STUDIES RELATED TO THE HEXAMINE NITROLYSIS REACTION

by

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University of Surrey,

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To my family

for their patience
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EXPERIMENTAL

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ABSTRACT.

The object of this work is to obtain a better understanding of the chemistry of the nitrolysis reaction of hexamine in nitric acid alone, this reaction giving primarily 3,5-dinitro-1,3,5-triazacyclohexane derivatives as final products.

Aspects of the nitrolysis reactions of hexamine, some related quarternary derivatives, and 7-nitro-1,3,5-triazadamanthane in nitric acid and nitric acid/ammonium nitrate solution are investigated.

The nitrosation, tosylation and methylation reactions of 7-nitro-1,3,5-triazadamanthane are studied and found to be similar to those of hexamine.

Preliminary variable temperature $^1$H NMR studies have been performed on the reactions of 1-methoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane, 3,7-dinitro-1,3,5,7-tetrazabicyclo(3,3,1)nonane and hexamine in nitric acid solution over the temperature range 243-303 K, in an attempt to follow the course of the reaction and characterise the intermediates.

In order to monitor these reactions the $^1$H NMR characteristics of certain N-nitramines, N-nitrosamines, 1,3,5,7-tetrazabicyclo(3,3,1)nonanes, hexamine and derivatives are studied, for compounds from these classes may be expected to participate in the nitrolysis reactions.

The nitrolysis reaction of 7-nitro-1,3,5-triazadamanthane gives either 1,3,7-triazabicyclo(3,3,1)nonane or 1,3,5-trinitro-1,3-diazacyclohexane derivatives as products. The nature of these products suggests that the mechanism of nitrolysis for this molecule occurs via a stepwise scission process.

Due to similarities between the chemistry of hexamine and 7-nitro-1,3,5-triazadamanthane, particularly with regards to the characteristics of the nitrolysis reaction, it is considered that the nitrolysis reaction of hexamine probably involves a similar mechanism.

$^1$H, $^{13}$C, $^{14}$N NMR and INDO molecular orbital studies are performed on selected molecules from the classes of compounds considered in this work with a view to the elucidation of their electronic structures.
CHAPTER ONE

INTRODUCTION
1.1 OBJECT OF THE WORK

The main object of the work described in this Thesis is to obtain a better understanding of the chemistry of the nitrolysis reaction of hexamine \((A)\)(1,1) in nitric acid alone, and to attempt to elucidate the mechanism of this reaction.

Considerable research effort has been expended in exploring the chemistry of the various nitrolysis reactions which hexamine undergoes, the emphasis being on the isolation and characterisation of the secondary N-nitramines which form the products of the reaction. These are found to be numerous and diverse in nature, indicating the complex nature of the reaction. From a consideration of the nature of the products formed under various reaction conditions several hypotheses have been forwarded concerning the mechanism of the reaction. These fall into two classes; the first involving a stepwise scission process, the principal features of which are illustrated in Fig 1.2; and the second involving the unselective degradation of the hexamine molecule to fragments, which then recombine to give the product. Either process enjoys a certain amount of experimental evidence to support its participation in the reactions.

![Diagram](image)

**Fig 1.1**

Studies are undertaken with a view to differentiating between these two types of mechanism, and characterising the intermediate(s) formed during the reaction.
1.2 TECHNIQUES EMPLOYED.

(A) $^1$H NMR SPECTROSCOPY.

The study of the hexamine nitrolysis reaction is hampered by the lack of suitable techniques for studying reactions in strong acid (these nitrolysis reactions generally employ 98-100% nitric acid). In this work preliminary studies involving the use of $^1$H NMR spectroscopy are undertaken in an attempt to monitor the reaction of substrates in nitric acid alone.

The simplest system involving the nitrolysis of hexamine is that with nitric acid alone, which gives 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) (B)(1,1) as the principal product. The chemistry of this system, and other systems involving the nitrolysis of the substrates (A) and (B)(1,3) in nitric acid alone, has been studied previously (1-4) over the temperature range 243-303 K. Product characterisation and dilution studies were employed in an attempt to characterise the intermediate(s) in the reactions, which make these systems useful for study by $^1$H NMR spectroscopy. Details of the relevant aspects of these reactions are summarised in Chapter Two.

![Fig 1.3](image)

In order to attempt a study of the nature of the nitrolysis reactions by $^1$H NMR spectroscopy, the spectroscopic features of the starting materials, expected products and possible intermediates need to be known and understood. Thus, the $^1$H NMR spectra of some available primary and secondary N-nitramines (A) and (B)(1,4)(Chapter Three, Part I, Section 3.2), hexamine and certain
Fig 1.4

(A) R - NO₂

(B) R

(C) R⁺ X⁻

(D) R - N

(E) R - NO

(F) R - N

(G) R - N

Fig 1.4
quaternary derivatives (C)(1.4)(Chapter Three, Part I, Section 3.5), and 1,3,5,7-tetraazabicyclo(3.3.1)nonane derivatives (D)(1.4)(Chapter Three, Part I, Section 3.4) have been recorded in suitable solvents. Their spectroscopic characteristics are interpreted on the basis of the structural features expected for these various classes of compounds. Included in this work are $^1\text{H NMR}$ studies of some secondary N-nitrosamines (E)(1.4)(Chapter Three, Part I, Section 3.3), since it is considered that secondary N-Nitrosamines are useful for the prediction of the $^1\text{H NMR}$ spectra of closely related N-nitramines.

A study of the variable temperature spectra of the substrates 1-methoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (A)(1.3), 3,7-dinitro-1,3,5,7-tetraazabicyclo(3.3.1)nonane (DPT)(B)(1.3) and hexamine (A)(1.1) in nitric acid alone (Chapter Three, Part I, Section 3.6) indicate that in all cases the substrate is rapidly attacked by the nitrating species and degrades to an intermediate (or intermediates), for in no case is a recognisable spectrum of the starting material present at the start of an NMR run at low temperature. The spectra are indicative of the latter stages of a reaction, which involves the slow step in the reaction, in these cases the formation of products. Due to the complexity of the spectra, the nature of the intermediate(s) cannot be ascertained with certainty at the present time.

(B) STUDIES OF THE NITROLYSIS REACTIONS OF HEXAMINE AND SOME STRUCTURALLY RELATED COMPOUNDS.

Hexamine occupies a somewhat unique position with regard to its chemistry. Due to its symmetrical nature and adamantane-like structure it can react to give either 1,3,5,7-tetraazabicyclo(3.3.1)nonane derivatives (D)(1.4) or 1,3,5-triazacyclohexane derivatives (F)(1.4). The former are obtained in alkaline, neutral or weakly acidic conditions, while the latter are generally obtained under more acidic conditions. In some reactions it may also form 1,3,5,7-tetraazacyclonctane derivatives (G)(1.4), presumably
via the appropriate 1,3,5,7-tetraazabicyclo(3.3.1)nonane derivative (D)(1.4).

There is a noticeable lack of data relating to the chemistry of structurally related compounds. Such data are often extremely useful when considering possible reaction mechanisms. To this end, aspects of the chemistry of hexamine (Chapter Three, Part III, Section 3.17), certain of its quarternary derivatives (C)(1.4)(Chapter Three, Part III, Section 3.18) and 7-nitro-1,3,5-triazaadamantane (A)(1.5)(Chapter Three, Part III, Section 3.15) are considered, particularly the nitration and nitrosation reactions. It is considered that features of the nitrosation reactions of hexamine and derivatives are related to aspects of the nitration reactions of these compounds. For 7-nitro-1,3,5-triazaadamantane (A)(1.5) it is found that nitration reactions give secondary N-nitramines of general structure (B)(1.5) under conditions similar to those used in the nitrolysis reactions of hexamine which give RDX.

From the nature of the reaction and the products obtained it is considered that the nitration reactions of 7-nitro-1,3,5-triazaadamantane (A)(1.5) proceed via a stepwise scission process, which suggests that the nitration of hexamine under similar conditions may also involve such a process.
(C) MOLECULAR ORBITAL CALCULATIONS.

Molecular orbital calculations, employing the INDO (Intermediate Neglect of Differential Overlap) method (5), have been performed on selected molecules from the various classes of compounds of interest in this work. It was hoped that such calculations might provide information on the energetics of the possible reaction pathways envisaged for the hexamine nitrolysis reaction. However, the failure of certain 1,3,5,7-tetraazabicyclo-(3.3.1)nonanes (D)(1,4) to achieve convergence conditions resulted in this approach being abandoned.

For selected primary and secondary N-nitramines (Chapter Three, Part II Section 3.10), secondary N-nitrosamines (Chapter Three, Part II, Section 3.11), and hexamine and derivatives (Chapter Three, Part II, Section 3.12), the calculations do provide reasonably good correlations with electronic properties, such as dipole moment and NMR data.

A secondary aim of this work is the investigation of the electronic structures of selected molecules from the classes of compounds considered in this work. In conjunction with the $^1$H NMR and molecular orbital studies, $^{14}$N and $^{13}$C NMR spectra of some primary and secondary N-nitramines, secondary N-nitrosamines, and hexamine and derivatives have been recorded (Chapter Three, Part I; Sections 3.7 and 3.8) with a view to an insight of the electronic structures of the molecules.
Chapter One describes the objects and techniques employed in this study of the nitrolysis of hexamine and other related tertiary amines in nitric acid alone.

Chapter Two provides an introduction to the relevant aspects of the chemistry of the nitrolysis reaction studied.

Chapter Three, Part I records and interprets the results of the $^1$H, $^{14}$N and $^{13}$C NMR studies performed on selected N-nitramines, N-nitrosamines, $1,3,5,7$-tetraazabicyclo(3.3.1)nonanes, and hexamine and derivatives.

Chapter Three, Part II records the results of the molecular orbital calculations performed on selected molecules.

Chapter Three, Part III records the results of the studies of aspects of the nitrolysis reactions of hexamine, its quarternary derivatives and 7-nitro-$1,3,5$-triazaadamantane.

Chapter Four, Part I discusses the results concerned with the nitrolysis of hexamine and related tertiary amines with a view to the elucidation of the mechanism of the reactions.

Chapter Four, Part II considers the molecular orbital and NMR data on selected molecules with a view to an understanding of the electronic structures of the molecules.

Chapter Five records the preparation and characterisation of the compounds considered in this work.
CHAPTER TWO

A REVIEW OF SOME RELEVANT ASPECTS OF THE HEXAMINE NITROLYSIS REACTION.
2.1 INTRODUCTION.

This Chapter summarises aspects of nitrolysis reactions which are relevant to that of hexamine. Thus the nitrolysis reactions of hexamine and other appropriate substrates in nitric acid alone, and in nitric acid/ammonium nitrate mixtures are considered. The nature of the products obtainable from these reactions are illustrated and the nature of the likely intermediates discussed in the light of available evidence.

2.2 SOME ASPECTS OF THE NOMENCLATURE OF NITRAMINES.

Nitramines may be considered as derivatives of nitric acid. The inorganic nitramine (A)(2.1) being regarded, formally, as the parent molecule of the group. When one of the hydrogen atoms of nitramine is replaced by an alkyl substituent, a primary nitramine (B)(2.1) is obtained. When both hydrogen atoms are replaced by alkyl substituents a secondary nitramine (C)(2.1) is obtained.

\[ \begin{align*}
\text{(A)} & \quad H \quad N - NO_2 \quad H \\
\text{(B)} & \quad R \quad N - NO_2 \\
\text{(C)} & \quad R \quad N - NO_2 \\
\end{align*} \]

Fig 2.1

The nomenclature used for nitramines is complicated by two potential sources of confusion. Firstly, the parent 'nitramine' (A)(2.1) was first named 'nitramide' by Thiele and Lachman (6). Secondly, many codified initials were used for ostensible secrecy during World War II and are now found in the chemical literature. As an example, 1,3,5-trinitro-1,3,5-triazacyclohexane (B)(2.2) is known as RDX (Research Department Explosive) in Britain, cyclonite in the U.S.A., T₄ in Italy and Hexogen in Germany, France and Belgium (7). Many other such initials are in use in the field of explosives, particularly for nitramines. Throughout this work most compounds are referred to by their names derived from current chemical nomenclature conventions (8). A few, however, are referred to by their common codified
initials, which have generally become accepted in the explosives literature. These are given in Fig 2.2.

Hexamine (Hexamethylenetetramine) (A)

RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) (B)

HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclododecane) (C)

Tetryl (N-nitro,N-methyl-2,4,6-trinitroaniline) (D)

DPT (3,7-dinitro-1,3,5,7-tetraazabicyclo(3,3,1)nonane) (E)
2.3 SOME ASPECTS OF THE HEXAMINE NITROLYSIS REACTION.

The term 'nitrolysis' was suggested by Linstead (9) and applies to a nitrating mechanism in which both the rupture of a C - N bond and the formation of an N-nitramine occur simultaneously. The other fragment may form an alcohol, which subsequently undergoes esterification to give a nitric ester. Alternatively, the nitric ester may be formed directly. These reactions are summarised in the following schemes (10).
\[
\begin{align*}
(R_1)_2 \text{NCH}_2 \text{R}_2 + \text{HONO}_2 & \rightarrow (R_1)_2 \text{N-NO}_2 + \text{HO-CH}_2 \text{R}_2 + \text{HNO}_3 \rightarrow \text{O}_2 \text{NOCH}_2 \text{R}_2 \\
(R_1)_2 \text{NCH}_2 \text{R}_2 + \text{NO}_2^+ & \rightarrow (R_1)_2 \text{N}^+\text{CH}_2 \text{R}_2 + \text{(R}_1)_2 \text{N-NO}_2 + \text{CH}_2 \text{R}_2 \rightarrow \text{O}_2 \text{NOCH}_2 \text{R}_2 
\end{align*}
\]

The nitration of hexamine to give RDX is thus a nitrolysis reaction.

The first nitramines to be synthesised appear to be by Griess (11) in 1869, however, the structure of the functional group was not elucidated until 1883. Romburgh (12) investigated the structure of the aromatic secondary nitramine, N-picryl-N-methyl nitramine (TETRYL)(D)(2.2), six years after it was first prepared by Mertens (13) in 1877. Franchimont et al (14) studied alkyl and acyl nitramines and first isolated a primary nitramine (B)(2.1), while the parent nitramine (A)(2.1) was isolated by Thiele and Lachman (6) in 1894. The major features of the chemistry of nitramines were established in the years 1883-1914 (9), a review of the work has been given by Backer (15). The trinitramine, 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX)(B)(2.2), a most powerful explosive, was first prepared during this period by Henning (16) from hexamine dinitrate and nitric acid, the hexamine dinitrate being obtained from hexamine. Hertz (17) proposed the correct structure for this compound in 1919 and also recognised its explosive properties.

In 1925, Hale (18) investigated the action of nitric acid on hexamine and hexamine dinitrate at different acid concentrations, reaction temperatures and addition times before dilution of the reaction with water, in order to establish favourable conditions for the production of RDX in high yield. In the case of hexamine dinitrate, nitration with acids of concentration 85-95% produces RDX, the higher concentrations of acid giving yields of up to 50% on the basis of one mole RDX formed from one mole of hexamine. Experimental data show that upon addition of hexamine to nitric acid (at temperatures of 303K or below) three separate and
distinct reactions may occur:

\[
C_6H_{12}N_4 \text{(HEXAMINE)} + 3\text{HNO}_3 \rightarrow C_6H_{12}N_6O_6 \text{(RDX)} + 3\text{CH}_2O + \text{NH}_3 \quad \text{(A)}
\]

\[
C_6H_{12}N_4 + 6\text{H}_2\text{O} \text{(acid)} \rightarrow 6\text{CH}_2O + 4\text{NH}_3 \quad \text{(B)}
\]

\[
C_6H_{12}N_4 + 2\text{HNO}_3 \rightarrow C_6H_{12}N_4(\text{2HNO}_3) \quad \text{(C)}
\]

With acid of comparatively low concentration, up to 70%, the reaction proceeds via reaction (B), involving hydrolysis of hexamine with little or no nitration. At higher acid concentrations, 80-85%, the reactions (B) and (C) apparently take place; while in the presence of 85-100% acid all three reactions may occur simultaneously, and RDX is produced in these cases.

The formation of RDX (reaction (A)) predominates at the highest acid concentrations (95-100%), when other conditions (above) are also favourable. The highest yields of RDX (75%) are obtained with the use of 100% nitric acid at low temperatures, when the absence of water reduces the participation of reactions (B) and (C). Losses of RDX are still incurred by formation of hexamine dinitrate, which once formed is considered to be fairly stable in nitric acid at low temperatures (18).

Chute et al (19) have re-examined the Hale nitrolysis reaction and find that the yield of RDX may be raised to 86% (average 83%) by careful attention to the rate of addition of hexamine so as to avoid local decomposition. Optimum yields result from the addition of hexamine (1 mole) to 21 moles of 99.5-99.9% nitric acid at 293-298 K over a 30 minute period. The product is obtained by drowning the reaction mixture in ice.

The addition of a small amount of ammonium nitrate (or sulphate) to the nitric acid is reported (20) to help stabilise the reaction and to produce higher yields of RDX. A yield of 85% has been recorded on addition of hexamine to a 27.25 molar excess of nitric acid (98%) containing 0.313 mole of ammonium nitrate at 276-283 K over 55 minutes. In these experiments the molar ratio of ammonium nitrate to nitric acid is very low. Increasing
the ratio results in an eventual decrease in RDX yields. When the ratio is
brought up to (1:1) the yield of RDX is drastically reduced. McKay et al (21)
have recorded a yield of only 19% RDX when hexamine is reacted with 20 molar
excess of (1:1) ammonium nitrate/nitric acid solution at 341 K for a total of
50 minutes. The drastic reduction of yield is presumably due to a decrease
in the effective strength of the acid on the addition of ammonium nitrate,
although no evidence is available concerning the pH of ammonium nitrate/
nitric acid mixtures.

Studies have been made concerning the mechanism of the Hale nitrolysis
of hexamine with nitric acid alone. Chute et al (19) have observed that
after RDX has been filtered from the drowned reaction liquor, careful
neutralisation of the filtrate to pH 5 in the cold with ammonia, or other
alkalis, precipitates the compound DPT (Fig 2.3) in yields up to 18%.

There is an indication that the formation of RDX and DPT may be related,
possibly by a common precursor. The formation of DPT in this manner is
considered (19) to result from the presence of dimethylolnitramine (A)(2-3),
its dinitrate ester (B)(2-3), or both in the aqueous diluate. The results
are summarised in Fig 2.3.
Winkler et al. (22, 23) have considered the nitrolysis of hexamine with nitric acid alone, (22) and with acetic acid as solvent (23). The results indicate that acetic acid has a harmful effect on the reaction rate and yield of RDX. This led to the postulate that acetic acid may suppress the formation of the active nitrolysing agent. Reaction of hexamine with nitric acid at 233 K, followed by rapid dilution of the reaction with ice-water produces a precipitate of PCX (K)(2.2), which has been considered by Vroom and Winkler (22) to be an intermediate in the nitrolysis reaction.

Wright et al. (24) have refuted this postulate, since they report that PCX cannot survive under nitrolysis conditions. PCX is considered to be formed by the action of water on the true intermediate present in the nitrolysis mixture at low temperatures (24).

Dunning and Dunning (3) have reported dilution studies of the hexamine dinitrate/nitric acid reaction mixture at low temperatures with ethyl ether at 213 K, and subsequent treatment of the product with methyl or ethyl alcohol or water. When hexamine dinitrate is added to 97% nitric acid with rapid stirring at 228 K and the temperature allowed to reach 244 K, followed by cooling to 213 K, and the addition of cold ether with the temperature kept below 223 K, a white gum separates. The gum is, however, only stable under ether at low temperatures. A portion of the gum is completely soluble in boiling water indicating the absence of RDX, however, some hexamine dinitrate is found to be present. The gum may be stabilised by stirring with cold ethyl alcohol, in which it immediately becomes granular.

Extraction of this white granular residue with ether gives 1-ethoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (A)(b)(2.4) while evaporation of the solution obtained by stirring the gum with ethyl alcohol gives the compound (B)(2.4). Similarly stirring with methyl alcohol produces the 1-methoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (A)(a)(2.4) and compound (B)(2.4).

When the gum is stirred with water the compound (C)(2.4) is isolated.
If it is stirred with acetic anhydride saturated with sodium acetate at 303 K only RDX is obtained. Interruption of the low temperature reaction between hexamine dinitrate and 97% nitric acid by dilution with ethyl alcohol below 233 K produces a granular precipitate, consisting of PCX (K)(2,2) and a small amount of (A)(b)(2,4); while a similar reaction with methyl alcohol gives PCX and a small amount of (A)(a)(2,4).

![Chemical Structures](image)

The results obtained from nitration studies of hexamine dinitrate are generally considered to be applicable to the study of the nitrolysis of hexamine. Kinetic studies (25,26) have indicated that the initial product of the hexamine nitrolysis reaction in nitric acid may be hexamine dinitrate (25), which is rapidly converted into an intermediate which, in turn, gives RDX by a relatively slow, rate-determining step (26).

Bell and Dunstan (2) have performed dilution studies on the hexamine/nitric acid reaction mixture over the temperature range 243-303 K, these are designed to detect and characterise unstable intermediates. The addition of water to nitrolysis mixtures prepared at 243 K give high yields of PCX (K) (2,2), while nitrolysis mixtures kept at 273 K for half a minute afford only low yields of PCX with a corresponding increase in the yields of RDX, reaching 83% after standing at 273 K for 120 minutes. Traces of the linear dinitrate (A)(2,5) are also detected in mixtures left to stand at 273 K for 30 and 180 minutes. On dilution with acetic anhydride, hexamine nitrolysis mixtures give RDX and acetoxy- and nitroxy-terminated triazahexatanes (B)(2,5).
Standing for long periods produces a small amount of the linear dinitrate (A)(2.5). Reaction mixtures treated with aqueous sodium nitrite at 243 K give high yields (75%) of the 1-nitroso-3,5-dinitro-1,3,5-triazacyclohexane (C)(2.5), and when the mixture is warmed to higher temperatures prior to the addition of the sodium nitrite solution lower yields of the nitrosamine are obtained, but increasing amounts of RDX result. The high yields of RDX obtained on warming reaction mixtures, and the formation of the nitrosamine (C)(2.5) favour the presence of the 3,5-dinitro-1,3,5-triazacyclohexane ring system in the intermediate.

![Chemical structure](image)

The formation of the acetoxy- and nitroxy-terminated linear triazaheptanes (B)(2.5) upon the addition of acetic anhydride to the reaction mixtures, requires that a methylene-linked side-chain be attached to the triazacyclohexane ring system (2). Bell and Dunstan (2) thus consider that the intermediate in the hexamine nitrolysis reaction is of the nature (A)(2.6), where the R group requires determination.

![Chemical structure](image)
Comparison of the results of the low temperature nitrolysis experiments on hexamine (2) with those on 1-acetoxyethyl- and 1-methoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (G) and (C)(2.6)(1)(see Section 2.4) shows that the nitrolysis intermediate for the latter compounds, considered to be 1-nitroxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (H)(2.6)(1), exhibits significant differences to that for hexamine on dilution with water and acetic anhydride. Different temperature dependencies are also noted. Thus, the intermediate in the hexamine nitrolysis reaction is considered to be less stable and more reactive than the simple nitroxymethyl intermediate (H)(2.6), which is postulated to explain the reactions for the 1-acetoxyethyl- and 1-methoxymethyl-3,5-dinitro-1,3,5-triazacyclohexanes.

Evidence that the side-chain of the hexamine nitrolysis intermediate may be the more complex bis(nitroxymethyl)aminomethyl group (A)(2.7) is provided by a consideration of the results of adding primary dinitramines (B)(2.7) to the nitrolysis mixture (2). Treatment of a cold (243 K) nitrolysis mixture with methylenedinitramine (B)(n=1)(2.7), followed by ageing the mixture at 303 K for 15 minutes gives yields of RDX which are almost doubled (from 85% to 145%, calculated on the basis of 1 mole hexamine going to 1 mole RDX). The RDX yield is similarly enhanced by the addition of hexamine to a solution of methylenedinitramine in nitric acid at 233 K or 273 K, followed by warming the mixture to 303 K. However, no enhancement is obtained when methylenedinitramine is added to hexamine nitrolysis mixtures previously warmed to 303 K. Higher members of the dinitramine series, ethylenedinitramine and trimethylene dinitramine (B) (n=2,3)(2.7) when added to the hexamine nitrolysis mixtures at 243 K give RDX in normal yield, together with the appropriate cyclic trinitramine (D) (n=2,3)(2.7). The dinitramines are considered to undergo condensation with the postulated intermediate (A)(2.7) to form the bicyclo compounds (C)(2.7), which then undergo nitrolysis to give RDX and the corresponding
HEXAMINE

(A)

(B) n=1,2,3

DINITRAMINE

(c) n=1,2,3

RDX

(d) n=1,2,3

Fig 2.7
cyclic trinitramine (D)(2.7). However, Chute et al (19) have postulated the presence of dimethylolnitramine or its dinitrate ester, (A) and (B)(2.3), in a Hale-type nitrolysis medium and it is thus possible that the reaction of the added dinitramines (B)(2.7) to give the trinitramines (D)(2.7) involves these entities and not the postulated intermediate (A)(2.7). A normal yield of RDX is still expected should this reaction occur.

2.4 SOME ASPECTS OF THE NITROLYSIS REACTIONS OF OTHER TERTIARY AMINES.

Studies on the nitration reactions of various derivatives of type (A) to (G)(2.6) have been performed. Chapman et al (27) have reported that reaction of the compounds (A) and (B)(2.6) with 98% nitric acid at 283 K, followed by subsequent dilution with water, gives the linear trinitramines (A)(a) and (A)(b)(2.8). Dunning and Dunning (28) have reported that the derivatives (C) to (F)(2.6) give RDX in high yield when treated with 99% nitric acid, and subsequently diluted with water. The reactions were performed at temperatures around 273 K with reaction times of about 30 minutes. Additionally, with the 1-methoxymethyl and 1-chloromethyl derivatives (C) and (E)(2.6) the addition of cold water to a cold (253 K) nitration mixture gives the compound PCX (K)(2.2)(4). The addition of cold (193 K) ether to a cold nitration mixture gives the bicyclo compound (B)(2.8). Reaction of (B)(2.8) with 96% nitric acid at 273 K gives RDX in 94% yield on subsequent dilution of the reaction mixture with water (4). RDX is also formed upon treatment of the bicyclo compound (C)(2.8) with 98% nitric acid at 233 K, followed by dilution of the reaction mixture with excess ice-water (4).

The derivative (A)(2.6) has been reported to give only RDX on reaction with nitric acid/ammonium nitrate solution (27).
Bell and Dunstan (11) have considered the nitration reactions of the acetoxymethyl and methoxymethyl compounds (G) and (C)(2,6), the action of 98% nitric acid being studied over the temperature range 243-303 K. Substrates are added to nitric acid at 243 K, and the products isolated from the reactions are found to depend on the subsequent treatment of the reaction mixture. Thus, addition of cold water to a cold (253 K) nitration mixture gives PCX, whereas addition of aqueous solution nitrite produces 1-nitroso-3,5-dinitro-1,3,5-triazacyclohexane (C)(2.5). When nitration mixtures are allowed to warm progressively to 303 K, before dilution with water or aqueous sodium nitrite, increasingly higher yields of RDX are obtained at the expense of PCX and the nitroso compound (C)(2.5).

These observations are considered to indicate that the true nitration product of the compounds (C) and (G)(2,6), which is stable only in cold concentrated nitric acid, is the nitrooxymethyl derivative (H)(2,6).

This was first suggested by Dunning and Dunning (4) on the basis of dilution studies. The compounds PCX and (C)(2.5) are considered to be formed by the action of the dilution reagent on the true intermediate. When the acetoxymethyl and methoxymethyl derivatives are added to a
preformed mixture of nitric acid/acetic anhydride the yields of products are affected by the nature of the substituent side-chain. Thus, the acetate (G)(2.6) gives the linear diacetate (B)(2.9)(85%); while the ether (C)(2.6) produces a mixture of linear diacetate (B)(2.9)(53%) and RDX (24%).

Further evidence for the presence of a cyclic nitrooxymethyl derivative in solution is provided by addition of acetic anhydride to the cold reaction mixtures (1). This leads to the formation of mixed acetoxy- and nitroxoy-terminated triazaheptanes at low temperature, presumably formed by the sequence given in Fig 2.9. At higher temperatures RDX is again progressively formed at the expense of the linear compounds.

Bell and Dunstan (1) have reported that the reaction of PHX (F)(2.2) with nitric acid below 273 K, followed by dilution with cold water gives no product; while much degradation occurs when the nitration mixture is warmed to 303 K. At this temperature the crude product, isolated by the addition of cold water, gives only low yields of HMX (C)(2.2) and the linear compound AcAn (G)(2.2) after treatment with het sodium acetate.
acetic acid. Reaction mixtures diluted with aqueous sodium nitrite afford good yields of the N-nitrosamine (B)(2.10), while the addition of acetic anhydride gives the mixed acetoxy- and nitroxy-terminated linear compounds (C)(2.10)(characterised as the linear diacetate, AcAn (G)(2.10)) in good yield at low temperature. Degradation occurs at higher temperatures producing HMX and AcAn in low yields. These reactions are summarised in Fig 2.10.

These results are considered to indicate the presence of the nitroxy-methyl intermediate (A)(2.10) in solution at low temperatures for this compound (1).

Similar studies have been performed on the reaction of DPT (E)(2.2) with nitric acid alone at various temperatures, the reactions again being terminated by the addition of water, aqueous sodium nitrite or acetic anhydride (1). It is found that DPT reacts similarly to PHX, in that reaction with nitric acid at low temperatures (253 K) appears to give solutions containing the nitrooxymethyl intermediate (A)(2.10)(1).

Evidence for the participation of fragments in the hexamine nitrolysis reaction is indirectly derived from studies of the reaction of hexamine with nitric acid/acetic anhydride/acetic acid/ammonium nitrate mixtures to form HMX (C)(2.2). Castorina et al (29,30) have performed $^{13}$C (29) and $^{15}$N (30) isotopic labelling tracer studies on such reactions and conclude from an analysis of the products for isotopic distribution that unselective degradation of hexamine occurs to give fragments, possibly of the type (A) (2.11). Fridman (31) has postulated the participation of fragments of the type (B) and (C)(2.11) for similar reactions.
Fig 2.10
The reaction of the compound (B)(2.4) with excess paraformaldehyde and acetic anhydride is reported (3) to give RDX in 61% yield. Chapman et al (32) have considered the nitration reactions of certain methylene-bis-amines. In the presence of nitric acid/ammonium nitrate/acetic anhydride both tetramethylmethylenediamine (A)(2.12) and methylenebis-morpholine (B)(2.12) give RDX in low yield.

Urbanski and Szyc-Lewanska (33) have reported that the reaction of hexamethylenetriperoxidiamine (A)(2.13) with nitric acid/ammonium nitrate below 313 K gives RDX in 26% yield. The reaction is summarised in Fig 2.13.
Attempts have been made to synthesise RDX from a variety of fragments under nitrating conditions (2, 3, 34), but without success.
CHAPTER THREE

EXPERIMENTAL RESULTS
PART I : NMR STUDIES.

3.1 INTRODUCTION.

The NMR spectra of the $^1$H, $^{13}$C and $^{14}$N nuclei in some of the various classes of compounds of interest in this work have been obtained and interpreted. The $^1$H NMR spectra of some available N-nitramines, N-nitrosamines, 1,3,5,7-tetraazabicyclo(3.3.1)nonanes, hexamine and derivatives have been recorded in suitable NMR solvents with a view to the application of $^1$H NMR spectroscopy to the interpretation of the reactions of such compounds in nitric acid solution. Characterisation of the various proton resonances found in these compounds is a necessary first step in an attempt to interpret the spectra obtained in nitric acid solutions. The spectra of secondary N-nitrosamines have been studied because the information obtained is meaningful when considering closely related N-nitramines, and may be used in some cases for the prediction of N-nitramine resonances. The $^1$H NMR spectra of some substrates in nitric acid solutions are recorded. The interpretations of the spectra obtained for these classes of compounds are made on the basis of the structural and electronic features possessed by them. An insight into the electronic structures of some selected molecules is obtained by a consideration of their $^{13}$C and $^{14}$N NMR spectra.

3.2 $^1$H NMR STUDIES OF N-NITRAMINES.

The $^1$H NMR spectra of some primary and secondary N-nitramines have been recorded. The data for some selected compounds are given in Fig 3.1. It may be seen from Fig 3.1 that the respective methylene protons in each N-nitramine grouping fall in comparatively narrow chemical shift ranges, although some classes do overlap. Chemical shifts are thus useful for the characterisation of N-nitramines. This point is discussed further in Chapter Four, Part I, Section 4.7. In general, N-nitramines are not particularly soluble in non-polar solvents, but are found to be readily
The letters in parentheses (a)(b)(c)(d) refer to the protons in the associated molecules.

Solvents: (DMSO)=dimethylsulphoxide; (CHCl₃)=chloroform; (d₆-DMSO)=hexadeuterodimethylsulphoxide.

(s)=singlet; (t)=triplet; (qt)=quintet

Chemical shifts are given in δ ppm with respect to TMS as internal standard.

Fig 5.1 (Continued)
soluble in dimethylsulphoxide or its deuterated derivative. This solvent
does possess certain disadvantages, for example in primary N-nitramines
the amino proton is labile and readily exchanges with any water in the
solvent. Some N-nitramines, such as RDX, are found to be unstable in wet
dimethylsulphoxide. Thus, reliable and reproducible spectra require a dry
solvent. For the six- and seven-membered ring compounds (A)(3,2), the
eight-membered ring compounds (B)(3,2) and the linear N-nitramines (C)(3,2)
the methylene protons (a) and (b) always exhibit singlet spectra. At
first sight these methylene protons might be expected to exhibit 'AB'
quartets due to geminal proton interactions. However, the N-nitramine
group is considered to be conjugated, with the $\text{C}_2\text{H}_4\text{NO}_2$ grouping
essentially planar (35,36), which implies some $sp^2$ character for the
amino type nitrogen atom in N-nitramines. For cyclic N-nitramines this
can lead to flattening of the ring and thus fast ring inversion making the
methylene protons equivalent. This postulate for the amino nitrogen atom
in the N-nitramine group implies that nitrogen inversion for this atom need
not be considered. The cyclic nitrogens may be considered to oscillate
about the planar ($sp^2$) position with little distortion (36). The
possibility of restricted rotation about the N-N bond in N-nitramines must
also be considered (Chapter Four, Part II, Section 4.10), although its
participation will not be apparent in the $^1H$ NMR spectra of these compounds
due to the symmetrical nature of the $\text{NNO}_2$ fragment. For the compounds
(A) and (B)(3,2), where the R groups are not considered conjugated
($R=\text{CH}_2R'$; $R'=\text{NO}_2$, $\text{NO}_2$, $\text{COR}'$), fast nitrogen inversion and ring inversion
are thought to occur in order to account for the methylene protons (b)
exhibiting singlet spectra for these compounds. The spectra of RDX and
HMX have been recorded over the temperature range 303 - 433 K, in each
case only a single line is shown, which progressively broadens on raising
the temperature, due to the interaction of the protons with the quadrupole
moments of the nitrogen atoms in the N-nitramine groupings. For the linear
N-nitramines (C)(3)2) protons in the methylene groups (a) and (b) appear equivalent, presumably due to an averaging mechanism such as molecular tumbling or a favorable molecular orientation of the compound. For the compounds (D)(3,2), containing the trimethylenedinitramine system, the methylene protons (a) and (b) are coupled (J=4-6 Hz). Geminal coupling is again absent but vicinal coupling occurs, the protons (a) appear as a quintet and the protons (b) as a triplet. Other features of the ¹H NMR spectra of N-nitramines are discussed in Chapter Four, Part II, Section 4.10.

![Chemical Structures](image)

3.3 ¹H NMR Studies of N-Nitrosamines.

The ¹H NMR spectra of the cyclic N-nitrosamines (A)-(D)(3,3) have been recorded at room temperature. The N-nitroso compounds (A)-(C)(3,3) show ¹H NMR spectra consistent with fast ring inversion, together with the effects of restricted rotation about the N-NO bonds in these molecules. The C₂N-NO groups in these molecules are considered to be planar (39, 40), which allows the effects of nitrogen inversion to be neglected. The presence of two or more N-nitroso groups in the ring system produces flattening of the ring, such that ring inversion is fast on the NMR time scale. Rotation about the N-NO bonds in these molecules is sufficiently
slow to enable the observation of individual signals from the possible conformational isomers; the observation also relies on the anisotropy of the N-nitrosamine group. For the compounds (A)-(C)(3.3) the presence of all possible syn/anti conformational isomers are found experimentally. The isomers are not in their statistical proportions, indicating the presence of unfavourable steric or electronic effects which determine the isomer ratios. It seems that a cis/cis orientation of two N-nitroso groups is extremely unfavourable, while the trans/trans orientation is highly favoured. The bicyclic N-nitrosamine (D)(3.3) is an example of an N-nitrosamine with a fixed molecular structure. This molecule is considered to exist in a flattened chair-chair conformation, as shown.

![Diagram](image)

(A)  (B)  (C)  (D)

Fig 3.3
### Table 3.1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Methylene group protons</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\alpha'_{cc}$</td>
</tr>
<tr>
<td>(A)</td>
<td>CDCl₃</td>
<td>3.83(s)</td>
</tr>
<tr>
<td>(B)</td>
<td>CDCl₃</td>
<td>2.0(m)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C)</td>
<td>(CD₃)₂SO</td>
<td>5.62(s)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bridge -CH₂-</th>
<th>H\text{ax}</th>
<th>H\text{eq}</th>
<th>J\text{ae (Hz)}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D)</td>
<td>(CD₃)₂CO</td>
<td>4.59(bs)</td>
<td>4.21(d)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.29(d)</td>
<td>5.50(d)</td>
</tr>
<tr>
<td></td>
<td>(CD₃)₂CO</td>
<td>4.59(bs)</td>
<td>4.29(d)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.42(d)</td>
<td>5.82(d)</td>
</tr>
<tr>
<td></td>
<td>(CD₃)₂SO</td>
<td>4.46(bs)</td>
<td>4.22(d)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.25(d)</td>
<td>5.45(d)</td>
</tr>
<tr>
<td></td>
<td>(CD₃)₂SO</td>
<td>4.46(bs)</td>
<td>4.29(d)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.35(d)</td>
<td>5.77(d)</td>
</tr>
</tbody>
</table>

Chemical shifts are in units of $\delta$ ppm relative to TMS as internal standard. Shifts to high frequency are considered positive.

* see Fig 3.3

(s)=singlet (bs)=broad singlet (d)=doublet (part of AB quartet)
(t)=triplet (m)=multiplet
The $^1$H NMR spectrum of 1,3-dinitroso-1,3-diazacycloheptane (A)(3,3) in CDCl$_3$ is given in Fig 3.5 and analysed in Table 3.1. It may be interpreted by a consideration of the three conformational isomers (A)-(C)(3,4). The assignments given in Table 3.1 are made from a consideration of the chemical shifts of the protons in the closely related compounds N,N'-dinitrosopiperazine (B)(3,3)(41, 42) and 1,3-dinitroso-1,3-diazacyclohexane, the spectrum of which has been assigned by Evans (43). The isomer ratio calculated from the respective integrals is (A):(B):(C) = 7:6:1, which is very different from the statistical ratio 1:2:1.

The $^1$H NMR spectrum of N,N'-dinitrosopiperazine (B)(3,3) in CDCl$_3$ is given in Fig 3.6 and analysed in Table 3.1. It may be interpreted by a consideration of the syn and anti forms (D) and (E)(3,4). The syn isomer produces two sharp singlets, an $A_x$ singlet at low frequency ($\alpha'^cc$ protons) and a $B_x$ singlet at high frequency ($\alpha'^tt$ protons). The anti isomer gives an (AA'BB')$_2$ pattern. The approximate chemical shift positions of the respective protons are given in Table 3.1, and the assignments are in agreement with those of other workers (41, 42). The isomer ratio is found to be (D):(E) = 5:8, which is different to the statistical value of 1:1.

The $^1$H NMR spectrum of 1,3,5-trinitroso-1,3,5-triazacyclohexane (C)(3,3) in d$_6$-DMSO exhibits a four line spectrum at room temperature. This consists of a 1:1:1 triplet and a singlet close to the centre line of the triplet. The chemical shift values of the respective protons are given in Table 3.1. The spectrum is interpreted by a consideration of the two conformational isomers (F) and (G)(3,4). The isomer (F)(3,4) gives a 1:1:1 triplet pattern for the three inequivalent methylene proton groupings, while the isomer (G)(3,4) gives a single line for the three equivalent methylene proton groupings. The isomer ratio is found to be (F):(G) = 2:1 which differs from the statistical value of 3:1. Variable temperature spectra of this compound over the range 193 - 365 K show that from 193 - 298 K a
four line spectrum may be distinguished, but at 315 K the two centre
lines have coalesced. From 313 - 353 K the three sharp lines broaden
and collapse, and at about 365 K have coalesced to give a broad singlet,
which sharpens on raising the temperature still further.

3,7-dinitroso-1,5,5,7-tetraazabicyclo(3,3,1)nonane (D)(3,3) is an
example of an N-nitrosoamine which possesses a fixed molecular structure.
Its $^1$H NMR spectra in (CD$_3$)$_2$CO and (CD$_3$)$_2$SO are given in Fig 3.7 and are
analysed in Table 3.1. The spectra are interpreted on the basis of
restricted rotation about the N-NO bonds linking the nitroso groups to
the bicyclo(3,3,1)nonane system.

For this compound the nitroso groups produce an anisotropic shielding
effect such that the spectrum may be interpreted in terms of the individual
contributions of the syn and anti isomers (II) and (I)(3,4), although
assignments as to which signals belong to which isomer have not been made.
The spectrum is complicated, in particular the high frequency signals,
since accidental degeneracy occurs in this region.

The cis axial ring methylene protons of the two isomers are both
deshielded, but to different degrees, by the magnetic anisotropy effect
of the nitroso group. The trans axial protons are also deshielded but to
a lesser extent, while the cis and trans axial protons appear at higher
frequencies, and are relatively unaffected by the presence of the nitroso
group. This is in agreement with the spectra of similar compounds (44, 45).
The spectrum of this compound was recorded in (CD$_3$)$_2$CO and (CD$_3$)$_2$SO and
shows some solvent shifts, particularly for the cis axial protons (Fig 3.7).
The assignments given in Table 3.1 are supported by decoupling experiments
and by a consideration of the integrated spectrum. The decoupling
experiments indicate that the equatorial protons may be coupled to the
appropriate bridge proton and also to each other. The cis and trans
equatorial protons and the bridge and equatorial protons are each linked
The definitions of $\alpha_{ct}$, $\alpha_{cc}$, $\alpha_{ct}$ and $\alpha'_{ct}$ are given in Fig. 3.4.

Fig 3.8
by a favourable \( U \) pathway permitting the observation of significant long-range coupling. A consideration of the long-range couplings and the geminal coupling constant data for this compound indicates that each isomer probably exists in a flattened chair-chair conformation (this Chapter, Section 3.4).

A correlation of the appropriate \( ^1H \) NMR data is found in the present work, between \( N \)-nitramines and the appropriate \( N \)-nitrosamine. With conformationally mobile molecules the following relationships apply:

(a) for mono \( N \)-nitrosamines the resonance positions of the corresponding protons in the \( N \)-nitramine are predicted by the relation

\[
\delta CH_2(N\text{-nitro}) = \frac{1}{2} (\delta CH_2('\text{cis}-N\text{-nitroso}) + \delta CH_2('\text{trans}-N\text{-nitroso}))
\]

(b) for di- and tri-\( N \)-nitroso compounds, where the \( N \)-nitroso groups are in a cyclic structure and separated by a single methylene unit, the relationship for the corresponding methylene protons in the \( N \)-nitramine is given by

\[
\delta CH_2(N\text{-nitro}) = \delta CH_2('\text{cis-trans}-N\text{-nitroso})
\]

\[
= \frac{1}{2} (\delta CH_2('\text{cis-cis}-N\text{-nitroso}) + \delta CH_2('\text{trans-trans}-N\text{-nitroso}))
\]

Some examples are given in Fig 3.8.

3.4 \( ^1H \) NMR STUDIES OF 1,3,5,7-TETRAAZABICYCLO(3.3.1)NONANES.

\( ^1H \) NMR data for a series of 3,7-disubstituted 1,3,5,7-tetraazabicyclo(3.3.1)nonanes are collected in Table 3.2. The data are interpreted on the basis of these molecules existing in chair-chair or flattened chair-chair forms. For the 1,3,5,7-tetraazabicyclo(3.3.1)nonane derivatives (A)-(D)(3.9), the \( ^1H \) NMR spectra exhibit a broad singlet for the methylene bridgehead protons and \( AB \) quartets, arising from the inequivalence of the axial and equatorial protons, for the ring methylene groups. The doublet to higher frequency is generally broadened, compared with the lower frequency
doublet, and is thus assigned to the equatorial protons, since these are connected by a 'W' bonding path to the bridgehead protons and to the other equatorial proton in the same ring. Such a pathway often favours the observation of long-range coupling effects in such molecules (46).

This assignment is consistent with the analysis of the $^1$H NMR data of 1,3-diazabicyclo(3.3.1)nonane derivatives (G)(3,9)(47).

For the compounds (C)(a) and (C)(b)(5,9) the signals of the ring methylene protons are considerably broadened. This presumably arises from quadrupolar relaxation induced by the nitrogen nuclei in the 3,7-substituents of these compounds. The spin-spin coupling is still resolvable in the spectrum of (C)(a)(3,9), but in the case of (C)(b)(5,9) the AB quartet is reduced to two very broad singlets (half-height width $\sim 50$Hz).

The dichloro derivative (A)(3,9) has the lowest value of the compounds in this series (9.5 Hz) for the geminal coupling constant $J_{ae}$. This is consistent with the molecule being in a chair-chair conformation such that the ring methylene protons have one adjacent nitrogen atom with its lone-pair axial and the other, the bridgehead nitrogen atom, with its lone-pair equatorial (48)(Chapter Four, Part II, Section 4.9).

The coupling constant data for all the other derivatives suggests that some progressive flattening of the rings occurs. A consideration of the electronic nature of the substituents in these compounds indicates that electron delocalisation could be concomitant with ring flattening, the hybridisation of the 3,7-ring nitrogen atoms moving from sp$^3$ towards sp$^2$. This could lead to effective flattening of the rings and higher values of $J_{ae}$.

In the case of the unsymmetrical molecule (E)(3,9), the $^1$H NMR spectrum (Fig 3.10) consists of a singlet for the bridgehead methylene protons and a singlet for the $\underset{N^+}{\text{CH}_2}$ protons, and two sets of AB quartets due to the pairs of ring methylene protons adjacent to the substituted and unsubstituted bridging nitrogen atoms. The pairs of lines at $\delta=6.42$ and 5.26 are shown.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$ (CH$_3$)</th>
<th>$\delta$ (H)</th>
<th>$\delta$ (H)</th>
<th>$\delta$ (H)</th>
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<tbody>
<tr>
<td>Ethane</td>
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<td>1.00</td>
<td>1.00</td>
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<tr>
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<tr>
<td>Pentane</td>
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<td>Nonane</td>
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<td>Other Compounds</td>
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</tr>
</tbody>
</table>

Table 2.3
Fig 3.9

(A) 

(B)(a) X=H
(b) X=\text{-o-Cl}
(c) X=\text{-m-Cl}
(d) X=\text{-p-Br}

(C)(a) X=H
(b) X=\text{-p-Br}

DPT (D)

(E)

(F)

(G)(a) R=\text{CH}_3
(b) R=\text{C}_5\text{H}_5
(c) R=\text{i-C}_5\text{H}_7
(d) R=\text{t-C}_5\text{H}_{11}
to be coupled, by decoupling experiments, and are attributed tentatively
to the methylene groups adjacent to the substituted bridging nitrogen atom.
The pairs of lines at 5.79 and 4.91 are also coupled, these are tentatively
assigned to the methylene protons adjacent to the unsubstituted bridgehead
nitrogen atom by comparison with the $^1$H NMR data for the closely similar
compound DPT (D)(3.9), the spectrum of which is given in Fig 3.11.

The spectrum of the 3,7-dinitroso derivative (F)(3.9) is given in Fig 3.7
and analysed in Table 3.1. This compound exhibits a room temperature
spectrum consistent with restricted rotation about the N-NO bonds in the
molecule, and is discussed in detail in Section 3.2.

3.5 $^1$H NMR STUDIES OF HEXAMINE AND DERIVATIVES.

The $^1$H NMR data for hexamine (A)(3.12) and some of its derivatives are
recorded in Table 3.3. Hexamine gives a sharp singlet. A consideration
of a molecular model shows that all of its protons are equivalent. On
protonation there is a shift to higher frequency for all of the ($\text{N-CH}_2\text{-N}^+$)
protons, a sharp singlet is still obtained. On going from hexamine mono-
nitrate (B)(3.12) to hexamine dinitrate (C)(3.12) there is little change
in the chemical shift of the ($\text{N-CH}_2\text{-N}^+$) protons, but for (B)(3.12) the
($\text{NH}^+$) signal appears as a broad peak, while for (C)(3.12) a sharp signal
is obtained. The position of these ($\text{NH}^+$) signals varies for different
samples. These protons are labile and presumably exchange rapidly with
water in the solvent (DMSO); thus, average chemical shift positions only
are obtained. The signals appear to high frequency of the ($\text{N-CH}_2\text{-N}^+$)
protons. The spectral characteristics of these compounds suggest that fast
exchange processes are occurring, which result in the averaging of all
methylene proton chemical shifts. In addition, it appears that all of the
nitrogen atoms experience an average positive charge in each molecule.

For hexamine dinitrate the appearance of the ($\text{NH}^+$) protons as a sharp
Fig 3.12
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>((\text{\text{N}}-\text{CH}_2-\text{H}))</th>
<th>((\text{\text{N}}^+-\text{CH}_2-\text{H}))</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>((\text{CH}_3)_2\text{CO})</td>
<td>4.72(s)</td>
<td>4.55(s)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>((\text{CH}_3)_2\text{SO})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B)</td>
<td>((\text{CH}_3)_2\text{SO})</td>
<td>4.80(s)</td>
<td>4.80(s)</td>
<td>7.1(bs)(1H)** ((\text{\text{N}}^+)^+)</td>
</tr>
<tr>
<td>(C)</td>
<td>((\text{CH}_3)_2\text{SO})</td>
<td>4.85(s)</td>
<td>4.85(s)</td>
<td>10.75(s)(2H)** ((\text{\text{N}}^+)^+)</td>
</tr>
<tr>
<td>(D)</td>
<td>((\text{CD}_3)_2\text{SO})</td>
<td>4.44(d) 4.64(d) (J = 12\ \text{Hz})</td>
<td>5.08(s)</td>
<td>2.50(s)((\text{\text{N}}^+)-\text{CH}_3)</td>
</tr>
<tr>
<td>(E)</td>
<td>((\text{CD}_3)_2\text{SO})</td>
<td>4.44(d) 4.64(d) (J = 12\ \text{Hz})</td>
<td>5.09(s)</td>
<td>2.50(s) 8.9(bs)(1H) ((\text{\text{N}}^+)^+) ((\text{\text{N}}^+)^+)</td>
</tr>
<tr>
<td>(F)</td>
<td>((\text{CD}_3)_2\text{SO})</td>
<td>4.44(d) 4.64(d) (J = 12\ \text{Hz})</td>
<td>5.09(s)</td>
<td>2.50(s) 9.7(bs)(2H) ((\text{\text{N}}^+)^+) ((\text{\text{N}}^+)^+)</td>
</tr>
<tr>
<td>(G)</td>
<td>((\text{CD}_3)_2\text{SO})</td>
<td>4.48(d) 4.63(d) (J = 13\ \text{Hz})</td>
<td>5.06(s)</td>
<td>2.86(qt) 1.20(t) (J = 8\ \text{Hz}) ((\text{\text{N}}^+)^+) ((\text{\text{N}}^+)^+)</td>
</tr>
<tr>
<td>(H)(a)</td>
<td>((\text{CD}_3)_2\text{SO})</td>
<td>(c \approx 4.51(t))**</td>
<td>5.02(s)</td>
<td>4.16(d) 9.01(t) (J = 8\ \text{Hz}) ((\text{\text{N}}^+)^+) ((\text{\text{N}}^+)^+) ((\text{\text{N}}^+)^+)</td>
</tr>
<tr>
<td>(I)</td>
<td>((\text{CD}_3)_2\text{SO})</td>
<td>(c \approx 4.52(t))**</td>
<td>5.00(s)</td>
<td>4.21(d) 8.89(t) (J = 8\ \text{Hz}) ((\text{\text{N}}^+)^+) ((\text{\text{N}}^+)^+) ((\text{\text{N}}^+)^+)</td>
</tr>
</tbody>
</table>

Chemical shifts are in units of \(\delta\) ppm relative to TMS as internal standard. Shifts to higher frequency are considered positive.
* see Fig 3.18. ** these NH protons are labile and exchange with any solvent water. *** near \(A_2\) pattern.
(s)=singlet (bs)=broad singlet (d)=doublet (part of AB quartet) (t)=triplet (qt)=quartet
signal indicates that formal protonation may be present, giving a symmetrical environment about each nitrogen nucleus, and hence sharp lines due to dipolar rather than quadrupolar processes dominating the nuclear relaxation (49, 50). A fast exchange process also takes place in order to give an average chemical shift for all of the \( \text{N-CH}_2^-\text{N}^- \) protons.

The effects of methylating hexammine may be seen from a consideration of the spectrum of (D)(3.12) compared with that of hexammine. Methylation produces a shift to higher frequency for the \( \text{N}^+\text{-CH}_2^-\text{N}^- \) methylene protons and inequivalence of the \( \text{N-CH}_2^-\text{N}^- \) protons, in accordance with the model (A)(3.13).

![Diagram](A)  ![Diagram](B)

**Fig 3.13**

For compounds of the type (A)(3.13) the axial protons \( \text{H}_a \) are considered to resonate at lower frequency compared to the equatorial \( \text{H}_e \) protons. Protonation of (D)(3.12), to give (E) and (F)(3.12), appears to have little effect, since the spectra are identical with that of (D)(3.12) apart from the additional \( \text{NH}^+ \) proton signals. A consideration of the series (A) \( \rightarrow \) (D) \( \rightarrow \) (G) \( \rightarrow \) (H)(I)(3.12) shows that the \( \text{N}^+\text{-CH}_2^-\text{N}^- \) methylene protons (which appear as a singlet) experience a shift to higher frequency in the order

\[ R = \text{CH}_3 > \text{CH}_2\text{CH}_3 > \text{CH}_2\text{NHCOCH}_3 > \text{CH}_2\text{NHCOCH}_2\text{CH}_3 \]
where R is the quaternary substituent on the hexamine molecule. For the 
(N-CH$_2$-N') methylene protons, 1-methylhexamine nitrate (D)(3.12) shows 
an AB quartet centred about the resonance position of the corresponding 
protons in hexamine. Upon following the above series of molecules the 
signals for the (N-CH$_2$-N') protons change from an AB quartet to a near 
$A_2$ singlet. This effect is presumably due to a progressive cancellation 
of the field effects of the positive pole of the molecule by the anisotropy 
effects of the substituents.

The values of the geminal coupling constants ($J = 12-14$ Hz) are considered 
to reflect the environment of the geminal protons, in that the adjacent 
nitrogen atoms each have an equatorially orientated lone pair (Chapter 
Four, Part II, Section 4.9).

The $^1$H NMR spectra of the 1,3,5-triazadamananes (J)(K) and (L)(3.12) 
are recorded in this work, and the data given in Table 3.4. The spectra 
of the compounds (J) and (K)(3.12) exhibit singlet resonances for the six 
(C-CH$_2$-N') protons, while the (N-CH$_2$-N') protons exhibit AB quartets 
to higher frequency, these are due to the interaction of the inequivalent 
axial and equatorial protons in the triazine methylene groups. From a 
consideration of the $^1$H NMR spectra of certain 1,3,5-triazines (52, 53) 
(Chapter Four, Part II, Section 4.9), in which the equatorial protons 
resonate at higher frequency than the axial protons, the equatorial protons 
are assigned to the higher frequency part of the AB quartet exhibited for 
the (N-CH$_2$-N') protons in these compounds. From a comparison of the 
spectra of (J) and (K)(3.12), protonation produces a shift to higher 
frequency for all protons. The spectrum of (J) in trifluoroacetic acid 
indicates that the molecule undergoes a greater degree of protonation in 
this solvent than the formally monoprotonated compound (K)(3.12).

For the compound (L)(3.12) the spectrum may be understood from a 
consideration of the structure (B)(3.13), which illustrates the equivalent
protons in this molecule. The assignments are given in Table 3.4.

Table 3.4

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>((\text{N-CH}_2\text{-N}))</th>
<th>((\text{C-CH}_2\text{-N}))</th>
<th>Others</th>
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</thead>
<tbody>
<tr>
<td>(J)</td>
<td>CF(_2)COOH</td>
<td>(4.75 \text{ (d)})</td>
<td>(5.07 \text{ (d)})</td>
<td>(6.25 \text{ (s)})</td>
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<tr>
<td></td>
<td></td>
<td>(J=13 \text{ Hz})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(K)</td>
<td>CD(_2)COOD</td>
<td>(4.35 \text{ (d)})</td>
<td>(4.65 \text{ (d)})</td>
<td>(3.75 \text{ (s)})</td>
</tr>
<tr>
<td>(L)</td>
<td>CD(_2)SO</td>
<td>(4.75 \text{ (d)})</td>
<td>(5.01 \text{ (d)})</td>
<td>(3.78 \text{ (d)})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(4.34 \text{ (s)}) (\text{H}_B) (\text{H}_C)</td>
<td>(4.2 \text{ (s)}) (\text{H}_A)</td>
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</table>

* see Fig 3.12 ** these assignments may be reversed

\((s)\)=singlet \((d)\)=doublet \((vb)\)=very broad

Chemical shifts are given in units of \(\delta\) ppm relative to TMS as internal standard. Shifts to higher frequency are considered positive.

3.6 \(\text{H}^1\) NMR STUDIES IN NITRIC ACID.

Some preliminary \(\text{H}^1\) NMR studies of substrates in 98\% nitric acid have been performed using two different procedures. The first involves the addition of the substrate to 98\% nitric acid at room temperature, which often results in a 'fume-off'. After gassing ceases the room temperature spectra of the resulting solutions are recorded in an attempt to discover the nature of fragments which are stable in nitric acid at room temperature. During the nitrolysis of hexamine in nitric acid alone to form RDX a fragment of the hexamine molecule is lost (this fragment comprises the \(\text{N(CH}_2\text{)}_3\) part of the molecule) and may form fragments in nitric acid solution which would be detectable in the \(\text{H}^1\) NMR spectrum. Such fragments may only be stable at low temperatures, while at higher temperatures they may decompose to give gaseous products. However, the presence of stable entities is
Fig 3.16

- 63 -
Fig 3.17

243 K

253 K

263 K

273 K

283 K

313 K

$\delta$ ppm

N-C$_2$H$_4$O in HNO$_3$

(HNO$_3$ at $\delta=10$ ppm)
Fig 3.18

123 K

233 K

263 K

253 K

273 K

283 K

303 K (after fume-off)

\[
\begin{array}{c}
\text{O}_2\text{N}-\text{N} \quad \quad \text{N}-\text{NO}_2 \quad \text{in} \quad \text{HNO}_3
\end{array}
\]

DPT
Fig 3.19

238 K 10

214.3 K 14

253 K 19

263 K 24

273 K 35

283 K 51

303 K 66

in HNO₃
possible in nitric acid solution, and would be expected to give signals in the room temperature spectra of substrates in nitric acid. The spectra obtained for some substrates using this technique are summarised in Figs 3.14 - 3.16.

The second approach involves the addition of the substrate to 98% nitric acid cooled to 223 K (dry ice/acetone cooling bath), pipetting a portion of the solution into a NMR tube and then inserting it into the probe preset at 233 K. The temperature is then raised to 303 K and the spectra recorded over the range 233 - 303 K. Three substrates have been chosen for this second approach, namely, 1-methoxyethyl-3,5-dinitro-1,3,5-triazacyclohexane (Fig 3.17), 3,7-dinitro-1,3,5,7-tetraazabicyclo-(3.3.1)nonane (DPT)(Fig 3.18) and hexamine (Fig 3.19). The chemistry of the reactions of these three compounds in nitric acid over the temperature range considered has been studied by Bell and Dunstan (1,2); who have characterised the products of the reaction and commented on the nature of the likely intermediates. In considering the hexamine nitrolysis reaction the likely intermediates may involve a 3,5-dinitro-1,3,5-triazacyclohexane derivative, or a 1,3,5,7-tetraazabicycle(3.3.1)nonane derivative, or both, thus the two former substrates may provide an indication of the presence of such entities in the hexamine nitrolysis reaction. If the intermediates involved are reactive fragments then the information obtained from Figs 3.14 - 3.16 may be indicative of the presence of such entities in the course of the reaction.

The use of 98% nitric acid as the solvent and reagent in these studies does provide some difficulties in recording spectra. At a temperature of 223 K the acid is near freezing point and thus spectra are only recorded at 233 K and above. Near room temperature, some gassing of the sample takes place and due to the hazardous nature of 98% nitric acid the sample is generally removed after the 233 K run, allowed to 'fume-off' at room temperature, and the 303 K spectrum recorded. It should be noted that the
temperatures reported are uncorrected. However, this is considered to be unimportant, since other factors influence the spectra which at best are only qualitatively correct. The most notable effect is the differences in absolute chemical shift positions possible. This is related to the nature of the nitric acid used and the extent of reaction which initially takes place on mixing the reactants (presumably both are related to the amount of water present in the sample or to the related concept of the acidity of the nitric acid used). On increasing the temperature there is a steady shift to higher frequency for all signals. However in most spectra the relative chemical shift differences between signals remain fairly constant, which enables comparisons to be made between the spectra of different samples. Some variation occurs between relative peak heights in spectra of the same material at comparable temperatures. This may be related to the extent of reaction and/or decomposition which takes place immediately on mixing the reactants.

The reaction is considered to be fast initially for in no case does a reactive substrate show a spectrum consistent with its presence at the beginning of the nitration reaction. The substrate is usually converted to an intermediate within 10 minutes of mixing at 223 K or higher temperatures. The spectra must therefore be considered to record the latter stages of the nitration reactions, and presumably the slow step in the reaction, that of conversion of intermediates to the product. The spectra are useful in that they extend the range of techniques available for the study of reactions in acidic media. The results are discussed further in Chapter Four, Part I, Section 4.7.

3.7 $^{14}$N NMR STUDIES.

The $^{14}$N NMR spectra of some N-nitramines and N-nitrosamines, nitric acid/ammonium nitrate solution ('NAN') and hexamine and some of its quaternary derivatives have been recorded. The results for the N-nitramines,
N-nitrosamines and nitric acid/ammonium nitrate solution are given in Table 3.5. The derivatives of hexamine considered are shown in Fig 3.20 and the data recorded in Table 3.6. The N-nitramines shown in Table 3.5 provide extensions and fill gaps in the data for other N-nitramines, which is conveniently summarised in Section 4.4.14, Chapter 4, reference (51).

The spectrum of 1,3,5-trinitros-1,3,5-triazaacyclononane provides an example of a cyclic N-nitrosamine. The available data for N-nitrosamines is summarised in Section 4.4.16, Chapter 4, reference (51). The spectrum of nitric acid/ammonium nitrate solution (‘NAN’) was recorded because little is known concerning the active species present in this nitrating mixture; and \(^{14}\)N NMR spectroscopy provides an insight to the nitrogen species present.

The \(^{14}\)N NMR spectra of certain quarternary salts of hexamine have been recorded with a view to providing an insight to the electronic structures of these molecules and to investigate the effects of substituents on the hexamine molecule. In all cases only the quarternary nitrogen atom gives a detectable \(^{14}\)N NMR signal under the conditions used, the other nitrogen atoms in these molecules presumably give signals which are too broad to be detected. No signals for hexamine or hexamine mononitrate have been detected when dimethylsulphoxide is used as solvent. In all cases the \(^{14}\)N NMR signal obtained for the quarternary nitrogen atom is relatively sharp (half-height width <150 Hz), as expected for a quadrupolar nucleus in a symmetrical environment (49). Similarly, for the N-nitramines considered the signals are relatively sharp (half-height width <100 Hz), indicating that the signals are for the nitro group nitrogen atom in these molecules. It is interesting to note that for 1-methyl-3,7-dinitro-1,3,5,7-tetraazaazabicyclo(3.3.1)nonane nitrate (Table 3.5) no signal is detected for the \(^{14}\)N-CH\(_3\) nitrogen atom, which, due to its seemingly symmetrical nature, might be expected to give a sharp signal. This may indicate a less symmetrical environment of this particular nitrogen atom, brought about by some distortion of the tetrahedral nitrogen environment, and thus the
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Chemical shift (ppm)*</th>
<th>Half-height width (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{NO}_3$</td>
<td>$(\text{CH}_3)_2\text{SO}$</td>
<td>0 (NO$_2^-$)</td>
<td>52 ± 5 **</td>
</tr>
<tr>
<td>$\text{CH}_2\text{NNO}_2$</td>
<td>$(\text{CH}_3)_2\text{SO}$</td>
<td>-22.5 ± 1 (NO$_2^-$)</td>
<td>52 ± 5 **</td>
</tr>
<tr>
<td>$\text{NO}_2$</td>
<td>$(\text{CH}_3)_2\text{CO}$</td>
<td>-33.2 ± 0.5 (NO$_2$)</td>
<td>91 ± 8 **</td>
</tr>
<tr>
<td>$\text{BSX}$</td>
<td>$(\text{CH}_3)_2\text{CO}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_2(\text{NNO}_2)_2$</td>
<td>$(\text{CH}_3)_2\text{SO}$</td>
<td>-29 ± 1 (NO$_2$)</td>
<td>60 ± 5 **</td>
</tr>
<tr>
<td>$\text{NNO}_2/\text{NH}_4\text{NO}_3$</td>
<td>neat</td>
<td>-360 ± 1 (quintet)</td>
<td>10 ± 5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-25 ± 2</td>
<td>46 ± 5</td>
</tr>
</tbody>
</table>

*Chemical shifts are quoted in units of 5 ppm with respect to NO$_2^-$ or CH$_3$NO$_2$ as internal standard. Shifts to higher frequency are considered positive.

**Spectrum recorded by Dr M. Witanowski, from a sample supplied by the author.
Fig 5.20
### Table 3.6

<table>
<thead>
<tr>
<th>Compound</th>
<th>Species</th>
<th>Chemical shift (ppm)**</th>
<th>Half-height width (Hz)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>$\leq N$</td>
<td>$-328 \pm 4$***</td>
<td>660 ± 30</td>
<td>CH$_3$OH</td>
</tr>
<tr>
<td>(B)</td>
<td>$\leq N^+ - H$</td>
<td>$-330 \pm 2$</td>
<td>42 ± 10</td>
<td>(CH$_3$)$_2$SO</td>
</tr>
<tr>
<td>(C)</td>
<td>$\leq N^+ - CH_3$</td>
<td>$-349 \pm 1$</td>
<td>63 ± 10</td>
<td>(CH$_3$)$_2$SO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-346 \pm 2$</td>
<td>28 ± 5</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>(D)</td>
<td>$\leq N^+ - CH_3$ and/or $\leq N^+ - H$</td>
<td>$-341 \pm 2$</td>
<td>50 ± 10</td>
<td>(CH$_3$)$_2$SO</td>
</tr>
<tr>
<td>(E)(a)</td>
<td>$\leq N^+ - CH_2 CH_3$</td>
<td>$-345 \pm 1$</td>
<td>42 ± 10</td>
<td>(CH$_3$)$_2$SO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-343 \pm 2$</td>
<td>17 ± 5</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>(E)(b)</td>
<td>$\leq N^+ - CH_2 CH_3$</td>
<td>$-347 \pm 1$</td>
<td>36 ± 4</td>
<td>(CH$_3$)$_2$SO</td>
</tr>
<tr>
<td>(F)</td>
<td>$\leq N^+ - CH_2 NHCOCH_3$</td>
<td>$-342 \pm 4$</td>
<td>150 ± 20</td>
<td>(CH$_3$)$_2$SO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-331 \pm 2$</td>
<td>43 ± 5</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>(G)</td>
<td>$\leq N^+ - CH_3$</td>
<td>$-332 \pm 3$</td>
<td>140 ± 30</td>
<td>(CH$_3$)$_2$SO</td>
</tr>
</tbody>
</table>

*see Fig 3.20. ** Chemical shifts are given in units of $\delta$ ppm relative to NO$_3^-$ or CH$_3$NO$_2$ as internal standard. Shifts to higher frequency are considered positive. *** Reference (54). © Spectrum recorded by Dr M. Witanowski, from a sample supplied by the author.
presence of a sizeable field gradient for this nucleus.

2.8 13C NMR STUDIES

13C NMR spectra of hexamine (A)(3.21) and certain of its quarternary salts (B) and (C)(3.21) have been recorded, together with those of 7-nitro-1,3,5-triazachexaazane (D)(3.21) and some other compounds containing methylene-bis-amine groupings (N-CH$_2$-N$^+$). The data are presented in Table 3.7. It may be seen that the assignments of the (N-CH$_2$-N$^+$) and (N$^+$-CH$_2$-N$^+$) carbon atom resonances for the quarternary salts of hexamine are not obvious, since hexamine gives a single resonance at $\delta = 77.73$ ppm for the (N-CH$_2$-N$^+$) carbon atoms, while other compounds containing this grouping have signals in the range $\delta = 61 - 72$ ppm.

Monoprotonation produces a shift to lower frequency, with the resonance position for hexamine mononitrate (B)(3.21) occurring at $\delta = 71.33$ ppm. On this basis either of the two signals for the methylene-bis-amine carbon atoms in the quarternary salts of hexamine could be assigned to the (N-CH$_2$-N$^+$) carbon atoms. A spectrum of the ethyl derivative (C)(b)(3.21) with proton coupling has been recorded. It was hoped to assign the spectrum on the basis of the $^1J(13C-H)$ coupling constants, but this has not proven possible since both types of carbon atoms are found to exhibit triplet patterns ($^1J(13C-H) \approx 160$ Hz), although the groupings appear as a quartet with the two central lines broadened, due to accidental degeneracy of some of the lines. The (N$^+$-CH$_2$-CH$_2$) carbon atoms exhibit a triplet ($^1J(13C-H) = 142$ Hz) and a quartet ($^1J(13C-H) = 128$ Hz), respectively.

In previous studies on protonation and methylation of tertiary nitrogen compounds (55,56) it has been considered that carbons bonded to a nitrogen atom, which is itself bonded to four carbons, are less shielded than those of structurally similar carbons bonded to a tertiary nitrogen atom (56). However, the systems studied here are of the type (N-CH$_2$ CH$_2$N(CH$_3$)$_3$-CH$_2$-C$^-$) and do not contain methylene-bis-amine groupings. If the above trend still holds for the compounds studied in this work then the (N-CH$_2$-N$^+$) carbon
atoms are expected to resonate at lower frequency than the (\(^{13}N\) CH\(_2\)-C\(^{13}\)) carbon atoms, as shown in Table 3.7. In support of this assignment is the fact that throughout the series of quaternary salts of hexamine the lower frequency singlet shows less variation on changing the substituent, which is in agreement with it being further away from the site of substitution and therefore less influenced by changes at that position. It should also be noted that the quaternary salts of hexamine are all highly polar molecules, while hexamine is non-polar; and thus the former compounds may interact with the polar medium (dimethylsulphoxide), whereas hexamine should be relatively unaffected. This may explain its apparently anomalous \(^{13}C\) NMR resonance position.

Data are given in Table 3.7 for some cyclic N-nitrosamines (G) and (H) (3.21), the spectra of which are complicated by the presence of restricted rotation about the N-NO bonds in the molecules. Assignments are given on the basis of the structures (A)-(D)(3.22), and are at best tentative. The other assignments given in Table 3.7 are relatively straightforward.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>(\textsuperscript{15}N-\text{CH}_2\textsuperscript{-}N\textsuperscript{15})</th>
<th>(\textsuperscript{15}N\textsuperscript{+}-\text{CH}_2\textsuperscript{-}N\textsuperscript{15})</th>
<th>Others</th>
</tr>
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<tbody>
<tr>
<td>(A)</td>
<td>(CD\textsubscript{3})\textsubscript{2}SO</td>
<td>77.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B)</td>
<td>(CD\textsubscript{3})\textsubscript{2}SO</td>
<td>71.13</td>
<td>71.13</td>
<td></td>
</tr>
<tr>
<td>(C)(a)</td>
<td>(CD\textsubscript{3})\textsubscript{2}SO</td>
<td>69.70</td>
<td>79.31</td>
<td>42.03</td>
</tr>
<tr>
<td>(C)(b)</td>
<td>(CD\textsubscript{3})\textsubscript{2}SO</td>
<td>68.89</td>
<td>76.41</td>
<td>4.64</td>
</tr>
<tr>
<td>(C)(c)</td>
<td>(CD\textsubscript{3})\textsubscript{2}SO</td>
<td>69.83</td>
<td>76.06</td>
<td>22.47</td>
</tr>
<tr>
<td>(C)(d)</td>
<td>(CD\textsubscript{3})\textsubscript{2}SO</td>
<td>69.83</td>
<td>76.06</td>
<td>8.90</td>
</tr>
<tr>
<td>(D)</td>
<td>CD\textsubscript{3}COOD</td>
<td>71.39</td>
<td></td>
<td>57.55</td>
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<tr>
<td>(E)</td>
<td>(CD\textsubscript{3})\textsubscript{2}SO</td>
<td>64.24</td>
<td></td>
<td>72.81</td>
</tr>
<tr>
<td>(F)\textsuperscript{a}</td>
<td>CDCl\textsubscript{3}</td>
<td>66.97</td>
<td></td>
<td>67.81</td>
</tr>
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</table>

\textsuperscript{a} CONT/1
Table 3.7 (Continued)

<table>
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<tr>
<th>Compound*</th>
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<th>Methylene group carbons</th>
<th>Comment</th>
</tr>
</thead>
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<td></td>
<td></td>
<td>( \alpha_{tt} ) ( \alpha_{cc} ) ( \beta )</td>
<td></td>
</tr>
<tr>
<td>(C) syn</td>
<td>(CD(<em>3)</em>(<em>2))(</em>{2})SO</td>
<td>69.7 59.5 68.1</td>
<td>All these assignments may be reversed; and are only tentative.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \alpha_{tc} ) ( \alpha_{ct} ) ( \beta' )</td>
<td></td>
</tr>
<tr>
<td>(C) anti</td>
<td></td>
<td>69.0 60.3 67.6</td>
<td>The values given are considered to be accurate to ( \pm 0.5 ) ppm.</td>
</tr>
<tr>
<td>(H) syn</td>
<td>(CD(<em>3)</em>(<em>2))(</em>{2})SO</td>
<td>55.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \alpha_{ct} ) ( \alpha_{cc} ) ( \alpha_{tt} )</td>
<td></td>
</tr>
<tr>
<td>(H) anti</td>
<td></td>
<td>56.4 45.9 64.6</td>
<td></td>
</tr>
</tbody>
</table>

Chemical shifts are given in units of \( \delta \) ppm (\( \pm 0.05 \)) relative to TMS as internal standard. Shifts to higher frequency are considered positive.

* see Fig 3.

** these assignments may possibly be reversed.

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A consideration of the spectrum of hexamine mononitrate (B)(3.21), which exhibits a single resonance signal, further substantiates the claim that for this molecule all of the atoms experience an averaged environment, as previously indicated by its $^1H$ NMR spectrum (Table 3.3). Methylation of hexamine appears to result in a shift to higher frequency for the ($^N^+\text{-CH}_2^N^-$) carbon atoms, while the ($^N\text{-CH}_2^N^{-}$) carbon atoms experience a low frequency shift compared with hexamine. 7-nitro-1,3,5-triazaadamantane (D)(3.21) exhibits a low frequency shift for the ($^N\text{-CH}_2^N^{-}$) carbon atoms compared to hexamine. For those compounds, which contain methylene-bis-amine units within a 1,3,5-triazacyclohexane ring system, the carbon atom signals appear within the range $\delta = 68 - 78 \text{ ppm}$. $^{13}C$ NMR spectra of other 1,3,5-triazacyclohexane systems have also been recorded; RDX (I)(3.21) has a value of $\delta = 64.60 \text{ ppm}$ (57) for the ($^{2}\text{NO}_2^\text{-N}\text{-CH}_2^N\text{-N}(\text{NO}_2^-)$) carbon atoms, while for the compound (J)(3.21) a value of $\delta = 80.20 \text{ ppm}$ has been reported (58) for the methylene carbons of ($^{3}\text{Cl}\text{-CS}\text{-N}\text{-CH}_2^N\text{-N}^\text{(SCCl}_3^-)$).

The other ($^N\text{-CH}_2^N^{-}$) groupings presented in Table 3.7 are found in aza-substituted bicyclo(3,5,1)nonane systems; and the carbon atom in the $(^N\text{-CH}_2^N^{-})$ methylene bridge resonates within the rather narrow range of $\delta = 64 - 69 \text{ ppm}$. For the quarternary salts of hexamine the ($^N^+\text{-CH}_2^N^-$) carbon atom resonances are considered to appear in the range $\delta = 58 - 80 \text{ ppm}$. It is interesting to note that for the $^{13}C$ NMR spectra of the quarternary salts of hexamine the ($^N^+\text{-CH}_2^N^-$) carbon atom resonances move to higher frequency, as $R$ changes, in the order

$$R = \text{CH}_3 \gg \text{CH}_2\text{CH}_3 \gg \text{CH}_2\text{NCOCH}_3 \gg \text{CH}_2\text{NCOCH}_2\text{CH}_3$$

where $R$ is the quarternary substituent on the hexamine cage.
Part I of this Chapter summarises the $^1$H, $^{14}$N and $^{13}$C NMR spectra obtained for some selected N-nitramines, N-nitrosamines, 1,3,5,7-tetramethylbicycle(3,3,1)nonanes, hexamine and derivatives. The $^1$H NMR spectra of these classes of compounds are recorded with a view to the interpretation of the $^1$H NMR spectra of substrates in nitric acid solutions. This technique is applied to the study of the hexamine nitrolysis reaction. The spectra obtained are interpreted on the basis of the structural and electronic features possessed by these classes of compounds.

The study of hexamine and derivatives is particularly rewarding, for molecular systems of well defined geometry provide the best models for the study of electronic effects on chemical shifts.

The study of the $^1$H NMR spectra of these classes of compounds allows predictions to be made concerning the spectral characteristics of the 1,3,5-triazine and hexahydropyrimidine ring systems, based upon the chemical shifts and coupling constants of the methylene-bis-amine geminal protons. This aids in the interpretation of the spectra of unknown compounds and gives an indication of their structural features.

Aspects of the results given in Part I are discussed further in Chapter Four, Parts I and II.
Molecular orbital calculations have been performed on some selected molecules from each of the classes of compounds of interest in this work. The object of these calculations is two-fold: Firstly it was hoped that computation of ground state electronic energies might give an insight into the mechanistic pathways possible (for example Fig 1.2) for the hexamine nitrolysis reaction. Secondly, the calculations are performed on selected N-nitramines, N-nitrosamines, hexamine and derivatives to provide an insight into their electronic structures and molecular conformations. Preliminary attempts to assign and interpret their NMR spectra with regard to the theoretical results are made. Molecular orbital calculations have been successfully performed for some selected primary and secondary N-nitramines, N-nitrosamines, hexamine and derivatives, but for the 1,3,5,7-tetraazabicyclo(3.3.1)nonane derivatives satisfactory convergence conditions could not be obtained. Thus the first object of the calculations has failed, and this approach to the hexamine nitrolysis reaction has been abandoned. However, the results of the calculations do give good results for the ground state properties, provide a good guide to molecular conformation for the molecules considered, and the preliminary attempts to assign and interpret the NMR spectra are encouraging.

The INDO (Intermediate Neglect of Differential Overlap) molecular orbital method is employed in these calculations. This method is excellently described by Pople and Beveridge (5). A modified INDO method, using finite perturbation theory, has been used to calculate the spin-spin coupling constants for some selected molecules; this procedure is described by Schaeffer and Wasylishen (61).
INDO molecular orbital calculations have been performed on the N-nitramines given in Fig 3.23.

For nitramine (A)(3.23) three conformations were employed in the calculation, these are illustrated in Fig 3.24.
Fig 3e25

(A) 

(B) Total energy = -75.964 eV
\( \mu \) calc = 4.49 D

(C) Total energy = -75.944 eV
\( \mu \) calc = 3.97 D

(D) 

\( \angle \text{NCH} = \angle \text{NCN} = 109^\circ 28' \)
\( \angle \text{CNO} = 126^\circ \)
\( \angle \text{CNN} = 117^\circ \)
\( \angle \text{CCN} = 122^\circ \)
\( \angle \text{CNN} = 119^\circ \)
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<th>Compound</th>
<th>( \text{NH}_2\text{-NO}_2 ) (3.24)</th>
<th>( \text{CH}_3\text{NH}-\text{NO}_2 ) (3.25)</th>
<th>( \text{CH}_2(\text{NHNO}_2)_2 ) (3.26)</th>
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<td>Bond Length (Å)</td>
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<td></td>
<td></td>
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<td>1.34</td>
<td>1.34</td>
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<tr>
<td>( \text{N}_1 - \text{C} )</td>
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<td>1.46</td>
</tr>
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<td>1.01</td>
<td>1.01</td>
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<tr>
<td>( \text{N}_2 - \text{O} )</td>
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<td>1.21</td>
<td>1.21</td>
</tr>
<tr>
<td>( \text{C} - \text{H} )</td>
<td></td>
<td>1.09</td>
<td>1.09</td>
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<tr>
<td>Total Energy</td>
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<td>-67.522</td>
<td>-125.177</td>
</tr>
<tr>
<td>Dipole Moment (D)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Calc</td>
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<td>4.42</td>
<td>5.68</td>
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<td>Exp</td>
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<td>~4.4 (64)</td>
<td>2.16 (65)</td>
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<td></td>
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<td>5.207</td>
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<td>4.303</td>
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<td>( \text{C}<em>2\text{H}</em>{av} )</td>
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<tr>
<td>Compound</td>
<td>(B)(3.25)</td>
<td>(D)(3.25)</td>
<td>(F)(3.23)</td>
</tr>
<tr>
<td>----------</td>
<td>-----------</td>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td><strong>Bond Lengths (Å)</strong></td>
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<td><strong>(CH)_2NNO_2</strong></td>
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<tr>
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<td>1.46</td>
<td>1.45</td>
<td>1.45</td>
</tr>
<tr>
<td>N₁ - H</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>N₂ - O</td>
<td>1.22</td>
<td>1.22</td>
<td>1.22</td>
</tr>
<tr>
<td>C - H</td>
<td>1.09</td>
<td>1.08</td>
<td>1.08</td>
</tr>
</tbody>
</table>

| **Total Energy (A.U)** | -75.964 | -198.323 | -180.642 |
| **Dipole Moment (D)** | **Calc** | **Exp** |
| | 4.49 | 4.94 | 4.72 |
| | 4.61 (66) | 5.78 (66) | 5.53 (67) |

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<th>nitroso</th>
<th>nitro</th>
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<td>4.306</td>
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<tr>
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<td>-</td>
<td>-</td>
</tr>
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</table>

* see Fig 3.23

** The total energies are recorded in atomic units (A.U)(Hartrees).

Conversion to eV or kcal/mole may be achieved using the following expressions: 1 AU = 27.12 eV; 1 eV = 23 kcal/mole.
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<td>( 2^{4} )</td>
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</tr>
<tr>
<td>( 2^{5} )</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.9

References:

- \( \text{CH}_3 \text{CN} \)
- \( \text{CH}_3 \text{CN} \)
- \( \text{NH}_3 \text{CN} \)

\( N_{\nu} \)
The staggered conformation \( (C)(3.24) \) is found to have the lowest energy, the results for it are given in Table 3.8. The predicted dipole moment of \( (C)(3.24) \) is 4.18D, this is somewhat higher than the experimental dipole moment values \( (3.57 \text{D (gas)}(62); 3.78 \text{D (solution)}(63)) \). Tyler (62) considers that the molecule possesses a somewhat 'flattened' conformation (with an angle of 52° between the \( \text{NH}_2 \) and \( \text{NO}_2 \) planes). Calculations performed on conformations of nitramine with this angle between the planes have total energies somewhat higher than those for the conformations \( (A) - (C)(3.24) \), but the predicted dipole moments for these forms are somewhat lower \( (\mu = 3.97\text{D for the staggered conformation analogous to } (C)(3.24)) \), in better agreement with experiment. Coupling constant calculations have been performed on the lowest energy conformation \( (C)(3.24) \) of nitramine. The results are given in Table 3.9.

For methyl nitramine \( (B)(3.23) \) twelve possible conformations have been examined. The conformation \( (A)(3.25) \) is found to have the lowest calculated total energy. The results for this conformation are given in Table 3.8, while those for the coupling constant calculation on this form are given in Table 3.9. The calculated dipole moments for all twelve conformations lie in a fairly narrow range \( (\mu = 4.14 - 4.42 \text{D}) \), with the lowest energy conformation \( (A)(3.25) \) having the highest value \( (\mu_{\text{calc}} = 4.42\text{D}) \), which is in good agreement with the experimental dipole moment \( (\mu_{\text{exp}} \approx 4.40 \text{D}) \) (64).

For dimethyl nitramine \( (C)(3.23) \) six possible conformations are considered, involving rotation about the C-N bonds and about the N-N bond. They fall into two groups:-

(a) those with the \( \text{C}_2\text{NNO}_2 \) fragment planar, with the \( \angle_{\text{NNO}} = 120^\circ \),

this group has the lowest total energies.
(b) those with the C<sub>N</sub>N fragment planar, but with the NO fragment inclined at an angle of 90° to the C<sub>N</sub>N plane, the angle FNO is also 120°.

The lowest energy conformations of each group are given in (B) and (C) (3.25). The conformation (B)(3.25) is found to have the lowest total energy for this molecule, and the results for this conformation are given in Table 3.8. The results of the coupling constant calculation for this conformation are given in Table 3.9, and are in good agreement with experiment. The calculated dipole moment for this conformation is also in good agreement with experiment.

For methylenedinitramine (D)(5.23) only three of the many possible conformations have been examined, these are illustrated in Fig 3.26. The results for the lowest energy form (A)(3.26) are reported in Table 3.8. The value predicted for the dipole moment of this form is considerably higher than that found experimentally for methylenedinitramine. However, the value predicted for the conformation (C)(3.26), which has the highest total energy of the three conformations considered, is much nearer to the experimental value. It is possible that a conformation exists for methylenedinitramine, similar to (C)(3.26), which gives a dipole moment in good agreement with experiment, and has the lowest total energy.

![Diagrams of conformations](image)
Fig 30.27
For RDX (E) (3.25) a modified chair form after Orloff et al. (70), illustrated in (D) (3.25), has been subjected to calculation by the INDO method. The results are recorded in Table 3.8. An INDO coupling constant calculation has been attempted for this molecule, but satisfactory convergence conditions could not be obtained.

For 1-nitroso-3,5-dinitro-1,3,5-triazacyclohexane (F) (3.25) the basic RDX structure, illustrated in (D) (3.25), has been used to obtain the coordinates for this compound, which were employed in the INDO calculation. The results for this molecule are given in Table 3.8.

For all the N-nitramines considered the calculated charge densities are conveniently summarised in Fig 3.27.

3.11 MOLECULAR ORBITAL CALCULATIONS ON N-NITROSAMINES.

In addition to the calculation for 1-nitroso-3,5-dinitro-1,3,5-triazacyclohexane (F) (3.25), calculations have been performed on dimethylnitrosamine (A) (3.28) and 1,3,5-trinitroso-1,3,5-triazacyclohexane (B) (3.28).

For dimethylnitrosamine (A) (3.28), twelve conformations are considered. They fall into three classes.

(a) those with a planar C_2NNO fragment, with \( \angle \text{NNO} = 120^\circ \), this group has the overall lowest calculated total energies.
(b) those with the \( C_2NN \) fragment planar, but with the NO fragment inclined at an angle of \( 90^\circ \) to the \( C_2NN \) planar fragment, with \( \angle NNO = 120^\circ \).

(c) those with a planar \( C_2NNO \) fragment, with \( \angle NNO = 180^\circ \) (linear NNO unit), this group has the highest overall calculated total energies.

The four conformations within each class involve rotation about the C - N bonds of the molecule. The three lowest energy forms for each class, which involve the same orientations of the two methyl groups, are illustrated by (A) - (C) (3.29). The results for the lowest energy form (A) (3.29) are given in Table 3.10. The calculated charge densities and bond orders for this conformation are summarised in Fig 3.31. An INDO coupling constant calculation has been attempted for this molecule, but satisfactory convergence conditions could not be obtained.
Table 3.10

<table>
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<tr>
<th>Compound*</th>
<th>(A)(3.29) (CH₂)₂NHO</th>
<th>(A)(3.31)</th>
<th>(B)(3.31)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond Lengths (Å)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>N₁ - N₂</td>
<td>1.34</td>
<td>1.34</td>
<td>1.34</td>
</tr>
<tr>
<td>N₁ - C</td>
<td>1.46</td>
<td>1.45</td>
<td>1.45</td>
</tr>
<tr>
<td>N₂ - O</td>
<td>1.24</td>
<td>1.22</td>
<td>1.22</td>
</tr>
<tr>
<td>C - H</td>
<td>1.09</td>
<td>1.08</td>
<td>1.08</td>
</tr>
<tr>
<td>Total Energy (A.U)**</td>
<td>-58.280</td>
<td>-145.274</td>
<td>-145.275</td>
</tr>
<tr>
<td>Dipole Moment (D)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calc</td>
<td>3.37</td>
<td>3.71</td>
<td>3.40</td>
</tr>
<tr>
<td>Exp</td>
<td>3.98 (71)</td>
<td>3.91-3.99 (67)</td>
<td>3.91-3.99 (67)</td>
</tr>
<tr>
<td></td>
<td>4.01 (66)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.22 (36)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atomic Populations</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>N₁</td>
<td>5.078</td>
<td>5.130 5.131 5.132</td>
<td>5.131</td>
</tr>
<tr>
<td>N₂</td>
<td>4.847</td>
<td>4.830 4.832 4.830</td>
<td>4.828</td>
</tr>
<tr>
<td>C₁(cis)</td>
<td>3.840</td>
<td>3.730 3.737 3.737</td>
<td>3.731</td>
</tr>
<tr>
<td>C₁av</td>
<td>1.021</td>
<td>1.030 1.021 1.021</td>
<td>1.029</td>
</tr>
<tr>
<td>C₂(trans)</td>
<td>3.837</td>
<td>3.724 3.724 3.730</td>
<td>3.731</td>
</tr>
<tr>
<td>C₂av</td>
<td>1.023</td>
<td>1.038 1.038 1.030</td>
<td>1.029</td>
</tr>
</tbody>
</table>

* see Fig 3.28.

** The total energies are recorded in atomic units (A.U)(Hartrees). Conversion to eV or kcal/mole may be achieved using the following expressions: 1 AU = 27.12 eV; 1 eV = 23 kcal/mole.
Fig 3e-20
For the trinitroso derivative (B)(3.28) the two possible conformational isomers (A) and (B)(3.31) have been considered. The coordinates for these forms were calculated using the basic RDX structure, illustrated in (D)(3.25). The results for these two forms are given in Table 3.10. A summary of their calculated charge densities is given in Fig 3.30.

![Diagram of molecular structures](image)

(A) anti

(B) syn

Fig 3.31

3.12 MOLECULAR ORBITAL CALCULATIONS ON HEXAMINE AND DERIVATIVES.

Molecular orbital calculations have been performed on hexamine, certain quarternary derivatives of hexamine, and 7-nitro-1,3,5-triazaadamantine (Fig 3.32), using the INDO molecular orbital method. For hexamine and its quarternary derivatives the geometries employed in the calculations are standard geometries, with all bond angles tetrahedral and bond lengths of C - N = 1.47 Å and C - H = N - H = 1.09 Å (4). For the 1-ethyl derivative the N⁺-CH₂-CH₂ side chain has bond lengths of N - C = 1.47 Å, C - C = 1.54 Å and C - H = 1.09 Å with all angles tetrahedral. For the 1-acetimidomethyl derivative, the N⁺-CH₂-NHCOCH₂ side chain has bond lengths N⁺-CH₂ = 1.47 Å, CH₂-NH = 1.46 Å, NH - CO = 1.32 Å, C - O = 1.36 Å, CO - CH₂ = 1.52 Å and C - H = N - H = 1.09 Å. All of the angles are taken to be tetrahedral with the exception of the NCC (= NCO = CCO), which are 120°. For 7-nitro-1,3,5-triazaadamantane the bond lengths are
**Fig. 3.32**

\[ \text{TE} = -95.586 \text{ a.u.} \]
\[ \mu_{\text{calc}} = 0.000 \text{ D} \]

\[ \text{TE} = -96.145 \text{ a.u.} \]
\[ \mu_{\text{calc}} = 10.93 \text{ D} \]

\[ \text{TE} = -96.499 \text{ a.u.} \]
\[ \mu_{\text{calc}} = 19.59 \text{ D} \]

\[ \text{TE} = -104.583 \text{ a.u.} \]
\[ \mu_{\text{calc}} = 11.39 \text{ D} \]

\[ \text{TE} = -104.947 \text{ a.u.} \]
\[ \mu_{\text{calc}} = 20.02 \text{ D} \]

\[ \text{TE} = -107.686 \text{ a.u.} \]
\[ \mu_{\text{calc}} = 3.41 \text{ D} \]

\[ \text{TE} = -115.015 \text{ a.u.} \]
\[ \mu_{\text{calc}} = 11.90 \text{ D} \]

\[ \text{TE} = -114.762 \text{ a.u.} \]
\[ \mu_{\text{calc}} = 13.93 \text{ D} \]
$N - C - (N) = 1.47 \, \AA$, $N - C - (C) = 1.50 \, \AA$, $C - C = C - NO_2 = 1.47 \, \AA$, $N - O = 1.34 \, \AA$ and $C - H = 1.09 \, \AA$. All angles are tetrahedral except $\angle ONO = \angle CNO$, which are $120^\circ$. For the 1-methyl derivatives the staggered conformation (as opposed to the eclipsed conformation) is found to be of lowest energy and the results for this form only are considered. For the 1-ethyl and 1-acetamidomethyl derivatives the staggered conformations only are presented. In order to obtain a realistic result for 7-nitro-1,3,5-triazasadamantane, the two forms involving rotation about the $\stackrel{\cdot}{C}NOS$ bond have been used in the calculations for this molecule. Taking average values of the charge densities for these staggered and eclipsed forms leads to a symmetrical charge density distribution (Fig 3.32), which is considered to best represent this molecule. The results of the calculations for hexamine and its derivatives are conveniently summarised in Fig 3.32.

5.13 ATTEMPTED INTERPRETATION OF NITROGEN NMR CHEMICAL SHIFTS.

Molecular orbital calculations have been performed on some selected N-nitramines, N-nitrosamines, hexamine and derivatives in an attempt to correlate their $^1H$ NMR chemical shift differences with calculated changes in the value of the local paramagnetic term of the screening tensor. Theoretical aspects of the approaches available for the calculation of chemical shifts may be found in reference (72). In this work the average excitation energy approximation has been used in an attempt to obtain a semi-quantitative account of the chemical shift differences. Within this approximation, the paramagnetic component of the nitrogen screening tensor, $\sigma_\text{N}^P$, changes of which may be considered to dominate the differences in chemical shifts of nuclei other than protons (73) in a closely related series of molecules, may be expressed (74, 75) as
\[ \sigma_N^p = - \frac{e^2}{2m^*c^2} \langle r^{-3} \rangle^p \sum Q_{NT} \]  

\[ \sum Q_{NT} = \frac{1}{3} \left( P_{X_{NT}} + P_{Y_{NT}} + P_{Z_{NT}} \right) \]

\[ = \frac{2}{3} \left( P_{X_{NT}}^2 + P_{Y_{NT}}^2 + P_{Z_{NT}}^2 \right) \]

\[ + 2 \left( P_{X_{NT}}^{*2} + P_{Y_{NT}}^{*2} + P_{Z_{NT}}^{*2} \right) \]

where \( P \) is the appropriate element in the charge density matrix and \( T \) are the atoms joined to the nitrogen atom under consideration. The \( \langle r^{-3} \rangle^p \) term, called the 'orbital expansion' term, may be calculated from Slater-type atomic orbitals as (76)

\[ \langle r^{-3} \rangle^p = \frac{1}{3} \left( \frac{Z_{2p}^2}{n^4 a_0} \right) \]

where \( Z_{2p} \) is the effective nuclear charge, \( n \) is the principal quantum number and \( a_0 \) is the Bohr radius. \( Z_{2p} \) has been calculated using the following expression (72):

\[ Z_{2p} = 5.35 - 0.5P_{2s2s} - 0.35(P_{2px2px} + P_{2py2py} + P_{2pz2pz}) \]

Another approach to the evaluation of the orbital expansion term is to use the equation reported by Velenik and Lynden-Bell (77)

\[ \langle r^{-3} \rangle^p = 3.099 - 0.732 q_{\text{net}} \]

where \( q_{\text{net}} \) is the total excess electron charge on the nitrogen atom.

Within the average excitation energy approximation, changes in \( \Delta E_{av} \) are considered negligible when a series of closely related compounds is examined. Consequently the observed \( ^{14}N \) NMR chemical shifts should be proportional to the product of \( \langle r^{-3} \rangle^p \) and \( \sum Q_{NT} \) under these conditions.
For N-nitramines and N-nitrosamines the values of the required parameters necessary for the calculations are given in Table 3.11. A plot of \( \left\langle r^{-3} \right\rangle _{2p} \sum Q_{\text{NT}} \) against \( \delta_N \) is given in Fig 3.35 for N-nitramines and Fig 3.35 for N-nitrosamines. Similarly, if \( \left\langle r^{-3} \right\rangle _{2p} \) is evaluated using the expression involving \( Z_{2p} \) (equation (d)) the observed \( ^{14} \mathrm{N} \) chemical shifts should be proportional to the product of \( (Z_{2p})^3 \) and \( \sum Q_{\text{NT}} \).

The values of the required parameters necessary for this calculation are recorded in Table 3.11, and a plot of \( (Z_{2p})^3 \sum Q_{\text{NT}} \) against \( \delta_N \) is given in Fig 3.34 for N-nitramines and Fig 3.36 for N-nitrosamines. It may be seen that the plots of \( \left\langle r^{-3} \right\rangle _{2p} \sum Q_{\text{NT}} \) and \( (Z_{2p})^3 \sum Q_{\text{NT}} \) against \( \delta_N \) for each class of compound are very similar.

Calculations have been performed on hexamino and certain quarternary derivatives, these are illustrated in Fig 3.37. For these calculations the orbital expansion term \( \left\langle r^{-3} \right\rangle _{2p} \) is calculated using the equation (e) only. The values necessary for the calculation and the results are given in Table 3.12. A plot of the calculated local paramagnetic term \( \left\langle r^{-3} \right\rangle _{2p} \sum Q_{\text{NT}} \) against the experimental chemical shifts \( \delta_N \) for these compounds is given in Fig 3.38.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Species</th>
<th>( \sum_{\text{NT}} )</th>
<th>( Z_{2p} )</th>
<th>( (Z_{2p})^2 )</th>
<th>( \langle r^{-3} \rangle_{2p} )</th>
<th>( \langle r^{-5} \rangle_{2p} \sum_{\text{NT}} )</th>
<th>Ref</th>
<th>Exp (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NO}_3^- )</td>
<td>( \text{NO}_3^- )</td>
<td>2.893</td>
<td>3.692</td>
<td>145.51</td>
<td>3.679</td>
<td>10.442</td>
<td>0</td>
<td>(110)</td>
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<tr>
<td>( \text{H}_2\text{N}-\text{NO}_2 )</td>
<td>N</td>
<td>2.034</td>
<td>3.303</td>
<td>73.26</td>
<td>2.933</td>
<td>5.964</td>
<td>-</td>
<td>(120)</td>
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<tr>
<td>( \text{NO}_2 )</td>
<td>NO</td>
<td>2.015</td>
<td>3.649</td>
<td>136.73</td>
<td>3.599</td>
<td>10.131</td>
<td>-</td>
<td>(121)</td>
</tr>
<tr>
<td>( \text{CH}_2\text{NHNO}_2 )</td>
<td>N</td>
<td>2.186</td>
<td>3.327</td>
<td>80.47</td>
<td>2.964</td>
<td>6.480</td>
<td>-20.6±8</td>
<td>(116)</td>
</tr>
<tr>
<td>( \text{NO}_2 )</td>
<td>NO</td>
<td>2.832</td>
<td>3.657</td>
<td>138.49</td>
<td>3.608</td>
<td>10.216</td>
<td>-23.2±6</td>
<td>(116)</td>
</tr>
<tr>
<td>( (\text{CH}_2\text{NHNO}_2)_2 )</td>
<td>N</td>
<td>2.365</td>
<td>3.341</td>
<td>88.22</td>
<td>2.979</td>
<td>7.103</td>
<td>-212±10</td>
<td>(117)</td>
</tr>
<tr>
<td>( \text{NO}_2 )</td>
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<td>3.655</td>
<td>138.03</td>
<td>3.595</td>
<td>10.111</td>
<td>-21.8±6</td>
<td>(58)</td>
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<tr>
<td>( (\text{CH}_2\text{NHNO}_2)_3 )</td>
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<td>2.365</td>
<td>3.341</td>
<td>88.22</td>
<td>2.952</td>
<td>6.981</td>
<td>-</td>
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<td>10.203</td>
<td>-34±1</td>
<td>(110)</td>
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<td>( \text{NO}_2^- )</td>
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<td>3.190</td>
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<tr>
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<td>8.815</td>
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<tr>
<td>( (\text{CH}_2\text{NNO})_3 )</td>
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<td>3.003</td>
<td>7.295</td>
<td>-130±10</td>
<td>**</td>
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<tr>
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<td>3.415</td>
<td>109.11</td>
<td>3.225</td>
<td>8.633</td>
<td>+132±15</td>
<td>**</td>
</tr>
</tbody>
</table>

* Chemical shifts are given in units of \( \delta \) ppm relative to \( \text{NO}_3^- \) or \( \text{CH}_2\text{NH}_2 \) as internal standard. Shifts to higher frequency are considered positive.

** Spectrum recorded by Dr M. Witanowski.
Fig 3.35

N-nitrosamines.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Species</th>
<th>(\sum_{\text{NT}})</th>
<th>(\delta_{\text{net}})</th>
<th>(&lt;r^{-3}&gt;_{2\rho})</th>
<th>(&lt;r^{-3}&gt;<em>{\Sigma</em>{\text{NT}}})</th>
<th>Exp (ppm)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>(\hat{N})</td>
<td>2.294</td>
<td>-0.265</td>
<td>2.905</td>
<td>6.665</td>
<td>-328±4***</td>
</tr>
<tr>
<td>(B)</td>
<td>(\hat{N}^+-\text{H})</td>
<td>2.134</td>
<td>-0.031</td>
<td>3.122</td>
<td>6.662</td>
<td>-330±2*</td>
</tr>
<tr>
<td>(C)</td>
<td>(\hat{N}^+-\text{CH}_3)</td>
<td>2.271</td>
<td>-0.038</td>
<td>3.127</td>
<td>7.101</td>
<td>-349±1*</td>
</tr>
<tr>
<td>(D)</td>
<td>(\hat{N}^+-\text{CH}_2\text{CH}_3)</td>
<td>2.264</td>
<td>-0.023</td>
<td>3.120</td>
<td>7.063</td>
<td>-345±1*</td>
</tr>
<tr>
<td>(E)</td>
<td>(\hat{N}^+-\text{CH}_2\text{NHCOCH}_3)</td>
<td>2.267</td>
<td>-0.019</td>
<td>3.113</td>
<td>7.055</td>
<td>-342±1*</td>
</tr>
<tr>
<td>(F)</td>
<td>(\hat{N}^+-\text{H})</td>
<td>2.194</td>
<td>-0.056</td>
<td>3.119</td>
<td>6.845</td>
<td>-341±2*</td>
</tr>
</tbody>
</table>

* see Fig 3.  ** experimental values are taken from Table 3, 6. Values in DMSO are used where available. Chemical shifts are given in units of \(\delta\) ppm relative to NO\textsubscript{2} or CH\textsubscript{2}NO\textsubscript{2} as internal standard. Shifts to higher frequency are considered positive. *** CH\textsubscript{3}OH as solvent, reference (54). @ Spectrum recorded by Dr. M. Witanowski.
The results of the foregoing calculations are discussed in Chapter Four, Part II, Section 4.10.

Part II of this Chapter summarises the results of the INDO molecular orbital calculations performed on selected N-nitramines, N-nitrosamines, hexamine and derivatives. The calculations give good results for the available ground state properties. The predicted lowest total energy forms for the individual molecules considered are found to represent reasonable ground state molecular conformations. Attempts to interpret the nitrogen chemical shift changes within these series of molecules are encouraging. The results of these calculations may also be used to obtain information concerning molecular properties, such as the barrier to rotation about the N-N bond in N-nitramines and N-nitrosamines. The predicted charge densities may also be used to study the effects of substituents on the hexamine molecule, and to follow changes in the electronic structures of a series of related molecules. These applications are discussed in Chapter Four, Part II, together with other aspects of the results summarised here.
PART III: SUMMARY OF THE REACTIONS OF HEXAMINE AND SOME STRUCTURALLY RELATED COMPOUNDS STUDIED.

3.14 INTRODUCTION.

Nitration reactions of hexamine, certain of its quarternary derivatives, and 7-nitro-1,3,5-triazaadamantane in nitric acid and nitric acid/ammonium nitrate solutions have been studied with a view to a better understanding of the nitrogen nitrolysis reaction.

Dilution studies have been performed on the reaction of 7-nitro-1,3,5-triazaadamantane with nitric acid alone. These are based upon the procedures described by Bell and Dunstan (2), which have been reported for the study of the reaction of hexamine with nitric acid alone.

The experimental conditions employed in the study of these nitration reactions, and the characterisation of the products of the reactions are given in Chapter Five.

3.15 NITRATION REACTIONS OF 7-NITRO-1,3,5-TRIAZAADAMANTANE.

Preliminary nitration reactions have been performed using the reagent 'NAN', which is prepared by the addition of ammonia to 99% nitric acid. Some evolution of gas occurs, but on standing a clear solution is obtained. This ammonium nitrate/nitric acid mixture (mole ratio about 3:4) is used industrially as the source of nitric acid for the production of RDX and HMX from hexamine. It is much safer to use than 99% nitric acid, since it does not fume appreciably at room temperature, is relatively non-corrosive, it does not burn the skin, and reactions may be carried out at room temperature, or higher.

When 7-nitro-1,3,5-triazaadamantane is added to an excess of 'NAN' at room temperature it dissolves completely in a few hours without stirring. On leaving the solution to stand at room temperature for two to three days, crystals of ammonium nitrate separate out. Filtration of the solution...
through a Gouch crucible into a large excess of ice-water or direct addition of the whole mixture to a large excess of ice-water, results in the formation of a white precipitate in high yield. This material is designated Nitronitramine II. Infra-red, \(^1\)H NMR spectra and micro-analytical data for this material (Experimental, Section 5.11) suggest that it may be characterised as the compound:

\[
\begin{array}{c}
\text{NO}_2 \\
\text{N} \ \\
\text{N} \\
\text{N} \\
\text{NO}_2 \\
\text{CH}_2\text{NH}_3^+\text{NO}_3^- \\
\end{array}
\]

In a similar experiment the 7-nitro-1,5,5-triazaadamantane is dissolved in an excess of 'NAN' over a period of one hour, with stirring. On addition of the solution to an excess of ice-water at this time no precipitate is obtained immediately, but on standing Nitronitramine II precipitates from the aqueous solution in low yield. If this experiment is repeated, but the solution is diluted with cold ethanol slowly with cooling (ice-bath), instead of dilution with water, a dense white precipitate of predominantly ammonium nitrate is produced. On filtration of the precipitate and addition of the solid obtained to an excess of water most of the material (ammonium nitrate) dissolves. Filtration of this solution gives a small residue, which is designated Nitronitramine III. Infra-red, \(^1\)H NMR spectra and microanalytical data (Experimental, Section 5.13), suggest that the material may be characterised as the compound:

\[
\begin{array}{c}
\text{O}_2\text{N} \ - \ - \\
\text{N} \\
\text{N} \\
\text{NH}_2^+\text{NO}_3^- \\
\text{NO}_2 \\
\end{array}
\]
When Nitronitramine III is added to NaN at room temperature, it dissolves completely after a few hours to give a clear solution. The mixture is then left to stand at room temperature for two days, whereupon addition to an excess of ice-water produces a white precipitate on shaking for a few minutes. This material is found to be Nitronitramine II.

Dilution studies, based on the procedures of Bell and Dunstan (2), have been performed on the reaction of 7-nitro-1,3,5-triazaadamantane with nitric acid alone.

The general procedure for these reactions consists of the addition of 1 gm of 7-nitro-1,3,5-triazaadamantane to 16 ml of fuming nitric acid (BDH grade with a concentration of 95% or better) below 233 K (dry ice/acetone cooling bath) with stirring, over a period of about five minutes. The reaction is then treated with the appropriate diluent as described below.

Dilution of the reaction mixture with 75 ml cold (213 K) ethanol slowly with a pipette, keeping the reaction temperature below 243 K, results in the initial precipitation of a white material which redissolves on further addition of the cold ethanol solution. Upon completion of the ethanol addition, the solution is filtered cold to give a small residue of 7-nitro-1,3,5-triazaadamantane-1-nitrate. By leaving the filtrate to stand at room temperature for about an hour, a white precipitate settles out. The solution is filtered to give the compound Nitronitramine III in high yield.

The addition of 50 ml cold water slowly with a pipette to a reaction mixture, keeping the temperature below 243 K, results in the initial formation of a white precipitate which redissolves on further addition of water. After the addition of water is complete, a clear solution results. Extraction of the aqueous solution with cold ethanol or ether affords low yields of Nitronitramine III. With the ether extraction the aqueous
extract also gives Nitronitramine III in low yield. The amounts of Nitronitramine III obtained on dilution with water at low temperatures are consistently lower than those obtained on dilution of the reaction mixture with ethanol, probably because the product is a nitrate and should be appreciably more soluble in the aqueous mixture.

On dilution of the nitration mixture with a cold aqueous solution of sodium nitrite (containing 3 gm NaNO₂ in 50 ml water) slowly with a pipette keeping the temperature below 248 K, a reaction appears to take place, since a bright yellow mixture is produced. After completion of the aqueous sodium nitrite addition the solution is filtered, but the yellow product rapidly decomposes in air to form a glue, and has not been characterised. In a similar experiment, the temperature of the reaction mixture was allowed to rise to 253 K during the addition of the aqueous sodium nitrite solution. The bright yellow colouration disappears at this temperature and a milky solution results. Addition of cold ethanol to the solution at this point precipitates a white solid, identified as sodium nitrate. Removal of this material and decantation of the ethanolic solution leaves a solid, identified as Nitronitramine III, possibly formed on addition of ethanol to the solution.

The reaction of Nitronitramine III with a nitrosation mixture consisting of sodium nitrite, dilute sulphuric acid, and water (2 gm, 10 ml, 10 ml) at about 283 K (ice-water bath), results in the formation of the mixed nitro-nitroso compound, characterised on the basis of its Infra-red, ¹H NMR spectra and microanalytical data (Experimental, Section 5.14).
If a nitration mixture is allowed to reach a temperature of 283 - 293 K after the addition of the 7-nitro-1,3,5-triazaadamantane to the fuming nitric acid below 233 K, then rapidly cooled to 233 K and 50 ml cold water added, keeping the temperature below 233 K, a white precipitate is obtained. This material is designated Nitromitramine I. The same material is obtained if the nitration mixture is either 'drowned out' in an excess of ice-water or ice-water is added to the reaction mixture. The Infra-red and $^1$H NMR spectra of this material are given in Fig 5.9. Inconsistent microanalytical data are obtained for this material which, together with the Infra-red and $^1$H NMR spectra indicate that this material is a mixture. Attempts to characterise the constituents of the mixture are described in the Experimental Section. It would seem, however, that the material may contain two compounds, both having the structure given below, where the group R requires assignment.

![Chemical structure](image)

In a similar experiment if the temperature is rapidly raised from 233 K to 293 K over 12 minutes, then the reaction mixture cooled rapidly to 233 K, and 50 ml cold water slowly added, keeping the temperature below 243 K, the precipitation of a white solid occurs. This material is designated Nitronitramine IV, it is also formed from nitration reactions of 7-nitro-1,3,5-triazaadamantane with 98% nitric acid, rather than the fuming nitric acid used previously, when the reaction mixture is diluted with cold water below 243 K or when it is 'drowned out' in an excess of ice-water. Reaction of Nitronitramine III with fuming nitric
acid at 233 K, followed by dilution of the reaction mixture with cold water below 243 K, gives an unstable solid from which Nitronitramine IV may be obtained. When first formed in the dilution of these reaction mixtures, Nitronitramine IV is often unstable, however it may be stabilised by dissolving the crude product in concentrated nitric acid. The Infrared and $^1$H NMR spectra of this compound are given in Fig 5.12. These, together with the microanalytical data, indicate that Nitronitramine IV may be characterised as the compound given below.

The addition of 1 gm of 7-nitro-1,3,5-triazadamantane to a mixture of acetic anhydride/nitric acid (20 ml/10 ml) at 233 K over 5 minutes, followed by the slow addition of cold water to the mixture, results in the formation of a white precipitate, identified as Nitronitramine I. The addition of 50 ml of cold (233 K) acetic anhydride to a cold (243 K) nitration mixture also results in the formation of Nitronitramine I.

1 gm of Nitronitramine III added to 25 ml acetic anhydride, with stirring, at room temperature dissolves after about an hour to give a clear solution. The addition of 75 ml of water to this mixture, followed by stirring for 30 minutes, results in the formation of a white precipitate. This material is designated Nitronitramine VII. (Experimental, Section 5.14).

The addition of 1-methyl-7-nitro-1,3,5-triazadamantane nitrate to fuming nitric acid at 263 K with stirring, followed by further stirring of the reaction mixture at 253 - 263 K for 30 minutes, results in dissolution of the material to give a clear solution. This is then added to a large
excess of crushed ice and left to stand for 30 minutes, whereupon a white precipitate slowly develops. This material is designated Nitronitramine VI. On the basis of Infra-red, $^1$H NMR and microanalytical data, (Experimental, Section 5.16), this material may be characterised as the compound given below.

\[
\begin{align*}
\text{CH}_3 & \quad \text{NO}_3^- \\
\text{O}_2\text{N} - \text{N} & \quad \text{N} - \text{NO}_2
\end{align*}
\]

3.16 OTHER SELECTED REACTIONS OF 7-NITRO-1,3,5-TRIAZADAMANTANE.

Details of the reactions described here and the characterisation of the products are given in Chapter Five.

The reaction of 7-nitro-1,3,5-triazadamantane with aqueous sodium nitrite in the presence of dilute sulphuric acid, hydrochloric acid or acetic acid over the pH range 1 - 6 produces only one product, 3,7-dinitroso-5-nitro-1,3,7-triazabicyclo(3,3,1)nonane in good yield.

\[
\text{NO}_2 \quad \text{NsNO}_2/\text{acid} / 283 \text{K} \quad \overset{\rightarrow}{\text{ON}} - \text{N} - \text{N} - \text{NO}_2
\]

Reaction of o-toluenesulphonyl chloride and 10% sodium hydroxide simultaneously with vigourous stirring to an aqueous solution of 7-nitro-1,3,5-triazadamantane with the temperature maintained at 363 - 373 K and the pH between 8 - 11, results in the formation of a compound which analyses as the ditosyl derivative.
When 7-nitro-1,3,5-triazaadamantane is refluxed in methanol containing methyl iodide and the reaction mixture is treated with powdered silver nitrate, 1-methyl-7-nitro-1,3,5-triazaadamantane nitrate is obtained, via the iodide.

The addition of cold (273 K) concentrated nitric acid to a cold (298 K) aqueous solution of 7-nitro-1,3,5-triazaadamantane with stirring, results in the immediate precipitation of 7-nitro-1,3,5-triazaadamantane nitrate.
In this work some reactions of hexamine in nitric acid and in nitric acid/ammonium nitrate solutions have been investigated. The dilution studies described by Bell and Dunstan (2) on the reaction of hexamine with nitric acid alone have been taken as the basis for these studies, and the reactions described by these authors (2) (summarised in Chapter Two, Section 2.3) have been confirmed in the present work. Supplementary to the reactions performed by Bell and Dunstan (2) the effect of the addition of ice-water all at once to a cold nitration mixture has been examined, as well as the reaction of hexamine with nitric acid/ammonium nitrate ('NAN').

The general procedure involves the addition of 2 g of hexamine to 16 ml 98% nitric acid below 243 K with stirring and cooling (dry ice/acetone cooling bath). Then 50 ml crushed ice is added all at once to the nitration mixture, this results in a temperature rise. A white precipitate is formed, which is filtered, washed with water, chilled ethanol and ether, and dried. An Infra-red spectrum of the product indicates a mixture of hexamine dinitrate and PCX.

If the material first obtained by the addition of water to the nitration mixture is filtered immediately and the product washed with a large excess of water, most of it dissolves, but a small amount of less soluble material remains on the filter. This is then washed with cold ethanol and ether, and dried. The material has a melting point of 335 - 336 K. An Infra-red spectrum of this material (Fig 5.1) indicates that it is neither
hexamine dinitrate nor PCX. The Infra-red data indicate the presence of 
\( \geq \text{N-NO}_2 \ (1530 \text{ cm}^{-1} \ (s)) \) and \( \geq \text{N-H} \ (3375 \text{ cm}^{-1} \ (v)) \) groupings. No suitable solvent has been found for recrystallisation or for a molecular weight determination, decomposition generally occurs. On the basis of its Infra-red and microanalytical data (Experimental, Section 5.1) the compound has been formulated as 1,3-dinitro-1,3,5-triazacyclohexane, given below.

\[ \text{N} \quad \text{N} \quad \text{N} \quad \text{NH} \]

The reaction of hexamine with nitric acid/ammonium nitrate solution has been investigated. Hexamine dissolves in nitric acid/ammonium nitrate solution ("NAN") at room temperature to give a clear solution. After standing at room temperature for 60 hours, rod-like crystals of ammonium nitrate are precipitated. The solution is then added to an excess of ice-water. A clear solution is obtained, no insoluble material is recovered. Hexamine mononitrate and hexamine dinitrate react similarly, no insoluble material being recovered. If the aqueous solution thus obtained is neutralised to pH 5 - 6 with aqueous ammonia and left to stand for several hours at room temperature, a very low yield of RDX (identified by comparison of the Infra-red spectrum of the material with that of an authentic sample (E.R.D.E.1)) is obtained in each case.

3.18 NITRATION REACTIONS OF QUARTERNARY DERIVATIVES OF HEXAMINE.

Nitration reactions of the quarternary derivatives (A) - (D)(Fig 3.39) have been studied.

The addition of 1-methylhexamine nitrate (A)(3.39) to 98% nitric acid at 263 K with stirring, followed by addition of the reaction mixture to an
An excess of crushed ice results in the formation of a white precipitate. This product is considered to be 1-methyl-3,7-dinitro-1,3,5,7-tetraazabicyclo(3.3.1)nonane nitrate (E) (Fig 3.39).

The reaction of 1-ethylhexamine nitrate (B) (Fig 3.39) with 98% nitric acid under these conditions gives the analogous 1-ethyl-3,7-dinitro-1,3,5,7-tetraazabicyclo(3.3.1)nonane (F) (Fig 3.39).

However, the reaction of 1-acetamidomethylhexamine nitrate (C) (Fig 3.39) and 1-propionamidomethylhexamine nitrate (D) (Fig 3.39) with nitric acid under these conditions produces no insoluble material on addition of the reaction mixture to ice-water.

When hexamine dinitrate is refluxed in water or an appropriate alcohol (RCH₂CH₂, R = CH₃, CH₂CH₃, CH₂CH₂CH₂ etc) the product is found to be 1-methylhexamine nitrate (A) (Fig 3.39) irrespective of the nature of the solvent (59, 60).

\[
\begin{align*}
\text{(A)} & \quad \begin{array}{c}
\text{CH}_3 \\
\text{N}^+ \\
\text{NO}_3^- \\
\end{array} \\
\text{(B)} & \quad \begin{array}{c}
\text{CH}_2\text{CH}_3 \\
\text{N}^+ \\
\text{NO}_3^- \\
\end{array} \\
\text{(C)} & \quad \begin{array}{c}
\text{CH}_2\text{N}^+\text{HCOCH}_3 \\
\text{N}^+ \\
\text{NO}_3^- \\
\end{array} \\
\text{(D)} & \quad \begin{array}{c}
\text{CH}_4\text{N}^+\text{HCOCH}_2\text{CH}_3 \\
\text{N}^+ \\
\text{NO}_3^- \\
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{(E)} & \quad \begin{array}{c}
\text{O}_2\text{N}^- \text{N}^+ \text{N}^+ \text{N}^- \text{NO}_2^- \\
\text{(F)} & \quad \begin{array}{c}
\text{O}_2\text{N}^- \text{N}^+ \text{N}^- \text{NO}_2^- \\
\text{(G)} & \quad \begin{array}{c}
\text{CH}_3 \\
\text{N}^+ \\
\text{NO}_3^- \\
\text{(H)} & \quad \begin{array}{c}
\text{CH}_3 \\
\text{N}^+ \\
\text{NO}_3^- \\
\end{array} \\
\end{array}
\end{align*}
\]

Fig 3.39
Evaporation of a solution of hexamine dinitrate in water or methanol, which has been refluxed for several hours, gives an oil. An infra-red spectrum of the oils obtained in each case indicates that the major product is 1-methylhexamine nitrate (A) (Fig 3-39). Further reaction of the oil with 70% nitric acid at 273 K gives 1-methylhexamine trinitrate (H) (Fig 3-39).

When hexamine dinitrate is refluxed in water for 3 hours, then the solution evaporated under reduced pressure, an oil is produced. This is then left to stand at 263 K overnight, when ammonium nitrate precipitates. The oil is then added to 70% nitric acid at 273 K with stirring, whereupon a white precipitate forms. This material is filtered using a Gouch crucible, and is considered to be 1-methylhexamine trinitrate (H) (Fig 3-39) on the basis of its infra-red, $^1$H NMR and microanalytical data (Experimental, Section 5.3). If an attempt is made to recrystallise this material from hot methanol, 1-methylhexamine dinitrate (G) (Fig 3-39) is obtained. By refluxing hexamine dinitrate in methanol for 3 hours, evaporating the solution under reduced pressure until an oil is obtained, leaving the oil to stand at 263 K overnight, the precipitation of 1-methylhexamine nitrate (A) (Fig 3-39), contaminated with ammonium nitrate is achieved. Filtration of this material and subsequent addition of the oil to 70% nitric acid at 273 K with stirring results in a solid product. The addition of cold methanol brings about complete precipitation of the product, which again is considered to be 1-methylhexamine trinitrate (H) (Fig 3-39).

The addition of the derivatives (A) - (D) (Fig 3-39) to a large excess of nitric acid/ammonium nitrate ("NAN") at room temperature, followed by standing for 60 hours, results in the precipitation of ammonium nitrate. The addition of the solution to an excess of ice-water gives no insoluble material in all cases. If the solution is then neutralised with aqueous ammonia and left to stand at room temperature for a few hours a small amount of RDX is recovered in each case.
It is interesting to note that, while all of the other compounds considered dissolve to give a clear solution, the addition of 1-methylhexamine nitrate to 'NAN' (or 90% nitric acid) results in the crystals becoming a deep purple colour, which on dissolution give a bright orange solution. It is also of interest that preliminary nitrosation studies on 1-methylhexamine nitrate give only unstable coloured products, which have not been characterised.

Part III of this Chapter summarises the reactions performed on hexamine, certain of its quarternary derivatives, and 7-nitro-1,3,5-triazaadamantane. In particular the results of nitration reactions are recorded, for it is considered that a knowledge of the nitration reactions of compounds structurally related to hexamine, such as the quarternary derivatives of hexamine and 7-nitro-1,3,5-triazaadamantane, will aid in the elucidation of the mechanism of the hexamine nitrolysis reaction. The results of the nitration reactions of the quarternary derivatives of hexamine are disappointing, for in few cases are isolatable products obtained. However, for 7-nitro-1,3,5-triazaadamantane it is found that this compound undergoes nitrolysis under conditions very similar to those employed for hexamine. The products obtained are either 1,3,5-trinitro-1,3-diazacyclohexane derivatives or 5-nitro-1,3,7-triazabicyclo(3,3,1)nonane derivatives and are thus comparable with the products obtained under similar conditions for hexamine. Other selected reactions of 7-nitro-1,3,5-triazaadamantane show that this compound undergoes similar reactions to hexamine, giving products comparable to those of hexamine. The results described here are further discussed in Chapter Four, Part I; and their implications to the hexamine nitrolysis reaction considered.
Introduction.

Part I of this Chapter is concerned with the results of the studies of the nitration reactions of hexamine (A)(4.1), certain of its quaternary derivatives (B)(4.1), tetraazabishomoadamantanane (C)(4.1) and 7-nitro-1,3,5-triazaadamantanene (D)(4.1).

A study of the nitration reactions of the compounds (B) - (D) (4.1), which are structurally related to hexamine, gives an indication of the nitration mechanisms possible for hexamine.

The results of the study of the $^1$H NMR spectra of substrates in nitric acid alone are discussed with a view to the elucidation of the mechanism of nitration of hexamine.

NITRATION REACTIONS OF QUARTERNARY DERIVATIVES OF HEXAMINE.

From the nitration reactions of 1-methylhexamine nitrate (B)(a)(4.1) and 1-ethylhexamine nitrate (B)(b)(4.1) in nitric acid alone at 263 K, described in Chapter Three, Part II, Section 3.18; it appears that the nitration reactions of these compounds proceed via a 1,3,5,7-tetraaza-bicycle(3.5.1)nonane derivative (A)(4.2), as illustrated by the isolation of 1-methyl and 1-ethyl-5,7-dinitro-1,3,5,7-tetraazabicycle(3.5.1)nonane.
from the appropriate reaction on the addition of the nitration mixture to ice-water. With 1-acetamidomethylhexamine nitrate (B)(c)(4.1) and 1-propionamidomethylhexamine nitrate (B)(d)(4.1) no product is isolated under the same conditions. However, as the yield and stability of 1-ethyl-3,5-dinitro-1,3,5,7-tetraazabicyclo(3.3.1)nonane is markedly less than the corresponding 1-methyl derivative, it is possible that, for these substituents, a decrease in the stability of the corresponding 1,3,5,7-tetraazabicyclo(3.3.1)nonane derivatives (A)(4.2) occurs. Consequently degradation takes place to give products which are water soluble and thus would not be detected under the conditions employed for these reactions.

Fig 4.2

For 1-methylhexamine nitrate (B)(a)(4.1), reaction with 70% nitric acid at 273 K gives 1-methylhexamine trinitrate (B)(4.2). This molecule is not very stable and easily loses a molecule of nitric acid to give 1-methylhexamine dinitrate (C)(4.2), which is stable. It is thus reasonable to assume that for 1-methylhexamine nitrate and also for the other quarternary derivatives of hexamine (B)(b - d)(4.1) the initial reaction of these compounds in 98% nitric acid will be protonation of the molecule, which then reacts to give a 1,3,5,7-tetraazabicyclo(3.3.1)nonane derivative (A)(4.2), this being isolated by the action of ice-water on the reaction mixture. A possible reaction scheme is given in Fig 4.3.
Norris (78) has investigated the nitrolysis reactions of the quarternary derivatives (A)(4.4) in nitric acid/acetic anhydride/acetic acid at 273 - 298 K. The final products of the reactions are the linear nitramines (B)(4.4).

This suggests that for 1-acetamidomethylhexamine nitrate (B)(c)(4.1) and 1-propionamidomethylhexamine nitrate (B)(d)(4.1), the reaction of these substrates in nitric acid alone may proceed via the intermediate (A)(4.3), this intermediate reacts further to give linear nitramines (B)(4.5), which would be expected to be water soluble.
The reaction of hexamine dinitrate (D)(4.2) with refluxing water or alcohols, such as methanol, ethanol, isopropanol and tertiarybutanol, followed by cooling to give 1-methylhexamine nitrate (B)(a)(4.1) as product (59, 60) has given rise to speculation concerning the mechanism of the reaction. Foss et al (59) consider that the reaction involves partial degradation of the hexamine dinitrate cage to give a 1,3,5,7-tetraazabicyclo(3.3.1)nonane derivative, which reacts with formaldehyde (produced by degradation of some of the hexamine dinitrate present) to form a 1-methyl-1,3,5,7-tetraazabicyclo(3.3.1)nonane derivative, which then recyclises to give 1-methylhexamine dinitrate, which furnishes 1-methylhexamine nitrate as the final product. Some possible steps in this scheme are illustrated in Fig 4.6.
However, Swissman and Weis (79) have reported that 3,7-diaza­ 
edrocyclo-(3,3.1) nonane sulphate undergoes reductive methylation to give 1-methyl-
1,3-diazaadamantane sulphate via initial cyclisation to form the diaza-
adamantane cage, followed by methylation. This scheme is illustrated 
below.

It is thus possible that the above reaction only involves methylation 
of the hexamine cage under reductive conditions furnished by the release 
of formaldehyde from some degradation of the hexamine dinitrate present.

Tschunke (80) reports that the reaction of hexamine with methyl deriv­
etives (such as the iodide, chloride, bromide, nitrate, etc.) results in 
the formation of the appropriate 1-methylhexamine salts. Instead of 
hexamine, these methyl derivatives may be reacted with ammonia and 
formaldehyde (or a source of formaldehyde, such as trioxane) to give the 
appropriate 1-methylhexamine salts. Another method of formation of these 
derivatives involves the reaction of formaldehyde and ammonia with suitable 
ammonium salts, these are probably methylated by the excess formaldehyde, 
and further reaction gives the appropriate 1-methylhexamine salts. These 
observations of Tschunke (80) appear to negate the schema of Foss et al 
(60)(Fig 4.6). However, the observations of Tschunke (80) and Foss et 
al (59, 60) represent two opposing views. Either the 1-methylhexamine 
derivatives are formed by reaction of appropriate fragments to give the 
product, or the fragments first form hexamine which is then reacted upon 
by a suitable reagent to give the desired product. In this particular 
case the evidence seems to slightly favour the reaction of an appropriate 
reagent upon hexamine; the reactions involving formaldehyde and ammonia 
presumably proceed via the initial synthesis of hexamine.
The condensation of formaldehyde and ethylenediamine in alkaline conditions gives tetraazabishomoadamantane (C) as the principal product (81). Simkins and Wright (82) have described nitration reactions of this compound, which are summarised in Fig 4. On reaction with nitric acid/acetic anhydride/ammonium nitrate at 338 K the only product is RDX in low yield. Reaction with hydrochloric acid in ether gives the monohydrochloride salt (A), which reacts with nitric acid/acetic anhydride/acetic acid at 273 K to give 1,5-dinitro-imidazolidine (B). Reaction of tetraazabishomoadamantane with nitric acid/acetic anhydride/acetic acid in the presence of acetyl chloride gives the linear compound (C) in good yield. A stable tetranitrate salt of tetraazabishomoadamantane (D) is also formed on the reaction of the unstable dinitrate (E) with 70% nitric acid in ethanol. This salt (D) gives the imidazolidine (B) on reaction with nitric acid/acetic anhydride/acetic acid/acetyl chloride. The tetranitrate salt was originally formulated as (B) by Simkins and Wright (82), because tetraazabishomoadamantane was first assigned the incorrect structure (A) by Bischoff (81). Kang et al (83) have re-investigated the synthesis and structure of the tetranitrate salt of tetraazabishomoadamantane and conclude that the compound is actually on the basis of its ¹H NMR data and % nitric acid content. Kang et al (83) conclude that tetraazabishomoadamantane (C) can undergo degradation to give ethylenediamine and formaldehyde, which may react further with suitable reagents to give imidazolidine derivatives. This type of reaction is shown (83) to occur readily in the presence of acylating agents and alkali, and presumably also occurs with the nitration reactions summarised in Fig 4.7.

![Fig 4.8](image-url)
NITRATION REACTIONS OF 7-NITRO-1,3,5-TRIAZAADAMANTANE

The reactions of 7-nitro-1,3,5-triazadamanante (D)(4.1) are described in Chapter Three, Part II, Section 3.15. The reaction of 7-nitro-1,3,5-triazadamanante with nitric acid/ammonium nitrate solution ('NAN') for 60 hours at room temperature, followed by dilution of the reaction mixture with excess ice-water, gives Nitronitramine II (E)(4.9) as the principal product. Studies involving the termination of the reaction by the addition of a diluent, such as water or ethanol, indicate that 7-nitro-1,3,5-triazadamanante nitrate (A)(4.9) and Nitronitramine III (C)(4.9) may be intermediates in this particular nitration reaction, for they have been isolated from the reaction. A possible scheme for this reaction is illustrated in Fig 4.9.
The pathway illustrated in Fig 4.9 is considered to be favoured in the presence of ammonium nitrate, which may act to decrease the effective acidity of the nitration species.

The reaction of 7-nitro-1,3,5-triazadadamantane (D)(4,1) with 98% nitric acid, followed by dilution of the reaction mixture with water, leads to the formation of either Nitronitramine I or Nitronitramine IV. Nitronitramine I is considered to be a mixture of compounds of general formula (A)(4,10), while Nitronitramine IV is thought to have the structure (B)(4,10). Studies on the low temperature reaction, involving dilution of the reaction mixture with cold water or ethanol below 243 K, result in the isolation of the 1,3,7-triazabicyclo(3,3,1)nonane derivative, Nitronitramine-III (C)(4,10). Dilution of the low temperature reaction mixture with aqueous sodium nitrite indicates that a reaction takes place (a bright yellow colouration develops), but the reaction product is unstable in air and has not been characterised.

One reaction of this type was finally terminated by the addition of cold ethanol, after the aqueous sodium nitrite addition. Some Nitronitramine III was detected as a reaction product in this case. However, Nitronitramine III (C)(4,10) forms the compound (D)(4,10) on reaction with acidified aqueous sodium nitrite solution, and thus it is reasonable to assume that the absence of (D)(4,10) from the reaction products of the nitration mixture diluted with aqueous sodium nitrite indicates that Nitronitrate III is not present in the normal nitration reaction. Similarly, the fact that Nitronitramine III is only precipitated after standing for a time from a nitration mixture diluted with cold water or ethanol, indicates that it is formed by the action of the diluent on a precursor to Nitronitramine III. Because sodium nitrite appears to participate in the reaction to form an unstable product, it is possible that it is reacting with a precursor to Nitronitramine III, the latter compound is only formed on the addition of ethanol to a reaction mixture containing aqueous sodium nitrite.
The nature of the products isolated from the nitration reaction of 7-nitro-1,3,5-triazaadamantane (D) with nitric acid alone, implies that the reaction proceeds via a stepwise scission process. It is thus instructive to consider possible stepwise scission pathways available in the nitration of 7-nitro-1,3,5-triazaadamantane. One such pathway is illustrated in Fig 4.9, for the formation of Nitronitramine II (E) from the reaction of 7-nitro-1,3,5-triazaadamantane with nitric acid/ammonium nitrate solution. An alternative nitration pathway is illustrated in Fig 4.11. It indicates that many possible products may be obtained on termination of the reaction at appropriate stages. It also indicates that the intermediate (B), present in Fig 4.9, can lead to the formation of (C) by stepwise scission, as well as to Nitronitramine III (F) by elimination of formaldehyde. The scheme given in Fig 4.9 is easily incorporated into the more general scheme shown in Fig 4.11. The compound (B) may be an intermediate in the reaction, the compound (F) being formed from it by the dilution of the nitration mixture with cold ethanol or water. It is also possible that a precursor such as (B) may be acted upon by aqueous sodium nitrite solution to give an unstable product, since the compound (B) has two tertiary alkylamine sites which could undergo nitrosation.
Fig 4.11
The scheme given in Fig 4.11 allows for the formation of final products involving rearrangement with elimination of formaldehyde. If, however, the reaction is to be considered to proceed with involvement of nitric acid only, the major pathway would be protonation of 7-nitro-1,3,5-triazaadamantane to give the mononitrate (A)(4.11), followed by the reactions (A) →(B) →(C) →(D) →(E)(4.11), with Nitronitramine IV as the true product of nitration. This compound may also be expected as the final product if compounds of the type (A)(4.12) are susceptible to scission at the exocyclic C-N bond, as shown below, under the influence of nitric acid.

The scheme given in Fig 4.11 represents the intermediates as containing the hydroxymethyl groupings. Under strong nitrating conditions in nitric acid alone it is perhaps more realistic to consider that the intermediates contain nitroxymethyl groupings where hydroxymethyl groupings are shown. The effect of this substitution may well alter the course of the reactions shown in Fig 4.11, but the formation of (E)(4.11) as final product may again be favoured. Under milder nitration conditions the hydroxymethyl intermediates may be relatively stable and other products may be formed. The formation of Nitronitramine II (E)(4.9) upon nitration with 'NAN', which is a relatively mild nitration medium, suggests that this may be the case. It should also be noted that the intermediates in the nitration reaction with nitric acid alone are expected to be temperature dependent. Raising the temperature not only increases the rate of the
of the reaction but also reduces the stability of some of the possible intermediates. This implies that nitration reactions carried out at higher temperatures or in nitration media other than nitric acid alone may not be directly comparable with the low temperature nitration reactions in nitric acid alone.

4.5 NITRATION REACTIONS OF HEXAMINE.

The major features of the reaction of hexamine with nitric acid alone are summarised in Chapter Two, Section 2.3. Evidence relating to the mechanism of this reaction, which gives RDX as the major product and can give rise to a variety of linear and cyclic by-products, has been summarised by several authors (2,7,9,10). Kinetic studies (25,26) have indicated that the initial product of the reaction, hexamine dinitrate, is rapidly converted into an intermediate. In turn this gives RDX by a relatively slow, rate-determining step. Previous studies (3, 24) have indicated that the intermediate has a cyclic structure with a side-chain containing at least one carbon atom. Intermediates of type (A)(a-f)(4,13) are favoured as the most probable ones (2,3,7,24).

Bell and Dunstan (1) have considered the reactions of 1-acetoxymethyl- and 1-methoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (A)(g) and (A)(h) (4,13) in nitric acid, and conclude from dilution studies (summarised in Chapter Two, Section 2.4) that for these substrates the intermediate in the
reaction is probably the nitrooxymethyl derivative (A)(a)(4,13).

A similar study on the reaction of hexamine in nitric acid alone (2) indicates the participation of the more complex bis(nitrooxymethyl)amino-
methyl derivative (A)(c)(4,13) in the reaction of hexamine with nitric
acid, although the evidence is not conclusive. Bell and Dunstan (2)
consider that, although the general features of the hexamine nitrolysis
reaction can be explained by the presence of the intermediate (A)(c)(4,13),
this is probably an over-simplification of a complex situation. For
example, the nature and relative stabilities and reactivities of inter-
mediate nitrolysis products may show a greater dependence on temperature
than is at first indicated.

The complexity of the reaction is further stressed by a consideration
of the products formed on the rapid addition of ice-water to the low-
temperature reaction mixture, this reaction is described in Chapter Three,
Part III, Section 3.12. Hexamine dinitrate and PCX are found to be the
major products; 3,5-dinitro-1,3,5-triazacyclohexane (B)(4,13) may also
be present in low yield, assuming it is not formed by the action of water
on the hexamine dinitrate/PCX mixture. Although it is possible that
3,5-dinitro-1,3,5-triazacyclohexane (B)(4,13) is formed by hydrolysis of
PCX brought about by the rapid dilution of the reaction mixture with
water, it is more likely that 3,5-dinitro-1,3,5-triazacyclohexane is the
precursor to PCX, the latter compound is considered to be formed by the
action of a suitable diluent on an intermediate present in the nitrolysis
mixture. If this latter situation occurs it is instructive to consider
the possible mode of formation of this compound. Its formation in a
stepwise degradation of hexamine may occur according to the scheme given
in Fig 4.14.
Alternatively, 3,5-dinitro-1,3,5-triazacyclohexane (B)(4.13) might be formed from suitable fragments. The formation of RDX or derivatives from hexamine on reaction with nitric acid also involves the loss of an N(CH₃)₃ fragment, the fate of which is not known.

The reaction emphasises that the nature and mode of addition of a diluent is important in determining the nature and yields of the products. The slow addition of water to a cold nitrolysis mixture kept below 243 K results in the formation of PCX in good yield. If a reaction mixture is allowed to reach 273 K before cooling and water added below 243 K, PCX is only a minor product and RDX is the major one. At higher temperatures RDX is formed almost exclusively. The use of the rapid addition of ice-water as a method for terminating a nitrolysis reaction is rather more drastic than those generally employed. There is a rapid temperature rise on the addition of the ice-water, but no RDX is detected in the products. The initial nitrolysis product, considered to be hexamine dinitrate, is, however, isolated. A scheme which might explain these
results is given in Fig 4.15. This scheme incorporates that given in Fig 4.14 and contains the bis(nitroxymethyl)aminomethyl compound (A)(c)(4.13), postulated as an intermediate in the reaction (2). The route summarised in Fig 4.14, and given in Fig 4.15, is considered to represent a 'low-temperature' route, and indicates the products expected from a low temperature nitrolysis reaction mixture. At temperatures above 273 K, RDX is the major product isolated from nitrolysis reaction mixtures. The intermediate (A)(c)(4.13) is considered to be the likely intermediate for nitrolyses carried out at higher temperatures (2). It is thus considered that the alternative route to that given in Fig 4.14, and shown in Fig 4.15, could be regarded as the 'high temperature' route. Where mixtures of RDX and PCX are obtained it is considered that both routes are possible.

The inference is that the mode of nitration of the bicyclic intermediate (A)(4.15) is temperature dependant; in other words, the stabilities of the intermediates (B) and (C)(4.15) are temperature dependant.

The participation of an intermediate such as (C)(4.15) does not invalidate the results of the dilution studies employing acetic anhydride, aqueous sodium nitrite or water as the diluent, nor the results of the addition of primary dinitramines to the nitrolysis reaction mixture, for if an intermediate such as (A)(c)(4.13) is considered to be a possible intermediate, then one such as (C)(4.15) is also possible, being structurally little different to (A)(c)(4.13).

4.6 NITROSATION REACTIONS OF HEXAMINE AND DERIVATIVES.

A feature of the reactions of hexamine is the possibility of the formation of derivatives of both 1,3,5,7-tetraazabicyclo(3.3.1)nonane and 1,3,5-triazacyclohexane. In alkaline, neutral or weakly acidic conditions, 1,5,5,7-tetraazabicyclo(3.3.1)nonane derivatives are formed while under more acidic conditions 1,3,5-triazacyclohexanes are obtained.
Fig 4.15
This is illustrated by the formation of 3,7-dinitro-1,3,5,7-tetraazabicyclo(3.3.1)nonane (DPT) from hexamine under nitration conditions which are mildly acidic, while under strongly acid conditions RDX is the major product. Similarly, under nitrosation conditions both types of derivatives may be formed. A consideration of the nitrosation reactions of hexamine may aid the elucidation of the mechanism of nitration of hexamine.

Bachmann and Deno (84) have rationalised the nitrosation experiments performed on hexamine and show that hexamine can give rise to two distinct nitrosation products, the formation of which is pH dependant. The dinitroso derivative (A) (4.16) may be formed in up to 76% yield at pH 3-6, a mixture of the dinitroso derivative and the trinitroso derivative (B) (4.16) is obtained at pH 2, while the trinitroso derivative is formed exclusively in 50% yield at pH 1.

\[ \text{A} \quad \text{B} \]
\[ \text{pH 3-6} \quad \text{pH 1} \]

Fig 4.16

Tada (85) has studied the kinetics of the acid decomposition of hexamine, including the effect of sodium nitrite. Acid decomposition of hexamine by aqueous hydrochloric acid over the pH range 3 - 7 is considered to involve monoprotonation of hexamine, followed by breakage of a C-N bond to give a 1,3,5,7-tetraazabicyclo(3.3.1)nonane derivative. In strong acid solution it presumably decomposes further to give 1,3,5-triazacyclo-hexane derivatives, which finally decompose to give formaldehyde and ammonia derivatives. The overall equation for the decomposition of
hexamine in aqueous hydrochloric acid is given by:–

\[ \text{C}_6\text{H}_{12}\text{N}_4\text{HCl} + 3\text{HCl} + 6\text{H}_2\text{O} \rightarrow 4\text{NH}_4\text{Cl} + 6\text{CH}_2\text{O} \]

The kinetics of the decomposition of hexamine in acid indicate a 'water' reaction, which in strong acid is accompanied by an acid catalysed reaction:

\[ k = k_{\text{water}} + k'[\text{H}^+] \]

In the presence of sodium nitrite a marked catalytic effect takes place. In acid solution the nitrite is considered to be present almost completely as molecular nitrous acid. With excess sodium nitrite an equilibrium is considered to exist between the nitrite anion and the monoprotonated hexamine to give the free amine and nitrous acid:

\[ \text{C}_6\text{H}_{12}\text{N}_4\text{H}^+ + \text{NO}_2^- \rightleftharpoons \text{C}_6\text{H}_{12}\text{N}_4 + \text{HNO}_2 \]

The results suggest that the catalytic action of nitrous acid is due to reaction with the C-N bond of the monoprotonated hexamine and cleavage of the bond by the reaction of nitrous acid with the secondary amine formed. This is summarised in Fig 4.17.

Fig 4.17
It is also possible that the dinitroso derivative is formed by initial attack of the nitronium ion on the free amine, hexamine.

The formation of the trinitroso derivative from hexamine under strong acid conditions presumably involves the degradation of the 1,3,5,7-tetraazabicyclo(3.3.1)nonane system to give the 1,3,5-triazacyclohexane system (85).

Preliminary nitrosation experiments on 1-methylhexamine nitrate resulted in the formation of unstable coloured products, which have not been characterised.

Nitrosation of 7-nitro-1,3,5-triazaadamantane results in the formation of 5-nitro-3,7-dinitroso-1,3,7-triazabicyclo(3.3.1)nonane (A)(4.18),

\[
\text{NaNO}_2/\text{H}_2\text{O}/\text{H}_2\text{SO}_4/ 278 \text{ K} \rightarrow
\]

![Reaction diagram](image)

Fig 4.18

presumably by a mechanism similar to that given for hexamine in Fig 4.17. Whereas hexamine may form either of the derivatives (A) or (B)(4.16), only (A)(4.18) is formed under the conditions employed. This may be due to the different protonation effects shown by 7-nitro-1,3,5-triazaadamantane compared to hexamine, or due to increased stability of the compound (A)(4.18) to acid decomposition, compared to compound (A)(4.16).

4.7 $^1H$ AND $^{14}N$ NMR STUDIES.

An examination of the available $^1H$ NMR data of N-nitramines (Chapter Three, Part I, Section 3.2; and references (37,38,49,86-91)) enables the characteristic chemical shift ranges for a variety of N-nitramine groupings to be elucidated, these are presented in Table 4.1. It may be seen from
Table 4.1 that the respective methylene protons in each N-nitramine grouping fall in comparatively narrow chemical shift ranges, although some classes do overlap.

The shielding effect of the \(-N(NO_2)\) grouping is considered to be very similar to that of oxygen in O-alkyl compounds \((37,38)\), this is best illustrated for groupings of the type \(-N(NO_2)-CH_2-X, X=H, C\) (Table 4.1). However, where \(X\) is a more electronegative atom, such as C, N or Halogen, the methylene protons are deshielded in the presence of this atom and appear at higher frequency. This is illustrated in Table 4.1, particularly for compounds containing the dinitramine grouping \(-N(NO_2)-CH_2-N(NO_2)\), the nitroso grouping \(-N(NO_2)-CH_2-N(O)\) and groupings of the type \(-N(NO_2)-CH_2-O-X\).

The chemical shift data in Table 4.1 are useful for the characterisation of N-nitramines and, together with a knowledge of the expected shielding effect of the \(-N(NO_2)\) grouping, it is possible to predict the spectrum of a given N-nitramine. Some examples of this approach are given in Fig 4.19. The compounds considered in Fig 4.19 are some possible intermediates or by-products expected in the nitrolysis reactions of hexamine and other related tertiary amines. These compounds might be expected to be stable in nitric acid solution at low temperature, but have not been isolated from nitrolysis reactions. The predicted chemical shifts given in Fig 4.19 for the respective protons in these molecules are those expected in a solvent such as dimethylsulphoxide. In nitric acid chemical shift differences might occur due to a change of solvent, but similar characteristic spectra are expected.

In order to investigate the nature of species stable in nitric acid at room temperature, a variety of substrates have been added to 98% nitric acid and their spectra recorded. The results of these experiments are recorded in Figs 3.14 - 3.16 (Chapter Three, Part I, Section 3.6).
Table 4.1

<table>
<thead>
<tr>
<th>Linear Nitramines</th>
<th>Chemical shift (ppm)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H-N(NO_2)^{-}$</td>
<td>8.0 - 14.0</td>
<td>variable with solvent and temperature</td>
</tr>
<tr>
<td>$H-CH_2-N(NO_2)^{-}$</td>
<td>3.0 - 3.6</td>
<td></td>
</tr>
<tr>
<td>$R_1R_2C-CH_2-N(NO_2)^{-}$</td>
<td>3.5 - 4.9</td>
<td></td>
</tr>
<tr>
<td>$-(NO_2)N-CH_2-CH_2-N(NO_2)^{-}$</td>
<td>4.1 - 4.4</td>
<td></td>
</tr>
<tr>
<td>$X-O-CH_2-N(NO_2)^{-}$</td>
<td>5 - 7</td>
<td>$X = \text{alkyl, }-\text{NO}_2,-\text{OCOCH}_3 \text{ }$</td>
</tr>
<tr>
<td>$-(R)H-CH_2-N(NO_2)^{-}$</td>
<td>5.45 - 6.10</td>
<td>$R = -\text{NO}_2,-\text{SO}_2$-$\text{X}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cyclic Nitramines</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$-\text{N(NO}_2\text{)}$</td>
<td>5.90 - 6.30</td>
<td>6,7,&amp; 8-membered rings</td>
</tr>
<tr>
<td>$\text{CH}_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$-\text{N(NO}_2\text{)}$</td>
<td>4.10 - 4.40</td>
<td>5 &amp; 7-membered rings</td>
</tr>
<tr>
<td>$\text{CH}_2\text{\underline{\text{\text{\text{\text}}}}}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$-\text{N(NO}_2\text{)}$</td>
<td>5.45 - 6.10</td>
<td>6,7,&amp; 8-membered rings</td>
</tr>
<tr>
<td>$\text{CH}_2\text{\underline{\text{\text{\text{\text}}}}}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$-\text{N(NO}_2\text{)}$</td>
<td>5.60 - 5.80 (cis)</td>
<td>6,7,&amp; 8-membered rings</td>
</tr>
<tr>
<td>$\text{CH}_2\text{\underline{\text{\text{\text{\text}}}}}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$-\text{N(NO}_2\text{)}$</td>
<td>6.20 - 6.40 (trans)</td>
<td>6,7,&amp; 8-membered rings</td>
</tr>
<tr>
<td>$\text{CH}_2\text{\underline{\text{\text{\text{\text}}}}}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$-\text{N(NO}_2\text{)}$</td>
<td>4.90 - 5.70</td>
<td>6,7,&amp; 8-membered rings</td>
</tr>
<tr>
<td>$\text{CH}_2\text{\underline{\text{\text{\text{\text}}}}}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$-\text{N(NO}_2\text{)}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Chemical shifts are given in units of $\delta$ ppm relative to TMS as internal standard. Shifts to higher frequency are considered positive.
Fig 4.19
The $^1$H NMR spectra of some primary and secondary linear N-nitramines, acetic acid and paraformaldehyde are illustrated in Fig 3.14. The room temperature (303 K) spectra of most of these compounds indicate that decomposition takes place to give molecular fragments. Only acetic acid appears stable in nitric acid at this temperature. For paraformaldehyde no signal is detected at room temperature, indicating that only gaseous products result from the violent 'fume-off' which takes place upon its addition to 98% nitric acid at room temperature. The addition of paraformaldehyde to nitric acid at 263 K results in decomposition, as indicated by its spectrum at this temperature. For methylnitramine, CH$_3$NHNO$_2$, a singlet is obtained at room temperature, presumably due to the species CH$_3$ONO$_2$. For the primary dinitramines, O$_2$N-HN-(CH$_2$)$_n$-NH-NO$_2$, the signals obtained may be due to species of the type O$_2$NO-(CH$_2$)$_n$-ONO$_2$. For ethylene-dinitramine, O$_2$N-HN-(CH$_2$)$_2$-NH-NO$_2$, it is possible that only partial decomposition takes place, for this compound is the most stable of the primary dinitramines, and might be expected to be present as a molecular entity in nitric acid. Upon the addition of BSX to nitric acid at room temperature decomposition occurs, as indicated by its spectrum at this temperature. When BSX and AcAn are added to nitric acid at 273 K, the spectra at this temperature indicate that these compounds react smoothly to give the linear nitroxyethyl derivatives ATX and 106.

\[
\begin{align*}
\text{BSX} & \quad n = 3 \\
\text{AcAn} & \quad n = 4 \\
\text{ATX} & \quad n = 3 \\
106 & \quad n = 4
\end{align*}
\]

Although acetic acid appears to be stable in nitric acid and gives a single resonance line, its position relative to the nitric acid proton is somewhat variable, particularly in the presence of other compounds. The proton in nitric acid may be considered to resonate at $\delta = 10$ ppm and the methyl protons in acetic acid at $\delta = 2$ ppm when it is added to nitric acid.
The presence of this signal serves as a useful secondary reference point, bearing in mind the extent of variation possible in the absolute chemical shift of species in nitric acid solutions. It is unfortunate that a suitable standard has not been found which gives a reliable chemical shift estimate of species present in nitric acid solutions. The nitric acid proton resonance is not suitable, for its position is variable when other labile protons are present in the sample. The lack of such a standard makes comparison of spectra of different substrates difficult, and thus the identification of common fragments difficult.

The spectra of some cyclic N-nitramines are illustrated in Fig 3.15. RDX and HMX are stable in nitric acid at room temperature and dissolve without effervescence to give singlet spectra. A mixture of RDX and HMX gives two resolvable signals, with the RDX singlet appearing to high frequency of the HMX singlet. 1,3-dinitro-1,3-diazacyclohexane (A)(3.15) dissolves readily in nitric acid at room temperature with no effervescence. However, the resulting spectrum indicates that some decomposition takes place, since fragments derived from the trimethylenedinitramine unit (Fig 3.14) are also present. The resultant room temperature spectra of solutions of 1-methoxymethyl-1,3,5-dinitro-1,3,5-triazacyclohexane (B)(3.15), 1-acetoxyethyl-1,3,6-dinitro-1,3,6-triazacycloheptane (C)(3.15), and 1-methyl-1,3,7-dinitro-1,3,7-triazacycloctane (D)(3.15) show the presence of breakdown products derived from methylenedinitramine, ethylenedinitramine and trimethylenedinitramine (Fig 3.14) respectively, and other fragment peaks presumably derived from the other half of these molecules.

The spectra of hexamine and related derivatives, and DPT at room temperature in nitric acid are given in Fig 3.16. Those of hexamine and hexamine mononitrate appear to be very similar, whilst that of hexamine dinitrate is somewhat simpler. 1-acetamidomethylhexamine nitrate gives a similar spectrum, with additional peaks presumably derived from the
-CH₂NHCOCH₃ side-chain. DPT also gives a spectrum apparently similar to those of hexamine and related derivatives.

Variable temperature spectra of 1-methoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane, DPT and hexamine are illustrated in Figs 3.17 - 3.19. The spectra of the compounds 1-methoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane and DPT were recorded with a view to the interpretation of the spectra of hexamine, for in a stepwise scission process hexamine is expected to degrade via a 1,3,5,7-tetraazabicyclo(3.3.1)nonane derivative to give RDX as the final product. Additionally, the chemistry of the nitrolysis reactions of these substrates has been investigated over the temperature range 243 - 303 K, and the nature of the likely intermediates indicated (1,2). These substrates are thus useful for study by ¹H NMR spectroscopy.

For 1-methoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane, the spectra (Fig 3.17) at all temperatures give fairly sharp lines. The singlet at about δ = 3.2 - 3.7 (slow shift to higher frequency on raising the temperature) may be due to the species CH₂ONO₂. The singlet at δ = 5.4 - 5.8 may be due to RDX, considered to be the product of the reaction (1). This peak is present in the first spectrum recorded at 243 K and increases in height throughout the reaction, at the expense of the peak at δ = 7.6 - 7.8 and others at δ = 5.4 - 5.6. These latter peaks may represent the entity PCX or a related compound, or they may represent the postulated intermediate 1-nitroxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (A)(4.20) (1,3,4). If these signals represent this latter entity, it is possible that the form (A)(4.20) may be in equilibrium with its ionic form (B)(4.20), with the equilibrium well to the right in nitric acid. The signals found experimentally do not agree with those predicted for this entity ((A)(4.19)), but for the form (B)(4.20) the exocyclic methylene protons could give rise to the high frequency signal.
For DPT (Fig 3.18) only two signals are present at 223 K, a fairly sharp signal at $\delta = 8.6$ and a broad signal at $\delta = 6.0$. On raising the temperature the signal at $\delta = 8.6$ diminishes and vanishes on reaching room temperature. The signal at $\delta = 6.0$ sharpens and splits into a series of peaks upon raising the temperature. A peak at $\delta = 6.1$ remains throughout the run. Above 243 K peaks at $\delta \approx 6.1 - 6.3$ appear (previously considered as shoulders to the $\delta = 6.1$ peak) and slowly diminish. A peak at $\delta = 5.8$ also appears and increases. This spectrum is difficult to interpret, due to its complexity. If the signal at $\delta = 6.1$ is considered to be due to HMX (1) it suggests that HMX forms very quickly at low temperatures; on raising the temperature competition takes place, with the intermediate forming some HMX but also side-products, such as the linear compound 106 and perhaps RDX. The side-products could decompose to give products.
related to formaldehyde and methylenedinitramine units. The signal at \( \delta = 8.6 \) is found to be present in the spectrum of DPT with DNO_3 (57) and is thus not due to an \( \text{NH} \) grouping. The intermediate may possibly be the postulated nitroxymethyl intermediate (C)(4.20)(1). However, it is again considered to exist in the appropriate ionic form (D)(4.20), in order to account for the high frequency signal at \( \delta = 8.6 \), and because the observed spectra do not indicate the presence of the form (C)(4.20), the predicted spectrum of which is given by (B)(4.19).

For hexamine (Fig 3.19) the spectrum at 233 K shows the presence of several broad peaks. Presumably hexamine reacts very quickly with nitric acid at low temperature to form an intermediate (or intermediates), which then reacts further to form products. On raising the temperature these broad peaks sharpen and those between \( \delta = 3 - 5 \) show fine structure. The peaks at \( \delta = 6.6 - 6.8 \) and 5.5 sharpen and slowly diminish on raising the temperature. The signal at \( \delta = 4.5 \) sharpens and increases throughout the run. Complex changes occur in the minor signals between \( \delta = 3 - 5 \) upon raising the temperature. Due to the complexity of the spectra, they are difficult to interpret. Many features are comparable with the variable temperature spectra of 1-methoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane and DPT (Figs 3.17 and 3.18), which suggests that the intermediates involved in the reactions of these compounds with nitric acid have similar characteristics. However, from the different temperature dependance of the groupings associated with the high frequency signal (between \( \delta = 8 - 9 \)) it would seem that for all three compounds the products are obtained from different intermediates, as suggested by Bell and Dunstan (1,2). The spectra of hexamine (Fig 3.19) do not show signals expected for the postulated intermediate (C)(4.19), nor for the possible intermediate (D)(4.19). An intermediate of the type (C)(4.15) could be considered to be involved, for a spectrum of this type of compound would be somewhat complex, in agreement
with the complex spectra recorded. The fragments of type (E) and (F) could also be present in nitric acid solutions.

While the spectra of 1-methoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane and DPT may possibly be considered to be indicative of the presence of the postulated nitroxymethyl intermediates (A) and (C) respectively, due to their complexity, the spectra of hexamine give little indication of the nature of the possible intermediate. This may suggest that the intermediate is complex or that more than one intermediate is present. From the complex changes which take place in the spectra between 253 and 283 K, it is possible that the true intermediate is only stable below a certain temperature, and that above this temperature other 'intermediates' may be formed from its decomposition. The number of signals found in the spectra between 253 and 283 K suggest the presence of numerous fragments of variable stability within this temperature range. The differences in the spectra of the three compounds also suggest that the formation of products from common fragments does not occur. However, the spectra do not rule out the possibility that the products are formed from different fragments obtained from each compound. In general terms, simpler spectra than those obtained are expected if product formation proceeds via the recombination of fragments, particularly for hexamine. It should be noted that fragments related to formaldehyde and methylenedinitramine units may be present in these spectra, but that neither of these species give rise to a signal at high frequency.

Similarly, species which contain a -CH₂OH grouping may be expected to undergo conversion to the corresponding -CH₂ONO₂ grouping in nitric acid and thus the signal at high frequency is probably not due to -OH. The fate of -CH₂NHNO₂ fragments, which could give rise to a high frequency signal, is not clear.

Little information is available concerning the nature of the nitrating species present in nitric acid and nitric acid/ammonium nitrate solutions.
NMR spectroscopy offers a technique for the study of the nitrogen species present in such solutions. The spectrum of nitric acid/ammonium nitrate (‘NAN’) has been recorded on a neat solution with a nitromethane capillary inserted in the tube as the internal standard. The spectrum has been calibrated using the sideband technique and additionally by sample replacement of a saturated ammonium nitrate solution to check the shift of the ammonium quintet. The results are given in Table 3.5. A value of -43 ppm (chemical shifts are quoted in ppm on the screening constant scale (51) relative to NO$_3^-$ or CH$_2$NO$_2$ as zero, with shifts to high frequency as positive) has been recorded for 100% nitric acid (92), while for 97% nitric acid a value of -47.5 ppm has been reported (73). These values may be considered to reflect average values resulting from rapid exchange of the species present. Pure nitric acid undergoes self-dissociation to a small extent:

\[
2\text{HNO}_3 \rightleftharpoons \text{H}_2\text{O} + \text{NO}_2^+ + \text{NO}_3^-
\]

On the addition of water the chemical shift becomes concentration dependant, due to ionisation of nitric acid taking place:

\[
\text{HNO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NO}_3^- + \text{H}_3\text{O}^+
\]

On dilution of nitric acid with water the chemical shift approaches zero, and on sufficient dilution only NO$_3^-$ is present and a value of zero is recorded. For 70% nitric acid a value of -28 ppm has been reported (93), while 65% nitric acid gives a resonance at -24 ppm (94). The presence of the nitronium ion as the principal nitrogen species in nitric acid is not indicated, for a value of -125 ppm has been recorded for a nitric acid/oleum mixture and -129 ppm has been recorded for nitrosonium fluorsulphate in fluorsulphonic acid (94), both of which contain the nitronium ion. For nitric acid/ammonium nitrate solution (‘NAN’), which is prepared by the
addition of gaseous ammonia to 98% nitric acid to give essentially a nitric acid/ammonium nitrate mixture, only two signals have been detected. These are an ammonium quintet at -360 ppm and a signal at -25 ppm due to a nitric acid species. Ammonium nitrate gives two signals (in acidified aqueous solution) at -355 ppm for the ammonium quintet and zero ppm for the nitrate anion; thus these two signals are modified by the presence of nitric acid. The presence of strong acid shifts the nitrate resonance to lower frequencies, but probably not to such an extent as that experienced by 'NAN' and thus the signal at -25 ppm must be considered to be derived from a nitric acid species. The shift of -5 ppm for the ammonium ion can be accounted for by the presence of nitric acid. The data may thus be interpreted in two ways. Firstly, due to the possibility of complex formation between nitric acid and the ammonium ion; and secondly, due to an ammonium ion resonance moved to lower frequency by the presence of strong acid; together with a nitric acid species, the resonance position of which indicates the relative acidity of the nitric acid.
PART II: ANCILLARY STUDIES.

4.8 INTRODUCTION.

Part II of this Chapter is concerned with the results of the studies of the electronic and molecular structures of some of the molecules in the classes of compounds considered in this work.

A study of the $^1$H NMR spectroscopy of the derivatives encountered in the nitrolysis reactions of hexamine and 7-nitro-1,3,5-triazaadamantane gives an insight into the conformational analysis of hexahydropyrimidines and and 1,3,5-triazacyclohexanes.

The $^1$H NMR characteristics of the N-nitramines and N-nitrosamines studied indicate significant electronic interaction within the N-nitro and N-nitroso groups; in particular, for N-nitrosamines effects due to restricted rotation about the N-NO bond are found, indicating appreciable double bond character for this bond. $^1$H NMR spectroscopy provides a suitable technique for the study of substituent effects for 1,3,5,7-tetraazabicyclo(3,3,1)nonanes and derivatives of hexamine.

In order to supplement the results of the $^1$H NMR studies in the investigation of these effects, the results of the $^{13}$C and $^{14}$N NMR studies on selected molecules are also considered.

Molecular orbital calculations also provide an insight to the electronic structures of molecules and the results of the calculations on selected N-nitramines, N-nitrosamines, hexamine and derivatives are discussed.

4.9 THE CONFORMATIONAL ANALYSIS OF HEXAHYDROPYRIMIDINES AND 1,3,5-TRIAZAADAMANTANES.

For hexahydropyrimidines (A)(4,21) the magnitude of the geminal coupling constant (|$J_{ax,ae}$|)(the sign of the coupling constant is generally considered to be negative (95)) between the axial and equatorial protons at the C2 position is considered useful as an indication of the
orientation of the N-substituents about the nitrogen atoms (47,96). For compounds of type (A)(4,21) the spectra at room temperature indicate that these molecules are undergoing rapid ring inversion; the C2 protons appear as a singlet in the $^1$H NMR spectra (97, 98). Low temperature spectra are required for separation of the C2 axial and equatorial proton signals (97). Inversion about the nitrogen atoms has to be taken into account for these molecules, which may be considered to exist with contributions from both the axial-equatorial and equatorial-axial forms (97). The substitution of two methyl groups at the C5 position, to give compounds (B)(4,21), is considered to force both N-substituents into the equatorial positions (97,98). However, low temperature spectra are still required to separate the axial and equatorial C2 protons. For these latter compounds it is found that the value of the geminal coupling constant falls in the range ($|J_{ae}|$) = 7 - 9 Hz at 190 - 200 K (97, 99), while for the former compounds of type (A)(4,21) the low temperature spectra give values in the range ($|J_{ae}|$) = 8 - 11 Hz (97, 99). The replacement of a methyl group at C5 by a nitro group to give the compounds (C)(4,21) slows down ring inversion and resolvable AB patterns for the C2 axial and equatorial protons are obtained at room temperature (47, 96, 100, 101). With alkyl substituents on the nitrogen atoms the C2 geminal coupling constant values are of the order ($|J_{ae}|$) = 8 - 9 Hz at room temperature (47). The effect of the nitro group at the C5 position is difficult to ascertain. Dipole moment and $^1$H NMR evidence (101 - 103) indicate that the nitro group is preferentially axial in the compounds (C)(4,21), and is thus not expected to affect the C2 protons to any great extent (47). It may, however, affect the N-substituents.
The nature of the N-substituents is found to have a direct effect upon the C2 protons (47). When the N-substituent \( R \) is a phenyl derivative there is a shift of the C2 axial and equatorial proton signals to higher frequency and a general increase in the value of \( |J_{ae}| \) (47). Such effects may generally be accounted for by a change of hybridisation of the ring nitrogen atoms (47). To account for these observations, it has been postulated that where \( R \) is an alkyl group there is a transfer of lone pair electrons from nitrogen into the C2(CH\(_2\)) anti-symmetric molecular orbital (see reference (95) for a discussion of the molecular orbital approach to the explanation of geminal coupling constants), resulting in \( |J_{ae}| \) values of the magnitude 7 - 10 Hz. When \( R \) is aryl the lone pairs of electrons on the nitrogen atoms overlap with the \( \pi \) electrons of the aromatic ring and are therefore not so readily available for donation into the C2(CH\(_2\)) group molecular orbital (47, 95). This results in an increase in \( |J_{ae}| \), with values in the range 10 - 13 Hz. There is also a relative shift to higher frequency in the resonance position of the C2 axial and equatorial protons. For other electron-withdrawing substituents on the nitrogen (for example, \( R = NO, NO_2, COC_6H_5, COR \)) a similar effect is expected. On going from compounds (C)(4.21) to (A)(4.22) the same analysis is expected to hold. Hence, for the hexahydrothiazole derived from 7-nitro-1,3,5-triazazaadamantane, of general formula (B)(4.22), ring inversion is expected to be slow at room temperature with resolvable
AB patterns for the C2 axial and equatorial protons. The nitro group is strongly electron-withdrawing and hence the signals are expected to come at high frequency and the AB quartets to have a relatively high value of \(|J_{ae}|\), in agreement with the spectra shown (Figs 5.10, 5.12 and 5.13). The values of \(|J_{ae}|\) for these compounds are of the order \(|J_{ae}| = 13\) Hz.

For compounds which, by virtue of their structure, have their N-substituents constrained either axially or equatorially, it is possible to comment on the values of \(|J_{ae}|\) under rigid conditions. For the molecule (A)(4.23) the N-substituents are constrained axially, and the di-equatorial N-lone pairs are considered to have no effect on the C2 position. This compound exhibits a \(|J_{ae}|\) value of 13 Hz (104, 105).

For the compounds (B)(4.23) one N-substituent is constrained axially and the low temperature values of \(|J_{ae}|\) are within the range 10 - 11 Hz (97, 99).

1,3,5-triazacyclohexane derivatives also provide a class of compounds in which to observe the effects of the orientation of substituents about the nitrogen atoms. For trialkyl derivatives room temperature spectra show singlets for the ring methylene protons. Low temperature spectra exhibit AB patterns for the \(\hat{N}\text{-CH}_2\text{-}\hat{N}\) geminal protons. Typical values of \(|J_{ae}|\) are in the range 10 - 11 Hz. These molecules are considered to undergo both ring and nitrogen inversions (52, 106, 109). From a recent report (55) of the variable temperature spectra of 1,3,5-trimethyl-1,3,5-triazacyclohexane it is apparent that previous reports (52, 106, 109) are
concerned with these molecules undergoing slow ring and fast nitrogen inversions. However, at very low temperatures (129 K) two sets of AB quartets are shown by the ($\text{N-CH}_2\text{N}^-$) geminal protons and two sets of methyl resonances are found. This is consistent with slow ring and slow nitrogen inversions. Conformation (C)(4.23) is considered to be present at this temperature. H$_a$ and H$_b$ give an AB quartet at $\delta = 2.13$, 3.65 ppm, ($|J_{ae}| = 7.9$ Hz (2H)) and H$_c$ and H$_d$ give an AB quartet at $\delta = 2.90$, 3.49 ppm, ($|J_{ae}| = 10.7$ Hz (4H)) (53). These values of ($|J_{ae}|$) are consistent with the previous analysis in that the value of ($|J_{ae}|$) for the methylene protons between two nitrogen atoms with equatorial substituents is lower than that of the methylene protons between one axial and one equatorial N-substituent. When the N-substituent are electron-withdrawing, a similar effect on the chemical shift of the methylene protons in 1,3,5-triazacyclohexanes compared to the C2 protons in hexahydropyrimidines takes place, in that the protons move to higher frequency (110). A singlet is still observed in the room temperature spectra of these molecules.

From a consideration of the spectra of the compound (D)(4.23)(111), which shows an AB quartet at room temperature with ($|J_{ae}| = 15$ Hz, and also of the spectra of 1,3,5-diazadamantane derivatives (E)(4.23)(112 - 115), 1,3,5-triazadamantane derivatives (Table 3.4) and the hexamine quarternary salts (Table 3.3), in which the ($\text{N-CH}_2\text{N}^-$) geminal coupling constants fall within the range ($|J_{ae}| = 12 - 14$ Hz), it is apparent that methylene protons between two nitrogen atoms with substituents axial, appear at the higher end of the coupling constant range at about ($|J_{ae}| = 12 - 15$ Hz).

In summary, the values of ($|J_{ae}|$) are a good guide to the orientation of the N-substituents in hexahydropyrimidines and 1,3,5-triazacyclohexane derivatives, providing due account is taken of the nature of the particular N-substituents, and that a series of closely related molecules is considered.
4.10 STUDIES RELATED TO THE ELECTRONIC STRUCTURES OF N-NITRAMINES, N-NITROSAMINES, HEXAMINE AND DERIVATIVES.

(A) $^{14}\text{N}$, $^{13}\text{C}$ and $^1\text{H}$ NMR STUDIES.

N-nitramines contain both amino and nitro nitrogen atoms, which may be studied by nitrogen NMR. In $^{14}\text{N}$ NMR spectra the resonance signal for the nitro group nitrogen is sharp (half-height width = 10 - 60 Hz) compared with that for the amino nitrogen atom, which is often broadened to such an extent that it is difficult to detect. Thus, most of the data available for N-nitramines is concerned with the resonance of the nitro nitrogen atom. A summary of the available data for N-nitramines may be found in Chapter Four, Sections 4.4.7 and 4.4.14, reference (51).

Spectra have been obtained for both types of nitrogen atom in methyl-nitramine and its sodium salt (116), N,2,4,6-tetranitroaniline (73), nitrourea (73), dimethylnitramine (117) and diethylnitramine (49), the results are summarised in Table 4.2. It may be seen from Table 4.2 that
Table 4.2

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Chemical Shift (ppm)</th>
<th>Half-height width (Hz)</th>
<th>$\Delta$ (ppm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{HNNO}_2$</td>
<td>$(\text{CH}_3\text{OCH}_2)_2$</td>
<td>$N$ $-208 \pm 8$ $\text{NO}_2$ $-23.2 \pm 0.8$</td>
<td>540</td>
<td>10</td>
<td>185 (116)</td>
</tr>
<tr>
<td>$\left[\text{CH}_3\text{HNNO}_2\right]^{\text{Na}^+}$</td>
<td>$\text{H}_2\text{O}$</td>
<td>$N$ $-145 \pm 15$ $\text{NO}_2$ $-26.3 \pm 1$</td>
<td>$\approx 1000$</td>
<td>43</td>
<td>119 (116)</td>
</tr>
<tr>
<td>$\text{O}_2\text{N}$</td>
<td></td>
<td>$N$ $-250$</td>
<td>broad</td>
<td></td>
<td>215 (73)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{NO}_2$ $-34.5 \pm 2$</td>
<td>32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{NH}_2\text{CONHNO}_2$</td>
<td>-</td>
<td>$N$ $-250 - -300$</td>
<td>broad</td>
<td></td>
<td>(73)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{NO}_2$ $-40 \pm 3$</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{NNO}_2$</td>
<td>neat</td>
<td>$N$ $-212 \pm 10$</td>
<td>**</td>
<td>180</td>
<td>(117)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{NO}_2$ $-32 \pm 10$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\text{CH}_3\text{CH}_2)_2\text{NNO}_2$</td>
<td>neat</td>
<td>$N$ $-$</td>
<td>***</td>
<td>1100</td>
<td>(49)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{NO}_2$</td>
<td>12</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Chemical shifts are quoted in $\delta$ ppm on the screening constant scale (118) relative to $\text{NO}_3^-$ or $\text{CH}_3\text{NO}_2$ as zero. Shifts to higher frequency are considered positive.

** Values obtained using the equation: $\delta$(NO$_3^-$) = $\delta$(NO$_2^-$) + 232 ppm (117)

*** No chemical shift values quoted, only chemical shift differences.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Chemical Shift (ppm)*</th>
<th>Half-height width (Hz)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₂NO₂</td>
<td>(C₂H₅)₂O</td>
<td>-12±2**</td>
<td></td>
<td>(120,121)</td>
</tr>
<tr>
<td>CH₃HNH₂NO₂</td>
<td>(CH₃OCH₂)₂</td>
<td>-23.2±0.5</td>
<td>10</td>
<td>(116)</td>
</tr>
<tr>
<td>(CH₂)₂NN₂O₂</td>
<td>CDCl₃</td>
<td>-21.8±1.5</td>
<td>-23</td>
<td>(38)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(121)</td>
</tr>
<tr>
<td>O₂NN</td>
<td>(CH₃)₂SO</td>
<td>-27±1</td>
<td>30</td>
<td>(119)</td>
</tr>
<tr>
<td>(DPT)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>(CH₃)₂SO</td>
<td>-22.5±1</td>
<td>52</td>
<td>***</td>
</tr>
<tr>
<td>O₂NN</td>
<td>(CH₃)₂SO</td>
<td>-29±1</td>
<td>60</td>
<td>***</td>
</tr>
<tr>
<td>CH₂(NH₂NO₂)₂</td>
<td>(CH₃)₂SO</td>
<td>-33.2±0.5</td>
<td>91</td>
<td>***</td>
</tr>
<tr>
<td>(BSX)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>(CH₂)₂CO</td>
<td>-34±1</td>
<td>25</td>
<td>(118)</td>
</tr>
<tr>
<td>N</td>
<td>(CH₂)₂SO</td>
<td>-36.5±1</td>
<td>35</td>
<td>(119)</td>
</tr>
<tr>
<td>(RDX)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>(CH₂)₂SO</td>
<td>-38±1</td>
<td>26</td>
<td>(118)</td>
</tr>
<tr>
<td>(HMX)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Chemical shifts (of the nitro group nitrogen atom only) are given in δ ppm relative to NO₂⁻ or CH₃NO₂ as zero. Shifts to higher frequency are considered positive.

**Estimated from published spectrum (120). *** See Table 3.5.
on going from methylnitramine to its sodium salt that there is a large high frequency shift for the amine nitrogen atom, but only a small low frequency shift for the nitro nitrogen atom. This, together with the $^{13}$C and $^{17}$O NMR results for these compounds (116), indicates that on ionisation of the nitramine a decrease in the N-O bond order and an increase in the N-N bond order occurs. This accounts for the large shift found for the amino nitrogen atom (and the oxygen atoms of the nitro group in the $^{17}$O NMR spectra (116)), while for the nitro nitrogen atom the two effects appear to mutually cancel, giving only a small resultant shift for this atom (116).

From a consideration of the series methylnitramine, N,2,4,6-tetranitroaniline and nitrourea, it appears that there is a progressive shift to low frequency for both the amine nitrogen atom and the nitro nitrogen atom. These shifts are presumably associated with the conjugative effects of the substituents attached to the amino nitrogen atom in these primary N-nitr-amines. There appears to be little change in the environment of either nitrogen atom in going from methylnitramine to dimethylnitramine. It is also reasonable to assume that the environment of the nitrogen atoms in diethylnitramine are very similar to those for dimethylnitramine. The chemical shift differences are comparable and the chemical shifts of the nitro group nitrogen atoms appear in a relatively narrow range.

Chemical shift data for some primary and secondary N-nitramines have been reported in Table 3,5. A comparison of this data with that of other related compounds is given in Table 4,3. The nitro group nitrogen atom resonance for N-nitramines occurs within the range $\delta = -12 \rightarrow -42$ ppm (screening constant scale (118), relative to $\text{NO}_2^-$ or $\text{CH}_3\text{NO}_2$ as zero, with shifts to high frequency considered positive). For primary nitramines the resonance position can occur throughout this range, but for secondary nitramines the resonance position occurs at the low frequency end of this range. The nitro group nitrogen atom resonates in the range $-22 \rightarrow -27$ ppm.
for compounds which contain adjacent methyl an isolated mononitramine grouping; however, for compounds containing adjacent methylenenitramine units (RDX, HMX, BSX) the nitro group nitrogen atom resonance occurs at lower frequency within the range $\delta = -33 \rightarrow -38$ ppm. Thus the nitro group nitrogen atom of secondary N-nitramines may be expected to resonate in the chemical shift range $\delta = -20 \rightarrow -40$ ppm. Overall, the nitrogen resonance signals of the nitro group for N-nitramines are found at the low frequency end of the rather narrow nitrogen chemical shift range of organic nitro compounds ($118$).

The trends shown in Table 4.3 may be accounted for by a consideration of the inductive electron withdrawal of the groups X in these $X-\text{NO}_2$ compounds. These trends are in essential agreement with the findings of Kintzinger et al (49) from a study of the $^{14}N$ nuclear quadrupolar relaxation of the nitro group nitrogen nucleus in organic nitro compounds, which includes dimethylnitramine and diethylnitramine. Quadrupolar relaxation of the $^{14}N$ nucleus generally washes out the $^{14}N$-$H$ spin-spin couplings and leads to more or less broadened proton resonances. The detection of $^{14}N$-$H$ spin-spin couplings, as in dimethylnitramine and diethylnitramine (37, 49), indicates a symmetrical environment of the $^{14}N$ nucleus leading to a small field gradient at the nucleus. This is indicated by sharp lines in the $^{14}N$ NMR spectrum. Conversely, the analysis of the proton line shape represents a way of obtaining the quadrupolar relaxation time of the $^{14}N$ nucleus, and the temperature dependance of the relaxation time leads to activation energies for molecular dynamical processes (50). For the nitramines considered (49) the results indicate a high symmetry for the electron distribution on the nitro group nitrogen of these nitramines. This could be due to the inductive electron withdrawal from the nitrogen 2p atomic orbital involved in the $X-\text{NO}_2$ bond by the electronegative $\text{-N(R)}_2$ substituents.
It is considered that for the dialkylnitramines considered strong conjugative effects may be present with appreciable double bond character for the N-N bond (49). A consequence of this is that rotation about the N-NO₂ bond should be restricted, as is the case for alkyl nitrates and N-nitrosamines. Although no barrier to rotation about the N-NO₂ bond in nitramines has been reported, the results are considered to indicate the presence of a considerable rotation barrier (probably >9 kcal/mole) for N-nitramines. Within a series of related molecules increasing negative inductive effects result in a shift to lower frequency (119), as shown for N-nitramines (Table 4.3).

¹⁴ N NMR measurements on N-nitrosamines are restricted to dimethyl-nitrosamine (A)(4,24)(123) and 1,3,5-trinitroso-1,3,5-triazacyclohexane (B)(4,24)(Table 3.5). A comparison of the data is given in Fig 4.24.

\[
\begin{align*}
\text{(A)} & \quad \text{N-NO} \\
& \quad \text{CH}_3 \\
& \quad \text{NO} \\
\text{N} & \quad \text{N-NO} \\
& \quad \text{CH}_3 \\
\text{(B)} & \quad \text{NO}
\end{align*}
\]

\[
\begin{align*}
\delta_{\text{NO}} &= +163 \text{ ppm} \\
\delta_{\text{N}} &= -141 \text{ ppm} \\
\delta_{\text{NO}} &= +132 \text{ ppm} \\
\delta_{\text{N}} &= -130 \text{ ppm}
\end{align*}
\]

The chemical shifts are quoted in ppm relative to NO₃⁻ as zero (screening constant scale (118)); shifts to high frequency are considered positive.

Due to the sparcity of the data it is difficult to comment constructively on the chemical shifts shown for these two compounds. However, comparison with the chemical shift data for the corresponding N-nitramines, dimethylnitramine (Table 4.2) and RDX (Table 4.3) shows a shift to lower
frequency for the amino type nitrogen atom on passing from dimethyl-
nitrosamine to dimethylnitramine. This is coupled with a shift to low
frequency on passing from the nitrogen atom of the nitroso group to the
nitrogen atom of the nitro group. A similar low frequency shift occurs
on passing from the nitrogen atom of the nitroso group in (B)(4,24) to the
nitrogen atom of the nitro group in RDX. It is interesting to note that
for dimethylnitrosamine the amino type nitrogen resonance is very similar
to that of the amino type nitrogen atom in the sodium salt of methyl-
nitramine (Table 4.2).

Sauer and Oja (106) have recorded the \(^{14}\)N nuclear quadrupole resonance
spectra of six N-nitrosamines and conclude from their results that there
is a considerable delocalisation of \(\pi\) charge throughout the N-nitrosamine
grouping. This indicates appreciable double bond character for the N-N
bond in these molecules.

The results of the \(^{14}\)N NMR measurements on hexamine and some related
derivatives are recorded in Table 3.6. The results show that in all
cases the quarternary nitrogen atom experiences a shift to low frequency
compared to that of the hexamine nitrogen atoms. This result is unexpected,
for in aliphatic systems quarternisation produces a shift to higher
frequency (118)(Table 4.4). An examination of the effects of quarter-
nisation in other nitrogen-containing alicyclic systems confirms these
findings(122). Furthermore, in certain aliphatic systems, such as the
enamino ketones (Table 4.4), the same trend is found. The trend in
going from primary amine to tertiary amine in these molecules (124) is
the same as that for other alkylamines (54, 118), a shift to higher
frequency occurring. However, on quarternisation a large shift to
lower frequency occurs (125). It may be that this latter effect is the
general case and that the opposite effect shown for trimethylamine and
triethylamine is a special case. This could be related to the ability
of these latter tertiary amines to undergo inversion about the nitrogen atom, while for alicyclic compounds inversion may be restricted. For the quarternary salts of hexamine the rigid cage structure prohibits inversion, while for the enamino ketones conjugation within the molecules may produce this effect. No satisfactory theoretical explanation of the trends shown by alkylamines and their corresponding ammonium ions is available (118), and the trends shown by the quarternary salts of hexamine and enamino ketones further complicate the situation. However, the recognition of these somewhat unexpected trends should lead to a better understanding of the $^{14}$N NMR spectra obtained for amines and their quarternary salts.

A consideration of nuclear spin-spin coupling constants between nitrogen and neighbouring nuclei ($^{1}J$) should provide a sensitive measure of the electron distribution in the bonds formed by the nitrogen atom (126). Long-range couplings ($^{2}J$ and $^{3}J$) give information concerning molecular structure (61).

The spectra of the protons on the $\alpha$-carbon atom in primary N-nitramines show a small coupling to nitrogen, which usually results in broadening of the proton signal (38). The nitrogen atom of the nitro group has been shown to be responsible for this coupling (38). For certain dialkyl-nitramines (Table 4.5) the protons on the carbon atoms are also found to couple to the nitro nitrogen atom, the coupling shows the expected temperature dependence for couplings between protons and a nucleus with a quadrupolar moment. The triplet splittings are better resolved at higher temperatures (37, 49).

$^{15}$N NMR studies (68, 69) have provided spin-spin coupling constants for some secondary N-nitramines. The coupling constant data available for some $^{15}$N-enriched N-nitramines are given in Table 4.6.
| Compound                  | Solvent       | Chemical Shift (ppm)* | Reference 
|--------------------------|---------------|-----------------------|----------------
| \(N(CH_3)_3\)            | neat          | -365 ± 1              | (54)           
| \(HN^+(CH_3)_3\)         | **            | -347                  | (118)          
| \(N^+(CH_3)_4\)          | **            | -334 ± 0.5            | (54)           
| \(N(C_2H_5)_3\)          | neat          | -327 ± 2              | (54)           
| \(HN^+(C_2H_5)_3\)       | **            | -314 ± 1              | (54)           
| \(N^+(C_2H_5)_4\)        | **            | -311 ± 0.5            | (54)           
| \(CH_3COCH=CHNH_2\)      | \(CH_3CN\)   | -294 ± 4              | (124)          
| \(CH_2COCH=CHNHCH_3\)    | \(CH_2Br_2/CH_3CN\) | -289 ± 5  | (124)          
| \(CH_2COCH=CHN(CH_3)_2\) | \(CH_2Br_2/CH_3CN\) | -269 ± 8  | (124)          
| \(CH_2COCH=CHN^+(CH_3)_3\)| \(H_2O\)       | -326                  | (125)          

* Chemical shifts are given in units of \(\delta\) ppm with respect to \(\text{NO}_2^-\) or \(\text{CH}_2\text{NO}_2\) as internal standard. Shifts to higher frequency are considered positive.

** Saturated solutions of the chloride in concentrated hydrochloric acid.
Axenrod et al. (127, 128) and Roberts et al. (129) have reported $^{15}_N$ coupling constant data for some $^{15}_N$-enriched N-nitrosamines. The data for dimethylnitrosamine, dibenzylnitrosamine and its protonated species are given in Table 4.6. The $^3J(^{15}_N-N-C-H)$ couplings show a cis/trans dependance associated with the restricted rotation about the N-N bond in these molecules. For all the $^3J(^{15}_N-N-C-H)$ couplings the trans coupling constant is consistently greater in magnitude than the cis coupling constant; the two being of the order 2 - 3 Hz and 0 - 1 Hz respectively.

For dimethylnitrosamine, Roberts et al. (129) have reported $^2J(^{13}_C-N-^{15}_NNO)$ coupling constants which again show a cis/trans dependance. The data reported for the $^3J(^{15}_N-N-C-H)$ coupling constants of this molecule, as observed by Axenrod (68), is the correct data, and previous reports (61,129)
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$^1J(^{15}\text{N}-^{15}\text{N})$ (Hz)</th>
<th>$^2J(^{15}\text{N}-\text{CH})$ (Hz)</th>
<th>$^3J(^{15}\text{N}-\text{NCH})$ (Hz)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{CH}_3)_2\text{N}-\text{NO}_2$</td>
<td>CDCl$_3$</td>
<td>4.9</td>
<td>0.9</td>
<td>2.2</td>
<td>(68,69)</td>
</tr>
<tr>
<td></td>
<td>$(\text{CH}_3)_2\text{SO}$</td>
<td>4.9</td>
<td></td>
<td></td>
<td>(68)</td>
</tr>
<tr>
<td>$\text{O}_2\text{N}-\text{CH}_2\text{NNO}_2$</td>
<td>$(\text{CH}_3)_2\text{SO}$</td>
<td>8.5</td>
<td></td>
<td></td>
<td>(68,69)</td>
</tr>
<tr>
<td>$\text{O}_2\text{NH}$</td>
<td>$(\text{CH}_3)_2\text{SO}$</td>
<td>8.9</td>
<td>0.6</td>
<td>2.8</td>
<td>(68,69)</td>
</tr>
<tr>
<td>$\text{CH}_2\text{NCH}_2$</td>
<td>$(\text{CH}_3)_2\text{SO}$</td>
<td>4.9</td>
<td>0.0</td>
<td>2.4</td>
<td>(68,69)</td>
</tr>
<tr>
<td>$\text{O}_2\text{N}_2$</td>
<td>$(\text{CH}_3)_2\text{SO}$</td>
<td>4.5</td>
<td>0.0</td>
<td>2.4</td>
<td>(68,69)</td>
</tr>
</tbody>
</table>

* all the N-nitramines are doubly labelled (amino and nitro nitrogens) having a $^{15}\text{N}$-enrichment of 95% at each nucleus.

** value for $^2J(^{15}\text{N}(0)-\text{N}-^{13}\text{C})$.
are in error. Axenrod et al (69, 127, 128) have reported coupling constant data for dibenzylnitrosamine and its protonated species.

Due to the lack of comparable data it is difficult to comment upon the significance of the available coupling constant data. For the $^{15}\text{N} - ^{15}\text{N}$ coupling constants it appears that the magnitude of the coupling constants can in principle be correlated with the hybridisation and/or effective nuclear charge at the nitrogen nucleus (69). However, for the nitramines given in Table 4.6 the $^{1}J(^{15}\text{N} - ^{15}\text{N})$ coupling constants may be considered to show no recognisable trend. They fall into two groups, one in which the $^{1}J(^{15}\text{N} - ^{15}\text{N})$ couplings are $\sim 5$ Hz and the other $\sim 9$ Hz. This is at the low end of the rather narrow range of the coupling constant values so far reported. From a consideration of the relative structures of the compounds there are no apparent reasons for the observed coupling constant differences. Dibenzylnitrosamine gives the largest $^{15}\text{N} - ^{15}\text{N}$ coupling constant so far recorded. This may reflect the high degree of partial double bond character in N-nitrosamines. A recent report (130) on $^{13}\text{C} - ^{15}\text{N}$ coupling constants in oximes shows that for these compounds $^{13}\text{C} - ^{15}\text{N}$ coupling constants are related to nitrogen lone pair orientation in structurally rigid molecules and that this property can markedly influence values of one-bond coupling constants. Additionally, the values of $^{1}J(^{13}\text{C} - ^{15}\text{N})$ may reflect subtle differences in bond lengths and angles. If such parameters are important in the consideration of $^{15}\text{N} - ^{15}\text{N}$ bonds, which seems likely, then the interpretation of such coupling constant data involves a complex situation. At the present time it is difficult to interpret the observed $^{15}\text{N}$ coupling constant data unambiguously.

The protonation studies on dibenzylnitrosamine (128) have shown that for nitrosamines the oxygen atom is the site of protonation, and not the amino nitrogen atom. It may be seen that protonation increases the magnitude of the trans coupling constant for this compound, reflecting a
change in the environment of the N-N bond upon protonation of the nitrogen oxygen atom. Nevertheless, partial double bond character is retained.

The $^{13}$C NMR spectra reported for N-nitramines is restricted to a study of methylnitramine and ethylenedinitramine and their sodium salts (116). For methylnitramine the resonance position of the methyl carbon atom occurs at $\delta = 32.3 \pm 0.5$ ppm, while for ethylenedinitramine the position of the methylene group carbon atom occurs at $\delta = 43.8 \pm 0.5$ ppm. Ionisation produces a shift to higher frequency for these carbon atoms. For DPT (Table 3.7) the ($N$-CH$_2$-$N$(NO$_2$)-) methylene carbon atoms resonate at $\delta = 67.8 \pm 0.5$ ppm. This progressive shift to higher frequency reflects the change in the electronegativity of the atom attached to the methylene group carbon atom in these molecules:

$$\text{H-CH}_2\text{-N(NO}_2\text{)-} \rightarrow \text{C-CH}_2\text{-N(NO}_2\text{)-} \rightarrow \text{N-CH}_2\text{-N(NO}_2\text{-)}$$

Pregosin and Randall (131) have reported the $^{13}$C NMR data for a series of secondary N-nitrosamines and N-nitrosoanilines. The carbon atom resonances show a cis/trans dependance on the orientation of the nitroso oxygen atom, with the cis carbon atom resonating at lower frequency to the trans carbon atom. This parallels the situation found for cis and trans protons in the $^1$H NMR spectra of these molecules. The chemical shift difference is of the order 6 - 10 ppm. This is a ten-fold increase compared to proton chemical shift differences and it is considered that this is evidence for the participation of electric field effects as well as the magnetic anisotropy effect in determining the resonance positions (131). For 3,7-dinitroso-1,3,5,7-tetraazabicyclo(3.3.1)nonane (G) (Table 3.7) the assignments are in accord with this previous work (131). The resonances come at the high frequency end of the chemical shift range shown for secondary N-nitrosamines and N-nitrosoanilines, and the chemical shift differences (9 - 10 ppm) are comparable. The assignments given for 1,3,5-trinitroso-1,3,5-triazacyclohexane (H) (Table 3.7) are considered
reasonable, for the syn isomer should give only one line (for the \( \alpha'_{ct} \) carbon atoms) and this is recognised from a consideration of the intensities of the four lines. The three lines assigned to the anti isomer are more intense than the other line. The position for the \( \alpha'_{ct} \) carbon atom is assigned by comparison with the \( \alpha'_{ct} \) carbon atom resonance, and the lower frequency signal then assigned to the \( \alpha_{cc} \) carbon atom. The chemical shift difference between the respective carbon atoms reflects the influence of two adjacent nitrosamine groupings on the carbon atoms. On passing from \( \alpha_{cc} \to \alpha_{ct} \to \alpha_{tt} \) an increment of about 10 ppm to higher frequency is observed for the respective carbon atoms.

The \( ^{13}C \) NMR spectra of hexamine, certain of its quarternary derivatives, 7-nitro-1,3,5-triazaadamentane and some other compounds containing methylene-bis-amine groupings are reported in Table 3.7. The assignments of the carbon atom resonances for hexamine and its quarternary derivatives are not straightforward, and a discussion is given in Chapter Three, Part I, Section 3.8. It appears that protonation of hexamine to give hexamine mononitrate results in a shift to lower frequency of 6.6 ppm, with retention of the single line spectrum. Methylation results in a shift to lower frequency for the \( \text{CH}^+_{-CH_2-N} \) carbon atoms, while a shift to higher frequency occurs for the \( \text{CH}^+_{-N-CH_2-N} \) carbon atoms. On passing from 1-methyl- to 1-ethyl- to 1-acetamidomethyl- to 1-propionamidomethylhexamine nitrate the resonance position of the \( \text{CH}^+_{-CH_2-N} \) carbon atoms remains fairly constant, while for the \( \text{CH}^+_{-N-CH_2-N} \) carbon atoms a gradual shift to lower frequency occurs. In the \( ^1H \) NMR spectra of these compounds (Table 3.3) the \( \text{CH}^+_{-CH_2-N} \) methylene protons exhibit singlet spectra and experience a small shift to lower frequency on passing along the above series. For the \( \text{CH}^+_{-N-CH_2-N} \) methylene protons, however, AB patterns are shown by the inequivalent axial and equatorial protons. On passing along the above series the AB quartets collapse to a near \( A_2 \) pattern for these protons. These effects are
considered to reflect the influence of the respective substituents upon the hexamine cage structure. There appears to be a progressive cancelation of effects of the positive pole on the quarternary nitrogen atom by the substituent attached to it. There is a pronounced inductive effect, for the influence of the substituent is felt throughout the molecule. For other molecules considered in Table 3.7 the assignments are relatively straightforward; as are the assignments of the carbon atoms in the substituent side-chain for the quarternary derivatives of hexamine. There are interesting comparisons between the spectra recorded for the quarternary derivatives of hexamine and other quarternary nitrogen compounds, such as those derived from acetylcholine, atropine and other cholinergic agents (56).

(B) MOLECULAR ORBITAL CALCULATIONS

Stains et al (64,132-135) have reported variable electronegativity, self-consistent field calculations, including configuration interaction (VESCFCI)(136,137), on nitramine, methylnitramine and dimethylnitramine (A)-(C)(3.23)(64,133) and have used the results to explain aspects of the electronic spectra of these molecules. The results have been extended to other primary and secondary N-nitramines to study many aspects of the chemistry of nitramines, particularly aspects of the chemistry of RDX and HMX (132,134,135). Aspects of the chemistry of nitramines considered include the electronic spectra (133), the intramolecular properties and crystal packing of nitramines (64), the electrophilic and nucleophilic reactions of nitramines (134) and aspects of the thermal, photochemical and mass spectral fragmentation of some secondary nitramines (132,134,135). CNDO/2 molecular orbital calculations (5) have also been performed for nitramine, methylnitramine and dimethylnitramine (64) to calculate electric dipole moments and ionisation potentials for these molecules. Orloff et al (70) have performed CNDO/2 molecular orbital calculations (5) on RDX with a view to an understanding of the electronic structure and spectrum of this
molecule. The results for the ground state properties of RDX indicate that an idealised chair form in which all three \( C_2N-NO_2 \) fragments are individually planar is probably the most stable form of the molecule, and predict a rotational energy barrier of about 10 kcal/mole for rotation about the N-N bond, very similar to that postulated by Kintzinger et al (49) for nitramines. The modified CNDO/2 method of Del Bene and Jaffe† (138) has been used to assign the electronic spectrum of RDX. The results confirm the approach of Stals et al (133) for the interpretation of the electronic spectra of nitramines.

Filhol et al (36) have studied the molecular conformation of RDX, particular interest being given to the conformation of RDX in solution. This study, using vibrational (I.R.), Raman and NMR spectroscopy, dipole moment and depolarised Rayleigh scattering measurements, and INDO molecular orbital calculations, suggests that the RDX molecule has approximately \( C_3v \) symmetry in solution, with some distortion due to the \( NO_2 \) groups. The ring is considered to undergo rapid interconversion in which the cyclic nitrogen atoms oscillate about the planar (sp\(^2\)) position, with little distortion (36). From the INDO calculations the conformation corresponding to the minimum energy form is that of an idealised chair with three planar \( C_2N-NO_2 \) groups. The bond lengths and angles for this form are N-N = 1.32 \( \AA \), C-N = 1.45 \( \AA \), N-O = 1.21 \( \AA \), C-H = 1.09 \( \AA \), and \( \angle \text{ONO} = 126^\circ \), \( \angle \text{CNC} = 120^\circ \), \( \angle \text{HCH} = \angle \text{NCN} = 109^\circ \), 28°. The calculated dipole moment for this form is 5.48 D, in good agreement with the value of 5.78 D found for RDX in dioxan (66). The basic difference between this form and that calculated by Orloff et al (70) is that the length of the N-N bond is much shorter, a value of 1.39 \( \AA \) being used by Orloff et al (70). The INDO calculations performed on RDX in this work (Table 3.8) employ the basic chair structure of Orloff et al (70) with a shorter N-N bond length of 1.34 \( \AA \). The total energy of this idealised chair form is lower than that of the corresponding form of Filhol et al (36), and also lower than that of the form of Orloff.
et al (70), as calculated by the INDO method. The dipole moment of this form is calculated to be 4.94 D, which is somewhat lower than the experimental value. The charge densities are in qualitative agreement with those of Orloff et al (70).

A consideration of the charge densities for the series of N-nitramines shown in Fig 3.27 gives interesting trends. For nitramine, methylnitramine and dimethylnitramine the charge densities are in qualitative agreement with those of Stals et al (133), but the charge density changes shown (Fig 3.27) are much more gradual than those reported previously (133). This is particularly true for the nitro oxygen atoms, whose charges change very little throughout the whole series of nitramines. Similarly, the nitro nitrogen atom charge densities change over a small range, while differences in the charge densities for the amino nitrogen atom and its adjacent carbon atoms are much more marked. For the whole series there is a high positive charge on the nitro nitrogen atom (+0.677 → +0.695) and the α carbon atoms are also positively charged. The amino nitrogen atom has a negative charge density, which varies over the range (-0.164 → -0.227), while the nitro oxygen atoms carry a fairly constant negative charge (-0.369 → -0.394) throughout.

For the primary nitramines the charge density of the amino hydrogen atoms remains fairly constant (+0.157 → +0.142); while for the carbon atom on going from \(\text{CH}_3\text{N}(\text{NO}_2^-)\) to \((-\text{NO}_2^-)\text{N}-\text{CH}_2-\text{N}(\text{NO}_2^-)\) there is an increase in positive charge density (+0.17 → +0.29), with a corresponding change in the negative charge density of the amino nitrogen atom (-0.16 → -0.21). On going from RDX to 1-nitroso-3,5-dinitro-1,3,5-triazacyclohexane the inclusion of the N-nitroso grouping in the molecule brings about a redistribution of charge. However, the charge densities within the two N-nitramine groups remain similar to those of the N-nitramine groups in RDX. For the α carbon atoms the carbon atom cis to the nitroso oxygen atom has the lowest positive charge, with that of the trans carbon atom slightly higher; both are lower than that of the methylene carbon atom between the
two N-nitramine groups. The charge densities of the protons on the \( \alpha \) carbon atoms for N-nitramines (Table 3.8) show no distinct trends, for the values change very little throughout the series of N-nitramines considered.

Nagata and Imamura (139) have calculated the electronic structures of methylethylnitrosamine and diallylnitrosamine and their \( \alpha \)-hydroxy derivatives, using the CNDO molecular orbital method (5). The charge densities reported for the lowest energy conformations of these molecules (139) are in qualitative agreement with those given for the N-nitrosamines considered in this work (Figs 3.27 and 3.30). On passing along the series dimethylnitrosamine (A)(3.29), 1,3,5-trinitroso-1,3,5-triazacyclohexane (B)(3.31) and 1-nitroso-3,5-dinitro-1,3,5-triazacyclohexane (F)(3.23), the negative charge density on the nitroso oxygen atom progressively decreases (from \(-0.267 \rightarrow -0.252 \rightarrow -0.234\)), while the positive charge density on the nitroso nitrogen atom progressively increases (from \(+0.153 \rightarrow +0.172 \rightarrow +0.176\)). The negative charge density on the amino nitrogen atom increases on going from dimethylnitrosamine to 1,3,5-trinitroso-1,3,5-triazacyclohexane and 1-nitroso-3,5-dinitro-1,3,5-triazacyclohexane (from \(-0.078 \rightarrow -0.131\)).

For the unsymmetrical N-nitrosamines a cis/trans dependence of the charge densities of the \( \alpha \) carbon atoms is shown, with the trans carbon atom having a consistently higher positive charge density than the cis carbon atom. A comparison of the charge densities of the two forms (A) and (B)(3.31) shows that the charge densities within the NNO groups remain constant, while the charge densities of the carbon atoms show an increase in the order \( \alpha_{cc} \leq \alpha_{ct} \leq \alpha_{ct} \leq \alpha_{tt} \). For the unsymmetrical N-nitrosamines the protons on the \( \alpha \) carbon atoms also show a cis/trans dependence, with the trans protons having a consistently higher negative charge density than the cis protons. The molecular orbital data for the lowest energy form of dimethylnitrosamine (A)(3.29) includes the charge densities and bond orders illustrated in Fig 3.30. The bond orders give support to the view that
there is considerable delocalisation of charge throughout the 
N-nitrosamine grouping (49,106), the value of the \( \pi \) bond order \((+0.485)\) 
indicates appreciable double bond character for this bond.

The results of the calculations on hexamine and derivatives are 
summarised in Chapter Three, Part I, Section 3.13; and the charge densities 
are given in Fig 3.32. Due to the complexity of these molecules it is 
difficult to comment upon the trends shown. However, the effects of 
quaternisation of hexamine are clear. The symmetrical distribution within 
hexamine is disturbed by the presence of the substituent and the changes are 
summarised in Fig 4.25, together with the related changes on going from 
hexamine to 7-nitro-1,3,5-triazaadamantane.
On passing from hexamine to a quarternary derivative there is a decrease of negative charge density on the hexamine type nitrogen atoms ($-0.265 \rightarrow -0.220$), and a much greater decrease on passing from a hexamine type nitrogen atom to a quarternary nitrogen atom ($((A)-(B))_{(4.25)}$, $-0.265 \rightarrow 0.058$). The ($N\text{-CH}_2\text{-N}$) carbon atoms show a decrease of positive charge on passing from hexamine to a quarternary derivative, as do the ($N^+\text{-CH}_2\text{-N}$) carbon atoms, but to a greater extent. There is a decrease of negative charge for all protons on going from hexamine to a quarternary derivative; with the ($N^+\text{-CH}_2\text{-N}$) protons showing the greatest decrease, while still remaining equivalent. The ($N\text{-CH}_2\text{-N}$) axial and equatorial protons show different charge densities, with the axial protons having a lower negative charge than the equatorial protons. Similar trends are shown by the respective nuclei on going from hexamine to 7-nitro-1,3,5-triazaadamantane. Within the series of quarternary derivatives there is a decrease in positive charge on the quarternary nitrogen atom on passing from (B)$\rightarrow$(C)$\rightarrow$(D)$_{(4.25)}$. Other nuclei have fairly constant charge densities within this series, although there are some very small changes which might be significant.

For dimethylnitramine (C)$_{(3.23)}$ and dimethylnitrosamine (A)$_{(3.28)}$ a study of the restricted rotation about the N-N bonds in these molecules has been performed. If rotation about the N-N bond in these molecules is considered, then the conformations which have the NO$_2$ or NO groups inclined at an angle of 90° to the C$_2$NN fragment may be considered to comprise the transition states in the respective interconversions. For dimethylnitramine the ground state conformation in the interconversion may be considered to be the form (B)$_{(3.25)}$, while the form (C)$_{(3.25)}$ may be considered to comprise the transition state. The calculated total energy difference between these two forms is about 12 kcal/mole, which is comparable with the value of 10 kcal/mole predicted for RDX by Orloff et al (70) and the value of $\geq 9$ kcal/mole expected for this rotation by Kintzinger et al (49). For dimethylnitrosamine the ground state and transition states in the
interconversion may be considered to be the forms (A) and (B)\(^{(3.29)}\), for which the calculated total energy difference is about 21 kcal/mole, which is in excellent agreement with the value of 21.1 kcal/mole found for the vapour phase free energy of activation for rotation about the N-N bond for dimethylnitrosamine (140).

The value of 12 kcal/mole may be considered a good estimate of the barrier of rotation about the N-N bond in dimethylnitramine, for the calculations for this molecule give very good agreement with the ground state properties of this molecule, such as the dipole moment (Table 3.8) and the coupling constant data (Table 3.9).

Attempts have been made to correlate the predicted charge densities for the N-nitramines, N-nitrosamines, hexamine and derivatives with their \(^1\)H, \(^{13}\)C and \(^{14}\)N NMR chemical shifts. For the N-nitramines considered there is no apparent correlation between the charge densities of the protons attached to the carbon atoms \(\alpha\) to the N-nitramine groupings. For the N-nitrosamines considered there is a correlation, for a proton shift to higher frequency is associated with an increase in the negative charge density for the appropriate protons. Thus the cis/trans dependence of the protons in N-nitrosamines is reflected in the calculated charge densities.

For hexamine and its quarternary derivatives, however, the calculations predict, on this basis, that the \((\text{N-CH}_\text{eq}^+ \text{-N})\) protons resonate at higher frequency to the \((\text{N-CH}_\text{ax}^- \text{-N})\) protons, and that these protons resonate at higher frequency to the \((\text{N}^+\text{-CH}_2^- \text{-N})\) protons; in complete contrast to the assignments given for these protons in Table 3.3. For 7-nitro-1,3,5-triazaadamantane, however, the trend predicted is \((\text{N-CH}_\text{eq}^- \text{-N}) > (\text{N-CH}_\text{ax}^+ \text{-N}) > (\text{N-CH}_2^- \text{-C})\), in agreement with the assignments given in Table 3.4. The possibility of additional electric field effects for N-nitrosamines also complicates the situation.

For N-nitramines, there is insufficient \(^{13}\)C NMR data to attempt a meaningful correlation, but it is possible that increasing positive charge on the carbon atom is associated with a shift to higher frequency.
For the N-nitrosamines considered a shift to higher frequency is associated with an increase in positive charge density at the carbon atom considered, and for dimethylnitrosamine and 1,3,5-trinitroso-1,3,5-triazacyclohexane (A)(3,31) the cis/trans dependences shown in the $^{13}$C NMR spectra are mirrored in the calculated charge densities. For hexamine and derivatives a similar situation to that indicated for protons exists. Higher positive charge density on a carbon atom appears to be associated with a shift to higher frequency, which for the (N=CH$_2$-N$^-$) and (N$^+$=CH$_2$-N$^-$) carbon atoms is the reverse of the assignments given in Table 3.7.

For the $^{14}$N NMR data there is no apparent correlation between the $^{14}$N NMR chemical shifts and the calculated charge densities for the respective nuclei. Attempts have been made to correlate the $^{14}$N NMR chemical shifts with the local paramagnetic term of the nitrogen screening constant tensor, the method and results are given in Chapter Three, Part I, Section 3.13. For the N-nitramines and N-nitrosamines considered (Table 3.11) it is difficult to interpret the results comprehensively, due to the lack of experimental data and of suitable compounds for comparison. For these molecules the two types of amino nitrogen atom and the nitro and nitroso nitrogen atoms have characteristic resonance positions well removed from each other in the $^{14}$N NMR spectrum. However, the absolute values of $(Z_{2p})^3\sum Q_{NT}$ and $\left<r^{-3}\right>_{2p}\sum Q_{NT}$ occur within the same range of values, which shows that absolute correlations cannot be made. The differences found in the $^{14}$N NMR resonance positions for these nuclei are presumably due to differences in the average excitation energy required for each type of nitrogen atom, for the values of the respective diamagnetic terms should be fairly constant. The differences are related to the fact that different transitions make contributions to the average excitation energy, $\Delta E_{av}$, depending on the chemical environment of the nitrogen atom under consideration. The results for these molecules reinforce a required approximation in the theoretical approach, which requires that a series of closely related molecules should be examined in order to predict the experimental shifts.
This is further emphasised by the results for hexamine and derivatives (Table 3.12), which show a good correlation between the experimental $^{14}$N NMR chemical shifts and the calculated local paramagnetic term, as represented by $\langle r^{-3} \rangle_{2p} \sum Q_{NT}$.
Attempts have been made to study the hexamine nitrolysis reaction by comparison with the nitration reactions of certain related quarternary derivatives of hexamine (B) and 7-nitro-1,3,5-triazaadamantane (D); and by \(^1\)H NMR studies of reactions of substrates in nitric acid. There are distinct comparisons between the reactions of hexamine and 7-nitro-1,3,5-triazaadamantane. These are summarised in Figs 4.26 and 4.27. Direct comparisons are possible for the various reactions, particularly with regards to the nature of the products.

For the various nitration reactions a consideration of the products formed from hexamine and 7-nitro-1,3,5-triazaadamantane proves interesting. Upon the addition of 70% nitric acid to an aqueous solution of hexamine at 273 K an immediate precipitate of hexamine dinitrate (A) results. For 7-nitro-1,3,5-triazaadamantane the mononitrate (B) is formed under the same conditions. With 98% nitric acid under conditions which give RDX (C) with hexamine, 7-nitro-1,3,5-triazaadamantane gives a 1,3,5-trinitro-1,3-diazacyclohexane derivative (D). Under the conditions which give PCX (E) with hexamine, 7-nitro-1,3,5-triazaadamantane gives the compound (F). While a cyclic N-nitroxyethyl derivative is not isolated from the hexamine nitrolysis reaction, for 7-nitro-1,3,5-triazaadamantane the derivative (D)(a) is obtained. Hexamine gives 1-nitroso-3,5-dinitro-1,3,5-triazacyclohexane (G) on treatment of a nitrolysis mixture with aqueous sodium nitrite below 243 K, but for 7-nitro-1,3,5-triazaadamantane a reaction appears to occur at low temperature but the product decomposes on attempted isolation from solution. With nitric acid/ammonium nitrate solution ('NAN') 7-nitro-1,3,5-triazaadamantane forms the derivative (D)(b), whereas hexamine gives no isolatable product on dilution of the reaction mixture with excess ice-water.
Fig 4.26
Fig 4.28
Despite the differences which occur for the respective nitration reactions of hexamine and 7-nitro-1,3,5-triazaadamantane, there are sufficient similarities to suggest that the nitration mechanism should be similar. From the nature of the products obtained from the nitration reactions of 7-nitro-1,3,5-triazaadamantane, this compound is considered to undergo nitration via a stepwise scission process, possible reaction mechanisms are given in Fig 4.11. This strongly supports the view that hexamine undergoes nitration via a similar stepwise scission process, and not by a mechanism involving the degradation of hexamine to suitable fragments, which then recombine to give the product. A possible mechanism is illustrated in Fig 1.2, although more complex pathways, such as those given in Fig 4.15, may exist.

The nitration reactions of the quaternary derivatives of hexamine (B)(4.1) provide little additional information concerning the possible nitration mechanism of hexamine. The isolation of the derivatives (A)(4.2)(R=CH₅, C₂H₆) from the reaction of 1-methylhexamine nitrate and 1-ethylhexamine nitrate with 98% nitric acid respectively does indicate the participation of 1,3,5,7-tetraazabicyclo(3.3.1)nonane derivatives in the nitration reactions, as postulated for hexamine.

In contrast, the nitration reactions of tetraazabishomoadamantane (C)(4.1) show that for this compound degradation of the molecule occurs to give fragments, which recombine to give products under appropriate conditions.

Although it seems possible that RDX may be formed from the reaction of suitable fragments (3,27,32,35), this compound has not been isolated from synthetic mixtures of fragments under nitrating conditions comparable with those employed for the nitrolysis of hexamine in nitric acid alone.

Studies of the variable temperature $^1$H NMR spectra of 1-methoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (H)(4.28), 3,7-dinitro-1,3,5,7-tetraazabicyclo(3.3.1)nonane (DPT) and hexamine in 98% nitric acid over the temperature range 243 - 303 K confirm some features of the hexamine nitrolysis reaction.
From the different temperature dependencies of the intermediate(s) present for each of these substrates, and from the differences in the nature and number of signals observed, it is concluded that different intermediates are present for each of these substrates in nitric acid. This confirms some of the observations of Bell and Dunstan (2) concerning the nature of the intermediate(s) present in the hexamine nitrolysis reaction. The complex changes which occur in the spectra of hexamine over the temperature range studied also suggest that there is a complex relationship between the species present and the temperature. Due to the complexity of the spectra obtained for these three substrates it is not possible to ascertain the nature of the species present in these nitrolysis reactions, nor to differentiate between a stepwise scission process or a recombination of fragments process for the mechanism of nitration of hexamine. Such information awaits the accumulation of more data concerning the characteristics of the spectra obtained from nitrolysis reactions.

From a consideration of the $^1\text{H}$, $^{13}\text{C}$ NMR and molecular orbital data of N-nitramines and their closely related N-nitrosamines it is reasonable to consider that the effects of the N-nitro and N-nitroso groups on neighbouring nuclei are very similar, in nature if not in degree. For N-nitrosamines, the $^1\text{H}$ and $^{13}\text{C}$ NMR data are interpreted on the basis of the magnetic anisotropy of the N-nitrosamine grouping, coupled with electric field effects. The polarity of the N-nitramine group is comparable with that of the N-nitroso group and thus similar electric field effects might be expected. However, the N-nitramine group is symmetrical and thus no effects due to magnetic anisotropy of the grouping are possible. Thus evidence of a barrier to rotation about the N-N bond in N-nitramines is difficult to obtain, whereas for N-nitrosamines variable temperature $^1\text{H}$ NMR spectroscopy provides such information. In the light of the molecular orbital data for dimethylnitramine (this work) and RDX (70) it appears that such a barrier probably exists, being of the order 9 - 12 kcal/mole. This may be compared with values of 20 - 25 kcal/mole (44, 45, 154) for N-nitrosamines.
The planarity of both the N-nitraniine and N-nitroso groupings (35, 40) is further substantiated by a consideration of the $^1H$ NMR spectra of cyclic systems containing these groupings. The spectra are consistent with fast ring inversion, brought about by flattening of the rings by the presence of the amino nitrogen atom, which possesses $sp^2$ character. Although the overall effects of these two groupings are similar, a consideration of the $^1H$ and $^{15}N$ NMR data for these compounds indicates that the electronic structures within the NNO$_2$ and NNO units are different, although both possess considerable delocalisation of charge.

For hexamine and derivatives, a consideration of the $^1H$, $^{13}C$, $^{14}N$ NMR and molecular orbital data provides a basis for the interpretation of the effects of substituents upon the tetraazaadamantane structure. However, such an interpretation awaits further confirmation of the assignments in the $^1H$ and $^{13}C$ NMR spectra for these molecules.

The $^1H$ NMR spectra of 1,3,5,7-tetraazabicyclo(3.3.1)nonane derivatives indicate that these molecules exist in chair-chair or flattened chair-chair conformations, with progressive flattening of the rings occurring with increasing conjugation of the 3,7-substituents with the ring nitrogen atoms.

### 4.12 FUTURE DEVELOPMENTS

From this study it is considered that further studies of the chemistry of 7-nitro-1,3,5-triazaadamantane (D)(4.1) and of other 7-substituted 1,3,5-triazaadamantanes will provide a better understanding of the chemistry of hexamine and other aza-substituted adamantanes.

From the synthetic methods available for the synthesis of 7-substituted 1,3,5-triazaadamantanes (141 - 145), the approach of Stetter and Bockmann (141) is of more general use. This method is illustrated in Fig 4.29. The low yield step in this procedure is the introduction of the amine residue, but recently Fleischer et al (146) have reported that the use of
the azide anion as the nucleophile for the introduction of the required amine residue gives appreciably better yields. This approach is also illustrated in Fig 4.29. This latter method has the disadvantage that the use of azides can be hazardous.

![Chemical structure diagram](image)

**Fig 4.29**

Hodge (142) has reported the synthesis of several 7-substituted 1,3,5-triataadamantanes from appropriate reactions of 7-nitro-1,3,5-triataadamantane, usually involving reduction to give 7-amino-1,3,5-triataadamantane (142 - 144), which may react further (Fig 4.30).

![Chemical structure diagram](image)

**Fig 4.30**
From the preliminary $^1$H NMR studies of the reactions of substrates in nitric acid, it is considered that this technique may provide an additional means of studying nitration reactions, and that further studies on additional substrates will lead to a better understanding of nitration reactions in general.

With regards to the hexamine nitrolysis reaction further data are required concerning the characteristic spectra of products found in the reaction, particularly for 3,5-dinitro-1,3,5-triazacyclohexane derivatives and linear nitramines. Data on the fate of fragments not concerned with the formation of major products in the reaction are also required for the interpretation of the $^1$H NMR spectra obtained. A useful technique for the identification of signals in a given spectrum involves 'doping' the sample with a known substrate and observing which peaks are enhanced. Such a technique is required for the identification of signals, for this has proved extremely difficult 'by inspection' due to the complexity of the spectra.

Studies directed towards the investigation of protonation effects in nitric acid are required, these might involve comparisons of spectra taken from reactions run in HNO$_3$ with those run in DNO$_3$.

$^1$H NMR spectroscopy may also provide a suitable technique for the study of nitrogen-containing species present in nitration reactions, and may give information concerning the nature of the nitrating species present in nitric acid.

An investigation of the nitration reactions of 7-nitro-1,3,5-triaza-adamantane and related derivatives employing $^1$H NMR spectroscopy may aid the elucidation of the mechanism of nitration of this compound and also of hexamine.
CHAPTER FIVE

PREPARATION AND CHARACTERISATION OF COMPOUNDS STUDIED.
PREPARATION AND CHARACTERISATION OF COMPOUNDS STUDIED.

Hexamine, hexamine mononitrate, and some available primary and secondary N-nitramines were supplied by E.R.D.E., Waltham Abbey, Essex; and used without further purification.

The other compounds studied were prepared and characterised as follows:

5.1 1,3-dinitro-1,2,5-triazacyclohexane.

In a preliminary experiment 2g hexamine was added to 16 ml 98% nitric acid at 246 K or below with stirring and cooling (dry ice/acetone cooling bath) over 6 minutes. Then 50 ml ice-water was added to the reaction mixture all at once, the temperature increased to about 288 K. Stirring and cooling was continued for a further 6 minutes, the temperature fell to 258 K. The cooling bath was then removed and stirring continued for a further 13 minutes, the temperature increased to 278 K. The precipitate which formed was filtered, washed with water, chilled ethanol and ether and then dried. An Infra-red spectrum of the material indicates that the principal constituents of this product are hexamine dinitrate and PCX.

On washing the material with a large excess of water, most of it dissolves, but a small amount of less soluble material remains on the filter. An Infra-red spectrum of this material is given in Fig 5.1.

The following procedure gives this compound in higher yield (up to 0.4 gm from 2 gm of hexamine).

2 gm hexamine is admixed with dry ice flakes and then added to 16 ml 98% nitric acid below 243 K with stirring and cooling (dry ice/acetone cooling bath) over 20 minutes. The cooling bath is then removed and crushed ice is added to the reaction mixture. Precipitation occurs and the temperature rises to about 293 K. The solution is stirred for 2 minutes, then filtered. The ice is then washed away with a large excess of water to leave the product (0.4 gm), which is washed with cold ethanol and ether, then dried. The product has a m.p. of 335-336 K.
Lower yields are obtained when hexamine dinitrate is used instead of hexamine, also when hexamine is used with no dry ice flakes.

No suitable solvent has been found for recrystallisation of this compound, since it appears to be unstable in air and in solvents. Good analysis figures are only obtained from samples less than 24 hours old. $^1$H NMR spectra in various solvents are not consistent, indicating possible decomposition. Microanalysis figures for this compound are:

Found: 
- C 20.6% H 4.1% N 39.7% (E.R.D.E.)
- C 20.8% H 3.5% N 40.0% (Surrey)

Calc. for $C_7H_5N_5O_4$; C 20.34% H 3.95% N 39.55%

The Infra-red spectrum (Fig. 5.1) indicates the presence of $\sim N-NO_2$ (1530 cm$^{-1}$), $\sim NH$ (3280 cm$^{-1}$) and possibly $-(NO_2)N-CH_2$-$N(NO_2)$-(3010 cm$^{-1}$) in a cyclic structure.

5.2 Reactions of Hexamine and Derivatives in "NAN".

In the general procedure 1 gm of sample is added to 20 ml "NAN" at room temperature and then left to stand for 60 hours. Crystals of ammonium nitrate are generally precipitated. The solution is then 'drowned out' in a large excess of ice-water.

For the samples hexamine, hexamine mononitrate, hexamine dinitrate, 1-methylhexamine nitrate, 1-ethylhexamine nitrate, 1-acetamidomethylhexamine nitrate and 1-propionamidomethylhexamine nitrate, no insoluble product is obtained on the addition of the reaction mixture to a large excess of ice-water.

If the aqueous solutions thus obtained are neutralised with aqueous ammonia and left to stand at room temperature for a few hours, a very small amount of material is precipitated for each sample. An Infra-red spectrum of this material indicates that it is RDX.
5.3 Preparation of 1-methylhexamine dinitrate and trinitrate.

(1) 30 gm hexamine dinitrate is refluxed for 3 hours in 75 ml of water, the volume of the solution is reduced under reduced pressure to give a light yellow oil. On standing at 273 K overnight no precipitation occurs. The oil is then slowly added with stirring to 50 ml of 70% nitric acid at 273 K to give a white precipitate. The mixture is then filtered and the residue dried in a desiccator. Yield 7.4 gms.

(2) 30 gm hexamine dinitrate is refluxed for 3 hours in 150 ml of methanol, the volume of the solution is reduced under reduced pressure to give a yellow oil. On standing at 273 K overnight a white precipitate slowly develops. This is filtered and dried. Yield 5.8 gms. The filtrate (yellow oil) is then added slowly to 50 ml of 70% nitric acid at 273 K with stirring, 50 ml of cold (273 K) methanol is carefully added to the solution to produce a white precipitate, which is filtered, washed with cold ethanol, then dried. Yield 2.4 gms.

In the above procedures the oils first obtained are considered to contain 1-methylhexamine nitrate (from an Infra-red spectrum of the oil (thin film)). In (2) above, the precipitate obtained on leaving the oil at 273 K overnight appears to be 1-methylhexamine nitrate contaminated with ammonium nitrate (from an Infra-red spectrum of this product). Only ammonium nitrate is precipitated on attempted isolation of the 1-methylhexamine nitrate on treatment with hot methanol. The products obtained from (1) and (2) on adding the respective oils to cold 70% nitric acid appear to be identical (Infra-red spectra). From the Infra-red (Fig 5.2) and $^1$H NMR spectra (reported in Table 3.3), and micro-analytical data, the compound is considered to be 1-methylhexamine trinitrate. It has a melting point of 420-425 K, with the following data:

<table>
<thead>
<tr>
<th>Found</th>
<th>C 23.81%</th>
<th>H 5.00%</th>
<th>N 28.68%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calc. for $C_{17}H_{17}N_9O_9$</td>
<td>C 24.49%</td>
<td>H 4.96%</td>
<td>N 28.57%</td>
</tr>
</tbody>
</table>
Fig 5.2
The material is not stable, attempted recrystallisation from hot methanol results in the recovery of a different substance which is considered, on the basis of its Infra-red (Fig 5.2) and $^1$H NMR spectra (reported in Table 3.3) and the microanalytical data, to be 1-methylhexamine dinitrate. Recrystallisation from hot methanol gives a product with melting point 406-410 K. The corresponding microanalytical data are:

<table>
<thead>
<tr>
<th>Element</th>
<th>Found</th>
<th>Calc</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>29.31%</td>
<td>30.04%</td>
</tr>
<tr>
<td>H</td>
<td>5.48%</td>
<td>6.02%</td>
</tr>
<tr>
<td>N</td>
<td>31.81%</td>
<td>30.34%</td>
</tr>
</tbody>
</table>

Calc for $C_7H_{16}N_6O_6$: C 30.00% H 5.71% N 30.00%

5.4 Preparation of 1-Methylhexamine Nitrate and 1-Methyl-3,7-Dinitro-1,2,5,7-Tetraazabicyclo(3.3.1)nonane Nitrate.

1-methylhexamine nitrate is prepared from the reaction of hexamine with methyl iodide in refluxing methanol, followed by treatment of the hot solution with powdered silver nitrate, after the method of Foss et al (59).

The compound is characterised by comparison of its melting point with the literature value, by comparison of its Infra-red spectrum (Fig 5.2) with that of an authentic sample (E.R.D.E.) and from its $^1$H NMR spectrum (recorded in Table 3.3).

1-methyl-3,7-dinitro-1,3,5,7-tetraazabicyclo(3.3.1)nonane nitrate is prepared from the reaction of 1-methylhexamine nitrate with cold (263 K) nitric acid, followed by addition of the reaction mixture to an excess of ice-water, after the method of Foss et al (60). The material has a m.p 423-433 K (literature value 415 K (60)). The microanalytical data for this compound are:

<table>
<thead>
<tr>
<th>Element</th>
<th>Found</th>
<th>Calc</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>24.29%</td>
<td>24.41%</td>
</tr>
<tr>
<td>H</td>
<td>4.60%</td>
<td>4.41%</td>
</tr>
<tr>
<td>N</td>
<td>33.62%</td>
<td>33.22%</td>
</tr>
</tbody>
</table>

Calc. for $C_6H_{15}N_7O_7$: C 24.41% H 4.41% N 33.22%

The Infra-red spectrum of this material is given in Fig 5.3 and its $^1$H NMR spectrum is recorded in Table 3.2.
5.5 Preparation of 1-Ethylhexamine Nitrate and 1-Ethyl-3,7-Dinitro-1,3,5,7-tetraazabicyclo(3.3.1)nonane Nitrate.

5.2 gm of 1-ethylhexamine iodide (Eastman Kodak) is refluxed in 150 ml of methanol, then 3 gm of powdered silver nitrate is added to the hot solution and the whole refluxed a further 30 minutes. The precipitated silver iodide is filtered off, and the filtrate left at 273 K overnight. Excess ether is added to produce a white precipitate, which is filtered, washed with ether, then dried. Yield 1 gm; m.pt 408-409 K. The microanalytical data for this compound are:

- **Found**: C 41.33% H 7.45% N 30.92%
- **Calc. for C<sub>6</sub>H<sub>17</sub>N<sub>5</sub>O<sub>3</sub>**: C 41.56% H 7.36% N 30.30%

The Infra-red spectrum of this compound is very similar to that of 1-methylhexamine nitrate. On the basis of the Infra-red and <sup>1</sup>H NMR spectra (reported in Table 3.3) and microanalytical data the compound is considered to be 1-ethylhexamine nitrate.

1-ethyl-3,7-dinitro-1,3,5,7-tetraazabicyclo(3.3.1)nonane nitrate is prepared from 1-ethylhexamine nitrate in a similar manner to that used in formation of 1-methyl-3,7-dinitro-1,3,5,7-tetraazabicyclo(3.3.1)-nonane nitrate from 1-methylhexamine nitrate (60).

1 gm 1-ethylhexamine nitrate is slowly added to 12 ml 98% nitric acid at 263 K with stirring, and the reaction mixture is stirred at this temperature for a further 30 minutes. It is added to an excess of ice-water and stirred for a further 30 minutes. The white precipitate which develops is filtered, washed with water and ethanol, then dried. Yield 0.6 gm; m.pt 301-302 K. The microanalytical data are:

- **Found**: C 27.13% H 5.00% N 31.97%
- **Calc. for C<sub>7</sub>H<sub>15</sub>N<sub>7</sub>O<sub>7</sub>**: C 27.18% H 4.85% N 31.71%
On the basis of this data, and by comparison of its Infra-red spectrum (Fig 5.5) with that of 1-methyl-3,7-dinitro-1,3,5,7-tetraazabicyclo(3.3.1) nonane nitrate (Fig 5.3), the compound is considered to be 1-ethyl-3,7-dinitro-1,3,5,7-tetraazabicyclo(3.3.1)nonane nitrate. This material is not stable in some solvents and decomposes with the evolution of a gas.

5.6 Other Compounds Related to Hexamine.

(1) Hexamine dinitrate is prepared after the method of Hale (18).

(2) 1-Acetamidomethylhexamine nitrate is prepared after the method of Bachmann et al (152).

These compounds are identified by comparison of their melting points with the appropriate literature values, by comparison of their Infra-red spectra with that of an authentic sample (spectra supplied by E.R.D.E.), and from a consideration of their $^1H$ NMR spectra (recorded in Table 3.3).

(3) 1-Propionamidomethylhexamine nitrate is prepared in a similar fashion to 1-acetamidomethylhexamine nitrate, after the method of Bachmann et al (152). The compound is identified on the basis of its melting point (443 K, literature value 451-3 K (152)), by comparison of its Infra-red spectrum with that of the closely similar compound 1-acetamidomethylhexamine nitrate, from its $^1H$ NMR (Table 3.3) and analytical data:

\[
\text{Found} : \quad C \quad 41.47\% \quad H \quad 7.02\% \quad N \quad 29.21\%
\]

\[
\text{Calc. for C}_{10}H_{20}N_6O_4 : \quad C \quad 41.67\% \quad H \quad 6.94\% \quad N \quad 29.17\%
\]

(4) 3,7-bis(phenylazo)-1,3,5,7-tetraazabicyclo(3.3.1)nonene (A) and 3,7-bis(p-bromophenylazo)-1,3,5,7-tetraazabicyclo(3.3.1)nonane (B) are prepared after the method of Duden and Scharff (150). (M. Passan).

Microanalytical data:

(A) m.p.t 493-494 K (recryst. benzene)

\[
\text{Found} : \quad C \quad 61.00\% \quad H \quad 5.98\% \quad N \quad 33.45\%
\]

\[
\text{Calc. for C}_{17}H_{20}N_8 : \quad C \quad 60.71\% \quad H \quad 5.95\% \quad N \quad 33.34\%
\]

(B) m.p.t 462-463 K (recryst. acetone)

\[
\text{Found} : \quad C \quad 41.26\% \quad H \quad 3.62\% \quad N \quad 22.81\%
\]

\[
\text{Calc. for C}_{17}H_{16}N_8Br_2 : \quad C \quad 41.30\% \quad H \quad 3.64\% \quad N \quad 22.68\%
\]
5.7 Preparation of 7-nitro-1,3,5-triazaadamantane.

A mixture of 125 ml ethanol (96%), 15 gm nitromethane, 23 gm paraformaldehyde and 58 gm ammonium acetate is stirred and refluxed for one hour, and 11 gm paraformaldehyde added to the solution. The mixture is then stirred and refluxed for a further 1 hour, and another 11 gm paraformaldehyde is added and the whole mixture is stirred and refluxed for a further 5 hours. The solution is filtered hot, any residue washed with IMS, and dried in a dessicator. The filtrate is cooled at 273 K for a period of hours, further product material is filtered, washed with IMS, and dried. The combined yield of crude product averages about 25 gm (49%). It may be purified by recrystallisation from hot ethanol, followed by further recrystallisation from boiling water containing decolourising charcoal. The final product is obtained as white needles, m.p. 563-583 K (literature 588 K (sublimation) (144)). The above procedure is after the method of Hodge (143).

The Infra-red and $^1$H NMR spectra of this compound are given in Fig 5.4. Microanalytical data are:

Found : C 45.36% H 6.68% N 30.34%

Calc. for C$_{12}$H$_4$N$_4$O$_2$: C 45.65% H 6.52% N 30.44%

Mass spec: m/e = 184 I.R. $\gamma$C-NO$_2$ 1550 cm$^{-1}$ (s)

The data are consistent with the proposed structure.

5.8 Nitrosation Reactions of 7-nitro-1,3,5-triazaadamantane.

(1) 1 gm 7-nitro-1,3,5-triazaadamantane is dissolved in 20 ml acetic acid, and 180 ml water added. The solution is cooled to 278 K in an ice-water bath and 50 ml of cold water containing 2 gm sodium nitrite is added. After about 10 minutes a precipitate forms. This is filtered to give 1 gm (80%) of product. Recrystallisation from hot methanol gives yellow needles, m.p. 480-482 K.
(2) 1 gm 7-nitro-1,3,5-triazaadamantane is dissolved in 50 ml water and added to 200 gm ice containing 10 ml concentrated hydrochloric acid. 50 ml of cold water containing 2 gm sodium nitrite are added. Precipitation takes place and the product is filtered off after 1 hour. The product is washed with water, ethanol and ether, and dried. This product is identical (I.R. analysis) with that from reaction (1). 

(3) 1 gm of 7-nitro-1,3,5-triazaadamantane is slowly added with stirring to a solution containing 2 gm sodium nitrite in 10 ml dilute sulphuric acid and 10 ml water at 283 K (ice-water bath). The resulting mixture is poured into excess ice-water and the product filtered, washed with water, ethanol and ether, and dried. The product is identical (I.R. analysis) with that from reaction (1). 

The Infra-red and $^1$H NMR spectra of this compound are given in Fig 5.5. 

The microanalytical data are:-

<table>
<thead>
<tr>
<th></th>
<th>Found</th>
<th>Calc. for C$<em>6$H$</em>{10}$N$_6$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>31.26% H 4.59% N 36.86% (Surrey)</td>
<td>C 31.1% H 4.41% N 37.0% (E.R.D.E.)</td>
</tr>
</tbody>
</table>

The mass spectrum of this compound gives a parent molecular ion at m/e 230. 

A molecular weight determination (in ethyl acetate by vapour pressure osmometry (E.R.D.E.)) gives a value of 221 compared with the calculated molecular weight of 230. 

Thus, this compound is considered to be 5-nitro-3,7-dinitroso-1,3,7-triazabicyclo(3,3,1)nonane.

5.9 Tosylation of 7-nitro-1,3,5-triazaadamantane.

To a solution containing 7 gm of 7-nitro-1,3,5-triazaadamantane in 100 ml of water, 20 gm of p-toluenesulphonyl chloride is added with vigorous stirring, together with sufficient 10% sodium hydroxide solution to maintain the pH of the mixture at 8-11. The temperature of the reaction is kept at
about 363-373 K throughout the addition. At the end of the addition a solid product is formed. The reaction mixture is poured into 200 ml of water containing 20 gm of sodium hydroxide and the mixture stirred for 15 minutes. The solid product is filtered, washed with water, and with acetone to remove any unreacted p-toluenesulphonyl chloride. The residue is recrystallised from hot dimethylsulphoxide to give a light yellow powder, m.pt 508-513 K. This compound is insoluble in most common organic solvents.

The microanalytical data are:

Found: C 50.23% H 4.93% N 11.71%
Calc. for C_{20}H_{24}N_{4}O_{6}S_{2}: C 50.00% H 5.00% N 11.67%

Thus, this compound is considered to be 5-nitro-3,7-di(p-toluenesulphonyl)-1,3,7-triazabicyclo(3.3.1)nonane.

5.10 Formation of Salts of 7-nitro-1,3,5-triazaadamantane.

(1) 2 gm 7-nitro-1,3,5-triazaadamantane is dissolved in 50 ml water and cooled to 278 K. Concentrated nitric acid (70%), cooled to 278 K, is gradually added with stirring. Precipitation occurs and the precipitate is filtered, washed with cold ethanol, and cold ether, and dried, to give 1.0 gm of product (37%), m.pt 483 K. The Infra-red and $^1$H NMR spectra of this compound are given in Fig 5.6. The microanalytical data are:

Found: C 34.75% H 5.27% N 29.05%
Calc. for C_{7}H_{13}N_{5}O_{5}: C 34.01% H 5.26% N 28.34%

Thus, the compound is considered to be 7-nitro-1,3,5-triazaadamantane nitrate.

(2) 7 gm of 7-nitro-1,3,5-triazaadamantane and 10 gm methyl iodide are refluxed in 125 ml methanol for 1 hour. 11 gm powdered silver nitrate are added and the mixture refluxed for a further 30 minutes. The precipitated silver iodide is filtered off, and the filtrate is cooled for several hours. White platelets precipitate. The solution is filtered to give 3.9 gm product (39%), m.pt 513 K.
The Infra-red and $^1$H NMR spectra of this compound are given in Fig 5.7.

The microanalytical data are:

**Found**

$\begin{align*}
\text{C} & : 36.63\% \\
\text{H} & : 5.77\% \\
\text{N} & : 26.97\%
\end{align*}$

**Calc. for $C_{15}H_5N_5O_5$**

$\begin{align*}
\text{C} & : 36.78\% \\
\text{H} & : 5.75\% \\
\text{N} & : 26.82\%
\end{align*}$

This compound is thus considered to be 1-methyl-7-nitro-1,3,5-triazaadamantane nitrate.

5.11 Reaction of 7-nitro-1,3,5-triazaadamantane with 'NAN'.

1 g m of 7-nitro-1,3,5-triazaadamantane is dissolved in 20 ml 'NAN' at room temperature and left to stand for 60 hours. Rod-like crystals of ammonium nitrate separate (I.R. analysis). The solution is 'drowned out' in excess ice-water or filtered through a Gouch crucible into an excess of ice-water to give a white precipitate. The precipitate is filtered, washed with water, ethanol and ether, and dried in a dessicator. This compound is designated Nitronitramine II. On average, a yield of about 1.3 gm (76%) of material is obtained. It is recrystallised from ethanol to give a compound with m.p. 418-422 K.

The Infra-red and $^1$H NMR spectra of this compound are given in Fig 5.10.

The microanalytical data are:

**Found**

$\begin{align*}
\text{C} & : 19.62\% \\
\text{H} & : 3.79\% \\
\text{N} & : 31.20\% (\text{Surrey})
\end{align*}$

**Calc. for $C_{11}H_9N_7O_9$**

$\begin{align*}
\text{C} & : 19.33\% \\
\text{H} & : 3.68\% \\
\text{N} & : 31.34\% (\text{E.R.D.E.})
\end{align*}$

The compound is soluble in warm water and gives a white precipitate with 'NITRON' reagent, indicating the presence of a nitrate. The method of Cope and Barab (151) has been used to estimate the nitrate content of this compound gravimetrically; a '% nitrate' composition of 19.1% was found experimentally, which is in good agreement with the calculated value of 19.81%.

The Infra-red spectrum indicates the presence of both $\gamma$N-NO$_2$ (1560(s) cm$^{-1}$) and $\gamma$C-NO$_2$ (1525 cm$^{-1}$(m)) groups, and the possibility of an ionic nitrate.
(1760 cm\(^{-1}\) (w)). Bands for the NH\(^+\) group (at \(\sim 3000\) cm\(^{-1}\) and 1650 cm\(^{-1}\)) are not well resolved. The presence of the weak absorptions of 3020 and 3080 cm\(^{-1}\) are indicative of the presence of \(\text{a-(NO}_2\text{)N-CH}_2\text{-N(NO}_2\text{)}\) linkage in a cyclic structure by comparison with the Infra-red spectra of some known cyclic nitramines.

The \(^1\)H NMR spectrum is considered to indicate the presence of the cyclic structure (A) (5.8).

The signals at \(\delta 3.64\) (2H) and \(\delta 8.44\) (3H) are considered to indicate the presence of the \(-\text{CH}_2\text{-NH}_+\) protons, respectively. The structure (B)(5.8) is thus considered to best represent Nitronitramine II.

5.12 Dilution Studies on the Nitration Reaction of 7-nitro-1,3,5-triazaadamantane

(1) 1 gm 7-nitro-1,3,5-triazaadamantane is added to 16 ml fuming nitric acid below 233 K (dry ice/acetone cooling bath) with stirring. 75 ml cold (213 K) ethanol is slowly added with a pipette, keeping the temperature below 243 K. The precipitate which first appears redissolves on further addition of the cold ethanol solution. On completion of the ethanol addition the solution is filtered cold. A small residue of 7-nitro-1,3,5-triazaadamantane nitrate (0.1 gm) is obtained. The filtrate is left to stand at room temperature for a few hours, whereupon a white precipitate settles out. The solution is filtered, the solid washed with ethanol, and dried. Yield 0.8 gm (53%). The compound may be recrystallised from hot ethanol to give white needles, m.pt. 443-444 K. This material is designated Nitronitramine III.

(2) 1 gm of 7-nitro-1,3,5-triazaadamantane is added to 16 ml fuming nitric acid below 233 K with stirring and cooling (dry ice/acetone cooling bath). 50 ml cold water (ice-bath) is slowly added with a pipette keeping the temperature below 243 K. The precipitate which first appears redissolves upon further addition of water. After the addition of water is complete,
the solution is left to stand at room temperature but no solid material has been obtained. Extraction of the aqueous solution with ethanol or ether and removal of the aqueous layer generally results in the precipitation of a white solid in low yield, this solid is identical to Nitronitramine III (I.R. analysis). Upon extraction with ether, Nitronitramine III is obtained from the aqueous layer.

(5) Dilution of the nitration reaction with aqueous sodium nitrite:
2 gm 7-nitro-1,3,5-triazaadamantane is added to 20 ml fuming nitric acid below 233 K with stirring and cooling (dry ice/acetone cooling bath). A cold solution containing 3 gm sodium nitrite in 50 ml water is slowly added with a pipette, keeping the temperature below 248 K. A reaction appears to take place since a bright yellow mixture results. After completion of the addition of the sodium nitrite solution, the mixture is filtered, the yellow product rapidly decomposes in air to form a glue. This compound has not been characterised.

5.13 Characterisation of Nitronitramine III.

The Infra-red and $^1$H NMR spectra are given in Fig 5.11. The Infra-red spectrum indicates the presence of $\nu$C-NO$_2$ (1550 cm$^{-1}$ (s)), $\nu$N-NO$_2$ (1520 cm$^{-1}$ (s)) and $\nu$NH$_2$ NO$_3$ (2200-3000 cm$^{-1}$ (broad), 1610 cm$^{-1}$ (m) (NH$_2^+$); 1745 cm$^{-1}$ (v) (NO$_3^-$)). The $^1$H NMR spectrum is complicated, which possibly indicates the presence of the 1,3,7-triazabicyclo(3,3,1)nonane structure. The $NH_2^+$ grouping is indicated by a very broad signal at $\delta$ 8.0 (2H).

The microanalytical data are given below. The formation of a white precipitate on the addition of 'NITRON' reagent to an aqueous solution of Nitronitramine III indicates the presence of a nitrate, and also enables the gravimetric estimation of the '% nitrate' content by the method of Cope and Barab (151).
Found: C 25.63% H 4.36% N 29.76% Nitrate 21.54%
Calc. for \( \text{C}_6\text{H}_{12}\text{N}_6\text{O}_7 \): C 25.71% H 4.29% N 30.00% Nitrate 22.14%

Thus the structure ((C)(Fig 5.8)) best represents Nitronitramine III.

5.14 Reactions of Nitronitramine III.

(1) Nitrosation:
1 gm Nitronitramine III is gradually added to a mixture of sodium nitrite (2 gm), dilute sulphuric acid (or hydrochloric acid) (10 ml) and water (10 ml) at about 283 K (ice-bath) with stirring. The solid material which is formed is washed with water and ethanol, then dried. Yield 0.4 gm (45%). Recrystallisation of the material from ethanol gives white needles, m.pt 467-469 K.

The Infra-red and \(^1\text{H} \text{NMR} \) spectra are given in Fig 5.16.

The microanalytical data are given below.

\[
\begin{array}{ccc}
\text{Found} & \text{Calc. for } \text{C}_6\text{H}_{12}\text{N}_6\text{O}_7 \\
\text{C} & 29.44\% & 29.27\% \\
\text{H} & 3.88\% & 4.07\% \\
\text{N} & 33.88\% & 34.15\% \\
\end{array}
\]

The structure (D)(5.8) is thus considered to best represent this compound.

(2) Reaction with 'NAN':
1 gm Nitronitramine III is added to 18 ml 'NAN' (ammonium nitrate/nitric acid) at room temperature. All solids dissolve after about an hour. The mixture is left to stand for two days. It remains clear. After filtering through a Gough crucible into ice-water, a white precipitate results on shaking the flask for a few minutes. The precipitate is filtered, washed with water, ethanol and ether, and dried. Yield 0.5 gm (45%). This compound is identified as Nitronitramine II (B)(5.8), on the basis of its Infra-red spectrum.

(3) Reaction with acetic anhydride:
1 gm Nitronitramine III is added with stirring to 25 ml acetic anhydride at
room temperature. The mixture is stirred for a further one and a half hours until all of the material is dissolved. 75 ml ice-water is added to the mixture all at once. A white precipitate results. The solution is stirred a further half-hour, filtered and dried. Yield 0.5 gm. The precipitate had a m.pt of 431-437 K. It is designated as Nitronitramine VII. The Infra-red and $^1$H NMR spectra are given in Fig.5.15. The microanalytical data are:

<table>
<thead>
<tr>
<th>Found</th>
<th>C 32.34%</th>
<th>H 4.58%</th>
<th>N 22.88%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calc. for $C_{10}H_{16}N_{6}O_9$</td>
<td>C 32.97%</td>
<td>H 4.40%</td>
<td>N 23.08%</td>
</tr>
</tbody>
</table>

The Infra-red spectrum indicates the presence of the groups $\nu\ C-NO_2$, $\nu\ N-NO_2$ (1550 cm$^{-1}$ (s)), $\nu\ N-COCH_3$ (1680 cm$^{-1}$ (s)) and $\nu\ N-CH_2OCOCH_3$ (1745 cm$^{-1}$ (s)), the latter two carbonyl frequencies are assigned by comparison with similar compounds. The weak signals at 3030, 3055 and 3080 cm$^{-1}$ may also be indicative of the presence of a cyclic structure containing $-(NO_2)N-CH_2-N(NO_2)$. The $^1$H NMR spectrum indicates the presence of the structure (A)(5.8). It is, however, difficult to interpret. The structure (E)(5.8) has tentatively been assigned to Nitronitramine VII, however, similar structures can be envisaged, and the material may possibly be a mixture. Thus the characterisation of this compound cannot be considered satisfactory.

(4) Reaction of Nitronitramine III with nitric acid; followed by the addition of water:

1 gm Nitronitramine III is added with stirring and cooling (dry ice/acetone cooling bath) to 16 ml fuming nitric acid below 233 K. 50 ml cold water (ice bath) is slowly added with a pipette keeping the temperature below 243 K. After the addition of about half the water a white precipitate forms and an exothermic reaction is indicated, since the temperature rises rapidly to 248 K. The mixture is quickly cooled to 243 K and the remainder of the water added. The precipitate is filtered and washed with water and cold ethanol. On standing for a short while the solid decomposes to a glue, the addition of the glue to cold concentrated nitric acid resulting in the
recovery of a small amount of Nitronitramine IV.

It is a general feature of nitration mixtures diluted with water that the rapid formation of a precipitate, accompanied by an associated heat rise in the system, results in products which tend to be unstable in air.

5.15 Reaction of 7-nitro-1,3,5-triazaadamantane with nitric acid at

temperatures greater than 233 K; followed by addition of water

1 gm of 7-nitro-1,3,5-triazaadamantane is slowly added to 16 ml fuming nitric acid below 233 K with stirring and cooling (dry ice/acetone cooling bath). The solution is allowed to reach a temperature of 283-293 K over a period of time (experiments have been performed using times of from 30 minutes to two hours). The reaction mixture is rapidly cooled to 233 K and 50 ml cold water slowly added, keeping the temperature below 253 K. A white precipitate results. This material is designated as Nitronitramine I. It may also be obtained if the nitration mixture is either 'drowned out' in excess ice-water, or if ice-water is added to the reaction mixture.

In a similar experiment, the reaction temperature is rapidly increased from 233 K to 293 K over 12 minutes, the reaction mixture is rapidly cooled to 233 K and cold water is slowly added below 253 K. A white precipitate is formed but the material is different to that produced in the above experiments (I.R. analysis). This material is designated Nitronitramine IV, and may be obtained from the previous experiments, instead of Nitronitramine I, by using 98% nitric acid in place of the fuming nitric acid. It may be purified by adding cold concentrated nitric acid, followed by dilution with water after standing for 30 minutes, and filtering. A white powder is obtained, m.pt 402-403 K. When first produced from a nitration reaction, Nitronitramine IV is often susceptible to decomposition in air, and may be stabilised by the addition of concentrated nitric acid.

The Infra-red and $^1$H NMR spectra of Nitronitramine IV are given in Fig 5.12
The microanalytical data are:

<table>
<thead>
<tr>
<th></th>
<th>Found</th>
<th>Calc. for $C_5H_8N_6O_9$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>20.66%</td>
<td>20.27%</td>
</tr>
<tr>
<td>H</td>
<td>2.89%</td>
<td>2.70%</td>
</tr>
<tr>
<td>N</td>
<td>27.70%</td>
<td>27.39%</td>
</tr>
</tbody>
</table>

The Infra-red spectrum indicates the presence of the $\text{C}-\text{NO}_2$ and $\text{N}-\text{NO}_2$ groups (1550 - 1560 cm$^{-1}$ (s)), together with the presence of $\text{-ONO}_2$ (1660 cm$^{-1}$ (s)). The presence of the cyclic $\text{-(NO}_2\text{)N-CH}_2\text{-N(NO}_2\text{)-}$ grouping is indicated by the weak signals at 3020, 3040 and 3080 cm$^{-1}$.

The $^1$H NMR spectrum is relatively simple, indicating the presence of the structure (A)$(5,8)$. The structure (F)$(5,8)$ has thus been assigned to the compound Nitronitramine IV, since this is in best agreement with the available data.

5.16 Reaction of 1-methyl-7-nitro-1,3,5-triazaadamantane nitrate with nitric acid; followed by the addition of water

1 gm of 1-methyl-7-nitro-1,3,5-triazaadamantane nitrate is gradually added to 12 ml fuming nitric acid with stirring and cooling (dry ice/acetone cooling bath), at a temperature between 253 and 263 K. All the material dissolves and the reaction mixture is stirred at this temperature for 30 minutes. The solution is added to 150 gm crushed ice, whereupon a white precipitate slowly develops. The mixture is left to stand for a further 30 minutes, and filtered. The solid residue is washed with water, ethanol and ether, and dried. Yield 0.65 gm (50%), m.pt 446-448 K. The material is designated Nitronitramine VI.

The Infra-red and $^1$H NMR spectra of the material are given in Fig 5.14.

The microanalytical data are:

<table>
<thead>
<tr>
<th></th>
<th>Found</th>
<th>Calc. for $C_7H_{15}N_9O_9$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>24.10%</td>
<td>24.78%</td>
</tr>
<tr>
<td>H</td>
<td>3.89%</td>
<td>3.33%</td>
</tr>
<tr>
<td>N</td>
<td>27.36%</td>
<td>28.91%</td>
</tr>
</tbody>
</table>

On the basis of the data the structure (G)$(5,8)$ is considered to best represent Nitronitramine VI.
**5.17 Attempted characterisation of Nitronitramine I**

The Infra-red and \(^1\)H NMR spectra of this material are given in Fig 5.9. When the material is first obtained from the nitration reaction, washed with water, ethanol and ether, and dried, it has a m.pt of about 393 K.

Microanalytical data for a single sample are given below as an example.

**Found:** C 21.34% H 3.72% N 27.99%

At first this material was considered to be a single compound, but consideration of the Infra-red and \(^1\)H NMR spectra for several samples indicate the presence of a mixture of compounds.

It may be seen from a comparison of the Infra-red and \(^1\)H NMR spectra of Nitronitramine I (Fig 5.9) and Nitronitramine II (Fig 5.10) that one of the constituents of the mixture is very similar to Nitronitramine II.

It is also apparent from a comparison of the spectra of Nitronitramine I with the spectra of Nitronitramine III and IV that these latter two compounds do not constitute part of the former mixture.

In the Infra-red spectrum of Nitronitramine I the band at 3250 cm\(^{-1}\) is characteristic of this material. It may be associated with either \(-\text{OH}\) or \(-\text{NH}\) groupings.

The \(^1\)H NMR spectrum (Fig 5.9) is complicated, and appears to consist of two compounds with a structure of type (A)(5.8); while the intense peak at \(\delta 5.07\) (s) may represent a third compound.

The attempted separation of the components of Nitronitramine I, by boiling the material in different solvents, has provided some interest. Boiling the material in ethanol or methanol, followed by cooling at 273 K results in the recovery of Nitronitramine II in low yield. Boiling the material in water gives a different compound, designated Nitronitramine V. It has been found that boiling Nitronitramine II in ethanol or methanol produces Nitronitramine II in good yield; while boiling Nitronitramine II in water results in the recovery of Nitronitramine V. The material is obtained as white platelets, m.pt 411-413 K.
The Infra-red and $^1$H NMR spectra of Nitronitramine V are given in Fig 5.13.

The microanalytical data for this compound are:

*Found:* C 21.67% H 3.20% N 30.63%

The characterisation of Nitronitramine V is not satisfactory. The Infra-red spectrum only indicates the presence of the $^2$C-NO$_2$ and $^4$N-NO$_2$ groups (1535 cm$^{-1}$ (sh), 1570 cm$^{-1}$ (s) and the cyclic $^5$(NO$_2$)$_2$N-CH$_2$-N(NO$_2$)$_2$- grouping 3010, 3030 3070 cm$^{-1}$ (w)); while the $^1$H NMR spectrum indicates the presence of the structure (A)(5.8). A possible structure for this compound is illustrated by (A)(5.17). The analytical data for this compound are satisfactory. (Required: C 22.15% H 3.38% N 30.15%), but aspects of the $^1$H NMR and Infra-red spectra are not consistent with this structure. It is difficult to envisage the formation of (A)(5.17) from Nitronitramine II (B)(5.8) upon reaction with boiling water. This latter reaction might result in the formation of the compound (B)(5.17), but the microanalytical data for this compound (C 23.90% H 3.58% N 24.70%) are very different from those found for Nitronitramine V. The formation of bicyclic compounds, such as (C) and (D)(5.17), might be considered possible. These compounds give microanalytical data (below) in good agreement with that for Nitronitramine V.

For the compound (D)(5.17) the Infra-red spectrum is expected to show an absorption for the $^3$NH$_2$ $+$ NO$_3$$^-$ grouping, but this is absent for Nitronitramine V. A signal for the $^3$NH$_2$$^+$ protons is not apparent in the $^1$H NMR spectrum of Nitronitramine V. However, the Infra-red and $^1$H NMR spectra of Nitronitramine V could be interpreted in terms of the structure (C)(5.17).

A comparison of the Infra-red and $^1$H NMR spectra of Nitronitramine I (Fig 5.9) with those of Nitronitramine V (Fig 5.13), indicate that Nitronitramine V is not a constituent of the mixture. However a comparison of their $^1$H NMR spectra suggests that a compound somewhat similar to Nitronitramine V may be present. It is thus apparent that the approaches used in an attempt to characterise Nitronitramine I have only hinted at the likely constituents present.
Fig 5-8
5.18 N-Nitroso Compounds.

(1) 1,4-dinitroso-piperazine is commercially available (Eastman Kodak).

(2) 1,4-dinitroso-1,4-diazacycloheptane is prepared by nitrosation of the parent diamine (commercially available from Aldrich Chemical Company) with NaNO₂/H₂O/dil H₂SO₄ at 283 K, after the method of Bell and Dunstan (147). 1 gm of 1,4-diazacycloheptane is quickly added to a cooled solution (283 K ice-water bath) containing 2 gm sodium nitrite in 10 ml water and 10 ml dilute sulphuric acid. A light yellow precipitate settles on top of the solution. The solution is stirred at 283 K for about ten minutes, and filtered. The material is dried to give 0.4 gm of product (25%), m.pt 364-365 K (recryst. methanol).
3,7-dinitroso-1,3,5,7-tetraazabicyclo(3.3.1)nonane is prepared by reaction of hexamine (1 gm) with NaNO$_2$/H$_2$O/dil H$_2$SO$_4$ (2 gm/10 ml/10 ml) at 283 K, after the method of Bell and Dunstan (147) (above). Yield 0.9 gm (67%), m.p. in the range 477-482 K (recryst. methanol) (literature value 480-488 K (84)). The Infra-red spectrum is identical with that of an authentic sample (E.R.D.E.). The material may also be prepared after the method of Bachmann and Deno (84).

1,3,5-trinitroso-1,3,5-triazacyclohexane is prepared after the method of Bachmann and Deno (84). The material obtained has a m.p. 378-379 K (recryst. water) (literature value 379-380 K (84)).

1-nitroso-3,5-dinitro-1,3,5-triazacyclohexane is prepared by the addition of aqueous sodium nitrite solution slowly to a low temperature nitrolysis mixture (233 K) containing either hexamine or 1-methoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane, keeping the temperature below 243 K, after the method of Bell and Dunstan (1,2). The material obtained has a melting point in the range 436-441 K (recryst. methanol) (literature value 424-441 K (148) (after repeated recrystallisation); 449-450 K (149)).

The $^1$H NMR data for these compounds are recorded and interpreted in Chapter Three, Part I, Section 3.3.

Mass spectra of these compounds have been recorded, the data being presented in Section 5.19.
Mass spectral studies have been performed on the five N-nitroso compounds listed in Section 5.18. Mass spectral data have only been reported for compounds containing a single N-nitroso group; whereas some of these compounds contain more than one N-nitroso group in a cyclic system. The mass spectra and possible fragmentation pathways for these compounds are illustrated in Figs 5.18 - 5.22.

For 1-nitroso-3,5-dinitro-1,3,5-triazacyclohexane, the spectrum shows a molecular ion at m/e 206, with intense peaks at m/e 132, 75, 56, 46, 42, 41, 30 and 28. Metastable peaks are notably absent from the spectrum. The data may be accounted for by the postulation of fragmentation pathways similar to some described for RDX by Bulusu et al (153). These are illustrated in Fig 5.18. Fragmentation appears to concern primarily the N-nitro functions and not the N-nitroso function, which seems to be little affected by electron-impact in this case. Accurate mass measurement on the m/e 133 ion which is present in the spectrum of the $^{15}$NO isotopomer (88) shows that this fragment has the constitution (C$_2$H$_4$N$_2$O$_3$($^{15}$NO)), which indicates that the fragment at m/e 132 for the $^{14}$NO compound has the constitution (C$_2$H$_4$N$_2$O$_3$(NO)), as shown in Fig 5.18.

For 1,4-dinitroso-1,4-diazacyclohexane and 1,4-dinitroso-1,4-diazacycloheptene, the primary decomposition pathways involve loss of an NO radical, followed by the loss of the other NO radical, then breakdown of the ring system. This pathway is confirmed by metastable peak analysis. There is also an indication that thermal decomposition may have taken place for these compounds. Line diagrams and possible fragmentation pathways for these compounds are given in Figs 5.19 and 5.20.

For 1,3,5-trinitroso-1,3,5-triazacyclohexane a very simple mass spectrum is obtained (Fig 5.21). A weak parent ion is present, with intense peaks at m/e 100, 42, 41, 30, 28 and 15, these peaks are generally present in the mass spectra of N-nitrosamines. The simplicity of the spectrum, together
with the lack of metastable peaks makes this spectrum very difficult to interpret. A possible scheme (indicated in Fig 5.21) may involve loss of the NO radical, followed by ring contractions, involving loss of N₂O and CH₂N₂O. Alternatively the peak at m/e 100 may correspond to the ion of 

constituition (CN₄O₂)⁺, while that at m/e 42 may be (CH₂=N⁺=CH₂).

For 3,7-dinitroso-1,3,5,7-tetraazabicyclo(3.3.1)nonane, the spectrum may be interpreted by the postulate of primary pathways involving (a) loss of CH₂N₂O and (b) loss of N₂O; these pathways are illustrated in Fig 5.22. Metastable peak analysis does tend to favour the pathways illustrated.
Fig. 5.18
EXPERIMENTAL

NMR Spectra

$^1$H NMR 100 MHz spectra were run on a Varian HA 100 instrument.

(Author)

90 MHz spectra were run on a Bruker WH-90 FT instrument.

60 MHz spectra were run on a Perkin-Elmer R10 instrument.

(Mr. J. Bloxsidge)

60 MHz spectra were run on a Varian V-4300-C instrument.

(Dr. N. Witanowski)

$^{14}$N NMR Spectra were run on a Varian HA 100 instrument, (Author), and on a Varian V-4300-C instrument (Dr. M. Witanowski) employing a $^{14}$N accessory operating at 7.22 MHz.

$^{13}$C NMR Spectra were recorded on a Bruker WH-90 Fourier-Transform instrument, operating at 22.64 MHz. (Dr. J. M. A. Al-Rawi)

Infra-red Spectra

Spectra were recorded on a Unicam SP 200 instrument (NaCl plates) or on a Perkin-Elmer 457 instrument (KBr plates). For solids Nujol Mulls were employed.

Mass Spectra

Spectra were recorded on an AEI MS 12 instrument, operating at 70 eV. (Mr. J. Delderfield)
**Microanalysis**

C, H and N analyses were determined at E.R.D.E. (Mr. R. Dukes) or at the University of Surrey Microanalytical Unit (Mr. E. J. Hopwood).

**Melting Points**

Melting points are recorded on an Electrothermal melting point apparatus. They are not corrected against reliable standards.

**Computing**

Molecular orbital calculations were performed using modified versions of Quantum Chemistry exchange program No. 141 (CNDO/INDO) and No. 224 (INDO incorporating the calculation of coupling constants). The programs were run on the University of Surrey ICL 1905 F, and the University of London CDC 7600 computers.
REFERENCES

(8) Chemical Abstracts.
(9) A.H. Lamberton. Quart. Revs. 5 (1951) 75
(11) P. Griess. Ber. 2 (1869) 434; 5 (1872) 192,855
(13) K.H. Mertens. Ber. 10 (1877) 995
(14) A.P.N. Franchimont and E.A. Klobbie. Rec. Trav. Chim. 7 (1888) 343
(15) H.J. Backer. Ahrens Sammlung. 18 (1912) 359
(16) G.F. Henning. German Patent. 104,280 (1899)
(18) G.C. Hale. J. Amer. Chem. Soc. 47 (1925) 2754
(34) J. Picard. Ind. Chem. Belge. NO 32. 3 (1967) 597
(38) P. Hampson and A. Mathias. J.C.S. Chem. Comm. (1968) 825
(42) R.K. Harris. J. Mol. Spec. 15 (1965) 100
(47) R.C. Cookson and T.A. Crabb. Tetrahedron. 24 (1968) 2385


(57) D.A. Gallagher. Private communication.


(64) J. Stals. Australian. J. Chem. 22 (1969) 2505

(65) P. G. Hall. Private communication.

(66) M.V. George and G.F. Wright. J. Amer. Chem. Soc. 80 1200 (1958)

(67) P.G. Hall and G.S. Horsfall. JCS. Perkin II. (1973) 1280

(68) T. Axenrod. Private communication.

(69) S. Bulusu, J.R. Autera and T. Axenrod. JCS. Chem. Comm. (1973) 602


(73) M. Witanowski. J. Amer. Chem. Soc. 90 5683 (1968)


(78) W.P. Norris. 'Nitrolysis of quarternary derivatives of hexamine'.

NOTS 1471. NAVORD REPORT 1261. China Lake, California, USA. (1956)
(79) E.E. Smissman and J. A. Weis. J. Hetero. Chem. 5 (1968) 405
(80) R. Tschunke. U.S Patent. 1,336,709 (1920)
(81) C.A. Bischoff. Ber. 21 (1898) 3248
(83) J-B. Kang, G. Sen and B.S. Thyagarajan. J. Hetero. Chem. 10 (1973) 439
(84) W.E. Bachmann and N.C. Deno. J. Amer. Chem. Soc. 73 2777 (1951)
(85) H. Tada. J. Amer. Chem. Soc. 82 (1960) 255, 263, 266
(87) T.G. Bonner, R.A. Hancock and J.C. Roberts. JCS. Perkin I. (1972) 1902
(90) H. Yoshida, G. Sen and B.S. Thyagarajan. J. Hetero. Chem. 10 (1973) 279
(91) H. Yoshida, G. Sen and B.S. Thyagarajan. J. Hetero. Chem. 10 (1973) 725
(92) N. Logan. Chapter Six. p 320, in reference (51).
(104) S. Shiotani and K. Mitsuhashi. Ykagaku Zasshi. **84** 656 (1964)
(122) M. Witanowski. Private communication.
(139) C. Nagata and A. Imamura. Gann. 61 (1970) 169
(141) H. Stetter and W. Bockmann. Chem. Ber. 84 (1951) 834
(143) E.B. Hodge. J. Org. Chem. 37 (1972) 320
(144) N.W. Gabel. U.S Patent. 3,301,854 (1967)
(145) R. Lukes and K. Syhora. Chem. Lis'ty. 46 731 (1952) (CA 47 12393i)
(149) F.J. Brockman, D.C. Downing and G.F. Wright. Canad. J. Res. 27B (1949) 469
(150) P. Duden and M. Scharff. Ann. der Chemie. 288 218 (1895)
(152) W.E. Bachmann, E.L. Jenner and L.B. Scott. J. Amer. Chem. Soc. 73 2775 (1951)