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Mechanistic Investigation of the [2+2] Cycloaddition-
Cycloreversion Reaction between 4-(N,N-
Dimethylamino)phenylacetylene and Arylated 1,1-
Dicyanovinyl Derivatives to Form Intramolecular Charge-
Transfer Chromophores

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Supporting Information for this article is available on the WWW under http://www.chemeurj.org or from the author.
Abstract: The kinetics and mechanism of the [2+2] cycloaddition-cycloreversion reaction between 4-(N,N-dimethylamino)phenylacetylene (1) and para-substituted benzyldenemalononitriles 2b–2l to form 2-donor-substituted 1,1-dicyanobuta-1,3-dienes 3b–3l via postulated dicyanocyclobutene intermediates 4b–4l have been studied experimentally by the method of initial rates and computationally at the unrestricted B3LYP/6-31G(d) level. The transformations were found to follow bimolecular, second-order kinetics, with $\Delta H_{\text{exp.}}^a = 10–28 \text{kcal/mol}$, $\Delta S_{\text{exp.}}^a = -26$ to $-37 \text{cal/K/mol}$, and $\Delta G_{\text{exp.}}^a = 21–28 \text{kcal/mol}$. These experimental activation parameters for the rate-determining cycloaddition step are close to the computational values. The rate constants show a good linear free energy relationship ($\rho = 2.0$) with the electronic character of the para-substituents on the benzyldiene moiety, which is indicative of a dipolar mechanism. Analysis of the computed structures and their corresponding solvation energies suggests that the attack of the nucleophilic, terminal alkyne carbon on the dicyanovinyl electrophile generates a transient zwitterion intermediate with the negative charge developing as a stabilized malononitrile carbanion. The computational analysis unexpectedly predicted that the cycloreversion of the postulated dicyanocyclobutene intermediate would become rate-determining if the 1,1-dicyanoethene electrophile is unsubstituted. The dicyanocyclobutene 4m could indeed be isolated as as the key intermediate from the reaction between alkyne 1 and 1,1-dicyanoethene (2m) and characterized by X-ray analysis. Facile first-order cycloreversion occurred upon further heating, yielding as the sole product the 1,1-dicyanobuta-1,3-diene 3m.
**Keywords:** cycloaddition · linear free energy relationships · kinetics · reaction mechanisms · push-pull chromophores

**Introduction**

π-Conjugated organic donor-acceptor (D-π-A) chromophores, featuring intense low-energy intermolecular charge-transfer (CT) absorptions in the visible to near-IR (infrared) spectroscopic range, are in high demand for applications in photonics and nonlinear optics.\(^1\) Versatile organic synthesis makes these dipolar organic push-pull molecules highly attractive for fine-tuning their optoelectronic properties and ultimately tailoring and optimizing advanced materials.

Organic D-π-A molecules not only need to feature desirable molecular properties but they should also be preparable on a larger scale through fast and efficient transformations. With this in mind, we developed over the last few years ‘click-chemistry’-type\(^2\) reactions which yielded new families of intramolecular CT chromophores. \([2+2]\) Cycloadditions between electron-rich alkynes, such as 4-ethynyl-N,N-dimethylaniline (1, Scheme 1), and strongly electron-accepting olefins such as tetracyanoethene (TCNE, 2a) or 7,7,8,8-tetracyanoquinodimethane (TCNQ) derivatives, followed by cycloreversion, provided non-planar, donor-substituted 1,1,4,4-tetracyanobuta-1,3-dienes (TCBDs, such as 3) and expanded TCNQ derivatives, featuring readily tunable CT absorption wavelengths, large non-linear optical responses, and high electron affinity.\(^3\) These transformations are generally fast, high-yielding, catalyst-free, 100% atom-economic, and the resulting products can be easily purified by precipitation.
or washing. Recently, a high-speed optical waveguide was prepared a donor-substituted TCBDs.\[^4\] The success of these molecules in materials applications arena stems from their ability to form amorphous films of excellent optical quality due to their molecular nonplanarity and sublimability.

More recently, we serendipitously discovered that 1,1-dicyanovinyl derivatives are sufficiently electron accepting to react with electron-rich alkynes in the same manner as TCNE or TCNQ, providing the nonplanar push-pull chromophores 3 in high yield (Scheme 1).\[^5\] A series of \textit{para}-substituted benzylidenemalononitriles (containing many of the compounds in the series 2b–2l) was successfully converted and the ease of reaction directly correlated with the electron-accepting power of the attached \textit{para}-substituent.

\[
\begin{align*}
\text{Me}_2\text{N} & \quad \text{Me}_2\text{N} \\
\text{CN} & \quad \text{CN} \\
\text{R}^1 & \quad \text{R}^1 \\
\text{R}^2 & \quad \text{R}^2 \\
\hline
\text{Me}_2\text{N} & \quad \text{Me}_2\text{N} \\
\text{CN} & \quad \text{CN} \\
\text{R}^1 & \quad \text{R}^1 \\
\text{R}^2 & \quad \text{R}^2 \\
\end{align*}
\]

\textbf{Scheme 1.} The proposed reaction mechanism for the \([2+2]\) cycloaddition-cycloreversion between 1 and cyanoolefins 2 through the zwitterionic (5) and cyclobutenyl (4)

intermediates to form charge-transfer chromophores (3) where $X$ is varied as defined (b−l).

The apparent net reaction for electrophiles 2a−2m is identical to the transition metal-catalyzed/mediated enyne metathesis reaction\cite{6} both of which provide buta-1,3-diene products. By analogy, we have proposed that the reaction between electron-rich acetylenes and cyanoolefins proceeds through the cyclobutene intermediate 4. Subsequent cycloreversion (4 $\rightarrow$ 3) of this transient intermediate gives the final cyanobutadienes. Moreover, based on the facts that (i) the direct and concerted [2+2] cycloaddition is thermally symmetry-forbidden, (ii) the transformation occurs in the absence of a transitional metal catalyst, and (iii) the reaction only proceeds between highly polarized components, we further proposed a stepwise, zwitterionic pathway whereby initial nucleophilic addition of the electron-rich alkyne forms a transient zwitterion (5) that quickly cyclizes to the cyclobutene. However, except for some information gained by our initial computational investigation\cite{5} of the reaction between 1 and 1,1-dicyanoethene (2m), TCNE (2a) and tricyanoethene (TCE) as electrophiles, little is known about the energetics and relative importance of these intermediates, and the transition-states (TS) which connect them, towards the overall efficiency and outcome of this versatile class of chemical transformations. Computation suggested that the reaction should be bimolecular in both reactants with a single rate-determining-step (RDS). The rate-determining TS, the addition of the alkyne to the electrophile in the case of TCNE and TCE, is strongly polarized according to natural bond orbital (NBO) analysis and is apparent by inspection of the optimized geometries. Additionally, the solvation energies
in acetonitrile of the TS for 1 + 2m and its immediate product 4m are quite large suggesting strong polarization (the addition step is not rate-determining in this case but rather the ring-opening step, as discussed below). However, there is no direct experimental evidence that proves this zwitterionic mechanism or indicates any of the intermediates. Additionally, there is no evidence that could rule out a thermally allowed diradical mechanism and the question remains to what extent the reactions proceed via zwitterionic or diradical intermediates.

Similar stepwise, zwitterionic mechanisms of pericyclic reactions are known and are especially efficient when highly polarized, nucleophilic and electrophilic unsaturated reactants are involved. However, compared to the reactions between olefins, far less attention has been paid to the triple bond in such polar, formal [2+2] cycloadditions. Previous studies on the triple bond employed the strongly activated ynamines as the nucleophilic reactants. In some cases, cyclobutenes have even been isolated as final products but the relationship between these cycles and the starting materials has been obscured by rearrangements of the peripheral substituents. In other cases, an enyne metathesis happened to give butadienes, but without detection or isolation of the cyclic intermediate. Thus, no mechanistic elucidation has been possible due to the complexity of the chemistry and the lack of a systematic approach to study the electronic and structural aspects of this transformation.

In this paper, we present a thorough mechanistic investigation of the [2+2] cycloaddition-cycloreversion reaction between electron-rich alkynes, such as 1, and electron-deficient dicyanoolefins, such as 2b-m, based on both experimental and computational methods. We provide strong evidence for the zwitterionic character of the
cycloaddition step and, in one case, report the isolation and characterization of the dicyanobutene intermediate which is converted to the 1,1-dicyanobuta-1,3-diene as the sole product.

Results and Discussion

Order of the reaction and the rate law: To gain more information about the course of the reaction, a real-time NMR study was performed for the transformation of the benzylidenemalononitriles 2b–2l in the temperature range from 298 K to 373 K. For a typical example, the $^1$H NMR spectral evolution of the solution of a 1:1 mixture of 1 and 2f ($R^1 = 4$-PhBr, $R^2 = H$) in (CD$_3$)$_2$SO at 373 K is shown in Figure 1. Similar spectral changes were observed for all the other para-substituted substrates. In all cases, the transformation is clean, directly from starting material to the corresponding s-trans, trans butadiene product, without any evidence of side-product or transient species formation on the NMR time-scale.
Figure 1. Partial time-dependent $^1$H NMR spectra (500 MHz, (CD$_3$)$_2$SO, 373 K) of the solution of 1 and 2f. The time interval between consecutive traces is 800 s. Structure-signal assignments are given.

The lack of a pre-equilibrium and the absence of any intermediate structure supports our previous computational studies, which predicted a bimolecular reaction mechanism with one key RDS. It is reasonable to rule out any reversibility after the RDS based on the high yields and the rapidness of the reaction under study. Moreover, when the extent of the reaction using NMR data was plotted against the reaction time, simple evolution curves were observed. Under the conditions, where the initial concentrations of 1 and 2 are identical, i.e. $[1]_0 = [2]_0$, the plot fits well to an overall second-order rate expression, meaning first-order in both 1 and 2 throughout the whole course of reaction (Figure 2; for plot-fitting, see Supporting Information). This was further confirmed by varying the reactant ratio (up to 3-fold excess of one component) and monitoring the rate of reaction of 2h with 1 by following the evolution of the CT band of the UV/Vis spectrum (see Supporting Information). The rate of product formation was found to be proportional to either [1] or [2h], i.e. first order in both reactants. Thus, the apparent rate law of the reaction subclass under question is bimolecular and first order in both reactants, eq. 1

$$v = k [1][2]$$  

(eq 1)
where $k$ is the observed rate constant. The simplicity of the rate expression in these cases further allows employment of initial-rate methods in the following kinetics studies without over-simplifying the reaction mechanism. Thus, the initial rate constants are calculated according to eq 2:

$$k = \frac{d[3]}{dt} \frac{1}{[1]_0[2]_0}$$  \hspace{1cm} (eq 2)

where $d[3]/dt$ is the observed rate and $[1]_0$ and $[2]_0$ are the initial concentrations of 1 and 2.

**Figure 2.** Time evolution of the reaction between 1 and 2f. The extent of reaction for the reactants is defined as the ratio between the number of one species at time $t$ to its initial number ($t = 0$); for the product, it is defined as the ratio between its number at time
to the initial number of the reactant. Can you make the triangle, ring, and square in the caption stronger; it is too weak there in the printout.

**Rate-dependency on the electronic nature of the substituents:** A series of para-substituted benzylidenemalononitriles 2b–2k were mixed with 1 in DMF (N,N-dimethylformamide) solution at 298 K, and the development of their characteristic CT bands around 450 nm was used to monitor the rate of product formation and to determine the rate constant by the method of initial rates employing eq. 2 as the kinetic model. As shown in the inset of Figure 3, the intensity of the CT band increases vertically, again suggesting a clean transformation without by-product formation.

The logarithms of the measured initial-rate constants of compounds 2b–2k with para-substituent X relative to the logarithm of the rate of 2h (X = H) were plotted against their corresponding Hammett substituent constants \( \sigma_p \) and a good linear correlation was found (\( R^2 = 0.97 \)), with slope \( \rho = 1.98 \pm 0.1 \) (Figure 1). The plot containing 2l at 373 K also exhibits a linear free-energy relationship. Data at 323 and 348 K including 2b–2k have also been obtained (see Supporting Information). As depicted in Figure 3, the good linearity implies that the same reaction mechanism is operating for all derivatives; the moderately positive \( \rho \) value reflects that the reaction is accelerated by electron-withdrawing substituents, and signifies a build-up of electron density around the benzylidene ring in the RDS, consistent with a stepwise, zwitterionic mechanism where nucleophilic addition to the 1,1-dicyanovinyl (DCV) moiety pushes electrons to the most stabilizing 1,1-dicyanomethylidine position.
Figure 3. Hammett plot of initial rates constants of the reaction of 1 with electrophiles 2b–2k relative to the initial rate constant for 2h versus the Hammett substituent constants $\sigma_p$ at 298 K. Inset (a) shows the time evolution (in the direction of the arrow) of the CT band for the reaction of 1 with 2h.

It was not possible to measure the rate of reaction of 1 and 2l at 298 K due to the sluggishness of the reaction; the evolution of the CT band was obscured by instrument noise. Kinetics at 373 K that include this data point are presented in the Supporting Information and shows a linear correlation.

Calculated free energy profile by density functional theory and activation parameters by Eyring analysis: In our previous report, a reaction free-energy profile was examined for the reaction between 1 and methylenemalononitrile (2m) at the
unrestricted B3LYP/6-31G(d) level\textsuperscript{[11]} in the gas-phase as well as using the polarizable continuum model (PCM) with acetonitrile to model solvent effects. Herein, this methodology is extended to the cases of the reaction of \textit{1} with the electrophiles having \textit{para}-nitrophenyl (\textit{2b}), phenyl (\textit{2h}), or \textit{para}-dimethylanilino (\textit{2l}) moieties attached to the DCV group, treating only the most relevant points along the reaction profile that are candidates for the RDS. The stability of the wavefunction was verified in each case. Geometries were optimized using the program Gaussian 03.\textsuperscript{[11]} Stationary points were characterized by harmonic vibrational frequency analysis.\textsuperscript{[12]} Molecular energies were calculated as the sum of the electronic energy and Gibbs free energy correction obtained from these analytical frequencies at 298.15 K. The Supporting Information gives all necessary numerical values used in this work along with zero-point and thermal corrections, gas-phase and solvated energies and geometries.

Irrespective of the substituent on the electrophile, the reaction consists of four basic steps (Figure 4). From unreacted components (\textit{1+2}), nucleophilic addition of the $\gamma$-carbon of the terminal alkyne (\textit{1}) to the $\beta$-position of the electrophile (\textit{2}) occurs to produce a high-energy intermediate (\textit{5}) through the bond-forming transition-state (TS) ([\textit{1+2} $\rightarrow$ \textit{5}]\textsuperscript{‡}) (see Scheme 1 for notation). From here, the ring-closed product (\textit{4}) is obtained by bond formation between the $\alpha$ and $\delta$ carbons through an electrocyclic TS ([\textit{5} $\rightarrow$ \textit{4}]\textsuperscript{‡}). For the reaction between \textit{1} and \textit{2m}, this happens through a barrier only slightly more energetic compared to the corresponding energy of \textit{5} and slightly less than the energy of [\textit{1+2m} $\rightarrow$ \textit{5m}]\textsuperscript{‡}, but the analogous TSs could not be located for the reaction with electrophiles \textit{2b}, \textit{2h} and \textit{2l}, presumably due to their shallow potential energy wells, which precluded optimization to their respective stationary-states. Moving forward, the
ring-opening cycloreversion step breaks the α–β bond ([5 → s-cis 3]‡) leading eventually to the final products (s-trans 3) by s-cis-to-s-trans isomerization ([s-cis 3 → s-trans 3]‡).

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Figure 4. Free-energy reaction profile at the B3LYP/6-31G(d) level (with PCM solvation in acetonitrile) for 2m (blue), 2b (red), 2h (orange), and 2l (green) with energies (kcal·mol⁻¹) provided for reactants (1+2) (reference energy), intermediates 5, 4, s-cis 3, and product s-trans 3) and transition-states barriers [1+2 → 5]‡, [5 → 4]‡, [4 → s-cis 3]‡, and [s-cis 3 → s-trans 3]‡ (energies referenced to their preceding intermediate).
Experimental Eyring activation parameters ($\Delta G^e_{\text{exp.}}$, $\Delta H^e_{\text{exp.}}$, and $\Delta S^e_{\text{exp.}}$) (see methods section) for the RDSs in DMF are also provided for comparison.

There is a considerable substitution effect on the TS energetics of the addition step $[1+2 \rightarrow 5]^\ddagger$. In the non-substituted case, 1,1-dicyanoethylene $2m$ reacts through a mechanism where the ring-opening process ($[4m \rightarrow s\text{-cis }3m]^\ddagger$; $\Delta G^e_{\text{calc.}} = 24.3 \text{ kcal}\cdot\text{mol}^{-1}$) is rate-determining based on comparison of the calculated free-energies of activation in acetonitrile ($\Delta G^e_{\text{calc.}}$) (compare to $[1+2m \rightarrow 5m]^\ddagger$; $\Delta G^e_{\text{calc.}} = 16.0 \text{ kcal}\cdot\text{mol}^{-1}$), while in the case of the 1,1-dicyanovinylphenylenes $2b$, $2h$, and $2l$ the RDS is the addition step ($[1+2 \rightarrow 5]^\ddagger$; $\Delta G^e_{\text{calc.}} = 29.9$, 25.6, and 23.0 kcal·mol$^{-1}$, respectively) (compare to $[4 \rightarrow s\text{-cis }3]^\ddagger$; $\Delta G^e_{\text{calc.}} = 7.1$, 11.6, and 14.0 kcal·mol$^{-1}$, respectively). Inclusion of a phenyl group at the $\beta$-position of the electrophile clearly raises the energy of $[1+2 \rightarrow 5]^\ddagger$ in all cases compared to $2m$ rendering it rate-determining overall. A secondary influence beyond this, presumably steric, effect of the phenyl ring is felt from the electronic nature of the attached substituent at its $para$-position; the nitro-substituted derivative ($2b$) reacts through the lowest barrier, followed by the phenyl group ($2h$) and finally the $N,N$-dimethylamino-substituted reactant ($2l$). Thus, the increased electrophilicity of the dicyanovinyl group caused by electron-withdrawal accelerates the reaction. This is in accordance with the experimental kinetic results.

In contrast, the $para$-phenyl substituent has a diminished influence on the ring-opening TS. The differences in this barrier $[4 \rightarrow s\text{-cis }3]^\ddagger$ for $2b$, $2h$, and $2l$ arise mostly from large changes in the energies of the cyclobutene intermediates themselves ($4$). The strongly donating DMA group destabilizes the cycle considerable ($4l$; $\Delta G^e_{\text{calc.}} = 1.3 \text{ kcal}\cdot\text{mol}^{-1}$).
the $\Delta G^\varphi$ is clearly wrong here, since it is a thermodynamic stability, so only $\Delta G_{\text{calc.}}$ placing its energy on the endergonic side of the reaction profile compared to this state along the reaction profile of $1+2m$ ($4m$; $\Delta G_{\text{calc.}} = -12.8$ kcal·mol$^{-1}$) again not a TS, but a "ground state"; no $\neq$. Both para-nitrophenyl ($4b$; $\Delta G_{\text{calc.}} = -7.2$ kcal·mol$^{-1}$) dito and phenyl ($4h$; $\Delta G_{\text{calc.}} = -4.0$ kcal·mol$^{-1}$) dito substitution also destabilize the cyclobutene, but to a lesser extent than for $4l$. It is important to notice that the electronic effects of the phenyl substituent on the barriers $[1+2\rightarrow 5]^\dagger$ and $[4\rightarrow s$-cis $3]^\ddagger$ are exactly reversed to each other. While $[1+2\rightarrow 5]^\dagger$ lowers upon increased electron-withdrawing character of the substituent, $[4\rightarrow s$-cis $3]^\ddagger$ raises (due mostly to effects in $4$). Thus, the kinetic results from the Hammett plot (positive $\rho$ value) are consistent with $[1+2\rightarrow 5]^\dagger$ as the RDS and rule-out any mechanism with $[4\rightarrow s$-cis $3]^\ddagger$ as the RDS since the $\rho$ value would be reversed to what is experimentally observed.

Solvation energies in acetonitrile for $[1+2\rightarrow 5]^\dagger$ occur at a relatively constant value ($\Delta G_{\text{solvation,ACN}}^\varphi = \Delta G_{\text{gas,calc.}}^\varphi - \Delta G_{\text{solv,calc.}}^\varphi \approx -3$ kcal·mol$^{-1}$)) replace ACN by MeCN! throughout and increase significantly for the immediate product $5$ ($\Delta G_{\text{solvation,ACN}}^\varphi = \Delta G_{\text{solv,calc.}}^\varphi - \Delta G_{\text{gas,calc.}}^\varphi$, MeCN = $-9.5$ ($5m$), $-10.9$ ($5b$), $-8.6$ ($5h$) and $-7.9$ ($5l$) kcal·mol$^{-1}$) (negative values indicate stabilization, solv = solvation, gas. = gasphase).

Thus, the zwitterionic character of the TS is corroborated, and to a greater extent, this character is prevalent in the intermediate ($5$) with the amount of stabilization increasing with the withdrawing power of the substituent. Solvation energies for $[4\rightarrow s$-cis $3]^\ddagger$ are positive and near 1 kcal·mol$^{-1}$ in all cases. Somewhat larger energies are found for the cyclobutenes ($4$), which are destabilized (positive $\Delta G_{\text{solvation, MeCN}}$ use your symbols) between 3.5 to 4.5 kcal·mol$^{-1}$. Based on the small and positive solvation energies of
[4→ s-cis 3]‡, the zwitterionic character of the ring-opening step should be small. Thus, a concerted diradical mechanism is most likely.

From variable temperature UV/Vis kinetic data, it was possible to perform Eyring analysis and extract the experimental activation parameters $\Delta H^\text{exp.}$, $\Delta S^\text{exp.}$, and $\Delta G^\text{exp.}$ (for a detailed description, see the Experimental, for the fitting analysis of the Eyring plots, see the Supporting Information). There is excellent quantitative agreement, in addition to the qualitative agreement, between the experimental activation parameters ($\Delta G^\text{exp.}$) obtained from Eyring analysis and these computed values (Figure 4). The initial rates of reaction for the reaction of 1 with electrophiles 2b, 2h and 2l were monitored at three or four temperatures (see Experimental) and the data fitted to the Eyring expression (see Supporting Information). The resultant parameters are presented in Figure 4 and agree with the calculated values to a standard deviation of 2.1 kcal·mol$^{-1}$. While this is not proof that the mechanism has been unambiguously assigned, it lends credence to the computational approach and methodology presented here. The negative entropies of activations ($\Delta S^\text{exp.} \approx -30$ cal·K$^{-1}$ mol$^{-1}$) support a mechanism involving a bimolecular RDS.

The activation parameters measured for the conversion of 4m to 3m (see next section) agree exceedingly well with the computed energy barrier [4m→ s-cis 3m]‡, and the entropy of activation ($\Delta S^\text{exp.} \approx -6.5$ cal·K$^{-1}$mol$^{-1}$) is consistent with a unimolecular RDS process.
Figure 5. Optimized geometries (B3LYP/6-31G(d) with PCM solvation in acetonitrile) of TSs $[1+2 \rightarrow 5]^\dagger$ for the reaction of 1 with 2m, 2b, 2h, and 2l. Relevant structural parameters are given (bond length in Å and bond angle (°) in °).

Optimized geometries of the addition step ($[1+2 \rightarrow 5]^\dagger$) along the reaction profile of the derivatives discussed above are shown in Figure 5. The geometric parameters strongly suggest zwitterionic character in the addition TS ($[1+2 \rightarrow 5]^\dagger$) for all derivatives. Pyramidalization about the methyldiene ($\alpha$) carbon of the acceptor portion is significant and decreases in the direction of lowering activation energy as the TS becomes earlier ($[1+2b \rightarrow 5b]^\dagger$ (2.7°) < $[1+2h \rightarrow 5h]^\dagger$ (2.9°) < $[1+2l \rightarrow 5l]^\dagger$ (3.4°)). How is this pyramidalization angle defined? This needs to be described. This pyramidalization is intermediate for the case of the reaction with 1,1-dicyanoethylene ($[1+2m \rightarrow 5m]^\dagger$ (2.8°)).

For the donor portion, a strong quinoid character$^{[13]}$ of the DMAA ($N,N$-dimethylanilinoacetylene) group in the TS, referenced to the structure of isolated DMAA ($\delta_r = 0.03$ Å) at this level of theory, ($\delta_r = 0.05$ Å for $[1+2b \rightarrow 5b]^\dagger$, $[1+2h \rightarrow 5h]^\dagger$, and $[1+2l \rightarrow 5l]^\dagger$) suggests that the donation from the dimethylamino substituent of the
dimethylanilino (DMA) residue is prominent. The quinoid character is slightly less when 1,1-dicyanoethylene is the electrophile ([1+2m → 5m]^‡ (δ = 0.04 Å)). Additionally, deviations in the linearity of the γ–δ–ε bond angles (see Scheme 1 for notation) for all considered TSs of ~8° places a considerable cationic character at the central δ carbon atom. This bond angle becomes linear for 5m, 5b, 5h, and 5l (see Supporting Information for Cartesian coordinates) where the charge becomes further delocalized through the π-system in the zwitterionic ground-state. Finally, the forming bond between the β and γ positions varies considerably ([1+2m → 5m]^‡ (2.15 Å) > [1+2b → 5b]^‡ (2.08 Å) > [1+2h → 5h]^‡ (2.04 Å) > [1+2l → 5l]^‡ (1.98 Å)), again as a function of accepting power of X. The TS [1+2m → 5m]^‡ has the earliest (longest bond) structure of all.

Comparing the bond distance of the computed cyclobutene moiety provides further insight into their tendency of ring-opening. The bond distances between β–γ, γ–δ and δ–α of all these cyclobutenes (4b, 4h, 4l, and 4m) are similar; however, the length of the α–β bond varies about 0.05 Å throughout the series. It is observed that the longer the α–β bond distance, the smaller the barrier to ring-opening. Comparing 4b, 4h, and 4l, we find a longer α–β bond length (1.65 Å) with the NMe₂ substituent, a shorter length with the NO₂ substituents (1.63 Å), and an intermediate value for the phenyl substituted cyclobutene (1.64 Å). This relatively small structural effect is presumably inductive in nature as the influencing substituent is separated by the sp³-hybridized β-carbon. Nonetheless the substituent effect, which may be acting on a partially diradical or zwitterionic electronic structure of the cyclobutene is sufficient to vary the cyclobutene energies in a range of ca. 9 kcal·mol⁻¹. Without any substituent (4m), this bond length is considerable shorter (1.60 Å). Given that electronic effects on the cyclobutene are
attenuated by poor communication over the β-position, it is reasonable to assume that this effect is predominantly steric in nature. In the case of 4m, the tight binding between the α and β positions caused by a lack of destabilizing phenyl substitution leads to an additional ca. 9 kcal·mol\(^{-1}\) stabilization allowing the isolation of the cyclobutene as a stable intermediate, as discussed in the following.

**Intermediate Identification:** Comparing the computational free energy profile in our previous report for the reaction of 2m with the results shown in the previous sections for 2b, 2h, and 2l, it is interesting to notice that the higher-barrier process changed from the ring-opening step to the ring-formation step upon phenyl-substitution. Since the cyclobutene intermediate was not found in any of the cases involving phenyl-substituted compounds which have the RDS in the addition step, this change in relative barrier-height suggested a possibility to isolate the cyclobutene using 2m as the electrophile.

To verify this postulate, 1 was mixed with 2m, which was *in situ* generated from malononitrile and aqueous formaldehyde in DMF solution at 50 °C overnight. A yellow solid was isolated after column chromatography in 76% yield, and is stable at ambient condition for weeks without decomposition. The peak at m/z 223 in the mass spectrum indicated a molecular formula of C\(_{14}\)H\(_{13}\)N\(_3\), corresponding to the 1:1 adduct between 1 and 2m. The very weak IR absorption of C≡N stretching at 2246 cm\(^{-1}\) suggests a non-conjugated cyano functional group. In the \(^1\)H NMR spectrum (CDCl\(_3\), 298 K), the aliphatic doublet signal at 3.3 ppm (2 H, \(J = 1.4\) Hz) together with the olefinic triplet signal at 6.2 ppm (1 H, \(J = 1.4\) Hz) immediately rule out the butadiene structure, but, to
our delight, point to a cyclobutene $4m$ which was further confirmed by X-ray analysis (Figure 6a).

This cyclobutene molecule was further transformed into the 1,1-dicyanobuta-1,3-diene $3m$ upon heating. In the real-time $^1$H NMR experiment in 1,1,2,2-tetrachloroethane-$d_2$, at 373 K, the two signals at 3.33 (d, $J = 0.9$ Hz) and 6.23 (t, $J = 0.9$ Hz) ppm of cyclobutene protons gradually vanished and three new sets of signals from terminal vinylic proton systems at 5.83 (dd, $J = 16.9, 0.8$ Hz), 6.06 (dd, $J = 10.6, 0.8$ Hz) and 7.08 (dd, $J = 16.9, 10.6$ Hz) ppm appeared (Supporting Information). The X-ray-quality crystal of butadiene was obtained by the diffusion method and shows the $s$-trans geometry with non-planarity between the $N,N$-dimethylanilino and the dicyanovinyl moieties as observed in other, phenyl-substituted analogs (Figure 6b). The transformation is clean and quantitative, without involving any other intermediate (at least on the NMR time-scale), and its kinetics fits well into a first order reaction (see Supporting Information). Thus, this dicyanocyclobutene was, for the first time, isolated and identified as the true intermediate of the formal [2+2] cycloaddition between electron-rich acetylene and cyanoolefins, giving cyanobuta-1,3-dienes as the final products.
Figure 6. ORTEP plots of (a) 4m (223 K) and (b) 3m (223 K) with thermal ellipsoids shown at the 50% probability level. Arbitrary numbering.

A closer look at the solid-state molecular structure of 4m provides deeper information on the cyclobutene properties. The DMA ring and the cyclobutene ring arrange almost in the same plane with a small twist of $6.68^\circ$, making the whole molecule quasi-$Cs$ symmetric. The double bond distance between C7–C8 is 1.329(4) Å, while the single bond-lengths between C8–C9, C7–C10, and C9–C10 are 1.501(4), 1.544(3), and 1.586(3) Å, respectively. These bond-distances are all in the range of known bond-length of cyclobutenes,[14] and the observed molecular geometry highly resembles that obtained from DFT calculation. However, it is noteworthy that the C7–C10 bond is significantly longer than the C8–C9 bond, and also than the typical $C_{sp3}$–$C_{sp2}$ bond distance in cyclobutene. ref. ???  It is known that, in x-phenyl-substituted cyclobutene, the phenyl substituted $C_{sp3}$–$C_{sp2}$ bond is usually longer than the other unsubstituted one and inversely correlated with the corresponding bond angle in the ring which again is influenced by the bulkiness of the substituents.
Conclusions

We have studied the reaction mechanism of the formal [2+2] cycloaddition-cycloreversion reaction between \( N,N \)-dimethylanilinoacetylene 1 and a series of phenyl-substituted 1,1-dicyanovinyl derivatives 2b–2l by means of UV/Vis and NMR spectroscopies and DFT calculations. From the experimental data, the reaction is clearly a quantitative transformation without by-product formation. The bimolecular, second-order kinetics show a good linear free energy relationship with respect to the electronic effects of the dicyanovinyl electrophiles, indicating a strong zwitterionic character in the rate-determining step, which is most probably due to a transition-state where the negative charge is located at the \( \text{gem} \)-dicyano-substituted homobenzylic position (\( \alpha \)-carbon) arising from nucleophilic attack of 1 onto the \( \beta \)-carbon of the dicyanovinyl moiety to form 5 according to the computed structures. For electrophiles 2b–2l, the activation free energies range 21.5–28.1 kcal·mol\(^{-1}\), with negative activation entropy contributions –26.1 to –36.5 cal·K\(^{-1}\)·mol\(^{-1}\) in DMF, on the order of those expected for a bimolecular reaction.

The cyclobutenyl molecule 4m generated from the cycloaddition between 1 and 2m was isolated as the true reaction intermediate and transformed into the ring-opening dicyanobuta-1,3-diene 3m upon heating. The small activation entropy (–6.5 cal·K\(^{-1}\)·mol\(^{-1}\)) of ring-opening indicates a unimolecular RDS.

Four reaction sub-steps were identified on the computational reaction free energy profiles, where the addition step and the ring-opening processes were shown to have more importance to the overall reaction kinetics. The energy barriers for the addition step process for 2b, 2h, and 2l are rate-determining as they are much higher in energy than
those of their subsequent steps. The finding of a high barrier in the early stage of the bimolecular, multi-step reaction is also in accordance with the fact that the reactions follow a simple second-order kinetics. Removing the phenyl substituent from the DCV group, however, changes the high-barrier step to the ring-opening process. As in the addition step, where the linear free energy relationship was found experimentally, there is also a substantial substituent effect on the ring-opening process. The barriers of this process were found to correlate with the ability of the substituent to affect the stability of the cyclobutene intermediates. The barrier heights calculated here were found to have a good quantitative agreement with the experimental values, suggesting the credibility of the proposed reaction mechanism.

While the mechanism for benzylidenemalononitriles has been treated in detail here, it would be too tenuous a generalization to assign the exact present mechanism to those reactions involving tricyanoethylene (TCE), TCNE, or TCNQ as the electrophiles nor do we offer a holistic mechanism for reactions involving metal acetylides as the nucleophiles. Our current finding suggests a reaction subclass that is highly sensitive to substitution with a roving rate-determining step. Additionally, a pre-equilibrium of the charge-transfer complexes for TCNE and TCNQ may be important. Preliminary kinetic experiments (unpublished results) for the reaction of 1 and TCNE (2a) offer an unclear picture as to whether the reaction is first or second order as both kinetic models give reasonable activation energies. It is reasonable that the addition step in this case would be considerably lower in energy than for the benzylidenemalononitriles and the ring-opening step much larger since the dicyanomethylidines flank both the forming positively and negatively charged positions as the ring opens. Thus, either addition or ring-opening
or both could be rate-determining in this case. Detailed mechanistic studies involving
these electrophiles are ongoing to further elaborate the exciting complexity and
sensitivity of this reaction subclass. As it stands, reactions involving electron-rich
acetylenes and electron-poor cyanoolefins should proceed through a stepwise process
involving zwitterionic and cyclobutenyl intermediates regardless of which TS is rate-
determining.

**Experimental Section**

**Materials and general methods:** Reagents were purchased at reagent grade from Acros,
Sigma-Aldrich, and Fluka and used as received. Anhydrous CH₂Cl₂ was freshly distilled
from CaH₂ under N₂ atmosphere. Column chromatography was carried out with SiO₂ 60
(particle size 0.040–0.063 mm, 230–400 mesh; Fluka) and technical solvents. Thin-layer
chromatography (TLC) was conducted on aluminum sheets or glass plate coated with
SiO₂ 60 F₂₅₄ obtained from Merck; visualization with a UV lamp (254 or 366 nm).

Melting points (M.p.) were measured on a Büchi B-540 melting-point apparatus in open
capillaries and are uncorrected. ¹H NMR and ¹³C NMR spectra were measured on a
Bruker AV 400 instrument at 20 °C. Chemical shifts are reported in ppm relative to the
signal of tetramethylsilane. Residual solvent signals in the ¹H and ¹³C NMR spectra were
used as an internal reference. Coupling constants (J) are given in Hz. The apparent
resonance multiplicity is described as s (singlet), d (doublet) and dd (doublet of doublet)
Infrared spectra (IR) were recorded on a Perkin-Elmer Spectrum BX instrument. UV/Vis
spectra were recorded on a Varian Cary-500 spectrophotometer in a quartz cuvette (1
cm). The absorption wavelengths are reported in nm with the extinction coefficient ε
(M$^{-1}$ cm$^{-1}$) in parenthesis; shoulders are indicated as sh. High-resolution HR-EI-MS spectra were measured on a Hitachi-Perkin-Elmer VG-Tribrid spectrometer. The signal of the molecular ion (M$^+$) is reported in m/z units. Compounds 3b, 3e, 3f, 3g, 3h, 3k, and 3l and their corresponding dicyanovinyl precursor molecules 2b, 2e, 2f, 2g, 2h, 2k, and 2l were prepared according to literature procedures$^{[5]}$ as were additional precursor molecules 2c,$^{[15a]}$ 2d,$^{[15b]}$ 2i,$^{[15c]}$ and 2j,$^{[15d]}$ their NMR data and melting points are in accord with the literature values. New charge-transfer chromophores 3c, 3d, 3i, and 3j were prepared by the General Method (see below). Compound 3m was prepared through in situ generation of precursor electrophile 2m to yield first 4m, as described below.

UV/Vis measurements. Initial-rate determination and Eyring analysis: The molar extinction coefficient and the initial-rate kinetics were measured with the Varian CARY 500 Scan UV-Vis-NIR Spectrophotometer, controlled by the CARY WinUV software in a Windows 2000 Professional operating system. The Scan application of CARY WinUV was used for molar extinction coefficient determination of a 5x10$^{-5}$ M solution in DMF at 298 K. For initial-rate measurement, the CARY Temperature Controller and Stir Control accessories were employed. The Scanning Kinetics application of CARY WinUV was used to control the appropriate temperature, the scan rate (600 nm/min), and scan range (550–400 nm), and to monitor the rate of product formation. The measured reactions were conducted in a 1 cm quartz cuvette charged with a stir-bar. For the formal cycloaddition reactions, 2b–2k were added into the pre-heated DMF (3 mL) solution of 1 at 298, 323, 348, and 373 K. For the exceedingly slow reaction of 2l, the temperatures were 353, 363, and 373 K. The concentration was 5.05x10$^{-3}$ M for each starting material.
The spectra were collected for every 1 min (typically monitored over 20–40 min), and the product concentrations used for initial-rate calculation were converted from the recorded absorbances based on the corresponding extinction coefficients at room temperature. Each data point was collected three times, and the average value is presented herein with the standard deviation indicating the experimental error. All experimental rate constants are given in the Supporting Information.

From these variable temperature kinetic data, it was possible to perform Eyring analysis and extract the activation parameters $\Delta H^{\text{exp.}}$, $\Delta S^{\text{exp.}}$ and $\Delta G^{\text{exp.}}$. The initial rate of the unimolecular reaction of $4\text{m}$ to $3\text{m}$ was monitored at 333, 353, and 373 K by adding $4\text{m}$ to the pre-heated neat DMF to obtain these parameters for the ring-opening step in this case using the same experimental conditions as for the other reactions. Fitting analyses of the Eyring plots are given in Supporting Information.

**Real-time NMR study of the reaction:** Real-time $^1\text{H}$ NMR snapshots of the reaction were measured on a Bruker Avance DRX 500 spectrometer operating at 500.1 MHz for the $^1\text{H}$ nucleus. The pulse angle was 30° and the acquisition time 5 s for each transient. The temperature was set by Bruker TopSpin, but the real temperature at the probehead region was measured externally with the Greisinger GMH 3710 high-precision thermometer connected to a platinum four-wire temperature sensor embedded in an NMR tube. A $4.6 \times 10^{-2}$ M solution of reactants in (CD$_3$)$_2$SO was freshly prepared and immediately charged into the pre-heated spectrometer for measurement. The temperature was assumed to reach equilibrium during the time of magnetic field adjustment. The
spectra were collected for every 20, 80, or 160 s, depending on the rapidness of individual reaction. Spectra procession was performed with MestReNova.

**X-ray analysis:** X-ray data collection was carried out on a Bruker KappaCCD diffractometer equipped with a graphite monochromator (MoKα radiation, λ = 0.71073 Å) and an Oxford Cryostream low-temperature device at 223(1) K. Cell dimensions were obtained by least-squares refinement of all measured reflections (HKL, Scalepack[16a]), θ_{max} = 27.5°. All structures were solved by direct methods (SIR97[16b]). All non-hydrogen atoms were refined anisotropically, H-atoms isotropically by full matrix least-squares with SHELXL-97[16c] using experimental weights (1/σ^2(Io)+(Io+Ic)^2/900)).

**X-ray crystal structure of compound 4m:** Single-crystals were obtained by slow diffusion of pentane into a solution of 4m in CHCl₃ at −20 °C: C_{14}H_{13}N₃, Mr = 223.28, crystal dimensions 0.42 x 0.2 x 0.06 mm, monoclinic space group P2₁/c (no. 14), Dc 1.199 g.cm⁻³, Z = 4, a = 6.7709 (4), b = 7.6141 (4), c = 24.105 (2) Å, β =95.336 (2)°, V =1237.35 (12) Å³. Number of measured and unique reflections 3716 and 2355, respectively (R_{int} =0.043). Final R(F) = 0.056, wR(F²) = 0.142 for 206 parameters and 1467 reflections with I > 2σ(I) (corresponding R-values based on all 2355 reflections 0.102 and 0.174). CCDC deposition number 744043.

**X-ray crystal structure of compound 3m:** Single-crystals were obtained by slow diffusion of pentane into a solution of 3m in CHCl₃ at −20 °C: C_{14}H_{13}N₃, Mr = 223.28, crystal dimensions 0.54 x 0.3 x 0.09 mm, orthorhombic space group Pbca (no. 61), Dc 1.173
$g.cm^{-2}$, $Z = 8$, $a = 14.1701$ (6), $b = 8.0015$ (3), $c = 22.3043$ (8) Å, $V = 2528.9$ (2) Å$^3$.

Number of measured and unique reflections 5681 and 2879, respectively ($R_{int} = 0.046$). Final $R(F) = 0.081$, $wR(F^2) = 0.186$ for 206 parameters and 1845 reflections with $I > 2\sigma(I)$ (corresponding $R$-values based on all 879 reflections 0.118 and 0.208). CCDC deposition number 744044.

**General Method for the synthesis of 3c, 3d, 3i, and 3j.**

A solution of DCV derivative 2c, 2d, 2i, or 2j (100 mg) in acetonitrile (6 mL) and 1 (1 equiv.) was stirred at reflux until complete conversion (determined by LC-MS). The solvent was removed first by rotary evaporation, then under higher vacuum to yield the crude product. The purification of each product is described below.

{(2E)-3-(4-Cyanophenyl)-1-[4-(dimethylamino)phenyl]-2-propen-1-ylidene}malononitrile (3c): Following General Method, 3c was obtained (175 mg, 96%) after passing the crude material through a short plug of SiO$_2$ with CH$_2$Cl$_2$ as eluent and collecting the red-colored band. M.p. 214–215 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta =$ 3.10 (s, 6 H; NMe$_2$), 6.76 (d, $J = 9.0$ Hz, 2 H; PhNMe$_2$), 7.01 (d, $J = 15.7$ Hz, 1 H; CH=CH), 7.41 (d, $J = 9.0$ Hz, 2 H; PhNMe$_2$), 7.56 (d, $J = 15.7$ Hz, 1 H; CH=CH), 7.62 (d, $J = 8.4$ Hz, 2 H; PhCN), 7.69 (d, $J = 8.4$ Hz, 2 H; PhCN) ppm; $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta =$ 40.03, 79.02, 111.42, 113.83, 113.91, 114.65, 118.18, 119.32, 128.54, 128.61, 131.71, 132.75, 138.86, 144.81, 152.99, 169.37 ppm; IR (neat): $\tilde{\nu} =$ 3050 (vw), 2986 (vw), 2938 (vw), 1717 (m), 1685 (m), 1265 (s), 1221 (m), 740 (vs), 631 (s);
UV/Vis (DMF): $\lambda_{\text{max}}$ / nm ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$) = 345 (26 400), 474 (9 400); HR-EI-MS $m/z$: calcd for C$_{21}$H$_{16}$N$_4^+$: 324.1369; found: 324.1369 ($M^+$).

**Methyl 4-[(1E)-4,4-dicyano-3-[4-(dimethylamino)phenyl]buta-1,3-dien-1-yl]benzoate (3d):** Following General Method, 3d was obtained (135 mg, 80%) after column chromatography (SiO$_2$, hexane:CH$_2$Cl$_2$ = 2:1) and collecting the red-colored band. M.p. 211–212 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 3.10 (s, 6 H; NMe$_2$), 3.94 (s, 3 H; CO$_2$Me), 6.76 (2, $J$ = 8.7 Hz, 2 H; PhNMe$_2$), 7.04 (d, $J$ = 15.7 Hz, 1 H; CH=CH), 7.41 (d, $J$ = 8.7 Hz, 2 H; PhNMe$_2$), 7.67-7.53 (m, 3 H; CH=CH, PhCO$_2$Me), 8.06 (d, $J$ = 8.2 Hz, 2 H; PhCO$_2$Me) ppm; $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ = 40.05, 52.36, 78.49, 111.40, 114.06, 114.85, 119.60, 127.44, 128.25, 130.25, 131.71, 131.87, 138.81, 146.24, 152.90, 166.27, 170.03 ppm; IR (neat): $\tilde{\nu}$ = 2951 (vw), 2905 (vw), 2824 (vw), 2361 (w) 2343 (w), 2216 (m), 1720 (s), 1600 (vs), 1492 (s), 1283 (s); UV/Vis (DMF): $\lambda_{\text{max}}$ / nm ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$) = 352 (27 100), 470 (9 300); HR-EI-MS $m/z$: calcd for C$_{22}$H$_{14}$N$_3$O$_2^+$: 357.1472; found: 357.1473 ($M^+$).

{(2E)-3-Biphenyl-4-yl-1-[4-(dimethylamino)phenyl]prop-2-en-1-ylidene}malononitrile (3i): Following General Method, 3i was obtained (139 mg, 86%) after washing with Et$_2$O. M.p. 200–202 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 3.10 (s, 6 H; NMe$_2$), 6.77 (d, $J$ = 9.0 Hz, 2 H; PhNMe$_2$), 7.07 (d, $J$ = 15.6 Hz, 1 H; CH=CH), 7.48–7.36 (m, 5 H, Ph), 7.56 (d, $J$ = 15.6 Hz, 1 H; CH=CH), 7.65–7.60 (m, 6 H, Ph) ppm; $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ = 40.06, 111.37, 114.33, 115.15, 119.96, 125.10, 127.06,
127.71, 128.12, 128.97, 129.07, 131.67, 133.74, 139.85, 143.86, 147.59, 152.77, 170.75 ppm (1 peak of C(CN)₂ is overlaped with the solvent peaks); IR (neat): \( \tilde{\nu} = 2923 \) (vw), 2860 (vw), 2826 (vw), 2360 (vw), 2208 (s), 1594 (vs), 1481 (s), 1376 (s), 1347 (s), 1172 (s); UV/Vis (DMF): \( \lambda_{\text{max}} / \text{nm} \ (\varepsilon / \text{M}^{-1} \text{cm}^{-1}) = 382 \ (31 \ 300), 454 \ (\text{sh}, 9 \ 900) \); HR-EI-MS
\[ m/z: \text{calcd for } C_{26}H_{21}N_{3}^{+}: 375.1730; \text{found: } 375.1729 \ (M^+). \]

\[(2E)-1-[4-(Dimethylamino)phenyl]-3-(4-methylphenyl)prop-2-en-1-ylidene]malononitrile (3j): Following General Method, 3j was obtained (150 mg, 81%) after washing with Et₂O. M.p. 151–154 °C; \(^1\)H NMR (CDCl₃, 400 MHz): \( \delta = 2.39 \) (s, 3 H; PhMe), 3.09 (s, 6 H; PhNMe₂), 6.76 (d, \( J = 9.0 \) Hz, 2 H; PhNMe₂), 7.00 (d, \( J = 15.6 \) Hz, 1 H; CH=CH), 7.21 (d, \( J = 8.2 \) Hz, 2 H; PhMe), 7.39 (d, \( J = 9.0 \) Hz, 2 H; PhMe); 7.44 (d, \( J = 8.2 \) Hz, 2 H; PhMe); 7.49 (d, \( J = 15.6 \) Hz, 1 H; CH=CH) ppm; \(^{13}\)C NMR (CDCl₃, 100 MHz): \( \delta = 21.57, 40.03, 111.32, 114.36, 115.19, 120.03, 124.23, 128.57, 129.87, 131.61, 132.12, 141.89, 148.22, 152.70, 171.04 \) (1 peak of C(CN)₂ is overlaped with the solvent peaks); IR (neat): \( \tilde{\nu} = 3055 \) (vw), 2987 (vw), 2868 (vw), 2821 (vw), 2217 (m), 1600 (s), 1491 (m), 1371 (m), 1345 (m), 1265 (m), 1172 (m), 735 (s); UV/Vis (DMF): \( \lambda_{\text{max}} / \text{nm} \ (\varepsilon / \text{M}^{-1} \text{cm}^{-1}) = 368 \ (22 \ 100), 460 \ (8 \ 300) \); HR-EI-MS \[ m/z: \text{calcd for } C_{21}H_{19}N_{3}^{+}: 313.1573; \text{found: } 313.1575 \ (M^+). \]

\[2-[4-(Dimethylamino)phenyl]cyclobut-2-ene-1,1-dicarbonitrile (4m): Alkyne 1 (100 mg, note, I cannot connect here or it goes into Symbol!?) 0.69 mmol) was added into a DMF (5 mL) solution of formaldehyde (36% solution in water, 63 µL, 0.83 mmol) and malononitrile (45.5 mg, 0.69 mmol). The mixture was
stirred at 50 °C for 18 h. DMF and water were removed under vacuum, and the residue was purified by column chromatography (SiO$_2$, CH$_2$Cl$_2$/hexane 1:1 → 2:1) to give 4m as a yellow solid (117 mg, 76%). $R_f = 0.25$ (CH$_2$Cl$_2$/hexane = 2:1); m.p. > 133 °C (the molecule opened into the corresponding butadiene around 100 °C at a discernable rate; thus the m.p. could not be recorded); $^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 3.01$ (s, 6 H; NMe$_2$), 3.30 (d, $J = 1.4$ Hz, 2 H; CH$_2$ in cyclobutene), 6.19 (t, $J = 1.4$ Hz, 1 H; CH=C in cyclobutene), 6.71 (d, $J = 8.9$ Hz, 2 H; PhNMe$_2$), 7.36 (d, $J = 8.9$ Hz, 1 H; PhNMe$_2$) ppm; $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 29.63, 39.27, 40.03, 111.88, 114.29, 116.65, 124.11, 125.76, 140.79, 151.27$ ppm; IR (neat): $\tilde{\nu} = 2245$ (vw), 1627 (m), 1603 (m), 1522 (m), 1364 (m); HR-EI-MS $m/z$: calcd for C$_{14}$H$_{13}$N$_3$+: 223.1109; found: 223.1102 (M$^+$); elemental analysis (%) calcd for C$_{14}$H$_{13}$N$_3$: C 75.31, H 5.87, N 18.82; found: C 75.25, H 5.83, N 18.66.

{1-[4-(Dimethylamino)phenyl]prop-2-en-1-ylidene}malononitrile (3m): not possible to connect without Font change

A 1,1,2,2-tetrachloroethane (5 mL) solution of 4m (50 mg, 0.22 mmol) was stirred at 80 °C for 10 h. The solvent was removed under vacuum to provide the product as a red solid (50 mg, 100%). $R_f = 0.17$ (CH$_2$Cl$_2$/hexane = 1:1); m.p. 115–116 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 3.07$ (s, 6 H; NMe$_2$), 5.79 (dd, $J = 16.9, 0.8$ Hz, 1H; CH=CH$_2$), 6.01 (dd, $J = 10.6, 0.8$ Hz, 1 H; CH=CH$_2$), 6.72 (d, $J = 9.0$ Hz, 2 H; PhNMe$_2$), 7.10 (dd, $J = 16.9, 10.6$ Hz, 1 H; CH=CH$_2$) 7.41 (d, $J = 9.0$ Hz; PhNMe$_2$) ppm; $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 39.94, 78.07, 111.19, 113.78, 114.71, 119.31, 131.86, 133.12, 134.22, 152.98, 170.43$ ppm; IR (neat): $\tilde{\nu} = 2218$ (m), 1600(m), 1503 (m), 1372 (m); UV/Vis
(DMF): $\lambda_{\text{max}}$ / nm ($\epsilon$ / M$^{-1}$ cm$^{-1}$) = 436 (16 800); HR-EI-MS m/z: calcd for C$_{14}$H$_{13}$N$_3^+$: 223.1109; found: 223.1103.

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References


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Mechanistic Investigation of the [2+2] Cycloaddition-Cycloreversion Reaction between 4-\((N,N\)-Dimethylamino)phenylacetylene and Arylated 1,1-Dicyanovinyl Derivatives to Form Intramolecular Charge-Transfer Chromophores

Yi-Lin Wu, Peter D. Jarowski, W. Bernd Schweizer and François Diederich*

**Substituent effects on activation barrier heights:** The detailed investigation of the cycloaddition/cycloreversion reaction between \(N,N\)-dimethylanilinoacetylene and arylated 1,1-dicyanovinyl derivatives elucidated its bimolecular, two-barrier reaction mechanism, where the relative height of reaction barriers is highly sensitive to the substituents. In one extreme case, the cyclobutene formed in the cycloaddition step was isolated as a crystalline solid (X-ray), thus disclosing the nature of the previously postulated reaction intermediate.
Keywords: cycloaddition · linear free energy relationships · kinetics · reaction mechanisms · chromophores