

Molecular Complexation and Kinetics for Diels–Alder Condensation of Naphthylalkenes with Tetracyanoethylene

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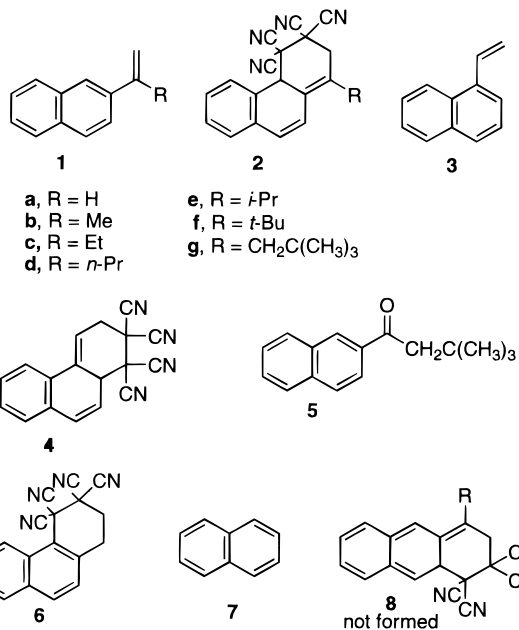
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The charge-transfer spectra of 1:1 molecular complexes of seven 1-alkyl-1-(2-naphthyl)ethenes (where R = alkyl group: H, Me, Et, *n*-Pr, *i*-Pr, *t*-Bu, Neopent) and 1-vinylnaphthalene with TCNE were determined in ClCH₂CH₂Cl as solvent at 27.1 °C. Equilibrium constants, *K*, for these complexes vary with *R*, as based on two opposing factors, viz. (a) the polar substituent factor σ^* and (b) the angle-of-twist θ between the planes of the naphthyl and vinyl groups. For R = Neopent (σ^* dominant) *K* is 50 times as large as for R = *t*-Bu (θ dominant). Except for R = *t*-Bu, kinetics of reaction conform with the equation D + TCNE \rightleftharpoons (*K*) D·TCNE \rightleftharpoons (*k*₁/*k*₋₁) P, where D is the donor alkene, P is the Diels–Alder 1,4-cycloaddition product, and *k*₁ and *k*₋₁ are first-order reaction rate constants. Values of *k*₁ vary from 0.71 min⁻¹ (R = H) to 55.5 min⁻¹ (R = Neopent) and the corresponding relative second-order rate constants *k*₂ (or *k*₁*K*) from 1 to 4000. The rate constant *k*₋₁ was measured only for **1b** (R = Me, 0.0017 min⁻¹) in the solvent mixture *p*-xylene/ClCH₂CH₂Cl. Formation of **1b**·TCNE complex gives $\Delta H = 10.0$ kcal/mol and $\Delta S = 38.4$ eu, and conversion to P shows an Arrhenius activation energy of $E_a = 7.24$ kcal/mol. It is proposed that the preferred conformation of a naphthylalkene for complexation has the R and vinyl groups projecting outward from opposite sides of the plane of the naphthalene ring. The TCNE molecule then aligns parallel to the naphthalene ring on the vinyl side where (except for R = *t*-Bu) it can slide into the geometry of the transition state to form P.

Introduction

There have been numerous studies of the molecular complexation of tetracyanoethylene (TCNE) with aliphatic and aromatic hydrocarbons. Extensive data are presented for these charge-transfer (CT) complexes by Frey and co-workers.^{1,2} Particularly pertinent to the present investigation are the results for styrene, α -methylstyrene, and 1- and 2-vinylnaphthalenes, which not only form CT complexes but also undergo Diels–Alder cycloaddition with TCNE. Thus, Japanese workers^{3–6} found that the equilibrium constant for complexation of styrene with TCNE is larger than that for α -methylstyrene in CHCl₃ at 25 °C but that the latter hydrocarbon undergoes thermal 1,4-cycloaddition faster than styrene does under the same conditions. Their adducts were not isolated, but the structures were ascertained by spectral investigation on solutions at elevated pressure. Considerably earlier, we reported the formation of isolable crystalline 1:1 adducts (**2a**, **4**) of the vinylnaphthalenes (**1a**, **3**), as well as those (**2b–f**) of the 2-alkenylnaphtha-

lenes **1b–f**, respectively.⁷ However, the lack of NMR spectral facilities at that time did not permit definitive establishment of the proposed structural formulas. We now present spectral data to confirm some representative structures from that array of compounds as well as for the additional 2-alkenylnaphthalene **1g** (R = neopentyl) and its TCNE adduct **2g**.



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This paper concerns primarily the effect of changing the R group (**1**) on the value of the equilibrium constant

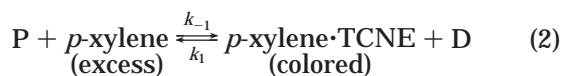
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K for 1:1 molecular complexation between **1** and TCNE and (2) on the kinetics of the Diels–Alder reaction to give **2**. For comparison purposes, 1-vinylnaphthalene (**3**) is also included in this study.

As based on investigations in the styrene^{5,6} and anthracene^{8,9} systems, the 1:1 CT complex has been shown to be an intermediate in the 1,4-cycloaddition process, as indicated by eq 1, where D is the hydrocarbon donor,



P is the Diels–Alder product, K is the equilibrium constant for CT complexation, and k_1 and k_{-1} are first-order rate constants for the conversion of $D \cdot \text{TCNE}$ into P, and its reverse process, respectively. Three separate investigations were made in order to corroborate and quantify eq 1 for the alkenylnaphthalenes, viz. (1) measurements of K and the attendant extinction coefficients ϵ in $\text{ClCH}_2\text{CH}_2\text{Cl}$ at 27.1 °C, (2) direct determination of k_1 by following the decrease in concentration of $D \cdot \text{TCNE}$ as a function of time t , and (3) direct determination of k_{-1} by following the equilibration of P with p -xylene, as in eq 2. Comparison of the results from



procedures (1) and (2) then provides justification for the intermediacy of $D \cdot \text{TCNE}$ (except for $D = \mathbf{1f}$), as shown in eq 1. Direct comparison of the relative rates of reaction of D and TCNE to form P is then given by the second-order rate constant k_2 , as calculated from eq 3.^{5,10a}

$$k_2 = k_1 K \quad (3)$$

In our previous paper,⁷ we presented data on (1) ultraviolet absorption spectra in absolute ethanol, (2) polarographic half-wave reduction potentials in aqueous dioxane, and (3) gas–liquid chromatographic retention times in Carbowax 20M (at a constant temperature) for alkenes **1a–f**. The data indicated that these compounds exist in varying conformations, i.e., in preferred angles of twist (θ) between the planes of the naphthalene ring and of the vinyl double bond. This order of twist, as given in terms of the R group, is $H(\theta \cong 0^\circ) < \text{Me} \leq \text{Et} = n\text{-Pr} < i\text{-Pr} \ll t\text{-Bu} (\theta \text{ near } 90^\circ)$. Despite these different inherent conformations, all of the alkenes were found to undergo Diels–Alder reactions with TCNE. The goal of the current study is further delineation of how the various angles of twist effect interaction between the alkene and TCNE.

New Syntheses and Structural Studies

Friedel–Crafts condensation of naphthalene (**7**) with 3,3-dimethylbutanoyl chloride gave a 64% yield of ketone **5**, identified as the 2-naphthyl derivative by ¹H NMR (singlet at 8.47 ppm) and by oxidation to 2-naphthoic acid. Wittig reaction of **5** produced **1g** (67%), which showed an ultraviolet absorption spectrum essentially superimposable in shape on those reported for **1c** (R = Et) and **1d** (R = $n\text{-Pr}$), albeit not identical in log ϵ values.

This situation implies that **1c**, **1d**, and **1g** have closely similar angles of twist (θ) in all three compounds.⁷ A cold equimolar mixture of **1g** and TCNE in CHCl_3 –EtOAc precipitated crystalline adduct **2g** (60%). Typical structures corroborated by ¹H NMR spectra are those of the 2-alkenylnaphthalenes **1b**, **1e**, and **1g** and the Diels–Alder adducts **2a**, **2f**, and **4**. Mass spectral data are also presented for **1a**, **1b**, **1g**, **2a**, **2f**, **2g**, and **4**. As noted previously,⁷ the primary adduct **2a** (mp 170.5–171.5 °C) undergoes base-catalyzed isomerization to the disubstituted naphthalene **6** (mp 201–202 °C). This structural transformation is now confirmed by ¹H NMR in that **2a** has four protons that resonate at $\delta > 7$ ppm, while **6** has six protons in this aromatic region. Both **2a** and **6** undergo the retro-Diels–Alder reaction on electron impact, but **2a** forms pertinent fragments at m/z 154 (for **1a**⁺) and 128 (for TCNE⁺), while **6** forms the most abundant peak at 204 (for $\text{C}_{14}\text{H}_8\text{N}_2^+$), with apparent loss of $\text{CH}_2=\text{C}(\text{CN})_2$. The isomerization of **2a** to **6** is also consistent with a change in ultraviolet absorption spectrum. Adduct **2f**, like **2a**, reverts to its ionized hydrocarbon precursor (**1f**⁺), m/z 210, in the mass spectrometer. It should be noted that there is no evidence that linear condensation of **1** to form adduct **8** occurs.

Charge-Transfer Data

Charge-transfer data for $D \cdot \text{TCNE}$ complexes (Table 1) were measured in 1,2-dichloroethane, rather than in CH_2Cl_2 or CHCl_3 (as used by many other research groups), because of its lower volatility and because of the relatively high solubility (about 0.11 mol/L at room temperature) of TCNE therein. The colored complex forms as rapidly as solutions of D and TCNE can be mixed.

Values of K and ϵ were obtained from Scott plots^{5,11} in the form of eq 4, where $[\text{TCNE}]_0$ and $[D]_0$ are the initial concentrations of TCNE and D (always the larger of the two), respectively, A_0 and A_∞ are initial and final absorbances, and l is the path length (in cm) through the absorption cell. From a plot of $[\text{TCNE}]_0/(A_0 - A_\infty)$ versus

$$\frac{[\text{TCNE}]_0}{(A_0 - A_\infty)} = \frac{1}{K\epsilon l [D]_0} + \frac{1}{\epsilon l} \quad (4)$$

$1/[D]_0$ one determines ϵ from the intercept and, thence, K from the slope of the straight line, with an average correlation coefficient of 0.998 for the nine hydrocarbons in Table 1 (see Figure 1).

The donor compounds are listed in Table 1 in order of increasing experimental value of the equilibrium constant K . Though irregularities occur, one notes a general increase in λ_{max} and a corresponding decrease in ϵ with increasing values of K for the series naphthalene (**7**), 1-vinylnaphthalene (**3**), and **1a–g**. The inverse relationship between ϵ and K is also seen in Table 2, where measurements were extended to temperatures other than 27.1 °C for three members of this series. Such general correlations were noted years ago by Orgel and Mulliken¹² and more recently for the TCNE complexes of styrene and its 4-methyl derivative.⁵ In comparing styrenes with their methylbenzene analogues, Frey et al.¹ observed that the former have much larger K values,

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Table 1. Charge-Transfer Data for Some Substituted Naphthalenes with TCNE in 1,2-Dichloroethane at 27.1 °C

donor compd (D) no.	substituent on naphthalene	short wavelength band λ_{\max}^a (nm)	long wavelength band		no. of data points ^d	exptl equil constant ^c K (L/mol) ^e	calcd equil constant ^f		
			λ_{\max}^a (nm)	molar extinction coeff, ϵ^b			angle of twist θ (deg) ^g	adjusted σ^* value ^h	K (L/mol)
7 ⁱ	none ^j	426	547	3060	7	0.20 ^k			
1f	2-(<i>t</i> -Bu-vinyl)	455	570	2980	8	0.23 ± 0.05	75.6	-0.79	0.23
1a ⁱ	2-vinyl ^l	472.5	577	3320	8	0.27 ± 0.04	18.6 ^m	0.00	
3 ⁱ	1-vinyl ⁿ	425	599	1720	9	0.32 ± 0.12			
1e	2-(<i>i</i> -Pr-vinyl)	480	580	820	6	1.09 ± 0.26	57.3	-0.68	1.29
1d	2-(<i>n</i> -Pr-vinyl)	487.5	600	375	7	5.6 ± 2.3	40.7 ^o	-0.61	9.1
1c	2-(Et-vinyl)	(500) ^p	600	155	10	7.5 ± 2.0	49.6 ^o	-0.59	3.6
1b	2-(Me-vinyl)	(506) ^p	594	100	6	10.5 ± 0.7	36.7	-0.49	18.5
1g	2-(Neopent-vinyl)	475	610	39	5	13.3 ± 2.9	39.4 ^o	-0.65	9.5

^a Determined from a 1:1 molar mixture of donor and TCNE. ^b Determined from Scott eq 4. ^c Determined from eqs 4 and 7 for long-wavelength bands only. ^d Used in eq 4. ^e Averaged values obtained from eqs 4 and 7, where the ± variation shown represents half of the difference between the two numbers obtained and not experimental accuracy in K . Donors are listed in order of increasing value of K . ^f Calculated by empirical eq 5 with $\rho^* = 1.018$ and $a = 2.75$ to give a least-squares fit of the data for **1b–g** combined. See: Bennet, C. A.; Franklin, N. L. *Statistical Analysis in Chemistry and Chemical Industry*; John Wiley: New York, 1954; pp 222–226. ^g Calculated for the parametric quantum mechanical model AM1: Dewar, M. J. S.; Zoebisch, E. G.; Healey, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. ^h Ballinger, P.; Long, F. A. *J. Am. Chem. Soc.* **1960**, *82*, 795. σ^* is adjusted algebraically to give $R = H = 0.00$, rather than $R = \text{Me} = 0.00$. ⁱ Reference 2 lists λ_{\max} and K values for these compounds in CH_2Cl_2 at 22 °C, as given in footnotes *j*, *l*, and *n*. ^j Reported data: 550–560 and 429–433 nm; $K = 0.6–1.19$. ^k Determined only by means of eq 4. Since **7** does not undergo Diels–Alder reaction, K cannot be calculated from eq 7 for comparison with this value. ^l Reported data: 580 and 465 nm; $K = 0.68 \pm 0.02$. ^m Previous experiments indicate that this is effectively 0° (ref 7). ⁿ Reported data: 603 and 432 nm, K not given. ^o Ultraviolet absorption spectra of these three compounds indicate that θ is effectively the same in all of them. ^p Shoulder.

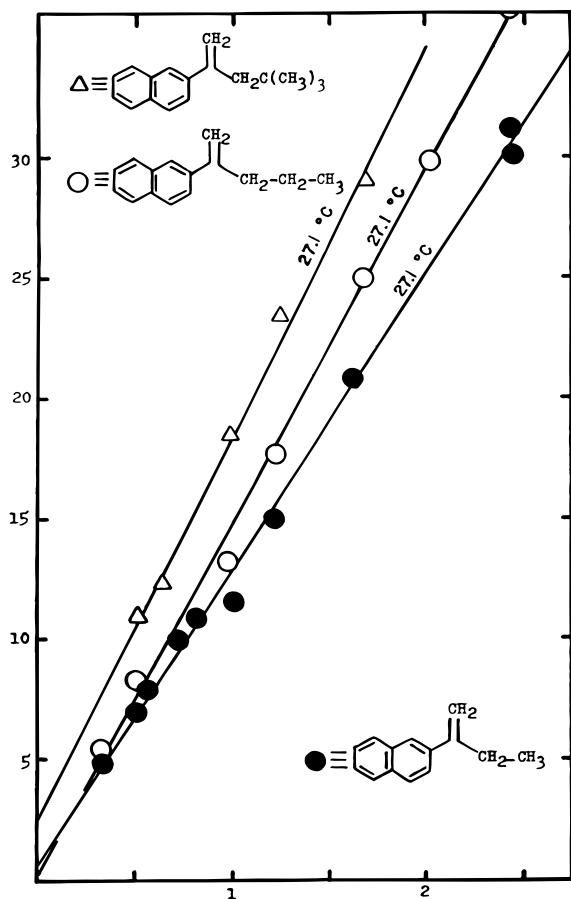


Figure 1. Scott plots (eq 4) of $1000[\text{TCNE}]_0/(A_0 - A_\infty)$ versus $100/[\text{D}]_0$ for three 1-alkyl-1-(2-naphthyl)ethenes in $\text{C}_1\text{H}_2\text{CH}_2\text{-Cl}$ at 27.1 °C. Calculated values of K and ϵ are included in Table 1. Concentrations (M).

while the latter have larger absorbances. In general, however, all alkyl substituents on benzene or naphthalene² tend to increase the value of K .

It is noteworthy from Table 1 that naphthalene (which does not undergo Diels–Alder reaction with TCNE), 2-vinylnaphthalene (nearly coplanar and highly conju-

Table 2. Temperature Dependence of TCNE Complexation with Naphthalene and Two 2-Alkenylnaphthalenes in 1,2-Dichloroethane

donor compd (D) no.	T °C	no. of measurements	molar extinction coeff, ϵ^a	$K^{a,b}$ (L/mol)
7	-29.6	5	3370	0.346
7	+0.5	7	2340	0.376
7	27.1	7	3060	0.20 ^c
1a	27.1	8	3320	0.27 ^c
1a	47.6	6	1720	0.538
1b	-29.6	9	5500	0.24
1b	+0.5	9	820	1.51
1b	8.7	7	525	6.1
1b	27.1	6	100	10.5 ^c

^a Average value for the correlation coefficient of the nine experiments is 0.998. Data refer to the long-wavelength CT bands. ^b A plot of $\ln K$ versus $1/T$ (where T is temperature on the Kelvin scale) for naphthalene (**7**) did not yield a straight line. This nonlinearity may be ascribed to experimental error in values of ϵ as determined by eq 4 or to an inherent property of the system. On the contrary, **1b** did give a reasonably straight line (Daniels, F.; Alberty, R. A. *Physical Chemistry*, 4th ed.; John Wiley: New York, 1975; pp 170–173). ^c See Table 1.

gated), and **1f** (effectively nonconjugated) have nearly identical K values. This situation, plus the order $R = i\text{-Pr} < n\text{-Pr} \leq \text{Et} < \text{Me} \leq \text{Neopent}$ for increasing stability of the complex, implies that electronic charge donation to the naphthalene ring by the group R operates through the vinyl group and will be altered by the angle of twist θ . In an attempt to rationalize the experimental values of K in a semi-quantitative manner, however, we assume, to a first approximation, that K is a function of both σ^* , the Taft polar substituent constant, and θ , acting independently of one another. The linear free-energy relationship, eq 5, is used for this calculation. In this

$$\log K = \rho^* \sigma^* + a \cos^2 \theta \quad (5)$$

equation, ρ^* and a are constants to be determined, and calculation is not applied to **1a** since σ^* is taken as zero in that case. The function $\cos^2 \theta$ satisfies the boundary conditions of 1 for $\theta = 0^\circ$ and 0 for $\theta = 90^\circ$. Also, it is consistent with the simple concepts that the CT band of longest wavelength involves electron transfer from the

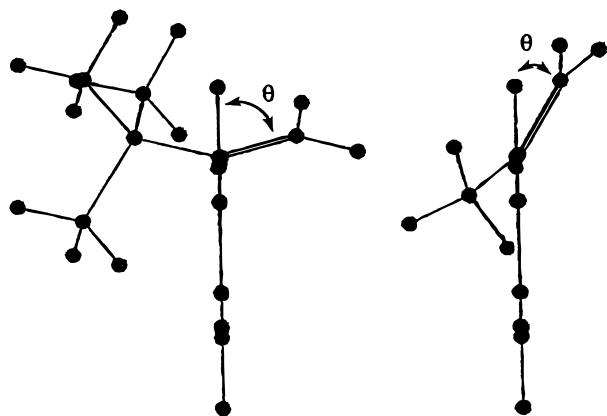


Figure 2. Proposed preferred conformations of **1b** (right-hand diagram) and **1f** (left-hand diagram) for complexation with TCNE. In these molecular mechanical (AM1) drawings, the naphthalene ring is viewed edgewise and the TCNE molecule is expected to align itself in a plane parallel to that of naphthalene and on the vinyl side.

HOMO of D to the LUMO of TCNE^{13–15} and that this transition can be regarded as occurring in a one-dimensional potential box of length y , where λ_{\max} is directly proportional to the square of y .¹⁶ Data used for θ and σ^* , the procedure for calculations, and the calculated values of K obtained are included in Table 1. It is apparent that calculated values have the correct order of magnitude, with good agreement for large values of θ (i.e., for **1e** and **1f**) and larger deviations from the experimental results for $\theta < 50^\circ$. It seems clear that some modification in the term $a \cos^2 \theta$ could improve the fit. However, one arrives at the overall conclusion that the stability of the complex D·TCNE increases with electronic donation by the R group and decreases with increasing angle of twist θ .

From Table 2, it is notable that naphthalene shows little change in K over a temperature range of 56.7 °C, while K increases 40-fold for **1b** over this same range and doubles for **1a** over a shorter range of 20.5 °C. A suggested geometrical interpretation for these differences, as well as for the K values in Table 1, is that both faces of naphthalene are open to unhindered approach by a TCNE molecule. 2-Vinylnaphthalene may be similarly situated. However, Figure 2, obtained by a molecular mechanics program,¹⁷ shows conformations for **1b** and **1f** that we suggest are preferred during TCNE complexation. In these cases, the R group (Me or *t*-Bu, respectively) protrudes outward to one side of the plane of the naphthalene ring, while the vinyl group protrudes outward from the other side of this plane. As proposed by Mobley et al.¹⁸ for complexation of asymmetrically substituted benzenes and naphthalenes, the TCNE will align itself in a parallel (or nearly parallel) plane on the vinyl (less hindered) face of the naphthyl group in a π - π

sandwich structure. This complexation will be more facile as conjugation by the vinyl group increases (for smaller θ) and as increasing π -electronic charge is driven from the alkyl side of the ring toward the acceptor TCNE molecule on the other side.

Measurement and Use of Rate Constant k_1

Kinetics of the reaction of the complex D·TCNE to give P were conducted on mixtures of D (used in large excess, such that $[D]_t \cong [D]_0$) and TCNE in $\text{CICH}_2\text{CH}_2\text{Cl}$ at constant temperature. Disappearance of the colored complex was followed spectrophotometrically as a function of time, t . Three typical linear plots of log absorbance (A) versus t , as shown in Figure 3, indicate that the reaction is first order in the concentration of the complex. For quantitative determination of k_1 we used eq 6, which assumes that k_{-1} is negligibly small, as compared to k_1 . Then if one lets k_{obs} represent the

$$-2.303 \log(A - A_\infty) = \left(\frac{k_1[D]_0}{K[D]_0 + 1} \right) t - 2.303 \log(A_0 - A_\infty) \quad (6)$$

coefficient of t in eq 6 one obtains eq 7, from which one calculates k_1 and a second value of K as derived from a linear plot of $1/k_{\text{obs}}$ versus $1/[D]_0$ (a modified Guggenheim plot^{6,19}). Illustrative data for one series of experiments

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_1} \left(\frac{1}{[D]_0} \right) + \frac{K}{k_1} \quad (7)$$

with donor **1b** are presented in Table 3 and typical kinetic plots are shown in Figure 4. In every case, good linearity was obtained over at least 2 half-lives, usually much longer. Comparative first-order rate constants k_1 and second-order rate constants k_2 are listed in Table 4.

One notes that 1- and 2-vinylnaphthalenes have comparable K , k_1 , and k_2 values. While the *tert*-butyl compound **1f** has similar stability in its complex, steric hindrance appears to slow its Diels–Alder addition by a factor of at least 20 times at 27.1 °C. At that standard temperature, k_1 values fall in the order for R of Neopent > Me > *n*-Pr > Et >> *i*-Pr >> *t*-Bu, and k_2 values, in the order Neopent > Me > Et > *n*-Pr > *i*-Pr >> *t*-Bu. The order of k_2 values is consistent with a general change in the domination of polar effects (for the neopentyl group) to that of domination of steric effects, i.e., hindrance to attainment of transition state geometry (for the *tert*-butyl group). Apparently, the presence of a methylene group between the naphthylvinyl and the *tert*-butyl portions of **1g** introduces sufficient flexibility in the molecule as to counteract hindrance by the bulky *tert*-butyl portion.

Figure 5 is a plot of log K (Table 1) versus log k_1 (Table 4) for reaction at 27.1 °C. This linear plot for compounds **1a–e** and **1g** with a positive slope implies that the complex D·TCNE is an intermediate on the pathway from reactants D and TCNE to Diels–Alder product P.^{6,20} The point for the *tert*-butyl compound **1f** (x, y coordinates at

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(17) See footnote g, Table 1.

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(19) Note that k_{obs} in eq 7 is different from k_{obsd} , as used in ref 6.

(20) The positive slope is consistent with the concept that the rate of Diels–Alder cyclization (as measured by k_1) increases as the instantaneous concentration of molecular complex (as measured by K) increases. If the slope were negative, the rate of cyclization would decrease with increasing concentration of complex and the kinetics should be more complicated.

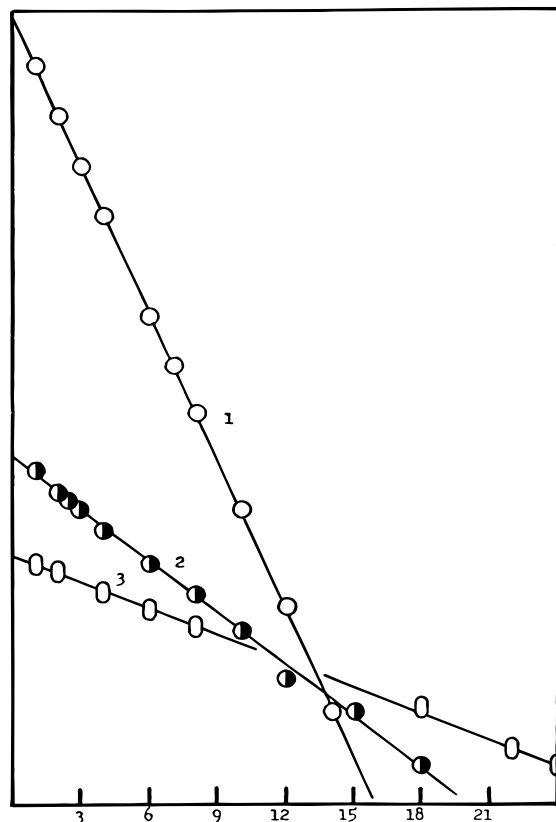


Figure 3. Linear plots of $\log A$ (arbitrary units) versus reaction time t (min) for disappearance of the molecular complex $D \cdot TCNE$ in first-order reaction kinetics in $CICH_2CH_2Cl$ plus excess TCNE at $27.1^\circ C$: curve 1 for $[3]_0$ of $0.1063 M$; curve 2 for $[3]_0$ of $0.0364 M$; curve 3 for $[1a]_0$ of $0.0272 M$.

Table 3. Illustrative Experimental Data for the Disappearance of $1b \cdot TCNE$ as a Function of Time at $27.1^\circ C$ in $CICH_2CH_2Cl$

expt no. ^a	$[1b]_0^b$ ($10^2 \times M$)	$[TCNE]_0^c$ ($10^4 \times M$)	$1/[1b]_0$ ($10^{-2} L/mol$)	$10^3 [TCNE]_0$ ($A_0 - A_\infty$)	$1/k_{obs}$ (min)
9a	1.03	5.00	0.971	10.87	2.78
9b	2.00	7.27	0.500	6.59	1.56
9c	3.00	7.27	0.333	3.84	1.03
9d	0.494	5.00	2.02	21.0	5.34
9e	0.618	5.00	1.62	18.3	4.16
9f	0.824	5.00	1.21	13.2	3.30

^a Listed in chronological order, as conducted. The subscript zero refers to conditions at $t = 0$. ^b A specific example of $[D]_0$ as given in eq 7. ^c This value is the sum of free, complexed, and reacted TCNE at any time, t .

$-0.34, 0.36$) falls far off the straight line, inasmuch as the rate of cycloaddition of **1f** is relatively very slow as compared to its equilibration. Thus, it seems likely that the kinetics for **1f** are more accurately represented by eq 8 than by general eq 1. However, for **1a–e**, and **g**, it



is proposed that the complex (with the TCNE molecule held on the vinyl side of the naphthalene ring) reacts further to give 1,4-cycloaddition by movement (sliding and, perhaps, rotating) of the TCNE addendum into the required geometry of the transition state.

Plots of $\ln k_1$ and of $\ln k_2$ (see Table 4) for compound **1b** versus $1/T$ (in Kelvin⁻¹) give linear relationships,

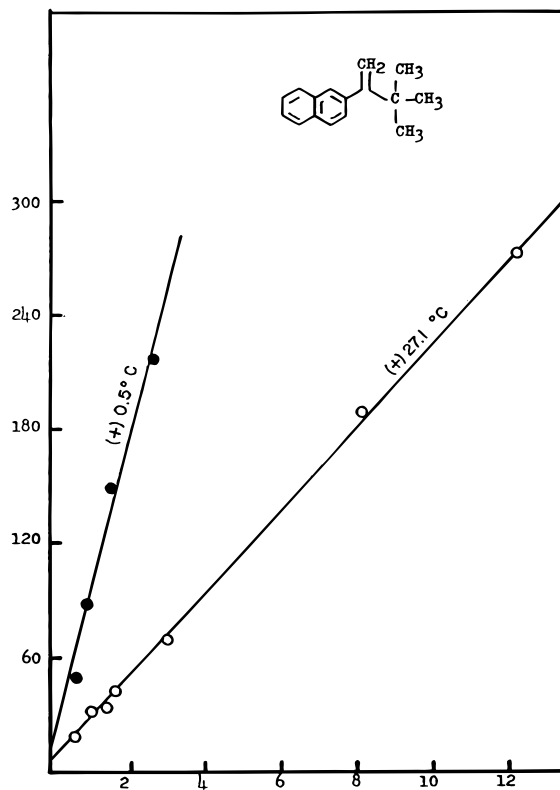


Figure 4. Plot of $1/k_{obs}$ (min) versus $1/[1f]_0$ (in units of $100/M$) (eq 7) for **1f** in excess TCNE plus $CICH_2CH_2Cl$ at two different temperatures. Calculated values for K and k_1 at $27.1^\circ C$ are included in Tables 1 and 4.

according to the Arrhenius eq 9.^{10b} From the slopes and

$$\ln k = \ln B - E_a/RT \quad (9)$$

the intercepts of these curves one calculates the activation energies E_a as 7.24 and 17.8 kcal/mol and the preexponential factors B^{21} as $6.58 \times 10^6 \text{ min}^{-1}$ and $4.31 \times 10^{15} \text{ L/mol/min}$ for $k = k_1$ and $k = k_2$, respectively.

Measurement and Correlation of Rate Constant k_{-1}

Measurement of the rate of dissociation of Diels–Alder product **P** was determined in one case, that of **2b** in $CICH_2CH_2Cl$ at $27.1^\circ C$ at three different initial concentrations. Since the solutions of **2b** are colorless, progress of the reaction was followed spectrophotometrically by adding a standard **2b**– $CICH_2CH_2Cl$ solution to excess *p*-xylene and obtaining the increase in the concentration of colored complex (*p*-xylene·TCNE) as a function of time. A calibration chart for the use of this procedure is shown in Figure 6. The approach to equilibrium is given by eq 2, and the rate constant, k_{-1} , is calculated as the slope of a linear plot of the left side of eq 10 versus time t ,²² where a is the initial concentration

$$\frac{X_e}{(2a - X_e)} \ln \left[\frac{aX_e + X(a - X_e)}{a(X_e - X)} \right] = k_{-1}t \quad (10)$$

of **2b**, X is the concentration of *p*-xylene complex at any time, and X_e is that of the complex when equilibrium is attained. Figure 7 shows the plot for one of the experi-

(21) B is used here, rather than A , so as to avoid confusion with absorbance.

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Table 4. Kinetic Results for the Conversion of Donor D and TCNE into the Diels–Alder 1,4-Cycloadduct (P) in CICH₂CH₂Cl

expt series no.	donor compd (D) no.	<i>T</i> °C	no. of measurements	<i>k</i> ₁ ^a (min ⁻¹)	standard deviation for <i>k</i> ₁	half-life, <i>t</i> _{1/2} (min)	<i>k</i> ₂ ^b (L/mol/min)	rel <i>k</i> ₂ value for 27.1 °C
1	3	27.1	9	1.11	0.01	0.613	0.36	1.9
2	3 ^c	27.1	6	1.15	0.01		0.37	1.9
3	1a	27.1	8	0.70	0.02	0.97	0.19	1 ^d
4	1a ^c	27.1	5	0.73	0.01		0.20	1 ^d
5	1a	47.6	7	2.08	0.07	0.333	1.12	
6	1b	-29.6	8	1.92	0.02	0.359	0.46	
7	1b	+0.5	9	11.8	0.25	0.059	17.8	
8	1b	8.7	7	20.8	0.31	0.033	127	
9	1b	27.1	6	40.3	1.13	0.017	423	2.23 × 10 ³
10	1b	46.5	6	64.5	5.81	0.011	^e	
11	1c	27.1	10	22.7	0.57	0.031	170	8.95 × 10 ²
12	1d	27.1	7	27.2	0.44	0.025	152	8.00 × 10 ²
13	1e	27.1	6	2.45	0.02	0.283	2.67	1.41 × 10 ¹
14	1f	0.5	4	1.22 × 10 ⁻²		56.8	^e	
15	1f	27.1	12	4.56 × 10 ⁻²	6 × 10 ⁻⁴	15.2	(1.05 × 10 ⁻²) ^f	(5.52 × 10 ⁻²) ^f
16	1g	27.1	6	55.5	2.78	0.012	738	3.89 × 10 ³

^a First-order rate constant for the reaction D·TCNE→P. ^b Second-order rate constant for the reaction D + TCNE → P (calculated by eq 3). ^c Duplicate series was conducted separately and at a different time from the previous series. ^d Arbitrarily chosen as a standard of reference. ^e *K* was not determined for this series. ^f It is likely that this datum is not directly comparable with other data in this column (see discussion of Figure 5).

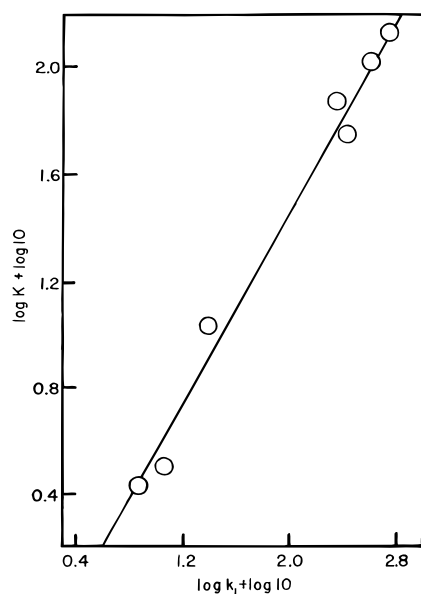


Figure 5. Linear plot of log (equilibrium constant *K*) versus log (first-order rate constant *k*₁) for donor alkenes **1a–e** plus **1g** to support the intermediacy of molecular complex D·TCNE as shown in eq 1. *T* = 27.1 °C.

ments; average correlation coefficient 0.994, *k*₋₁ = 1.72 ± 0.13 × 10⁻³ min⁻¹; *t*_{1/2} = 403 min. The ratio of *k*₁/*k*₋₁ = 2.34 × 10⁴ confirms that *k*₋₁ can be neglected as shown in eq 6.

Experimental Section

Purification of alkenes **1a–f**, TCNE, and their condensation products **2a–f** was conducted as described previously.⁷ Analytical-grade 1,2-dichloroethane was distilled twice through a packed fractionating column, stored over a mixture of anhydrous CaCl₂/K₂CO₃ for 1 week, and finally refractionated, bp 84.0 °C. Chemically pure *p*-xylene was dried with Na wire and fractionated, bp 136.4–136.6 °C.

NMR spectra were determined on CDCl₃ solutions at 300 MHz; MS spectra were obtained by impact with 70 V electrons. Coupling constants (*J*) are given in Hz. Miscellaneous spectra on previously reported alkenes and Diels–Alder adducts are presented here.

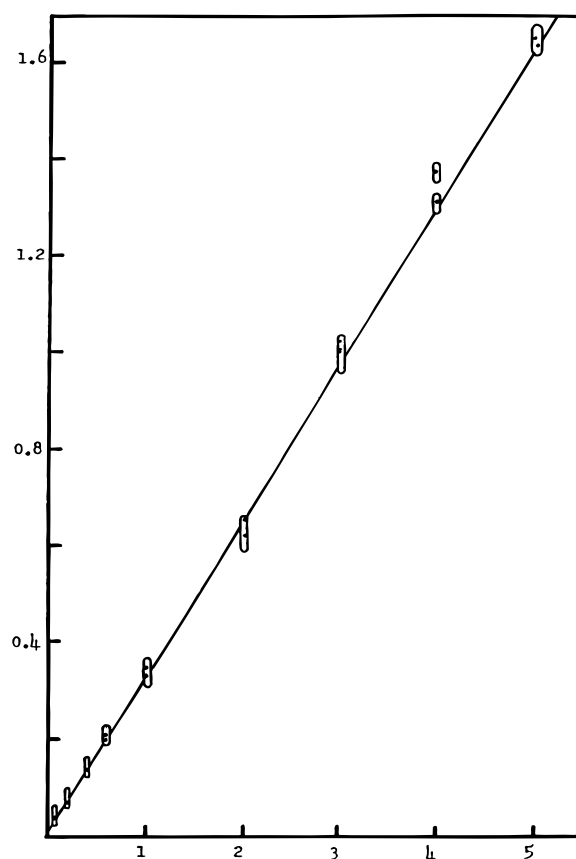


Figure 6. Calibration curve for absorbance *A* of the complex *p*-xylene·TCNE versus 1000[TCNE] in excess *p*-xylene. Used in conjunction with Figure 7.

2-(2-Naphthyl)-1-ethene (1a):⁷ IR (CHCl₃) 1640, 1600, 1490, 1420, 900 cm⁻¹; MS *m/z* 154 (100), 153 (51), 152 (33), 128 (13).

2-(2-Naphthyl)-1-propene (1b):⁷ ¹H NMR δ 7.8–9.6 (m, 4H), 7.73 (dd, *J* = 1.8, 6.9, 1H), 7.45–7.56 (m, 2H), 5.60 and 5.26 (2d, *J* = 0.9, 2H), 2.33 (s, 3H); MS *m/z* 168 (100), 153 (50), 128 (38).

3-Methyl-2-(2-naphthyl)-1-butene (1e):⁷ ¹H NMR δ 8.01 (m, 4H), 7.64–7.73 (m, 3H), 5.51 and 5.36 (2 split s, 2H), 3.18 (m, 1H), 1.36 (2d, *J* = 6–7, 6H).

2,3,4,4a-Tetrahydrophenanthrene-3,3,4,4-tetracarbo-

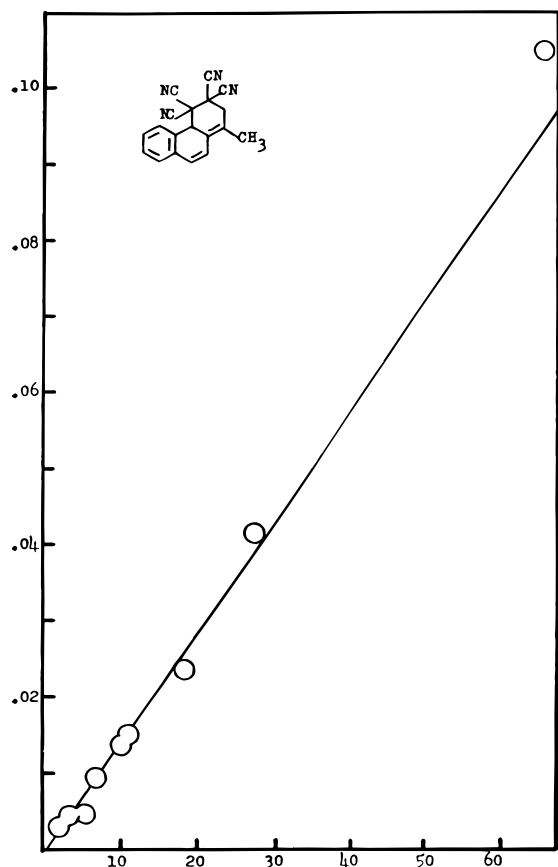


Figure 7. Plot of first-order dissociation kinetics of Diels–Alder adduct **2b** as per eq 10. The vertical axis corresponds to the left-hand side of eq 10 and is a pure number without units. The horizontal axis is time t (min). The solvent is $\text{ClCH}_2\text{CH}_2\text{-Cl}/p$ -xylene at 27.1°C .

nitride (2a):⁷ ES (100% EtOH) λ_{max} (log ϵ) 231.5 (4.42), 251.5 (4.04), 285 (3.90), 296 (3.96), 313 (3.96), 325 (3.63); $^1\text{H NMR}$ δ 7.88 (dd, $J = 2.1, 6.3, 1\text{H}$), 7.38–7.5 (m, 2H), 7.24–7.3 (m, 1H), 6.45 (dd, $J = 1, 8.3, 2\text{H}$), 5.77 (m, 1H), 4.88 (bs, 1H), 3.2–3.6 (m, 2H); MS m/z 282 (19), 154 (100), 153 (50), 152 (30), 128 (26).

1-(1,1-Dimethylethyl)-2,3,4,4a-tetrahydrophenanthrene-3,3,4,4-tetracarbonitrile (2f):⁷ $^1\text{H NMR}$ δ 7.70 (dd, 1H), 7.35–7.45 (m, 2H), 7.2–7.3 (m, 1H), 6.70 (dd, $J = 10, 59, 2\text{H}$), 4.68 (bs, 1H), 3.44 (dd, $J = 4, 18.9, 1\text{H}$), 3.20 (dd, $J = 1.6, 18.9, 1\text{H}$), 1.34 (s, 9H); MS m/z 338 (8), 210 (100), 195 (57), 153 (97).

1,2,3,4-Tetrahydrophenanthrene-3,3,4,4-tetracarbonitrile (6):⁷ ES (100% EtOH) λ_{max} (log ϵ) 227.5 (4.70), 266 (3.55), 277 (3.74), 286 (3.78), 307 (3.15), 316 (2.17), 322 (2.90); $^1\text{H NMR}$ δ 8.38 (d, $J = 9, 1\text{H}$), 8.04 (t, $J = 9, 2\text{H}$), 7.87 and 7.74 (2t, $J = 7.5, 2\text{H}$), 7.38 (d, $J = 9, 1\text{H}$), 3.53 and 2.92 (2t, $J = 6.3, 4\text{H}$); MS m/z 282 (41), 204 (100).

Syntheses of New Compounds. 3,3-Dimethyl-1-(2-naphthyl)butanone (5). Naphthalene (56 g, 0.44 mol) was acylated with 3,3-dimethylbutanoyl chloride²³ (59 g, 0.44 mol) by a general Friedel–Crafts procedure.²⁴ The crude product (bp $115\text{--}124^\circ\text{C}/0.11$ Torr, 64%) was converted to a monopicate (yellow needles, mp $90.5\text{--}91.5^\circ\text{C}$), which was dissociated on a column of alumina with $\text{C}_6\text{H}_6\text{--CHCl}_3$ (1:1). Crystallization from MeOH gave needles: mp $43\text{--}44^\circ\text{C}$; IR ($\text{CCl}_4\text{--CS}_2$) 1675, 858, 825, 746 cm^{-1} ; $^1\text{H NMR}$ δ 8.47 (s, 1H), 8.03 (dd, $J = 1.4, 8.7, 1\text{H}$), 7.98 and 7.89 (2d, $J = 7.8, 2\text{H}$), 7.91 (d, $J = 8.7, 1\text{H}$), 7.62 and 7.57 (2 dt, $J = 1.1, 6.7, 2\text{H}$), 3.00 (s, 2H),

1.12 (s, 9H); MS m/z 226 (31), 170 (71), 155 (100), 127 (71). Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}$: C, 84.91; H, 8.02. Found: C, 85.04; H, 7.83.

Oxidation of **5** by means of $\text{KO-}t\text{-Bu}$ and O_2 ²⁵ gave 2-naphthoic acid, mp $184\text{--}185^\circ\text{C}$ (lit.²⁶ mp 185.5°C).

4,4-Dimethyl-2-(2-naphthyl)-1-pentene (1g). This alkene was prepared from **5** by the Wittig procedure as used for **1e**.⁷ The crude product from chromatography (mp $44\text{--}47^\circ\text{C}$, 67%) formed needles (mp $49\text{--}50^\circ\text{C}$) from MeOH: IR ($\text{CCl}_4\text{--CS}_2$) 1622, 1599, 1506, 860, 822, 753 cm^{-1} ; ES (100% EtOH) λ_{max} (log ϵ) 239 (4.74), 265 sh (3.56), 274.5 (3.68), 284.5 (3.71), 292 sh (3.54), 296 nm (3.55); $^1\text{H NMR}$ δ 7.5–7.9 (m, 4H), 7.2–7.5 (m, 3H), 5.40 and 5.15 (2s, 2H), 2.61 (s, 2H), 1.89 (s, 9H); MS m/z 224 (37), 168 (100), 57 (93). Anal. Calcd for $\text{C}_{16}\text{H}_{20}$: C, 91.01; H, 8.99. Found: C, 90.64; H, 8.92.

1-(2,2-Dimethylpropyl)-2,3,4,4a-tetrahydrophenanthrene-3,3,4,4-tetracarbonitrile (2g). An equimolar mixture of alkene **1g** (2.24 g) and TCNE (1.28 g) was dissolved in a 1:1 mixture of $\text{CHCl}_3\text{--EtOAc}$ in a vessel protected from the light. When the solution was concentrated and cooled to -10°C , needles (2.04 g, 60%) of **2g** precipitated: mp $143\text{--}143.5^\circ\text{C}$; MS m/z 352 (0.1), 224 (21), 168 (73), 128 (37), 76 (35), 57 (100). Anal. Calcd for $\text{C}_{23}\text{H}_{20}\text{N}_4$: C, 78.38; H, 5.72; N, 15.90. Found: C, 78.59; H, 5.53; N, 15.60.

1,2,3,10a-Tetrahydrophenanthrene-1,1,2,2-tetracarbonitrile (4). Following essentially the same procedures as used for **2g**, a mixture of purified 1-vinylnaphthalene²⁷ (**3**) and TCNE deposited a 93% yield of adduct **4**, obtained as light-sensitive prisms on recrystallization from CHCl_3 : mp $182\text{--}183^\circ\text{C}$; IR (KBr) 2260, 1655, 1570, 1488, 755, 675 cm^{-1} ; ES (100% EtOH) λ_{max} (log ϵ) 245 (4.52), 295 (3.63), 305 (3.59); $^1\text{H NMR}$ δ 7.43 (d, $J = 7.5, 1\text{H}$), 7.33 (pentet, $J = 7.5, 2\text{H}$), 7.14 (d, $J = 7.5, 1\text{H}$), 6.77 (dd, $J = 3, 9.6, 1\text{H}$), 6.0–6.15 (m, 2H), 4.45 (split s, 1H), 3.35–3.58 (dm, 2H); MS m/z 282 (29), 204 (26), 154 (100). Anal. Calcd for $\text{C}_{18}\text{H}_{10}\text{N}_4$: C, 76.58; H, 3.57; N, 19.85. Found: C, 76.33; H, 3.95; N, 19.99.

Charge-transfer spectra of the TCNE complexes of **1**, **3**, and naphthalene were obtained on equimolar mixtures (ca. 1×10^{-3} M) of the two components in 1,2-dichloroethane contained in a 10-cm quartz cell, thermostated to $27.1 \pm 0.1^\circ\text{C}$ in a Cary 11 spectrophotometer. Solutions of the components were mixed rapidly, and measurements were made by scanning the region 750–400 nm as rapidly as possible (3–4 min) in order to minimize Diels–Alder reaction. Wavelengths for the two absorption maxima found in each case are given in Table 1.

Determinations of K and ϵ for the long-wavelength maximum for each donor hydrocarbon (D) were made from the Scott plots, as shown in eq 4 and Figure 1. $[\text{D}]_0$, the initial molar concentration of D (4×10^{-3} to 1.6), was always larger (8–1100 times) than the initial molar concentration of TCNE, i.e., $[\text{TCNE}]_0$ (1×10^{-4} to 4×10^{-3}). Measurements at 27.1°C and 47.6°C were made in a thermostated bath as above. However, a specially designed Dewar jacketed absorption cell²⁸ with Pyrex glass windows (cutoff point at 300 nm in the ultraviolet region) was used for measurements below room temperature (see Tables 2 and 4). The volume of the sample compartment was 10 mL, and the light path through the sample was 2.02 cm. Temperature control was furnished by adding a coolant (ice–water slurry for 0.5°C , boiling Freon-12 for -29.6°C) to the Dewar flask to a height sufficient to bathe the sample cell. Solutions of D and TCNE in $\text{ClCH}_2\text{--CH}_2\text{Cl}$ were prepared just prior to the experiment. For experiments above room temperature, the cell compartments were thermally equilibrated for 2 h and the solutions (in separate cells of a “quick-mix” vessel) for 20–30 min. Mixing of the reactants and starting of a stopwatch were conducted

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simultaneously, and the mixture was rapidly transferred into the spectrometer. Absorbance, A , was obtained versus time, t . A_{∞} was obtained after 8 half-lives (30 min to several hours). For experiments below room temperature, the D solution (10 mL) was equilibrated in the cell for 20–30 min. Then 100–200 μ L of TCNE at room temperature was added with vigorous stirring (magnetic stir bar) and simultaneous start of timing. Stirring was stopped, and A was measured versus t . Concentrations were corrected for change in density of the solvent with temperature.

Representative plots of $\log A$ versus t are shown in Figure 3 and of $1/k_{\text{obs}}$ versus $1/[D]_0$ in Figure 4. Data for k_{obs} and k_1 (see eqs 6 and 7) and k_2 (see eq 3) are presented in Tables 3 and 4. A log–log plot of K versus k_1 occurs in Figure 5.

Determination of k_{-1} was made (as per eq 2) in only one case, that of the retrogression of **2b** to **1b** and TCNE (measured spectrophotometrically as the complex with excess *p*-xylene) at 27.1 °C. To a reference cell and to a sample cell were added 3 mL of *p*-xylene and 0.5 mL of $\text{ClCH}_2\text{CH}_2\text{Cl}$ and counterbalanced for absorbance at 408 nm, the λ_{max} for absorbance by *p*-xylene·TCNE, to obtain a cell correction for the sample cell. Then into each of several sample cells were placed 3 mL of *p*-xylene plus 0.5 mL of a measured quantity of TCNE in $\text{ClCH}_2\text{CH}_2\text{Cl}$, and the calibration curve of Figure 6 was determined over a range of [TCNE] of 10^{-3} to 10^{-5} M.

The dissociation of **2b** was conducted in a round-bottomed flask fitted with a water-cooled glass stirrer and a short water-cooled condenser through which one could withdraw samples. Into 24 mL of thermally stabilized $\text{ClCH}_2\text{CH}_2\text{Cl}$ was washed 74.2 mg of **2b** with 1 mL of this solvent. Timing and vigorous stirring were started. All solid dissolved in 10–20 s. Periodically, 0.5 mL aliquots were withdrawn and added to 3 mL of *p*-xylene in a sample cell, and time and absorbance were immediately recorded. Data are plotted according to eq 10 (see Figure 7). The reaction was essentially complete in 30 min.

Computations. Calculations were made by means of a mainframe computer, and linear plots were obtained from a Mathcad program,²⁹ which provides corresponding values for the intercept, slope, and correlation coefficient for the line.

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