The results of the $(CH_3)_2Be-BeCl_2$ nmr study are even more convincing (Table IV, Figure 4). At 35° only an average signal is observed for all of the mixtures due to the rapid exchange at this temperature. When $(CH_3)_2Be$ and $BeCl_2$ are in 1:1 ratio only one signal is observed at −85° which is 4 cps different from $(CH_3)_2Be$ at the same temperature. Once again the convincing experiments are the nmr observations at 2:1 and 3:1 ratio. When $(CH_3)_2Be$ and $BeCl_2$ are in 2:1 ratio two signals are observed, one is characteristic of $(CH_3)_2Be$ and the other for what must be CH_3BeCl since the signals bear a 1:1 ratio. When $(CH_3)_2Be$ and $BeCl_2$ are added in 3:1 ratio the signal indicative of the excess $(CH_3)_2Be$ increases and the signal indicative of CH_3BeCl remains constant. Thus the nmr evidence alone appears conclusive to establish redistribution in the $(CH_3)_2Be-BeX_2$ systems.

The nmr spectra of similar mixtures of $(C_6H_5)_2Be-BeBr_2$ were also determined. The spectra obtained are qualitatively like those found for C_6H_5Li, $(C_6H_5)_2Mg$, and $(C_6H_5)_2Zn$.[25] The effect of replacing C_6H_5 by halogen was observed in slight upfield shifts of the bands, but the complexity of the AB_2C_2-type pattern made detailed and clear-cut analysis of the variable-temperature spectra beyond the scope of this paper.

The conclusion therefore is that the nmr evidence, in addition to selective precipitation and association studies, indicates strongly that rapid redistribution in the system $R_2Be-BeX_2$ where $R = CH_3, C_2H_5, C_6H_5$ and $X = Cl, Br$ does take place.

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Charge-Transfer Complexes of Tetracyanoethylene with Acenaphthylene Photodimers. The ω Technique as an Approach to Transannular Interaction

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Abstract: The tetracyanoethylene charge-transfer complex of the *cis* photodimer of acenaphthylene shows a slight red shift in its two absorption bands relative to those of the *trans* isomer. The difference is greater for the higher energy band than for the lower one. ω-Technique calculations performed with an initially unsymmetrical positive ion afford a simple approach to the problem of transannular interaction and predict the observed behavior.

Electron donor–acceptor (EDA) complexes between aromatic compounds and Lewis acids have been studied extensively because of their sensitivity to relatively small steric and electronic changes in both donor and acceptor. For a series of methylated benzenes with tetracyanoethylene (TCNE), Merrifield and Phillips showed an increase in both the extent of complexation and the absorption wavelength for the complex with increased substitution.[2] The initial work of Mulliken[3] has resulted in several experimental and theoretical studies which have illustrated the relationship between the ionization potential of the donor, among other things, with both the free energy of formation and the energies of spectral transitions (E_{EDA}) of these complexes.[4] In particular, several workers have demonstrated a relationship between the energy of the highest occupied molecular orbital (HOMO) with E_{EDA}, using either simple Hückel[5] or more sophisticated calculations.[6]

Our interest in this topic involves the use of EDA complexes as measures of the extent of transannular interaction (TI). That such interaction results in significant differences in these complexes was shown by Cram in the paracyclophane series.[7] However, the problem of puckered rings encountered with these compounds renders them less than ideal, especially with regard to adaptation to π-electron calculations.[8]

We have investigated the behavior of the two acenaphthylene photodimers I and II, along with acenaphthene (III). In I, there is no puckering of the benzene rings

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Table I. Corrections of Wavelength and Absorbance for the Short-Wavelength Band of TCNE Complexes of Compounds I, II, and III

Donor	λ_{max}, mμ		— Max absorb[a] —	
	Obsd	Cor	Obsd	Cor
I	457 ± 1	459 ± 1	0.306	0.300
II	424 ± 3	439 ± 3	0.231	0.174
III	426 ± 1	446 ± 1	0.210	0.195

[a] For a run of intermediate values of the absorbance/donor concentration ratio.

metric flask, heating to ensure complete dissolution of the TCNE, then adjusting the volume and taking measurements at 23 ± 1°. The concentration of donor was 3.0 × 10⁻⁴ M in all cases, while the concentration of TCNE was varied from 8.3 × 10⁻³ to 2.1 × 10⁻² M in the six or more samples used for each donor. Optical density was measured with a Cary Model 14 spectrophotometer in a 12.90 ± 0.03 cm Pyrex glass-stoppered cell which was carefully positioned reproducibly in the sample chamber. For the long-wavelength bands, no corrections were necessary for absorption of either component, but such corrections became appreciable in the lower wavelength region, especially for II–TCNE (Table I).

Solid II–(TCNE)₂ was isolated by slow evaporation of an equi-

Table II. Treatment of the Data Obtained for TCNE Complexes of Compounds I, II, and III by the Methods of Benesi–Hildebrand and of Scott

Donor	λ_{max}, mμ	E_{EDA}, 10⁻³ cm⁻¹	Benesi–Hildebrand			Scott			Av K
			K	ϵ	SD[a]	K	ϵ	SD[a]	
I	671 ± 2	14.9	8.3	1100	2.8	8.9	1100	1.4	
	459[b]	21.8	7.5	860	2.3	8.0	820	1.2	8.2 ± 0.4
II	663 ± 1	15.1	2.3	1900	3.7	3.3	1400	1.1	
	439[b]	22.8							2.8 ± 0.5
III[c]	664 ± 1	15.1	6.9	730	2.3	5.8	850	1.7	
	446[b]	22.4	7.0	590	2.2	6.4	650	1.1	6.5 ± 0.4

[a] Standard deviation in y, expressed in per cent. For Benesi–Hildebrand $y \equiv$ ([donor]/absorbance)l; for Scott, $y \equiv$ ([TCNE][donor]/absorbance)l. [b] See Table I. [c] Reported[10] to absorb at 440 and 655 mμ in CH₂Cl₂.

and also no twisting of one ring relative to the other. Dziewonski has reported significant differences for the picrates of I and II,[9] and a solid 1:1 complex of TCNE with III (III–TCNE) has been isolated.[10] The complex of II promises to be a nearly ideal compound, since differences in strain and bond angles between I and II are expected to be very small if not negligible.

I   II   III
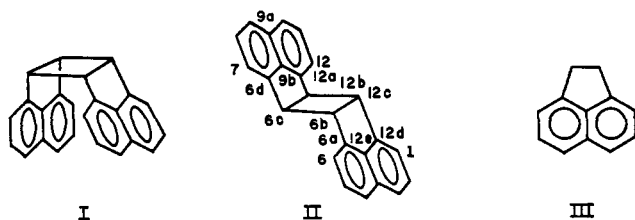
Experimental Section

Compound II[11] was recrystallized four times from benzene, mp 305.5–306.5° (uncor) (lit.[9] 306–307°). Compound I was prepared by 60-hr irradiation of a cyclohexane solution of acenaphthylene with a Hanovia 450-W medium-pressure Hg lamp with a Pyrex filter, while the solution was continuously purged with oxygen saturated with solvent.[12] After removal of the solvent, the monomer was allowed to sublime under vacuum. The residue was treated with hot ethanol and filtered, and the solution was cooled to afford I, mp 224–228°. Recrystallization from benzene was repeated six times until the melting point stayed constant at 228.5–231.5° (uncor) (lit.[9] 232–234°). Prolonged heating at 200° results in partial reversion to monomer. Tetracyanoethylene (EK) was sublimed under vacuum, recrystallized twice from chlorobenzene, and sublimed just before use. Chloroform (Baker Analyzed, containing about 1% ethanol) was used without further purification; all measurements were made with the same batch. Acenaphthene (EK) was sublimed under vacuum, recrystallized three times from ethanol, then kept under vacuum for several hours to remove any residual ethanol.

Solutions were prepared by mixing a known amount of stock solution of the donor with a weighed amount of TCNE in a volu-

molar CHCl₃ solution of the two components. *Anal.*[13] Calcd for TCNE:II (2:1): N, 19.99. Found: N, 20.86. The complex I–TCNE could not be isolated in a pure state because of coprecipitation of the uncomplexed components. However, a Nujol mull of the impure green solid showed broad absorption maxima centered at 420 and 620 mμ, in contrast to the uniform absorption of the dark purple II–(TCNE)₂.

Hückel and ω calculations were performed at The Ohio State University Computer Center, using a program written by G. Pettit and D. Lazdins, as modified by D. Fleckner for use with heteroatoms. Least-squares treatments of data were performed with an Olivetti 101 Programma desk computer.[14]

Results

Chloroform solutions of TCNE with I, II, or III are green. The absorbance data were treated using both the Benesi–Hildebrand[15] and Scott[16] equations to yield values of K and ϵ for the complexes, as shown in Table II. The extensive corrections required for the short-wavelength band of II–TCNE result in negative values of K and ϵ for both plots. The differences in the values of K at one wavelength calculated by the two methods are comparable to the differences between that calculated by one method for the two bands.

As shown in Table I, the energy of the short-wavelength bands of both II–TCNE and III–TCNE involves considerable uncertainty because of the absorption of the components. Clearly, however, both complexes absorb at shorter wavelength in both regions of the spectrum than does I–TCNE.

Since TCNE and II form a 2:1 solid complex, it may seem surprising that good linear plots were obtained in the treatments of the data for the long-wavelength band, assuming 1:1 stoichiometry. However, at the concentrations employed, only 2–6% of the total complex would have 2:1 stoichiometry, even if formation of this complex from the 1:1 complex were as

(9) K. Dziewonski and C. Paschalski, *Chem. Ber.*, 46, 1986 (1913).

(10) H. Kuroda, M. Kobayashi, M. Kinoshita, and S. Takemoto, *J. Chem. Phys.*, 36, 457 (1962).

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(13) Analysis was performed by Midwest Microlab, Inc., Indianapolis, Ind.

(14) We are indebted to Professor D. L. Leussing for the use of this computer.

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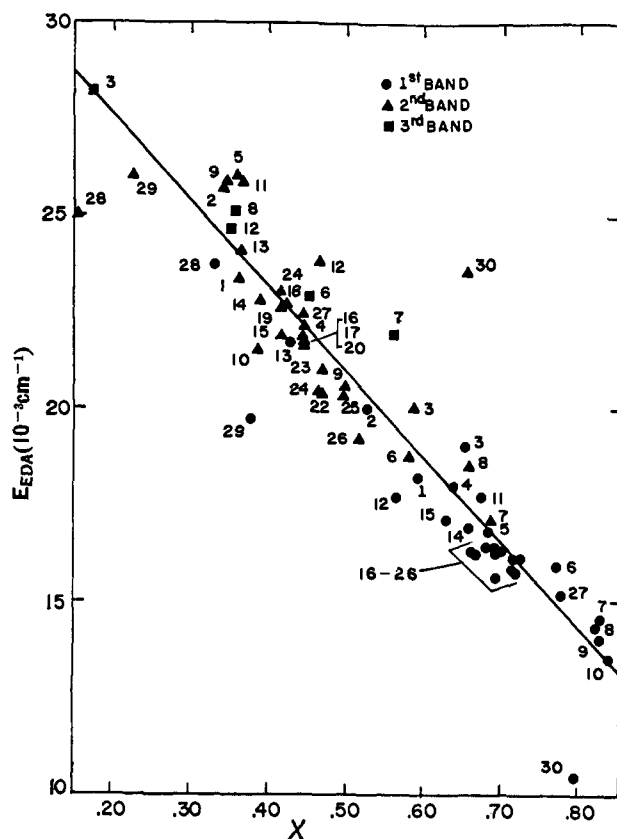
(16) R. L. Scott, *Rec. Trav. Chim.*, 75, 787 (1956).

Figure 1. Relationship between E_{EDA} and χ using the ω technique. Data are taken from Table III.

favorable as is formation of the 1:1 complex itself. This problem has been treated in detail.[17]

Comparison of K values for II-TCNE (K_{II}) and III-TCNE (K_{III}) shows that whereas the two donors differ only slightly with respect to E_{EDA}, there is a destabilizing factor decreasing K_{II} below the expected value which is equal to twice K_{III}. If complexation involves the positioning of TCNE so that its C-C axis is parallel to the 9a-9b bond,[18] then the presence of the cyclobutane ring in II would prevent formation of the complex in two of its four a priori possible configurations (on either side of each ring), reducing K_{II} to the same as K_{III}. Further reduction is probably due to strain in II caused by the cyclobutane ring, reflected in the slight hypsochromic shift observed for the short-wavelength band of II-TCNE relative to III-TCNE.

Discussion

Two charge-transfer bands have been reported for the TCNE-naphthalene complex, near 18,000 and 23,400 cm^{-1}.[19] Table II shows that III-TCNE exhibits a decrease in transition energy of about 3000 and 1000 cm^{-1}, respectively, compared to naphthalene-TCNE. The larger effect of 1,8 substitution in naphthalene derivatives on the lower energy band rather than the higher energy one is consistent with the reports of Lepley, who was able to explain this effect in methylnaphthalenes using perturbation theory.[18,20]

Transannular interaction in I is expected to involve mainly positions 6a-6d and 12a-12d, with about one-third of this amount of interaction in the three pairs of adjacent carbons (6-7, 9b-12e, and 12a-12d) because of the bending of the two naphthalene rings away from each other (vide infra). Thus, one might expect the same trend in the differences between I-TCNE and II-TCNE; namely, a larger effect on the lower energy band than at higher energy. The opposite is in fact observed.

A suitable theoretical model must be able to account for this discrepancy while providing a satisfactory picture of the complex with and without TI. An additional difficulty is that one is dealing with an alkyl-substituted aromatic system, thereby necessitating consideration of the substituents.

We have selected the ω technique[21] as the procedure of choice, since it has been shown to be quite successful in correlating ionization potentials of alkyl-substituted hydrocarbons.[22] Further, it is operationally convenient, requiring nothing more than a simple Hückel calculation with a variable coulomb integral, α. The parameters used are those recommended by Streitwieser[22] ($\omega = 1.40$, $h_x = 3.0$, $k_{c-x} = 0.7$, with x contributing two electrons to the π system) with the additional assignment of $k_{x-x} = 0.7$, where x is any alkyl group. Unless specified otherwise, only one iteration was used, since this has been shown to be sufficient for most purposes.[22]

The validity of this method for multiple transitions in EDA complexes is shown in Table III and Figure 1, in which χ is defined[21] as the difference in π-electron energy between positive ion (with the appropriate orbital half-filled) and the hydrocarbon, after one ω cycle for each. In principle, values of χ for the second and third absorption bands should be obtained by adjustment of α using charge densities (obtained from the Hückel calculation) calculated with the appropriate orbital (second or third highest occupied) half-filled. In practice, it is much simpler to transfer an electron from the appropriate orbital to the HOMO after the ω iteration has been performed using a half-filled HOMO. This approach gives a correlation which is at least as good as the former one and thus was used exclusively.

Clearly, not only does the lowest energy EDA band correlate with χ but also the second and third bands for all compounds except heteroatom molecules. Such a correlation has been reported recently for alternant hydrocarbons by Lepley and Thompson using other semiempirical approaches.[6] The fit of the ω technique with the compounds reported in that work is comparable to that obtained by those workers with the Pariser-Parr-Pople method, PPP1.[6] For the heteroatom molecules 29 and 30, it is not possible to fit both points of any compound on the best line by adjustment of α and β for the heteroatoms. These transitions apparently involve irregularities such as the implication of the n electrons of the heteroatom.[23] The suitability of this technique for the complexes of I and II is shown in Table IV, in which both unsubstituted and alkyl-substituted hydrocarbons are seen to

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(21) A. Streitwieser, Jr., and P. M. Nair, Tetrahedron, 5, 149 (1959).
(22) A. Streitwieser, Jr., J. Am. Chem. Soc., 82, 4123 (1960).
(23) E. M. Voigt, ibid., 86, 3611 (1964).

Table III. Charge-Transfer Excitation Energies and Values of χ for Compounds Reported to Have More than One Charge-Transfer Band with TCNE

No.	Compound	Band	E_{EDA}, 10^{-3} cm^{-1}	Ref	χ
	Unsubstituted Hydrocarbons				
1	Naphthalene	1	18.2	5b	0.592
		2	23.4		0.359
2	Biphenyl	1	20.0	5b	0.525
		2	25.7		0.341
3	Phenanthrene	1	19.0	5b	0.653
		2	20		0.586
		3	28.2		0.173
4	Triphenylene	1	18.0	5b	0.640
		2	22.1		0.445
5	Stilbene	1	16.8	5b	0.683
		2	26.0		0.357
6	Chrysene	1	15.9	5b	0.771
		2	18.8		0.580
		3	22.9		0.451
7	1,2,5,6-Dibenzanthracene	1	14.5	5b	0.826
		2	17.1		0.687
		3	21.9		0.560
8	1,2-Benzanthracene	1	14.3	5b	0.821
		2	18.5		0.658
		3	25.1		0.354
9	Pyrene	1	14.0	5b	0.826
		2	20.5		0.496
		3	25.8		0.344
10	Anthracene	1	13.5	5b	0.839
		2	21.5		0.385
11	p-Terphenyl	1	17.7	5g	0.675
		2	25.9		0.364
	Alkyl-Substituted Hydrocarbons				
12	Fluorene	1	17.7	5b	0.565
		2	23.8		0.466
		3	24.7		0.351
13	p-Xylene	1	21.7	2	0.425
		2	24.1		0.363
14	1-Methylnaphthalene	1	16.9	20	0.658
		2	22.8	18	0.389
15	2-Methylnaphthalene	1	17.1	20	0.629
		2	21.9	18	0.415
16	1,2-Dimethylnaphthalene	1	16.3	20	0.700
		2	21.8	18	0.442
17	1,3-Dimethylnaphthalene	1	16.4	20	0.691
		2	21.7	18	0.443
18	1,4-Dimethylnaphthalene	1	16.1	20	0.725
		2	22.7	18	0.421
19	1,5-Dimethylnaphthalene	1	16.1	20	0.716
		2	22.6	18	0.415
20	1,6-Dimethylnaphthalene	1	16.3	20	0.693
		2	21.6	18	0.443
21	1,8-Dimethylnaphthalene	1	15.8	20	0.714
		2	23.0	18	0.414
22	2,3-Dimethylnaphthalene	1	16.4	20	0.658
		2	20.4	18	0.470
23	2,6-Dimethylnaphthalene	1	16.2	20	0.668
		2	21.0	18	0.466
24	2,7-Dimethylnaphthalene	1	16.3	20	0.661
		2	20.4	18	0.466
25	2,3,5-Trimethylnaphthalene	1	15.7	20	0.718
		2	20.3	18	0.496
26	2,3,6-Trimethylnaphthalene	1	15.6	20	0.693
		2	19.2	18	0.517
27	Acenaphthene	1	15.1	This work	0.777
		2	22.4		0.443
	Heteroatom Molecules				
28	Pyridine	1	23.7	2	0.330
		2	25.0		0.151
29	Anisole	1	19.7	2	0.376
		2	26.0		0.224
30	Tetramethyl-p-phenylene-diamine	1	10.4	a	0.795
		2	23.5		0.655

[a] W. Liptay, G. Briegleb, and K. Schindler, Z. Elektrochem., **66**, 331 (1962).

fit the same least-squares line, within the limits of error, for the equation: E_{EDA} (10^{-3} cm^{-1}) $= m\chi + b$. Kuroda, et al., have observed a relationship between E_{EDA} and ionization potential for a series of hydrocarbon-TCNE complexes.[10] Combination of this with the correlation of ionization potential and χ reported by Streitwieser and Nair[21] affords a relationship between E_{EDA} and χ which is included in Table IV. Lack of correspondence between this and the observed relationship is at least partly due to lack of agreement between the above sets of authors as to appropriate values of the ionization potentials; in some cases they vary by as much as 0.8 eV from each other.

Table IV. Slope and Intercept for the Equation: $E_{EDA}(10^{-3}$ cm$^{-1})= m\chi + b$ for the Compounds Included in Table III and Figure 1

Class of hydrocarbon	m	b	Std dev (% of E)
Unsubstituted	−22.2	32.5	4.6
Alkyl substituted	−22.7	31.9	3.6
Both	−22.3	32.1	4.7
Literature[a]	−14.8	30.1	

[a] References 10 and 21.

Application of this technique to TI in I–TCNE requires assignment of overlap integrals between rings. From the known crystal structure of III[24] and a 1.54-Å $C_{6b}-C_{6c}$ bond distance, and Mulliken's tables,[25] assuming proportionality of β with overlap, the following interactions were included.

$$\beta_{6a-6d} = \beta_{12a-12d} = 0.34$$

$$\beta_{1-12} = \beta_{9b-12e} = \beta_{6-7} = 0.13$$

Transannular interaction of the other aromatic atoms was calculated to be negligible. Since II–TCNE and III–TCNE have almost identical spectra and since II–TCNE is being used as the standard compound, interaction between $C_{6b}-C_{6c}$ and between $C_{12b}-C_{12c}$ was neglected.

Calculation using the above parameters yields two values of χ corresponding to the two EDA bands, 0.786 and 0.447. The complex of II is used to provide an example of the noninteracting system, the total π-electron energy of its cations being taken as the sum of that of a neutral acenaphthene molecule (26.023β) and either of those of the two acenaphthene cations involved (26.800β and 26.466β) after one ω cycle. The π-electron energy of the hydrocarbon is taken to be twice that of acenaphthene, 52.046β. Thus, χ_1 and χ_2 are the same as for acenaphthene, 0.777 and 0.443. Thus, this result predicts a larger effect on the lower energy band than on the higher energy one ($\Delta\chi = 0.009$ for the first band, 0.004 for the second). Clearly, such an approach is unsatisfactory.

The presence of the acceptor nearer to one ring than to the other undoubtedly results in an unsymmetrical positive donor ion in the state in which charge transfer is complete. The effect of TI, then, is to allow partial charge dispersal into the second ring, and may be considered as a perturbation of the initial "localized"

(24) H. W. W. Ehrlich, Acta Cryst., 10, 699 (1957).
(25) R. S. Mulliken, C. A. Reike, D. Orloff, and H. Orloff, J. Chem. Phys., 17, 1248 (1949).

Table V. Values of χ for I-TCNE Calculated Using the ω Technique

	χ_1	χ_2	Charge in one ring, %
Initial	0.777	0.443	100
After one iteration	0.779	0.469	78
After two iterations	2.376	2.061	57

ion. This situation can be simply analogized within the ω-technique framework by considering first a localized donor ion, then examining the effect of successive iterations. Hückel calculations of neutral III and its cation provide values of the charge density on all 24 atoms, which values are then used to vary α in the usual way[21] for the first ω iteration.

Results of such a calculation are shown in Table V for the first and second iterations. Clearly, extension even only this far leads to an unacceptable description. After only one iteration, however, differences in χ caused by TI are only 0.002β and 0.026β for the first and second EDA bands, respectively. From Table IV, this corresponds to an energy difference of 45 and 570 cm^{-1}. The observed difference, 200 and 1000 cm^{-1}, is somewhat higher. An increase in the overlap integrals between rings improves the fit. In fact, calculation of β between rings by application of Simonetta and Winstein's relationship between β and overlap[26] yields a calculated energy difference of 330 and 890 cm^{-1} for the two bands. This improvement is of questionable significance considering the crudity of the method, especially the rather arbitrary but convenient designation of one cycle of iteration as a measure of perturbation due to TI. Nevertheless, consideration of the unsymmetrical ion as described above does effect a reversal in the relative magnitudes of the energy differences from those calculated ignoring this feature.

The model described here clearly requires further application to demonstrate its generality or lack thereof. Its main advantage over other semiempirical SCF methods lies in its operational simplicity, which has been shown not to appreciably impair its relative ability to fit data such as are included in Figure 1.

(26) M. Simonetta and S. Winstein, *J. Am. Chem. Soc.*, 76, 18 (1954).

Perdeuteriostilbene. The Triplet and Singlet Paths for Stilbene Photoisomerization[1]

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Abstract: A comparative study of the direct and sensitized *trans* → *cis* photoisomerization of perhydro- and perdeuteriostilbene solutions in benzene has been carried out. Perdeuteration does not affect *cis–trans* decay ratios of stilbene S^1 and T^1 states. The effect of azulene on stationary states of the benzophenone-sensitized photoisomerization has been determined, and it is inferred that upon perdeuteration the lifetime of stilbene T^1 states increases 30% at 25 and 60°. These observations are accounted for by a modified triplet mechanism for sensitized isomerization and a new singlet mechanism for direct photoisomerization. The two mechanisms involve radiationless decay from common twisted T^1 and S^1 electronic states, respectively. Loss of triplet excitation through interaction with *trans*-stilbene ground states is shown not to occur.

Theory predicts that deuteration should decrease the rate of T^1 → S^0 and S^1 → S^0 radiationless transitions.[2] The deuterium effect is attributed to inhibition of a kind of tunneling between the zero vibrational level of the electronically excited state and high vibrational levels of the ground state.[2] Spectroscopic studies of rigid perhydro and perdeuterio aromatic compounds provide abundant experimental support for the theory.[3] Perdeuteration leads to large increases in T^1 lifetimes of aromatic hydrocarbons and, as expected,[2] the effect diminishes as the energy separation between electronic states decreases.[3] Corresponding deuterium effects on S^1 lifetimes and fluorescence quantum yields are not generally found.[4–6] This is because S^1 → S^0 radiation-less transition in rigid aromatic hydrocarbons is not an important decay process even for the perhydro compounds.[5–7] No deuterium effect on S^1 → T intersystem crossing is expected because of small energy gaps between the zero vibrational level of S^1 and lower lying triplet states.

Information concerning radiationless decay paths of electronically excited intermediates is required for a detailed understanding of the mechanisms of photochemical reactions. In this work deuteration has been utilized in evaluating the nature of the excited states and the radiationless decay paths involved in the sensitized and direct *cis–trans* photoisomerization of the stilbenes.

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