

The Lowest Triplet State of Stilbene^{1a}

William G. Herkstroeter^{1b} and Donald S. McClure

Contribution from the James Franck Institute and Department of Chemistry,
University of Chicago, Chicago, Illinois 60637. Received February 27, 1968

Abstract: The lowest triplet state of stilbene has been observed by means of its absorption spectrum following flash excitation of stilbene in glassy solvents at liquid nitrogen and liquid argon temperatures. The triplet lifetime is a strong function of solvent viscosity and decreases rapidly as the solvent becomes more fluid. Evidence that the transient absorption is truly the triplet-triplet absorption is: (1) similar transient spectra are found in several stilbene derivatives and nonisomerizable model compounds including perdeuteriostilbene, 1,2-dihydro-3-phenyl-naphthalene, 4,4'-dichlorostilbene, and 5H-dibenzo[*a,d*]cycloheptene; (2) deuteration markedly increases the lifetime; (3) the observed spectrum has approximately the correct energy and *f* number according to Pariser-Parr-type calculations.

The lowest triplet state of stilbene is of considerable interest because of its role in the *cis-trans* isomerization of this molecule. Numerous attempts have been made to study this electronically excited state by either phosphorescence or triplet-triplet absorption, but without success.²⁻⁵

The origin of the first singlet-triplet transition in *trans*-stilbene lies at 2.2 eV (17,300 cm⁻¹), according to absorption spectra taken in ethyl iodide^{6a} and in oxygen under high pressure.^{6b} The corresponding transition in the *cis* isomer of stilbene appears without structure even in heavy-atom solvents, but the origin has been estimated to occur at 2.5 eV (20,000 cm⁻¹).^{7,8} The lowest triplet state is believed to be a reactive intermediate in the photochemical isomerization of stilbene upon both direct irradiation and triplet energy transfer from appropriate sensitizers.^{2b,3,6a,7,9-17} Although spectroscopic transitions involve no change in geometry, isomerization leads to a 180° twist about the central bond. This raises the question of the shape of the potential surface of the lowest stilbene triplet state in the twisting coordinate. A barrier to twisting 90° from

the *trans* triplet to a geometry intermediate between *cis* and *trans* is predicted experimentally by the work of Hammond and Saltiel¹² as well as Stegemeyer¹⁰ and also theoretically from the calculations of Ting,⁴ although this barrier is probably small. The intersection of the potential surfaces for triplet and ground states upon twisting 90° may well be responsible for highly facile, radiationless return to the isomeric ground states, a likely path for the isomerization.^{2a,4,12,18} Aside from the inability to detect phosphorescence or triplet-triplet absorption, there is, in fact, experimental evidence that the lifetime of the stilbene triplet in solution at room temperature is on the order of 10⁻⁷ sec or even less.^{12,19,20}

The quantum yield for fluorescence of *trans*-stilbene varies inversely with temperature.^{4,6a,11,13,14} Fischer and coworkers^{11,13,14} have further demonstrated the inverse interdependence of the quantum yields of fluorescence and isomerization from *trans*- to *cis*-stilbene. They have evidence that the process of intersystem crossing in *trans*-stilbene from the first excited singlet to the triplet *via* intermediate singlet and triplet states is temperature dependent with an activation energy of about 1.2 kcal/mol. Such a barrier is also predicted by the calculations of Ting.⁴

Fischer^{13,14} also has observed that the quantum yield of isomerization from *trans*- to *cis*-stilbene is reduced at higher viscosities, but that the reverse process is largely independent of viscosity. He proposed that this is consistent with the fact that *cis*-stilbene has a larger van der Waals volume than the *trans* isomer. He further hypothesizes that the viscosity dependent step is either the conversion of the lowest energy *trans* triplet to the twisted triplet or the deactivation of the twisted triplet to ground-state *cis*-stilbene.

Curiosity about the various processes involved in the triplet-state population and depopulation and their relationship to photoisomerization in stilbene helped to prompt this investigation. It would appear that the lifetime of the lowest triplet of *trans*-stilbene depends upon its resistance to rotation about the central double bond and the resistance to radiationless transitions to the ground state. For this reason, we decided to look

(1) (a) Supported by Public Health Service Research Grant No. RO/GM 13519, NIGMS, RGB. (b) National Science Foundation Postdoctoral Fellow, 1965-1966. Address correspondence to this author: Research Laboratories, Eastman Kodak Co., Rochester, N. Y. 14650.

(2) (a) G. Porter, unpublished results as reported in (b) D. Schulte-Frohlinde, H. Blume, and H. Güsten, *J. Phys. Chem.*, **66**, 2486 (1962).

(3) W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966).

(4) C. H. Ting, Ph.D. Thesis, University of Chicago, 1965.

(5) Just prior to submission of this paper, we read the preliminary results of G. Heinrich, H. Blume, and D. Schulte-Frohlinde, *Tetrahedron Letters*, 4693 (1967), who tentatively conclude that the transient absorption observed by them is the triplet-triplet absorption of *trans*-stilbene. In the light of our work, we feel that their interpretation is correct.

(6) (a) R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962); (b) D. F. Evans, *J. Chem. Soc.*, 1351 (1957).

(7) E. Lippert, *Z. Physik. Chem.* (Frankfurt), **42**, 125 (1964).

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(11) S. Malkin and E. Fischer, *ibid.*, **68**, 1153 (1964).

(12) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

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(15) Saltiel^{16,17} recently presented evidence that the direct photoisomerization of stilbene proceeds through the first excited singlet state rather than the triplet.

(16) J. Saltiel, E. D. Megarity, and K. G. Kneipp, *ibid.*, **88**, 2336 (1966).

(17) J. Saltiel, *ibid.*, **89**, 1037 (1967).

(18) P. Borrell and H. H. Greenwood, *Proc. Roy. Soc. (London)*, **A298**, 453 (1967).

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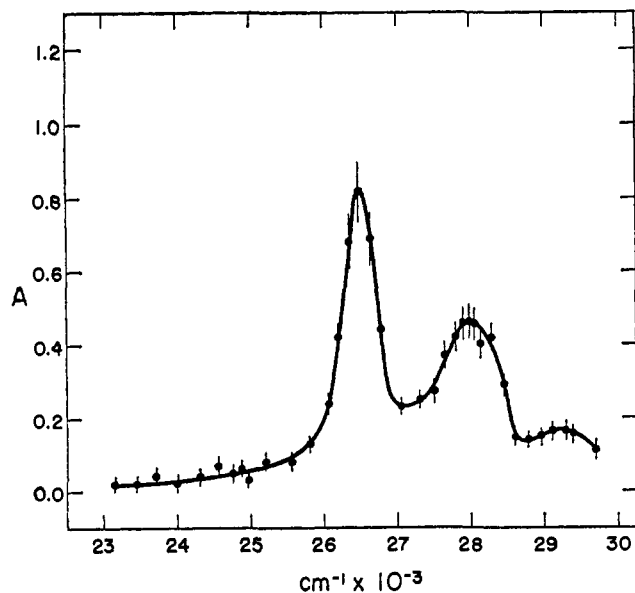


Figure 1. The triplet-triplet absorption spectrum of *trans*-stilbene. The spectrum was recorded in units of absorbance following flash excitation of 4.3×10^{-6} M *trans*-stilbene in glass 1 at 77°K in a cell of 8-cm optical length.

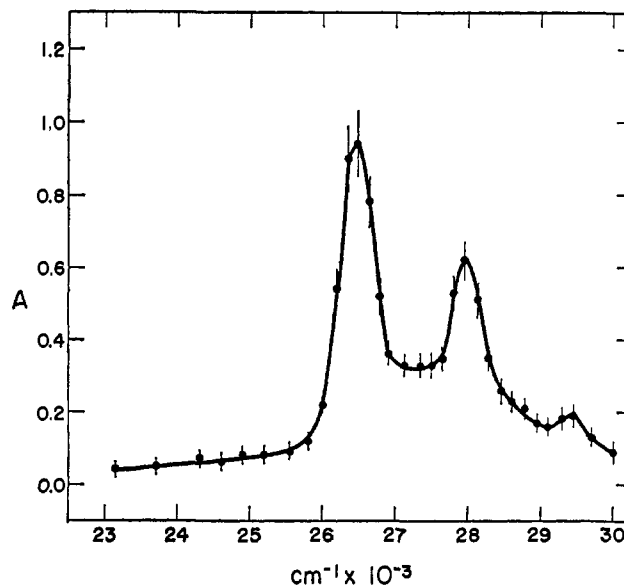


Figure 2. The triplet-triplet absorption spectrum of *trans*-stilbene- d_{12} . The spectrum was recorded in units of absorbance following flash excitation of 7.2×10^{-6} M *trans*-stilbene- d_{12} in glass 1 at 77°K in a cell of 8-cm optical length.

for metastability of the stilbene triplet under conditions where we believed such rotation would be restricted.

Results and Discussion

If the stilbene triplet lifetime is indeed short, the radiative lifetime would well be expected to be orders of magnitude longer than the nonradiative lifetime, which could readily explain the inability to detect phosphorescence from stilbene. Detection of the triplet by viewing its absorption, however, requires only that the triplet lifetime be increased to the point where it can be resolved by flash-excitation methods. Since previous attempts at viewing the triplet-triplet absorption of stilbene had all been with fluid solvents, we attempted the same objective in rigid host media.

In the first experiment, carried out in conjunction with Ottolenghi,²¹ a transient species with an absorption maximum near $26,300 \text{ cm}^{-1}$ (3800 Å) was detected both in EPA²² and 3-methylpentane solutions of *trans*-stilbene at 77°K following flash excitation. The calculations of Ting⁴ predict a strong triplet-triplet absorption band in *trans*-stilbene at $29,500 \text{ cm}^{-1}$ (3400 Å) with no other strong band in the visible. It seemed likely that this band was, indeed, being observed.

In order to make possible a more positive identification of the transient observed, similar experiments were repeated in other rigid host media and the absorption spectrum itself was resolved as shown in Figure 1. This transient could not be detected at higher temperatures where the solvents became fluid. Nothing appeared in the absence of stilbene. Photochemical reaction between stilbene and solvent also seemed unlikely. In order to test for possible hydrogen abstraction from the alkane solvents, a glass made up of a mixture of *n*-pentane and 2,2-dimethylbutane containing no tertiary carbon atoms²³ was employed as solvent. No

(21) M. Ottolenghi, W. G. Herkstroeter, and D. S. McClure, unpublished results.

(22) EPA is a 5:5:2 mixture of diethyl ether, isopentane, and ethanol.

(23) K. Rosengren and S. Sunner, *Acta Chem. Scand.*, 16, 521 (1962).

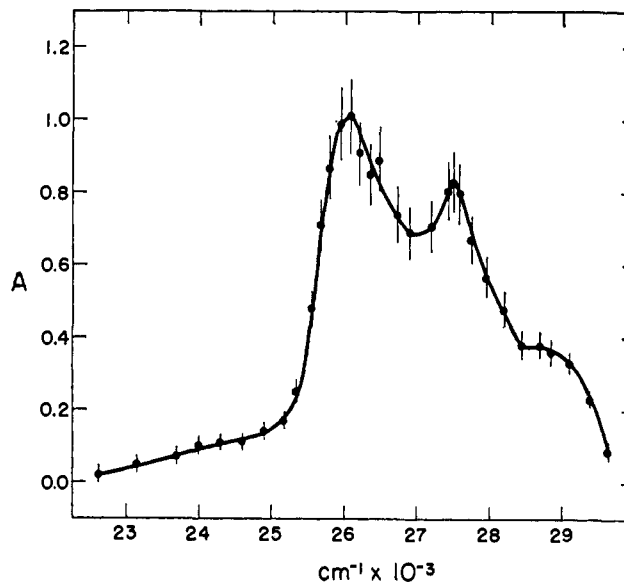


Figure 3. The triplet-triplet absorption spectrum of 1,2-dihydro-3-phenyl-naphthalene. The spectrum was recorded in units of absorbance following flash excitation of 5×10^{-6} M 1,2-dihydro-3-phenyl-naphthalene in glass 1 at 77°K in a cell of 8-cm optical length.

differences in the stilbene transient spectra were observed relative to those obtained with two other alkane solvent mixtures containing tertiary carbon atoms.

Similar transient spectra were obtained for molecules structurally closely related to *trans*-stilbene. The transient spectra with *trans*-stilbene and *trans*-stilbene- d_{12} , shown in Figures 1 and 2, respectively, have absorption peaks near $26,500$, $27,950$, and $29,400 \text{ cm}^{-1}$ (3780, 3580, and 3410 Å), which appears to represent a progression of a 1450-cm^{-1} vibration. This compares with 1635- and 1599-cm^{-1} vibrational progressions of the central double bond in the ground state and first excited singlet state, respectively.^{8a} The transient spectrum of 1,2-dihydro-3-phenyl-naphthalene (1) (Fig-

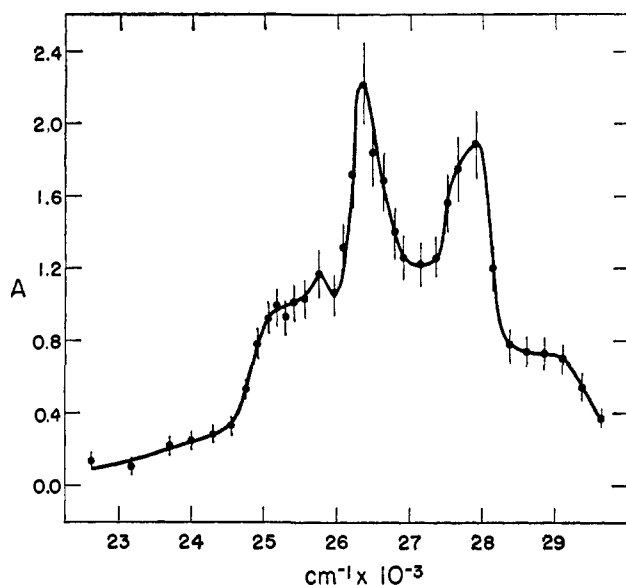
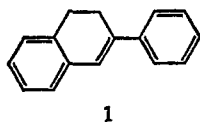


Figure 4. The triplet-triplet absorption spectrum of 4,4'-dichlorostilbene. The spectrum was recorded in units of absorbance following flash excitation of $6.2 \times 10^{-6} M$ 4,4'-dichlorostilbene in glass 1 at 77°K in a cell of 8-cm optical length.

ure 3) is similar to the first two, but red-shifted by approximately 400 cm^{-1} , while that of 4,4'-dichlorostilbene (Figure 4) is shifted by 150 cm^{-1} and has a vibrational progression of 1550 cm^{-1} .



The decay of transient absorption was first order in all cases, and the rate constants measured for the various species are listed in Table I. Strong evidence for

Table I. First-Order Rate Constants for Triplet-State Depopulation and Their Variation with Viscosity, Temperature, and Isotopic Substitution

	Temp, °K	k_1, sec^{-1}		
		Glass 1 ^a	Glass 2 ^a	Glass 3 ^a
<i>trans</i> -Stilbene	77	190	170	56
<i>trans</i> -Stilbene- <i>d</i> ₁₂	77	88	50	11
k_H/k_D	77	2.2	3.4	5.1
<i>trans</i> -Stilbene	87	$>10^4$ ^b	$>10^4$	200
<i>trans</i> -Stilbene- <i>d</i> ₁₂	87	$>10^4$	$>10^4$	40
k_H/k_D	87	5.0
1,2-Dihydro-3-phenyl-naphthalene	77	290	...	75
1,2-Dihydro-3-phenyl-naphthalene	87	$>10^4$...	190
1,2,5,6-Dibenzanthracene	77	...	0.76	...
1,2,5,6-Dibenzanthracene	87	...	0.85	...
4,4'-Dichlorostilbene	77	210
5H-Dibenzo[<i>a,d</i>]cycloheptene	77	140

^a See text and Table II. ^b Since no transient was observed, the rate constant must be greater than 10^4 sec^{-1} .

the identification of these transients as triplets is provided by the deuterium effect on the lifetime of the *trans*-

stilbene transient. The triplet lifetime enhancement upon substitution of deuterium for hydrogen is a confirmed fact in many hydrocarbons and is controlled by the influence of C-H and C-D vibrational modes on the magnitude of the overlap of the zero-point vibrational wave function of the triplet state and the isoenergetic, vibrational wave functions of the ground state.²⁴

The rate constants listed in Table I for the decay of the triplets of *trans*-stilbene, *trans*-stilbene-*d*₁₂, and 1,2-dihydro-3-phenyl-naphthalene are quite sensitive to the viscosity of the host medium. These rate constants were measured employing as solvents three different glass-forming hydrocarbon mixtures at both liquid nitrogen and liquid argon temperatures. In Table II are listed the compositions of the three glasses together with their viscosity values at 77 and 87°K, which were determined as follows. Rosengren²⁷ found that, over a range of low temperatures, the relative viscosities of the solvents are in the numerical order assigned in Table II

Table II. Glass-Forming Hydrocarbon Solvents^a and Their Estimated Viscosities

Glass no.	Composition	Estimated log viscosity, poise	
		77°K	87°K
1	6 parts isopentane and 1 part 3-methylpentane	6.8	5.0
2	3 parts <i>n</i> -pentane and 8 parts 2,2-dimethylbutane	7.3	5.5
3	3-Methylpentane	12.0	10.2

^a See ref 27.

and that, for each solvent, the temperature dependence of viscosity is nearly identical, with the viscosity decreasing by a factor of 3 for a 2.5°K rise in temperature. The viscosities of glasses 1 and 3 at 77°K can be assigned as 6.9×10^6 and 9.4×10^{11} poise, respectively.²⁸ The relationship $\log \eta = A + B/T$ (where η is the viscosity, A and B are constants, and B is the same for all glasses) can be applied in order to calculate the viscosities of glasses 1 and 3 at 87°K. From Rosengren's work,²⁷ glass 2 has the same viscosity at 86°K as glass 1 at 83°K, and this relationship can be extrapolated in order to estimate the viscosity of glass 2 at 77 and 87°K. The triplet lifetimes of *trans*-stilbene, *trans*-stilbene-*d*₁₂, and 1,2-dihydro-3-phenyl-naphthalene are, with one exception, in the same order as the viscosities of the host media. This correlation confirms the dependence of triplet lifetime upon viscosity of the solvent.

Also included in Table I are rate constants for the triplet-state depopulation of 1,2,5,6-dibenzanthracene measured in glass 2 at both 77 and 87°K. Since these rate constants are, first of all, smaller than those measured for stilbene and its derivatives and also independent within experimental error of the change in viscosity and temperature, one can discount the possibility that the lifetime differences in stilbene are controlled by the diffusion of adventitious quenchers

(24) See ref 25 and 26 and other references therein.

(25) J. D. Laposa, E. C. Lim, and R. E. Kellogg, *J. Chem. Phys.*, **42**, 3025 (1965).

(26) S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, **66**, 199 (1966).

(27) K. Rosengren, *Acta Chem. Scand.*, **16**, 1421 (1962).

(28) J. R. Lombardi, J. Raymonda, and A. C. Albrecht, *J. Chem. Phys.*, **40**, 1148 (1964).

present in the hydrocarbon solvents. In solvents as viscous or more viscous than isopentane, Hilpern, Porter, and Stief²⁹ also observed that impurity quenching is not noticeable below 90°K.

The extinction coefficients of the phototransient absorption maxima, determined by the method of McClure,³⁰ are listed in Table III. Since, for unknown

Table III. Molar Extinction Coefficients of Strongest Triplet-Triplet Bands

Substance	Wavelength, nm	ϵ
<i>trans</i> -Stilbene	378	3.4×10^4
<i>trans</i> -Stilbene- <i>d</i> ₁₂	378	2.8×10^4
1,2-Dihydro-3-phenylnaphthalene	384	4.0×10^4
4,4'-Dichlorostilbene	359	2.8×10^5
5H-Dibenzo[<i>a,d</i>]cycloheptene	426	2.0×10^4
Naphthalene	413	1.4×10^4

reasons, this method has given incorrect results in the past,³¹ the extinction coefficient of the naphthalene triplet-triplet band at 24,200 cm⁻¹ was also determined for reference purposes. The value obtained here of 1.4×10^4 is within our estimated experimental error ($\pm 50\%$) of the values reported by Craig and Ross³¹ and Porter and Windsor,³² who utilized other experimental procedures. The integrated absorption strength of the triplet-triplet band of *trans*-stilbene yields an *f* value of 0.51 as compared with the calculated oscillator strength of 0.93.⁴

The cisoid isomer of stilbene was converted to the transoid isomer in glass 2 at liquid nitrogen temperatures so rapidly that no transient absorption could be attributed to the starting material. The observed intensity of transient absorption increased with repeated flashing and soon reached a limit. The absorption spectrum and rate of decay of the transient species were identical within experimental error with those obtained directly upon flashing the transoid isomer. The isomerization at liquid nitrogen temperatures was further confirmed by spectrophotometric analysis of the solution following the flash experiments. Fischer and coworkers^{11,13,14} have shown that the quantum yield of *trans*-*cis* isomerization at 90°K in a hydrocarbon solvent is much less than for the reverse process, so that the photostationary state largely favors *trans*-stilbene. If the data of these authors are extrapolated to liquid nitrogen temperatures, the photostationary state would be expected to be even richer in *trans*-stilbene. This fact has been verified by independent studies in these laboratories.⁴ There also was no evidence for the formation of 4a,4b-dihydrophenanthrene. This can readily be explained by Fischer's observation that at low temperatures the quantum yield of formation of this substance is much less than that of the reverse photochemical conversion to *cis*-stilbene.^{33,34}

No transient absorption whatsoever could be detected in similar experiments with 1,2-diphenylcyclo-

(29) J. W. Hilpern, G. Porter, and L. J. Stief, *Proc. Roy. Soc. (London)*, **A277**, 437 (1964).

(30) D. S. McClure, *J. Chem. Phys.*, **19**, 670 (1951).

(31) D. P. Craig and I. G. Ross, *J. Chem. Soc.*, 1589 (1954).

(32) G. Porter and M. W. Windsor, *Proc. Roy. Soc. (London)*, **A245**, 238 (1958).

(33) E. Fischer, *Fortschr. Chem. Forsch.*, **7**, 605 (1967).

(34) K. A. Muszkat and E. Fischer, *J. Chem. Soc., B*, 662 (1967).

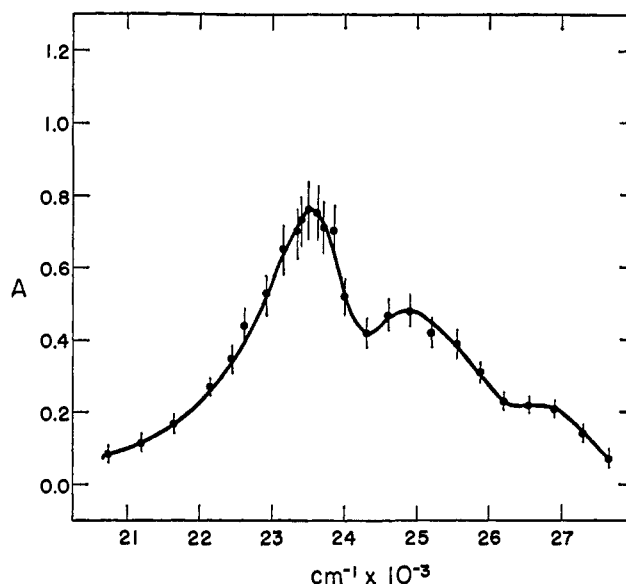
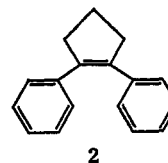
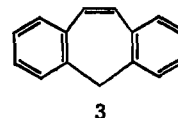


Figure 5. The triplet-triplet absorption spectrum of 5H-dibenzo[*a,d*]cycloheptene. The spectrum was recorded in units of absorbance following flash excitation of $6.8 \times 10^{-6} M$ 5H-dibenzo[*a,d*]cycloheptene in glass 1 at 77°K in a cell of 8-cm optical length.

pentene (2) selected as a nonisomerizable model for



cis-stilbene. Another model compound, 5H-dibenzo[*a,d*]cycloheptene (3), also incapable of isomerization



but also less flexible than 1,2-diphenylcyclopentene, did produce a phototransient at 77°K, the spectrum of which is shown in Figure 5. The absorption peaks are close to 23,500 and 24,900 cm⁻¹ (4260 and 4020 Å), a 1400-cm⁻¹ spacing, whereas the calculated triplet-triplet absorption maximum of *cis*-stilbene is near 25,500 cm⁻¹.⁴ Measured extinction coefficients are close in magnitude to those of *trans*-stilbene. These observations are consistent with the assignment of this transient to a triplet, since triplet-triplet absorption in the *cis*-stilbene model would be expected to be close to that computed for *cis*-stilbene.

trans-Stilbene forms crystalline solutions with bibenzyl which remain solid up to 50°. Crystalline solutions of 0.5% *trans*-stilbene in bibenzyl were subjected to flash excitation at room temperature, and a transient absorption spectrum, also believed to be that of the triplet of *trans*-stilbene, was observed as illustrated in Figure 6. At 250°K the decay is exponential over two mean lifetimes with a first-order rate constant of 60 sec⁻¹. This is approximately the same as the lifetime of the *trans*-stilbene triplet in glass 3 at 77°K. At higher temperatures the decay becomes increasingly

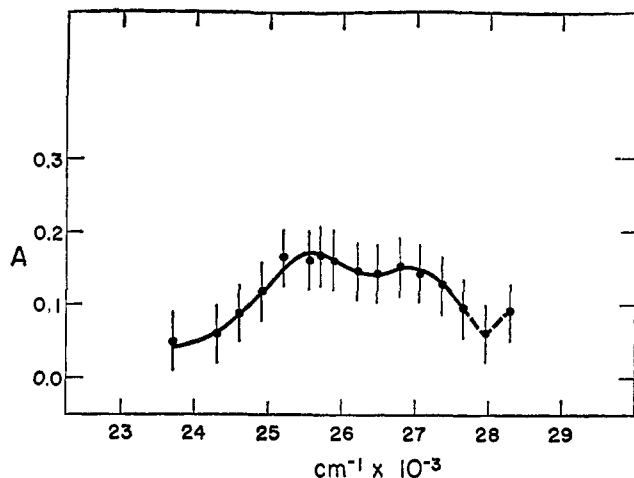


Figure 6. The triplet-triplet absorption spectrum of *trans*-stilbene. The spectrum was recorded in units of absorbance following flash excitation at 22° of 0.5% *trans*-stilbene in a bibenzyl crystal of 6.5-cm optical length.

nonexponential, as the decay rate increases with time more rapidly than is consistent with a first-order decay.

In order to make certain that the transients observed were formed from the parent compounds, the individual solutions were monitored over the range of absorption from the ground state. Following flash excitation in all cases, the ground states were partially depopulated and the rates of the ground-state repopulation matched those of the decay of the individual transients.

The transients assigned as triplets showed maximum absorption intensity initially, but upon repeated flash excitation there was a gradual decrease. This phenomenon has been reported previously for triplets of other aromatic hydrocarbons³¹ and was also confirmed here in experiments with naphthalene, phenanthrene, and 1,2,5,6-dibenzanthracene. In solutions of aromatic compounds in rigid, aliphatic hydrocarbon glasses, the ionization of the solute and sensitized dissociation of the solvent to give free radicals and hydrogen atoms are known to occur as a result of biphotonic processes involving absorption by metastable, excited, triplet states.^{35,36} It is to be expected that such reactions be enhanced by repeated pulsing with high-intensity, flash lamps. Our solutions were analyzed spectrophotometrically before and after the flash excitation experiments, and it was found that some reaction had occurred. The photoproducts had structureless absorption in the region below 3000 Å. Of all compounds examined here, *trans*-stilbene-*d*₁₂ and *trans*-stilbene showed the least such reaction. Less than 10% of a $1.7 \times 10^{-5}M$ solution of *trans*-stilbene-*d*₁₂ in glass 2 was consumed after several hundred flashes at both liquid nitrogen and liquid argon temperatures.

Transients tentatively attributed to photochemical reaction products were observed in experiments with *trans*-stilbene, *trans*-stilbene-*d*₁₂, and 1,2-dihydro-3-phenylnaphthalene. In addition to the triplets, phototransients with lifetimes of approximately 2 sec appeared, but only after repeated flash excitation of glassy solutions of the three parent compounds. The absorption

(35) S. Siegel and K. Eisenthal, *J. Chem. Phys.*, **42**, 2494 (1965).

(36) B. Brocklehurst, W. A. Gibbons, F. T. Lang, G. Porter, and M. I. Savadatti, *Trans. Faraday Soc.*, **62**, 1793 (1966).

maxima of all three of the longer lived intermediates were near 4200 Å and, although neither concentrations nor extinction coefficients were known, the absorbance was greatest in the 1,2-dihydro-3-phenylnaphthalene solution and least in the *trans*-stilbene-*d*₁₂ solution. Unlike the triplets, these longer-lived species were insensitive to changes in solvent viscosity and temperature.

The triplet lifetimes we have measured must be controlled almost entirely by nonradiative contributions, since the radiative lifetime of stilbene would hardly be expected to be less than 1 sec. The nonradiative process must lead through various vibrational degrees of freedom to the ground state. From our data, we can draw some conclusions as to the nature of this process.

The data of Table I show that the deuterium isotope effect on the rate constants for triplet-state depopulation is greater the more rigid the solvent. In interpreting this fact, it is reasonable to assume, first of all, that in a less viscous solvent the torsional motions of the molecule achieve larger displacements than in a more viscous solvent. Second, the torsional displacement into nonplanar configurations about the central double bond decreases the singlet-triplet separation, because the energy of the ground state increases with twisting more than that of the triplet state.⁴ In a twisted or partly twisted conformation, therefore, the effect of deuterium substitution is reduced, because the vibrational overlap of the two states involves smaller numbers of quanta and the importance of C-C vibrations relative to C-H vibrations becomes greater.

Experimental Section

Materials. The hydrocarbon solvents *n*-pentane, isopentane, 2,2-dimethylbutane, and 3-methylpentane were all Phillips, Pure Grade. They were extracted with concentrated sulfuric acid until the layer no longer became colored and were then neutralized, dried, and passed over a column made up of activated alumina and silica gel (Woelm) in separate layers. The criterion for purity of these solvents was the absorbance at short wavelengths. Those samples used showed only weak absorption in a 2-cm cell at 2200 Å.

Two different samples of *trans*-stilbene were used. The first (Matheson Coleman and Bell, Scintillation Grade) was recrystallized three times from ethanol. The second sample of *trans*-stilbene (James Hinton, Ph.D., zone refined), *trans*-stilbene-*d*₁₂ (Merck Sharpe and Dohme), *cis*-stilbene (Aldrich), and bibenzyl (J. Hinton, zone refined) were used as received. 1,2-Dihydro-3-phenylnaphthalene and 1,2-diphenylcyclopentene were obtained through the courtesy of Dr. F. B. Mallory. 4,4'-Dichlorostilbene was prepared by Dr. C. H. Ting from 4,4'-diaminostilbene by diazotization in hydrochloric acid followed by reaction with cuprous chloride. The product was recrystallized from a mixture of toluene and ethanol and sublimed under vacuum. 5H-Dibenzo[*a,a'*]cycloheptene was prepared from 5H-dibenzo[*a,a'*]cyclohepten-5-one by a Huang-Minlon variation of the Wolff-Kischner reduction³⁷ and purified by sublimation and three recrystallizations from methanol.

Procedure. The apparatus was similar to that used in earlier investigations.³⁰ A helically shaped, xenon flashlamp (Kemlite), capable of discharging 1000 J within 40 μsec, surrounded a cylindrically shaped, quartz dewar having plane windows on the bottom. The lower half of the dewar was transparent to the exciting light. The energy output of the flashlamp was variable between 360 and 1000 J by choice of voltage on a 5 μF, low-inductance, storage capacitor (Line Material Industries). Between the dewar and the flash lamp was positioned a concentric quartz filter container with an annulus of 2.5 mm. A filter solution composed of 240 g of

(37) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Longmans, Green, and Co., New York, N. Y., 1957, p 516.

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 45.0 g of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ per liter of water reduced the exciting light in the visible and near-infrared.³⁸ The dc monitoring source was either a 100-W tungsten filament lamp or a 150-W xenon arc lamp (Hanovia). Samples were contained in cylindrical quartz cells having plane windows on the ends and positioned vertically in the center of the dewar and were cooled with either liquid nitrogen or liquid argon. The dimensions of the cells were 8 cm optical length and 13 mm id. The cells were connected to bulbs where the solutions were contained during the degassing procedure. The collimated monitoring light passed through a shutter, the sample cell, and the bottom of the Dewar, reflected 90° from a plane mirror and then focused on the entrance slit of a Bausch and Lomb 250-mm grating monochromator. An RCA 1P28 photomultiplier tube, mounted on the exit slit of the monochromator, served as detector. The optics of the monitoring light beam had narrow aperture so as to reduce the quantity of stray light reaching the detector. Because of the low fractional output of the xenon arc lamp in the ultraviolet, it was necessary to include in the optical path a cell 50 mm in length containing the above $\text{NiSO}_4\text{-CoSO}_4$ filter solution in order to reduce stray light to a tolerable level when monitoring signals at wavelengths shorter than 3200 Å. The signal from the detector was dc coupled through a cathode-follower amplifier to a Tektronix wide-band oscilloscope where it was displayed and recorded photographically.

The oscilloscope transparencies were enlarged by projection and traced onto graph paper in order to facilitate more precise measurement of the transient phenomena. In recording a transient absorption spectrum, the amplitude of the absorbance was measured at a series of closely spaced wavelengths at a constant time interval following initiation of the flash. The lifetime of a transient species was measured by the recovery rate of the monitoring beam after the flash. Kinetic analysis was by the method of Linschitz and Sarkanen.³⁹

(38) M. Kasha, *J. Opt. Soc. Am.*, **38**, 929 (1948).

(39) H. Linschitz and K. Sarkanen, *J. Am. Chem. Soc.*, **80**, 4826 (1958).

The relative intensities of the excitation flash were monitored with a photoelectric detector as a function of discharge energy. Duplicate determinations were within 15% of each other. With the photochemical reaction of anthracene in carbon tetrachloride as actinometer,⁴⁰⁻⁴² the absolute flash intensities were also measured. Table IV lists the quanta per flash incident upon the sample cell within the absorption spectra of both anthracene and *trans*-stilbene.

Table IV. Flash Intensities

Pulse energy, J	Quanta/ml $\times 10^{-16}$ in reaction cell	
	Within anthracene spectrum	Within <i>trans</i> - stilbene spectrum
360	9.0	6
490	11	7
640	14	9

The crystalline solution of *trans*-stilbene in bibenzyl was prepared by doping a zone-refined sample of bibenzyl with a small quantity of stilbene. The two substances were pulverized, mixed together in a tube, and then melted and degassed under a partial atmosphere of helium. A single crystal, 65 mm in length and 6 mm in diameter, was grown by slowly lowering the melt in the tube into a cooled bath. The crystal was contained in a Pyrex tube with open ends during the flash experiments. The concentration of *trans*-stilbene in the crystal was later determined spectrophotometrically to be 0.5%.

(40) E. J. Bowen and K. K. Rohatgi, *Discussions Faraday Soc.*, **14**, 146 (1953).

(41) R. Livingston and D. W. Tanner, *Trans. Faraday Soc.*, **54**, 765 (1958).

(42) R. J. Charlson, H. Harrison, and R. Hardwick, *Rev. Sci. Instr.*, **31**, 46 (1960).

The Partial Molal Volume of Polyelectrolytes

Norio Ise and Tsuneo Okubo

Contribution from the Department of Polymer Chemistry, Kyoto University, Kyoto, Japan. Received March 14, 1968

Abstract: The densities of aqueous solutions of polyelectrolytes were measured by a pycnometric method. The materials used were polyacrylates (PAA), polystyrenesulfonates (PSt), polyethylenesulfonates (PES), and salts of polyethylenimine (PEI) and its low molecular weight analogs having various gegenions. The apparent molal volumes of the polyelectrolytes were practically concentration independent. From the partial molal volume obtained, the individual molal volume of macroions was calculated and discussed in terms of three contributions, namely intrinsic volume of macroions, hydrophobic structural effect (P_{2p}), and electrostrictional hydration (E_{2p}). P_{2p} was negative for all polyelectrolytes studied, ranging from about -20 to 0 ml monomole⁻¹. The magnitude of P_{2p} was in the order PEI < PES < PAA < polymethacrylate < PSt < polyphosphate. E_{2p} , which was also negative, varied from -50 to 0 ml monomole⁻¹, depending on the macroion. The magnitude of E_{2p} increased in the order PSt < PEI < PAA < polyphosphate < polymethacrylate < PES. It was found that the P_{2p} term was influential in determining thermodynamic properties of polyelectrolyte solutions, as was the electrostrictional hydration term, which was already known to be exclusively important in the ordinary simple electrolytes.

In previous papers the mean activity coefficients of polyelectrolytes were determined by the isopiestic equilibration method¹⁻⁶ and electrochemical measurements.⁷⁻⁹ The results show that the mean activity

(1) N. Ise and T. Okubo, *J. Phys. Chem.*, **71**, 1287 (1967).

(2) N. Ise and T. Okubo, *ibid.*, **71**, 1886 (1967).

(3) T. Okubo, N. Ise, and F. Matsui, *J. Amer. Chem. Soc.*, **89**, 3697 (1967).

(4) N. Ise and T. Okubo, *J. Phys. Chem.*, **72**, 1361 (1968).

(5) N. Ise and K. Asai, *ibid.*, **72**, 1366 (1968).

(6) N. Ise and T. Okubo, *ibid.*, **72**, 1370 (1968).

coefficients were largely influenced by solute-solvent interaction. It is feasible that there are two types of solute-solvent interaction, namely electrostrictional hydration by electric charges of gegenion or macroion, *i.e.*, charge effect, and hydrophobic structural enhancement or "iceberg" formation by hydrophobic parts of the electrolytes, *i.e.*, hydrophobic effect. Using the

(7) N. Ise and T. Okubo, *ibid.*, **69**, 4102 (1965).

(8) N. Ise and T. Okubo, *ibid.*, **70**, 1930 (1966).

(9) N. Ise and T. Okubo, *ibid.*, **70**, 2400 (1966).