being augmented by $\sigma\sigma''$ and $(p')^2$, we obtain the transition energies 4.62, 2.14, and 0.64 eV for CF_2, FCH, and CH_2 and the results labeled CI in Figures 9–11 and Tables I–III. While we are encouraged by the agreement with experiment, we consider it somewhat fortuitous since it is quite likely that the correlation energy loss upon dissolution of the σ^2 lone pair is greater[32] than the 0.25 eV we find from the minimal CI.

D. Singlet–Triplet Transition. In going from the $^3B_1$ state of CF_2 or CH_2 to the corresponding $^1B_1$ state we neither disrupt any existing nor form any new electron pairs and we therefore expect the correlation energy in these two states to be comparable. Consequently, we anticipate that the energy difference $^1B_1 - {}^3B_1$ or $^1A'' - {}^3A''$ should be adequately represented by the various CI functions we have described. To the extent that this is true we note that the reliability of our $^1A_1$–$^3B_1$ or $^1A'$–$^3A''$ separations may be estimated by observing how well we account for the various singlet–singlet transitions. Since we do very well in estimating this transition in CF_2 ($^1B_1 \leftarrow {}^1A_1$) and FCH ($^1A'' \leftarrow {}^1A'$) (see Table IV), we expect the singlet–triplet separations to be accurate, so in CF_2 we predict that the $^3B_1$ is 39 kcal above the $^1A_1$ state, while in FCH the $^1A'$ and $^3A''$ are separated by a very small ($\simeq$0 kcal) energy. Also, since our computed energy for the $\tilde{A}\,{}^1B_1 \leftarrow \tilde{X}\,{}^1A_1$ transition in CH_2 is too low by 5 kcal we expect the $^3B_1$ to be 19 kcal below the $^1A_1$ state even though our raw data predict this separation to be 24 kcal.

Our estimate is in disagreement with recent experimental results[33] which indicate a separation of 1–2 kcal, and on the basis of the above arguments this would imply an error of 18 kcal in the $^1B_1$–$^3B_1$ separation, which seems unreasonable. However, since this discrepancy must be resolved, we are undertaking a detailed study of the correlation energy contribution to the various states of CH_2 and will report the results as soon as possible.[34]

Acknowledgment. The contour plots were constructed with routines written by Dr. Vincent Nicely, and it is a pleasure to acknowledge their use.

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(32) Indeed E. A. Scarzafava, Ph.D. Thesis, Indiana University, 1969, estimates the correlation energy in an oxygen lone pair in the water molecule as approximately 1 eV.

(33) R. W. Carr, Jr., T. W. Eder, and M. G. Topor, *J. Chem. Phys.*, **53**, 4716 (1970).

(34) NOTE ADDED IN PROOF. Recently, O'Neil, Schaefer, and Bender, manuscript in preparation, have used the iterative natural orbital technique [C. F. Bender and E. R. Davidson, *J. Phys. Chem.*, **70**, 2675 (1966)] to construct wave functions for various states of CH_2. Using Huzinaga's (9s5p/4s) basis [(S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965)] contracted to [4s2p/2s] as recommended by Dunning [T. H. Dunning, Jr., *J. Chem. Phys.*, **53**, 2823 (1970)], a 298 and a 408 configuration representation of the $^1A_1$ and $^3B_1$ states, respectively, were constructed as a function of geometry. Their result for the $^3B_1$–$^1A_1$ splitting, $E[{}^3B_1\ (133.3°)] - E[{}^1A_1\ (104.4°)] = -0.96$ eV (-22 kcal), is in substantial agreement with ours but is still in conflict with the interpretation of the experimental data of ref 33. I thank Professor Schaefer for forwarding the results of his study before publication.

Viscosity Dependence of Fluorescence Quantum Yields

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Contribution from the Department of Chemistry,
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Basel, Switzerland. *Received October 28, 1970*

Abstract: The normally nonfluorescent *cis*-stilbene and sterically hindered *trans*-stilbenes become strongly fluorescent in very viscous media. Thus a maximum fluorescence quantum yield (ϕ_F) of 0.75 is measured for *cis*-stilbene in a hydrocarbon glass. The fluorescence of these compounds is a steep function of the viscosity, due to a solvent free volume (and viscosity) dependent rate constant for the internal conversion ($S_1 \rightarrow S_0$) process. This dependence is traced to the effect of enhanced solvent viscosity in reducing the probability and amplitude of the twisting and out-of-plane-bending modes about the central double bond. The theoretical dependence of ϕ_F on viscosity is developed along the lines of the free volume theory of viscosity and is obeyed accurately by the experimental results. An uncoupling of fluorescence and intersystem crossing at high viscosities is observed for *trans-p*-bromostilbene and for *trans*-hexamethylstilbene. The photochemical significance of this uncoupling is examined.

The quantum yields of the trans to cis photoisomerization, ϕ_t, of planar stilbenes were recently found to depend very strongly on the viscosity of the medium.[2] The effect was shown to be due to a solvent free volume dependent intramolecular rearrangement process subsequent to the $S_1 \rightarrow T_2$ or $S_1 \rightarrow T_1$ intersystem crossings,[2–4] and the theory[2] for a process of this type was developed along the lines of the free volume theory of the viscosity of liquids.[5]

In the present paper we wish to describe the results of an investigation of the dependence of the fluorescence quantum yields ϕ_F on the viscosity in a number of nonpolar aromatic compounds.[6] We have observed a

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(1) The Weizmann Institute.

(2) D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Amer. Chem. Soc.*, **90**, 12 (1968).

(3) K. A. Muszkat, D. Gegiou, and E. Fischer, *ibid.*, **89**, 4814 (1967).

(4) D. Gegiou, K. A. Muszkat, and E. Fischer, *ibid.*, **90**, 3907 (1968).

(5) (a) M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, **31**, 1164 (1959); (b) D. B. Davies and A. J. Matheson, *ibid.*, **45**, 1000 (1966).

(6) Other investigators have observed effects of viscosity on ϕ_F in the following systems: (a) diphenylmethane dyes, G. Oster and Y. Nishijima, *J. Amer. Chem. Soc.*, **78**, 1581 (1956); (b) tetraphenylbutadienes, M. A. El-Bayoumi and F. M. Abdel-Halim, *J. Chem. Phys.*, **48**, 2536

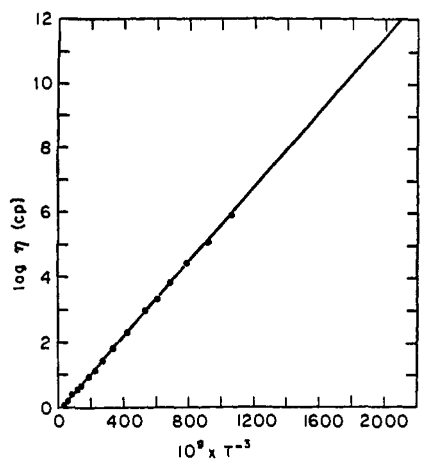


Figure 1. Temperature dependence of the viscosity of MCH/MCP (1:1) plotted according to eq 1.

strong dependence of ϕ_F on the viscosity only in stilbenes, and for these compounds we treat the effect in terms of the theory of free volume controlled monomolecular processes. The study of viscosity dependent photochemical processes has important mechanistic implications if two concurrent processes show independent behavior. This is the case for fluorescence and trans to cis photoisomerization in several stilbenes, and the conclusions to be drawn from this research will be discussed.

Experimental Section

Most of the experimental details are described in the previous publications.[2,4,7] 1,2-Diphenylcyclobutene was obtained from Dr. DeBoer.[8] A considerably purer grade of glycerol (Matheson Coleman and Bell, Spectroquality, anhydrous) was used in the present study. *cis*-Stilbene was purified by fractional distillation *in vacuo*. The purity of the compounds was checked by gas chromatography. The solutions in glycerol were prepared by a 100-fold dilution with glycerol of stock solutions in ethanol. Control experiments indicate that this amount of ethanol does not affect the viscosity nor the results to any significant extent. The solutions were degassed *in vacuo*. For this study we have used two fluorescence standards. *p*-Terphenyl, $\phi_F = 0.93$,[9] was used for compounds with emission centered in the range 310 to 420 nm, and 9,10-diphenylanthracene, $\phi_F = 1.00$,[9] was used for the 390–520-nm range. The quantum yields were corrected for the change of refractive index of the solution with the temperature. It was found in this study that too low ϕ_F values were reported previously[2,3] for *trans*-stilbene in hydrocarbon glasses at 90°K, and in glycerol at and below room temperature. The differences were traced to the lack of correction for refractive index *vs.* temperature changes and to the relatively high internal light filtering by the previously used glycerol samples.

In most of the present experiments the viscosity of a given glass-forming solvent was changed by changing the temperature. The range of viscosity values required in the present study extends beyond the experimentally determined values for glycerol[10] and for the methylcyclohexane-methylcyclopentane (1:1) mixture,[11] MCH–MCP. These viscosity values (η) were estimated by extrapolation of the experimental values[10,11] using the empirical equation of Litovitz[12]

$$\log \eta = A + B/T^3 \tag{1}$$

which represents very accurately the experimental behavior for glycerol[12] and for MCH–MCP (Figure 1) for viscosities up to 10^6 cP.

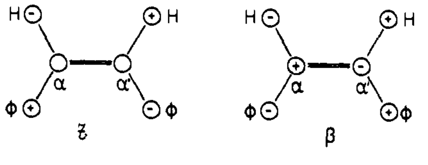
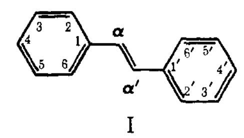


Figure 2. Schematic description of the twisting (τ) and out-of-plane bending (β) vibration modes of stilbenes.

In the present paper the solute molecules will be denoted as follows: I, *trans*-stilbene; II, 3,3′,5,5′-*trans*-tetramethylstilbene; III, *cis*-stilbene; IV, *trans*-α-methylstilbene; V, *trans*-α,α′-dimethylstilbene; V′, *cis*-α,α′-dimethylstilbene; VI, *trans*-2,4,6-trimethylstilbene; VII, *trans*-2,4,6,2′,4′,6′-hexamethylstilbene; VII′, cis isomer of VII; VIII, triphenylethylene; IX, tetraphenylethylene; X, diphenylcyclopentene; XI, diphenylcyclobutene; and XII, *trans*-4-bromostilbene. Typical fluorescence and absorption spectra



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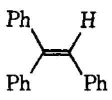

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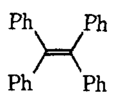

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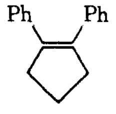

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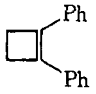

XI

of stilbenes (*e.g.*, for I;[13] III, VIII, and IX;[14] VI and VII;[4] X;[7,15] and XI[16]) have been described previously. The emission of stilbenes is known to be due exclusively to fluorescence.[14,15]

Results and Discussion

Structural Studies. We have previously described the difference in the ϕ_F values at low viscosities between planar *trans*-stilbenes and the necessarily nonplanar *cis*-stilbenes and sterically hindered trans isomers.[4] The planar molecules are fluorescent at room temperature (or slightly below) while the nonplanar compounds are in most cases nonfluorescent down to *ca.* 120°K. We tend to attribute this difference to increased rates of intersystem crossing and of internal conversion in the nonplanar molecules. The role of planarity on fluorescence has been examined at length in other systems.[17,18]

An important aspect of the present work is the identification of the vibration modes in the first excited singlet states which are responsible for the low ϕ_F values in the nonplanar stilbenes at low viscosities. It is further assumed that when these motions are absent altogether (*i.e.*, in rigid nonplanar molecules) high ϕ_F values are observed even at very low viscosities. In flexible non-

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(1968); (c) adenine, J. W. Eastman and E. J. Rosa, *Photochem. Photobiol.*, 7, 189 (1968); (d) triphenylmethane dyes, G. Hoffmann, Dissertation, Universität Stuttgart, 1969, and private communication from Professor Th. Förster.

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

(8) We are grateful to Dr. C. D. DeBoer, Research Laboratories, Eastman Kodak Co., Rochester, N. Y., for providing a sample of this compound.

(9) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965.

(10) G. Tamman and W. Hesse, *Z. Anorg. Allg. Chem.*, **156**, 245 (1926).

(11) G. A. von Salis and H. Labhart, *J. Phys. Chem.*, **72**, 752 (1968).

(12) T. A. Litowitz, *J. Chem. Phys.*, **20**, 1088 (1952).

(13) S. Malkin and E. Fischer, *J. Phys. Chem.*, **68**, 1153 (1964).

(14) H. Stegemeyer, *Ber. Bunsenges. Phys. Chem.*, **72**, 335 (1968).

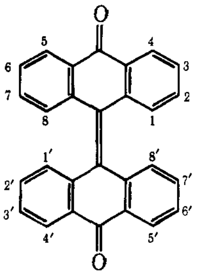
(15) A. A. Lamola, G. S. Hammond, and F. B. Mallory, *Photochem. Photobiol.*, **4**, 259 (1965).

(16) C. D. DeBoer and R. H. Schlessinger, *J. Amer. Chem. Soc.*, **90** 803 (1968).

(17) C. A. Parker, "Photoluminescence of Solutions," Elsevier, Amsterdam, 1968, p 428.

(18) I. B. Berlman, *J. Phys. Chem.*, **74**, 3085 (1970); *J. Chem. Phys.*, **52**, 5616 (1970).

planar molecules, at high viscosities, these molecular motions are decreased and an increase in ϕ_F is observed. The results of this study indicate that these are the twisting, (τ), and probably the out-of-plane bending (β) modes, both about a central essential double bond (*cf.* Figure 2; there are two β-type vibrations, *cf.* ref 19). In hindered stilbenes, where a remarkable increase in ϕ_F is observed at high viscosities, the effect is thus correlated with the probability of the τ and β vibrations. This conclusion is based on the following results. (a) In the rigid aromatic systems[20] anthracene, naphthalene, and azulene, ϕ_F is not influenced by increased viscosities. (b) ϕ_F values in compounds with essential *single* bonds are not dependent on the viscosity. This was observed in the present study for biphenyl and for β,β'-binaphthyl.[20] (c) In the 1,3,1′,3′,-tetramethyl derivative of bianthrone (XIII) a strong increase of ϕ_F values

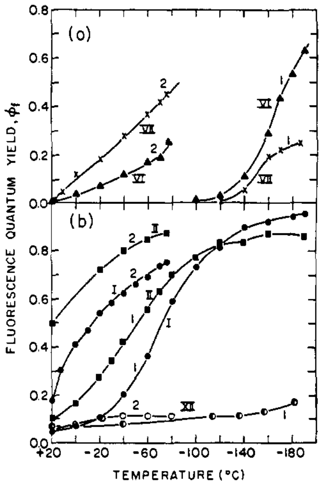


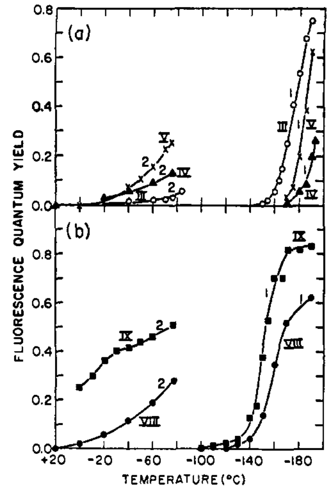
XIII

at high viscosities is observed.[21] In this compound only the τ and β vibrations involving the central double bond in the excited state are possible. (d) The role played by the τ and β vibrations on the magnitude of ϕ_F *at low viscosities* is shown by the following data. For XI, ϕ_F = 1.0 at 294°K in *n*-hexane.[16] For X, at 153°K, ϕ_F = 0.07 (in MCH–isohexane, 1:3).[7] For III at 153° in the same solvent, ϕ_F = 0. Thus as the ring size decreases and the potential barriers for the τ and β modes in the excited state increase one notes a corresponding strong increase in ϕ_F.

In-plane bending vibrations do not involve a considerable change in molecular volume or in the shape of the molecular cavity and therefore are assumed to be only of little importance in the present context. Thermal population of modes τ and β in the S_1 state at low viscosities is expected to be considerable, even at 77°K. Dyck and McClure have reported that in stilbenes the frequency of the β mode in the S_1 state is *ca.* 200 cm^{-1}.[22] The frequency of τ is also probably of a similar magnitude, as can be judged from the frequency of this mode in the mechanically analogous *trans*-CHBr=CHBr.[19]

Fluorescence Quantum Yields in Stilbenes. As in the previous work,[2,3] the effects of viscosity were determined by comparing results obtained in a high-viscosity solvent (glycerol) at higher temperatures (300–195°K) with results obtained in a fluid solvent (MCH–MCP) at these and at lower temperatures (300–77°K). Thus the range of high viscosities accessible in glycerol at about 200°K is reached in MCH–MCP at about 77°K. Therefore intrinsic effects of temperature on ϕ_F at temperatures accessible in glycerol may be detected in the control studies at low viscosities over the same temperature range in MCH–MCP. This approach was elaborated in the previous paper.[2] In common with the previous study a search was made for chemical effects which could possibly be due to the high polarity of glycerol. Such effects were ruled out by control measurements in low-viscosity alcohol solvents. The experimental results for solutions in MCH–MCP and in glycerol are shown in Figures 3 and 4. On the basis of these results, stilbenes may be broadly classified into two groups.





Figures 3 (top) and 4. Experimental fluorescence quantum yields at different temperatures in MCH–MCP (1) or glycerol (2) solutions. The compounds are denoted with Roman numerals (see text).

(a) ***trans*-Stilbene and Derivatives with No Substituents on the α,α' or 2,6,2′,6′ Carbon Atoms.** These molecules are planar in the ground state as there is no steric hindrance between atoms or groups attached at these positions.[23] These compounds have considerable ϕ_F values (in particular I and II) at low viscosities. In the case of I and II the ϕ_F values in glycerol at a given temperature are higher than in MCH–MCP, though to a much smaller extent than in the sterically hindered compounds (case b). Also, I and II show an increase in ϕ_F on cooling at much lower viscosities than compounds in group b. Thus even at 293°K the ϕ_F's of I

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(19) J. M. Dowling, P. G. Puranik, A. G. Meister, and S. I. Miller, *J. Chem. Phys.*, 26, 233 (1957).

(20) Absorption and fluorescence spectra and ϕ_F values at low viscosities and at room temperature are reported in ref 9.

(21) T. Bercovici, R. Kornstein, K. A. Muszkat, and E. Fischer, *Pure Appl. Chem.*, 24, 531 (1970).

(22) R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, 36, 2326 (1962).

(23) H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press, New York, N. Y., 1967.

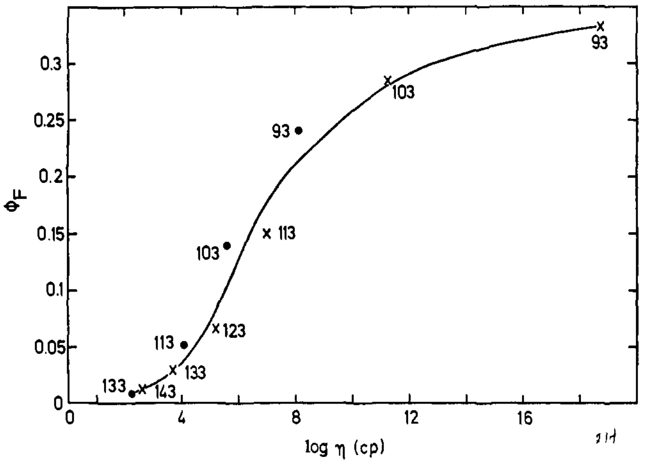

Figure 5. Dependence of fluorescence quantum yields of *cis*-stilbene on viscosity and temperature. Points denoted with ● refer to solutions in ethanol + 6.6% water, while × indicates results for *n*-propyl alcohol solutions. Temperatures (in °K) are indicated for each point.

and II in glycerol are higher than in MCH–MCP. The results for low-viscosity solvents indicate that fluorescence in this group is intrinsically dependent on temperature (*i.e.*, in addition to any dependence on viscosity). The temperature dependence of the fluorescence of unhindered stilbenes,[2,4,13] will be reexamined in the present study.

(b) Sterically Hindered Compounds. Figures 3a, 4a, and 4b show that III or *trans*-stilbenes substituted at any of the α,α′; 2,6,2′; or 6′ positions are completely nonfluorescent at low viscosities (*i.e.*, down to *ca.* 170°K in MCH–MCP). The fluorescence observed in glycerol solutions of these compounds is thus due entirely to enhanced viscosity. An obvious problem that arises in the present context is whether the high ϕ_F values in MCH–MCP are due to the low temperatures, to the high viscosities prevailing at these temperatures, or to both factors combined. The solution to this problem is suggested by the results of a comparative study of the fluorescence of III in two alcoholic solvents of different viscosities (Figure 5). Ethanol + 6.6% water[10] (E) was chosen as the fluid solvent and *n*-propyl alcohol[10,24] (P) as the viscous solvent. These results indicate that for any given temperature ϕ_F is larger in the more viscous solvent. Thus at 123, 113, and 103°K the ratios ϕ_F^P/ϕ_F^E are equal respectively to 3.9, 2.7, and 2. Very similar results were obtained when comparing solutions of *cis*-stilbene in 3-methylpentane (3-MP) and in a mixture of 3-MP and MCH (1:20). Thus $\phi_F = 0.40$ in 3-MP at 91°K and in MCH-3-MP at 102°K. The viscosity of these two solvent systems at the above temperatures is about 10^7–10^8 cP.[24] These results indicate that high viscosity is the most important factor over this temperature range. However, some temperature dependence is also evident. Obviously, this reasoning is based on the assumption that, apart from different viscosities, these two solvent pairs would show similar specific effects, if any, due to their chemical similarity.

The two cis isomers of the hindered compounds V and VII were also studied. Their fluorescence spectra are red shifted in comparison with those of the trans isomers, and the quantum yields are very low, so that emission is discernible only at very low temperatures and high viscosities.

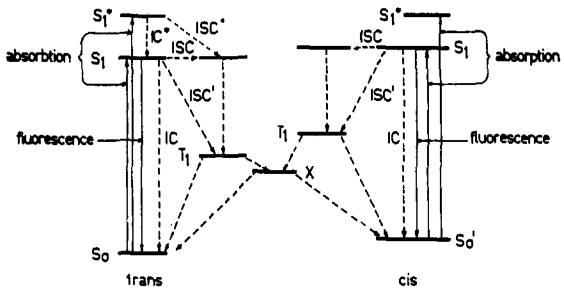

Figure 6. Jablonski-type scheme for the stilbene system.

Analysis of the Temperature Dependent Fluorescence in Planar *trans*-Stilbenes. The experimental data on which is based the schematic description (Figure 6) of the different processes in the stilbene system have been described previously.[2–4] Further information about two radiationless processes of the singlet excited trans form is made available by the following analysis of the temperature dependence of ϕ_F (in I and II) at low viscosities in MCH–MCP.

We assume that at low viscosities the temperature dependent behavior of ϕ_F is due to the presence of the intersystem crossing process $S_1 \rightarrow T_2$ (ISC) which requires an activation energy (E_a) of a few kilocalories per mole. In the previous study a value of E_a = 1–4 kcal/mol was obtained from the temperature dependence of ϕ_t.[4] The radiationless processes which compete with fluorescence (F) are IC, an internal conversion process ($S_1 \rightarrow S_0$), and ISC and ISC′, $S_1 \rightarrow T_2$ and $S_1 \rightarrow T_1$ intersystem crossings. Evidence for the existence of an intersystem crossing process which can populate the triplet manifold at 77°K was presented by Herkstroeter and McClure.[25] On the basis of the enhancement of the temperature independent intersystem crossing by an *n*-butyl bromide solvent[3] we now identify the process reported by Herkstroeter and McClure[25] as the temperature independent $S_1 \rightarrow T_1$ process (ISC′). Evidence for a slightly temperature dependent IC ($S_1 \rightarrow S_0$) is provided by the temperature dependent behavior of ϕ_F in XII, where ISC is temperature independent. This process is therefore assumed by analogy for I and II. The ϕ values of the above mentioned processes add up to unity.

$$\phi_{ISC'} + \phi_{ISC} + \phi_{IC} + \phi_F = 1 \tag{2}$$

We denote the maximal ϕ_F at 77° as ϕ_F^0. At this temperature $\phi_{ISC} = 0$ and we further assume that $\phi_{IC} = 0$. Therefore we obtain at 77°

$$\phi_{ISC'} + \phi_F^0 = 1 \tag{3a}$$

and for any other temperature

$$\phi_{ISC} + \phi_{IC} + \phi_F = \phi_F^0 \tag{3b}$$

and

$$\phi_{ISC} + \phi_{IC} = \phi_F^0 - \phi_F \tag{3c}$$

By expressing the quantum yields as ratios of rate

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(24) A. C. Ling and J. E. Willard, *J. Phys. Chem.*, 72, 1918, 3349 (1968).

(25) W. G. Herkstroeter and D. S. McClure, *J. Amer. Chem. Soc.*, 90, 4522 (1968).

constants k we obtain that

$$\phi_F/(\phi_F^0 - \phi_F) = k_F/(k_{ISC} + k_{IC}) \qquad (4)$$

We expect a range of temperatures for which $k_{ISC} \gg k_{IC}$. Therefore at these temperatures

$$\phi_F/(\phi_F^0 - \phi_F) \approx k_F/k_{ISC}^0 e^{-E_a/RT} \qquad (5)$$

This is indeed the situation (Figure 7) at $T > 200°$K. At lower temperatures the function $\phi_F/(\phi_F^0 - \phi_F)$ changes less, as then $k_{IC} \approx k_{ISC'}$ or even $k_{IC} > k_{ISC}$. This is observed at $T < 200°$K. The activation energy values for ISC (in the linear part of Figure 7) are 4.1 kcal/mol for I (*cf.* with $E_a = 3$ kcal/mol from the temperature dependence of ϕ_t[4]) and 3.8 kcal/mol for II.

Analysis of the Viscosity Dependence of ϕ_F. We limit our treatment to the *cis*-stilbenes and the sterically hindered *trans*-stilbenes. These molecules have nonplanar ground states,[23] and intersystem crossing is independent of the viscosity and of the temperature. This is inferred from the behavior of ϕ_t (for the trans isomers) and of ϕ_c (for the cis isomers).[2-4] As in these compounds ϕ_{ISC} is constant but ϕ_F is not, we conclude that at high viscosities intersystem crossing (ISC*) proceeds from a *higher energy singlet state* (S_1*, *cf.* Figure 6). This state is converted into the S_1 state by the internal conversion process IC*. Stegemeyer has recently reported that high-viscosity solvents freeze down the molecular relaxation processes in III, VIII, IX, and in similar compounds.[14] Therefore, final states having geometries similar to that of the initial states (Franck–Condon states) are obtained either on emission or on absorption in high-viscosity solvents. These observations lead us to conclude that the S_1* state is a Franck–Condon state with a nuclear configuration similar to that of the ground state. From these considerations we conclude that at any temperature and viscosity

$$\phi_{IC} + \phi_{ISC*} + \phi_F = 1 \qquad (6)$$

For any solvent the limiting fluorescence quantum yield, ϕ_F^0, is achieved at the highest viscosities. We assume that then $\phi_{IC} \rightarrow 0$. Then

$$\phi_{IC} = \phi_F^0 - \phi_F \qquad (7)$$

and

$$\phi_F/(\phi_F^0 - \phi_F) = \phi_F/\phi_{IC} = k_F/k_{IC} \qquad (8)$$

We limit our treatment to cases where the fluorescence is determined by the viscosity. IC is the process whose rate constant k_{IC} is viscosity dependent. According to a previous publication[2] the dependence of k_{IC} on the mean free volume of the solvent, V_f, is given by

$$k_{IC} = k_{IC}^0 e^{-aV_0/V_f} \qquad (9)$$

In eq 9 k_{IC}^0 is the free volume independent rate constant, V_0 is the critical free volume for a motion of the solvent, and a is the fraction of V_0 required for a motion of the solute. By adopting eq 9 for the present case we assume that a molecular vibration (*e.g.*, τ or β) can be treated much the same way as a molecular geometry change such as the trans-to-cis isomerization around a double bond.[2] The viscosity η is given by[5a]

$$\eta = \eta_0 e^{V_0/V_f} \qquad (10)$$

Thus k_{IC} may be expressed in terms of the viscosity as

$$k_{IC} = k_{IC}^0(\eta_0/\eta)^a \qquad (11)$$

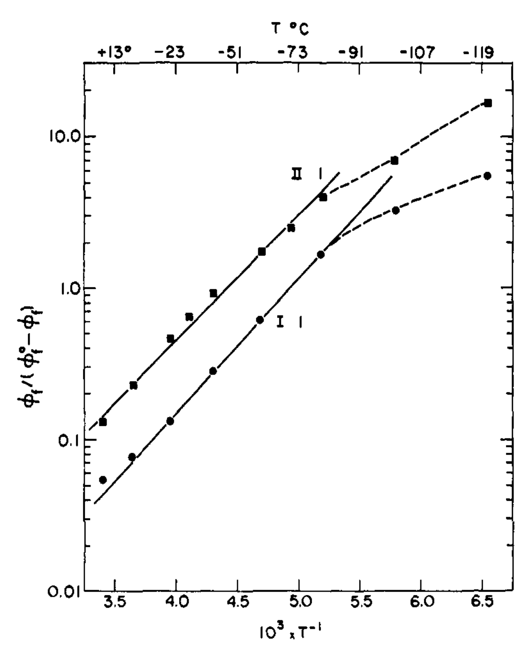


Figure 7. Plot of $\phi_F/(\phi_F^0 - \phi_F)$ *vs.* $1/T$ for *trans*-stilbene and *trans*-tetramethylstilbene (MCH–IH solutions).

Substitution for k_{IC} in eq 8 results in

$$\phi_F/(\phi_F^0 - \phi_F) = k_F/[k_{IC}^0(\eta_0/\eta)^a] \qquad (12)$$

The absorption spectra of the present compounds are independent of the viscosity. Thus k_F as well as $k_F/(k_{IC}^0\eta_0^a)$ are constant. $k_F/(k_{IC}^0\eta_0^a)$ will be denoted by A. Our final expression is then

$$\phi_F/(\phi_F^0 - \phi_F) = A/\eta^a \qquad (12a)$$

Figures 8, 9, and 10 show the linear dependence of log $[\phi_F/(\phi_F^0 - \phi_F)]$ on log η for III, IV, V, VI, VIII, IX, and X, as required by eq 12a. The slope of the curves, a, is larger for MCH–MCP than for glycerol. Thus for IX a is 1 in MCH–MCP but 0.2 in glycerol. a is in general a function both of the solvent and of the solute.

Correlation between the Theory of Radiationless Transitions and the Viscosity Dependence of ϕ_F. We have shown in the previous sections that the molecular motions which have a direct influence on ϕ_F are the twisting (τ) and the out-of-plane bending (β) motions of the α–α' double bond, in the excited state. The process whose rate constant depends on the viscosity (and on τ and β) was furthermore identified as the IC radiationless transition. In the present section we wish to examine the reasons for the strong effect of these vibrations on the rate constant of the IC transition.

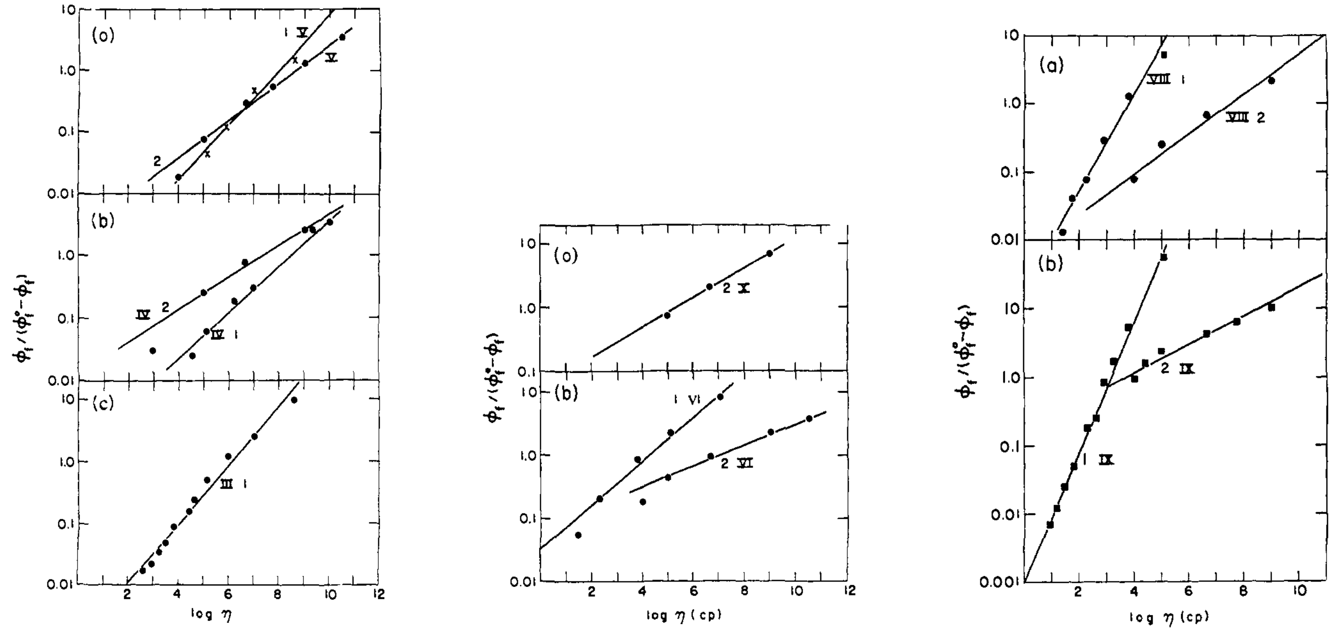
Of the many theories of radiationless transitions,[26] we chose for the present discussion the well-known formulation of Robinson and Frosch.[27a] According to this theory, the rate constant k for a radiationless transition (k_{IC} in the present case) is given by

$$k = (2\pi\beta_{el}^2/\alpha\hbar)\sum_n \langle\phi_n''/\phi_0'\rangle^2 \qquad (13)$$

In this equation the summation represents the overall

[26] (a) B. R. Henry and M. Kasha, *Annu. Rev. Phys. Chem.*, **19**, 161 (1968); (b) J. Jortner, S. A. Rice, and R. M. Hochstrasser, *Advan. Photochem.*, 7, 149 (1969).

[27] (a) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962); **38**, 1187 (1963); (b) W. Siebrand and D. F. Williams, *ibid.*, **49**, 1860 (1968), and literature cited therein.



Figures 8 (left), 9 (center), and 10 (right). Plots of $\phi_F/(\phi_F^0 - \phi_F)$ on logarithmic scale *vs.* log (viscosity). The compounds are denoted with Roman numerals (see Experimental Section). The solvents are MCH–MCP (1) and glycerol (2).

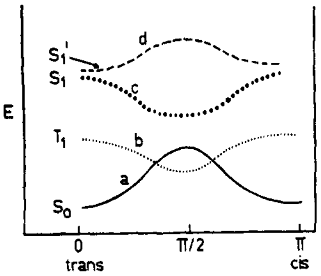


Figure 11. Schematic energy profiles for the twisting mode of stilbene. Curve d refers to a molar volume equal to that of the trans form.

vibrational overlap factor (Franck–Condon factor), β_{el} is the matrix element of the electronic perturbation Hamiltonian H' between the final and initial wave functions, and α is an inverse measure of the density of final states.

In the present discussion we shall be mainly concerned with the Franck–Condon (FC) factor of eq 13. This factor accounts for overlap of the lowest vibrational wave function of the higher electronic state (designated by a single prime), ϕ_0', with all the n different wave functions of the lower electronic state (designated by a double prime), ϕ_n''.

Siebrand and Williams have recently investigated several of the factors which strongly increase the magnitude of FC factors for the $S_1 \rightarrow S_0$ internal conversion.[27b] Among these factors are included the anharmonicity of the excited vibrations in the lower electronic state, the extent of change in the frequencies of the excited modes between the two states (distortions), and the extent of change in the normal coordinates proper to the excited normal modes (displacements).[27b] Low-frequency modes are expected to be particularly effective.[27b] All these requirements are obviously fulfilled by the τ mode[28] and probably by the out-of-plane-bending modes. However, this approach is unable to explain why modes τ and β are of particular importance for the nonplanar molecules. It seems that for these other factors have also to be considered.

The experimental data of Auwers[29] on the molar volumes of sterically nonhindered (planar) and sterically hindered (nonplanar) isomers in solution point toward the general trend that planar molecules have smaller molar volumes than nonplanar molecules. We have therefore attributed the difference in the viscosity dependence of the quantum yields of geometrical photoisomerization between planar *trans*-stilbenes and the nonplanar *cis*- or *trans*-stilbenes to a difference in the molar volumes.[2]

According to this approach[2] the combined molecular volume of the solute and the mean free volume of the solvent are sufficient at all viscosities for the rotation about the central double bond in the nonplanar compounds. However, in the planar compounds this motion mode is probable only at low viscosities (*i.e.*, at high values of the solvent mean free volume). Thus at intermediate viscosities the probability of the twisting motion in a triplet state and therefore the photoisomerization quantum yield should show a dependence on the viscosity.

This same approach provides an immediate explanation of the present experimental results. In the previous sections we have seen that the motions involving the double bond (τ and the β's) are closely related to the magnitude of ϕ_{IC} and to its dependence on the viscosity. We therefore wish to suggest that an important path for internal conversion in stilbenes is through tunneling of molecules twisted by 90° about the central double bond in S_1 (Figure 11) to the perpendicular ground state. Figure 11 gives a qualitative description of the energy profiles of several electronic states important for the present context as a function of the angle of twist of the central double bond.[30,31] The lowest energy

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(28) A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).

(29) K. v. Auwers, *Chem. Ber.*, **68B**, 1346 (1935).

gap S_1–S_0 is between the perpendicular forms, and a radiationless transition $S_1 \rightarrow S_0$ would be the most probable for this geometry. Curve c describes the energy of the S_1 state at low viscosities. However, at high viscosities, depending on the solute and on the viscosity, a potential barrier of varying height which is required for a free volume limited motion will be superimposed on the potential curve of the S_1 state of the isolated molecule (curve d). Therefore, planar *trans*-stilbenes which have low molar volumes will experience high viscosity dependent barriers to the τ motion and will show a decrease of ϕ_{IC} even at relatively low viscosities (Figure 3b). The nonplanar stilbenes which have higher molar volumes will show a decrease of ϕ_{IC} only at much higher viscosities because they experience much lower free volume dependent barriers to rotations.

The present approach can also be applied to another chapter of the photochemistry of stilbene. Herkstroeter and McClure have observed that the lifetime of the triplet state of *trans*-stilbene is very strongly dependent on viscosity.[25] On the other hand, it is considerably increased by deuteration, but only at the α and α' positions (I).[32] These two observations can easily be correlated by assuming that a preferred path for the radiationless transition $T_1 \rightarrow S_0$ (trans) which determines the lifetime of the triplet also involves a twisted or bent upper state. This state is converted to the isoenergetic lower state excited with one or several of the out-of-plane vibrations involving the double bond. These correspond respectively to the modes ν_6 (a_u), ν_7 (a_u), and ν_8 (b_g) of CHBr=CHBr.[19] The transition $T_1 \rightarrow S_0$ is, however, not a simple surface crossing but also requires some quantum mechanical tunneling. The frequencies of the out-of-plane bending vibrations a_u and b_g are probably strongly decreased by deuteration at α and α' (*cf.* the effect in CHBr=CHBr[19]), while in the V state of ethylene deuteration is known to reduce considerably the frequency of the double bond twisting mode.[33] Energy profiles qualitatively similar to that for the twisting deformation (Figure 11) are also expected for the out-of-plane-bending modes.

The two effects on the lifetime of the triplet state of stilbene—that of viscosity and that of deuteration at the α and α' positions—are thus ascribed to the participation of the twisting and of the out-of-plane-bending modes in the radiationless $T_1 \rightarrow S_0$ transition.

Conclusion about the Mechanism of the Direct Cis–Trans Photoisomerization of Stilbenes. The involvement of triplet levels in the direct photoisomerization of stilbenes has been a subject of controversy.[2–4,13,22,25,34] Mainly on the basis of quenching experiments of the sensitized and of the direct photoisomerization of stilbene, Saltiel, *et al.*, infer[34] that the unsensitized photoisomerization proceeds in an excited singlet level. However, studies of triplet sensitization[13,35] and of the effects of internal and external heavy-atom enhancement[2–4,36] on $S_1 \rightarrow T_1$ and on $S_0 \rightarrow T_1$ indicate that a triplet level is involved which may be directly observed by triplet–triplet absorption in flash photolysis.[25] The present investigation supports this last conclusion: the effects of high viscosity on ϕ_F and on ϕ_t values in VI and XII show that there is complete uncoupling of fluorescence and trans-to-cis photoisomerization in both VII and XII,[37] as well as in III, IV, V, and VI. Thus in VI ϕ_t is independent both of temperature and of viscosity[2,4] while ϕ_F is strongly dependent on the viscosity and to a lesser degree on the temperature (Figure 3). In XII in glycerol solutions at −80° ϕ_t is decreased to almost zero while ϕ_F is approximately equal to its value at this temperature in the fluid MCH–MCP (*cf.* Figure 3).

Acknowledgments. K. A. M. wishes to thank Professor E. Heilbronner for his hospitality at the Physikalisch-Chemisches Institut der Universität Basel and the Bank J. Bär and Co. (Zürich) for support. Both authors are indebted to Professor E. Fischer for many discussions and for his interest in this work.

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(30) P. Borrell and H. H. Greenwood, *Proc. Roy. Soc., Ser. A*, **298**, 453 (1967).

(31) *Cf.* the diagram based on the semiempirical π MO calculation (Figure 5 in ref 30) and the analogous situation in ethylene (Figure 3 of ref 28).

(32) G. Heinrich, G. Holzer, H. Blume, and D. Schulte-Frohlinde, *Z. Naturforsch. B*, **25**, 496 (1970).

(33) R. McDiarmid and E. Charney, *J. Chem. Phys.*, **47**, 1517 (1967).

(34) (a) J. Saltiel, *J. Amer. Chem. Soc.*, **89**, 1037 (1967); **90**, 6394 (1968); (b) J. Saltiel, E. D. Megarity, and K. G. Kneipp, *ibid.*, **88**, 2336 (1966); (c) J. Saltiel, O. C. Zafiriou, E. D. Megarity, and A. A. Lamola, *ibid.*, **90**, 4759 (1968).

(35) (a) G. S. Hammond, *et al.*, *ibid.*, **86**, 3197 (1964); (b) G. S. Hammond and J. Saltiel, *ibid.*, **84**, 4984 (1962).

(36) G. Fischer, K. A. Muszkat, and E. Fischer, *Israel J. Chem.*, **6**, 965 (1968).

(37) The present ϕ_F values for *trans*-stilbene (I) show that here no *experimental* proof is available of uncoupling of fluorescence and of photoisomerization at high viscosities. At high viscosities, in glycerol solutions, ϕ_t drops,[2] while ϕ_F *increases* (see Figure 3), implying a viscosity dependent ISC process. An uncoupling of fluorescence and trans-to-cis photoisomerization at high viscosities[2,3] was deduced erroneously for I from the previous set of ϕ_F values.[2,3] For I these are superseded by the present measurements (*cf.* Experimental Section)