

Separation of Viscosity and Temperature Effects on the Singlet Pathway to Stilbene Photoisomerization^{1a}

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Abstract: Fluorescence quantum yields of *trans*-stilbene (**1**) and a fused-ring analog, *trans*-1,1'-biindanylidene (**2**), were obtained in glycerol over a 90° temperature range from -25 to +65°. A marked increase in fluorescence quantum yield (ϕ_f) was observed on lowering the temperature, indicating that the processes of fluorescence and *trans* → *cis* isomerization remain coupled with changing temperature in a highly viscous solvent. Contributions from the thermal and the viscosity-dependent processes of geometric twist have been determined by employing a model which assumes that the over-all activation energy observed in a viscous solvent is the sum of an inherent thermal barrier (E^\ddagger_t) and a solvent-dependent viscosity barrier (E^\ddagger_v). Rate constants for the activated process are proportional to expressions of the form $1/\phi_f - \kappa$, where $\kappa = 1 + \text{constant}$, with the constant term representing contribution from a nonactivated decay process (*i.e.*, intersystem crossing). Arrhenius and Andrade equations are used to describe the variations of rate constant and viscosity (η) with temperature. Plotting $\ln(1/\phi_f - \kappa)$ values *vs.* the appropriate abscissas gives the following slopes: (a) *vs.* $1/T$, slope = $(E^\ddagger_v + E^\ddagger_t)/R$; (b) *vs.* $\ln \eta$ at varying temperature, slope = $(E^\ddagger_v + E^\ddagger_t)/E^\ddagger_\eta$; (c) *vs.* $\ln \eta$ at constant temperature, slope = $E^\ddagger_v/E^\ddagger_\eta$, where E^\ddagger_η is a solvent parameter which may be obtained for any solvent by evaluation of the expression $\ln \eta = \ln A_\eta + E^\ddagger_\eta/RT$. In glycerol it was found that $E^\ddagger_v = 6.2$ kcal/mol and $E^\ddagger_t = 3.5$ kcal/mol for **1**, while $E^\ddagger_v = 9.9$ kcal/mol and $E^\ddagger_t = 2.4$ kcal/mol for **2**. Intercepts of the plots are interpreted in terms of Arrhenius frequency factors A_t and A_v for the thermal and viscosity-dependent processes, respectively. The model is applied to decay processes of other excited molecules with resulting Arrhenius parameters suggesting the isokinetic relationship: $\log A_v = 0.71 E^\ddagger_v$. For systems conforming to this isokinetic relationship the onset of viscosity dependence can be related to the rate of solvent relaxation.

The mechanism of stilbene isomerization by direct irradiation has been the subject of much controversy.²⁻⁶ While proposals of the triplet mechanism date back to 1952,² recent findings⁵ have cast considerable doubt on the ability of this mechanism to explain all the data. We present here an analysis of viscosity and temperature effects on the fluorescence efficiency of *trans*-stilbene and a fused-ring analog which supports the previous conclusion^{5b} that the isomerization process competing with fluorescence occurs within the singlet manifold of stilbene. In addition, a model is proposed which accounts for viscosity effects on excited state behavior and explains these effects in our study.

Based on the Förster² model for stilbene photoisomerization, Fischer and coworkers⁴ interpreted their results and those of other workers^{2,3} by proposing that population of the first excited singlet state of *trans*-stilbene leads to fluorescence or to intersystem crossing to the triplet manifold, from which *trans* → *cis* isomerization occurs *via* a common triplet state. The tem-

perature-dependent coupling of fluorescence and isomerization quantum yields was attributed to a small thermal barrier in the intersystem crossing process.^{3,4a} Perhaps the most convincing evidence in support of the triplet mechanism was the observation^{4b,c} that the quantum yield for *trans* → *cis* isomerization decreases in solvents of high viscosity while the fluorescence quantum yield is relatively unchanged. This viscosity effect was ascribed^{4c} to an increase in molecular volume during the *trans* → *cis* photoconversion. Because the isomerization and fluorescence quantum yields were apparently not coupled in highly viscous media, assignment of the observed viscosity effect to some step within the triplet manifold was required, *i.e.*, a viscosity-dependent change in molecular geometry followed the thermally activated step assigned to intersystem crossing.^{4c}

In contrast, the singlet mechanism^{5b} for the *cis*-*trans* isomerization by direct irradiation involves rotation of the central bond in the first excited singlet state to form a common twisted singlet. The thermally activated process which competes with fluorescence and leads to isomerization is assigned to formation of the twisted singlet from the fluorescing *trans*-oid form. Theoretical calculations^{6,7} support this assignment by predicting a small barrier in the potential energy surface for twisting in the first excited singlet state of *trans*-stilbene. Experimental evidence consistent with the singlet mechanism was provided by the differing azulene quenching effects on the photo-stationary state compositions of direct and sensitized irradiations,^{5e} and by the observation that the fluorescence quantum yield at 25° is unity for indeno[2,1-*a*-

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(2) Th. Förster, *Z. Elektrochem.*, **56**, 716 (1952).

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

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

(b) K. A. Muszkat, D. Gegiou, and E. Fischer, *J. Amer. Chem. Soc.*, **87**, 4814 (1967); (c) D. Gegiou, K. A. Muszkat, and E. Fischer, *ibid.*, **90**, 12 (1968); (d) *ibid.*, **90**, 3907 (1968); (e) S. Sharafy and K. A. Muszkat, *ibid.*, **93**, 4119 (1971).

(5) (a) J. Saltiel, E. D. Megarity, and K. G. Kneipp, *ibid.*, **88**, 2336 (1966); (b) J. Saltiel, *ibid.*, **89**, 1036 (1967); (c) J. Saltiel, O. C. Zafriou, E. D. Megarity, and A. A. Lamola, *ibid.*, **90**, 4759 (1968); (d) J. Saltiel, *ibid.*, **90**, 6394 (1968); (e) J. Saltiel and E. D. Megarity, *ibid.*, **91**, 1265 (1969).

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

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

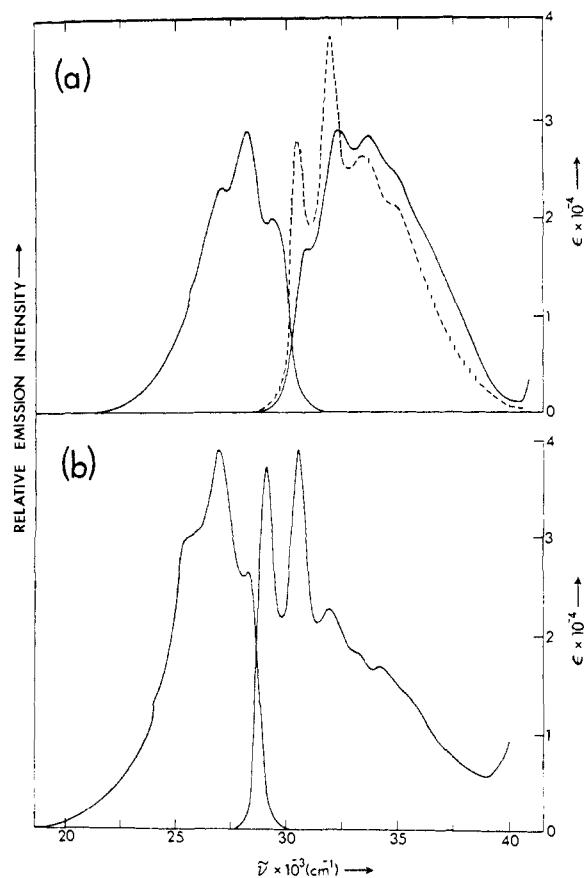


Figure 1. Absorption and fluorescence spectra of **1** (a) and **2** (b) in glycerol at 25°. Dashed curve in (a) is 77°K absorption spectrum of **1** (intensity is only relative) taken from ref 3.

indene,^{3e,8} a fused-ring analog of *trans*-stilbene which is restricted to a planar configuration in both ground and excited states.

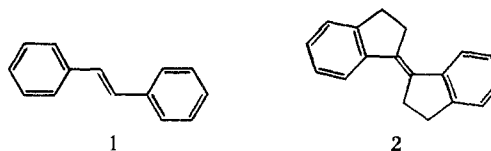
The singlet mechanism requires the thermally activated and the viscosity-dependent steps leading to isomerization to be one and the same, namely, twisting of the excited singlet from its transoid geometry.^{5d} Hence, in solvents of high viscosity, the mechanism predicts that a decreased isomerization quantum yield will be accompanied by an increased fluorescence quantum yield. This prediction is at odds with the relatively small viscosity effect reported for fluorescence.^{4b,c} However, interpolation of earlier fluorescence quantum yields^{4a} had suggested^{5c} an inconsistency with the more recently published values^{4c,9} in glycerol.

A reexamination of the fluorescence quantum yields of *trans*-stilbene (**1**) in glycerol over a temperature range of +65 to -25° was therefore undertaken. For comparison, the fluorescence of *trans*-1,1'-biindanylidene¹⁰ (**2**) in both glycerol and methylcyclohexane at various temperatures was also studied. The structure of **2** requires that complete π overlap between each benzene ring and the p orbital of the ethylenic carbon to which it is attached be maintained throughout the twisting of the central bond in the excited state.

(8) I. B. Beriman has informed us that he has obtained a value of $\phi_f = 0.92$ for indeno[2,1-*a*]indene at room temperature.

(9) Cf., also, ref 4e, footnote 37.

(10) The synthesis and photochemistry of **2** will be presented in a forthcoming publication by J. Saltiel, O. C. Zaffriou, and K. Neuberger, in preparation.



Results and Discussion

Absorption and Fluorescence Spectra. The room temperature absorption spectrum of **2** is strikingly similar to the 77°K spectrum of **1** (see Figure 1). This confirms the earlier suggestion by Platt¹¹ that the spectrum of **1** at room temperature contains some short wavelength absorption in the ¹B band¹² which results from coupled higher energy vibrational transitions due to twisting of the phenyl groups about the 1, α and 1', α' bonds. As the viscosity of the medium is increased by lowering the temperature, the probability of phenyl group twist in **1** decreases and the resulting spectrum shows the vibrational components of the ¹B band to be far better resolved.

Changing the solvent from a nonviscous hydrocarbon to glycerol has the expected effects on the absorption spectra (Figure 1). The ¹B band undergoes a bathochromic shift of 2–4 nm (0.5 and 0.9 kcal/mol for **1** and **2**, respectively) due to stabilization of the excited state by the more polar solvent. The spectrum of **1** also shows greater resolution among the vibrational components of the ¹B band (all three are resolved maxima), consistent with the hypothesis of Platt.¹¹

The corrected fluorescence spectra of **1** and **2** in glycerol at 25° are also shown in Figure 1. (These spectra in hydrocarbon solvents are somewhat less structured and displaced slightly to higher energy.) Lowering the temperature increases the resolution only subtly and at no temperature investigated in this work did the resolution of emission approach that of the corresponding absorption spectrum. Interestingly, the emission spectrum of **1** in glycerol is somewhat better resolved (three maxima and one shoulder) than that of **2** (two maxima and two shoulders).

Fluorescence Quantum Yields. Fluorescence quantum yields for **1** and **2** in glycerol at various temperatures are reported in Table I. Table II presents fluorescence and isomerization data from the earlier work^{4c,e} along with our ϕ_f values for several temperatures. Our ϕ_f values are much higher than the early values of Fischer and coworkers^{4c} which prompted this work. The agreement is better with the recent values of Sharafy and Muszkat.^{4e} Comparison of the *trans* \rightarrow *cis* isomerization quantum yields ($\phi_{t \rightarrow c}$)^{4c} with our ϕ_f values or those in ref 4e shows that the processes of fluorescence and isomerization remain coupled with varying temperature in a highly viscous solvent such as glycerol.^{9,13}

In Table III are listed ϕ_f values at 25° which were obtained for **1** and **2** in two solvents of widely differing viscosity.¹⁴ The ϕ_f of **2** is profoundly affected by this

(11) R. N. Beal and E. M. F. Roe, *J. Chem. Soc.*, 2775 (1953).

(12) D. L. Beveridge and H. H. Jaffé, *J. Amer. Chem. Soc.*, **87**, 5340 (1965).

(13) See ref 5c for some reservations concerning the accuracy of the $\phi_{t \rightarrow c}$ quantum yields.

(14) Previously reported⁴ fluorescence studies of **1** in methanol indicate that the increased ϕ_f values observed in glycerol should not be ascribed to the protic or polar nature of this solvent, but to its high viscosity.

Table I. Temperature Dependence of Fluorescence Quantum Yields for **1** and **2** in Glycerol

| 1 | | 2 | |
|---------------------|----------|---------------------|----------|
| $T, ^\circ\text{C}$ | ϕ_f | $T, ^\circ\text{C}$ | ϕ_f |
| 63 | 0.058 | 67 | 0.016 |
| 57 | 0.069 | 55 | 0.018 |
| 50 | 0.087 | 46 | 0.044 |
| 43 | 0.11 | 35 | 0.085 |
| 36 | 0.16 | 28 | 0.12 |
| 30 | 0.20 | 24 | 0.16 |
| 28 | 0.22 | 14 | 0.29 |
| 25 | 0.26 | 10 | 0.37 |
| 20 | 0.32 | 7 | 0.45 |
| 15 ^a | 0.38 | 4 | 0.50 |
| 11 | 0.43 | -1 | 0.60 |
| 10 | 0.44 | -4 | 0.64 |
| 6 | 0.48 | -9 | 0.74 |
| 5 | 0.49 | -13 | 0.80 |
| -1 | 0.58 | -17 | 0.85 |
| -7 | 0.65 | -20 | 0.89 |
| -11 | 0.67 | -24 | 0.91 |
| -16 | 0.71 | | |
| -20 | 0.73 | | |
| -25 | 0.76 | | |

^a Two determinations at this temperature gave the same value for ϕ_f .

Table II. Fluorescence and Trans \rightarrow Cis Isomerization Quantum Yields of Stilbene in Glycerol at Various Temperatures

| $T, ^\circ\text{C}$ | ϕ_f^a | $\phi_{t \rightarrow c}^a$ | ϕ_f^b |
|---------------------|-------------|----------------------------|-------------------|
| 50 | (0.075) | 0.55 | 0.09 |
| 25 | 0.15 (0.16) | 0.52 | 0.26 |
| 0 | 0.27 (0.42) | 0.25 | 0.56 |
| -25 | 0.37 (0.57) | 0.10 | 0.76 |
| -80 | 0.46 (0.75) | 0.01 | 0.83 ^c |

^a Data taken from ref 4c, data in parentheses are from ref 4e.
^b Data from this work. ^c A limiting value predicted by our data; *vide infra*.

Table III. Viscosity Dependence of Fluorescence Quantum Yields for **1** and **2** at 25^o

| Solvent | η^a | ϕ_f of 1 | ϕ_f of 2 |
|-------------------|---------------------|----------------------|----------------------|
| Methylcyclohexane | 0.0069 ^b | 0.05 | 0.002 |
| Glycerol | 7.0 ^c | 0.26 | 0.14 |

^a Viscosity coefficient at 25^o, in poise. ^b Value obtained from ref 28. ^c Value obtained from ref 27.

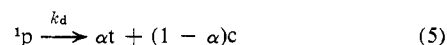
viscosity change.¹⁵ Note that while the fluorescence efficiency of **1** has increased fivefold in going to the more viscous medium, the ϕ_f of **2** has increased by a factor of 70 for the same solvent change. Consistent with this viscosity dependence, lowering the temperature (and thereby increasing the viscosity of glycerol) causes a much steeper rise in the ϕ_f of **2** relative to **1** so that at -25^o, ϕ_f of **2** has reached a value of 0.92.

Kinetics of the Singlet State. The above results remove any serious reservations concerning the validity of the singlet mechanism⁵ as the route to unperturbed¹⁶ stilbene isomerization by direct irradiation. The sug-

(15) The ϕ_f of **2** in degassed glycerol was found to be the same as for the undegassed solution, indicating that diffusional quenching by oxygen is not responsible for the variation in fluorescence efficiency.

(16) Heavy atom substitution as in *p*-bromostilbene enhances intersystem crossing and leads to a substantial triplet contribution in the direct photoisomerization. J. Salties and E. D. Megarity, manuscript in preparation.

gested mechanism for decay of *trans*-stilbene singlets follows



Here *t*, *c*, and *p* represent *trans*, *cis*, and twisted (phantom) geometries, while k_f , k_{is} , k_{obsd} , and k_d are the rate constants for fluorescence, intersystem crossing, twisting, and decay, respectively. The fluorescence yield is given by eq 6. Since step 4 is temperature dependent, k_{obsd} may be described by the Arrhenius eq 7,

$$\phi_f = k_f / (k_f + k_{is} + k_{obsd}) \quad (6)$$

with substitution into eq 6 yielding expression 8. If

$$k = A e^{-E^\ddagger/RT} \quad (7)$$

with substitution into eq 6 yielding expression 8. If

$$\frac{1}{\phi_f} - 1 + \left(\frac{k_{is}}{k_f} \right) = \frac{A e^{-E^\ddagger/RT}}{k_f} \quad (8)$$

$k_{is}/k_f < 1$ (*i.e.*, the rate of intersystem crossing is slow relative to that of fluorescence), plots of $\ln(1/\phi_f - 1)$ vs. $1/T$ will be linear, with a slope of $-E^\ddagger/R$ and intercept of $\ln(A/k_f)$. An expression analogous to eq 8 has been employed by Dyck and McClure,³ but their approach favored assignment of the temperature-dependent step to intersystem crossing rather than to geometric twist within the singlet manifold. These authors also determined the fluorescence rate constant (k_f) to be $4 \times 10^8 \text{ sec}^{-1}$ from integration of the ¹B band in the absorption spectrum of **1**.^{3,17}

Using the above treatment, Megarity¹⁹ plotted the fluorescence and isomerization data reported by Malkin and Fischer^{4a} for **1** in methylcyclohexane. The results were averaged to give an activation energy of 2.7 kcal/mol and a frequency factor of $4.1 \times 10^{11} \text{ sec}^{-1}$.

Table IV. Temperature Dependence of the Fluorescence Quantum Yield for **2** in Methylcyclohexane

| $T, ^\circ\text{C}$ | $\phi_f \times 10^3$ | $T, ^\circ\text{C}$ | $\phi_f \times 10^3$ |
|---------------------|----------------------|---------------------|----------------------|
| 54 | 1.7 | 24 | 2.3 |
| 45 | 1.8 | 15 | 2.6 |
| 36 | 2.0 | 8 | 2.8 |
| 29 | 2.2 | | |

Values of ϕ_f for **2** in methylcyclohexane over a 45^o temperature range are shown in Table IV. The plot of $\ln(1/\phi_f - 1)$ vs. $1/T$ (^oK⁻¹) is linear, giving an ac-

(17) The assumption of a temperature and medium independent k_f , made throughout this discussion, is supported by the relative insensitivity of the absorption and emission spectra of **1** and **2** to these changes (see above). Although this assumption appears to be valid for several other systems as well (see below), variations in k_f have been found in several polyenes.¹⁸

(18) J. P. Dalle and B. Rosenberg, *Photochem. Photobiol.*, **12**, 151 (1970).

(19) E. D. Megarity, Ph.D. Thesis, Florida State University, Tallahassee, Fla., 1969.

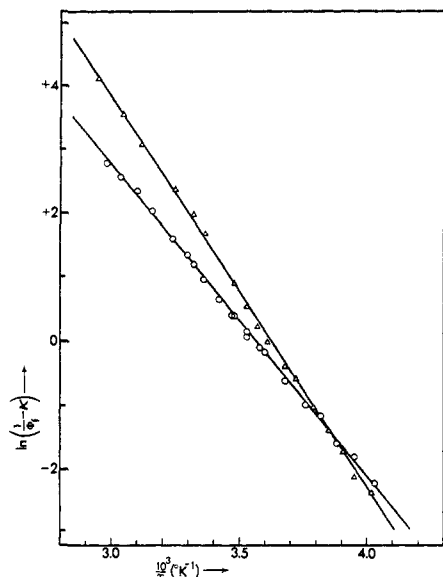


Figure 2. Arrhenius plots for 1 (O) and 2 (Δ) in glycerol. The κ values on the ordinate scale are 1.20 and 1.00 for 1 and 2, respectively.

tivation energy of 2.0 kcal/mol and, using $k_t = 4 \times 10^8 \text{ sec}^{-1}$ for 2,²⁰ a frequency factor of $4.8 \times 10^{12} \text{ sec}^{-1}$.

The fluorescence data for 1 and 2 in glycerol (Table I) were also treated by application of eq 8 and the resulting plots are shown in Figure 2. The assumption that $k_{is}/k_t \ll 1$ does not hold for 1 in glycerol, since a plot of $\ln(1/\phi_t - 1)$ vs. $1/T$ gives an upward curvature (decreased negative slope) at lower temperatures. Values for k_{is}/k_t were estimated by using the method of Kirby and Steiner²² and the best straight line relationship was obtained for $k_{is}/k_t = 0.20$. This ratio of temperature-independent rate constants predicts a limiting ϕ_t of 0.83 for 1 in glycerol at low temperatures where the rate of twisting is too slow to compete with fluorescence (see footnote c of Table II). It may also be shown from the above ratio that at 25°, 5% of the transoid excited states arising from 1 undergo intersystem crossing in glycerol.²³ Further application of this reasoning²³ to quantum yield studies in a nonviscous solvent such as methylcyclohexane (see Table III), where much photoisomerization work has been conducted,⁴ predicts that only 1% of the first excited planar states originating from 1 enter the triplet state at 25°, *i.e.*, the room temperature photochemical processes available to 1 arise almost exclusively within the singlet manifold in nonviscous media. An excellent linear relationship for 2 is obtained assuming $k_{is}/k_t \ll 1$, Figure 2, predicting a limiting $\phi_t \approx 1.0$ in glycerol at low temperatures for this molecule.

Assuming the k_t values to remain unchanged in going from methylcyclohexane to glycerol,¹⁷ Arrhenius parameters were obtained from the glycerol plots in Figure 2: for 1, $E^\ddagger = 9.7 \text{ kcal/mol}$, $A = 1.3 \times 10^{16} \text{ sec}^{-1}$; for 2 $E^\ddagger = 12.3 \text{ kcal/mol}$, $A = 2.1 \times 10^{18} \text{ sec}^{-1}$.

(20) The k_t for 2 was determined to be $4 \times 10^8 \text{ sec}^{-1}$ by measuring the relative areas of the ¹B bands in 1 and 2, using a k_t of $4 \times 10^8 \text{ sec}^{-1}$ for 1, and applying the Einstein equation for the probability of spontaneous emission.²¹

(21) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 173.

(22) E. P. Kirby and R. F. Steiner, *J. Phys. Chem.*, **74**, 4480 (1970).

(23) Since $k_{is}/k_t = \phi_{is}/\phi_t$, given that $\phi_t = 0.26$ at 25° from Table I, it follows that $\phi_{is} = 0.05$ at 25°.

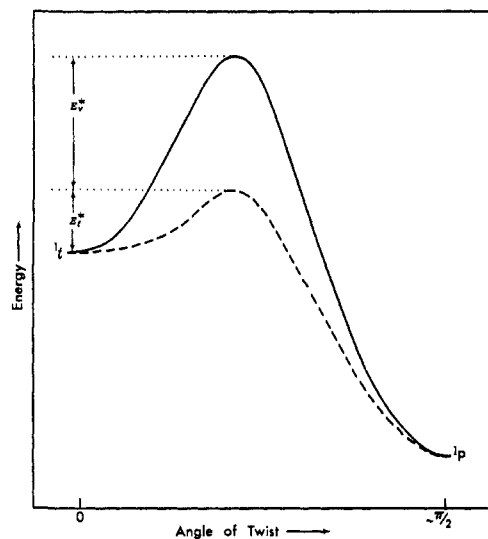


Figure 3. Proposed potential energy curves for first excited state twisting of 1 in solvents of low (---) and high (—) viscosity; the depth of the energy minimum at 1^1p is arbitrary.

Two things become immediately apparent when considering these values. (1) The activation energies are considerably higher than corresponding values in methylcyclohexane, suggesting that the high viscosity of glycerol has played a major role in restricting the twisting process in the excited transoid states of 1 and 2;¹⁴ (2) the frequency factors obtained in glycerol are far too large to be assigned to a unimolecular twisting or isomerization process,²⁴ suggesting that they may actually be composed of two or more frequency factors.

Model to Account for Viscosity Effects. The model depicted in Figure 3 explains the data. In solvents of low viscosity (*i.e.*, methylcyclohexane) there is an inherent thermal barrier to twisting about the central bond, E_t^\ddagger , in the first excited state of 1 and 2, with which a temperature-dependent rate constant, k_t , is associated. In certain viscosity regions the solvent imposes an additional barrier which must also be overcome before twisting may take place. This viscosity-dependent barrier, E_v^\ddagger , has associated with it a viscosity-dependent rate constant, k_v , and is presumed to arise from a restriction of changes in solute geometry by the slower rate at which the solvent cage is capable of rearranging. The over-all activation energy observed in viscous media may therefore be expressed as the arithmetic sum of an inherent thermal barrier and a solvent-dependent viscosity barrier, *i.e.*, $E_{\text{obsd}}^\ddagger = E_t^\ddagger + E_v^\ddagger$.

In testing this model, three basic equations (9–11) have been applied to the system from which relationships are derived permitting examination of the observed rate constant for twist with changes in temperature and viscosity. Since the thermal and viscosity-dependent steps are assumed to be one and the same, the over-all rate constant for twist, k_{obsd} , can be expressed as the product of thermal and viscosity-dependent rate constants, k_t and k_v , respectively, eq 9. For an

$$\ln k_{\text{obsd}} = \ln k_t + \ln k_v \quad (9)$$

activated process, the temperature dependence of the

(24) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1953.

rate constant may be defined in terms of the Arrhenius equation, eq 10. The temperature dependence of

$$\ln k_t = \ln A_t - E^\ddagger_t/RT \quad (10)$$

viscosity may be approximately expressed in terms of the Andrade equation, eq 11, where η is the viscosity

$$\ln \eta = \ln A_\eta + E^\ddagger_\eta/RT \quad (11)$$

coefficient in poise, E^\ddagger_η is the energy barrier which must be overcome by the solvent before the elementary flow process can occur (*i.e.*, activation barrier for viscous flow), and A_η is a constant for a given solvent system. Since eq 11 relates $\ln \eta$ to $1/T$, we may solve this equation for $1/T$ and substitute into the Arrhenius equation in unsubscripted form to obtain eq 12 which

$$\ln k = \ln A + E^\ddagger/E^\ddagger_\eta \ln A_\eta - E^\ddagger/E^\ddagger_\eta \ln \eta \quad (12)$$

expresses the rate constant in viscosity terms. If eq 12 is applied to a system where viscosity is varied while the temperature is held constant, then the changes in rate constant observed under these conditions may be ascribed solely to viscosity dependence, eq 13, where

$$\ln k_v = \ln A_v + E^\ddagger_v/E^\ddagger_\eta \ln A - E_v/E_\eta \ln \eta \quad (13)$$

k_v and E_v are the viscosity-dependent rate constant and activation barrier, respectively, A_v is a frequency factor associated with k_v and other terms are as previously described.

In order to solve for E^\ddagger_v uniquely, it was necessary to conduct an experiment which allowed variation of the viscosity of the medium at constant temperature. A mixed solvent system of glycerol-water was chosen for this purpose. Several ϕ_t values for 1 and 2 were obtained from neat glycerol to 70% glycerol-water at 20° and are given in Table V.²⁵

Table V. Viscosity Dependence of Fluorescence Quantum Yields for 1 and 2 in Glycerol-Water at 20°

| Wt % glycerol | η , poise | ϕ_t for 1 | ϕ_t for 2 |
|---------------|----------------|-------------------|-------------------|
| 100 | 14.99 | 0.32 | 0.19 |
| 97.5 | 8.85 | 0.27 | 0.14 |
| 95.0 | 5.45 | 0.24 | 0.12 |
| 90.0 | 2.35 | 0.19 | 0.07 ₀ |
| 85.0 | 1.13 | 0.15 | 0.047 |
| 80.0 | 0.62 | 0.12 | 0.031 |
| 75.0 | 0.36 | 0.10 | 0.023 |
| 70.0 | 0.23 | 0.07 ₅ | 0.017 |

Expressions 14–16 follow from eq 9–11 and 13 and may be used in interpreting all of the above ϕ_t values for 1 and 2.

Effect of Varying Temperature on k_{obsd} . A plot of \ln

$$\ln k_{\text{obsd}} = \ln A_t + \ln A_v - (E^\ddagger_t + E^\ddagger_v)/RT \quad (14)$$

k_{obsd} vs. $1/T$ will be linear (see Figure 2)²⁶ so long as the experiment is carried out in the same solvent (thereby ensuring that E^\ddagger_v and $\ln A^\ddagger_v$ remain constant) and

(25) ϕ_t values below 70% glycerol are not reported because solubility becomes a problem and refractive index corrections become important.

(26) The Arrhenius plots in Figure 2 are actually plots of $\ln(k_{\text{obsd}}/k_t)$ vs. $1/T$ (see eq 3), where k_t is assumed independent of temperature and viscosity.¹⁷ While division of k_{obsd} by a constant has no effect on the slopes of these plots, the $\ln k_t$ term must be added to the intercepts in order to obtain the frequency factors. This operation is required as well for application of eq 15 and 16, Figures 3 and 4, respectively.

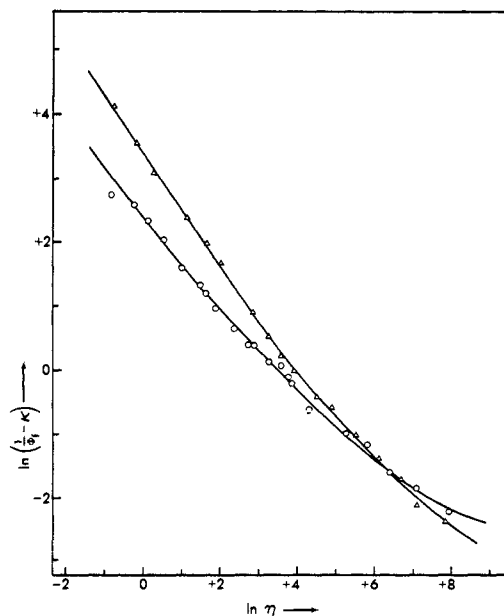


Figure 4. Plot of $\ln(k_{\text{obsd}}/k_t)$ vs. $\ln \eta$ in neat glycerol at varying temperatures for 1 (O) and 2 (Δ). κ values are 1.20 and 1.00 for 1 and 2, respectively.

provided that both thermal and viscosity-dependent barriers remain fully operative over the entire temperature range investigated (see Application of the Model for deviations from linearity). The slope of the plot is proportional to the sum of thermal and viscosity-dependent barriers. The intercept represents a product of frequency factors arising from thermal and viscosity effects, thus explaining the large magnitude of the observed frequency factors predicted from these plots.

Effect of Varying Viscosity on k_{obsd} at Varying Temperatures. Plots of $\ln(k_{\text{obsd}}/k_t)$ ²⁶ vs. $\ln \eta$ for 1 and 2 are

$$\ln k_{\text{obsd}} = \ln A_t + \ln A_v + \frac{E^\ddagger_t + E^\ddagger_v}{E^\ddagger_\eta} \ln A_\eta - \frac{E^\ddagger_t + E^\ddagger_v}{E^\ddagger_\eta} \ln \eta \quad (15)$$

shown in Figure 4. These plots will be linear only to the extent that $1/T$ varies linearly with $\ln \eta$, eq 11. A plot of $\ln \eta$ vs. $1/T$ for glycerol²⁷ indicates that, strictly speaking, this is not true over the wide temperature range employed here. The plots in Figure 4 reflect this nonlinearity, giving decreased slopes at high values of $\ln \eta$ where E^\ddagger_η for glycerol increases. At any given viscosity, however, the slope and intercept may be determined graphically. A graphic determination of slopes and intercepts for 1 and 2 was carried out at 20° ($\ln \eta = 2.3$) for comparison with the constant temperature experiment. Using 20° values for glycerol of $E^\ddagger_\eta = 15.1$ kcal/mol and $\ln A_\eta = -24.75$,²⁷ the following activation barriers were obtained from eq 15: $E_t + E_v = 9.7$ kcal/mol for 1, 13.0 kcal/mol for 2.

Effects of Varying Viscosity on k_{obsd} at Constant Temperature. A plot of $\ln k_{\text{obsd}}$ vs. $\ln \eta$ at constant temperature is not expected to be linear over a wide viscosity range (see Figure 5),²⁶ since varying the viscosity by

(27) For representative values on the variation of η with temperature, see T. A. Litovitz, *J. Chem. Phys.*, 20, 1088 (1952).

Table VI. Activation Energies and Frequency Factors for 1 and 2 in Glycerol

| Source | Parameter | Activation energies, kcal/mol | | Parameter | Log frequency factors | |
|--------|-----------------------------------|----------------------------------|------|-----------------------|--------------------------|------|
| | | 1 | 2 | | 1 | 2 |
| a | $E^{\ddagger}_t + E^{\ddagger}_v$ | 9.7 | 12.3 | $\text{Log}(A_t A_v)$ | 16.1 | 18.3 |
| b | E^{\ddagger}_v | 6.2 | 9.9 | $\text{Log}(A_t A_v)$ | 16.4 | 18.2 |
| c | E^{\ddagger}_t | 3.5 | 2.4 | | | |
| d | $E^{\ddagger}_t + E^{\ddagger}_v$ | 9.7 | 13.0 | $\text{Log}(A_t A_v)$ | 16.4 | 19.2 |

^a Equation 14. ^b Equation 16. ^c Predicted. ^d Equation 15.

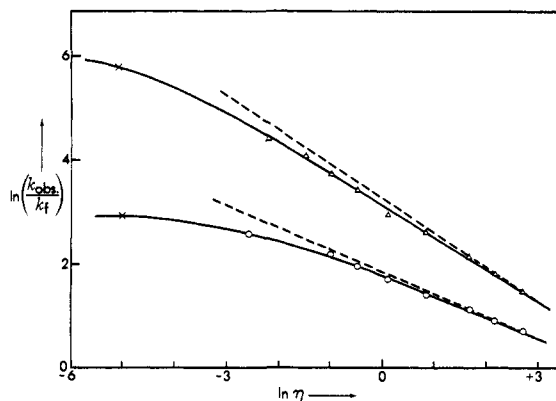


Figure 5. Plot of $\ln(k_{\text{obsd}}/k_t)$ vs. $\ln \eta$ at 20° in glycerol-water mixed solvent system for 1 (O) and 2 (Δ) with κ 's of 1.20 and 1.00, respectively. Dashed lines represent slopes in the region of neat glycerol. Points at low viscosity (X) were obtained in methylcyclohexane (Table III).

$$\ln k_{\text{obsd}} = \ln A_t + \ln A_v -$$

$$\frac{E^{\ddagger}_t}{RT} + \frac{E^{\ddagger}_v}{E^{\ddagger}_\eta} \ln A_\eta - \frac{E^{\ddagger}_v}{E^{\ddagger}_\eta} \ln \eta \quad (16)$$

changing the solvent medium will vary E^{\ddagger}_η and A_η which, in turn, affect the magnitude of E^{\ddagger}_v and A_v . Note also that at reduced viscosities, even if $E^{\ddagger}_v/E^{\ddagger}_\eta$ is constant, E^{\ddagger}_v must certainly be reduced so that in the presence of a second thermal barrier, the $\ln k_{\text{obsd}}$ values will change less rapidly than at higher viscosities where E^{\ddagger}_v plays a major role. This reasoning justifies inclusion of the methylcyclohexane points at $\ln \eta = -5$ in Figure 5. In this region, the effect of viscosity on the rate of twist is considerably reduced. The significance of eq 16 rests on the fact that a determination of the slope ($E^{\ddagger}_v/E^{\ddagger}_\eta$) over a limited viscosity range will give a measure of E^{\ddagger}_v in this range. (Here, as with eq 15, E^{\ddagger}_η is a function only of solvent and may be determined independently.) Since the value of E^{\ddagger}_v in neat glycerol is desired (for purposes of applying it to the variable-temperature work done in this solvent), the initial slopes for 1 and 2 were graphically obtained in the region from 95 to 100% glycerol. Using a value of 15.1 kcal/mol for E^{\ddagger}_η of neat glycerol at 20°,²⁷ the E^{\ddagger}_v values were found to be 6.2 kcal/mol for 1 and 9.9 kcal/mol for 2.

Discussion of Results for the Model. The kinetic parameters obtained by applying eq 14–16 to the experiments conducted with 1 and 2 are collected in Table VI. Comparison of the over-all activation energies from eq 14–15 shows them to be in excellent agreement. Since the same fluorescence data were used in both these equations, this agreement, while not surprising, speaks well for the self-consistency of the equations used to reach it.

In terms of the over-all rate constant for the twisting process, evaluation of the kinetic parameters obtained from eq 14 shows that the mean lifetimes for twist ($1/k_{\text{obsd}}$) in glycerol are 1×10^{-9} and 5×10^{-10} sec for 1 and 2, respectively, at 25°. This compares with lifetimes of 2×10^{-10} and 5×10^{-12} sec for 1 and 2, respectively, in methylcyclohexane, *i.e.*, the increased viscosity of the medium has produced a fivefold decrease in the rate of twist for 1, and a 100-fold decrease in this rate for 2.

The E^{\ddagger}_v values obtained for 1 and 2 from eq 16 reflect the marked dependence of the twisting process of these molecules on the solvent viscosity. Note that for 2 in glycerol, 81% of the $E^{\ddagger}_{\text{obsd}}$ may be assigned to a viscosity-dependent barrier while for 1, 64% of the observed barrier arises from viscosity. The greater sensitivity of 2 to solvent viscosity is consistent with the fact that it is a somewhat larger molecule requiring a greater volume for twisting and hence must interact more strongly with the surrounding solvent cage in order to accomplish this task.

Determination of E^{\ddagger}_v from eq 16 allows the prediction of the intrinsic thermal barrier which is still operative in glycerol. These predicted E^{\ddagger}_t values may be compared with the observed activation energies for 1 and 2 in methylcyclohexane, a solvent of low viscosity where contributions from E^{\ddagger}_v may be considered small to negligible. The $E^{\ddagger}_{\text{obsd}}$ values in methylcyclohexane, 2.7 and 2.0 kcal/mol for 1 and 2, respectively, are in very good agreement with the predicted E^{\ddagger}_t values (Table V).

A more refined comparison between predicted E^{\ddagger}_t values in glycerol and $E^{\ddagger}_{\text{obsd}}$ values in methylcyclohexane is possible by examining the plot for 2 in Figure 5 and utilizing solvent effects on the absorption spectra of 1 and 2. Note in Figure 5 that while the slope of the viscosity curve for 1 approximates zero at methylcyclohexane viscosity, the viscosity curve for 2 is just beginning to level off in this region. This suggests that $E^{\ddagger}_{\text{obsd}}$ for 2 in methylcyclohexane contains contributions from an E^{\ddagger}_v term (further evidence that 2 is highly sensitive to solvent viscosity). Graphic determination of the slope at methylcyclohexane viscosity (slope = -0.22) may be combined with an E^{\ddagger}_η for this solvent of 2.4 kcal/mol²⁸ to yield a value for E^{\ddagger}_v of 0.5 kcal/mol for 2 at this viscosity. Hence, of the measured $E^{\ddagger}_{\text{obsd}} = 2.0$ kcal/mol for 2 in methylcyclohexane, the inherent thermal barrier $E^{\ddagger}_t = 1.5$ kcal/mol.

Next, we recall that the absorption spectra of 1 and 2 undergo bathochromic shifts of 0.5 and 0.9 kcal/mol in going from methylcyclohexane to glycerol, presum-

(28) For representative values which allow this determination, see "International Critical Tables," Vol. VII, E. W. Washburn, Ed., McGraw-Hill, New York, N. Y., 1930.

ably due to the increased stabilization of the excited state by the more polar solvent. If solvent stabilization effects on the transition state leading to 1p are assumed to be the same as those experienced by the ground state, then this additional stabilization to the transoid excited state must also be overcome before twisting can occur, *i.e.*, the thermal barriers for **1** and **2** will be higher by 0.5 and 0.9 kcal/mol, respectively, in glycerol than in methylcyclohexane. This adjustment to the predicted E_t values in glycerol gives expected thermal barriers in methylcyclohexane of 3.0 and 1.5 kcal/mol for **1** and **2**, respectively. The refined experimental methylcyclohexane values for E_t are 2.7 and 1.5 kcal/mol for **1** and **2**, respectively, in excellent agreement with the solvent adjusted predictions.

The difference in E_t values for **1** and **2** suggests that preventing the phenyl groups from twisting about the $1,\alpha$ and $1',\alpha$ bonds aids in the energetics of twisting about the central bond by lowering the inherent thermal barrier. Apparently, maintaining π overlap between the benzene ring and the central ethylenic bond stabilizes the transition state leading to the twisted form. This conclusion may seem surprising when one considers that in those stilbenes where the phenyl groups are forced out of coplanarity by alkyl substitution in the ortho or α positions (steric effect) the thermal barrier to twisting is found to be negligible.^{4b} However, in these cases we most likely start from a different place on the potential energy surface for twist and pass through a different transition state.¹⁰ Alternatively, the difference in E_t for **1** and **2** could be due entirely to alkyl substitution (electronic effect) causing greater stabilization of the transition state for twist than of the planar transoid 1S state.

The frequency factors obtained from eq 14–16 are in remarkable agreement (Table VI). The apparent $\log A_v$ values are considerably smaller than those for $\log A_t$ and, unlike the latter, they appear to be directly related in magnitude to the size of E^{\ddagger}_v (compare the E^{\ddagger}_v terms for **1** and **2** with the corresponding $\log A_t A_v$ values in Table VI). Application of eq 14–16 does not permit a unique solution for $\log A_v$. However, the paralleled variation of E^{\ddagger}_v with $\log A_t A_v$ does suggest that the viscosity-dependent parameters exhibit an isokinetic relationship²⁹ which may be used to determine the magnitude of $\log A_v$ independently (see below).

Application of the Model to Other Singlet State Systems. It is interesting to note that, as early as 1955, Becker and Kasha³⁰ predicted the existence of a viscosity-dependent barrier on the potential energy surface for twisting in the first excited state of **1**. Viscosity effects are not unique to stilbene, having been observed in several other singlet state unimolecular rate processes.^{31–34}

Oster and Nishijima studied the effects of viscosity on the fluorescence intensity of auramine O (4,4'-dimethylaminodiphenylketimine hydrochloride, **3**) in

(29) (a) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955); (b) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, pp 315–402.

(30) R. S. Becker and M. Kasha, "Luminescence of Biological Systems," F. H. Johnson, Ed., AAAS, Washington, D. C., 1955.

(31) G. Oster and Y. Nishijima, *J. Amer. Chem. Soc.*, **78**, 1581 (1956).

(32) E. J. Bowen and J. Sahu, *J. Phys. Chem.*, **63**, 4 (1959).

(33) J. W. Eastman and E. J. Rosa, *Photochem. Photobiol.*, **7**, 189 (1968).

(34) D. G. Whitten, private communication. We thank Professor Whitten for bringing these data to our attention.

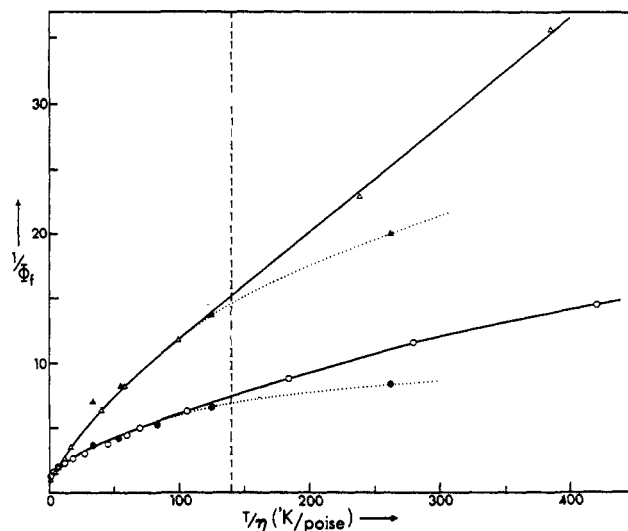
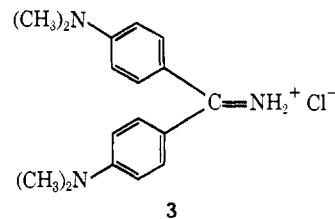


Figure 6. Plot of $1/\phi_f$ vs. T/η for **1** (O) and **2** (Δ) in glycerol. Solid points represent data from constant temperature experiments. The range of T/η values covered in ref 31 is to the left of the dashed vertical line.



glycerol at various temperatures (6–30°) and in dextrose–glycerol–water mixtures at 25°. An increase in ϕ_f was observed with increasing viscosity of the medium and was attributed to a reduction in the rate of rotation of the phenyl groups. Applying the Stokes–Einstein relation, eq 17 was derived,³¹ where α is the

$$1/\phi = 1 + \alpha + \beta(T/\eta) \quad (17)$$

ratio of nonradiative to radiative rate constants (analogous to k_{is}/k_f for the stilbenes, eq 8) and β is a proportionality constant. A plot of $1/\phi_f$ vs. T/η was found to give a good straight line between 10 and 30°, with higher and lower temperatures showing positive and negative deviations from linearity, respectively. A limiting ϕ_f of 0.05 was predicted from the intercept of the extrapolated straight line and the observation of ϕ_f values higher than this predicted limiting value was attributed to delayed fluorescence.

The relationship proposed by Oster³¹ was applied to the fluorescence data for **1** and **2** in glycerol. The appropriate values are plotted in Figure 6, with the dashed line representing the range of T/η values covered by the Oster study. The plot shows that, at least for **1** and **2**, a linear relationship does not hold over the wider temperature range investigated in this work. Further a downward curvature of both lines occurs for low values of T/η , just as was observed for **3**.³¹ In the case of **1** and **2** (and probably **3**) delayed fluorescence cannot account for the high ϕ_f values obtained in this range. The data from the constant temperature–varying viscosity experiment agree quite well with data from the variable temperature experiments (Tables I and V) over the temperature range encompassed in the Oster

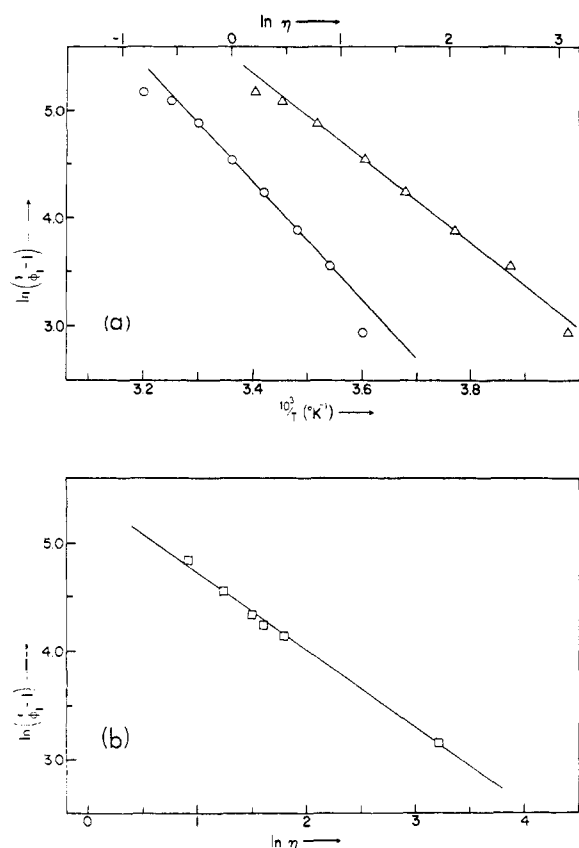


Figure 7. (a) Plot of $\ln(k_{obsd}/k_f)$ vs. $10^3/T$ (O, lower scale) and vs. $\ln \eta$ (Δ , upper scale) for **3** in glycerol at varying temperature. (b) Plot of $\ln(k_{obsd}/k_f)$ vs. $\ln \eta$ at 25° for **3** in dextrose-glycerol-water solutions. Data taken from ref 31.

work, and could have led to the conclusion that ϕ_f is independent of temperature in all three systems. A reduced slope is observed for the constant temperature points only at high values of T/η . Finally, extrapolation of a straight line drawn through points in the T/η range from 10 to 70°K/P predicts limiting ϕ_f values of only 0.44 for **1** and 0.71 for **2**.

In short, eq 17 is unsatisfactory in accounting for the fluorescence data of **1** and **2** since it does not give the predicted linearity and does not distinguish between temperature and viscosity dependence unless a wide temperature range is examined. In addition, it leads to very low estimates of limiting quantum yields.

The model proposed in this work has been used to treat the fluorescence data for **3** in glycerol³¹ and the results are plotted in Figure 7. Application of eq 14 (Figure 7a) gives a linear relationship between 10 and 30°,³⁵ the same range where Oster obtained linearity. At higher temperatures (where $T/\eta > 140$) a decreased slope is obtained while lower temperatures give an increased slope (this is the region where enhanced fluorescence was reported).³¹ The reported low-temperature ϕ_f values may indicate that some new mechanism is operative below 10°, and such values should not be considered further until the temperature range is extended. At temperatures above 10°, however, the results are entirely consistent with the model proposed in this work. The viscosity effect becomes fully operative only at 30°, with higher temper-

(35) In treating these data, $\kappa = 1$ was found to give a good straight line within this region, thus predicting a limiting $\phi_f = 1$.

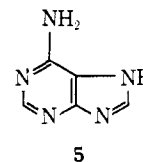
atures showing a decreased activation energy for internal rotation in **3** due to a reduction in the viscosity effect (see earlier discussion of eq 14). In the region analogous to that treated in the original work,³¹ the E_{obsd}^\ddagger is 11.0 kcal/mol and $\log A_{obsd}$ is 18.4.

Application of eq 15 (Figure 7a) was accomplished using the viscosity values determined in ref 31.³⁶ The slope of the linear portion of the plot gives $E_{obsd}^\ddagger/E_\eta = 0.82$, thus predicting $E_{obsd}^\ddagger = 10.9$ kcal/mol³⁶ in excellent agreement with the results of eq 14.

In Figure 7b, ϕ_f values for **3** in dextrose-glycerol-water solutions at 25° are plotted, along with the 25° ϕ_f in glycerol, by application of eq 16. The slope of the resulting straight line, E_{obsd}^\ddagger/E_η , is 0.72, indicating that $E_{obsd}^\ddagger = 9.5$ kcal/mol³⁶ in glycerol. This independent determination of E_{obsd}^\ddagger affords the conclusion that an inherent thermal barrier of 1.5 kcal/mol exists for phenyl group rotation in the first excited state of **3**. Summarizing, application of the proposed model to the 3-glycerol system³¹ predicts that (a) the limiting $\phi_f \approx 1$ ³⁵ and (b) at higher temperatures or in solvents of lower viscosity, there remains an inherent thermal barrier of 1.5 kcal/mol.

Bowen and Sahu studied the effects of temperature and viscosity on ϕ_f for several substituted anthracenes.³² The observations were treated using an expression analogous to eq 8, but the measurements were not considered sufficiently accurate to allow evaluation of contributions to the decay from temperature independent processes and $\kappa = 1$ was assumed.³² Arrhenius parameters for 9-substituted anthracenes are substituent dependent and generally enhanced in the more viscous media. For 9-methylanthracene (**4**), the results give E_{obsd}^\ddagger values of 2–4 kcal/mol and $\log A_{obsd}$ values of 9.2–10.5.^{32, 37} The system **4**-ethanol was reinvestigated by Bennett and McCartin³⁹ and by Lim, Laposa, and Yu.⁴⁰ The activated process has been assigned to $^1S \rightarrow ^2T$ intersystem crossing^{39–42} and the following Arrhenius parameters were obtained: $E_{obsd} = 2.23$ ³⁹ and 2.3 kcal/mol,⁴⁰ and $\log A_{obsd} = 9.7$ ³⁹ and 9.8.⁴⁰ No data are available from which E_ν can be obtained, and it may well be that a significant fraction of E_{obsd} in ethanol is due to E_t .

Eastman and Rosa³³ determined the ϕ_f of adenine (**5**) in several alcoholic glasses over a 200° temperature



range (77–298°K). They found three distinct temperature regions: (1) a low-viscosity region in which the radiationless decay ratio appeared to be proportional

(36) These values are somewhat lower than those reported by Litovitz³⁷ and give an $E_{obsd}^\ddagger = 13.3$ kcal/mol and $\log A_\eta = -9.64$ over the temperature range employed.³¹

(37) Beriman's value of $k_f = 7.36 \times 10^7$ sec⁻¹ in cyclohexane was assumed in calculating $\log A_{obsd}$ values.³⁸

(38) I. B. Beriman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965, p 128.

(39) R. G. Bennett and P. J. McCartin, *J. Chem. Phys.*, **44**, 1969 (1966).

(40) E. C. Lim, J. D. Laposa, and J. M. H. Yu, *J. Mol. Spectrosc.*, **19**, 412 (1966).

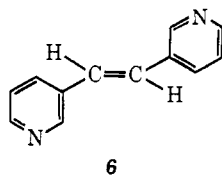
(41) R. E. Kellogg, *J. Chem. Phys.*, **44**, 411 (1966).

(42) R. S. H. Liu and R. E. Kellogg, *J. Amer. Chem. Soc.*, **91**, 250 (1969), and previous papers in this series.

to T/η ; (2) an intermediate-viscosity region where the increase in ϕ_f parallels the increase in viscosity with rate constants following an Arrhenius behavior, giving $E^{\ddagger}_{\text{obsd}}$ of 1–10 kcal/mol and $\log A_{\text{obsd}}$ of 13–14 in the various solvents studied; and (3) a high-viscosity region where the radiationless decay rate constant is much less sensitive to changes in temperature.

Application of eq 14 to the 5-glycerol system³³ was carried out in the intermediate-viscosity region over a 100° temperature range (+50 to -50°) and a linear plot was obtained ($\kappa = 1$) which gives $E^{\ddagger}_{\text{obsd}} = 4.8$ kcal/mol and $\log A_{\text{obsd}} = 14.8$. In the absence of data for a constant temperature-varying viscosity experiment, it is not possible to uniquely solve for E^{\ddagger}_v . However, since $E^{\ddagger}_{\text{obsd}}$ values as low as 1 kcal/mol were observed in the more fluid media, E^{\ddagger}_t must be less than or equal to 1 kcal/mol. Further treatment of these data (see below) will therefore assume that virtually all of the observed barrier arises from an E^{\ddagger}_v term, *i.e.*, $E^{\ddagger}_t = 0$.

Whitten has studied the fluorescence of *trans*-1,2-bis(3-pyridyl)ethylene (6), a nitrogen heterocyclic analog



of 1, over a 40° temperature range in *tert*-butyl alcohol.³⁴ Application of the model to this system gives preliminary results⁴³ which are in very good agreement with those already discussed for the 1-glycerol system. At high temperatures (low η), where the viscosity effect is apparently not operative, an inherent thermal barrier of 2.5 kcal/mol with $\log A_t$ of 11.3 is obtained.⁴⁴ At lower temperatures the viscosity effect becomes operative and $E^{\ddagger}_{\text{obsd}}$ is found to be 6.7 kcal/mol with $\log A_{\text{obsd}} = 14.3$.⁴⁴ Subtraction of E^{\ddagger}_t from $E^{\ddagger}_{\text{obsd}}$ yields $E^{\ddagger}_v = 4.2$ kcal/mol for 6 in *tert*-butyl alcohol.

Taken together, results from the above-cited works indicate a fundamental correlation between E^{\ddagger}_v and $\log A_v$ values. In Figure 8 are plotted the E^{\ddagger}_v values obtained for compounds 1–6 *vs.* the logarithm of observed frequency factors ($\log A_t A_v$). Of the nine points plotted, seven are found to give a good linear fit with a slope of 0.71 and intercept of 11.5. Inherent in the good fit of this plot is the requirement that $\log A_t$ values for these rate processes be very similar, *i.e.*, $\log A_t \approx 11.5$. This is certainly the expectation for 1, 2, 3, and 6, where geometric twisting in the excited state is the process being examined. The fact that the value for 5 falls on this same line suggests that in this compound too a geometric deformation, occurring with an inherent frequency factor similar in magnitude to that observed for twisting, competes with fluorescence. The deviation of the value for 4 from the line was expected since a smaller $\log A_t$ value is involved (see below).

The straight-line relationship in Figure 8 illustrates the existence of an isokinetic relationship²⁹ for the viscosity-dependent parameters determined from the model. This plot may be expressed mathematically

(43) A more extensive temperature range is required for a complete analysis.

(44) The frequency factor was obtained by assuming a radiative rate constant identical with that of 1, $k_f = 4 \times 10^8 \text{ sec}^{-1}$.

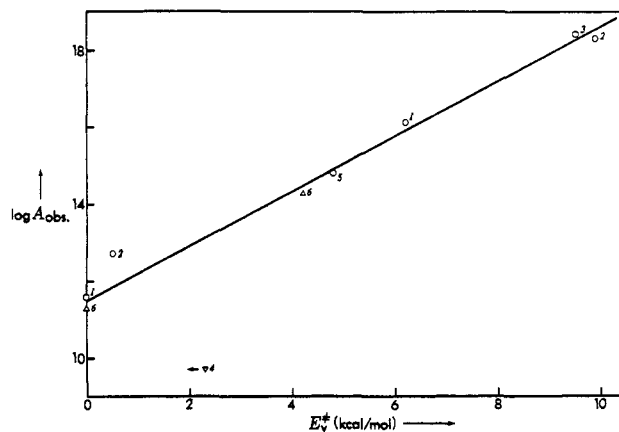


Figure 8. Plot of $\log A_{\text{obsd}}$ *vs.* E_v^{\ddagger} for compounds 1–6 in various solvents: glycerol (O), *tert*-butyl alcohol (Δ), methylcyclohexane (\square), and (∇) ethanol.

by eq 18, where α is the slope of the straight line. Since

$$\log (A_t A_v) = \log A_t + \alpha E_v^{\ddagger} \quad (18)$$

the $\log A_t$ value is approximately constant for the series of rates being considered, *i.e.*, for 1, 2, 3, 6, and probably 5, eq 19 follows and Figure 8 gives $\alpha = 0.71$. In

$$\log A_v = \alpha E_v^{\ddagger} \quad (19)$$

terms of transition state theory, the analogous isokinetic relationship is given by eq 20, where β is de-

$$\delta \Delta H^{\ddagger} = \beta \delta \Delta S^{\ddagger} \quad (20)$$

defined as the isokinetic temperature.²⁹ Where this relationship (eq 20) applies, a series of related reactions involving moderate changes in either structure or solvent show changes in enthalpies and entropies of activation which parallel each other. Equation 19 is a specific example of the more general eq 20.⁴⁵

The very existence of the linear relationship is strong evidence supporting a constant mechanism for the related series of rates. Hence, viscosity appears to affect the kinetics of these processes in the same way. It is probably more than coincidental that for a large number of molecules Arrhenius activation parameters for fluorescence quenching processes cluster in the vicinity of the straight line: $\log A_{\text{obsd}}/k_f = 0.8 E_v^{\ddagger}_{\text{obsd}}$.⁴⁶ It seems likely that the solvent effects treated here underlie Kazakov's relationship with deviations reflecting differences in A_t and k_f values.

Failure of the 2-methylcyclohexane point to fall on the line in Figure 8 may be due to some inaccuracy in determining the low ϕ_f 's and the very approximate fashion in which E_v^{\ddagger} was obtained for this system. Alternatively, the $\log A_t$ for this system could differ somewhat from 11.5. The large deviation of the point for 4-ethanol from the line can be readily rationalized (note that the uncertainty in E_v^{\ddagger} does not greatly affect the deviation of this point from the line). In the case of 4 the thermal process competing with fluorescence is $^1S \rightarrow ^2T$ intersystem crossing^{39–42} and the $\log A_t$ value associated with it must reflect the multiplicity

(45) The Arrhenius-type parameters plotted in Figure 8 have been converted to transition state parameters and β was found to be 294°K, with values of ΔH^{\ddagger}_v and $\Delta S^{\ddagger}_{\text{obsd}}$ ranging from 0 to 9.4 kcal/mol and -8.0 to +23.8 eu, respectively.

(46) V. P. Kazakov, *Opt. Spectrosc. (USSR)*, 18, 27 (1965).

Table VII. Separation of Viscosity and Temperature Effects for Singlet State Systems

| Compd | Solvent | $E_{\text{obsd}}^{\ddagger}$, kcal/mol | Log A_{obsd} | E_{t}^{\ddagger} , kcal/mol | Log A_{t}^{\ddagger} | E_{v}^{\ddagger} , kcal/mol | Log A_{v}^{\ddagger} | $E_{\text{v}}^{\ddagger}/E_{\eta}^{\ddagger}$ | $10^3/T$ range, $^{\circ}\text{K}^{-1}$ | Ref |
|-------|----------------------------|--|--------------------------|---|----------------------------------|---|----------------------------------|---|--|-----------|
| 1 | Methylcyclohexane | 2.7 | 11.6 | 2.7 | 11.6 | 0 | 0 | 0 | 3.3–7.5 | 4a, 17 |
| 2 | Glycerol | 9.7 | 16.1 | 3.5 ^b | 11.7 ^c | 6.2 ^d | 4.4 | 0.41 | 3.0–4.0 | This work |
| | Methylcyclohexane | 2.0 | 12.7 | 1.5 ^b | 12.3 ^c | 0.5 ^d | 0.4 | 0.22 | 3.3–3.7 | This work |
| 3 | Glycerol | 12.3 | 18.3 | 2.4 ^b | 11.2 ^c | 9.9 ^d | 7.1 | 0.66 | 3.0–4.0 | This work |
| | Glycerol | 11.0 | 18.4 | 1.5 ^b | 11.6 ^c | 9.5 ^d | 6.8 | 0.72 | 3.2–3.5 | 30 |
| 4 | Ethanol | 2.3 | 9.7 | | | | | | 3.4–6.2 | 39, 40 |
| 5 | Glycerol | 4.8 | 14.8 | ~0 ^e | 11.4 ^c | 4.8 ^e | 3.4 | 0.32 | 2.9–4.4 | 33 |
| 6 | <i>tert</i> -Butyl alcohol | 2.5 | 11.3 | 2.5 | 11.3 | | | ~0 | <3–3.2 | 34 |
| | <i>tert</i> -Butyl alcohol | 6.7 | 14.3 | 2.5 | 11.3 ^c | 4.2 ^f | 3.0 | 0.34 | 3.3–3.5 | 34 |

^a Calculated from eq 19. ^b Predicted by subtracting E_{v}^{\ddagger} from $E_{\text{obsd}}^{\ddagger}$. ^c Predicted by subtracting log A_{v} from log A_{obsd} . ^d Determined from a constant temperature experiment. ^e Based on assumption that all $E_{\text{obsd}}^{\ddagger}$ is due to viscosity dependence. ^f Predicted by subtracting E_{t}^{\ddagger} at low η from $E_{\text{obsd}}^{\ddagger}$ at high η .

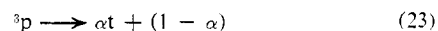
forbiddenness of the process and is expected to be considerably smaller than 11.5. A plot of log A_{obsd} vs. $E_{\text{obsd}}^{\ddagger}$ for 4 in several media reveals the expected trend but the linear correlation is poor.^{32,39,40} A straight line of slope 0.7 may be drawn through the points, with points corresponding to the lower and the higher $E_{\text{obsd}}^{\ddagger}$ values falling below the line. If it is assumed that $E_{\text{t}}^{\ddagger} \leq 2$ kcal/mol the results require log A_{t} to be less than or equal to 9.5.

Arrhenius parameters for compounds 1–6 are summarized in Table VII. Equation 19 was used to calculate log A_{v} values from the observed (or assumed) E_{v}^{\ddagger} 's in those cases where the model was deemed to apply. It is interesting to consider the relative magnitude of the $E_{\text{v}}^{\ddagger}/E_{\eta}^{\ddagger}$ ratios in Table VII. This ratio may be thought to be a measure of the extent of the solute–solvent interaction, a gauge on the microscopic viscosity experienced by the “guest” solute. The greater the physical interaction of a given solute geometric change with the solvent cage, the more nearly the $E_{\text{v}}^{\ddagger}/E_{\eta}^{\ddagger}$ ratio is expected to approach unity. The values in Table VII are consistent with this expectation. Inhibition of ring deformations is probably responsible for the viscosity effect on 5 (and probably 4), which shows a lower ratio than 1 (in the same solvent) where geometric twisting is the viscosity-dependent step. The large volume required for twist in 2 is reflected in a higher ratio than for 1, while a combination of bulk and the alternate twisting of phenyl groups is sufficient to explain the relatively high ratio obtained for 3.

Application of the Model to Triplet State Systems. Triplet–triplet absorption^{47–53} and phosphorescence^{49,53,54} measurements have revealed large viscosity effects on radiationless decay processes of the lowest triplet states of many compounds, which are generally manifested in a strong temperature depen-

dence of the apparent first-order rate constant for triplet decay, with the particular temperature range depending upon the solvent. However, most of these effects are almost certainly due to changes in intermolecular quenching rates involving small concentrations of unknown impurities and/or photoproducts,^{48,51,55} and do not represent viscosity effects on unimolecular decay processes of the triplet state.

The model can be applied straightforwardly to those triplet systems in which the rate-determining step for radiationless decay is not multiplicity forbidden and can be associated with a change in the geometry of the molecule. The decay of *trans*-perhydro- and *trans*-perdeuteriostilbene triplets in glassy hydrocarbon media at 77–87°K provides a possible example.^{52,56} Decay of *trans*-stilbene triplets has been represented by eq 21–23, where step 22 is analogous to step 4 de-



scribing torsional displacement into nonplanar configurations.^{5d} A large deuterium isotope effect in triplet decay rates is observed in the highest viscosity medium studied (3-methylpentane, 77°K).⁵² As the viscosity of the medium is decreased, the lifetime of perhydrostilbene triplets decreases from 1.8×10^{-4} to less than 10^{-4} sec, suggesting that twisting about the central bond is less hindered and formation of twisted triplets (${}^3\text{p}$) competes with decay from planar triplets (${}^3\text{t}$). Correspondingly, the deuterium isotope effect on the decay rate also decreases. Under these conditions decay from ${}^3\text{p}$ is too fast to allow any reversal of step 22, so that its formation becomes rate limiting with respect to *trans*-stilbene triplet decay. Although the data are too limited to allow a quantitative separation of temperature and viscosity effects, they do suggest the presence of a small thermal barrier in the ${}^3\text{t} \rightarrow {}^3\text{p}$ conversion. We are in the process of extending Herkstroeter and McClure's observations so that a

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(56) A second example may be provided by the interesting viscosity dependence of the decay processes of 1,3,1',3'-tetramethyldianthrone triplets.⁵⁴ We thank Professor E. Fischer for bringing this to our attention.

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detailed application of the model to stilbene triplet decay may be attempted.⁵⁷

Lifetimes of stilbene triplets in solution at 30° have been estimated from azulene quenching observations.^{56,58} Under these conditions the ³t to ³p interconversion is freely reversible and intersystem crossing from ³p, k_{23} , is rate limiting.^{54,58} Effective lifetimes $(K_{22}k_{23})^{-1}$ of 10⁻⁸ and 10⁻⁷ sec have been obtained in benzene ($\eta = 0.561$ cP) and *tert*-butyl alcohol ($\eta = 3.32$ cP), respectively. It is not presently known whether the lifetime increase in *tert*-butyl alcohol should be attributed to k_{23} , K_{22} , or to both of these constants. An attractive possibility is that the lifetime difference is associated with medium effects on the molecular geometry change rather than on the intersystem crossing process. However, since intersystem crossing is the rate-limiting step, solvent inhibition of the rate of twisting, although expected, will not affect the effective triplet lifetime. The above kinetic model must be replaced with a thermodynamic model for solvent-solute interaction. It is tentatively suggested that the more viscous media will favor solute conformations having minimum volume requirements. Applied to the stilbene system, this modified model predicts that at equilibrium a larger fraction of the triplets will exist in transoid conformations when solvents with large E_η 's are employed; *i.e.*, K_{22} would be smaller in the more rigid media and more stilbene triplets would be stored in the planar ³t form.

Since it is likely that crossing between different electronic states occurs most efficiently from preferred molecular geometries,^{42,52} the mechanism of solvent interaction suggested above for stilbene triplets in solution may generally apply whenever the radiationless transition is sufficiently forbidden to allow prior equilibration among different molecular geometries.

Mechanism of Viscosity Effect. Since reliable unimolecular triplet lifetime measurements are rather limited, remarks in this section will be confined to those singlet systems which define the isokinetic relationship in Figure 8. It is noteworthy that in all these systems the rate constant for the activated process at the onset of its viscosity dependence falls within an order of magnitude of the rate constant for solvent relaxation, Table VIII. Eastman and Rosa have alluded to this relation-

ship in discussing their results with adenine.³³ It appears that the solvent does not interfere with the rate of the process (low-viscosity region) if the mobility of solvent molecules is fast relative to the rate of a

solute relaxation process. On the other hand, the activated process requires cooperative solvent rearrangement in order to occur if the rate of solvent relaxation is similar to, or somewhat slower than, that of the rate being studied. This physical interaction between the solute and its solvent shell gives rise to the increased activation energy ascribed to a viscosity effect (intermediate-viscosity region).

The close parallelism between relaxation rate and viscosity has been well documented in dielectric studies on pure liquids.⁵⁹⁻⁶¹ Kauzmann⁵⁹ has shown for several liquids that log-log plots of dielectric relaxation rate *vs.* viscosity, both obtained at various temperatures, result in a family of parallel straight lines of unit slope. Hence, the temperature dependence of solvent relaxation equals that of viscosity for many liquids. The observations of viscosity effects on rate constants approaching in magnitude those of solvent relaxation should therefore not be surprising if these rate constants can be associated with some change in solute geometry. Furthermore, dielectric relaxation studies of rigid organic molecules in viscous media⁶² have been found to exhibit viscosity effects analogous to those described in this work with ratios equivalent to $E^\ddagger_\nu/E^\ddagger_\eta$, ranging from 0.17 to 1.1.

In Table VIII observed rate constants are compared with appropriate solvent relaxation rate constants. The temperature used for this comparison represents the highest value for which the viscosity effect is observed. It seems reasonable to conclude that the close similarity between solvent relaxation rates and viscosity-dependent rates is more than coincidental.

It is also noted that this concept of solvent relaxation times may be extended to account for the viscosity-dependent behavior in the high viscosity region 3 of the Arrhenius plots discussed earlier.³³ Here solvent relaxation times are very long, the solvent is highly ordered, and the cooperative nature of solute-solvent interactions found in region 2 is "frozen out."³³ In this solid solution the relaxing solute experiences hindrance from the walls of its now-rigid solvent cage. The result is a decreased probability for reorientation (lower A_i) accompanied by a substantially reduced barrier (tunnelling). An analogous situation has been observed in dielectric studies of guest molecules in solid solution where the E^\ddagger_{obsd} for the solute's relaxation has been found to be < 0.5 kcal/mol.⁶¹

An alternative viscosity treatment has been proposed by Fischer and coworkers.^{40,6} In their approach, a plot of the appropriate quantum yield expression *vs.* $\ln \eta$ gives a slope a , which is designated as the additional free volume (over and above the van der Waals volume of the solute molecule) required for the rearrangement to occur. This additional free volume was expected to be only a fraction of the critical free volume needed for the motion of a solute molecule. Based on this definition, the corresponding parameter in our model is $E^\ddagger_\nu/E^\ddagger_\eta$, the slope obtained from application of eq 16. This ratio may be shown, by analogy to the

Table VIII. Comparison of Solute with Solvent Relaxation Rate Constants

| Compd | Solvent | 10 ³ /T | Log k_{obsd}^a | Log k_{relax}^b |
|-------|-------------------|--------------------|-------------------------|--------------------------|
| 1 | Glycerol | 3.0 | 9.7 | 10.2 |
| 2 | Methylcyclohexane | 3.3 | 11.2 | ~11 ^c |
| | Glycerol | 3.0 | 10.2 | 10.2 |
| 3 | Glycerol | 3.3 | 10.5 | 9.7 |
| 5 | Glycerol | 2.9 | 11.8 | 10.4 |

^a Calculated from kinetic parameters in Table VII. ^b Unless otherwise noted, obtained from ref 59. ^c Estimated from ref 61.

ship in discussing their results with adenine.³³ It appears that the solvent does not interfere with the rate of the process (low-viscosity region) if the mobility of solvent molecules is fast relative to the rate of a

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Fischer approach, to represent that fraction of the critical free volume of solvent required for the twisting process of the solute molecule. The problem with the Fischer treatment^{4c} is that the value of a is obtained by plotting $\ln \eta$ at varying temperatures. Under these conditions the slope of the resulting curve is $(E_{\nu}^{\ddagger} + E_{\nu}^{\ddagger})/E_{\nu}^{\ddagger}$ based on our model (see eq 15). Since no attempt was made to remove contributions from the thermal barrier in treating the earlier data, our $E_{\nu}^{\ddagger}/E_{\nu}^{\ddagger}$ values in glycerol of 0.41 and 0.66 for **1** and **2**, respectively, are more meaningful estimates of the magnitude of the a parameter described in the Fischer scheme.

Experimental Section

Materials. The synthesis of **2** will be described elsewhere;¹⁰ it was recrystallized four times from ether prior to use. *trans*-Stilbene, K & K scintillation grade, was recrystallized from ethanol and sublimed twice. It was shown by glpc to contain less than 0.3% of the *cis* isomer. Spectroquality reagent grade methylcyclohexane from Matheson Coleman and Bell was further purified by passing through a AgNO₃-coated alumina column. Baker's reagent grade glycerol was vacuum-distilled with minimum heat (to avoid bumping) and the middle fractions were collected in a flask cooled to -80°. To remove fluorescing impurities still present in the distillate, the glycerol was washed eight times with spectroquality grade benzene and five times with spectroquality grade methylene chloride. The residual solvent washings were removed by "drying" the glycerol under vacuum (<10⁻³ mm) for 3 days with constant stirring. Quinine sulfate was obtained from Matheson Coleman and Bell and was used without further purification.

Spectra. Ultraviolet absorption spectra were recorded on a Cary 14 spectrophotometer. Spectra above ambient temperature were obtained in 10-mm jacketed quartz cells connected to a constant temperature circulating bath; spectra below ambient temperature were taken using quartz plates spaced 2.5 mm apart and equipped with circulating jackets. Over the temperature ranges investigated, the extinction coefficients for **1** and **2** varied 3% or less at the exciting wavelengths used in the fluorescence work. Fluorescence spectra were recorded on a Hitachi MPF-2A fluorescence spectrophotometer equipped with 150 W Xenon lamp, R-106 photomultiplier, and thermostated sample cell holder. Cylindrical quartz cells (i.d. = 0.125 in., precision bore), mounted with 1-cm² fused quartz cells containing either water or methanol, were used for both quantum yield and variable temperature emission work. Temperatures were monitored with a thermometer using a reference cell and were accurate to ±1°.

Quantum Yield Determinations. Fluorescence quantum yields for **1** and **2** were obtained relative to quinine sulfate in 0.1 N H₂SO₄ ($\phi_f = 0.55^{63-65}$) at 28°. Fluorescence spectra of this actinometer and the stilbenes were corrected for phototube and monochromator response and normalized to the maximum intensity. Relative areas of emission spectra were obtained by weighing the corrected, normalized spectra. Refractive index corrections were made to adjust for the different solvents used with the actinometer and unknown. Concentrations of solutions used for quantum yield measurements (~10⁻⁵ M) were adjusted so that the optical densities of actinometer

and stilbene were equal at the exciting wavelength (290 nm). The absorbance measurements were obtained in 5-cm cells and, when transferred to the fluorescence cells used for emission work (~0.33 cm), the solutions had an absorbance of 0.03 or less at the exciting wavelength. A wavelength of equal emission intensity was determined by comparing actinometer and stilbene corrected spectra. This wavelength was used to monitor relative emission intensities. Relative fluorescence quantum yields for **1** and **2** were then obtained by measuring the relative intensities of emission for actinometer and unknown at this predetermined wavelength and applying eq 24 where I , w , and n are emission intensity, area

$$\phi_x = \phi_a I_x W_x n_x^2 / I_a W_a n_a^2 \quad (24)$$

(weight) of the corrected spectrum, and refractive index of the solvent used, respectively, with subscripts a and x designating actinometer (quinine sulfate) and unknown (**1** and **2**), respectively, and $\phi_a = 0.55^{63-65}$. The fluorescence intensities of **1** and **2** decreased slowly with irradiation time probably owing to *trans* → *cis* isomerization and extrapolation to zero excitation time was used to obtain the I_x values used in eq 24.

Relative fluorescence quantum yields for **1** and **2** at various temperatures were obtained by monitoring the emission intensity at a fixed wavelength (λ_{max}) and assuming that the intensity is proportional to the area of the emission curve at that temperature. (Emission spectra were virtually unchanged with respect to band shape and position over the temperature range studied.)

Solutions for variable viscosity (at constant temperature) fluorescence work were made from glycerol-water mixed solvents which had been prepared by weighing and from aliquots of glycerol stock solutions for **1** and **2**. To adjust for small variations in stilbene concentrations among these solutions, the fluorescence intensity at each viscosity was corrected for difference in optical density at the exciting wavelength. Viscosity coefficients for the mixed solvents used were those of Sheeley.⁶⁶

In all the quantum yield work, fresh solutions were used for each intensity reading since exposure of the sample to exciting light results in *trans* → *cis* isomerization and concomitant loss of fluorescence intensity.

Graphic Data. A least squares analysis of Arrhenius plots gave the following slopes (M), intercepts (b), and correlation coefficients (R)

| Systems | In ordinate (vs. 1/T) | No. of data points | m | b | R |
|----------------------------------|--------------------------|-----------------------|--------|-------|-------|
| 1 -Glycerol | $1/\phi_f - 1.20$ | 21 | -4.87 | 17.35 | 0.999 |
| 2 -Glycerol | $1/\phi_f - 1.00$ | 17 | -6.18 | 22.41 | 0.999 |
| 2 -Methyl- cyclohexane | $1/\phi_f - 1.00$ | 7 | -0.994 | 9.42 | 0.999 |

Graphic solution of viscosity plots at varying temperature in glycerol (see Figure 4) gave the following values at 20° (where $\ln \eta$ is 2.3): for **1**, $m = 0.640$ and $b = 2.19$; for **2**, $m = 0.860$ and $b = 3.26$.

Graphic solution of viscosity plots at constant temperature in glycerol-water mixed solvent system at 20° (see Figure 5) gave the following values in the region of neat glycerol: for **1**, $m = 0.410$ and $b = 1.79$; for **2**, $m = 0.656$ and $b = 3.23$; in the region of methylcyclohexane viscosity, for **2**, $m = 0.220$ and $b = 4.70$.

Acknowledgment. We thank Dr. E. D. Megarity for preliminary fluorescence investigations of **1** and Drs. O. C. Zafriou and K. R. Neuberger for the synthesis of **2**. J. T. D. thanks Dr. J. Arnett for helpful discussions.

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