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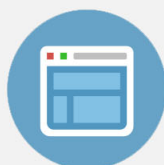
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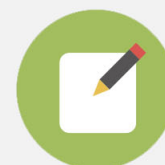


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Photochemical isomerization in solution. Photophysics of diphenyl butadiene

Stephan P. Velsko and Graham R. Fleming^{a)}

Department of Chemistry and the James Franck Institute, The University of Chicago, Chicago, Illinois 60637
(Received 15 October 1981; accepted 18 December 1981)

We have examined the radiative and nonradiative decay rates of diphenyl butadiene in hydrocarbon and polar solvents as a function of temperature and pressure. We demonstrate that the radiative rate constant has a small dependence on solvent polarizability, in contrast to what is observed for diphenylhexatriene. We make an explicit separation of the internal molecular barrier to isomerization and the barrier due to frictional forces in the solvent. The energy of the internal barrier to isomerization is less than the activation energy observed in solution, and depends on the polarizability and polarity of the solvent. In contrast to diphenylhexatriene, it *decreases*, in more polar solvents. We compare the viscosity dependence of the barrier crossing process with Kramers' theory, the recent kinetic theory result of Skinner and Wolynes [J. Chem. Phys. **69**, 2143 (1978)], and the free volume theory of Gegiou, Muzkat, and Fischer, [J. Amer. Chem. Soc. **90**, 12 (1968)]. Our data clearly show that the isomerization process is in the intermediate friction limit and we obtain experimental values for the parameters of the three theories. Over the viscosity region studied, Kramers' and Skinner and Wolynes' equations coincide exactly and do not reproduce the functional dependence of the radiationless rate pre-exponential factor as well as the free volume theory. We speculate that it may be necessary to consider the frequency dependence of medium viscosity.

I. INTRODUCTION

Recently, a great deal of attention has been given to the effects of solvents on the radiationless decay of molecules which are thought to undergo large amplitude structural changes in their excited states. Among these are the triphenyl methane dyes, the cyanine dyes, and the class of diphenyl polyenes. This last class of compounds is of special interest for two reasons. First, because polyenes play important roles in mediating the interaction of light with many natural biological systems, and second, because a consistent theoretical picture of polyene spectroscopy and photoisomerization has emerged over the last ten years. Such a consistent picture of the photophysical kinetics and reaction mechanism is clearly necessary before the interpretation of the solvent influence on a particular measurement (e.g., fluorescence lifetime, ground state recovery rate, etc.) can be made, and theories for solvent effects on various rate processes tested.

Orlandi and Siebrand first suggested that the singlet surface (S_1), on which stilbene photoisomerization occurred, might be the result of an avoided crossing along the isomerization coordinate of a 1B_u state with a 1A_g state which lies above it in the planar configuration of the molecule.¹ Quantum mechanical calculations lend support to this idea.² Birks subsequently realized the importance of the A , B state orderings to the photophysical properties of the series of all-*trans* diphenyl polyenes.³ In Birks' scheme, the relative order of, and energy gap between, the A and B states has two implications: first, it determines the size of the barrier to internal rotation in the isolated molecule, and second, it can determine the radiative rate constant from the S_1 electronic state in which photoisomerization occurs. This last effect arises because emission from an A_g excited state to the A_g ground state is symmetry for-

bidden, and the radiative properties of a state with mixed A_g , B_u character will depend critically on the degree of B_u character it contains. Thus, in Birks' scheme, an important solvent influence is the relative stabilization of the B and A states, affecting their energy separation and, hence, the degree to which they are mixed.

Theoretical considerations point to another possible solvation effect which may influence the nature of the S_1 surface: polarization of the twisted form.⁴ While there is no direct experimental evidence, some quantum mechanical calculations suggest that the twisted form of the excited A state in polyenes may be unstable with respect to charge separation, since the A state arises from a doubly excited electronic configuration in which the electrons are highly correlated.⁵ Stabilization of the twisted form by polar or polarizable solvents may change the *shape* of the A surface along the twisting coordinate, and, hence, the energy of the "crossing point" with the B state. Thus, the magnitude of the internal barrier to isomerization can be affected.

Finally, within the general picture of isomerization, the solvent may have a *direct* influence on the dynamics through the "frictional forces" exerted on the twisting coordinate. This has been discussed extensively in the literature on cyanine dyes⁶ and triphenyl methane dyes.⁷ However, aside from the quantum yield measurements made on stilbene by Gegiou *et al.*,⁸ and the high pressure experiments of Brey *et al.*,⁹ there has been little effort to isolate a viscosity effect in the diphenyl polyenes by a systematic study of solvent effects. There has, of course, been considerable activity directed towards the theoretical description of isomerization dynamics in liquids. The best known model is that of Kramers¹⁰ who derived expressions for the escape of particles over a barrier in various limiting cases. More recently, there have been some important kinetic theory calculations of isomerization dynamics.¹¹⁻¹³

^{a)}Alfred P. Sloan Foundation Fellow.

These treatments have dealt with the transition from the "weak coupling limit," when the rate of barrier crossing is proportional to the friction (collision rate), to the diffusive or Smoluchowski limit, when the rate is inversely proportional to the friction. It is pointed out that the low friction limit of Kramers' theory is incorrect, since it goes to the transition state theory limit which is not correct at *any* coupling strength. These studies also imply that for many realistic cases, one cannot expect the high friction (Smoluchowski) limit to apply. This conclusion was also reached by McCaskill and Gilbert in their theoretical study of the twisting dynamics in biphenyl.¹¹ However, with the latter exception, there has been little contact between theory and experiment—particularly for photochemical isomerizations. While, in some senses, the diphenyl polyenes are ideal candidates for testing theories of photoisomerization dynamics, previous studies have shown that their photophysics is somewhat complex, with very pronounced differences in the lower and higher members of the series.

Stilbene has been studied by many workers in different solvents, changing both temperature and pressure. Birks¹⁵ had proposed that thermal equilibration between *trans* and twisted forms occurs on the S_1 surface, but these more recent studies have shown that the fluorescence decay kinetics are consistent with rapid thermal equilibration in the metastable planar form, followed by *irreversible* passage over the S_1 barrier.¹⁶ This is in accord with the notion that the twisted form is a "photochemical funnel" efficiently channeling population to the ground electronic surface.⁵

Sumitani¹⁷ and co-workers combined the temperature dependent quantum yield measurements of Malkin and Fischer¹⁸ with their own measured fluorescence lifetimes to show that the radiative rate constant k_r is essentially independent of temperature ($k_r = 6.3 \times 10^8 \text{ s}^{-1}$). In addition to the work of Sumitani *et al.*, Heisel¹⁹ and Taylor²⁰ have also made independent streak camera measurements of the temperature dependence of the fluorescence lifetimes of stilbene in methylcyclohexane-iso-hexane (MCH/IH) solution. The result of the three independent measurements of τ_F in MCH/IH at 298 K is $84 \pm 21 \text{ ps.}$; the Arrhenius parameters derived from the temperature studies are $3.0 \pm 0.5 \text{ kcal/mol}$ for the activation energy, and a pre-exponential factor of $2.0 \pm 0.9 \times 10^{12} \text{ s}^{-1}$. The temperature ranges were somewhat different, but overlapped, for the three studies.

Taylor, *et al.*²¹ studied the fluorescence lifetimes of stilbene in mixtures of ethanol and glycerol. They found that the lifetime increased as the percentage of ethanol was reduced and, thus, established a correlation with viscosity, although they did not analyze the viscosity dependence in an explicit way. Hochstrasser, however, has claimed that the low viscosity results are consistent with the Kramers theory of barrier crossing in the presence of hydrodynamic friction.¹⁶

A more direct assessment of the effects of viscosity on the isomerization rate of excited *trans*-stilbene was made by Brey, Schuster, and Drickamer,^{9(a)} who studied the fluorescence quantum yield as a function of pres-

sure. They noted that, while increasing viscosity (via high pressure) implied a slower radiationless decay rate in a given solvent, the rate was generally faster in polar than nonpolar solvents of a given viscosity. They attributed this to a direct solvent effect on the size of the internal barrier to twisting. They noted that there must be both internal and solvent contributions to the observed activation energy in solution, but did not attempt to separate them experimentally. Finally, they showed that the intersystem crossing channel for isomerization could become significant at high viscosities and low temperatures.

In contrast to stilbene, the higher diphenyl polyenes, diphenyl-hexatriene (DPH) and diphenyloctatetraene (DPO) show unusual fluorescence lifetime effects as a function of temperature and solvent.^{22,3(a)} These compounds show large solvent shifts in absorption wavelength, while the fluorescence spectra are solvent independent. The radiative rate constant is much smaller than that estimated from the integrated absorption intensity using the Strickler-Berg relation, and shows a marked solvent dependence. Cehelnick *et al.*²² found that the fluorescence lifetime of DPH depended on solvent, but not on temperature for a range of nonpolar solvents, while in polar solvents, τ_f increased with decreasing temperature. The quantum yield was monotonically increasing with decreasing temperature in all solvents.

To explain this, Birks^{3(a)} postulated that the *A* state lay below the *B* state in the planar configuration, and that the primary role of the solvent in these molecules is to change the energy gap between *A* and *B*. From the data of Cehelnick *et al.*, Birks calculated the activation energies for radiationless decay of the *A* state and found them to be in the range 0.4 kcal/mol in hydrocarbon solvents to 3.4 kcal/mol in acetonitrile. This increase with more polar or polarizable solvents could be correlated with the magnitude of the shifts in the absorption spectrum. In Birks picture, excitation to the 1B_u state in DPH (DPO) is followed by a rapid internal conversion to *A* which forms a "bottleneck," having both slow radiative and nonradiative channels. This picture has been corroborated by two-photon spectroscopy²³ and by time resolved fluorescence measurements.²⁴

Perhaps the most striking difference between the photophysical behavior of DPH and stilbene is seen in the effect of high pressure on the nonradiative rate constant: the measurements of Brey *et al.* show that k_{nr} increases with increasing pressure.^{9(b)} It is hard to reconcile this observation with the idea that the rate limiting step for radiationless decay from the *A* state is a large amplitude twisting motion, as Birks proposed.^{3(a)}

In this paper, we present a study of the fluorescence properties of diphenyl butadiene (DPB). A question which arises naturally is whether DPB is "stilbene like" or "DPH like." A recent two-photon excitation study has placed the *A* state of DPB slightly below the one photon allowed *B* state in a low temperature, polar glass (EPS, 77 K).²⁵ However, the measured radiative rate constant agrees closely with one calculated from the integrated absorption spectrum.²⁶ A ground state recov-

ery experiment has been reported in the literature, but measurements were made in only a few solvents of unrelated types at a single temperature, so that the origin of the observed lifetime variations could not be identified.²⁷ Therefore, we have measured the temperature and solvent dependence of the DPB absorbance and fluorescence spectra, fluorescence quantum yields, and lifetimes with the aim of untangling the various solvent influences on the radiative and nonradiative rates.

The purpose of this work is twofold. Firstly, as an important prerequisite to the photoisomerization study, we present data bearing on the nature of the excited electronic surface in DPB. We show that the radiative rate of DPB is relatively solvent independent and, thus, that the emitting state is not of significantly different character from the absorbing state. Secondly, we present the results of a systematic attempt to isolate the influence of solvent viscosity on the isomerization process, and to determine the intrinsic internal molecular barrier for twisting. We present evidence for a major viscosity effect in the alkane solvents and compare our data with Kramers' theory for diffusive barrier crossing, with a free volume theory advanced by Gegiou *et al.*⁸ and with the recent kinetic theory results¹¹⁻¹³ and obtain experimental values for the parameters of the three theories. We derive an estimate of the *internal* barrier to rotation which is less than the observed activation energy in solution. In the present study, we have examined primarily alkane solvents, as these should have the simplest interactions with the solute. However, even among the alkanes, we see significant variations in fluorescence lifetimes.

Evidence for specific (nonhydrodynamic) solvent effects is presented, and it is argued that these depend on the molecular polarity and polarizability of the solvent.

II. EXPERIMENTAL

Diphenyl butadiene (scintillation grade) was obtained from Eastman. The purity was confirmed by TLC and, following Hochstrasser,¹⁶ by wavelength independence of the quantum yield. The alkane solvents were purified by shaking with concentrated sulfuric acid, washing with distilled water, and drying over anhydrous magnesium sulfate. Some of the higher alkane solvents we used contained contaminants which absorbed at $\lambda < 330$ nm and had weak fluorescence interfering with DPB. Therefore, excitation was restricted to $\lambda \geq 330$ nm in these solvents.

Absorbance spectra were recorded on a Cary 219 spectrophotometer, excitation and emission spectra on a Perkin-Elmer MPF-4 connected fluorimeter with thermostated cell compartment. Quantum yields were obtained from integrated fluorescence spectra. The quantum yield of DPB in cyclohexane against quinine sulfate in 1 N. H₂SO₄ was found to be 0.44 in agreement with literature values.²⁸

Fluorescence lifetimes were measured by time correlated single photon counting. The apparatus has been described elsewhere.²⁹ For these experiments, we generated ultraviolet excitation pulses by focusing red dye

laser pulses (Rhodamine 640 or DCM dyes) into a lithium iodate crystal. Fluorescence photons at "magic angle" polarization were detected using an Amperex XP2020 photomultiplier. The instrument function was 300 ps. All decay profiles fit well to single exponential kinetics.

Temperature control from -20 to 100 °C was obtained with a Neslab RTE-4 circulating bath and temperature control from 10 to -70 °C with a Neslab ULT-80. Temperatures were monitored with an Omega 199 Digital thermometer with copper constantan thermocouple which was calibrated by immersion in dry ice/acetone (-78 °C), ice/water (0 °C) and boiling water (100 °C).

The high pressure measurements were made using a cell constructed according to the design of Jonas.³⁰ Hydraulic pressure was generated with a H.I.P. pump, type 10-600-50. The range of pressures used in these experiments was from atmospheric pressure to 3 kbar.

Values of the index of refraction and viscosity of the solvents studied was obtained from standard tables³¹ and the viscosity of octane as a function of pressure was obtained by interpolating the data given by Bridgeman.³²

III. RESULTS AND DISCUSSION

A. Spectral shifts and the radiative rate constant

Andrews and Hudson have proposed an expression based on perturbation theory to explain the variation of radiative rate with solvent in the case of polyenes where the *A* state lies below the *B* state.³³ They postulate that the energy gap between the *A* and *B* states and the ground state (*G*) vary as

$$\Delta E_{BG} = \Delta E_{BG}^0 - hc\alpha(P_B - P_G), \quad (1a)$$

$$\Delta E_{AG} = \Delta E_{AG}^0 - hc\alpha(P_A - P_G), \quad (1b)$$

where E_{AG}^0 is the energy gap between *A* and *G* in the isolated molecule, P_A , P_B , and P_G are measures of the polarizability of the *A*, *B*, and *G* states. α is a measure of the solvent polarizability, calculated via

$$\alpha = (n^2 - 1)/(n^2 + 2). \quad (2)$$

The energy gap between *A* and *B* is then

$$\Delta E_{BA} = \Delta E_{BA}^0 - hc\alpha(P_B - P_A). \quad (3)$$

The radiative rate constant for emission from the *A* state is given by

$$k_{GA} \propto \frac{|M_{GB}|^2 h_{AB}}{(\Delta E_{AB}^0 - hc\alpha\Delta P_{BA})} \quad (4)$$

when h_{AB} is the perturbation which mixes *A* and *B* and M_{GB} is the *B*-*G* transition dipole matrix element. This expression has been shown to apply to DPH and DPO by Birks^{3(a)} and Andrews and Hudson.³³ The striking observation made by these authors is that for the higher polyenes

$$P_B - P_G \gg P_A - P_G \quad (5)$$

by a factor of 5 to 20.

In Fig. 1, we have plotted the peak absorbance frequency $\bar{\nu}_a$ and peak emission frequency $\bar{\nu}_e$ against α for DPB in a range of alkane solvents. We have used the spectral maxima rather than the "0-0" transition fre-

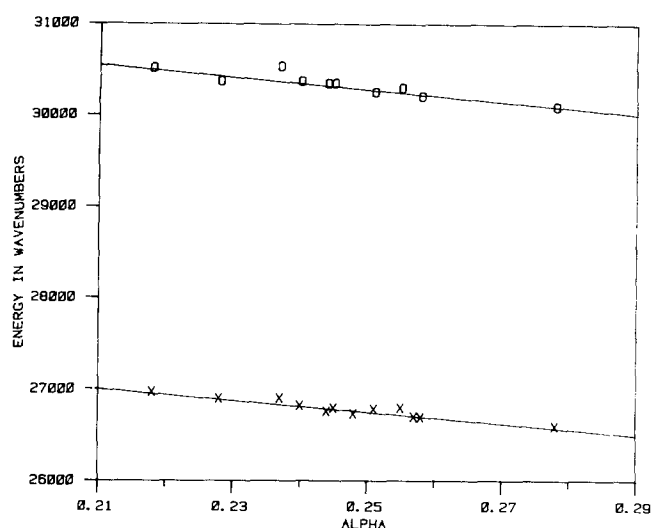


FIG. 1. Variation of the peak absorption frequency ν_a (x) and emission frequency ν_e (o) of DPB with solvent polarizability α in alkane solvents. Values of the linear least squares fit parameters are given in the text.

quency because these have more well defined positions (being sharper) and there is no evidence for a substantial change in vibronic spacing in these solvents.

Linear least squares fits of these data to Eqs. (1a) and (1b) give $P_A - P_C = 6338 \pm 1000 \text{ cm}^{-1}$ and $P_B - P_C = 6975 \pm 1300 \text{ cm}^{-1}$. Thus, the difference in $P_A - P_B$ is only a few hundred wave numbers, compared with 8830 cm^{-2} for DPH.⁴¹ We have observed that the cyclic alkanes show a larger value of ΔP_{AD} than the linear alkanes (2000 cm^{-1} vs $\sim 300 \text{ cm}^{-1}$), but the uncertainties in our measurements prevent us from deciding if this is significant or not.

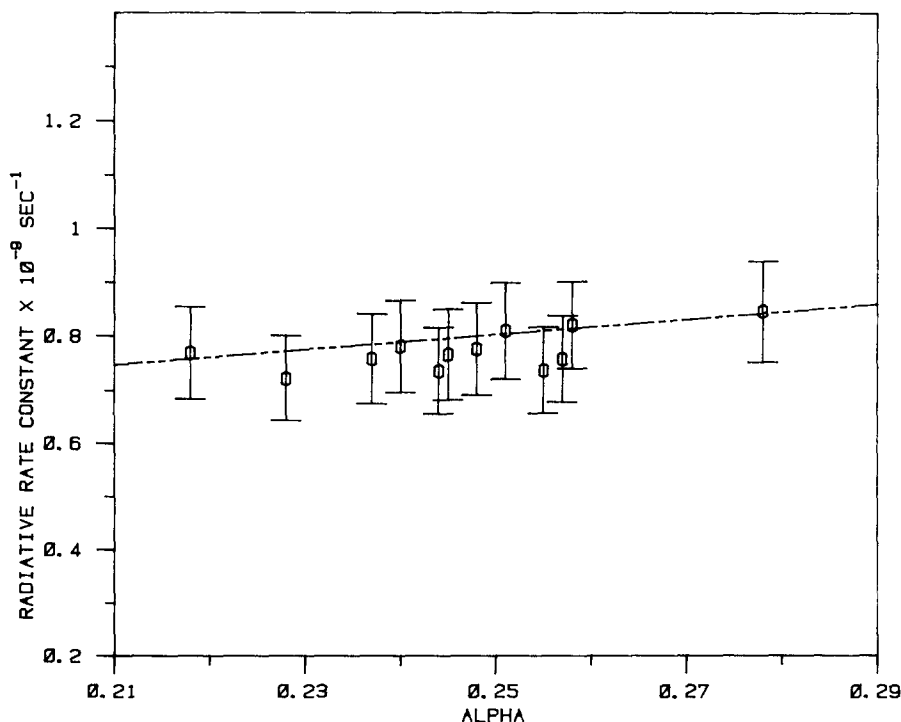


FIG. 2. Variation of the radiative rate constant k_r of DPB with solvent polarizability α in alkane solvents. The line is the linear least squares fit of $k = A\alpha + B$ with $A = 1.4 \times 10^9 \text{ s}^{-1}$, $B = 0.43 \times 10^9 \text{ s}^{-1}$.

The variation of the radiative rate constant with α is shown in Fig. 2. This should be compared with the variation of k_r with α for DPH shown in Fig. 2 of Ref. 33. Over the same range of α , k_r increases by nearly a factor of 3 in DPH. The mean value of k_r for all the alkanes is $0.77 \pm 0.4 \times 10^9 \text{ s}^{-1}$ and nearly all the points lie within one standard (SD) deviation of the mean, so that the variation over the full range of α is only about 10%. This could easily be accounted for by a simple n^2 index of refraction dependence. Because of the small variation k_r , we have used the mean value to compute non-radiative rates from our measured fluorescence lifetimes.

From these results, it seems likely that the absorbing and emitting states in DPB are the same and, although it is possible that the state has some mixed character, from the size of the radiative rate constant it is probably primarily of B_u character. Very recently, Birch and Imhoff have reached a similar conclusion.³⁴

B. Nonradiative decay

Table I lists the fluorescence lifetimes of DPB in various solvents at 27°C , along with the viscosity and α for each solvent. There is clearly considerable variation in the lifetimes even among the alkanes. The lifetime we have measured for DPB in benzene agrees well with the ground state recovery time measured by Morand *et al.* (305 ps).²⁷ The lifetimes observed in benzene and ethanol are relatively short compared to lifetimes in alkanes of similar viscosity, which is easy to rationalize in terms of the different "chemical" nature of these solvents. However, even in the nonlinear alkanes, the lifetimes are anomalously short for the viscosities compared to the linear alkanes. Thus, although the lifetimes correlate well with viscosity within the series of linear alkanes, there is clearly some other property

TABLE I. Fluorescence lifetimes and quantum yields at 24°C.

Solvent	τ_F (ps)	ϕ_F	η (cp)	α
Pentane	450	0.35	0.24	0.218
Hexane	485	0.35	0.33	0.228
Octane	580	0.45	0.54	0.240
Decane	630	0.51	0.92	0.248
Undecane	690	0.56	1.17	0.251
Dodecane	710	0.253
Tetradecane	740	0.56	2.25	0.257
Pentadecane	755	0.62	2.81	0.258
2,2,4 tri-methyl pentane	475	0.36	0.51	0.237
Cyclopentane	535	0.41	0.46	0.245
Cyclohexane	570	0.42	0.98	0.255
<i>Trans</i> -decalin	680	0.58	2.13	0.278
Ethanol	60 ^a	0.042	1.2	0.222
Benzene	290	...	0.63	0.294

^a $T = 20^\circ\text{C}$.

which is important to the radiationless decay which does not correlate with viscosity outside the homologous series. Brey *et al.* have made a similar observation for stilbene in linear and cyclic alkanes.^{9(a)}

In order to elucidate the nature of this property and to evaluate better the role of viscosity, we undertook a study of the temperature dependence of the nonradiative rate constant k_{nr} in various solvents. Figure 3 shows

TABLE II. Activation energies and pre-exponential factors.

Solvent	E_{act} (kcal/mol)	A (s^{-1})
Hexane	5.6 ± 0.6	$17 \pm 7 \times 10^{12}$
Hexane ^a	1.7 ± 1.3	$7 \pm 2 \times 10^9$
Octane	5.7 ± 0.7	$16 \pm 2 \times 10^{12}$
Dodecane	6.2 ± 0.7	$23 \pm 25 \times 10^{12}$
Pentadecane	5.9 ± 0.35	$13 \pm 7 \times 10^{12}$
Cyclohexane	5.3 ± 0.7	$8.4 \pm 9 \times 10^{12}$
Ethanol	4.0 ± 0.2	$14 \pm 9 \times 10^{12}$

^aFit to four low temperature points.

the Arrhenius behavior of the nonradiative rate constant for DPB in selected solvents. Table II contains the activation parameters derived from linear least squares fits to the data for a range of linear alkanes and cyclohexane and ethanol.

The Arrhenius plot for hexane shows clearly the presence of two decay channels, one of which dominates at high temperatures, the other at low temperatures. We were unable to study systematically this low temperature behavior because of the high freezing points of the other alkanes relative to hexane. Below the freezing points, the fluorescence lifetimes tended to be independent of temperature, or decreased slightly with decreasing T . The mean "limiting" fluorescence lifetime we obtained under these circumstances was $\tau_F = 1.02 \pm 0.05$ ns. This implies a nonradiative rate constant of about $2 \times 10^8 s^{-1}$ for this channel and it seems likely that this

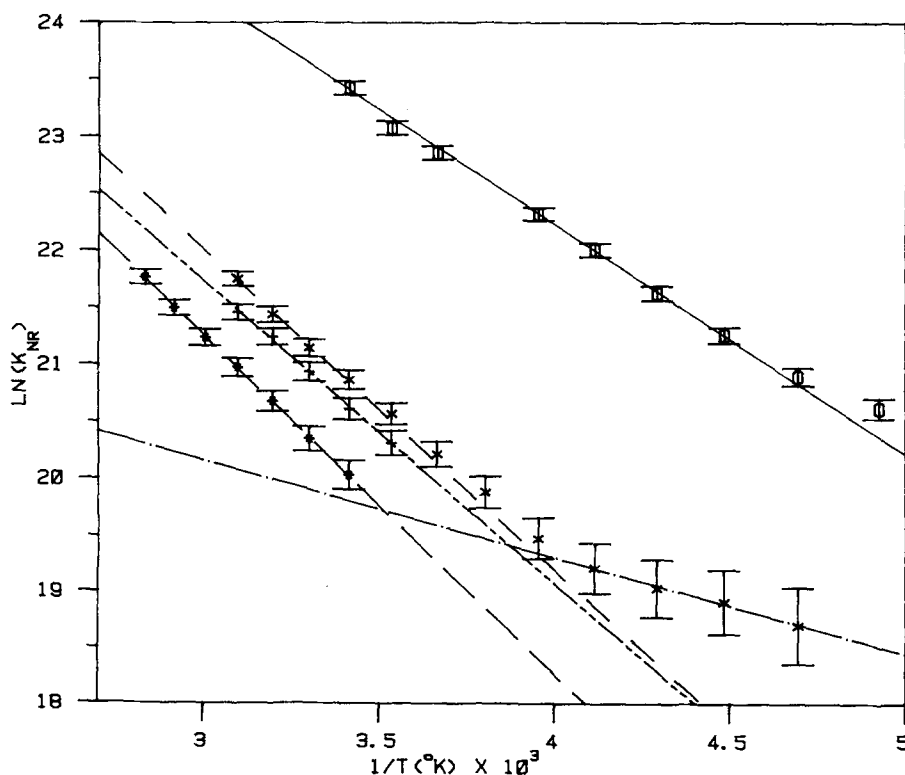


FIG. 3. Arrhenius plots of k_{nr} for DPB in various alkane solvents. \circ -ethanol, \times -normal hexane, $+$ -cyclohexane, $*$ -pentadecane. The dashed lines are linear least squares fits to the high temperature data, the dotted line is the fit to the low temperature data of *n*-hexane.

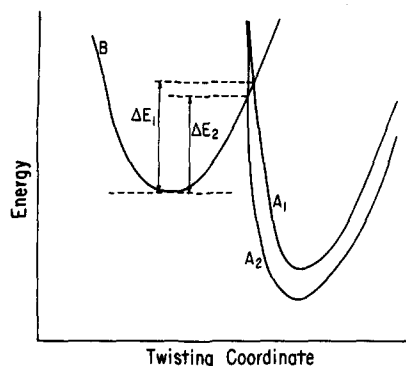


FIG. 4. Variation of crossing point energy E_0 with relative stabilization of hypothetical A surface with respect to B.

is the analog of the process identified by Brey *et al.* as intersystem crossing in stilbene.^{9(a)}

Table II indicates that the activation energies and pre-exponential factors tend to increase in the more viscous solvents of the series of linear alkanes, and are "anomalously" low in cyclohexane and ethanol. This may be due to the stabilization of the polar, twisted A state which will lower the crossing point of A and B and, hence, the activation energy as shown in Fig. 4. Such an effect must, of course, also occur within the series of linear alkanes, but this is evidently masked by a competing effect of solvent viscosity, as evidenced by the following argument.

Models which have been proposed for the viscosity dependence of isomerization suggest that for $E_0 > RT$ the rate constant can be written

$$k = F(\eta) e^{-E_0/RT} \quad (6)$$

If this is true, then the internal barrier E_0 can be extracted by plotting $\ln k$ vs $1/T$ for a series of solvent, temperature pairs such that $\eta = \text{constant}$. We have constructed such plots for a series of linear alkanes (hexane, octane, decane, dodecane, pentadecane) and these are shown in Fig. 5, along with the normal Arrhenius plot for pentadecane for comparison.

If the variations in E_0 from solvent to solvent are small compared with the influence of the frictional forces, these isoviscosity plots should yield a constant E_0 independent of the particular alkanes used or of the particular fixed viscosity selected. The plots in Fig. 5 are at 0.69 cp and 0.97 cp and their very similar slopes suggest that the above condition is quite closely fulfilled for DPB in linear alkanes. A more rigorous test would be to measure the temperature dependence of the radiationless decay rate in a single solvent at constant volume, since for many nonpolar liquids, the viscosity and index of refraction are nearly constant over large temperature ranges under these conditions.³⁵

The activation energy calculated from the isoviscosity series data was 4.7 ± 0.5 kcal/mol, which is appreciably lower than the activation energies obtained from the normal Arrhenius plots. Since these plots are constructed from only a few points, the absolute value of E_0 is somewhat uncertain, but the results strongly suggest that part of the observed activation energy observed in the linear alkanes may be due to solvent hindrance of the large amplitude motion associated with isomerization.

In order to examine the correlation between the non-radiative decay rate and viscosity in the series of linear alkanes in more detail, we have plotted

$$F = (k - k_B) e^{E_0/RT} \quad (7)$$

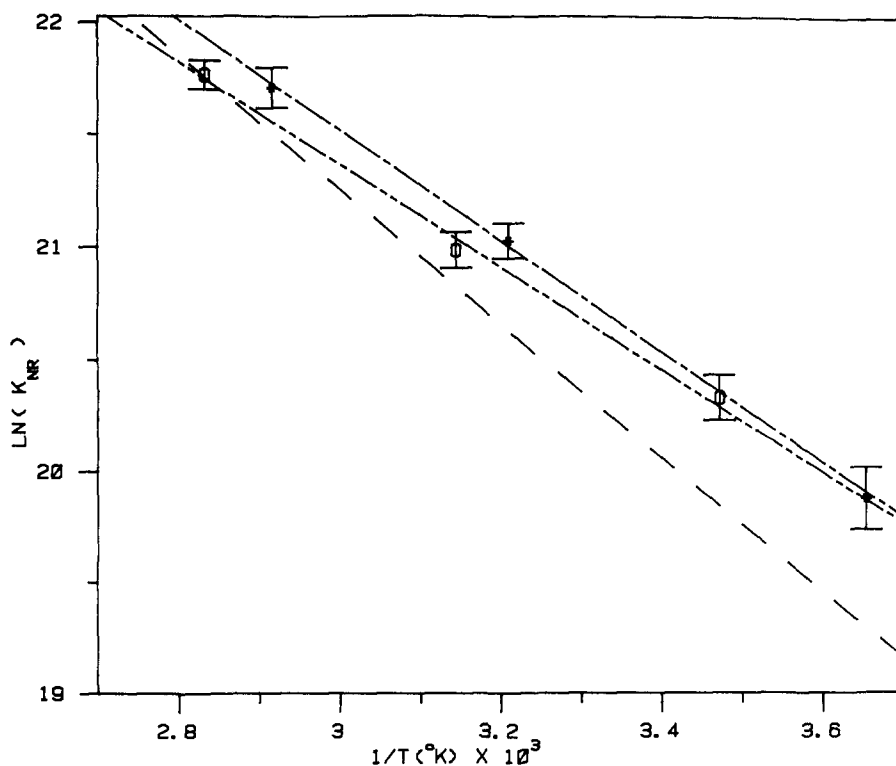


FIG. 5. Isoviscosity plots for DPB radiationless rate constant in normal alkanes. * = 0.69 cp, ○ = 0.97 cp, the separate dashed line is the least squares fit to the normal Arrhenius plot for pentadecane, shown here for comparison.

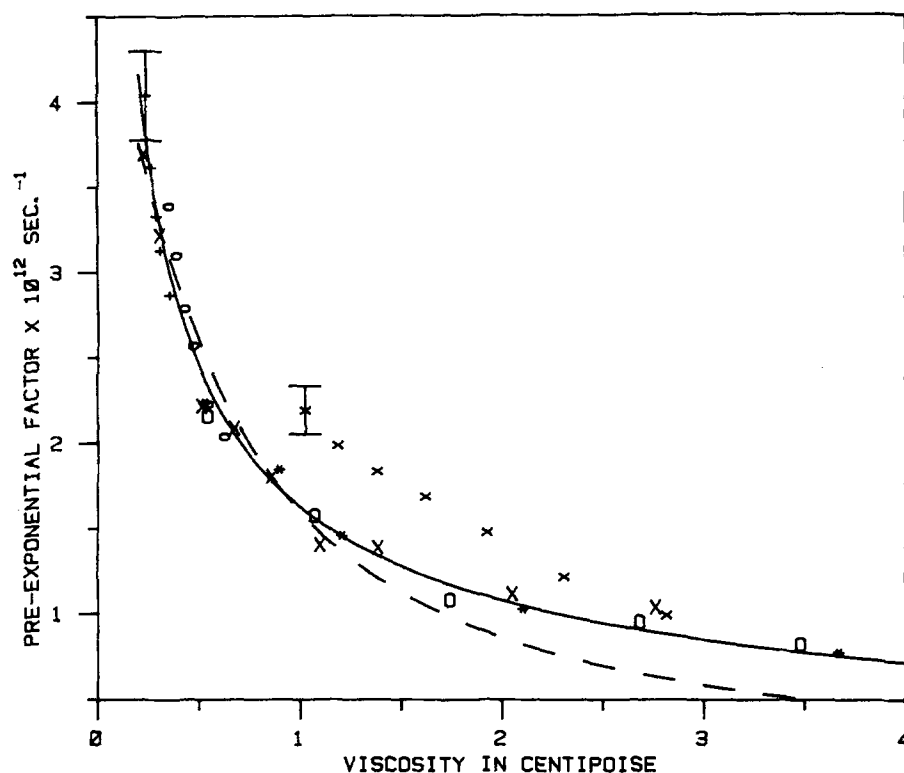


FIG. 6. Pre-exponential factor for the radiationless decay rate constant for DPB in normal alkanes. X—normal alkanes at room temperature; +—hexane varying temperature; o—octane varying temperature; •—octane varying pressure, $T=20^{\circ}\text{C}$; 0—octane varying pressure, $T=22^{\circ}\text{C}$; x—pentadecane, varying temperature. The dashed line in the nonlinear least squares fit of all points excluding the pentadecane data to the Kramers expression (9b). The solid line is the nonlinear least squares fit to the same data of the free-volume expression (13).

against viscosity for a large number of measurements where the viscosity was varied by changing the solvent, the temperature, and the pressure. k_B is a temperature independent baseline which we take to be $0.2 \times 10^9 \text{ s}^{-1}$ to account roughly for the low temperature channel we have mentioned previously. This channel will also become important at high viscosities, where it begins to compete effectively with the isomerization channel. We have taken $E_0 = 4.7 \text{ kcal/mol}$ as deduced from the isoviscosity plots. Figure 6 shows that the data fall on a fairly smooth curve over a range of viscosity of more than an order of magnitude. A significant deviation from the curve defined by the room temperature measurements can be seen in the data for pentadecane as a function of temperature. Since the polarizability of pentadecane is large, the intrinsic barrier to isomerization E_0 might be smaller than the estimated 4.7 kcal/mol. However, if we were overestimating the internal barrier energy, one would expect the pentadecane data to exhibit less of a slope with decreasing viscosity than the room temperature data in the same viscosity range. Without the more accurate estimate of the internal barrier in a given solvent which constant volume measurements can provide, it is difficult for us to interpret the observed trends. Considering what is ignored in this plot, i.e., possible changes in the S_1 potential surface with solvent and temperature, and the uncertainty in the "baseline" correction, the correlation of the various types of measurements with viscosity is remarkable. This is rather strong evidence that, when the temperature variation of the rate constant due to the internal barrier is removed, the pre-exponential factor seems to be determined primarily by the solvent viscosity.

Figure 7 shows the pressure dependence of the non-radiative rate constant of DPB in octane at 22°C . The

important qualitative feature of these measurements is that k_{nr} decreases as the pressure is increased and, thus, that DPB is clearly more like stilbene in its relaxation mechanism than like DPH. Following Le Noble,³⁶ we have fit $\ln k_{nr}$ vs p to the cubic equation

$$\ln k_{nr} = a + bp + cp^3 \quad (8)$$

and calculated the activation volume for the nonradiative decay process as

$$\Delta V^\ddagger = -bRT \quad (9)$$

For two separate runs near room temperature, we ob-

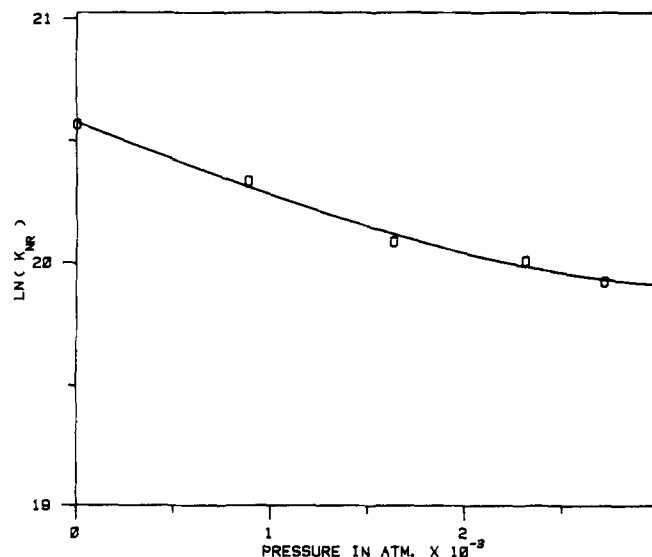


FIG. 7. Pressure dependence of the nonradiative rate constant of DPB in octane at 22°C . The line is the least squares fit of Eq. (8) to the data.

tained $\Delta V^\ddagger = 7.6 \pm 0.4 \text{ cm}^3/\text{mol}$. This is in reasonable agreement with the range of values of ΔV^\ddagger reported for stilbene in alkane solvents by Brey *et al.*^{9(a)}

C. Models for the viscosity dependence of k_{nr}

In this section, we compare the data of Fig. 6 with models which have been proposed for the viscosity dependence of radiationless processes involving large amplitude motion, in particular, the Kramers model^{10,14} and the free volume theory of Gegiou *et al.*⁸

The Kramers expression for diffusive barrier crossing is

$$k_{nr} = \frac{\omega}{\omega' \tau_v} \{ [1 + (2\omega' \tau_v)^2]^{1/2} - 1 \} e^{-E_0/RT}, \quad (10)$$

where ω = frequency of the initial well, ω' = curvature at the top of the barrier, τ_v = velocity relaxation time for the isomerization motion, and E_0 is the height of the barrier. This formula is derived by considering the steady state flux of particles undergoing Brownian motion across a barrier.

For the particular case of photochemical isomerization, where the final state is short lived, return to the initial state can be neglected and Eq. (10) is appropriate. In ground state isomerizations which are described by a double minimum potential with very similar or identical energies for the two states, Eq. (10) is inappropriate and needs to be modified to allow for two way passage over the barrier.¹¹ The velocity relaxation time is linearly related to the friction felt by each particle, which, in turn, is the time integral of the autocorrelation function of the random forces exerted by the solvent on the diffusing degree of freedom. The hydrodynamic model for the friction sets

$$1/\tau_v \propto \eta. \quad (11)$$

So that,

$$k e^{E_0/RT} = A/(B/\eta) \{ [1 + (B/\eta)^2]^{1/2} - 1 \}, \quad (12)$$

where $A = \omega/2\pi$ and $B/\eta = 2\omega' \tau_v$. It should, perhaps, be emphasized that this hydrodynamic model for τ_v is added *ad hoc* to the Kramers expression proper. Recent work by McCaskill and Gilbert¹⁴ has suggested that this expression can be applied to molecular barrier crossing.

However, in testing the validity of Kramers' theory, it is important to distinguish between tests of Eq. (10) and of the hydrodynamic approximation to it [Eq. (12)].

We have done a nonlinear least squares fit of Eq. (10) to the data of Fig. 6 and the result is the dashed line. The best fit parameters were $\omega = 660 \text{ cm}^{-1}$ and $\omega' \tau_v \sim 0.71 \text{ cp}^{-1}/\eta$. In our viscosity range $\omega' \tau_v \sim 1$. As we have shown in a previous study, this is consistent with the observation that the sum of the intrinsic barrier energy E_0 and the activation energy of the solvent viscosity is less than the activation energy measured in solution.³⁷

An Arrhenius plot of the twisting rate calculated according to Eq. (10) with τ_c assumed proportional to η^{-1} when $\omega' \tau_c \sim 1$ is slightly convex and, over a temperature range corresponding to our measurements, has a slope significantly less than the sum of E_0 and the viscosity

activation energy (E_η). Only when $\omega' \tau_c \ll 1$ does the observed activation energy = $(E_0 + E_\eta)$. A more stringent test of the Kramers equation (12) may be made by comparing the shape of the experimental plot with that of Eq. (12). As can be seen in Fig. 6, the Kramers function cannot account well for the flattening of the curvature of the data at high viscosity. It is possible that this flattening is caused by significant contribution to the nonradiative rate at higher viscosities from a viscosity independent process. However, we reject this explanation since our low temperature studies allow an estimate of the rate of such a process and as mentioned earlier a baseline of 0.2×10^{-9} has already been subtracted in constructing Fig. 6. Hochstrasser has mentioned a similar observation about the data of Taylor *et al.*,¹⁶ although their data applies to a viscosity range 10–50 times higher than that studied here.

Skinner and Wolynes have derived an approximate expression for the barrier crossing rate which interpolates between the correct low friction limit and the diffusive limit.^{11(a)} The expression is

$$k = \frac{\omega}{2\pi} gT \left[1 + \frac{gT}{2} + \frac{(gT)^2}{2\pi} \right]^{-1} e^{-E_0/RT}, \quad (13)$$

where, to compare with the Kramers formula $gT = (\omega' \tau_v)^{-1}$ and ω as in Eq. (10). A fit of Eq. (13) to the data in Fig. 6, with $gT = A' \eta$, gives a result indistinguishable from that of the Kramers formula, and the values of the best fit parameters are in exact correspondence. This observation, combined with the monotonic negative pressure dependence of the nonradiative rate constant shown in Fig. 7, implies that the isomerization is well into the strong coupling (although not Smoluchowski) region with the solvent. This is quite consistent with the picture of the nonradiative rate limiting step being a rather large amplitude structural rearrangement.

Finally, we must mention in this context, the work of Grote and Hynes¹³ who considered the effects of non-Markovian random forces on the rate constant for barrier crossing. Because the motion along the isomerization coordinate is partially governed by an internal potential surface and, hence, by fairly rapidly changing internal forces, one must consider, in general, the frequency dependent response of the medium, i.e., $\zeta(\omega)$ the frequency dependent friction coefficient. For a simple model of a parabolic barrier, Grote and Hynes found that

$$k = (\lambda/2\pi) e^{-E_0/RT}, \quad (14)$$

where the pre-exponential factor and the high frequency friction coefficient obey the following self-consistent equation:

$$\lambda = \left(\left\{ \left[\frac{\zeta(\lambda)}{2\mu} \right]^2 - \omega^2 \right\}^{1/2} - \frac{\zeta(\lambda)}{2\mu} \right). \quad (15)$$

Since Fig. 6 is essentially a plot of λ , we can see that $\lambda \approx 1 \times 10^{12} \text{ s}^{-1}$ and the "consistent" value of the friction is actually located at a fairly high frequency. It is well known from studies of simple liquids that $\zeta(\omega)$ falls off quite rapidly with frequency and hence an adequate hydrodynamic model for ζ might be required to use the frequency dependent viscosity, as using the zero frequency value will overestimate the solvent drag on the

isomerization coordinate.^{38,39} While this is a possible explanation for the deviation of the ordinary hydrodynamic Kramers equation from our data, we cannot, at present, test this idea more rigorously.

In their paper on viscosity effects on the quantum yields of stilbene, Gegiou *et al.*^{8(a)} proposed that the rate of molecular rearrangement in the presence of solvent could be written

$$k = k_0 e^{-a V_0/V_f} \quad (16)$$

Here, V_0 is the critical free volume for molecular translation diffusion, V_f is the free volume of the solvent, a is the fraction of the critical free volume necessary to allow the rearrangement of the isomerizing molecule, and k_0 is the limiting rate constant at zero viscosity. The fraction a is less than one since the motion involved in twisting is much smaller than that involved in translational diffusion of the entire molecule. This formula has a basis in the free volume theory of the viscosity advanced by Cohen and Turnbull.³⁵ Doolittle⁴⁰ showed that the viscosity of hydrocarbons could be related to the free volume via

$$\eta = A e^{V_0/V_f} \quad (17)$$

so that, combining Eqs. (16) and (17), one finds

$$k = k_0 (A/\eta)^a \quad (18)$$

If we write $k_0 = B e^{-E_0/RT}$, then

$$k e^{E_0/RT} = (BA^a) 1/\eta^a \quad (19)$$

Since the coefficient A is supposed to vary from solvent to solvent,⁴⁰ Eq. (19) cannot properly be applied to data obtained in different solvents. However, Doolittle found that $A = 4.76 \times 10^{-4} \text{ p}^{-1}$ for heptadecane, and Cohen and Turnbull³⁵ list parameters for 2,3-dimethylbutane which will give $A = 3.5 \times 10^{-4}$ at $T = 298 \text{ K}$ so that for hydrocarbons, the mean value of $4.1 \times 10^{-4} \text{ p}^{-1}$ appears to be reasonable. Another problem with the free volume expression is that it does not reproduce the viscosity of a solvent well near its freezing point.³⁵ In fact, most of our measurements are *not* in the range of validity of Eq. (17) cited by Doolittle. However, it is a useful expression to consider, since it is a simple, few parameter realization of the more complex theoretical ideas discussed by Kivelson in a recent review.⁴¹

In spite of its limitations, we have found that Eq. (19) fits the data of Fig. 6 over the entire viscosity range. The parameters from the least squares fit are $a = 0.59 \pm 0.14$ and $BA^a = 0.7149 \pm 0.337 \times 10^{12} \text{ s}^{-1}$. Using the value for A quoted above, we can extract the pre-exponential factor $B = 2400 \pm 1100 \text{ cm}^{-1}$. This is a factor of 3–4 larger than the frequency factor derived from the fit of Kramer's formula, but both pre-exponentials are in a reasonable range (i.e., $2 \times 10^{13} \text{ s}^{-1}$ and $7.2 \times 10^{13} \text{ s}^{-1}$, respectively).

IV. CONCLUDING REMARKS

The photophysical properties of DPB appear to be more closely related to stilbene than to DPH. Our evidence indicates that the radiative rate constant is relatively solvent independent and that the apparent activation energy for the nonradiative rate constant *de-*

creases in polar and polarizable solvents. This may be due to the stabilization of the twisted form, which recent theories suggest, has polar character. We are currently studying DPB in polar and polarizable solvents to test these ideas.

Part of the activation energy for the nonradiative decay processes in DPB in solution is due to the temperature dependence of the viscosity, although we have not taken into account the possible solvent influence on the barrier height via its polarizability, there is excellent correlation between the pre-exponential factor of the nonradiative decay constant and the solvent viscosity.

In terms of our fit to Kramers' equation, the parameters of the theory derived from our data show that the barrier crossing process in DPB is in the intermediate friction limit. In this limit, the rate decreases with increasing viscosity, but the Smoluchowski equation does not provide an adequate description of the process. We do not have an exact hydrodynamic model for the specific twisting motion involved, but if the simple inverse viscosity dependence of τ_c [Eq. (11)] is used, the observed dependence on viscosity at higher viscosities is less quickly varying than the hydrodynamic Kramers' model can account for. We suggest that it may be necessary to consider the frequency dependent viscosity to provide a correct theoretical description of the barrier crossing process. A possible alternative interpretation is provided by the good fit of a free volume expression to our data. In terms of the free volume theory, the isomerization processes requires that a volume corresponding to about 60% of the DPB molecular volume be displaced for the twisting process to occur, a result which seems physically reasonable if the isomerization process involves twisting of one of the two phenyl rings.

Recently, we have examined the solvent dependence of the nonradiative decay of the cyanine dye DODCI in alcohols,³⁷ and it seems appropriate to comment here on certain similarities between the results of that study and the ones we have presented for DPB in alkanes. The radiationless decay kinetics of both molecules are consistent with an activated barrier crossing in which the dynamics are partially controlled by solvent viscosity. While there have been no studies of the origin of the internal barrier in cyanine dyes, superficial similarity between their structures and those of the diphenyl polyenes is suggestive. Since Dahne⁴² has pointed out an analogy between the electronic structures of cyanine and triphenyl methane dyes, there is the possibility of unifying the photophysical properties of all of these classes in one consistent scheme. One may also note the similarity between our results for the viscosity dependence derived from the free volume model and the fractional dependence on viscosity found by other workers for both the cyanines⁶ and triphenyl methane dyes.⁷ Both fundamental theoretical and further careful experimental studies along these lines should prove illuminating.

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