

Excited State Intramolecular Torsional Relaxation.¹ Viscosity, Temperature, and Medium Effects on the Fluorescence Characteristics of a Sterically Crowded Molecule

Joseph Kordas² and M. Ashraf El-Bayoumi*

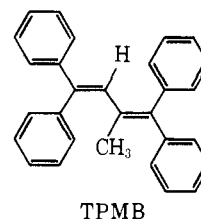
Contribution from the Departments of Biophysics and Chemistry, Michigan State University, East Lansing, Michigan 48823. Received November 7, 1973

Abstract: *trans*-1,1,4,4-Tetraphenyl-2-methylbutadiene (TPMB) undergoes an intramolecular twisting relaxation after excitation. The extent of this relaxation depends on the viscosity of the medium. The fluorescence energy maximum exhibits a blue shift and the fluorescence intensity is greatly enhanced as the medium becomes rigid. We have focused our attention on the quantitative aspects of fluorescence energy and intensity dependences on viscosity and temperature of the medium with the purpose of explaining the effect of each of these parameters on radiationless processes of the excited state of TPMB and similar molecules. Of particular interest is the separation of viscosity and temperature effects. While the fluorescence energy depends only on the viscosity of the medium, the quantum yield depends both on viscosity and temperature. Fluorescence intensity variation as the viscosity is changed by lowering temperature is interpreted in terms of solvent as well as solute activation energies. Solvent activation energies correspond to viscosity activation energies obtained from the macroscopic viscosity dependence on temperature. Solute activation energies correspond to torsional frequencies in the excited state of TPMB. A selective red-quenching mechanism is proposed to account for anomalous shifts that are dependent on the temperature and polarity of the medium. Selective red quenching appears to be a general phenomenon occurring in situations where excited molecules undergo geometrical relaxation during their lifetime.

Flexible molecules that undergo intramolecular torsional vibration around a bond linking two interacting moieties of the chromophore are weakly or non-fluorescent. The low-frequency oscillations lead to efficient radiationless deactivation of the excited molecule in fluid media. Upon "freezing" these modes or limiting their amplitudes, the molecule becomes strongly fluorescent. This may be accomplished by using media of high viscosities or by rendering the molecule rigid *via* a chemical bond.

In addition to the fluorescent enhancement effect, flexible molecules may undergo a change in their equilibrium geometry configuration upon excitation, such as in sterically crowded molecules where the steric strain can be relieved by internal rotation. In these cases a large Stokes shift of the fluorescence maximum is observed in fluid media. The fluorescence emission may originate from the equilibrium excited state, Franck-Condon state, or an intermediate geometric configuration depending on the relative magnitudes of the rate constants of the rotational relaxation process (k_r) and fluorescence (k_f). If k_r is viscosity dependent one may expect the fluorescence maximum to be a sensitive function of the viscosity provided that $k_f \ll k_r$. As the medium becomes more viscous the fluorescence maximum shifts progressively to higher energies and a maximum blue shift is observed in rigid media.

In an earlier study³ we have shown that the fluorescence maximum of a sterically crowded molecule, namely *trans*-1,1,4,4-tetraphenyl-2-methylbutadiene (TPMB), lies 3700 cm^{-1} at higher energies in rigid glass at 77°K compared to its maximum in fluid medium at room temperature as shown in Figure 1. The results



were interpreted in terms of an intramolecular twisting relaxation process that is fast in fluid medium. In rigid glass, however, the twisting relaxation is slowed down due to the high viscosity of the medium and the emission originates from an excited molecule which has a geometric configuration similar to that of the ground state, *i.e.*, from the Franck-Condon state which lies at higher energies relative to the equilibrium excited state. Potential-energy curves are drawn qualitatively by considering both the variation of the resonance energy and the steric energy as a function of the angle of twist about an essential single bond.³ These curves for the ground and excited state are shown in Figure 2. The curve in the upper state is a steeper function of the angle of twist reflecting the enhanced double bond character of the bond in question. The curves demonstrate the large Stokes shift in fluid medium, compared to that in rigid medium. Emissions from relaxed, intermediate, and Franck-Condon states (shown in Figure 2) demonstrate the blue shift of fluorescence as the medium becomes more rigid.

In addition to the blue-shift phenomenon, we presently show that TPMB exhibits also a remarkable fluorescence enhancement effect as the viscosity of the medium is increased. We have focused our attention on the quantitative aspects of fluorescence energy and intensity dependences on viscosity and temperature of the medium with the purpose of explaining the role of each of these parameters on the radiationless processes of the excited state of TPMB and similar molecules. Of particular interest is the separation of viscosity and

(1) Supported by U. S. Atomic Energy Commission Contract No. AT(11-1)2039.

(2) Supported by National Institute of Health Training Grant GM-01422 and by funds from the College of Osteopathic Medicine and the College of Human Medicine of the Michigan State University.

(3) M. A. El-Bayoumi and F. M. A. Halim, *J. Chem. Phys.*, **48**, 2536 (1968).

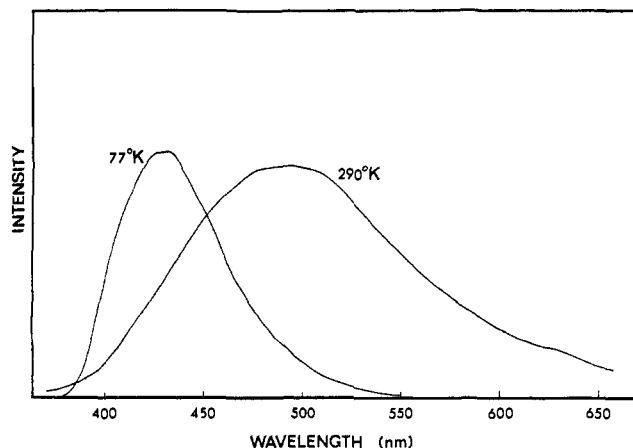


Figure 1. Emission spectra of TPMB in 3-methylpentane at room temperature (fluid medium) and at 77°K (rigid glass). Emission at room temperature is much less intense and is recorded at a higher sensitivity.

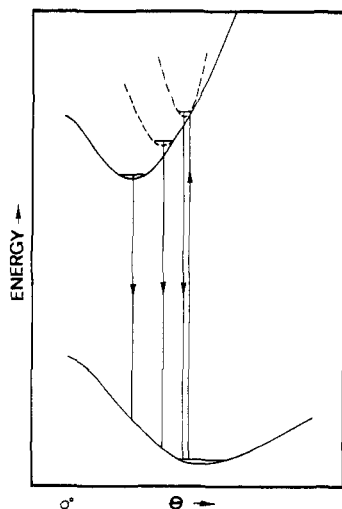


Figure 2. Qualitative potential-energy curves for the ground and excited states of TPMB. Emissions from a relaxed state (fluid medium), a Franck-Condon state (rigid medium), and an intermediate state are demonstrated.

temperature effects. To accomplish this, we used various approaches. 1. Use of mixtures of solvents with different viscosities at constant temperature. 2. Use of solvents whose viscosity dependences on temperature are different. 3. Studying temperature effects on luminescence of a sample in a plastic matrix.

Experimental Section

Materials. Phillips pure grade 3-methylpentane (3MP) was purified by distillation and by passing through an activated silica gel column.

Spectroquality isopentane (IP), methylcyclohexane (MCH), and glycerol (obtained from Matheson Coleman and Bell) were used without further purification. Ethanol, 1-propanol, and butanol were distilled while octanol and triacetin were vacuum distilled. Paraffin oil (obtained from Baker) was used without further purification. All solvents were spectrally transparent above 350 nm and exhibited no fluorescence when excited above 350 nm. In Figure 3 the viscosities of three solvents are plotted as $\log \eta$ vs. $1/T$. The data for 1-propanol are taken from Denny⁴ while those for triacetin and methylcyclohexane/isopentane (3:1) are taken from von Salis.⁵

(4) D. J. Denny, *J. Chem. Phys.*, **30**, 159 (1959).

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

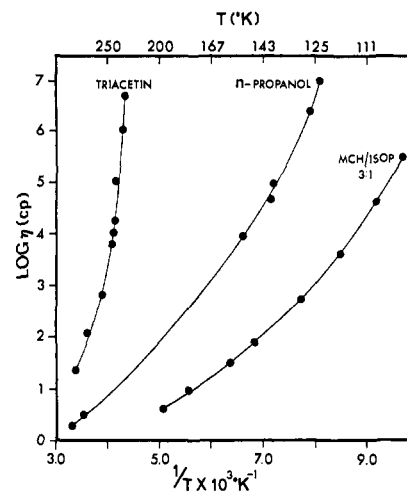


Figure 3. Viscosity-temperature data for triacetin, 1-propanol, and methylcyclohexane/isopentane mixture 3:1. These data are taken from the references cited in the text.

A pure sample of TPMB was further purified by successive recrystallizations from ethanol. The plastic samples were formed by dissolving both TPMB and the plastic (either polystyrene or polyvinyl acetate) in spectroquality CHCl_3 and evaporating off the solvent. A thin transparent plastic film was formed with the TPMB embedded in the matrix.

Methods. The Aminco-Keirs spectrophosphorimeter (1P28 Phototube) was utilized to obtain the emission intensity as a function of temperature. Relative quantum yields were obtained by measuring areas under emission curves and are uncorrected for phototube and monochromator response. In a limited temperature range, where only little shift of emission occurs, these correction factors are identical. A quartz dewar with a flat quartz excitation window and a 1-cm square suprasil cuvette were used. The temperature of the sample was controlled by boiling liquid nitrogen using a power resistor and allowing the N_2 gas to flow into the sample dewar. The temperature of the sample was monitored through a thermocouple (copper, constantan) attached to the outside of the cuvette immediately above the point of excitation. Fifteen minutes were allowed for equilibration at every point after the thermocouple reached the appropriate temperature. Comparing readings of the thermocouple on the outside and the inside of a cuvette containing solvent, one finds not more than 1° difference between thermocouples over wide ranges of temperature (room temperature down to -151°).

A 750-mm Czerny-Turner spectrometer (Spex 1700-II) in conjunction with a PAR lock-in amplifier (HR-8) and an EMI 9558 QA phototube was used to obtain the energy of the fluorescence maximum $\bar{\nu}_F$. These spectra also are presented uncorrected for phototube and monochromator response.

Absolute quantum yields for TPMB in various solvents at room temperature were obtained by utilizing a double-beam quantum yield instrument interfaced with a PDP 11 computer.⁶ This instrument measures both emission and absorption and corrects for both monochromator and phototube response. It is programmed to correct for innerfilter effects for solutions with optical densities up to 1.0. All solutions used here were 10^{-4} M. The excitation wavelength was again 360 nm. Quinine sulfate (10^{-6} M) in 1 N H_2SO_4 was used as the quantum yield standard with a value of 0.54. Because this apparatus uses phototubes with a weak red response and because the measured quantum yields are very small, these absolute quantum yields are only approximate ($\pm 20\%$).

It was noticed that a slow photochemical process occurs as a result of excitation at short wavelengths. This leads to changes in the intensity of absorption and emission spectra. The excitation wavelength of 360 nm was used throughout our study; at this wavelength, minimal changes occurred upon excitation. Fresh undegassed solutions were used. Degassing the samples produced no change in quantum yields.

(6) J. F. Holland, R. E. Teets, and A. Timnick, *Anal. Chem.*, **45**, 145 (1973).

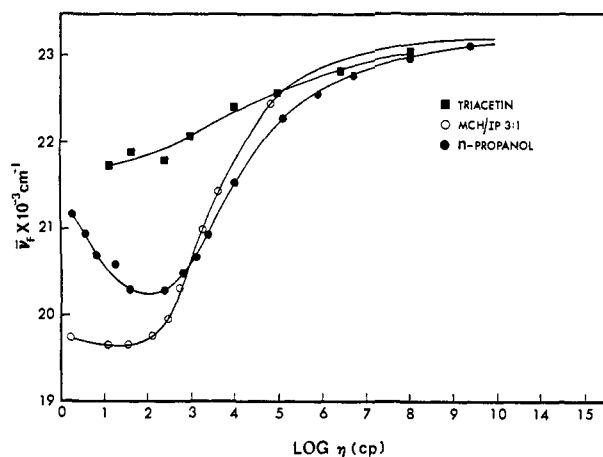


Figure 4. The variation of the energy of the fluorescence maximum ($\bar{\nu}_F$) in three different solvents as a function of viscosity. The viscosity was varied by lowering the temperature.

Viscosity Dependence of Fluorescence Energy

The fluorescence frequency maximum $\bar{\nu}_F$ was measured in three different media as a function of temperature. The viscosities of the solvents used, namely 1-propanol, triacetin, MCH/IP mixture (3:1), are plotted as a function of temperature in Figure 3. The differences in viscosities of these media at a given temperature enable us to distinguish between temperature and viscosity effects. The fluorescence energy is plotted *vs.* the logarithm of viscosity in Figure 4. At $\eta \geq 100$ cP the fluorescence maximum exhibits a blue shift, the magnitude of which increases continuously in all three media as the viscosity is increased, reaching a maximum value of about 23,200 cm^{-1} at very high viscosities. Plots of fluorescence energy maximum, $\bar{\nu}_F$, *vs.* temperature in the three media are shown in Figure 5. In general $\bar{\nu}_F$ increases rapidly in a narrow temperature range which differs from one medium to the other. In contrast these large changes of $\bar{\nu}_F$ occur at nearly the same viscosity. The inflection point of $\bar{\nu}_F$ *vs.* temperature plots occurs at approximately the same viscosity (the arrows in Figure 5 mark a viscosity of 10^4 cP), in spite of the fact that such viscosity is reached at widely different temperatures varying from 120°K up to 250°K, depending on the medium. This clearly demonstrates that $\bar{\nu}_F$ depends primarily on viscosity and not on temperature.

In mixtures of 3MP and paraffin oil, the fluorescence energy maximum of TPMB remains essentially the same up to viscosities of about 30 cP. In pure paraffin oil at 298°K ($\eta = 77$ cP) the observed blue shift is about 530 cm^{-1} . At 270°K in paraffin oil the spectrum is further blue shifted by 480 cm^{-1} and the half-width decreases. These effects are attributed solely to viscosity changes since 3MP solution begins to exhibit a blue shift below 150°K and since the viscosity of 3MP is little affected by cooling down to 200°K. The frequency maxima $\bar{\nu}_F$ and half-widths $\Gamma_{1/2}$ of the fluorescence band are compared under various conditions in Table I. At low viscosities, the fluorescence spectra are appreciably broader than at high viscosities. This broadening is in part due to emission from excited molecules at various stages of relaxation and in part due to the detailed shapes and relative displacements of the potential surfaces involved in emission.

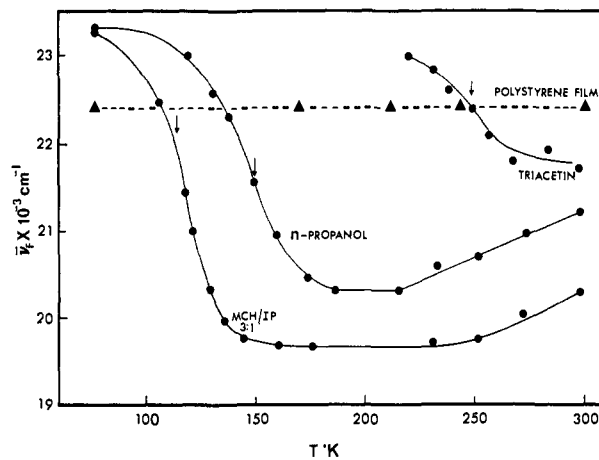


Figure 5. The variation of the energy of the fluorescence maximum ($\bar{\nu}_F$) as a function of temperature in four different media. Arrows indicate the temperature at which the viscosity of the medium is 10^4 cP. The dashed line indicates the values of $\bar{\nu}_F$ in polystyrene film at different temperatures.

Table I. Fluorescence Energy Maximum $\bar{\nu}_F$ and Half-Band Widths $\Gamma_{1/2}$ of TPMB in 3MP, Paraffin Oil (PO), and a Plastic Matrix at Various Temperatures

	3MP (77°K)	3MP (298°K)	PO (298°K)	PO (270°K)	Plastic (298°K, 77°K)
$\bar{\nu}_F$, cm^{-1}	23,256	20,325	20,859	21,340	22,271
$\Gamma_{1/2}$, cm^{-1}	3,500	5,680	4,840	4,340	4,325

Samples of TPMB in plastic matrices (in polystyrene and polyvinyl acetate) were studied at different temperatures. The fluorescence frequency maximum exhibits very little change as shown in Figure 5, which further supports our earlier conclusion of temperature invariance of $\bar{\nu}_F$. The value of $\bar{\nu}_F$ in plastic is 22,400 cm^{-1} which corresponds to a macroscopic viscosity of $\sim 10^6$ cP. An increase in microscopic viscosity by lowering the temperature would have been observed since $\bar{\nu}_F$ in plastics is about 1000 cm^{-1} lower than its value in rigid glasses. This indicates that excited TPMB exhibits some intramolecular twisting relaxation in its plastic cage. Our observations also support the expectation that the microscopic viscosities of plastics are essentially invariant with temperature in the region of our study.

It should be noted that in the low-viscosity region, $\bar{\nu}_F$ has a different value depending on the polarity of the medium. This behavior is anomalous since one would not expect polarity effects for the nearly nonpolar TPMB molecule. Moreover, Figures 4 and 5 show that the fluorescence maximum in 1-propanol and hydrocarbon solvents initially red shifts upon increasing the viscosity (in the range 0–100 cP) before it blue shifts as the viscosity is further increased. An interpretation of these observations will be discussed later in terms of a *selective red-quenching phenomenon* which is more prominent in polar solvents.

Fluorescence Intensity

Fluorescence intensities in two different media, namely MCH/IP (3:1) and 1-propanol, were measured as a function of viscosity. The viscosity was changed by lowering the temperature and its value was obtained

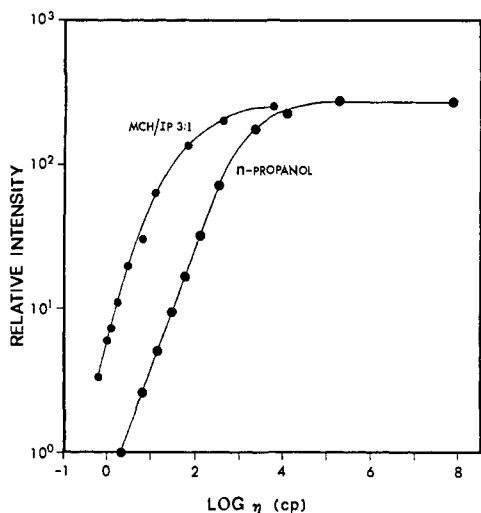


Figure 6. The change of fluorescence intensity of TPMB in 1-propanol and in MCH/IP (3:1) as a function of viscosity. The intensity is measured relative to the value at 298°K in 1-propanol.

from the viscosity-temperature data discussed in the Experimental Section. Intensities (corrected for changes in absorption due to temperature variation) are plotted as $\log I_F$ vs. \log viscosity in Figure 6 and as $\log I_F$ vs. temperature in Figure 7. The values given are relative to the fluorescence intensity at room temperature in 1-propanol. It should be noted that the fluorescence intensity at room temperature in 1-propanol is lower than that in hydrocarbon solvent although their viscosities are comparable. The reverse is true at lower temperatures due to the higher viscosity of 1-propanol. Fluorescence intensity gradually increases as a function of viscosity, reaching a maximum value which is the same for both solvents. Since degassing does not have any effect on fluorescence intensities at any temperature, one may assume that the only radiationless process which deactivates the excited singlet occurs directly to the ground state and not *via* a triplet state; *i.e.*, deactivation occurs mainly *via* the internal conversion process $S_1 \rightsquigarrow S_0$. The quantum yield at high viscosity is probably unity since no phosphorescence is observed under any conditions and since the intensity levels off at viscosities where some relaxation can still occur. Assuming that the quantum yield is 1 at high viscosity, the extrapolated room temperature quantum yields in 1-propanol and MCH/IP mixture are 0.004 and 0.013, respectively. Measured quantum yields at room temperature in these two solvents are 0.003 and 0.009, respectively. The measured quantum yields are only approximate with an error of almost 20%. The fluorescence intensity (corrected for changes of optical density with temperature) increases by a factor of 270 in 1-propanol in the temperature range 298–135°K and by a factor of 75 in MCH/IP mixture in the temperature range 298–117°K. In plastic, the corrected fluorescence intensity remains nearly constant in the same temperature range. However, one must note that the frequency maximum in plastic corresponds to macroscopic viscosities where the quantum yield has already achieved its maximum value in the two solvent systems.

In order to separate temperature from viscosity effects, the fluorescence intensities were measured in

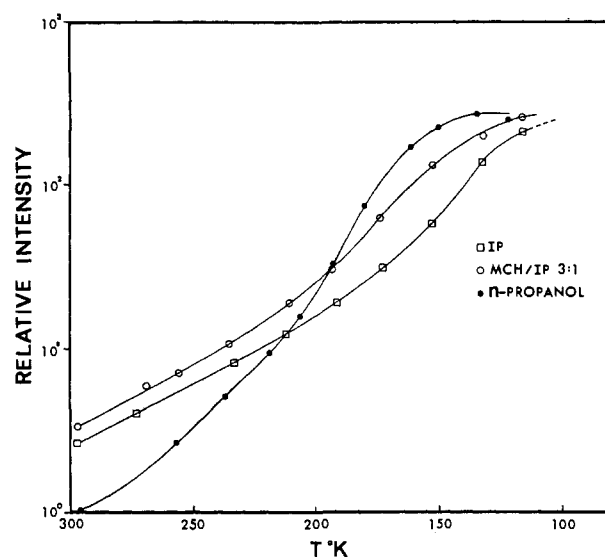


Figure 7. The change of fluorescence intensity of TPMB in 1-propanol, MCH/IP (3:1), and IP as a function of temperature. The intensity is measured relative to the value at 298°K in 1-propanol.

mixtures of paraffin oil and 3MP at room temperature, where the viscosity range varied from 0.5 in 3MP to 45 cP in paraffin oil/3MP mixture (9:1). The fluorescence intensity increases by a factor of 7.2 over this range in these mixtures. This change is attributed solely to viscosity. In MCH/IP mixture the fluorescence intensity increases by a factor of 33 over the same viscosity range when the temperature is lowered from 298°K down to 160°K; and therefore, one may attribute a factor of 4.5 as being due to temperature effects on luminescence yield. This value is obtained assuming a linear variation of $\log \eta$ with per cent volume of paraffin oil in the mixture.

In ethanol/glycerol mixtures where the viscosity at room temperature varies from 1.2 cP for ethanol to 63 cP for ethanol/glycerol mixture (4:6), the intensity increases by a factor of 8.7. In an experiment where the viscosity of propanol was increased from 2.3 cP at room temperature to 63 cP at 205°K, the intensity has increased by a factor of 18. Thus a factor of approximately 2 may be attributed to lowering temperature from 298 to 205°K. Here we assumed that the polarity of ethanol/glycerol mixtures is invariant and is the same as that of propanol.

Selective Red Quenching

As mentioned before the fluorescence energy maximum $\bar{\nu}_F$ decreases as the viscosity is decreased until it reaches a minimum value at viscosities around 100 cP where complete relaxation occurs during the lifetime of the excited state. Further lowering of the viscosity should not have any effect on $\bar{\nu}_F$. Indeed if the viscosity is varied in the range of 1–30 cP by mixing 3MP and paraffin oil in various proportions at room temperature, $\bar{\nu}_F$ remains invariant. However, in Figures 4 and 5, it is clear that as the viscosity is lowered $\bar{\nu}_F$ decreases reaching a minimum value near viscosities of about 100 cP, but then it begins to increase upon further warming of the sample. This clearly demonstrates that the increase in $\bar{\nu}_F$ in a fluid medium is due to temperature and does not reflect a real change in transition energies.

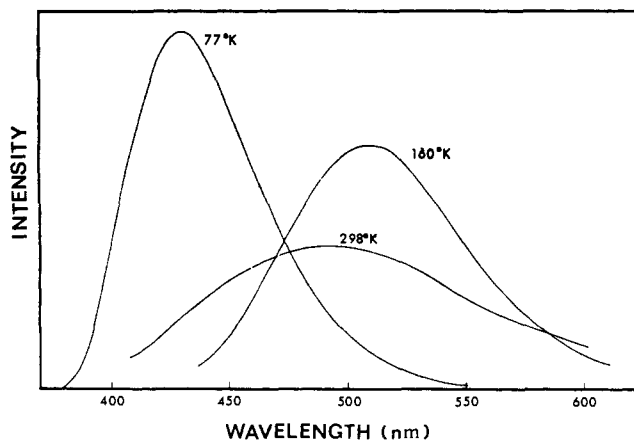


Figure 8. Emission spectra in MCH/IP (3:1) at three different temperatures 298, 160°, and 77°K. The relative sensitivities at which the spectra were recorded are $\times 180$, $\times 7$, $\times 1$, respectively.

This behavior was also observed for arylethylenes⁷ but no interpretation was given.

To interpret this behavior one should make the following points. (1) Emission is composite in nature; *i.e.*, it originates from excited molecules which have different geometric configurations depending on the extent of relaxation at the time of the transition. Although in a fluid medium most of the molecules relax to the equilibrium excited state geometric configuration before emission occurs, a few molecules still emit from partially relaxed geometric configurations. This explains in part the fact that the emission in a fluid medium is broad (see Table I), corresponding to various degrees of relaxation. In a rigid medium emission arises from one geometric configuration which corresponds approximately to that of the ground state. This accounts for the relative small half-width of the emission in a rigid medium at 77°K. (2) The paths of energy degradation (*i.e.*, radiative *vs.* radiationless transitions) will depend on the excited state geometric configuration. A Franck-Condon (unrelaxed) state is expected to have a small radiationless rate constant since the overlap factor⁸ of the vibrationless level of the upper state with the isoenergetic levels of the ground state is small; the radiative processes will therefore dominate. Therefore, in a rigid medium ($\eta \geq 10^8$ cP) the fluorescence is intense, the band is relatively narrow, and the maximum occurs at higher energies. The equilibrium excited state geometric configuration is expected to have a large radiationless rate constant due to a large overlap factor arising from the displacement of the excited state potential surface relative to that of the ground state. Therefore, in a fluid medium the fluorescence yield is low, the band is broad, and the fluorescence maximum lies at lower energies. Since the fluorescence yield of completely relaxed molecules is very small compared to nonrelaxed molecules, emission originating from the latter will contribute more significantly than their proportions. (3) Increasing the temperature will change the Boltzmann distribution of completely relaxed molecules among the accessible torsional modes in the ex-

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

(8) The overlap factor in the rate equation for radiationless transitions depends on the extent of displacement of the potential energy surfaces of the upper and lower states relative to each other and is expected to be minimum for the Franck-Condon state configuration.

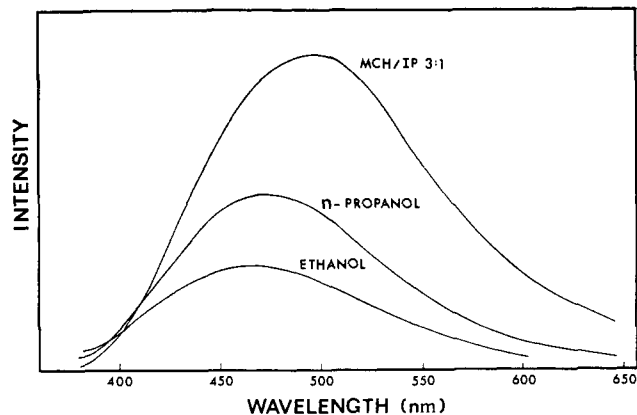


Figure 9. Emission spectra at 298°K in three solvents, MCH/IP (3:1), 1-propanol, and ethanol. The emission in 1-propanol and ethanol was recorded at the same sensitivity ($\times 1$) while that in MCH/IP (3:1) was recorded at a lower sensitivity ($\times 0.5$)

cited state. If radiationless decay from upper torsional modes in the excited state is more efficient (larger rate constant), one would expect fluorescence quenching of molecules emitting at longer wavelengths as the temperature is increased.

Therefore, the apparent blue shift which occurs at low viscosities as a result of warming the sample is really a selective red-quenching phenomenon. Increasing the temperature leads to a preferential quenching of fluorescence of completely relaxed molecules. Partially relaxed molecules will progressively contribute more to the emission intensity as the temperature is increased. Since their emission occurs at higher energies, an apparent blue shift of the fluorescence maximum is observed as the yield decreases with temperature, giving rise to a selective red-quenching effect. This is demonstrated in Figure 8 where the fluorescence spectra in MCH/IP (3:1) at different temperatures are shown.

Medium Polarity Effects. Comparing the fluorescence spectra in 1-propanol, MCH/IP (3:1), and ethanol at room temperature one notices a decrease in intensity and a blue shift of the $\bar{\nu}_F$ as the polarity of the medium is increased. As shown in Figure 9, the half-width of the fluorescence band is larger in hydrocarbon medium. One should note that TPMB is practically nonpolar and therefore the observed blue shifts in the polar media could not be attributed to energy changes of the states involved in emission.

The selective red quenching observed when the medium is made polar is interpreted in terms of a larger solvent-solute coupling (mainly due to dipole-induced dipole interactions) in polar media. One may therefore expect more efficient radiationless decay in polar medium particularly for completely relaxed molecules where radiationless processes are dominant.

We believe that the selective red-quenching phenomenon observed when temperature is increased or when the medium is made polar is a general one and will occur in situations where excited molecules undergo geometric relaxation during their lifetime.

Discussion

From the previous sections, it is apparent that the fluorescence intensity depends on both the temperature and the viscosity of the medium. By lowering the tem-

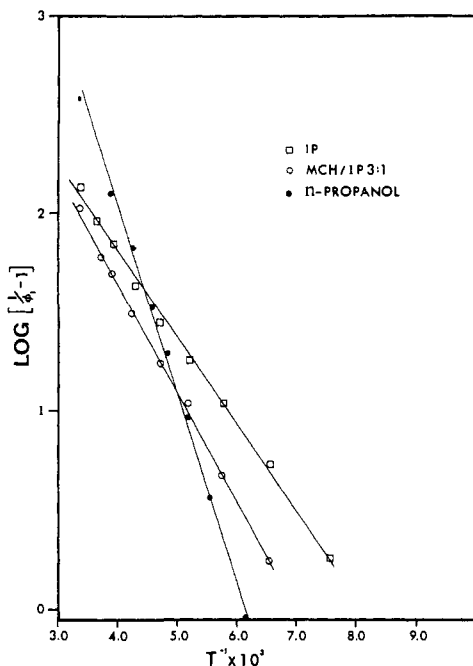


Figure 10. A plot of $\log((1/\phi_F) - 1)$ vs. T^{-1} for TPMB in three solvents, MCH/IP (3:1), 1-propanol, and IP, where ϕ_F is the absolute quantum yield at temperature T . The activation energies determined from the plots are 890, 1530, and 710 cm^{-1} , respectively.

perature the upper torsional modes of the equilibrium excited state become less populated and, if one makes the reasonable assumption that radiationless decay from these levels is more efficient compared to the lowest level in the excited state, one would expect the fluorescence intensity to increase as temperature is lowered.

In the viscosity range where no shifts are observed the increase in viscosity will have no effect on the excited state geometric configuration. However, the torsional oscillations will be damped and their maximum amplitudes will be smaller at higher viscosities, *i.e.*, the shape of the potential energy surface will be dependent on the viscosity. In the excited state this will affect the overlap integrals that govern the rates of radiationless decay. At low viscosities the excited state potential energy surface is broader and the overlap integrals

larger than at relatively higher viscosities. Solute-solvent coupling may also be dependent on viscosity to some extent particularly in polar medium. Further increase in the viscosity will alter the relative positions of the upper and lower potential surfaces causing a change in the overlap integral and leading to enhanced intensities as well as blue shifts of fluorescence.

In order to get some idea regarding the nature of the nonradiative process, plots of $\log((1/\phi_F) - 1)$ vs. $1/T$ in three different media were obtained and are shown in Figure 10. The activation energies obtained are 890 cm^{-1} (MCH/IP, 3:1), 710 cm^{-1} (IP), and 1530 cm^{-1} (1-propanol). The intensity data were obtained by changing the viscosity of the solvent by lowering temperature in a region where no shifts in $\bar{\nu}_F$ are observed; *i.e.*, solute molecules may completely relax and equilibrate among the various excited state torsional modes. Solvent activation energies obtained from macroviscosity vs. temperature data are 1000 for MCH/IP and 1950 cm^{-1} for 1-propanol.

To separate the dependence of fluorescence on temperature from viscosity, it is necessary to use intensity data obtained as a function of viscosity at constant temperature. The fluorescence intensity change due to temperature alone is then plotted as $\log((1/\phi_F) - 1)$ vs. $1/T$. The activation energies thus obtained are 527 and 700 cm^{-1} , in propanol and MCH/IP, respectively. Considering the approximations involved (namely that the η is a linear function of per cent volumes of paraffin oil and that the polarity of ethanol/glycerol mixtures is invariant and is the same as that of 1-propanol) one may only state that the activation energy is a few hundred wave numbers. This corresponds probably to the torsional frequency in the excited state and indicates that a bond with double-bond character is involved which is consistent with our earlier conclusion.⁸ Thus the variation of fluorescence intensity as the viscosity is varied by lowering the temperature is interpreted in terms of activation energies which combine a solvent (viscosity) activation energy as well as a solute activation energy, the solute activation energy being related to the torsional frequency in the excited state.

Acknowledgment. We are grateful to Dr. J. F. Holland for the use of his double-beam quantum yield instrument.