HIGH PRESSURE PHOTOPHYSICS
OF ORGANIC MOLECULES

MASTER

BY

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INTRODUCTION

A simple photophysical process begins with the absorption of a quantum of light to form an electronically excited state. The release of energy occurs on a time scale ranging from thousands of years (a phenomenon which has been used in archeological dating) to shorter than several picoseconds (10^{-12} seconds). Three primary mechanisms result in the release of energy for organic compounds: the emission of light, chemical reaction, and non-radiative transitions. Because these processes occur competitively, their efficiencies are interrelated.

The scientific value in understanding photophysical processes is enormous. The optical properties of luminescent materials such as dyes and phosphors are intimately associated with the function of devices such as fluorescent lamps, light-emitting diodes and lasers. Photochemical reactions represent another area of proved and growing importance for which applications of current interest are abundant. Photochemical synthesis also provides a means of producing compounds which are not readily manufactured by conventional thermal routes.

Most of the work described here deals with the effect of solvent viscosity on the non-radiative deactivation rates from electronically excited states. Pressure was utilized to attain high viscosities in organic solvents at room temperature. Studies of viscosity dependent processes in fluid media are usually carried out by varying the composition or the temperature of the solvent. The problem then arises of separating the viscosity dependence from purely temperature and/or solvent effects. The use of pressure allows a significant range of viscosities to be

attained in a single solvent at a single temperature. If a wider range of viscosities is desired, chemically similar solvents for which the attainable viscosities overlap can be utilized. In this way, a very large viscosity range can be investigated at one temperature with only a few solvents.

The following section gives a brief account of the background and theoretical basis of high pressure research and organic photophysics in general. Next, the high pressure emission apparatus and sample preparation are described. Experimental techniques for recording and analyzing both steady state and emission lifetime experiments are included in the discussion. The following three sections deal with the effect of solvent viscosity on the photophysics of several organic solutes. In the last section, the effect of pressure on the radiative and non-radiative deactivation rates for several linear polyenes is investigated.

GENERAL BACKGROUND AND THEORY

1. Historical Review and Background

1.1 High Pressure Research High pressure has become an important tool for the investigation of interatomic interactions and the electronic structure of condensed media [1,2]. Pressure can significantly alter mean interatomic distances in solids and liquids and thereby affect the numerous chemical and physical properties which are dependent on these distances.

The unit of pressure used here is the kilobar (kbar), which is defined as 10^9 dynes/cm², or about 986.9 atmospheres. Bridgman [3] first extended the range of accessible pressures to about 100 kbar in 1941 by using a two stage piston-cylinder apparatus [4]. This employed the "cascade" principle by enclosing a small piston and cylinder assembly within progressively larger cylinders so that each member in the series of nested vessels is subject only to the difference in stress between the internal and external cells. Practical design considerations limit the device to two stages.

Bridgman has also been credited with the principle of massive support. This principle states that a material can be locally stressed far beyond the yield point if the surrounding support material is below its yield point.

Drickamer et al. [5,6] have constructed supported taper cells which apply the principle of cascading and massive support. The cells permit optical study of small sample volumes at pressures up to 150 kbar. Recent modifications have extended the temperature range from 77°K to 450°K without restricting the pressure range [7]. The development of

Diamond-anvil type cells has enabled investigators to extend the pressure range for optical work to 1.7 megabar [3].

Materials under high pressure have been probed by electrical resistance, X-ray diffraction, Mossbauer resonance and ultra-violet (UV), visible and infrared (IR) spectroscopy. Much of this work and its applications has been presented in the monograph by Drickamer and Frank [2]. Additional reviews of high pressure techniques are also available [9-12].

1.2 Optical Spectroscopy In modern absorption spectroscopy, the absorbance of a material is generally recorded as a function of wavelength. The phenomenon which results in this absorption is the transition between the ground state, which is almost always a singlet state, and an electronically excited state. When electron spins are paired, the state is said to be a singlet state. If a set of unpaired electrons exists, the molecule is said to be in a triplet state because there are three possible spin orientations; however, these orientations are indistinguishable in the absence of strong electric or magnetic fields. Transitions between singlet and triplet states are said to be "forbidden" because electromagnetic radiation is only weakly coupled to the spin vector.

The most readily observed absorption transitions are those between the ground state and excited singlet states. Because of the forbidden nature of the transition involved, singlet-triplet absorption can only be observed for very pure samples, and in spectral regions which are not masked by the more intense singlet-singlet absorptions. Emission spectroscopy often yields information about the nature of states which are not apparent in absorption spectra. In particular, the radiative transition from an excited triplet state to the ground state (phosphorescence), and the transition from an excited singlet state to the ground state (fluorescence) often occur with comparable intensities. Kasha [13] generalized that irrespective

If the state initially excited, the emission usually occurs only from the lowest excited state of a given multiplicity.

Several methods have been employed to investigate relaxation kinetics from excited states. The most commonly used technique is the observation of emission intensities and lifetimes. This yields information about both radiative and non-radiative transition rates from emitting states. Non-emitting states can also affect the photophysics and have been investigated in a variety of ways. For example, the recent development of lasers with short duration (<10 psec), high intensity pulses has enabled the observation of transient absorption associated with repopulation of the ground state. Energy transfer and chemical quenching studies are other techniques which have found application in the investigation of decay mechanisms. Birks has edited comprehensive reviews on the subject of photophysics [14] and reviews of photochemistry appear annually [15].

1. Luminescence of Organic Molecules

2.1 Photophysical Processes and Parameters

Radiative transitions occur between states of different energy. In complex molecules there are also radiationless transitions which occur between different electronic states of the same energy induced by intramolecular vibrations and perturbations by surrounding solvent molecules. A spin-allowed radiationless transition between two states of the same multiplicity is called internal conversion (IC). A spin-forbidden radiationless transition between two states of different multiplicity is called intersystem crossing (ISC). After the initial excitation or after a radiationless transition, the molecule is usually in a vibrationally excited level of a particular electronic state. In a condensed phase, the excess vibrational energy

is quickly dissipated (10^{-12} to 10^{-13} sec) and all photophysical processes occur from an equilibrated system of molecules.

Figure 1 shows schematically the photophysical processes that can occur in an organic molecule in dilute solution following excitation into the lowest excited singlet state S_1 . S_1 can decay: (a) by $S_1 \rightarrow S_0$ fluorescence with rate k_f ; (b) by ISC to a vibrationally excited level of T_1 followed by vibrational relaxation to T_1 with rate k_{ISC} ; or (c) by IC to a vibrationally excited level of S_0 followed by vibrational relaxation to S_0 with rate k_{IC} . T_1 , from (b), decays: (d) by $T_1 \rightarrow S_0$ phosphorescence with rate k_p ; or (e) by ISC to a vibrationally excited level of S_0 followed by vibrational relaxation to S_0 . Fluorescence, phosphorescence, ISC, and IC are the rate-determining processes, since vibrational relaxation is so much faster.

The S_1 decay rate is given by

$$k_{tot} = k_f + k_{ISC} + k_{IC} \equiv 1/\tau_f \quad (1)$$

where τ_f is the observed S_1 lifetime. The fluorescence efficiency from S_1 is given by

$$\phi_f = k_f / (k_f + k_{ISC} + k_{IC}) \equiv k_f \tau_f \equiv \tau_f / \tau_0 \quad (2)$$

where $\tau_0 (=1/k_f)$ is the so-called natural radiative lifetime.

2.2 The Fluorescence Rate Parameter A theoretical expression for ϕ_f has been derived from the Einstein radiation relation using the zero-order Born-Oppenheimer approximation [16,17]

$$k_f^{theor} = 2.88 \times 10^{-9} \frac{n_F^3}{n_A} \langle \bar{\nu}_F^{-3} \rangle_{AV}^{-1} \int \frac{\epsilon(\bar{\nu}) d\bar{\nu}}{\bar{\nu}} \quad (3)$$

Figure 1. Decay of Electronically Excited States
(From reference 14)

where n_F and n_A are the mean refractive indices of the solvent over the $S_0 \rightarrow S_0$ fluorescence and $S_0 \rightarrow S_1$ absorption spectra, respectively, $\frac{-1}{T_{AV}}$ is the reciprocal of the average value of $\bar{\nu}^{-3}$ over the fluorescence spectrum, $\epsilon(\bar{\nu})$ is the decadic molar extinction coefficient, and the integral is taken over the $S_0 \rightarrow S_1$ absorption spectrum. This expression has been extensively tested for a number of molecules and excellent agreement between the theoretical and experimental k_f values has been obtained. If $n_F \approx n_A = n$, expression (3) can be simplified to

$$k_f^{\text{theor}} = n^2 (k_f^{\text{theor}})_0 \quad (4)$$

where $(k_f^{\text{theor}})_0$ is a molecular constant, independent of solvent and temperature. This relation has been verified for several solutes in different solvents over a wide temperature range [18].

For some molecules such as biphenyl and the higher diphenylpolyenes, there are large discrepancies between the theoretical and observed k_f values. Detailed studies of these cases have revealed the presence of "hidden" electronic states [19,20].

EXPERIMENTAL APPARATUS AND PROCEDURE

1. High Pressure Apparatus

1.1 High Pressure Liquid Cell The high pressure liquid emission cell used in this work is a modification of the cell described by Okamoto [21]. It is constructed of Vascomax steel and is equipped with sapphire windows. The cell is sketched in Figure 2. An inner cell made of stainless steel with fixed sapphire windows contains the sample. A stainless steel piston sealed with a teflon o-ring transmits the pressure from the pressurizing fluid (spectral grade hexanes) to the sample. A collar around the side window holds the inner cell in place in the pressure cell. The hexane is pressurized using an intensifier and is transmitted to the cell via a high pressure line. The intensifier uses hydraulic pumps to apply pressure against a 3 1/3 inch piston. This piston pushes against a one inch piston which is forced against the hexane. For experiments in which accurate pressure data is needed at low pressures (less than about 2.5 kbar) a 50,000 psi gauge is used to monitor the hexane pressure directly. For work at higher pressures, the applied hydraulic pressure is read from a Heise Bourdon gauge and the hexane pressure obtained from a calibration curve of hexane pressure versus applied pressure. The calibration curve is checked regularly with a manganin gauge. Details of the intensifier pressure seals and design are given by Okamoto [21]. The cell is operated at ambient room temperature.

The sample is deoxygenated by purging it with argon for about five minutes in a nitrogen filled glove bag. The inner cell is loaded in the glove bag by setting the o-ring in position and filling the cell with

CELL

SAPPHIRE
WINDOW

WINDOW PLUG

Figure 2a. High Pressure Liquid Cell. Seal rings and inner cell positioning collar are not shown. Drawn approximately to scale.

Figure 2b. Detail of Inner Cell

sample solution. The piston is then placed against the o-ring and is pushed in until the piston and o-ring snap together. The inner cell is then removed from the glove bag, placed in the pressure cell, and the remaining collar is put into place. The side window plug and its seal are then assembled and the plug is torqued to 1200 inch-pounds to set the seal. The pressure cell is then filled with hexane. Air bubbles are removed by forcing hexane into the recesses of the cell using a Pasteur pipet with a rubber bulb. The front window is then sealed.

1.2 High Pressure Solid State Cell The solid state high pressure cell used in this work is a modification of the cell developed by Fitch, Flythe, and Drickamer [6]. For emission measurements, the optical windows are located 90 degrees apart. They are filled with optical grade sodium chloride which is transparent to radiation in the region of interest here. The sodium chloride also serves as the pressure transmitting medium. The cell has a one-eighth inch diameter piston and yields an internal pressure up to 40 kbar. Pressure is applied to the cell by means of a hydraulic press with a 4 1/2 inch diameter ram. The external applied pressure is measured with a Heise Bourdon gauge.

The calibration of internal pressure versus external applied pressure has been determined by means of the R_1 ruby fluorescence shift [22]. This shift is $-0.75 \text{ cm}^{-1}/\text{kbar}$ to 195 kbar as determined by the National Bureau of Standards [23]. The calibration is given by eq (5)

$$P_{\text{int}} (\text{kbar}) = 0.08 P_{\text{ext}} (\text{psi}) \quad (5)$$

Further details concerning the high pressure cell and its calibration are given by Drottning [22].

The samples used in this work were dissolved in plastic films. For mounting, the films were cut into 1/8 inch squares. A 1/8 inch diameter by 1/8 inch high cylinder of sodium chloride is carved and then cleaved into two half-cylinders. The sample film is sandwiched between the two half-cylinders. This composite cylinder is then inserted into the cell so that the front face of the film is at a 45 degree angle to the windows. The assembly is press-fused with the top piston by applying about 5 kbar of pressure. A retaining ring is then placed between the fused assembly and the piston. The pressure is cycled between a high pressure and 5 kbar; the high pressure begins at 30 kbar and is progressively lowered 5 to 10 kbar each cycle. This cycling procedure is particularly necessary for accurate intensity measurements.

2. Optical Emission Apparatus

2.1 Steady State Spectroscopy The apparatus used for steady state emission measurements is shown in Figure 3. The light source for optical excitation is housed in a Schoeffel LH150 lamp housing and powered by a Schoeffel LPS271 Lamp Power Supply. All work described here was done using either a Hanovia 150-watt or an Illumination Industries 75-watt xenon arc lamp. Light leaving the housing is focussed into the first of two excitation monochromators (Jarrel-Ash Model 82-410 quarter-meter Ebert driven in tandem). These monochromators contain two gratings, one blazed at 300 nm with a reciprocal linear dispersion (RLD) of 1.65 nm/mm and a second blazed at 600 nm with an RLD of 3.3 nm/mm. The monochromatic light leaving these monochromators is focussed through the high pressure entrance window onto the sample.

Figure 3. Emission Apparatus

The emitted light is observed at a right angle to the incident light path, through the exit window. It is first filtered, if necessary, by one of a number of Corning or Schott glass filters to remove reflected exciting light, which might lead to excessive scattered light or second-order interferences within the emission monochromator. After filtering, the light is focussed onto the entrance slit of a Bausch and Lomb half-meter monochromator. A grating blazed at 500 nm with an RLD of 3.3 nm/mm was used throughout this work. The dispersed light exits the emission monochromator through a variable slit with a typical bandpass of 5 to 10 nm and is focussed on the face of a cooled EMI 9558Q photomultiplier tube operated at -1200 volts. The photomultiplier output is detected by an Ortec photon counting system, with the photons per unit time displayed digitally. Data are taken in a point-by-point fashion by the photon scanner as a function of wavelength. The data are then computer analyzed by a program SKEW [24]. This program corrects for spectral response of the detection apparatus [22,25] and plots the corrected data as relative number of quanta per unit time per unit energy interval versus energy. The least squares fitting routine in SKEW is then used to fit one or more skewed Gaussians [26,27] to the experimental data. Output from the program includes (for each peak) the absolute area of the peak, the peak location, the peak halfwidth, and the peak skewness. Calculations are performed on a DEC-20 computer. Additional detailed information on the apparatus is given by Drotning [22].

2.2 Lifetime Measurements The apparatus used for luminescence lifetime measurements is shown in Figure 4. Several light sources are available for pulsed excitation of the sample, but the short lifetimes of

Figure 4. Transient Emission Apparatus

The molecules studied made it necessary to use a Photochemical Research Associates model 510 nanosecond source which can be flashed up to 20 kHz with flash widths as short as 2 nsec. The excitation wavelength is selected by either a Schoeffel GM 250 quarter-meter grating monochromator or by Schott UV bandpass reflectance filters; either or both of which may be used. Triggering is provided by a 1P28 photomultiplier tube located in the flashlamp housing.

Emission from the high pressure cell can be directed at two detection systems. Filters can be placed in the light path in order to select broad band observation at photomultiplier #1 which is directly in line with the emission window of the high pressure cell. Alternatively, a mirror may be positioned to direct the emission into a Spex model 1870 half-meter grating monochromator and subsequently to photomultiplier #2. Two photomultiplier tubes 9558Q and 9813Q are used; the latter tube is preferred for single photon counting due to the short rise-time and high gain.

For the fast decays encountered in this work, it is necessary to use a single photon counting technique to obtain fluorescence lifetimes. Photon generated output pulses from both the trigger and signal photomultipliers are amplified and converted to uniform pulses by Ortec model 9302 discriminators and then fed into the "start" and "stop" inputs on an Ortec model 467 time-to-pulse-height converter (TPHC). The resultant TPHC output pulse, whose height is proportional to the time between the flash and the detected photon arrival at the signal PM, is received by the multichannel analyzer (MCA) operating in the pulse height analysis mode. One count is then added to the channel number corresponding to the TPHC pulse height. If light levels are kept so low that only one photon is detected every 100 flashes (to minimize the probability that two or more photons will

arrive during the measurement time), a decay curve characteristic of the sample can be generated with 5000 to 10000 counts. The final accumulated decay curve is transferred to a model 33 teletype which punches the data onto paper tape. A program for iterative deconvolution supplied by PRA was used to extract lifetimes from the observed decays.

Crystal Violet

methyl violet

Auramine - O

*dyes
amines*Figure 5. Structure of Crystal Violet
and Auramine O

VISCOSITY EFFECT ON FLUORESCENCE EFFICIENCY IN CRYSTAL VIOLET AND AURAMINE O

1. Introduction

Many non-rigid aromatic molecules in which the aromatic groups are linked by bonds of partial multiple order or polyene chains exhibit a marked enhancement of fluorescence efficiency in fluid solution as the viscosity of the solvent is increased. This effect has been observed in the di- and tri-phenylmethane dyes, the polymethine cyanine dyes, substituted benzophenones, and sterically hindered stilbenes and tetraphenylbutadienes. The dependence of the fluorescence efficiency of the diphenylmethane dye auramine O (AO) and the triphenylmethane dye crystal violet (CV) on solvent viscosity at room temperature has been investigated using pressure to vary the viscosity. Figure 5 shows the structure of the molecules. Mastrangleo and Offen [29] have recently published a similar study of these dyes, but over a much smaller range of viscosities.

Studies of viscosity dependent processes in fluid media are usually carried out by varying the composition or the temperature of the solvent. The problem then arises of separating the viscosity dependence from purely temperature and/or solvent effects. The use of pressure allows a significant range of viscosities to be attained in a single solvent at a single temperature. If a wider range of viscosities is desired, chemically similar solvents for which the attainable viscosities overlap can be utilized. In this way a very large viscosity range can be investigated at one temperature with only a few solvents.

Experimental Procedure

In this paper pressures to 11 kbar on methanol, iso-propanol, iso-butanol, and glycerol are used to obtain solvent viscosities from less than 10^{-2} poise to more than 10^{+3} poise at room temperature. The methanol and iso-butanol (MC/B), the iso-propanol (Aldrich), and the glycerol (Mallinckrodt) were all spectral grade and showed no interfering fluorescence in the spectral region of interest. Care was taken to avoid absorption of atmospheric water by these hygroscopic solvents. The pressure dependence of the viscosities of the solvents is given by Bridgman [30] at 30 and 75°C. This data is used to correct the viscosities to ambient temperature. The currently accepted value for the viscosity of glycerol at 30°C (6.29 poise) was used rather than that given by Bridgman (3.8 poise). The more recent work by Zolotych [31] on the pressure-viscosity relation of carefully dried glycerol to 7 kbar shows excellent agreement with Bridgman's data.

The crystal violet (MC/B) was purified by the method of Lewis et al. [32]. The auramine O (Aldrich) was recrystallized twice from ethanol. All solutions of crystal violet were 4×10^{-6} M. The auramine O solutions were 2×10^{-6} or 4×10^{-6} M. The high pressure liquid cell and emission equipment are described elsewhere [33,34]. CV solutions were excited into the absorption band with maximum at about 590 nm. For AO, the second absorption band with maximum at about 370 nm was used. The excitation wavelengths were adjusted at each pressure to give maximum fluorescence intensity. The shift of the excitation maximum was never more than 8 nm over the 11 kbar viscosity range. The fluorescence intensities were obtained by integration of the corrected emission spectra. All intensities were corrected for the change in concentration due to solvent compressibility using Bridgman's data [35]. Table I gives the position of the emission

Table I. Peak Shifts and Half Width Changes with Pressure

	$\nu_{0.5}^a$	$\Delta\nu^b$ Pressure (kbar)		FWHM ^c Pressure (kbar)		
<u>Crystal Violet</u>		<u>5.0</u>	<u>10.0</u>	<u>0.5</u>	<u>5.0</u>	<u>10.0</u>
methanol	15.94	-0.230	-0.410	2.5	2.6	2.6
iso-propanol	16.07	-0.170	-0.265	2.6	2.4	2.2
iso-butanol	16.07	-0.230	-0.315	2.6	2.3	2.1
glycerol	15.74	-0.100	-0.100	2.9	2.3	2.1
<u>Pyranine 0</u>						
methanol	20.14	-0.350	-0.615	3.6	3.1	3.3
iso-propanol	20.31	-0.285	-0.415	3.1	3.3	3.3
iso-butanol	20.27	-0.360	-0.450	3.2	3.3	3.2
glycerol	19.51	-0.185	-0.090	3.7	3.45	3.40

^aPeak energy (10^3 cm^{-1}) at $P = 0.5 \text{ kbar}$

^b $\Delta\nu$ = peak shift (10^3 cm^{-1}) from 0.5 kbar

^cFull width at half maximum (10^3 cm^{-1})

at 0.5 kbar in each solvent for both dyes, the shift in peak position with pressure and the change in peak width with pressure. The shifts agree well with those indicated by Offen et al. [29].

Results and Discussion

Förster and Hoffman (FH) [28] have investigated the fluorescence efficiency of several triphenylmethane dyes including CV in a variety of solvents at different temperatures. They found that the only relevant solvent property was the viscosity and that for each dye there was a range of "low" viscosities for which the quantum efficiency ϕ was given by $\phi = C\eta^{2/3}$ where C is a constant for a particular dye. For CV, $C = 2.75 \times 10^{-3}$ poise^{-2/3} and the equation holds for $\eta < 200$ poise. At higher viscosities ϕ approaches a limiting value (0.35). FH propose a model to explain the observed dependence of ϕ on η in which the dye molecule is excited to a Franck-Condon vertical state with the phenyl rings still at the ground state equilibrium angle θ_0 . The rings then rotate towards a new equilibrium angle θ'_0 at a rate controlled by Stokes-like viscous damping. $(\theta - \theta'_0)$ therefore decreases exponentially with time with a relaxation time proportional to η . The nonradiative viscosity dependent deactivation rate of the excited singlet is taken to be proportional to $(\theta - \theta'_0)^2$. (For stilbenes, Marafy and Muszkat [36] attribute this deactivation to the effect of η on the twisting and out-of-plane bending motions of the double bond in the excited state. These vibrations are thought to have a strong effect on the Franck-Condon factor and hence on the rate of the IC transition $S_1 \rightarrow S_0$.) There is also a nonradiative viscosity independent deactivation which accounts for the limiting value of ϕ in highly viscous media. The relative emission rate is independent of θ so ϕ is proportional to the excited state lifetime.

In solvents of very low viscosity, the model predicts a viscosity independent minimum value for ϕ . FH calculate an approximate minimum ϕ for these dyes of about 2×10^{-6} . This limiting case was not observed. In more viscous solvents in which the excited singlet is deactivated nonradiatively before ring rotation proceeds very far, there are two limiting cases. The most interesting is where deactivation by η dependent nonradiative processes predominates (intermediate η). This gives $\phi = C\eta^{2/3}$. The other limiting case is where radiative deactivation is dominant (high η). Here $\phi = \tau_0/\tau_s$ where τ_0 is the characteristic time for deactivation of the excited singlet by radiative and η independent nonradiative processes and τ_s is the natural radiative lifetime of the excited singlet.

The data for CV and AO are shown in log-log form in Figures 6 and 7. The CV data in Figure 7 has been displaced along the arbitrary intensity axis to show that for $\log \eta > -0.5$ the two dyes exhibit identical dependence of fluorescence efficiency on solvent viscosity. The dashed line in Figure 7 indicates the deviation of the AO intensities at low η . The line of slope 0.7 drawn in Figure 7 shows excellent agreement with the CV data over 3.5 orders of magnitude in viscosity. At very low η there is a small but definite deviation from linearity and at high η the intensities begin to level off. The AO data is also linear with a slope of 0.7 over a smaller range of 2.5 orders of magnitude in viscosity. It exhibits identical limiting behavior at high η , but much larger deviations from linearity at low η . It should be noted that the deviation at low viscosity is towards a larger viscosity dependence of the fluorescence intensity. The FH theory predicts a leveling, i.e., a lower viscosity dependence at low viscosities. We do not at present have an explanation for this discrepancy. Oster and Nishijima [37] have measured ϕ for AO in glycerol

Figure 6. Log Intensity vs. Log Viscosity-Auramine O

Figure 7. Log Intensity vs. Log Viscosity-Crystal Violet

function of temperature from about 5 to 35°C. Their experimentally determined viscosities varied from about 2 to 25 poise in this temperature range. Analysis of their data also shows that ϕ is proportional to $\eta^{2/3}$. The FH model is thus shown to adequately describe the dependence of ϕ on η for AO and CV over a large viscosity range with deviations occurring only at low viscosities.

Fluorescence quantum efficiencies in glycerol at 25°C ($\eta = 9.5$ poise) were measured relative to quinine sulfate in 1 N H_2SO_4 ($\phi = 0.55$) [38] for AO and relative to rhodamine B in ethanol ($\phi = 0.66$) [25] for CV as described in reference [39]. Values obtained were 0.030 for AO and 0.019 for CV. These compare to a value for CV of 0.012 calculated using the FH data and a value for AO of 0.022 from ref. 37.

The theory of Förster and Hoffman does not bear directly on the mechanism of the energy loss other than giving the quadratic interaction discussed above. Clearly, because of the viscosity dependence it is an intermolecular process. The results do not contain any detailed information on the mechanism but one can gain some insight from peak shifts and half-width changes in terms of a single configuration coordinate diagram. The coordinate in question would presumably involve the interaction of the dye with neighboring solvent molecules. The peak shift and half-width can be expressed as follows [33,34]:

$$\Delta h\nu_e = \frac{Pq_0}{R} + \frac{(R-1)P^2}{2w^2} \quad (6)$$

$$(\delta E_{1/2})_e = N \left| \frac{Wq_0}{R^{1/2}} + P \frac{(R-1)}{wR^{3/2}} \right| \quad (7)$$

Here q_0 is the displacement of the excited state potential well relative to the ground state well along the coordinate of interest at $P = 0$. k is the force constant of the ground state, and $R = (w'/w)^2$ is the ratio of excited state to ground state force constants. R and w^2 may be pressure dependent but it is difficult to extract information on this point. Let us consider the crystal violet data. In methanol one observes an essentially linear red shift and a half-width independent of pressure. This would imply a negative q_0 and $R \approx 1$. As the solvents become more viscous, there is an increasing tendency for the rate of shift to decrease with increasing pressure and for the half-width to decrease also as P increases. Both these observations are consistent with q_0 being negative and with an R which is increasingly greater than one, i.e., the excited state potential well becomes increasingly stiffer with increasing solvent viscosity. The same trends are noted for auramine O. Since R and w^2 are very probably pressure dependent, a detailed discussion is difficult.

In Figure 8 the effect of stiffening the wells is shown, everything else being constant. One must keep in mind that, because there is a shift of the emission peak to lower energy with increasing pressure and, in some cases, a narrowing of the peak, the excited state potential well at high pressure (and high viscosity) will, in fact, be displaced both vertically and horizontally from its position at low pressure (low viscosity). In Figure 8 we do not show these displacements because we are trying to emphasize the effect of increasing R on the barrier height for internal conversion. As one can see, an increase in R could profoundly effect both the probability of internal conversion and the reversibility of the process by raising the energy of the intersection of the ground and excited state surfaces.

Figure 8. Schematic Configuration Coordinate Diagram

VISCOSITY EFFECT ON THE QUENCHING OF NAPHTHALENE FLUORESCENCE BY BIACETYL

1. Introduction

The quenching of naphthalene fluorescence by biacetyl in fluid solution has been shown to occur by energy transfer from naphthalene to biacetyl [40,41]. The low extinction coefficient of biacetyl rules out the possibility of any appreciable long range singlet-singlet energy transfer [41,42] at least up to the viscosities used in this work. The critical radius R_0 for dipole-dipole resonance transfer from naphthalene to biacetyl in methylcyclohexane ($\sim 7 \text{ \AA}$) is about equal to the collisional intermolecular separation ($5.8 \text{ \AA}$) calculated from the van der Waals volumes of the molecules [43,44]. This suggests that the quenching can be treated as a diffusion controlled process with unit quenching probability per encounter.

2. Experimental Procedure

In this work pressures to 10 kbar on methylcyclohexane (MC/B Spectroquality) are used to obtain solvent viscosities from less than 10^{-2} to about 10 P at room temperature. Other pressure studies of diffusion controlled energy transfer have been made, but over much smaller viscosity ranges [45,46]. The pressure dependence of the viscosity of methylcyclohexane to 8 kbar is given by Bridgman at 30 and 75°C. [47]. This data was extrapolated to 10 kbar and used to correct the viscosities to ambient temperature. Naphthalene (Aldrich, zone-refined 99.9 + %) was used as received. Biacetyl (Aldrich) was fractionally distilled under a nitrogen atmosphere and the middle fraction was retained and stored in

the dark. The naphthalene concentrations used in the pressure experiments were 1×10^{-3} or 2×10^{-3} M. The biacetyl concentrations were 1.14×10^{-2} or 2.28×10^{-2} M. Solutions were excited at 300 nm. At the concentrations used both self-quenching of naphthalene and distortion of its fluorescence spectrum by biacetyl absorption are negligible. Solution degassing was accomplished by several repetitions of a vacuum freeze-thaw cycle. The high pressure liquid cell and emission equipment are described elsewhere [33,34].

The relative naphthalene fluorescence yields I_p at each pressure were determined from the peak fluorescence intensity at $\lambda \approx 335$ nm. The emission spectrum is virtually unchanged with respect to position and shape over the 10 kbar pressure range. All intensities and concentrations entering into the calculations are corrected for solvent compressibility using Bridgman's data [48].

In order to obtain k_p the experimental quenching rate parameter at pressure P from the pressure quenching experiments the Stern-Volmer equation is used in the form

$$\frac{I_{P0}}{I_p} = \frac{1 + k_p \tau_p [Q]_p}{1 + k_{p0} \tau_{p0} [Q]_{p0}} \quad (8)$$

Here the subscripts P_0 and p indicate that the subscripted variables are evaluated at 1 atm and pressure p , respectively. τ is the donor fluorescence lifetime in the absence of quencher. τ_{p0} is taken as 109 nsec [49]. τ_p is calculated from the data of Offen and Phillips [50], which indicates an approximately 15% decrease in the fluorescence lifetime of naphthalene over 10 kbar. The quenching rate at 1 atm (k_{p0}) in methylcyclohexane was obtained from Stern-Volmer experiments at a

naphthalene concentration of $4 \times 10^{-3} \text{ M}$ and biacetyl concentrations up to $4.56 \times 10^{-3} \text{ M}$. At these concentrations only a small amount of incident light is absorbed by the quencher. The Stern-Volmer plots were linear in this concentration range, and gave a rate of $1.3 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. The pressure runs required the use of more concentrated biacetyl solutions to insure that even at the highest viscosities there is a reasonable probability that an excited donor molecule will encounter a quencher molecule during its lifetime. The good agreement of runs made at two biacetyl concentrations indicates the absence of a significant internal filter effect. The emission of naphthalene without quencher ($Q = 0$) is constant to $\pm 1\%$ over 10 kbar. The experimental and calculated parameters appear in Table II.

3. Results and Discussion

A plot of $\log k_p$ against $\log \eta$ is shown in Figure 9. Also shown is data from Birks and Leite [43], who determined the quenching rates for this system in ten pure solvents and solvent mixtures of varying viscosities by relative fluorescence yield and lifetime measurements. Over much of the viscosity range there is good agreement of the quenching constants obtained through pressure experiments on a single solvent and those from Stern-Volmer experiments on different solvents. The pressure technique has obvious advantages in that it allows a significant range of viscosities to be attained in a single solvent at a single temperature in one experiment.

It is interesting to look at what can be said about the mutual diffusion coefficient D_{AB} from this data. It has been shown [51-53] that in the limit of low quencher concentrations the Stern-Volmer equation reduces to

Table II. Experimental and Calculated Parameters

	Pressure (kbar)											
	0.0	0.5	1	2	3	4	5	6	7	8	9	10
$[Q]_p/[Q]_{p_0}$	1.00	1.04	1.08	1.11	1.17	1.19	1.20	1.22	1.24	1.25	1.28	1.30
$\tau_p/\tau_{p_0}^a$	1.00	0.99	0.98	0.97	0.95	0.94	0.93	0.91	0.90	0.88	0.87	0.85
l_p/l_{p_0}												
b	1.00	1.55	1.76	2.53	3.39	4.39	5.41	6.67	7.75	8.93	9.71	10.3
c	1.00	...	1.54	2.38	...	4.17	...	6.53	...	8.62	9.35	10.2
d	1.00	1.44	1.66	2.50	3.58	4.98	6.67	8.55	10.6	12.6	14.2	15.3
$kc\lambda_p (M^{-1} \text{sec}^{-1})$												
b	10.11	9.89	9.82	9.62	9.46	9.31	9.18	9.05	8.93	8.81	8.73	8.66
c	10.11	...	9.86	9.66	...	9.34	...	9.06	...	8.84	8.77	8.68
d	10.11	9.93	9.86	9.65	9.47	9.30	9.15	9.01	8.98	8.76	8.67	8.59
$\eta_p/\eta_{p_0}^e$	1.0	1.7	2.4	5.1	10.2	20	38	71	129	240	437	813

^a $\tau_{p_0} = 109 \text{ nsec.}$ ^b $[Q]_{p_0} = 1.14 \times 10^{-3} M.$ ^c $[Q]_{p_0} = 1.14 \times 10^{-2} M.$ ^d $[Q]_{p_0} = 2.28 \times 10^{-3} M.$ ^e $\eta_{p_0} = 7.1 \times 10^{-3} P (T = 23^\circ C).$

Figure 9. Plot of $\log k_p$ vs. $\log \eta$

$$\frac{I_0}{I} = 1 + 4\pi N' R D_{AB} \tau_0 [Q] \left[1 + \frac{R}{(D_{AB} \tau_0)^{1/2}} \right], \quad (9)$$

where N' is the number of particles per mole and R is some interaction distance. Thus, the experimentally obtained quenching constants should be given by

$$k_{\text{exp}} = 4\pi N' R D_{AB} \left[1 + \frac{R}{(D_{AB} \tau_0)^{1/2}} \right]. \quad (10)$$

Using a reasonable value of $7 \text{ \AA}$ for R , D_{AB} is calculated to be $2.4 \times 10^{-5} \text{ cm}^2/\text{sec}$ for $\eta = 0.7 \text{ cP}$ ($P = 1 \text{ atm}$) and $5.8 \times 10^{-7} \text{ cm}^2/\text{sec}$ for $\eta = 550 \text{ cP}$ ($P = 10 \text{ kbar}$). This compares to values of 2.7×10^{-5} and $3.4 \times 10^{-8} \text{ cm}^2/\text{sec}$ calculated from the Stokes-Einstein equation with slip.

$$D_{AB} = D_A + D_B = \frac{k_B T}{4\pi\eta} \left(\frac{1}{r_A} + \frac{1}{r_B} \right) \quad (11)$$

taking $r_A = r_B = 3.5 \text{ \AA}$. If the Stokes-Einstein equation is valid and if $D_{AB} = D_A + D_B$, then Eq. (10) predicts that for low viscosities where the term in parentheses is about equal to 1 the slope of a plot of $\log k_{\text{exp}}$ against $\log \eta$ should be -1. The observed initial slope is -0.65. In order to account for this and similar discrepancies observed by other workers Alwattar et al. [54] assert that the Stokes-Einstein equation is inadequate when applied to particles of molecular size. However, self-diffusion and viscosity data on tetramethylsilane and benzene obtained by Parkhurst and Jonas [55] over a 5 kbar range indicate that the Stokes-Einstein equation is adequate for self-diffusion. Another possibility is that $D_{AB} \neq D_A + D_B$. If the solutions are thermodynamically nonideal, factors of the form $\partial \ln a / \partial \ln X$ should be included, where a is the activity and X the mole

fraction. At the high dilutions used here this could be a very large factor and one sensitive to the solution properties.

Nemjek and Ware [49] have used fluorescence decay measurements to obtain the encounter radius and mutual diffusion coefficient of a donor-acceptor pair by analysis of the nonexponential decay of the donor fluorescence in a viscous solvent. A high pressure study of this type would provide information on the viscosity dependence of these parameters and allow comparisons with results from steady-state quenching experiments.

VISCOSITY EFFECT ON FLUORESCENCE AND
PHOTOISOMERIZATION OF TRANS-STILBENE

1. Introduction

The photoisomerization of stilbene is of considerable interest from both a theoretical and a practical point of view, particularly as a prototypical example of polyenes such as vitamin A and the visual pigments which play an important role in photobiology. Light absorption in the stilbene system is followed by a rapid change in molecular configuration due to twisting about the double bond. This change in molecular geometry upon excitation gives rise to the unusual emission properties observed in stilbene and the polyenes. Such a process involving rotation about a double bond has the advantage of possessing a reaction coordinate easily separable from other molecular coordinates, thereby facilitating theoretical description.

Early work by Dyck and McClure [56] and Malkin and Fischer [57] on the temperature dependence of trans-stilbene fluorescence and isomerization quantum yields established that almost all decay from the first excited trans singlet ($^1t^*$) can be accounted for by fluorescence or by crossing into the state from which subsequent isomerization occurs. Great controversy arose over the identification of the process competing with fluorescence from $^1t^*$. Förster [58] proposed a model in which the process was assigned to intersystem crossing (ISC) into the triplet stilbene manifold ($^3t^*$) followed by isomerization via a triplet state common to both isomers. Saltiel [59] assigned the competing process to activated rotation about the central bond to form a twisted (perp) singlet ($^1p^*$) from which isomerization occurs by efficient internal conversion to the

ground state S_0 . This singlet mechanism (eq. 12-16) has received additional theoretical and experimental support and is the currently accepted model for direct trans-stilbene photoisomerization.

A consequence of this mechanism is the prediction of very short lifetimes for stilbene fluorescence at moderate temperatures. This is in conflict with recently reported fluorescence lifetime work by Birch and Birks [60] in which a two component exponential decay was reported. At room temperature the long component was found to be 1.65 nsec and the short component less than 0.2 nsec in methylcyclohexane/isohexane. In order to account for this, it was proposed that during the singlet (S_1) lifetime, thermal equilibrium is established between $^1I_t^*$ and $^1I_p^*$ by reversible internal conversion across the potential barrier. Preliminary fluorescence data by Teschke and co-workers [61] seem to indicate such an equilibrium between a fluorescing and a non-fluorescing state. However, a recent picosecond study [62] of the effect of temperature on trans-stilbene fluorescence lifetimes (in which a careful search for a long decay component was made) and our observations on these lifetimes at room temperature in various solvents show only a single very short simple exponential decay. Until further data are available to resolve this question, we assume that the

$1_t^* \rightarrow 1_p^*$ internal conversion is effectively unidirectional as originally proposed by Saltiel. A small degree of reversibility would not affect the general conclusions reached herein.

Two pieces of evidence were instrumental in establishing the singlet mechanism. One was the observation by Saltiel and Megarity [63] that the effect of azulene on the photostationary states for direct stilbene photoisomerization is small and independent of solvent viscosity, while the effect of azulene on sensitized stilbene photoisomerization is large and viscosity dependent. In the sensitized experiments the azulene acts as an efficient acceptor of triplet excitation from 3_t^* at the diffusion controlled rate resulting in a large enhancement of the amount of trans isomer in the photostationary state mixture. The small viscosity independent enhancement of the trans isomer in the direct isomerizations is attributed to long range singlet-singlet energy transfer. These experiments established that ISC is not an important (< 5%) decay path for unperturbed trans-stilbene in non-viscous solvents at room temperature.

The second key piece of evidence for the singlet mechanism was the observation by Saltiel and D'Agostino [64] that fluorescence and isomerization yields remain coupled in a highly viscous solvent upon lowering the temperature. On the basis of these experiments they postulated the existence in viscous solvents of a viscosity dependent barrier to $1_t^* \rightarrow 1_p^*$ rotation giving an overall activation energy for this process of $E^\ddagger = E_t^\ddagger + E_v^\ddagger$ where $E_t^\ddagger$ is the inherent thermal barrier and $E_v^\ddagger$ is the viscosity dependent barrier. The individual activation energies were then extracted by use of the Arrhenius and Andrade equations to analyze the dependence of the fluorescence quantum yields upon temperature and upon

viscosity (at varying temperature and at constant temperature using glycerol/water mixtures).

The ordering of the lowest energy excited singlet states of the all-trans polyenes has been the subject of much study [65,66]. In these molecules the excited $\pi\pi^*$ states are of either A_g or B_u symmetry and the only allowed electric dipole transitions from the A_g ground state are to u states. It was thought that the excited A_g state would be located at much higher energy than the B_u state due to its doubly excited character, but recent theoretical work has shown that when doubly excited configurations are included in the configuration interaction this state exists at an energy much lower than previously supposed [65-67]. In fact these calculations predict that in the higher polyenes the doubly excited A_g singlet should be the lowest singlet lying just below the singly excited B_u state [66]. The B_u state has considerable Rydberg character while the excited A_g state is covalent suggesting that the B_u state is much more sensitive to solvent changes than is the A_g excited state [65]. The very strong solvent dependence of the quantum yields and fluorescence lifetimes of all-trans-1,6-diphenyl-1,3,5-hexatriene (DPH) has been attributed to the modification of the energy gap between these states by solvent polarizability [68,69].

Orlandi and Siebrand [70] have proposed a potential energy diagram for trans-stilbene isomerization based upon such a low energy doubly excited singlet state. This A_g state which for trans-stilbene arises from an electronic excitation mainly localized in the ethylenic fragment, has higher energy than the lowest B_u state for planar geometry, but lower energy for twisted geometries. The two potentials intersect at some angle $\theta = \theta_s < 90^\circ$ leading to a reversal of the state order. Birch and

Birks have used this potential energy diagram in their discussion of stilbene isomerization. Birks [71] has recently presented this semi-empirical model in more detail and applied it to the higher polyenes. Figure 10 shows schematically the angular dependence of the ground and excited singlet state potentials in trans-stilbene based on this model.

In this report we investigate the effect of solvent viscosity on fluorescence and isomerization quantum yields of stilbene at room temperature by using high pressure to alter solvent viscosities. Viscosities from less than 10^{-2} poise to more than 10^3 poise were obtained by application of pressures to 11 kbar on organic solvents. The use of pressure allows a clean separation of the viscosity effect from purely temperature and solvent effects — both of which are important in this system.

2. Experimental Procedure

2.1 Materials trans-stilbene (Aldrich) was recrystallized twice from $\text{CHCl}_3/\text{EtOH}$ and then sublimed. Analysis by glpc showed no volatile impurities other than a trace of cis-stilbene. A pure sample of cis-stilbene was obtained by preparative glpc. 600 ml of spectral glycerol (Mallinckrodt) was mixed with 200 ml water and filtered through activated charcoal to remove UV absorbing impurities. The anhydrous glycerol was recovered by fractional distillation at high vacuum. Methanol, isobutanol, n-hexane, and MCH were all MC/B fluorometric solvents and were used without further purification in the fluorescence experiments. HMN (Aldrich) and paraffin oil (Amoco #31-U.S.P.) were used to attain high viscosities in a non-polar solvent. The HMN was used without further purification. The paraffin oil was stirred 12 hours over fuming sulfuric acid (30% SO_3), washed, neutralized, and filtered through silica gel and alumina. This

Figure 10. Potential energy diagram of ground and two lowest excited singlet states of trans-stilbene as a function of rotation angle θ . After refs. 60 and 71.

treatment reduced the fluorescence background by a factor of about 20 for 313 nm irradiation. The alcohols for the isomerization experiments were distilled over BaO to remove trace acidic impurities which catalyzed cis to trans isomerization upon concentration of the irradiated solutions. The MCH was distilled to remove small amounts of high boiling substances which interfered with the glpc analysis.

2.2 Atmospheric Fluorescence Yields Fluorescence quantum yields at atmospheric pressure for trans-stilbene in methanol were obtained relative to quinine sulfate in 1 N H_2SO_4 ($\phi_f = 0.55$) [38] at 23°C. Fluorescence spectra of stilbene and the standard were taken on a previously described emission spectrometer [33,34] using photon counting at very low excitation intensities. Loss of fluorescence intensity while the spectrum was being taken (due to trans to cis photoisomerization) was negligible. The relative fluorescence intensities were obtained by integration of the corrected emission spectra. Refractive index corrections were made to adjust for the different solvents used with the standard and the stilbene solution. Concentrations of solutions were adjusted so that optical densities were approximately equal at the exciting wavelength (295 nm) and the fluorescence intensities were corrected for small differences in optical density. Fluorescence quantum yields for trans-stilbene in other solvents were determined by comparison with the quantum yield in methanol. This was done on an uncorrected fluorometer (Farrand Mk II) by monitoring the emission intensity at the wavelength of maximum intensity in each solvent and assuming that the intensity is proportional to the area of the emission spectrum in that solvent. (Emission spectra changed only slightly in position and half-width in the solvents studied.) Refractive index corrections were made as above.

2.3 High Pressure Fluorescence Yields The high pressure liquid cell and associated emission equipment have been described elsewhere [33,34]. Trans-stilbene solutions (4×10^{-6} M) were excited into the absorption band with maximum at about 308 nm. The excitation wavelength (bandwidth 0.5 nm) was adjusted at each pressure and for each solvent to give maximum fluorescence intensity. The shift of the excitation maximum was never more than 3 nm over the 11 kbar pressure range. Photon counting at very low excitation intensities was used to minimize trans to cis isomerization. In order to further reduce the time that the solution was irradiated during a pressure run, only the emission intensity at the wavelength of maximum intensity was taken at each pressure. This emission intensity was corrected for photomultiplier and monochromator response, and taken to be proportional to the area of the emission spectrum at that pressure. The emission spectrum undergoes a red shift with increasing pressure, but the halfwidth is little changed. Intensities were corrected for the increase in solution concentration due to solvent compressibility using Bridgman's data [35,47]. The compressibility of n-heptane was used for HMN and paraffin oil was assumed to be 85% as compressible as n-heptane. It is unlikely that these estimated values differ by more than 10% from the actual compressibilities. No correction for the approximately 10% increase in refractive index [86] from atmospheric pressure to 11 kbar has been applied to the high pressure intensity data. The design of the collection optics in the high pressure emission equipment makes this correction negligible.

2.4 High Pressure Isomerization Rates Solutions at pressure were irradiated in a cylindrical stainless steel inner cell designed for high pressure absorption work [21] with path length of about 1.5 cm. The sapphire window assembly at one end of the cell was replaced with a

polished stainless steel plunger to reflect exciting light back into the solution. It was verified that the extent of photoisomerization was directly proportional to irradiation time for small conversions showing the absence of any appreciable dead volume in the cell. All solutions were deoxygenated by bubbling argon through them for several minutes. Trans-stilbene solutions (4×10^{-6} M) were irradiated at the wavelength of maximum emission intensity for each pressure and solvent as determined in the fluorescence experiments. Cis-stilbene solutions (1×10^{-5} M) were irradiated at 277 nm. A solution was brought to pressure, irradiated for the time necessary to bring about approximately 10% isomerization at 0.5 kbar, the pressure was released, and the sample set aside while the process was repeated at another pressure. After several pressure runs, the solutions were concentrated on a hotplate under a stream of argon. This treatment was shown not to affect cis/trans ratios if carefully done. The solutions were then analyzed by glpc for the per cent conversion (glass 3 ft $\times$ 1/8 in column of 3% SE-30 on Chromosorb P, T 155°C).

2.5 High Pressure Viscosities The pressure dependence of the viscosities of the solvents in Figure 11 is given by Bridgman at 30 and 75°C [47]. The Andrade equation is used to correct the viscosities to ambient temperature at each pressure. The currently accepted value for the viscosity of glycerol at 30°C (6.29 poise) is used rather than that used by Bridgman (3.8 poise) which he took from the International Critical Tables. The more recent work by Zolotykh [31] on the pressure-viscosity relation of carefully dried glycerol to 7 kbar shows excellent agreement with Bridgman's data.

2.6 Fluorescence Lifetimes The picosecond laser, streak camera, and digitizing system have been previously described [87]. The Nd^{3+} : YAG

laser 4th harmonic (265 nm) was used to excite trans-stilbene (5×10^{-5} M) in various solvents at room temperature. Streak camera optics were quartz, allowing observation of the entire trans-stilbene fluorescence spectrum. Ten decay curves were obtained in each solvent, summed, and fitted to a single exponential decay. In each case a good fit was obtained.

3. Results and Discussion

3.1 Fluorescence Quantum Yields and Lifetimes Fluorescence lifetimes and quantum yields obtained for trans-stilbene in various solvents at 23°C (λ_{exc} 295 nm) are shown in Table III. Also shown are quantum yield data from Saltiel's work. Agreement between the two sets of data is very good. Figure 11 shows the fluorescence quantum yield as a function of solvent viscosity at room temperature in several solvents. Figure 12 is a plot of ϕ_f versus P in 2,2,4,4,6,8,8-heptamethylnonane (HMN) and paraffin oil — solvents for which the pressure dependence of viscosity is not known. The 10 kbar point in HMN was disregarded as it seemed inconsistent with the other data. This was the last point taken and it is likely that some photoisomerization occurred resulting in a low ϕ_f . Solutions were deoxygenated although fluorescence yields in solution are almost unchanged even under an oxygen atmosphere. $\phi_f^{\text{Ar}} / \phi_f^{\text{O}_2} = 1.03 \pm 0.02$ in n-pentane; [68] $\phi_f^{\text{Ar}} / \phi_f^{\text{O}_2} = 1.01 \pm 0.02$ in paraffin oil (this work).

The dependence of the fluorescence yields on viscosity indicates the presence of a viscosity barrier to $1_t^* \rightarrow 1_p^*$ rotation even in the non-viscous solvents studied. There is also an inherent thermal barrier to the twist which is not addressed in these experiments. It should be noted that even quite non-viscous solvents such as the commonly used 1:1 methylcyclohexane/methylcyclopentane (MCH/MCP) mixture become significantly

Table III. Fluorescence Quantum Yields and Lifetimes at 23°C

Solvent	ϕ_f	τ_f (p sec)
methanol	0.026	
isobutanol	0.032	70
<u>tert</u> -butanol	0.035 [63]	
glycerol	0.26 0.26 (T = 25°C) [64]	650
<u>n</u> -pentane	0.043 (T = 20°C) [72]	
<u>n</u> -hexane	0.043	
MCH	0.047 0.046 (T = 25°C) [72]	
HMN	0.048	85
paraffin oil	0.15

Figure 11. ϕ_f vs. log viscosity: trans-stilbene in several solvents.

Figure 12. ϕ_f vs. pressure: trans-stilbene in paraffin oil and in 2,2,4,4,6,8,8-heptamethylnonane

are viscous at low temperatures. For example, MCH/MCP attains a viscosity of about 10^4 poise at -175°C [73]. When a solvent such as this is used in a low temperature fluorescence yield experiment to extract the thermal activation energy via an Arrhenius plot, the observed ϕ_f must contain both thermal and viscosity dependent contributions.

In order to explain the $\eta^{2/3}$ dependence of the fluorescence yield in the triphenylmethane dyes, Förster and Hoffman [28] proposed a model in which the phenyl rings rotate to a new equilibrium position after excitation at a rate controlled by Stokes-like viscous damping. The non-radiative, viscosity dependent deactivation rate of the excited singlet was taken to be quadratically proportional to the angle of ring rotation. Although this model accounts for the emission quantum yields, it predicts a fluorescence decay of the form $\exp(-bt^3/\eta^2)$ where b is a constant. However, a simple exponential decay has been observed in the triphenylmethane dye malachite green [74]. It is difficult to see how any model in which there is a time dependent rate of excited state deactivation could give rise to a simple exponential fluorescence decay as observed in trans-stilbene and malachite green. We, therefore, assume that the rate of viscosity dependent t^* deactivation is time independent and assign it the value k_c . Whether or not this is also the rate of rotation about the central bond k_{tp} postulated by Birch and Birks [60], Saltiel and D'Agostino [64], and others, is unknown.

It is evident from Figure 11 that in addition to the viscosity dependence of the fluorescence yields, there is also a strong solvent dependence. For example, at a viscosity of 0.1 poise in isobutanol, MCH, and n-hexane, the fluorescence yields are 0.045, 0.080, and 0.13, respectively. This large enhancement of ϕ_f in hydrocarbon solvents over

that in polar solvents has received little attention. Saltiel and Megarity [63] noted the low ϕ_f in the viscous tert-butanol in comparison to the higher ϕ_f in the non-viscous n-pentane, but attached no particular significance to it. A similar solvent effect has been observed in trans-1,1,4,4-tetraphenyl-2-methylbutadiene [75] and in DPH [76].

The solvent effect can be rationalized in terms of Birk's potential diagram (Figure 10). An increase in solvent polarizability decreases the $^1B_u^*$ energy thereby lowering the S_1 potential barrier to rotation. This increases the rate of non-radiative $^1t^*$ deactivation resulting in a lower ϕ_f . Also the angle θ_s at which the avoided crossing occurs increases -- making viscosity more effective at hindering deactivation of $^1t^*$ in a polar solvent than in a non-polar solvent. This may explain the large slope of the ϕ_f versus $\log \eta$ plot for the highly polar methanol. As expected, the absorption spectrum of trans-stilbene undergoes a bathochromic shift of about 175 cm^{-1} upon changing the solvent from a hydrocarbon to glycerol due to stabilization of the excited state by the more polar solvent [64]. The findings for the two hydrocarbon solvents n-hexane and MCH are rather puzzling. The data show that the slope is larger in n-hexane. The smaller ϕ_f in MCH could be due to its greater molecular polarizability (note that at low viscosities the difference in ϕ_f is not large). Phenomonologically, this indicates that an increase in viscosity is much less effective in hindering twisting in MCH than it is in n-hexane. This may perhaps be connected with the shape of the molecule -- the other solvent molecules are much more "cylindrical" than MCH.

From our ϕ_f and τ_f data at room temperature we calculate the radiative rate k_f as $4.0 \times 10^8 \text{ sec}^{-1}$ in glycerol; $4.6 \times 10^8 \text{ sec}^{-1}$ in isobutanol; and $5.6 \times 10^8 \text{ sec}^{-1}$ in HMN. A theoretical value of k_f in

n-pentane of $5.9 \times 10^8 \text{ sec}^{-1}$ has been obtained by Marinari and Saltiel [77] from the integrated absorption spectrum using the Birks-Dyson relation [17]. The small solvent dependence observed is supported by the relative insensitivity of the trans-stilbene absorption and fluorescence spectra to solvent changes [63]. A similar insensitivity to pressure is the justification for taking k_f to be pressure independent.

Figures 11 and 12 show that at the highest viscosities attained, ϕ_f has reached a limiting value in glycerol and paraffin oil. The ϕ_f in HMN shows signs of limiting at some value near that for the paraffin oil. At these high viscosities the excited trans-stilbene molecule experiences hindrance to twisting from the walls of its now rigid solvent cage. The rotational deactivation path from 1_t^* is closed off and the excited molecule either fluoresces or undergoes ISC to 3_t^* . The cessation of molecular twist in the excited singlet is consistent with the observation that the excited state absorption of 1_t^* shows no decay in the 120 psec after excitation in a polymethylmethacrylate (PMMA) matrix in contrast to the fast decay observed in n-hexane solution. It should be noted that the complete inhibition of the $1_t^* \rightarrow 1_p^*$ rotation does not necessarily mean that trans to cis photoisomerization has also ceased. As Birks has pointed out [78], isomerization via a triplet mechanism could still occur. The reduction in the rate of the process $3_t^* \rightarrow 3_p^*$ would be less important than in the corresponding singlet process because of the longer 3_t^* lifetime. Such a triplet mechanism is operative in the trans to cis photoisomerization of the styrylnaphthalenes [79,80] which occurs even in rigid media such as polystyrene [81]. A similar triplet mechanism for isomerization also seems to be operative in trans-stilbene at high viscosities and

at room temperature. Irradiation at these viscosities leads to loss of fluorescence intensity indicative of trans to cis isomerization.

The rate of ISC at room temperature k_{is} can be calculated from the limiting ϕ_f values at high viscosity by use of eq. 17.

$$(\phi_f)_{\eta \rightarrow \infty} = k_f / (k_f + k_{is}) \quad (17)$$

Calculated k_{is} values are $3.3 \times 10^8 \text{ sec}^{-1}$ in glycerol and $2.4 \times 10^8 \text{ sec}^{-1}$ in paraffin oil (using $k_f = 5.6 \times 10^8 \text{ sec}^{-1}$ in this solvent). The difference between these values is probably not significant, but both are much larger than the generally quoted values. These range from about $2 \times 10^7 \text{ sec}^{-1}$ (the value for β -styrylnaphthalene) [82] to about $6.4 \times 10^7 \text{ sec}^{-1}$ (from computer assisted curve fitting of ϕ_f vs T) [72]. However, the large k_{is} values obtained are not in conflict with the photochemical behavior of trans-stilbene at room temperature (see below). The near unity ϕ_f in hydrocarbon solvents at -190°C [36] is explained by assuming that k_{is} decreases as the temperature is lowered. At these low temperatures the trans to cis isomerization yield $\phi_{t \rightarrow c}$ is small ($\phi_{t \rightarrow c} = 0.006$ at -183°C) [57] so k_{is}^0 can be calculated as above. At about -190°C , $k_f^0 = 5.8 \times 10^8 \text{ sec}^{-1}$ from low temperature ϕ_f [36] and τ_f [62] data giving $k_{is}^0 = 3.1 \times 10^7 \text{ sec}^{-1}$.

Knowing k_f , k_{is} , and ϕ_f at some viscosity allows calculation of the rate of configuration dependent $^1t^*$ decay (k_c) via the relation:

$$\phi_f = k_f / (k_f + k_{is} + k_c) \quad (18)$$

In n-hexane at atmospheric pressure and room temperature, k_c is $1.2 \times 10^{10} \text{ sec}^{-1}$. Values in the other non-viscous solvents studied are not far different. Calculation of the ISC quantum yield ϕ_{is} in these solvents shows that only about 2% of the $^1t^*$ states undergo ISC to $^3t^*$. This is well below the 5% ISC yield which could have been detected in

Megarity and Saltiel's azulene quenching experiments [63]. In glycerol k_c is $8.1 \times 10^8 \text{ sec}^{-1}$ giving an ISC yield of 21%. Thus, the triplet mechanism plays a significant role in trans-stilbene photoisomerization in glycerol and other viscous solvents at room temperature.

Since the yield of cis- and trans-stilbene from $^1p^*$ and $^3p^*$ are identical [83], measurements of the photostationary states in a particular solvent give no information on whether the isomerization proceeds via a singlet mechanism, a triplet mechanism, or both simultaneously. This explains why the same photostationary states are observed in glycerol and in non-viscous solvents. The use of a triplet interception method to determine the ISC yield in glycerol would be extremely difficult as the high viscosity would result in a much smaller rate of triplet quenching and thereby cause only slight trans enhancement for reasonable quencher concentrations. The high pressure technique described here seems the best way to approach the problem.

3.2 Initial Isomerization Rates In Figure 13 the effect of viscosity on the initial rate of trans to cis photoisomerization relative to the initial rate at a viscosity corresponding to a pressure of 0.5 kbar is shown in several solvents at room temperature. The data represent the relative rates during the first 10% of the trans to cis conversion. Also shown are data obtained for the cis to trans conversion in isobutanol. The fraction (about 0.1) of excited cis molecules which undergo photocyclization and oxidation by traces of oxygen giving phenanthrene seemed little affected by pressure and was ignored in the calculation of the relative rates.

Although there is a fair amount of scatter in the data, several conclusions can be drawn. In all solvents studied, the rate of trans to cis conversion decreases at the highest solvent viscosities showing that ϕ_f

Figure 13. Relative $\phi_{t \rightarrow c}$ vs. $\log \eta$ in several solvents and $\phi_{c \rightarrow t}$ in isobutanol.

and $\phi_{t \rightarrow c}$ are indeed coupled in moderately viscous media at room temperature in accordance with the singlet mechanism (eq. 12-16). The slope of the $\phi_{t \rightarrow c}$ vs. $\log$ plot is greater in methanol than in the other solvents. This is consistent with the large viscosity effect on ϕ_f in methanol as discussed above -- solvent viscosity is more effective at hindering $1_t^* \rightarrow 1_p^*$ in polar solvents. In some cases it appears that at intermediate pressures (2-5 kbar) $\phi_{t \rightarrow c}$ actually increases as the viscosity increases. A likely explanation is that pressure alters the cis/trans decay ratio from 1_p^* further in favor of the cis isomer ($1-\alpha = 0.59$ in non-viscous solvents at atmospheric pressure) [83]. At higher viscosities the decrease in the rate of twist giving rise to 1_p^* overpowers the increase in cis/trans decay ratio from 1_p^* resulting in a lower $\phi_{t \rightarrow c}$. The fast drop in the rate of the cis to trans conversion between 0.5 and 4 kbar is consistent with an increase in the cis/trans decay ratio in this pressure range. From 5 to 10 kbar, $\phi_{c \rightarrow t}$ seems independent of both solvent viscosity and pressure. The viscosity independence is in agreement with the results of Gegiou, Muszkat, and Fisher [84] in glycerol at temperatures down to -80°C implying that the rate of the process $1_c^* \rightarrow 1_p^*$ is much less sensitive to solvent viscosity than that of $1_t^* \rightarrow 1_p^*$. This is illustrated by the observation that the cis to trans conversion occurs rapidly in a PMMA matrix at pressures to 100 kbar as shown by the rapid growth of trans-stilbene fluorescence intensity upon irradiation [85].

4. Conclusion.

Trans-stilbene direct photoisomerization proceeds predominately via the singlet mechanism (ISC yield $\approx 2\%$) in nonviscous solvents at room temperature. As solvent viscosity is increased at room temperature,

isomerization via the triplet mechanism becomes increasingly competitive due to inhibition of the $^1t^* \rightarrow ^1p^*$ process. In glycerol at room temperature about 21% of the $^1t^*$ states undergo ISC to $^4t^*$. If the $^3t^* \rightarrow ^1t$ radiationless decay is negligible as suggested by the identical photostationary states observed for perhydro- and perdeuterio- stilbenes with high energy sensitizers [59] then 21% of the isomerization occurs via the triplet mechanism in glycerol. The ability of high pressure to alter solvent viscosities at one temperature is a very useful tool in the investigation of photochemical processes involving changes in molecular geometry upon excitation.

PHOTOPHYSICS OF POLYENES AT HIGH PRESSURE

1. Introduction

Linear conjugated polyenes have a characteristic strongly allowed $\pi\pi^*$ transition ($B_u \leftarrow A_g$ in point group C_{2h}) in the near UV or visible region. MO models of polyene electronic structure incorporating only singly excited configurations predict that this strongly allowed transition is lowest in energy followed at higher energies by two states of A_g symmetry to which transitions from the A_g ground state are symmetry forbidden. Many of the linear polyenes fluoresce and interpretation of the fluorescence data on the basis of the above state ordering leads to certain anomalies. The observed fluorescence lifetimes of the diphenylpolyenes are found to be much longer than the lifetimes calculated from the absorption intensities of the $B_u \leftarrow A_g$ transition. Also anomalous are the large Stokes shifts and the very different solvent shifts of absorption relative to emission.

The observation in 1972 by Hudson and Kohler [88] of a structured weak absorption at an energy lower than that of the strong absorption and the publication by Schulten and Karplus [89] of the results of an MO calculation including CI with all singly and doubly excited states led to a fundamental re-evaluation of polyene photophysics. The calculations indicated that a low energy singlet A_g state is a general feature of linear polyenes and in some cases could be the lowest excited singlet. Hudson and Kohler assigned the weak absorption ($f \approx 0.05$) to the symmetry forbidden $A_g \leftarrow A_g$ ($S_1 \rightarrow S_0$) transition. They proposed that the transition responsible for fluorescence is $A_g \rightarrow A_g$ ($S_1 \rightarrow S_0$) which gains

oscillator strength through intensity borrowing from the allowed ${}^*B_u \rightarrow A_g$ ($S_2 \rightarrow S_0$) transition.

The apparent anomalous fluorescence behavior of linear polyenes is easily explained by this model. The discrepancy between the observed and calculated natural fluorescence lifetimes is due to the different states involved in absorption and emission. The large Stokes shifts which increase with polyene length are only the energy difference between the *B_u (S_2) and *A_g (S_1) states. The large absorption shifts are consistent with the large dipole transition moment for the ${}^*B_u \rightarrow A_g$ ($S_2 \rightarrow S_0$) transition. The much smaller solvent and temperature shifts of the fluorescence spectrum are a reflection of the small transition dipole for the ${}^*A_g \rightarrow A_g$ ($S_1 \rightarrow S_0$) transition.

Hudson and co-workers [88,90] have shown that for many polyenes the positions of the 0-0 absorption and fluorescence bands in solution are given by an expression of the form $\nu = \nu_0 - \alpha K$ (19) where ν_0 is the energy of the transition in the gas phase, α is the solvent polarizability $(n^2-1)/(n^2+2)$ and n is the solvent index of refraction, and K is a constant related to the oscillator strength of the transition. The strong absorption occurs in solution 2000 - 3000 cm^{-1} to the red of its gas phase position giving a value for K of about 10^4 cm^{-1} per unit change in α . Values of K obtained from plots of fluorescence frequency vs α are typically a factor of 5 - 20 smaller [88]. Therefore as α is increased, the 0-0 energy gap ΔE_{0-0} between the allowed *B_u (S_2) and forbidden *A_g (S_1) state rapidly decreases. Since this gap is only 1000 - 2000 cm^{-1} in the lower polyenes, a significant perturbation can be introduced by fairly small changes in α .

Andrews and Hudson [91] have used a perturbation theory approach to derive an expression for the solvent dependence of the radiative rate of a forbidden transition in the presence of vibronic mixing. Their expression has the form

$$k_f = \frac{9n^3}{(n^2+2)^2} \frac{\Gamma^2}{(\Delta E_{0-0})^2} \quad (20)$$

where Γ is a constant for a given molecule and ΔE_{0-0} is the energy difference between the 0-0 bands of absorption and emission. As mentioned above, ΔE_{0-0} is a strong function of solvent α so that eq. 20 predicts a radiative rate which is very sensitive to solvent polarizability. Analysis of radiative rate data for DPH and trans-retinol in several solvents and over a large temperature range gave quantitative agreement with theory.

Birks and co-workers [68,69] have used a similar expression

$$k_f = \frac{k_{f2} v^2}{(\Delta E_{0-0})^2} = \frac{n^2 k_{f20} v^2}{(\Delta E_{0-0})^2} \quad (21)$$

to describe the solvent and temperature effect on the $S_1 \rightarrow S_0$ radiative rate k_f in DPH and DPO. In this expression v is the matrix element coupling the $S_1 \rightarrow S_0$ and $S_2 \rightarrow S_0$ transitions. k_{f2} is the $S_2 \rightarrow S_0$ radiative rate in cyclohexane obtained from the experimental absorption spectrum via the Birks-Dyson relation [17]. k_{f20} ($= k_{f2}/n^2$) has been observed to be independent of solvent and temperature for many organic solutes in several solvents [18]. Plots of k_f vs $(\frac{n}{\Delta E_{0-0}})^2 \equiv \beta$ were found to be linear giving v values of 745 cm^{-1} for DPH and 500 cm^{-1} for DPO. As β increased from about $20 \times 10^{-8} \text{ cm}^2$ to about $85 \times 10^{-8} \text{ cm}^2$, the radiative rate for DPH increased from about $3 \times 10^7 \text{ sec}^{-1}$ to about $12 \times 10^7 \text{ sec}^{-1}$. For DPO, β ranged from

about $15 \times 10^{-8} \text{ cm}^2$ to $30 \times 10^{-8} \text{ cm}^2$ while k_f increased from about $0.7 \times 10^6 \text{ sec}^{-1}$ to $2.1 \times 10^7 \text{ sec}^{-1}$ [69].

We report here the results of high pressure spectroscopic studies on DPH, DPO, and retinyl acetate in which pressure is used to modulate the energy gap between the borrowing and lending states through its effect on the solvent-chromophore dispersion interactions. Studies were made to 10 kbar in fluid solution and to 40 kbar in polymer films. The use of high pressure allows a wide range of α to be attained at room temperature in a single solvent. In addition, pressure studies in plastic media permit the attainment of higher α values than are available by the temperature variation method.

2. Experimental Procedure

2.1 Materials DPH (Aldrich) was recrystallized twice from benzene/hexane and DPO (Aldrich) twice from toluene. All-trans retinyl acetate (Sigma) was purified by liquid chromatography on silica gel. After removal of solvent the oily yellow liquid was crystallized and recrystallized from methanol giving fine yellow crystals which were stored under high vacuum in the dark. Methylcyclohexane (MC/B Spectroquality), toluene (Baker Photrex), and perfluoro-n-hexane (Pierce) were used as received. None exhibited significant fluorescence in the spectral region of interest. The polymethylmethacrylate (PMMA) and polystyrene (PS) used in this work were prepared and purified by Mitchell [92]. Plastic films of about 0.02 cm thickness containing the solutes under study were prepared by dissolving the solutes and polymer in methylene chloride and evaporating the solvent over several days under a stream of nitrogen. All films were prepared and stored at room temperature and in the dark.

2.2 Atmospheric Quantum Yields Fluorescence quantum yields at atmospheric pressure for DPH and DPO in the fluid solvents studied were obtained relative to quinine sulfate in 1 N H_2SO_4 ($\phi_f = 0.55$) at 23°C. Fluorescence spectra of the polyenes and the standard were taken on a previously described emission spectrometer [33,34] using photon counting at very low excitation intensities. A bandpass of 0.5 nm was used both in taking the optical densities and the emission spectra in order to reduce the uncertainties in the effective absorbance arising from the highly structured polyene absorption spectra. Loss of fluorescence intensity while the spectra were being taken (due to trans to cis photoisomerization) was negligible. Data were taken in a point-by-point fashion as a function of wavelength. The data were then analyzed by a program SKEW. This program corrects for spectral response of the detection apparatus and plots the corrected data as relative number of quanta per unit time per unit energy interval versus energy [22,]4]. The least squares fitting routine in SKEW was then used to fit a skewed Gaussian curve to the experimental data. Although the DPH and DPO emission spectra have considerable vibrational structure, the integrated intensities for the Gaussian and the observed spectrum were not significantly different. The n^2 refractive index corrections were made to adjust for the different solvents used with the standard and the polyene solutions. Concentrations of solutions were adjusted so that optical densities were approximately equal and less than 0.05 at the exciting wavelength (350 nm). The fluorescence intensities were corrected for small differences in the optical densities. All polyene solutions were deoxygenated by bubbling argon through them for several minutes. Atmospheric fluorescence yields in the polymeric media were made on optically dense ($\text{OD} > 2$) polyene films relative to an optically

dense 9,10-diphenylanthracene film in PMMA ($\phi_f = 1.0$) [93]. The films were held at an angle of 45° to the incident light and fluorescence was also observed at this angle. Schott cutoff filters were used to prevent scattered exciting light from reaching the detector. DPH and RAc films were excited at 345 nm, and DPO films at 375 nm.

2.3 High Pressure Emission Experiments The high pressure liquid cell and associated emission equipment have been described elsewhere [21]. Polyene solutions (5×10^{-7} M to 1×10^{-6} M) were excited into the most intense absorption band. The excitation wavelength (bandpass 0.5 nm) was adjusted at each pressure and for each solvent to give maximum fluorescence intensity. The shift of the excitation maximum was fairly large over the 10 kbar pressure range necessitating the correction of the observed fluorescence intensities for the output of the xenon lamp-monochromator combination. The fluorescence intensities were obtained as above. All intensities were corrected for the change in concentration due to solvent compression. The compressibility of methylcyclohexane (MCH) was taken from Bridgman [48]. The Tait equation was used to calculate the compressions of toluene and perfluoro-n-hexane. For toluene the Tait B and C constants of Andersson [94] were used. For perfluoro-n-hexane the 1 atm compressibility was estimated from the value given for perfluoro-n-heptane by Smith and Hildebrand [95] by multiplying this value by the ratio of the compressibility of n-hexane to that of n-heptane. The Tait C was taken to be 0.21 which is the usual value for non-polar liquids. All polyene solutions were deoxygenated as above.

The solid state high pressure cell used for attaining pressures from 4 to 40 kbar has been described elsewhere [6]. The optically dense films used had concentrations between 2 and 5×10^{-3} M.

2.4 High Pressure Excitation Experiments The high pressure apparatus is as above. Polyene solutions were between 5×10^{-7} and 1×10^{-6} M. The concentrations of the optically dilute polyene films were between 2 and 5×10^{-5} M. At each pressure the emission monochromator was set at the wavelength of maximum emission and the excitation monochromator was scanned from 300 nm to longer wavelengths. Cutoff filters were used to block scattered exciting light. The observed fluorescence intensities were corrected for the output of the xenon lamp-monochromator combination at each excitation wavelength. The correction factors were obtained by using optically dense PMMA films containing various organic fluorophores as quantum counters. The most useful were azulene (250 nm to 340 nm) and dicarboethoxyaminoazulene (290 nm to 460 nm). A comparison between the dicarboethoxyaminoazulene film and a 3 g/l solution of rhodamine B in ethylene glycol both observed at 45° to the front surface showed agreement to 5% from 290 to 390 nm and to 10% from 400 to 460 nm. The 1 atm excitation spectra are virtually identical in shape and in position of the band maxima with the corresponding absorption spectra. The same agreement was observed between high pressure absorption and excitation spectra in the polymer films. A correction for the optical characteristics of the apparatus was determined each time that an excitation spectrum was taken. A skewed Gaussian was fit to each spectrum as above. Solutions were deoxygenated.

2.5 Fluorescence Lifetime Measurements Fluorescence lifetimes were determined by the single-photon technique. The basic set-up has been described [96]. A PRA model 510 nanosecond flashlamp was used for excitation. Fluorescence was isolated with cutoff filters and viewed at 90° to the direction of excitation by an EMI 9813Q fast photomultiplier. A Schoeffel high intensity monochromator was used to excite DPO and RAC

solutions at the nitrogen 381 nm and 337 nm bandheads respectively. For DPH a deuterium flash at 350 nm was used. Lifetimes were obtained by iterative deconvolution using a program obtained from PRA. Measurements were made on deoxygenated solutions (1×10^{-6} to 5×10^{-6} M) and on the optically dense films.

2.6 ΔE_{0-0} Determination In all cases the shift in the 0-0 absorption band with pressure was obtained by fitting the excitation spectra with a skewed Gaussian curve and assuming the shift in the Gaussian maximum was the same as the shift of the 0-0 band. The relative intensities of the different maxima changed little with pressure. Up to 10 kbar in the liquid cell for DPH and DPO, the fluorescence bands were sufficiently well resolved to be taken directly from the observed spectra. A computer fit was not used because there was a significant redistribution of intensity into the higher energy vibronic bands with pressure causing large apparent blue shifts. Pressure broadening of the vibronic bands in the polymer films at high pressures (> 16 kbar) made it very difficult to determine the 0-0 band location in emission. In these cases, shifts obtained from computer fits and shifts obtained by eye from the broad spectral maximum were averaged. The experimental values of $\Delta E_{\text{max-max}}$ at each pressure were normalized to the known 1 atm values of ΔE_{0-0} . These values were calculated using experimental values for the 0-0 band absorption maxima in each solvent studied determined on a Cary 14, and Birks' values of $\nu_F^\circ = 24800 \text{ cm}^{-1}$ for DPH and 22035 cm^{-1} for DPO [69]. In the absence of any vibrational structure in the RAc spectra, ΔE_{0-0} was crudely approximated by subtracting one-half the sum of the widths of the absorption and emission spectra.

2.7 Refractive Indices The pressure dependence of refractive index for toluene has been measured by Vedam and Limsuwan [86]. For MCH the change in refractive index with pressure was assumed to be the same as for n-heptane and was also taken from Vedam. Changes in n for C_6F_{14} and the polymer films were calculated from the Lorentz-Lorenz equation. The compression of PMMA was taken from Stephens [97] and of PS from Bridgman [98]. Initial densities used were 1.492 for PMMA and 1.594 for PS.

3. Results and Discussion

Table IV summarizes the 1 atm fluorescence quantum yield, lifetime, and ΔE_{0-0} values obtained for each polyene in each solvent studied. Our experimental fluorescence quantum yields for DPH in MCH, toluene, and C_6F_{14} are a factor of 1.25 ± 0.04 greater than those for DPH in MCH, benzene, and C_6F_{14} given in ref 99 where 9,10-diphenylanthracene ($\phi_f = 0.83$) was used as a quantum standard. When the experiment was repeated using 9,10-diphenylanthracene as the standard ($OD < 0.05$) a fluorescence yield of 0.63 was found for DPH in MCH in good agreement with ref 99. Our results are similar to those obtained by Berlan [100] and Birks and Dyson [17]. DPH lifetimes and both DPO yields and lifetimes in fluid solution are in excellent agreement with literature values [68,69,99]. Preliminary work on RAC in fluid solution showed that even at very low excitation intensities in deoxygenated solutions, photodecomposition was fast. In addition, fluorescence decays in MCH and toluene were highly non-exponential. Therefore this polyene was studied only in polymer films where it showed excellent photostability and fluorescence decays were exponential. No references to polyene yields or lifetimes when dissolved in polymeric media could be located in the literature.

Table IV. 1 Atm Fluorescence Yields, Lifetimes, and ΔE_{0-0} Values

		ϕ_f	τ_f (nsec)	ΔE_{0-0} (10^3 cm^{-1})
DPH in:	MCH	0.83	13.2	1.97
	TOL	0.87	6.1	1.55
	C ₆ F ₆	0.64	31.2	3.13
	PMMA	0.96	9.1	1.63
	PS	1.0	5.6	1.25
DPO in:	MCH	0.09	6.6	3.12
	TOL	0.14	7.2	2.72
	PMMA	0.11	7.1	2.78
	PS	0.10	7.0	2.40
RAC in:	PMMA	0.11	8.7	5.7
	PS	0.09	8.5	3.1

The peak positions obtained by computer fitting of a skewed Gaussian curve to the corrected excitation spectra are plotted versus solvent α in Figure 14. The plots are fairly linear (correlation coefficient $> .99$) in accordance with eq 19. Slopes are 14600 for DPH and DPO, and 29300 for RAc. These compare to slopes of 10600 for DPH [91] and 10909 for octatetraene [101] from solvent and temperature variation studies. A slope of about 6500 for RAc can be obtained from data in ref 102. The reason for the very large pressure-induced shifts in RAc is unknown.

Figure 15 shows the shifts of the excitation and emission spectra for DPH and DPO to 10 kbar versus solvent compression. The much larger shift of absorption relative to emission is quite evident. Also of interest are the almost identical absorption shifts of DPH and DPO in the solvents studied. In Figures 16 and 17 are shown the shifts to 40 kbar in PMMA and PS. The absorption shifts for DPO and RAc are much larger than the emission shifts. However, this is not the case for DPH. The DPH emission shift is comparable to the absorption shift and even appears to be increasing faster than the absorption shift at high pressures. This shift is much larger than any attainable for DPH by solvent variation or low temperature experiments and is unexpected. One possibility based on Birks' [103] general model for polyenes of potential interaction of the *A and *B potentials via a vibrational mode of b_u symmetry, is that sufficiently high pressures distort the potential surfaces so as to cause increased mixing of the *A and *B wavefunctions resulting in a more " *B -like" S_1 potential. In general, shifts are larger in the more polarizable PS than in PMMA.

Figure 18 exhibits the effect of solvent compression on the absolute fluorescence yields and lifetimes of DPH in MCH and toluene. DPH yields

Figure 14. Energy of Absorption Spectrum Centroid vs. Solvent α

Figure 15. Absorption and Emission Shifts vs. Solvent Compression

Figure 16. Absorption and Emission Shifts in PMMA

Figure 17. Absorption and Emission Shifts in PS

Figure 18. DPH Fluorescence Yields and Lifetimes vs. Solvent Compression

decrease about 30% in the 10 kbar pressure range while the lifetime drops to 1/4 of its 1 atm value in MCH and to 1/3 of its 1 atm value in toluene. It is interesting to compare these data with those obtained by Cehelnik and co-workers [99] in MCH at temperatures from 100°C to about -100°C. The solvent volume contraction in this range is approximately the same as that produced by a pressure of 10 kbar. However, the effect on ϕ_f and τ_f is quite different. ϕ_f increases by a factor of about 2 while τ_f decreases about 20%. The radiative rates ($= \phi_f/\tau_f$) in both experiments therefore increase by about the same factor as predicted by the Lorentz-Lorenz equation and eqs 19 and 20. The striking differences in the observed behavior of ϕ_f and τ_f must be ascribed to large pressure and/or temperature effects on the non-radiative rates. For example, in MCH the non-radiative rate k_{nr} ($= 1/\tau_f - k_f$) decreases from $4.2 \times 10^7 \text{ sec}^{-1}$ at about 100°C to about $0.8 \times 10^7 \text{ sec}^{-1}$ at -100°C. When roughly the same volume decrease is obtained upon application of 10 kbar pressure, k_{nr} increases from about $1.1 \times 10^7 \text{ sec}^{-1}$ to about $12.1 \times 10^7 \text{ sec}^{-1}$. The nature of the non-radiative transition in the high pressure experiments is not clear. It is unlikely to be $S_1 \rightarrow S_0$ internal conversion because the theoretical value for the internal conversion rate k_{IC} is only about 10^6 sec^{-1} for a molecule such as DPH with an S_1 energy of about 25000 cm^{-1} . In the simplest diphenylpolyene, trans-stilbene, the dominant S_1 radiationless transition is the thermally activated internal rotation around the central ethylenic bond [60]. Birks and co-workers [69] have proposed a similar pathway for DPH. Such a model is consistent with the observed decrease in k_{nr} as the temperature is lowered. In stilbene, however, the rate of the internal rotation has also been found to be significantly viscosity-dependent [64,104]. As solvent viscosity is increased by high pressure or other means, the rate

of rotation decreases and at very high viscosities, ceases entirely [104]. The increase in MCH viscosity in 10 kbar is sufficient to cause a factor of about 4 decrease in k_{nr} for stilbene. For the same increase in viscosity, a factor of 10 increase in k_{nr} is observed for DPH. The same large increases in k_{nr} are observed in the plastic films. It therefore seems likely that high pressure is opening an important new radiationless pathway in DPH. One possibility is intersystem crossing to the triplet manifold. This would require that the 1 atm $S_1 \rightarrow T_1$ yields ($\phi_{ISC} \approx 0.02$) [105] increase dramatically with pressure. No experimentally significant change in k_{nr} was observed for DPO in fluid solutions. In the polymer films, k_{nr} for DPO increased from about $1.3 \times 10^8 \text{ sec}^{-1}$ at 1 atm in both PMMA and PS to $1.8 \times 10^8 \text{ sec}^{-1}$ in PMMA and $2.9 \times 10^8 \text{ sec}^{-1}$ in PS. For RAc, k_{nr} increased from about $1.0 \times 10^8 \text{ sec}^{-1}$ in both PMMA and PS to $1.4 \times 10^8 \text{ sec}^{-1}$ in PMMA and $2.0 \times 10^8 \text{ sec}^{-1}$ in PS.

Figure 19 shows ϕ_f and τ_f for DPO in the liquid cell. ϕ_f increases by about 70% while τ_f decreases about 5% over the 10 kbar pressure range. Figures 20 and 21 are plots of ϕ_f and τ_f vs pressure in the plastic films. For DPH, ϕ_f shows an initial decrease with pressure followed by an increase. τ_f decreases rapidly with pressure as it did in fluid solution. At high pressures in PS, τ_f seems to reach a limiting value of about 1.7 nsec. The changes in ϕ_f and τ_f for DPO in the plastics are qualitatively similar to those observed in the liquid cell only of greater magnitude. RAc shows a moderate gain in ϕ_f finally levelling off and perhaps even decreasing slightly at the highest pressures. τ_f is observed to increase slightly at low pressure, but to decrease at a rate about equal to that of DPO at higher pressures.

Figure 19. DPO Fluorescence Yields and Lifetimes vs. Solvent Compression

Figure 20. Polyene Fluorescence Yields and Lifetimes in PMMA vs. Pressure

Figure 21. Polyene Fluorescence Yields and Lifetimes in PS vs. Pressure

Figure 22 presents quantum yields, fluorescence lifetimes, and the shifts in absorption and emission for DPH in perfluoro-n-hexane to 10 kbar. At room temperature this solvent freezes at a pressure between 1.5 and 2.5 kbar. There was considerable variation of freezing pressure within these limits from run to run. The 1 atm τ_f (31.2 nsec) is considerably larger than that observed in other solvents. As pressure is applied, it rapidly decreases until at about 1.5 kbar it is 22 nsec. Upon further application of pressure the solvent freezes and τ_f suddenly drops to about 11 nsec and continues to decrease as the ice is further compressed. There is also a discontinuous red shift of about 1500 cm^{-1} in the position of the absorption maximum upon freezing.

In Figures 23 and 24 are shown the effect of pressure on the radiative rates k_f for each polyene in each solvent. In each case k_f increases with pressure. This is in accord with eq 21 since the 0-0 gap between S_1 and S_2 (ΔE_{0-0}) in the right hand denominator of eq 21 is decreasing with pressure. Of lesser importance is the increase of n with pressure. The highest values of k_f for DPH and DPO observed in the pressure experiments are approximately 5 times larger than the highest k_f attainable by other methods.

Figures 25 and 26 plot k_f vs β . Figure 25 shows data for DPH and DPO in the liquid cell all to 10 kbar except for DPH in C_6F_{14} (which freezes above 1.5 kbar) and DPH in toluene. For DPH in toluene only the 1 atm and 0.5 kbar points are shown. At higher pressures ΔE_{0-0} becomes so small (650 cm^{-1} at 9 kbar) that β blows up. The dashed lines are the best fit to temperature and solvent variation data from reference 69. They are extended to the limit of the data in reference 69. The close agreement between our data and Birks' for DPH is somewhat fortuitous since our ϕ_f

Figure 22. DPH Fluorescence Yields, Lifetimes, and Shifts in C_6F_{14}

Figure 23. Polyene Radiative Rates in Fluid Solution vs. Solvent Compression

Figure 24. Polyene Radiative Rates in Plastic Media vs. Pressure

Figure 25. Polyene Radiative Rates in Fluid Solution

vs. $\left(\frac{n}{\Delta E_{0-0}}\right)^2$

Figure 26. Polyene Radiative Rates in Plastic Media
vs. $(\frac{n}{\Delta E_{0-0}})^2$

values are a factor of 1.25 ± 0.04 greater than those used by Birks which were taken from reference 99 (see experimental section). Our data for DPO closely follow Birks' extrapolated data over much of the experimental range. The fairly small deviation at high β values is judged to be within the possible experimental error. Figure 26 presents the data for the three polyenes in polymeric media to 40 kbar. The dashed lines are extrapolated from Birks. Note the larger range of β attained in the plastics over that in fluid solution, except for DPH in toluene, for which ΔE_{0-0} decreases to about 650 cm^{-1} at 9 kbar due to the much larger red shift of absorption relative to emission. Although the absorption red shift in the plastics is equal or greater to that in toluene, it is counterbalanced by the large emission red shift resulting in smaller values of β . For DPH our data and the extrapolation of Birks' data are in good agreement. The scatter at high values is due both to the increased uncertainty in determining ΔE_{0-0} at high pressures as the result of pressure broadening of the emission and to the sensitivity of β to the exact ΔE_{0-0} used for small ΔE_{0-0} .

The pressure data for DPO fall to either side of the extrapolated line. The differences in behavior between the PMMA and PS films appear to be larger than can be accounted for by any likely experimental error. Although small errors in ΔE_{0-0} can cause large changes in the calculated parameters at high pressures (i.e., ΔE_{0-0} small) their effect is much smaller at low pressures. The observation that even at low pressures the data points in PMMA and PS do not fall on the same line suggests that the discrepancy is a real one.

A similar situation arises for RAC. Although the crude procedure used to obtain ΔE_{0-0} from these structureless spectra (see experimental

section) may result in large errors, the low pressure values of 3 should be fairly insensitive to them. Again, the data points fall on different curves as for DPO.

4. Conclusions

High pressure can be used to perturb significantly the ionic *B_u state in all linear polyenes studied, while leaving the covalent *A_g state essentially unaffected in DPO and RAc. If the unexpectedly large pressure-induced shifts in *B_u for RAc are a general feature of the retinyl polyenes, potentially interesting changes in their photochemical behavior could be produced by high pressure.

Eq 21 can be used to calculate the changes in radiative rate k_f for DPH upon modulation of the energy gap between the lending (*B_u) and borrowing (*A_g) states by high pressure just as it can for solvent and temperature induced gap changes. It appears to also hold to a slightly lesser degree for DPO, but to fail for RAc.

The DPH non-radiative rate is affected by high pressure in a very different way than by lowering the temperature contrary to expectations based on simple solvent density arguments. The non-radiative rates for DPO and RAc are much less affected by pressure.

SUMMARY

High pressure spectroscopic studies on several classes of organic compounds were made both in fluid solution (to 100 kbar) and in polymeric media (to 40 kbar). The first three studies were conducted in fluid solution and concern the effect of solvent viscosity on the non-radiative deactivation rates from electronically excited states. Pressure was utilized to attain high viscosities in organic solvents at room temperature. The primary experimental technique used was fluorescence emission spectroscopy. In the fourth and last study observations were made both in fluid solution and in plastic films. The focus of this study was the effect of pressure on the solvent-chromophore dispersion interaction in several polyenes and the concomitant changes in both the radiative and non-radiative rates from the excited states. Extensive use was made of fluorescence lifetime measurements and excitation spectra.

~~In the first study it was observed that the fluorescence efficiency of the dyes crystal violet and auramine O shows a large increase as solvent viscosity is increased. This is interpreted to indicate that high viscosity slows some non-radiative deactivation rate of the excited singlet state (probably involving a torsional mode of the phenyl rings).~~

~~The effect of solvent viscosity on the rate of quenching of naphthalene fluorescence by biacetyl in degassed methylcyclohexane at room temperature was investigated using pressure to alter the viscosity from 10^{-2} poise to about 10 poise. Rates obtained are in good agreement with those measured by other workers in several solvents and solvent mixtures of varying viscosities at atmospheric pressure.~~

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High pressure spectroscopic studies on several classes of organic compounds were made both in fluid solution (to 100 kbar) and in polymeric media (to 40 kbar). The first three studies were conducted in fluid solution and concern the effect of solvent viscosity on the non-radiative deactivation rates from electronically excited states. Pressure was utilized to attain high viscosities in organic solvents at room temperature. The primary experimental technique used was fluorescence emission spectroscopy. In the fourth and last study observations were made both in fluid solution and in plastic films. The focus of this study was the effect of pressure on the solvent-chromophore dispersion interaction in several polyenes and the concomitant changes in both the radiative and non-radiative rates from the excited states. Extensive use was made of fluorescence lifetime measurements and excitation spectra.

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The fluorescence quantum yields and the initial photoisomerization rates for trans-stilbene in several deoxygenated solvents were obtained as a function of solvent viscosity at room temperature by using pressures to 11 kbar to alter solvent viscosity. At high viscosities in paraffin oil and glycerol, the fluorescence yield approaches a limiting value associated with the complete inhibition of molecular twist. Analysis of the data gives the rates of intersystem crossing and of viscosity dependent deactivation via twist of the planar excited singlet.

In many polyenes, transitions to the lowest excited singlet state are symmetry forbidden while transitions to the next highest singlet are strongly allowed. Emission occurs from the lowest excited singlet. The radiative rate from this state is a strong function of the energy gap between the two states. Pressure is used to modulate the energy gap and the resultant changes in the radiative rate are compared to those predicted from a simple intensity-borrowing expression.

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APPENDIX A

TABULATED POLYENE SPECTRAL DATA

In this appendix are presented the smoothed experimental fluorescence yields ϕ_f , lifetimes τ_f , and energy gap ΔE_{0-0} for each polyene in each solvent studied at several pressures.

Table A-1. DPH in C_6F_{14}

P(kbar)	ϕ_f	τ_f (nsec)	$\Delta E_{0-0}(10^3 \text{ cm}^{-1})$
0	0.64	31.2	3.13
0.5	0.61	27.4	2.93
1.0	0.59	24.4	2.82
1.5	0.58	22.1	2.76
2.0	0.56	20.0	2.72

Table A.2. DPH in toluene

P	ϕ_f	τ_f	ΔE_{0-0}
0	0.87	6.1	1.55
0.5	0.83	4.7	1.44
2	0.76	3.6	1.22
4	0.70	2.9	1.02
6	0.66	2.5	0.89
8	0.62	2.2	0.74
9	0.61	1.9	0.63

Table A-3. DPH in MCH

0	0.83	13.2	1.97
0.5	0.80	10.9	1.90
1	0.78	9.8	1.80
2	0.74	8.0	1.72
4	0.68	5.4	1.57
6	0.66	4.7	1.50
8	0.63	4.1	1.39
10	0.59	3.3	1.35

Table A-4. DPH in PS

P	ϕ_f	τ_f	ΔE_{0-0}
0	1.0	5.6	1.25
4	0.90	3.3	1.12
8	0.83	2.5	0.94
16	0.77	1.9	0.91
24	0.79	1.7	0.91
32	0.83	1.7	1.04
40	0.86	1.7	0.97

Table A-5. DPH in PMMA

0	0.96	9.1	1.63
4	0.89	5.5	1.38
8	0.86	4.0	1.18
16	0.83	2.9	1.07
24	0.83	2.5	1.06
32	0.84	2.2	1.13
40	0.87	2.1	1.22

Table A-6. DPO in toluene

P	ϕ_f	τ_f	ΔE_{0-0}
0	0.14	7.2	2.72
1	0.16	7.1	2.48
2	0.18	7.0	2.36
4	0.20	6.9	2.21
6	0.22	6.9	2.08
8	0.23	6.8	1.99
9	0.24	6.8	1.95

Table A-7. DPO in MCH

0	0.09	6.6	3.12
1	0.10	6.5	2.93
2	0.11	6.4	2.82
4	0.13	6.4	2.67
6	0.13	6.3	2.50
8	0.14	6.3	2.36
10	0.15	6.2	2.30

Table A-8. DPO in PS

P	ϕ_f	τ_f	ΔE_{0-0}
0	0.10	7.0	2.40
4	0.13	6.5	2.20
8	0.15	5.9	1.97
16	0.19	4.7	1.66
24	0.24	3.6	1.44
32	0.26	2.9	1.26
40	0.26	2.6	1.19

Table A-9. DPO in PMMA

0	0.11	7.1	2.78
4	0.13	6.9	2.57
8	0.16	6.6	2.30
16	0.21	5.8	2.04
24	0.25	5.1	1.88
32	0.29	4.4	1.79
40	0.33	3.7	1.64

Table A-10. RAc in PS

P	ϕ_f	τ_f	ΔE_{0-0}
0	0.09	8.5	3.1
4	0.12	8.9	2.7
8	0.14	8.4	2.4
16	0.17	7.2	1.9
24	0.17	6.1	1.5
32	0.16	5.1	1.2
40	0.13	4.4	0.96

Table A.11. RAc in PMMA

0	0.11	8.7	5.7
4	0.13	9.0	4.9
8	0.14	8.9	4.4
16	0.16	8.2	3.8
24	0.18	7.1	3.3
32	0.19	6.3	3.0
40	0.19	5.7	2.8