

spectrum due to the phenyl adduct of 4-*tert*-butyl PBN (4-*t*-BPBN) in 1% SDS is included for comparison (Figure 7c). The steady increase in line width of the high-field branch of the aminoxyl triplet in comparing Ph/PBN, Ph/4-*t*-BPBN, and Ph/4-DoPBN is evidence of increased immobilization with increase in size of the hydrocarbon group in the 4 position of PBN.

In a recent study of the solvent effect on Ph/PBN, a plot of a_{H}^{β} vs. a_{N} was shown to be linear.²⁹ This plot is given here with a few extra points included (Figure 10). If one assumes that the 4-*tert*-butyl or the 4-dodecyloxy group will not noticeably affect the hyperfine coupling constants of Ph/PBN, the values for these spin adducts can be placed on the line of best fit and the polarity of the environment of the SDS micelle where these spin adducts find themselves deduced. The arrows of Figure 10 show the positions of the following a_{H}^{β} and a_{N} values:

adduct	a_{N} , G	a_{H}^{β} , G
Ph/PBN (H ₂ O)	15.98	4.21
Ph/PBN (micelle)	15.60	3.87
Ph/4- <i>t</i> -BPBN (micelle)	15.50	3.62
Ph/4-DoPBN (micelle)	15.29	3.56

Although the region where the phenyl spin adducts reside in the SDS micelle becomes more hydrophobic with substitution of hydrocarbon groups, the environment probed by the nitroxyl function is still very polar and approximately that of pure methanol. The same conclusion was reached by Walter et al.¹⁶ for the spin trap-4-DoPBN itself; namely, the nitron function appears to reside in a region of the micelle with a polarity of that of ethanol.

Conclusions

Spin-trapping experiments indicate that 2-SSPBN can be used to probe radical events in the aqueous phase of SDS micelles whereas 4-DoPBN is useful for detecting radicals produced in the

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hydrocarbon phase. Since the nitronyl function of 4-DoPBN is believed to reside in the polar region of the micelle,¹⁶ radicals which are formed here or which diffuse in from the aqueous phase will be detected by this trap. PBN traps radicals both in the aqueous phase as well as in the interior of the micelle. Sulfate radicals (SO₄^{•-}) do not penetrate SDS micelles and are not detected by 4-DoPBN. No evidence of radicals derived from hydrogen atom abstraction from SDS molecules was found.

Although undoubtedly other spin traps will be found which can be used to study radical events in the aqueous exterior or hydrocarbon interior of SDS micelles, 2-SSPBN and 4-DoPBN appear to be the only pair of spin traps (with persistent spin adducts) which because of their solubility will not "cross-over" and complicate the observed results. PBN is soluble in both phases where 4-M₄A PBN already associates with SDS before cmc.

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Registry No. PBN, 3376-24-7; 2-SSPBN, 73475-11-3; 4-PyBN, 69396-90-3; 4-*t*-BPBN, 88888-33-9; 4-M₃APBN, 88888-34-0; 4-DoPBN, 80311-20-2; Ph/PBN, 21572-75-8; Ph/2-SSPBN, 88888-37-3; Ph/4-*t*-BPBN, 88888-38-4; HO/PBN, 55482-05-8; Ph/4-DoPBN, 82981-31-5; HO/2-SSPBN, 88888-39-5; HO/4-M₃APBN, 88888-36-2; HO/4-DoPBN, 88888-40-8; SO₄/4-M₃APBN, 88904-41-0; Na₂S₂O₈, 7775-27-1; H₂O₂, 7722-84-1; PA-4-PD, 88888-35-1; Ph-, 2396-01-2; SO₄^{•-}, 12143-45-2; HO-, 3352-57-6; C₄H₉N(O)H, 22665-15-2; SDS, 151-21-3.

Effect of High Pressure on Intramolecular Electron-Transfer Luminescence of 9,9'-Bianthryl in Different Solvents

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Abstract: The effects of high pressure on the fluorescence from the intramolecular electron-transfer state of 9,9'-bianthryl were investigated in different solvents. In low-viscosity solvents an increase of pressure affects the emission similarly to an increase of solvent polarity. In moderately viscous solvents the formation of the electron-transfer state is quenched as pressure is increased. In highly viscous solvents, as in glycerol, the emission is only from the locally excited state at atmospheric pressure, and no change except for peak shift is observed with pressure increase. Freezing of solvents at high pressure strictly quenches the formation of the electron-transfer state.

Introduction

There is a possibility that electron transfer occurs between molecules in the excited state and in the ground state even in the case where it does not occur between the ground-state molecules. This is because the ionic potential of molecules in the excited state becomes smaller and the electron affinity becomes larger than those in the ground state. For the excited-state complex (so-called "excimer" or "exciplex"), the two molecules are considered to interact spatially to form a sandwich-like conformation with a

separation of 3.0-3.5 Å. Also possible is an intramolecular interaction such as reported for α,ω -diaryllkanes,¹ aryl- ω -N,N'

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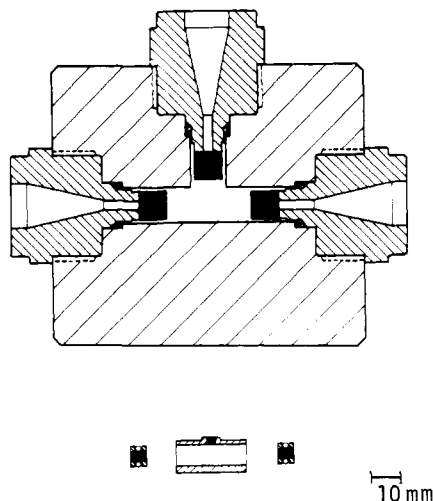


Figure 1. High-pressure optical cell (maraging steel) and inner cell (stainless steel).

dialkylaminoalkanes,² and other similarly related compounds.³

9,9'-Bianthryl (BA), for which such a sandwich-like conformation is unlikely to be formed, has been suggested to form an intramolecular electron-transfer state in polar solvents, which is characterized by a new red-shifted excimer-like emission.^{4,5} Further, it has been proposed that the twisted angle between the two anthracene molecular planes along the 9-9' bond changes at the excited state.^{4,6} It has been reported for *p*-cyano-*N,N*-dimethylaniline derivatives⁷ that the change of intramolecular conformation has an important contribution to the formation of an intramolecular charge-transfer state.

The investigation of the effect of environment on the excited electronic states of electron-transfer compounds is an interesting problem and also the goal of this research. In these systems solvent polarity plays an important role due to the charge separation associated with the electron-transfer interaction. The application of high pressure is also useful for perturbing these systems,⁸ since geometric restrictions may contribute. Fluorescence properties were measured to monitor the effects of these perturbations on the electronic states. The present paper reports on the solvent and pressure effects of the fluorescence spectra of BA and clarifies the behavior of the intramolecular electron-transfer state.

Experimental Section

Materials. BA was prepared according to the literature procedure⁹ and was purified by sublimation. No impurity was detectable both in the absorption and emission spectra of the purified samples. All solvents were spectroscopic grade quality and were used after distillation in vacuo. All solutions were prepared immediately prior to use.

Apparatus and Methods. The high-pressure optical cell for fluorescence measurements made from hardened maraging steel (YAG 300) is shown in Figure 1. The windows are sapphire seated directly on the window plugs. The seals on the window plugs are back-up rings and Teflon O-rings. The pressure-transmitting fluid is spectral grade hexane. High pressures transmitted from an intensifier were measured by using a manganin gauge, which is housed in another separate cell of hardened maraging steel. The stainless steel inner cell in which the sample solution is placed is also shown in Figure 1. The sapphire piston is sealed with Teflon O-rings.

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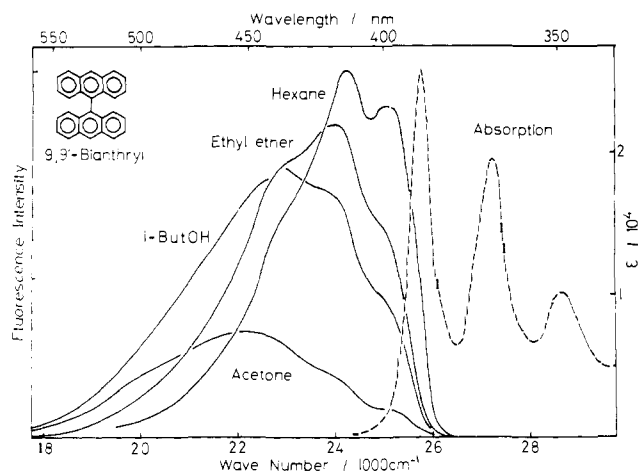


Figure 2. Fluorescence and absorption spectra in different solvents at atmospheric pressure.

The emission apparatus is the same as that reported before.^{10,11} Fluorescence was excited by radiation from a 200-W Hg-Xe arc lamp, the 366-nm line of which was isolated by a monochromator.

Each spectrum consisted of 60–100 times-averaged data points spaced 3.0 nm apart. The spectra were fit to several Gaussians. Quinine sulfate-0.1 *N* sulfuric acid was used as a reference standard for quantum yield measurements of solutions. The measurements were carried out for air-saturated samples of concentration 1.0×10^{-5} M at 288 K, unless otherwise specified.

Results and Discussion

Solvent Effects. The absorption and excitation spectra of BA were measured in various solvents at atmospheric pressure. The excitation spectra are in agreement with the absorption spectra. These spectra show no difference between polar and nonpolar solvents as shown in Figure 2. Namely, the location of the excitation peaks as well as of the absorption peaks, is insensitive to solvent polarity. In addition, these spectra are identical with those of anthracene except for a small peak shift of 890 cm^{-1} to the red, and small differences in the vibronic structure. This result reflects that there is no measurable interaction in the ground state between the two anthracene chromophores of BA. This fact has been also suggested by the measurements of polarizability,¹² dipole moment,¹² half-reduction potential,¹³ molecular refraction,¹⁴ and combustion energy.¹⁵ Further, this may be evidence that the torsional angle between the two anthracene molecular planes along the 9-9' bond is a right angle in the ground state, and that the π -electron clouds of both anthracene chromophores do not interact with each other, as reported by Schneider and Lippert.⁴

The fluorescence spectra, on the other hand, are strongly dependent on the polarity of the solvent, as shown for hexane and acetone in Figure 2. From this study we can find the existence of two clearly different emitting states. One of them which appears in nonpolar solvents shows its peak maximum at around 24000 cm^{-1} with vibrational structure that is apparently the mirror image of the excitation spectra. This fluorescence can be attributed to the locally excited state (LE state) corresponding to S_1 of anthracene, while the emission spectrum in polar solvents consists of a structureless broad band with a maximum at around $22000\text{--}23000 \text{ cm}^{-1}$.

The dependence of the Stokes shift ($\Delta\bar{\nu}_{\text{Stokes}} = \bar{\nu}_{\text{abs}} - \bar{\nu}_{\text{fl}}$) on the solvent parameter

$$\Delta f(\epsilon, n) = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (1)$$

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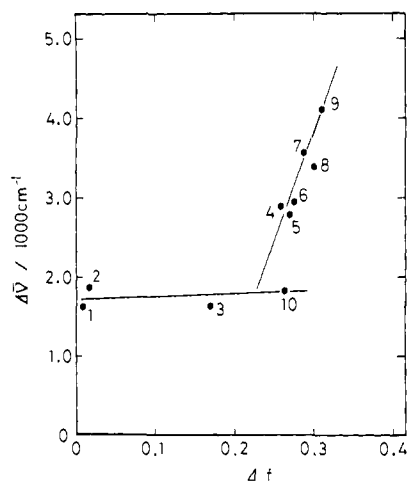


Figure 3. Plots of Stokes shift against solvent polarity parameter Δf : (1) hexane, (2) toluene, (3) ethyl ether, (4) isoamyl alcohol, (5) isobutyl alcohol, (6) isopropyl alcohol, (7) acetone, (8) methanol, (9) acetonitrile, (10) glycerol.

Table I. Ratio of Quantum Yield ϕ_{ET}/ϕ_{LE} , Fluorescence Maximum of ET Band $(\bar{\nu}_{fl})_{ET}^{max}$, Dielectric Constant ϵ , and Coefficient of Viscosity η^a

	ϕ_{ET}/ϕ_{LE}	$(\bar{\nu}_{fl})_{ET}^{max}$, 10^3 cm^{-1}	ϵ^b	$\eta,^b \text{ cp}$
acetone	19.8	22.20	20.70	0.3040
MeOH	11.5	22.38	32.70	0.5445
acetonitrile	19.0	21.65	37.50	0.375
<i>i</i> -PrOH		22.79	19.92	2.859 (15 °C)
<i>i</i> -BuOH	4.9	22.90	17.93	4.703 (15 °C)
<i>i</i> -AmOH	4.2	22.85	14.70	4.810 (15 °C)
glycerol	0.3		42.50	945

^a Temperature is 25 °C for ϵ and η unless otherwise specified.

^b Riddick, J. A.; Bunger, W. B. "Techniques of Chemistry", Vol. II, "Organic Solvents", Wiley-Interscience: New York, 1970.

is plotted in Figure 3, where ϵ and n are the dielectric constant and refractive index of solvents, respectively. The absorption maximum $\bar{\nu}_{abs} = 25\,750 \text{ cm}^{-1}$ was adopted for all the solvents. As can be seen in Figure 3, the relation is expressed by two straight lines with different slopes reflecting two different emitting states.

According to Lippert's theory,¹⁶ the relation between the Stokes shift and Δf is expressed as

$$\Delta\bar{\nu}_{\text{stokes}} = \frac{2}{hca^3}(\mu_e - \mu_g)^2 \Delta f \quad (2)$$

where μ_e and μ_g are the dipole moments of excited and ground states, respectively, and a is the radius of the solvent cage. A large slope in Figure 3 indicates a large dipole moment in the excited state.

According to Beens and Wellers,¹⁷ on the other hand, the shift of the fluorescence peak maximum with changing the solvent polarity can be related to the dipole moment of the excited states as follows:

$$\bar{\nu} = \bar{\nu}(0) - \frac{2\mu_e^2}{hca^3} \left(\frac{\epsilon - 1}{2\epsilon + 1} - \frac{1}{2} \frac{n^2 - 1}{2n^2 + 1} \right) \quad (3)$$

Plots of $\bar{\nu}$, measured in solvents of different polarity, vs. $\Delta f(\epsilon, n)$ in eq 3 allow the calculation of μ_e^2/hca^3 . This yields by least-squares evaluation of $17\,500 \text{ cm}^{-1}$ for BA. The large value can be understood as due to the large charge separation. An $S_n \leftarrow$

Table II. Effect of Pressure on Excitation Peak Location and Stokes Shift in Hexane and Acetone

pressure, kbars	hexane		acetone	
	E_{exc} , 10^3 cm^{-1}	$\Delta\bar{\nu}_{\text{stokes}}$, 10^3 cm^{-1}	E_{exc} , 10^3 cm^{-1}	$\Delta\bar{\nu}_{\text{stokes}}$, 10^3 cm^{-1}
0	25.77	1.52	25.72	3.55
1	25.64	1.61	25.61	3.77
2	25.58	1.70	25.52	3.89
3	25.51	1.74	25.47	3.93
4	25.50	1.79	25.43	4.03
5	25.45	1.83	25.41	4.05
6	25.43	1.87	25.37	4.16
7	25.42	1.90	25.35	4.23
8	25.38	1.94	25.32	4.11
9	25.37	1.97	25.28	3.95
10	25.34	1.99	25.28	3.78

Table III. Effect of Pressure on the Ratio of Quantum Yield ϕ_{ET}/ϕ_{LE} in Different Solvents

pressure, kbars	ϕ_{ET}/ϕ_{LE}			
	hexane	ethyl ether	<i>i</i> -BuOH	<i>i</i> -AmOH
0	0.45	1.50	4.88	4.15
2	0.50	1.78	5.25	
4	0.64	2.13	6.14	
6	0.72	2.22	7.33	5.21
8	0.85	2.45	5.66	
10	1.00	2.45	2.70	2.55

S_1 absorption spectrum similar to anthryl anion has been reported in acetone solution.⁵ Thus, we refer to this state of a large excited dipole moment as an electron-transfer state (ET state) in the excited state.

The ratios of the quantum yields for emission from the electron-transfer state, ϕ_{ET} , and from the locally excited state, ϕ_{LE} , were determined from integrated area ratios. Representative data at atmospheric pressure are presented in Table I for the polar solvents, whose dielectric constants are high enough to cause the ET state. It also contains the emission peak maximum of the ET state $(\bar{\nu}_{fl})_{ET}^{max}$, the dielectric constant ϵ , and the coefficient of viscosity η . The low-viscosity solvents such as acetone, methanol, and acetonitrile give a large value of the relative yield of the ET state, while in moderately viscous solvents, such as isopropyl, isobutyl and isoamyl alcohols, the ratio decreases to approximately 5. In glycerol the yield of the ET state is almost completely quenched and the emission spectrum consists only of the LE state. Its peak maximum lies just on the line of the LE state in Figure 3, although the dielectric constant is high enough for the ET state to be formed. In addition, $(\bar{\nu}_{fl})_{ET}^{max}$ is higher for the moderately viscous solvents as compared with the low-viscosity solvents. Thus, these results suggest that the solvent viscosity may play an important role in the formation of the ET state in addition to the effect of solvent polarity.

Pressure Effects. The excitation peaks shift uniformly to lower energy with increasing pressure in all the solvents irrespective of their polarity ($-120 \pm 10 \text{ cm}^{-1}/\text{kbar}$) (see Table II). These observations indicate that the state emitting electron-transfer fluorescence is not directly populated by excitation, but justifies the $S_0 \rightarrow LE$ assignment.

The effects of pressure on the fluorescence spectra of BA in hexane, ethyl ether, and acetone are shown in Figure 4a-c as typical examples. Changes in fluorescence peak locations with pressure are presented in Figure 5. Spectral maxima have been employed because these have more well-defined positions (being sharper) and there is no evidence for substantial change in vibronic spacing in these solvents. The fluorescence energy of the LE state such as in hexane shifts monotonously toward "red" (to lower energy) with increasing pressure ($-90 \text{ cm}^{-1}/\text{kbar}$). This amount of shift is almost identical with the excitation peak shift. The initial peak shift for acetone, methanol, and acetonitrile which can be attributed to that of the pure ET state is larger than that of the pure LE state ($-220 \text{ cm}^{-1}/\text{kbar}$). Thus, we can conclude that the

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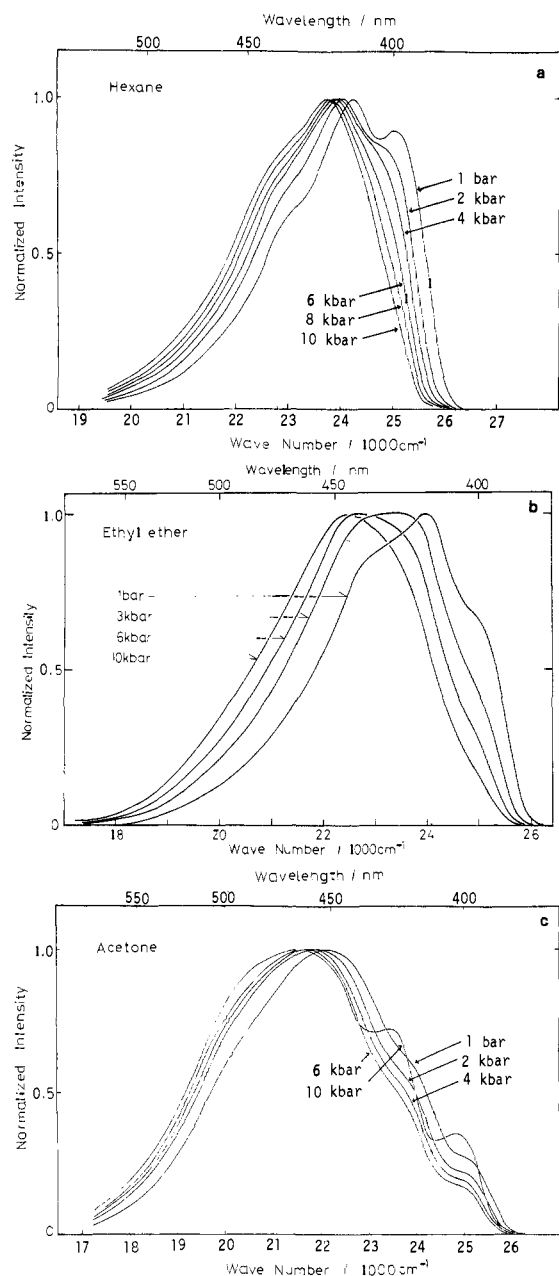


Figure 4. Fluorescence spectra of BA at various pressures in (a) hexane, (b) ethyl ether, and (c) acetone.

ET state is more sensitive to pressure than the LE state. The discontinuous peak shift in ethyl ether for 15 °C at 3–4 kbars originates from the replacement of the peak maximum from the LE to ET band. The drastic blue shift in acetonitrile at 3 kbars and the gradual blue shift in acetone at 6 kbars are caused by the freezing of the solvents.

The effect of pressure on ϕ_{ET}/ϕ_{LE} is presented in Table III. In hexane and ethyl ether the ratio increases uniformly with pressure. In isopropyl, isobutyl, and isoamyl alcohols it increases in the first 6 kbars, and then decreases beyond that pressure. In acetone and acetonitrile it is almost constant in the liquid-phase range.

The relative increase of the ET fluorescence yield with increasing pressure in hexane and ethyl ether indicates the stabilization of the ET state caused by the increased dipole moment of the solvents with pressure. In methanol, however, the trend is opposite. The ratio decreases with increasing pressure. The relative enhancement of the ET peak seems to produce an apparent blue shift at higher pressures. In this case specific solute-solvent interaction may have an effect, but it is difficult to explain clearly at this time.

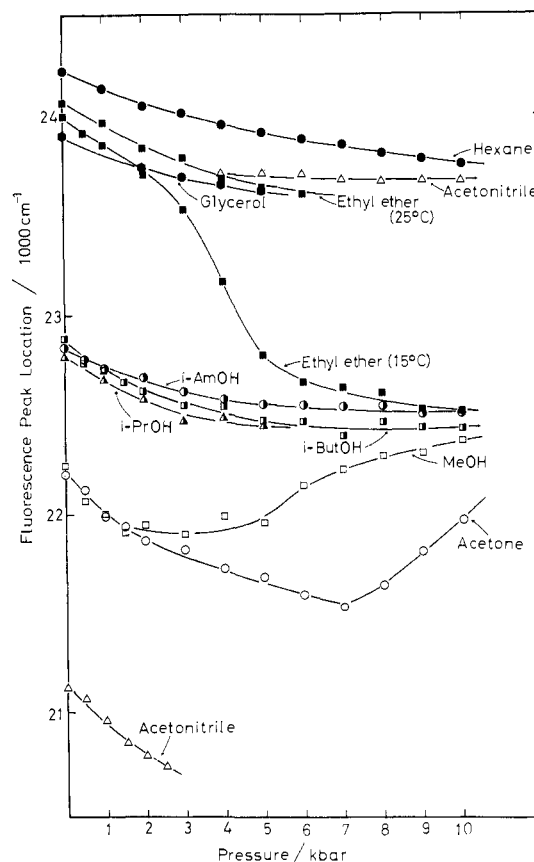
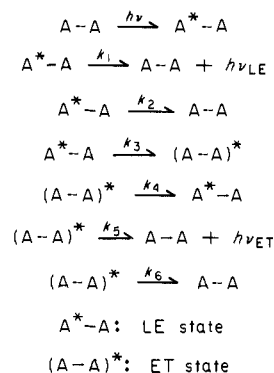


Figure 5. Effect of pressure on the fluorescence peak location in different solvents.

Scheme I



When the kinetic scheme for the formation of the intramolecular ET state as shown in Scheme I is adopted, the ratio of the quantum yield is given by

$$\frac{\phi_{ET}}{\phi_{LE}} = \frac{k_5}{k_1} \frac{k_3}{k_4 + k_5 + k_6} \quad (4)$$

At sufficiently high temperatures where k_4 is larger than $(k_5 + k_6)$, the process is thermodynamically controlled and this equation can be simplified to

$$\frac{\phi_{ET}}{\phi_{LE}} = \frac{k_5}{k_1} \frac{k_3}{k_4} \quad (5)$$

It has been reported for intramolecular exciplex formation that 288 K is in the high-temperature range for this assumption to be safely applied.^{2a} When we can assume further that the pressure effect on k_5/k_1 is small,¹⁸ the pressure effect is expressed by

$$\frac{d \ln (\phi_{ET}/\phi_{LE})}{dP} = - \frac{\Delta V}{RT} \quad (6)$$

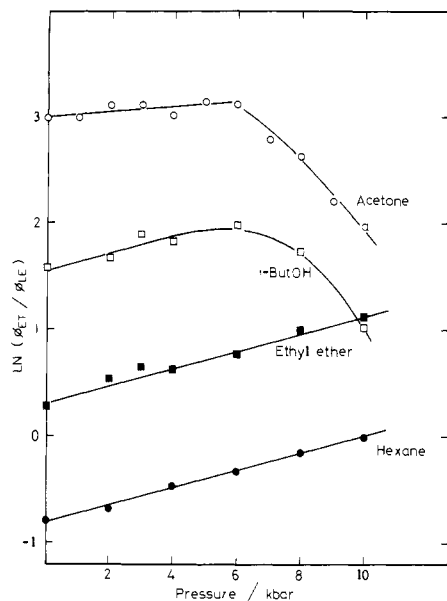


Figure 6. Effect of pressure on $\ln(\phi_{ET}/\phi_{LE})$.

Thus, the volume change of the ET state formation, ΔV , can be estimated. Figure 6 shows a plot of $\ln(\phi_{ET}/\phi_{LE})$ against pressure for hexane, ethyl ether, isobutyl alcohol, and acetone. The value of ΔV obtained from the initial slope is $-1.9 \text{ cm}^3/\text{mol}$ for hexane, ethyl ether, and isobutyl alcohol. This volume change can be attributed to increased interaction with solvent associated with the increase of dipole moment in the ET state with the LE state.

The relative decrease of the ratio of the quantum yields and the apparent blue shift in acetone beyond 6 kbars and in acetonitrile beyond 3 kbars are caused by freezing of the solvents. The freezing of solvents is accompanied by a quenching in the formation of the ET state. The ratio of the yield decreases in isopropyl, isobutyl, and isoamyl alcohols at higher pressure range. The viscosity of isobutyl alcohol increases $10^{2.075}$ times at 8 kbars.¹⁹ Deviations from the straight lines in Figure 6 at the higher pressure range in acetone and in isobutyl alcohol are caused by these effects. In this region the high-temperature approximation (eq 5) could not be applied since k_4 is not always larger than $(k_5 + k_6)$. If $k_4 \ll (k_5 + k_6)$, then eq 4 is reduced to

$$\frac{\phi_{ET}}{\phi_{LE}} = \frac{k_5}{k_1} \frac{k_3}{k_5 + k_6} \quad (7)$$

When k_3 is decreased in this situation, $\ln(\phi_{ET}/\phi_{LE})$ decreases.

With the highly viscous solvent glycerol, only the LE band is observed even at high pressures and shows the peak shift analogous to that in hexane. The emissions in moderately viscous solvents as isopropyl, isobutyl, and isoamyl alcohols, on the other hand, can be assigned as the mixed bands of the LE and ET states, because of the apparent peak location and the larger half-width as compared with other polar solvents. No change in peak shift or a slight blue shift at high pressures correlates with the quenching of the ET formation since the increase in viscosity becomes effective. We can conclude as a whole that the electron-transfer emission is quenched in the rigid matrix as in the frozen state or in high-viscosity solvents.

When the formation of the ET state is accompanied by a change of molecular conformation, we can expect that the rigidity or

(18) It has been understood for some intramolecular charge-transfer states that radiative rates of LE and charge-transfer states decrease slightly with almost the same rate when pressure is increased, while nonradiative rates show different characteristic behavior between them.⁸

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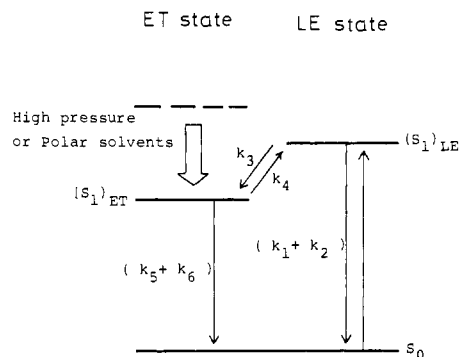


Figure 7. Schematic potential energy diagram.

viscosity of solvents should have a direct influence. This explanation is also confirmed from the solvent effects at atmospheric pressure in Table I. The drastic quenching of the ET emission with increasing solvent-viscosity or solvent-rigidity by freezing at high pressures suggests the existence of some geometrical restrictions during the relaxation process. Namely, in the rigid matrix the intramolecular rotational motion of the bulky solute is necessary for the resonance interaction to occur between the two anthracene chromophores. The amount of change in the twisted angle has been estimated as $\pm 12^\circ$ by Schneider and Lippert.⁶ Salem²⁰ has reported, however, that π -electron conjugation in polyenes is very sensitive to the angular change and that $\pm 2^\circ$ is sufficient to cause any interaction. If the rotational change occurs easily and relatively faster than the emission lifetime of the LE state, the dielectric relaxation of the solvent would become the rate-determining process.

From the considerations mentioned above, the potential energy diagram shown in Figure 7 seems to be the case that represents the electronic energy states of BA. By the application of high pressure, the ET state lowers relatively faster than the LE state, so that the feeding barrier to the ET state becomes lower. In polar solvents the ET level is low enough even at atmospheric pressure to emit dominantly from this state. In highly viscous solvents or rigid matrices that are produced at high pressures, however, the relaxation process is retarded, possibly predominantly. Similar behavior has been observed in some intramolecular charge-transfer compounds. As compared with *p*-(9-anthryl)dimethylaniline reported by Rollinson and Drickamer,⁸ the LE and ET states of BA are more clearly separated in energy with each other, and consequently more well-defined solvent effects of polarity and viscosity were observed.

Summary

The formation of the ET state is fed through the LE state. Application of high-pressure affects the emission of BA similarly to an increase of solvent polarity and solvent rigidity. The formation and quenching of the ET state with pressure in different solvents are observed continuously. The behavior can be explained by a potential energy diagram. Viscosity dependence in the formation of the ET state suggests a conformational change at the excited state during the feeding relaxation process. Apparent volume changes accompanying formation of the ET state can be estimated as $-1.9 \text{ cm}^3/\text{mol}$.

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Registry No. MeOH, 67-56-1; *i*-PrOH, 67-63-0; *i*-BuOH, 78-83-1; *i*-AmOH, 123-51-3; 9,9'-bianthryl, 1055-23-8; acetone, 67-64-1; acetonitrile, 75-05-8; glycerol, 56-81-5; hexane, 110-54-3; ethyl ether, 60-29-7.

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