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Effect of Pressure on the Fluorescence of 9-Carbonyl Substituted Anthracenes

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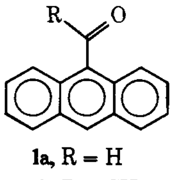
Abstract: The pressure dependence of the fluorescence intensity of 9-anthraldehyde, acetylanthracene, and 9-benzoylanthracene was investigated. It was observed that for each of these compounds the intensity of fluorescence increased remarkably as the external pressure was raised. In each case the energy of the fluorescent transition decreased with increasing pressure, leading to a large red shift in the emission spectrum. These data are interpreted to indicate that a change in the energy separating the lowest excited singlet and upper triplet energy levels occurs when these compounds are subjected to high pressure.

The fate of an electronically excited molecule is determined by the relative rates of the various paths available for its eventual return to the ground state. Thus, the net result of electronic excitation (fluorescence, phosphorescence, chemical reaction, radiationless decay, etc.) depends upon those factors that control the rates of the decay paths. External variables have proved useful in directing the decay of an excited molecule toward a particular path. For example, the external heavy atom effect has been used to enhance the rate of intersystem crossing and hence to increase the quantum efficiency for triplet formation.[1] We have investigated the effect of external pressure on the competition among various decay paths for a series of 9-carbonyl substituted anthracenes (**1**).



1a, R = H
1b, R = CH_3
1c, R = Ph

Aldehyde **1a** is reported to fluoresce only weakly in nonpolar solution at room temperature and atmospheric pressure.[2] Ketones **1b** and **1c** are totally nonfluorescent under these conditions. As the temperature is lowered the fluorescence efficiency of **1a** and **1b** increases but benzoylanthracene **1c** is nonfluorescent even at 77 K.[3] It has been suggested that the dominant decay path for the excited singlet of these 9-carbonyl substituted anthracenes is an intersystem crossing to an upper triplet. The temperature dependence of fluorescence is therefore a result of a thermal barrier to this intersystem crossing.[4] The height of the barrier is dependent upon the particular substituent, which accounts for the different thermal behavior of anthracenes **1b** and **1c**.

External pressure has been observed to affect the energy levels of excited states in a predictable and regular fashion. It has been shown that increased pressure causes singlet–singlet transitions to decrease in energy relative to singlet–triplet transitions.[5] This effectively raises the energy of the triplet relative to the excited singlet. Johnson and Offen[6] have exemplified this effect by showing that the fluorescence lifetime of anthracene in polymethylmethacrylate (PMMA) increases by a factor of three when the external pressure is varied from 1 atm to 30 kbars. Shaw and Nicol[7] confirmed that this was the result of the inhibition of intersystem crossing due to displacement of the excited singlet and upper triplet levels.

In this paper we report our results which show that the external pressure may be used to control the selection of decay modes by the electronically excited singlet state of the 9-carbonyl substituted anthracenes. By varying the applied pressure we have succeeded in converting the nonfluorescent anthracene derivatives **1a**, **1b**, and even **1c** to efficiently emitting molecules at room temperature.

Experimental Section

9-Anthraldehyde (**1a**) and 9-acetylanthracene (**1b**) were purchased from Aldrich Chemical Co. and purified by column chromatography,

Table I. Summary of Relative Fluorescence Yield and Spectral Shift Data[a] for 9-Carbonyl Derivatives of Anthracene in Plastic Solution at 297 K

	ϕ_f[b] Pressure, kbars								ν_0	$\Delta\nu$		
	4	10	20	40	60	80	100	120		40	80	120
							1a					
PMMA	0.40	1.2	3.4	15	36	60	82	100	19 800	−605	−955	−1300
(PS)[d]	0.29	0.81	3.7	24	55	85	96	100	20 300	−1570	−2390	−3200
							1b					
PMMA	0.36	2.0	9.0	34	59	77	91	1100	22 900	−1970	−3410	−4780
PS	0.16	1.2	9.8	48	80	93	98	100	22 600	−2300	−4280	−5680
							1c					
PMMA	0.43	1.3	6.1	36	65	81	94	100	21 500	−1800	−2780	−3630
PS	0.42	1.5	7.7	4.0	77	95	100	100	22 200	−2180	−3260	−5090
							Anthracene					
PMMA										(−1020)	(−1650)[c]	

[a] ν_0 and $\Delta\nu$ are given in cm^{-1}. ν_0 is taken as the centroid of emission energy extrapolated to 1 atm (effectively zero pressure). [b] ϕ_f is normalized to equal 100 at 120 kbar and 297 K. [c] Anthracene data are taken from ref 13. [d] Polystyrene.

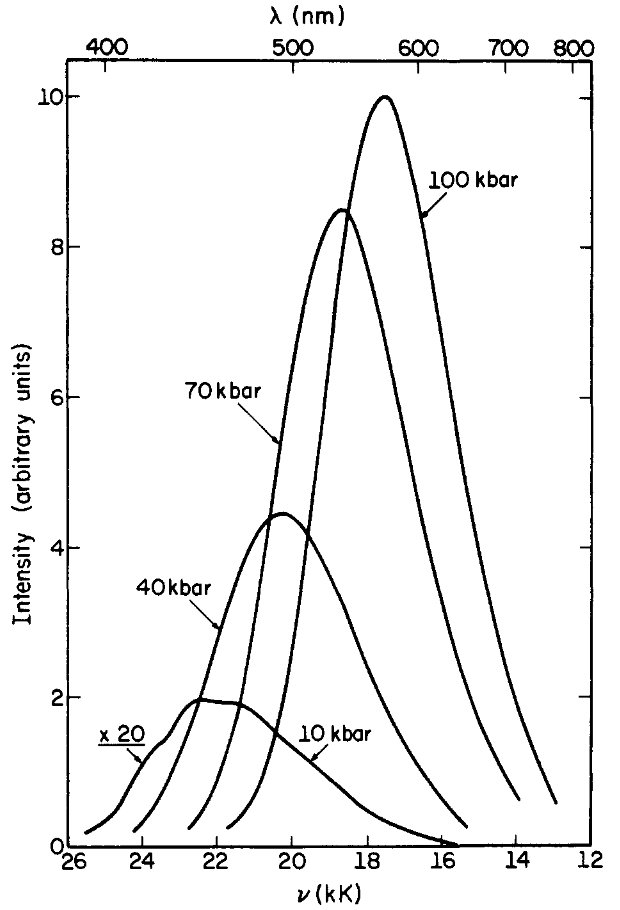


Figure 1. Pressure response of fluorescence emission for 9-acetylanthracene in polystyrene.

followed by repeated recrystallization from hexane. 9-Benzoylanthracene was prepared according to the literature procedure and recrystallized from ethanol.[8] Inhibitor was removed from methylmethacrylate monomer (Aldrich) by five washings with alkaline solution (5% NaOH, 20% NaCl) and five washings with distilled water, followed by two distillations at reduced pressure.[9] The middle fraction was photopolymerized at room temperature in 80% methanol solution after degassing with four freeze-thaw cycles. Styrene monomer was purified as above and thermally polymerized in bulk at 110 °C. Volatile components were removed from both plastics by baking at approximately 10^{-6} Torr and elevated temperatures (80 °C for PMMA, 110 °C for polystyrene).

Approximately 0.01 M, 0.15 mm thick plastic films were prepared by dissolving both compound and plastic in methylene chloride and evaporating the solvent at reduced pressure. No effect of concentration on the luminescence[10] was observed in the concentration range 0.001 to 0.1 M. Care was taken to avoid prolonged contact with air. The high-pressure cell and emission equipment, as well as methods of processing and analyzing the data, are described elsewhere.[11] The low-temperature techniques were developed by Tyner.[12]

Relative quantum yields were determined by integrating the intensity of emitted light. Intensities were calibrated against the emission of $Ca_3(Po_4)_2$:Tl, which was used as an internal reference. Tyner[12] has shown that the fluorescence intensity of $Ca_3(PO_4)_2$:Tl is virtually independent of pressure and independent of temperature below 300 K. All quantum yields were normalized to 120 kbar and 297 K, which was arbitrarily assigned the value 100. Peak shifts were determined by the change in location of the centroid of emission energy.

Results and Discussion

A series of typical fluorescence spectra as a function of pressure for acetylanthracene **1b** in a polystyrene matrix are shown in Figure 1. Relative quantum yields for fluorescence and the spectral shifts of the emission for **1a**, **1b**, and **1c** as a function of pressure are listed in Table I. A plot of the log of the relative fluorescence quantum yield against the log of the applied pressure for benzoylanthracene (**1c**) is shown in Figure 2. It is clear from these data that the fluorescence efficiency for each of these three anthracene derivatives increases remarkably as the pressure is raised. In the highest pressure region the increase in emission intensity begins to level off and approach a limiting value. Differences in behavior exist among the three compounds and between the two solvents investigated (Table I); however, they are small compared with the overall effect of increasing pressure.

Shown also in Table I are the pressure dependent shifts of the energy for the fluorescence emission for anthracenes **1a**, **1b**, and **1c**. The previously measured spectral shift of anthracene in PMMA is included for comparison.[13] The pressure dependence of the centroid of emission energy (ν) was extrapolated to give the value at atmospheric pressure (ν_0).

At least four potential paths are available for the depletion of the electronically excited singlet states of anthracenes **1a**, **1b**, and **1c**. These are: internal conversion to the ground state, intersystem crossing to the lowest triplet state (T_1), intersystem crossing to an upper triplet level (T_2), or fluorescence. It is generally agreed that internal conversion is slow relative to the other processes available and therefore does not usually contribute significantly to the overall decay of the lowest excited singlet state.[14] Anthracene and its derivatives have an energy

Table II. Temperature Dependence of Relative Fluorescence Efficiency for 9-Carbonyl Derivatives of Anthracene at Various Pressures in a Plastic Solution

			ϕ_f[a]				
			T, K				
Molecule	Medium	*P*, kbars	297	250	200	150	110
1a	PMMA	8	0.88	1.4	2.6	5.8	11
	PMMA	40	15	23	37	54	73
1b	PMMA	8	1.2	2.3	5.5	16	45
	PMMA	40	34	51	83	130	190
1c	PMMA	8	0.91	1.4	2.3	4.0	6.0
	PMMA	40	36	58	86	120	140
	PMMA	80	81	100	120	160	190
	PS[b]	100	100	140	170	190	200

[a] The fluorescence efficiency is normalized to equal 100 at 120 kbar and 297 K. [b] Polystyrene.

gap between the lowest singlet and lowest triplet states that is rather large, greater than 33 kcal/mol for unsubstituted anthracene.[15] According to the accepted theory of radiationless decay processes, this large energy gap causes the rate of intersystem crossing to the lowest triplet state to be slowed.[16] It is for these reasons that the general lack of fluorescence from 9-carbonyl derivatives of anthracene is ascribed to a rapid intersystem crossing to an upper triplet state. Values of the fluorescence efficiency at a series of temperatures and pressures are listed in Table II. At high pressures, only small increases in fluorescence were observed to occur as a result of lowering the temperature from 297 to 110 K. For example, the fluorescence intensity of benzoylanthracene **1c** in polystyrene was found to reach an upper limit at 100 kbars and 297 K. Decreasing the temperature to 110 K increased the fluorescence intensity by only a factor of 2. This observation indicates that thermally activated intersystem crossing to the upper triplet state ceases to occur to an appreciable extent at 100 kbars. There is evidently a small additional temperature dependent, radiationless decay pathway depleting the excited singlet at this pressure, but it is not possible to determine the identity of this path from the present data.

For acetylanthracene **1b** in PMMA, it has previously been shown that the quantum yield for fluorescence is 0.17 at 77 K and 1 atm.[3] With the conservative assumption that this yield is no larger than that which would be observed at 8 kbar and the same temperature, it is possible to estimate a lower limit for the fluorescence quantum yield in the limiting high-pressure region. This may be done by extrapolating the temperature dependence of the fluorescence efficiency of **1b** at 8 kbar to 77 K and comparing this to the reported value at atmospheric pressure. This leads to a value for the absolute quantum yield of fluorescence at 120 kbar and 297 K of not less than 0.3. Although it is difficult to compare the relative yields for the various compounds, the high-pressure values all appear to be at least of the same magnitude as that obtained for **1b.**

The exceptionally large spectral red shift for anthracenes **1b** and **1c** shown in Table I indicate that a large change occurs in the dipole moment upon excitation of these compounds. The direction of the shift confirms our initial speculation that the lowest singlet of the substituted anthracenes moves to lower energy relative to the ground state with increasing pressure. In some cases, vibrational structure is observed, while in others, individual vibrational components are not discernible (see Figure 1). Because of this, quantitative analysis of the shift data is not practical. Qualitatively, however, the pressure dependence of the peak shift is similar to that of anthracene[13] for each of the compounds studied. The magnitude of the spectral shift for transitions to singlet π,π^* states are generally larger than those to singlet n,π^* states.[17] Therefore, a crossing of the two states would be anticipated if the π,π^* singlet were slightly higher in energy than n,π^* singlet at low pressure. There is no evidence of the discontinuity in the pressure dependence of the fluorescence efficiency that a state crossing would cause for these anthracene derivatives. This is consistent with the recent conclusion that the π,π^* singlet is the lowest excited singlet for these structures.[4]

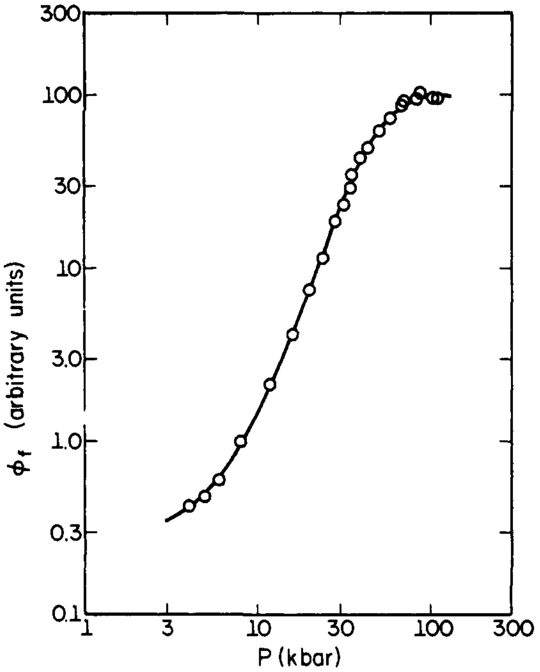


Figure 2. Pressure dependence of the relative fluorescence yield for 9-benzoylanthracene in polystyrene.

It is seen from Table I that the magnitude of the red shift of the emission is roughly correlated with the fluorescence efficiency. For polystyrene solution, in which the emission from each of the compounds shifts more rapidly then in PMMA, the fluorescence efficiency approaches a limiting value at lower pressure. Also, aldehyde **1a,** which is characterized by the smallest shift, is the compound for which increasing fluorescence efficiency persists to the greatest extent in the high pressure region (indicating that the pressure dependent radiationless process has not been extinguished).[18]

The effect of pressure on the intersystem crossing rate constants for these molecules may involve at least two important factors. The exact form of the theoretical rate expression for intersystem crossing is still being developed. El-Sayed has proposed selection rules for estimating the magnitude of the intersystem crossing rate constant based upon an analysis of the effect of a change in configuration ($n\pi^*$ to $\pi\pi^*$, etc.) on the spin-orbit coupling operator. The result of this analysis indicates that when a change in spin multiplicity is accompanied by a change in electron configuration the process is

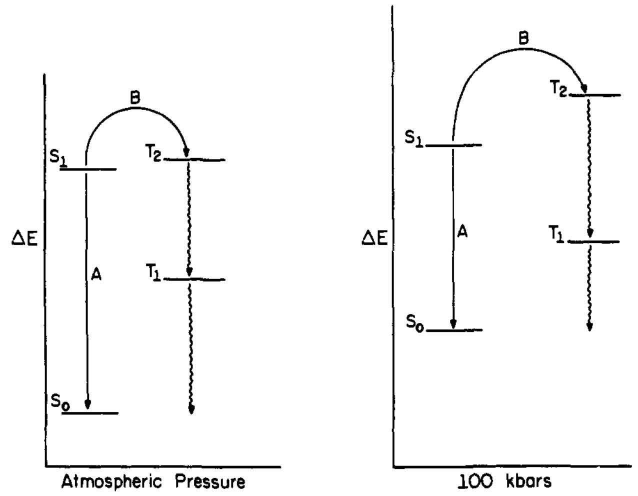


Figure 3. Pressure dependence of energy levels for 9-carbonyl anthracenes. Path A is fluorescence; path B is an activated intersystem crossing.

rapid.[19] Recently, an alternative theoretical approach has been developed that implicates the nuclear kinetic energy operator as controlling the rate of intersystem crossing.[20] In this system, mixing of states of the same multiplicity but with different electronic configurations determines the rate of intersystem crossing. Recent experimental results seem to favor spin-orbit coupling as being dominant in determining the rate of intersystem crossing.[21]

These two models predict opposite effects of pressure on the intersystem crossing rate for the carbonyl substituted anthracenes. Since the $\pi\pi^*$ singlet transition presumably shifts to lower energy faster than the $n\pi^*$ singlet transition, the energy gap between these states widens with pressure. The increased gap reduces the mixing of the $n\pi^*$ and $\pi\pi^*$ singlet state and hence the rate of intersystem crossing is predicted to decrease by this model. However, if spin-orbit coupling is the dominating factor, then pressure is not expected to have a large influence on the rate of intersystem crossing because triplet states of both $\pi\pi^*$ (T_2) and $n\pi^*$ configuration are available from the lowest excited singlet state.[22]

The second, and perhaps dominating, effect of pressure on the rate of intersystem crossing is the relative energetic displacement of the lowest excited singlet state and the available triplet states. At atmospheric pressure the temperature dependence of the fluorescence of these 9-carbonyl substituted anthracenes clearly indicates that intersystem crossing is a thermally activated process (vide supra). Increased pressure is expected to shift the triplet states to higher energy faster than it moves singlet states.[6,7] Thus the endothermicity of the intersystem crossing transition will increase, slowing this process and permitting fluorescence to compete. This interpretation is consistent with the observed decrease in the temperature dependence of fluorescence efficiency in the limiting pressure region. Furthermore, this analysis permits simultaneous rationalization of both the temperature and pressure dependence of the fluorescence for these carbonyl substituted anthracenes. This interpretation of the data is summarized in Figure 3. It should be noted that this diagram is only schematic. The upper triplet may actually lie slightly above or below the lowest excited singlet depending upon the compound. In the latter case, the thermal barrier to fluorescence would be a result of the relative displacement of the potential wells for S_1 and T_2 along the relevant configuration coordinate. Note that the absolute energies of all electronic states increase with increasing pressure; however, the rate of increase is dependent upon the nature of the particular state.[23]

At atmospheric pressure, benzoylanthracene **1c** is nonfluorescent even at 77 K. The pressure derivative of the emission shift is so large for this compound that the atmospheric condition is overcome even at low pressure. It was observed, however, that at 8 kbars, the fluorescence efficiency for **1c** in PMMA does not increase to the extent observed for the other compounds as the temperature is decreased. This may indicate the existence of efficient radiationless decay pathways with low or zero (tunneling) activation energies for this compound. Attempts to model the temperature dependence of fluorescence for these systems with single activation energy rate expressions for intersystem crossing have proved to be unsatisfactory. This may indicate the presence of multiple paths for decay even at atmospheric pressure.

Conclusion

We have discovered a strong pressure dependence of the fluorescence efficiency for a series of 9-carbonyl substituted anthracenes. Increased pressure results in a remarkable increase in the fluorescence efficiency as well as a shift of the emission spectrum to lower energy for each of the compounds studied. We attribute the increased fluorescence to a decrease in the rate of the competing intersystem crossing process. The rate of intersystem crossing appears to be very strongly dependent upon the relative energetic displacement of the relevant states. Thus at high pressure, where the critical triplet levels have been displaced upward relative to the singlet, endothermic intersystem crossing ceases to occur. The temperature dependence of the fluorescence efficiency indicates that at elevated pressure the remaining radiationless decay paths have only very small temperature coefficients.

The ability of the external pressure to rearrange the electronic energy levels of organic molecules provides an important tool for the direction of photochemical or photophysical reactions toward a specific path. We are currently investigating the pressure response of other chemical systems.

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