

Proximity Effect and Excited-State Dynamics of 9-Carbonyl-Substituted Anthracenes

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Abstract: It is shown that 9-carbonyl-substituted anthracenes exhibit photophysical properties that are characteristic of the proximity effect.

Substituent, solvent, temperature, and pressure dependence of photophysical properties of nitrogen heterocyclic and aromatic carbonyl compounds can be rationalized in terms of the electronic factors for singlet \rightarrow triplet intersystem crossing and the Franck-Condon factors for internal conversion.¹

The electronic selection rule for the intersystem crossing (El-Sayed's rule)² predicts that due to the much greater $n\pi^*-\pi\pi^*$ spin-orbit coupling, relative to $n\pi^*-n\pi^*$ and $\pi\pi^*-\pi\pi^*$ couplings, the photophysical properties of the lowest excited singlet state (S_1) of $\pi\pi^*$ character (or $n\pi^*$ character) are largely determined by the disposition of $n\pi^*$ ($\pi\pi^*$) triplet states relative to S_1 . Thus, the absence or extreme weakness of fluorescence from the $S_1(\pi\pi^*)$ state of several aromatic carbonyl compounds has been rationalized in terms of an efficient singlet \rightarrow triplet intersystem crossing resulting from the presence of an $n\pi^*$ triplet state below the $\pi\pi^*$ singlet state.^{3,4} Similarly, the increasing intensity of $\pi\pi^*$ fluorescence, in certain 9-carbonyl-substituted anthracenes, with decreasing temperature⁵ and increasing pressure⁶ have been interpreted in terms of diminishing intersystem crossing to an $n\pi^*$ triplet state lying above $S_1(\pi\pi^*)$. If an $n\pi^*$ triplet state lies slightly below or slightly above $S_1(\pi\pi^*)$, an $n\pi^*$ singlet state must lie close to $S_1(\pi\pi^*)$ since singlet-triplet splitting is relatively small for $n\pi^*$ states. As shown in a number of earlier publications,^{1,7,8} the close proximity of $n\pi^*$ and $\pi\pi^*$ singlet states can lead to an efficient internal conversion to the ground state (S_0). This phenomenon, which we have termed the proximity effect, is a consequence of $n\pi^*-\pi\pi^*$ vibronic coupling, which renders vibronically active out-of-plane vibrations exceptionally good accepting modes for a large energy-gap radiationless transition (e.g., $S_1 \rightarrow S_0$ internal conversion).⁷⁻¹⁰ The internal conversion rate was found to increase dramatically with vibrational excitation of the out-of-plane modes in the lowest excited state.⁹ Thus, the absence of the fluorescence and the thermal quenching of the fluorescence, previously attributed to the manifestation of the selection rule for intersystem crossing, could also be rationalized in terms of the proximity effect. The relative importance of these two mechanisms (in determining photophysical properties of aromatic carbonyl compounds) can be determined from the measurements of fluorescence and triplet formation since the proximity effect primarily influences $S_1 \rightarrow S_0$ internal conversion, while the electronic selection rule affects singlet \rightarrow triplet intersystem crossing. Employing this criterion, we have shown that the solvent and temperature dependence of

thioxanthone¹¹ and psoralens (8-methoxypsoralen and trioxsalen)¹² are due primarily to the manifestation of the proximity effect, rather than the intersystem crossing selection rule as previously assumed. Despite these developments, the emission characteristics of 9-carbonyl-substituted anthracenes continue to be interpreted in terms of the spin-orbit coupling arguments alone.¹³ While this may appear justified on the basis of the well-known efficiency of singlet \rightarrow triplet intersystem crossing in aromatic carbonyls, the possibility of $S_1 \rightarrow S_0$ internal conversion competing with very fast intersystem crossing cannot be dismissed, even in these molecules, in view of the expected close proximity of the lowest energy $n\pi^*$ and $\pi\pi^*$ singlet states.

In this paper we present measurements of the temperature and solvent dependence of fluorescence and triplet formation for several 9-carbonyl-substituted anthracenes. The results demonstrate that the proximity effect is an important factor in determining the photophysical properties of these compounds, especially at elevated temperatures. For large $S_2(n\pi^*)-S_1(\pi\pi^*)$ gaps and at low temperatures, where the proximity effect becomes much less important, the disposition of an $n\pi^*$ triplet state relative to $S_1(\pi\pi^*)$ appears to have an important influence on the photophysics of these molecules, consistent with a manifestation of the selection rule for intersystem crossing.

Experimental Section

The experimental apparatus and technique have been described.¹² Briefly, fluorescence decays and time-resolved fluorescence spectra were measured with use of time-correlated photon counting. The light source was a cavity-dumped dye laser which was synchronously pumped by a mode-locked argon ion laser. The temperature dependence of the quantum yield of fluorescence was deduced, relative to that of 9,10-diphenylanthracene ($\Phi_F = 1$), with a conventional spectrofluorometer. The temperature dependence of the quantum yield of triplet formation was measured by triplet-triplet absorption, on the assumption that the molar extinction coefficient of the absorption is independent of temperature. A laser-photolysis system, utilizing the third harmonic of a Nd:YAG laser as the pump beam and a xenon arc lamp as the probe beam, was used for the transient absorption experiments.

9-Benzoylanthracene and its derivatives were the gifts of Professor S. Hirayama of Kyoto Technical University, and they were vacuum sublimed prior to use.

Results and Discussion

Three classes of carbonyl-substituted anthracenes were investigated in the present study: 9-benzoylanthracene and its 10-halogeno (Cl and Br) derivatives, which do not fluoresce at any temperature;¹⁴ 9-benzoyl-10-cyanoanthracene, which fluoresce at all temperatures; and 9-anthrylalkyl ketones which fluoresce only at low temperatures. The results on these three classes of compounds will be described separately.

A. 9-Benzoylanthracene and 9-Benzoyl-10-X-anthracenes (X = Cl, Br). Studies of temperature dependence of triplet formation

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(14) 9-Benzoylanthracene fluoresce with high yield as a supercooled gas: V. Swayambunathan, V.; Lim, E. C. *J. Chem. Phys.*, in press.

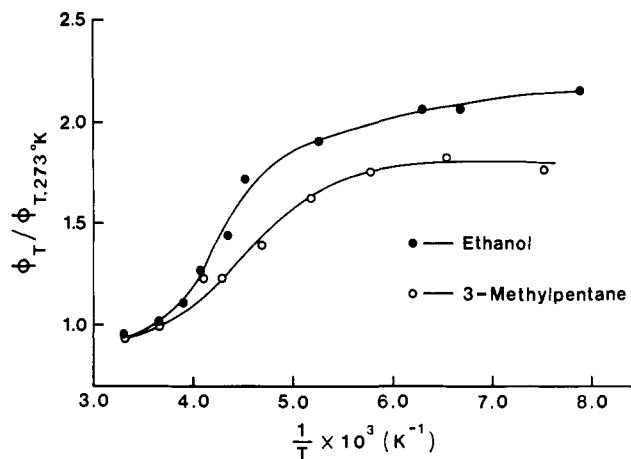


Figure 1. Temperature dependence of triplet formation yield (relative to the value at 273 K) for 9-benzoylanthracene in ethanol and 3-methylpentane. The triplet formation was monitored by triplet-triplet absorption at 430 nm.

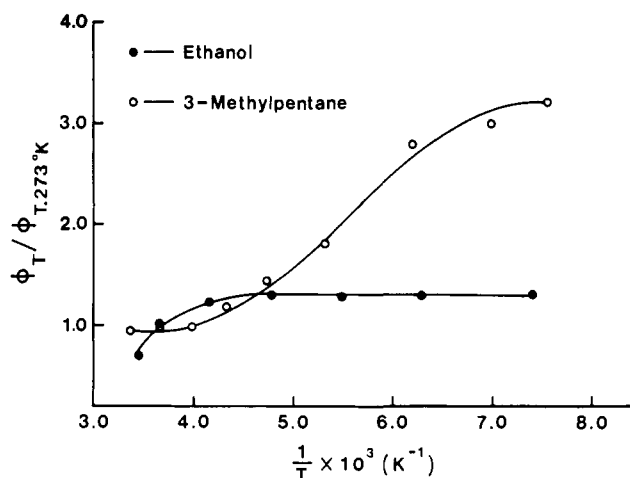


Figure 2. Temperature dependence of triplet formation yields (relative to the value at 273 K) for 9-benzoyl-10-bromoanthracene in ethanol and 3-methylpentane. The triplet formation was monitored by triplet-triplet absorption at 425 and 415 nm, respectively.

in these compounds reveal that $S_1 \rightarrow S_0$ internal conversion is an important nonradiative decay channel at elevated temperatures. Figures 1–3 show the temperature dependence of triplet-triplet absorption in ethanol and 3-methylpentane. It should be noted that the triplet formation yield, as probed by triplet-triplet absorption, exhibits significant increase with decreasing temperature. When the low-temperature limit of the triplet formation (i.e., singlet \rightarrow triplet intersystem crossing) yield is taken to be unity, the maximum quantum yield of singlet \rightarrow triplet intersystem crossing, Φ_{ISC}^{\max} , at room temperature is seen to be substantially less than unity. Thus, the minimum value of $S_1 \rightarrow S_0$ internal conversion yield (Φ_{IC}^{\min}) at room temperature, as deduced from $\Phi_{IC}^{\min} = 1 - \Phi_{ISC}^{\max}$, ranges from ~ 0.5 to ~ 0.7 in 3-methylpentane and ~ 0.3 to ~ 0.5 in ethanol. Clearly, $S_1 \rightarrow S_0$ internal conversion is an important, if not dominant, nonradiative decay process at elevated temperatures. This conclusion represents a fundamental departure from the earlier explanation of Hirayama et al.,⁵ which attributes the weakness of fluorescence in these compounds to the efficient intersystem crossing from $S_1(\pi\pi^*)$ to an $n\pi^*$ triplet state.

The occurrence of an important $S_1 \rightarrow S_0$ internal conversion at elevated temperatures is most probably due to the excitation of sequence bands which results in a prepared state which has a large contribution of out-of-plane bending modes and hence a large proximity effect (due to their low frequencies^{1,15} a significant

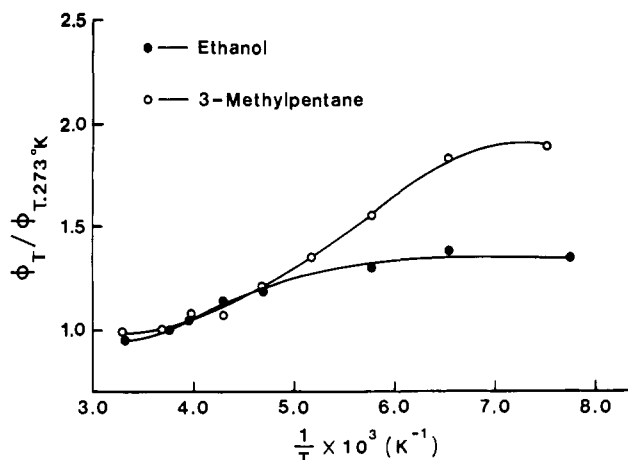


Figure 3. Temperature dependence of triplet formation yields (relative to the value at 273 K) for 9-benzoyl-10-chloroanthracene in ethanol and 3-methylpentane. The triplet formation was monitored by triplet-triplet absorption at 420 nm.

fraction of out-of-plane modes are thermally populated at elevated temperatures). On the basis of the measured rise times (20–50 ps) of triplet-triplet absorptions,¹⁶ a lower limit of $S_1 \rightarrow S_0$ internal conversion rates at room temperature can be set at about 10^{10} s^{-1} . This is more than three orders of magnitude greater than the upper limit ($\sim 10^7 \text{ s}^{-1}$)¹⁷ of the $S_1 \rightarrow S_0$ internal conversion rates in anthracene, and it demonstrates the importance of the presence of an $n\pi^*$ singlet state in the vicinity of the lowest energy $\pi\pi^*$ singlet state. The observation that the temperature dependence of Φ_{ISC} for 9-benzoyl-10-chloroanthracene and 9-benzoyl-10-bromoanthracene, as measured by $\Phi_{ISC}(\text{low temp})/\Phi_{ISC}(\text{room temp})$, is greater in 3-methylpentane than in ethanol implies that the ${}^1n\pi^* \rightarrow {}^1\pi\pi^*$ electronic energy gap is smaller in the former solvent. For 9-benzoylanthracene, the value of $\Phi_{ISC}(\text{low temp})/\Phi_{ISC}(\text{room temp})$ is similar in 3-methylpentane and in ethanol. Since the $S_2(n\pi^*) \rightarrow S_1(\pi\pi^*)$ gap is expected to be increased in polar solvents, the observation suggests that the ordering of $n\pi^*$ and $\pi\pi^*$ states may be reversed in the two solvents. The possible presence of a low-lying $n\pi^*$ singlet state in aprotic solutions of 9-benzoylanthracene is suggested by the appearance of a low-intensity, long-wavelength tail in the room-temperature absorption spectrum of the compound. For the purpose of our argument concerning the importance of $S_1 \rightarrow S_0$ internal conversion, related to the proximity effect, the energy ordering of $n\pi^*$ and $\pi\pi^*$ singlet states is immaterial so long as these states are in close proximity.

B. 9-Benzoyl-10-cyanoanthracene. Since this compound fluoresces even at room temperature, both the fluorescence yield and intersystem crossing yield can be measured over a wide range of temperature to deduce information concerning $S_1 \rightarrow S_0$ internal conversion, related to the proximity effect.

Figure 4 presents the temperature dependence of fluorescence and triplet formation in ethanol. Unlike fluorescence, whose yield increases first slowly and then rapidly with decreasing temperature, Φ_{ISC} first increases and then decreases as the temperature is lowered from room temperature to 77 K. The onset of the decrease in Φ_{ISC} appears to coincide with the onset of the sharp increase in Φ_F , indicating that the rate of singlet \rightarrow triplet intersystem crossing decreases very sharply below about 175 K. The simplest explanation of the decreased intersystem crossing rate at low temperatures is that singlet \rightarrow triplet intersystem crossing proceeds from $S_1(\pi\pi^*)$ to an $n\pi^*$ triplet state lying slightly above S_1 . The thermally activated intersystem crossing is expected to be greatly reduced at low temperatures, hence accounting for the decrease in Φ_{ISC} and the large increase in Φ_F . We estimate Φ_F to be ~ 0.5

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(17) The upper limit of the quantum yield of $S_1 \rightarrow S_0$ internal conversion is ~ 0.1 ($\Phi_F + \Phi_{ISC} \sim 1.0$, experimentally). Since the measured fluorescence decay rate is $\sim 10^8 \text{ s}^{-1}$, the maximum $S_1 \rightarrow S_0$ internal conversion rate is $\sim 10^7 \text{ s}^{-1}$.

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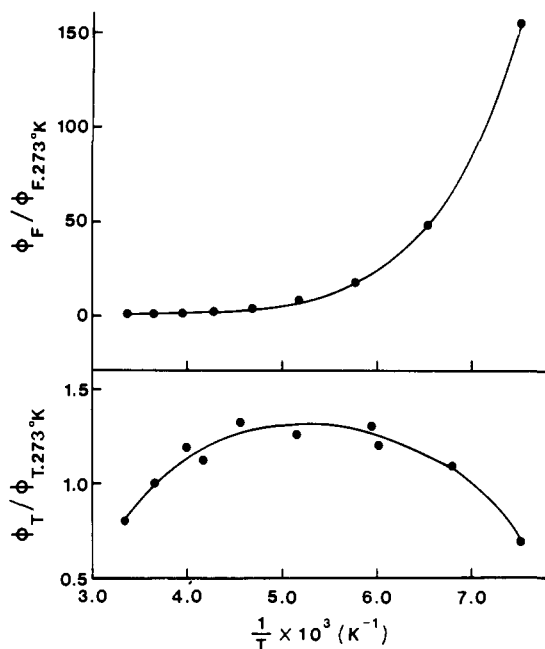


Figure 4. Temperature dependence of fluorescence and triplet formation yields (both relative to the value at 273 K) for 9-benzoyl-10-cyanoanthracene in ethanol. The triplet formation was monitored by triplet-triplet absorption at 430 nm.

Table I. Temperature Dependence of Fluorescence Lifetime of 9-Benzoyl-10-cyanoanthracene in Ethanol

temp, °C	τ_F , ns		
	410 nm	450 nm	500 nm
22	0.24	0.24	0.24
0	0.26	0.26	0.26
-20	0.25	0.25	0.25
-40	0.28	0.28	0.28
-60	0.42	0.42	0.42
-80	0.37	0.73 ^a	0.86 ^a
-100	0.70 ^a	1.82 ^a	2.13 ^a
-120	2.21 ^a	2.82 ^a	3.00 ^a
-140	4.49 ^a	5.69	5.74
-160	5.69 ^a	7.04	6.84
-196	8.80	9.00	9.00

^aThe decay is nonexponential; only the lifetime of the dominant component is given.

at 77 K (Hirayama reports $\Phi_F = 1.0$ at 77 K¹⁸), based on the comparison with the known fluorescence yield ($\Phi_F = 1.0$) of 9,10-diphenylanthracene.

Measurements of the fluorescence decay rate in ethanol show that the temporal characteristics of fluorescence are exponential only at elevated temperatures or in low-temperature rigid matrices. At intermediate temperatures, the fluorescence exhibits nonexponential decay, as shown in Figure 5 and Table I. The energy-resolved fluorescence decay, shown in Table I, indicates that the lifetime is shorter for the shorter wavelength region of the fluorescence spectrum. The shorter lifetime of the emission observed at shorter wavelengths is confirmed by the time-resolved fluorescence spectra which are shown in Figure 6. These results suggest that at least two emitting species contribute to the observed fluorescence at lower temperatures. We believe (as will be shown elsewhere¹⁹) that the shorter wavelength component with shorter lifetime is due to the electronically excited species having a conformation very similar to the ground-state species, while the longer wavelength component represents the species which have undergone substantial geometry changes (from less coplanar to more coplanar) during the excited-state lifetime. The proportion

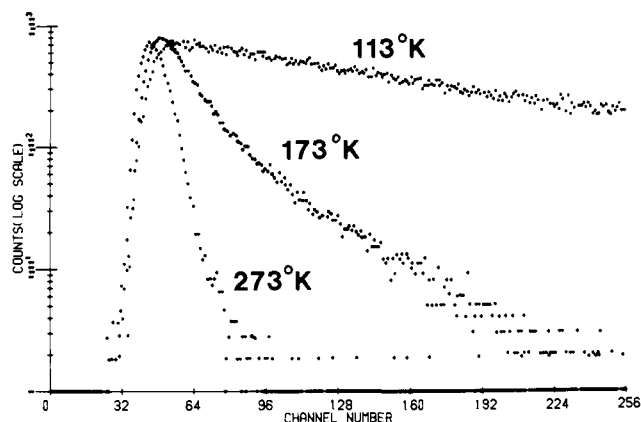


Figure 5. Temporal characteristics of fluorescence of 9-benzoyl-10-cyanoanthracene in ethanol at the different temperatures (1 channel = 0.0125 ns). The fluorescence was monitored at 450 nm.

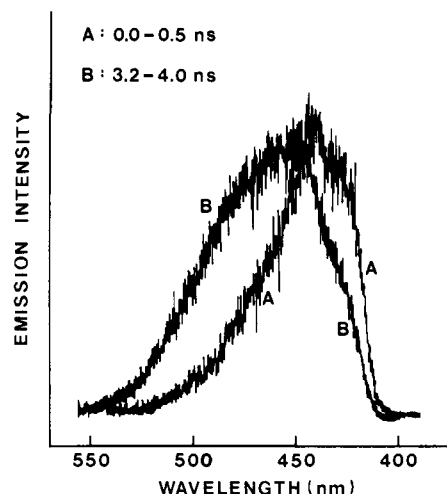


Figure 6. Time-resolved fluorescence spectra of 9-benzoyl-10-cyanoanthracene in ethanol at 173 K.

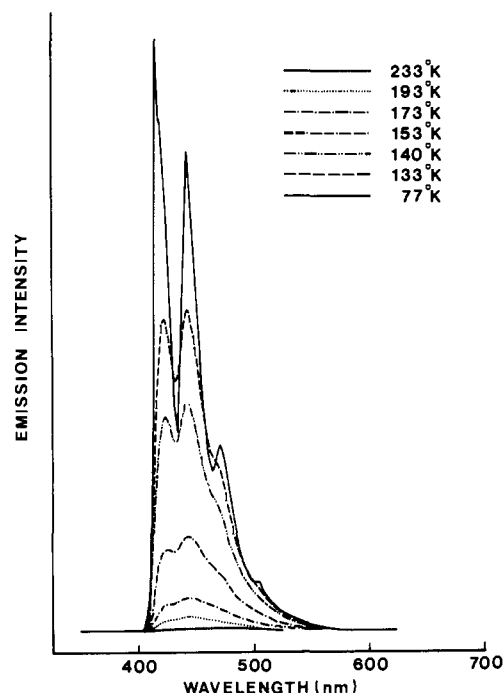


Figure 7. Temperature dependence of steady-state fluorescence of 9-benzoyl-10-cyanoanthracene in ethanol.

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of the longer wavelength component, relative to that of the shorter wavelength component, is expected to be viscosity dependent, since

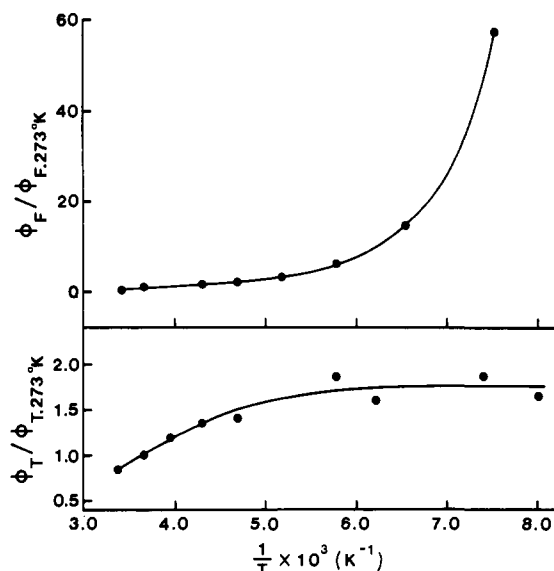


Figure 8. Temperature dependence of fluorescence and triplet formation yields (both relative to the value at 273 K) for 9-benzoyl-10-cyanoanthracene in 3-methylpentane. The triplet formation was monitored by triplet-triplet absorption at 435 nm.

the rotation of the bulky carbonyl group (during the short excited-state lifetime) should not be effective in high-viscosity medium. This conjecture is supported by the temperature dependence of the steady-state fluorescence, shown in Figure 7, which shows that the shorter wavelength, 0-0 band-like feature of the emission becomes much more prominent as the temperature is lowered (i.e., as the viscosity of the medium is increased). A detailed account of this aspect of the work is not warranted here, as the conformational changes accompanying $S_0 \rightarrow S_1(\pi\pi^*)$ excitation of 9-carbonylanthracenes is the subject of a future paper.¹⁹ It is sufficient to point out that the longer lifetime of the longer wavelength component is consistent with the greater $S_2(n\pi^*)-S_1(\pi\pi^*)$ electronic energy gap expected for the more coplanar conformation of the molecule (coplanar structure is expected to stabilize $^1\pi\pi^*$ relative to $^1n\pi^*$, leading to an increase in the S_2-S_1 electronic gap).

The temperature dependence of fluorescence and triplet formation in a 3-methylpentane solution is shown in Figure 8. As in ethanol, both the fluorescence intensity and the fluorescence lifetime increase greatly with decreasing temperature. However, the quantum yield and lifetime (these quantities have only qualitative connotations as the fluorescence decay is nonexponential in a certain temperature range) in 3-methylpentane are substantially smaller than those in ethanol, consistent with the smaller $S_2(n\pi^*)-S_1(\pi\pi^*)$ gap expected in aprotic solvents.

C. 9-Anthryl Alkyl Ketones. The temperature and solvent dependence of fluorescence and triplet formation in 9-anthryl alkyl ketones (e.g., 9-acetylanthracene) are in between those in class A and class B compounds. Thus, the class C compounds fluoresce only at low temperatures both in ethanol and in hydrocarbon solvents (with fluorescence efficiency increasing with decreasing

temperature). Measurements of the temperature dependence of the triplet-triplet absorption indicate that the lack of fluorescence at elevated temperatures is caused not so much by an efficient intersystem crossing but by an efficient internal conversion. The thermal quenching of fluorescence can again be attributed to the sequence-band excitations (of out-of-plane modes) which leads to a large enhancement of $S_1 \rightarrow S_0$ internal conversion via the increase in the proximity effect. As expected from the greater $S_2(n\pi^*)-S_1(\pi\pi^*)$ gap, the onset of fluorescence lies at higher temperatures in ethanol relative to hydrocarbon solvents (i.e., these compounds fluoresce at higher temperatures in ethanol).

When the $S_2(n\pi^*)-S_1(\pi\pi^*)$ gap is large, as in strongly hydrogen-bonding solvents (e.g., solvents containing a small amount of trichloroacetic acid), the temperature dependence of fluorescence is small and the emission is observed with high yields even at room temperatures.

Conclusion

We have shown that the diverse emission characteristics of 9-carbonyl-substituted anthracenes can be rationalized on the basis of relative proximity of the lowest energy $n\pi^*$ and $\pi\pi^*$ singlet states and temperature, which influence the efficiency of $S_1 \rightarrow S_0$ internal conversion via the proximity effect. When the $n\pi^*-\pi\pi^*$ gap is very small, $S_1 \rightarrow S_0$ internal conversion is so rapid that even the fast singlet \rightarrow triplet intersystem crossing has yields which are substantially less than unity. Under these conditions, fluorescence is not observed even at low temperatures, and the location of the higher lying $n\pi^*$ triplet states relative to $S_1(\pi\pi^*)$ appears to have no major consequences on the photophysical properties of the carbonyl compounds. The latter conclusion is consistent with the extensive $n\pi^*-\pi\pi^*$ vibronic coupling (in the singlet manifold) which leads to a breakdown of the electronic selection rule for spin-orbit coupling. When the $S_2(n\pi^*)-S_1(\pi\pi^*)$ gap is large, fluorescence is observed even at elevated temperatures and the energy level disposition of an $n\pi^*$ triplet state relative to $S_1(\pi\pi^*)$ becomes an important factor in determining photophysical properties of the molecules. The pressure dependence of fluorescence at different temperatures⁶ can also be adequately rationalized in terms of the proximity effect, either taken alone or in combination with the electronic selection rule for intersystem crossing.

Acknowledgment. The work described in this paper was completed a number of years ago with samples generously donated (in 1975) by Professor S. Hirayama of Kyoto Technical University. Because the photophysical properties of these molecules are not very different from those of other carbonyl compounds which we have already described and interpreted, we have refrained from putting these materials into print. However, because of the persistent interpretation of the photophysical properties of these compounds in terms of singlet \rightarrow triplet intersystem crossing (alone), we have felt compelled to publish these results at this late date. This work was supported by a grant from the Department of Energy.

Registry No. 9-Benzoylanthracene, 1564-53-0; 9-benzoyl-10-bromoanthracene, 1564-51-8; 9-benzoyl-10-chloroanthracene, 22970-73-6; 9-benzoyl-10-cyanoanthracene, 22970-75-8.