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# Photophysical Properties of Biologically Important Molecules Related to Proximity Effects: Psoralens[†]

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**Abstract:** Evidence is presented that indicates that the strong temperature and solvent dependence of fluorescence and triplet formation in psoralens is due to efficient $S_1 \rightarrow S_0$ internal conversion that arises from the proximity of the lowest energy $n\pi^*$ and $\pi\pi^*$ singlet states. The $S_1 \rightarrow S_0$ internal conversion rate increases with increasing temperature and decreasing solvent polarity, in conformity with the predictions of the model calculations on the proximity effect and the photophysical behavior of simpler aromatic ketones with close-lying $n\pi^*$ and $\pi\pi^*$ singlet states. Time-resolved fluorescence spectra and energy-resolved fluorescence decays demonstrate the importance of solvent relaxation in determining the relative importance of the proximity effect via its influence on the $n\pi^*-\pi\pi^*$ electronic energy gap.

Many nitrogen heterocyclic and aromatic carbonyl compounds possess a lowest energy $n\pi^*$ state that is close in energy to the lowest energy $\pi\pi^*$ state. The close proximity of these states has been found to lead to a very efficient radiationless decay from the lower of the two excited states.[1] This phenomenon, which we have termed "proximity effect", is believed[2-5] to be a consequence of vibronic interaction between the $n\pi^*$ and $\pi\pi^*$ states, which leads to the potential energy distortion (frequency change)[6] and displacement (geometry change)[6] along the vibronically active out-of-plane bending modes. Theoretical investigations of the proximity effect indicate that for a sufficiently large interaction strength and sufficiently small energy separation between the interacting states, the vibronically active mode could become the dominant accepting mode for the radiationless transition.[2-5] The radiationless decay rate was found to increase dramatically with vibrational excitation of the out-of-plane modes in the lowest excited state.[7] An interesting conclusion to come out of the model calculations is that the proximity effect, as well as the effects of vibrational excitation thereon, is greater the larger the electronic gap for a radiationless transition.[2-5,7] Since the $S_1 \rightarrow S_0$ electronic energy gap is much greater than the $S_1$–$T_1$ gap, it follows that the proximity effect will have much greater effects on $S_1 \rightarrow S_0$ internal conversion than on $S_1 \rightarrow T_1$ intersystem crossing. Thus, the $(S_1 \rightarrow S_0)/(S_1 \rightarrow T_1)$ branching ratio in the radiationless transition is predicted to be greatly enhanced by optical excitation of the out-of-plane bending modes under collision-free conditions of a low-pressure gas phase or by thermal excitation of the out-of-plane modes in a condensed phase. The measurements of the temperature dependence of fluorescence and triplet formation for several polycyclic azines and aromatic carbonyls indeed indicate that the quantum yield of both processes decreases sharply with increasing temperature.[8-10] Since the temperature dependence is quantitatively very similar for fluorescence and triplet formation, the observed temperature effects must be due to a process other than fluorescence or intersystem crossing. In the absence of any evidence for photochemistry, the temperature dependence of the quantum yields has therefore been attributed[8-10] to the thermal enhancement of $S_1 \rightarrow S_0$ internal conversion, which is predicted by the model calculation of the proximity effect. The importance of the proximity effect in molecular systems exhibiting these temperature effects is further demonstrated by the observation that the fluorescence is very weak or absent in hydrocarbon solvents, while it is moderately strong in polar and/or hydrogen-bonding solvents. The fluorescence activation in polar solvents has been argued[1] in terms of a larger $^1n\pi^*-^1\pi\pi^*$ electronic energy gap in these solvents, which render the proximity effect in radiationless transition less important. These results, as well as others, suggest that the proximity effect may play a dominant role in electronic relaxation of a large number of N-heterocyclic and aromatic carbonyl compounds.

Since many biologically, or photobiologically, important molecules (e.g., nucleic acid bases and retinal) can also possess the lowest energy $n\pi^*$ singlet state that is close in energy to the lowest energy $\pi\pi^*$ singlet state, it is possible that the proximity effect also plays an important role in electronic relaxation, and hence in the photochemistry and photobiology, of these species. As part of a research program directed toward the understanding of radiationless transitions in molecules with close-lying excited states, we have therefore initiated an experimental study of photophysical properties of biologically important molecules. In this paper, which represents the first of the series, we discuss solvent, temperature, and viscosity dependence of fluorescence and triplet formation in psoralens, which appear to demonstrate the occurrence of an important proximity effect.

Because of the importance of psoralens (furocoumarins) in the treatment of psoriasis and vitiligo, the photophysical properties of the lowest excited states (singlet and triplet) of furocoumarins and coumarins have been extensively investigated in recent years.[11] These studies indicate that the lowest excited singlet state of 8-methoxypsoralen is a $\pi\pi^*$ state,[12] the fluorescence from which is strongly dependent upon the nature of solvent.[13] In nonpolar solvents, such as 3-methylpentane, the fluorescence is too weak to be detected, while in polar solvents the fluorescence is observed with moderate intensity.[13] The result, which is reminiscent of the behavior of simpler carbonyls,[9,10] was interpreted[13] in terms of the energy level disposition of an $n\pi^*$ triplet state relative to the lowest energy $\pi\pi^*$ singlet state. In nonpolar solvents, the $n\pi^*$ triplet state was assumed[13] to lie below the $\pi\pi^*$ singlet state, and the $^1\pi\pi^* \rightarrow {}^3n\pi^*$ intersystem crossing, which is efficient due to relatively strong $n\pi^*-\pi\pi^*$ spin-orbit coupling, was proposed[13] to render the observation of the fluorescence difficult. In polar solvents, the energy level ordering was assumed[13] to be reversed, so that the fluorescence becomes competitive with intersystem crossing. This explanation requires the solvent effect on

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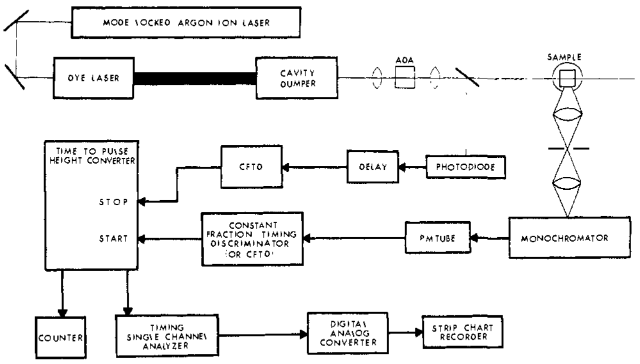

**Figure 1.** Block diagram of the experimental arrangement used to measure time-resolved fluorescence spectra.

fluorescence to be inversely correlated with the solvent effect on the corresponding singlet → triplet intersystem crossing.

It will be shown here that the solvent dependence of fluorescence in psoralens has little to do with the changes in singlet → triplet intersystem crossing but is a consequence of the changes in $S_1 \rightarrow S_0$ internal conversion. Comparison of the temperature and solvent dependences of steady-state fluorescence with those of the triplet formation as well as the time-resolved fluorescence spectra and the energy-resolved fluorescence decays in polar solvents indicates that the efficiency of $S_1 \rightarrow S_0$ internal conversion is strongly dependent upon the ${}^1n\pi^*$–${}^1\pi\pi^*$ electronic energy gap, as expected from the proximity effect in radiationless transitions.

## Experimental Section

Fluorescence decays and time-resolved fluorescence spectra were measured by using time-correlated photon counting. The light source was a Spectra-Physics synchronously pumped, cavity-dumped dye laser system operating at 820.19 kHz. The ultraviolet (~300 nm) beam of ~8-ps duration and ~6-cm$^{-1}$ width was generated by frequency doubling the visible output of the Rhodamine 6G dye laser with temperature-tuned ADA crystals (Lasermetrics). The description of the timing electronics and the optical arrangements for the decay measurements is given elsewhere.[14] For the time-resolved fluorescence spectra, we used the experimental arrangement[15] shown in the block diagram of Figure 1. The time interval was selected by the window of the single channel analyzer. Steady-state fluorescence spectra were measured with an Aminco SPF-500 spectrofluorometer. The quantum yield of fluorescence at room temperature was deduced relative to that of 9,10-diphenylanthracene, which was taken as unity. The relative quantum yields of triplet formation in various solvents were measured by triplet–triplet absorption by using third harmonics of a Nd:YAG laser as the pump beam and a xenon arc lamp as the probe beam. An assumption was made that the molar extinction coefficient of the triplet–triplet absorption is not sensitive to the nature of the solvent. Both in the absorption and emission experiments, the temperature of the sample was maintained to within ±1 °C by flowing cold nitrogen gas.

8-Methoxypsoralen (Pfaltz and Bauer) was purified by vacuum sublimation, while trioxsalen (Calbiochem) was used as received. Solvents were either spectrograde or the best research grade, and they were purified as described previously.[8,16] All solutions were degassed by several freeze–pump–thaw cycles on a mercury-free vacuum line. All spectroscopic measurements were made by using dilute solutions (~8 × 10$^{-5}$ M) of psoralens.

## Results and Discussion

Figure 2 presents the solvent dependence of absorption and fluorescence spectra for 8-methoxypsoralen. The spectral and decay characteristics of the fluorescence from the $S_1$ state of 8-methoxypsoralen are strongly dependent upon the nature of the solvent. In nonpolar solvents, the fluorescence is too weak to be detected. Increasing polarity of the solvent leads to an increase in the fluorescence yield, an increase in the fluorescence lifetime, and a shift of the fluorescence maximum to longer wavelengths, as shown in Table I. Since the fluorescence yield ($\Phi_F$) is very small even for polar solvents, it is the change in nonradiative decay rate that is primarily responsible for the observed solvent dependence of the fluorescence lifetime. The nonradiative decay rate therefore decreases with increasing polarity of the solvent. The nonradiative decay process of $S_1$ that is sensitive to the solvent polarity is most likely internal conversion to the ground state since the solvent effects on the relative quantum yield of triplet formation ($\Phi_T$) are similar to those of $\Phi_F$ (Table I).

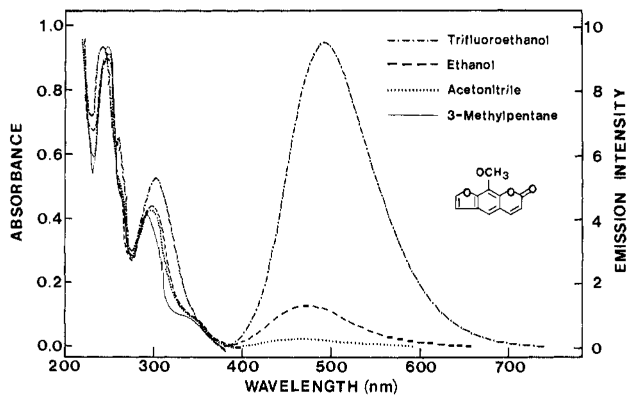

**Figure 2.** Absorption (left) and fluorescence (right) of 8-methoxypsoralen in various solvents at 298 K.

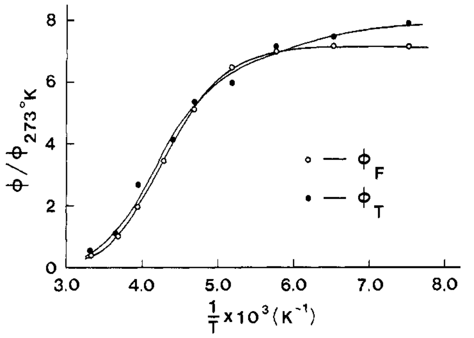

**Figure 3.** Temperature dependence of fluorescence and triplet formation yields (both relative to the value at 273 K) for 8-methoxypsoralen in ethanol. The triplet formation was monitored by triplet–triplet absorption at 400 nm.

**Table I.** Wavelength of Fluorescence Maximum ($\lambda_{max}$), Fluorescence Mean Lifetime ($\tau_F$), Relative Fluorescence Yield ($\Phi_F$), and Relative Triplet Formation Yield ($\Phi_T$) for 8-Methoxypsoralen in Various Solvents[a]

| solvent | $\lambda_{max}$, nm | $\tau_F$, ns | $\Phi_F$[c] | $\Phi_T$[c] |
|---|---|---|---|---|
| 3-methylpentane | not observed<br>(452.5)[b] | | | |
| acetonitrile | 462.5 | <0.10 | 0.2 | 0.3 |
| ethanol | 470 | 0.39 | 1.0 | 1.0 |
| trifluoroethanol | 492.5 | 2.30 | 8.7 | 2.6 |

[a] Data were obtained at 298 K. The triplet formation was monitored by triplet–triplet absorption at 400 nm. [b] Lower temperature value taken from Figure 4. [c] Relative to the value in ethanol. Actual quantum yield of fluorescence is 0.0013 (this work), while that of triplet formation is 0.04 (ref 20), in ethanol at room temperature.

It should be noted from Table I that the radiative lifetime ($\tau_r = \tau_F/\Phi_F$) of the $S_1$ state is nearly independent of the nature of the solvent. The magnitude of the radiative lifetime (~300 ns in ethanol), as well as the solvent dependence of the fluorescence maximum, indicates that the lowest excited singlet state is $\pi\pi^*$, consistent with the assumptions of earlier workers.[11-13]

The importance of $S_1(\pi\pi^*) \rightarrow S_0$ internal conversion is also indicated by the temperature dependence of $\Phi_F$ and $\Phi_T$, which are shown in Figure 3 for 8-methoxypsoralen in ethanol. As the temperature is lowered initially, both $\Phi_F$ and $\Phi_T$ increase in nearly identical fashion, thereby yielding the $\Phi_F/\Phi_T$ ratio, which remains essentially independent of temperature. The result confirms that

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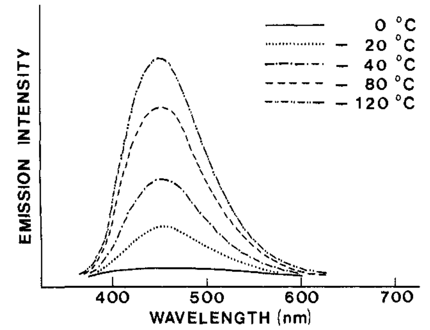

**Figure 4.** Temperature dependence of steady-state fluorescence of 8-methoxypsoralen in 3-methylpentane.

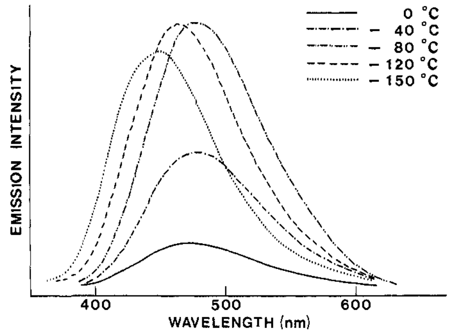

**Figure 5.** Temperature dependence of steady-state fluorescence of 8-methoxypsoralen in ethanol.

the dominant nonradiative decay process, which is sensitive to temperature changes, is definitely not the singlet → triplet intersystem crossing. Since 8-methoxypsoralen is photochemically stable under the experimental conditions, the temperature-sensitive radiationless transition can be identified as $S_1 \rightarrow S_0$ internal conversion. The rate of the $S_1 \rightarrow S_0$ internal conversion therefore decreases with decreasing temperature. The fluorescence of 8-methoxypsoralen is too weak to be detected in hydrocarbon solvents at room temperature, but it can be activated by cooling the solution to lower temperatures, as illustrated in Figure 4. Although the triplet–triplet absorption is too weak to be measured (at any temperature) in hydrocarbon solvents, the results for related trioxsalen (vide infra) indicate that the "fluorescence activation by cooling" in hydrocarbon solvents is due to a decreased $S_1 \rightarrow S_0$ internal conversion at lower temperatures.

An interesting feature of the steady-state fluorescence in polar solvents is that the emission spectrum shifts to the blue when the viscosity of the solvent becomes high at lower temperatures (see Figure 5). This is in sharp contrast to the behavior of nonpolar solvents, where the spectral position remains essentially independent of temperature (Figure 4). The fluorescence spectra in polar hydrogen-bonding solvents are further complicated by the appearance of emission from hydrogen-bonded (in the ground electronic state) species. This emission, which occurs at the blue edge of the main fluorescence spectrum, becomes quite important at low temperatures (being the dominant emission at 77 K). The results and the discussion to follow refer only to the excited-state dynamics of non-hydrogen-bonded species.

The temporal characteristics of fluorescence in 8-methoxypsoralen are also strongly influenced by the nature of the solvent and by temperature. In nonpolar solvents, the decay of fluorescence (where observable) is exponential at all temperatures, and its rate (which is very fast) decreases with decreasing temperature. In polar solvents, however, the decay (which is considerably slower than that in nonpolar solvents) is exponential only at elevated temperatures (Table II). At lower temperatures, the fluorescence exhibits nonexponential decay, as shown in Figure 6 and Table II. The energy-resolved fluorescence decays, shown in Figure 7, indicate that the lifetime is shorter for the shorter wavelength region of the fluorescence spectrum. Interestingly, the time dependence of the emission observed at longer wavelengths exhibits a clear rise time (see Figure 7), suggesting that the species responsible for the longer wavelength component(s) of the emission is not formed instantaneous to the excitation by the light source. The shorter lifetime of the emission observed at shorter wavelengths is confirmed by the time-resolved fluorescence spectra, which are shown in Figure 8. These results suggest that at least two emitting species contribute to the observed fluorescence at lower temperatures.

The solvent and temperature dependences of fluorescence and triplet formation in trioxsalen are qualitatively similar to those

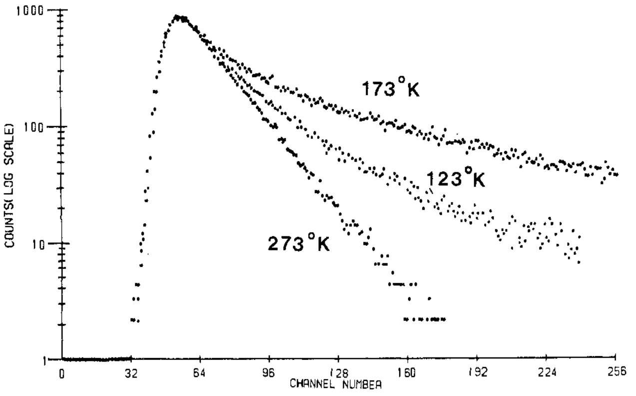

**Figure 6.** Temporal characteristic of fluorescence of 8-methoxypsoralen in ethanol at the different temperatures.

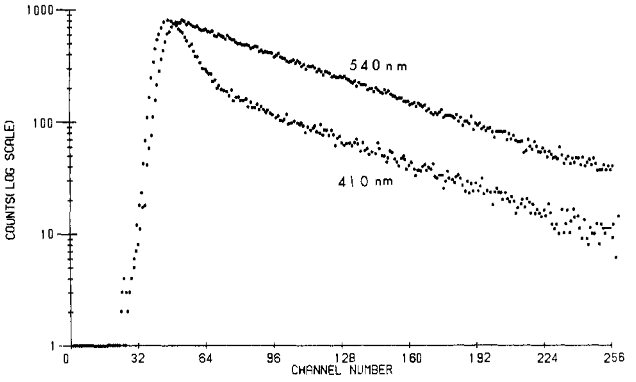

**Figure 7.** Energy-resolved fluorescence decay of 8-methoxypsoralen in ethanol at -40 °C.

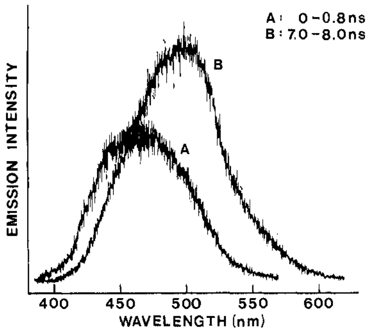

**Figure 8.** Time-resolved fluorescence spectra of 8-methoxypsoralen in ethanol at -100 °C.

Table II. Temperature Dependence of Fluorescence Lifetime of 8-Methoxypsoralen in Ethanol[a]

| temp, °C | $\tau_F$, ns | temp, °C | $\tau_F$, ns |
|---|---|---|---|
| 24 | 0.39 | -80 | *6.04*, 1.12 |
| 0 | 0.92 | -100 | 5.88, 1.14 |
| -20 | 1.77 | -120 | 4.20, *1.11* |
| -40 | 3.22 | -140 | 3.04, *1.06* |
| -60 | *4.60*, 0.67 | -150 | 2.18, *0.79* |

[a] The observation wavelength is 540 nm. Where the decay is clearly nonexponential, the dominant component is in italics.

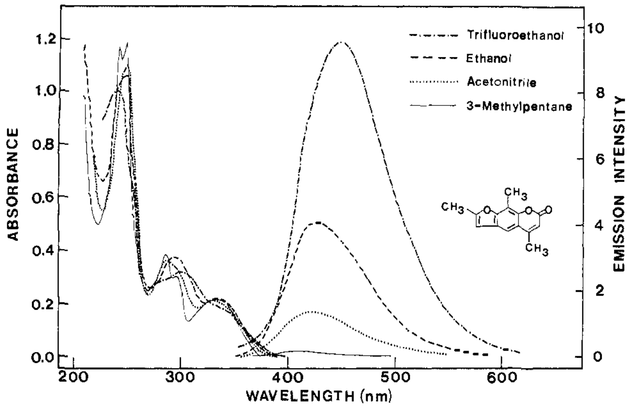

Figure 9. Absorption (left) and fluorescence (right) of trioxsalen in various solvents at 298 K.

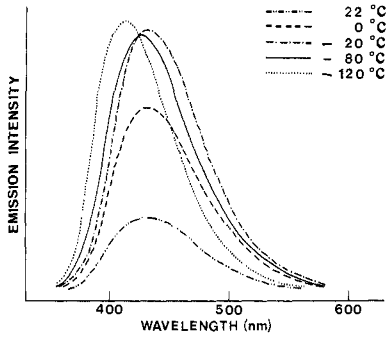

Figure 10. Temperature dependence of steady-state fluorescence for trioxsalen in ethanol.

Table III. Wavelength of Fluorescence Maximum ($\lambda_{max}$), Fluorescence Mean Lifetime ($\tau_F$), Relative Fluorescence Yield ($\Phi_F$), and Relative Triplet Formation Yield ($\Phi_T$) for Trioxsalen in Various Solvents[a]

| solvent | $\lambda_{max}$, nm | $\tau_F$, ns | $\Phi_F$[b] | $\Phi_T$[b] |
|---|---|---|---|---|
| 3-methylpentane | 402.0 | <0.10 | 0.02 | 0.2 |
| acetonitrile | 422.5 | 0.30 | 0.32 | 0.6 |
| ethanol | 427.5 | 0.62 | 1.0 | 1.0 |
| trifluoroethanol | 452.5 | 2.14 | 3.0 | 0.8 |

[a] Data were obtained at 298 K. The triplet formation was monitored by the peak of the triplet-triplet absorption at 460 nm. [b] Relative to the value in ethanol. Actual fluorescence yield in ethanol is 0.044.

Table IV. Temperature Dependence of Fluorescence Lifetime of Trioxsalen in Ethanol[a]

| temp, °C | $\tau_F$, ns | temp, °C | $\tau_F$, ns |
|---|---|---|---|
| 23 | 0.67 | -80 | *2.12*, 0.63 |
| 0 | 0.79 | -100 | 2.68, *0.81* |
| -20 | 0.90 | -120 | 2.40, *0.69* |
| -40 | 1.30 | -140 | 2.70, *0.75* |
| -60 | 1.65 | | |

[a] The observation wavelength is 525 nm. Where the decay is clearly nonexponential, the dominant component is in italics.

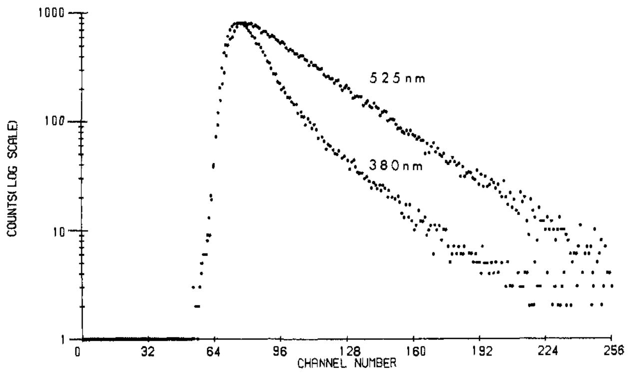

Figure 11. Energy-resolved fluorescence decay of trioxsalen in ethanol at -60 °C.

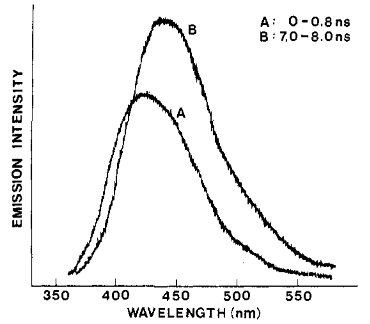

Figure 12. Time-resolved fluorescence spectra of trioxsalen in ethanol at -100 °C.

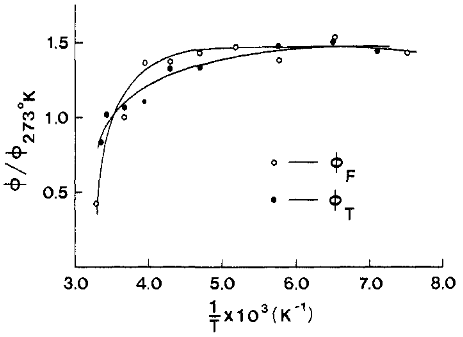

Figure 13. Temperature dependence of fluorescence and triplet formation yields for trioxsalen in ethanol (both relative to the value at 273 K). The triplet formation was monitored by the peak of the triplet-triplet absorption at 460 nm.

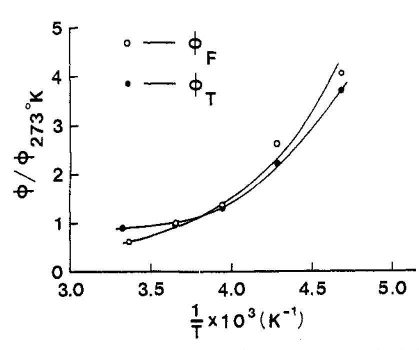

Figure 14. Temperature dependence of fluorescence and triplet formation yields (both relative to the value at 273 K) in 3-methylpentane. The triplet formation was monitored by the peak of the triplet-triplet absorption at 460 nm.

in 8-methoxypsoralen. In trioxsalen, however, the quantum yield of fluorescence is much greater (e.g., ~30 times in ethanol at room temperature) and its temperature dependence significantly smaller than those in 8-methoxypsoralen. This is probably due to the combination of greater radiative decay rate of the $S_1(\pi\pi^*)$ state and larger $S_2(n\pi^*)$-$S_1(\pi\pi^*)$ electronic gap of trioxsalen relative to those of 8-methoxypsoralen (the oscillator strength of the $S_0 \rightarrow S_1$ absorption is much greater for the former), as is the fact that fluorescence and triplet-triplet absorption of trioxsalen are observable even in hydrocarbon solvents at room temperature. Some of the pertinent emission data for trioxsalen are given in Tables III and IV and Figures 9-12. The temperature dependence of $\Phi_F$ and $\Phi_T$ in trioxsalen (Figures 13 and 14) again indicates that the $S_1 \rightarrow S_0$ internal conversion rate decreases with decreasing temperature.

The results presented above demonstrate that the photophysical properties of the psoralens are strongly influenced by $S_1 \rightarrow S_0$ internal conversion, the rate of which is sensitively dependent upon

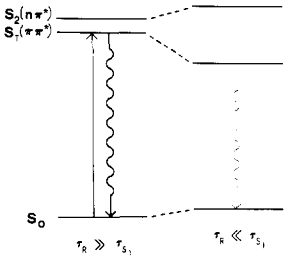

**Figure 15.** A schematic representation of the dependence of $S_1 \rightarrow S_0$ internal conversion rate on solvent relaxation. The left-hand side illustrates the case in which the relaxation time ($\tau_R$) is much longer than the lifetime ($\tau_{S_1}$) of the lowest excited singlet state, while the right-hand side illustrates the opposite situation. The thickness of the wavy vertical lines reflects the relative efficiency of the $S_1 \rightarrow S_0$ internal conversion (the thicker the line, the more efficient the internal conversion).

the solvent polarity, solvent viscosity, and temperature.

The dependence of the $S_1 \rightarrow S_0$ internal conversion rate upon the solvent polarity can be rationalized in terms of the orientation of the polar solvent molecules in the reaction field of the electronically excited psoralens, which stabilize $S_1(\pi\pi^*)$ relative to the higher lying $n\pi^*$ singlet state. The increased $^1\pi\pi^*$–$^1n\pi^*$ electronic energy gap resulting from this solvent reorientation (or relaxation) leads to a reduced proximity effect, and hence to a diminished $S_1 \rightarrow S_0$ internal conversion rate. This accounts for the inverse correlation of $\Phi_F$ and $\tau_F$ with $S_1$ energy ($\lambda_{max}$), which has been observed for the series of solvents with different polarity (Tables I and III). The extreme weakness of the fluorescence and triplet–triplet absorption in hydrocarbon solvents can be traced to the small $^1\pi\pi^*$–$^1n\pi^*$ gap, which renders the proximity effect (and hence $S_1 \rightarrow S_0$ internal conversion) very important. (Even in polar solvents, $S_1 \rightarrow S_0$ internal conversion in 8-methoxypsoralen is an important, if not dominant, decay process at elevated temperatures.[17])

At low temperatures, where the viscosity of the solvent is high, the reorientation of polar solvent molecules is slow enough for the decay processes to compete with the solvent relaxation. This leads to the nonexponential decay of fluorescence and the appearance of at least two spectrally distinct fluorescence spectra (Figures 7, 8, 11, and 12). The longer wavelength fluorescence with longer lifetime can be attributed to the relaxed species (i.e., the species for which the solvent reorientation has occurred), while the shorter wavelength fluorescence with shorter lifetime can be associated with the unrelaxed, or only partially relaxed, species. The shorter lifetime of the unrelaxed species can be rationalized in terms of a smaller $^1\pi\pi^*$–$^1n\pi^*$ electronic energy gap, which leads to a greater proximity effect. The rise time of the longer wavelength fluorescence (Figures 7 and 11) is consistent with the solvent reorientation, which competes with the decay processes of the $S_1(\pi\pi^*)$ state. At low temperatures, the fluorescence spectrum is dominated by the faster decaying unrelaxed species. Conversely, the fluorescence of the relaxed species dominates at elevated temperatures. A schematic representation of the dependence of the proximity effect on solvent relaxation is given in Figure 15.

The short fluorescence lifetime of the relaxed species at elevated temperatures can be accounted for in terms of thermal excitation of the vibronically active out-of-plane bending modes, which renders proximity effects even more important.[7] The thermal enhancement of the proximity effect can be considerable since the vibronically active modes are expected to be of low frequencies in $S_1$ (the low frequencies of these modes are direct consequences of vibronic interactions[6]). The rate of $S_1 \rightarrow S_0$ internal conversion is therefore expected to be the smallest when the temperature is low enough to render the thermal effect not very important, but high enough for the solvent relaxation to occur prior to electronic relaxation. This accounts for the observation that fluorescence lifetime of the dominant emitting species in ethanol is the longest at about −80 °C for the two psoralens (see Tables II and IV).

In nonpolar solvents, where the solvent reorientation is not important, the temperature dependence of $S_1 \rightarrow S_0$ internal conversion is predicted to be even larger (than in polar solvents) since the thermal enhancement of the proximity effect is not countered by the solvent relaxation that reduces the importance of the proximity effect. Indeed, in 3-methylpentane, the quantum yield of $S_1 \rightarrow S_0$ internal conversion (which is essentially unity for 8-methoxypsoralens at room temperature) decreases much more rapidly with decreasing temperature than in ethanol (Figures 3 and 4).

The decrease in $\Phi_F$ and $\Phi_T$ with increasing temperature and decreasing solvent polarity, as well as the viscosity effects on $\Phi_F$ and $\Phi_T$, have previously been observed in some N-heterocyclics and aromatic carbonyls with close-lying $n\pi^*$ and $\pi\pi^*$ singlet states.[8-10,15] The results of the present investigation are therefore consistent with the supposition that the photophysical behavior of the psoralens is controlled by the proximity effect. More specifically, the strong solvent (polarity and viscosity) effects on fluorescence and triplet formation can be accounted for in terms of the solvent-dependent $^1\pi\pi^*$–$^1n\pi^*$ electronic energy gap, which affects the $S_1 \rightarrow S_0$ internal conversion rate. Similarly, the strong temperature dependence of $\Phi_F$ and $\Phi_T$ can be rationalized in terms of the thermal excitation of the vibronically active out-of-plane bending modes, which leads to a large increase in the $S_1 \rightarrow S_0$ internal conversion rate. Although the location of the $^1n\pi^*$ state has not been experimentally established (a pitfall not unique to these psoralens), a CNDO calculation on related coumarin predicts[12] that there is an $n\pi^*$ singlet state lying only slightly above the lowest energy $\pi\pi^*$ singlet state. That there may be an $n\pi^*$ singlet state in close proximity to $S_1(\pi\pi^*)$ in the psoralens is suggested by the appearance of out-of-plane hydrogen bending modes in the $\pi\pi^*$ phosphorescence spectrum of 8-methoxypsoralen[12] and the appearance of the out-of-plane $CH_3$ bending modes in the $\pi\pi^*$ phosphorescence spectrum of trioxsalen.[12] An out-of-plane bending mode can couple the $^3\pi\pi^*$ state with a higher lying $^3n\pi^*$ state, whereby $^3\pi\pi^* \rightarrow S_0$ radiative transition borrows intensity from the more allowed $^3n\pi^* \rightarrow S_0$ radiative transition.[18] In coumarins and furocoumarins, the out-of-plane bending mode, which is especially effective in the $^3\pi\pi^*$–$^3n\pi^*$ vibronic coupling, is expected to be the one that involves displacements of hydrogens (or $CH_3$ groups) attached to the ethylenic carbons ($C_3$ and $C_4$) of the pyrone group. This follows from the expectation[19] that the transition density $\langle n|\pi\rangle$, which is proportional to the matrix elements of the $^3\pi\pi^*$–$^3n\pi^*$ vibronic coupling, is large in the vicinity of these C–H or C–$CH_3$ groups. Since $^1n\pi^*$–$^3n\pi^*$ splitting is generally smaller than $^1\pi\pi^*$–$^3\pi\pi^*$ splitting, the presence of an $^3n\pi^*$ state above $T_1(\pi\pi^*)$ requires that there ought to be an $n\pi^*$ singlet state in the vicinity of $S_1(\pi\pi^*)$. Independent of these arguments, the photophysical similarities of the psoralens to simpler aromatic carbonyls with nearby $^1n\pi^*$ and $^1\pi\pi^*$ states are compelling evidence that the lowest energy $n\pi^*$ and $\pi\pi^*$ singlet states are in close proximity in the singlet manifold of the psoralens.

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**Registry No.** 8-Methoxypsoralen, 298-81-7; trioxsalen, 3902-71-4.

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[17] The lower limit of $\Phi_{IC}$, $\Phi_{IC}^{min}$, at room temperature (RT) can be deduced from the temperature dependence of the relative triplet yield ($\Phi_T$) by using $\Phi_{IC}^{min}(RT) = 1 - \Phi_F(RT) - \Phi_T^{max}(RT)$, where $\Phi_T^{max}$ represents the maximum possible value of $\Phi_T$. $\Phi_T^{max}(RT)$ can be deduced from the measured temperature dependence of $\Phi_T$ (e.g., Figure 3) on the assumption that the largest observed $\Phi_T$ is unity. The value of $\Phi_{IC}^{min}(RT)$ so obtained is ~0.94 for 8-methoxypsoralen in ethanol.

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