STUDIES ON THE TEMPERATURE DEPENDENCE OF METHYL ANTHROATE FLUORESCENCE

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Summary

The temperature dependence of the fluorescence quantum yield ϕ_f of methyl-1-, methyl-2- and methyl-9-anthroate was investigated. For the former two esters, the trend of ϕ_f *versus* temperature is consistent with the mechanism proposed earlier to account for the temperature dependence of ϕ_f for *meso*-substituted anthracene. In this mechanism, an activated intersystem crossing to a nearby upper triplet is the only significant non-radiative decay mode. The activation energy E_A for fluorescence is a measure of the gap between the emitting singlet S_1 and the accepting triplet. Since the former state is more solvent dependent, solvents which lower the S_1 energy increase E_A and thereby increase ϕ_f. Thus E_A and ϕ_f are inversely related to the S_1 energy and directly related to each other. The situation for methyl-9-anthroate is quite different from that of the other esters. While E_A is inversely related to the S_1 energy, ϕ_f is not, and hence there is no correlation between E_A and ϕ_f. It appears that the ϕ_f of methyl-9-anthroate is more dependent on the nature of the solvent than on the measured E_A in that solvent. The inclusion of a temperature-independent non-radiative decay mode in the analysis does not produce results consistent with the above mechanism. It is suggested that the difference in behavior for these esters may in some way be related to an excited state geometry change which occurs for methyl-9-anthroate but not for the other two compounds.

1. Introduction

The temperature dependence of the fluorescence quantum yield ϕ_f of substituted anthracenes has been studied extensively [1 - 8]. In general, ϕ_f for *meso*-substituted anthracenes shows significant temperature dependence, while that for side-substituted anthracenes such as 2-methylanthracene and 1,5-dichloroanthracene exhibits little, if any, temperature dependence.

The ϕ_f temperature dependence for *meso*-substituted anthracenes is thought to arise because intersystem crossing (ISC) is thermally activated. In support of this, Bennett and McCartin [2] and Lim *et al.* [3] have reported similar thermal dependences for the fluorescence and triplet–triplet absorption of 9-methylanthracene. Since the lowest triplet state T_1 of 9-methyl-anthracene is about $11\,000\ cm^{-1}$ below the lowest singlet S_1, these workers suggested that crossing to the second triplet T_2 was responsible for the activated process [2, 3]. Results from a combination of phosphorescence and triplet–triplet absorption experiments are indeed consistent with the placement of a triplet level slightly above S_1 for 9-methylanthracene and 9,10-dichloroanthracene [9]. More recently, Gillispie and Lim [10] have reported evidence for the existence of two triplet levels T_2 and T_3 in the vicinity of S_1, an assignment consistent with theoretical calculations by Pariser [11]. Whether both of these triplets are involved in ISC is not known.

In *meso*-substituted anthracenes containing a carbonyl or nitro group, the $T_{n,\pi*}$ level of the carbonyl or nitro group is assigned the accepting triplet role in thermally activated ISC [4, 12]. For anthracene itself and the side-substituted anthracenes 2-methylanthracene and 1,5-dichloroanthracene, the accepting triplet level, located by triplet–triplet absorption, is at least $600\ cm^{-1}$ below S_1 [9]. This accounts for the lack of significant temperature dependence for the ϕ_f values of these compounds. It has been assumed that only for *meso*-substituted anthracenes, where substitution is along the transverse axis of the $S_1 (^1L_A)$ state, does S_1 lie below an accepting triplet thereby leading to activated ISC [10].

The solvent dependence of ϕ_f for several *meso*-substituted anthracenes has also been explained by assuming the existence of a temperature-dependent ISC. The Arrhenius activation energy E_A for the $S_1 \rightarrow T_x$ crossing is assumed to be a measure of the S_1–T_x gap [2]. Since solvents generally affect the S_1 energy more than triplet energies, E_A should increase as S_1 is red shifted by the solvent. As a result, ϕ_f and τ_f at a given temperature should increase with the S_1 red shift. This has indeed been observed for several *meso*-substituted anthracenes [5, 8, 13].

We have been studying the fluorescence properties of carboxyl-substituted anthracenes for the past several years. Unlike other similar electronic withdrawing groups, the carboxyl group can cause the ϕ_f of anthracene to increase substantially. In the course of our work, we have measured the temperature dependence of the ϕ_f of methyl-1-anthroate (1-COOMe), methyl-2-anthroate (2-COOMe) and methyl-9-anthroate (9-COOMe). We have found a substantial contrast between our data and those reported by other workers for anthracene derivatives. For example, the ϕ_f values of the side-substituted anthroates 1- and 2-COOMe exhibit a temperature dependence analogous to that observed previously for *meso*-substituted anthracenes. However, the E_A and ϕ_f for the *meso* derivative (9-COOMe) are not well correlated with S_1 energy. We report here the results of this work.

2. Experimental details

2.1. Chemicals and solvents

9-COOMe, 1-COOMe and 2-COOMe were prepared as described previously [13].

Acetonitrile, dimethyl formamide, dimethyl sulfoxide, ethyl acetate, isopropanol, butyl acetate, hexane and cyclohexane were Matheson, Coleman and Bell Spectroquality or Omnisolv solvents. Ethanol from U.S. Industrial Chemicals was distilled from CaH_2 before use. Tetrahydrofuran from Mallinckrodt was refluxed over CuCl and then distilled from CaH_2.

2.2. Instrumentation

The UV–visible absorption measurements were made on a Cary model 118 spectrophotometer. The fluorescence emission measurements were recorded on a Perkin–Elmer MPF-2A spectrofluorometer using excitation and emission bandpasses of 7 nm and 3 nm respectively. The emission spectra were corrected for the response function of the instrument as described earlier [13].

An FTS Systems Inc. Flexi Cool unit was used to circulate 95% ethanol through thermostatted cell blocks to obtain emission spectra as a function of temperature. The temperature was monitored by a copper–constantan thermocouple and read out on an Omega model 2160A digital thermometer. Since sealed and degassed sample cells were used, the thermocouple was placed in an unsealed cell containing an identical solvent and located in the thermostatted block.

2.3. Procedures

The procedures used to determine the room temperature ϕ_f values and the temperature dependence of ϕ_f have been described elsewhere [4, 13]. For both measurements, samples were degassed by the freeze–thaw–degas method and sealed off at a pressure below 5×10^{-4} Torr after 3 - 4 cycles. The room temperature quantum yield reference was 9-COOMe in ethanol ($\phi_f = 0.173$) [4]. The temperature range for the ϕ_f measurements extended from 15 - 17 °C to 8 - 10 °C below the boiling point of a given solvent.

3. Results

ϕ_f is given by

$$\phi_f = \frac{k_f}{k_f + k_{ic} + k_{isc}} \tag{1}$$

where k_f, k_{isc} and k_{ic} are the rate constants for fluorescence, ISC and internal conversion respectively. For anthracene and several anthracene derivatives, the results of quenching experiments [14], deuteration experiments [15], Arrhenius plots [3] and triplet formation quantum yield

measurements [2] indicate that k_f and k_{isc} are much greater than k_{ic}. Thus, eqn. (1) reduces to

$$\phi_f = \frac{k_f}{k_f + k_{isc}} \tag{2}$$

Since k_f is relatively temperature independent, the temperature dependence of k_{isc} is responsible for the observed variation in ϕ_f with temperature. It is assumed that k_{isc} can be fitted by the usual Arrhenius relation

$$k_{isc} = k_{isc}{}^0 + A \exp\left(-\frac{E_A}{RT}\right) \tag{3}$$

where $k_{isc}{}^0$ is the temperature-independent ISC rate constant. Insertion of eqn. (3) into eqn. (2) with subsequent rearrangement yields

$$\log\left(\frac{1}{\phi_f} - \frac{1}{\phi_f{}^0}\right) = \log\left(\frac{A}{k_f}\right) - \frac{E_A}{2.3RT} \tag{4}$$

where $\phi_f{}^0$ is the low temperature limit of the quantum yield:

$$\phi_f{}^0 = \frac{k_f}{k_f + k_{isc}{}^0} \tag{5}$$

Since the value of $\phi_f{}^0$ for several *meso*-substituted anthracenes is unity [9], eqn. (4) is usually simplified to

$$\log\left(\frac{1}{\phi_f} - 1\right) = \log\left(\frac{A}{k_f}\right) - \frac{E_A}{2.3RT} \tag{6}$$

If the above assumptions are valid, a plot of $\log(1/\phi_f - 1)$ *versus* $1/T$ will be linear, yielding E_A from the slope and A from the intercept. This analysis is virtually identical with that used by most workers who have studied the temperature dependence of substituted anthracene fluorescence.

Table 1 contains the E_A and A values obtained when ϕ_f *versus* temperature data for the three esters in various solvents are plotted according to eqn. (6). In all cases, the correlation coefficients for the Arrhenius plots exceeded -0.99. Solvents were chosen to include a large range of room temperature (23 °C) ϕ_f values for the esters. However, solvents where ϕ_f was 0.85 or more at room temperature were not included, since a small absolute error in the value for these high room temperature ϕ_fs leads to a very large error in E_A. For this reason, Arrhenius data for 2-COOMe are reported for only two quite non-polar solvents. Increasing solvent polarity caused the ϕ_f of 2-COOMe to exceed 0.85 at room temperature.

Also included in Table 1 are the room temperature ϕ_f values and the mean frequency of fluorescence $\bar{\nu}_m$ as defined by [16]

$$\int_{\bar{\nu}_i}^{\bar{\nu}_f} F(\bar{\nu})\, d\bar{\nu} = 2 \int_{\bar{\nu}_i}^{\bar{\nu}_m} F(\bar{\nu})\, d\bar{\nu} \tag{7}$$

TABLE 1

Values of the Arrhenius activation energy E_A, the pre-exponential factor A, the room temperature fluorescence quantum yield ϕ_f and the mean frequency of fluorescence $\bar{\nu}_m$ for 1-, 2- and 9-COOMe in various solvents

Ester	Solvent	ϕ_f (23 °C)	E_A (cm^{-1} (kcal mol^{-1}))	A ($\times 10^{10}$ s^{-1})	$\bar{\nu}_m$ ($\times 10^4$ cm^{-1})
1-COOMe	Cyclohexane	0.12	769 (2.20)	1.6	2.31
	Butyl acetate	0.41	1210 (3.47)	2.5	2.24
	Tetrahydrofuran	0.46	1320 (3.77)	3.2	2.22
	Acetonitrile	0.81	1810 (5.17)	7.9	2.17
2-COOMe	Hexane	0.33	958 (2.74)	1.0	2.39
	Cyclohexane	0.49	1230 (3.53)	2.0	2.38
9-COOMe	Cyclohexane	0.76	934 (2.67)	0.16	2.23
	Butyl acetate	0.72	1060 (3.03)	0.32	2.19
	Ethyl acetate	0.66	1350 (3.85)	1.6	2.18
	Acetonitrile	0.39	1440 (4.11)	7.9	2.15
	Dimethyl formamide	0.70	1580 (4.53)	5.0	2.14
	Dimethyl sulfoxide	0.56	1390 (3.98)	4.0	2.12
	Isopropanol	0.24	1320 (3.78)	10	2.11
	Ethanol	0.17$_3$	1490 (4.27)	32	2.10

In this equation, $\bar{\nu}_i$ is the initial frequency, $\bar{\nu}_f$ is the final frequency, $\bar{\nu}_m$ is the mean frequency and $F(\bar{\nu})$ is the fluorescence intensity at a given frequency. A computer program was used to convert the corrected fluorescence spectra from quanta per unit bandpass in wavelength to quanta per unit bandpass in frequency and thus to perform the calculation of $\bar{\nu}_m$ according to eqn. (7). The $\bar{\nu}_m$ value is taken to be a measure of the S_1 energy.

Plots of ϕ_f and E_A *versus* $\bar{\nu}_m$ are shown in Fig. 1 for 1-COOMe. There is a clear inverse relation between $\bar{\nu}_m$ and both E_A and ϕ_f for this ester. The dependence of ϕ_f on $\bar{\nu}_m$ for 9-COOMe, which is also plotted in Fig. 1, is actually directly opposite to that observed for 1-COOMe, showing a direct rather than an inverse dependence on $\bar{\nu}_m$. In addition, the E_A values for 9-COOMe do not show a monotonic decrease with increasing $\bar{\nu}_m$ as observed for 1-COOMe. While a general decrease in E_A is observed with increasing $\bar{\nu}_m$ value for 9-COOMe, there is considerable scatter (Table 1).

From the plot of ϕ_f *versus* E_A for 1-COOMe in Fig. 2 it is clear that these two parameters are highly correlated for this ester (correlation coefficient, 0.999). If the data points for 2-COOMe are included in the plot, good correlation (correlation coefficient, 0.986) between ϕ_f and E_A is still observed. In contrast, there is quite poor correlation between ϕ_f and E_A for 9-COOMe as shown by the plot in Fig. 2.

As mentioned earlier, E_A is thought to be a measure of the gap between S_1 and the accepting triplet which we arbitrarily assign here as T_2. Thus the sum $E_A + \bar{\nu}_m$ should be an estimate of the T_2 energy in a given
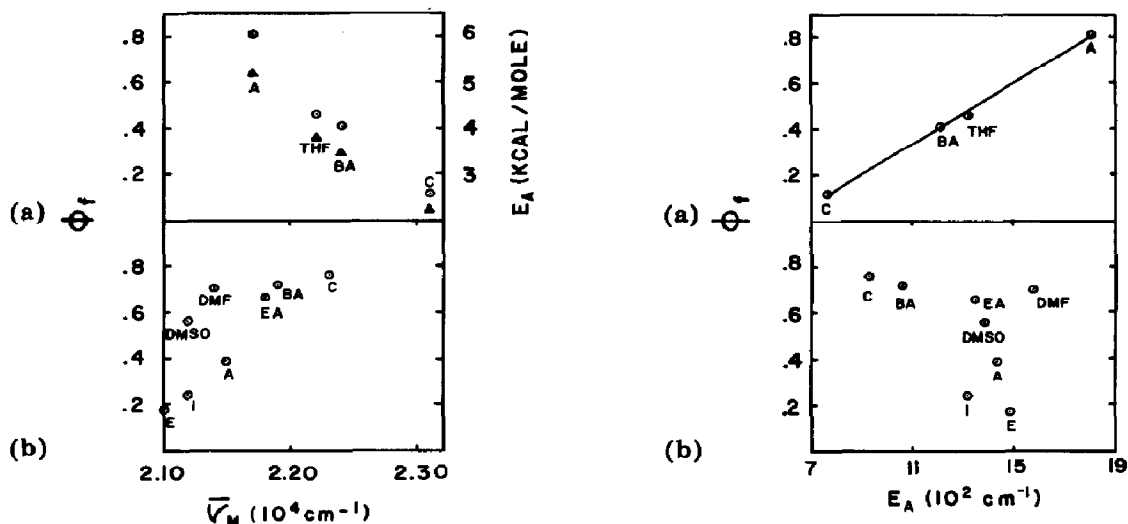
Fig. 1. (a) The fluorescence quantum yield ϕ_f (⊙) and the activation energy E_A (△) for thermal quenching as a function of the S_1 energy $\bar{\nu}_m$ for 1-COOMe; (b) ϕ_f vs. $\bar{\nu}_m$ for 9-COOMe: C, cyclohexane; THF, tetrahydrofuran; BA, butyl acetate; A, acetonitrile; EA, ethyl acetate; E, ethanol; DMF, dimethyl formamide; DMSO, dimethyl sulfoxide; I, isopropanol.

Fig. 2. The fluorescence quantum yield ϕ_f vs. the activation energy E_A for thermal quenching for (a) 1-COOMe and (b) 9-COOMe. The solvent abbreviations are defined in the caption to Fig. 1.

solvent. Plots of $\bar{\nu}_m$ and $E_A + \bar{\nu}_m$ *versus* E_A are given in Fig. 3 for 1-COOMe. The greater slope of the $\bar{\nu}_m$ line is consistent with the expected greater solvation effect on the S_1 ($\bar{\nu}_m$) state than on the T_2 ($E_A + \bar{\nu}_m$) state. The ratio $\Delta(E_A + \bar{\nu}_m)/\Delta\bar{\nu}_m$ of the slopes is 0.29, indicating that the T_2 level is only 29% as solvent sensitive as the S_1 level. Interestingly, Wu and Ware [8] found that the T_2 level for 9,10-dibromoanthracene is only 30% as solvent sensitive as its S_1 level.

Figure 3 also contains plots of S_1 and the estimated T_2 energies $E_A + \bar{\nu}_m$ *versus* the experimental E_A values for 9-COOMe. The data points are too scattered to yield a quantitative estimate of the relative solvent sensitivity of these two states although the S_1 level is more solvent sensitive.

Attempts were made to determine the triplet state energies for the esters in several solvents by a combination of phosphorescence and triplet–triplet fluorescence measurements. These measurements were made on a photon-counting spectrofluorometer in the laboratory of Dr. Gregory Gillispie at the State University of New York at Albany. Unfortunately neither emission could be detected for any of the esters. This was not un-expected. At the low temperatures used for phosphorescence the quantum yield of triplet state formation should be low. In addition, the fraction of triplets which decay by phosphorescence should be quite low, since the $T_1 \rightarrow S_0$ energy gap is small. Triplet–triplet fluorescence has been observed on the long wavelength tail of the $S_1 \rightarrow S_0$ emission for anthracene and
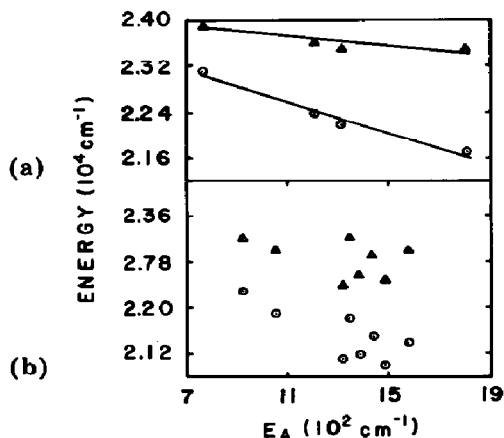
Fig. 3. The S_1 energy $\bar{\nu}$ (⊙) and the sum $E_A + \bar{\nu}_m$ (⊿) as functions of the activation energy E_A for thermal quenching for (a) 1-COOMe and (b) 9-COOMe.

several haloanthracene $S_1 \rightarrow S_0$ emissions [10]. The carboxyl group causes a larger red shift of the fluorescence than halosubstitution does. Since substituents generally affect excited singlet levels more than triplet levels, it is likely that the red-shifted tail of the $S_1 \rightarrow S_0$ fluorescence completely swamps the triplet–triplet fluorescence in the case of the anthroates studied here.

4. Discussion

The ϕ_f versus temperature data for 1-COOMe are clearly in agreement with the mechanism proposed to account for the temperature dependence of meso-anthracene ϕ_f values [2, 3]. In this mechanism, activated ISC from S_1 to a nearby upper triplet (T_2) level is the only process which competes with fluorescence. Since S_1 should be more solvent sensitive than T_2, increasing solvent polarity should increase E_A (a measure of the S_1-T_2 gap) and thus, ϕ_f at a given temperature. The plots in Figs. 1 - 3 are all consistent with this mechanism. Despite the fact that only two data points are available for 2-COOMe, it also appears that this mechanism can account for the temperature-dependent ϕ_f of 2-COOMe.

Although the carboxyl group in 1- and 2-COOMe does not lie along the ^1L_A transition axis, there is sufficient electronic interaction between the ring and the carboxyl group to lower the $S_1(^1L_A)$ state below the accepting triplet level. For carbonyl-substituted anthracenes, a new accepting triplet, the $T_{n, \pi*}$ of the carbonyl group, becomes the accepting triplet in ISC [12]. However, since the n,π^* transition of an aldehyde or a ketone is substantially lower in energy than that of an ester [17], the $T_{n, \pi*}$ level of the carboxyl group should be too high in energy to participate in significant ISC for 1- and 2-COOMe. Therefore activated ISC for these esters must occur to the same triplet level involved in meso-substituted anthracene ISC. In support of

this, the A values for 1- and 2-COOMe in Table 1 are similar to those reported for several *meso*-substituted anthracenes which do not contain a $T_{n, \pi*}$ level [5]. Activated ISC from S_1 to T_2 has previously been proposed to account for the solvent dependence of ϕ_f for 2-COOMe and to account for the efficiency with which external heavy atoms quench 2-COOMe fluorescence [13].

It is readily apparent from the plots in Figs. 1 - 3 that the assumptions used to rationalize the ϕ_f *versus* temperature data for 1- and 2-COOMe are not valid for 9-COOMe. While E_A does generally decrease with decreasing $\bar{\nu}_m$ (Table 1), a similar trend is not observed for ϕ_f (Fig. 1). The lack of any correlation between ϕ_f and E_A in Fig. 2 suggests that non-radiative decay in 9-COOMe is more dependent on the nature of the solvent than on the magnitude of E_A in that solvent. Excluding the cyclohexane and butyl acetate data, we find that ϕ_f varies over a fourfold range while E_A changes by only 20% for the remaining eight solvents in Table 1.

If a small but significant number of excited states continue to decay by a non-radiative mode even at low temperatures then the data should be analyzed according to eqn. (4) rather than eqn. (6). Measurement of the low temperature quantum yield limit ϕ_f^0, however, is subject to serious uncertainties for 9-COOMe. The change to a more coplanar conformation which occurs for 9-COOMe in S_1 is known to be inhibited at low temperatures [18]. If this geometry change has any effect on the rate of non-radiative decay then the ϕ_f^0 value is not relevant for the more coplanar 9-COOMe S_1 level which exists at room temperature and above.

To see how a ϕ_f^0 value below unity would affect the trend of E_A values, we re-evaluated our ϕ_f *versus* temperature data according to eqn. (4) assuming $\phi_f^0 = 0.9$. Plots of eqn. (4) showed good linearity with correlation coefficients comparable with the plots of eqn. (6). For all solvents the E_A values were observed to increase, but the range of E_A values decreased from that shown in Table 1. The resulting new E_A values showed no relation with $\bar{\nu}_m$ or ϕ_f in a given solvent. It is possible that ϕ_f^0 may be substantially less than 0.9 in solvents such as isopropanol and ethanol; however, this would produce even larger E_A values which would still be inconsistent with the low ϕ_f values in these solvents. Thus we think it unlikely that a temperature-independent non-radiative decay mode could account for the difference between the 9-COOMe data and those for the other *meso*-substituted anthracenes.

We do not wish to indulge in undue speculation about the origin of the exceptional behavior for 9-COOMe. However, since the 1- and 2-COOMe derivatives appear to behave as predicted, it is useful to point out a significant difference between these esters and 9-COOMe. The S_0, S_1 and T_2 states will undoubtedly be nearly coplanar for 1- and 2-COOMe. By contrast, the S_0 state of 9-COOMe has the carboxyl group nearly perpendicular to the ring while in S_1 the ring and the carboxyl group approach coplanarity to accommodate the increased charge transfer character of the S_1 state [13]. If, as expected, charge transfer effects are smaller in T_2 than in S_1, it is pos-

sible that the T_2 state maintains the same conformation as S_0. In sum, then, the S_1 and T_2 states of 1- and 2-COOMe will have similar geometries while the geometries of the S_1 and T_2 states for 9-COOMe can differ significantly. In view of this difference in the shapes of the excited state surfaces, it is probable that the factors which control ISC will be different for 9-COOMe compared with 1- and 2-COOMe. For example, for a given E_A, the Franck–Condon overlap integrals which govern the rate of ISC may differ substantially for 9- and 1-COOMe. Moreover, if the shape of the S_1 surface for 9-COOMe is somewhat solvent dependent, a greater dependence on the nature of the solvent than on the E_A value is not unexpected. The unusually large A value for 9-COOMe in ethanol (Table 1) may reflect this situation.

Finally, it should be noted that recent work on benzyl-9-anthroate and 9-methoxyanthracene challenges the assumption of negligible internal conversion in *meso*-substituted anthracenes [19, 20]. In addition, the latter molecule appears to have both ISC and internal conversion modes which are temperature dependent [20]. Unfortunately, information about the triplet manifold energies and population efficiencies for 9-COOMe is still unknown. In the future, we hope to be able to measure triplet formation efficiencies for 9-COOMe by triplet–triplet absorption to gain more insight into this problem.

Acknowledgments

References

1 E. Bowen and J. Sahu, *J. Phys. Chem.*, *63* (1959) 4.
2 R. Bennett and P. McCartin, *J. Chem. Phys.*, *44* (1966) 1969.
3 E. C. Lim, J. D. Laposa and J. M. Yu, *J. Mol. Spectrosc.*, *19* (1966) 412.
4 T. C. Werner, W. Hawkins, J. Facci, R. Torrisi and T. Trembath, *J. Phys. Chem.*, *82* (1978) 298.
5 H. Dreeskamp and J. Pabst, *Chem. Phys. Lett.*, *61* (1979) 262.
6 B. Hammerich, R. Schmidt and H. Brauer, *Ber. Bunsenges. Phys. Chem.*, *83* (1979) 198.
7 S. Schoof, H. Güsten and C. von Sonntag, *Ber. Bunsenges. Phys. Chem.*, *81* (1977) 305.
8 K. Wu and W. Ware, *J. Am. Chem. Soc.*, *101* (1979) 5906.
9 R. S. Becker, *Theory and Interpretation of Fluorescence and Phosphorescence*, Wiley-Interscience, New York, 1969, Chap. 11.
10 G. Gillispie and E. C. Lim, *Chem. Phys. Lett.*, *63* (1979) 355.

11 R. Pariser, *J. Chem. Phys.*, *24* (1956) 250.
12 K. Hamanoue, S. Hirayama, T. Nakayama and H. Teraniski, *J. Phys. Chem.*, *84* (1980) 2074.
13 T. C. Werner, T. Matthew and B. Soller, *J. Phys. Chem.*, *80* (1976) 533.
14 T. Medinger and F. Wilkinson, *Trans. Faraday Soc.*, *61* (1965) 620.
15 J. Laposa, E. Lim and P. Kellogg, *J. Chem. Phys.*, *42* (1965) 3025.
16 I. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, New York, 2nd edn., 1971, Chap. 1.
17 S. Suzuki, *Electronic Absorption Spectra and the Geometry of Organic Molecules*, Academic Press, New York, 1967, Chap. 21.
18 T. C. Werner, in E. L. Wehry (ed.), *Modern Fluorescence Spectroscopy*, Vol. 2, Plenum, New York, 1976, Chap. 7.
19 S. M. de B. Costa, A. L. Maçanita and M. J. Prieto, *J. Photochem.*, *11* (1979) 109.
20 S. Schoof and H. Güsten, *J. Photochem.*, *9* (1978) 246.