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SOLVATOCHROMIC EFFECTS IN THE FLUORESCENCE AND TRIPLET–TRIPLET ABSORPTION SPECTRA OF XANTHONE, THIOXANTHONE AND *N*-METHYLACRIDONE

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Summary

While the fluorescence of xanthone, thioxanthone and *N*-methylacridone shows the customary red shift with increasing solvent polarity, as measured by a polarization function, indicating an increase in dipole moment on excitation, the triplet–triplet (T_1–T_n) absorption spectra are strongly blue shifted, indicating a decrease in dipole moment on excitation.

1. Introduction

The very substantial redistribution of electronic charge consequent on excitation from the S_0 to the S_1 state of many organic molecules is manifest in the solvatochromic effect on the reverse transition $S_0 \leftarrow S_1$, *i.e.* fluorescence. According to various treatments (Von Lippert [1], Bilot and Kawski [2], Bakhshiev [3], Block and Walker [4], all reviewed by Koutek [5, 6] and Lakowicz [7]), the Stokes shift depends linearly on a polarization function incorporating the dielectric constant ϵ and the refractive index n of the solvent medium, although hydroxylic solvents usually show considerable deviance from the regression line linking the other solvents, an effect normally attributed to specific donor and acceptor hydrogen bonding [7]. The solvatochromic effect on fluorescence normally takes the form of a red shift with increase in solvent polarity, signifying an increase in dipole moment on excitation to the S_1 state. The $S_0 \rightarrow S_1$ absorption spectrum of certain molecules is blue shifted by an increase in solvent polarity, indicating a reduction in the dipole moment on excitation. This is found with molecules with a sizable ground state dipole moment, while the most familiar case is the n–π^* transition of carbonyl compounds, where the shift is up to about 10 nm [8]; for highly polar molecules the shift becomes hundreds of nanometres, *e.g.* for the solvent "probe" molecules such as pyridinium *N*-phenol betaine [9] and 1-ethyl-4-carbomethoxypyridinium iodide [10].

Rather few systematic studies of solvatochromic effects on triplet–triplet (T–T) spectra have been carried out. Thus for 1-nitronaphthalene this

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absorption features a red shift of 90 nm in going from *n*-hexane to *N*-methylformamide, indicating an increase in dipole moment of 5.6 debyes [11]. Garner and Wilkinson [12] report a small blue shift in the T_1–T_n absorption of xanthone in going from hydrocarbon solvents (λ_{max} = 610 nm) to ethanol and water–ethanol (10 wt.% H_2O) (λ_{max} = 605 nm and λ_{max} = 590 nm respectively).

We report that, while the fluorescence maxima of xanthone, thioxanthone and *N*-methylacridone are red shifted by an increase in solvent polarity, the T_1–T_n absorption spectra exhibit strong blue shifts.

2. Experimental details

All organic solvents used were either of spectroscopic or AnalaR grade and were used without further purification. Xanthone (Hopkin and Williams Ltd.) was recrystallized twice from ethanol (melting point, 173 - 175 °C (174 °C reported in ref. 13)). Thioxanthone (Aldrich) was recrystallized twice from petroleum ether (60 - 80 °C) (melting point, 212 - 215 °C (212 °C reported in ref. 13)). *N*-Methylacridone (Aldrich) was recrystallized twice from ethanol (melting point, 205 - 207 °C (203 °C reported in ref. 14)). Fluorometry and laser flash photolysis experiments were carried out on deoxygenated solutions using the procedures described in our previous papers [15, 16]. Triplet–triplet absorption spectra were taken point-by-point by varying the monochromator setting; most of the spectra were compiled using an Oxford Lasers model KX2 excimer laser (249 nm, 250 mJ per pulse, 15 ns duration), while a ruby laser (347 nm, 75 mJ per pulse, 50 ns duration) was used in the construction of the triplet–triplet absorption spectra of those ketones where the absorbance of the solvents was relatively high at 249 nm.

3. Results and discussion

The absorption and fluorescence data for xanthone and thioxanthone in various solvents are given in Tables 1 and 2 respectively. In order to estimate the values of the excited singlet state dipole moment μ_{S_1} of xanthone and thioxanthone, analyses of these data were performed according to the treatment of Bilot and Kawski [2]:

$$\Delta\bar{\nu}_{SS} = \frac{(\vec{\mu}_{S_1} - \vec{\mu}_{S_0})^2}{hca^3}\,\mathrm{BK} + \text{constant} \qquad (1)$$

where

$$\mathrm{BK} = \left[\frac{(\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1)}{\{(n^2 - 1)/(2n^2 + 1)\}\{(\epsilon - 1)/(2\epsilon + 1)\}}\right]$$

TABLE 1

Solvent effect on the Stokes shift in the fluorescence of xanthone

Solvent	BK[a]	λ_A (nm)	λ_F (nm)	$\Delta\bar{\nu}_{SS}$ (cm^{-1})
(1) *n*-Hexane	0.002	337	375	3007
(2) Benzene	0.008	339	380	3183
(3) Carbon tetrachloride	0.023	337	389	3967
(4) Dioxan	0.043	333	367	2782
(5) Bromobenzene	0.365	336	366	2439
(6) Diethyl ether	0.365	336	375	3095
(7) Chlorobenzene	0.399	334	366	2618
(8) Tetrahydrofuran	0.55	333	371	3076
(9) Dichloromethane	0.586	340	380	3096
(10) 2-Methyl-2-propanol	0.673	335	376	2063
(11) 2-Propanol	0.766	335	373	3041
(12) Acetone	0.793	337	391	4098
(13) Ethanol	0.812	336	373	2952
(14) Dimethylformamide	0.836	334	369	2840
(15) Methanol	0.858	335	382	3673
(16) Acetonitrile	0.864	337	390	4033

[a] Calculated from data in ref. 13 according to the Bilot–Kawski equation (eqn. (1)); values of ϵ and n refer to 293 K.

TABLE 2

Solvent effects on the Stokes shift in the fluorescence of thioxanthone

Solvent	BK[a]	λ_A[b] (nm)	λ_F[b] (nm)	$\Delta\bar{\nu}_{SS}$[c] (cm^{-1})
(1) *n*-Hexane	0.002	378	395	1139
(2) Benzene	0.008	380	405	1624
(3) Carbon tetrachloride	0.023		400	1316
(4) Diethyl ether	0.365		398	1190
(5) Dichloromethane	0.586		409	1866
(6) Acetone	0.793		405	1624
(7) Acetonitrile	0.864	380[d]	409	1866
(8) 2-Methyl-2-propanol	0.673		418	2392
(9) 2-Propanol	0.766		423	2675
(10) Ethanol	0.812	380[d]	428	2951
(11) Methanol	0.858		431	3114

[a] Calculated from data in ref. 13 according to the Bilot–Kawski equation (eqn. (1)); values of ϵ and n refer to 293 K.
[b] Values for λ_A and λ_F are from ref. 17.
[c] λ_A is taken to equal 380 nm.
[d] From ref. 18.

The value of μ_{S_1} for *N*-methylacridone has been reported recently by Koutek [6] (see Table 3). The Stokes shifts $\Delta\bar{\nu}_{SS}$ are positively correlated with the polarizability function designated BK in eqn. (1), although the data for xanthone are subject to considerable scatter and the value for μ_{S_1} is

TABLE 3

Dipole moments of heterocyclic ketones in different electronic states

Molecule	μ_{S_0} (debyes)	μ_{S_1} (debyes)	μ_{T_n} (debyes)
Xanthone	3.1[a]	5.10	3.51
Thioxanthone	5.4[a]	7.64	6.64
N-Methylacridone	5.39[b,c]	7.287[b]	5.85

[a] From ref. 19.

[b] From ref. 6; 1 debye ≡ 3.336 × 10^{-30} C m.

[c] Ref. 19 gives μ_{S_0} = 3.5 debyes.

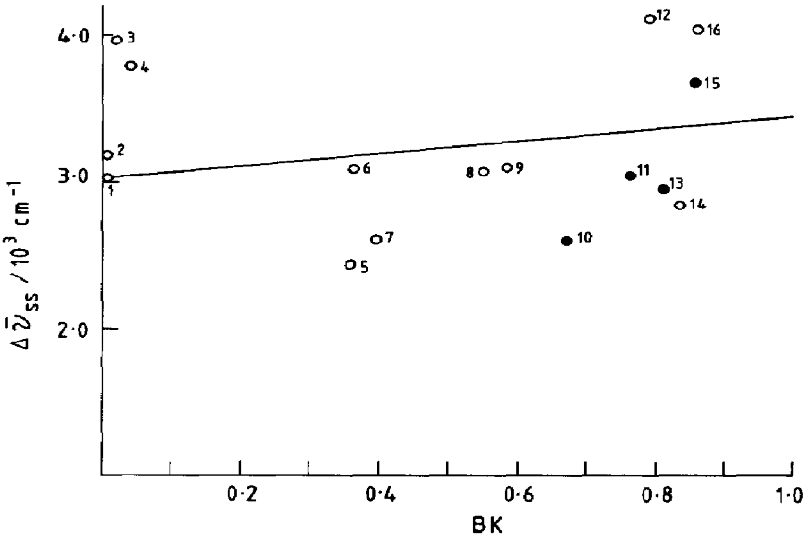

Fig. 1. Correlation of the Stokes shift $\Delta\tilde{\nu}_{SS}$ for xanthone with the value of the function BK (see eqn. (2)): ●, alcoholic solvents (excluded from the regression analysis). The numbering of the solvents is as in Table 1.

correspondingly less certain. The regression lines for xanthone (Fig. 1) and thioxanthone (Fig. 2) are given respectively by

$$\Delta\tilde{\nu}_{SS}\ (\text{cm}^{-1}) = (3011 \pm 262) + (435 \pm 512)\text{BK} \tag{2}$$

$$\Delta\tilde{\nu}_{SS}\ (\text{cm}^{-1}) = (1313 \pm 137) + (543 \pm 267)\text{BK} \tag{3}$$

From the coefficients of eqns. (2) and (3) and the values reported in the literature for the dipole moments μ_{S_0} of the ground states (see Table 3), μ_{S_1} can be estimated as 5.1 debyes for xanthone and 7.6 debyes for thioxanthone. (The solute cavity radius *a* was taken as 3.6 Å for both xanthone and thioxanthone, a value originally utilized [6] for the *N*-methylacridone molecule.)

The marked solvatochromic effects on the T_1–T_n absorption spectra of the various heterocyclic ketones are collated in Table 4, from which is

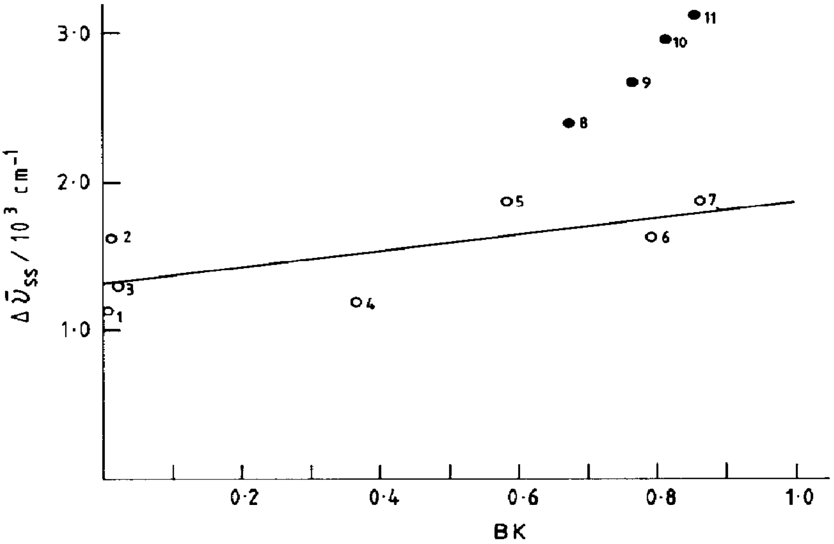

Fig. 2. Correlation of the Stokes shift $\Delta\bar{\nu}_{SS}$ for thioxanthone with the value of the function BK (see eqn. (3)): ●, alcoholic solvents (excluded from the regression analysis). The data source of λ_F is taken from ref. 17. The numbering of the solvents is as in Table 2.

TABLE 4

Solvent dependence of the triplet–triplet absorption spectral maxima of xanthone and related molecules at room temperature

Solvent	$\Delta f(\epsilon)$	*Thioxanthone*		*Xanthone*		*N-Methylacridone*	
		λ (nm)	ν_S (cm^{-1})	λ (nm)	ν_S (cm^{-1})	λ (nm)	ν_S (cm^{-1})
(1) Cyclohexane	0.405	650	15385			640	15625
(2) Carbon tetrachloride[a]	0.452	662 ± 5	15105				
(3) Benzene[a]	0.461	660 ± 5[b]	15150	655 ± 5[c]	15270	640	15625
(4) Dioxan	0.446	650	15385			625	16000
(5) Chloroform[a]	0.758	640 ± 5	15625	637 ± 3	15700	623 ± 2	16050
(6) Dichloromethane	0.843	645 ± 5	15505	645 ± 5	15505		
(7) Acetone[a]	0.929	645 ± 5	15505			615 ± 5	16260
(8) Acetonitrile	0.961	630 ± 10[b]	15875	635 ± 5[d]	15750	610 ± 5	16390
(9) 2-Propanol	0.931	620 ± 20	16130				
(10) Ethanol	0.940	610 ± 5	16390	610 ± 5	16390		
(11) Methanol	0.956	608 ± 8	16450	610 ± 5	16390	582 ± 3	17182
(12) 2,2,2-Trifluoroethanol	—	508 ± 5	17240				

[a] Results obtained using a ruby laser because the transmittances of the solvents are higher at 347 nm (an excimer laser (249 nm) was used for the other solvents).

[b] Ref. 20 gives 650 nm in benzene and 620 nm in acetonitrile.

[c] Ref. 12 gives 610 nm in benzene.

[d] Ref. 21 gives 620 nm in acetonitrile.

apparent the unusual feature of a strong blue shift on increasing the solvent polarity (clearly demonstrated in Figs. 3 - 5). The change $\Delta\mu(T_1 \rightarrow T_n)$ in dipole moment accompanying the transition $T_1 \rightarrow T_n$ can be calculated according to the treatment of Suppan [22 - 24], making the simplification

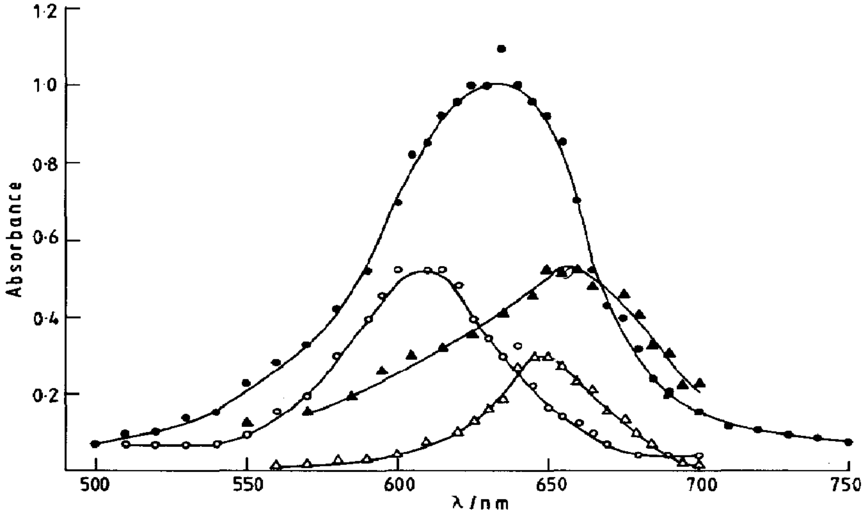

Fig. 3. Triplet–triplet absorption spectra of xanthone (about 2×10^{-4} mol dm^{-3}) obtained on laser flash photolysis of deaerated solutions: ●, in acetonitrile measured 2 μs after the end of the excimer laser pulse; ○, in methanol measured 2 μs after the end of the excimer laser pulse; ▲, in benzene measured 200 ns after the end of the ruby laser pulse; △, in dichloromethane measured 1 μs after the end of the excimer laser pulse.

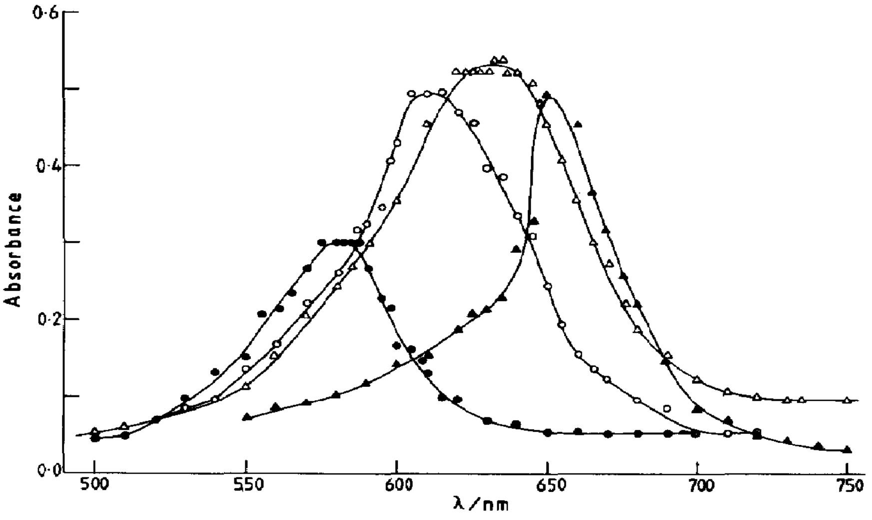

Fig. 4. Triplet–triplet absorption spectra of thioxanthone (about 2×10^{-4} mol dm^{-3}) obtained on laser flash photolysis of deaerated solutions: △, in acetonitrile measured 5 μs after the end of the excimer laser pulse; ○, in ethanol measured 2 μs after the end of the ruby laser pulse; ●, in 2,2,2-trifluoroethanol measured 2 μs after the end of the ruby laser pulse; ▲, in cyclohexane measured 500 ns after the end of the excimer laser pulse.

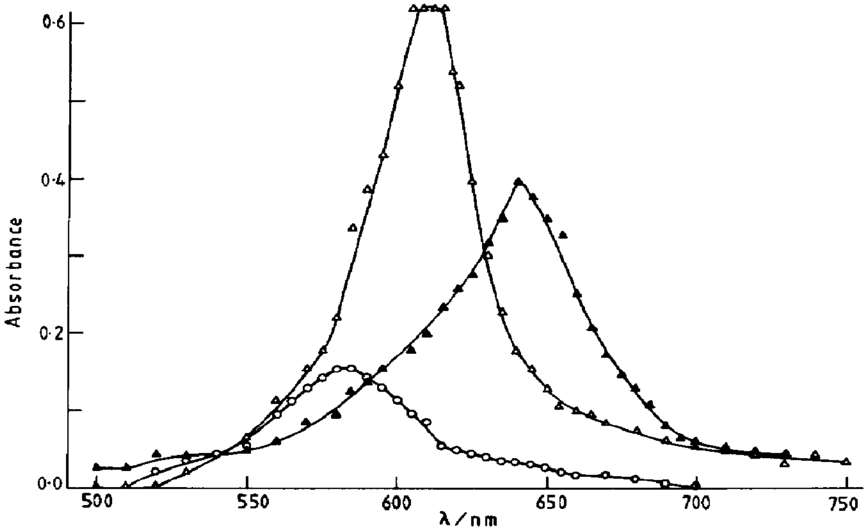

Fig. 5. Triplet–triplet absorption spectra of *N*-methylacridone (about 1 × 10^{-4} mol dm^{-3}) obtained on laser flash photolysis of deaerated solutions: △, in acetonitrile measured 10 μs after the end of the excimer laser pulse; ○, in methanol measured 10 μs after the end of the excimer laser pulse; ▲, in benzene measured 2 μs after the end of the ruby laser pulse.

that the dipole moment of the state S_1 approximates to that of the state T_1 (following Capellos and Porter [11]). While such an assumption must be seen as tentative, its validity does not affect arguments concerned with changes in the dipole moment:

$$\bar{\nu}_S = \bar{\nu}_V + \frac{\vec{\mu}_{T_1}(\vec{\mu}_{T_1} - \vec{\mu}_{T_n})}{hca^3}\,\Delta f(\epsilon) \tag{4}$$

Here $\bar{\nu}_S$ (cm^{-1}) represents the absorption band maximum for a solvent of dielectric constant ϵ, $\bar{\nu}_V$ represents the absorption band *in vacuo* (or in the gas phase) and $\Delta f(\epsilon) = 2(\epsilon - 1)/(2\epsilon + 1)$ where ϵ is the dielectric constant of the solvent at 293 K taken from ref. 13. Recently, the expression of Suppan has been modified to eqn. (4) in order to improve the reliability of the estimated excited state dipole moment [25], Prabhumirashi [25] recommends plotting $\bar{\nu}_S$ (rather than $\bar{\nu}_S - \bar{\nu}_V$) *versus* $f(\epsilon)$ in order to reduce the standard deviation. The plots of $\bar{\nu}_S$ *versus* $\Delta f(\epsilon)$ (Figs. 6 and 7) show good correlations for all three heterocyclic ketone molecules, and the corresponding regression lines are given by

$$\bar{\nu}_S = (14\,888.6 \pm 288) + (880.4 \pm 370.2)\,\Delta f(\epsilon) \tag{5}$$

$$\bar{\nu}_S = (14\,898.4 \pm 178) + (826.2 \pm 256.8)\,\Delta f(\epsilon) \tag{6}$$

and

$$\bar{\nu}_S = (15\,247.6 \pm 191.2) + (1125.4 \pm 273.3)\,\Delta f(\epsilon) \tag{7}$$

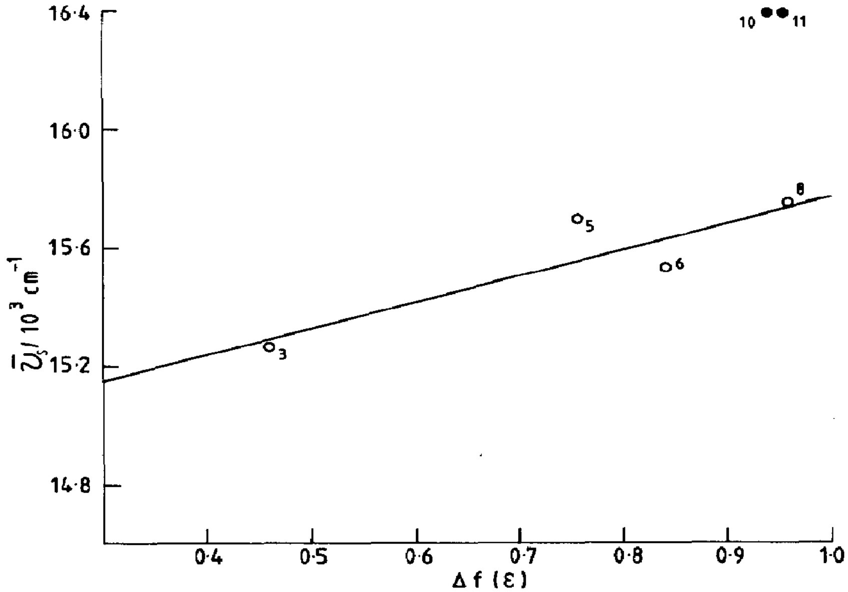

Fig. 6. Correlation of the triplet–triplet energy band maxima $\bar{\nu}_S$ of xanthone with the polarizability function $f(\epsilon) = 2(\epsilon - 1)/(2\epsilon + 1)$ (see eqn. (5)): ●, alcoholic solvents (excluded from the regression analysis). For key to the numbering of the solvents see Table 4.

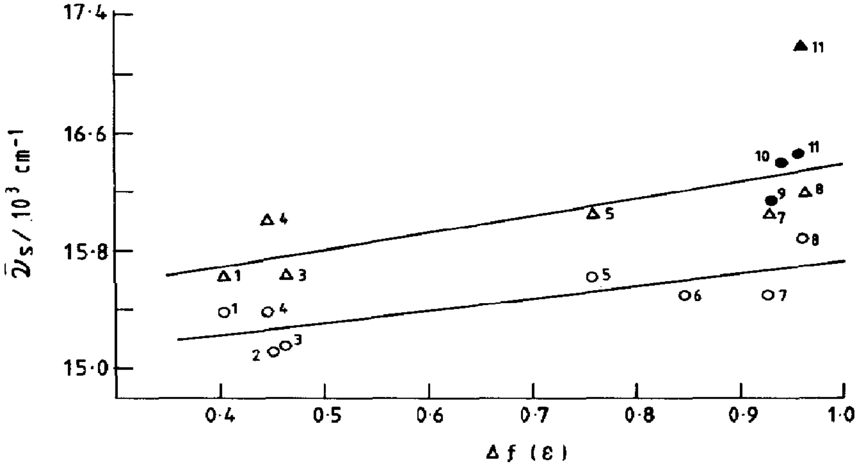

Fig. 7. Correlation of the triplet–triplet energy band maxima $\bar{\nu}_S$ of thioxanthone (○) and *N*-methylacridone (△) with the polarizability function $f(\epsilon) = 2(\epsilon - 1)/(2\epsilon + 1)$ (see eqns. (6) and (7) for thioxanthone and *N*-methylacridone respectively): ●, ▲, alcoholic solvents (excluded from the regression analysis). For key to the numbering of the solvents see Table 4.

for xanthone, thioxanthone and *N*-methylacridone respectively. The estimated changes in dipole moment for the $T_1 \rightarrow T_n$ and $S_1 \rightarrow S_0$ transitions for the three molecules are summarized in Table 3, *i.e.* the observed blue shift in the $T_1 \rightarrow T_n$ transition maxima is explained by a decrease in the dipole moment of T_n over that of T_1 for all three molecules.

Interestingly, the (0,0) band of the transition $T_1 \rightarrow S_0$ (phosphorescence) of xanthone [26] experiences a red shift of about 1100 cm^{-1} on going from a non-polar solvent (3-methylpentane) to a polar solvent (ethanol–isopentane–ether, 5:2:2) at 77 K, implying a larger dipole moment for the T_1 than for the S_0 state, although an alternative explanation [27] favours solvent effects on the relative position of approximate n–π^* and π–π^* states.

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References

1 E. Von Lippert, *Z. Electrochem.*, *61* (1957) 962.
2 L. Bilot and A. Kawski, *Z. Naturforsch.*, *Teil A*, *17* (1962) 621.
3 N. G. Bakhshiev, *Opt. Spectrosc.*, *19* (1965) 196.
4 M. Block and S. M. Walker, *Chem. Phys. Lett.*, *19* (1973) 363.
5 B. Koutek, *Collect. Czech. Chem. Commun.*, *43* (1978) 2368.
6 B. Koutek, *Collect. Czech. Chem. Commun.*, *49* (1984) 1680.
7 J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Plenum, New York, 1983, Chapter 7.
8 D. H. Williams and I. Fleming, *Spectroscopic Methods in Organic Chemistry*, McGraw-Hill, London, 1980, Chapter 1.
9 C. Reichardt, *Angew. Chem.*, *Int. Edn. Engl.*, *18* (1979) 98.
10 E. M. Kosower, *An Introduction to Physical Organic Chemistry*, Wiley, New York, 1968, pp. 259 - 384.
11 C. Capellos and G. Porter, *J. Chem. Soc., Faraday Trans. II*, *70* (1974) 1159.
12 A. Garner and F. Wilkinson, *J. Chem. Soc., Faraday Trans. II*, *72* (1976) 1010.
13 R. C. Weast (ed.), *Handbook of Chemistry and Physics*, CRC Press, Cleveland, OH, 58th edn., 1975 - 1976.
14 J. R. A. Pollock and R. Stevens (eds.), *Dictionary of Organic Compounds*, Eyre and Spottiswoode, London, 1965.
15 K. A. Abdullah and T. J. Kemp, *J. Photochem.*, *30* (1985) 363.
16 K. A. Abdullah and T. J. Kemp, *J. Chem. Soc., Perkin Trans. II*, (1985) 1279.
17 J. C. Dalton and F. C. Montgomery, *J. Am. Chem. Soc.*, *96* (1974) 6230.
18 T. Lai and E. C. Lim, *Chem. Phys. Lett.*, *73* (1980) 244.
19 A. L. McClellan, *Tables of Experimental Dipole Moments*, Freeman, San Francisco, 1963.
20 S. F. Yates and G. B. Schuster, *J. Org. Chem.*, *49* (1984) 3349.
21 J. C. Scaiano and N. Kim-Thuan, *Can. J. Chem.*, *60* (1982) 2286.
22 P. Suppan, *J. Chem. Soc. A*, (1968) 3125.
23 P. Suppan and M. B. Ledger, *Spectrochim. Acta, Part A*, *23* (1967) 41.
24 P. Suppan, *J. Mol. Spectrosc.*, *30* (1969) 17.
25 L. S. Prabhumirashi, *Spectrochim. Acta, Part A*, *39* (1983) 91.
26 H. J. Pownall and J. R. Huber, *J. Am. Chem. Soc.*, *93* (1971) 6429.
27 R. E. Connor and W. R. Christian, *J. Phys. Chem.*, *86* (1982) 1524.