FLUORESCENCE YIELDS OF N,N'-DIMYRISTOYLINDIGO: EFFECT OF SOLVENT POLARITY

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Summary

The fluorescence yields at room temperature of the hydrophobic indigo derivative N,N'-dimyristoylindigo have been measured in 14 organic solvents. Like the *trans → cis* photoisomerization quantum yields reported in our earlier publication (G. R. Seely and E. R. Shaw, *J. Photochem.*, 24 (1984) 383), the fluorescence yields vary with the polarity of the solvent, being greatest in hydrocarbons and least in highly polar solvents. There is in fact a near proportionality between these two yields. There is also a broadly linear relation between the Stokes shift and the polarity of the solvent as expressed by the equation of Bilot and Kawski. It is argued that it is the rate of internal conversion that is sensitive to solvent polarity and that strong multipolar forces between the excited indigo and the solvent molecules surrounding it are responsible for accelerating this rate in polar solvents.

1. Introduction

In connection with our work on the photochemistry of chlorophyll in heterogeneous systems, we have investigated N,N'-dimyristoylindigo (DMI) as a probe for photochemical rates in hydrocarbon systems. In our previous paper [1] we reported that the quantum yield of *trans → cis* isomerization, unlike that of *cis → trans* isomerization, was dependent on the nature of the solvent, being greatest in hydrocarbons and least in highly polar solvents, particularly alcohols. Since solutions of DMI are usually distinctly fluorescent, it was considered that a survey of fluorescence quantum yields in the same solvents would give valuable information about the photophysical processes preceding isomerization. We here present results of a survey of fluorescence quantum yields in 14 of the solvents used previously and discuss them with reference to the *trans → cis* isomerization yields.

2. Experimental details

2.1. Materials

The preparation and purification of DMI are described in ref. 1. Rhodamine 101 was purchased from Exciton Chemical Company, Dayton, OH, as Rhodamine 640 chloride. Solvents were generally of research grade; however, tetrahydrofuran, acetonitrile, 1-propanol and hexane were purified by appropriate procedures, which included a fractional distillation, and dimethyl sulfoxide and tetradecane were subjected to fractional crystallization.

2.2. Fluorometry

The quantum yields were determined by integration of fluorescence spectra recorded on a locally assembled apparatus constructed to have good sensitivity in the red region. Exciting light from a 150 W xenon lamp was dispersed by a Beckman DU monochromator to a beam of 9 nm bandwidth and focused on the front face of the sample solution in a quartz cuvette of 1 mm nominal path length. The focused fluorescence from the front face was dispersed by a Spex 0.5 m grating monochromator, blazed for 750 nm, and operated at a bandwidth of 1.6 nm. The signal was detected with a cooled Hamamatsu R928 photomultiplier, amplified and recorded and integrated by a Kipp and Zonen BD 12 recorder. The sensitivity of the apparatus to wavelength was calibrated with a tungsten lamp, and corrections were made to the integrated fluorescence spectra as described below.

Aliquots of a stock solution of DMI in acetone were evaporated and redissolved in the test solvents. Solutions were prepared under nitrogen, and nitrogen was circulated through the sample compartment of the fluorescence apparatus. The temperature was monitored, and most spectra were recorded in the range 290 - 292 K. Usually, fluorescence was excited at 550, 530 and 510 nm, in different parts of the first electronic excitation band of DMI. The absorption spectrum was recorded before and after fluorescence measurement, to verify that the extent of isomerization was not significant.

2.3. Quantum yield calculation

The quantum yields were determined by comparing the integrated fluorescence intensity of DMI with that of Rhodamine 101 in basic 95% ethanol, the quantum yield of which was taken to be 0.96 [2] (this is considered to be a conservative value, since Frank et al. [3] found a quantum yield of 0.99 in methanol, and Karstens and Kobs [4] obtained 1.0 in ethanol, independent of temperature). A highly scattering paste of mannitol and glycerol in a 5 mm cuvette served as a working standard for the incident light intensity, calibrated against Rhodamine 101.

The quantum yields were calculated from

$$\phi_f = F \frac{(I_f \times 1.05)\lambda_f(1/2)S(\lambda_s)n^2}{I_s(1 - 10^{-\rho})\lambda_s S\{\lambda_f(1/2)\}n_{et}^2} \tag{1}$$

In eqn. (1), F is the calibration factor, obtained from the fluorescence yield of Rhodamine 101, I_f is the integrated fluorescence intensity of the sample excited in a band about λ_s, I_s is the integrated scattering intensity of the working standard excited at λ_s, $\lambda_f(1/2)$ is the midway point in the recorder integration of fluorescence, $S(\lambda_s)$ and $S\{\lambda_f(1/2)\}$ are instrumental sensitivities to light of λ_s and $\lambda_f(1/2)$ in energy units and ρ is the absorbance of the sample along the incident light path in the 1 mm cuvette. This path length was estimated to be 1.05 mm from the angle of incidence. Another factor of 1.05 appears in the numerator; this was found empirically to compensate for the inequivalence in the variation of instrumental sensitivity about the midway point $\lambda_f(1/2)$. The refractive index n correction was applied, relative to the refractive index n_{et} of ethanol.

The peak sample absorbance did not generally exceed 0.20 - 0.25. The fluorescence spectrum of DMI is a good mirror image of the absorption spectrum, and fairly well separated from it, so reabsorption effects were small and not noticeable in our front surface viewing set-up. The advantage of using lower absorbances is offset by the loss of sensitivity. The most serious source of systematic error was instability of the calibration factor (*i.e.* alignment of the apparatus). The data presented are believed to compose a consistent set, as indicated by internal checks, and we consider that the quantum yields are accurate at least to within 10%.

3. Results and discussion

3.1. Quantum yields

Data pertaining to the spectra of fluorescence in 14 solvents are collected in Table 1; the fluorescence quantum yields in the same solvents are listed in Table 2. The solvents were chosen to represent a variety of types among those listed in ref. 1, Tables 1 and 2. Solvents such as amines in which quenching by electron transfer might occur [5] have been avoided.

Considering first the data of Table 2, it is seen that there is generally good agreement among the quantum yields excited at the three wavelengths, 550, 530 and 510 nm, within the estimated accuracy of 10%. Values of $\phi_f(530)$ are systematically greater than those of $\phi_f(550)$; there is reason to believe that the calibration factor varies slightly with wavelength, in such a way as to account for this apparent discrepancy. The yields in acetone were measured toward the beginning and the end of the series; the two sets of values agree quite well.

Of particular interest is the parallel between the quantum yields of fluorescence and those of *trans* → *cis* isomerization, drawn from ref. 1, Table 2. There is a distinct decline in both as the solvent polarity increases. The parallelism is made graphic in the plot of $\phi_f(550)$ and $\phi_f(530)$ against $\hat{\phi}_{tc}$ (excited at 559 nm) in Fig. 1. The regression

$$\phi_f = 0.0006 + 1.52\hat{\phi}_{tc} - 3.87\hat{\phi}_{tc}^2 \tag{2}$$

TABLE 1

Spectral data for dimyristoylindigo in various solvents[a]

Solvent	Symbol	λ_a (nm)	λ_f (nm)	$\Delta\nu_{ss}$ (cm^{-1})	ϵ	n	BK
Hexane	hx	565	609	1280	1.89	1.3749	0
Tetradecane	td	567	607	1160	2.01	1.4216	−0.003
Cyclohexane	ch	565	607.5	1240	2.02	1.4235	−0.002
Benzene	bz	569	616	1330	2.28	1.4979	+0.008
Chloroform	cf	567	624	1600	4.81	1.4429	0.372
Tetrabromoethane	tbe	574	629	1520	7.0	1.6323	0.420
Tetrahydrofuran	tf	560	614.5	1590	7.58	1.405	0.550
Acetone	ac	556	616	1750	20.7	1.356	0.791
Dimethyl sulfoxide	ms	555	624	1990	46.68	1.4773	0.842
Acetonitrile	an	557	617.5	1750	37.5	1.3416	0.864
Dimethylformamide	df	555	621.5	1930	36.61	1.4282	0.836
Pyridine	py	565	622.5	1620	12.4	1.5075	0.628
1-Propanol	np	564	624	1700	20.33	1.3837	0.780
Cyclohexanol	cxl	567	620.5	1510	15.0	1.4648	0.697

[a]Listed are the solvents in the order in which they appeared in ref. 1, their symbols as used on the figures, the peak wavelengths of absorption and fluorescence, the Stokes shift, the dielectric constant, the refractive index and the derived quantity called BK in eqns. (3) and (4).
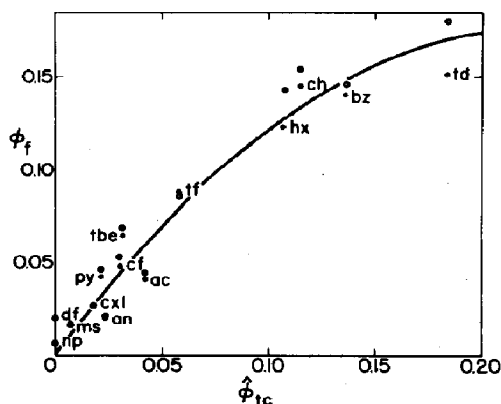

Fig. 1. Correlation of the fluorescence quantum yields ϕ_f measured at 550 nm (●) and 530 nm (○) with median $trans \rightarrow cis$ photoisomerization yields $\hat{\phi}_{tc}$ from ref. 1. The regression curve is eqn. (2) of the text.

relates these points, with a standard error of 0.0123. The variation of the points from the regression curve is not unreasonable, when the variety of solvent types employed is considered.

The solvent conferring the lowest quantum yield is 1-propanol, and alcohols are known to quench the fluorescence of thioindigos, probably by a proton transfer mechanism [6, 7]. In ref. 1 we reported that alcohols greatly accelerated the dark $cis \rightarrow trans$ isomerization rate of acylindigos. In

TABLE 2

Fluorescence yield information for dimyristoylindigo in various solvents[a]

Solvent	$\lambda_f(1/2)$ (nm)	$\phi_f(550)$	$\phi_f(530)$	$\phi_f(510)$	$\hat{\phi}_{tc} \pm \Delta IQ$	k_{IC}/k_f
Hexane	616	0.123	0.143	0.132	0.107 ± 0.010	4.96
Tetradecane	616	0.151	0.179	0.173	0.184 ± 0.003	2.58
Cyclohexane	614.5	0.145	0.154	0.156	0.115 ± 0.012	3.91
Benzene	624	0.140	0.146	0.143	0.136 ± 0.004	3.72
Chloroform	632	0.048	0.053	0.054	0.0305 ± 0.0025	18.2
Tetrabromoethane	637	0.065	0.069	0.066	0.0318 ± 0.0003	13.2
Tetrahydrofuran	623	0.088	0.086	0.086	0.058 ± 0.006	8.7
Acetone	625	0.0411[b]	0.0438	0.0457	$.0.0424 \pm 0.0016$	20.8
		0.0409	0.0451	0.0371		
Dimethyl sulfoxide	633	0.0171	0.0165	0.0228	0.0073 ± 0.0005	56.4
Acetonitrile	625.5	0.0200	0.0217	0.0224	0.0233 ± 0.0026	46.1
Dimethylformamide	629	0.0208	0.0207	0.0194	0	47
Pyridine	631	0.0421	0.0466	0.0504	0.0212 ± 0.0063	21.5
1-Propanol	629	0.0067	—	—	0	148
Cyclohexanol	627	0.0267	0.0269	—	0.0180 ± 0.0004	34.8

[a]Quantities listed for each solvent are the median fluorescence wavelengths, the fluorescence quantum yields excited at 550, 530 and 510 nm, the median *trans* → *cis* photoisomerization quantum yield, excited at 559 nm, from ref. 1, Table 2, together with its probable error estimated by the interquartile separation, and the relative internal conversion rate calculated by eqn. (7).
[b]The first set of data in acetone was taken near the beginning of the series, the second near the end.

the present context, we felt some concern that the low fluorescence yields in polar solvents might be due to traces of alcohol or amine impurities. Fluorescence yields were therefore measured in tetrahydrofuran containing 0.1, 0.6 and 1.1% 1-propanol; the fluorescence quantum yield (at 550 nm) fell from 0.088 to 0.078 in the last mixture, which does not suggest great sensitivity to traces of hydroxylic impurities. Therefore the quantum yields reported are not likely to be related to residual quenching impurities in the solvents, with one exception: chloroform contained 0.5% ethanol as preservative, which had not been removed and which might be sufficient to reduce the quantum yields somewhat in this solvent.

3.2. Wavelength dependence

In ref. 1, the photoisomerization quantum yields in acetonitrile and benzene were reported to vary with the excitation wavelength by amounts greater than the uncertainty of measurement. We checked the fluorescence quantum yields excited over a range of wavelength in these two solvents, to see whether the variation in the photoisomerization yields could be traced to this source. With acetonitrile, the results were $\lambda = 560$ nm ($\phi_f = 0.0202$), $\lambda = 550$ nm ($\phi_f = 0.0200$), $\lambda = 540$ nm ($\phi_f = 0.0209$), $\lambda = 530$ nm ($\phi_f = 0.0217$), $\lambda = 520$ nm ($\phi_f = 0.0214$), $\lambda = 510$ nm ($\phi_f = 0.0224$), $\lambda = 500$ nm ($\phi_f =$

0.0216) and $\lambda = 490$ nm ($\phi_f = 0.0219$), for an average over the first DMI absorption band of $\phi_f = 0.0213 \pm 0.0008$. In benzene, the results were $\lambda = 570$ nm ($\phi_f = 0.121$), $\lambda = 560$ nm ($\phi_f = 0.115$), $\lambda = 550$ nm ($\phi_f = 0.113$), $\lambda = 540$ nm ($\phi_f = 0.107$), $\lambda = 530$ nm ($\phi_f = 0.123$) and $\lambda = 520$ nm ($\phi_f = 0.115$), for an average of $\phi_f = 0.116 \pm 0.006$ over the first absorption band (the lower value of ϕ_f than that recorded in Table 2 is accounted for by a change, and probably an error, in the calibration factor F). It cannot be said with much probability that there is a real variation in the quantum yield with wavelength over the first absorption band of DMI. It can be said that, if a variability exists, it does not exceed about 10%, and does not account for the reported variation in the *trans → cis* photoisomerization yields with wavelength.

3.3. Stokes shift

It was reported earlier [1] that there was no discernible dependence of the DMI absorption band peak wavelength λ_a on the polarity of the solvent, except that in a few aprotic highly polar solvents it was unusually short. It is evident from Table 1 that the fluorescence band peak wavelength λ_f and more particularly the Stokes shift $\Delta\nu_{ss} = 1/\lambda_a - 1/\lambda_f$ are positively correlated with solvent polarity.

The expression of Bilot and Kawski [8]

$$\Delta\nu_{ss} = \frac{(M_e - M_g)^2}{hca^3}\left[\frac{(\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1)}{\{1 - \beta(n^2 - 1)/(2n^2 + 1)\}^2\{1 - \beta(\epsilon - 1)/(2\epsilon + 1)\}} \right] +$$

$$+ \text{constant} \qquad (3)$$

has been useful in correlating Stokes shifts with dielectric functions through the difference $M_e - M_g$ between ground and excited state dipole moments [9 - 12]. In eqn. (3), ϵ and n are the solvent dielectric constant and refractive index, β is a factor approximated by unity, a is the solute cavity radius and h and c have their usual meanings. Values of the bracketed quantity, designated BK, are listed in Table 1, eighth column, and $\Delta\nu_{ss}$ is plotted against these values in Fig. 2. From the slope of the regression line
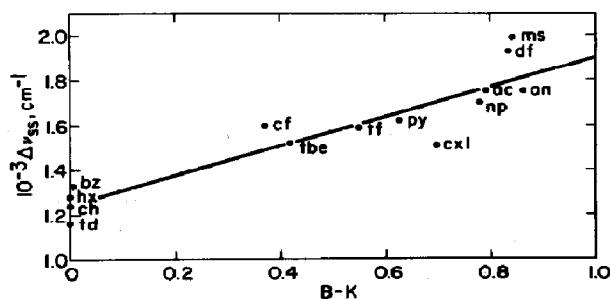

Fig. 2. Correlation of the Stokes shift $\Delta\nu_{ss}$ with the value of the quantity designated BK in eqn. (3) and Table 1. The regression line is eqn. (4) of the text.

$$\Delta\nu_{ss} \ (\text{cm}^{-1}) = 1251 + (657 \pm 82)BK \tag{4}$$

we conclude that, if a is at least 5 Å, $|M_e - M_g|$ must be at least 4.0 debyes. Since DMI has a center of symmetry in the ground state and almost surely in the excited state as well, the difference $M_e - M_g$ must not correspond to a real dipole moment change, but to an "equivalent" change in quadrupole and higher moments on excitation.

3.4. Kinetics

In the absence of quenching by electron transfer from the solvent, the only paths for deactivation of singlet excited *trans*-DMI are fluorescence, internal conversion and intersystem crossing, with rate constants k_f (s^{-1}), k_{IC} (s^{-1}) and k_{ISC} (s^{-1}). It seems to be well established that the *trans* → *cis* isomerization of thioindigos is a triplet state reaction only [13 - 15], and the apparently analogous reaction of diacylindigos is also likely to be so. The fluorescence yield is

$$\phi_f = \frac{k_f}{k_f + k_{IC} + k_{ISC}} \tag{5}$$

and the *trans* → *cis* isomerization yield is

$$\phi_{tc} = \frac{\alpha k_{ISC}}{k_f + k_{IC} + k_{ISC}} \tag{6}$$

where α is the probability that a triplet state will relax into the *cis* configuration.

The radiative decay rate k_f is determined by the integral of the absorption spectrum, which for DMI is insensitive to solvent. Since the yield of *cis* isomer declines proportionately to the yield of fluorescence, it is likely that k_{ISC} is also relatively constant and that it is k_{IC} which increases in more polar solvents.

The at present unknown k_{ISC} can be eliminated and eqns. (5) and (6) can be solved for the relative internal conversion rate:

$$\frac{k_{IC}}{k_f} = \frac{1}{\phi_f}\left(1 - \frac{\phi_{tc}}{\alpha}\right) - 1 \tag{7}$$

The value of α is unknown but a reasonable estimate is 0.4, similar to values reported for thioindigo dyes [15]. The values of k_{IC}/k_f can be calculated and are listed in the seventh column of Table 2. The dependence on solvent polarity is very clear. A plot of these values against the solvent dielectric constant is presented in Fig. 3. If the points for 1-propanol, cyclohexanol and chloroform are omitted, the remaining points for aprotic solvents are correlated by

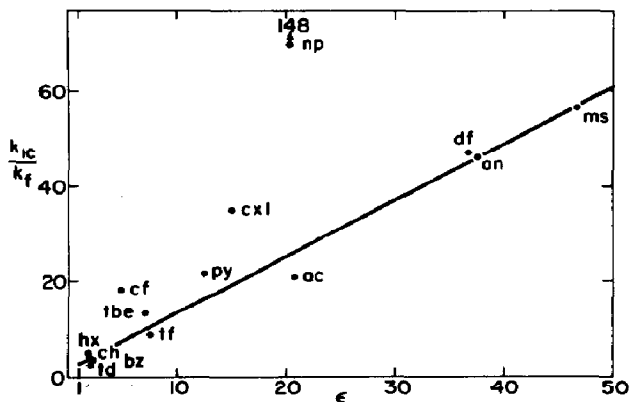$$\frac{k_{IC}}{k_f} = 3.055 + (1.179 \pm 0.055)(\epsilon - 1) \tag{8}$$

Fig. 3. Correlation of the relative internal conversion rate k_{IC}/k_f, calculated by eqn. (7) of the text, with the solvent dielectric constant ϵ. Only fluorescence data $\phi_f(550)$ were used. The regression line (eqn. (8)) ignores points for propanol, cyclohexanol and chloroform, because the presence of alcohol opens an additional channel of internal conversion.

with a correlation coefficient of 0.99. In alcohols, k_{IC}/k_f is large because of quenching through hydrogen bond displacement. Chloroform is excluded because of its small alcohol content.

To explain the strong dependence of k_{IC} on ϵ, it is assumed that the solvent molecules are to some extent ordered with respect to the charge distribution in the ground state of DMI. On excitation, the change in charge distribution in DMI exerts torques on the adjacent solvent molecules, and they in turn exert stresses on the structure of DMI that set in motion vibrational modes conducive to internal conversion. To put it another way, the electrical strain in the immediately excited solute–solvent system offsets the activation energy of internal conversion.

Recently, Birckner *et al.* [16] have examined the fluorescence of thioindigo in eight solvents and found results which were similar in some respects to ours, but dissimilar in others. The Stokes shift correlates with solvent polarity in such a way as to correspond to a dipole moment of less than 2 debyes in the excited states; however, by further analysis they showed that it was not the dipole moment as such but the polarizability of thioindigo in the excited state that was responsible for the correlation. The fluorescence quantum yields of thioindigo are higher than those of DMI in polar and nonpolar solvents, and there is less decrease with increase in polarity. Apparently for thioindigo, internal conversion is a slower and less important process than for DMI, and is less affected by solvent polarity.

Acknowledgments

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