BEHAVIOUR OF THE LASER DYE 4-DICYANOMETHYLENE-2-METHYL-6-DIMETHYLAMINOSTYRYL-4*H*-PYRAN IN THE EXCITED SINGLET STATE

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(Received January 20, 1984; in revised form July 28, 1984)

Summary

The spectral and temporal behaviour of the excited singlet state of 4-dicyanomethylene-2-methyl-6-dimethylaminostyryl-4*H*-pyran (DCM) in a variety of solvents was studied. The results obtained enable us to propose a possible mechanism for the behaviour of DCM in the excited singlet state.

1. Introduction

The compound 4-dicyanomethylene-2-methyl-6-dimethylaminostyryl-4*H*-pyran (DCM), which is used as a laser dye in the red region, has recently received much attention owing to its high efficiency and wide frequency tunability [1 - 4]. Attempts to understand the lasing process of DCM require that the spectral and temporal parameters of the excited state of this dye molecule should be known. However, information of this kind for DCM is not yet available in the literature.

In this paper we present the spectral and temporal behaviour of the excited singlet state of DCM in a variety of solvents. The results obtained enable us to propose a mechanism describing the behaviour of DCM in the excited singlet state. This is also of interest with respect to the general understanding of some intramolecular processes of excited molecules in the condensed phase and for chemical and biological applications.

2. Experimental details

In our experiment laser dye grade DCM (Exciton) was used without further purification. All the solvents used were of spectroscopic grade and were carefully checked for fluorescent impurities.

The absorption and fluorescence spectra of DCM were measured using a Specord visible–UV spectrophotometer (Jena Zeiss, G.D.R.) and an MPF-4 spectrofluorometer (Hitachi, Japan) respectively. The fluorescence decay profile and time-resolved emission spectra were recorded using

0047-2670/85/$3.30

a nanosecond fluorescence spectrometer (Model SP-7/8X, Applied Photophysics Ltd., Gt. Britain) in which low intensity excitation of the sample was achieved using a 337 nm light pulse generated by a thyratron-gated discharge in nitrogen at frequencies up to 80 kHz. The duration of the exciting light pulse was about 5 ns. The fluorescence was monitored by a photomultiplier through a monochromator and was recorded by a single-photon counting system consisting of a time-to-amplitude convertor (TAC) and a multichannel analyser (MCA). The decay profile of the emission at the wavelength of interest was obtained by setting the monochromator at this wavelength and storing the output signal from the TAC in the appropriate MCA channel according to the amplitude. The emission decay time was evaluated by analysing the data stored in the MCA on a PDP 11/05 computer using a non-linear least-squares deconvolution procedure. The transient emission spectra at a given time interval were recorded by scanning the monochromator over the wavelength interval of interest and storing in the MCA only those output signals representing the photons emitted at short time intervals which were discriminated by the TAC output. The instrument used in the time-resolved measurement was calibrated to have a reproducibility of ± 0.15 ns.

3. Results

The behaviour of the low-lying excited singlet state of DCM was investigated by measuring the photostationary and time-resolved emission spectra in an aerated solution at ambient temperature. The frequencies of the absorption and fluorescence maxima observed in various solvents are listed in Table 1.

The solvents have no detectable effect on the absorption band shape. However, the absorption maximum undergoes a red shift on increasing the dielectric constant of the aprotic solvents used, but this solvatochromic effect is less obvious in protic solvents. The solvatochromic effect observed for fluorescence shows a regular correlation with the dielectric constant of the solvent used, but is different for each solvent. As shown in Fig. 1, the fluorescence maximum of DCM in non-polar aprotic solvents shifts from 560 nm to 580 nm with increasing dielectric constant of the solvent used, whereas in dipolar aprotic and protic solvents the location of the fluorescence maximum in the red region, *i.e.* 610 nm, undergoes little change and is accompanied by a new fluorescence band with its maximum at 630 nm. This longer-wavelength fluorescence band generally appears as a shoulder in the short-wavelength band, but it becomes dominant when solvents of high dielectric constant such as dimethyl sulphoxide (DMSO) and dimethylformamide (DMF) are used. Unfortunately, we cannot yet perform a quantitative evaluation of the intensities of the fluorescence bands separately and correlate them with the dielectric constant of the solvent; nevertheless it is evident that the solvent dependence of the intensities

TABLE 1

Spectral and temporal parameters of 4-dicyanomethylene-2-methyl-6-dimethylaminostyryl-4*H*-pyran in various solvents

Solvent	*Concentration* ($\times 10^{-4}$ M)	*Absorption maximum* (kilokaysers)	*Fluorescence maximum* (kilokaysers)		*Decay time constant* (ns)		
					580 nm	*610 nm*	*630 nm*
Benzene	1.58	21.42	17.85		0.3	–	–
1,4-Dioxane	1.20	21.68	17.60		0.3	–	–
Diethyl ether	1.58	21.79	17.79		0.5	–	–
Ethyl acetate	1.28	21.63	17.30		0.8	–	–
Pyridine	1.00	20.70	16.44	15.90[a]	–	1.9	2.0
2-Butanol	1.00	21.38	16.50	15.90[a]	–	1.9	2.0
Acetone	1.20	21.28	16.50	15.90[a]	–	2.0	2.1
Acetonitrile	1.20	21.36	16.39	15.90[a]	–	1.8	1.8
DMF	1.00	20.78	16.40[a]	15.88	–	2.1	2.2
DMSO	1.23	20.40	16.40[a]	15.88	–	2.0	2.1
t-Butanol	1.36	21.12	16.72	15.90[a]	–	2.2	2.2
i-Propanol	1.32	20.97	16.53	15.90[a]	–	2.0	2.1
n-Propanol	1.20	20.89	16.39	15.90[a]	–	1.9	2.0
Ethanol	1.56	21.00	16.39	15.90[a]	–	1.6	1.8
Methanol	1.43	21.06	16.39	15.90[a]	–	1.2	1.4
Formamide	1.40	20.64	16.40	15.88	–	1.3	1.4

[a]The shoulder of the fluorescence band.

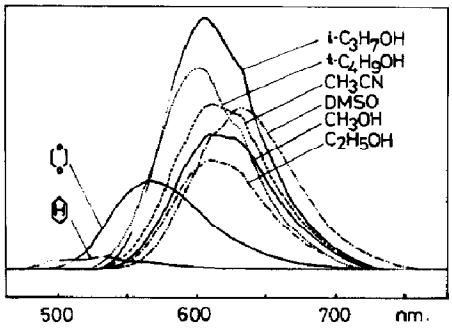

Fig. 1. Fluorescence spectra of DCM in selected solvents: DCM concentration, 1×10^{-4} - 1.6×10^{-4} M.

of the short-wavelength fluorescence and the total fluorescence exhibits a maximum, and that the intensity of the longer-wavelength band seems to be enhanced monotonically with increasing dielectric constant of the solvent. Similar behaviour is observed in dioxane with various concentrations of a polar additive such as ethanol or DMSO. The addition of ethanol to the DCM–dioxane solution shifts the fluorescence band from its original position in pure dioxane to that in pure ethanol and concomitantly produces a longer-wavelength fluorescence with a maximum at 630 nm even at low ethanol concentrations compared with the DCM concentration, *i.e.* about 10^{-4} M. Increasing the concentration of ethanol added, with a consequent increase in the dielectric constant of the medium, has no effect on the position of the longer-wavelength fluorescence maximum but produces an increase in intensity. However, the intensity of the shorter-wavelength band and the total emission each increases to a maximum and then decreases to that of DCM in pure ethanol.

Variation of the concentration of DCM in polar solvents has little effect on either the band shape or the positions of the absorption and fluorescence maxima but, as expected, produces marked fluorescence quenching (Table 2).

The decay profile of DCM fluorescence at various wavelengths in all solvents used was found to be described exactly by a single-exponential function, although in the experiments special attention was paid to the possibility of non-exponential decay in polar solvents owing to the fact that there is a strong overlap between the two fluorescence bands. The fluorescence decay of DCM can therefore be characterized by a single decay time constant τ obtained from the best fit of the experimental decay profile to the theoretical single-exponential function. The τ values measured at various wavelengths in various solvents are given in Table 1. These data clearly show that the value of τ for DCM in the same solvent is independent of the fluorescence wavelength at which the measurement was made. However, the solvent concentration dependences vary from solvent to solvent.

TABLE 2

Concentration dependence of the absorption and fluorescence of 4-dicyanomethylene-2-methyl-6-dimethylaminostyryl-4*H*-pyran in ethanol

Concentration (M)	*Absorption maximum* (kilokaysers)	*Extinction coefficient* (M^{-1} cm^{-1})		*Fluorescence maximum*[a] (kilokaysers)	*Decay time*[b] (ns)
		475 nm	337 nm		
5.0×10^{-6}	21.00	4.2×10^4	1.2×10^4	13.69	1.6
7.5×10^{-6}	21.00	4.2×10^4	1.2×10^4	13.69	1.6
1.0×10^{-5}	21.00	4.2×10^4	1.2×10^4	13.69	1.5
5.0×10^{-5}	21.00	4.2×10^4	1.2×10^4	13.69	1.1
7.5×10^{-5}	21.00	4.2×10^4	1.2×10^4	13.69	0.9

[a]With a shoulder at 15.90 kilokaysers.
[b]Excitation wavelength, 337 nm; measurement wavelength, 610 nm.

The solvent dependence of τ for DCM in non-polar aprotic solvents resembles the solvatochromic effect for DCM in these solvents, *i.e.* τ increases with increasing dielectric constant ϵ of the solvent used and can be described by the linear equation

$$\tau = 0.0014 + 0.127\epsilon$$

The correlation coefficient r is 0.97. The value of τ for DCM in dipolar aprotic solvents is larger and seems to be independent of the dielectric constant of the solvent, whereas in protic solvents τ decreases linearly with increasing dielectric constant of the solvent. The linear least-squares analysis of τ for DCM in protic solvents presented in Table 1 leads to the following equation for the solvent effect:

$$\tau = 3.01 - 0.055\epsilon \qquad r = 0.98$$

To obtain more information about the nature of the emitting states of DCM in polar solvents, the fluorescence spectra of DCM in DMSO were recorded at various times after excitation. Typical time-resolved emission spectra are shown in Fig. 2. It can clearly be seen that both short- and long-wavelength fluorescence bands appear during the first 0.75 ns after excitation; however, their relative intensity changes with time until a time-independent intensity ratio is reached at about 2 ns. Whereas experiments with a higher time resolution, *i.e.* on the picosecond timescale, have not yet been performed and the build-up times of the two emission bands cannot be followed separately, the spectra presented in Fig. 2 suggest that the dual fluorescence observed in the polar solvents is generated from two physically different emitting states of DCM.

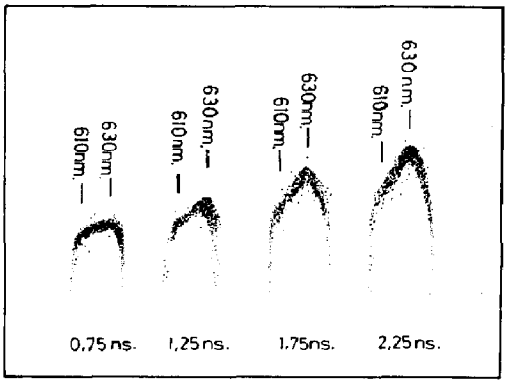

Fig. 2. Time-resolved emission spectra of DCM in aerated DMSO: DCM concentration, 1.2×10^{-4} M.

4. Discussion

Of greatest interest in the behaviour of DCM in the low-lying excited state is the fact that dual fluorescence is observed in polar solvents. The variations in the effects of the solvent on the spectral as well as the temporal behaviour of DCM is fairly convincing evidence that photoexcited DCM can exist in various emitting states in polar solvents. The single-exponential decay of dual fluorescence with wavelength-independent τ can be regarded as an indication that the two emitting species responsible for the dual fluorescence are in dynamic equilibrium which is established during the lifetime of these excited states. Phenomenologically similar decay kinetics have been observed for monomer–excimer fluorescence [5]. However, the nature of these emitting species remains to be clarified.

It is tempting to characterize the excited species responsible for the dual fluorescence in terms of differences in aggregation. However, the independence of the spectral profiles for both absorption and fluorescence indicates that neither of these emitting species is generated from aggregates in either the ground state or the low-lying excited singlet state.

Another possible explanation for the appearance of the additional long-wavelength fluorescence is that it is due to a DCM–solvent exciplex. However, this is unlikely because the additional emission appears even at polar additive concentrations as low as 10^{-4} M. It can be argued that a 1:1 DCM–solvent complex could be formed at low concentrations of the additive if the polar molecule has the correct location and orientation in the solvent shell of DCM at the time of excitation. However, the probability that this will occur is rather small. A decrease in the fluorescence intensity upon increasing the dielectric constant of the solvent is, indeed, a general feature of exciplex fluorescence, but it is not sufficient evidence for the assignment of the additional long-wavelength fluorescence to a solute–solvent exciplex

since a solvent dependence of this type also occurs for radiating intramolecular charge transfer complexes. Moreover, if the additional fluorescence originated from a DCM–solvent exciplex the position of the maximum would be expected to depend on the solvent used. However, no solvent dependence was observed in our experiments. In addition, the separation between the maxima of the dual fluorescence seems to be too small (about 500 cm^{-1}) compared with the red shift observed in typical exciplex fluorescence spectra.

It is reasonable to consider DCM as an ionic merocyanine-like dye molecule in which an electron-donating moiety D (*i.e.* the dimethylamino group) is linked by a conjugated π electron system to an electron-accepting moiety A (*i.e.* the dicyanomethylene group). Electronic excitation of molecules of this type generally occurs via intramolecular charge transfer (ICT) transitions, but π–π^* transitions also contribute, particularly in non-polar solvents. Therefore the radiating DCM molecules in non-polar solvents are probably in locally excited states formed via π–π^* transitions and have an electronic configuration similar to that of the ground state. In polar solvents, however, excited DCM molecules in the ICT state, which are characterized by a planar molecular conformation, are formed immediately after excitation under the influence of the electric polarization of the surrounding solvent molecules and are responsible for the short-wavelength fluorescence. This explains why an abrupt shift in the position of the fluorescence band is observed on changing from a non-polar aprotic solvent to a polar solvent. The additional long-wavelength fluorescence seems to be difficult to explain other than by a tentative hypothesis that it is generated from excited DCM in a novel ICT state which forms during the lifetime of the lowest excited singlet state and equilibrates with the ICT state emitting at 610 nm. Without further information we cannot yet exclude the possibility that the dual fluorescence arises from excited DCM in the ^1L_a and ^1L_b states as proposed originally by Lippert *et al.* [6] to explain the dual fluorescence observed in *p*-*N*,*N*-dimethylaminobenzonitrile. However, the independence of the long-wavelength fluorescence maximum leads us to believe that it originates from excited DCM in the ICT state with a twisted conformation formed by internal rotation of the D moiety with simultaneous ICT from this group to a suitable acceptor orbital. This twisted intramolecular charge transfer state (TICT) was first reported by Grabowski and coworkers [7] in an investigation of dual fluorescence in a number of structurally different compounds such as *p*-cyano and *p*-(9-anthryl) derivatives of *N*,*N*-dimethylaniline in polar solvents. However, it should be noted that the difference between the short- and long-wavelength maxima of the dual fluorescence of DCM is somewhat smaller than that calculated for *p*-*N*,*N*-dimethylaminobenzonitrile. This may be because the larger separation between the D and A moieties in DCM leads to a smaller fraction of charge transfer than that for the TICT state characterized by a perpendicular conformation of D and A moieties.

Therefore the experimental data presented in this paper enable us to conclude that locally excited DCM and DCM in ICT states with planar and

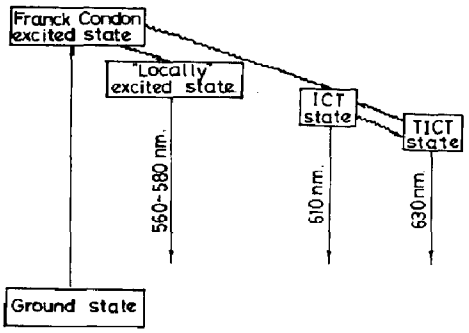

Fig. 3. Schematic diagram of the dynamic behaviour of low-lying excited singlet states of DCM.

twisted conformations are responsible for the fluorescence observed in various solvents. The dynamic behaviour of the low-lying excited singlet state of DCM is shown in Fig. 3.

Acknowledgments

The authors are indebted to Professor S. H. Lin, Arizona State University, and Professor Qian Renyuan for helpful discussions.

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