

PHOTOPHYSICAL PROPERTIES OF THE DCM AND DFSBO STYRYL DYES CONSEQUENCE FOR THEIR LASER PROPERTIES

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The two styryl dyes, 4-dicyanomethylene-2-methyl-6-*p*-dimethylaminostyryl-4H-pyran (DCM) and 7-dimethylamino-3-(*p*-formylstyryl)-1,4-benzoxazin-2-one (DFSBO) exhibit similar solvent-induced shifts of their absorption and emission spectra related to a large intramolecular charge transfer (ICT) in the first singlet excited state. From the Stokes shift values ($\nu_A - \nu_F$) and a vectorial analysis of their ground state dipole moment ($\mu_g = 6.1$ D for DCM and 5.8 D for DFSBO), and using the Lippert-Mataga theory, we have estimated the dipole moments of their fluorescent excited states S_1 ($\mu_e = 26.3$ D for DCM and 27.6 D for DFSBO). Intersystem crossing to the triplet state is totally inefficient in DCM but significant in DFSBO. Moreover the absorption of the DFSBO triplet is quite large in the emission band (600–650 nm), which makes of DFSBO a poor laser dye. Although DCM *trans-cis* photoisomerization can be quite efficient in non polar solvents (chloroform, tetrahydrofuran), DFSBO does not photoisomerize probably due to steric hindrance and to the S_1 character which should be more “benzoxazinone” than ethylenic. DFSBO is also shown to exhibit rotamerism.

INTRODUCTION

The two styryl dye molecules, 4-dicyanomethylene-2-methyl-6-*p*-dimethylaminostyryl-4H-pyran (DCM) and 7-dimethyl-amino-3-(*p*-formylstyryl)-1,4-benzoxazin-2-one (DFSBO) have very similar absorption spectrum maxima in the 450–500 nm range which depend strongly on the solvent polarity. It was interesting to compare their photophysical and photochemical properties since DCM is a widely used laser dye^{1,2} because of its broad tunability and high conversion efficiency under flash-lamp,^{3,4} XeCl,⁵ argon ion laser,⁶ second harmonic output of a Q-switched Nd: YAG laser^{7,8} and copper vapor laser^{9,10} pumping. DCM spectral properties are remarkable as regards the weak overlap between the absorption spectrum and the emission spectrum, i.e. to the large Stokes shift ($\nu_A - \nu_F$)³ which is also valuable in luminescent solar concentrators.^{11–14} The DCM spectral shift of the absorption and fluorescence spectra with solvent polarity^{15–23} is related to the intramolecular charge transfer due to the presence of an electron donor group and an electron acceptor group on each side of the ethylenic bond.²⁴ In a preliminary study,¹⁸ we have determined the dipole moment increase upon DCM electronic excitation using the DCM Stokes shift values ($\nu_A - \nu_F$) in 25 solvents and the Lippert-Mataga theory.^{25–28}

$\mu_e - \mu_g = 20.2$ D. A vectorial analysis enabled us to estimate the DCM ground state dipole moment $\mu_g = 6.1$ D and thus that of the DCM fluorescent singlet state $\mu_e = 26.3$ D.¹⁸ More recently in an attempt to describe fully the photophysical properties of DCM and the surprising monoexponential behaviour of the fluorescence decay obtained in time correlated single photon counting (TCSPC) experiments with nanosecond flashlamp excitation,^{15,16} we undertook TCSPC measurements using tunable picosecond laser pulse excitation.^{20,21,23} They clearly showed the existence of a trans-cis equilibrium in various solvents under ambient light, in good agreement with the findings of Drake *et al.*, who were able to identify the two photoisomers using high performance liquid chromatography (HPLC) and nuclear magnetic resonance spectroscopy (NMR).^{15,17} We thus found that the nonradiative deactivation is governed by two competing processes, $S_1 \longrightarrow S_0$ internal conversion (ic) to the ground state and $S_1 \longrightarrow P^* \longrightarrow$ cis photoisomerization (P^* is the perpendicular excited state). We found that the efficiency of the latter decreases in more polar solvents as due to the lowering of the S_1 zwitterionic potential energy surface which creates a double well potential model and a higher energy barrier to isomerization.^{23,29–32} Our results thus substantiate the theoretical model of Salem *et al.*^{29–32} who took into account the suggestion of Wulfman and Kumei³³ that the presence of any electron-attracting or repelling ion, molecule or group near either end of the double bond will cause more highly polarizable perpendicular 1A_1 (Z) and 1B_2 (v) excited singlet states of alkenes, according to the symmetry designations of Mulliken³⁴ and Kaldor-Shavitt.³⁵ The doubly excited state 1A_1 (Z) is replaced by a low energy S_2 state in the Orlandi-Siebrand model of the photoisomerization of stilbene.³⁶ According to these authors, in low viscosity solvents, S_2 relaxes towards the perpendicular configuration and then undergoes internal conversion to S_0 with an equal chance to relax towards a cis or a trans configuration. This model does not explain the solvent polarity effect on the DCM photoisomerization. Hsing-kang *et al.* have interpreted their fluorescence data by considering two different intramolecular charge transfer (ICT) states of DCM in dynamic equilibrium: a short wavelength emission was assigned to a planar conformation and a long wavelength emission to a twisted (TICT) conformation.¹⁶ More recently the fluorescence decay of DCM was found nonexponential in dibutylether (5 and -35°C) and the main fluorescent state was described as a TICT state.²²

We believe that more experiments are needed to clarify the nonradiative processes in DCM: twisting of the dimethylaminogroup, twisting around the double bond, direct internal conversion and solvent relaxation.

The other dye, DFSBO which belongs to the benzoxazinone family also possesses an electron donor group (dimethylamino) and an electron acceptor group (carbonyl).^{37,38} Le Bris *et al.* have analyzed the shift of the fluorescence spectrum induced by the solvent polarity using the solvent polarity-polarizability parameter π^* of Taft and Kamlet.³⁷ A good correlation was found between the wavenumber of the fluorescence maximum and π^* in aprotic solvents. Despite the small overlap between the absorption spectrum and the emission spectrum and the high fluorescence quantum yield,³⁷ DFSBO did not show a high laser yield under N_2 laser or 532 nm pumping.³⁸

In the present paper in the light of our recent DCM results,²³ we present some new data on DCM and extend our study to DFSBO. We thus gained a better understanding of the effects of the molecular structure and of the solvent which may help to design suitable styryl dye molecules possessing appropriate photochemical reactivity and laser properties.

EXPERIMENTAL SECTION

The nanosecond laser absorption spectroscopy setup has already been described.³⁹ The DCM and DFSBO triplet states were populated via triplet-triplet energy transfer from naphthalene which was excited by the 4th harmonic of a Q-switched Nd: YAG laser.²³

Fluorescence decay profiles were obtained using a TCSPC apparatus which has been described elsewhere.^{20,21,23}

UV-visible absorption spectra were measured with a Beckman UV 5240 spectrophotometer. Fluorescence spectra were obtained with a Perkin Elmer MPF 66 spectrofluorometer. More recently fluorescence quantum yields were measured with a fully corrected Spex Fluorolog 2F111A spectrofluorometer using an ethanolic solution of rhodamine 101 as a reference.⁴⁰

RESULTS AND DISCUSSION

Absorption Spectra

The absorption spectrum and the uncorrected fluorescence spectrum of DFSBO in methanolic solution are given in Figure 1. The absorption spectrum consists of a first electronic transition $S_0 \longrightarrow S_1$ located at 483 nm and two other electronic transitions

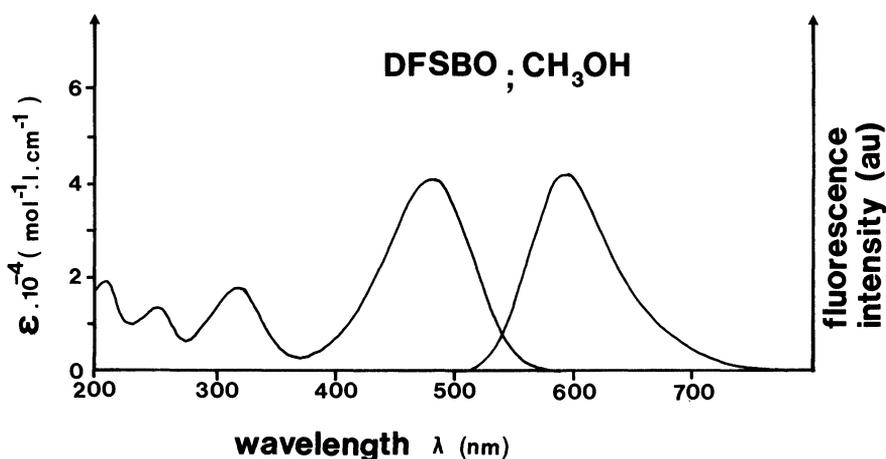


Figure 1 Absorption and fluorescence of DFSBO in methanol.

Table 1 Comparison of some DFSBO properties in different solvents: maximum absorption and fluorescence wavelengths λ_A and λ_F , energies E_A and E_F , Brooker's parameter χ_R , Stokes shift ($\nu_A - \nu_F$), refraction index n_D^{20} , static dielectric constant ϵ , function $\Delta f(\epsilon, n_D^{20})$

Solvent	λ_A (nm)	λ_F (nm)	E_A (kcal/mol)	E_F (kcal/mol)	χ_R (kcal/mol)	$(\nu_A - \nu_F)$ (cm^{-1})	n_D^{20}	ϵ (20°C)	Δf
Cyclohexane	* 1	468	61,11	56,52	50,0	1650	1,4266	2,023	-0,001
Isooctane	2	469	60,98	56,87	50,9	1441	1,3915	1,94	0,00047
Benzene	* 3	481	59,46	52,48	46,9	2440	1,5011	2,284	0,003
CCl ₄	5	474	60,34	54,79	48,7	1940	1,4601	2,238	0,011
Toluene	* 6	481	59,46	52,57	47,2	2410	1,4961	2,379	0,013
Dioxane	* 7	473	60,47	52,19	48,4	2890	1,4224	2,218	0,021
Bromobenzene	8	492	58,13	51,16	44,6	2436	1,5597	5,47	0,130
Trichloroethylene	9	484	59,09	53,06		2108	1,4760	3,42	0,088
Chlorobenzene	10	489	58,49	51,44	45,2	2464	1,5241	5,708	0,145
Chloroform	*11	488	58,61	51,25	44,2	2570	1,4459	4,806	0,149
Ethyl ether	12	470	60,85	52,57	48,3	2894	1,3526	4,335	0,167
Butyl Acetate	13	478	59,83	51,07	47,5	3063	1,3941	5,01	0,171
Pyridine	*14	492,5	58,07	48,81	43,9	3240	1,5095	12,5	0,212
Dichloromethane	15	489	58,49	50,57	44,9	2766	1,4242	9,08	0,219
Dimethyl sulfoxide	*16	496	57,66	47,43	42,0	3578	1,4770	48,9	0,265
Dimethyl formamide	*17	491,5	58,19	48,15	43,7	3510	1,4305	37,6	0,275
Ethylene glycol	*18	499	57,31	46,50	40,4	3780	1,4318	38,7	0,275
Acetonitrile	19	484	59,09	48,97	45,7	3538	1,3442	38,8	0,306
Methanol	20	483	59,21	48,15	43,1	3869	1,3288	33,62	0,309
Ethanol	21	485,5	58,91	48,47	43,9	3648	1,3611	25,07	0,290
Propanol	22	484	59,09	48,72	44,1	3625	1,3350	20,79	0,275
Isopropanol	23	484	59,09	48,81	44,5	3596	1,3776	18,96	0,274
1-butanol	24	484	59,09	48,81	44,5	3596	1,3993	17,8	0,264
1-pentanol	26	483	59,21	49,06		3551	1,4101	14,27	0,250
1-hexanol	27	483	59,21	49,14		3522	1,4178	13,85	0,248
1-octanol	29	483	59,21	49,31	45,4	3463	1,4295	10,3	0,226
1-décanol	31	481	59,46	49,57		3459	1,4372	8,1	0,205
Propargyl Alcohol	32	502	56,97	47,75	38,9	3226	1,4322	21,6	0,26

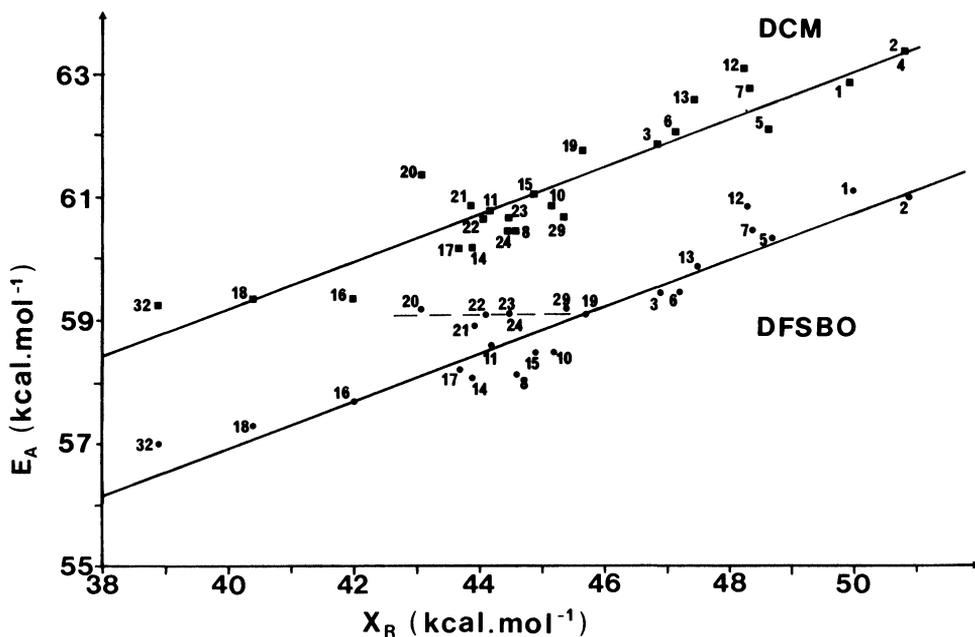


Figure 2 Energies E_A of the absorption transitions $S_0 \longrightarrow S_1$ of DCM and DFSBO as a function of the χ_R Brooker's parameter.

at ~ 320 and 250 nm which are well separated from the first one. This behaviour is very different from that met in DCM which presents badly defined absorption bands below 400 nm.²³ The DFSBO absorption spectrum is reminiscent of the absorption spectra of homologous benzoxazinone derivatives which do not possess the *p*-formylstyryl group in the 3-position.³⁸ Although the DFSBO absorption and fluorescence spectra are largely red-shifted with respect to those of the 3-methyl-substituted benzoxazinone, they indicate that the first excited singlet state S_1 of DFSBO keeps more benzoxazinone than ethylenic character. Such a behaviour has been already demonstrated in the case of naphthyl and phenanthryl stilbene derivatives.^{41–46} Mazzucato pointed out that the rotation around their ethylenic bridge is thus hindered by high activation energies and resulting low rate constants k_{tp} for the twisting from the *trans* (*t*) to the perpendicular (*p*) configuration. Mazzucato concluded that choosing the S_1 energy of a side group was a way to transform a highly photoreactive material in a nonreactive highly fluorescent one.⁴⁵ The energy E_A of the DFSBO absorption maximum (*Table 1*) correlates excellently with the χ_R solvent property indicator (transition energy of Brooker's merocyanine VII^{18,47} as shown in *Table 1* and *Figure 2*. χ_R is to be used for the red shift of the absorption maximum of weakly polar merocyanine dyes in solvents of increasing polarity.⁴⁷ The plot of E_A (in kcal mol⁻¹) versus the available values of χ_R is a straight line with a correlation coefficient of 0.97 .²⁴

$$E_A (\text{DFSBO}) = 0.386 \chi_R + 41.47 \quad (1)$$

The difference of the E_A values in isooctane and propargyl alcohol is 4.0 kcal.mol⁻¹ in DFSBO, about the same as in DCM¹⁸ but much smaller than the one registered by Brooker for merocyanine VII ($\Delta\chi_R = 12$ kcal.mol⁻¹).⁴⁷ In the case of DCM, a similar plot gave¹⁸

$$E_A (\text{DCM}) = 0.386 \chi_R + 43.72 \quad (2)$$

The fact that the slopes are equal is fortuitous but it shows that both dyes absorption spectra behave similarly with respect to the solvent polarity. The observed red shift of the absorption maximum arises from the combination of a blue shift due to the stabilization of the electronic ground state induced by the orientation of the solvent molecules around the solute and a red shift due to the stabilization of the Franck-Condon electronic excited singlet state resulting from the electronic polarization of the solvent (dispersion term). Short range interactions such as hydrogen bonding are not taken into account as one can see in Figure 2 for *n*-alcohols (solvents 20–24) which induce a slightly different behaviour. The effect of the solvent electronic polarization can be expressed following the theory based on the reaction field of Onsager that Bayliss applied to merocyanines in apolar solvents.⁴⁸ The plot of the DFSBO transition energy E_A (in kcal.mol⁻¹) versus the $(n^2 - 1)/(2n^2 + 1)$ function of the solvent refractive index in 9 apolar solvents is a straight line with a correlation coefficient of 0.94 (Figure 3)

$$E_A = -60.03 \frac{n^2 - 1}{2n^2 + 1} + 72.84 \quad (3)$$

We have also estimated the effect of the electron acceptor group (CHO) on the absorption transition maximum by calculating in acetonitrile the difference (2.6 kcal.mol⁻¹) between the energies of the absorption transition maxima of DFSBO, $\lambda_{\text{max}} = 484$ nm, i.e., $E_A = 59.1$ kcal.mol⁻¹ (this work) and BOZ-H or 7-dimethylamino-3-styryl-1,4-benzoxazin-2-one, $\lambda_{\text{max}} = 463$ nm, i.e., $E_A = 61.7$ kcal.mol⁻¹.⁴⁹ It must be emphasized that the simple picture of a charge transfer from the dimethylamino electron donor group to the formyl electron acceptor end group is not correct since the para-substitution of the styryl by a dimethylamino group gives a compound BOZ-NMe₂ which exhibits a greater red shift of the absorption maximum, $\lambda_{\text{max}} = 488$ nm, i.e., $E_A = 58.6$ kcal.mol⁻¹.⁴⁹

Fluorescence Spectra

Pure solvents

The DFSBO fluorescence spectra are largely red shifted with respect to its absorption spectra.³⁷ The wavelengths of the fluorescence maxima λ_F in 28 solvents are gathered in Table 1, together with the transition energies E_F , Stokes shift values ($\nu_A - \nu_F$) (in cm⁻¹) and solvent properties, refraction index *n*, static dielectric constant ϵ and Δf values of the Lippert and Mataga theories.^{25–28,18} A plot of $(\nu_A - \nu_F)$ versus Δf gives a straight line for solvents 8–32 in the range $0.09 \leq \Delta f \leq 0.31$, with a correlation coefficient of 0.93 (Figure 4).

$$10^{-3} (\nu_A - \nu_F) = 7.43 \Delta f + 1.56 \quad (4)$$

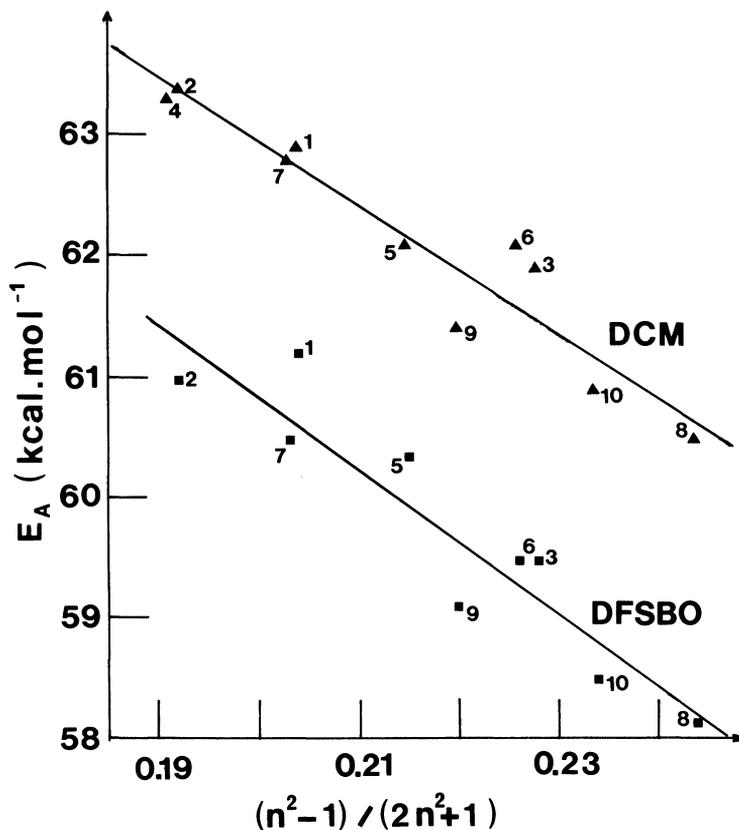


Figure 3 Energy E_A of the absorption transition $S_0 \rightarrow S_1$ of DCM and DFSBO as a function of $(n^2 - 1)/(2n^2 + 1)$.

The non polar solvents (1–7) must be excluded since according to Lippert some additional terms cannot be neglected in equation (4) when $\epsilon \sim n^2$.

We must confess that the wavelengths of the fluorescence maxima are only average of the values obtained for two excitation wavelengths situated on both sides of the absorption band. We shall see later that the DFSBO fluorescence spectrum depends on the excitation wavelength due to the coexistence of rotamers.

From the slope m of the straight line, we calculated $(\mu_e - \mu_g)$ the difference between the dipole moment of the excited state and that of the ground state using equation (5)

$$m = \frac{2}{h c_o} \frac{(\mu_e - \mu_g)^2}{a^3} = 7.94 \times 10^3 \text{ cm}^{-1} \quad (5)$$

where a is the radius (in Å) of the spherical cavity in Onsager's theory of the reaction field, h is Planck's constant and C_o is the speed of light. With a $\sim 8.6 \text{ Å}$, obtained from the estimation of the ellipsoid half long axis, we found $(\mu_e - \mu_g) = 21.8 \text{ D}$. The

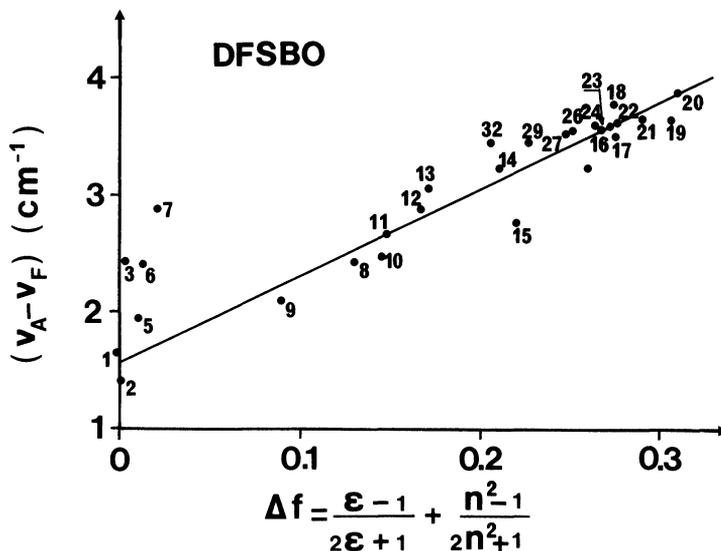


Figure 4 DFSBO Stokes shift ($\nu_A - \nu_F$) as a function of Δf Lippert's parameter.

DFSBO ground state dipole moment was calculated using a vectorial analysis of the various group dipole moments,^{18,24} $\mu_G = 5.8$ D. Therefore $\mu_e = 27.6$ D. These values are different from those obtained by Valeur *et al.* in a PPP (Pariser-Parr-Pople) calculation $\mu_g = 8.7$ D and $\mu_e = 20.5$ D.⁵⁰ Our experimentally estimated value ($\mu_e - \mu_g$) is thus much higher than the theoretically calculated value $\mu_e - \mu_g = 11.8$ D of Valeur *et al.* A more precise estimation is not possible at the present time.

We however conclude that DCM^{18,19,23} and DFSBO (this work) both undergo a large intramolecular charge transfer upon excitation in their fluorescent excited state.

Solvent mixtures

Because of the large shifts of the absorption and fluorescence spectra in increasing polarity solvents, it appeared to us interesting to study the spectral behaviour of DCM and DFSBO in solvent mixtures. We chose methanol-dimethylsulfoxide (DMSO) mixtures since DCM is largely used as a laser dye in both pure solvents. The wavelengths λ_A , the transition energies E_A of the maxima of the absorption spectra, the wavelengths λ_F , and the transition energies E_F of the maxima of the fluorescence spectra of DCM and DFSBO are gathered in Table 2 together with the volumic percentages of methanol. E_A and E_F of both dyes are linearly related to the methanol volumic percentages (X) as shown in Figure 5 and Figure 6. These data indicate that there is no preferential solvation of DCM or DFSBO and that the solvent shell is an homogeneous mixture. Therefore methanol which might induce hydrogen bonding with these solutes does not look like playing a particular role in the binary methanol-DMSO mixtures.

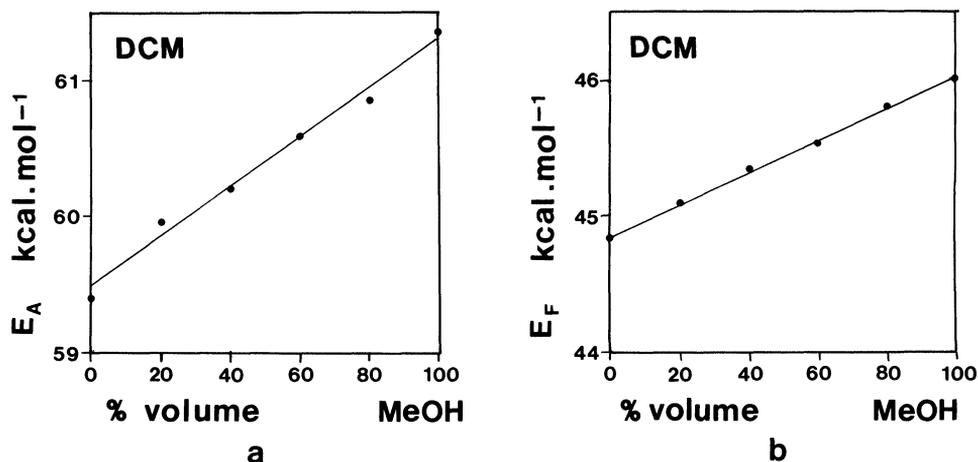


Figure 5 Transition energies of DCM as a function of the methanol volumic percentage in methanol-DMSO mixtures (a) E_A (absorption), (b) E_F (fluorescence).

We have also calculated the relative fluorescence yield R_F of DCM in these binary mixtures by taking Φ^F (DMSO) as a reference. R_F decays linearly with X according to equation (6) with a correlation coefficient of 0.965

$$R_F = -0.0036 X + 0.953 \quad (6)$$

$$0 < X < 100$$

Our R_F value for DCM in pure methanol (0.61 ± 0.06) is in good agreement within the uncertainty errors with the ratio (0.54) one can calculate from the DCM

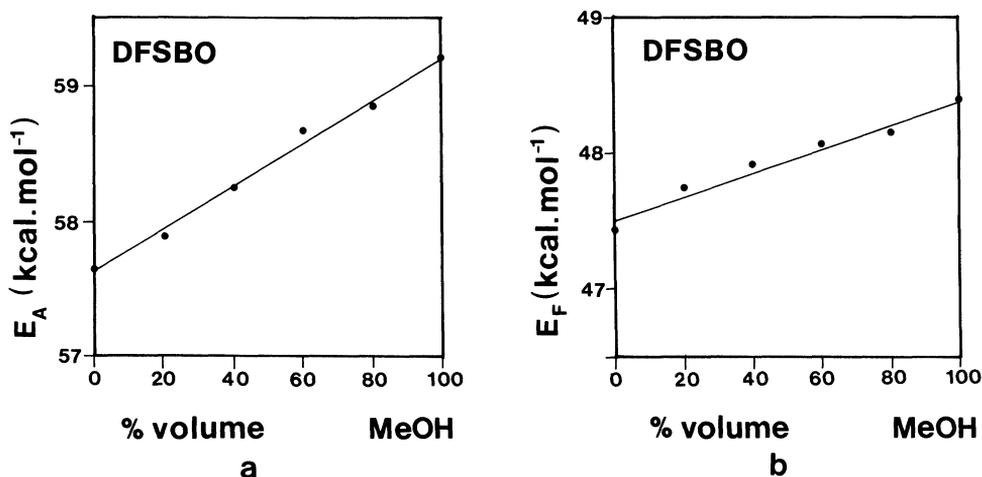


Figure 6 Transition energies of DFSBO as a function of the methanol volumic percentage in methanol-DMSO mixtures (a) E_A (absorption), (b) E_F (fluorescence).

Table 2 Spectral properties of DCM and DFSBO in binary methanol-DMSO mixtures. Maximum absorption and fluorescence wavelengths λ_A and λ_F , energies E_A and E_F , relative fluorescence yields R_F as a function of the volumic percentage of methanol.

DCM					
% Vol. methanol	λ_A (nm)	λ_F (nm)	E_A (kcal.mol ⁻¹)	E_F (kcal.mol ⁻¹)	$R_F = \frac{\Phi_{\text{solvent}}}{\Phi_{\text{DMSO}}}$
0	482	638	59.4	44.8	1
20	477	634	60.0	45.1	0.86
40	475	630	60.2	45.4	0.75
60	472	628	60.6	45.5	0.75
80	470	625	60.9	45.8	0.67
100	466	622	61.4	46.0	0.61

DFSBO				
% Vol. methanol	λ_A (nm)	λ_F (nm)	E_A (kcal.mol ⁻¹)	E_F (kcal.mol ⁻¹)
0	496	603	57.7	47.4
20	494	599	57.9	47.8
40	491	597	58.3	47.9
60	487	595	58.7	48.1
80	486	594	58.9	48.2
100	483	591	59.2	48.4

fluorescence quantum yields Φ^F (DMSO) = 0.80 ± 0.05 and Φ^F (CH₃OH) = 0.43 ± 0.08 measured by Drake *et al.* in 10^{-4} M DCM solutions which contained also cis-isomer.¹⁵ The Φ^F (DMSO) value given by Hammond is 0.71^3 and the recent value Φ^F (CH₃OH) = 0.44 ± 0.04 of Valeur *et al.*⁸ lead to $R_F = (0.62 \pm 0.10)$.

These curves are of a particular interest if by using a solvent mixture one intends to shift the DCM absorption spectrum for a better pumping by a copper vapor laser for example or to get more gain at a particular wavelength in the red.

DFSBO Fluorescence and Excitation Spectra

As we indicated above, the maxima and the bandwidths (FWHM) of the DFSBO fluorescence spectra depend largely on the excitation wavelength (*Table 3*). The fluorescence and excitation spectra of DFSBO in butyl acetate solution are given as an example in Figure 7. In non polar solvents, isooctane, CCl₄, trichloroethylene, the number and the intensity of well resolved vibronic bands dramatically depend on the observation wavelength. The DFSBO fluorescence spectra in isooctane solution are given in Figure 8a, for two excitation wavelengths 420 and 490 nm. When exciting at 490 nm, the first fluorescence band at 479 nm completely disappears but the band at 534 nm increases significantly. The DFSBO excitation and absorption spectra in isooctane solution given in Figure 8b and c show also distinct features. The excitation wavelength dependent fluorescence spectra cannot be interpreted on the basis of "edge-excitation-red-shifts" which are sometimes observed in viscous solvents when the solvent reorientation process is much slower than the emission process.^{51,52} The reorientation time constant of the molecules of the low viscosity solvents under study

Table 3 DFSBO maximum fluorescence wavelengths (λ_{em}) and bandwidths (FWHM) observed in various solvents for different excitation wavelengths.

<i>Solvent</i>		λ_{ex} (nm)	λ_{em} (nm)	<i>FWHM</i>
Isooctane	2	420	479, 502, 534	
		510	502, 534	
CCl ₄	5	400	502, 521, 553	
		460	502, 521, 553	
		500	521, 553	
Bromobenzene	8	450	557	79
		490	559	77
		510	560	72
Trichloroethylene	9	420	512, 538	
		520	540, 575	
Chlorobenzene	10	440	554	77
		520	558	70
Ethyl ether	12	390	540	75
		530	547	72
Butyl Acetate	13	400	555	80
		530	568	74
Dichloromethane	15	430	562	79
		500	565	75
		520	569	70
Acetonitrile	19	450	581	82
		510	590	79
Methanol	20	400	589	85
		550	598	76
Ethanol	21	410	585	81
		540	593	78
Propanol	22	420	585	81
		430	585	85
		530	593	80
Isopropanol	23	450	583	81
		520	590	79
Butanol	24	440	582	82
		520	590	80
Pentanol	26	470	581	82
		500	585	81
Hexanol	27	450	579	82
		500	586	82
Octanol	29	440	576	84
		520	583	79
Decanol	31	450	573	86
		500	580	84
Propargyl Alcohol	32	440	598	81
		520	601	81

is indeed much shorter (<100 ps) than the fluorescence lifetime which is on the order of one nanosecond. Moreover the observation of different vibronic bands is certainly the best proof that several configurations of DFSBO are involved.

Fluorescence Lifetimes

The fluorescence lifetimes of DCM measured using the TCSPC apparatus have been published elsewhere.^{20,21,23} Some observed two exponential decays showed that an

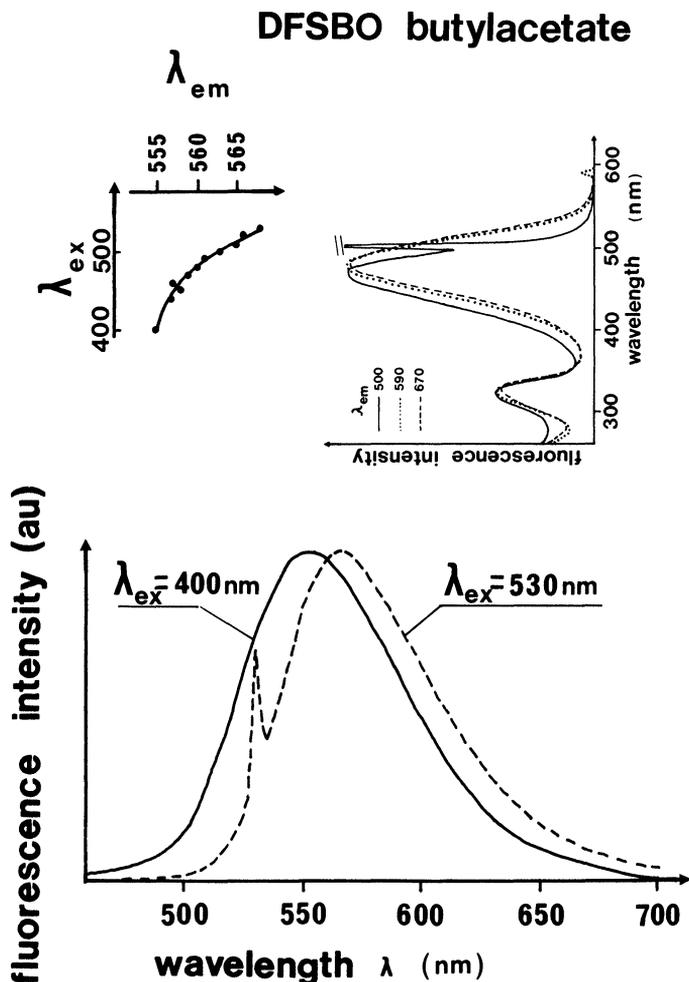


Figure 7 Fluorescence spectra of DFSBO in butylacetate for two excitation wavelengths. On top, excitation spectra for three emission wavelengths.

equilibrium between two trans-cis isomers could be attained very rapidly under room light even in methanol although the photoisomerization quantum yield was very low. For solutions which were freshly prepared and kept in the dark, the DCM decay lifetime was found monoexponential. We recently found in methanol solutions that the monoexponential decay time was depending on the presence of oxygen. In methanolic solutions flushed with argon, the DCM fluorescence decay time was $\tau = (1.41 \pm 0.01)$ ns but in aerated methanolic solutions, it was $\tau = (1.36 \pm 0.01)$ ns⁵³ in perfect agreement with the value of the trans-isomer fluorescence decay (1.37 ± 0.01) ns obtained in our previous two exponentials decay analysis of room light exposed aerated solutions.²¹ The DCM fluorescence lifetime in methanol is thus shorter than that of DFSBO in ethanol $\tau = 2.9$ ns as measured by Le Bris *et al.*³⁷

Photostability under Laser Pulse Excitation

The UV-visible absorption spectra of freshly prepared solutions of DFSBO in methanol or DMSO and submitted to laser pulse excitation at 532 nm indicate a decrease of the absorbance around 490 nm and 320 nm and an absorbance increase between 350 and 420 nm. Isosbestic points are found at 317, 353 and 440 nm. The spectral change is found irreversible. In order to understand the nature of the new species formed under light irradiation, we compared the NMR spectra of DFSBO in

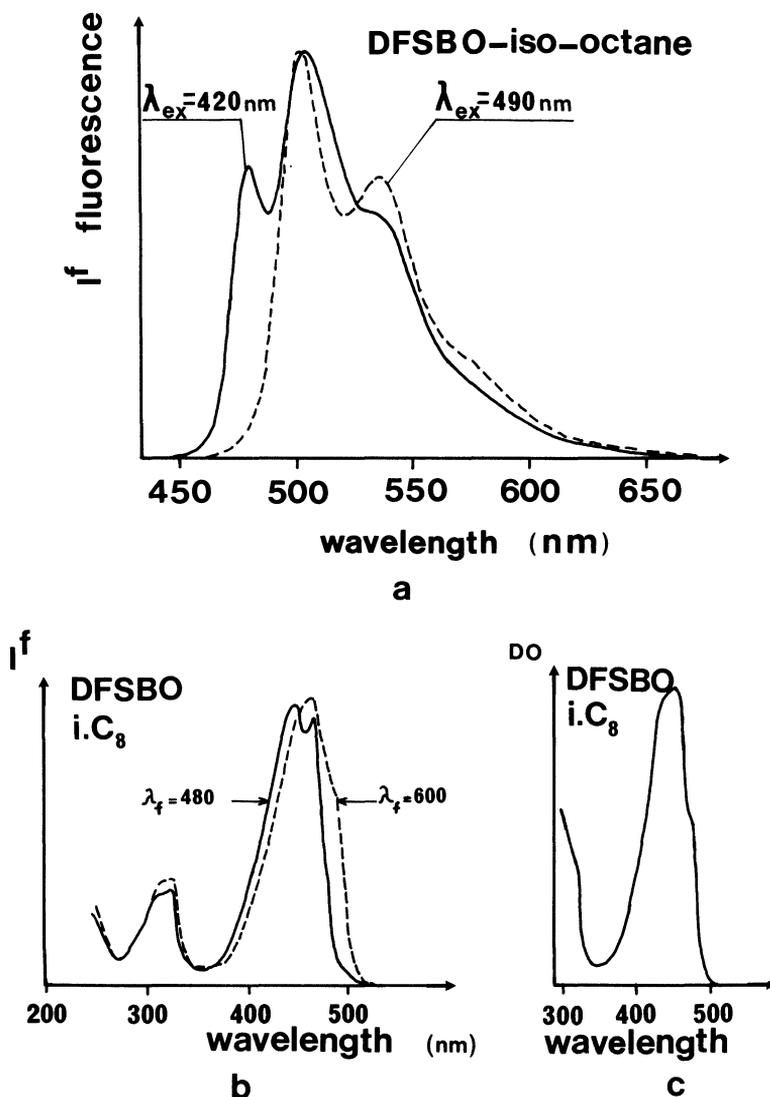


Figure 8 DFSBO-iso-octane. (a) Fluorescence spectra for two excitation wavelengths. (b) Excitation spectra for two emission wavelengths. (c) Absorption spectrum.

deuterated chloroform solutions freshly prepared and kept in the dark to those of solutions submitted to the visible light ($420 < \lambda < 580$ nm) of a xenon arc lamp during three hours. Although new peaks could be observed, they did not present the characteristics of a cis-isomer²⁴ as observed in the case of DCM.²³ Moreover the photostability of solutions flushed with argon was largely improved.

Nanosecond Laser Photolysis

Absorption spectrum of the first singlet excited state of DFSBO.

The DFSBO excited singlet state generated in $10^{-5} - 2 \times 10^{-5}$ M DFSBO methanolic solutions using nanosecond laser excitation at 532 nm presented a differential absorption spectrum with a minimum at 480 nm (photobleaching of the ground state), a maximum around 380 nm and two isosbestic points at 410 and ~ 515 nm, as shown in Figure 9. The S_1 absorbance appeared significant for wavelengths greater than 515 nm but an accurate determination of the absorption spectrum in this wavelength range was made impossible due to the amplification of the analyzing light in the fluorescence band. After the fast decay of S_1 within the resolution time of our apparatus (~ 5 ns), a transient absorption spectrum remained at $t \sim 200$ ns showing the photobleaching of the ground state absorbance, a wide absorption band around 400 nm and an isosbestic point at 440 nm. The absorbance change was however very small. The same behaviour was also found in DMSO (Figure 10).

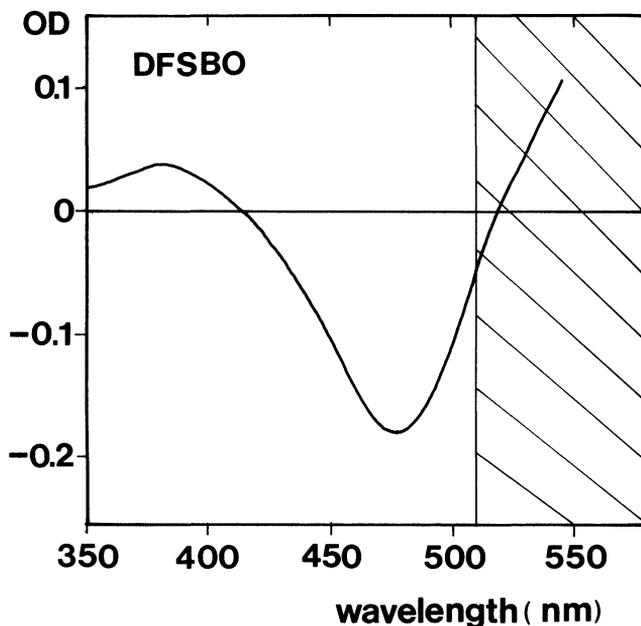


Figure 9 Difference absorption spectrum of the first singlet excited state of DFSBO in methanol. $t \ll 5$ ns.

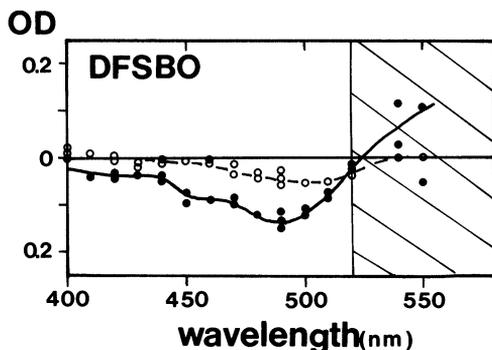


Figure 10 Difference absorption spectra of DFSBO in DMSO. —●—●—●— $t \ll 5$ ns (S_1), —○—○—○— $t = 200$ ns.

Intersystem crossing to the triplet state

532 nm nanosecond laser excitation of a 10^{-5} M DFSBO methanolic solution flushed with argon gave a significant 650 nm transient absorbance which disappeared in aerated solution (Figure 11). The difference absorption spectrum presents an absorbance maximum at 660 nm, a large photobleaching at 490 nm and two isosbestic points at 440 and 535 nm. It decays with a lifetime $\tau = (52 \pm 5) \mu\text{s}$. This spectrum was already observed in the nanosecond time range after the S_1 decay. At $t = 400 \mu\text{s}$, a small residual absorbance is observed below 450 nm and over 530 nm together with a small photobleaching of the DFSBO ground state absorbance.

In order to ascertain that the $52 \mu\text{s}$ lifetime transient absorbance was that of the DFSBO triplet state, we also used naphthalene as a sensitizer in triplet-triplet energy transfer experiments as we did before in the case of DCM.²³ The kinetics of the energy transfer was analyzed at 480 nm, the wavelength of the absorption maximum of the DFSBO ground state which gave a better signal. The plot of the pseudo first order rate constant k of the DFSBO ground state photobleaching versus the DFSBO

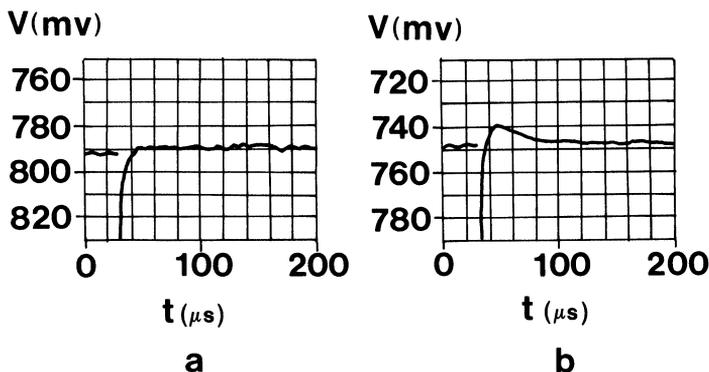
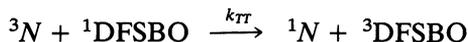


Figure 11 Oxygen effect on the 650 nm transient absorbance of DFSBO in methanol. (a) Aerated solution, (b) Deaerated solution.

concentration gave the bimolecular second order rate constant $k_{TT} = (2.3 \pm 0.3) \times 10^{10} \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$. The energy transfer is thus diffusion controlled.



Using this method we were able to determine the absorption spectrum of the DFSBO triplet state in methanolic solutions containing $1.8 \times 10^{-4} \text{ M}$ naphthalene and $2.5 \times 10^{-5} \text{ M}$ DFSBO. The DFSBO triplet molar extinction coefficient was calculated using the literature molar extinction coefficient of the naphthalene triplet $\epsilon^{415\text{nm}} = 4 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ and the naphthalene initial triplet absorbance obtained in DFSBO free methanolic solutions containing only naphthalene. We indeed assumed a complete energy transfer since the naphthalene triplet lifetime was respectively 70 and $1.4 \mu\text{s}$ in the absence and in the presence of DFSBO. The DFSBO triplet molar extinction coefficient is thus $\epsilon_T^{660\text{nm}} = (5.0 \pm 0.5) 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$. The difference absorption spectrum and the calculated absorption spectrum of the DFSBO triplet are given in Figure 12.

The DFSBO intersystem crossing quantum yield $\Phi_{S_1 \rightarrow T_1}$ was then calculated using 3,3'-diethyloxadicarbocyanine iodide (DODCI) as an actinometer.^{23,54,55} DODCI and DFSBO were alternatively excited at 532 nm in deaerated methanolic solutions which were adjusted to a 0.15 absorbance. We verified that the concentrations of the resulting species, DODCI photoisomer and DFSBO triplet were linear with the laser intensity. The DODCI photoisomer was monitored at 620 nm ($[P] = 5.1 \times 10^{-7} \text{ mol} \cdot \text{dm}^{-3}$) and the DFSBO triplet at 660 nm ($[T] = (5.6 \pm 1.0) \times 10^{-8} \text{ mol} \cdot \text{dm}^{-3}$). Using the DODCI photoisomerization quantum yield in

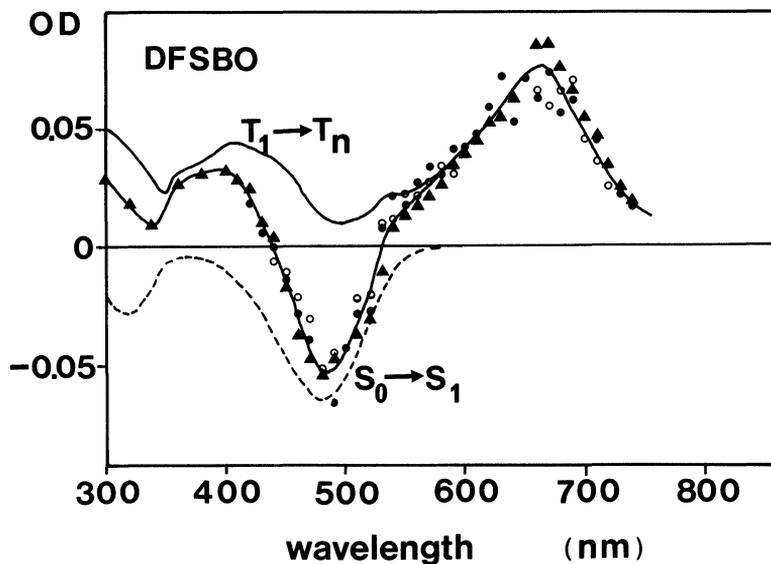
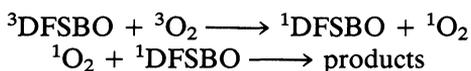


Figure 12 Normalized difference absorption spectra of the DFSBO triplet state in methanol —●—●—●—, calculated absorption spectrum of the triplet state ———, corresponding photobleaching of the ground state - - - -.

methanol, $\Phi_p = 0.07$,⁵⁶ we thus calculated $\Phi_{S_1 \rightarrow T_1}^{\text{DFSBO}} = (8 \pm 2) \cdot 10^{-3}$ which is definitely higher than the DCM estimated upper value $\Phi_{S_1 \rightarrow T_1}^{\text{DCM}} \ll 3 \times 10^{-3}$.²³

DCM and DFSBO Photophysical and Photochemical Properties

Unlike DCM which exhibits a very low quantum yield of intersystem crossing to the triplet state and a low triplet molar extinction coefficient in the 600–650 nm laser wavelength range, $\epsilon_{T, \text{DCM}}^{600-650\text{nm}} < 10^4 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{cm}^{-1}$,²³ DFSBO is characterized by a significantly larger $\Phi_{S_1 \rightarrow T_1}^{\text{DFSBO}} = (8 \pm 2) \times 10^{-3}$ and a more important triplet molar extinction coefficient $\epsilon_{T, \text{DFSBO}}^{600-650\text{nm}} > 2.5 \times 10^4 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{cm}^{-1}$. The build up of a significant DFSBO triplet population under laser pumping will thus reduce the population of the excited singlet state (i.e. the gain) and enhance the absorption losses.^{57,58} Moreover, we found that DFSBO degrades in aerated solutions, probably via chemical reactions involving the triplet state and the excited singlet oxygen $^1\text{O}_2$



We did not find any evidence of a trans-cis photoisomerization. Our nanosecond laser absorption studies did not show any absorbance than one may ascribe to a short lived cis-isomer. Moreover, NMR experiments did not show the typical doublet of the ethylenic protons of a stable cis-isomer that we observed in the case of DCM.²³

Two major reasons may account for the lack of trans-cis photoisomerization. The first one is the trivial steric hindrance that one may expect by inspection of the molecular structure of the cis-isomer. The second one is the nature of the first singlet excited state. We indicated above that it had more benzoxazinone than ethylenic character. This behaviour should enhance the energy barrier for the twisting from the trans to the perpendicular configuration, as pointed out by Mazzucato for other substituted styrenyl compounds.⁴⁵

Now if one considers the “benzoxazinone” character of the first singlet excited state of DFSBO, one must also keep in mind the resonance structures A and B of coumarin derivatives, as pointed out by Drexhage⁵⁸ (Figure 13). In their first excited singlet state S_1 , the polar form B is predominant. The opposite is true in the ground state. A large Stokes shift is thus observed in coumarine derivatives, particularly coumarins substituted by an heterocyclic substituent into the 3-position (coumarin 6, coumarin 30).⁵⁸ As we indicated above, the simple picture of a charge transfer from the dimethylamino group of the benzoxazinone to the formyl end group is not correct

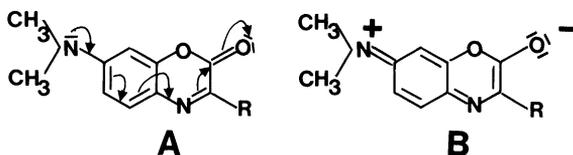


Figure 13 Resonance structures of benzoxazinone derivatives.

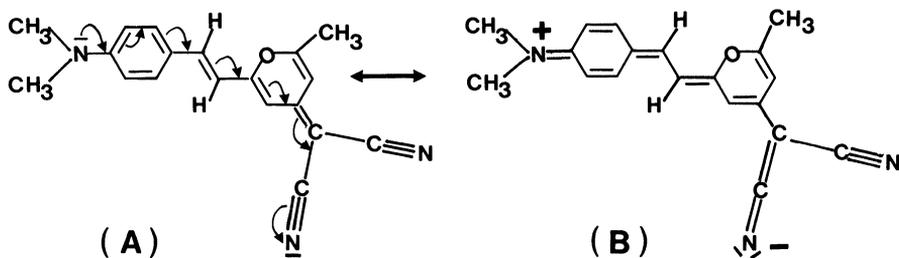


Figure 14 Resonance structures of DCM.

since the para-substitution of the styryl by a dimethylamino group gave an even greater red shift of the absorption maximum. The large Stokes shift of DFSBO has thus a different origin from that of DCM and we conclude that the predominant mesomeric forms of DFSBO and DCM are those represented in Figure 13 and Figure 14.

Let us now come back to the fluorescence and excitation spectra of DFSBO in non viscous solvents. They are dramatically dependent on the observation wavelength. We ascribed the band shifts and the different vibronic bands observed to several configurations of DFSBO. Because we have now rejected the hypothesis of a cis-isomer formation, we believe that these configurations are those of two rotamers resulting from the rotation of the benzoxazinone moiety around the single bond. The occurrence of the rotamers of trans-diarylethylenes is well documented.^{42-46,59-64} The rotamers of compounds which exhibit a variation in the fluorescence spectrum with the excitation wavelength should be almost isoenergetic,⁶³ i.e., they must show a similar steric interaction. One of the two DFSBO rotamers might be stabilized by intramolecular hydrogen bonding, as indicated in Figure 15. The mesomeric form (B) (Figure 13) probably favours this intramolecular hydrogen bonding. In many cases a two exponentials decay has been observed in the fluorescence of trans-diarylethylenes.^{42-44,46,61,63,64} The existence of rotamers is reinforced by the recent observation of a two exponentials decay in cyclohexane according to very recent experiments of Valeur *et al.*⁶⁵ Several simultaneous processes including solvent relaxation probably blurred the analysis in more polar solvents.

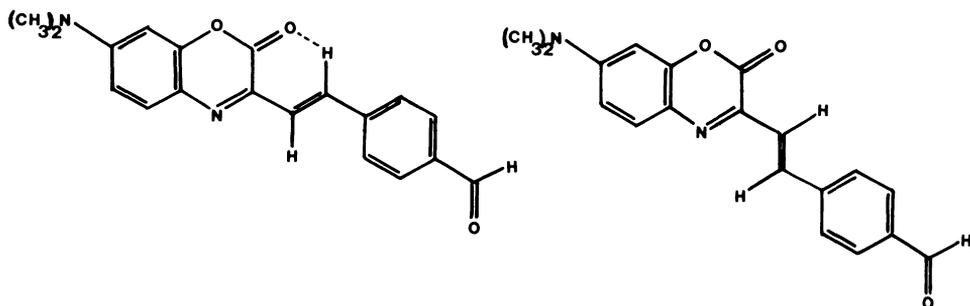


Figure 15 Planar molecular structures of the DFSBO rotamers.

CONCLUSION

Despite the similar behaviour of their absorption and fluorescence spectra in solvents of increasing polarity indicating a large intramolecular charge transfer, the styryl dyes DCM and DFSBO undergo quite different photophysical processes. The nature of the intramolecular charge transfer is different. In DCM the charge is flowing from the dimethylamino end group to the dicyanomethylene end group. In DFSBO, the charge is probably flowing from the dimethylamino end group to the carbonyl group in the 2-position of the benzoxazinone. Intersystem crossing is totally inefficient in DCM but significant in DFSBO. The trans-cis photoisomerization of DCM is efficient in solvents of low polarity (chloroform, tetrahydrofuran) but we have no evidence of a cis-isomer of DFSBO. However, the existence of conformers of DFSBO is clearly demonstrated. They are probably two rotamers resulting from the rotation of the benzoxazinone moiety around the single bond.

We believe that the different behaviour of DFSBO with respect to DCM is related to the "benzoxazinone" rather than ethylenic character of the first singlet excited state of DFSBO.

We have also explained the poor laser action of DFSBO by the significant quantum yield of intersystem crossing to the triplet state and by the high molar extinction coefficient of the triplet state in the emission wavelength range.

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