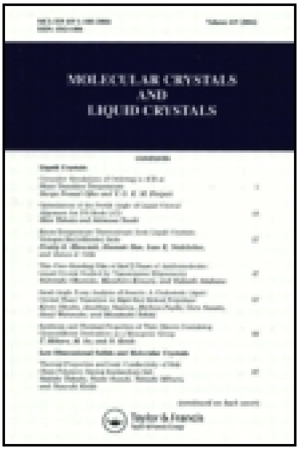

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CHEMICAL ENGINEERING OF FLUORESCENCE DYES

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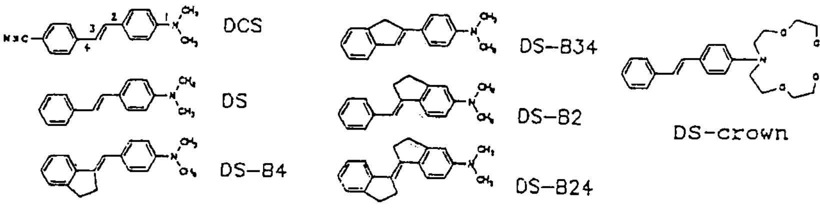
Abstract 4-(N,N-dimethylamino)stilbene (DS), 4-(1-aza-15-crown-5)stilbene (DS-Crown) and four, new, regioselectively bridged 4-(N,N-dialkylamino)stilbene derivatives (DS-B2, DS-B4, DS-B24, DS-B34) have been synthesized and their solvatochromism measured. In ethanol the fluorescence quantum yields were obtained at room temperature (RT) while the lifetimes were measured from 77 K to RT. When the single bond connecting the dialkyanilino group to the double bond is bridged, strong fluorescence quenching is observed; when this bond is flexible the fluorescence quenching is strongly reduced and the lifetime maxima at intermediate temperature indicate the involvement of a further emitting state (TICT). The resulting kinetic scheme led to the design of fluorescence probes for calcium sensing (DS-Crown).

INTRODUCTION

Substituted stilbenes possess several flexible bonds, and it has been shown previously[1,2] that the donor-acceptor compounds like 4,4'-dimethylaminocyano stilbene (DCS), are strongly affected in their photophysical properties by the flexibility or non-flexibility of these bonds. In DCS, double bond twisting leads to fluorescence quenching whereas twisting the adjacent single bonds (bonds 2 and 4 in scheme 1) leads to population of lower-lying fluorescent charge transfer states which competes with fluorescence quenching and therefore raises the fluorescence quantum yield and lengthens the lifetimes[3]. If the cyano group is taken away, as in DS, it can be predicted, on energetic grounds, that only one of the two channels (bond 2) should remain active. We therefore undertook the synthesis of various bridged model compounds of DS (scheme 1) with the expectation that the bridged compounds DS-B2 and DS-B24, where the stabilizing channel is missing, should behave similarly and show much smaller fluorescence quantum yields and lifetimes than the other compounds with flexible bond 2 (DS, DS-B4, DS-B34).

EXPERIMENTAL

The structure of the stilbenes investigated are shown in scheme 1. A Wittig reaction between benzyltriphenylphosphonium chloride and 4-dimethylaminobenzaldehyde led to DS[4] and between benzyltriphenylphosphonium chloride and 4-(1-aza-15-crown-5) benzaldehyde to DS-Crown. The bridged compounds DS-B2, DS-B4 and DS-B24 were synthesized by cross coupling of the corresponding aldehydes and ketones with low valent titanium[5].



SCHEME 1 Molecular structure of donor stilbenes and bridged model compounds.

General procedure for the preparation of the bridged compounds[6]

Titanium tetrachloride (10 mmol) was added dropwise to a stirred suspension of zinc powder (40 mmol) in THF at -10°C under dry argon. The resulting dark mixture was heated under reflux for 2 hours. The suspension was cooled to 18°C and the mixture of carbonyl derivatives[7] (6 mmol) in THF (20 cm^3) was added. The mixture was refluxed and stirred for 2h, cooled and poured into 10% aqueous K_2CO_3 (30 cm^3). The aqueous layer was extracted with ether and the combined extracts were dried and evaporated. Chromatography on silica gel, crystallisation in ethanol and sublimation afforded the following pure trans compounds.

(E)-1-(5-N,N-dimethylamino-1-indanyl)-2-phenylethylene: DS-B2

m.p. = 139°C; Anal. $C_{18}H_{19}N$ requires C,86.7; H,7.68; N,5.62; Found: C,86.6; H,7.81; N,5.46; ^{1}H-NMR (C_6H_6) δ 2,54 (CH_3,s,6H); 2.78-2.91 (CH_2,m,4H); 6.51-7.57 (Ar-H,m,9H). ^{13}C-NMR (C_6D_6) δ 31.3,31.4 [CH_2]; 40.4 [CH_3-N]; 108.4,112.3,115.7, 121.5,125.6 [CH]; 132,139.8,146,147.8,151 [Cq]. MS (m/e): 249 (M^+, 100); 158 (66).

(E)-1-(4-N,N-dimethylaminophenyl)-2-(1-indanyl)ethylene: DS-B4

m.p. = 126°C; Anal. $C_{18}H_{19}N$ requires C,86.7; H,7.68; N,5,62; Found: C,86.33; H,7.65 ; N,5.71; ^{1}H-NMR ($CDCl_3$) δ 3.00 (-CH_3,s,6H); 3.12 (-CH_2-,s,4H); 6.77-7.61 (Ar-H,m,9H). ^{13}C-NMR ($CDCl_3$) δ 30.6,30.9 [-CH_2-]; 40.6 [CH_3-N]; 112.5,119.0,119.7, 125.1,126.5,127.3,129.6 [CH]; 140.0,143.3,145.2,148.9 [Cq]. MS (m/e): 249 (M^+, 100); 134 (18).

(E)-1-(5-N,N-dimethylamino-1-indanyliden)indan: DS-B24

m.p. = 150°C; Anal. $C_{20}H_{21}N$ requires C,87.22; H,7.69; N,5.09; Found: C,86.4; H,7.64; N,5.13; ^{1}H-NMR (C_6H_6) δ 2,59 (CH_3,s,6H); 2.91-3.05 (CH_2,m,8H); 6.60-7.62 (Ar-H,m,7H). ^{13}C-NMR (C_6D_6) δ 31.3,31.7,32.1,32.4 [CH_2]; 40,4 [CH_3-N]; 108.9,111.6, 124.4,125.2,125.8,126.2,126.6 [CH]; 131.4,144.4,146.8,149.1,150.4 [Cq]. MS (m/e): 275 (M^+, 100); 158 (67); 115 (37).

RESULTS AND DISCUSSION

Electronic absorption spectra

The electronic absorption spectra of DS, and DS-B24, in 2-methyltetrahydrofuran (MTHF) at room temperature and at 77 K are presented in figure 1. The sharpening and the red shift of the vibrational sub-bands indicate a larger decrease in the torsion angles of the C-Ph bonds for DS than for DS-B24[8]. DS-B2 and DS-B4 resemble DS. Probably all the compounds have a nearly planar geometry in the glassy solution.

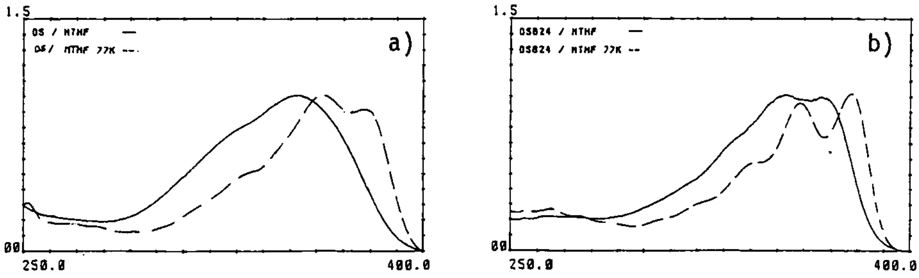


FIGURE 1 Electronic absorption spectra of DS derivatives: a) DS (10^{-4} M in MTHF) at RT (–), at 77 K (- -); b) DS-B24 (10^{-4} M in MTHF) at RT (–), at 77 K (- -).

Fluorescence Spectra:

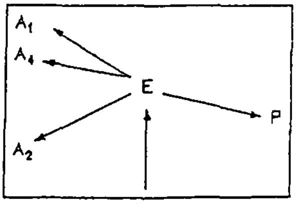
Contrary to the absorption, the emission is strongly redshifted when the polarity of the solvent is increased. The dipole moment of the excited state can be calculated from the Liptay[9] equation (1): $\nu_{fluo} = -2\mu_e(\mu_e - \mu_g)\Delta f/hc\rho^3$ + Const; where $\Delta f = [(\epsilon - 1)/(2\epsilon + 1) - 0.5(n^2 - 1)/(2n^2 + 1)]$ represents a measure for solvent polarity and polarisability. The slope (m) of the plot of ν_{fluo} versus Δf gives the value of $-2\mu_e(\mu_e - \mu_g)/hc\rho^3$, where ρ is the cavity radius estimated from the molecular volume as calculated from the molecular weight and the specific mass of N,N-dimethylaniline (0.95 g/cm^3). Adding the experimental ground state dipole moment of DS (2.41 D[10]) yields μ_e for all the DS derivatives (table 1). The excited state dipole moments of all the DS derivatives (12-14.3 D) are equal within the margin of error of the solvatochromic method.

TABLE 1 Solvatochromic slopes (m; in 10^3 cm$^{-1}/\Delta f$) and dipole moments (Debye units) of DS derivatives obtained according to equation (1) taking into account diethylether, n-butylchloride, dichloromethane and acetonitrile.

	DS	DS-B4	DS-B34	DS-B2	DS-B24
ρ (Å)	4.53	4.70	4.61	4.70	4.86
Slope (m)	-12898	-14348	-13326	-16960	-13843
μ_e	12.01	13.23	12.47	14.27	13.63

Fluorescence quantum yields and lifetimes

They are shown in table 2: in rigid matrix (77 K), the twisting motions are frozen, and only fluorescence from the primary excited state E* results (scheme 2) leading to long lifetimes (1.7 to 2.2 ns) for all compounds. When viscosity gets small enough that intramolecular rotation becomes effective and the increased temperature can help to overcome activation barriers, compounds DS-B2 and DS-B24 efficiently react via the photochemical channel P* (double bond twisting, scheme 2) which shows up in the shortened lifetimes at 163 K. But at that temperature DS and DS-B4 still possess long lifetimes in spite of channel P* being open. This is evidence that in these compounds a further photochemical channel (fluorescence state A_2, reached through twisting around



Scheme 2

bond 2, scheme 2) is available, which protects against non radiative decay via P*. In DS-B2 and DS-B24, this channel (TICT) is absent because of the bridge.

TABLE 2 Fluorescence quantum yields and lifetimes of DS and various bridged derivatives in ethanol at different temperature.

	DS	DS-B4	DS-B34	DS-B2	DS-B24
Φ_f (300 K)	0.035	0.030	0.67	0.002	0.002
τ_f (300 K)/ns	0.11	< 0.1	1.86	< 0.1	< 0.1
(163 K)/ns	1.91	1.80	1.96	0.19	0.12
(77 K)/ns	1.72	2.23	1.90	1.94	1.69

The comparison of the compounds also shows that other possible channels (A_1 and A_4) are not effective presumably because they are energetically too high lying (scheme 2). As the temperature raises further, also A_2 is depopulated via temperature-activated decay towards P* (short lifetimes, low quantum yields at room temperature). Only in DS-B34, where this channel is blocked the lifetime remains long and the quantum yield large at all temperatures.

A DERIVED PROBE CALCIUM SENSING

The substitution of the dimethylaminogroup by the 5-azacrown might allow modulation of the electron donating property of the nitrogen by cation complexation[11]. Indeed the absorption band of DS-Crown is hypsochromically shifted by alkali and alkaline earth metal ions due to an attraction of the lone pair of the nitrogen atom of the crown by the cation which reduces or suppresses the charge transfer.

Fluorescence spectrum of the complexed ligand with calcium perchlorate in CH_3CN and of the free ligand are very close at room temperature and even at -45°C. However in CH_2Cl_2 at room temperature a small band attributed to the complexed probe was detected at short wavelength (figure 2). This fluorescence band increases when the temperature decreases with an isoemissive point.

This behaviour of the excited state can be assigned to a replacement of the crown nitrogen-Ca^{2+} coordination by a CH_3CN-Ca^{2+} interaction at all

This behaviour of the excited state can be assigned to a replacement of the crown nitrogen-Ca^{2+} coordination by a CH_3CN-Ca^{2+} interaction at all temperatures, whereas in CH_2Cl_2 the crown nitrogen-Ca^{2+} interaction is disrupted at high temperature only due to the less favorable CH_2Cl_2-Ca^{2+} interaction.

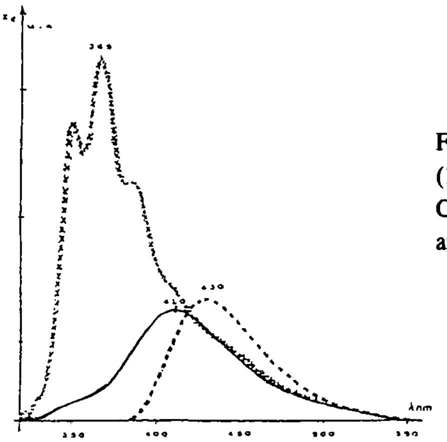


FIGURE 2: Fluorescence spectra of DS-Crown (10^{-6} M in CH_2Cl_2): (- -) free ligand at RT; Complexed ligand with $Ca(ClO_4)_2$, (—) at RT and (***) at 183 K.

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