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Influence of a second donor and of rotational isomers on the solvatochromic properties of ketocyanine fluorophores

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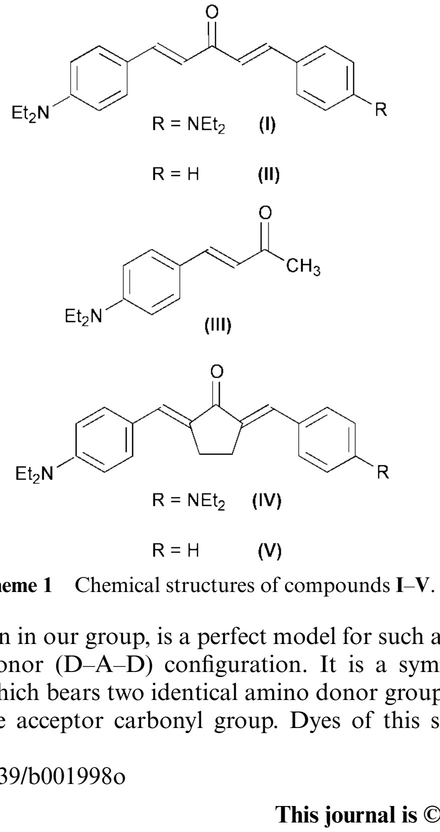
The solvatochromic behaviour of the donor–acceptor–donor system 1,5-bis[4-(diethylamino)phenyl]penta-1,4-dien-3-one (**I**), and two closely related donor–acceptor systems (1-[4-(diethylamino)phenyl]-5-phenylpenta-1,4-dien-3-one (**II**) and 1-[4-(diethylamino)phenyl]but-1-en-3-one (**III**)) was examined in 15 organic solvents. Two rigid analogues of the cyclopentadienone series were examined too. The UV/Vis spectroscopic data were correlated using different polarity scales. It was shown that the presence of a strong second donor induced the Vis absorption maximum to shift to higher wavelengths, and bestowed high sensitivity with respect to the solvent hydrogen-bond donor character. In return, the fluorescence solvatochromism was much reduced. Compounds **I**, **II**, and **III** exist as a mixture of conformational isomers. Therefore, the consequences of this equilibrium upon the solvatochromic properties were investigated through comparison with the blocked analogues. Rigidity resulted in a decrease of sensitivity to solvent variations.

Introduction

The incorporation of distinct donor and acceptor moieties at both ends of a conjugated π-system has long been known to induce long-wavelength emission and sensitivity to the environment. Compounds based on this principle occupy a most important place as dyestuffs, laser dyes, non-linear optical materials, and as fluorescent sensors.[1] Surprisingly, much less attention has been paid to molecules containing two electron-donating groups and a single acceptor group on the same conjugated π-system, and no clear tendency emerges from the reported results.[2,3]

The ketocyanine dye 1,5-bis[4-(diethylamino)phenyl]-penta-1,4-dien-3-one (**I**, Scheme 1), which is presently under investigation in our group, is a perfect model for such a donor–acceptor–donor (D–A–D) configuration. It is a symmetrical molecule which bears two identical amino donor groups linked to only one acceptor carbonyl group. Dyes of this series, as well as closely related ones, are used as photosensitizers,[4] in photopolymer imaging systems,[5,6] and we recently showed that the crown-ether derivatives are efficient fluoroionophores for alkali and alkaline-earth cation recognition.[7] Above all, many authors reported a pronounced dependence of the UV/Vis absorption and emission spectra on the solvent,[4,8–11] so that the use of some of these compounds as polarity probes has been proposed. Therefore, it seemed interesting to us to thoroughly examine the solvatochromic behaviour of **I**, in the hope of getting a better insight into the ground and excited state properties of a D–A–D system. In that aim, **I** was successively studied by UV/Vis absorption and emission spectroscopy, using a large number of solvents, and correlations with classical solvatochromic scales were made. The same study was performed on molecule **II** which lacks one of the amino groups, and chalcone **III** which bears a decreased conjugated π-system.



Scheme 1 Chemical structures of compounds **I**–**V**.

Additional interest in this study emerges from the fact that **I** exists in solution as a mixture of two rotational conformers, *cis,cis* (11%) and *cis,trans* (89%), which differ by the carbonyl–carbon quasi-single bond, as shown in a previous work.[12] The presence of these rotamers has to be taken into account to explain some absorption and emission characteristics of this compound. In particular, it has been shown that UV/Vis absorption is due to both conformers, while emission only results from an excited *cis,cis* species. Consequently, it is important to know whether the solvatochromic properties are affected by the presence of conformers or not. In the present study, we firstly searched for evidence of the existence of such conformers in solutions of **II** and **III**. Afterwards, solvatochromic investigations were extended to analogues **IV** and **V**, which can be considered as blocked *cis,cis* conformers of **I** and **II**, respectively. Comparison indicated the extent to which the loose compounds can be considered as homogeneous polarity probes.

Results

Existence of rotational conformers for II and III

Before undertaking the solvatochromic study, the presence of conformers was investigated for **II** and **III**. Their infrared

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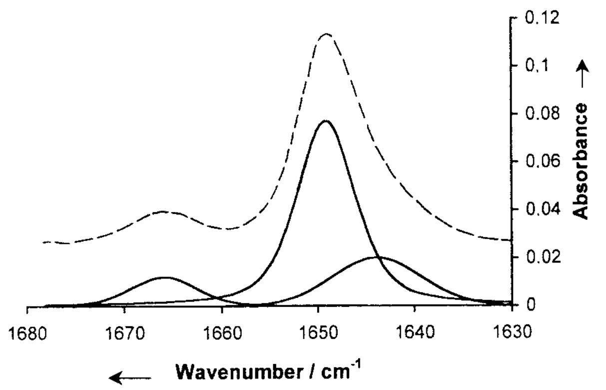
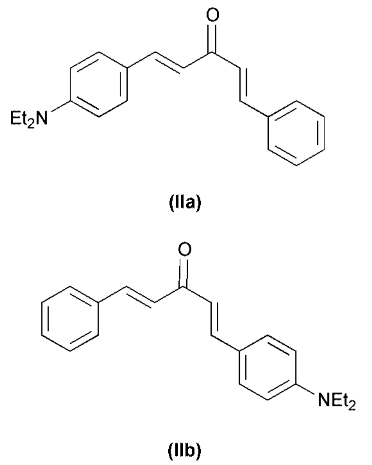


Fig. 1 Infrared spectrum of **II** measured in acetonitrile. Top: spectrum before deconvolution identical to the fit of the reconvoluted spectrum. Bottom: deconvoluted spectrum.

spectra were recorded in a dipolar solvent, acetonitrile, and in a solvent of low polarity in which the dyes are soluble, toluene. Each spectrum displayed a split carbonyl band, indicating the presence of rotamers for these compounds. For **III**, the deconvolution of the IR spectra resulted in two bands which peaked at 1681 and 1658 cm^{-1} in acetonitrile. They were assigned to the *cis* and *trans* conformers, respectively, according to the literature which indicates that *trans* conjugation produces a lowering of the C=O frequency.[13] From the area under the peaks, the *trans* rotamer was estimated to be in a much higher proportion (75% in acetonitrile) than the *cis* rotamer. This agrees well with the conclusions of Venkateshwarlu and Subrahmanyam,[14] who have shown that chalcones bearing electron-releasing substituents mainly exist as the *trans* derivative, where electrostatic repulsions between the C=O and C=C bonds are assumed to be reduced. For compound **II** in acetonitrile, good fits were only obtained when the IR spectrum was deconvoluted with three bands (Fig. 1).

The band centred at 1666 cm^{-1} can then be assigned to the *cis,cis* conformer, while the two bands at lower frequency probably correspond to two different *cis,trans* conformers (forms a and b) of the unsymmetrical compound **II** (Scheme 2), the latter two species being highly predominant. Note that with a toluene solution, a satisfactory fit was obtained with two bands, although this does not exclude the presence of a third band.



Scheme 2 Two rotational conformers for compound **II**.

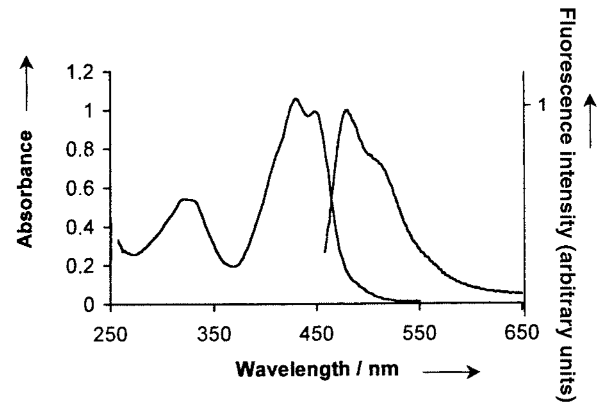


Fig. 2 UV/Vis absorption (around 10^{-5} M, left) and emission (around 10^{-6} M, right) spectrum of **V** in CCl_4. λ_{ex} = 448 nm.

Table 1 Dipole moments (μ) obtained by AM1-MOPAC calculations for the different conformers and infrared characteristics in acetonitrile and toluene: frequency (ν) and relative area of the peaks after deconvolution

Compound		μ/D	Acetonitrile		Toluene	
			ν/cm^{-1}	%	ν/cm^{-1}	%
I[a]	*cis,cis*	4.2	1660	11	1664	23
	cis,trans	5.3	1641	89	1645	77
II	*cis,cis*	4.3	1666	11	1670	25
	cis,trans (a)	4.8	1649, 1644	89	1651	75
	cis,trans (b)	4.4				
III	*cis*	4.9	1681	23	1686	25
	trans	5.4	1658	77	1663	75
IV[a]	*cis,cis*	4.5	1679	100	—	—
V	*cis,cis*	4.1	1685	100	—	—

[a] Ref. 12.

Assignment of the bands was also supported by the fact that their frequency and intensity were affected by the nature of the solvent. The less polar isomers of **II** and **III**, that is the *cis,cis* and *cis* isomers, respectively, according to AM1-MOPAC calculations, were stabilized when decreasing the solvent polarity, as previously shown for **I**. Results are gathered in Table 1, together with those of **I**, which are given for the sake of comparison. It is interesting to note that **III** is less sensitive to a polarity change than the two other compounds. It must also be specified that the infrared spectrum of blocked analogues **IV** and **V** displayed only one C=O band, which is in line with the existence of only one species in these solutions.

Analysis of the UV/Vis absorption data

All five compounds were firstly studied by UV/Vis absorption spectroscopy in 15 different solvents. Aromatic solvents were excluded since they are known to occasionally offer a different solvation mechanism than other solvents.[15] It was shown previously that the spectrum of **I** encompasses the spectra of the *cis,cis* and *cis,trans* conformers, the *cis,trans* species absorbing at slightly lower wavelengths.[12] A similar behaviour can be expected for **II** and **III**, which are also mixtures of conformational isomers. As for **IV** and **V**, the absorption spectrum is that of the pure *cis,cis* species.

Attention was focused on the intense long-wavelength band which has been assigned to a charge transfer from the amino groups to the carbonyl group.[8] A vibrational structure appeared in apolar solvents for all five compounds, particularly well-defined for **IV** and **V**, which is probably due to the rigidity of the molecule. The absorption maximum was recorded for **I**, **II**, **III**, and **IV** in each solvent. For **V**, the relative intensity of two adjacent vibrational bands was inverted in apolar and polar solvents. So, the high-wavelength band was regarded in each case, although it was not the most intense in apolar solvents (Fig. 2).

The absorption maxima λ_{abs} are displayed in Table 2. As expected, the absorption spectrum of **I** peaked at higher wavelengths than that of **II** and **III**, in descending order, which is in line with the extension of the conjugated π-system between

Table 2 Maximum UV/Vis absorption wavelength λ_{abs}, maximum excitation wavelength λ_{ex}, Taft and Kamlet π^* and a parameters (from refs. 16 and 17)

	I		II		III		IV	V		
Solvent	λ_{abs}/nm	λ_{ex}/nm	λ_{abs}/nm	λ_{ex}/nm	λ_{abs}/nm	λ_{ex}/nm	λ_{abs}/nm	λ_{abs}/nm	π^*	a
Diethyl ether	424	426	410	422	370	/	452	444	0.24	0.00
Tetrachloromethane	428	432	414	435	376	377	456	448	0.21	0.00
Trichloroethene	438	445	428	440	384	385	466	452	0.48	0.00
Ethyl acetate	432	437	416	429	374	377	458	442	0.45	0.00
1,4-Dioxane	434	438	418	433	376	379	460	444	0.49	0.00
Tetrahydrofuran	436	437	422	431	378	374	464	446	0.55	0.00
Acetone	440	446	424	440	380	383	466	448	0.62	0.08
Acetonitrile	444	454	428	447	380	383	470	450	0.66	0.19
Chloroform	456	455	438	448	390	395	480	460	0.69	0.44
Dichloromethane	454	456	436	448	386	383	476	456	0.73	0.30
N,*N*-Dimethylformamide	450	453	432	445	384	386	478	456	0.88	0.00
Formamide	486	498	456	468	399	400	506	476	0.97	0.71
Butan-1-ol	466	473	444	453	394	405	488	466	0.47	0.79
Ethanol	466	476	444	454	392	402	492	466	0.54	0.83
Methanol	472	480	446	455	393	398	494	468	0.60	0.93

Table 3 Linear correlations obtained by plotting ν *vs.* π^* and a according to the Taft and Kamlet equation (r = correlation coefficient)

	Absorption				Excitation				Emission			
Compound	$10^{-4}\nu_0$/ cm^{-1}	$10^{-3}s$/ cm^{-1}	$10^{-3}a$/ cm^{-1}	r	$10^{-4}\nu_0$/ cm^{-1}	$10^{-3}s$/ cm^{-1}	$10^{-3}a$/ cm^{-1}	r	$10^{-4}\nu_0$/ cm^{-1}	$10^{-3}s$/ cm^{-1}	$10^{-3}a$/ cm^{-1}	r
I	2.40	−1.91	−1.85	0.99	2.38	−1.93	−2.04	0.97	2.16	−3.98	−3.71	0.97
II	2.46	−1.65	−1.46	0.97	2.37	−1.47	−1.13	0.94	2.11	−5.17	−1.90	0.91
III	2.69	−0.90	−1.17	0.94	—[a]	—[a]	—[a]	—[a]	2.41	−2.75	−2.36	0.95
IV	2.84	−1.53	−1.44	0.98	—[a]	—[a]	—[a]	—[a]	2.15	−3.64	−3.62	0.97
V	2.28	−0.75	−1.13	0.94	—[a]	—[a]	—[a]	—[a]	2.10	−4.49	−1.88	0.91

[a] The excitation maxima being very close or similar to the absorption maxima, the data were not processed again.

these structures. The absorption spectra of **IV** and **V** peaked at higher wavelengths than those of the loose analogues. In the case of **IV**, this effect was previously attributed to the planarity of the molecule, which facilitates π-electron delocalization, while the *cis,trans* conformers of **I** and **II** are twisted molecules.[12] It was shown here by AM1 calculation that **V** was a planar structure too.

For all five compounds, the long-wavelength Vis absorption maximum was shifted to the red on increasing the solvent's polarity and acidity. The absorption data were quantitatively analysed. Among many available polarity scales, the Taft and Kamlet scale offers the distinct advantage of separately assessing the effect of both the dipolarity and hydrogen-bonding capacity of the medium.[16,17] It uses the empirical parameters π^*, a, and β, which, respectively, measure the solvent dipolarity/polarizability, hydrogen-bond donor acidity, and hydrogen-bond acceptor basicity. The original equation also uses the δ parameter which is a "polarizability correction term" applied to chlorinated and aromatic solvents. However, abstraction can be made of the β parameter, since the compounds investigated in this work contain no hydrogen-bond donor groups, and of the δ parameter, the coefficient of which is zero for all electronic spectra that are shifted bathochromically on increasing the solvent dipolarity.[17] So, the Taft and Kamlet equation reduces to eqn. (1), in which s and a are the coefficients affected by the

$$\nu = \nu_0 + s\pi^* + aa \qquad (1)$$

π^* and a parameters, respectively. They can be considered as a measure of solvatochromism. The spectrophotometric data were processed according to this equation. Coefficients s and a were determined by multiple linear regression analysis of the absorption maxima of the fluorophores. The results are gathered in Table 3.

Comparing the loose analogues, it appears that the sensitivity to both the dipolarity/polarizability and acidity parameters increased in the order **III** < **II** < **I**. For the rigid compounds **IV** and **V**, the same order was observed, but the s and a values were slightly weaker, especially for **V**.

Analysis of the excitation data

Studying the excitation spectra is particularly interesting for the following reasons. In our former study, the fluorescence of **I** was exclusively attributed to a *cis,cis* excited species. Both excitation and emission spectra were assigned to this species. Hence, differences were found between the excitation spectrum, which arises from the *cis,cis* rotamer, and the absorption spectrum, which reflects the mixture of conformers.

The excitation spectra were recorded in each solvent, setting the emission wavelength at the emission maximum (Table 2). As previously observed for **I**, the excitation spectra of **II** and **III** (to a lesser extent) were red-shifted with respect to the absorption spectra. This is totally in line with the presence of rotamers for these species too, and suggests that the rotamers behave the same way as in **I**. It is noteworthy that plotting the excitation data *versus* the absorption data gives a straight line. This correlation is probably due to the fact that both conformers, having close dipolar moments, display a similar solvatochromic behaviour. After analysis with the Taft and Kamlet scale, a shift of the ν_0 value was observed with respect to the absorption ν_0 for **I** and **II**, but the a and s values remained very close to those found when processing the absorption data (Table 3). Calculations were carried out neither for **III**, since absorption and excitation values were very close, nor for **IV** and **V**, the absorption and excitation specta of which were exactly superimposed.

Analysis of the emission data

In emission, only one intense band was observed for all five compounds. The wavelengths of the maxima are collected in

Table 4 Maximum emission wavelength λ_{em}, Stokes shift ($\nu_{ex} - \nu_{em}$ for **I**, **II** and **III**, $\nu_{abs} - \nu_{em}$ for **IV** and **V**), solvent orientational polarizability parameter $f(D, n)$ (from ref. 20)

	I		**II**		**III**		**IV**		**V**		
Solvent	λ_{em}/nm	Stokes shift/ cm^{-1}	λ_{em}/nm	Stokes shift/ cm^{-1}	λ_{em}/nm	Stokes shift/ cm^{-1}	λ_{em}/nm	Stokes shift/ cm^{-1}	λ_{em}/nm	Stokes shift/ cm^{-1}	$F(D, n)$
Diethyl ether	478	2554	508	4012	/	/	476	1115	505	2720	0.366
Tetrachloromethane	476	2140	479	2112	429	3215	479	1053	480	1488	0.036
Trichloroethene	513	2979	523	3607	438	3279	515	2042	519	2856	0.209
Ethyl acetate	511	3314	550	5128	438	3694	509	2188	543	4208	0.489
1,4-Dioxane	494	2588	521	3901	431	3183	494	1496	517	3180	0.043
Tetrahydrofuran	517	3541	557	5249	437	3855	508	1867	544	4039	0.551
Acetone	549	4206	593	5864	459	4323	547	3178	579	5050	0.790
Acetonitrile	572	4544	615	6111	473	4968	563	3415	598	5500	0.860
Chloroform	549	3763	562	4527	462	3671	549	2618	554	3689	0.372
Dichloromethane	557	3977	580	5080	460	4370	548	2760	567	4293	0.592
N,*N*-Dimethylformamide	562	4281	617	6265	470	4630	555	2902	596	5151	0.836
Formamide	646	4600	651	6007	506	5237	636	4040	631	5160	0.895
Butan-1-ol	611	4775	602	5464	485	4073	604	3935	589	4481	0.751
Ethanol	620	4879	609	5606	489	4426	611	4091	601	4820	0.814
Methanol	640	5208	622	5901	491	4759	632	4420	606	4866	0.855

Table 5 Correlations with the solvent orientational polarizability parameter $f(D, n)$ using eqn. (2) (r = correlation coefficient). Calculated cavity radius a_0 and excited state dipole moment μ_e. For **I**, **II**, and **III**, the ground-state dipole moment μ_g was taken to be that of the *cis,cis* and *cis* conformers

Compound	a_0/pm	$\mu_e - \mu_g$/D	μ_e/D	r
I	512	5.7	9.9	0.86
II	477	6.5	10.8	0.97
III	437	4.4	9.3	0.94
IV	523	5.9	10.4	0.75
V	491	6.5	10.6	0.96

Table 4. The quantitative analysis of the emission data with the Taft and Kamlet scale showed a neat increase of the *s* and *a* values compared with the absorption and excitation data, for all five compounds.

Since emission is due to a *cis,cis* species, the loose analogues were expected to emit close to their corresponding rigid compounds. Actually, the spectra were almost similar in apolar solvents and quantitative analysis confirmed that ν_0 was exactly the same for **I** and **IV**, on the one hand, and for **II** and **V**, on the other hand. However, the gap between the spectra of the loose and rigid compounds widened on increasing the solvent's polarity and acidity. This suggests some differences in the solvatochromic behaviour, as expressed by the *s* and *a* values which were found to be weaker for the blocked analogues.

Among the compounds considered, **III** emitted at the lowest wavelengths. Now, regarding the other compounds, an interesting phenomenon appears. In aprotic solvents, **II** and **V** emitted at higher wavelengths than **I** and **IV**. In protic solvents, the reverse trend was observed, **I** and **IV** emitting at higher wavelengths than **II** and **V**. This behaviour was related to a strong coefficient *s* for **II** and **V** (Table 3), while high values of *a* were found for **I** and **IV**. In other words, in the excited state, mono-amino substituted **II** and **V** became much more sensitive to the dipolarity/polarizability parameter than the other analogues, while bis-amino substituted **I**, and to a lesser extent **IV**, remained the most sensitive to the solvent acidity.

Note that other solvatochromic scales, such as the $E_T(30)$ scale of Dimroth and Reichardt,[18,19] gave excellent linear correlations with the emission data, provided that protic solvents were excluded.

Excited-state dipole moments

A strong positive solvatochromism of fluorescence, like the one encountered here, generally indicates marked intramolecular charge transfer in the excited state. This charge transfer is responsible for solvent reorientation, which results in large Stokes shifts ($\nu_{abs} - \nu_{em}$). Kawski's equation (2) relates the

$$\nu_{abs} - \nu_{em} = (2/hca_0^3)(\mu_e - \mu_g)^2 f(D, n) + \text{const} \qquad (2)$$

Stokes shift of an ellipsoidal fluorophore with the solvent orientational polarizability.[20] In this formula *h* is Planck's constant, *c* is the speed of light, and $f(D, n)$ is the orientational polarizability, defined by eqn. (3), where *D* and *n* are the relative

$$f(D, n) = [(D - 1)/(D + 2) - (n^2 - 1)/(n^2 + 2)]\,[(2n^2 + 1)/(n^2 + 2)] \qquad (3)$$

permittivity and the refractive index, respectively.[21] From eqns. (2) and (3), a plot of the Stokes shift *versus* $f(D, n)$ yields a slope *m* from which the excited-state dipole moment can be calculated [eqn. (4)], provided that the ground-state dipole moment (μ_g) and the cavity radius (a_0) are known.

$$m = 2(\mu_e - \mu_g)^2/hca_0^3 \qquad (4)$$

This processing was undertaken here with well-behaved solvents, *i.e.* aprotic solvents and solvents without a special dispersive force.[22] It was assumed that emission arises from a *cis,cis* species in **I** and **II,** and from a *cis* species in **III**. For this reason, the excitation data which are assumed to correspond to these species, were used instead of the absorption data for **I**, **II**, and **III**. Calculations were carried out by taking the *cis,cis* and *cis* species into account.† The solute cavity radius (a_0) was calculated using the molecular mass of each compound and the density of benzophenone for **I**, **II**, **IV**, and **V**, and of acetophenone for **III**.[23] Good correlations were obtained, with the exception of **IV**, the correlation coefficient of which was not satisfactory. The gap between μ_e and μ_g was particularly wide for **II** and **V** and then narrowed for **IV** and **I**, and even more so for **III**. The calculated dipole moment in the excited state, μ_e, was high for **II** and **V** (Table 5), and slightly lower for **IV**, **I** and **III**.

Discussion

Each compound covered in this work may be regarded as a conjugated D–A–D system. In **I** and **IV**, both amino groups are

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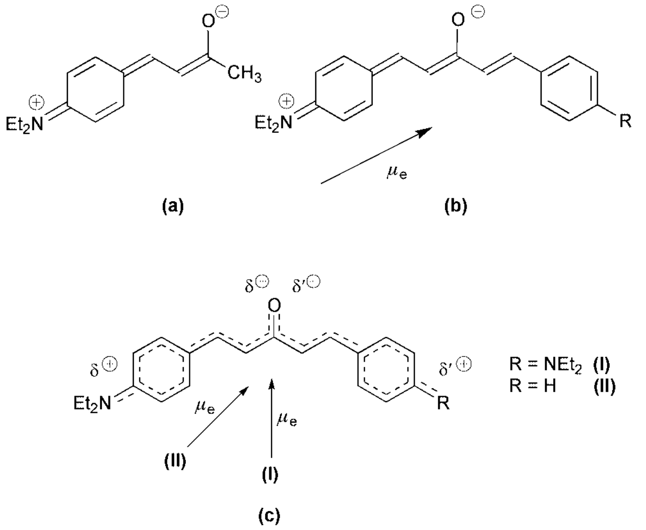
† The possibility that the *cis,trans* and *trans* conformers isomerize to *cis,cis* and *cis* forms, respectively, in the excited state was not considered here. In this case, two rotamers, at least, would be involved in the excitation spectrum. Each rotamer having its own μ_g and *a* values, and its respective proportion being unknown and variable with the solvent, this treatment would be unenforceable.

strong electron donors. In the other analogues, the second donor is very weak, with the difference that the styryl group encountered in **II** and **V** is highly polarizable, which is not the case for the methyl group borne by **III**.

Some information about the structure of these compounds is provided by their dipole moments. These must be considered as the sum of all the dipole moments localized within the molecule. The orientation of the ground-state dipole moments obtained by calculations is known. Let us consider the plane which is perpendicular to the molecule plane and contains the C=O group. For **I**, where the two strong electron donors are symmetrically arranged, the dipole moment lies exactly in this plane. For **III**, the dipole moment describes an angle of 42.3° with respect to this plane. The angle is 34.3° for **II**, indicating that the contribution from the styryl group is not negligible. Regarding the simplest structure, the μ_g values of **III** were found to be around 5 D. For the sake of comparison, the dipole moment of acetone is reported to be 2.88 D, and that of aniline 1.53 D.[24] It can also be calculated that a total charge transfer on **III** would result in a dipole moment of around 40 D. So, for **III** in the ground state, the charge transfer between the amino and carbonyl groups is moderate. Therefore, a form close to the non-ionic structure (Scheme 1) is predominant, in particular in apolar solvents. It may be assumed that a weakly ionic structure is also encountered in the other molecules. This does not exclude the involvement of the *l* orbitals of nitrogen with the π-system, as particularly well evidenced by the wavelength shift observed when passing from dibenzylideneacetone ($\lambda_{abs} = 325$ nm in CH_2Cl_2)[25] to **I**, and then from **I** to **II**. It is interesting to note that the ν_0 value, which corresponds to the $S_0 \rightarrow S_1$ transition in the absence of an interaction with the solvent, is quite close for **I** and **II**. It is identical when only the *cis,cis* species is considered, either by regarding the excitation ν_0 for **I** and **II** or the absorption ν_0 for **IV** and **V**. So, the presence of one amino group makes the first transition easy, owing to charge transfer, but the introduction of a second amino group leads to very little modification of this transition energy.

All five compounds exhibit strong positive solvatochromism. A bathochromic wavelength shift was observed in absorption and in emission, when increasing the solvent's polarity and hydrogen-bond donor acidity. As already noted by some authors, this implies that the first transition is of the π–π* type.[8,10] On the contrary, the n–π* transition often encountered with amino aromatics and carbonyl compounds is known to induce an opposite solvatochromic effect.[26]

It is generally accepted that a dipolar/polarizable solvent stabilizes dipolar solutes by electrostatic interactions. In the same way, the hydrogen bonds formed with a protic solvent stabilize the negative charges localized on atoms and on the unsaturated part of the molecules. The solvatochromic behaviour observed here is typical of an increase of the molecules' dipolarity in the excited state. Processing the UV/Vis spectrophotometric data allowed the value of the excited-state dipole moments μ_e to be estimated. However, these values must be handled carefully. The treatment undertaken assumes that the direction of the dipole moment is unchanged from ground to excited state. As a matter of fact, this direction depends on the involvement of the second donor group, which may vary from ground to excited state. So, the μ_e value must not be regarded as an absolute value of the excited-state dipole moment, but rather as an estimate of solvent reorganization around the solute. For compound **III** only, it can be assumed that the direction of the dipole moment hardly changes upon excitation and that the μ_e value gives a good estimation of the excited-state dipole moment. This value still does not correspond to total charge delocalization. So, the zwitterionic resonance structure (a, Scheme 3) is only approached, and probably favoured by dipolar and protic solvents. Concerning **I** and **II**, the widely delocalized resonance structure b pictured in Scheme 3 may be considered. It corresponds to a dipole moment essentially directed along the D–A axis. However, no element allows a choice to be made between this structure and structure c in which both donor groups participate in the charge transfer. In this last case, a dipole moment orientated closer to the axis of the C=O bond, or lying exactly in this axis, can be expected for **II** and **I**, respectively. It is probable that the molecular structure is indeed intermediate between these extremes.



Scheme 3 Dipolar mesomeric structures of **I**–**III** (a and b) and inductive effect in **I** and **II** (c).

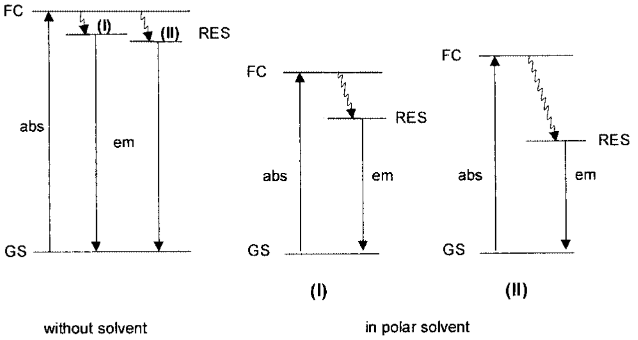
Now, both qualitative and quantitative approaches highlight some differences in the behaviour of the five compounds.

i) The relative proportion of each conformer depends on the solvent. However, despite the existence of this equilibrium, good correlations were obtained between the UV/Vis absorption data and the solvatochromic scales for **I**, **II**, and **III**. Therefore, the loose compounds show no anomalous behaviour as polarity probes.

ii) Rigid compounds **IV** and **V** displayed a loss of sensitivity to solvent variations, both in absorption and emission, with respect to the loose analogues. In particular, *s* values are much reduced. Loose compounds have more vibrational and rotational levels than rigid analogues. In the course of time, their flexibility allows them to take up many instant conformations, each corresponding to an instant dipole moment. It is possible that a dipolar/polarizable solvent may stabilize these fluctuating states better.

iii) The absorption properties of **I** and **IV** strongly depend on the dipolarity/polarizability of the solvent. Above all, these compounds are especially sensitive to solvent acidity, both in absorption and in emission. It is likely that these molecules bear strong localized charges in the excited state, due to the involvement of both amino groups which transfer their charge to the carbonyl group, reinforcing this negative pole.

iv) Mono-amino molecules **II** and **V** become very sensitive to the solvent dipolarity/polarizability, as far as their emission properties are concerned. This means that their *relaxed* excited state is mainly ionic, even if the charges are not as precisely localized as in **I**. It is interesting to see how the relaxed state of **II** is reached, in comparison with **I**. The energy levels are pictured in Scheme 4. The ν_0 values obtained with the emission data indicate that, in the absence of interactions with the solvent, the energy of the $S_1 \rightarrow S_0$ transition is only slightly lower for **II** than for **I**. This difference increases strongly in polar solvents. For instance, in acetonitrile, once the Franck–Condon state has been formed, significant solvent reorganization takes place, especially for **II**, as indicated by the μ_e values. This suggests that the charge distribution, and hence the direction of the dipole moment, varies strongly for **II** between ground and excited state. It can be noticed that this charge redistribution



Scheme 4 Schematic representation of the energy levels for **I** (left) and **II** (right) in vacuum and in acetonitrile. GS = ground state; FC = Frank-Condon state; RES = relaxed excited state.

was much weaker for **III**, and so may be linked to the presence of a polarizable weak donor.

Comparison can be made between this work and that of Anstead and Katzenellenbogen,[3] who studied *trans*-4,4′-methoxynitrostilbenes and methoxynitroindenes. In the latter molecules, both donor groups are placed roughly symmetrically with respect to the acceptor group, as is the case for the molecules investigated here. These authors showed that the monodonor derivatives exhibited larger Stokes shifts than the dual donor analogues, which agrees well with our results. The magnitude of this effect was higher when the donor was more closely conjugated with the acceptor. In contrast, a larger Stokes shift has been reported for a dual donor than for a monodonor benzoxazinone, but the molecule geometry strongly differed from that of the structures studied here.[2]

Conclusion

The solvatochromic scales used in this work allowed the UV/Vis-spectroscopic behaviour of the three compounds to be analysed in a large number of solvents. It was shown that the addition of a strong second donor directly conjugated with the electron-withdrawing group induced the Vis absorption maximum to shift to high wavelengths, but in return the fluorescence solvatochromism was much reduced. Additionally, it appeared that rigidity decreases the sensitivity to solvent variations. The presence of rotational conformers does not prevent the use of these compounds as polarity probes. Therefore, the properties of a polarity probe for a given application can be optimized by modulating the strength and polarizability of the second donor, and by bringing minor structural changes to the rigidity of the molecule. This result is particularly important for the design of sensors which are built on donor–acceptor interactions, like a large number of fluoroionophores.

Experimental

Materials

Spectroscopic grade solvents (Merck and SDS) were used for the spectrophotometric measurements. Dyes were prepared according to the general procedure of Olomucki and Le Gall.[27] They were recrystallized from tetrachloromethane (**I** and **IV**), petroleum ether (bp 40–65 °C) (**II**), hexane (**III**), and diethyl ether (**V**).

Measurements

The measurements were conducted at 25 °C in a thermostatted cell. Absorbance spectra were recorded on a Hewlett-Packard 8452 A diode array spectrophotometer. Steady state fluorescence work was performed on a Photon Technology International (PTI) Quanta Master 1 spectrofluorometer. All fluorescence spectra were corrected. Infrared spectroscopy was performed with a Perkin-Elmer 1760-X Infrared Fourier Transform spectrometer using CaF_2 cells of 100 μm pathlength. AM1 Calculations using MOPAC 6.0 were carried out assuming that the nitrogen free electron pair was involved in conjugation.

References

1 For example, see: J. R. Lakowicz, *Topics in Fluorescence Spectroscopy, Vol. 4: Probe Design and Chemical Sensing*, Plenum Press, New York, 1994.
2 S. Fery-Forgues, M. T. Le Bris, J. C. Mialocq, J. Pouget, W. Rettig and B. Valeur, *J. Phys. Chem.*, 1992, **96**, 701.
3 G. M. Anstead and J. A. Katzenellenbogen, *J. Phys. Chem.*, 1990, **94**, 1328.
4 M. V. Barnabas, A. Liu, A. D. Trifunac, V. V. Krongauz and C. T. Chang, *J. Phys. Chem.*, 1992, **96**, 212.
5 W. J. Chambers and D. F. Eaton, *J. Imaging Sci.*, 1986, **30**, 230.
6 M. D. Baum and C. P. Henry (Du Pont de Nemours), *Ger. Offen.*, 2,133,515, 13 Jan. 1972; U.S. Appl. 53,686, 09 Jul. 1970; *Chem. Abstr.*, 1972, **77**, 27427w.
7 N. Marcotte, S. Fery-Forgues, D. Lavabre, S. Marguet and V. G. Pivovarenko, *J. Phys. Chem.*, 1999, **103**, 3163.
8 A. A. Khalaf, S. H. Etaiw, R. M. Issa and A. K. El-Shafei, *Rev. Roum. Chim.*, 1977, **22**, 1251; *Chem. Abstr.*, 1978, **88**, 5759f.
9 M. A. Kessler and O. S. Wolfbeis, *Spectrochim. Acta, Part A*, 1991, **47**, 187.
10 J. M. Eisenhart and A. B. Ellis, *J. Org. Chem.*, 1985, **50**, 4108.
11 R. J. De Voe, M. R. V. Sahyun, E. Schmidt, M. Sadrai, N. Serpone and D. K. Sharma, *Can. J. Chem.*, 1989, **67**, 1565.
12 N. Marcotte and S. Fery-Forgues, *J. Photochem. Photobiol., A: Chem.*, 2000, **130**, 133.
13 G. Venkateshwarlu and B. Subrahmanyam, *Proc. Indian Acad. Sci., Chem. Sci.*, 1987, **99**, 419; *Chem. Abstr.*, 1988, **109**, 128261x.
14 G. Venkateshwarlu and B. Subrahmanyam, *Proc. Indian Acad. Sci., Chem. Sci.*, 1990, **102**, 45; *Chem. Abstr.*, 1990, **112**, 215864b.
15 M. L. Horng, J. A. Gardecki, A. Papazyan and M. Maroncelli, *J. Phys. Chem.*, 1995, **99**, 17311.
16 C. Laurence, P. Nicolet, M. T. Dalati, J.-L. M. Abboud and R. Notario, *J. Phys. Chem.*, 1994, **98**, 5807.
17 M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877.
18 K. Dimroth, C. Reichardt, T. Siepmann and F. Bohlmann, *Justus Liebigs Ann. Chem.*, 1963, **661**, 1.
19 C. Reichardt, *Chem. Rev.*, 1994, **94**, 2319.
20 A. Kawski, *Acta Phys. Pol.*, 1966, **29**, 507; *Chem. Abstr.*, 1967, **66**, 24152g.
21 J. A. Riddick, W. B. Burger and T. K. Sakano, *Organic Solvents: Physical Properties and Methods of Purification*, Techniques of Chemistry, Wiley (Interscience), New York, 1986, Vol. 2.
22 J.-L. M. Abboud, M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, 1977, **99**, 8325.
23 P. Suppan, *Chem. Phys. Lett.*, 1983, **94**, 272.
24 *Handbook of Chemistry and Physics*, 65th edn., CRC Press, Boca Raton, 1984, p. E60.
25 K. Moseley and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1971, 982.
26 P. Suppan and N. Ghoneim, *Solvatochromism*, The Royal Society of Chemistry, Cambridge, 1997, pp. 69–72 and 101–105.
27 M. Olomucki and J. Y. Le Gall, *Bull. Soc. Chim. Fr.*, 1976, 1467.