Dyes and Pigments **13** (1990) 11–19

Photophysical Characteristics of Some 2-Styrylindolium Dyes

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(Received 1 March 1989; accepted 24 April 1989)

ABSTRACT

The absorption and fluorescence characteristics of some 2-styrylindolium dyes are reported. Depending on the nature of the substituent, a change from a polyene-type structure to a polymethine type is observed. This is accompanied by a significant change of colour, and a considerable decrease of the half-bandwidth of the longest-wavelength absorption maximum and Stokes' shift $\Delta\nu_{st}$. *Quantum-chemical calculations by the PPP (SCF–CI) method support the conclusions concerning the bond alternation change of the central styryl fragment. The spectral data suggest that the preferred configuration in the compounds studied is* s-trans. *By incorporating the dyes into a polymeric PVC film a strong enhancement of the fluorescent intensity is observed.*

1 INTRODUCTION

The 2-styrylindolium dyes studied belong to the class of unsymmetrical polymethine dyes[1] having the general formula shown in Fig. 1, where R^1 and R^2 are alkyl or substituted alkyl groups, X is H, CH_3, OCH_3, Cl, NO_2 or $N(Alk)_2$, and Y is I or BF_4 (Table 1).

These compounds are of practical interest since they have application as dyes for PAN materials[2,3] and are used as additives to daylight fluorescent

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Dyes and Pigments 0143-7208/90/$03·50

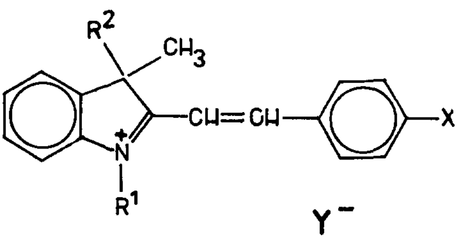


Fig. 1. General formulae of compounds **1**–**12**.

pigments.[4,5] Despite the fact that the spectral characteristics of some representatives of this group are known,[6] there are no systematic and detailed investigations of their absorption and fluorescence properties.

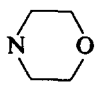
The purpose of this work is to study in detail the absorption and fluorescent characteristics of this class of compounds with respect to the nature of substituents, medium, temperature and matrix effects.

The dyes studied, **1**–**12**, are shown in Table 1. In order to establish a relation between electronic structure and spectral properties, quantum-chemical calculations by the SCF–CI–MO method in PPP approximation for compounds **1**, **3** and **7** were also performed.

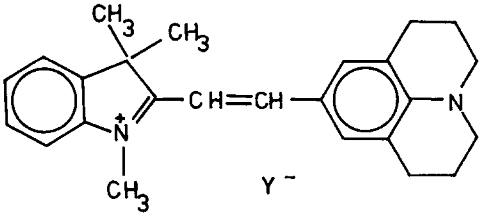
2 EXPERIMENTAL

The synthesis of compounds **1**–**12** is described in Refs 7 and 8. In order to evaluate the effect of structural factors on their spectral properties,

TABLE 1
Compounds **1**–**12**

Compd no.	*R^1*	*R^2*	*X*	*Y*
1	CH_3	CH_3	H	I
2	CH_3	CH_3	CH_3	I
3	CH_3	CH_3	OCH_3	I
4	CH_3	CH_3	Cl	I
5	CH_3	CH_3	NO_2	I
6	CH_3	CH_3	$N(CH_3)_2$	I
7	CH_3	CH_3	$N(CH_2CH_3)_2$	I
8	CH_2CH_2CN	CH_3	$N(CH_3)_2$	BF_4
9	CH_3	CH_3	$N(CH_2CH_2CN)CH_3$	I
10	CH_3	CH_3	 N O	I
11	CH_2CH_3	CH_2CH_2CN	$N(CH_3)_2$	I
12	CH_2CH_2CN	CH_2CH_2CN	$N(CH_3)_2$	BF_4

compounds **13** (having a fixed nitrogen atom in the dialkylamino group), **14** and **15** (having a fixed *s-cis* configuration of the styryl fragment with respect to the 3*H*-indole one) were synthesized.[8,9]



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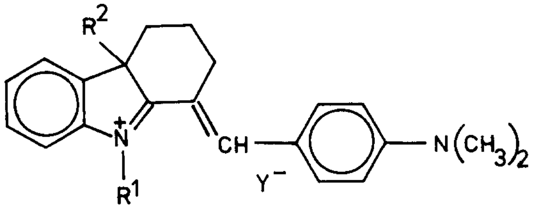

14 $R^1 = R^2 = CH_3$

15 $R^1 = R^2 = CH_2CH_2CN$

The absorption spectra were recorded on a Specord M-40 spectrophotometer (Carl Zeiss, Jena) at dye concentrations less than 10^{-4} M. The luminescence characteristics at room temperature and 77K were determined using a Perkin–Elmer MPF-44B spectrofluorimeter. The low-temperature luminescence measurements were performed at 77K using the standard phosphorescence accessory to the MPF-44B. The emission of the compounds in a polymer film was measured at an angle of 30°/60° between the normal to the surface and the exciting/emitted light.

The quantum-chemical calculations, taking into account the positive charge on the N-atom in the 3*H*-indole ring, were performed with parameters used by Nishimoto *et al.*[10] and the parameters for the OCH_3 and $N(C_2H_5)_2$ groups are according to Griffiths.[11]

3 RESULTS AND DISCUSSION

3.1 Absorption characteristics

The energies of the longest-wavelength absorption Frank–Condon transition ν^A and the respective molar absorptivities ε in C_2H_5OH,

TABLE 2
Experimental Spectral Characteristics of the Compounds in Ethanol[a]

Compd no.	ν^{A} (*cm*$^{-1}$)	ε (*litre mol*$^{-1}$ *cm*$^{-1}$)	$\Delta\nu^{A}_{1/2}$ (*cm*$^{-1}$)	*f*	ν^{F} (*cm*$^{-1}$)	$\frac{I^{F}(77K)}{I^{F}(293K)}$
1	25 840	27 230	5 440	0·64	19 610	900
2	25 000	27 750	4 960	0·59	19 530	200
3	23 580	19 120	5 200	0·43	18 870	250
4	25 510	28 520	5 240	0·65	19 610	200
5	25 320	21 970	4 640	0·44	19 800	300
6	18 020	81 320	2 560	0·90	17 000	100
7	17 790	91 900	2 400	0·95	16 810	30
8	17 420	60 740	2 080	0·71	16 860	300
9	18 760	88 050	2 960	1·16	16 860	100
10	18 870	54 690	3 600	0·85	16 610	30
11	17 600	51 530	2 400	0·53	16 470	300
12	17 270	41 820	2 080	0·38	16 340	300
13	17 000	100 180	1 840	0·80	16 390	300
14	17 980	6 810	2 880	0·08	16 780	100
15	18 550	3 260	4 160	0·06	No fluorescence	

[a] Abbreviations: ν^{A}, ν^{F}, energy of the Franck–Condon absorption and fluorescence transition; ε, molar absorptivity; I^{F}, fluorescence intensity at the respective ν^{F}; *f*, oscillator strength; $\Delta\nu^{A}_{1/2}$, half-band width.

determining the colouristic properties of the compounds are given in Table 2. The longest-wavelength maxima show the highest intensity, the molar absorptivities being over 20 000 litre mol^{-1} cm^{-1} except for compounds **14** and **15** having a fixed *s-cis* configuration.

The absorption spectrum of **1** and the results of the PPP–SCF–CI calculations are presented in Fig. 2. The vertical lines denote the computed energies of the singlet π–π^* transitions. The heights of the corresponding lines are proportional to the computed oscillator strengths *f*.

The effect of the substituent X on the longest-wavelength absorption maximum can be evaluated from the spectral data of compounds **1**–**12** (Table 2).

The electron-releasing substituents X decrease the energy of the longest-wavelength FC transition in the order $\Delta E_{H} > \Delta E_{CH_3} > \Delta E_{OCH_3} > \Delta E_{N(Alk)_2}$. This effect is most pronounced for the N(Alk)$_2$ derivatives **6**–**12**. Most probably this observation is connected with the changeover from a polyene-like structure in the case of compounds **1**–**5** to a polymethine type for compounds **6**–**12**, which is accompanied usually by a progressive deepening of colour.[1]

The half-bandwidth of the longest-wavelength absorption band $\Delta\nu_{1/2}$ of

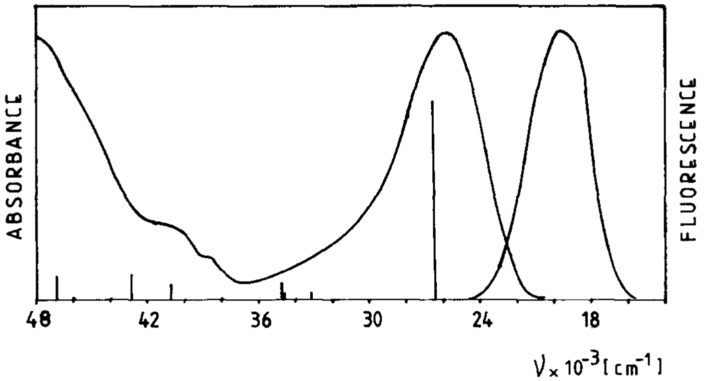

Fig. 2. Electronic spectrum of compound **1** in C_2H_5OH at 293K. The vertical lines denote the computed energies of the π–π^* transitions and the corresponding oscillator strengths.

compounds **1–5** is approximately $5000\,cm^{-1}$ whilst in the case of compounds **6–12** this value is about $2000\,cm^{-1}$. As noted by Suzuki,[12] the longest-wavelength absorption bands of symmetrical cyanines are structureless, with a half-bandwidth $\sim 1000\,cm^{-1}$ [13] which is due to the lack of bond alternation. The marked bond alternation in conjugated polyenes results in a considerably greater half-bandwidth of the longest-wavelength absorption band—about $5000\,cm^{-1}$.[14]

The differences in the half-bandwidth of the longest-wavelength absorption bands for compounds **1–5** and **6–12** are in accord with the assumption that the polyene-like structure is dominant in the case of **1–5**, whilst the polymethine-like structure with a progressive bond equalization along the chain occurs in the dialkylamino-substituted compounds **6–12**. An analogous conclusion is drawn by Fabian[1] on the basis of his study of the absorption spectra of styryl dyes with a similar structure.

In contrast to symmetrical cyanines, the two extreme resonance structures **A** and **B** (Fig. 3) of the unsymmetrical polymethines are not equivalent. This suggests some bond alternation, leading to a relatively greater half-bandwidth of the longest-wavelength absorption band.

In this respect, the 2-styrylindolium dyes investigated, being unsymmetrical polymethines, behave intermediately between cyanines and polyenes.

The quantum-chemical calculations for compounds **1** and **7** support the conclusions concerning a bond alternation change of the central styryl fragment. A marked bond alternation upon transition from the S_0 to the S_1 state is observed in the unsubstituted derivative **1**, whilst the changes of the corresponding bond orders of the central styryl fragment upon excitation in **7** are less pronounced (Fig. 4).

As noted by Brooker[15] and Suzuki,[12] the two extreme mesomeric

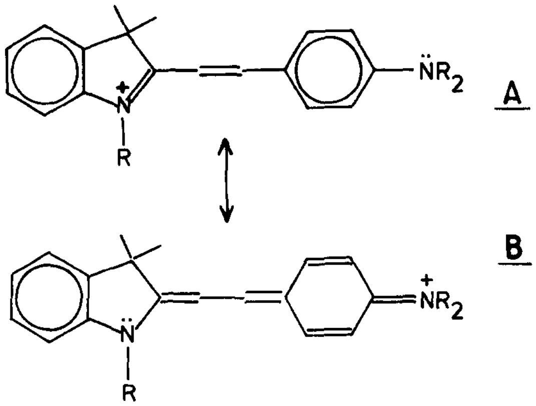

Fig. 3. Extreme resonance structures **A** and **B** for the *p*-dialkylamino-2-styrylindolium dyes.

structures (Fig. 3) of styryl dyes are not energetically equivalent. Structure **A** predominates in the ground state and the contribution of structure **B** is greater in the first excited singlet state (Fig. 4).

A similar conclusion could be drawn from the influence of the *β*-cyanoethyl group as a substituent in the electron-releasing $N(Alk)_2$ group and/or electron-withdrawing 3*H*-indolium ring, representing both ends of the parent chromophore system of compounds **6**–**12**. Assuming the molecule of **6** as a basic unsubstituted structural unit, substitution of one CH_3 group

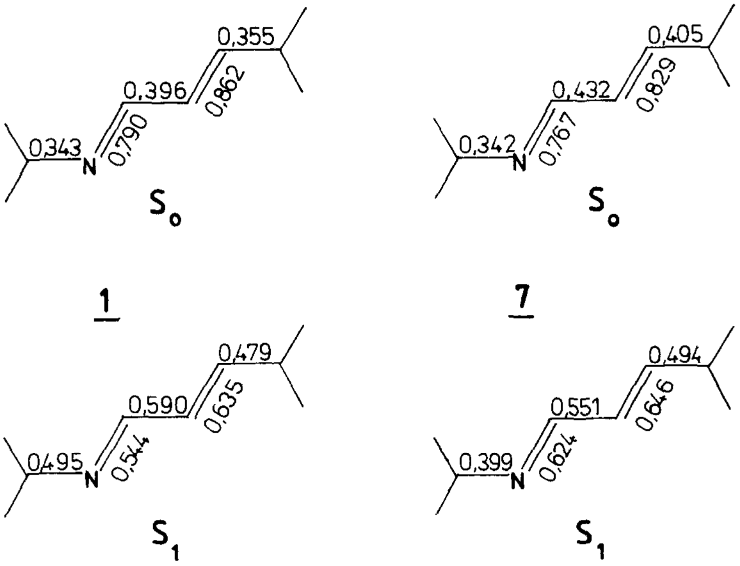

Fig. 4. Calculated *π*-bond orders of the styryl fragment for compounds **1** and **7** in the ground and first excited singlet states.

in $N(CH_3)_2$ with CH_2CH_2CN in **9** leads to a 20-nm hypsochromic shift (~700 cm^{-1}). The introduction of CH_2CH_2CN group in the 3*H*-indolium ring leads to a bathochromic effect, larger in compound **8** ($R_1 = CH_2CH_2CN$) and relatively smaller in the case of **11** ($R_2 = CH_2CH_2CN$). When both R_1 and R_2 are CH_2CH_2CN (**12**) the most pronounced bathochromic shift is observed.

Thus, in accordance with one of the basic rules in the colour concept, weakening of the electron-releasing properties of the $N(Alk)_2$ group and the enhancement of the electron-withdrawing character of the 3*H*-indolium fragment confirm the dominating contribution of structure **A** in the styryl dyes studied. If structure **B** were predominant, then the effects observed would be the opposite, as in the structurally similar diazastyryl dyes, where the same substitution with a CH_2CH_2CN group causes a small effect (±5 nm), due to the relative equivalence of structures **A** and **B**.[16,17]

Fixing of the N-atom in the dialkylamino group with a methylene bridge, as in compound **13**, leads to a marked bathochromic shift of about 35 nm (1000 cm^{-1}) in comparison with compound **6**, in accord with the above conclusions. It should be noted that the half-bandwidth $\Delta\nu_{1/2}$ (Table 2) of the longest-wavelength band of **13** has the smallest value, thus resembling the features of a cyanine band.

The spectral properties of compounds **14** and **15** with a fixed *s-cis* configuration provide a possibility to estimate the preferred configuration of the styryl dyes studied. For example, the molar absorptivity of the longest-wavelength transition in **15** (Table 2) is lower by approximately an order of magnitude than that of **12**, which is accompanied by a hypsochromic shift of 40 nm (1300 cm^{-1}). On the other hand, the fixing of the styryl fragment in the *S-trans* configuration[18] does not lead to substantial changes in the spectral behaviour with respect to the unfixed styryl dyes. From these data it can be suggested that the preferred configuration in compounds **1**–**13** is *S-trans*, as in the case of cyanine dyes.[19]

The absorption spectra of **6**–**13** measured in solvents with different polarity (CH_2Cl_2, C_2H_5OH, H_2O) show a slight hyposochromic shift of the longest-wavelength band (15–30 nm) on passing from the less polar CH_2Cl_2 to the more polar C_2H_5OH or H_2O. This slight negative solvatochromic effect suggests that the ground state is more polar than the first excited singlet state.

3.2 Luminescence characteristics

The energies of the fluorescence FC transitions ν^F and the ratios of the fluorescence intensities at 77K and 293K are presented in Table 2. Similarly to the substituent effect on ν^A, the enhancement of the electron-releasing properties of the substituent X in compounds **1–6** leads to a bathochromic shift of ν^F (Table 2).

The fluorescence quantum yield Q_f in solution (CH_2Cl_2, C_2H_5OH, H_2O) at 293K of all compounds studied is low, about 0·01. This could be explained in principle by high-amplitude intramolecular motions in the unfixed styryl fragment and/or of the substituent X. The compounds **14** and **15** with fixed *s-cis* configuration show a substantially weaker fluorescence which, together with the above-mentioned differences in their absorption spectra, confirms the assumption that in compounds **1–13** the *s-trans* configuration is preferred.

The influence of the possible rotation of the substituent X on the fluorescence capacity of the styryl dyes can be estimated from a comparison of the fluorescence properties of **6** and **7** with those of **13**. The fluorescence intensity of **13** is half those of **6** and **7**. Consequently, the rotation of the dialkylamino substituent $N(Alk)_2$ is not responsible for the low fluorescence quantum yields observed.

The fixing of the compounds studied by freezing of the solutions at 77K leads to the known[20] hypsochromic shift of the corresponding FC fluorescence transitions of about 20 nm (600 cm^{-1}) and to a considerable enhancement of the fluorescence intensity up to three orders of magnitude (Table 2).

Incorporating the compounds **1–15** into polymeric PVC film one can expect that the quenching emission intramolecular motions would be very much restricted. Indeed, along with the slight bathochromic shift of the longest-wavelength absorption and the FC fluorescent bands, a strong enhancement of the fluorescent intensity is observed.

Therefore, the most probable reason for the low quantum yields in solution at room temperature is connected with the quenching emission rotations in the styryl fragment.

No phosphorescence from the frozen ethanol solutions at 77K for any of the compounds studied was recorded.

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