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Monomethine Cyanine Dyes Containing Benz[c,d]indole and Pyrylium End-Groups

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ABSTRACT

Asymmetric monomethine cyanine dyes with benz[c,d]indole and pyrylium end-groups were prepared. The dyes absorb in the region 633–688 nm and are among the most deeply coloured monomethine cyanine dyes containing nitrogen heterocycles synthesized so far. Quantum-chemical considerations show that electronic excitation to the first-singlet-excited state is localized in the polymethine fragment and is connected with a considerable decrease in electronic polarizability.

1 INTRODUCTION

Dyes containing the ben[c,d]indole moiety are known to be amongst the most deeply coloured polymethine dyes that contain nitrogen heterocycles. A symmetric monomethine dye containing the benz[c,d]indole

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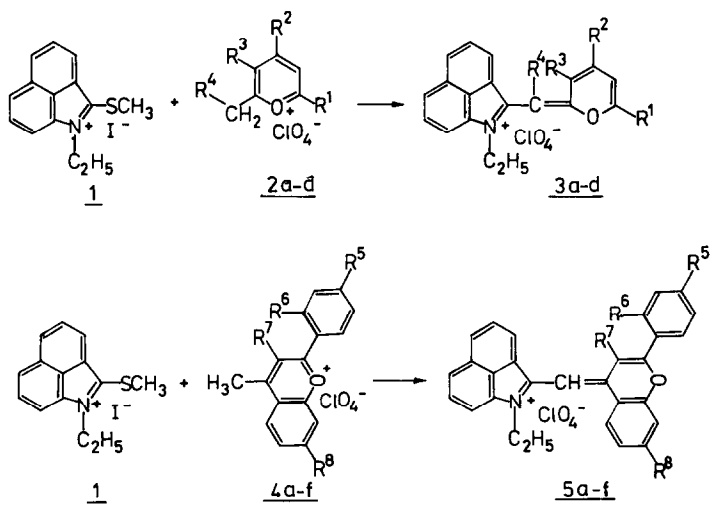
heterocycle has been described;[1] this compound absorbs at 645 nm, with molar absorptivity of 37300 L mol^{-1} cm^{-1}. Asymmetric monomethine dyes containing the benz[c,d]indole system and other different nitrogen heterocycles, and which absorb in the 535–596 nm, region are also known.[2] Recently, dyes containing the benz[c,d]indole residue have attracted much interest,[3–6] since these dyes absorb in the red and near-infrared region despite the relatively short polymethine chain. This is a prerequisite for the preparation of more stable and more deeply coloured polymethine cyanine dyes.

The synthesis, physical properties, and quantum-chemical investigations of new asymmetric monomethine cyanine dyes containing benz[c,d]indole and pyrylium end-groups are described in this present paper.

2 RESULTS AND DISCUSSION

2.1 Preparation of dyes

The asymmetric monomethine cyanine dyes **3a–d** and **5a–f** (Table 1) with benz[c,d]indole and pyrylium end-groups were prepared by the interaction of 1-ethyl-2-methylthiobenz[c,d]indolium iodide **1** with the corresponding pyryluium salts **2a–d** and **4a–f** in pyridine (Scheme 1).



Scheme 1

The method has been used for the preparation of symmetric and asymmetric monomethine nitrogen heterocyclic dyes.[7] The process proceeds smoothly for 15 min with moderate-to-good yields. The dyes

TABLE 1
Subsituents in **3a–d** and **5a–f**

Dye	R^1	R^2	R^3	R^4	*Dye*	R^5	R^6	R^7	R^8
3a	p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	H	H	5a	H	H	H	H
3b	p-ClC_6H_4	p-ClC_6H_4	H	H	5b	CH_3O	H	H	H
3c	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	H	H	5c	CH_3O	H	H	OH
3d	C_6H_5	C_6H_5	—$CH_2CH_2CH_2$—		5d	Cl	H	H	H
					5e	CH_3O	—CH_2CH_2—		H
					5f	CH_3O	—CH_2CH_2—		H

3a–d and **5a–f** absorb in the region 633–688 nm and have molar absorptivity 30 000–40 000 liter mol^{-1} cm^{-1}. The compounds are among the most deeply coloured monomethine cyanine dyes containing nitrogen heterocycles synthesized and so far described. Melting points, yields, λ_{max}, molar absorptivities, and analysis for dyes **3a–d** and **5a–f** are given in Table 2.

TABLE 2
Melting Points, Yields, Molar Absorptivities, and Analysis for Dyes **3a–d** and **5a–f**

Dye	*m.p.* (°C)	*Yield* (%)	λ_{max} (nm)	ε (liter mol^{-1} cm^{-1})	*Molecular formulae*	*Analysis %* (calc./found)		
						C	*H*	*N*
3a	268–269	43	646	40 000	$C_{33}H_{28}ClNO_5$	*71·5*	*5·1*	*2·5*
					(553·5)	71·2	5·2	2·4
3b	319–321	93	634	35 200	$C_{31}H_{22}Cl_3NO_5$	*62·6*	*3·7*	*2·4*
			675sh	32 600	(594·5)	62·3	3·8	2·6
3c	278–280	73	665	45 000	$C_{33}H_{28}ClNO_7$	*67·6*	*4·8*	*2·4*
					(585·5)	67·5	5·0	2·0
3d	280–282	79	688	27 700	$C_{34}H_{28}ClNO_5$	*72·1*	*5·0*	*2·5*
					(565·5)	72·0	5·2	2·3
5a	280–282	79	633	37 900	$C_{29}H_{22}ClNO_5$	*68·2*	*5·1*	*2·6*
					$\cdot C_2H_5OH$ (545·5)	67·9	4·7	2·4
5b	253–256	78	612sh	34 300	$C_{30}H_{24}ClNO_5$	*67·3*	*4·9*	*2·5*
			652	42 000	$\cdot$ 0·5 C_2H_5OH	67·2	4·6	2·9
					(552·5)			
5c	244–246	72	612sh	29 800	$C_{30}H_{24}ClNO_7$	*66·0*	*4·4*	*2·6*
			648	40 200	(545·5)	66·1	4·5	1·9
5d	295–297	60	598sh	26 700	$C_{29}H_{21}Cl_2NO_5$	—	—	*2·6*
			633	28 400	(534)			2·5
5e	253–255	58	648	36 400	$C_{31}H_{24}ClNO_5$	*70·8*	*4·6*	*2·7*
			710sh	14 600	(525·5)	71·1	4·9	2·8
5f	235–237	77	665	34 000	$C_{32}H_{26}ClNO_6$	—	—	*2·5*
					(555·5)			2·4

All dyes were recrystallized from ethanol.

2.2 Quantum-chemical results

Theoretical studies carried out are exemplified for structures **3a–d** and **5a–d**. These are shown in Scheme 1. Quantum-chemical calculations employing the semi-empirical method of Pariser, Parr, and Pople[8,9] (PPP method) were performed with the molecular geometry as obtained by the molecular-mechanic method MM2.[10] Optimization of the geometry of the structures studied, **3a–d** and **5a–d**, shows that these molecules are quasi-planar. This is most probably due to their extended conjugated system.

The singlet electronic transitions and corresponding oscillator strengths are determined with parameters for the Coulomb and resonance integrals, presented in detail in a semi-empirical study[11] on the absorption spectra of different groups of azomethine dyes. The electron-density distribution and transition energies of the structures studied were calculated by the configuration-interaction method (PPP–CI approximation). In all cases, up to 120 monoexcited configurations were taken into account. In Table 3, the wavelength of the longest absorption maxima (λ_{max}), the corresponding oscillator strengths (f), and π-electronic components of the average static polarizability (α) for the ground (S_0) and the first-excited-singlet (S_1) states are collected. A good correlation between the calculated and observed wavelengths for the first optical transition of the systems studied can be seen from the data shown.

Analysis of the total molecular wave function shows that, in the MO-approach, the first-singlet transition of all calculated molecules is determined by the promotion of an electron between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital

TABLE 3

Values of Experimental (λ_{exp}) and Calculated (λ_{calc}) Wavelengths (in nm) for the Longest Optical Transition, Oscillator Strength (f) and Average π-Electronic Polarizability (α in A^3) of the Different Structures for the Ground (S_0) and the First-Excited-Singlet (S_1) States (Results from PPP–CI Calculations)

Structure	λ_{exp}	λ_{calc}	f	$\alpha(S_0)$	$\alpha(S_1)$
3a	646	624	0·889	47·3	23·4
3b	634	625	0·896	47·7	23·9
3c	665	632	0·883	49·5	27·1
3d	688	639	0·719	46·8	22·9
5a	633	629	0·795	43·9	18·5
5b	652	637	0·922	47·4	22·2
5c	648	640	0·790	47·1	22·4
5d	633	632	0·859	45·7	19·8

(LUMO). The square of the HOMO–LUMO coefficients in the CI wave function corresponding to this electronic configuration varies in the range 0·92–0·98. On the other hand, study of the electronic-transition localization in the molecular carried out by Luzanov's method[12] shows that the first-singlet transition is localized in a polymethine fragment, of the type:

$$\overset{+}{\mathrm{N}} \cdots\cdots (\mathrm{CH})_n \cdots\cdots \overset{-}{\mathrm{O}}$$

For all calculated structures, the values of the electronic-localization parameter of this fragment are about 0·78. This indicates that the rest of the molecule does not participate in the first-excitation process.

The average static-electronic polarizability has been determined by the perturbative SOS formalism described in our previous paper.[13] In the present study, this important molecular characteristic was calculated for different groups of charged and neutral polymethine compounds. From the data presented in Table 3, it can be seen that, in all cases, there is a significant decrease in the polarizability in the first-excited-singlet state. This is in accord with previous results for the polymethine cyanines ions.[13] This suggests that the conjugation in the molecules studied may be disturbed. As a result, the stabilization of the molecules in polar media is expected to be much less effective.

3 EXPERIMENTAL

3.1 General

Melting points were determined in a Koffler apparatus and were uncorrected. The absorption spectra were taken on a Lambda 17 Perkin–Elmer spectrophotometer in ethanol at 2×10^{-5} mol liter^{-1}.

3.2 General procedure for preparation of dyes 3a–d and 5a–f

Ethyl-2-thiomethylbenz[c,d]indolium iodide (1 or 0·0028 mol) and the appropriate pyrylium salt (0·0028 mol) were refluxed in pyridine (5 ml) for 15 min. The reaction mixture was cooled to room temperature and left overnight in a refrigerator. The precipitate was filtered, washed with 20—30 ml diethyl ether, and dried. If the dye did not crystallize, diethyl ether (30 ml) was added to the reaction liquor prior to overnight refrigeration.

Some physical data dyes **3a–d** and **5a–f** are shown in Table 2.

REFERENCES

1. Steinberg, Ja. B. & Dokunikhin, N. S., *Zh. Obshch. Chim.*, **30** (1960) 1989.
2. Ficken, G. E. & Kendall, J. D., *J. Chem. Soc.* (1960) 1537.
3. Mihailenko, F., Vasilenko, N., Kachkovski, A. & Rozhinski, Y., *Zh. Org. Chim.*, **18** (1982) 438.
4. Steinberg, Y., *Khim. Geterocycl. Soedin.*, (1970) 340.
5. BASF A. G., German Offen 3 631 843 (*Chem. Abstr.*, **109** (1988) 75205y).
6. Gadjev, N. I., Deligeorgiev, T. G. & Drexhage, K. H., *Dyes & Pigm.*, **17** (1991) 53.
7. Kendall, J. D. & Suggate, H. G., *J. Chem. Soc.*, (1949) 1503.
8. Pariser, R. & Parr, R., *J. Chem. Phys.*, **21** (1953) 466–767.
9. Pople, J., *Trans. Faraday Soc.*, **49** (1953) 1375.
10. Allinger, N., *J. Am. Chem. Soc.*, **99** (1977) 975.
11. Griffiths, J., *Dyes & Pigm.*, **3** (1982) 211.
12. Luzanov, A., *Theor. Exp. Khimia*, **13** (1977) 579.
13. Kanev, I. & Neykov, G., *J. Chim. Phys.*, **79** (1982) 115.