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Styryl Dyes Containing the Benz[c,d]Indolium Heterocycle

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ABSTRACT

The synthesis of some new styryl benz[c,d]indolium heterocycle dyes is described. The dyes absorb in the region from 636 to 686 nm. The structure of the compounds was confirmed by elemental analysis, electronic absorption spectra, IR and in some cases by ^{1}*H-NMR spectroscopy.*

1 INTRODUCTION

Some data on cyanine dyes based on benz[c,d]indole has been reported,[1-8] and these dyes have the greatest effective length (L) among the nitrogen-containing heterocyclic dyes. The effective length is a term representing the parameter of the shift of the absorption maximum to longer wavelength for dyes derived from a given heterocycle.[4] For the same length of the polymethine chain, benz[c,d]indole-based cyanine dyes are characterised by a longer wavelength absorption than other nitrogen-containing heterocycles. This property is of importance in the preparation of photostable dyes absorbing in the longer wavelength spectral region, since it is known[9] that, because of cis-trans isomerisation, the stability of polymethine dyes decreases with increase in length of the polymethine chain.

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Benz[c,d]indolium styryl dyes have been applied in the dyeing of polyacrylonitrile fibres[10] and as a medium for optical information recording with a diode laser emitting in the near IR region.[6]

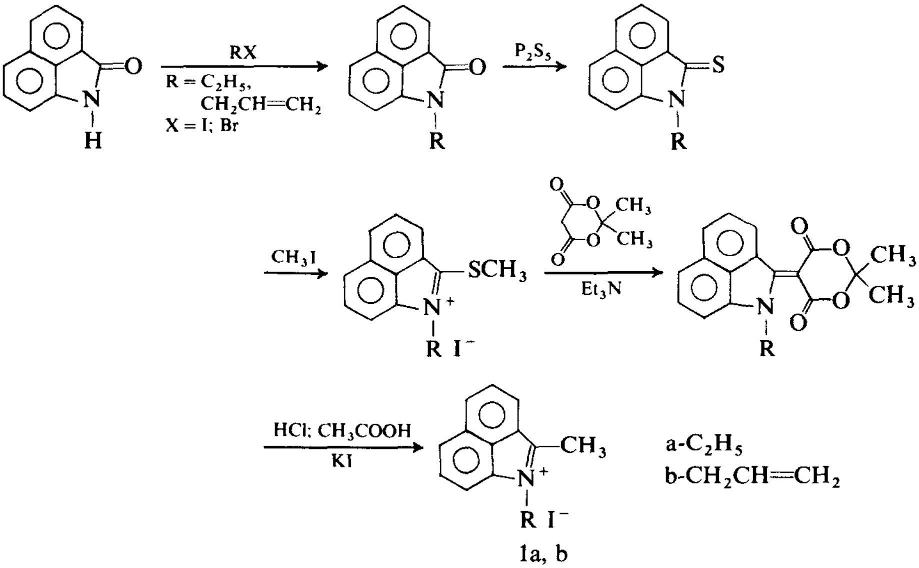
We have used styryl dyes as a passive non-linear absorber in the mode-locking Rhodamine 6G dye laser for the generation of ultra-short light pulses.[11-12] These dyes exhibit a remarkable photochemical stability allowing the laser to operate for more than eight months without changing its parameters. Laser action with these dyes is achieved by pumping with ultra-short light pulses in a double mode-locked Rhodamine 6G dye laser.[13]

A diode laser emitting in the visible region (670–680 nm) has recently been described,[14] thus providing the possibility of improving the density of optical information recording. Dyes useful as active media for recording with a diode laser emitting in the visible 670–680 nm spectral region have also been described.[15]

As a part of our research program to obtain ultra-short pulses in other spectral regions and to develop dyes as active media for optical information recording, this present paper reports the synthesis of novel styryl dyes containing the benz[c,d]indolium moiety.

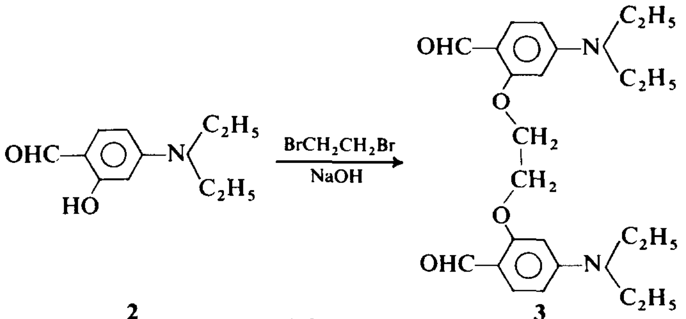
2 RESULTS AND DISCUSSION

1-Allyl- and 1-ethyl-2-methyl-benz[c,d]indolium salts were used as starting compounds. They were prepared following a previously reported reaction



1a, b

Scheme 1

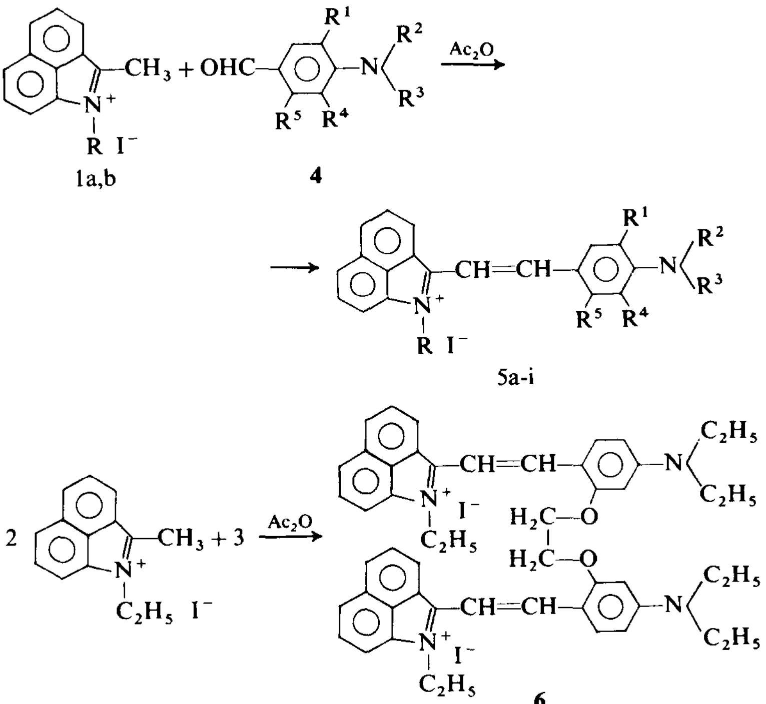


Scheme 2

scheme.[4,16] The synthesis of 1-ethyl-2-methyl-benz[c,d]indolium bromide has been described[4] and 1-allyl-2-methyl-benz[c,d]indolium iodide was prepared according to Scheme 1.

The required benzaldehydes were either commercial products or they were prepared by known methods.[17,18] A new benzaldehyde was also prepared as outlined in Scheme 2. The product yield was low (21·4%), but no experiments to effect its optimization were carried out.

The styryl dyes were obtained by condensation of 1-ethyl- or 1-allyl-2-methyl-benz[c,d]indolium salts with the respective benzaldehydes (Scheme



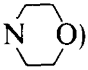
Scheme 3

TABLE 1
Substituents in Dyes **5a–5i**

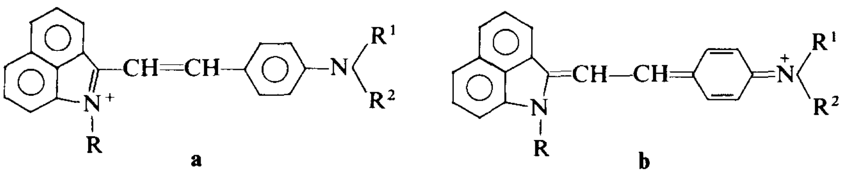
Dye	*R*	*R^1*	*R^2*	*R^3*	*R^4*	*R^5*
5a	$CH_2CH{=}CH_2$	H	C_2H_5	C_2H_5	H	OC_2H_5
5b	C_2H_5	H	C_2H_5	C_2H_5	H	OCH_3
5c	C_2H_5	H	C_2H_5	C_2H_5	H	OH
5d	C_2H_5	H	C_2H_5	C_2H_4CN	H	H
5e	C_2H_5	H	$-(CH_2)_4-$		H	H
5f	C_2H_5	H	$-(CH_2)_5-$		H	H
5g	C_2H_5	H	$-C_2H_4-O-C_2H_4-$		H	H
5h	C_2H_5	$-(CH_2)_3-$		C_2H_5	H	H
5i	C_2H_5	$-(CH_2)_3-$		$-(CH_2)_3-$		H

3). The substituents in dyes **5a–5i** are shown in Table 1. The dyes absorbed in the 629–686 nm region and exhibited high molar absorptivities (62 000–110 000) (Table 2).

Kiprianov & Michailenko[19] have studied the benzothiazole styryl dyes and their conclusions are pertinent to the styryl dyes derived from benz[c,d]indole. The limiting structures (Scheme 4) can be adopted for the dyes prepared in this present investigation.

It has been established that **a** is the prevailing structure and that the essential factor determining the electron state of the cation is the tendency of the benzene ring to preserve its π-electron sextet. In the case where the NR^1R^2 fragment comprises electron-acceptor substituents (e.g. C_2H_4CN or ) the conjugation of the electron pair at the nitrogen atom is hindered and structure **b** is less clearly expressed. Thus the two structures are inequivalent and **5d** and **5g** exhibit a hipsochromic shift compared to the other dyes.

In cases where the limiting structures have the same energy, the delocalisation in the molecule is maximal. Increase in the electron-donor character of the NR^1R^2 moiety results in a bathochromic shift, and when the lack of rotation of the alkyl substituents (as in julolidine and tetrahydroguinoline) is taken in conjunction with this increased electron-donor effect, the largest bathochromic effect is observed (analyses **5h** and **5i**).



Scheme 4

TABLE 2
Absorption Maxima (nm), Molar Extinction Coefficients (litre mol^{-1} cm^{-1}), Melting Points,[a] Yields and Elemental Analysis Data for **5a**–**5i** and **6**

Dye	λ_{max}	*E*	*MP* (°C)	*Yield* (%)	*Molecular formula*	*Analysis* (%) *found* (*calculated*)		
						C	*H*	*N*
5a	677	97 150	212–213	87	$C_{28}H_{31}IN_2O$	62·6 (62·45)	5·5 (5·8)	5·0 (5·2)
5b	673	86 900	186–187	94	$C_{26}H_{29}IN_2O.C_2H_5OH$	60·1 (60·2)	6·4 (6·3)	4·6 (5·0)
5c	668	110 900	242–244	91	$C_{23}H_{23}IN_2O$	59·7 (60·2)	5·5 (5·5)	5·4 (5·6)
5d	636	74 400	220–222	88	$C_{26}H_{26}IN_3$	61·7 (61·5)	5·4 (5·2)	8·5 (8·3)
5e	664	82 450	>350	94	$C_{25}H_{25}IN_2$	63·0 (62·5)	5·5 (5·2)	5·2 (5·8)
5f	661	61 700	>350	94	$C_{26}H_{27}IN_2$	63·3 (63·2)	5·6 (5·5)	5·4 (5·7)
5g	629	53 600	>350	96	$C_{25}H_{27}IN_2O.CH_3OC_2H_4OH$	58·4 (58·85)	5·6 (5·6)	4·7 (4·9)
5h	681	99 500	220–221	90	$C_{26}H_{27}IN_2$	63·0 (63·2)	5·6 (5·5)	5·45 (5·7)
5i	686	80 800	>350	98	$C_{27}H_{27}IN_2$	63·8 (64·0)	5·6 (5·4)	5·2 (5·5)
6	686	110 200	220–223	94	$C_{52}H_{56}IN_4O_2.H_2O$	59·8 (60·0)	5·9 (5·6)	5·9 (5·4)

[a] **5a**–**5d** and **6** were recrystallised from ethanol, **5e**–**5i** from methoxyethanol.

A similar situation is also observed with dye **6**, which absorbs at the same wavelength as dye **5i** (λ_{max} 686 nm). Here, the absence of rotation of the benzene rings probably contributes to a more complete conjugation of the electron pair of the nitrogen atom or the dialkylamino group with the π-electron sextet of the benzene ring.

The IR spectra of the dyes in nujol show a medium intensity band at about 1620 cm^{-1}, which is ascribed to the azomethine group in the heterocycle. Other characteristics in these spectra were the out-of-plane deformation vibration of C—H in the —CH=CH— group (at about 965 cm^{-1}) and out-of-plane deformation vibrations of C—H in the benzene rings (at 815–820 cm^{-1} for the 1,4-substituted dyes and at 825–870 cm^{-1} for the 1,2,4-substituted dyes). The spectrum of **5c** showed the hydroxy group as a broad band at about 3200 cm^{-1} due to intermolecular hydrogen bonding. A low-intensity peak at about 2240 cm^{-1} (CN group) was observed in the IR spectrum of **5d**.

^{1}H-NMR spectra are recorded for some of the dyes (**5d–5i**) and similar signals were apparent for all the dyes (see Experimental). The vicinal coupling constant $J = 14{\cdot}8–15{\cdot}4$ Hz suggests the presence of E trans isomer.

3 EXPERIMENTAL

3.1 General

Melting points were determined on a Kofler apparatus and are uncorrected. ^{1}H-NMR spectra were recorded on a Brucker WM 250 MHz instrument in DMSO-d_6, with TMS as internal reference. The absorption spectra were recorded on a Carl Zeiss Jena Specord M40 spectrophotometer (2×10^{-5} M/l in ethanol) and the IR spectra in nujol on a Specord 71 IR instrument.

3.2 Preparation of 1-allylbenz[c,d]indole-2(1H)-thione

1-Allylbenz[c,d]indole-2(1H)-one (3·8 g, 0·02M) and diphosphorus pentasulphide (4·4 g, 0·02M) were dissolved in pyridine (40 cm^3) and refluxed for 1·5 h. The cooled solution was acidified with concentrated hydrochloric acid and the dark-red precipitate which formed on cooling was filtered and dried. The yield was 3·8 g (93%); m.p. 86–87°C (ethanol).

Elemental analysis for $C_{14}H_{11}NS$. 1/3 C_2H_5OH:

Found: C, 73·4; H, 5·65; N, 6·0.
Calculated: C, 73·2; H, 5·4; N, 5·8.

3.3 Preparation of 1-allyl-2-thiomethylbenz[c,d]indolium iodide

Methyl iodide (6·25 cm^3, 0·1M) was added to 1-allylbenz[c,d]indole-2(1H)-thione (3 g, 0·02M) and the mixture kept for 12 h at room temperature and then filtered. Since the product was unstable, it was used in the next stage without further isolation and purification.

3.4 Preparation of 1-allyl-2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-1(H)-benz[c,d]indole

2,2-Dimethyl-1,3-dioxan-4,6-dione (3·17 g, 0·022M) and triethylamine (3·05 cm^3, 0·022M) were added to a solution of 1-allyl-2-thiomethylbenz[c,d]indolium iodide (4·1 g, 0·011M) in 55 cm^3 absolute ethanol. The reaction mixture was stirred at 50°C for 1·5 h and after cooling two parts of water were added. The resultant precipitate was filtered and washed with water until neutral. The yield was 3·5 g (86%). After recrystallisation from ethanol/water 1:1, m.p. was 178–179·5°C.

Elemental analysis for $C_{20}H_{17}NO_4$:

Found: C, 71·55; H, 5·0; N, 3·8.
Calculated: C, 71·6; H, 5·5; N, 4·2.

3.5 Preparation of 1-allyl-2-methylbenz[c,d]indolium iodide

1-Allyl-2-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-1(H)-benz[c,d]indole (3 g, 0·01 M) and acetic acid 10 cm^3 were refluxed and concentrated acid added dropwise to the refluxing mixture until the colour changed from red to yellow-green. Saturated potassium iodide solution (40 cm^3) was added to the cooled mixture and the precipitate which formed was filtered and dried. The yield was 3·2 g (92%); m.p. >350°C (water).

Elemental analysis for $C_{15}H_{14}IN$:

Found: C, 53·9; H, 4·25; N, 4·1.
Calculated: C, 53·75; H, 4·2; N, 4·2.

3.6 Preparation of 1,2-bis-(4-N,N-diethylaminobenzaldehyde-2-yl)-dioxyethane

4-*N*,*N*-Diethylamino-2-hydroxybenzaldehyde (19·3 g, 0·1 M), dibromoethane (9·4 g, 0·02M), sodium hydroxide (4 g, 0·1M) and triethylbenzylammonium chloride (2·28 g, 0·01 M) were dissolved in 100 cm^3 acetone and refluxed for 6 h. Water (500 cm^3) was added to the cooled reaction mixture and the pH adjusted to 10–11. The precipitate was filtered and dried. The yield was 4·3 g (21·4%); m.p. 147·5–148°C (ethanol).

After the filtration the mother liquor was acidified and unreacted 4-*N*,*N*-diethylamino-2-hydroxybenzaldehyde recovered.

3.7 General procedure for preparation of the styryl dyes

1-Ethyl-2-methylbenz[c,d]indolium iodide[4] (1·6 g, 0·005M) or 1-allyl-2-methylbenz[c,d]indolium iodide (1·7 g, 0·005M), the respective aldehyde (0·005M), acetic acid (10 cm^3) and acetic anhydride (5 cm^3) were refluxed for 4 h. The precipitate which formed on cooling was filtered and dried.

Some characterisation data for the dyes thus prepared is given in Table 2.

3.8 ^{1}H-NMR (DMSO-d$_6$) δ ppm data

5d—1·20 (t, 3H, N—$CH_2\underline{CH_3}$), 1·47 (t, 3H, =N—$CH_2\underline{CH_3}$), 2·90 (t, 2H, CH_2CN), 3·65 (q, 2H, N—$\underline{CH_2}CH_3$), 3·89 (t, 2H, N—$\underline{CH_2}CH_2CN$), 4·72 (q, 2H, $=N-\underline{CH_2}CH_3$), 7·65, 8·80 (d, d, H, H, $-CH=CH-$, J = 15·3 Hz), 7·03–9·22 (m, 10H, 2Ar).

5e—1·46 (t, 3H, $=N-CH_2\underline{CH_3}$), 2·02 (t, 4H, $-)\,CH_2\,(_2-)$, 3·51 (t, 4H, CH_2NCH_2), 4·66 (q, 2H, $=N-\underline{CH}CH_3$), 7·54, 8·74 (d, d, H, H, $-CH=CH-$, J = 15·0 Hz), 6·74–9·14 (m, 10H, 2Ar).

5f—1, 46 (t, 3H, $=N-CH_2\underline{CH_3}$), 1·66 (s broad, 6H, $-)\,CH_2\,(_3-)$, 3·66 (t, 4H, CH_2NCH_2), 4·69 (q, 2H, $=N-\underline{CH_2}CH_3$), 7·59, 8·74 (d, d, H, H, $-CH=CH-$, J = 15·2 Hz), 7·12–9·17 (m, 10H, 2Ar).

5g—1·48 (t, 3H, $=N-CH_2\underline{CH_3}$), 3·57 (t, 4H, CH_2NCH_2), 3·77 (t, 4H, CH_2OCH_2), 4·75 (q, 2H, $=N-\underline{CH_2}CH_3$), 7·71, 8·80 (d, d, H, H, $-CH=CH-$, J = 15·4 Hz), 7·14–9·24 (m, 10H, 2Ar).

5h—1·20 (t, 3H, $N-CH_2\underline{CH_3}$), 1·44 (t, 3H, $=N-CH_2\underline{CH_3}$), 1·94 (t, 2H, $CH_2\underline{CH_2}CH_2$), 2·80 (t, 2H, $Ar\underline{CH_2}$), 3·52–3·65 (m, 4H, CH_2NCH_2), 4·63 (q, 2H, $=N-\underline{CH_2}CH_3$), 7·41, 8·69 (d, d, H, H, $-CH=CH-$, J = 14·9 Hz), 6·90–9·10 (m, 9H, 2Ar).

5i—1·46 (t, 3H, $=N-CH_2\underline{CH_3}$), 1·98 (t, 4H, $2CH_2\underline{CH_2}CH_2$), 2·82 (t, 4H, CH_2ArCH_2), 3·56 (t, 4H, CH_2NCH_2), 4·61 (q, 2H, $=N-\underline{CH_2}CH_3$), 7·44, 8·62 (d, d, H, H, $-CH=CH-$, J = 14·8 Hz), 7·75–9·06 (m, 8H, 2Ar).

3.9 IR ν cm^{-1} (nujol)

5a—825, 870, 965, 1630; **5b**—825, 870, 965, 1620; **5c**—825, 870, 965, 1620, 3200; **5d**—820, 965, 1620, 2240; **5e**—815, 965, 1625; **5f**—820, 970, 1620; **5g**—815, 970, 1620; **5h**—825, 965, 1630; **5i**—850, 965, 1630.

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