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Styryl Dyes Containing an Aza-15-Crown-5 Macroheterocycle Moiety

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ABSTRACT

Seven new styryl dyes containing an aza-15-crown-5 moiety were synthesized and characterized by means of elemental analysis, m.p., UV, IR and ^{1}H-NMR spectra. The colour change in the presence of metal salts was investigated.

INTRODUCTION

Chromoionophores are an important class of crown ethers; the presence of both chromophore and ionophore groups also results in such compounds having applicability as analytical reagents.[1] It is well documented that in the presence of metal ions the visible absorption bands of chromoionophores are shifted as a result of the complexation process and it has been shown that the band shift depends on the relationship between the metal ion and the cavity dimensions and steric structure of the compound.[2,3]

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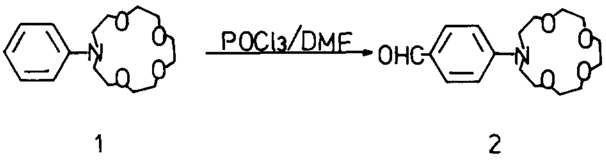
Recently some styryl dyes including a 15-crown-5 fragment were prepared and their structure and reversible *trans-cis* isomerization on visible light irradiation discussed. The λ_{max} shift resulting from the addition of alkaline and alkaline-earth metal salts addition indicated a selective interaction of the compounds with the appropriate metal ions.[4–6]

In this present paper the synthesis of seven new styryl dyes containing an aza-15-crown-5 macrocycle is reported, together with some spectrophotometric data concerning their complex formation with alkaline and alkaline-earth metal ions.

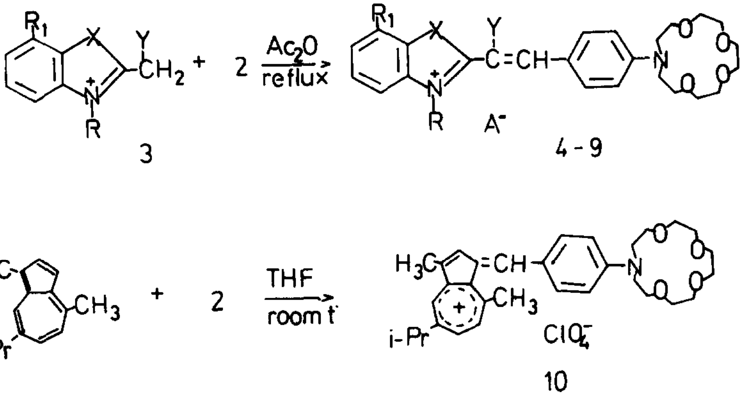
RESULTS AND DISCUSSION

N-Phenyl-aza-15-crown-5 (**1**) (Scheme 1) was used as starting material and formylated according to the Vilsmeier procedure[7] resulting in the formation of 4-formylbenzo-aza-15-crown-5 (**2**) (Scheme 1).

Some of the heterocycles used were commercial products (**4**, **10**), while the others were obtained by alkylation of the heterocyclic bases with ethyl iodide[8] (**7**, **8**), 2-bromoethanol[9] (**9**) and dimethyl sulphate[10,11] (**5**) respectively. 1-Ethyl-2-methyl-benz[cd] indolium iodide was synthesized as previously detailed.[12]



Scheme 1



Scheme 2

Table 1
Substituents in Dyes **4–9**

Dye	*R*	*R_1*	*X*	*Y*
4	CH_3	H	$C(CH_3)$	H
5	CH_3	H	$N—CH_3$	CN
6	C_2H_5	—CH=CH—		H
7	C_2H_5	H	S	H
8	C_2H_5	H	—CH=CH—	H
9	C_2H_4OH	H	$C(CH_3)_2$	H

The styryl dyes (**4–9**) (Table 1) were obtained by condensation of **2** with the corresponding heterocycle at reflux in acetic anhydride. Dye **10** was prepared in tetrahydrofuran in the presence of $HClO_4$ at room temperature[13] (Scheme 2).

The compounds thus obtained were characterized by elemental analysis, m.p., IR and ^{1}H-NMR spectroscopic data. The IR spectra of the dyes in $CHCl_3$ show a low intensity peak at 1610 nm or a shoulder at 1600 cm^{-1} due to the stretching vibrations of the —CH=CH— group. A high intensity peak at 1100 cm^{-1} can be ascribed to the stretching vibrations of

Table 2
Absorption Maxima (nm), Molar Extinction Coefficients (litre/mol/cm), Melting Points, Yields and Elemental Analysis Data for **4–10**

Dye	*λ_{max} (nm)*	*ε*	*Yield (%)*	*M.p. (°C)*	*Molecular formula*	*Analysis (%) found (calculated)*		
						C	*H*	*N*
4	547	43 400	52	109–110	$C_{29}H_{39}ClN_2O_8$	60·15 (59·95)	6·79 (7·10)	4·84 (4·73)
5	445	36 000	63	209–212	$C_{28}H_{35}ClN_4O_8$	56·89 (56·70)	5·97 (5·60)	9·48 (9·03)
6	662	80 000	55	259–260	$C_{41}H_{37}IN_2O_4$	59·24 (59·45)	5·93 (6·24)	4·46 (4·27)
7	528	65 900	85	227–228	$C_{27}H_{35}ClN_2O_8S$	55·62 (55·53)	6·05 (6·22)	4·80 (4·70)
8	528	66 000	80	242–244	$C_{28}H_{35}ClN_2O_8$	59·73 (59·55)	6·27 (6·11)	4·98 (4·51)
9	556	80 500	72	133–134	$C_{30}H_{41}ClN_2O_9$	59·16 (58·96)	6·78 (6·65)	4·59 (4·34)
10	645	48 260	82	187–189	$C_{32}H_{43}ClNO_8$-C_2H_5OH	62·70 (62·73)	7·58 (7·16)	2·15 (1·92)

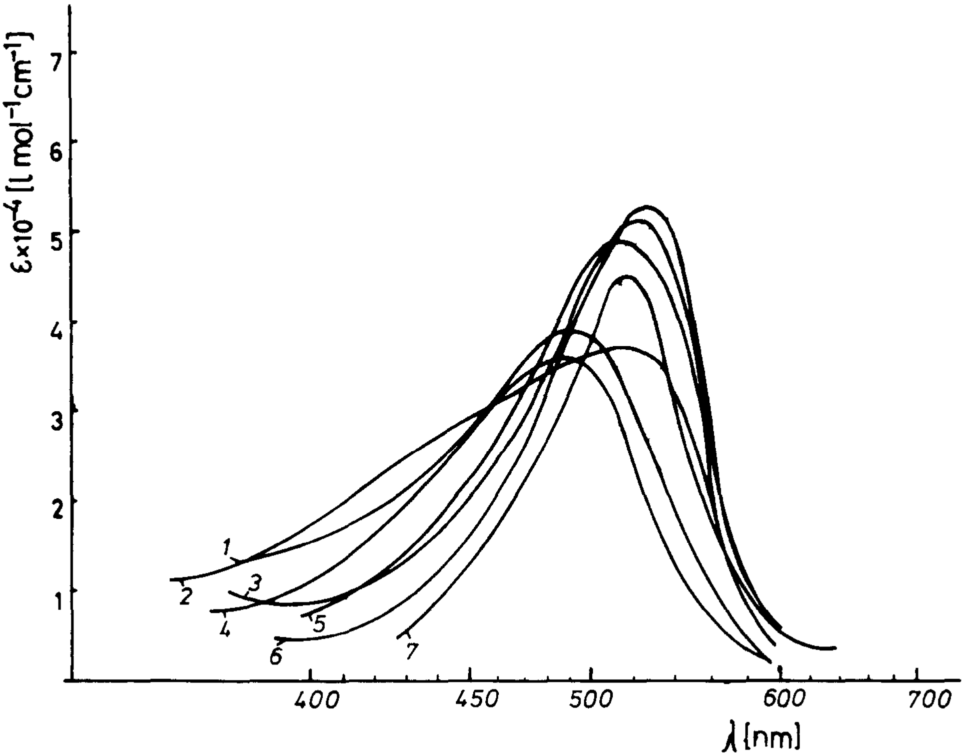


Fig. 1. Absorption spectra of the chromoionophore **7**: free ligand and in the presence of metal salts in acetonitrile: 1, $Mg(NO_3)_2$; 2, $Ba(SCN)_2$; 3, KSCN; 4, $Ca(NO_3)_2$; 5, NaSCN; 6, free ligand; 7, $LiNO_3$.

the —C—O— group and in the spectrum of **5**, a low-intensity peak at 2200 cm^{-1} (CN^- group) was observed.

^{1}H-NMR spectra were compatible with the assigned structures. Signals at 3·60–3·80 ppm indicated that at least three groups of non-equivalent protons in the crown moiety were present. The vinyl protons appeared downfield (7·20–8·60 ppm) as doublets and the vicinal coupling constant (15–15·5 Hz) indicated that only *trans*-isomers were obtained.

Electronic absorption spectral data in ethanol are shown in Table 2 and in order to obtain information about the complexation properties of the dyes their electronic spectra were also recorded in the presence of some alkaline and alkaline-earth metal salts. For this purpose, acetonitrile solutions of the metal salts were added to the corresponding dye solutions in acetonitrile to give a metal ligand ratio >100:1. The data thus obtained (Figs 1 and 2) showed that all the dyes exhibited hypsochromic shifts in the presence of the metal ions, the shifts also being combined with hypochromic effects. It was apparent that compounds **4**,

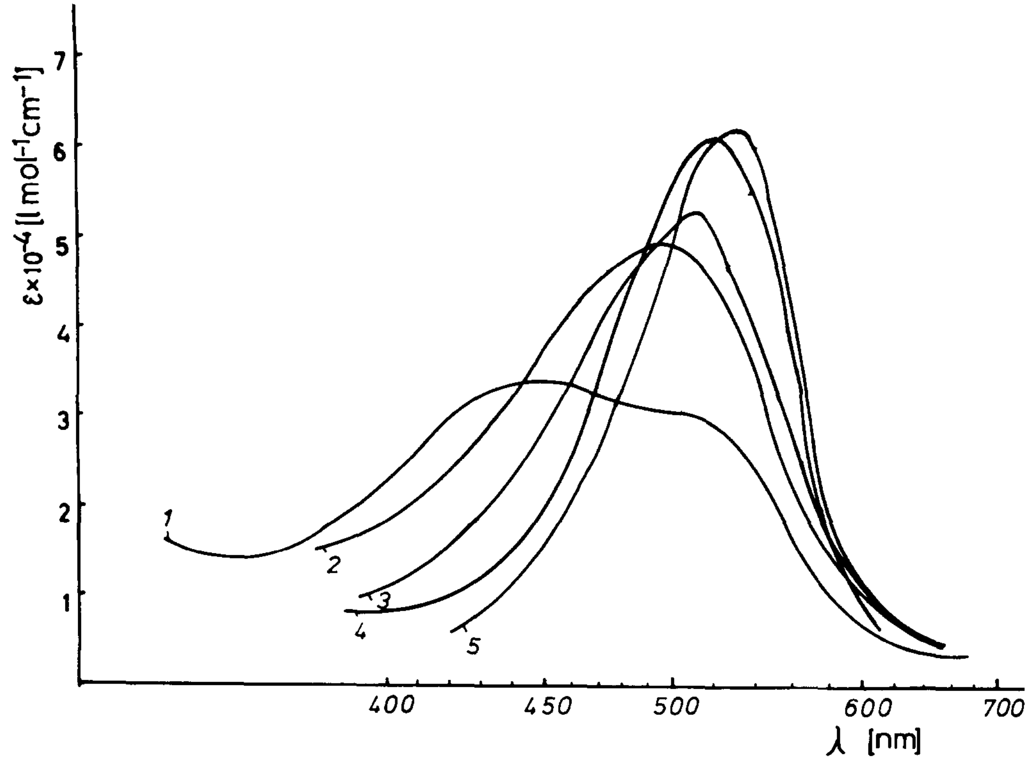


Fig. 2. Absorption spectra of the chromoionophore **8**: free ligand and in the presence of metal salts in acetonitrile: 1, $Ba(SCN)_2$; 2, NaSCN; 3, KSCN; 4, $LiNO_3$, 5, free ligand.

6, **9**, **10** were only slightly influenced by the cations used, λ_{max} shifts of only 5–10 nm in the presence of Na^+, K^+ and Ba^{2+} being observed; the λ_{max} shifts of **5** in the presence of Na^+ and K^+ (10 nm) and of Ba^{2+} (20 nm) were slightly larger. It should be noted that, in all cases, the Ba^{2+} interaction with the dyes studied was accompanied by a significant change in the band shape (Figs 1 and 2).

The largest λ_{max} shift was observed as a result of Na^+, Ca^{2+} and Mg^{2+} interaction with dyes **7** and **8** (30 nm). These compounds also reacted with Li^+ with a shift of 10 nm (Figs 1 and 2).

The relationship between the cavity dimensions and ionic radii in crown ether–metal ions complexation is well documented for aza-15-crown-5, the best fit being observed for Na^+.[14] For that reason it might be assumed, that, in the cases studied, non-specific interaction proceeded, e.g. metal binding to the heterocyclic moiety and not to the aza-crown ether fragment. The same conclusion has been made concerning complexes formed as extraction species between compound (**7**) and Hg^{2+}, Pd^{2+}, etc.[15]

EXPERIMENTAL

General

Melting points were determined on a Kofler apparatus and are uncorrected. ^{1}H-NMR spectra were recorded on a Bruker WM 250 MHz instrument in $CDCl_3$ and DMSO-d_6 with TMS as internal reference. The absorption spectra were recorded on a Carl Zeiss Jena Specord M40 spectrophotometer (2×10^{-5} mol/litre in ethanol) and IR spectra on a Specord 71.

Preparation of 4-formilbenzo-aza-15-crown-5 (2)

N-phenyl-(aza-15-crown-5) (1 g, 3·4 mmol) was dissolved in 3 ml (2·9 g, 40 mmol) DMF. After cooling to −10°C, 0·521 g (0·31 ml, 3·4 mmol) $POCl_3$ was added dropwise. The mixture was stirred for 10 min at −10°C, then for 1 h at room temperature, finally for 4 h at 100°C. The reaction mixture was cooled, poured onto ice and the pH adjusted to 7 with 40% NaOH. The solid product thus obtained was purified by dissolving in ethyl acetate and precipitating with petroleum ether: yield 70%, m.p. 85–86°C (lit. m.p. 86–87°C).[7]

Preparation of 10

Guajazulene (0·290 g, 1·5 mmol) and (**2**) (0·500 g, 1·5 mmol) were dissolved in THF. A few drops of $HClO_4$ were added and the mixture was stirred at room temperature for 3 h. The precipitate was filtered, washed with dry ether and air-dried.

General procedure for styryl dyes 4–9

Compound **2** (0·500 g, 1·5 mmol) and the appropriate heterocycle (1·5 mmol) were refluxed for 30 min in 10 ml acetic anhydride. The reaction mixture was then cooled and the precipitate was filtered and dried. In cases where a precipitate did not occur, the reaction mixture was diluted with 10–20 ml ether, and the resultant solid collected and dried. The compounds were purified by recrystallization from ethanol, and converted to the perchlorate salts by adding an equimolar quantity of $NaClO_4$ to a hot solution of the compound.

^{1}H-NMR spectra (TMS int., δ (ppm))

4 ($CDCl_3$)—1·77 (s, 3H, —$C(CH_3)$), 3·63–3·81 (m, 20H, —CH_2O CH_2—, —N—CH_2—), 4·05 (s, 3H, —$\overset{+}{N}$—CH_3—), 7·23, 8·03 (d, d, H, H, —CH=CH—, J = 15·5 Hz), 7·38–7·54 (m, 4H, Ar).

5 (DMSO-d_6)—3·64–3·80 (m, 20H, —CH_2OCH_2—, —N—CH_2), 4·08 (s, 6H, —N—CH—$_3$), 6·72, 8·16 (d, d, 2H, 2H, Ar, J = 9·2 Hz), 7·53–7·70 (m, 4H, Ar), 8·29 (s, 1H, =CH—.

6 ($CDCl_3$)—1·59 (t, 3H, —$CH_2\underline{CH_3}$—), 4·84 (q, 2H, —$\underline{CH_2}CH_3$—), 3·61–3·75 (m, 20H, —CH_2—OCH_2—, —N—CH_2—), 6·66, 8·23 (d, d, 2H, 2H, Ar), 7·57–7·84 (m, 3H, Ar), 7·61, 8·62 (d, d, H, H, —CH=CH—, J = 15 Hz), 8·23–9·06 (m, 3H, Ar).

7 ($CDCl_3$)—1·57 (t, 3H, —$CH_2\underline{CH_3}$), 3·63–3·77 (m, 20H, —CH_2OCH_2—, —N—$\underline{CH_2}$—), 5·06 (q, 2H, —$\underline{CH_2}$—CH_3), 6·65, 8·02 (d, d, H, H, Ar, J = 9 Hz), 7·55–8·0 (m, 4H, Ar), 7·76, 7·88 (d, d, H, H, —CH=CH—, J = 15 Hz).

8 ($CDCl_3$)—1·64 (t, 3H, —$CH_2\underline{CH_3}$—), 3·63–3·81 (m, 20H, —CH_2OCH_2—, —N—CH_2—), 4·87 (q, 2H, —$\underline{CH_2}CH_3$), 6·78–7·80 (d, d, 2H, 2H, Ar, J = 9 Hz), 7·55–8·0 (m, 4H, Ar), 7·48, 7·79 (d, d, H, H, —CH=CH—, J = 15 Hz).

9 ($CDCl_3$)—1·76 (s, 6H, —$C(CH_3)_2$—), 3·60–3·84 (m, 20H, —CH_2OCH_2—, —N—CH_2—), 4·82, 4·68 (t, t, —$\underline{CH_2}$—$\underline{CH_2}OH$), 6·86, 7·89 (d, d, 2H, 2H, Ar), 7·27, 8·08 (d, d, H, H, —CH=CH—, J = 15·2 Hz), 7·37–7·47 (m, 4H, Ar).

10 ($CDCl_3$)—1·46 (d, 6H, $(CH_3)_2CH$), 2·6 (s, 6H, —CH_3), 3·32 (m, 1H, $(CH_3)_2\underline{CH}$), 3·63–3·89 (m, —CH_2OCH_2—), 7·02, 7·94 (d, d, 2H, 2H, Ar, J = 9 Hz), 8·04, 8·12 (d, d, 2H, 2H, Ar) 8·34 (s, =CH—).

Ir spectra (ν (cm^{-1}))

4 ($CHCl_3$)—1110, 1600, 1600 (sh); **5** (nujol)—1110, 1580, 1610, 2200; **6** ($CHCl_3$)—1110, 1580, 1610; **7** ($CHCl_3$)—1120, 1580, 1610; **8** ($CHCl_3$)—1120, 1580, 1610; **9** ($CHCl_3$)—1100, 1580, 1600; **10** ($CHCl_3$)—1100, 1600, 1600 (sh).

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