Dyes and Pigments **19** (1992) 215–222

Benzothiazolium Cyanine Dyes Containing a Trimethylene Bridge in the Polymethine Chain

T. Deligeorgiev, N. Gadjev

Department of Chemistry, University of Sofia, 1126 Sofia, Bulgaria

&

A. Lugade

Molecular Probes Inc., 4849 Pitchford Ave, Eugene, OR 97402, USA

(Received 11 February 1992; accepted 20 March 1992)

ABSTRACT

The synthesis of two benzothiazolium intermediates and derived cyanine dyes with a trimethylene bridge in the polymethine chain is described. The dyes absorb in the region from 451 to 650 nm. The structure of the new compounds is confirmed by elemental analysis, electron-absorption spectra, and, in some cases, ^{1}*H-NMR spectroscopy.*

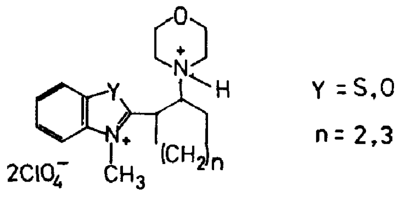
1 INTRODUCTION

One of the pathways for the synthesis of photostable polymethine dyes is the inclusion in the polymethine chain of cyclohexene or cyclopentene rings. This can be achieved by using dialdehydes containing such cyclic fragments as intermediates.[1,2] Fanghaenel and Behrmann[3] have described another synthetic approach using enamines to build cyclohexene and cyclopentene rings in the polymethine chain. With the same method,[3] the synthesis of some new styryl dyes is described. Thus the synthetic application of the method has been extended.

Dyes and Pigments 0143-7208/92/$05.00

2 RESULTS AND DISCUSSION

Fanghaenel and Behrmann have prepared reactive onium salts for the synthesis of symmetrical trimethinecyanine dyes (Scheme 1).



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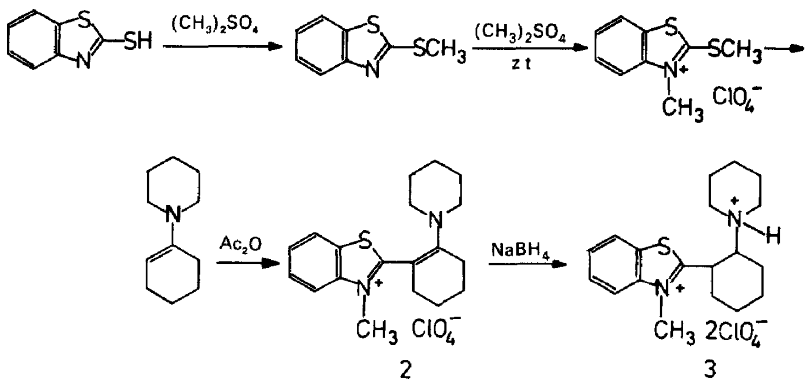
Scheme 1.

Applying this pathway, we prepared **2** and **3** (Scheme 2) by using 1-piperidinocyclohex-1-ene instead of 1-morpholinocyclohex-1-ene. In this case, we obtained **3** in 57% yield, i.e. a yield considerably higher than that reported by Fanghaenel and Behrmann.[3]



2 3

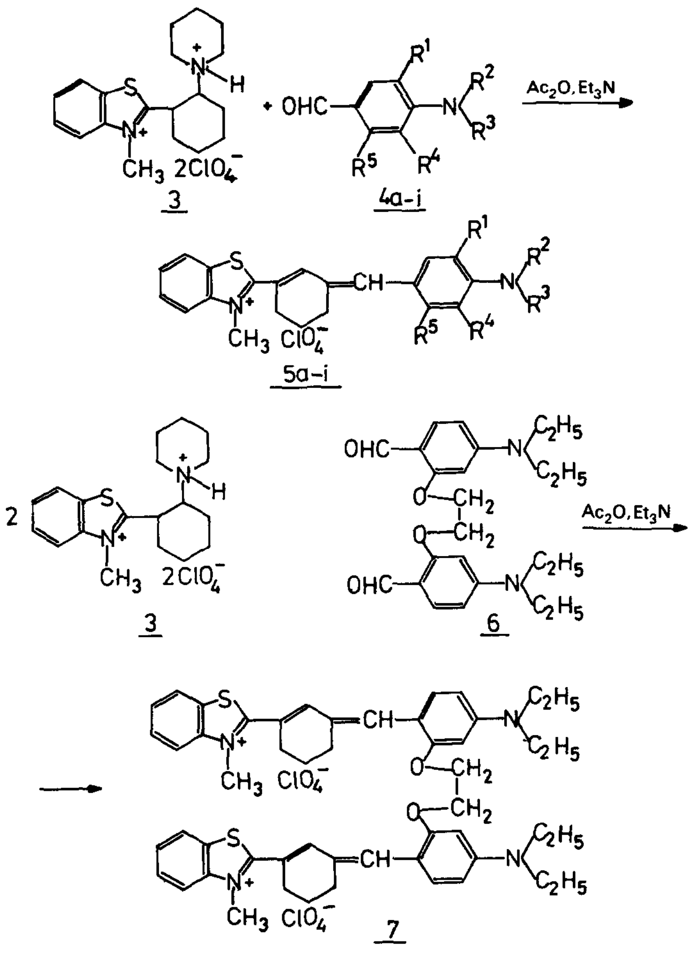
Scheme 2.

The preparation of the styryl dyes **5a**–**5i** by condensation of **3** with aldehydes **4a**–**4i** is shown in Scheme 3.

A pentamethinecyanine dye **9** was synthesized by condensation of 3-methyl-2-(2-piperidiniocyclohexyl)benzothiazolium diperchlorate **3** with 1(1H)-ethyl-2-formylmethylidenebenz[c.d.]indole[4] **8** (Scheme 4).

The substituents of dyes **5a**–**5i** are shown in Table 1.

The styryl dyes **5a**–**5i** and **7** absorb in the region 451–556 nm and have molar absorptivity from 19 000 to 56 000 (Table 2). A similar Styzyl 8[5] laser dye has λ_{max} equal to 570 nm (Scheme 5).



Scheme 3.

The hypsochromic shifts of the dyes **5a–5i** and **7** can be explained by steric hindrance of the benzothiazolium ring and the cyclohexene fragment, which is responsible for the decreased planarity of the molecule.[6] Dye **7** absorbs at 532 nm and has the highest molar absorptivity of 56 700. This can be assigned to the doubled dye molecule connected with the dioxyethylene bridge.

Compound **9** is a polymethine dye and absorbs at 650 nm. The lower molar absorptivity (50 200) indicates the presence of steric hindrance in this molecule, too.

The ^{1}H-NMR spectra of some of the dyes in DMSO-d_6 were recorded. The signals for the methyl protons at the nitrogen atom of the benzothiazolium ring appear as a singlet at 4·25–4·27 ppm with an intensity

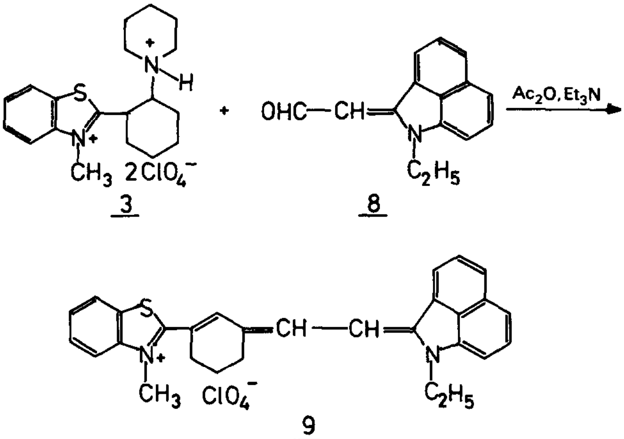
TABLE 1
Substituents of Dyes **5a–5i**

Dye	R_1	R_2	R_3	R_4	R_5
5a	H	CH_3	CH_3	H	H
5b	H	C_2H_5	C_2H_5	H	H
5c	H	$-(CH_2)_2-$		H	H
5d	H	$-(CH_2)_3-$		H	H
5e	H	$C_2H_4-O-C_2H_4$		H	H
5f	H	C_2H_5	C_2H_5	H	OCH_3
5g	H	C_2H_5	C_2H_5	H	OC_2H_5
5h	$-C_6H_4-$		C_2H_5	H	H
5i	$-(CH_2)_3-$		$-(CH_2)_3-$		H

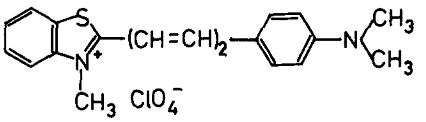
TABLE 2
Absorption Maxima (nm), Molar Extinction Coefficients (litre mol^{-1} cm^{-1}), Melting Points,[a] Yields, and Elemental-Analysis Data for **5a–5i**, **7**, and **9**

Dye	λ_{max}	*E*	*M.P.* (°*C*)	*Yield* (*%*)	*Molecular formula*	*Analysis found/calc. %*		
						C	*H*	*N*
5a	502	35 300	218–220	76	$C_{23}H_{25}ClN_2O_4S$	60·0	5·2	6·0
						59·9	5·4	6·1
5b	519	38 900	176–178	87	$C_{25}H_{29}ClN_2O_4S$	61·5	6·1	5·5
						61·4	5·9	5·7
5c	518	38 300	242–244	55	$C_{25}H_{27}ClN_2O_4S$	62·2	5·7	5·4
						61·7	5·5	5·7
5d	483	27 700	206–208	80	$C_{26}H_{29}ClN_2O_4S$	62·1	5·5	5·5
						62·3	5·8	5·6
5e	458	25 800	217–219	40	$C_{25}H_{27}ClN_2O_5S$	60·0	5·4	5·3
						59·9	5·4	5·6
5f	537	32 400	206–208	82	$C_{26}H_{31}ClN_2O_5S$	60·4	6·0	5·4
						60·2	6·0	5·4
5g	538	25 200	182–183	97	$C_{27}H_{33}ClN_2O_5S$	61·1	6·0	5·3
						60·8	6·2	5·3
5h	451	19 200	280–282	38	$C_{29}H_{27}ClN_2O_4S$	65·3	5·2	4·7
						65·1	5·1	5·2
5i	556	31 500	216–218	89	$C_{27}H_{29}ClN_2O_4S$	63·3	5·9	5·3
						63·2	5·7	5·5
7	532	56 700	260–262	82	$C_{52}H_{60}Cl_2N_4O_{10}S$	60·0	5·6	5·2
						60·3	5·8	5·4
9	650	50 200	249–252	89	$C_{29}H_{27}ClN_2O_4S$	65·3	4·9	4·9
						65·1	5·0	5·2

[a] **5b**, **5c**, **5f**, **5g**, **5h**, **7**, and **9** were recrystallized from methanol, **5a** from acetone, **5d** and **5e** from acetonitrile/ethanol 1:1, and **5i** from methoxyethanol.



Scheme 4.



Styzyl 8

Scheme 5.

for three protons. The methylene proton signals from the cyclohexene fragment are recorded as multiplets at 1·89–1·92 ppm (with an intensity for two protons) for the central CH_2 group and as a triplet (with an intensity for four protons) at 2·74–2·78 ppm for the two other CH_2 groups.

The proton from the cyclohexene fragment and the proton of the =CH–Ar moiety appear as singlets at 7·39–7·45 ppm and 6·84–7·14 ppm, respectively, each of them with an intensity for one proton.

The aromatic protons show up as multiplets in the region 6·72–8·43 ppm with intensities for six (**5i**), seven (**5f**, **5g**), and eight (**5b**, **5c**, **5e**).

3 EXPERIMENTAL

3.1 General

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

3.2 Preparation of 2-thiomethylbenzothiazole

2-Mercaptobenzothiazole (20 g, 0·12M) was dissolved in sodium hydroxide solution (50 ml, 10%) with stirring. Dimethylsulphate, freshly washed with ice-water (11·5 ml, 0·12M), was added for 1 h to the alkaline solution. During the addition, the temperature was kept at about 40°C. After completion of the addition, the reaction mixture was cooled to 5–10°C (ice-water) with continuous stirring. The precipitated oil crystallized and was filtered by suction. The yield of the crude product was 20·3 g (94%), m.p. 44–46°C (lit. m.p. 46°C[7]).

3.3 Preparation of 2-thiomethyl-3-methylbenzothiazolium perchlorate[3]

2-Thiomethylbenzothiazole (7·2 g, 0·04M), acetic acid (12 ml), and dimethylsulphate (7·6 ml, 0·08M) were kept at room temperature for 12 h. The product was extracted with ether (120 ml) and filtered by suction, and the precipitate was dissolved in water. Sodium perchlorate (9·8 g, 0·04M) dissolved in the minimum amount of water was added to this solution. The precipitate was filtered and air-dried. The yield of the crude product was 11·3 g (95%), m.p. 168–175°C. After recrystallization from methanol, the product had m.p. 179–181°C (lit. m.p. 180°C[3]).

3.4 Preparation of 3-methyl-2-/2-piperidinocyclohex-1-enyl(2-pi... enyl)-benzothiazolium perchlorate

2-Thiomethyl-3-methylbenzothiazolium perchlorate (6 g, 0·02M), acetic anhydride (30 ml), and 1-piperidinocyclohex-1-en (10 ml, 0·04M) were refluxed for 10 min. The product was kept overnight in a freezer to crystallize and the precipitate formed was filtered, washed thoroughly with ether, and dried at 70–80°C. The yield was 7·6 g (92%), m.p. 231–236°C. After recrystallization from methanol, the m.p. was 240–242°C.

Analysis for $C_{19}H_{25}ClN_2O_4S$(M-412·5)
Found: %C—55·3 H—6·2 N—6·6
Calc.: %C—55·3 H—6·1 N—6·8

3.5 Preparation of 3-methyl-2-(2-piperidiniocyclohexyl)benzothiazolium diperchlorate 3

3-Methyl-2-(2-piperidinocyclohex-1-enyl)-benzothiazolium perchlorate (10·3 g, 0·0025M) and sodium borohydride (1·3 g, 0·035M) in acetonitrile (80 ml) were dissolved with stirring. Two portions of acetic acid (5 ml) were added dropwise at time intervals of 7 min and 15 min; after the second addition, 70% perchloric acid (6 ml) was also added. The reaction mixture was stirred for 1 h and then poured into ether (200 ml). After being left overnight in a freezer, the precipitate was filtered and washed with ether and methanol/ether 1:1. The yield of the product was 7·5 g (58%), m.p. 185–193°C. Recrystallization from methanol/acetonitrile 1:1 gave the pure product, m.p. 196–198°C.

Analysis for $C_{19}H_{28}Cl_2N_2O_8S$ (M—515)
Found: %C—44·5 H—5·7 N—5·5
Calc.: %C—44·3 H—5·4 N—5·4

3.6 Preparation of dyes 5a–5i, 7, and 9

3-Methyl-2-(2-piperidiniocyclohexyl)benzothiazolium diperchlorate (1 g, 0·002M), acetic anhydride (5 ml), triethylamine (0·7 ml), and the corresponding aldehyde (0·002M) were refluxed with stirring for 10 min, and, after cooling to room temperature, left for 12 h in a freezer. In cases when the product remained in solution, diethylether (50–60 ml) was added. The dyes were filtered, washed with ether, and dried (Table 2).

3.7 ^{1}H-NMR (DMSO-d_6) δ ppm data

5b—1·12 (t, 6H, $2CH_2\mathbf{CH_3}$); 1·92 (m, 2H, $CH_2\mathbf{CH_2}CH_2$); 2·78 (t, 4H, $\mathbf{CH_2}CH_2\mathbf{CH_2}$); 3·37 (q, 4H, $2\mathbf{CH_2}CH_3$); 4·26 (s, 3H, N–CH_3); 6·93 (s, H, =CH–Ar); 7·44 (s, H, =CH–); 6·72–8·36 (m, 8H, 2Ar).

5c—1·92 (m, 2H, $CH_2\mathbf{CH_2}CH_2$); 2·75 (t, 4H, $\mathbf{CH_2}CH_2\mathbf{CH_2}$); 3·28–3·42 (m, 8H, $(CH_2)_4$); 4·27 (s, 3H, N–CH_3); 6·93 (s, H, =CH–Ar); 7·44 (s, H, =CH–); 6·59–8·39 (m, 8H, 2Ar).

5e—1·89 (m, 2H, $CH_2\mathbf{CH_2}CH_2$); 2·78 (t, 4H, $\mathbf{CH_2}CH_2\mathbf{CH_2}$); 3·22 (t, 4H, CH_2OCH_2); 3·75 (t, 4H, CH_2NCH_2); 4·25 (s, 3H, N–CH_3); 6·94 (s, H, =CH–Ar); 7·39 (s, H, =CH–); 6·99–8·43 (m, 8H, 2Ar).

5f—1·14 (t, 6H, $2CH_2\mathbf{CH_3}$); 1·90 (m, 2H, $CH_2\mathbf{CH_2}CH_2$); 2·74 (t, 4H, $\mathbf{CH_2}CH_2\mathbf{CH_2}$); 3·37 (q, 4H, $2\mathbf{CH_2}CH_3$); 3·85 (s, 3H, OCH_3); 4·27 (s, 3H, N–CH_3); 7·14 (s, H, =CH–Ar); 7·45 (s, H, =CH–); 6·23–8·38 (m, 7H, 2Ar).

5g—1·13 (t, 6H, $2CH_2\mathbf{CH_3}$); 1·38 (t, 3H, $OCH_2\mathbf{CH_3}$); 1·87 (m, 2H, $CH_2\mathbf{CH_2}CH_2$); 2·74 (t, 4H, $\mathbf{CH_2}CH_2\mathbf{CH_2}$); 3·37 (q, 4H, $2\mathbf{CH_2}CH_3$); 4·10 (q, 2H, $O\mathbf{CH_2}CH_3$); 4·27 (s, 3H, N–CH_3); 7·16 (s, H, =CH–Ar); 7·45 (s, H, =CH–); 6·21–8·38 (m, 7H, 2Ar).

5i—1·88 (m, 6H, $2CH_2\mathbf{CH_2}CH_2N + CH_2\mathbf{CH_2}CH_2$); 2·69 (m, 8H, $2ArCH_2 + \mathbf{CH_2}CH_2\mathbf{CH_2}$); 3·25 (q, 4H, CH_2NCH_2); 4·25 (s, 3H, N–CH_3); 6·84 (s, H, =CH–Ar); 7·43 (s, H, =CH–); 6·98–8·35 (m, 6H, 2Ar).

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