Dyes and Pigments **11** (1989) 21–35

Synthesis and Characterization of Deep-Coloured Squarylium Dyes for Laser Optical Recording Media

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(Received 21 April 1988; accepted 2 June 1988)

ABSTRACT

The synthesis and characterization of some deep-coloured squarylium dyes was studied with respect to the development of media in optical recording systems.

The reaction of 3-ethyl-2-methylbenzothiazolium iodide and squaric acid in benzene/1-butanol gave 2,4-bis[(3-ethyl-2-benzothiazolylidene)methyl]-cyclobutadienylium-1,3-diolate (λ_{max}*667 nm) and its iodide adduct type compound as by-product. The latter was a new compound and had an absorption maximum at 796 nm. Similarly an iodide adduct of 2,4-bis[(3-ethyl-2-benzoselenazolylidene)methyl]cyclobutadienylium-1,3-diolate was also synthesized from 3-ethyl-2-methylbenzoselenazolium iodide and squaric acid. This compound had an absorption maximum at 815 nm, i.e. in the infrared wavelength region. Thus, these new dyes with an iodine atom and a butoxy group generally absorbed at a much longer wavelength (120–130 nm) than the corresponding parent dyes. The structures of the dyes is also discussed on the basis of IR and ESCA analyses.*

1 INTRODUCTION

There is current interest in the development of near-infrared-absorbing dyes for use in optical information-recording media for semiconductor lasers in electronics. Since the gallium–arsenic (Ga/As) diode laser emits infrared light at 780–850 nm, the dyes have to absorb light over 700 nm. The infrared dyes are used as a recording single layer in the optical recording systems, and

Dyes and Pigments 0143-7208/89/$03·50

some pits on the dye layer are formed by laser irradiation. The recorded information can be reproduced at the same wavelength by means of the reflection changes on the dye-layer reflection.

Recently some infrared dyes such as pentamethinecyanine,[1,2] napthoquinonoid,[3] anthraquinoid,[4] phthalocyanine[5] and nickel complex dyes[6,7] have been reported as functional dyes for optical recording media for semiconductor lasers.[8-11]

The syntheses of squarylium dyes having absorption maxima below 700 nm have been reported by Sprenger & Ziegenbein[12] and Tanaka *et al.*[13] More recently, Law & Bailey[14,15] have reported the synthesis and xerographic properties of bis(4-methylbenzylaminophenyl)squaraines having absorption maxima in the region 626–631 nm. However, little has been done to synthesize deep-coloured squarylium dyes.[16,17]

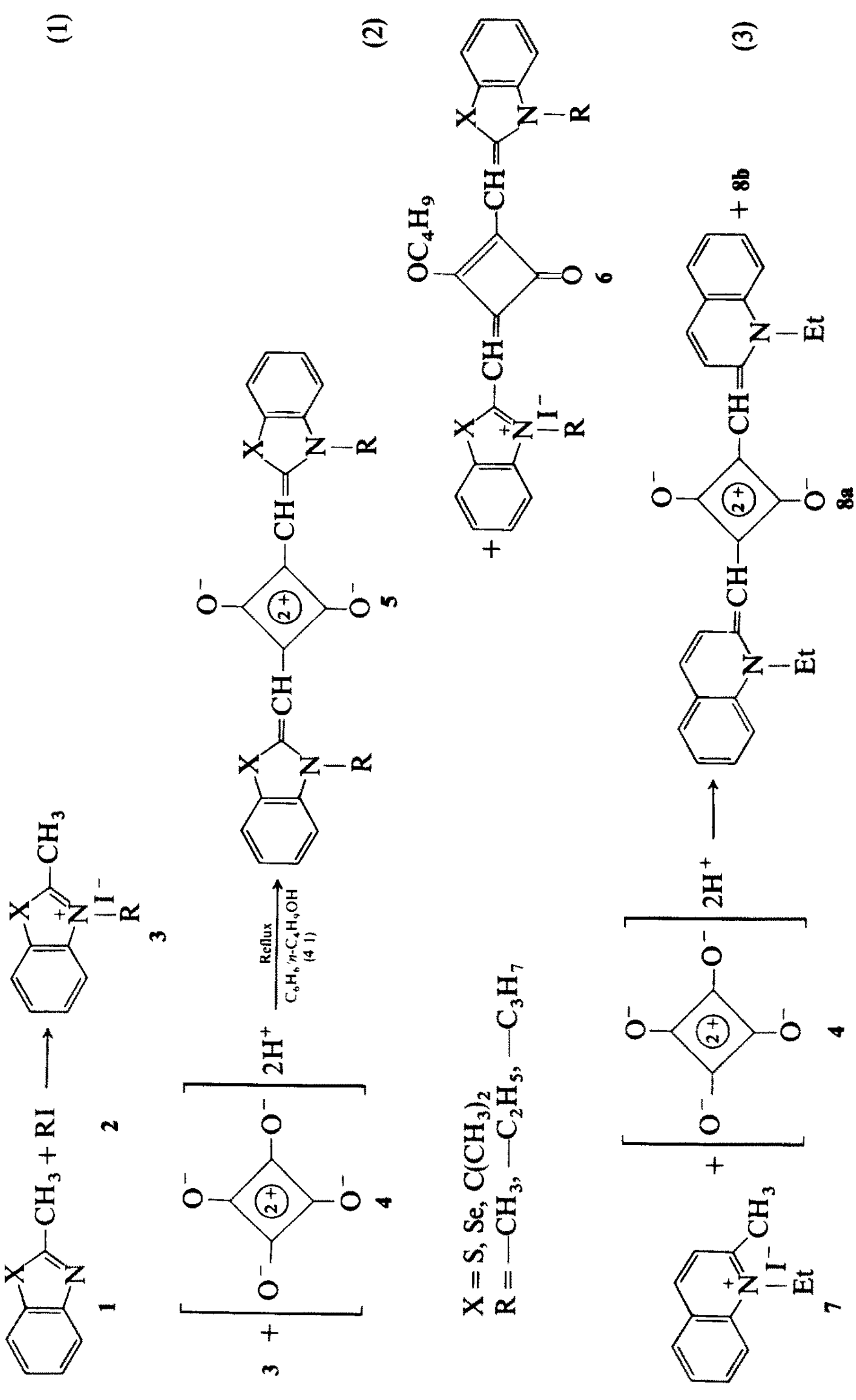
In this paper we report the syntheses of new infrared-absorbing squarylium dyes, and we discuss also the structures of the dyes on the basis of their visible absorption and IR spectra and electron spectroscopy for chemical analysis (ESCA).

2 RESULTS AND DISCUSSION

2.1 Preparations of squarylium dyes

Virtually all squarylium dyes in this work were synthesized from squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione) and 2-methylbenzothiazole, 2-methylbenzoselenazole, 2,3,3-trimethylindoline or 2-methylquinoline according to modified literature procedures.[12,13] The general procedures to prepare the squarylium dyes are shown in Scheme 1.

Typically, the reaction of 2-methylbenzothiazole (**1**, X = S) with ethyl iodide (**2**, $R = C_2H_5$) in ethanol gave 3-ethyl-2-methylbenzothiazolium iodide (**3b**, $R = C_2H_5$). A mixture of **3b** and squaric acid **4** in 1-butanol/benzene (4:1, v/v) containing a small amount of quinoline as catalyst was refluxed for 15 h to give a green-coloured solution, which contained **5b**, 2,4-bis[3-ethyl-2-benzothiazolylidene)methyl]cyclobutadienylium-1,3-diolate and **6b**. Dyes **5b** and **6b** were fractionated by solubility difference and by alumina column chromatography using chloroform as eluent. After these treatments, **5b** (bluish-green powder) was obtained in 35% yield, and **6b** (golden-coloured powder) was obtained in 12% yield as a by-product. In Fig. 1, the visible spectra of the reaction mixture and of the isolated dyes are shown. The absorption maximum for dye **5b** occurred at 667 nm, i.e. as described by Sprenger & Ziegenbein.[12] On the other hand, the new dye **6b** sharply absorbed near-infrared light at 796 nm in dichloromethane and at


(1)
1
2
3
(2)
4
5
Reflux
$C_6H_6/n\text{-}C_4H_9OH$ (4:1)
$2H^+$
6
OC_4H_9
(3)
7
8a
+ 8b
Et
$X = S, Se, C(CH_3)_2$
$R = —CH_3, —C_2H_5, —C_3H_7$

Scheme 1

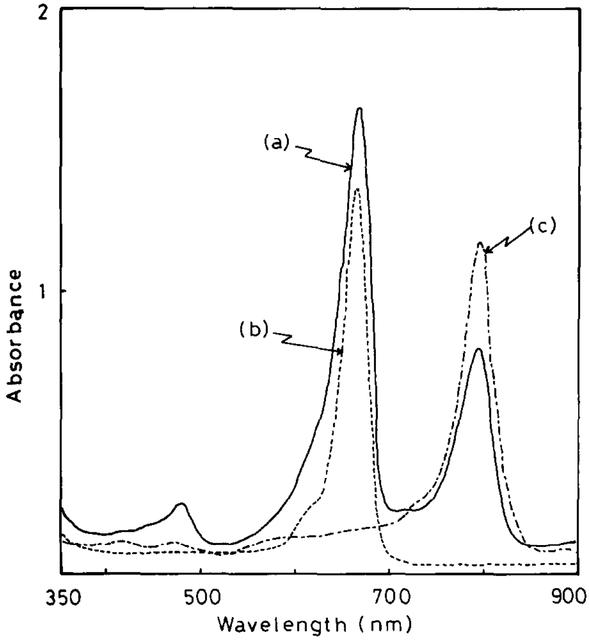


Fig. 1. Absorption spectra of reaction products obtained from squaric acid and 3-ethyl-2-methylbenzothiazolium iodide. These spectra were measured in chloroform. (a) The reaction mixture; (b) the isolated dye **5b**; (c) the isolated dye **6b**.

825 nm under solid conditions. Thus, **6b** is a deep-coloured dye, and absorbs at much longer wavelength than the corresponding main product **5b**. Elemental analysis of **6b** revealed the presence of an iodine atom and ESCA analysis also suggested it was an iodide adduct. Thus **6b**, having an iodine atom and a butoxy group compared **5b**, is a new dye which is able to absorb the emitted light of the gallium–arsenic laser.

In this reaction system, the yields of **5a–5c** and **6a–6c** decreased depending on the type of *N*-alkyl group on the 3-position of 2-methylbenzothiazolium iodide (**3**, X = S) in the following order; $—CH_3 > —C_2H_5 > —C_3H_7 > —C_4H_9$. These results are summarized in Table 1.

In the same manner the reaction of 3-ethyl-2-methylbenzoselenazolium iodide (**3d**, X = Se) with squaric acid in the presence of quinoline gave **5d**, 2,4-bis[(3-ethyl-2-benzoselenazolylidene)methyl]cyclobutadienylium-1,3-diolate (λ_{max} 683 nm) in 18% yield and its derivative (dye **6d**, yield 32%). Dye **6d** absorbs infrared light at 815 nm in dichloromethane and exhibits a bathochromic shift of 132 nm in comparison with the corresponding dye **5d**, which has no iodine atom or butoxy group.

Similarly the reaction of 1-ethyl-2,3,3-trimethylindolinium iodide (**3e**, X = CMe_2) with squaric acid gave **5e**, 2,4-bis[(1-ethyl-3,3-dimethyl-2-indolinylidene)methyl]cyclobutadienylium-1,3-diolate, in *c*. 60% yield. Dye

TABLE 1

Preparation and Properties of Some Squarylium Dyes

Compound	*Yield*[a] (%)	*M.p.* (°C)	λ_{max}[b] (*nm*)	ε (× 10^5)	*IR*[c] (*cm*$^{-1}$)
5a (X = S, R = CH_3)	49·5	>300	667	1·2	1 570(s)
6a (X = S, R = CH_3)	12·4	290–292	796	1·1	1 745, 1 624
5b (X = S, R = C_2H_5)	34·7	280–282	667	1·6	1 596 (s)
6b (X = S, R = C_2H_5)	13·6	290	796	1·3	1 735, 1 621
5c (X = S, R = C_3H_7)	3·0	>300	668	0·9	1 580(s)
6c (X = S, R = C_3H_7)	Trace	—	797	—	1 742, 1 620
5d (X = Se, R = C_2H_5)	18·0	>300	683	1·0	1 570 (s)
6d (X = Se, R = C_2H_5)	32·0	>300	815		1 748, 1 620
5e (X = CMe_2, R = C_2H_5)	60·3	295–297	634	3·3	1 593 (s)
6e (X = CMe_2, R = C_2H_5)	Not produced				
8a Quinaldine deriv.	55·4	>300	732	1·2	1 618 (s)
8b Quinaldine deriv.	10–15		833		

[a] The percentage (%) was based on the respective **3** used.
[b] In chloroform.
[c] In KBr; (s), sharp.

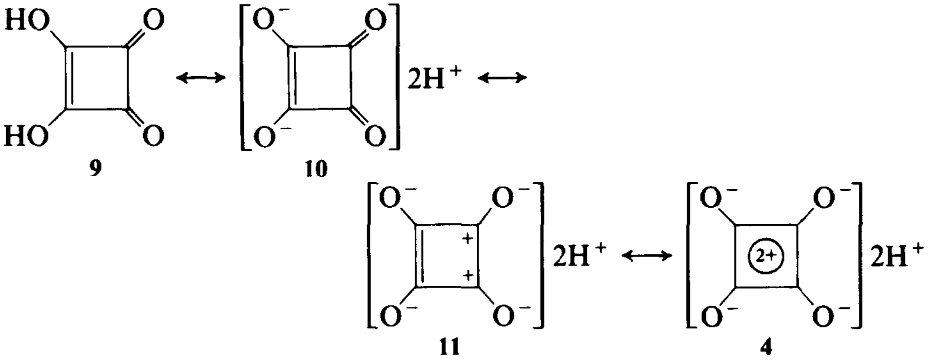
5e separated from the reaction mixture had visible absorption bands at 634 and 590 nm in chloroform. In this case, however, the by-product with an iodine atom was not produced.

Moreover, similar reaction of 1-ethyl-2-methylquinolinium iodide **7** with squaric acid gave **8a**, 2,4-bis[(1-ethyl-2(1*H*)-quinolylidene)methyl]-1,3-cyclobutadienylium-1,3-diolate and **8b**, depending on the reaction conditions. When the starting materials were refluxed in 1-butanol/benzene (4 : 1, v/v) containing small amounts of quinoline, **8a** was obtained preferentially. Dye **8a** was obtained in *c.* 55% yield, after separation from the reaction mixtures by column chromatography. The formation of **8b** (λ_{max} 833 nm) was indicated by the absorption spectrum, when a small amount of iodine was added to the solvents. Dye **8b** was obtained in 10–15% yield after appropriate treatments as described.

2.2 Visible and IR spectra of the products

It is well known that squaric acid **4** is represented in resonance limiting structures such as **9–11**. The interesting anion **9** would be expected to have much resonance stabilization since all four oxygen atoms should become equivalent through resonance.

As dyes derived from squaric acid, the production of two kinds of 1,2-type

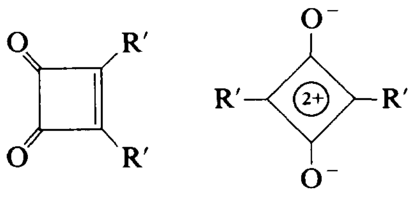


9 10 11 4

Scheme 2

12 and 1,3-type **13** is theoretically possible. The 1,2- and 1,3-type derivatives were distingushed by visible, NMR and IR spectra.[12,15,18] In IR analysis, Treibs & Jacob[18] have reported that the 1,2-type compound has two carbonyl absorptions in the 1700–1800 cm^{-1} region, and that the 1,3-type compound has a band based on a four-membered ring (C_4O_2) in the region of 1600 cm^{-1}. Dye **5b** obtained in this present study exhibits only a strong IR-absorption band at 1596 cm^{-1} (Fig. 2). Similarly dyes **5a**, **5c–5e** and **8a** exhibit a band only at 1570–1620 cm^{-1}. These bands are attributable to the C—C band stretching of the phenyl ring and the four-membered ring in the dye molecule. The absence of any C═O stretching at ~1740 cm^{-1} is a strong indication of extensive bond delocalization in the dye structure.[15] These results suggest that the dyes (**5a–5e** and **8a**) are 1,3-type compounds.

On the other hand, dye **6b** showed two bands at 1621 cm^{-1} and 1735 cm^{-1} (Fig. 2), but these bands differed from those described for the 1,2-type compound.[18] The former band is attributable to the C—C bond stretching of the phenyl ring and the four-membered ring. The latter band is assigned to a carbonyl group (C═O), depending on the contribution of the additional iodine atom and butoxy group in the dye structure. As described above, the dye **6b** (λ_{max} 795 nm) is a deeper colour than the corresponding 1,2-type compound (λ_{max} 520 nm).[18] From these wide differences in IR and visible spectra, it seems that **6b** is also a 1,3-type compound, having the same



12 13

Scheme 3

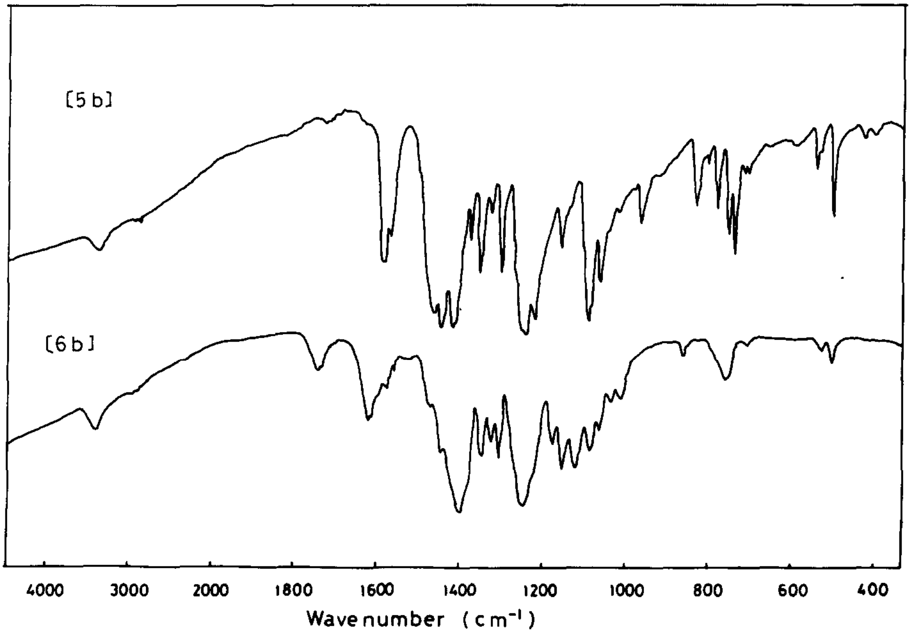


Fig. 2. IR spectra (KBr) of **5b** and **6b**.

differences as **5b** in the molecular structure. It can similarly be assumed that the other dyes (**6a**, **6c–6d** and **8b**) are also 1,3-type compounds.

2.3 ESCA analysis

In order to elucidate further the structural differences between **5b** and **6b**, ESCA analysis was carried out. The ESCA spectra of these dyes are shown in Fig. 3 and the results are summarized in Tables 2 and 3.

In Fig. 2, four peaks based on C_{1s}, N_{1s}, S_{2p} and O_{1s} were apparent for dye **5b**, and for dye **6b** an additional $I_{3d\,5/2}$ peak was present. The binding energy of $I_{3d\,5/2}$ in dye **6b** was 618·3 eV, and the value was approximately identical with that for the iodine in 3-ethyl-2-methylbenzothiazolium iodide **3b**, a starting material. The energy was also smaller (2·6 eV) than that for the iodine atom (covalent bond) in Rose Bengal. These facts suggest that the iodine atom in dye **6b** carries some negative charge (I^-). On the other hand, the binding energy for N_{1s} in **6b** was 400·8 eV. This value has a fairly good approximation to that for **3b**, but is larger than the value (399·4 eV) for N_{1s} of pyridine, which is not a pyridinium ion compound. This result suggests that there is a positive charge on a nitrogen atom in dye **6b**.

Table 3 shows the elemental composition ratios estimated for the compounds **3b**, **5b** and **6b** by ESCA analyses. The N/S/I ratios were 1 : 1 : 0 for

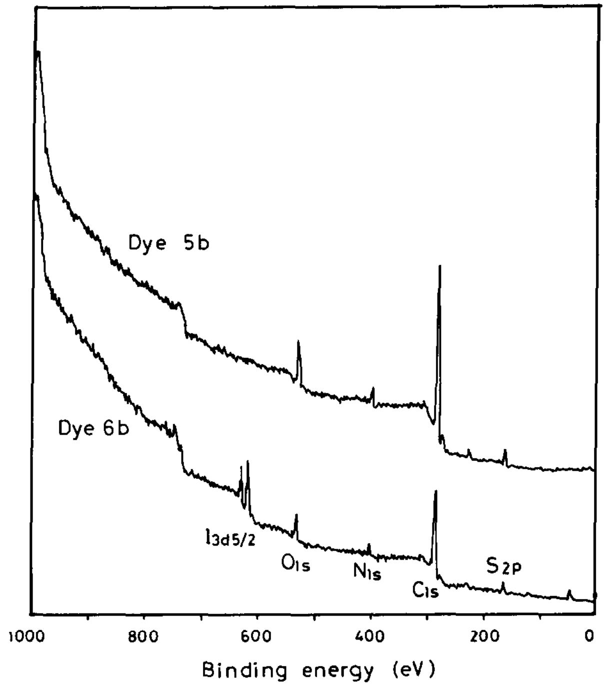


Fig. 3. Electron spectra (ESCA) of **5b** and **6b**: Mg Kα-radiation, power 10 kV, 30 mA, 10^{-5} Pa.

TABLE 2
Binding Energy (eV) for Some Compounds by ESCA Analyses[a]

Compound	*Element*					
	C_{1s}	O_{1s}	N_{1s}	S_{2p}	Se_{3d}	$I_{3d\,5/2}$
3b[b]	285·0	—	401·4	164·9	—	618·2
5b	285·0	533·2	400·3	164·3	—	—
6b	285·0	531·9	400·8	164·5	—	618·3
3d[c]	285·0	—	401·3	—	56·5	618·4
5d	285·0	531·0	400·4	—	56·2	—
6d	285·0	532·2	400·6	—	56·2	618·2
Pyridine[d]			399·4			
Pyridinium ion[d]			401·4			
Rose Bengal[d]						620·8

[a] X-ray (magnesium K α-ray), power 10 kV, 30 mA, 10^{-5} Pa.
[b] 3-Ethyl-2-methylbenzothiazolium iodide.
[c] 3-Ethyl-2-methylbenzoselenazolium iodide.
[d] Reference sample.

TABLE 3
Composition Ratios of Elements in Some Dyes and Intermediates by ESCA Analyses

Compound	*Element ratio*[a]				*N/S (or Se)/I ratio*[b]
	N	*S*	*Se*	*I*	
3b	1·0	0·9		1·1	1:1:1
5b	1·0	0·9		0·0	1:1:0
6b	1·0	1·1		0·5	1:1:0·5
3d	1·0		1·4	1·2	
5d	1·0		0·9	0·0	1:1:0
6d	1·0		0·9	0·4	1:1:0·5

[a] These values are given by comparison with the peak-height of N_{1s}.
[b] The N/S (or Se)/I ratios were calculated approximately.

5b, and 1:1:0·5 for **6b**. From these observations, it is concluded that a nitrogen atom on the dye **6b** has a pyridinium salt-type structure.

In a similar manner, the ESCA analyses for dyes **5d** and **6d** were carried out and the results are shown in Table 3. Consequently, the new deep-coloured dyes obtained in this study are proposed to have the structures **6a**–**6d** as shown in Scheme 1.

2.4 A consideration of the reaction mechanism

The squarylium dye synthesis described above was reported about two decades ago,[12] but has been little studied with respect to the reaction mechanism. Recently, Law & Bailey have reported that the reaction of squaric acid and *N*,*N*-dimethylaniline in 1-butanol/toluene proceeds via *n*-butyl squarate as an intermediate.[15]

In this work, using squaric acid and 3-alkyl-2-methylbenzothiazolium iodide 3 as model reactants, and 1-butanol/benzene as solvents, we have studied the reaction mechanism.

Since the synthesis of the squarylium dye described above starts with squaric acid, one can refer to this procedure as the acid route [eqn (2) in Scheme 1]. Both of **5b** and **6b** were produced by this procedure (Table 1). Additional experiments for the acid route exhibit that the yield of **6b** decreases as the concentration of the quinoline catalyst in the reaction medium increases. The addition of sulphuric acid catalyst at low concentration ($[H_2SO_4] = 0{\cdot}004\text{M}$) improved the yields of both dyes, but decreased the yields of the dyes at higher sulphuric acid concentration ($[H_2SO_4] \geq 0{\cdot}02\text{M}$). The yield of **6b** was however, increased by ~20% when a small amount of iodine was added to the reaction medium.

Furthermore, di-*n*-butyl squarate (**14**) was synthesized by the published procedure,[12] and then the reaction with **3a** was attempted (ester route). When the mixture was heated for 8 h at refux in 1-buthanol/benzene (4:1, v/v), **5a** and **6a** were formed with varying yields, depending on the reaction conditions. In the ester route procedure, **5a** was also formed preferentially. The formation of **5a** was found to be affected by the catalytic effects of quinoline (1 ml) or Naffion NR-50 (Superacid catalyst; Du Pont). Although the addition of sulphuric acid (0·1 M) was not effective, the catalytic effect at lower concentration ($[H_2SO_4] = 0{\cdot}004$ M) was apparent. The formation of **6a** decreased in presence of quinoline and increased in solvents containing iodine. When benzene alone was used as solvent, this reaction did not occur. These results are summarized in Table 4.

The most probable mechanism for the formation of **5a** and **6a** from di-*n*-butyl squarate in the ester route is shown in Scheme 4. It seems that the formation of **5a** involves steps **14** → **13** → **15** → **5a**. On the other hand the formation of **6a** involves steps **14** → **13** → **16** → **6a** or **14** → **16** → **6a**.

These observations on the ester route suggest that the mechanism for the acid route, using squaric acid as a starting material, involves the ester route process. That is, it seems that *n*-butyl squarate(s) is the precursor of the formation of squarylium dyes in both routes.

TABLE 4

Synthesis of Squarylium Dyes from Di-*n*-butyl Squarate by the Ester Route[a]

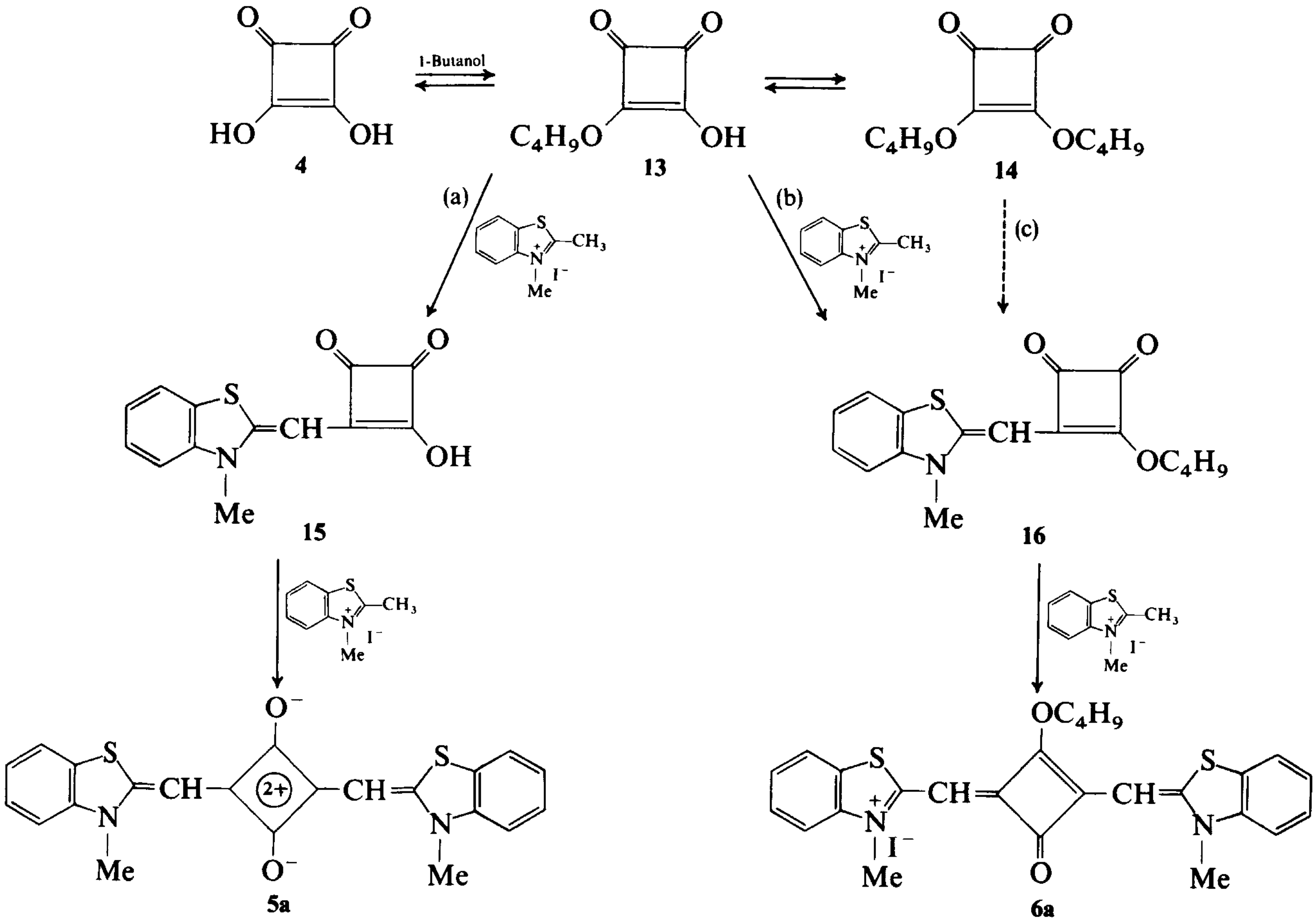
Reaction conditions		*Yield*[d]	
Solvents	*Catalyst*	**5a**	**6a**
1-Butanol/benzene[b]	None	67·2	6·1
1-Butanol/benzene	Quinoline (1 ml)	81·7	1·6
1-Butanol/benzene	Iodine (0·12 g)	60·1	9·6
1-Butanol/benzene	Naffion NR-50 (0·1 g)	81·0	6·8
1-Butanol/benzene	H_2SO_4 (0·1 M)[c]	Not produced	
1-Butanol/benzene	H_2SO_4 (0·004 M)[c]	71·8	3·8
Benzene	None	Not produced	
Benzene	Naffion NR-50 (0·1 g)	Not produced	

[a] The mixture of 2,3-dimethylbenzothiazolium iodide (2·6 mmol), di-*n*-butyl squarate (1·3 mmol) and various additives was refluxed for 10 h in the respective solvent.

[b] A mixture of 1-butanol (40 ml) and benzene (10 ml) was used.

[c] Molar concentrations in the solvent are shown.

[d] These values were calculated from the peak-heights in visible spectra of the reaction mixture.



Scheme 4

Whilst the reaction mechanism in the acid route is expected to be more complicated owing to contributions of other processes such as the electrophilic reaction[13] between **4** and **4**, it appears reasonable to investigate it in the context of the detailed mechanism of the reaction.

Application in optical recording systems of compounds **6b** and **6d** as described elsewhere.[19]

3 EXPERIMENTAL

The visible and IR spectra were measured using a Shimadzu UV-250 and an IR-420 spectrophotometer, respectively. Elemental analyses were recorded on a Yanaco CHN recorder MT-2. ESCA analyses were measured using a Shimadzu ESCA-850 type electron spectroscopy unit operating at 10 kV, 30 mA. The data were analysed using an ESPAC-200 computer. Column chromatography was carried out on activated aluminium oxide or silica gel (about 300-mesh) using chloroform as eluent.

3.1 Materials

Squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione; Aldrich) was reagent-grade and used without further purification. 2-Methylbenzothiazole, 2-methylbenzoselenazole, 2-methylquinoline and 2,3,3-trimethylindoline (Tokyo Chemical Co. Ltd) were used without further purification. Organic solvents were reagent-grade and were used after distillation.

3.2 *N*-Alkylation of 2-methylbenzothiazole and 2-methylbenzoselenazole

2-Methylbenzothiazole (14·9 g, 0·1 mol) and ethyl iodide (31·2 g, 0·2 mol) were refluxed for 7 h in 20 ml of ethanol. After the reaction, 3-ethyl-2-methylbenzothiazolium iodide **3b** was obtained in 56% yield (17·0 g, m.p. 224–225°C) by filtration. In a similar manner 3-methyl- and 3-propyl-2-methylbenzothiazolium iodide were in 60% (**3a**) and 5% (**3c**) yields, respectively. 3-Ethyl-2-methylbenzoselenazolium iodide **3d** was also obtained in 36% yield using a similar procedure.

3.3 Preparation of 2,4-bis[(3-alkylbenzothiazolylidene)methyl]cyclobutadienylium-1,3-diolate 5a–5c and their related compounds 6a–6c

3-Ethyl-2-methylbenzothiazolium iodide **3b** (2·0 g, 0·7 mmol) was reacted with squaric acid **4** (0·32 g, 3 mmol) by refluxing for 15 h in 40 ml of 1-butanol/benzene (4:1, v/v) containing 1 ml of quinoline and removing water of reaction. The reaction mixture was cooled to room temperature. After leaving overnight, the precipitated crude product and mother liquor were separated by filtration. The crude product contained **6b** together with **5b**. Dye **6b** was isolated from the crude product by washing with diethyl ether, benzene and/or ethyl acetate. Further **6b** was recrystallized from chloroform/ethyl acetate (1:1, v/v). After purification, **6b** was obtained in 12% yield as golden-coloured crystals, m.p. 282°C.

The above mother liquor, after filtering the product from the reaction mixture, was combined with the washing liquors and solvents were removed on a rotary evaporator. The residue was disolved in 5 ml of diethyl ether. Dye **5b** was separated from this residue solution by column chromatography (alumina) using chloroform as eluent. After evaporation, **5b** was obtained in 35% yield as bluish-green crystals, m.p. >300°C.

In a similar manner, dyes **5a**, **5c**, **6a** and **6c** were obtained. These reactions did not occur when using only benzene without 1-butanol.

Analysis:
5a, Found: C, 66·0; H, 4·0; N, 6·6; S, 15·0. Calculated for $C_{22}H_{16}N_2S_2O_2$: C, 65·3; H, 4·0; N, 7·0; S, 15·85%.
5b, Found: C, 66·7; H, 4·35; N, 6·3; S, 14·1. Calculated for $C_{24}H_{20}N_2S_2O_2$: C, 66·3; H, 4·7; N, 6·5; S, 14·8%.
6a, Found: C, 53·0; H, 3·6; N, 4·7; S, 10·35; I, 20·9. Calculated for $C_{26}H_{25}N_2S_2O_2I$: C, 53·1; H, 4·3; N, 4·8; S, 10·9; I, 21·6%.
6b, Found: C, 54·0; H, 3·5; N, 4·6; S, 10·8; I, 19·4. Calculated for $C_{28}H_{29}N_2S_2O_2I$: C, 54·5; H, 4·5; N, 4·6; S, 10·4; I, 20·6%.

3.4 Preparation of 2,4-bis[(3-ethylbenzoselenazolylidene)methyl]cyclobutadienylium-1,3-diolate 5e and its related dye 6e

A mixture of **3d** (2·0g) and squaric acid (0·32 g) in 30 ml of 1-butanol/benzene (4:1, v/v) containing quinoline (1 ml) was refluxed for 8 h at an oil-bath temperature of ~140°C. Water was removed by a water measuring trap. After reaction, diethyl ether was added to the reaction mixture, which was then kept for 12 h at room temperature. After similar treatments to those described above, **5d** and **6d** were isolated.

Analysis:
5d, Found: C, 54·9; H, 4·1; N, 4·7. Calculated for $C_{24}H_{20}N_2Se_2O_2$: C, 54·8; H, 3·8; N, 5·3%.
6d, Found: C, 47·8; H, 3·4; N, 3·9; I, 17·9. Calculated for $C_{28}H_{29}N_2Se_2O_2I$: C, 47·3; H, 4·1; N, 3·9; N, 3·9; I, 17·1%.

3.5 Preparation of 2,4-bis[(1-ethyl-3,3-dimethyl-2-indolinylidene)methyl]-cyclobutadienylium-1,3-diolate 5e

1-Ethyl-2,3,3-trimethylindoleninium iodide **3e** was obtained from the reaction of 2,3,3-trimethylindoline and ethyl iodide in ethanol. Compound **3e** (0·53 g, 1·8 mmol)and squaric acid (0·1 g, 0·9 mmol) were dissolved in 50 ml of 1-butanol/benzene (4:1, v/v) containing a small amount of quinoline, and the mixture was then heated for 2 h, with removal of water. After reaction, the mixture was cooled and the precipitated product was filtered. Dye **5e** was isolated from the crude product in 60·3% yield by alumina column chromatography using chloroform. The crystals of **5e** had a golden colour, but their solution was green. In this reaction the formation of an iodide adduct **6e** was not evident from the visible spectrum.

Analysis:
5e, Found: C, 80·8; H, 7·3; N, 5·7. Calculated for $C_{30}H_{32}N_2O_2$: C, 79·6; H, 7·1; N, 6·2%.

3.6 Preparation of squarylium dyes from di-*n*-butyl squarate

Squaric acid (3·42 g, 0·03 mol) was refluxed for 8 h in a mixture of 1-butanol (50 ml) and toluene (50 ml). Water was distilled off azeotropically and removed by a water-measuring tube. After the reaction, solvents were removed on a rotatory evaporator. Dibutyl squarate was then isolated by vacuum distillation (b.p. ~145°C at 0·5 Torr, yield 80%).

Di-*n*-butyl squarate (0·29 g, 1·3 mmol), 2,3-dimethylbenzothiazolium iodide (0·73g, 2·6 mmol), 1-butanol (40 ml) and benzene (10 ml) were stirred for 8 h at an oil-bath temperature of ~130°C. After cooling the mixture to room temperature, the precipitated product was filtered. The crude product contained **5a** and **6a**. It was dissolved in chloroform, and the components were measured spectro-photometrically. The results are summarized in Table 4.

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