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Cyanine Dyes from Polynitro- and Poly(trifluoromethylsulphonyl)-benzenes

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SUMMARY

New monomethine and trimethine cyanine dyes with benzothiazole or indole and polynitro- or poly(trifluoromethylsulphonyl)-substituted benzene rings attached to the ends of the polymethine chain have been synthesised. Atoms of fluorine or methyl groups were introduced to the α-position of the polymethine chain. The influence of nitro and trifluoromethylsulphonyl groups on the colour of these dyes is compared. It is shown that the CF_3SO_2 *group is a weaker auxochrome than the nitro group.*

1. INTRODUCTION

Organic dyes contain in their molecules a system of conjugated bonds with electron-withdrawing and donating groups attached to the ends of the chain of conjugation. The growth of electron effects of these groups produces a bathochromic shift in an absorption band. The nitro group is one of the strongest electron-withdrawing substituents and a very good auxochrome. The colour of many types of nitro dyes is determined by the presence of this group and its electronic influence.[1] The trifluoromethylsulphonyl group is an even stronger acceptor of electrons than the nitro

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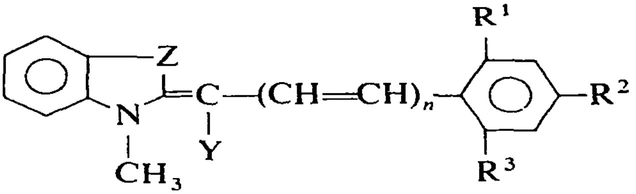
group,[2] but the properties of this substituent as an auxochrome have been much less extensively investigated.[3–5]

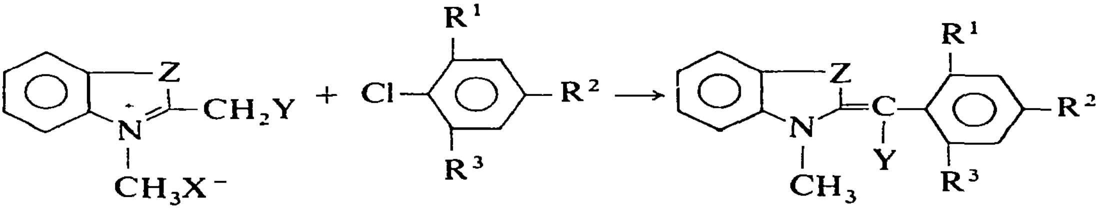
2. RESULTS AND DISCUSSION

In the present work the influence of trifluoromethylsulphonyl and nitro groups on the absorption spectra of asymmetric cyanine dyes derived from polysubstituted benzenes and benzothiazole or indoline is compared.



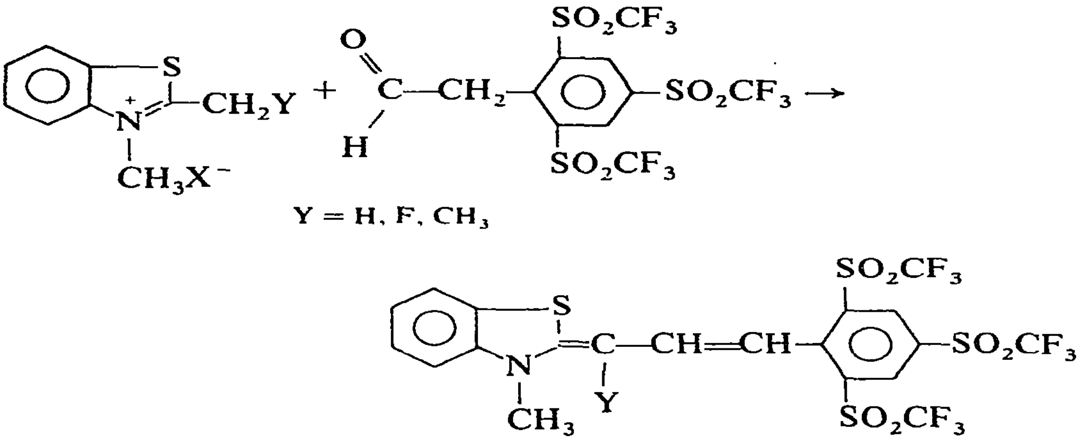
$Y = H, F, CH_3$;
$Z = S, C(CH_3)_2$;
$R^1, R^2, R^3 = H, SO_2CF_3, NO_2$
$n = 0, 1$

Monomethine dyes ($n = 0$) were obtained by condensation of quaternary salts of 2-methyl-, 2-fluoromethyl- and 2-ethyl-benzothiazole or 2,3,3-trimethylindoline with 2,6-dinitro-4-(trifluoromethylsulphonyl),[6] 2-nitro-4,6-bis(trifluoromethylsulphonyl)[7] or 2,4,6-tris(trifluoromethylsulphonyl)-chlorobenzene[8] in the presence of triethylamine or pyridine.



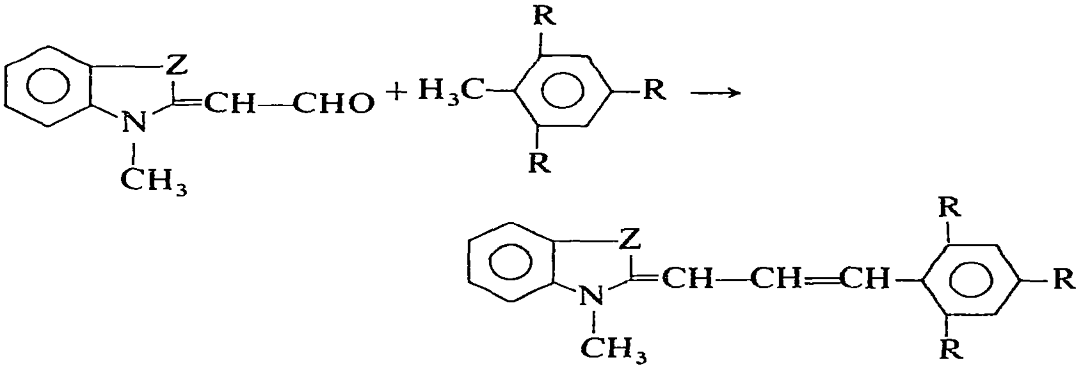
$Y = H, F, CH_3$; $Z = S, C(CH_3)_2$; $R^1, R^2, R^3 = H, SO_2CF_3, NO_2$

Several such nitro dyes derived from indoline and quinoline were previously synthesised,[9] but their absorption maxima were not determined. Benzothiazole derivative dyes containing di- and tri-nitrophenyl rings also have been described earlier by one of the authors.[10] Trimethine tris(trifluoromethylsulphonyl)-substituted dye derivatives of benzothiazole were prepared by condensation of the corresponding quaternary salts with 2,4,6-tris(trifluoromethylsulphonyl)phenylacetaldehyde[8] in acetic anhydride.



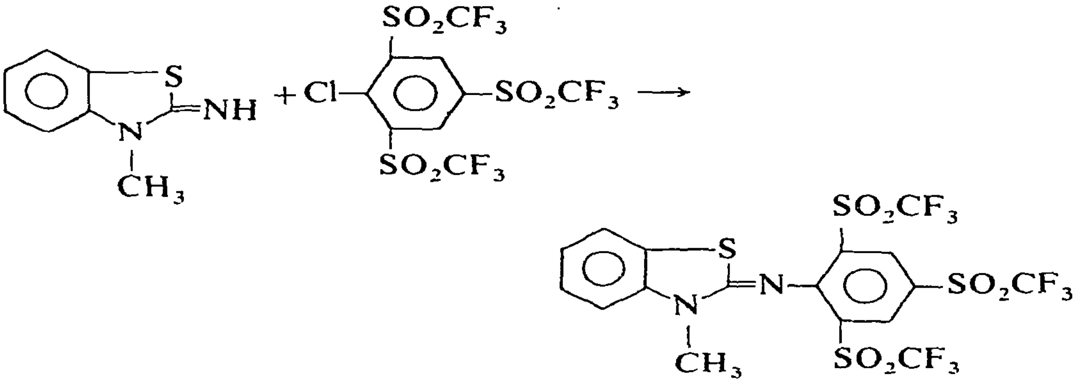
$Y = H, F, CH_3$

Trimethine dyes were also obtained by condensation of formylmethylene derivatives of benzothiazole or indoline with trinitrotoluene or 1,3,5-tris(trifluoromethylsulphonyl)toluene.[8]



$Z = S, C(CH_3)_2;\ R = NO_2, SO_2CF_3$

The absorption maxima (λ) of the synthesised dyes in benzene and ethanol, their difference ($\Delta\lambda$) and extinction (ε) in benzene are summarised in Tables 1–3. The interaction of 2-imino-3-methyl-3*H*-benzothiazole with 2,4,6-tris(trifluoromethylsulphonyl)chlorobenzene gives the dye with a nitrogen atom in the chain.



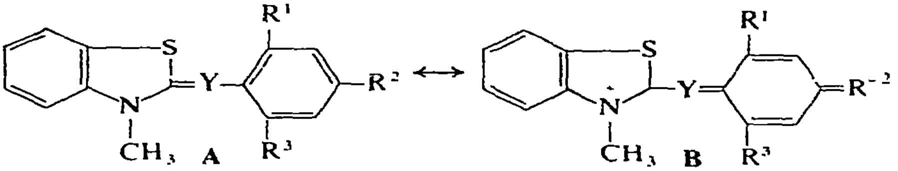
Dyes **1**–**4** and **14**–**17** reveal a negative solvatochromism.[11] The replacement of the nonpolar solvent (benzene) by a polar one (ethanol) causes a hypsochromic shift of the absorption band. This confirms the fact that the distribution of the electronic density in the ground state of these dyes may be described by the superposition of two limiting structures (**A**, **B** and **C**, **D**) with predominance of the charge-separated form. It should be noted that the slight solvatochromism of the dye **1** points to the energetic equivalence of two limiting structures (**A** and **B**). The gradual substitution of the nitro group for CF_3SO_2 in the benzene moiety of the dyes results in the growth of the absolute value of $\Delta\lambda$, characterising its negative solvatochromism. This gives evidence for a considerable shift of the equilibrium between the nonionic and ionic structures in favour of the latter. This fact is connected with the greater shift of the electron density from the heterocyclic ring to the benzene moiety of the molecule under the influence of the CF_3SO_2 groups in comparison with the nitro groups. At the same time the CF_3SO_2 group is a weaker auxochrome than the nitro group, as the dyes with CF_3SO_2 groups absorb at shorter wavelengths than the analogous dyes with nitro groups. This becomes evident when the absorption maxima of the pairs of dyes (**1**–**2**, **2**–**3**, **1**–**4**, **14**–**15**, **14**–**16**, **14**–**17**, etc.) are compared.

Apparently, π-electron conjugation in dyes with CF_3SO_2 groups reaches only the sulphur atom and is not passed on to the oxygen atoms owing to the tetrahedral configuration of the CF_3SO_2 group. This results in a shorter chain of conjugation in these dyes in comparison with nitro analogues.

Ionic limiting structure prevails only in the dyes with three nitro or CF_3SO_2 groups in the benzene moiety. In the case of only two such

TABLE 1

3-Methyl-2-poly(nitro- and trifluoromethylsulphonyl-)phenylmethylene-3*H*-benzothiazoles

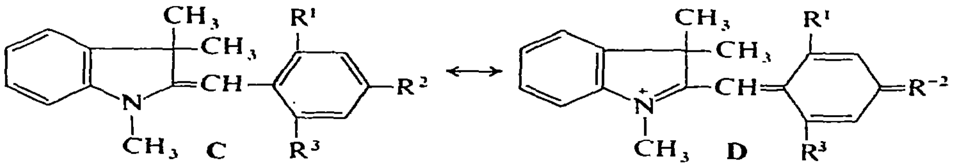


Dye	*Y*	*R*^{1}	*R*^{2}	*R*^{3}	λ_{max} (*nm*)		$\Delta\lambda$ (*nm*)	$\varepsilon \times 10^{-4}$
					Benzene	*Ethanol*		
1	CH	NO_2	NO_2	NO_2	552	550	−2	3
2	CH	NO_2	SO_2CF_3	NO_2	526	518	−8	1·12
3	CH	NO_2	SO_2CF_3	SO_2CF_3	512	507	−5	1·62
4	CH	SO_2CF_3	SO_2CF_3	SO_2CF_3	504	487	−17	3·02
5	CH	H	NO_2	NO_2	508	519	+11	—
6	CH	H	SO_2CF_3	SO_2CF_3	470	475	+5	—
7	CF	H	SO_2CF_3	SO_2CF_3	524	524	0	—
8	CF	NO_2	NO_2	NO_2	617	610	−7	—
9	CF	SO_2CF_3	SO_2CF_3	SO_2CF_3	554	482	−72	1·86
10	$C(CH_3)$	NO_2	NO_2	NO_2	605	605	0	1·25
11[a]	$C(CH_3)$	SO_2CF_3	SO_2CF_3	SO_2CF_3	431	392	−39	0·04
12	N	NO_2	NO_2	NO_2	430	—	—	—
13	N	SO_2CF_3	SO_2CF_3	SO_2CF_3	388	356	−32	0·03

[a] Dye **11** was obtained from the *N*-ethyl-substituted salt.

TABLE 2

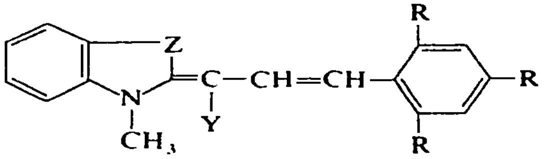
1,3,3-Trimethyl-2-poly(nitro- and trifluoromethylsulphonyl-)phenyl-2*H*-indoles



Dye	*R*^{1}	*R*^{2}	*R*^{3}	λ_{max} (*nm*)		$\Delta\lambda$ (*nm*)	$\varepsilon \times 10^{-4}$
				Benzene	*Ethanol*		
14	NO_2	NO_2	NO_2	540	536	−4	1·27
15	NO_2	SO_2CF_3	NO_2	522	616	−6	1·03
16	NO_2	SO_2CF_3	SO_2CF_3	510	502	−8	1·5
17	SO_2CF_3	SO_2CF_3	SO_2CF_3	506	434	−12	3·07

TABLE 3

2-3-Poly(nitro and trifluoromethylsulphonyl)phenylallyliden-3-methyl-3*H*-benzothiazoles and -1,3,3-trimethyl-2*H*-indoles



Dye	*Z*	*Y*	*R*	λ_{max} (*nm*)		Δλ (*nm*)	ε × *10*$^{-4}$
				Benzene	*Ethanol*		
18	S	H	NO_2	640	638	−2	2·31
19	S	H	SO_2CF_3	616	579	−37	5·28
20	S	F	SO_2CF_3	639	588	−51	14·74
21[a]	S	CH_3	SO_2CF_3	614	526	−88	6·85
22	$C(CH_3)_2$	H	NO_2	605	605	0	3·43
23	$C(CH_3)_2$	H	SO_2CF_3	610	602	−8	6·34

[a] Dye **21** was obtained from the *N*-ethyl-substituted salt.

substituents (dyes **5** and **6**) the nonpolar structure prevails, as is shown by the positive solvatochromism of these dyes.

The fluorine atom at the α-position of the chain usually produces a bathochromic shift (dyes **7–9**, in comparison with **1**, **4**, **6**). This fact is in good accordance with the Ferster–Dewar–Knott rules.[12–14] The electron-donating ability of the benzothiazole moiety after introduction of the atom of fluorine to the α-position is increased,[15] which leads to electronic asymmetry of the dye and results in negative solvatochromism. But at the same time the fluorine atom can produce a hypsochromic shift in strongly electronic asymmetric dyes,[15] as it does for example in the case of the solution of **9** in ethanol. If the bulky electron-donating methyl group attached to the α-position does not rotate the chain out of conjugation, the bathochromic shift is produced. It is observed, for example, in the case of the dye **10**, where the steric hindrance is decreased as the result of rotation of the nitro group at the *ortho*-position of the benzene ring. The benzene moiety of the dye **11** is sterically hindered by the methyl group at the α-position, the molecule is not coplanar and as a result the hypsochromic shift is observed. This shift is especially great (−95 nm) in ethanol solution and is caused mainly by rotation about a primary single bond between the benzothiazole ring and the carbon atom at the α-position.[16] In trimethine dyes (**20** and **21**) the spectral effects of introduction of the fluorine atoms or the methyl group are of the same nature as in the monomethine dyes, but smaller in value. Solvatochromic effects in these dyes are especially great as they are caused by the solvation of the polymethine chain.[17] The substitution of indolyl for the more electron-donating benzothiazolyl radical causes a bathochromic shift and leads to the growth of negative solvatochromism. The only exception is observed in cases when the electronic asymmetry is especially great (**20** and **23** in ethanol).

The nitrogen atoms at α-position of the chain (**12** and **13**) in accordance with the Ferster–Dewar–Knott rule produce a considerable hypsochromic shift.

3. EXPERIMENTAL

Electronic absorption spectra were recorded on a VSU-2P spectrometer.

3.1. 2-Nitro-4,6-bis(trifluoromethylsulphonyl)chlorobenzene (1)

A mixture of 2-nitro-4,6-bis(trifluoromethylsulphonyl)anisole (0·5 mmol) and pyridinium hydrochloride (1 mmol) was heated for 5–6 min at 150 °C. The reaction mixture was cooled to 80 °C and anhydrous benzene (5 ml) followed by phosphorus oxychloride (2 ml) were added. The solution was refluxed for 15 min, cooled and diluted with ether. The ether layer was separated and dried. After removal of ether in vacuum, the product was recrystallised from benzene. Yield: 79 %; m.p. 100–102 °C. Analysis found (%): Cl 8·56, 8·61. Calculated for $C_8H_2F_6ClNO_6S_2$: Cl 8·42.

3.2. Monomethine cyanine dyes (2–4, 11, 13–17)

A mixture of corresponding quaternary salt (0·5 mmol), corresponding chloronitro- or chlorotrifluoromethylsulphonyl-benzenes (0·5 mmol) and anhydrous triethylamine (1 mmol) in ethanol (7 ml) was stirred for 20 min at 20–25 °C. After removal of ethanol in vacuum, dyes were washed with water and recrystallised.

3.3. Monomethine cyanine dyes (6, 7, 9)

A mixture of quaternary salt of 2-fluoromethylbenzothiazole (0·5 mmol), 2,4,6-tris(trifluoromethylsulphonyl)chlorobenzene (0·5 mmol) or 2,4-bis(trifluoromethylsulphonyl)chlorobenzene (0·5 mmol) and anhydrous

TABLE 4
Some Properties and Elemental Analysis Data of the Synthesised Dyes

Dye	*Yield* (%)	*Melting point* (°C) *solvent*	*Found* (%)		*Formula*	*Required* (%)	
2	75	205–206, ethanol	N	8·69 8·80	$C_{16}H_{10}F_3N_3O_6S_2$	N	9·11
3	77	195–196, ethanol	C	37·01 37·10	$C_{17}H_{10}F_6N_2O_6S_3$	C	37·22
			H	1·92 1·97		H	1·82
4	78	206–208, ethanol	C	33·93 34·08	$C_{18}H_{10}F_9NO_6S_4$	C	34·01
			H	1·70 2·82		H	1·57
6	66	186–187, ethanol	C	39·92 39·97	$C_{17}H_{11}F_6NO_4S_3$	C	40·35
			H	2·16 2·36		H	2·18
7	55	174–176, benzene	C	39·17 39·25	$C_{17}H_{10}F_7NO_4S_3$	C	39·15
			H	2·10 2·30		H	1·91
9	53	192–193, benzene	C	32·75 33·00	$C_{18}H_9F_{10}NO_6S_4$	C	33·07
			H	1·50 1·36		H	1·37
11	71	225–227, ethanol	C	36·45 36·28	$C_{20}H_{14}F_9NO_6S_4$	C	36·19
			H	2·21		H	2·11
13	75	200–203, ethanol	C	31·87 31·98	$C_{17}H_9F_9N_2O_6S_3$	C	32·12
			H	1·36 1·40		H	1·41
14	74	175–177, benzene	N	14·42 14·60	$C_{18}H_{16}N_4O_6$	N	14·58
15	75	177–178, ethanol	C	47·88 48·07	$C_{19}H_{16}F_3N_3O_6S$	C	48·40
			H	3·38 3·44		H	3·39
16	78	158–160, benzene	C	43·20 43·40	$C_{20}H_{16}F_6N_2O_6S_2$	C	43·01
			H	2·90 2·70		H	2·86

TABLE 4—*continued*

Dye	*Yield* (%)	*Melting point* (°C) *solvent*	*Found* (%)		*Formula*	*Required* (%)	
17	80	165–167,	C	33·93	$C_{21}H_{16}F_9NO_6S_3$	C	34·01
		benzene		34·08		H	1·57
			H	1·80			
18	40	175–176,	N	13·62	$C_{17}H_{12}N_4O_6$	N	14·00
		ethanol					
19	57	195–196,	C	36·22	$C_{20}H_{12}F_9NO_6S_4$	C	36·30
		ethanol		36·28		H	1·88
			H	1·80			
				1·90			
20	59	197–198,	F	27·86	$C_{20}H_{11}F_{10}NO_6S_4$	F	27·98
		ethanol		28·06			
21	61	203–205,	C	38·53	$C_{22}H_{16}F_9NO_6S_4$	C	38·31
		ethanol		38·60		H	2·32
			H	2·10			
22	55	217–218,	N	13·49	$C_{20}H_{18}N_4O_5$	N	13·65
		acetone		13·67			
23	63	191–192,	C	40·64	$C_{23}H_{18}F_9NO_6S_3$	C	41·13
		ethanol		40·84		H	2·68
			H	2·50			
				2·53			

pyridine (1 mmol) in anhydrous benzene (5 ml) was refluxed for 1 h. The residue was sucked off, the solution was concentrated and the precipitated dye was recrystallised.

3.4. Trimethine cyanine dyes (18, 22)

A mixture of the corresponding formylmethylene derivative (0·5 mmol) and trinitro- or tris(trifluoromethylsulphonyl)-toluene (0·5 mmol) in acetic anhydride (5 ml) was refluxed for 1 h. The reaction mixture was cooled, diluted with water, and the dye was filtered off, dried and crystallised.

3.5. Trimethine cyanine dyes (19–21, 23)

A mixture of the corresponding quaternary salt (0·5 mmol) and tris(trifluoromethylsulphonyl)phenylacetaldehyde (0·5 mmol) in acetic anhydride (5 ml) was refluxed for 1 h. The reaction mixture was diluted with water, the dye was filtered off, dried and crystallised.

3.6. 3-Methyl-2-tris(trifluoromethylsulphonyl)phenylbenzothiazolonimine (13)

This was prepared as described above for the dye **2** by condensation of *N*-methylbenzothiazolonimine and 2,4,6-tris(trifluoromethylsulphonyl)-chlorobenzene.

Some physical properties, yields and the results of the microanalysis of the synthesised dyes are summarised in Table 4.

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