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Novel Synthesis of Methine Dyes Absorbing in the Near-Infrared Region

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ABSTRACT

*By reaction of 2-(1-cyano-1-methylthio)methyleneindan-1,3-dione (**2**) with nucleophiles, the corresponding substituted compounds (**10–16**) as typical donor–acceptor chromogens were obtained. Novel methine dyes (**24, 25**) absorbing in the near-IR region (650–850 nm) were synthesized by condensation of **16** and malononitrile with $TiCl_4$ and pyridine.*

1 INTRODUCTION

Appropriately functionalized (cyano, methoxycarbonyl, sulphonyl, nitro, acyl, etc.) ketene dithioacetals are versatile electrophilic reagents which have been extensively utilized in organic synthesis.[1–3] One such compound, 2-bis(methylthio)methyleneindan-1,3-dione (**1**), has been synthesized and studied with respect to the nucleophilic substitution of its methylthio group.[4–10]

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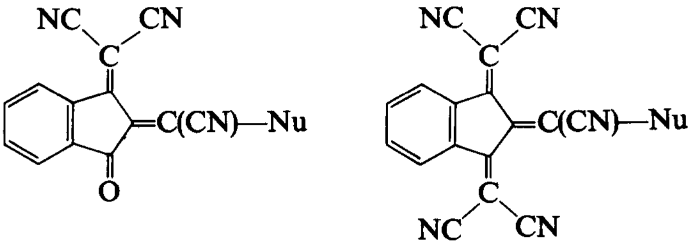


17a **Scheme 1** **17b**

As an extension of our previous studies on the ketene dithioacetal (**1**), we report here the synthesis of 2-(1-cyano-1-methylthio)-methyleneindan-1,3-dione (**2**) as an interesting synthon, and the substitution of its methylthio group with nucleophiles (**3**–**9**) to give the corresponding substituted products (**10**–**16**). These products **10**–**16**, based on indan-1,3-dione, are typical donor–acceptor chromogens[11–13] and replacement of one or two of the carbonyl groups in them by the more powerful electron acceptor dicyanovinyl group can give dyes of general structure (**17**) (Scheme 1).

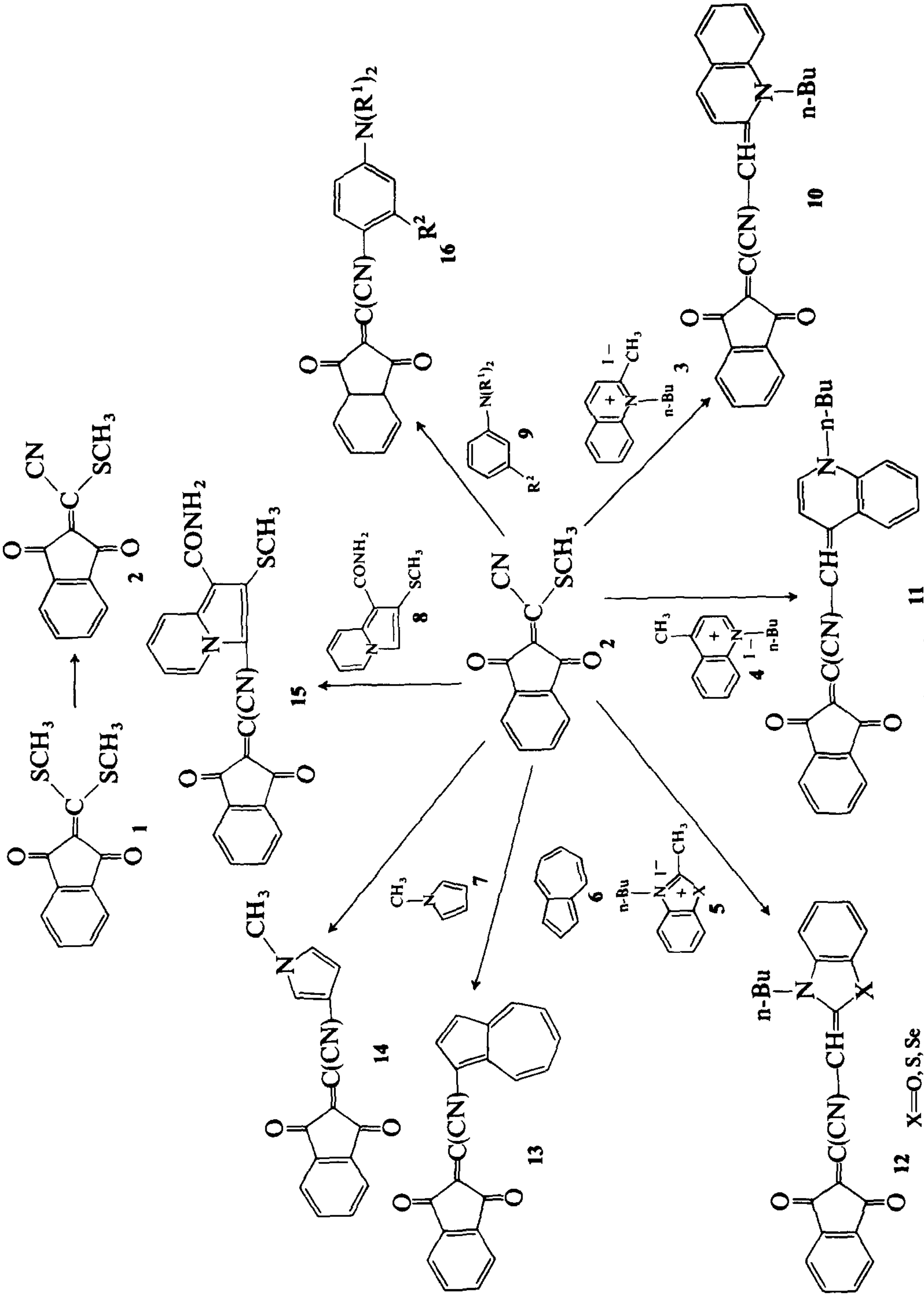
The report also examines the condensation of compound **16** with malononitrile in presence of $TiCl_4$ and pyridine, leading to the formation of the new near-infrared (IR) dyes (**24**, **25**), absorbing up to 850 nm.

2 RESULTS AND DISCUSSION

2.1 Synthesis of 2 and its substitution reactions

The starting material **2** was readily obtained in high yield by the reaction of **1** with sodium cyanide in dimethyl sulphoxide (DMSO) for 3 min. We also examined the reaction of **2** with the active methyl group of the quinolinium halides **3** and **4**. Thus, a solution of **2** with **3** or **4** in $CHCl_3$ in the presence of K_2CO_3 was stirred at room temperature for 48 h to give the derivatives **10** and **11** respectively in good yields. Similar reactions of **2** with N-butyl-2-methyl benzazolium iodides (**5a**–**c**) in $CHCl_3$ in presence of K_2CO_3 gave the desired products (**12a**–**c**) in 49–70% yield.

We also found that compound **2** was an effective electrophile for the substitution of azulene (**6**), N-methylpyrrole (**7**), the indolizine derivative (**8**)[14] or dialkylanilines (**9a**–**c**). Thus, when a mixture of **2** and **6** in AcOH was heated under reflux for 48 h, 2-(1-azulen-1-yl-1-cyano)methyleneindan-1,3-dione (**13**) was obtained in 53% yield. Compounds **14**, **15** and **16** were similarly prepared from the appropriate nucleophiles **7**, **8** and **9**. It was observed that the reaction of **2** and dialkylanilines (**9a**–**c**) could be effected smoothly with $TiCl_4$ and pyridine in CH_2Cl_2 at ice-bath temperature to give **16a**–**c** in


1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
X=O,S,Se
n-Bu
N(R¹)₂
R²
C(CN)
CONH₂
SCH₃
CN
CH₃

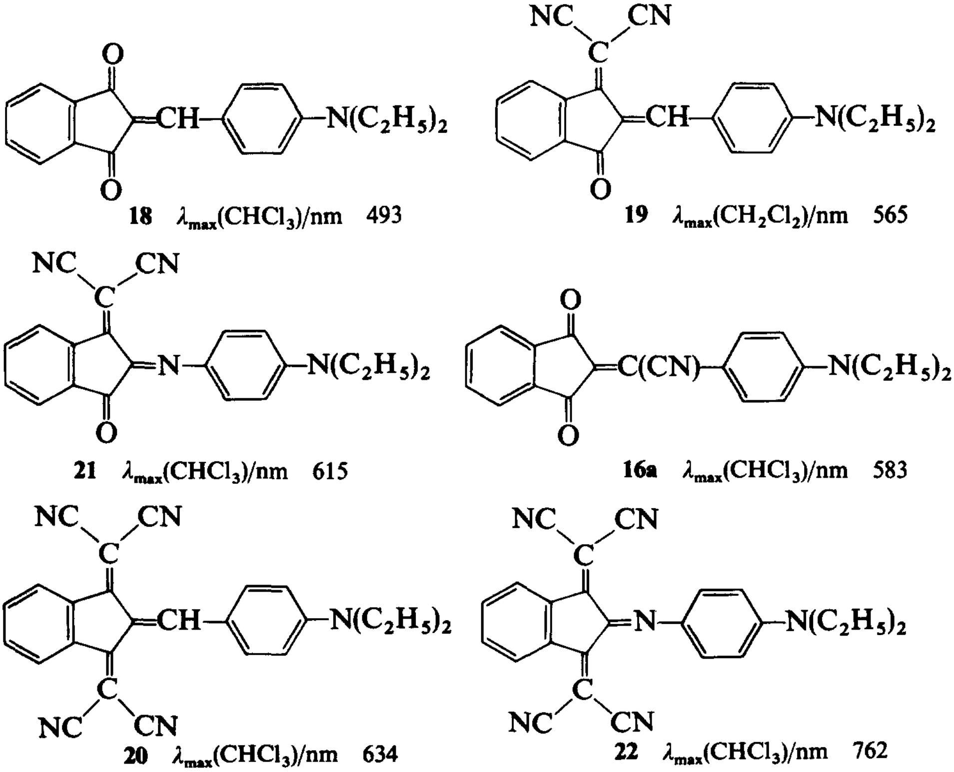
Scheme 2

68–72% yields (Scheme 2). The synthesis of **16a** using 2-(1,1-dicyanomethyleneindan)-1,3-dione has been previously reported by Junek *et al.*[15]

2.2 Synthesis of dyes

At the present time, dyes absorbing in the near-IR region (800–830 nm) are of particular interest for use in diode-laser optical storage systems. Methine dyes (**16a**, **18–22**) based on indan-1,3-dione have already been synthesized.[12,15–17] (Scheme 3).

Griffiths has pointed out that replacement of the central CH unit of compound **18** by C(CN) or that of the CH unit of compounds **19** or **20** by a more electronegative group (e.g. —N═) causes a bathochromic shift. This prompted us to synthesize the dicyanomethylene derivatives (**24**, **25**) in which the dicyanomethylene substituent was expected to produce a bathochromic shift. Attempts to obtain dyes **24** and **25** from **16** by the use of acetic anhydride or AcOH-piperidine, etc., in the condensation with malononitrile were fruitless. For example, reaction of **16a** with malononitrile, using AcOH-piperidine, gave only the tricyanoethylene derivative **23**.[18]



18 λ_{max}(CHCl$_3$)/nm 493

19 λ_{max}(CH$_2$Cl$_2$)/nm 565

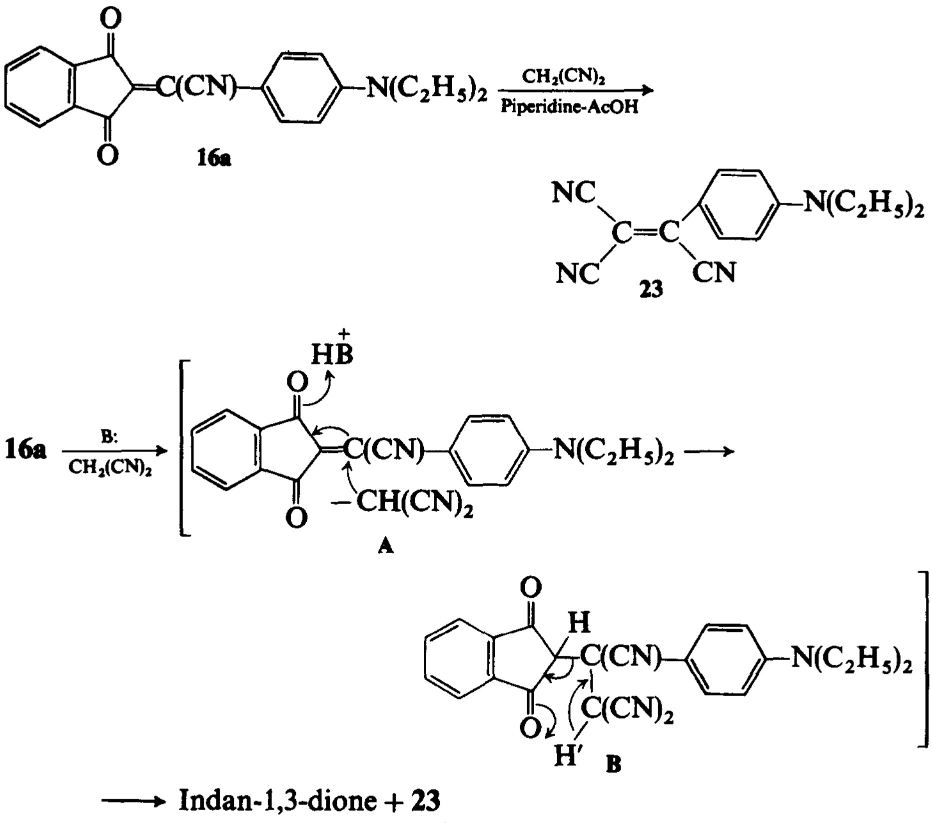
21 λ_{max}(CHCl$_3$)/nm 615

16a λ_{max}(CHCl$_3$)/nm 583

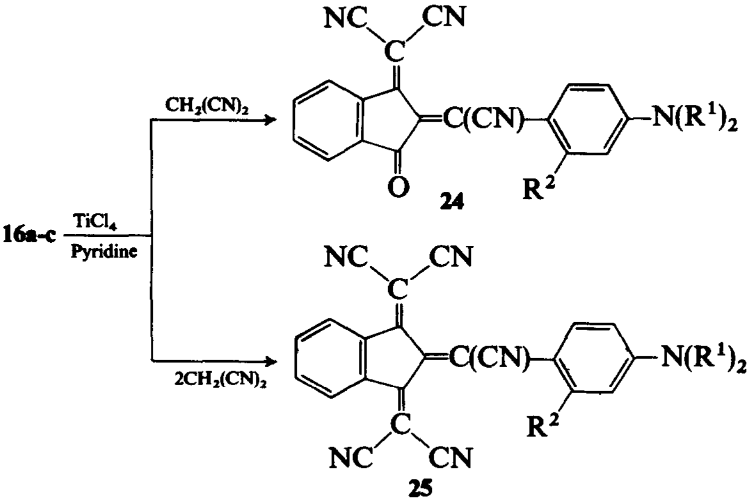
20 λ_{max}(CHCl$_3$)/nm 634

22 λ_{max}(CHCl$_3$)/nm 762

Scheme 3



Scheme 4



	R^1	R^2
24a	Et	H
24b	Et	Me
24c	n-Bu	H

	R^1	R^2
25a	Et	H
25b	Et	Me
25c	n-Bu	H

Scheme 5

The formation of **23** can be rationalized as follows: addition of malononitrile to **16a** would form the Michael adduct (**B**). The retro Michael reaction with elimination of indan-1,3-dione then gives **23** (Scheme 4). After much investigation, the synthesis of dyes **24** and **25** was achieved on employing the procedure of Ong & Keoshkerian.[19] Reaction of **16** with 1 equivalent of malononitrile in the presence of $TiCl_4$ and pyridine in CH_2Cl_2 at ice-bath temperature to room temperature gave 2-(1-aryl-1-cyano) methylene-3-(1,1-dicyano)methyleneindan-1-one (**24**) in good yield. In a similar manner reaction of **16** with excess of malononitrile gave 2-(1-aryl-1-cyano)methylene-1,3-bis(1,1-dicyanomethylene)indan (**25**) in high yield (Scheme 5).

2.3 Absorption of the dyes

The absorption spectra of these dyes (**24**, **25**) were recorded in $CHCl_3$ (see Table 1). In spite of the simple donor group, the dyes **24** and **25** absorb at 652–850 nm in $CHCl_3$. When one of the carbonyl groups of **16a** is replaced by a dicyanovinyl group (dye **24a**), the absorption band is shifted to a longer wavelength by *c.* 70 nm. Replacement of the second carbonyl group by a dicyanovinyl group causes a remarkable shift of *c.* 200 nm. Thus, **25a** absorbs at 849 nm in $CHCl_3$. As pointed out by Bello *et al.*,[12] this large shift is largely electronic in origin and cannot be attributed to any major enhancement of molecular planarity, since the intensity of **25a** is no higher than that of **16a**.

Replacement of the carbon bridge in **19** by nitrogen to give **21**[12] produces a bathochromic shift of 50 nm. However replacement of the central nitrogen in **21** by C(CN) to give **24a** produces an additional bathochromic shift of 37 nm. By analogy with **21** and **24a**, replacement of the central nitrogen in **22**[12] to give **25a** produces a large shift of 87 nm. These results suggest that, as pointed out by Bello *et al.*,[12] replacement of the central CH unit in **19** or **20**

TABLE 1
Visible Absorption Spectroscopic Data of Methine Dyes

Dye	λ_{max} *($CHCl_3$) (nm)*	ε_{max} *($l\,mol^{-1}\,cm^{-1}$)*
24a	652	51 000
24b	665	35 000
24c	658	49 000
25a	849	21 000
25b	833	11 000
25c	850	21 000
28a	655	59 000
28b	663	63 000

TABLE 2
Spectral Data for New Compounds

Compound	*IR* (*KBr*) (*cm*$^{-1}$)	*UV* λ_{max} (*nm*) (*log* ε)	^{1}H *NMR* ($CDCl_3$) δ(*ppm*)
10	2 200 (CN), 1 680 (C=O)	250 sh,[a,b] 258, 608	1·08 (3H, t, $J = 7$ Hz, $CH_2\underline{CH}_3$), 1·34–2·03 (4H, m, CH_2CH_2), 4·32–4·48 (2H, m, NCH_2), 7·50–7·86 (8H, m, Ar–H), 8·39–8·58 (2H, m, Ar–H), 9·03 (1H, s, =CH)
11	2 200 (CN), 1 680 (C=O)	239 (4·73)[b], 255 (4·54), 540 (4·67), 577 (4·91)	1·25 (3H, t, $J = 7$ Hz, $CH_2\underline{CH}_3$), 1·60–2·23 (4H, m, CH_2CH_2), 4·41–4·59 (2H, m, NCH_2), 7·51–8·52 (9H, m, Ar–H), 8·40–8·75 (2H, m, Ar–H)
12a	2 250 (CN), 1 680 (C=O)	251 (4·48)[b], 495 (4·79), 523 (5·00)	1·04 (3H, t, $J = 7$ Hz, $CH_2\underline{CH}_3$), 1·34–2·17 (4H, m, CH_2CH_2), 4·14 (2H, t, $J = 7$ Hz, NCH_2), 7·26–7·83 (8H, m, Ar–H), 7·86 (1H, s, =CH)
12b	2 000 (CN), 1 680 (C=O)	254,[a,b] 522 555	1·07 (3H, t, $J = 7$ Hz, $CH_2\underline{CH}_3$), 1·47–2·06 (4H, m, CH_2CH_2), 4·37 (2H, t, $J = 7$ Hz, NCH_2), 7·33–7·88 (8H, m, Ar–H), 8·56 (1H, s, =CH)
12c	2 000 (CN), 1 680 (C=O)	255,[a,b] 527, 561	1·08 (3H, t, $J = 7$ Hz, $CH_2\underline{CH}_3$), 1·56–2·09 (4H, m, CH_2CH_2), 4·38 (2H, t, $J = 7$ Hz, NCH_2), 7·34–7·80 (8H, m, Ar–H), 8·72 (1H, s, =CH)
13	2 200 (CN), 1 700 (C=O)	235,[a,b] 258 572	7·45 (1H, d, $J = 4$ Hz, $C_{3'}$–H), 7·65–8·14 (7H, m, $C_{5',6',7'}$–H and Ar–H), 8·36 (1H, d, $J = 4$ Hz, $C_{2'}$–H), 8·50 (1H, d, $J = 9$ Hz, $C_{4'}$–H), 8·60 (1H, d, $J = 8$ Hz, $C_{8'}$–H)
14	2 250 (CN), 1 680 (C=O)	249 (4·31),[b] 277 (4·26) 490 (4·37)	3·78 (3H, s, CH_3), 6·19 (1H, d, $J = 4$ Hz, $C_{4'}$–H), 7·16 (1H, s, $C_{2'}$–H), 7·19 (1H, d, $J = 4$ Hz, $C_{5'}$–H), 7·72–8·22 (4H, m, Ar–H)
15	2 250 (CN), 1 720 (C=O). 1 670 (C=O),	228 (4·44),[b] 260 (4·41), 335 (4·05), 585 (4·15)	2·44 (3H, s, SCH_3), 7·01 (1H, t, $J = 7$ Hz, $C_{6'}$–H), 7·38 (1H, t, $J = 7$ Hz, $C_{7'}$–H), 7·78–8·15 (7H, m, Ar–H), 8·64 (1H, d, $J = 7$ Hz, $C_{5'}$–H)
16a	2 200 (CN), 1 710 (C=O) 1 680 (C=O)	583 (4·51)[c]	1·28 (6H, t, $J = 7$ Hz, $NCH_2\underline{CH}_3$ × 2), 3·53 (4H, q, $J = 7$ Hz, NCH_2 × 2), 6·71 (2H, d, $J = 10$ Hz, $C_{3',5'}$–H) 7·76–7·99 (4H, m, Ar–H), 8·08 (2H, d, $J = 10$ Hz, $C_{2',6'}$–H)

(*continued*)

TABLE 2—*contd.*

Compound	*IR (KBr)* *(cm^{-1})*	*UV λ_{max} (nm)* *(log ε)*	*^1H NMR ($CDCl_3$)* *δ (ppm)*
16b	2 200 (CN), 1 710 (C=O), 1 680 (C=O)	607 (4·46)[c]	1·24 (6H, t, $J = 7·2$ Hz, $NCH_2\underline{CH}_3 \times 2$), 2·41 (3H, s, CH_3), 3·46 (4H, q, $J = 7·2$ Hz, NCH_2), 6·50–6·60 (2H, m, $C_{3',5'}$–H), 7·42 (1H, d, $J = 9·4$ Hz, $C_{6'}$–H), 7·73–8·06 (4H, m, Ar–H)
16c	2 200 (CN), 1 710 (C=O), 1 680 (C=O)	590 (4·17)[c]	0·99 (6H, t, $J = 7·2$ Hz, $CH_2\underline{CH}_3 \times 2$), 1·21–1·81 (8H, m, $CH_2CH_2 \times 2$), 3·44 (4H, t, $J = 7·2$ Hz, $NCH_2 \times 2$), 6·68 (2H, d, $J = 9·4$ Hz, $C_{3',5'}$–H), 7·79–8·03 (4H, m, Ar–H), 8·12 (2H, d, $J = 9·4$ Hz, $C_{2',6'}$–H)
27a	2 220 (CN), 1 680 (C=O)	564 (4·72)[c]	1·25 (6H, t, $J = 7$ Hz, $CH_2\underline{CH}_3 \times 2$), 3·57 (4H, q, $J = 7$ Hz, $NCH_2 \times 2$), 6·77 (2H, d, $J = 10$ Hz, $C_{3',5'}$–H), 7·76–8·15 (4H, m, $C_{4,5,6,7}$–H), 8·27 (2H, d, $J = 10$ Hz, $C_{2',6'}$–H)
27b	2 220 (CN), 1 680 (C=O)	570 (4·78)[c]	1·06 (6H, t, $J = 7$ Hz, $CH_2\underline{CH}_3 \times 2$), 1·21–1·83 (8H, m, $CH_2CH_2 \times 2$), 3·45 (4H, t, $J = 8$ Hz, $NCH_2 \times 2$), 6·75 (2H, d, $J = 9$ Hz, $C_{3',5'}$–H) 7·76–8·16 (4H, m, $C_{4,5,6,7}$–H), 8·27 (2H, d, $J = 9$ Hz, $C_{2',6'}$–H)

[a] Concentration unknown because of poor solubility.
[b] In EtOH.
[c] In $CHCl_3$.

by a more electronegative group (—N=, C(CN)) gives a bathochromic shift and that the C(CN) group is superior to the nitrogen as an electronegative group.

For comparison purposes, similar reactions of cyclic sulphone derivatives (**27**)[20,21] and malononitrile with $TiCl_4$ and pyridine readily gave dyes (**28**) in 65–68% yields. The products (**28**) had λ_{max} 655–663 nm in $CHCl_3$. When the carbonyl group of **27a** is replaced by a dicyanovinyl group (dye **28a**), the absorption band is shifted to longer wavelengths by 91 nm. In addition, the dye **28a** has a bathochromic shift of 3 nm relative to the carbonyl derivative (**24a**), which seems to be an interesting characteristic of cyclic sulphone derivatives (Scheme 6).

These dyes (**24**, **25**, **28**) are readily prepared excellent nonionic dyes with good solubility in organic solvents. We are in the process of preparing other dyes from **10** to **15** with the aim of extending our understanding of these interesting compounds (Tables 2–4).

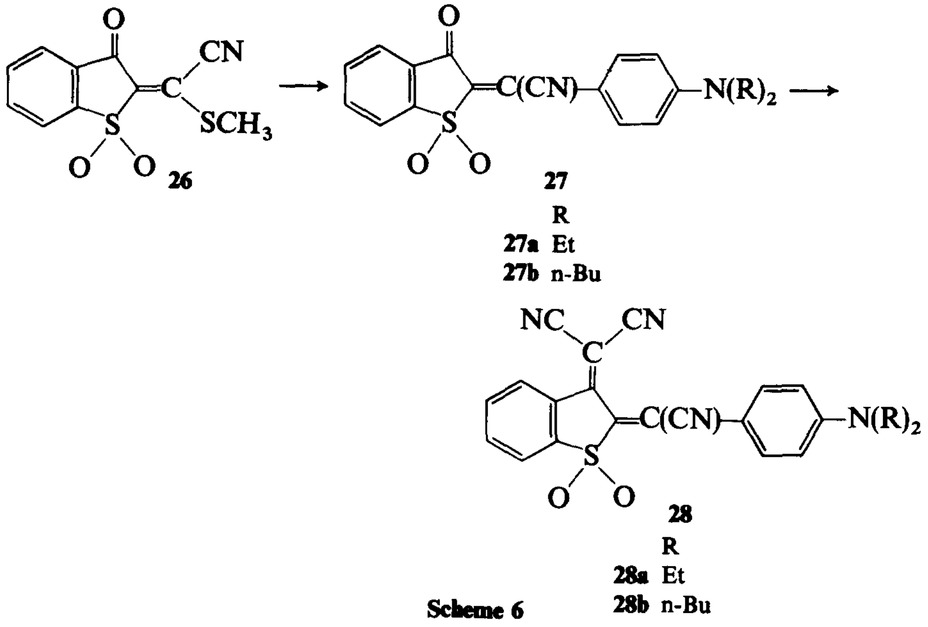
TABLE 3
Spectral Data for New Compounds

Compound	*IR (KBr)* (*cm*$^{-1}$)	^{1}*H NMR* (*CDCl*$_3$) δ (*ppm*)
24a	2 200 (CN), 1 680 (C=O)	1·25 (6H, t, J = 7·2 Hz, $NCH_2\underline{CH}_3$ × 2), 3·56 (4H, q, J = 7·2 Hz, NCH_2 × 2), 6·74 (2H, d, J = 9·7 Hz, $C_{3',5'}$_H), 7·62–7·88 (5H, m, Ar–H), 8·44–8·54 (1H, m, Ar–H)
24b	2 200 (CN), 1 720 (C=O)	1·27 (6H, t, J = 7·3 Hz, $NCH_2\underline{CH}_3$ × 2), 2·48 (3H, s, CH_3), 3·50 (4H, q, J = 7·3 Hz, NCH_2 × 2), 6·48 (2H, m, $C_{3',5'}$–H), 7·66–7·86 (4H, m, Ar–H), 8·42–8·48 (1H, m, Ar–H)
24c	2 200 (CN), 1 680 (C=O)	1·07 (6H, t, J = 6·1 Hz, $CH_2\underline{CH}_3$ × 2), 1·22–1·78 (8H, m, CH_2CH_2 × 2), 3·49 (4H, t, J = 6·3 Hz, NCH_2 × 2), 6·73 (2H, d, J = 9·5 Hz, $C_{3',5'}$–H), 7·62–7·82 (5H, m, Ar–H), 8·42–8·67 (1H, m, Ar–H)
25a	2 200 (CN)	1·27 (6H, t, J = 7·2 Hz, $NCH_2\underline{CH}_3$ × 2), 3·73 (4H, q, J = 7·2 Hz, NCH_2 × 2), 7·77–7·88 (4H, m, Ar–H), 7·88–7·89 (2H, m, Ar–H), 8·45–8·55 (2H, m, Ar–H)
25b	2 200 (CN)	1·32 (6H, t, J = 7·3 Hz, $NCH_2\underline{CH}_3$ × 2), 2·48 (3H, s, CH_3), 3·55 (4H, q, J = 7·3 Hz, NCH_2 × 2), 6·63–6·68 (2H, m, Ar–H), 7·15 (1H, d, J = 9·7 Hz, $C_{6'}$–H), 7·60–7·77 (2H, m, Ar–H), 8·43–8·52 (2H, m, Ar–H)
25c	2 200 (CN)	1·03 (6H, t, J = 6·3 Hz, $CH_2\underline{CH}_3$ × 2), 1·24–1·78 (8H, m, CH_2CH_2 × 2), 3·50–3·80 (4H, m, NCH_2), 6·91 (2H, d, J = 9·7 Hz, $C_{3',5'}$–H), 7·55–7·65 (2H, m, Ar–H), 7·70–7·94 (2H, m, Ar–H), 8·45–8·55 (2H, m, Ar–H)
28a	2 200 (CN)	1·31 (6H, t, J = 6 Hz, $CH_2\underline{CH}_3$ × 2), 3·57 (4H, q, J = 7 Hz, NCH_2 × 2), 6·80 (2H, d, J = 10 Hz, $C_{3',5'}$–H), 7·73–7·99 (5H, m, $C_{2',6',5,6,7}$–H), 8·56–8·66 (1H, m, C_4–H)
28b	2 200 (CN)	1·00 (6H, t, J = 6 Hz, $CH_2\underline{CH}_3$), 1·25–1·74 (8H, m, CH_2CH_2 × 2), 3·49 (4H, t, J = 6 Hz, NCH_2 × 2), 6·78 (2H, d, J = 7 Hz, $C_{3',5'}$–H), 7·78–8·00 (5H, m, $C_{2',6',5,6,7}$–H), 8·56–8·66 (1H, m, C_4–H)

TABLE 4
Yields and Characterization Data for New Compounds

Compound	*mp (°C)*	*Yield (%) (synthetic procedure*[a]*)*	*Molecular formula*	*Elemental analysis (%)*			
					C	*H*	*N*
10	243	98 (A)	$C_{25}H_{20}N_2O_2$	Calcd	78·93	5·30	7·36
				Found	78·75	5·42	7·40
11	285	56 (A)	$C_{25}H_{20}N_2O_2$	Calcd	78·93	5·30	7·36
				Found	78·83	5·40	7·30
12a	300>	49 (A)	$C_{23}H_{18}N_2O_3$	Calcd	74·58	4·90	7·56
				Found	74·79	5·00	7·66
12b	273	75 (A)	$C_{23}H_{18}N_2O_2S$	Calcd	71·48	4·69	7·25
				Found	71·38	4·79	7·21
12c	260	62 (A)	$C_{23}H_{18}N_2O_2Se$	Calcd	63·75	4·19	6·46
				Found	63·68	4·27	6·39
13	250	53 (B)	$C_{21}H_{11}NO_2$	Calcd	81·54	3·58	4·53
				Found	81·26	3·77	4·48
14	210	67 (B)	$C_{16}H_{10}N_2O_2$	Calcd	73·27	3·84	10·68
				Found	73·09	4·06	10·63
15	240	63 (B)	$C_{21}H_{13}N_3O_3S$	Calcd	65·11	3·38	10·85
				Found	65·01	3·39	10·80
16a[b]	125	53 (B)	$C_{21}H_{18}N_2O_2$	Calcd	76·34	5·49	8·48
		71 (C)		Found	76·50	5·85	8·20
16b	130	52 (B)	$C_{22}H_{20}N_2O_2$	Calcd	76·72	5·85	8·13
		72 (C)		Found	76·87	5·91	8·08
16c	105	49 (B)	$C_{25}H_{26}N_2O_2$	Calcd	77·69	6·78	7·25
		68 (C)		Found	77·49	6·81	7·23
24a	245	82	$C_{24}H_{18}N_4O$	Calcd	76·17	4·79	14·81
				Found	76·23	4·99	14·58
24b	230	90	$C_{25}H_{20}N_4O$	Calcd	76·51	5·14	14·28
				Found	76·55	5·30	14·25
24c	146	73	$C_{28}H_{26}N_4O$	Calcd	77·39	6·03	12·89
				Found	77·38	6·15	12·87
25a	242	77	$C_{27}H_{18}N_6$	Calcd	76·04	4·25	19·71
				Found	75·81	4·55	19·43
25b	220	75	$C_{28}H_{20}N_6$	Calcd	76·35	4·58	19·08
				Found	76·41	4·77	18·97
25c	210	85	$C_{31}H_{26}N_6$	Calcd	77·15	5·43	17·41
				Found	76·85	5·61	17·15
27a	207	69 (B)	$C_{20}H_{18}N_2O_3S$	Calcd	65·56	4·95	7·64
				Found	65·47	5·07	7·59
27b	213	50 (B)	$C_{24}H_{26}N_2O_3S$	Calcd	68·22	6·20	6·63
				Found	68·18	6·21	6·55
28a	238	65	$C_{23}H_{18}N_4O_2S$	Calcd	66·65	4·38	13·52
				Found	66·44	4·49	13·37
28b	224	68	$C_{27}H_{26}N_4O_2S$	Calcd	68·91	5·57	11·91
				Found	68·64	5·44	11·63

[a] See experimental section.
[b] Ref. 15, mp not given.



Scheme 6

3 EXPERIMENTAL

Melting points were determined with a Mitamura Mel-Temp and are uncorrected. Infrared (IR) spectra were recorded in KBr discs on a JASCO IRA-2 spectrometer. Ultraviolet (UV) spectra were recorded on a Hitachi EPS-2 spectrometer and a Hitachi U-3400 spectrometer. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained on a JNM-FX-90 (90 MHz) spectrometer with tetramethylsilane as internal standard. Chemical shifts are reported in part per million (δ). Apparent shapes of signals are described as s (singlet), d (doublet), t (triplet), q (quartet), dd (double doublet), m (multiplet). Elementary analyses (C, H, N) of all compounds described here were performed on a Yanagimoto MT-2 CHN recorder.

3.1 2-(1-Cyano-1-methylthio)methyleneindan-1,3-dione(2)

A mixture of 2-bis(methylthio)methyleneindan-1,3-dione(1)[5,7] (50 mmol) and sodium cyanide (150 mmol) in DMSO (50 ml) was stirred at room temperature for 3 min. The reaction mixture was poured into ice-water (300 ml) and the solution was acidified to litmus with 10% HCl. After stirring for 8 h, the solid was collected by filtration, washed with water, dried, and recrystallized from MeOH, to give **2** (82%), mp 220°C; IR (K Br) 2200

(CN), 1680 (C=O) cm^{-1}; UV λ_{max} (EtOH) 244 ($\log \varepsilon$ 4·26), 272 (4·20), 373 (4·35) nm; ^{1}H NMR ($CDCl_3$) δ 2·79 (3H, s, SCH_3), 7·75–8·06 (4H, m, Ar-H).

3.2 General procedure for the substitution of 2 with nucleophiles (3–9)

3.2.1 Procedure A

A mixture of **2** (2 mmol) and the appropriate quaternary nitrogen compound **3–5** (2 mmol) and K_2CO_3 (4 mmol) in $CHCl_3$ (50 ml) was stirred at room temperature for 48 h. The precipitate was filtered, washed with water, dried, and recrystallized from $CHCl_3$ to give products **10–12** respectively. For experimental and spectral data, see Tables 2 and 4.

3.2.2 Procedure B

A mixture of **2** (2 mmol) and compounds **6–9** (2 mmol) in AcOH (20 ml) was refluxed for 48 h and the mixture was then evaporated under reduced pressure. To the residue was added water (100 ml) and the mixture was made basic to litmus with $NaHCO_3$ and extracted with $CHCl_3$ (3 x 30 ml). The combined extracts were washed with water (50 ml), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was submitted to column chromatography on silica gel. From a benzene–$CHCl_3$ (2:1) fraction, the corresponding products (**13–16**) were obtained. For experimental and spectral data, see Tables 2 and 4.

3.2.3 Procedure C

To a well-stirred mixture of **2** (2 mmol) and **9** (2 mmol) in CH_2Cl_2 (50 ml) at ice-bath temperature and under a nitrogen atmosphere was added dropwise $TiCl_4$ over 10 min. After stirring for 5 min, a solution of pyridine (10 mmol) in CH_2Cl_2 (10 ml) was added dropwise over 30 min to the ice-cooled mixture. After the addition, the ice bath was removed to allow the reaction to continue at room temperature for another 24 h and ice-water (50 ml) was added. The mixture was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic phase was washed with aqueous $NaHCO_3$, dried (Na_2SO_4), and evaporated under reduced pressure. The residue was submitted to column chromatography on silica gel. From a benzene–$CHCl_3$ (2:1) fraction, the products **16a**–**16c** were obtained. For experimental and spectral data, see Tables 2 and 4.

3.3 1-(4-N,N-Diethylaminophenyl)-1,2,2-tricyanoethylene (23)

A mixture of **16a** (1 mmol), malononitrile (2 mmol) and AcOH-piperidine (5:1) (1 ml) in EtOH (30 ml) was refluxed for 6 h, the mixture was poured into ice-water (100 ml) and extracted with $CHCl_3$ (3 × 50 ml). The combined extracts were washed with water (50 ml), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was submitted to column chromatography on silica gel. From a benzene fraction, compound **23** was obtained in 72% yield: mp 171°C (lit.,[18] mp 164°C); IR (KBr) 2200 (CN) cm^{-1}; UV λ_{max} (EtOH) 257 ($\log \varepsilon$ 4·04), 396 (4·26), 526 (4·24) nm; ^1H NMR ($CDCl_3$) δ 1·28 (6H, t, $J = 7{\cdot}2$ Hz, $CH_2\underline{CH_3} \times 2$), 3·35 (4H, q, $J = 7{\cdot}2$ Hz, $\underline{CH_2}CH_3 \times 2$), 6·67–6·81 (2H, m, Ar-H), 7·97–8·15 (2H, m, Ar-H).

3.4 General procedure for the preparation of 24

Compound **24** was prepared by reaction of **16** (1 mmol) and malononitrile (1 mmol) with $TiCl_4$ (3 mmol) and pyridine (6 mmol) using procedure C above for the synthesis of **16**. After column chromatography on silica gel, **24** was obtained from a benzene–$CHCl_3$ (1:1) fraction. For experimental and spectral data, see Tables 1, 3 and 4.

3.5 General procedure for the preparation of compound 25

Compound **25** was prepared by reaction of compound **16** (1 mmol) and malonotrile (2·2 mmol) with $TiCl_4$ (3 mmol) and pyridine (6 mmol) using procedure C above for the synthesis of **16**. After column chromatography on silica gel, compound **25** was obtained from a $CHCl_3$–acetone (10:1) fraction. For experimental and spectral data, see Tables 1, 3 and 4.

3.6 2-(1-Aryl-1-cyano)methylene-2,3-dihydro-3-oxobenzo[b]thiophene 1,1-dioxides (27a, b)

Compounds **27a** and **27b** were prepared by reaction of 2-(1-cyano-1-methylthio)methylene-2,3-dihydro-3-oxobenzo[b]thiophene-1,1-dioxide (**26**)[21] (1 mmol) with N,N-diethylaniline or N,N-dibutylaniline (1 mmol) using procedure B above for the synthesis of **16**. For experimental and spectral data, see Tables 2 and 4.

3.7 2-(1-Aryl-1-cyano)methylene-3-(1,1-dicyano)methylene-2,3-dihydrobenzo[b]thiophene 1,1-dioxides (28a, b)

Compounds **28a** and **28b** were prepared by reaction of **27** (1 mmol) with malononitrile (1 mmol) in $TiCl_4$ (3 mmol) and pyridine (6 mmol) using procedure C above for synthesis of **16**. After column chromatography on silica gel, **28a**, **28b** were obtained from a benzene–$CHCl_3$ (1:1) fraction. For experimental and spectral data, see Tables 1, 3 and 4.

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