Near-infrared Absorbing Methine Dyes based on Dicyanovinyl Derivatives of Indane-1,3-dione

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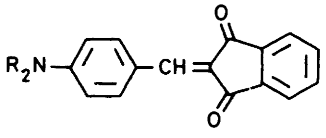
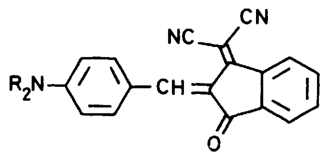
The synthesis, colour, and constitution of methine dyes formed by condensation of benzaldehydes and nitrosobenzenes with dicyanovinyl analogues of indane-1,3-dione have been investigated. 3-Dicyanovinylindan-1-one (**3**) and 1,3-bisdicyanovinylindane (**5**) give magenta ($\lambda_{max.}$ *ca.* 560 nm) and blue ($\lambda_{max.}$ *ca.* 600 nm) dyes respectively with 4-dialkylaminobenzaldehydes. Aza analogues formed from (**3**) and (**5**) and 4-dialkylaminonitrosobenzenes are significantly more bathochromic, and the exceptional shift in the case of dyes formed from (**5**) (*ca.* 150 nm) permits the synthesis of a new class of dyes absorbing in the near-i.r. region, with absorption maxima in the range 700—850 nm.

Methine dyes (**1**) based on indane-1,3-dione are typical donor–acceptor chromogens, and are generally yellow to orange in colour with a high absorption intensity.[1] Replacement of one of the carbonyl groups in (**1**) by the more powerful electron acceptor dicyanovinyl group gives dyes of general structure (**2**), which absorb some 70 nm to longer wavelengths than (**1**), with reduced intensity.[2] The donor–acceptor character of the chromophoric system of (**2**) suggests that further pronounced bathochromic shifts should be attainable by one or more of the following structural modifications: (a) replacement of the remaining carbonyl group in (**2**) by a second dicyanovinyl group; (b) modification of the arylamine ring to enhance its electron-donating properties; (c) replacement of the carbon bridge by a more electronegative grouping (*e.g.* -N=).


(1)


(2) a; R = Me
b; R = Et

Modifications (a) and (b) are self-evident but (c) requires some comment. In so far as the fundamental chromophore of (**2**) can be related to the isoconjugate odd alternant hydrocarbon anion, the bridging carbon is at an 'unstarred' position, and perturbational MO theory predicts that an increase in electronegativity at this site will cause a bathochromic shift.[3] Such an effect is well demonstrated in the case of (**1**; R = Me), where replacement of the CH bridge by C(CN) causes a colour change from orange to violet, corresponding to a bathochromic shift of *ca.* 80 nm.[4]

The synthesis of methine dyes absorbing in the near-i.r. region (*i.e.* beyond 700 nm) may be feasible by application of modifications (a)—(c). Dyes with such light absorption properties are of particular interest at the present time, for example in dye lasers, optical filters, optical data storage, and other electro-optical applications. Non-ionic examples with a low molecular weight, and consequently with good solubility in organic solvents and polymers, are of greatest value, but are rare. The light absorption properties of analogues of (**2**) incorporating modifications (a)—(c) have been investigated, and this has permitted the synthesis of a new class of i.r. dyes absorbing up to 850 nm. These have good solubility in organic solvents.

Results and Discussion

Synthesis of Dyes.—For comparison purposes dyes (**2a** and **b**) were prepared. Thus 3-dicyanovinylindan-1-one (**3**)[2,5] was heated under reflux with the appropriate 4-dialkylaminobenzaldehyde in alcohol without catalyst giving (**2**) in high yields. The dimethoxy analogues (**4**) were prepared similarly from the appropriate aldehydes.

When similar condensations with 1,3-bisdicyanovinylindane (**5**)[6] were attempted, there was no reaction, even with the addition of base catalysts such as piperidine. However it was found that the reaction could be effected smoothly in acetic anhydride, and for example (**6**) was obtained from 4-dimethylaminobenzaldehyde in 98% yield.

Aza-analogues (**7**) of dyes (**2**) could be prepared most conveniently by reaction of (**3**) with the corresponding 4-nitroso-*NN*-dialkylaniline in alcohol, again without added catalyst. Reaction between the bisdicyanovinyl compound (**5**) and 4-nitroso-*NN*-dialkylanilines was surprisingly easy, and occurred in most cases in dichloromethane at room temperature to give dyes (**8**) in good yield. This contrasts with the low reactivity of (**5**) towards aldehydes in dichloromethane.

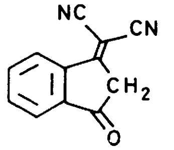
Visible Absorption Spectroscopic Properties.—Absorption spectra were recorded in dichloromethane and the results are summarised in Table 1. Pariser–Parr–Pople SCF-CI MO calculations were carried out on the planar parent structures (**2a**) and (**7a**), using parameters described elsewhere,[7] with the exception of slightly modified cyano parameters (electron affinity of N 5.5 rather than 3.5 eV). It was found that reasonable results could be obtained using an approximate geometry, in which all C–C bond lengths were given an averaged value of 1.4 Å. All such bonds were also given an averaged resonance integral of −2.4 eV. Derivatives (**6**) and (**8**), which must necessarily be non-planar, were not handled satisfactorily by the PPP method. The calculations included a configuration interaction treatment involving the first nine singly excited singlet states.

The parent dye (**2a**) showed an intense absorption band at 533 nm in cyclohexane, with a shoulder at 505 nm, and a distinct, much weaker, second band at 440 nm. In dichloro-

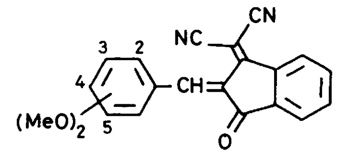
Table 1. Visible absorption spectroscopic properties of methine dyes

Dye	$\lambda_{max.}(CH_2Cl_2)$/nm	$\varepsilon_{max.}(CH_2Cl_2)$/l mol^{-1} cm^{-1}
(2a)	557 (533)^a	55 200
(2b)	565 (543)^a	62 900
(4a)	477	9 200
(4b)	475	24 800
(4c)	435	13 400
(4d)	406	13 700
(6)	608	33 000
(7a)	609 (575)^a	48 200
(7b)	615	54 100
(7c)	621	57 300
(7d)	607	54 600
(7e)	586	45 500
(7f)	676	44 900
(7g)	680	49 200
(8a)	755	25 500
(8b)	762	30 100
(8c)	770	31 200
(8d)	753	26 100
(8e)	718	25 600
(8f)	794	39 800
(8g)	800	41 800
(9)	812	39 400
(10)	850	*b*
(12)	696	68 000
(13)	686	51 100

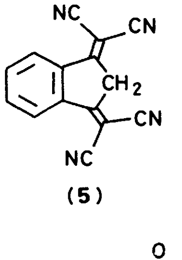
^{a} In cyclohexane. ^{b} Unstable.



(3)



(4) a; 2,5-(MeO)$_2$
b; 2,4-(MeO)$_2$
c; 3,5-(MeO)$_2$
d; 2,6-(MeO)$_2$



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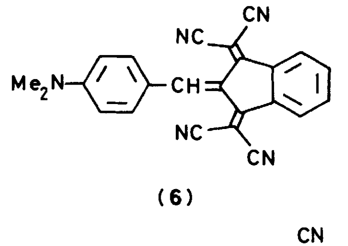

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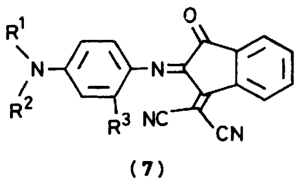

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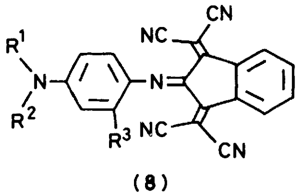


(8)

	R^1	R^2	R^3
a;	Me	Me	H
b;	Et	Et	H
c;	Bu^n	Bu^n	H
d;	C_2H_4OH	C_2H_4OH	H
e;	Et	C_2H_4CN	H
f;	Et	Et	NHAc
g;	Pr^n	Pr^n	NHAc

methane the main band is displaced to 557 nm and the second band is less distinct, forming a shoulder at *ca.* 470 nm. This pattern is found for all the derivatives **(2)**. PPP calculations for **(2a)** predict an intense band at 530 and a weaker band at 431 nm, in good agreement with the experimental values in cyclohexane. The calculations indicate that the first absorption band is approximated by the HOMO ⟶ LUMO transition, and the second band by the HOMO ⟶ LUMO + 1 transition. Electron density changes for the two transitions are shown in the Figure, and it is evident that both processes effectively involve electron density migration from the amino donor group into the rest of the chromophoric system. The more intense longer wavelength band involves migration mainly to the central bridging carbon atom and into the dicyanovinyl group, whereas the shorter wavelength band involves electron density migration to the bridging carbon atom and the carbonyl group. The calculations also reveal a large increase in the π-dipole moment in the two resultant excited states, which account for the shift of the bands to longer wavelengths in dichloromethane.

The somewhat longer wavelength absorption of the diethylamino analogue **(2b)**, $\lambda_{max.}(CH_2Cl_2)$ 565 nm, relative to **(2a)** typifies the donor–acceptor character of the system.

The dimethoxy derivatives **(4)** absorb at much shorter wavelengths than **(2)** and with a reduced intensity (Table 1), reflecting the relatively weak electron-donating strength of the methoxy group. The most bathochromic substitution pattern is found with **(4a)**, $\lambda_{max.}(CH_2Cl_2)$ 477 nm, where the methoxy groups are in positions 2 and 5 relative to the acceptor residue. This was also the most bathochromic pattern noted with analogous dimethoxy dyes derived from indane-1,3-dione.[8] It is evident that the bathochromic effect of an amino group cannot be duplicated by two suitably located methoxy groups.

The electron density changes shown in the Figure indicate the important role that the bridging carbon atom plays in the chromophoric system of **(2)**. Thus there is a pronounced increase in π-electron density at this position in the first and second excited states, and simple perturbational MO considerations predict that any factor increasing the electronegativity of this position will cause a bathochromic shift of both absorption

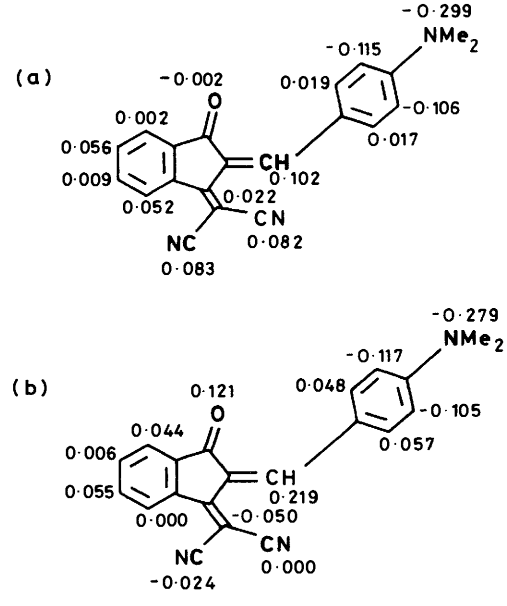


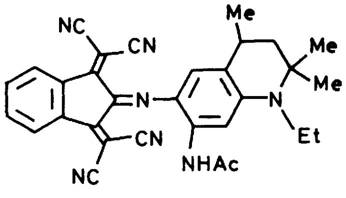
Figure. π-Electron density changes for the two visible absorption bands of **(2a)**: (a) band 1, $\lambda_{max.}(C_6H_{12})$ 533 nm ($\lambda_{max.}^{calc.}$ 530 nm) (HOMO ⟶ LUMO); (b) band 2, $\lambda_{max.}(C_6H_{12})$ 440 nm ($\lambda_{max.}^{calc.}$ 431 nm) (HOMO ⟶ LUMO + 1) bands. This was confirmed experimentally with dyes (**7**). Thus replacement of the carbon bridge in (**2a**) by nitrogen to give (**7a**) results in a displacement of the two visible bands from 533 and 440 nm to 575 and 476 nm, respectively. PPP calculations predict the effects of this perturbation well, with calculated absorption maxima at 574 and 473 nm. As with dyes (**2**), the shorter wavelength band is relatively weak and makes an insignificant contribution to the colour of the dyes. Series (**7**) shows the same positive solvatochromism as (**2**), and for example in dichloromethane the longer wavelength intense band of (**7a**) is displaced to 609 nm. Thus in dichloromethane (**7**) are turquoise, whereas (**2**) are magenta. Aza substitution causes a small decrease in absorption intensity, and the molar absorption coefficients of (**7a**) and (**7b**) are *ca.* 12—14% lower than those of corresponding dyes (**2**).

When one of the carbonyl groups of indane-1,3-dione dyes (**1**) is replaced by a dicyanovinyl group, giving (**2**), the absorption band is moved to longer wavelengths by *ca.* 70 nm. Replacement of the second carbonyl group by dicyanovinyl causes a further shift of *ca.* 50 nm. Thus (**6**) absorbs at 608 nm in dichloromethane, and is similar in colour to (**7a**). However, there is considerable steric crowding in the former structure and this is reflected in its lower molar absorption coefficient (33 000 l mol^{-1} cm^{-1}).

By analogy with (**2**) and (**7**) one might expect that replacement of the central CH unit of (**6**) by nitrogen would produce an additional bathochromic effect of *ca.* 50 nm. In fact such a structural change produces a remarkable shift of *ca.* 150 nm, and for example the 608 nm band of (**6**) in dichloromethane is displaced to 755 nm in the aza analogue (**8a**). The latter gives green solutions. This large shift is largely electronic in origin and cannot be attributed to any major enhancement of molecular planarity, since the intensities of (**8**) are no higher than that of (**6**). In addition, (**6**) and (**8**) have similar band widths, which are significantly larger than those of (**2**) and (**7**). Thus aza substitution in (**6**) affords a simple means of obtaining near-i.r. absorbing dyes, and several examples (**8**)—(**10**) were prepared (Table 1). Of the derivatives containing a single amino donor group, the *NN*-di-n-butylamino derivative (**8c**) was the most bathochromic, absorbing at 770 nm in dichloromethane.

Additional shifts could be obtained by enhancing the electron-donor properties of the arylamine ring, for example by introducing an acetylamino group *ortho* to the nitrogen bridge. Thus (**8f**) has $\lambda_{max.}$ 794 nm, a red shift of 39 nm relative to (**8a**). Alternatively, the electron-donating effect of the amino group in (**8**) can be enhanced by including the nitrogen atom in a fused six-membered ring, as in the tetrahydroquinoline derivative (**9**). This maximises overlap between the lone pair orbital on nitrogen and the π-electron system of the molecule. Derivative (**9**) absorbs at 812 nm in dichloromethane. The absorption band can be displaced further by using a naphthalene ring in place of a phenyl ring, which both enhances transmission of the $+M$ effect of the amino group and also introduces increased lateral conjugation. Thus the rather unstable compound (**10**), prepared by condensation of (**5**) with 4-nitroso-1-dimethylaminonaphthylamine, has an absorption maximum at 850 nm in dichloromethane.

The cyclic sulphone (**11**) has been used commercially to produce intense blue dyes by condensation with 4-dialkylaminobenzaldehydes.[9] The corresponding reaction between (**11**) and a 4-nitrosodialkylaminobenzene was examined in order to compare the chromophoric effect of the sulphone system with that of (**5**). 7-Acetylamino-6-nitroso-1-ethyl-2,2,4-trimethyltetrahydroquinoline reacted readily with (**11**) to give (**12**) in 60% yield. The product had $\lambda_{max.}$ 696 nm in dichloromethane, which is significantly less bathochromic than (**9**), and only slightly more bathochromic than (**13**). The intensity of (**12**) is greater than that of (**9**) and (**13**), however, which seems to be a useful characteristic of the sulphone system. Methine dyes derived from (**11**) have little potential as near-i.r. absorbers.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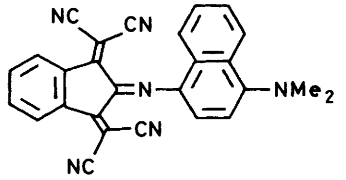
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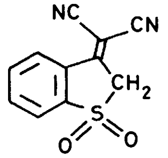
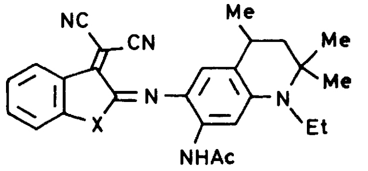

(11)


(12) X = SO$_2$

(13) X = CO

Experimental

*3-Dicycanovinylindan-*1*-one* (**3**).—Anhydrous sodium acetate (1.6 g) was added to a stirred mixture of indane-1,3-dione (2.19 g), malononitrile (1.98 g), and absolute ethanol (25 cm^3) at 22 °C. An immediate red coloration occurred and the suspended solid slowly dissolved. After 40 min the mixture was diluted with water (50 cm^3) and acidified to pH 1—2 by addition of hydrochloric acid. The suspension was stirred for 10 min, the solid material filtered off, and washed thoroughly with water. The crude material was recrystallised twice from acetic acid to give (**3**) (2.64 g, 90%), m.p. 232 °C (lit.,[2] 223—229 °C).

1,3-*Bisdicyanovinylindane* (**5**).—A mixture of indane-1,3-dione (4.38 g) and malononitrile (5.94 g) in ethanol (50 cm^3) was stirred at room temperature for 15 min and sodium acetate trihydrate (6.12 g) was added. The mixture was heated under reflux for 5 h. After cooling, the blue solution was filtered to remove the monocondensation product (**3**). The filtrates were diluted with water (120 cm^3) and acidified with hydrochloric acid to pH 1—2. The precipitate was filtered off, washed with water until the washings were blue, and dried, giving (**5**) as an off-white solid (6.5 g, 88%). An analytically pure sample was obtained by recrystallisation from acetic acid followed by vacuum sublimation, and had m.p. 257 °C (decomp.) (Found: C, 74.3; H, 2.55; N, 22.8. $C_{14}H_6N_4$ requires C, 74.4; H, 2.5; N, 23.1%).

Condensation of (**3**) *with Benzaldehydes.—Procedure A.* A mixture of the aldehyde (6 mmol) and (**3**) (5 mmol) was dissolved in absolute ethanol (50 cm^3) with warming and then stirred at room temperature until precipitation of the product was complete. The product was filtered off, washed with ethanol,

Table 2. Yields and characterisation data for new compounds

					Found (%)			Required (%)		
Compound	Synthetic procedure[a]	Yield (%)	M.p. (°C)[b]	Formula	C	H	N	C	H	N
(2a)	A	85	233—234	$C_{21}H_{15}N_3O$	77.2	4.6	13.0	77.5	4.6	12.9
(2b)	A	87	160—162	$C_{23}H_{19}N_3O$	78.1	5.3	12.1	78.2	5.4	11.9
(4a)	A	67	202—204	$C_{21}H_{14}N_2O_3$	73.9	4.1	8.3	73.7	4.1	8.2
(4b)	A	63	237—239	$C_{21}H_{14}N_2O_3$	73.6	4.2	8.1	73.7	4.1	8.2
(4c)	A	55	209—211	$C_{21}H_{14}N_2O_3$	73.5	4.3	8.2	73.7	4.1	8.2
(4d)	A	35	196—198	$C_{21}H_{14}N_2O_3$	73.7	4.1	8.2	73.7	4.1	8.2
(7a)	B	82	263[c]	$C_{20}H_{14}N_4O$	73.1	4.1	17.6	73.6	4.3	17.2
(7b)	B	87	202[c]	$C_{22}H_{18}N_4O$	74.8	4.9	15.9	74.6	5.1	15.8
(7c)	B	85	157[c]	$C_{26}H_{26}N_4O$	75.9	6.2	13.8	76.1	6.4	13.7
(7d)	B	63	204[c]	$C_{22}H_{18}N_4O_2$	71.3	4.8	15.0	71.3	4.9	15.1
(7e)	B	51	196[c]	$C_{23}H_{17}N_5O$	72.9	4.6	18.2	72.8	4.5	18.5
(7f)	C	82	209—210	$C_{24}H_{21}N_5O_2$	70.0	5.1	17.8	70.1	5.1	17.0
(7g)	C	66	202	$C_{26}H_{25}N_5O_2$	71.5	5.7	15.7	71.1	5.7	15.9
(8a)	D	70	214[c]	$C_{23}H_{14}N_6$	73.9	3.8	22.1	73.8	3.8	22.4
(8b)	D	85	188—189	$C_{25}H_{18}N_6$	74.7	4.5	20.7	74.6	4.5	20.9
(8c)	D	97	202—203	$C_{29}H_{26}N_6$	75.8	5.7	18.7	75.9	5.7	18.3
(8d)	D	60	190[c]	$C_{25}H_{18}N_6O$	71.6	4.3	19.8	71.75	4.3	20.1
(8e)	D	35	205[c]	$C_{26}H_{17}N_7$	73.4	4.0	22.1	73.05	4.0	22.9
(8f)	E	82	215	$C_{27}H_{21}N_7O$	70.3	4.5	21.1	70.6	4.6	21.3
(8g)	E	70	275	$C_{29}H_{25}N_7O$	71.2	5.1	20.5	71.4	5.2	20.1
(9)	E	96	255	$C_{31}H_{27}N_7O$	72.7	5.3	19.0	72.5	5.3	19.1
(10)	E	60	178	$C_{27}H_{16}N_6$	76.8	3.7	19.4	76.4	3.8	19.8
(13)	C	64	242	$C_{28}H_{27}N_5O_2$	72.1	5.8	15.4	72.2	5.85	15.0

[a] See Experimental section. [b] Uncorrected, except where stated. [c] By differential scanning calorimetry.

and recrystallised once from ethanol. Yields, m.p.s, and microanalytical data are summarised in Table 2.

Condensation of **(5)** with 4-dimethylaminobenzaldehyde. 4-Dimethylaminobenzaldehyde (4 mmol) was added to a solution of **(5)** (3 mmol) in acetic anhydride (30 cm^3) at 60 °C with vigorous stirring. The mixture was heated at 60—70 °C for 1 h and cooled. The precipitated solid was filtered off, washed with a little acetic anhydride, and recrystallised from the same solvent to give 1,3-*bisdicyanovinyl*-2-(4-*dimethylbenzylidene*)*indane* **(6)** as dark crystals (98%), m.p. 246—248 °C (Found: C, 76.9; H, 4.0; N, 18.6. $C_{24}H_{15}N_5$ requires C, 77.2; H, 4.05; N, 18.75%).

Procedure B. Condensation of **(3)** with 4-nitroso-*NN*-dialkylarylamines. A mixture of nitroso compound (6 mmol) and **(3)** (5 mmol) in absolute ethanol was stirred at room temperature for 1 h. It was advantageous to maintain a slight excess of the nitroso compound at the end of the reaction to ensure complete conversion of **(3)**, which is difficult to remove from the product. The suspension was filtered and the precipitate washed with ethanol until the yellow nitroso compound was completely removed. The product was recrystallised from ethanol. Yields, m.p.s, and characterisation data are given in Table 2.

Procedure C. A mixture of nitroso compound (6 mmol) and **(3)** (5 mmol) in acetic anhydride (30 cm^3) was stirred at room temperature for 1 h. The precipitated dye was filtered off, washed thoroughly with ethanol to remove all traces of the anhydride, and recrystallised from toluene. Yields, m.p.s, and characterisation data are summarised in Table 2.

Procedure D. Condensation of **(5)** with 4-nitroso-*NN*-dialkylarylamines. A mixture of nitroso compound (6 mmol) and **(5)** (5 mmol) was dissolved in dichloromethane (50 cm^3) and stirred at room temperature for *ca.* 4 h. The solution was filtered and the residue washed with a small amount of dichloromethane. The combined filtrates and washings were evaporated *in vacuo* to half their original volume and ethanol (50 ml) was added. The precipitated deep green solid was recrystallised by redissolving in dichloromethane and carefully diluting the solution with ethanol. Yields and characterisation data are summarised in Table 2.

Procedure E. A mixture of nitroso compound [or, in the case of **(10)**, the hydrochloride of the nitroso compound] (5 mmol) and **(5)** (6 mmol) in acetic anhydride (30 cm^3) was stirred at room temperature for 1 h. The precipitated dye was filtered off, washed with ethanol to remove all traces of the anhydride, and recrystallised from toluene. Yields and characterisation data are summarised in Table 2.

7-*Acetylamino*-6-(3-*dicyanovinyl*-1,1-*dioxobenzo*[b]*thiophen*-2-*ylideneamino*)-1-*ethyl*-2,2,4-*trimethyltetrahydroquinoline* **(12)**.—This was prepared by condensing **(11)** with 7-acetylamino-6-nitroso-1-ethyl-2,2,4-trimethyltetrahydroquinoline using procedure D. The product was obtained as a dark blue solid (60%), m.p. 247 °C (Found: C, 65.05; H, 5.3; N, 14.2. $C_{27}H_{27}N_5O_3S$ requires C, 64.8; H, 5.4; N, 14.0%).

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