Compounds containing Sulphur Chromophores. Part V. Complex Cyanines.*

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Complex cyanines derived from 1 : 3-dithia*cyclo*pentan-4-one have been prepared. Their absorption spectra indicate that the thiol-ester (·CO·S·) bridge of the above nucleus functions as an efficient transmitter of electrons between the auxochromes of the dyes. The absorptions of these dyes have been compared with those of related complex cyanines derived from tetrahydroglyoxaline and thiazolid-4- and -5-one.

Previous Parts of this series * have been concerned with the synthesis of compounds designed to show that a sulphur atom, by expanding its electron octet and utilizing its *d*-orbitals, may function as a resonance transmitter and form part of a chromophoric system. The present paper deals with known and new dyes in which a sulphur atom, attached to a carbonyl group, may function as an electron transmitter without utilizing its *d*-orbitals.

In its simplest form the system to be considered is represented by the thiol ester (I*a*; X = S), the ester resonance (I*a* ⟷ I*b*) being a fundamental requirement for any electronic transition between A and B. A is a $-M$ group and B a $+M$ group or *vice versa*, and the extreme structures of the hybrid to be considered may then be represented by (I*a* ⟷ I*b*) and (I*c*) or (I*d*) respectively. Similar systems are equally feasible in which X in (I*a*) is an oxygen atom or an ·NR· group.

$$\underset{(\mathrm{I}a)}{\mathrm{A{\cdot}CO{\cdot}X{\cdot}B}} \longleftrightarrow \underset{(\mathrm{I}b)}{\mathrm{A{\cdot}C(\overset{-}{O}){:}\overset{+}{X}{\cdot}B}} \longleftrightarrow \underset{(\mathrm{I}c)}{\mathrm{\overset{+}{A}{:}C(\overset{-}{O}){\cdot}\overset{+}{X}{\cdot}\overset{-}{B}}} \qquad \underset{(\mathrm{I}d)}{\mathrm{\overset{-}{A}{:}C(\overset{-}{O}){\cdot}\overset{+}{X}{:}\overset{+}{B}}}$$

Cilento (*J. Amer. Chem. Soc.*, 1953, **75**, 3748) has described certain substituted phenyl thiolbenzoates (I*a*; A = *p*-$NO_2{\cdot}C_6H_4$; B = *p*-$MeO{\cdot}C_6H_4$; X = S). He assigned

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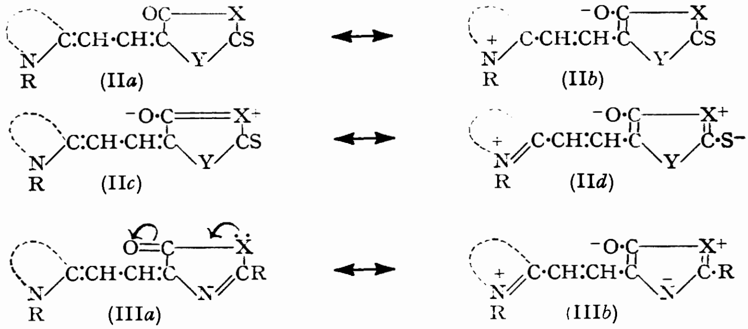
* Parts I—IV, preceding papers.

absorption bands to four electronic transitions in the molecule, including one involving the sulphur *d*-orbitals, but did not consider transitions of the type (I*b* $\longleftrightarrow$ I*d*). There is no evidence from his absorption curves (*loc. cit.*, Fig. 3) that such a transition occurs. This is perhaps not unexpected since, from models or scale drawings, it appears that the benzene ring in group B of (I*a*) is strongly crowded out of planarity with the rest of the molecule. The same non-planarity would also hinder or exclude contributions involving a sulphur decet.

The most suitable compounds for the examination of this effect, free from steric hindrance, are those containing a cyclic thiol-ester group. *mero*Cyanine dyes containing this group as part of a 3-substituted thiazolid-5-one nucleus (II*a*; X = S, Y = NR′) (Doyle, Lawrence, and Kendall, B.P. 622,775; Jeffreys and Knott, *J.*, 1952, 4632) or of a thiazol-5-one nucleus (III*a*; X = S) (Cook, Harris, and Shaw, *J.*, 1948, 1435; Aubert, Knott, and Williams, *J.*, 1951, 2185) are already available.

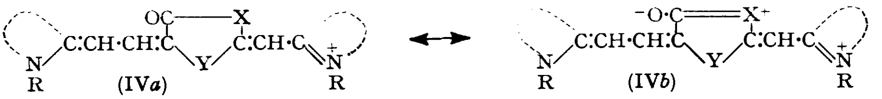
The long wave-length absorption band of *mero*cyanines is generally ascribed to the resonance system (II*a* $\longleftrightarrow$ II*b*) (see, *e.g.*, Brooker, Keyes, Sprague, Van Dyke, Van Lare, Van Zandt, White, Cressman, and Dent, *J. Amer. Chem. Soc.*, 1951, **73**, 5332). This is indeed the fundamental system common to all such dyes. However, if a series of dimethin*mero*cyanines is considered, in which the basic nucleus remains constant but the ketonic nucleus varies, then it will be observed that the theoretical values of $\lambda_{max.}$ at the point of degeneracy of their resonance systems will vary greatly from case to case (cf. Brooker *et al.*, *loc. cit.*). This is often an indication that significant contributions are made by structures in which the electron passes beyond the ketonic oxygen atom. For (II*a*) where X = O, S, or NR it may be more accurate to represent the hybrid by (II*a* $\longleftrightarrow$ II*b*) $\longleftrightarrow$ (II*d*) with a similar system for (III*a*) in which X is a part of the main chromophoric chain. In general, except when Y is oxygen the ketonic nuclei which can function in this way give rise to the dyes with the deepest colours when their absorption is taken at the point of degeneracy.

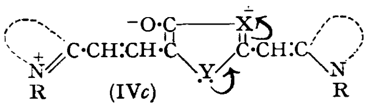

(II*a*) (II*b*)
(II*c*) (II*d*)
(III*a*) (III*b*)

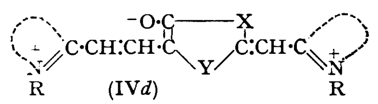
Impressive evidence of the truth of the above assumption is provided by the absorption characteristics of the complex cyanines (IV*a*) obtained by the replacement of the thionic sulphur atom of (II*a*) by a cationic residue. (Similar evidence which will not be discussed here is also provided by the related complex *mero*cyanines.) The synthesis of such dyes where X = S and Y = NR has been described by Doyle *et al.* (*loc. cit.*) and by Knott and Jeffreys (*J.*, 1952, 4762); where X = Y = NR by Riester and Willmanns (U.S.P. 2,440,119); and where X = NR, Y = S by Kendall (B.P. 487,051), Brooker (Mees, " The Theory of the Photographic Process," New York, Macmillan, 1942) and by Knott and Jeffreys (*loc. cit.*). The very large bathochromic and hyperchromic shifts obtained when we pass from (II*a*; X = S, Y = NR) to (IV*a*; X = S, Y = NR) have been ascribed by the last-named authors to the extension of the resonance system to give the hybrid represented by (IV*a* $\longleftrightarrow$ IV*b*) $\longleftrightarrow$ (IV*c*).

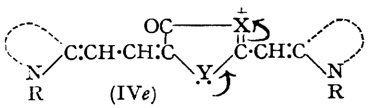
To complete the series of complex cyanines (IV*a*; X and Y = NR or S) the synthesis of (IV*a*; X = Y = S) was required. 2-Methylbenzothiazole ethiodide was condensed with carbon disulphide and triethylamine to give a solution of the salt of the acid (V) (cf. Kendall and Majer, B.P. 549,201) and thence the acid ester (VI), which was cyclized by phosphorus trichloride or tribromide to the quaternary salt (VII). Condensation of (VII) at the reactive methylene group with a 2′-acetanilidovinyl derivative of a cyclic quaternary ammonium salt in an inert solvent then gave the required dyes—both (VII) and (IV; X = Y = S) are decomposed by hot alcohol or pyridine. A similar reaction series was carried out from 2-methylthiazoline methiodide.

As the Table shows, the changes in (IV*a*) from X = Y = NMe to X = S, Y = NMe to X = Y = S result in marked bathochromic shifts. The accompanying shifts in $\varepsilon_{max.}$ do

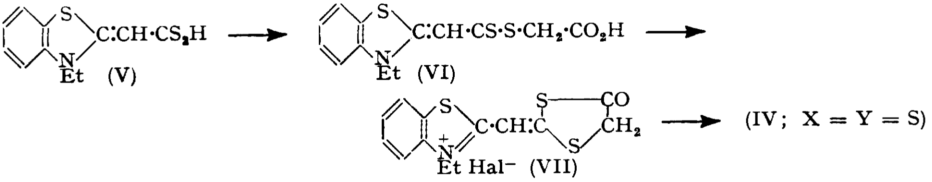

(IV*a*) (IV*b*)


(IV*c*)


(IV*d*)


(IV*e*)

not follow the same pattern, for all the dyes in which X = S, Y = NMe show substantially higher values than the other dyes. An increase in solvent polarity always results in a hypsochromic shift, particularly for those dyes in which X = S, Y = NR or S. This sensitivity to changes in solvent polarity is unusual in ionic dyes and must be ascribed in the present cases to the importance of dipolar contributing structures, particularly (IV*d*), in the hybrid. Any factor, such as an increase in solvent polarity which decreases

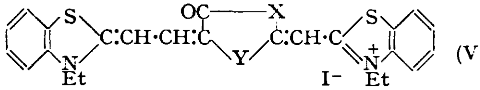
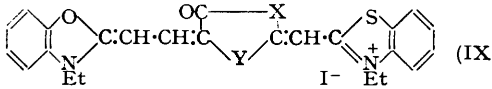
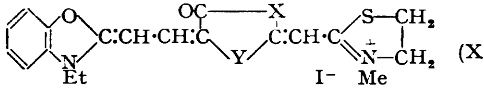

(V) (VI) (VII)

the energy of such excited structures will result in a hypsochromic shift (Knott, *J.*, 1951, 1024). Alternatively, since this increase in the significance of (IV*d*) will also increase the significance of the extreme structure (IV*a*), the hypsochromic solvent effect may be a result of increasing the energetic asymmetry of the dye by bringing the energy of (IV*c*) below that of (IV*a*). The fact that the hypsochromic shift is not always accompanied by a hypochromic shift does not agree, however, with this explanation.

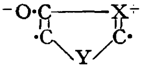
The changes in the absorption of (IV*a*) on variation of X and Y are doubtless due in part to differences in the energetic asymmetry of the dyes. From a consideration of the values of ε, however, it appears that this factor can only be of minor importance. Much more probably such changes are due to changes in the relative energies of all the contributing resonance structures. If these are assessed empirically on the basis of the higher —*M* effect of ·NMe· compared with that of ·S·, any change in X or Y from ·NMe· to ·S· will affect the energies of certain important excited structures represented by the curved arrows of (IV*e*) in much the same way as that of the hybrid extreme structure represented by the curved arrows of (IV*c*). Since these two factors tend to cancel out each other's effect on the absorption of the dye, a further factor must be considered which is not common to both excited and extreme structures. This may be the effect of changes in X and Y on the aromatic stabilization of the extreme structure (IV*c*) by the central nucleus. Thus it is known (Knott, *J.*, 1951, 1024) that any factor which decreases the energy of an extreme structure with respect to that of an excited structure will result in a bathochromic shift.

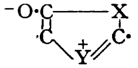
If structures involving charged carbon atoms are neglected, then the central ring of (IV*c*) is stabilized by the contributions of the principal structures (XI*a* and *b*) when X = Y = NMe. The replacement of X = NMe by X = S then stabilizes the ring by allowing the additional structures (IX*d* and *f*) to participate by virtue of the ability of a sulphur atom to expand its electron octet. The replacement of Y = NMe by Y = S allows structures (XI*c*, *e*, and *g*) to contribute in addition to (XI*a* and *b*), whilst in the dye where X = Y = S all the structures (XI*a*—*g*) contribute to the stabilization. This treatment would explain the differences found in the colour of the dyes with the exception that (IV*a*; X = NR, Y = S) would be deeper than (IV*a*; X = S, Y = NR).

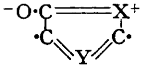
The absorption in solvents of different polarities of dyes (IV*a*).
($\lambda_{max.}$ *in* mμ, $10^{-4}\varepsilon$ *in parentheses.*)

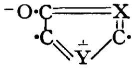
	Nitrobenzene	*o*-Chlorophenol–acetone (1 : 4)	Aq. formamide (1 : 2)
 (VIII)			
X = Y = NMe	595(14·25)	588(12·4)	587(10·2)
X = NMe, Y = S	608(11·2)	600(11·45)	602(9·0)
X = S, Y = NMe	630(18·2), 584(6·55)	615(18·5), 572(7·45)	613(10·6), 569(5·7)
X = Y = S	646(9·0)	624(7·95)	615(5·1)
 (IX)			
X = Y = NMe	558(9·85)	548(11·0)	550(10·4)
X = NMe, Y = S	580(7·85)	568(9·2)	570(7·7)
X = S, Y = NMe	591(17·9), 551(7·3)	570(21·2), 533(8·9)	572(13·7), 540(6·9)
X = Y = S	610(7·6)	600(7·9)	589(5·2)
 (X)			
X = Y = NMe	530(9·7)	524(10·8)	523(10·5)
X = NMe, Y = S	552(5·75)	540(7·05)	544(6·4)
X = S, Y = NMe	559(15·0), 527(6·8)	550(16·1), 515*i*(7·1)	548(13·0), 512(6·25)
X = Y = S	577(6·65)	568(6·7)	565(6·4)

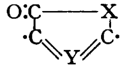
(*i* = Inflexion.)

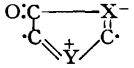

(XI*a*)

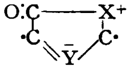

(XI*b*)


(XI*c*)


(XI*d*)


(XI*e*)


(XI*f*)


(XI*g*)

The parent dye (II*a*; X = Y = S) from which (IX; X = Y = S) may be considered to be derived was synthesized some years ago by Dr. L. G. S. Brooker and in nitrobenzene it has $\lambda_{max.}$ 530 mμ (ε 6·5 × 10^4) (personal communication). The increase in ε on proceeding from this dye to (IX; X = Y = S) (ε 7·6 × 10^4) is much less than in the related dyes where X = S, Y = NMe. The evidence of interaction between electrons from either side of the sulphur bridges is shown, however, apart from the depth of colour of the complex dye by the strong effect on the absorption of a change in the nature of the right-hand nucleus, *e.g.*, from (IX) to (X) (see Table).

EXPERIMENTAL

Analyses are by Mr. C. B. Dennis.

2-(*Carboxymethylthio*)*thiocarbonylmethylene*-3-*ethylbenzothiazoline* (VI).—3-Ethyl-2-methylbenzothiazole toluene-*p*-sulphonate (28 g., 0·08 mole), ethanol (100 c.c.), carbon disulphide (6 c.c., 0·1 mole), and triethylamine (24 c.c., 0·16 mole) were heated to 60° and set aside for 30 min. Sodium chloroacetate (9·6 g., 0·083 mole) was added and the whole refluxed for 15 min. A cheesy mass separated. Water (400 c.c.) was added to dissolve most of the solid, and the solution was filtered and acidified with acetic acid. The orange crystals (20·4 g., 81·6%) which separated formed fine red needles, m. p. 198°, from acetic acid (Found : N, 4·6; S, 31·05. $C_{13}H_{13}O_2NS_3$ requires N, 4·5; S, 30·9%).

2-(*Carboxymethylthio*)*thiocarbonylmethylene*-3-*methylthiazolidine*.—2-Methylthiazoline methiodide (24·3 g.), ethanol (100 c.c.), carbon disulphide (7·0 c.c.), and triethylamine (30 c.c.) were warmed together to 60°, sodium chloroacetate (12·0 g.) was added, and the whole was refluxed for 20 min. A bright yellow sodium salt was formed gradually. The latter (16·5 g.) was collected and washed with ethanol, dissolved in water (100 c.c.), and the solution filtered to remove some yellow grains (2·3 g.). The filtrate was acidified with acetic acid. The yellow powder which then crystallized (6·6 g., 26·6%) formed brown needles, m. p. 175—176°, from acetic acid (Found : N, 5·5; S, 38·7. $C_8H_{11}O_2NS_3$ requires N, 5·6; S, 38·55%).

[3-*Ethyl*-2-*benzothiazole*][5-(3-*ethylbenzothiazolin*-2-*ylidene*-*ethylidene*)-2-(1 : 3-*dithia*cyclo*pentan*-4-*one*)]*methincyanine Iodide* (VIII; X = Y = S).—The finely powdered benzothiazoline thiol-ester (above) (3·1 g.), dry dioxan (30 c.c.), and phosphorus trichloride (1·5 c.c.) were ground together at 60°. The solid softened, then hardened after a few minutes. After chilling, the dioxan was decanted and the residual solid washed with ether by decantation. Finely ground 2-2′-acetanilidovinylbenzothiazole ethiodide (4·5 g.) was added, followed by cold methanol (100 c.c.) and triethylamine (1·8 c.c.). The whole was stirred for 5 min. and the solid was collected. It was dissolved in nitrobenzene (20 c.c.), and benzene (15 c.c.) was added to give 3·3 g. of *dye*. It (0·7 g., 11·5%) was obtained as black crystals, m. p. 275°, from nitromethane (Found: C, 47·4; H, 3·3; N, 4·4; I, 21·2; S, 21·3. $C_{24}H_{21}ON_2IS_4$ requires C, 47·3; H, 3·45; N, 4·6; I, 20·9; S, 21·05%).

[3-*Ethyl*-2-*benzothiazole*][5-(3-*ethylbenzoxazolin*-2-*ylidene*-*ethylidene*)-2-(1 : 3-*dithia*cyclo*pentan*-4-*one*)]*methincyanine Iodide* (IX: X = Y = S).—The benzothiazoline thiol-ester (1·55 g.), dry dioxan (10 c.c.), and phosphorus tribromide (0·5 c.c.) were ground together until the solid which softened initially had become hard again. Ether (10 c.c.) was added and the solid washed with ether by decantation. 2-2′-Acetanilidovinylbenzoxazole ethiodide (2·2 g.), methanol (10 c.c.), and triethylamine (1 c.c.) were added to the above solid, and the whole was ground together with water cooling. After 2—3 min. the black solid was collected and washed with acetone. The *dye* (1·15 g., 39%) formed green crystals, m. p. 270°, from nitrobenzene (Found: C, 50·5; H, 3·7; N, 5·75; I, 17·45; S, 13·6. $C_{24}H_{21}O_2N_2IS_3,C_6H_5{\cdot}NO_2$ requires C, 50·3; H, 3·65; N, 5·85; I, 17·75; S, 13·45%). From nitromethane the solvent-free *product* formed green crystals, m. p. 262° (Found : N, 4·5; I, 21·7; S, 16·05. $C_{24}H_{21}O_2N_2IS_3$ requires N, 4·75; I, 21·4; S, 16·2%).

[4-(3-*Ethylbenzoxazolin*-2-*ylidene*-*ethylidene*)-1 : 3-*dithia*-2-cyclo*pentan*-5-*one*][3-*methyl*-2-*thiazoline*]*methincyanine Iodide* (X; X = Y = S).—The thiazolidine thiol-ester (1·1 g.), dioxan (15 c.c.), and phosphorus trichloride (0·5 c.c.) were ground together at 25° to give a tar. This was washed with ether and ground at 25° for 3 min. with 2-2′-acetanilidovinylbenzoxazole ethiodide (2·0 g.), ethanol (15 c.c.), and triethylamine (0·7 c.c.). The *dye* was washed with ethanol and benzene and formed magenta threads (0·1 g., 4·3%) with a bronze reflex, m. p. 261°, from nitromethane (Found: N, 5·1; I, 24·1; S, 18·3. $C_{19}H_{19}O_2N_2IS_3$ requires N, 5·3; I, 23·95; S, 18·1%).

[3-*Ethyl*-2-*benzothiazole*][5-(3-*ethylbenzothiazolin*-2-*ylidene*-*ethylidene*)*dihydro*-1 : 3-*dimethyl*-4-*oxo*-2-*glyoxaline*]*methincyanine Iodide* (VIII; X = Y = NMe).—5-(3-Ethylbenzothiazolin-2-ylidene-ethylidene)-1 : 3-dimethyl-2-thiohydantoin (0·7 g.) and methyl sulphate (0·4 c.c.) were fused together on a steam-bath for 20 min. The solid quaternary salt was heated with 2-methylbenzothiazole ethotoluene-*p*-sulphonate (0·8 g.), pyridine (10 c.c.), and triethylamine (0·35 c.c.) on a steam-bath for 15 min. Saturated aqueous potassium iodide (1 c.c.) and then ethanol (25 c.c.) were added to the solution. The *dye* (1·1 g., 82%) crystallized on chilling and formed olive-green crystals, m. p. 275°, from methanol (Found: N, 9·2; I, 21·2; S, 10·6. $C_{26}H_{27}ON_4IS_2$ requires N, 9·3; I, 21·1; S, 10·6%).

[3-*Ethyl-2-benzothiazole*][5-(3-*ethylbenzoxazolin-2-ylidene-ethylidene*)*dihydro*-1 : 3-*dimethyl*-4-*oxo*-2-*glyoxaline*]*methincyanine iodide* (IX; X = Y = NMe) was obtained similarly and formed violet needles (62·5%), m. p. 253°, from methanol (Found: N, 9·4; I, 21·8; S, 5·7. $C_{26}H_{27}O_2N_4IS$ requires N, 9·55; I, 21·65; S, 5·45%).

[5-(3-*Ethylbenzoxazolin-2-ylidene-ethylidene*)*dihydro*-1 : 3-*dimethyl*-4-*oxo*-2-*glyoxaline*][3-*methyl*-2-*thiazoline*]*methincyanine iodide* (X; X = Y = NMe) was obtained in 68% yield as red needles, m. p. 251°, from methanol–ether (Found: N, 10·5; I, 24·3; S, 6·2. $C_{21}H_{25}O_2N_4IS$ requires N, 10·7; I, 24·25; S, 6·1%).

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