

# The Influence of Bridging on the Colour of Polymethin and Aza-methin Dyes

By G. E. FICKEN and J. D. KENDALL\*

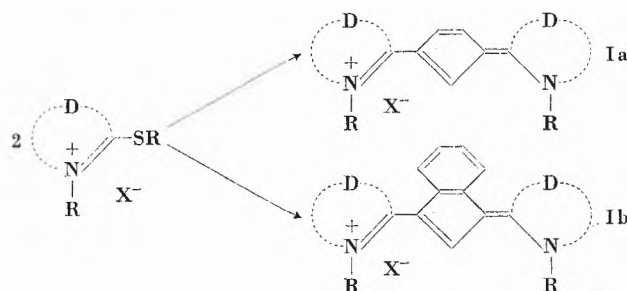
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For many years now it has been known that the introduction of a substituent in the polymethin chain of a cyanine dye can markedly affect the photographic properties of the dye. Because of this a considerable amount of work has been carried out in the laboratories of the manufacturers of photographic materials on the preparation of dyes with chain substituents. In the *Ilford* laboratories in particular, we have been engaged for a number of years on a systematic study of the effects of bridging polymethin chains. Although many of the systems with which we shall deal have been the subject of Patent Specifications, very little has been published in scientific journals.

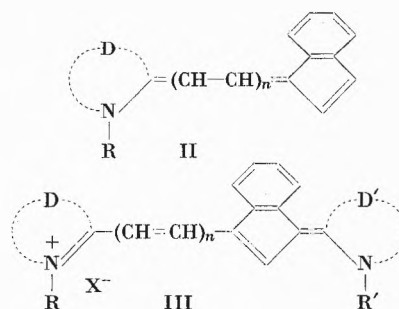
## Methods of Synthesis

Dealing firstly with the synthesis of tri- and pentamethincyanines bridged by a chain of carbon atoms, examples are known in which this bridging chain is either saturated or unsaturated. The most readily prepared dyes are those with a two- or three-carbon bridge, which may be across the  $\alpha$   $\alpha'$  atoms in a trimethincyanine, or across the  $\alpha\gamma$ ,  $\beta\beta'$ , or  $\alpha\beta'$  atoms in a pentamethincyanine.

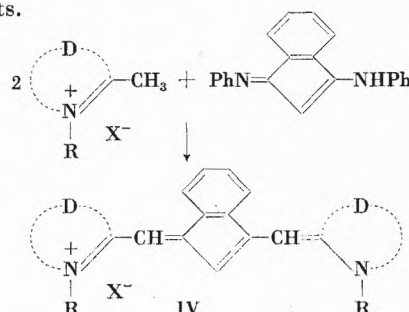
The original method for the preparation of trimethincyanines possessing an unsaturated hydrocarbon bridge consisted in heating cyclopentadiene or indene with the quaternary salt of a 2-alkylthio heterocyclic base.<sup>1</sup> Reaction occurs in the 1,3-positions of the



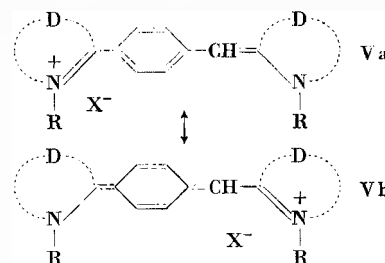
hydrocarbon to give symmetrical dyes (I). Reaction of one mole of the quaternary salt with one mole of the hydrocarbon gave intermediates of type II ( $n = 0$ ), whilst use of acetanilidovinyl intermediates gave compounds of type II ( $n = 1$ ).<sup>2</sup> By reaction of these intermediates with the quaternary salts of different alkylthio-bases, unsymmetrical trimethincyanines and penta-



methincyanines could be obtained.<sup>3</sup> The latter possessed an  $\alpha\gamma$  bridge, but the dyes with a  $\beta\beta'$  bridge (IV) could be obtained by the method shown. Here also, unsymmetrical dyes could be obtained by reacting indandione dianil in two stages with two different quaternary salts.



Dyes V in which the pentamethin chain is bridged at the  $\alpha\beta'$  carbon atom have been prepared by both BROOKER of *Eastman Kodak*<sup>4</sup> and KIPRIANOV in Russia<sup>5</sup> by dehydro-halogenation of the bis-quaternary salt obtained by quaternisation of the condensation product of homoterephthalic acid and *o*-aminothiophenol.



Trimethin and pentamethin cyanines bridged by a saturated chain of carbon atoms can be synthesized by a number of different methods. Dyes in which the bridge forms a 5- or 6-membered ring are again easiest to prepare. The earliest method described is that of the *I.G.*

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<sup>1</sup> KENDALL, Brit. Pat. 431,187 / 1933.

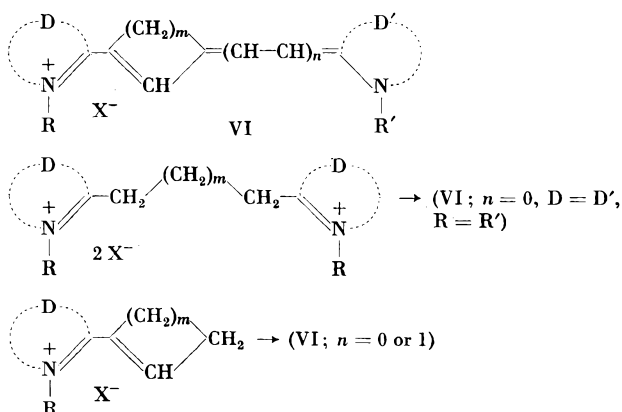
<sup>2</sup> KENDALL, Brit. Pat. 526,892 / 1939.

<sup>3</sup> KENDALL, Brit. Pat. 526,893 / 1939.

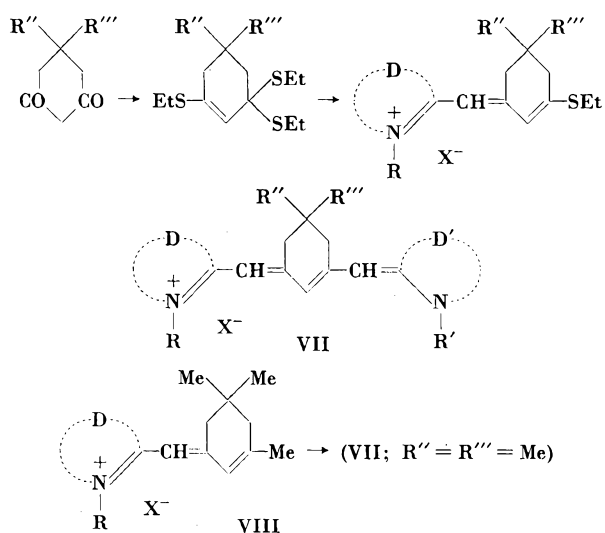
<sup>4</sup> BROOKER and SPRAGUE, U.S. Pat. 2,356,445 / 1942.

<sup>5</sup> KIPRIANOV, USCHENKO, and GERSCHUN, *J. Gen. Chem. Russia* 14 (1944) 865.

*Farbenindustrie*,<sup>6</sup> who condensed an appropriate aliphatic dicarboxylic acid, e.g. glutaric or adipic acid, with two molecules of an *o*-aminophenol or thiophenol to give a bis-heterocyclic alkane which was quaternised and condensed with ethyl *o*-formate in the presence of a base. This method gave symmetrical dyes (VI;  $n=0$ ) and was applicable only to bridged benzothiazole or benzoxazole cyanines. Gevaert extended the method to other heterocycles.<sup>7</sup> An alternative method devised in our Laboratories which was applicable to the synthesis of symmetrical and unsymmetrical dyes was to condense *o*-aminophenol or -thiophenol with  $\Delta^1$ -cyclopentenyl- or cyclohexenyl-carboxylic acid. The resultant 2-cyclopentenyl or cyclohexenyl base was quaternised and reacted with a quaternary salt of the same or different heterocyclic base containing a 2-alkylthio- or alkylthio vinyl group to give  $\alpha\gamma$  bridged tri- or pentamethincyanines.<sup>8</sup>

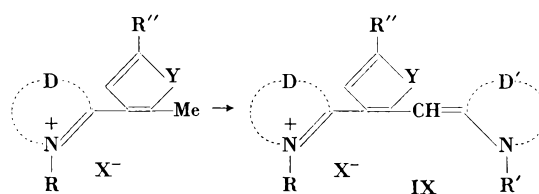


Pentamethincyanines (VII) bridged by a saturated chain in the  $\beta\beta'$  position have also been synthesized in our Laboratory via cyclohexane-1:3-diones and their reaction products with mercaptan. Intermediates con-

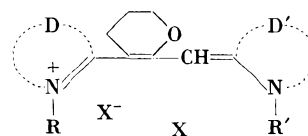


taining one heterocyclic ring are also readily preparable, and from these unsymmetrical dyes can be obtained.<sup>9</sup> Recently BROOKER and HESELTINE in the Kodak Laboratories have been able to obtain similar dyes and also those with longer chains from related intermediates (VIII) containing a terminally reactive methyl group.<sup>10</sup>

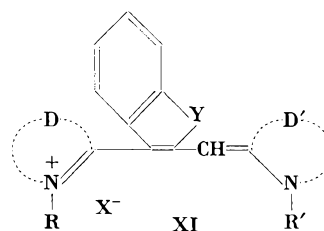
In addition to bridging by hydrocarbon chains it is also possible to bridge by chains containing either an oxygen, sulphur or nitrogen atom. In these cases it has proved easiest to bridge the  $\alpha\beta$  and  $\beta\gamma$  carbons of the polymethin chain. Thus, reaction of 2-methyl-3-furoic acid with *o*-aminothiophenol gave an intermediate, the quaternary salt of which possessed a reactive methyl group, enabling dyes IX ( $Y=O$ ,  $R''=H$ ) to be prepared. Similarly obtained were dyes IX ( $Y=S$ ,



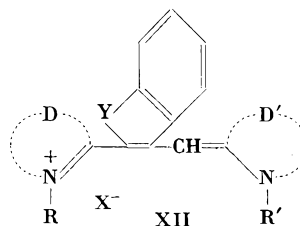
$R''=Me$ ) and dyes X containing a dihydropyran bridge.



In all of these dyes the hetero-atom is linked to the  $\beta$ -atom of the chain, as it is also in dyes XI ( $Y=S$ ). The corresponding dyes in which  $Y=O$  could not



be prepared owing to the unavailability of the required benzofuran-3-carboxylic acid. Use of the appropriately substituted coumarilic acid, however, gave the dyes XII ( $Y=O$ ) where the oxygen is linked  $\alpha$ .



<sup>6</sup> I. G. Farbenindustrie AG, Brit. Pat. 483,045 / 1936.

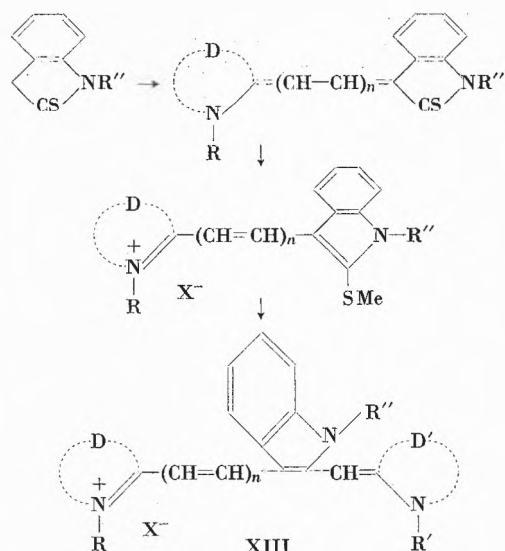
<sup>7</sup> Gevaert Photo-Producten N. V., Brit. Pat. 511,940 / 1937.

<sup>8</sup> KENDALL, SUGGATE, and WOOD, Brit. Pat. 546, 565-6 / 1941.

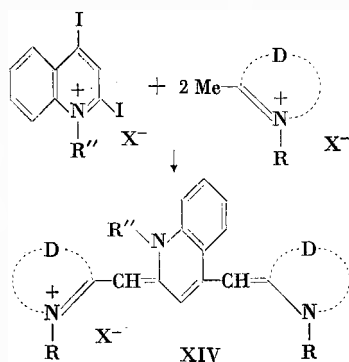
<sup>9</sup> KENDALL and DOYLE, Brit. Pat. 595,783-5; 604,217 / 1945.

<sup>10</sup> BROOKER and HESELTINE, U.S. Pat. 2,756,227 / 1953.

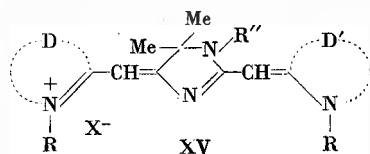
Pentamethincyanines (XIII;  $n = 1$ ) in which the conjugated chain passes through an indole ring have been prepared as shown. The corresponding trimethincyanines (XIII;  $n = 0$ ) could not be obtained.



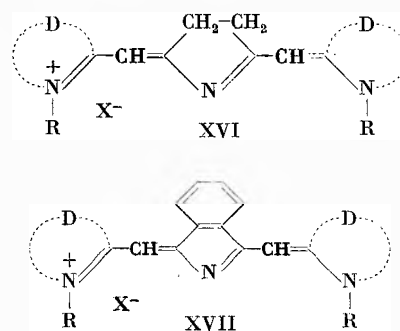
BROOKER<sup>11</sup> has described pentamethincyanines (XIV) bridged across the  $\beta\beta'$  carbon atoms by a nitrogen-containing chain, which were obtained by making use of the two reactive groups in either 2,4-diiodo or 2,4-dimethyl-quinoline quaternary salts, e.g.



We have also synthesised a few bridged aza-poly-methincyanines, such as those of structure XV.<sup>12</sup>



More recently we have prepared  $\gamma$ -azapentamethincyanines in which the  $\beta\beta'$  carbon atoms are bridged by a hydrocarbon chain. Thus, reaction of 2,5-diimino-pyrrolidine with quaternary salts of methyl heterocyclic bases gave dyes XVI; dyes XVII were obtained similarly from 1,3-diiminoisindoline, and unsymmetrical dyes could also be prepared.



### Light Absorption

Bridging of the polymethin chain of a cyanine dye could affect the light absorption in two distinct ways:

a) There will in every case be an electronic effect due to the bridge, which can in some cases be considered simply as two substituents on the chain.

b) In addition to the above effect, there may sometimes be a steric effect, which can show itself in two ways. Firstly, the dye molecule may remain planar, but will be forced to adopt some configuration which is not normally associated with a cyanine dye. Secondly if steric hindrance is severe, the molecule may be forced to adopt some non-planar form. In the latter case, there will result not only a shift of the wavelength of maximum absorption, but also a drop in the extinction coefficient.

Using the above considerations as a basis, the light absorption of bridged cyanines can be discussed. Although the discussion below has particular reference to  $N,N'$ -dimethylbenzothiazole dyes, similar conclusions can be drawn from dyes possessing other heterocyclic rings.

**Hydrocarbon chains.** BROOKER<sup>13</sup> has shown that the dye VI ( $m = 2$ ,  $n = 0$ ,  $D = D' =$  benzothiazole) forms a "compact" molecule with little or no steric hindrance. The same appears to be true of the dyes possessing a 3-carbon bridge, a phenylene bridge and a vinylene bridge (the latter however forms a rather "loose" molecule). This is true of most other heterocycles, with the exception of some of the quinoline dyes, where there is appreciable steric hindrance to planarity.

Dealing with the saturated chains first, it might be expected in view of the absence of steric hindrance that these dyes would resemble dyes possessing two small alkyl substituents on the  $\alpha\alpha'$  atoms. This is shown in Table 1 to be accurately true for dyes possessing a 3-carbon bridge, the bathochromic shift (compared to the unsubstituted dye XVIII [ $R'' = H$ ]) being almost exactly that caused by two methyl substituents. The 2-carbon bridged dye, however, shows an additional small bathochromic shift, presumably associated with a slight strain in the unsaturated five-membered ring.

<sup>11</sup> BROOKER and SMITH, *J. Amer. Chem. Soc.* 59 (1937) 67.

<sup>12</sup> DUFFIN and KENDALL, *Ind. Chim. Belge* 20 (1955) Special No. 599.

<sup>13</sup> BROOKER, WHITE, HESELTINE, KEYES, DENT, and VAN LARE, *J. Photogr. Sci.* 1 (1953) 173.

Table 1<sup>a</sup>: Trimethincyanines with saturated hydrocarbon bridges

Dye	D = } D' = } BT <sup>b</sup>	} BO	BT BO	BT 2-Q
Unsubstituted (XVIII; R'' = H) . . . . .	5580 (5.09)	4840 (4.97)	5200 <sup>c</sup>	5780 <sup>c</sup>
Methyl-substituted (XVIII; R'' = Me) . . . . .	5720 (4.88)			
2-Carbon-bridge (VI; m = 2, n = 0) . . . . .	5900 (5.21)	5380 (4.99)	5670 (5.06)	
3-Carbon-bridge (VI; m = 3, n = 0) . . . . .	5730 (5.11)	5050 <sup>d</sup>	5400 (4.98)	6280 (4.83)

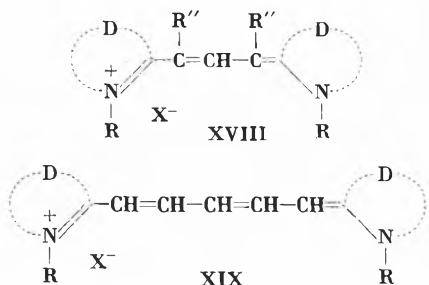
<sup>a</sup> This and the following Tables give  $\lambda_{max}$  (Å) and  $\log \epsilon_{max}$  for the dyes in ethanolic solution.

<sup>b</sup> The following abbreviations are used in the tables:

BT = 2-benzothiazole      BO = 2-benzoxazole  
MeT = 4-Methyl-2-thiazole      PhT = 4-phenyl-2-thiazole  
NT =  $\beta$ -naphthothiazole-2      Q = Quinoline

<sup>c</sup> N,N'-Diethyl dyes (BROOKER, SPRAGUE, and CRESSMAN, *J. Amer. Chem. Soc.* 67 (1945) 1889.

<sup>d</sup> N,N'-Diethyl dye (I.G. Farbenindustrie AG, Brit. Pat. 483, 045/1935).



In the pentamethincyanines two cases arise, depending on whether the bridge is  $\alpha\gamma$  or  $\beta\beta'$ . A dye of the former type can be considered as a vinylogue of a bridged trimethincyanine, and likewise absorbs bathochromically compared to the unsubstituted dye (XIX) (see Table 2). On the other hand, the isomeric  $\beta\beta'$ -bridged dye shows a smaller hypsochromic shift. These results are in agreement with the rules linking light absorption with the nature and position of the substituents, which have been deduced from the electronic theory.<sup>14</sup> The dye XVI (D = benzothiazole, R = Me) showed the large hypsochromic shift characteristic of a  $\gamma$ -azapentamethincyanine, absorbing at 5550 Å ( $\log \epsilon$  4.57).

Table 3: Trimethincyanines with unsaturated hydrocarbon bridges

Dye	BT	MeT	PhT	NT	2-Q	4-Q
Unbridged (XVIII, R'' = H) . . . . .	5580 (5.09)	5550 (4.91)	5620 (4.72)	5980 (5.12)	6050 (5.24)	7070 (5.35)
Vinylene-bridged (Ia) . . . . .	4700 (4.87)	4475 (4.71)	4580 (4.77)	4900 (4.83)	5350 (4.87)	6100 (4.94)
Phenylene-bridged (Ib) . . . . .	5180 (4.94)	4950 (4.77)	5040 (4.79)	5460 (4.88)	6230 (4.82)	6875 (4.90)

<sup>14</sup> DEWAR, *Chem. Soc. Special Publication No. 4* (1956) 64.

According to DEWAR,<sup>14</sup> a + E substituent (e.g. Ph) at any position of the polymethin-chain causes a bathochromic shift in the absorption maximum. On a simple view therefore a phenylene bridge might be considered to be equivalent to two phenyl substituents and hence to lead to a large bathochromic shift. That this is in fact not the case is shown in Table 3 for a series of symmetrical dyes possessing both phenylene (Ib) and vinylene (Ia) bridges. In every case but one, there is a hypsochromic shift compared with the unbridged cyanine, the shift being particularly pronounced with the vinylene-bridged dyes. The exception is the phenylene-bridged 2-quinoline dye; this dye is exceptional in this series in that it shows quite large steric hindrance to planarity. It is of interest that the large bathochromic

Table 2: Trimethylene-bridged benzothiazole pentamethincyanines

Unbridged dye (XIX) . . . . .	6525 (5.30)
$\alpha\gamma$ -bridged dye (VI, m = 3, n = 1) . . . . .	6680 (5.12)
$\beta\beta'$ -bridged dye (VII, R'' = R''' = H) . . . . .	6480 (5.05)

shift observed on proceeding from dye Ia to its dihydro derivative VI (m = 2, n = 0) is paralleled in other fields e.g. the change porphyrin  $\rightarrow$  chlorin is known to produce a large bathochromic shift.\*

When we examine the phenylene-bridged pentamethincyanines, we once again encounter a difference between the  $\alpha\gamma$  and  $\beta\beta'$  bridges. The  $\alpha\gamma$  bridged dye (III; n = 1) again shows a hypsochromic shift due to the bridge, whereas the isomeric dye (IV) shows a very large bathochromic shift, sufficient to bring the absorption up into the heptamethincyanine region (Table 4).

\* This phenomenon has been discussed in terms of the quantum theory at this Symposium by Professor PULLMAN.

It is of interest that Professor KIPRIANOV had predicted quantum-mechanically that these two dyes would show the hypsochromic and bathochromic shifts respectively which we have observed.<sup>15</sup> Introduction of an aza link

Table 4: Phenylene-bridged benzothiazole pentamethincyanines

Unbridged dye (XIX) . . . . .	6525 (5.30)
$\alpha\gamma$ -bridged dye (III, $n = 1$ ) . . . . .	6150 (5.04)
$\beta\beta'$ -bridged dye (IV) . . . . .	7550 (4.91)

in the  $\gamma$ -position of the  $\beta\beta'$ -bridged dye produces the expected large hypsochromic shift, the resulting dye XVII absorbing at 6250 Å ( $\log \epsilon$  4.86).

The dyes V described by BROOKER and by KIPRIANOV can be considered as another type of vinylene-bridged pentamethincyanine ( $\alpha\beta'$  linked). There is here a profound hypsochromic shift, dye V (D = benzothiazole, R = Et) absorbing at 5300 Å.<sup>5</sup> BROOKER<sup>4</sup> has ascribed this to the highly unsymmetrical nature of the dye cation, the resonance hybrid strongly favouring the form Va, which possesses an intact benzene ring, rather than the  $p$ -quinonoid form Vb.

**Heterocyclic bridges.** Table 5 gives the light absorption data for a number of trimethincyanines in which the  $\alpha\beta$  atoms are fused to a heterocyclic ring. Apart from the two dyes in the last row, of type XII, all of the dyes possess an oxygen or sulphur atom attached to the  $\beta$ -carbon atom. Of these, models show that there is only slight steric hindrance in the dyes with furan (IX; Y = O) and dihydropyran (X) bridges, and the extinction coefficients for these dyes are consequently fairly high. In the case of the thiophen (IX, Y = S) and thionaphthen (XI, Y = S) dyes, however, steric hindrance is very much greater, the extinction coefficients being consequently very low. The benzofuran dyes (XII, Y = O) show a similar degree of crowding, and again the extinction coefficients are very low. Models indicate that dyes XII (Y = S) would show a very much greater degree of steric hindrance to planarity. It is perhaps not

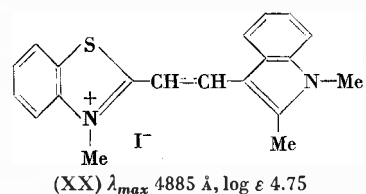
surprising therefore that attempts to prepare these dyes have so far proved unsuccessful; although the transient formation of blue colours was observed, the dyes decomposed too rapidly to allow of their isolation.

We ascribe to the same cause, viz. very great steric hindrance, our inability to prepare trimethincyanines with an indole bridge (XIII,  $n = 0$ ). The pentamethincyanines XIII ( $n = 1$ ) possess absorption spectra characterised by two bands; the shorter-wavelength band is sharp and of high intensity, whilst the longer-wavelength band is very broad and flat and of low intensity (two examples are given in Table 6). We assign the long-wavelength band to the pentamethincyanine system, the low intensity being due to steric hindrance, which is still very considerable in these dyes. Owing to the presence of the additional basic nitrogen atom however, another resonating system is possible, viz. a 3-indole-dimethincyanine (cf. XX), and we consider that the lower-wavelength band is due to this.

Table 6: Heterocyclic-bridged pentamethincyanines

Dye	D = } D' = } BT	2-Q	BO BT
XIII, $n = 1$ R'' = Et	4590, 5940 (4.45, 4.24)		4610, 5850 (4.46, 3.96)
XIV	4514, 5475 <sup>a</sup> (4.70, 4.61)	4800, 6150 <sup>a</sup> (4.77, 4.66)	
XV	3860, 4680 (4.52, 4.79)	4180, 5000, 5250 (4.65, 4.71, 4.96)	

<sup>a</sup> BROOKER *et. al.*, Ref. 11.



Also characterised by a two-banded spectrum are the dyes XIV obtained by BROOKER with a quinoline

Table 5: Heterocyclic-bridged trimethincyanines

Dye	D = } D' = } BT	BT BO	BT NT	BT 2-Q
Unbridged (XVIII, R'' = H) . . . . .	5580 (5.09)	5200 <sup>a</sup>	5765 <sup>a</sup>	5780 <sup>a</sup>
Furan (IX, Y = O, R'' = H) . . . . .	5430 (4.68)			
(IX, Y = O, R'' = Ph) . . . . .	5630 (4.57)	5390 (4.45)	5820 (4.48)	6200 (4.37)
Dihydropyran (X) . . . . .	5230 (4.85)			
Thiophen (IX, Y = S, R'' = Me) . . . . .	5625 (4.25)	5380 (4.22)		
Thionaphthen (XI, Y = S) . . . . .	5440 (4.21)	5320 (4.23)		
Benzofuran (XII, Y = O) . . . . .	5900 (4.19)			6220 (4.14)

<sup>15</sup> KIPRIANOV, Personal communication.

<sup>a</sup> See footnote c to Table 1.

bridge. Formally bridged pentamethincyanines, the light absorption is complicated by the fact that there is appreciable steric hindrance (with the heterocyclic ring at position 4) and that the central quinoline ring can also share the positive charge. The longer-wavelength band is considerably hypsochromic compared with the unsubstituted pentamethincyanine.

The iminazolenine dyes (XV) also show two bands (3 in the case of the 2-quinoline dye) of moderate intensity,

the longer-wavelength band being very hypsochromic compared with that of a pentamethincyanine. Much of this shift can be associated with the  $\gamma$ -aza link. Once again the iminazolenine ring can carry the positive charge, and models indicate that in these dyes there is little or no steric hindrance.

We thank Mr. R. M. HAWKINS for the preparation of some of the dyes, and Mr. L. R. BROOKER for the light absorption measurements.