of the order of 5 times at 12,000 kg/cm^2. The acceleration in this class appears to be due mainly to a decrease in the activation energy.

(*b*) "*Slow*" *Reactions*—Where pressure has a much greater accelerating influence, which increases with increasing pressure, the increase in velocity being of the order of 10 times at 5000 kg/cm^2, and 45 times at 8500 kg/cm^2. In this class the constants A and E of the Arrhenius equation both increase with increasing pressure.

(*c*) *Unimolecular Decompositions*—The decomposition of phenyl-benzyl-methyl-allyl ammonium bromide in chloroform solution is retarded 1·5 times at 3000 kg/cm^2.

The magnitude of the pressure effect on the ethyl alcohol and acetic anhydride reaction varies with change of solvent, but is always of the same order.

The results are in good agreement with the predictions given by the transition state method of calculating reaction velocities.

A Comparison of the Absorption Spectra of Some Typical Symmetrical Cyanine Dyes

By Nellie I. Fisher and Frances M. Hamer

(*Communicated by Sir William Pope, F.R.S.—Received December* 17, 1935)

INTRODUCTION

Compounds of the cyanine type show a wide variation in colour, whilst possessing comparatively simple chemical structures. They are, therefore, particularly suitable for a study of the relationship between colour and constitution. Such a study, for certain fairly simple series of cyanine dyes, free from substituents, forms the subject of the present paper.

The cyanines are characterized by possessing two heterocyclic nuclei containing nitrogen. One of our objects was to find how the colour varies according to the nature of the nuclei, but we restricted the investigation to those series in which the two nuclei are identical.

According to static formulae for compounds of the cyanine type, the nitrogen atom of one heterocyclic nucleus is tertiary, and that of the other is quaternary; the nitrogen atoms are joined by a chain of conjugated linkages, so that the number of carbon atoms in the chain is necessarily uneven. Our second object was to find out how the colour varies according to the length of the chain joining the nuclei, for compounds of the following classes: (i) cyanines of the simplest type, in which the nuclei are linked by one :CH. group; (ii) carbocyanines, where the nuclei are linked by the three-carbon chain, :CH.CH:CH.; (iii) dicarbocyanines, with linking by the five-carbon chain :CH.CH:CH.CH:CH.; (iv) tricarbocyanines, with linking by the seven-carbon chain, :CH.CH:CH.CH:CH.CH:CH..

In the quinoline nucleus, linking in either of two positions is possible, with the result that, for a given chain joining the nuclei, the length of the chain joining the nitrogen atoms can yet be varied: this point also seemed worth investigation.

Ethiodides were chosen for the work, and the preparation of eleven series of dyes, each comprising four members, was attempted. The series differ from one another in the nature of the heterocyclic nuclei, whilst the various members of a series differ in the length of the polymethine chain joining the nuclei. Some account of most of the compounds is to be found by a search in the literature. Most emphatically, however, our object was not merely to fill in the gaps in the subject by examining those members of the series which have not hitherto been described, but rather to compare all the members under standard conditions, working throughout with purified specimens of dyes. Methyl alcohol was selected as solvent.

EXPERIMENTAL

The names and graphic formulae of the dyes prepared are given below, with a literature reference wherever possible, even although the previously published information be scanty; where we ourselves have described a preparation, the reference is to our own method only, without any attempt at a complete bibliography. Only thirty-nine of the forty-four compounds sought were actually obtained; the lowest member of the indo-series was rejected because it failed to come up to the criterion of purity which we had set ourselves, and we were unable to prepare tricarbocyanines containing β-naphthaquinoline, benzoxazole, or naphthoxazole nuclei.

I—*Oxa-Series* (fig. 1).

2:2′-Diethyloxacyanine iodide (I),* (x = CH).

2:2′-Diethyloxacarbocyanine iodide (II),† (x = CH.CH:CH).

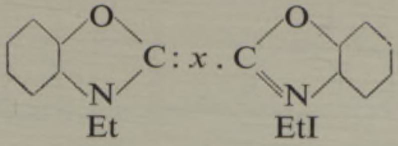
---

* Fisher and Hamer, 'J. Chem. Soc.,' p. 962 (1934).

† Hamer, *ibid.*, p. 2796 (1927).

2 : 2′-Diethyloxadicarbocyanine iodide (III),
(x = CH . CH : CH . CH : CH).

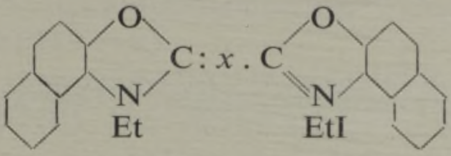
(I–III)



IA—Oxa-Series, 3 : 4 : 3′ : 4′*-dibenz-derivatives* (fig. 2).

2 : 2′-Diethyl-3 : 4 : 3′ : 4′-dibenzoxacyanine iodide (IV),* (x = CH).
2 : 2′-Diethyl-3 : 4 : 3′ : 4′-dibenzoxacarbocyanine iodide (V),
(x = CH . CH : CH).
2 : 2′-Diethyl-3 : 4 : 3′ : 4′-dibenzoxadicarbocyanine iodide (VI),
(x = CH . CH : CH . CH : CH).

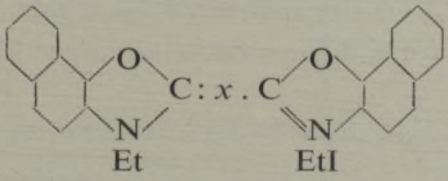
(IV–VI)



IB—Oxa-Series, 5 : 6 : 5′ : 6′*-dibenz-derivatives* (fig. 3).

2 : 2′-Diethyl-5 : 6 : 5′ : 6′-dibenzoxacyanine iodide (VII),* (x = CH).
2 : 2′-Diethyl-5 : 6 : 5′ : 6′-dibenzoxacarbocyanine iodide (VIII),†
(x = CH . CH : CH).
2 : 2′-Diethyl-5 : 6 : 5′ : 6′-dibenzoxadicarbocyanine iodide (IX),
(x = CH . CH : CH . CH : CH).

(VII–IX)



II—Thia-Series (fig. 4).

2 : 2′-Diethylthiacyanine iodide (X),‡ (x = CH).
2 : 2′-Diethylthiacarbocyanine iodide (XI),§ (x = CH . CH : CH).
2 : 2′-Diethylthiadicarbocyanine iodide (XII),||
(x = CH . CH : CH . CH : CH).

---

* Fisher and Hamer, 'J. Chem. Soc.,' p. 962 (1934).

† Brooker and Eastman Kodak Company, U.S. Patent, 1,939,201 ; 1,962,123.

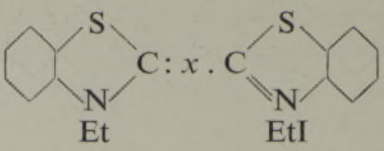
‡ Fisher and Hamer, 'J. Chem. Soc.,' p. 2502 (1930).

§ Hamer, *ibid.*, p. 2796 (1927).

|| Ogata, 'Proc. Imp. Acad. Tokyo,' vol. 9, p. 602 (1933); 'Bull. Inst. Phys. Chem. Res.,' vol. 13, p. 528 (1934); Ogata and Kimura, *ibid.*, vol. 13, p. 537 (1934).

2 : 2′-Diethylthiatricarbocyanine iodide (XIII),*
(x = CH . CH : CH . CH : CH . CH : CH).

(X–XIII)



IIA—Thia-Series, 3 : 4 : 3′ : 4′-*dibenz-derivatives* (fig. 5).

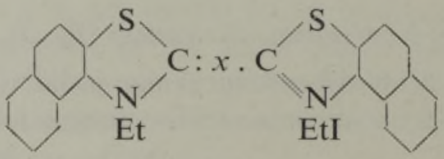
2 : 2′-Diethyl-3 : 4 : 3′ : 4′-dibenzthiacyanine iodide (XIV), (x = CH).

2 : 2′-Diethyl-3 : 4 : 3′ : 4′-dibenzthiacarbocyanine iodide (XV),†
(x = CH . CH : CH).

2 : 2′-Diethyl-3 : 4 : 3′ : 4′-dibenzthiadicarbocyanine iodide (XVI),
(x = CH . CH : CH . CH : CH).

2 : 2′-Diethyl-3 : 4 : 3′ : 4′-dibenzthiatricarbocyanine iodide (XVII),*
(x = CH . CH : CH . CH : CH . CH : CH).

(XIV–XVII)



IIB—Thia-Series, 5 : 6 : 5′ : 6′-*dibenz-derivatives* (fig. 6).

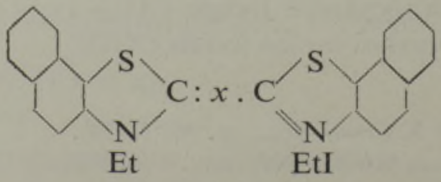
2 : 2′-Diethyl-5 : 6 : 5′ : 6′-dibenzthiacyanine iodide (XVIII),‡ (x = CH).

2 : 2′-Diethyl-5 : 6 : 5′ : 6′-dibenzthiacarbocyanine iodide (XIX),†
(x = CH . CH : CH).

2 : 2′-Diethyl-5 : 6 : 5′ : 6′-dibenzthiadicarbocyanine iodide (XX),
(x = CH . CH : CH . CH : CH).

2 : 2′-Diethyl-5 : 6 : 5′ : 6′-dibenzthiatricarbocyanine iodide (XXI),*
(x = CH . CH : CH . CH : CH . CH : CH).

(XVIII–XXI)



---

* Fisher and Hamer, ‘J. Chem. Soc.,’ p. 189 (1933).

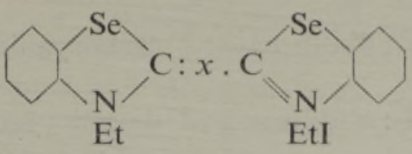
† Hamer, *ibid.*, p. 2598 (1929).

‡ Fisher and Hamer, ‘J. Chem. Soc.,’ p. 2502 (1930).

III—Selena-Series (fig. 7).

2 : 2′-Diethylselenacyanine iodide (XXII),[*] ($x = \mathrm{CH}$).
2 : 2′-Diethylselenacarbocyanine iodide (XXIII),[†] ($x = \mathrm{CH\,.\,CH:CH}$).
2 : 2′-Diethylselenadicarbocyanine iodide (XXIV), ($x = \mathrm{CH\,.\,CH:CH\,.\,CH:CH}$).
2 : 2′-Diethylselenatricarbocyanine iodide (XXV),[‡] ($x = \mathrm{CH\,.\,CH:CH\,.\,CH:CH\,.\,CH:CH}$).

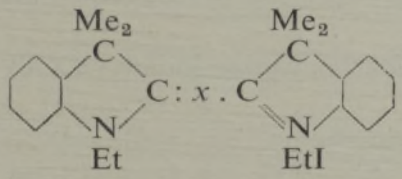
(XXII–XXV)



IV—Indo-Series (fig. 8).

3 : 3 : 3′ : 3′-Tetramethyl-1 : 1′-diethylindocarbocyanine iodide (XXVI),[§] ($x = \mathrm{CH\,.\,CH:CH}$).
3 : 3 : 3′ : 3′-Tetramethyl-1 : 1′-diethylindodicarbocyanine iodide (XXVII), ($x = \mathrm{CH\,.\,CH:CH\,.\,CH:CH}$).
3 : 3 : 3′ : 3′-Tetramethyl-1 : 1′-diethylindotricarbocyanine iodide (XXVIII), ($x = \mathrm{CH\,.\,CH:CH\,.\,CH:CH\,.\,CH:CH}$).

(XXVI–XXVIII)



V—2 : 2′-Series (fig. 9).

1 : 1′-Diethyl-2 : 2′-cyanine iodide (XXIX),[‖] ($x = \mathrm{CH}$).
1 : 1′-Diethyl-2 : 2′-carbocyanine iodide (XXX),[§] ($x = \mathrm{CH\,.\,CH:CH}$) .
1 : 1′-Diethyl-2 : 2′-dicarbocyanine iodide (XXXI),[¶] ($x = \mathrm{CH\,.\,CH:CH\,.\,CH:CH}$).

---

[*] I. G. Farbenind. A.-G., British Patent 380,702/1931.

[†] Clark, ' J. Chem. Soc.,' p. 2313 (1928).

[‡] Fisher and Hamer, ' J. Chem. Soc.,' p. 189 (1933).

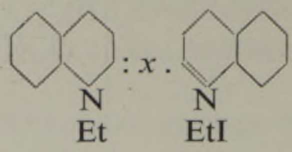
[§] Hamer, ' J. Chem. Soc.,' p. 2796 (1927).

[‖] *Ibid.*, p. 206 (1928).

[¶] Ogata, ' Proc. Imp. Acad. Tokyo,' vol. 8, p. 421 (1932); Ogata and Shiosaki, ' Bull. Inst. Phys. Chem. Res.,' vol. 13, p. 511 (1934); Ogata and Kimura, *ibid.*, vol. 13, p. 537 (1934).

1 : 1′-Diethyl-2 : 2′-tricarbocyanine iodide (XXXII),[*]
(x = CH . CH : CH . CH : CH . CH : CH).

(XXIX–XXXII)



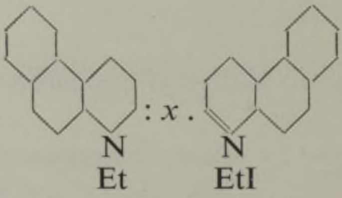
VB—2 : 2′-*Series*, 5 : 6 : 5′ : 6′-*dibenz-derivatives* (fig. 10).

1 : 1′-Diethyl-5 : 6 : 5′ : 6′-dibenz-2 : 2′-cyanine iodide (XXXIII),[†]
(x = CH).

1 : 1′-Diethyl-5 : 6 : 5′ : 6′-dibenz-2 : 2′-carbocyanine iodide (XXXIV),[‡]
(x = CH . CH : CH).

1 : 1′-Diethyl-5 : 6 : 5′ : 6′-dibenz-2 : 2′-dicarbocyanine iodide (XXXV),
(x = CH . CH : CH . CH : CH).

(XXXIII–XXXV)



VI—4 : 4′-*Series* (fig. 11)

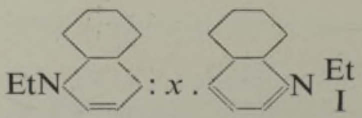
1 : 1′-Diethyl-4 : 4′-cyanine iodide (XXXVI),[§] (x = CH).

1 : 1′-Diethyl-4 : 4′-carbocyanine iodide (XXXVII),[||][¶]
(x = CH . CH : CH).

1 : 1′-Diethyl-4 : 4′-dicarbocyanine iodide (XXXVIII),[**][††]
(x = CH . CH : CH . CH : CH).

1 : 1′-Diethyl-4 : 4′-tricarbocyanine iodide (XXXIX),[††][‡‡]
(x = CH . CH : CH . CH : CH . CH : CH).

(XXXVI–XXXIX)



---

[*] Fisher and Hamer, ‘J. Chem. Soc.,’ p. 189 (1933).

[†] Hamer and Kelly, ‘J. Chem. Soc.,’ p. 777 (1931).

[‡] Mees and Gutekunst, ‘Brit. J. Photogr.,’ vol. 69, p. 474 (1922).

[§] Hoogewerff and van Dorp, ‘Rec. trav. chim. Pays-Bas.,’ vol. 2, p. 317 (1882).

[||] Hamer, ‘J. Chem. Soc.,’ p. 2796 (1927).

[¶] Hamer, *ibid.*, p. 1472 (1928).

[**] Ogata, ‘Proc. Imp. Acad. Tokyo,’ vol. 8, p. 421 (1932); Ogata and Shiosaki, ‘Bull. Inst. Phys. Chem. Res.,’ vol. 13, p. 511 (1934); Ogata and Kimura, *ibid.*, vol. 13, p. 537 (1934).

[††] König, ‘Z. wiss. Photogr.,’ vol. 34, p. 15 (1935).

[‡‡] Brooker, Hamer, and Mees, ‘Photogr J.,’ vol. 73, p. 258 (1933).

For obtaining the absorption curves, solutions were always freshly prepared, by dissolving accurately-weighed samples of the dyes in pure methyl alcohol.

For the ultra-violet region, the Hilger rotating sector photometer attached to a quartz spectrograph was employed; of two 1 cm cells, one contained the solution and the other the solvent: hence the results are corrected for reflexion losses and any possible absorption of the solvent.

For the visible region, the Hüfner and the König-Martens spectrophotometers were employed. A Schultz cell was used with the former and the light source was a 4·5 amp right-angle carbon arc with a clock feeding-mechanism. With the König-Martens instrument, the solution and solvent were contained in 1 cm cells.

For the deep red and infra-red regions a Heele triple-prism spectrograph was used, with a Bellingham and Stanley polarization photometer.* A 1 cm cell was placed in a single beam; these curves are without correction for reflexions at the two cell surfaces. At first F, N, P, and Q type Eastman spectroscopic plates† were used, but subsequently the necessity for selecting different types of plates according to the different regions of absorption was avoided by adopting L type plates throughout, these being hypersensitized and exposed to an incandescent tungsten lamp at 2800° K; with them, by giving an exposure through a No. 34 Wratten filter, a nearly uniform density from λ 400 to 900 mμ resulted. With some of the tricarbocyanines, the solutions became paler on exposure to light of short wave-lengths; hence, whenever possible, a yellow or red filter was put in front of the cell. With the longer exposure required for the high density readings, fresh samples of dye were taken frequently from the stock solution, which was kept in a darkened bottle. Even with this precaution, the densities may have been lowered, owing to fading.

In the following absorption curves, wave-length (mμ) is plotted against density. In every figure the dotted line refers to the simple cyanine in which the nuclei are linked by one : CH . group; the curve with alternative dots and dashes refers to the corresponding carbocyanine; the curve outlined by dashes is that of the dicarbocyanine, and the continuous line depicts the absorption of the tricarbocyanine.

The arrows in the figures indicate the positions of the absorption maxima of corresponding closely related compounds and were inserted in order that the shift of the maximum caused by especially interesting changes in chemical constitution might be read off from the figures.

---

* Schoen, ' J. Opt. Soc. Amer.,' vol. 14, p. 179 (1927).

† Mees, ' J. Opt. Soc. Amer.,' vol. 23, p. 229 (1933).

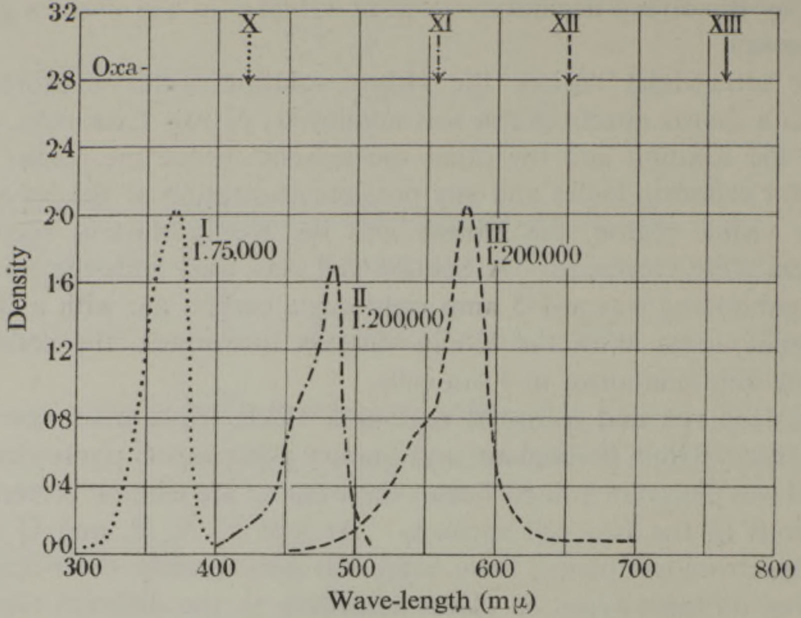

3·2
2·8
2·4
2·0
1·6
1·2
0·8
0·4
0·0
Density
Oxa-
X
XI
XII
XIII
I
1:75,000
II
1:200,000
III
1:200,000
300
400
500
600
700
800
Wave-length (mμ)

FIG. 1.

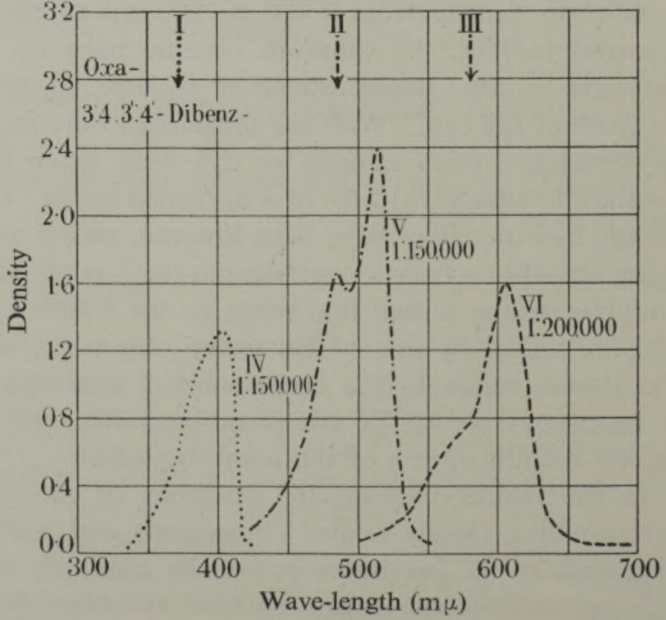

3·2
2·8
2·4
2·0
1·6
1·2
0·8
0·4
0·0
Density
Oxa-
3:4:3':4'-Dibenz-
I
II
III
IV
1:150,000
V
1:150,000
VI
1:200,000
300
400
500
600
700
Wave-length (mμ)

FIG. 2.

Thus in figs. 1, 7, and 8, the arrows mark the positions of the absorption maxima of the corresponding dyes of the thia-series, from fig. 4, whence can be read the effect upon absorption of replacing the two sulphur atoms by two oxygen atoms, fig. 1, by two selenium atoms, fig. 7, or by two :CMe$_2$ groups, fig. 8.

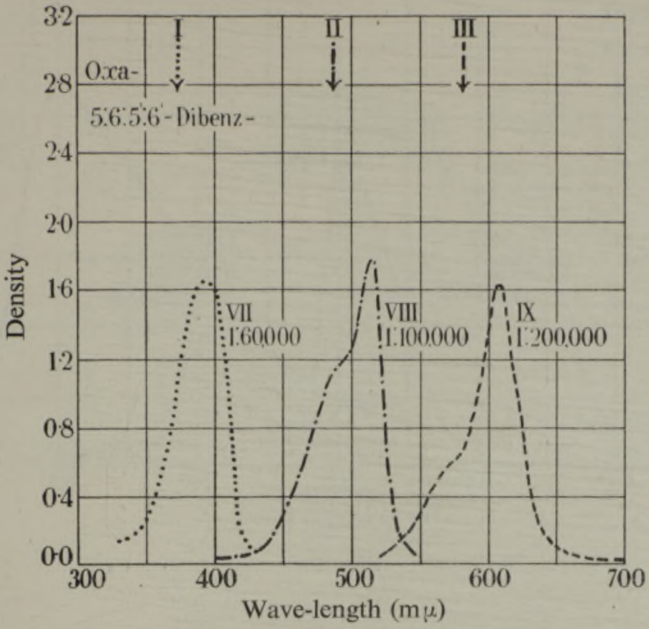


FIG. 3.

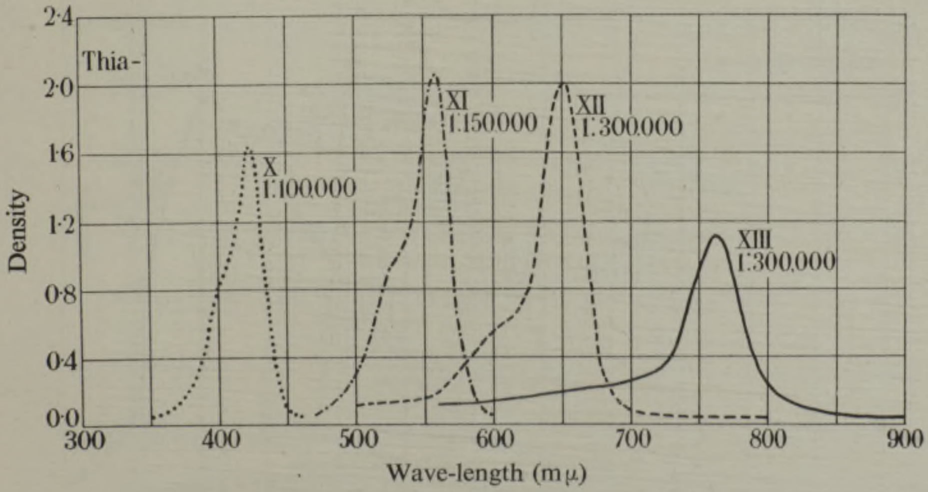


FIG. 4.

In figs. 2 and 3, the arrows show the absorption maxima of the simpler compounds from fig. 1, and thus make clear the shift which occurs when

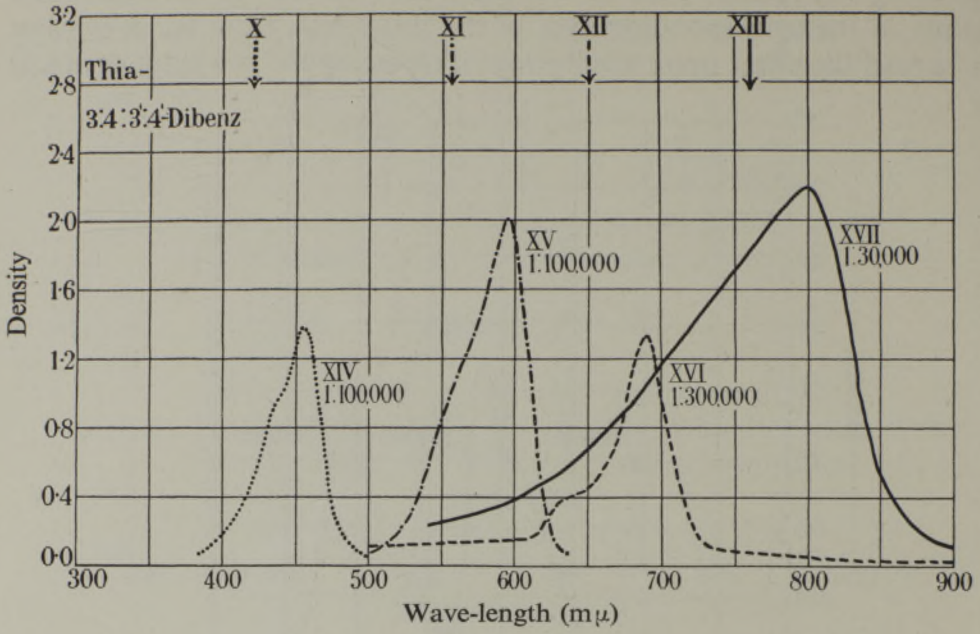

X
XI
XII
XIII
Thia-
3:4:3′:4′-Dibenz
XIV
1:100,000
XV
1:100,000
XVI
1:300,000
XVII
1:30,000
Density
3·2
2·8
2·4
2·0
1·6
1·2
0·8
0·4
0·0
300
400
500
600
700
800
900
Wave-length (mμ)

FIG. 5.

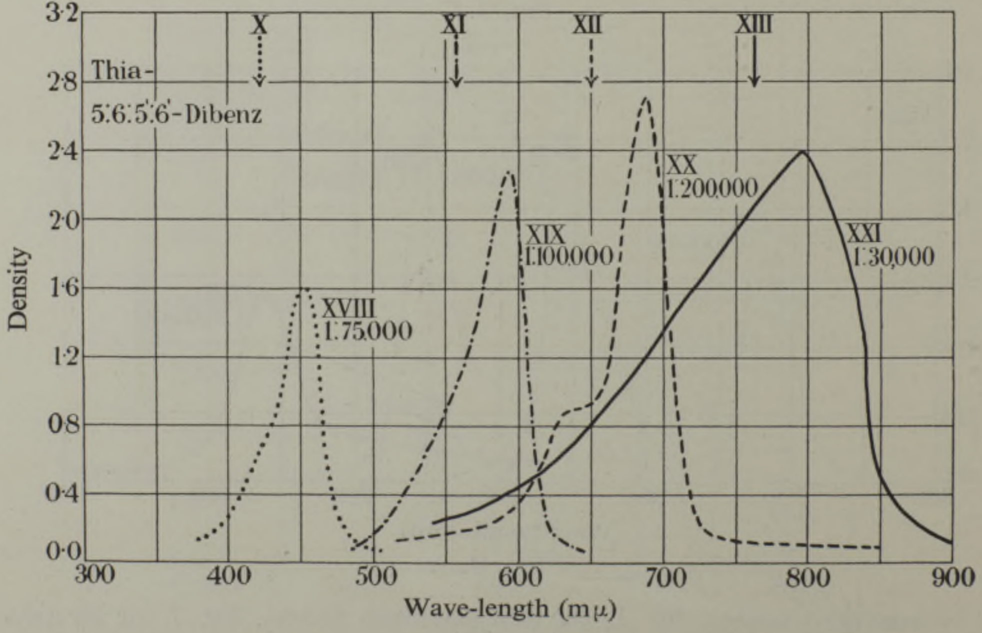

X
XI
XII
XIII
Thia-
5:6:5′:6′-Dibenz
XVIII
1:75,000
XIX
1:100,000
XX
1:200,000
XXI
1:30,000
Density
3·2
2·8
2·4
2·0
1·6
1·2
0·8
0·4
0·0
300
400
500
600
700
800
900
Wave-length (mμ)

FIG. 6.

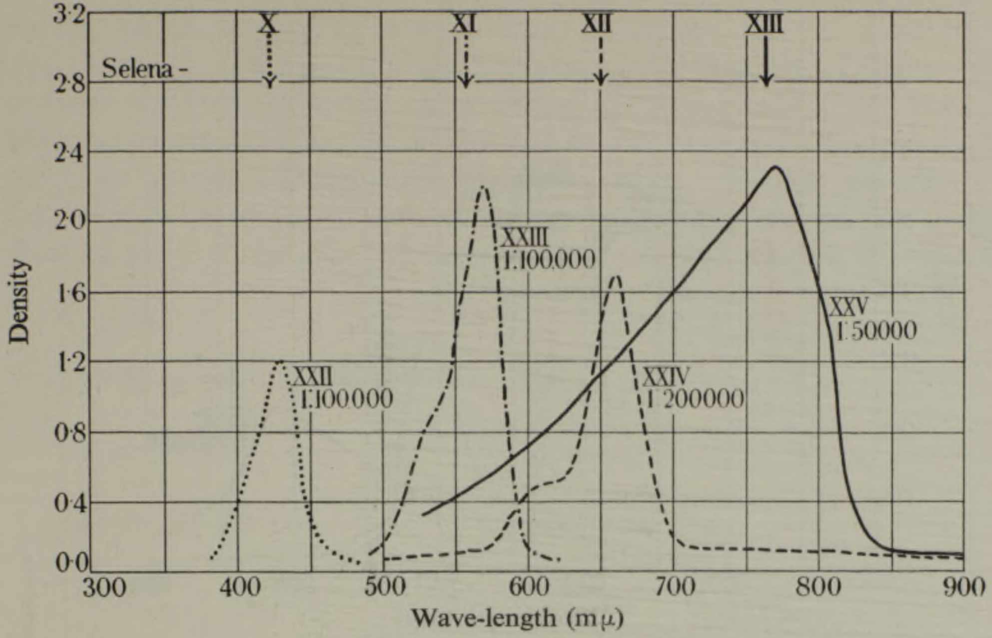

Density
3·2
2·8
2·4
2·0
1·6
1·2
0·8
0·4
0·0
300
400
500
600
700
800
900
Wave-length (mμ)
Selena -
X
XI
XII
XIII
XXII
1:100000
XXIII
1:100,000
XXIV
1:200000
XXV
1:50000

FIG. 7.

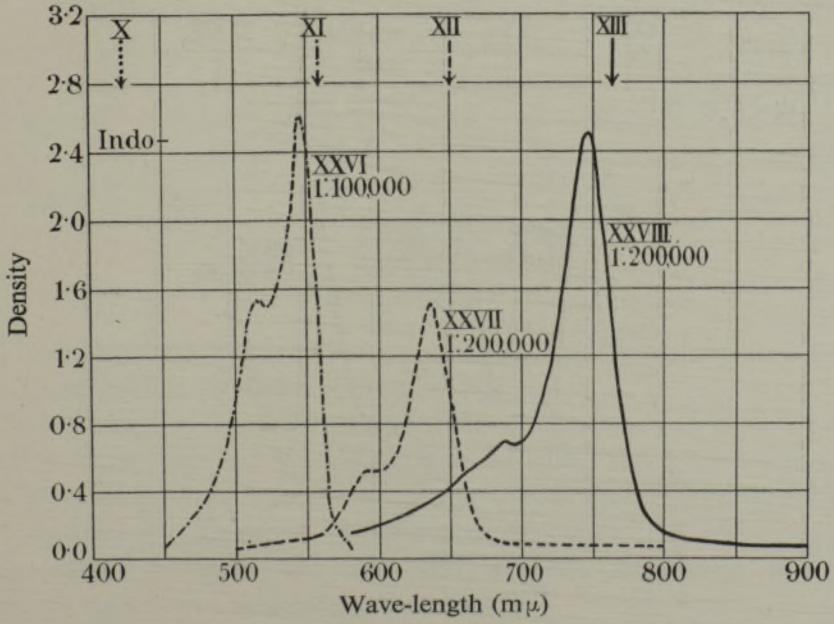

Density
3·2
2·8
2·4
2·0
1·6
1·2
0·8
0·4
0·0
400
500
600
700
800
900
Wave-length (mμ)
Indo-
X
XI
XII
XIII
XXVI
1:100,000
XXVII
1:200,000
XXVIII
1:200,000

FIG. 8.

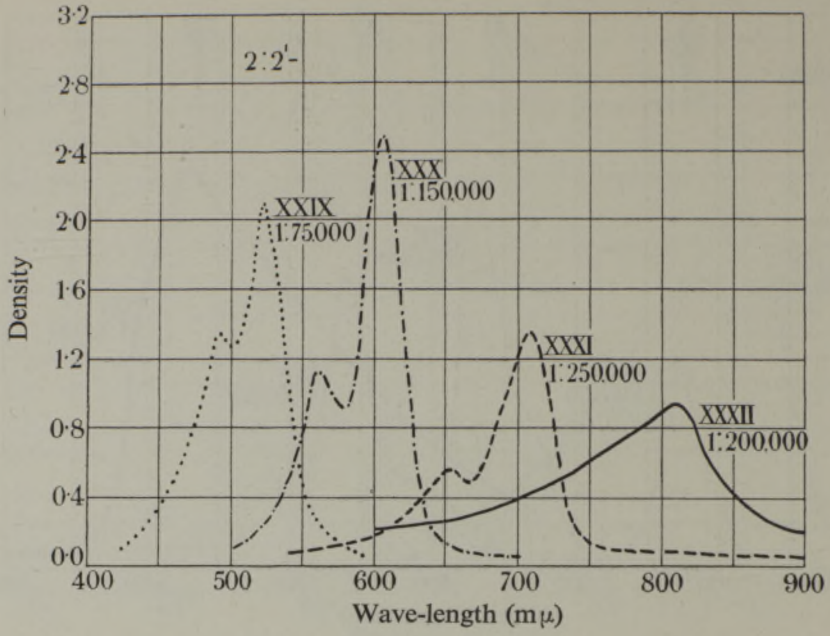

2:2'-
XXIX
1:75,000
XXX
1:150,000
XXXI
1:250,000
XXXII
1:200,000
Density
3·2
2·8
2·4
2·0
1·6
1·2
0·8
0·4
0·0
400
500
600
700
800
900
Wave-length (mμ)

FIG. 9.

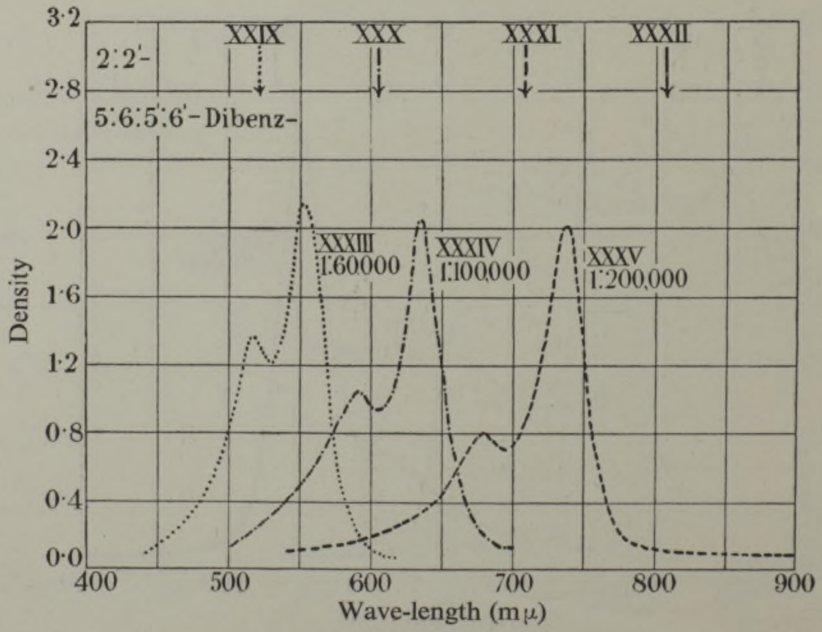

XXIX
XXX
XXXI
XXXII
2:2'-
5:6:5':6'-Dibenz-
XXXIII
1:60,000
XXXIV
1:100,000
XXXV
1:200,000
Density
3·2
2·8
2·4
2·0
1·6
1·2
0·8
0·4
0·0
400
500
600
700
800
900
Wave-length (mμ)

FIG. 10.

the two benzoxazole nuclei of series I are replaced by two β-naphthoxazole nuclei, fig. 2, or by two α-naphthoxazole nuclei, fig. 3. Similarly in figs. 5 and 6, the arrows show the absorption maxima of the simpler compounds from fig. 4, and make evident the shift produced by replacing the two benzthiazole nuclei of series II by two β-naphthathiazole nuclei, fig. 5, or by two α-naphthathiazole nuclei, fig. 6. So also, the arrows in fig. 10 indicate the positions of the absorption maxima of the simpler dyes of series V, so that the magnitude of the shift caused by replacing two quinoline nuclei, linked through their 2-positions, by two β-naphthaquinoline nuclei, similarly linked, is shown.

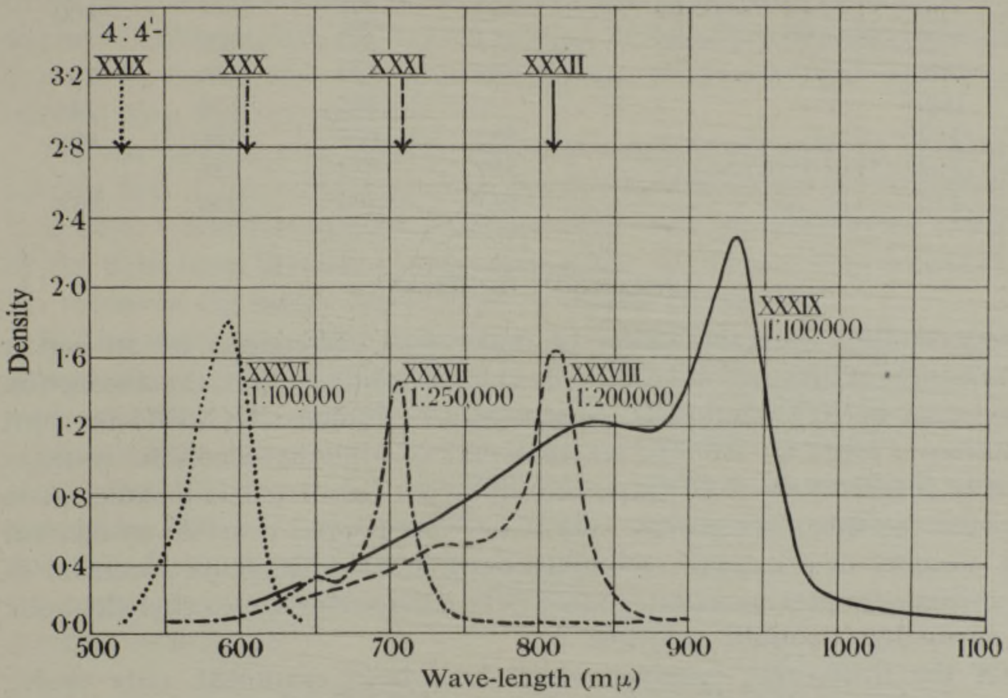


FIG. 11.

The arrows in fig. 11 represent the absorption maxima of the compounds from fig. 9: the comparison between these two series, both of which contain two quinoline nuclei, but with a 2: 2′-linking in one and a 4: 4′-linking in the other, is an especially interesting one.

In Table I are given the exact values of the absorption maxima of the dyes, as read from our original curves.

TABLE I

	Dyes	Length of chain joining nuclei CH	 3CH	 5CH	 7CH
		Wave-lengths (mμ) of maximum absorption			
I	Oxa-	372	485	580	—
IA	Oxa-, 3:4:3′:4′-dibenz-	402	513	606	—
IB	Oxa-, 5:6:5′:6′-dibenz-	395	515	608	—
II	Thia-	422	557	650	762
IIA	Thia-, 3:4:3′:4′-dibenz-	456	597	691	800
IIB	Thia-, 5:6:5′:6′-dibenz-	453	593	687	797
III	Selena-	429	570	660	770
IV	Indo-	—	545	636	745
V	2:2′-	522	605	708	808
VB	2:2′-, 5:6:5′:6′-dibenz-	553	635	738	—
VI	4:4′-	593	704	810	932

DISCUSSION OF RESULTS

Opportunity must be taken to make two corrections in an earlier publication of absorption spectra.* (1) According to that, the absorption maximum of 1:1′-diethyl-4:4′-carbocyanine iodide (XXXVII) in spirit solution is given as 716 mμ, whereas that of a methyl-alcoholic solution is now found to lie at 704 mμ; the difference in solvent is insufficient to account for this discrepancy. (2) It has not proved possible to confirm the presence of a marked secondary band in the absorption spectrum of 2:2′-diethylthiacarbocyanine iodide (XI), either in absolute ethyl alcoholic or in methyl alcoholic solution,

Of the thirty-nine cyanines which have been examined, only twelve (Nos. V, XXVI, XXVIII–XXXI, XXXIII–XXXV, and XXXVII–XXXIX) possess a definite secondary absorption band. Some of the other curves show an inflexion which, at different concentrations, might either be less marked or, on the other hand, develop into a secondary band. In every instance the secondary band, or inflexion, lies on the short wave-length side of the principal band. Apparently the presence of quinoline nuclei tends to produce a secondary band, since of the twelve dyes which show double-banded absorption, nine belong either to the 2:2′-series (V), to the series of 5:6:5′:6′-dibenz-derivatives of these (VB), or to the 4:4′-series (VI).

The absorption maxima of three unsubstituted dicarbocyanines (Nos. XII, XXXI, and XXXVIII) have been compared with those of certain of

---

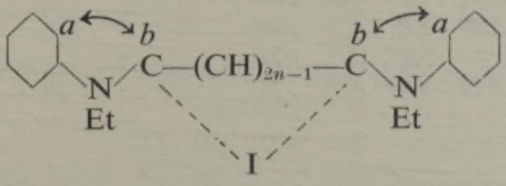
* Bloch and Hamer, ' Photogr. J.,' vol. 68, p. 21 (1928).

their derivatives, which were described by Beattie, Heilbron, and Irving,* in which the hydrogen on the central carbon atom of the chain had been replaced by bromine; similarly one unsubstituted dicarbocyanine (No. III) has been compared with the corresponding chain-substituted chloro-derivative. With not one of these pairs is there adherence to Nietzki's rule, that increase in molecular weight shifts the absorption band towards the region of longer wave-length; with one pair, the maxima of the substituted and parent dyes are identical in position, while with the other three pairs the maximum of the parent dye is actually further into the less refrangible region, by 3–10 mμ, than is that of its bromo-derivative. It must be noted, however, that the solvent which was used for the substituted dyes was not recorded.

The use of frequency in place of wave-length is essential to analysis of spectra and is becoming common practice in presenting spectral absorption data. The frequencies corresponding with the absorption maxima of the dyes have therefore been calculated. To obtain true frequencies, the values in the tables below must be multiplied by 10^{12}.

Before discussing the relationship between frequencies of maximum absorption and chemical constitution, the essential structure of the cyanine molecule must be considered. The occurrence of virtual tautomerism in the cyanine series is well known,†‡§||¶ we are therefore forced to conclude that the iodine atom is not attached to one nitrogen atom rather than to the other, and that the chain of alternate double and single bonds has not the fixity implied by our graphic formulae. According to the resonance theory, the members of series I–V may be represented by the general formula (XL).

(XL)



Within a series, n varies from 1–4, in those sets of dyes which we have studied here, and the number of carbon atoms in the chain joining the nitrogens varies from 3–9; of these carbon atoms, the two in positions b

---

* 'J. Chem. Soc.,' p. 260 (1932).

† Hamer, 'J. Chem. Soc.,' p. 206 (1928).

‡ Mills and Wishart, 'J. Chem. Soc.,' vol. 117, p. 579 (1920).

§ Mills and Braunholtz, 'J. Chem. Soc.,' vol. 121, p. 1489 (1922).

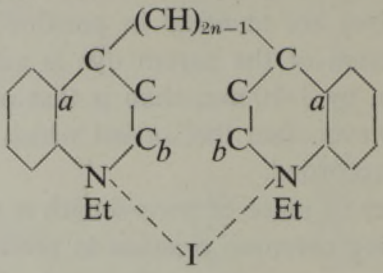
|| Kuhn, Winterstein, and Balser, 'Ber. dtsch. chem. Ges.,' B, vol. 63, p. 3176 (1930).

¶ Ogata, 'Proc. Imp. Acad. Tokyo,' vol. 8, p. 119 (1932).

are cyclic. The series vary according to the atoms or groups which bridge the positions *a–b*; in series I it is the oxygen atom, in series II sulphur, in III selenium, in IV the group $:CMe_2$, and in V the group $.CH:CH..$

Series VI cannot be represented by the same general formula, since the nuclei are not linked through the carbon atoms at *b* (2-position) but in the 4-position, as in formula XLI:

(XLI)



Although in series VI also, *n* varies from 1–4, the number of carbon atoms in the chain joining the nitrogens varies from 7–13: not two, but six of these are cyclic carbon atoms.

TABLE II

Series	$\overset{\curvearrowleft\curvearrowright}{a\quad b}$ in formula XL	Number of C atoms in chain joining N atoms						Frequency differences when number of C atoms varies from				
		3	5	7	9	11	13	3 to 5	5 to 7	7 to 9	9 to 11	11 to 1
		Frequencies of maximum absorption										
I	—O—	807	619	517	—			188	102	—		
II	—S—	711	539	462	394			172	77	68		
III	—Se—	699	526	455	390			173	71	65		
IV	$:CMe_2$	—	550	472	403			—	78	69		
V	$.CH:CH.$	575	496	424	371			79	72	53		
VI	Formula XLI	—	—	506	426	370	322	—	—	80	56	48

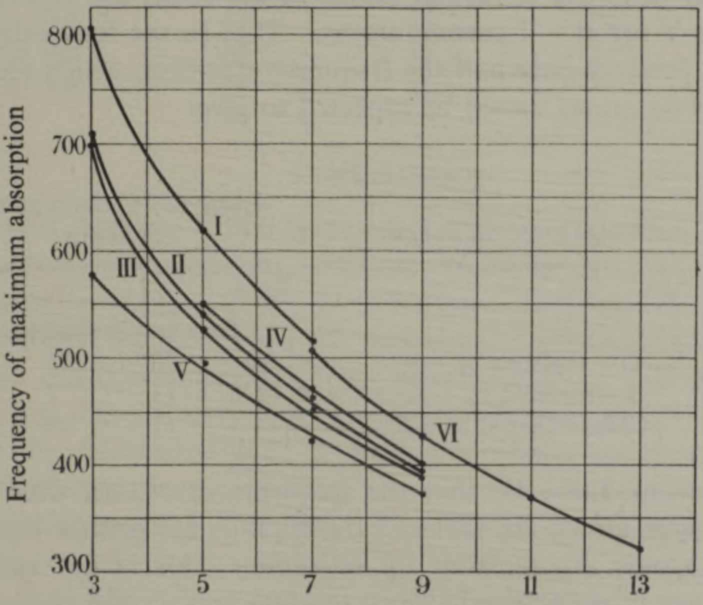
The variation of frequency of maximum absorption with the number of carbon atoms in the chain joining the nitrogen atoms is given in Table II for the six main series, and the results are also plotted in fig. 12.

Table III gives the frequencies of maximum absorption for the more complex series of compounds.

Tables II and III and fig. 12 bring out the fact that the frequencies of maximum absorption depend both upon the nature of the nuclei, and upon the length of the chain joining the nitrogen atoms, being, in general, decreased (1) by increasing the weight of the molecule or (2) by lengthening

TABLE III

Series	$\overset{\curvearrowright}{a\quad b}$ in formula XL	Number of C atoms in chain joining N atoms				Frequency differences when number of C atoms varies from		
		3	5	7	9	3 to 5	5 to 7	7 to 9
		Frequencies of maximum absorption						
IA	—O—	746	585	495	—	161	90	—
IB	—O—	760	583	494	—	177	89	—
IIA	—S—	658	503	434	375	155	69	59
IIB	—S—	662	506	437	376	156	69	61
VB	. CH : CH .	543	472	406	—	71	66	—



Number of C atoms in chain joining N atoms

FIG. 12.

the chain. In each series, the effect of each increase in n decreases with increasing length of the chain, as is shown by the flattening of the curves in fig. 12; this is comprehensible, for each increment is a successively smaller fraction of the total chain. Omitting the three series of dyes (V, VB, and VI) which contain quinoline nuclei, the frequency-decrease caused in the remaining eight series varies from 188–155, and from 102–69, when the number of carbon atoms in the chain joining the nitrogen atoms increases from 3–5 and from 5–7, respectively; in each of these series, the highest value is for the lightest nuclei (series I) and the lowest value for the heaviest nuclei (series IIA and IIB). The frequency-decrease, in four series, varies from 69–59 when the number of carbon atoms in the chain increases from 7–9.

Of the series containing quinoline nuclei, V and VB differ from the eight series already considered, in that the decrease in frequency caused by each increase in length of the chain is anomalously low. In series V and VB, an increase of n (formula XL) from A to $A + 1$ produces only that frequency-decrease which is caused by a change from $A + 1$ to $A + 2$ in the other series.

A comparison of series VI with series V in Table II shows that the carbon atoms of the chain joining the nitrogen atoms cause less frequency-decrease when an additional four of them are cyclic. The frequencies in series VI when there are B carbon atoms in the chain are equivalent to those of series V for $B - 1$ carbon atoms. That is, the four extra cyclic carbon atoms produce only half the frequency-decrease, which four extra non-cyclic carbon atoms would be expected to give.

TABLE IV

Series	Change involved in both groups $a \frown b$	Length of C chain joining N atoms			
		3	5	7	9
		Decrease in frequency			
I and II	—O— replaced by —S—	96	80	55	—
II and III	—S— replaced by —Se—	12	13	7	4
IV and II	: CMe_2 replaced by —S—	—	11	10	9

It is clear from Table IV that the frequency-decreases, which occur when two oxygen atoms are replaced by sulphur, are greater than when two sulphur atoms are replaced by selenium. This is not surprising, since the change in properties between the first and second elements in a column of the periodic table is always greater than the succeeding changes. There is a small decrease in frequency when the sulphur atoms are replaced by : CMe_2 groups.

The shift of the absorption maximum which occurs on replacing two benzthiazole nuclei by two α- or β-naphthathiazole nuclei, or two benzoxazole by two α- or β-naphthoxazole nuclei, is one which we have previously studied.* Table V contains all the information of this kind, relating to the present series, expressed on a frequency basis.

Apart from the quinoline series (V and VB), the frequency decreases caused by introducing two phenylene groups vary in four instances from

---

* Fisher and Hamer, 'J. Chem. Soc.,' p. 962 (1934); p. 2502 (1930); Hamer, *ibid.*, p. 2598 (1929).

61–47, from 36–33, and from 28–22, when the carbon chain has 3, 5, and 7 members, respectively; when it has 9 members, the two values are 18 and 19. Whether the extra nuclei are in the 3 : 4- or 5 : 6- positions seems immaterial. As before, the frequency-changes are anomalously low in the quinoline series.

TABLE V

Series	Length of C chain joining N atoms			
	3	5	7	9
	Decrease in frequency			
I and IA	61	34	22	—
I and IB	47	36	23	—
II and IIA	53	36	28	19
II and IIB	49	33	25	18
V and VB	32	24	18	—

FLUORESCENCE

Alcoholic solutions of the three oxadicarbocyanines (Nos. III, VI, and IX) are strongly fluorescent, and fluorescence is also apparent with the dibenzoxacarbocyanines (Nos. V and VIII). Although fluorescence has not previously been recorded for any dyes of the cyanine group apart from the oxadicarbocyanines,* an examination of the present series showed that this property is by no means uncommon.

When the thirty-nine dyes, in methyl alcoholic solution, were tested for visible fluorescence excited by an ultra-violet light source, only nine gave negative results: these were Nos. XXIX–XXXIII, and XXXVI–XXXVIII, *i.e.*, they are confined to the series containing quinoline nuclei (V, VB, and VI).

The solutions were also examined in a collimated beam of white light from a 100 c.p. pointolite lamp. Under these conditions, negative results were obtained in twenty instances and positive in nineteen. The positive results are embodied in Table VI, where the strength of fluorescence is marked as either intense (i), strong (s), moderate (m), or weak (w). There are several interesting points to be noted: (1) no dye of series V, VB, or VI is fluorescent; (2) in the remaining eight series, all the carbocyanines and all the dicarbocyanines are fluorescent; (3) in the three oxa-series, not only is the fluorescence of certain dyes especially striking, but the simple cyanines also, as well as the carbocyanines and dicarbocyanines are fluorescent.

---

* Konig, ' Z. wiss. Photogr.,' vol. 34, p. 15 (1935).

TABLE VI

Series	No. of C atoms in chain joining N atoms	Colour of solution	Colour of fluorescence	Strength of fluorescence
I	3	Colourless	Violet	w
	5	Deep yellow	Yellow-green	s
	7	Purple	Orange	s
IA	3	Very pale yellow	Violet-blue	m
	5	Pale orange	Yellow-green	s
	7	Deep blue	Orange-red	i
IB	3	Very pale yellow	Blue	m
	5	Pale orange	Yellow-green	s
	7	Deep blue	Orange-red	i
II	5	Pink	Orange-red	s
	7	Deep blue	Red	s
IIA	5	Bluish-purple	Red	s
	7	Blue	Dark red	s
IIB	5	Bluish-purple	Red	s
	7	Blue	Red	s
III	5	Purplish-pink	Orange-red	m
	7	Blue	Red	s
IV	5	Pink	Orange-yellow	m
	7	Blue	Red	s

We are deeply indebted to our colleagues of the Eastman Kodak Company for their generous help; to Dr. L. A. Jones, Messrs. H. P. Cleveland, E. E. Richardson, and A. L. Schoen, for carrying out the work on the absorption spectra, to Dr. B. H. Carroll and Dr. J. A. Leermakers for their suggestions as to the method of presenting the results, and to Dr. L. G. S. Brooker for providing the data concerning dye No. XXXIX. In addition we wish to thank Dr. E. E. Jelley for his help with the work on fluorescence, and Mr. E. D. Eyles, both of Kodak Limited. Most especially are we indebted to Dr. W. H. Mills for his helpful criticism.

SUMMARY

Eleven sets of symmetrical cyanine dyes have been prepared, of which each set differs from the other ten in the nature of the heterocyclic nuclei. In general, each set comprises four members which differ from one

another in the method of linking of the nuclei; this is either by one : CH ., or by a chain composed of three, five, or seven such groups. Thirty-nine of the forty-four compounds aimed at have been prepared, some of them for the first time, and absorption spectra of their methyl-alcoholic solutions have been examined under standard conditions. The frequencies of maximum absorption have been calculated, and correlated with changes in chemical constitution. Data concerning fluorescence are recorded.