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Absorption Spectra of Organic Dyes Containing Two Chromophores

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The Review begins with consideration of the absorption spectra of dyes whose molecules contain non-conjugated (isolated) chromophores. The major portion of the Review, however, is devoted to the spectra of dyes having two conjugated chromophores. According to the view adopted until recently the interaction of conjugated chromophores is apparent in a displacement of the absorption band to longer wavelengths and in an increase in its intensity. The Reviewer and his coworkers have recently established that this view is valid only for the particular case of conjugated chromophores which absorb similar light quanta and lie on the same straight line.

If the light quanta absorbed by the conjugated chromophores are very different, the chromophores do not interact. If the conjugated chromophores are at an angle, their absorption bands do not merge into a single band: on the contrary, they either split or move apart. The intensities of the two new bands are then determined by the angle between the interacting chromophores.

The spectra of bis-dyes which illustrate these principles are examined, and an elementary theory is given for the interaction of conjugated chromophores. A list of 61 references is included.

The concept of colour carriers (chromophores) and of groups of atoms that intensify the colour (auxochromes), which was introduced by Witt into the chemistry of colouring matters almost a century ago, has retained its value until the present time, although we now give a different content to these terms. The name *chromophore* is now applied to a system of conjugated single and double bonds whose presence in sufficient length causes the absorption of visible light even in hydrocarbon molecules. *Auxochromes* are atoms or groups of atoms containing delocalised electron pairs (electron donors—NH_2, NR_2, OH, O^-) and negative [sic] groups of atoms (electron acceptors—NO_2, $CO:NR_2^+$). Auxochromes are located at the ends of the conjugated chain of the dye molecules: donors supply their electrons to the chain of conjugation; acceptors withdraw them.

In the present Review we shall for brevity apply the term *chromophore* to the whole part of the dye molecule which is responsible for its colour, i.e. to the actual chromophore together with the auxochromes (Aux). Thus, when discussing how electronic interaction of two chromophores is revealed in the absorption spectra, we shall have in mind the mutual influence of two systems A and B, both of which absorb visible light, linked together through a series of conjugated or non-conjugated covalent bonds C (Fig. 1) into a single molecule of a bis-dye.

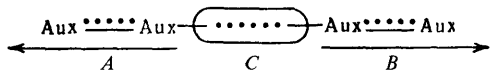


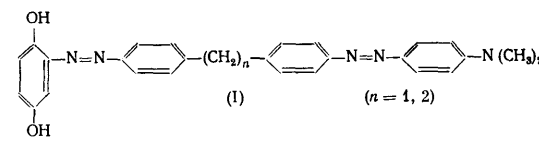
Figure 1.

We shall not be concerned in this Review with the synthesis of the compounds discussed, which can easily be found in the papers cited.

Very many dyes containing two chromophores have been described in the periodical and patent literature, among them the immense group of bisazo-dyes. Unfortunately, only a few such compounds have been examined spectrographically.

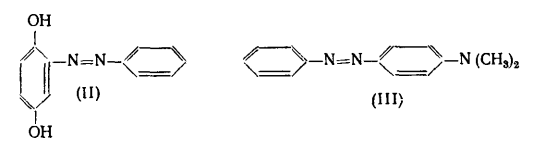
Two chromophores which are separated from each other by saturated groups of atoms ($CH_2.CH_2$, $CH_2.O$, CH_2, etc.) absorb light additively. The absorption spectrum of the solution of such a dye is almost identical with that of a solution of equimolecular proportions of the two corresponding component dyes (parent dyes)[1]. Isolated chromophores absorb light independently of one another: they do not influence each other.

This has been shown by Brode and his coworkers on bisazo-dyes. The absorption curve of the unsymmetrical bisazo-dye (I)



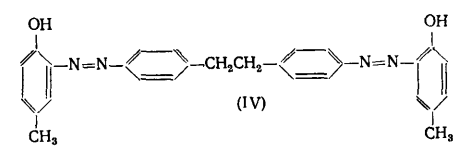
(I) ($n = 1, 2$)

coincides with that of an equimolecular mixture of the two parent monoazo-dyes (II) and (III) [2]



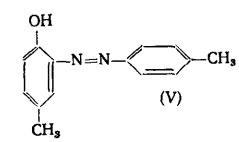
(II) (III)

The spectrum of the symmetrical bisazo-dye (IV)



(IV)

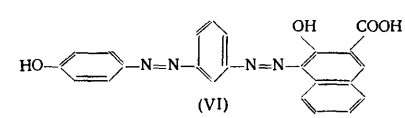
is indistinguishable from that of dye (V)



(V)

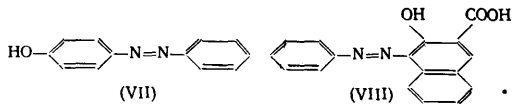
at double the concentration [3].

According to Funkhouser and Brode[4] two chromophoric systems are isolated when linked together through *meta*-positions in a benzene ring: the absorption curve of the bisazo-dye (VI)



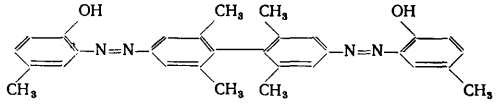
(VI)

is identical with the curve of a mixture of the dyes (VII) and (VIII)



(VII) (VIII)

Isolation of the two azo-chromophores in bisazo-dyes obtained from benzidine derivatives may be due to steric hindrance between the biphenyl rings: the absorption spectrum of the bisazo-dye (IX)

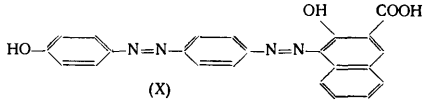


does not differ from that of the bisazo-dye (IV) [5].

All that has been said about the spectra of bisazo-dyes containing isolated chromophores applies also to bis-dyes of other classes—bismerocyanines[6], bisazomethines[7], etc.

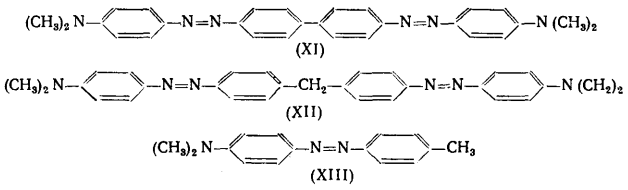
We shall not deal in this Review with the vast number of papers by the eminent Soviet scientist V. A. Izmail'skii, in which he showed that an intense colour can arise also when two auxochromes (donor and acceptor of electrons), present in the same molecule, are isolated from each other by saturated groups of atoms. This type of coloration is observed only in the solid state and in concentrated solutions. It is due not to intramolecular electron transitions but to intermolecular exo-interactions of donor and acceptor groups, and is explained by the formation of complexes with partial transfer of charge. If two chromophores in a dye molecule are not isolated from each other, but are in some measure conjugated, the absorption spectrum usually differs markedly from those of the component dyes. According to ideas current until recently the interaction of conjugated chromophores is shown by a shift in the absorption band to longer wavelengths and in an increase in the intensity of absorption[8].

Brode and his coworkers showed, for example, that the bisazo-dye (X)



(X)

in which the arylazo-groups are interlinked through a *para*-phenylene ring, absorb considerably further towards the red end of the spectrum and more strongly than the isomer (VI), in which the same chromophores are joined in the *meta*-position[4]. Fig. 2 shows the absorption curves† of two symmetrical bisazo-dyes (XI) and (XII) and also of the corresponding component dye (XIII) (at double the concentration). Here, too, a bathochromic shift in the band due to dye (XI) is clearly evident in comparison with the bands of dyes (XII) and (XIII), which show close similarity[3].



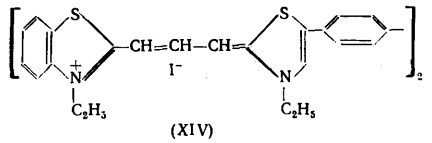
(XI)

(XII)

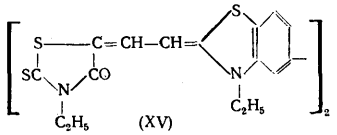
(XIII)

† Here and subsequently absorption curves and maxima are given for alcoholic solutions, where no solvent is specially mentioned.

A similar deepening of colour has been observed in symmetrical biscyanines (XIV) [9] and bismerocyanines (XV) [10]



(XIV)



(XV)

in comparison with the corresponding mono-dyes.

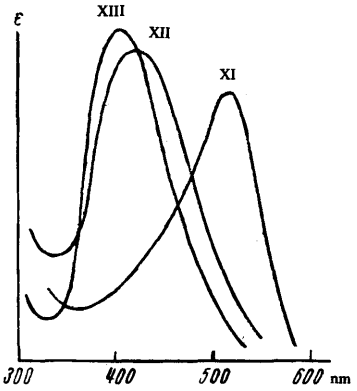
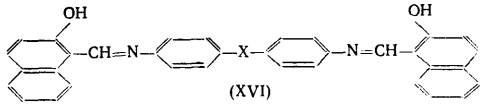


Figure 2.

The effect of the nature of the bridge X on the degree of conjugation between azomethine chromophores has been investigated on bisazomethines of formula (XVI) [11]



(XVI)

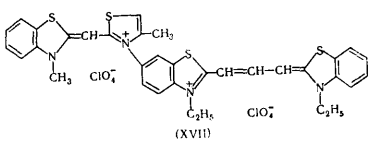
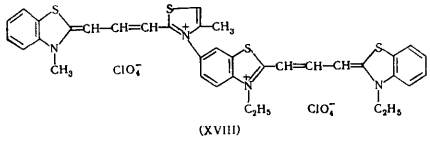
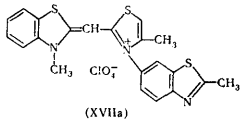
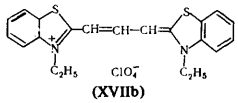
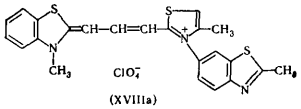
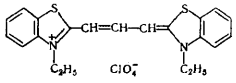
Table 1.

X	Abs. max., nm	$10^{-4}\varepsilon$	X	Abs. max., nm	$10^{-4}\varepsilon$
CH_2	345	2.86	S	358	3.70
O	350	3.60	NH	413	4.83

Such conjugation is apparent in a displacement of the absorption maximum (abs. max.) and an increase in molecular extinction. Table 1 shows that oxygen, sulphur, and nitrogen atoms, with their lone pairs of electrons, do not have an isolating effect like that of the methylene group. However, the effect of conjugation through bridges of this type is relatively small in bisazomethines, as well as in bisazo-dyes[12,13] and in biscyanines[14].

We shall not cite other published examples of the interaction of bound chromophoric systems. The view held until recent years was that two conjugated chromophores in a dye molecule lose their individuality, delocalise into one conjugated system, and absorb light as a single chromophore having a longer conjugated chain. As a result the absorption bands corresponding to each individual chromophore merge to form a single more intense band displaced to lower frequencies[15].

Table 2.

Biscyanines	Abs. max., nm
 (XVII)	422 563
 (XVIII)	581 522
Component cyanines	**Abs. max., nm**
 (XVIIa)	420
 (XVIIb)	558
 (XVIIIa)	562
 (XVIIIb)	558

It has been found recently, however, that this view is valid only for the particular case in which the conjugated chromophores when separated (in the parent dyes) absorb closely similar light quanta, and also when these chromophores lie on the same straight line (Fig. 1). If the quanta absorbed by the two chromophores differ greatly, the chromophores do not interact at all, even when conjugated with each other. If the conjugated chromophores do not lie on a straight line, but are inclined at an angle, their absorption bands do not merge into a single band, but on the contrary split or move apart. The intensities of the two new bands will then depend on the angle between the interacting chromophores. We shall now discuss these previously unknown phenomena.

In 1964 Kiprianov and Mushkalo[16] synthesised six biscyanine dyes in which the nitrogen atom of the thiazole ring of one cyanine was covalently bound to the benzothiazole ring of a second cyanine. Two biscyanines of this type—dyes (XVII) and (XVIII)—are given as examples in Table 2. The absorption spectra of each of the six biscyanines of this series contained two intense bands. It would naturally be assumed that the maxima of these bands would approximate in some measure to those of the corresponding parent dyes, which were also prepared (e.g. XVIIa and XVIIb in Table 2). However, comparison of the absorption maxima of the biscyanines with those of the corresponding parent dyes led to an unexpected result.

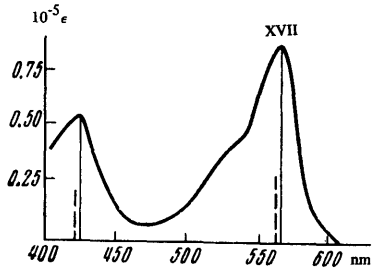


Figure 3.

With biscyanines in which the two chromophoric chains differed in length, e.g. (XVII), the maxima on the absorption curve (Fig. 3) almost coincided with those of the corresponding component dyes (XVIIa) and (XVIIb) (these maxima are indicated by the broken lines in Fig. 3). This implies that the chromophores in such biscyanines do not interact, although they are conjugated.

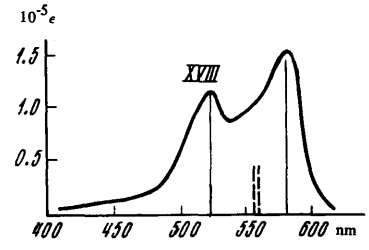


Figure 4.

With biscyanines which contain two chromophores of the same length, e.g. (XVIII), on the other hand, the maxima on the curve (Fig. 4) differed markedly from the absorption maxima of their component dyes (denoted by broken lines). The shorter-wavelength maximum of the biscyanine was shifted to still shorter wavelengths, and the longer-wavelength maximum to still longer wavelengths, than in the component dyes. Thus the chromophores in biscyanines with polymethine chains of the same length interact. The interaction, however, does not lead to coalescence of the absorption bands but to their

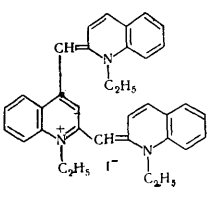
moving apart (or resolution, as has since been shown with biscyanines of symmetrical structure).

Despite the paucity of experimental results these workers[16] permitted themselves the conclusion that the interaction of two conjugated chromophores depends on the light quanta which each chromophore absorbs separately. If the quanta differ greatly, the chromophores do not interact. If the quanta differ little, the chromophores interact in such a way that the frequency absorbed by one chromophore increases, while that absorbed by the other decreases, the absorption bands moving apart. The authors mention the theory of perturbations and its application to electronic spectra[17].

Kiprianov and Dyadyusha[18] examine the physical nature of these phenomena, starting to a first approximation from the principles of classical wave mechanics. Two conjugated chromophores are two coupled oscillators, analogous e.g. to two loosely connected pendulums. If such pendulums differ in length, they have little influence on each other, and each oscillates at its characteristic frequency. But if the pendulums have the same or similar lengths, they interact, which is apparent in a change in their vibration frequency. When isolated from each other, the pendulums oscillated at frequency ν; now that they are coupled, they are able to oscillate only at the two new frequencies $\nu - e$ and $\nu + e$. In one case oscillations of the pendulums are in phase; in the other case they are of opposite phase.

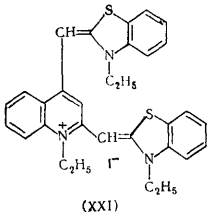
Electrons oscillate in the conjugated chromophores of bis-dyes. If the vibration frequencies of the electrons in the isolated chromophores are the same or similar, the conjugation of such chromophores should result in their vibration and absorption of light at two new frequencies, one higher and the other lower than the original frequency.

Two cases are known of the observation by other workers of analogous phenomena to those observed by Kiprianov and Mushkalo above. In 1953 Shibata[19] prepared the distyryl dye (XIX) and the corresponding two monostyryl dyes (XIXa) and (XIXb) (Table 3). He took no notice of the fact that the bands corresponding to the monostyryl derivatives had moved apart in the spectrum of the distyryl compound. Perhaps this was because such separation was inconsistent with his quantum-mechanical calculations.



(XX)

Abs. max. 615, 480 nm
(550, 520 nm)

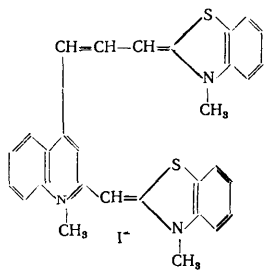


(XXI)

Abs. max 547, 450 nm
(509, 480 nm)

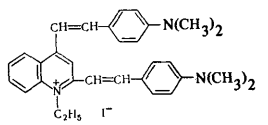
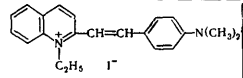
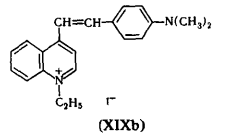
Still earlier Brooker and Smith[20] had noted something similar in the spectra of the two biscyanines (XX) and (XXI). With both dyes the two absorption maxima were farther apart than those of the corresponding monocyanines (indicated in parentheses). The authors tried to explain why the longer-wavelength bands of their dyes had shifted towards the red end of the spectrum, but the displacement of the shorter-wavelength bands in the opposite direction remained incomprehensible to them.

Kiprianov and Mushkalo showed[21] that the parting of the absorption bands in the spectra of Brooker and Smith's biscyanines was due to the same cause as in the spectra of the biscyanines which they themselves had described[16]. While it is true that the two chromophoric chains in (XX) and (XXI) differ in length and that the absorption maxima of the corresponding component dyes do not coincide, it must be borne in mind that conjugation of the chromophores, including the common methine groups, is far stronger here than in Kiprianov and Mushkalo's bis-dyes. In fact it was found that in the spectra of dyes of the same type, but with a still greater difference in length between the chromophoric chains, e.g. in the spectrum of the biscyanine (XXII)



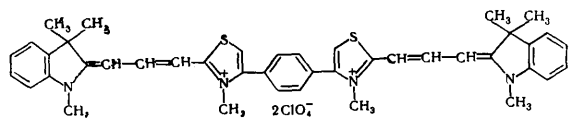
(XXII)

Table 3.

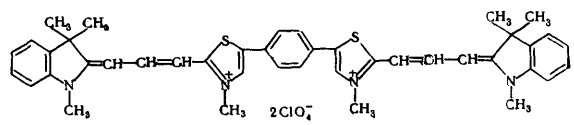
Distryl dye	Abs. max., nm	Monostyryl dye	Abs. max., nm
 (XIX)	500 570	 (XIXa)  (XIXb)	527 546

there is hardly any separation of the absorption maxima relative to those of the component dyes.

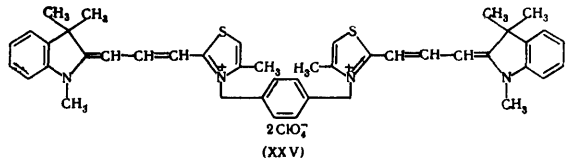
The biscyanines in which the separation of absorption bands due to conjugated chromophores was discovered proved to be a convenient subject for studying the new phenomenon. This applies especially to symmetrical biscyanines, in which the bands due to the two identical component dyes do not move apart but are resolved.



(XXIII)



(XXIV)



(XXV)

have been synthesised[22]. Figs. 5–7 show their absorption curves (full lines) and those of the corresponding parent monocyanines (XXIIIa)–(XXVa) (broken curves). The curves for (XXIII) and (XXIIIa) (Fig. 5) have the same shape and the same position of the maxima, differing only in intensity. The chromophores in the molecule (XXIII) are not formally conjugated, and hardly interact at all. In contrast, curves (XXIV) and (XXIVa) in Fig. 6 are completely different: here the chromophores are conjugated, so that the band of the parent cyanine is split in the spectrum of the biscyanine into two new bands of different intensities. Interaction between the chromophores is observed also in the biscyanine (XXV) (Fig. 7), but it is far weaker, and the two bands have moved apart less.

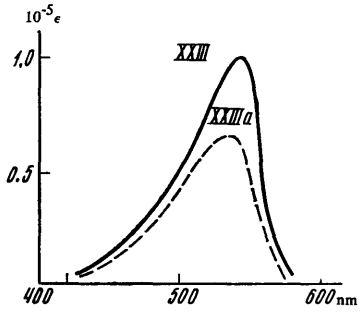
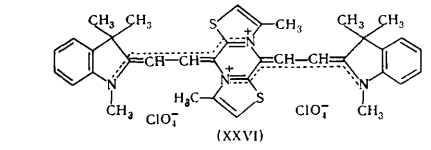
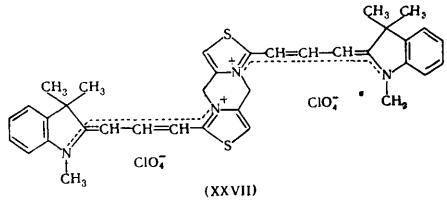


Figure 5.

It has been shown[23] how different are the spectra of biscyanines with conjugated and non-conjugated chromophores by the synthesis of two biscarbocyanines (XXVI) and (XXVII)

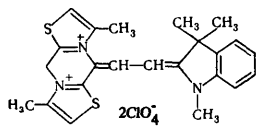


(XXVI)

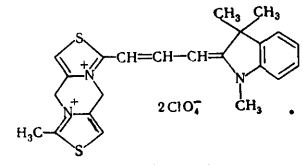


(XXVII)

of generally similar structure together with the corresponding parent cyanines (XXVIa) and (XXVIIa)



(XXVIa)



(XXVIIa)

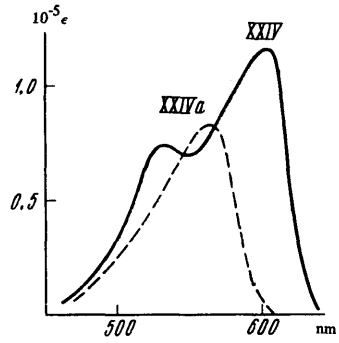


Figure 6.

The chromophoric chains in the bis-dyes are shown as broken lines in the structural formulae. They are conjugated in the first of these biscyanines, but separated by methylene groups in the second biscyanine.

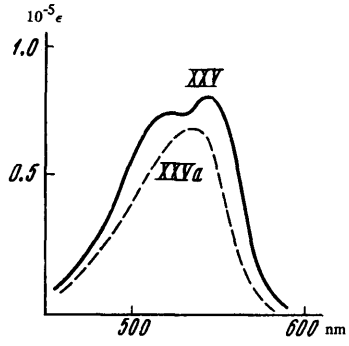


Figure 7.

Fig. 8 shows the absorption curve of the biscyanine (XXVI) and the absorption maximum of the component cyanine (XXVIa) (broken curve). This is a typical picture of strongly interacting chromophores: the absorption bands of the cyanine (XXVIa) (maximum at 552 nm) are split into two mutually remote bands (maxima at 490 and 642 nm).

Fig. 9 shows that the absorption curves of the biscyanine (XXVII) and the component cyanine (XXVIIa) are very similar in shape, with only one band of almost double

the intensity in the biscyanine. Both indicate absence of interaction between the chromophores, but the biscyanine maximum is displaced 19 nm to longer wavelengths. Consequently the methylene group does not completely isolate the chromophores in this case, some mutual influence being preserved.

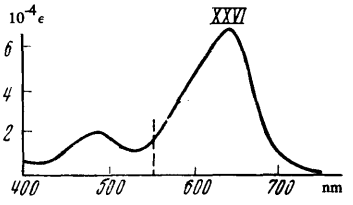


Figure 8.

It must be supposed that the degree of interaction of the chromophores in bis-dyes is defined by the increase in separation or the resolution of their absorption bands. If we denote by Δ_1 the difference between the absorption maxima of the two component dyes and by Δ_2 the difference between the maxima of the two bands of the bis-dye, the degree of interaction of the chromophores in the latter should be measured by $\Delta = \Delta_2 - \Delta_1$. In the case of bis-dyes of symmetrical structure $\Delta_1 = 0$ and $\Delta = \Delta_2$.

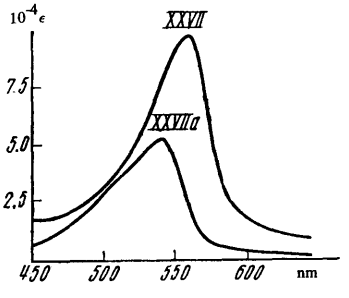
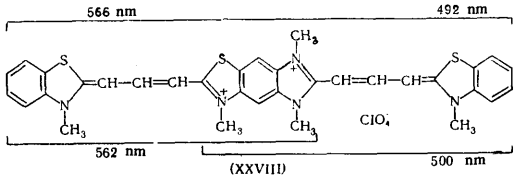


Figure 9.

In order to elucidate the factors determining the degree of interaction of chromophores in biscyanines, a series of nine dyes of the type (XXVIII)

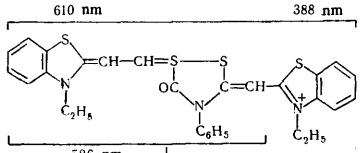


(XXVIII)

and the corresponding parent monocyanines were prepared[24,25]. Above the formula of the bis-dye (XXVIII) are indicated the maxima of its two absorption bands, and below the formula those of the component monocyanines. In the present case the maxima move apart by $\Delta = 12$ nm. Both central and terminal heterocycles were varied in biscyanines of this type, the corresponding Δ values being determined each time.

This work confirmed the correlation already mentioned between the increase Δ in the separation of the absorption maxima of the chromophores in the biscyanines and the difference Δ_1 in the maxima of the component cyanines: the smaller is Δ_1 the larger is Δ. The mutual withdrawal of the bands is largest in symmetrical biscyanines. The interaction of the chromophores is influenced also by the mobility (degree of delocalisation) of the π-electrons in the polymethine chromophore: the more delocalised are these electrons, the more strongly the chromophores interact‡. However, there is yet another important factor influencing the increased separation of absorption bands in dyes having conjugated chromophores. It can be termed "the degree of conjugation of the chromophores", a name which has not yet been fully defined.

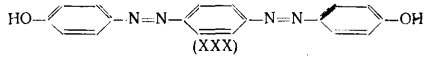
An example of bis-dyes with a high degree of conjugation between the chromophores is provided by the trinuclear rhodacyanines[27]. Spectroscopic investigation[21] of the dye (XXIX)



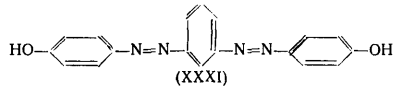
(XXIX)

showed that, despite the very large difference between the maxima of the two component dyes of this rhodacyanine ($\Delta_1 = 87$ nm) and the absence of formal conjugation between the polymethine chains, the mutual withdrawal Δ of the maxima reaches 135 nm. The probable reason for such strong interaction of the chromophores through the rhodanine ring is that this ring is present in both component dyes. Investigation of a series of analogous trinuclear cyanines (bismerocyanines) shows[28] very considerable withdrawal of the absorption bands in all of them, which is also larger the smaller the difference between the maxima of the component dyes.

Hitherto we have been considering the resolution of absorption bands in biscyanine dyes. However, this phenomenon should be common to bis-dyes of all classes. It seemed surprising that it had not been noted in any of the many known bisazo-dyes. It was therefore of especial interest to study, more carefully than had been done previously, at least the simplest members of this immense group of colorants. In 1968 the two bisazo-dyes (XXX) and (XXXI)



(XXX)



(XXXI)

were investigated spectroscopically[29].

Fig. 10 shows the absorption curves of the bisazo-dye (XXX) and of the component dye *p*-hydroxyazobenzene (XXXa). These curves were obtained in alcohol alone (full curves) and with added alkali (broken curves). In both solvents we observe the long known pattern: the

‡ The degree of delocalisation of π-electrons in unsymmetrical cyanines is determined by their deviation[26].

bands of the bis-dye are displaced to longer wavelengths, especially in the alkaline solution§. No splitting of the band is seen in the bisazo-dye (XXX).

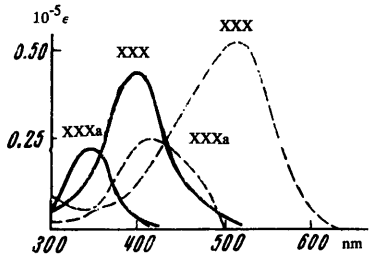


Figure 10.

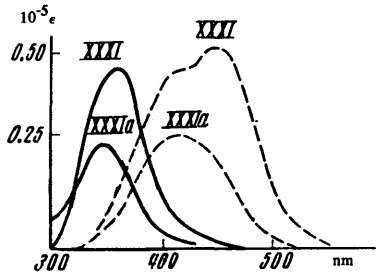


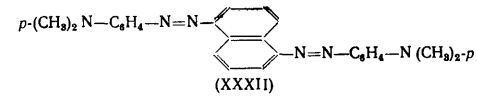
Figure 11.

The absorption curves of the bisazo-dye (XXXI) in neutral and alkaline alcoholic solutions are at first glance unexpected (Fig. 11). Here the two azo-groups are linked through the *meta*-position of a benzene ring, so that formally they are not conjugated. Nevertheless, the absorption band of the bisazo-dye (XXXI) is displaced towards the red end of the spectrum with respect to that of the component dye (XXXa)¶, and in alkaline solution there is even appreciable resolution into two bands. It has also been shown in several other experiments—dyes (XLIII), (XLVII), (LVI), and (LVII)—that the interaction of chromophores linked through the *meta*-positions of a benzene ring is weak but not entirely absent. The situation is probably similar to that observed with rhodacyanine dyes. As we shall see later, the absence of band splitting in the bisazo-dye (XXX) and its presence in (XXXI) are connected with the linear structure of the former molecule and the angular structure of the latter.

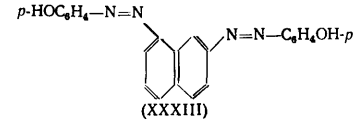
§ Delocalisation of π-electrons is greater in dye anions and cations than in the unionised molecules[26].

¶ Although Brode had stated[4] that azo-chromophores in *meta*-positions do not influence each other.

The interaction of two azo-chromophores has been studied also in the bisazo-dyes from naphthylene-1,5-diamine (XXXII) and from naphthylene-1,7-diamine (XXXIII)[30]



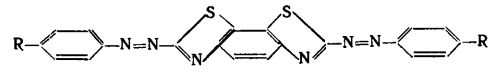
(XXXII)



(XXXIII)

Contrary to earlier results[31], no conjugation has been detected between the azo-chromophores in the spectrum of the bisazo-dye (XXXII). On the other hand, the chromophores are conjugated in (XXXIII), as is seen from the distinct splitting of the absorption band (angular molecular structure).

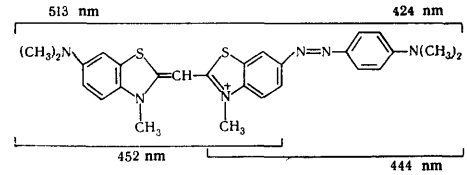
Two bisazo-dyes have been prepared from thiazolobenzothiazolediamine—(XXXIV) and (XXXV)[32]



(XXXIV: R=OH) (XXXV: R=N(CH3)2)

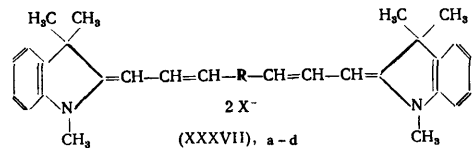
Both these symmetrical bisazo-dyes show, in neutral alcoholic solution and still better in alkaline (XXXIV) or acid (XXXV) solutions, the splitting of the absorption band of their component dyes which is typical of conjugated bis-dyes.

The interaction of a polymethine chromophore with an azo-chromophore has been studied[33] in azo-cyanine dyes. Here, too, maximum interaction was observed in dyes where the two component dyes absorbed similar light quanta, e.g. (XXXVI)



(XXXVI)

Very interesting results on the band intensities of dyes containing two conjugated chromophores were obtained[34,35] from an investigation of the spectra of biscyanines synthesised from isomeric dimethylthiazolobenzothiazoles. Four isomeric bistrimethinecyanines (XXXVII)



(XXXVII), a–d

were obtained, in which the central ring R was one of the fused systems (a)–(d) (Fig. 12), as well as several other symmetrical biscyanines and distyryl derivatives containing the same ring systems (a)–(d). The absorption curves of the biscyanines (XXXVIIa–d) are reproduced in Fig. 13.

The spectrum of the biscyanine (XXXVIIa) was found to contain two bands *a* and *a'* of almost equal intensity; with (XXXVIIb) the intensity of the shorter-wavelength band *b'* fell, whereas the longer-wavelength band *b* increased sharply in intensity; the shorter-wavelength band *c'* of the biscyanine (XXXVIIc) was hardly noticeable;

and finally (XXXVIId) exhibited only a strong longer-wavelength band *d*, while the shorter-wavelength band had almost disappeared†. Comparison of the structural formulae of these biscyanines (XXXVIIa–d), taking into account X-ray data on the thiacyanines [38,39], clearly reveals a correlation between the intensity ratio of the two bands of each biscyanine and the angle between the directions of its polymethine chromophores (from one auxochrome to the other). This angle is smallest (80°) in the isomer (XXXVIIa) (Fig. 14); it is 180°, i.e. a maximum, in (XXXVIId), whose molecule is centrosymmetric.

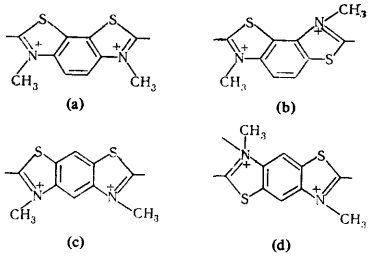


Figure 12.

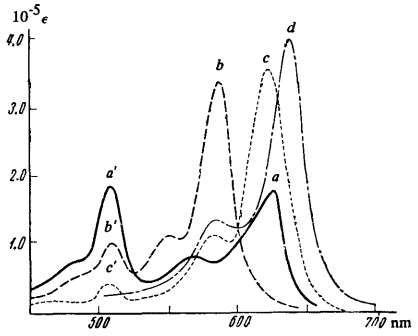
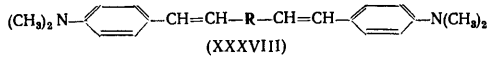


Figure 13.

The intensity ratio of the two bands in the biscyanine (XXXVIIa) remains almost unchanged with increase in the length of its chromophoric chains. In the distyryl dye (XXXVIII)

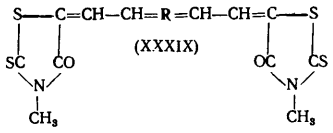


(XXXVIII)

containing the same central ring (R = a), however, the intensity of the longer-wavelength band, in contrast to the biscyanine (XXXVIIa), is almost double that of the shorter-wavelength band (Fig. 15). In fact, the angle between the chromophoric chains is far larger in (XXXVIII) than in (XXXVIIa) (Fig. 16).

† Inflexions on the short-wavelength portion of the absorption curves, in the present case in the range 550–600 nm, are characteristic of most cyanine dyes and are due to vibrational transitions [36]. This origin of such inflexions has recently been proved by the luminescence spectra at low temperatures [37].

Investigation of the spectra of the bismerocyanines (XXXIX)



(XXXIX)

where R represents one of the ring systems (a)–(c) (see above) revealed the same dependence of the intensities of the absorption bands on the angles between the chromophores [40].

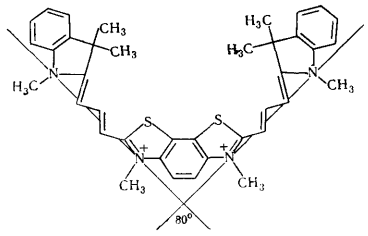


Figure 14.

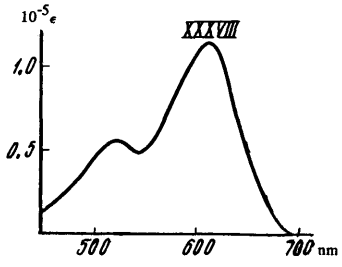
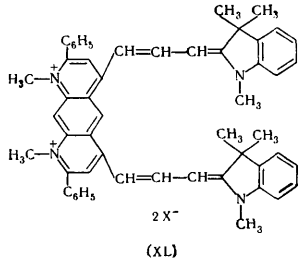


Figure 15.

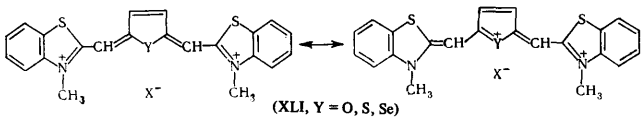
In 1968 it proved possible to synthesise [41] the first biscyanine (XL) in which the directions of the chromophoric chains formed an acute angle



(XL)

In conformity with expectation the shorter-wavelength band of this dye was considerably more intense than the longer-wavelength band (Fig. 17). Since then simpler bis-dyes have been obtained with acute angles between the chromophores—see (XLII) and (XLVI).

Unusual bis-dyes of general formula (XLI)



(XLI, Y = O, S, Se)

have recently been described[42]. Fig. 18 shows that two bands—a more intense longer-wavelength band with a fine structure and a weaker shorter-wavelength band—are present in the absorption spectra of all three compounds.

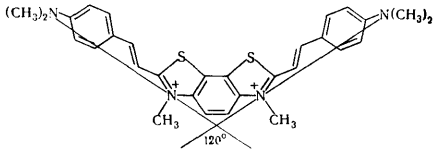


Figure 16.

This corresponds to obtuse angles between the chromophores. The intensity ratio of the two bands indicates that the selenophen derivative has the largest angle and the furan derivative the smallest: this was to be expected. Similar observations have been made[43] on biscyanines obtained from dimethyloxazolobenzoxazole and dimethylthiazolobenzothiazole.

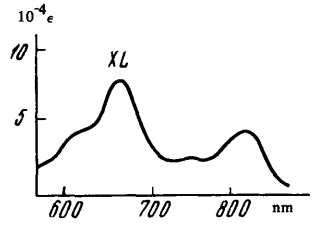


Figure 17.

The experimental results discussed in this Review leave no doubt that the intensity ratio of the two absorption bands which appear on electronic interaction between two combined chromophores is determined by the angle between the chromophores in space‡.

The elementary theory of the interaction of chromophores (Kiprianov and Dyadyusha[18,44]) is consistent with this generalisation. The oscillations of a positive or a negative charge excited in the chromophores by the alternating electric field of a light wave are equivalent to vibrations of a dipole. Because of the repulsion of like charges, the excitation of oscillations in which the like charges in chromophores joined at the ends come together (*a* and *d* in Fig. 19) requires more energy than with the opposite phase relationship (*b* and *c*). The former corresponds to high-frequency or short-wavelength absorption bands, the latter to low-frequency or long-wavelength bands.

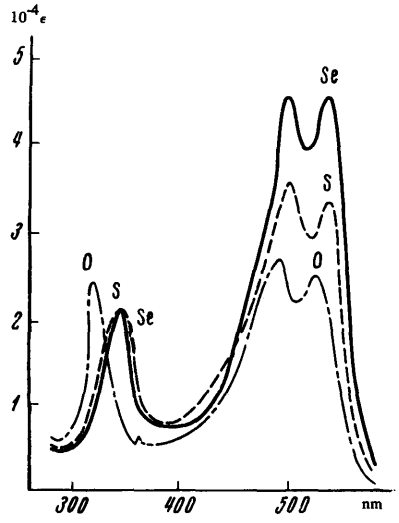


Figure 18.

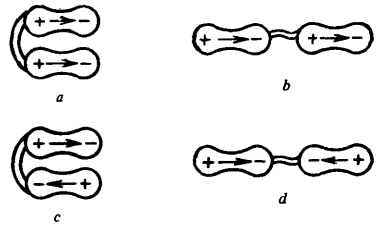


Figure 19.

If the angle between the chromophores is either 0 or 180°, the oscillations depicted as *a* and *b* (Fig. 19) are equivalent to vibrations of a dipole having double the charge. They interact strongly with the field of the light wave. With oscillations of types *c* and *d*, on the other hand, the aggregate dipole remains unchanged, and these vibrations cannot be actively involved in the absorption of light. With the chromophores arranged parallel (angle 0°), therefore, only the short-wavelength band can be intense. If, however, one chromophore constitutes a prolongation of the other (angle 180°), only the long-wavelength band can be intense. With intermediate angles between the chromophores (Fig. 20) both absorption bands should be observed, with the short-wavelength band more intense at acute angles, and the long-wavelength band at obtuse angles.

It is desirable that models for study of a new phenomenon should be as simple as possible. In the case of

‡ At least in bis-dyes of symmetrical structure. The intensities of the component dyes must also be taken into account in the case of unsymmetrical bis-dyes.

dyes having two linked chromophores this condition was met by bishemicyanines. A considerable number of dyes of this group have been reported in the patent literature[45], but their absorption spectra have not been investigated.

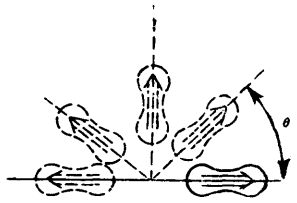
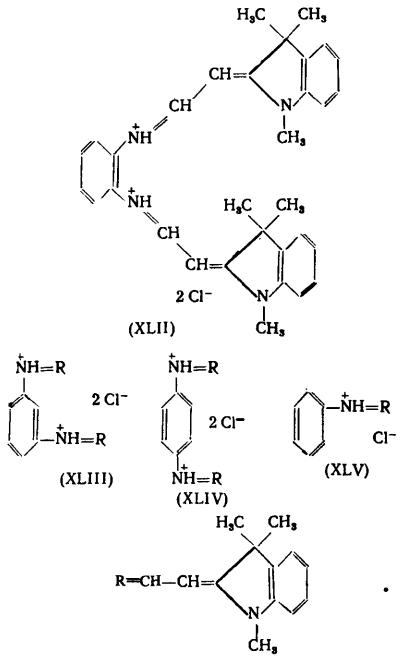
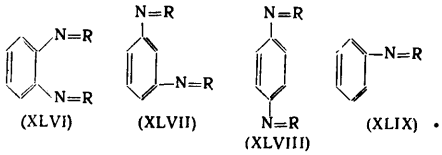


Figure 20.

Kiprianov and Buryak[46] determined the absorption curves of three simple isomeric bishemicyanines (XLII)–(XLIV) and also that of the component hemicyanine (XLV). We give the structure of the first of these dyes in full, and the other structures in abridged form:



These dyes are converted by alkali into the corresponding bases (XLVI)–(XLIX)



The absorption curves of these bases show (Fig. 21) that the chromophores interact in every case. In the spectrum of the *ortho*-derivative (XLVI) the band of the component base (XLIX) is split into two new bands, of which the shorter-wavelength band is by far the more intense. This intensity relationship was to be expected, since the two chromophores should form an acute angle in this *o*-phenylenediamine derivative.

No splitting of the band due to the component hemicyanine is observed in the spectrum of the base (XLVII) (a derivative of *m*-phenylenediamine). However, the chromophores do interact, as is evident from the shift in the band to longer wavelengths.

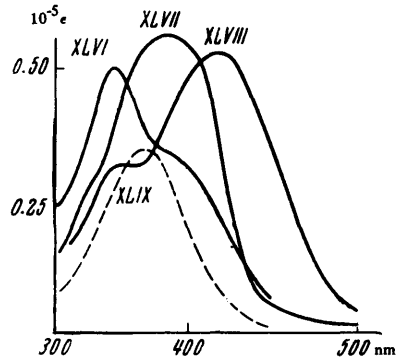


Figure 21.

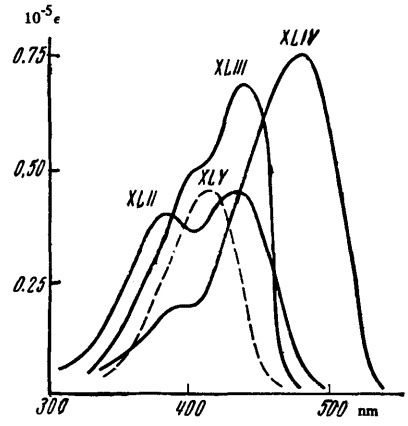


Figure 22.

In the base (XLVIII) the chromophores are conjugated, but they are arranged in diametrically opposed directions. Here an intense long-wavelength band would be expected with disappearance of the short-wavelength band. Nevertheless, although the former is strong, we see also a weak but distinct short-wavelength band. It is probable that not all the equilibrium conformations of this molecule have a centrosymmetric structure§.

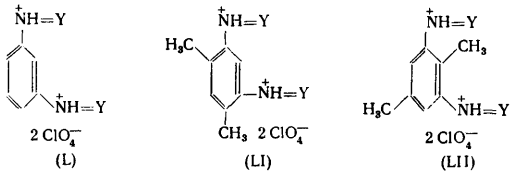
Fig. 22 shows the absorption spectra of the bishemicyanines themselves (XLII)–(XLIV) and of the hemicyanine (XLV). As usual, the absorption bands of the salts

§ Like the dimethyl ether of quinol, in which the dipole moment differs from zero.

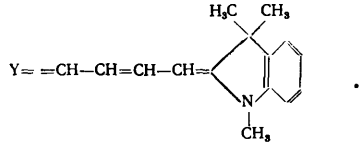
are more intense than those of the bases, and are displaced towards the red end of the spectrum. The absorption curves underwent interesting changes on passing from the bases to the salts. The longer-wavelength band—not the shorter-wavelength band—is more intense in the spectrum of the *ortho*-derivative (XLII) in contrast to the spectrum of the base (XLVI). The appearance of like cationic charges on the nitrogen atoms pushed the latter apart. The absorption curve of the *meta*-derivative (XLIII) exhibits not only a general shift in the band to longer wavelengths but also a distinct splitting with the formation of a shorter-wavelength maximum, in spite of the absence of formal conjugation. The absorption curve of the *para*-derivative (XLIV) resembles that of the corresponding base (XLVIII).

The spectra of bishemicyanines revealed steric effects on the introduction of methyl groups *ortho* to the chromophoric chains. These effects are readily evident in the methyl and dimethyl derivatives of the bishemicyanines just described[47], but they become especially strong as the polymethine chromophores become longer. Let us give a few examples[48].

m-Phenylenediamine and its dimethyl derivatives have been used to prepare the bishemicyanines (L)–(LII)



where



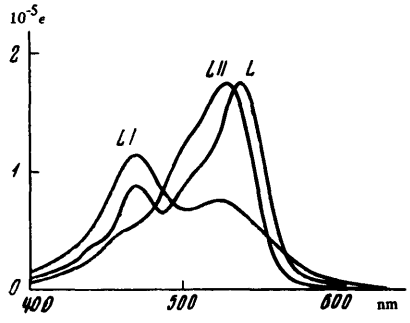
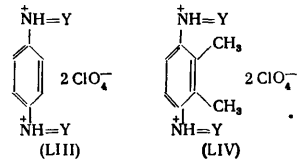


Figure 23.

From Fig. 23 it can be seen how the volume of the methyl groups affects the angle between the chromophores. The intensities of the absorption bands indicate that, as was to be expected, this angle is obtuse in the bishemicyanine (L). The introduction of two methyl groups into positions 4 and 6 of the benzene ring (bishemicyanine LI) forces the chromophoric chains together and makes the angle between them acute. But if a methyl group is placed between the chromophores (dye LII), the angle between them increases almost to 180°.

Similar changes in angle between the chromophores under the influence of adjacent methyl groups are observed also in the bishemicyanine from *p*-phenylenediamine (LIII) and its dimethyl analogue (LIV)



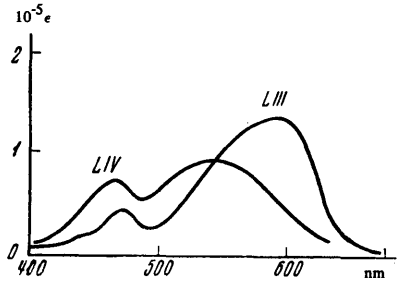
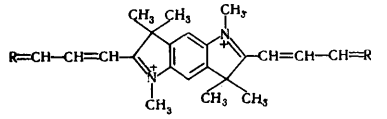
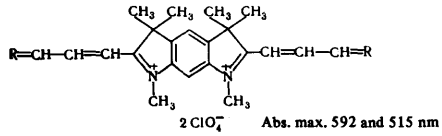


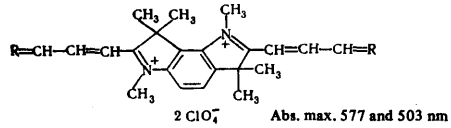
Figure 24.

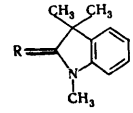
The chromophores in (LIII) lie in opposite directions (cf. preceding footnote §). This is apparent in the spectrum (Fig. 24) as an intense long-wavelength band and a weakly defined short-wavelength band. Two methyl groups introduced into positions 2 and 3 in the benzene ring (bishemicyanine LIV) reduce this angle almost to a right-angle (two maxima of almost equal intensity).

We have already noted—dyes (XXXI) and (XLIII)—that spectral interaction of two chromophores is observed when they are linked not only through the *ortho*- and *para*-positions of a benzene ring but also through the *meta*-position. A special investigation has been made of this last case[49]. Three symmetrical biscyanines (LV)–(LVII)



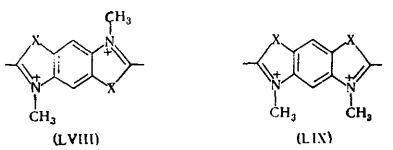






were prepared from isomeric dimethyldiazaindacene derivatives. Mutual separation of the absorption bands is observed with all three bis-dyes, but its value Δ, representing the degree of interaction of the combined chromophores, is 139 nm in (LV), in which the chromophoric chains are conjugated through the *para*-position of the benzene ring, whereas it is 77 and 74 nm, i.e. only half, in the biscyanines (LVI) and (LVII), where the same chains are combined through the *meta*-position.

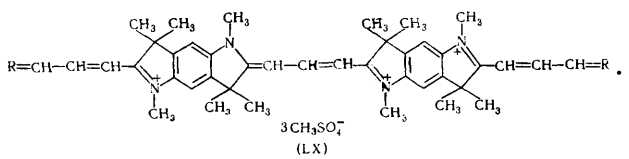
In the analogous biscyanines containing fused thiazolobenzothiazole or oxazolobenzoxazole rings as central nucleus the structures (LVIII) and (LIX)



(LVIII) (LIX)

(where X = S, O) show little difference in mutual separation of the bands. In these dyes, however, conjugation can be accomplished not only through the nitrogen atoms but also through the sulphur or oxygen atoms.

In concluding this survey we note that it has recently proved possible[50] to synthesise the first triscyanine dye (LX)



(LX)

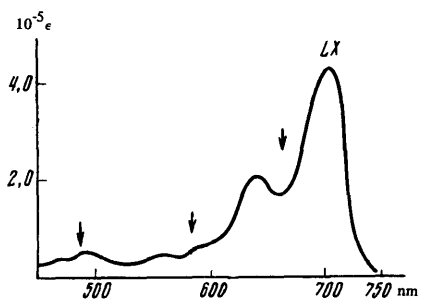


Figure 25.

Fig. 25 shows that the absorption curve of this dye in nitromethane contains bands corresponding to three electronic transitions (indicated by arrows).

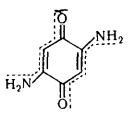
From all that has been stated concerning the interaction of conjugated chromophores it must be concluded that a cautious approach is necessary to the use of spectral methods to determine the structure of organic compounds. In the infrared and nuclear magnetic resonance spectra each group of atoms is represented by a band or region of characteristic absorption, so that these methods are extremely valuable for the determination of structure. But the attempts of many chemists to establish such characteristic frequencies in electronic spectra, e.g. for substituents in aromatic and heterocyclic ring systems, have been unsuccessful. For the most part conjugated chromophores do not absorb at all in the spectral region in which the isolated chromophores absorb. It was therefore supposed that on conjugation the individual chromophores merge into a single longer chromophore, which absorbs at longer wavelengths. We now know that the situation is more complicated, and that the conjugation of two chromophores results in the formation of two new absorption bands, for each of which both interacting chromophores are responsible.

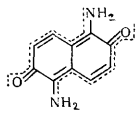
This interaction of chromophores has been discussed in the quantum theory of the spectra of organic compounds[16,51]. The probable reason why it has not been observed hitherto in the spectra of simple conjugated systems, e.g. the absorption spectra of aromatic hydrocarbons and polyenes, is that such spectra are too complicated, consisting of a large number of closely spaced bands. However, the splitting of bands has been observed by Davydov in the spectra of molecular crystals of naphthalene and anthracene at low temperatures, when the bands are especially narrow, and has been brilliantly explained by him (Davydov splitting)[52,53]. It must also be borne in mind that, according to London's theory, electrical interaction between oscillators in molecules should be greater the stronger the oscillators and the longer the longest wavelengths of absorption bands due to the molecule. Consequently resonance interactions should be more clearly developed between dye molecules than between aromatic hydrocarbon molecules containing conjugated systems of the same length[54]. Earlier spectroscopic investigations on bisazo-dyes have not resulted in the discovery of splitting of their absorption bands, for the dyes studied mostly had linear molecules, in which splitting should not have been observed. Furthermore—probably the most important reason—the absorption bands of azo-dyes are broad, overlapping, and devoid of distinct maxima. It is not surprising that cyanine dyes, with their narrow and intense absorption bands, provided greater success.

As early as 1944 Förster[55,56] used the interaction of π-electron systems to explain the absorption bands of dimeric cyanine dyes, which lay at shorter wavelengths than the bands due to the monomers. The chromophores were arranged parallel to each other in the molecules of these dimers. Recently Kuhn[57] has shown that, in monomolecular layers of simple cyanine dyes deposited on a glass surface in such a way that the chromophoric chains of two neighbouring molecules A and B are contiguous, the chromophores begin to interact as coupled oscillators. As a result, the absorption band of dye A is displaced in one direction, and that due to dye B in the other, so that the bands move apart.

Whether in Davydov's molecular crystals, in dimers of cyanines, or in Kuhn's monolayers of dyes, the interacting molecules only approach one another, but do not form covalent bonds. Recently, however, Dähne has shown[58] that the deep and intense colour of certain aromatic and heterocyclic compounds, including Indigo Blue, Indanthren Blue, and Alizarin, can be regarded as resulting from the interaction of two electronic oscillators bound covalently into a single cyclic system

(coupling effect). This has been shown especially convincingly for red 2,5-diamino-*p*-benzoquinone (LXI) and blue 1,5-diamino-2,6-naphthaquinone (LXII)





336 and 488 nm 321 and 581 nm

Absorption maxima in $(CH_3)_2SO$

(LXI) (LXII)

which, according to Dähne, are doubly bound merocyanine molecules. This has been confirmed by appropriate quantum-mechanical calculations of the absorption maxima of these compounds, investigation of their ultraviolet and nuclear magnetic resonance spectra, and X-ray examination of the crystals [59-61].

Nevertheless, as is evident from the present review, it is only by investigating the spectra of bis-dyes in which the two component dye molecules are combined into a single open conjugated chain that we were able to establish that not all combined chromophoric systems interact spectroscopically, but only those which absorb similar quanta of light energy, that the intensities of the two absorption bands of a bis-dye can be used to estimate the direction of its chromophores in space, that these directions are easily changed by steric and electronic factors, etc.

The investigation of bis-dyes having conjugated chromophores has opened a new chapter in the theory of colour and constitution.

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