173. F. Eisenkolb, "Fortschritte der Pulvermetallurgie", Akademie Verlag, Berlin, 1963, Vol. II, p. 851.
174. "Metallography of Reactor Materials. Survey by Battelle Memorial Institute", Book 3, "Materials for Moderating, Reflector, and Control Assemblies" (Translated into Russian), Atomizdat, Moscow, 1962.
175. I. I. Kornilov, "Metallidy i Vzaimodeistvie Mezhdu Nimi" (Metallides and Reactions between Them), Izd. Nauka, Moscow, 1964.
176. I. V. Bersuker and A. V. Ablov, "Khimicheskaya Svyaz' v Kompleksnykh Soedineniyakh" (The Chemical Bond in Complex Compounds), Izd. Akad. Nauk Moldav. SSR, Kishinev, 1962.
177. A. Z. Men'shikov and S. A. Nemnionov, Fiz. Metallov i Metalloved., 19, 57 (1965).
178. H. J. Goldsmid and W. M. Ham, J. Less Common Metals, 10, 57 (1966).
179. E. Ganglberger, E. Laube, and H. Nowotny, Monatsh., 96, 242 (1965).

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THE COLOUR OF DYES AND STERIC HINDRANCE IN THEIR MOLECULES

A. I. Kiprianov, G. G. Dyadyusha, and F. A. Mikhailenko

Steric hindrance in the molecules of organic dyes has a marked influence on their colour, ability to fluoresce, solubility, and many other physical and chemical properties. The presence of steric hindrance in the molecule quite often makes a dye unsuitable for practical application. With direct dyes the rule exists [1,2] that factors — including steric hindrance — which disturb bond conjugation weaken the affinity of the dye for the fibre, and may result in complete loss of this affinity. Moreover, steric hindrance lowers the intensity of absorption, so that dyes having non-planar molecules yield weaker colours [3]. Steric hindrance in the molecules of cyanine dyes sharply diminishes their ability to sensitise a silver halide emulsion [4]. Thus the problem of steric hindrance in the molecules of organic dyes is of great practical importance.

The chief method for detecting steric hindrance in dye molecules, as in other organic compounds, consists in examining their absorption in the visible or the ultraviolet region of the spectrum.

The absorption spectra of organic compounds depend to a considerable extent on the spatial arrangement of the atoms in their molecules, and sometimes this factor is dominant. The intense and longer-wavelength absorption bands typical of dyes (Burawoy's *K* bands [5]) are associated with $\pi-\pi^*$ electronic transitions, and are caused by the presence in the molecule of an extended system of conjugated double and single bonds, the chromophore [6]. Henceforward we shall confine our discussion to these bands.

Hückel [7] and Pauling [8] showed that the maximum conjugation of multiple bonds is achieved when the molecule has a planar structure, since the axes of the *p* orbitals are then parallel, and the orbitals overlap to the maximum extent. This theoretical conclusion was subsequently confirmed by the X-ray examination of a large number of compounds containing systems of conjugated bonds (*trans*-stilbene, phthalocyanines, cyanine dyes, etc.).

According to the conclusions of quantum-mechanical theory and the results of X-ray structural analysis, the principal structural features of an organic dye molecule are: (1) atoms forming part of the conjugated bond system lie in the same plane; (2) the angles between the bonds involving atoms in the conjugated chain are close to 120°; (3) double bonds in conjugated chains are usually arranged in *trans-trans*-positions; and (4) the lengths of bonds between directly linked atoms in the conjugated chain lie within the range 1.34–1.48 Å (the lengths of bonds between carbon atoms in buta-1,3-diene).

These rules may break down when bulky substituents are present in the conjugated system or adjacent to it. The departures from the normal geometry of the molecule are due to steric hindrance and the mutual repulsion of atoms which are not directly interlinked. If normal angles and a planar structure had been preserved in the molecule, these atoms would have been very close together.

Repulsive forces fall off very rapidly with increase in the interatomic distance. When the latter exceeds the sum of the van der Waals radii, repulsion between the atoms dies away. The van der Waals radii correspond to the minimum distances between atoms in various molecules and molecular crystals, and can be determined from X-ray data.

According to Kitaigorodskii [9] the van der Waals radii of atoms and radicals remain constant to within 0.01 Å on passing from the molecule of one substance to that of another. The van der Waals radii of several atoms and radicals, determined by the above method, are listed in Table 1. [10]

It must be remembered, however, that, as a result of some compression of the electron clouds, atoms can approach, without any considerable consumption of energy, to distances less than the sum of the van der Waals radii. Magat [11] introduced the concept of "effective" radii of atoms and radicals as a limit closer than which atoms could not approach. These effective radii or radii of action depend on the temperature in the sense that the higher the temperature the greater the energy of the colliding atoms, and the more strongly are they deformed on collision.

Although repulsive forces begin to act at distances equal to the sum of the van der Waals radii, the radii of action are in practice more suitable for detecting steric hindrance

TABLE 1.

H 1.20 Å	S 1.85 Å
C 1.80 Å	CH_3 2.00 Å
N 1.50 Å	(C_6H_5) 1.70 Å*
O 1.40 Å	

* Half the thickness of an aromatic ring.

in a molecule. The radii of action of atoms and radicals are known only very roughly. In the case of atoms containing π electrons, they have different values parallel and perpendicular to the plane of the molecule. In view of the difficulty of determining radii of action, somewhat diminished van der Waals radii are often employed[12]. Some workers[13] use the relationship

$$R_{act} = R_{cov} + 0.8 \text{ Å}.$$

The presence or absence of steric hindrance in a planar conjugated molecule is established by drawing the molecule graphically to scale with the normal bond lengths and valency angles. Around each atom or radical is described a circle of radius corresponding to the radius of action. Steric hindrance is then detected from the overlapping of circles belonging to atoms or radicals which are not directly interlinked.

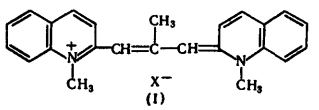
Table 2 gives bond lengths, bond angles, and radii of action for the most important atoms and radicals occurring in dye molecules†.

Fig. 1 shows as example a graphical representation of the cation of 2,2′,9-trimethylcarbocyanine (I).[15] It indicates that a coplanar conformation of this cation is impossible.

More accurate information on steric hindrance is provided by Stuart–Briegleb molecular models[16], which not only enable steric hindrance to be detected in a molecule but also permit the extent of breakdown of molecular coplanarity to be estimated. In these models interatomic

TABLE 2.

Length of bond, Å[13,14]		Radius of action, Å[12]		Angle[12]	
C=C	1.543	H	1.08	C C	
C...C (benzene)	1.397	C	1.40	\ /	125°
				C	
C=C	1.353	N	1.35	C C	
C—O	1.43	O	1.26	\ /	105°
				S	
C—N	1.475	S	1.67	C C	
C...N (pyridine)	1.37	CH_3	1.80	\ //	120°
				N	
C=N	1.29—1.31	C_3H_5	2.20	C C	
C—S	1.78—1.82			\ /	105°
C—H	1.007—1.10			O	



(I)

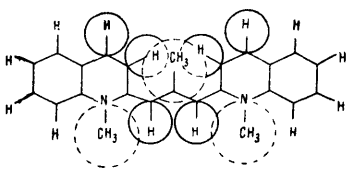
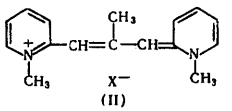


Fig. 1.

† Fuller data on bond lengths and angles in various organic compounds can be found in Wheland's book[14].



(II)

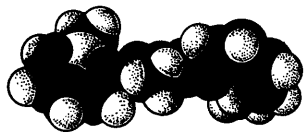
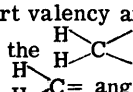
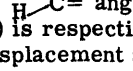


Fig. 2.

distances and angles are strictly fixed, while atoms are incompressible. The only variable parameters are provided by the angles of displacement about bonds. By constructing the model in such a way that atoms are located as close as possible to a single common plane, we can measure or calculate angles of displacement about individual bonds. Fig. 2 illustrates a Stuart–Briegleb model of the dye (II).

From simple geometrical considerations it may be supposed that steric hindrance changes the structure of a molecule in three ways — (1) by the stretching of bonds between atoms, (2) by the distortion of valency angles in a plane, and (3) by displacement about a bond, with one part of the molecule emerging from the plane of the remainder.

Actually, however, bond lengths remain almost unchanged, since the energy required to stretch C–C and C=C bonds is very large (3.25 and 7.05 kcal mole^{-1} respectively to lengthen these bonds by 0.01 Å[17]). Considerably less effort is necessary to distort valency angles in a plane. The energy of deformation of the  angle in the methane molecule and of the  angle in the ethylene molecule by 5.73° (0.1 radian) is respectively 0.39 and 0.26 kcal mole^{-1}.[17] However, displacement about a bond occurs most easily, as about an axis of rotation. The energy of displacement by 0.1 radian about an ethylenic (C=C) and an aromatic (C–C) bond is respectively 0.24 and 0.08 kcal mole^{-1}.[18] For a bond which approximates to a single bond, this energy is close to zero. It follows from these results that the primary effect of steric hindrance will generally be displacement about bonds, which will occur more readily the closer a given bond approximates to a single bond.

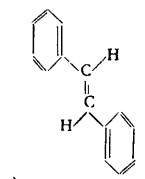
When considering the effect of steric hindrance on the absorption spectrum of a molecule containing a system of conjugated bonds, we must also bear in mind that the stretching of bonds and the distortion of valency angles have relatively little effect on the conjugation of π electrons[19], whereas rotation about a bond reflects the axes of p-electron orbitals from their parallel arrangement. The π-electron interaction energy varies with the square of the cosine of the angle of deflection[20–22]. On rotation through 90°, the atomic p orbitals cease to interact.

Let us now examine the changes in absorption spectrum resulting from steric hindrance and the breakdown of molecular coplanarity in the light-absorbing substance. These changes consist firstly in a displacement in the absorption band, which is usually characterised by the change in wavelength corresponding to maximum absorption (λ_{max}). Secondly a change, usually a decrease, occurs

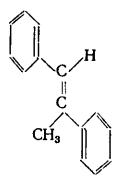
in the intensity of absorption, which is characterised by the molecular extinction at the absorption maximum (ϵ_{max}).

The decrease in absorption intensity is a direct consequence of the diminished mutual overlap of p orbitals in the conjugated system when its coplanarity breaks down. A fall in molecular extinction is therefore the first sign of the appearance of steric hindrance in the absorbing molecule.

The displacement of the absorption band is rather more complicated, since it may occur either towards longer or towards shorter wavelengths. Thus methyl-*trans*-stilbene (IV) absorbs at shorter wavelengths than does *trans*--stilbene (III)[23]:

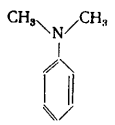


λ_{max} 294 nm, logϵ 4.44
(III)

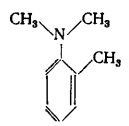


λ_{max} 272 nm, logϵ 4.30
(IV)

NN-Dimethyl-*o*-toluidine (VI) absorbs at shorter wavelengths than does dimethylaniline (V)[24]:

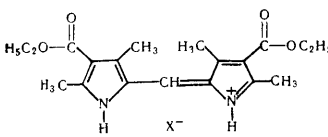


λ_{max} 300 nm, ϵ 13.9 × 10³
(V)

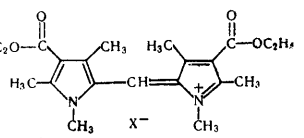


λ_{max} 277 nm, ϵ 6.0 × 10³
(VI)

In 1942 Brunings and Corwin[25] were the first to show that steric hindrance in the dipyrrylmethene (VIII) produces not a hypsochromic but a bathochromic shift:

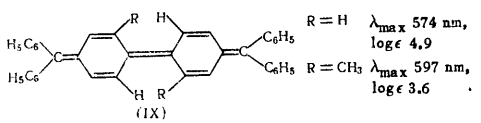


λ_{max} 470 nm, ϵ 13.5 × 10⁴
(VII)



λ_{max} 510 nm, ϵ 5.7 × 10⁴
(VIII)

A bathochromic shift has been observed to accompany steric hindrance in Chichibabin's hydrocarbon (IX)[26]:



R = H λ_{max} 574 nm, logϵ 4.9
R = CH₃ λ_{max} 597 nm, logϵ 3.6
(IX)

Absorption of light occurs in the visible and ultraviolet regions when the energy of the quanta of incident light coincide with that of the electronic transitions of the molecule from the ground state to an excited state. The frequency of the adsorbed light is determined by the difference in energy between ground and excited states according to the well--known Bohr formula

$$\nu = \frac{c}{\lambda} = \frac{E' - E_0}{h}.$$

Hence, in order to ascertain how the frequency (or wavelength) absorbed by the molecule changes under the influence of steric hindrance, we must know what changes are produced thereby in the energy of the ground and of the excited states (steric hindrance always increases the energy of a molecule in comparison with one that is free from steric hindrance).

If steric hindrance increases the energy of the excited state more than it does that of the ground state, the molecule will absorb light of higher frequency: i.e. the absorption band will shift to shorter wavelengths, and a hypsochromic shift in the absorption band will be observed. In the opposite case, when steric hindrance increases the energy of the ground state more than that of the excited state, the molecule will absorb light of lower frequency: the absorption band will be displaced to longer wavelengths (bathochromic shift).

Applying the LCAO approximation[27], we determine the order of the mobile (π-electron) bond p'_{rs} as the derivative of the energy E of the π electrons with respect to the exchange integral β_{rs} of the π-electron orbitals of the atoms r and s forming the given bond:

$$p_{rs} = \frac{1}{2}\frac{\partial E}{\partial \beta_{rs}}.$$

As we have seen, the influence of steric hindrance on absorption spectra is due to the disturbance of π-electron conjugation, represented by a decrease in the absolute magnitude of the exchange integral β_{rs}. If the change in the exchange integral is small, the corresponding change in the π-electron energy is[28]:

$$dE = \frac{\partial E}{\partial \beta_{rs}} d\beta_{rs} = 2p_{rs}\, d\beta_{rs}.$$

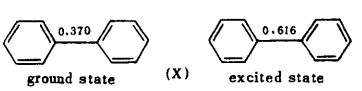
Since excitation involves no change in the relative positions of atoms, the change in exchange integral produced by steric hindrance is the same in ground and excited states. The difference in the change in energy of ground E_0 and excited E' states should depend on the difference in bond order between ground $p_{0,rs}$ and excited p'_{rs} states:

$$d(E' - E_0) = 2d\beta_{rs}\,(p'_{rs} - p_{0,rs}).$$

The exchange integral is a negative quantity. When it decreases in absolute magnitude, $d\beta_{rs}$ is positive. If, therefore, the bond order is greater in the excited than in the ground state, i.e. if $p'_{rs} - p_{0,rs} > 0$, the energy of the transition $E' - E_0$ increases, since $d(E' - E_0) > 0$, and we should observe a hypsochromic shift. When, on the other hand, $p'_{rs} - p_{0,rs} < 0$ and $d(E' - E_0) < 0$, a bathochromic shift should be observed. In the particular case in which $p'_{rs} - p_{0,rs} = 0$ and $d(E' - E_0) = 0$, steric hindrance does not affect the position of the absorption maximum, although it may influence the fine structure and the intensity of absorption.

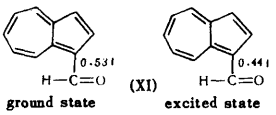
The bond order in the chain of conjugation in a molecule in its ground state can be determined[29] by X-ray examination of its length. Some information can be obtained from infrared and Raman spectra[30]. The experimental determination of bond orders in the excited state of a molecule is difficullt, but some information can be obtained from the vibrational structure of the absorption bands[31].

However, the order of the bonds in which we are interested (only the contribution of the π electrons to the bond order is taken into account), in both ground and excited states, can be calculated to a sufficiently close approximation by quantum-mechanical methods. Calculations by the molecular orbital method are most readily available. They show that the order of the central bond in biphenyl (X) increases on excitation. This is consistent with the observed hypsochromic shift when the coplanarity of the phenyl groups breaks down:

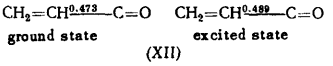


ground state (X) excited state

In just the same way calculation shows, in agreement with experiment, that the order of the bond between the cyclic system and the carbonyl group in azulene-1-aldehyde (XI) is lower in the excited state than in the ground state [28]:

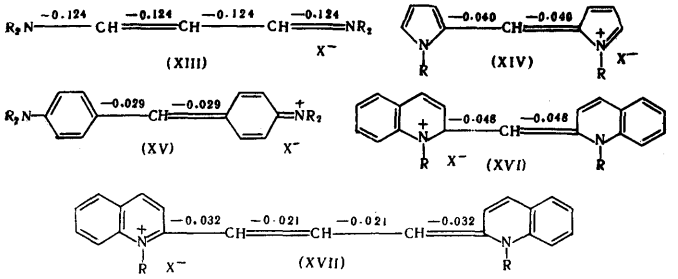


The comparatively small change in order of the similar bond in acryladehyde (XII) explains why no shift in its absorption maximum under the influence of steric hindrance is observed in its derivatives [28]:



(XII)

Similar calculations (with the usual values for the parameters $\alpha_N = \alpha + \beta$ and $\beta_{CN} = \beta$ [32]) show that the excitation of symmetrical polymethine dyes is accompanied by a decrease in order of all bonds in the polymethine chain, for example (with only the differences $p'_{rs} - p_{0,rs}$ indicated)



This rule does not extend to unsymmetrical dyes. For the 4-*p*-dimethylaminostyrylpyridinium cation (XVIII) calculation indicates that excitation will be accompanied by an increase in order of the "single" bonds and a decrease in that of the "double" bond:

Similar calculations have been made for bianthronyl [33], stilbene [34], and nitro-derivatives [35].

Quantum-chemical methods are also useful in enabling general tendencies and regularities to be detected in the changes in bond order accompanying excitation. It has been shown from symmetry considerations, for example, that the order of the central bond in compounds of general formula A–A increases on excitation if this bond is single when the formula is written in the usual way, and decreases if the bond is double or triple (except in the case of cumulenes) [36]. Similar principles have been formulated for the central bonds of symmetrical compounds of general formula Hal–X=Hal$^+$, i.e. for dyes [36].

If we have data on bond orders only in the ground state, we can guess the most probable direction of the change. In fact, if the bond about which deflection occurs is of low order in the ground state, cases in which this bond will have a still lower order should be more rarely met than cases in which it will be of a higher order in the excited state. If, one the other hand, the bond is of high order in the ground state, it is more likely to have a lower order in the excited state. It must be borne in mind here that, on the average, bond orders are lower in an excited state than in the ground state.

This follows from the fact that the energy of a molecule is an additive function of the bond energies, which are proportional to the bond orders. According to the definition of bond order which we have adopted, the coefficient of proportionality between the energy and the order of a bond should be double the exchange integral. Actually, if

$$E' = E_0 + 2\sum_{r<s} p_{rs}\beta_{rs},$$

we have

$$\frac{\partial E}{\partial \beta_{rs}} = 2p_{rs}.$$

The mean decrease in bond order on excitation depends on the transition energy and the number of bonds n involved in the absorption of light. Writing the mean values $\bar{p}$ and $\bar{\beta}$, we obtain

$$2\sum_{r<s} p_{rs}\beta_{rs} = 2n\bar{p}\bar{\beta};\ \bar{p}' - \bar{p}_0 = \frac{E' - E_0}{2n\bar{\beta}}.$$

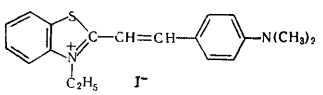
Substituting in this formula $\bar{\beta}$ = 73.2 kcal mole^{-1} [32], the transition energy, and n = 4 for the dye (XIII) (λ_{max} 409 nm), we obtain $\bar{p}' - \bar{p}_0 = -0.119$, in good agreement with the value of -0.124 calculated by the molecular orbital method. It follows from the relationship which has been obtained that the smaller the transition energy and the larger the number of bonds, the smaller is the difference in bond order between ground and excited states. This means that, as the molecule becomes more complicated and the colour of the substance deeper, steric hindrance exerts an ever diminishing effect on the transition energy (the displacement of the absorption band expressed in frequency units decreases). But this does not mean that the shift in the absorption maximum expressed in wavelength units should be smaller, under otherwise similar conditions, in more deeply coloured substances, since the sensitivity of the wavelengths of absorption maxima to changes in transition energy increases rapidly with increase in wavelength. In fact if follows from $\lambda_{max} = \nu_{max}^{-1}$ that $d\lambda_{max} = -\lambda^2_{max} d\nu_{max}$.

The conclusion that bond orders on the average decrease on excitation indicates a tendency of steric hindrance to cause bathochromic shifts. However, deflection about a bond which approaches a single bond in character requires less energy, and occurs first if there is a choice [37]. On the same principle sterically hindered compounds have a smaller energy content and are more stable the lower the order of the bond, rotation about which destroys the conjugation. Therefore we more often meet hypsochromic shifts.

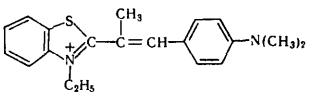
Bond orders in ground and excited states can be estimated also by other quantum-chemical methods, e.g. the valence bond method. With this method it must be borne in mind that the "percentage double-bondedness" is ambiguous owing to a certain arbitrariness in the choice of canonical structures, and bond orders must be determined by Penney's method [38]. The inconvenience associated with this last method, as well as the necessity of taking into account ionic structures for the excited state, complicate application of the valence bond method in comparison with the molecular orbital method. Nevertheless, an empirical approximation of this method, known as the theory of resonance, enables the relative orders of difference bonds in the ground state, or the ratio of the orders of the same bond in ground and excited states, to be determined simply and clearly. The conclusions of this simple method do not usually differ qualitatively from those of the molecular orbital method. Thus the general conclusion that deflection about bonds of low order should result in hypsochromic

shifts, whereas deflection about bonds of high order should result in bathochromic shifts, was first obtained by Wheland[39] on the basis of this particular method.

We can illustrate the application of resonance theory by an example[40]: the change from the styryl dye (XIX), having an unsubstituted chain, to its methyl derivative (XX) is accompanied by a diminished intensity of absorption and a marked displacement of the absorption band to shorter wavelengths:

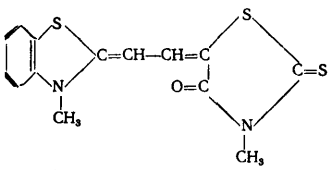


λ_{max} 528 nm, ϵ 11.0×10^4 (XIX)

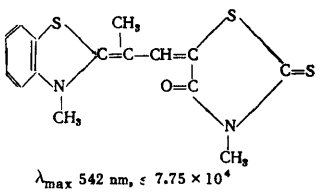


λ_{max} 481 nm, ϵ 6.2×10^4 (XX)

In the latter dye (XX) steric hindrance arises between the methyl group in the chain and the sulphur atom or the *N*-alkyl group. This interference forces the benzothiazole ring system to be deflected through a certain angle about its bond with the neighbouring carbon atom in the chain as axis, this bond being predominantly single in the ground state. On the other hand, the absorption maximum is displaced to longer wavelengths in merocyanine dyes, e.g. on passing from (XXI), whose chain is unsubstituted, to its methyl derivative (XXII):



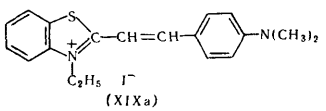
λ_{max} 521 nm, ϵ 9.13×10^4 (XXI)



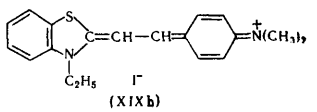
λ_{max} 542 nm, ϵ 7.75×10^4 (XXII)

In contrast to (XX), the bond about which the ring system turns in the dye (XXII) in the ground state approximates to a double bond, not a single bond.

The structure of the molecule of (XIX) in both ground and excited states is intermediate between the structures (XIXa) and XIXb)

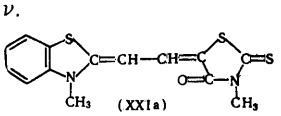


(XIXa)

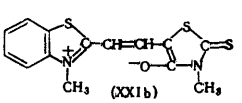


(XIXb)

the former predominating in the ground state, and the latter in the excited state. A similar situation is found in the dye (XX). Denoting by E_0 the energy of compound (XIX) in the ground state and by E_0' that of compound (XX), and by E_{ex} and E_{ex}' the energies of these compounds in the excited state, we find that E_0' differs little from E_0, since deflection about a single bond requires no great consumption of energy. But E_{ex}' exceeds E_{ex}, since deflection about a double bond requires a considerable consumption of energy. Consequently the quantum of energy absorbed by the molecule (XX) $h\nu' = E_{ex}' - E_0'$ exceeds that absorbed by the molecule (XIX) $h\nu = E_{ex} - E_0$. Hence $\nu' > \nu$.



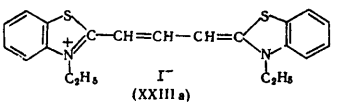
(XXIa)



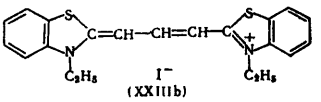
(XXIb)

In the case of merocyanines in which a non-polar structure, e.g. (XXIa), predominates in the ground state, whereas a polarised structure (e.g. XXIb), predominates in the excited state, the energy relationships between ground and excited states are the reverse of those above, and $\nu' < \nu$.

In the case of symmetrical polymethine dyes, all carbon–carbon bonds in the polymethine chain have the same length of 1.40–1.41 Å, as has been shown for the thiacarbocyanine (XXIII)[41]

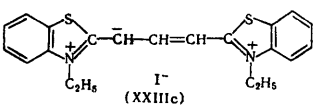


(XXIIIa)



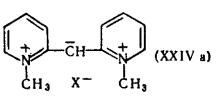
(XXIIIb)

The fact that steric hindrance in these dyes produces bathochromic shifts[42] is explained by the theory of resonance in terms of diminished interaction between the limiting structures — (XXIIIa) and (XXIIIb)[43] — resulting from the breakdown of conjugation. The same effect can be explained by a decrease in bond order in the excited state in comparison with the ground state owing to the great weight of bipolar structures of the type (XXIIIc) in the excited state[44].



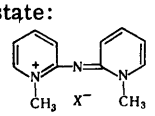
(XXIIIc)

These explanations do not contradict, but on the contrary supplement, one another. It is impossible to say in advance which of the effects should be the more important. This depends on the structure of the given dye. Contrary to Scheibe's original idea[44], it must be remembered that completely symmetrical structures, e.g. (XXIVa)

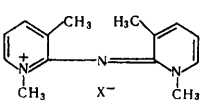


(XXIV a)

cannot be involved in an incompletely symmetrical excited state[45]. Therefore increase in the weight of such structures, as e.g. in the compounds (XXV) and (XXVI), results in a decrease in bond order not in the excited but in the ground state:



λ_{max} 388 nm, ϵ 3.04×10^4 (XXV)



λ_{max} 364 nm, ϵ 2.26×10^4 (XXVI)

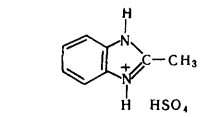
As a consequence, steric hindrance in these compounds produces hypsochromic shifts[46], instead of the bathochromic shifts which are usual for symmetrical dyes.

In the examination of experimental data, it is often difficult to assess the "pure" effect of steric hindrance, especially if it is caused by strong electron-donor or electron-acceptor substituents. In cases of this kind, steric and electronic effects are superposed, and are difficult to separate. In the investigation of steric effects, therefore, they are usually produced by introducing bulky alkyl groups, whose electronic effect is minimal[47].

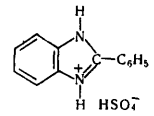
Data known to us on the effect of steric hindrance on the colour of dyes can be separated, to some extent arbitrarily, into two groups. The first group comprises cases in which steric hindrance prevents conjugation of a substituent with the main chromophore of the molecule. The second group consists of cases in which the coplanarity of parts of the chromophore itself is destroyed by steric hindrance.

The effect of steric hindrance on a substituent in a dye molecule is in general fairly simply revealed. The steric hindrance forces the substituent out of coplanarity with the chromophore, and thus diminishes or altogether eliminates

its effect on the absorption of light. An example is provided by replacing the methyl group in the 2-methylbenzimidazolium cation (XXVII) by phenyl, which produces a bathochromic effect[48]:

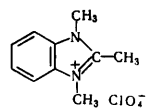


λ_{max} 275 nm, ϵ 0.096 × 10^4 (XXVII)

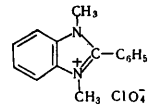


λ_{max} 300 nm, ϵ 2.76 × 10^4 (XXVIII)

This effect almost disappears if methyl groups are attached to the nitrogen atoms, for they prevent the phenyl from lying in the plane of the heterocycle:

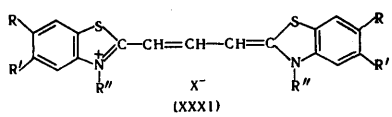


λ_{max} 277 nm, ϵ 0.84 × 10^4 (XXIX)



λ_{max} 280 nm, ϵ 1.52 × 10^4 (XXX)

Introduction of a substituent *ortho* to a dialkylamino- or a nitro-group in an aromatic ring produces a hypsochromic displacement of the absorption band owing to steric hindrance[49]. Let us examine in this connection the absorption of thiacarbocyanines of general formula



(XXXI)

which were investigated by Kiprianov and Zhmurova[50]. Comparison of dyes *4* and *1* in Table 3 shows that the introduction of two dimethylamino-groups into the thiacarbocyanine cation considerably deepens the colour and diminishes its intensity (the latter effect being associated with a broadening of the absorption band). If methyl radicals are introduced *ortho* to the dimethylamino-groups (dye *5*), some breakdown occurs in the coplanarity and conjugation of the dimethylamino-groups with the benzene rings, and their influence on the colour is somewhat weakened. In fact we see that the absorption maximum of dye *5* approaches that of dye *2*, and the intensity of absorption increases. The more bulky t-butyl groups force the dimethylamino-groups still further out of the plane of the benzene rings, and practically eliminate their effect on the colour. The narrow and intense absorption band of dye *6* almost coincides with that of dye *3*. In this case steric hindrance has a similar effect to protons binding unshared electron pairs in dimethylamino-groups (dye *7*).

Similar rules were observed by Levkoev et al.[51] on the introduction of halogen atoms *ortho* to dimethylamino--groups in thiacarbocyanines.

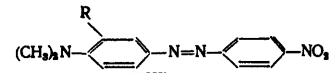
TABLE 3.

Dye No.	R	R′	R″	λ_{max}, nm	$10^{-4}\epsilon$
1	H	H	C_2H_5	558	16.5
2	CH_3	H	C_2H_5	563	14.5
3	$C(CH_3)_3$	H	CH_3	563	14.9
4	H	$N(CH_3)_2$	C_2H_5	608	8.2
5	CH_3	$N(CH_3)_2$	CH_3	575	10.1
6	$C(CH_3)_3$	$N(CH_3)_2$	CH_3	570	14.1
7	H	$\overset{+}{N}H(CH_3)_2$	C_2H_5	558	16.4

TABLE 4.

R	λ_{max}, nm	$10^{-4}\epsilon$
H	475	3.20
CH_3	438	2.20
C_2H_5	425	2.18
iso-C_3H_7	420	1.86

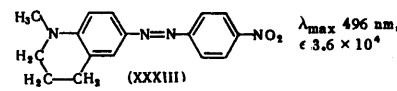
In azo dyes having the structure



(XXXII)

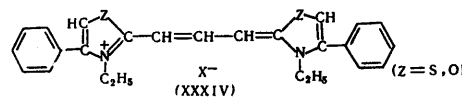
substituents R *ortho* to the dimethylamino-group diminish its auxochromic action and weaken the colour[52] (Table 4).

If the substituent forms a ring with the amino-group, fixing the latter in the plane of the benzene ring (dye XXXIII), it intensifies instead of weakening the colour:



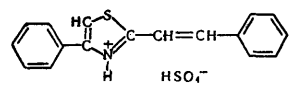
λ_{max} 496 nm, ϵ 3.6 × 10^4 (XXXIII)

Aryl radicals in the 4,4′-positions of the cations of thiazolo- and oxazolo-cyanines have little effect on the absorption of light by these dyes, whereas the same aryls in the 5,5′-positions greatly deepen the colour[53–55]. It was suggested that, as a result of steric hindrance, aryl groups in the 4,4′-positions are not coplanar with the thiazole or oxazole rings:

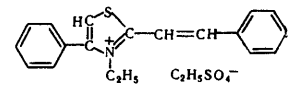


(XXXIV)

This hypothesis could be confirmed[56] by comparing the absorption curves of the sulphate (XXXV) and the ethyl sulphate (XXXVI) of 4-phenyl-2-styrylthiazoles:



λ_{max} 358 nm, ϵ 2.4 × 10^4 (XXXV)



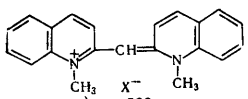
λ_{max} 355 nm, ϵ 1.82 × 10^4 (XXXVI)

Steric hindrance was practically absent in the cation of the sulphate, and the phenyl group produced a bathochromic displacement of the absorption maximum.

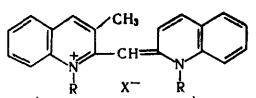
Experimental data on the effect of steric hindrance in the chromophores of dyes are far more varied. Cyanine dyes form the most convenient subject for investigations of this type. In them the length of the conjugated chain can be altered comparatively easily, as can substituents differing in bulk and electronic character be introduced into it, and hydrogen atoms substituted in the heterocyclic rings. Displacements of maxima resulting from the appearance of steric hindrance can be very conveniently observed in cyanine dyes, with their narrow and intense absorption bands.

The first systematic investigation in this field was undertaken by Scheibe[57]. He found that introduction of a methyl group into position 3 of the pseudocyanine dye (XXXVII), with the formation of (XXXVIII), produces no shift in the absorption maximum if methyl groups are

attached to the nitrogen atoms. Replacement of these methyl by ethyl groups produces a bathochromic shift:

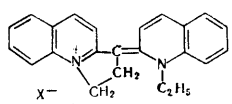


λ_{max} 522 nm
(XXXVII)

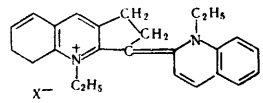


R = CH_3, λ_{max} 523 R = C_2H_5 λ_{max} 535 nm
(XXXVIII)

The substantial change in the absorption maximum on passing from methyl to ethyl groups attached to the nitrogen atoms in itself shows that steric hindrance is involved here. Passing from (XXXVII) to the dyes (XXXIX) and (XL) will give an increase in steric hindrance and a sharp increase in the bathochromic shift:

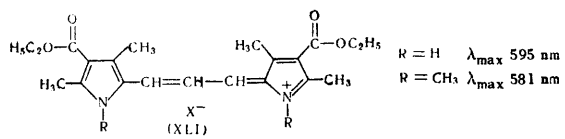


λ_{max} 575 nm
(XXXIX)



λ_{max} 583 nm
(XL)

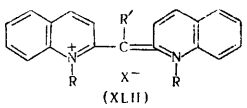
Brooker et al.[43] showed that the previously mentioned Brunings–Corwin effect was associated with a loss of coplanarity, not with the electronic character of the methyl group. In the vinylogue (XLI) of dipyrrylmethane, replacement by methyl groups of the hydrogen atoms attached to the nitrogen atoms produces merely a slight hypsochromic shift, since the coplanarity of the molecule is not thereby disturbed:



(XLI)

R = H λ_{max} 595 nm
R = CH_3 λ_{max} 581 nm

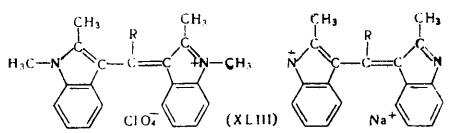
Brooker found an effect, similar to that described for dyes (XXXVII) and (XXXVIII), on introducing an alkyl radical into the methine group of pseudocyanines:



(XLII)

R	R′	λ_{max} nm
CH_3	H	520
CH_3	CH_3	574.5
C_2H_5	H	522.5
C_2H_5	C_2H_5	584

Similar facts had been observed even before Brooker's work. They had either remained unnoticed, as occurred, for example, with the indocyanines

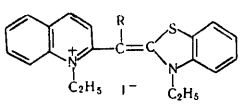


(XLIII)

R = H λ_{max} 482 nm
R = C_6H_5 λ_{max} 518 nm

R = H λ_{max} 482 nm
R = C_6H_5 λ_{max} 526 nm

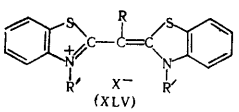
synthesised by König[58] in 1925, or were puzzling. Thus Götze[59] in 1936 was the first to prepare *meso*-methylthia--2-quinocyanine (XLIV, R = CH_3), but he thought that he was dealing with a more complicated substance, since its violet colour differed sharply from the orange colour of the unsubstituted dye‡:



R = H λ_{max} 486 nm; R = CH_3 λ_{max} 545 nm[60]
(XLIV)

Bathochromic shifts accompanying the introduction of bulky alkyl substituents into the methine groups of monomethinecyanines were observed by Kiprianov and Ushenko[42] and by Fry and Kendall[62] in thiacyanines, by Jeffreys and Knott[63] in pyrrolocyanines, and by Hamer[60] in unsymmetrical cyanines.

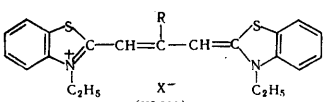
Kiprianov et al.[64] showed that this effect is actually associated with steric hindrance. Studying the monomethinecyanines (XLV), they found that replacement of the methine hydrogen atom by a methyl group produces no steric hindrance if hydrogen atoms are attached to the nitrogen atoms. Such replacement results in a loss of coplanarity and a bathochromic shift only when alkyl groups are attached to the nitrogen atoms:



(XLV)

R	R′	λ_{max} nm
H	H	425
CH_3	H	425
H	CH_3	425
CH_3	CH_3	465

A *meso*-methyl group does not give rise to steric hindrance in the thiacarbocyanines (XLVI, R = CH_3)[4]. The slight hypsochromic shift without appreciable decrease in intensity is explained by its electronic effect[65]. In the dye (XLVI, R = C_6H_5) the phenyl group, because of steric hindrance, lies in a plane perpendicular to the rest of the molecule. Conjugation of the phenyl group with the chromophore of the dye disappears, and the group has no significant effect on the colour[66]:



(XLVI)

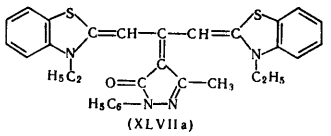
R = H λ_{max} 558 nm, R = CH_3 λ_{max} 543 nm,[67] R = C_6H_5 λ_{max} 560 nm

Even the introduction of polar substituents — $N(CH_3)_2$, OH, O^- — into the *para* position of this phenyl group does not significantly affect the absorption maximum[68].

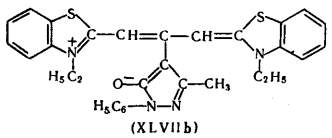
Brooker observed an interesting phenomenon, which he termed allopolar isomerism[69], in some trinuclear dyes. The dye (XLVII) can be represented by three limiting structures, a non-polar form (XLVIIa) and two bipolar

‡ The non-planar structure of this dye was confirmed in 1960 by X-ray examination, the angle between the planes of the quinoline and the benzothiazole rings being 60°.[61]

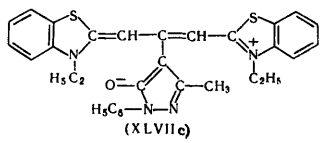
structures — (XLVIIb) and (XLVIIc) — having the same energy:



(XLVIIa)



(XLVIIb)

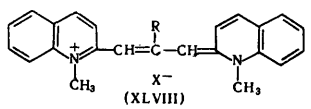


(XLVIIc)

As can be seen from Fig. 3, it is not possible for all three ring systems in the dye (XLVII) to lie in the same plane: at least one of them must be perpendicular to the other two.

In a polar solvent (methanol) this dye gives an absorption curve (Fig. 4*B*) which is typical of thiacarbocyanines. Hence the molecule is polarised in methanolic solution, the two benzothiazole systems lying in one plane, while the pyrazolone ring, with a negative charge on the carbonyl oxygen atom, is deflected from this plane as a result of rotation about the single bond, as in structures (XLVIIb) and (XLVIIc) (Fig. 3*B*). In a non-polar solvent (lutidine) the absorption curve (Fig. 4*C*) is quite different in shape, resembling that of a merocyanine based on a benzothiazole and a pyrazolone ring. It is obvious that in lutidine solution the benzothiazole and pyrazolone systems lie in the same plane, while the second benzothiazole ring system is deflected out of this plane — structures (XLVIIa) and (XLVIIb) (Fig. 3*C*).

Introduction of a methyl group into the *meso* position of the 2,2′-carbocyanine (XLVIII) now causes steric hindrance[70], which is eliminated by deflection of the quinoline rings about the bonds of the polymethine chain. The consequence is a bathochromic shift:



(XLVIII)

R = H λ_{max} 607 nm,[71]
R = CH_3 λ_{max} 649 nm,[7]
R = C_6H_5 λ_{max} 648 nm,[71]

In the dye (XLVIII) with R = C_6H_5 the phenyl group lies in a plane perpendicular to that of the chromophore, but even in this position it, like the methyl group, causes steric hindrance.

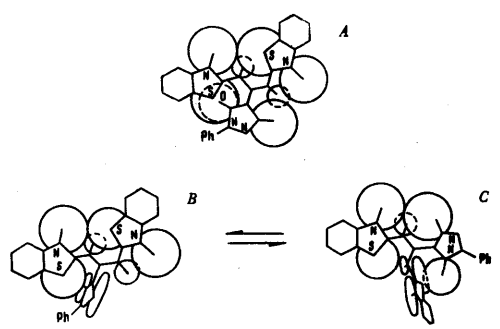


Fig. 3.

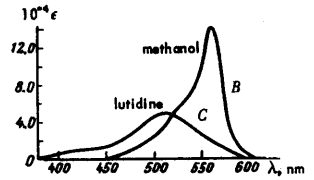
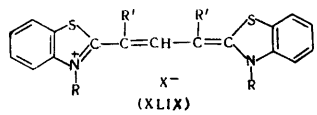


Fig. 4.

Kiprianov and his coworkers have shown that alkyl or aryl groups in the $\alpha\gamma$ positions of the polymethine chain of thiacarbocyanines (XLIX) cause steric hindrance[42,72]:

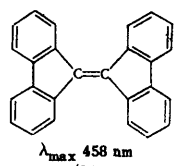


(XLIX)

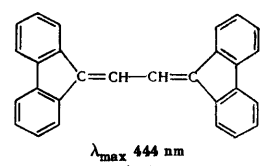
R	R′	λ_{max} nm
CH_3	H	559
CH_3	CH_3	577
CH_3	C_2H_5	571
CH_3	iso-C_3H_7	576
CH_3	C_6H_5	580
C_6H_5	H	565
C_6H_5	CH_3	602

Deflection of the benzothiazole ring systems about the bonds of the polymethine chain results in a bathochromic shift, which is especially marked if phenyl radicals are attached to the nitrogen atoms.

An interesting case occurs when steric hindrance present in a lower vinylogue because of the large volume of the ring systems of the dye disappears when the polymethine chain is lengthened. For example, 9,9′-bifluorenylidene (L) is more deeply coloured than is its vinylogue (LI)[73]. In the non-coplanar dye (L) the ring systems have been deflected about a bond which approximates to a double bond. This has led to a bathochromic shift in the absorption maximum exceeding the vinylene shift in the maximum on passing from (L) to (LI).

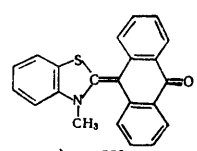


λ_{max} 458 nm
(L)

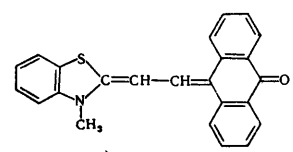


λ_{max} 444 nm
(LI)

A similar phenomenon is observed in the quinone methides (LII) and (LIII)[74].

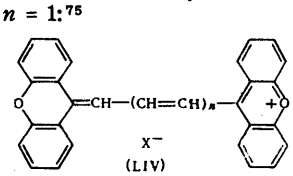


λ_{max} 551 nm
(LII)



λ_{max} 537 nm
(LIII)

In xanthocyanine (LIV, n = 0) the bathochromic shift due to breakdown of coplanarity is detected from the decrease in the vinylene shift on passing from n = 0 to n = 1:[75]

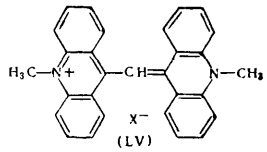


(LIV)

		$\Delta\lambda_{max}$
n = 0	λ_{max} 648 nm	
		57 nm
n = 1	λ_{max} 705 nm	
		80 nm
n = 2	λ_{max} 785 nm	
		80 nm
n = 3	λ_{max} 865 nm	

The considerable breakdown in coplanarity in acridinomethinecyanine (LV) is detected from the very low extinction

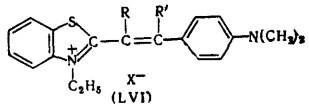
of this dye and the wide absorption band without any distinct maximum[43]:



(LV)

In dyes having a high degree of electronic asymmetry the effect of steric hindrance will depend on the order of the bond about which the ring systems of the dye have been deflected.

In styryls (LVI) with substituents in the β or α position, deflection of the benzothiazole and benzene ring systems occurs about bonds of diminished order, resulting in a hypsochromic shift[76]:

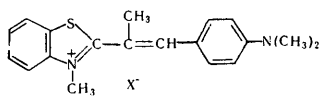


(LVI)

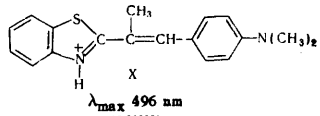
R=H R′=H λ_{max} 530 nm
R=CH_3 R′=H λ_{max} 481 nm
R=H R′=CH_3 λ_{max} 518 nm

Similar results were obtained by Brooker[43] and by Hamer[60].

The presence of steric hindrance in the styryl dye (LVII) has been confirmed by Kiprianov and Tolmachev, who showed that its analogue (LVIII), in which steric hindrance should not be present, absorbs at considerably longer wavelengths[77]:

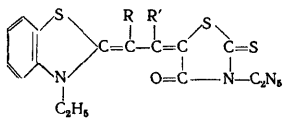


λ_{max} 478 nm
(LVII)



λ_{max} 496 nm
(LVIII)

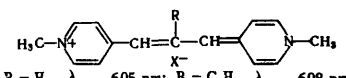
The bonds between the heterocyclic systems and the neighbouring methine groups in merocyanines (LIX) are of high order, and deflection of the rings about these bonds results in bathochromic shifts[78]:



(LIX)

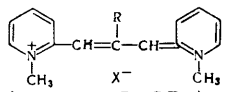
R	R′	λ_{max} nm
H	H	524
CH_3	H	540
C_6H_5	H	536
H	CH_3	532
H	C_6H_5	542

Kiprianov and Dyadusha[15] made a spectroscopic study of steric hindrance in symmetrical and unsymmetrical *meso*-phenylcarbocyanines. They showed that in the 4,4′-pyridocarbocyanines (LX) a *meso*-phenyl group produces no change in the absorption maximum, as in the case of the thiacarbocyanines discussed earlier:



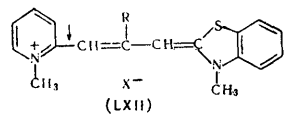
R = H λ_{max} 605 nm; R = C_6H_5 λ_{max} 608 nm
(LX)

A phenyl group in the same position in 2,2′-pyridocarbocyanines (LXI) results in appreciable steric hindrance, as in the dye (XLVIII, R = C_6H_5). Deflection of the rings about bonds in the polymethine chain produces a bathochromic shift:



R = H λ_{max} 559 nm; R = C_6H_5 λ_{max} 606 nm
(LXI)

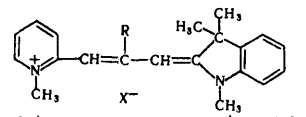
In unsymmetrical dyes (LXII) bonds of higher and lower order alternate in the chain. The degree of non-equivalence of the bonds is measured by the deviation[79,80] (the displacement, towards shorter wavelengths, of the absorption maximum of the unsymmetrical dye from the arithmetic mean of the absorption maxima of the corresponding symmetrical dyes):



(LXII)

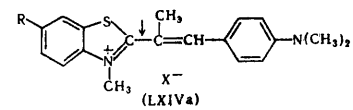
R=H λ_{max} 536 nm deviation 22.5 nm
R=C_6H_5 λ_{max} 544 nm deviation 39 nm

In the dye (LXII) with R = C_6H_5 steric hindrance between the pyridine ring and the phenyl group is removed by rotation about a bond (shown by the arrow in the formula) of rather diminished order. This results in a smaller bathochromic shift on passing from the dye (LXII) with R = H to the corresponding dye with R = C_6H_5 compared with the similar bathochromic shift in the dye (LXI). Deflection of the pyridine ring about a bond of diminished order results in a still greater decrease in the order of this bond, and hence in an increase in the deviation. With a sufficiently large difference in basic character between the ring systems, as e.g. in the dye (LXIII), the bathochromic shift is replaced by a hypsochromic shift:

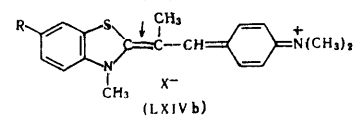


R = H λ_{max} 509 nm; R = C_6H_5 λ_{max} 460 nm
(LXIII)

Kiprianov and Mikhailenko have investigated, on polymethine dyes of several types, how displacement of the absorption maximum changes with variation in the order of the bond about which the ring systems of the dye are deflected. In styryl dyes (LXIV)[40] the first of the two limiting structures



(LXIVa)



(LXIVb)

predominates in the ground state, and deflection of the benzothiazole ring system caused by interference with the methyl group takes place about a bond which approaches a single bond in character. The consequence of this is a hypsochromic shift in the absorption maximum on passing from the dye with an unsubstituted chain to its methyl derivative. However, the order of this bond — marked by an arrow in formula (LXIVa) — can be to some extent varied by introducing various polar substituents into the benzothiazole system. The electron-donor dimethylamino-group, where R = $N(CH_3)_2$, by increasing the basic strength of the benzothiazole moiety still further stabilises structure (LXIVa), lowers the order of the bond shown by the arrow, and increases the hypsochromic displacement of the maximum to 80 nm. The electron-acceptor nitro-group (R = NO_2) will give the opposite effect (hypsochromic shift decreases to 50 nm) (Table 5).

In the unsymmetrical carbocyanine (LXV) having an unsubstituted chain (R = R′ = H) the cationic charge is located predominantly on the more basic ring system (with the dimethylamino-group in position 6), and the bond *a* is

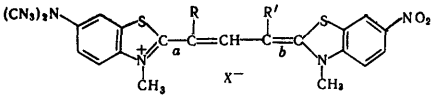
TABLE 5.

R	$\Delta\lambda_{max}(H \rightarrow CH_3)$, nm
$N(CH_3)_2$	80
H	61
NO_2	50

TABLE 6.

Solvent	$\Delta\lambda_{max}(H \rightarrow CH_3)$, nm	Solvent	$\Delta\lambda_{max}(H \rightarrow CH_3)$, nm
Water	—65	Acetone	+ 4
Methanol	—57	Chloroform	+12

closer to a single bond, while bond *b* is closer to a double bond (deviation 15 nm)[81]:

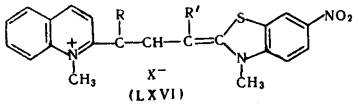


R=H R′=H λ_{max} 586 nm, deviation 15 nm,
R=CH_3 R′=H λ_{max} 556 nm, deviation 44.5 nm,
R=H R′=CH_3 λ_{max} 601 nm, deviation 7 nm.

(LXV)

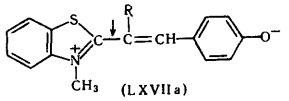
Replacement by methyl of the methine hydrogen adjacent to the bond *a* — dye (**LXV**) with R = CH_3 and R′ = H — shifts the absorption maximum to shorter wavelengths, whereas similar substitution in the methine group adjacent to bond *b* (R = H and R′ = CH_3) displaces the absorption maximum to longer wavelengths, compared with the dye having an unsubstituted chain, although the steric hindrance is the same in the two dyes. In dye (**LXV**) with R = CH_3 and R′ = H, as also in dye (**LXII**) with R = C_6H_5, deflection of the left-hand benzothiazole system about a bond of lower order increases the deviation to 44.5 nm. Deflection of the right-hand ring system about bond *b* in dye (**LXV**) with R = H and R′ = CH_3 lowers the order of this bond. The electronic asymmetry of the dye is diminished, as is evident from the decrease in the deviation to 7 nm.

Similar phenomena are observed in unsymmetrical carbocyanines (**LXVI**) made up of quinoline ring system (the more basic) and a 6-nitrobenzothiazole system (the less basic).

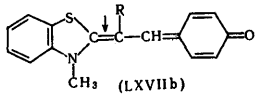


(LXVI)

In the zwitterionic anhydro-bases of the *p*-hydroxystyrenes



(LXVIIa)



(LXVIIb)

the order of individual bonds in the conjugated chain can be varied as desired by dissolving the dye in solvents of different polarities. This is the explanation of the solvatochromism of zwitterionic dyes[82]. The bond marked by the arrow in formulae (**LXVIIa**) and (**LXVIIb**) is closer to a single bond in polar solvents, and closer to a double bond in non-polar solvents. In conformity with this, substitution of methyl for hydrogen as the radical R in the dye (**LXVII**) will give different displacements of the absorption maximum depending on the solvent, as can be seen from Table 6.[74]

If the zwitterionic dyes — (**LXVII**), R = H and R = = CH_3 — are dissolved not in pure solvents but in mixtures of the weakly polar pyridine and the strongly polar water, smooth curves are obtained showing how the displacement (H → CH_3) in the absorption maximum varies

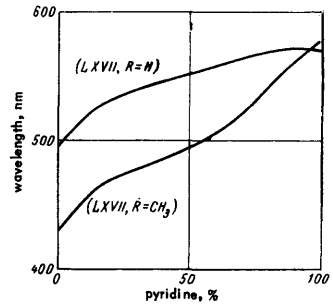
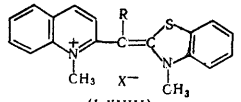


Fig. 5.

with the percentage of pyridine in the water. It is seen from Fig. 5 that, as the pyridine content increases (the polarity decreases), the colour of the anhydro-bases deepens, the order of the bond marked by an arrow increases, and the curve of the dye with R = CH_3 approaches the curve for the anhydro-base having an unsubstituted chain (the hypsochromic shift decreases). With a mixture containing 90% of pyridine, the bonds in the chromophore of the anhydro-base level out (the colour being the deepest), and in this region the hypsochromic shift changes to a bathochromic shift.

Bulky polar substituents may have two effects — steric and electronic — and it is often difficult to determine the proportion of each. The introduction of phenyl and *p*-nitrophenyl radicals into the methine group of a monomethinecyanine (**LXVIII**, R = H) causes a bathochromic shift. These radicals undoubtedly lie in a plane perpendicular to that of the heterocyclic ring systems, and the observed bathochromic shifts are due, as in the case of the methyl group, solely to steric effects[60]:

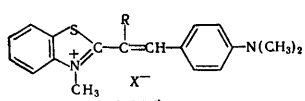


(LXVIII)

R	λ_{max} nm
H	486
CH_3	545
C_6H_5	552
$p\text{-}C_6H_4NO_2$	548
$COOC_2H_5$	474

When, however, the hydrogen atom is substituted by an ethoxycarbonyl group, a hypsochromic instead of a bathochromic shift is observed, owing to the predominating electronic effect of the ethoxycarbonyl group. It is known that negative substituents in the α position of a chain should give a hypsochromic displacement of the absorption band[83,84].

In the styryls (**LXIX**), the two effects act in the same direction, which explains the comparatively large hypsochromic shift when R = $COOC_2H_5$:

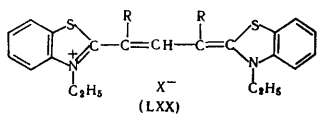


(LXIX)

R=H λ_{max} 525 nm
R=CH_3 λ_{max} 460 nm
R=$COOC_2H_5$ λ_{max} 418 nm

The effect of polar substituents in the *meso* position of thiacarbocyanines is determined solely by the electronic effect: electron-donor substituents produce a hypsochromic shift[85], whereas electron-acceptor substituents produce a bathochromic shift[86,87].

Alkoxy- and aroxy-groups in the $\alpha\gamma$ positions of the thiacarbocyanine (LXX) cause a bathochromic shift[72,88,89], the magnitude of which is little affected by the nature of the aryl:

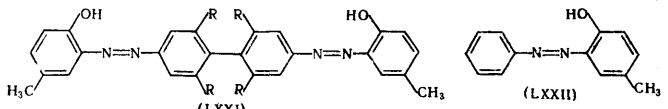


(LXX)

R	λ_{max} nm
H	558
OCH_3	586
OC_6H_5	589
p-OC_6H_4Cl	585
p-$OC_6H_4OCH_3$	590
OH	565

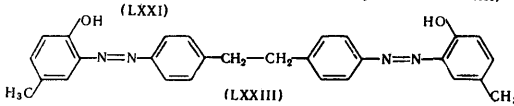
The slight decrease in intensity compared with the dye having an unsubstituted chain and the fact that the dye with R = C_6H_5 is a good sensitiser[4] indicate that the electronic effect predominates in this case.

The effect of steric hindrance on the colour of dyes of other classes has been far less studied than in the case of polymethine dyes.



(LXXI)

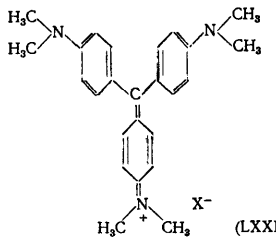
(LXXII)



(LXXIII)

Brode and his coworkers[90,91] studied the effect of steric hindrance in bisazo dyes which are derivatives of biphenyl. They found that the absorption curve of the dye (LXXI) with R = CH_3 resembles that of the dyes (LXXII) and (LXXIII): i.e. there is no conjugation between the biphenyl rings in the first of these three dyes. Similar results have been reported in a series of papers by Krasovitskii[92].

Di- and tri-arylmethane dyes having a symmetrical distribution of the electron cloud resemble symmetrical polymethine dyes. In Crystal Violet



(LXXIV)

only the nitrogen and the central carbon atom lie in the same plane, owing to steric interference (of the *ortho*--hydrogen atoms). The benzene rings have been turned relative to one another in such a way that the structure of the dye resembles a three-bladed propeller. Calculation shows that each benzene ring should turn through 18°.[93]

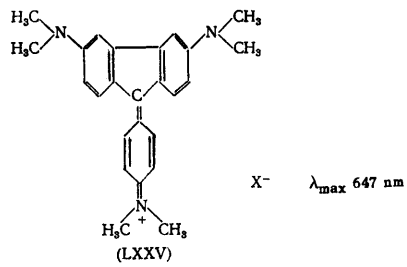
The introduction of methyl groups *ortho* to the central carbon atom results in further deflection of the rings about bonds of enhanced order, which leads to an increase in the bathochromic shift (Table 7)[94]. The uniform displacement of the absorption maximum with increasing number of *o*-methyl groups suggests that all three rings have been deflected to the same extent (in the 2,2',2"-trimethyl derivative the angle of deflection should be about 34°). But the 2,6-dimethyl derivative gives a larger shift per methyl group. It is possible that in this case the xylidine

TABLE 7.

Methylated Crystal Violets	λ_{max}, nm	Methylated Crystal Violets	λ_{max}, nm
Crystal Violet (LXXIV)	589	2,2',2"-Trimethyl	614
2-Methyl	597	2,6-Dimethyl	614.5
2,2'-Dimethyl	605		

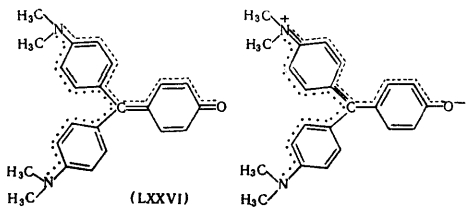
ring has been greatly rotated, and the charge is concentrated on the two dimethylaniline rings, as in Malachite Green. Similar results have been obtained for Michler's Hydrol Blue.

Barker[95] fixed two rings of Crystal Violet in a plane by means of an additional valency bond, but obtained an unexpected result: the dye (LXXV) proved to be more deeply coloured than Crystal Violet. This result was subsequently explained by formation of the new C–C bond and the greater possibility of conjugation of the rings[96,97].



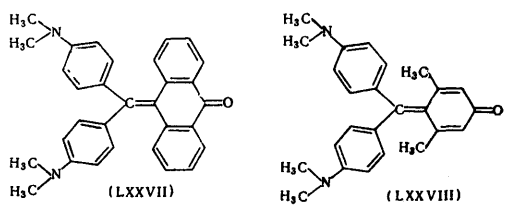
(LXXV)

A phenomenon analogous to Brooker's allopolar isomerism was observed by Hünig[98] in sterically hindered triphenylmethane dyes. Of the two possible systems of conjugation in tetramethyldiaminofuchsone (LXXVI) — the dimethylaminofuchsone system (broken line in the formula) and the Malachite Green system (dotted line in the formula) — only the former is developed. The dye has one absorption maximum, which migrates with change in the polarity of the solvent:



(LXXVI)

In the dyes (LXXVII) and (LXXVIII), which exhibit great steric hindrance, the quinone ring is turned relative to the rest of the molecule, and partly emerges from conjugation:

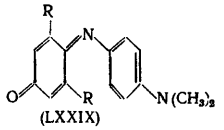


(LXXVII) (LXXVIII)

The spectra of these dyes now reveal two systems of conjugation (the dyes each have two absorption maxima, one of which migrates with change in the polarity of the medium). When acid is added to solutions of the dyes, only the absorption maximum remains which does not vary with

change in the solvent, and this undoubtedly belongs to the conjugation system of Malachite Green.

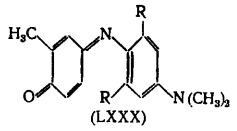
In the indaniline dye (LXXIX, R = H) the C⋱N⋰C angle is less than 180°, and a value of 120° has been assumed[99] by analogy with *cis*-azobenzene:



(LXXIX)

R = H λ_{max} 634 nm
R = CH_3 λ_{max} 653 nm

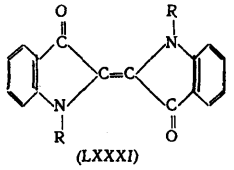
Steric hindrance in the dye (LXXIX, R = CH_3) between one of the *o*-methyl groups and the dimethylaniline ring is eliminated only by turning the quinone ring about the double bond, which causes a bathochromic shift. Rotation of the dimethylaniline ring about the single bond does not eliminate steric hindrance, which remains between one of the methyl groups and the plane of the benzene ring of the dimethylaniline[100]. In the dye (LXXX, R = CH_3), on the other hand, the dimethylaniline ring turns about a bond which is close to a single bond, with a hypsochromic shift as a consequence[101]:



(LXXX)

R = H λ_{max} 630 nm
R = CH_3 λ_{max} 610 nm

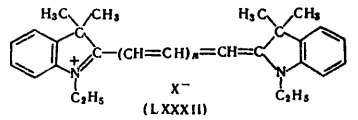
Although the order of the central bond in indigo (0.628)[102] is less than that of an aromatic bond (0.667), it should decrease on excitation, as has been shown by Dyadyusha[36]. This explains the bathochromic shift on passing from indigo (LXXXI, R = H) to dimethylindigo (LXXXI, R = CH_3), in which Weinstein and Wyman assume the presence of steric hindrance[103]:



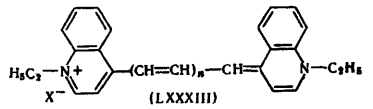
(LXXXI)

R = H λ_{max} 591 nm
R = CH_3 λ_{max} 644.5 nm

Hofer et al.[12] showed that steric hindrance inhibits the fluorescence of cyanine dyes. Indocyanines (LXXXII) and 4-quinocyanines (LXXXIII) fluoresce only when $n = 2$ or above. This observation was confirmed by Kiprianov and Ushenko[104], who also observed that sterically hindered dyes show practically no fluorescence.

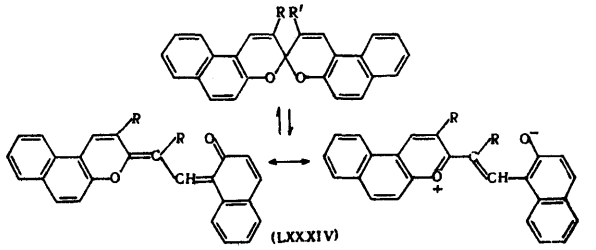


(LXXXII)



(LXXXIII)

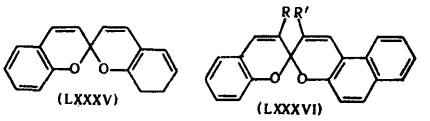
Finally, the effect of steric hindrance on the thermochromism of spiropyrans (LXXXIV), which has been studied by Koelsch[105], must be noted. The thermochromism of colourless spiropyrans (LXXXIV, R = H) is due to their conversion with ring-opening into a coloured form:



(LXXXIV)

In the spiropyran (LXXXIV) with R = CH_3, the form with opened rings exhibits greater steric hindrance than the spiro-form, in which the rings are mutually perpendicular: therefore ring-opening does not occur, and thermochromism is not observed.

Dibenzospiropyran (LXXXV) is non-thermochromic, since conversion into the form with open rings involves the formation of an unstable *o*-benzoquinone ring. Benzonaphthospiropyran (LXXXVI, R = R′ = H) exhibits thermochromism, probably with the formation of a naphthaquinone ring.



(LXXXV) (LXXXVI)

In this connection, the difference between the spiropyrans (LXXXVI, R = CH_3 and R′ = H) and (LXXXVI, R = H and R′ = CH_3) is interesting. The former is thermochromic, since formation of the modification with open rings occurs without strain. The latter compound does not exhibit thermochromism, since formation of the modification with open rings involves steric hindrance.

1. E.Schirm, J.prakt.Chem., [2], 144, 69 (1935).
2. B.M.Krasovitskii, Doctoral Thesis, Kharkov University, 1960.
3. K.Venkataraman, "The Chemistry of Synthetic Dyes" (Translated into Russian), Vol. 2, Goskhimizdat, 1957, p. 1462.
4. L.G.S.Brooker, F.L.White, D.W.Heseltine, G.H.Keyes, S.G.Dent, and E.I.van Lare, J.Phot.Sci., 1, 173 (1953).
5. A.Burawoy, J.Chem.Soc., 1177 (1939).
6. M.Pestemer, in Houben–Weil's, "Methoden der organischen Chemie", Stuttgart, 1955, Vol. 3, Part 2, p.618.
7. E.Hückel, Z.Elektrochem., 43, 752, 857 (1937).
8. L.Pauling and J.Sherman, J.Chem.Phys., 1, 679 (1933).
9. A.I.Kitaigorodskii, "Organicheskaya Kristallokhimiya" (Organic Crystal Chemistry), Izd.Akad.Nauk SSSR, 1958, p.17.
10. L.Pauling, "The Nature of the Chemical Bond", p. 245.
11. M.Magat, Z.phys.Chem., B 16, 1 (1932).
12. L.J.E.Hofer, R.J.Grabenstetter, and E.O.Wiig, J.Amer. Chem.Soc., 72, 207 (1950).
13. H.Staab, "Einführung in die theoretische organische Chemie", Weinheim, 1959, pp.531, 193, 197.
14. G.W.Wheland, "Resonance in Organic Chemistry", New York, 1955, p.165.
15. A.I.Kiprianov and G.G.Dyadyusha, Zhur.Obshch.Khim., 30, 3655 (1960).
16. G.Briegleb, see Ref. 6, Vol. 3, Part 1, p. 549.
17. C.A.Coulson and S.Senent, J.Chem.Soc., 1813 (1955).
18. H.Staab, see Ref. 13, p.270.

19. R.S.Mulliken, J.Amer.Chem.Soc., 72, 4493 (1950).
20. I.Guy, J.Chim.phys., 46, 469 (1949).
21. L.Pauling and R.B.Corey, J.Amer.Chem.Soc., 74, 3964 (1952).
22. M.J.S.Dewar, J.Amer.Chem.Soc., 74, 3341 (1952).
23. H.Suzuki, Bull.Chem.Soc., Japan, 25, 146 (1952).
24. W.Remington, J.Amer.Chem.Soc., 67, 1838 (1945).
25. K.J.Brunings and A.H.Corwin, J.Amer.Chem.Soc., 64, 593 (1942).
26. W.Theilacker and W.Ozegowsky, Ber., 73, 901 (1940).
27. C.A.Coulson and H.C.Longuet-Higgins, Proc.Roy.Soc., A191, 39 (1947).
28. E.Heilbronner and R.Gerdil, Helv.Chim.Acta, 39, 1996 (1956).
29. H.Staab, see Ref. 13, p.196.
30. T.Anno, J.Chem.Phys., 28, 944 (1958).
31. C.K.Ingold and G.W.King, J.Chem.Soc., 2744 (1953).
32. M.J.S.Dewar, J.Chem.Soc., 2330 (1950).
33. W.T.Grub and G.B.Kistiakowsky, J.Amer.Chem.Soc., 72, 419 (1950).
34. H.H.Jaffe and M.Orchin, J.Chem.Soc., 1078 (1960).
35. T.K.Rebane, Zhur.Fiz.Khim., 35, 1681 (1961) [Russ.J. Phys.Chem., 827 (1961)].
36. G.G.Dyadyusha, Ukrain.Khim.Zhur., 30, 930 (1964).
37. M.J.S.Dewar, "Steric Effects in Conjugated Systems" (Edited by G.W.Gray), Butterworth, London, 1958, p.46.
38. G.W.Penney, Proc.Roy.Soc., A169, 413 (1939).
39. G.W.Wheland, see Ref. 14, p.314.
40. A.I.Kiprianov and F.A.Mikhailenko, Zhur.Obshch.Khim., 31, 781 (1961).
41. P.J.Wheatley, J.Chem.Soc., 4100 (1959).
42. A.I.Kiprianov and I.K.Ushenko, Zhur.Obshch.Khim., 20, 134 (1950).
43. L.G.S.Brooker, F.L.White, R.H.Sprague, S.G.Dent, and G.van Zandt, Chem.Rev., 41, 325 (1947).
44. G.Scheibe and D.Brück, Z.Elektrochem., 54, 403 (1950).
45. W.E.Moffit, Proc.Phys.Soc., 63, 700 (1950).
46. G.G.Dyadyusha, T.M.Verbovskaya, and A.I.Kiprianov, Ukrain.Khim.Zhur., 32, 357 (1966).
47. M.S.Newman (Editor), "Steric Effects in Organic Chemistry" (Translated into Russian), Inostr.Lit., Moscow, 1960, p.573.
48. A.I.Kiprianov and V.A.Shrubovich, Zhur.Obshch.Khim., 29, 1290 (1959).
49. A.I.Kiprianov and I.N.Zhmurova, Uspekhi Khim., 22, 1246 (1953).
50. A.I.Kiprianov and I.N.Zhmurova, Zhur.Obshch.Khim., 23, 493 (1953).
51. I.I.Levkoev, N.N.Sveshnikov, and N.S.Barvyn', Dokl.Akad. Nauk SSSR, 85, 805 (1952).
52. A.I.Kiprianov and I.N.Zhmurova, Zhur.Obshch.Khim., 23, 626 (1953).
53. E.B.Knott, J.Chem.Soc., 4099 (1952).
54. R.A.Jeffreys, J.Chem.Soc., 4825 (1952).
55. E.D.Sych, Ukrain.Khim.Zhur., 22, 80 (1956).
56. A.I.Kiprianov and E.D.Sych, Zhur.Obshch.Khim., 31, 3927 (1961).
57. G.Scheibe, Z.Elektrochem, 47, 73 (1941).
58. W.König, Z.angew.Chem., 38, 743, 868 (1925).
59. I.Götze, Z.angew.Chem., 49, 563 (1936).
60. F.M.Hamer, J.Chem.Soc., 1480 (1956).
61. J.Effinger, G.Germain, J.Meunier, J.Vanderauwera, and G.van Meersche, Bull.Soc.chim.belges, 69, 387 (1960).
62. D.I.Fry and J.D.Kendall, J.Chem.Soc., 503 (1954).
63. R.A.Jeffreys and E.B.Knott, J.Chem.Soc., 1028 (1951).
64. A.I.Kiprianov, Yu.S.Rozum, and L.P.Yakovleva, Zhur. Obshch.Khim., 22, 302 (1952).
65. H.C.Barany and M.Pianka, J.Chem.Soc., 2217 (1953).
66. A.van Dormael, Ind.chim.belge, 15, 146 (1950).
67. L.G.S.Brooker and F.L.White, J.Amer.Chem.Soc., 57, 2482 (1935).
68. I.K.Ushenko, Zhur.Obshch.Khim., 29, 3364 (1959).
69. L.G.S.Brooker, Experientia, Suppl.II, 254 (1955).
70. L.G.S.Brooker and P.W.Vittum, J.Phot.Sci., 7, 76 (1957).
71. A.I.Kiprianov and G.G.Dyadyusha, Dokl.Akad.Nauk Ukrain. SSR, 1122 (1959).
72. A.I.Kiprianov and M.G.Suleimanova, Ukrain.Khim.Zhur., 31, 1281 (1965).
73. E.D.Bergmann and J.Hirschberg, Bull.Soc.chim.France, [5], 17, 1096 (1950).
74. A.I.Kiprianov and F.A.Mikhailenko, Zhur.Obshch.Khim., 31, 1334 (1961).
75. R.Wizinger and P.Arni, Chem.Ber., 92, 2309 (1959).
76. A.I.Kiprianov and I.K.Ushenko, Zhur.Obshch.Khim., 20, 514 (1950).
77. A.I.Kiprianov and A.I.Tolmachev, Ukrain.Khim.Zhur., 25, 340 (1959).
78. M.V.Deichmeister, Z.P.Sytnik, I.I.Levkoev, and E.B.Lifshits, Zhur.Obshch.Khim., 24, 900 (1954).
79. A.I.Kiprianov and G.T.Pilyugin, Uch.Zap.Khar'kovsk.Gos. Univ., 10, 91 (1937).
80. L.G.S.Brooker, Rev.Mod.Phys., 14, 275 (1942).
81. A.I.Kiprianov and F.A.Mikhailenko, Zhur.Obshch.Khim., 31, 786 (1961).
82. A.I.Kiprianov, Uspekhi Khim., 29, 1336 (1960) [Russ.Chem. Rev., 618 (1960)].
83. E.B.Knott, J.Chem.Soc., 1024 (1951).
84. M.J.S.Dewar, J.Amer.Chem.Soc., 74, 3350 (1951).
85. N.N.Sveshnikov, I.I.Levkoev, B.S.Portnaya, and E.B.Lifshits, Dokl.Akad.Nauk SSSR, 84, 733 (1952).
86. P.Bruylants and A.van Dormael, Rec.Trav.chim., 69, 321 (1950).
87. K.Meyer, German P. 725 825; Chem.Zentr., I, 242 (1943).
88. A.I.Kiprianov, Zh.M.Ivanova, and S.G.Fridman, Ukrain. Khim.Zhur., 20, 641 (1954).
89. V.M.Zubarovskii, Zhur.Obshch.Khim., 21, 2063 (1951).
90. R.J.Morris and W.R.Brode, J.Amer.Chem.Soc., 70, 2485 (1948).
91. W.R.Brode, "The Roger Adams Symposium, University of Illinois, 1954", Wiley, New York, 1955, p.21.
92. B.M.Krasovitskii, Ukrain.Khim.Zhur., 20, 646 (1954); 22, 72 (1956); 23, 497 (1957); Dokl.Akad.Nauk SSSR, 108, 93 (1956).
93. W.Theilacker and W.Berger, Chem.Ber., 89, 965 (1956).
94. C.C.Barker, M.H.Bride, and A.Stamp, J.Chem.Soc., 3957 (1959).
95. A.Barker and C.C.Barker, J.Chem.Soc., 1308 (1954).
96. D.A.Brown and M.J.S.Dewar, J.Chem.Soc., 2134 (1954).
97. G.G.Dyadyusha, Ukrain.Khim.Zhur., 30, 1186 (1964).
98. S.Hünig, H.Schweeberg, and H.Schwarz, Annalen, 587, 132 (1954); 599, 131 (1956).
99. G.Brown, B.Graham, P.W.Vittum, and A.Weissberger, J.Amer.Chem.Soc., 73, 919 (1951).
100. P.W.Vittum and G.Brown, J.Amer.Chem.Soc., 69, 152 (1947).
101. S.Hünig and P.Richters, Annalen, 612, 283 (1958).
102. M.Klessinger and W.Lüttke, Tetrahedron, 19, Suppl.II, 327 (1963).
103. I.Weinstein and G.M.Wyman, J.Amer.Chem.Soc., 78, 4007 (1956).
104. A.I.Kiprianov and I.K.Ushenko, Izv.Akad.Nauk SSSR, Otd. Khim.Nauk, 499 (1950).
105. C.F.Koelsch, J.Org.Chem., 16, 1362 (1951).

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