673. *The Colour of Organic Compounds. Part V.*[*] *Thermochromic Spirans.*

By EDWARD B. KNOTT.

The factors affecting the thermochromic behaviour of certain spirans containing one or more pyran residues have been analysed. It is shown that, whereas the ease of intramolecular ionization resulting in dye formation increases with an increasing $-M$ effect of the heterocyclic *spiro*-component (cf. Wizinger and Wenning, *Helv. Chim. Acta*, 1940, **23**, 247), it may be affected in either direction by changes in the $+M$ effect of the ketonic fragment resulting from the ring-opening and is largely independent of the degree of degeneracy of the resonance system responsible for the colour of the dye. The inhibitory effect of the introduction of substituents into certain positions of the pyran rings is explained on the basis of steric hindrance to planarity of the dye molecules. Certain colour phenomena associated with Wizinger's dyes are explained on the basis of their strongly dipolar nature.

THE thermochromic behaviour of certain colourless *spiro*bispyrans is well known (for references see Mustafa, *Chem. Reviews*, 1948, **43**, 509), and the explanation of the formation of colour is now generally accepted as being due to an intramolecular ionization proceeding according to (I; X = O) $\longrightarrow$ (II; X = O),[†] the broken line denoting the atoms necessary to complete the heterocyclic ring. Dickenson and Heilbron (*J.*, 1927, 1699) have shown that the property of thermochromicity is only exhibited by those spirans (I; X = O) which contain at least one naphthopyran ring and a free 3-position (I; X = O, R = H). The same process also appears to be involved in related spirans in which X = NR (Wizinger and Wenning, *Helv. Chim. Acta*, 1940, **23**, 247).

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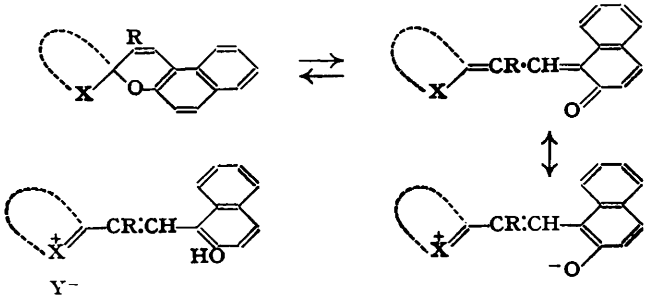
[*] Part IV, *J. Soc. Dyers and Colourists*, 1951, in the press.

[†] Hukins and Le Fèvre (*J.*, 1949, 2088) and Bergmann, Weizmann, and Fischer (*J. Amer. Chem. Soc.*, 1950, **72**, 5009) have shown that the expected increase in dipole moment of *spiro*bispyrans when heated to give colour is not measurable. These authors suggest, therefore, that the least unacceptable hypothesis for the structure of the coloured molecule is the quinone (*e.g.*, II*a*). Bergmann *et al.* also refer to the stable dye [1-methyl-2-quinoline][1 : 2-dihydro-2-ketonaphthalene]dimethin*mero*cyanine as *N*-methylquinolino-β-naphthopyrylospiran. They appear thus to be unaware of three fundamental principles involved : (*a*) That in the spiran there is no π-electron orbital overlap between the two halves at right angles to each other. Consequently atomic movement towards planarity is required in order that (II*a*) and (II*b*) can contribute. (*b*) That in such a case there must be a resonance system with (II*a*) and (II*b*) as extreme structures. (*c*) That for deep and intense colour near-planarity of the molecule is required with not greatly dissimilar contributions by both extreme structures.

The experimental results of the above authors can thus best be explained on the basis of the relatively small percentage of spiran molecules excited to dye molecules at any particular moment at the relatively low temperatures employed (60° and 90° respectively).

Wizinger and Wenning concluded that the ease of ionization would increase as the electron donating properties (−*M* effect) of the atom or group X increased. Thus they found that compounds where X = NR are more thermochromic than those in which X = O and that in the extreme case the coloured, " ionic " form was stable at room temperature. They called the latter dyes, spirains, but in this paper they will be given the more usual name of dimethin*mero*cyanines. They were obtained by these authors by employing 1-formyl-2-naphthol in the well-known reaction between aldehydes and cyclic quaternary ammonium salts carrying a reactive methyl group (König, *J. pr. Chem.*, 1912, **86**, 166; Barbier, *Bull. Soc. chim.*, 1920, **27**, 429). The resultant stable 1-(2-hydroxy-1-naphthyl)vinyl derivative of the quaternary salt (III; X = NR) gave (II) on treatment with a base. In two cases this treatment resulted in spontaneous isomerisation to the spiran (I; X = NR), namely, in those dyes containing the 1 : 3 : 3-trimethylindoline and 9 : 10-dihydro-10-methylacridine nuclei. No such isomerization occurred, however, in the dyes containing the 3-ethylbenzothiazoline, 3-ethylbenzoselenazoline, 1 : 2-dihydro-1-methylquinoline, or 1 : 2-dihydro-1 : 4 : 6-triphenylpyridine nuclei. The increased ease of ionization of these spirans (I; X = NR), compared with (I; X = O), was demonstrated by the development of colour even in cold solutions in polar solvents and by the thermochromic behaviour of the benzopyran (as I; X = NR, less one benzene ring).



(I) (II*a*) (III) (II*b*)

We shall now consider the electronic processes which occur on ionization in order to determine those factors which will favour or inhibit such ionization.

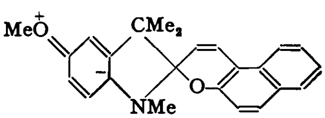
The Electronic Processes and Energy Considerations affecting Ionization.—As with any reaction, the ease of intramolecular ionization of these spirans would be expected to depend on the relative energy levels of the ground states of the dye and of the spiran. If such extramolecular factors as temperature and solvent polarity (which will be of importance in determining the spiran–dye equilibrium) are excluded, it may be argued that the stability of the dye relative to that of the spiran will depend on the free energy associated with (*a*) the −*M* effect of the heterocyclic component containing X, (*b*) the +*M* effect of the carbocyclic (ketonic) residue, and (*c*) the resultant interaction of these two effects, *i.e.*, the resonance (II*a* ⟶ II*b*) responsible for visible absorption. The effect, on ionization, of changes in these three factors resulting from structural alterations will now be examined.

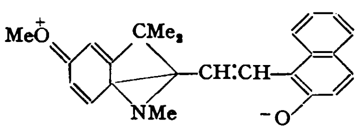
The factor (*a*). This factor, applied to the spiran, is that given by Wizinger and Wenning (*loc. cit.*), who refer to it as a change in the " Positivierung " of the carbon atom of the spiran molecule common to both *spiro*-components. They give no fundamental theoretical explanation of the effect, which is believed to be as follows. The −*M* effect of the heterocyclic system is related to the free energy involved in the process (II*a* ⟶ II*b*) and will increase with increasing free-energy change; it involves the ionization potential of the atom X and the simultaneous changes in the resonance energy of the nucleus itself. Any structural changes in the heterocyclic system which alter the strength of its −*M* effect in the direction of the *spiro*-carbon atom cannot affect the ground state level of the spiran by virtue of such a change in −*M* effect, since it cannot operate. On the other hand, such a change will affect the resonance energy, and hence the ground-state level, of the dye in which the −*M* effect is operative. As the latter increases, so will this level fall, with a resultant increase in ease of ionization of the corresponding spiran. This may be pictured as an increased stabilization of the extreme structure (II*b*) of the dye and of all excited structures containing the quaternary-nitrogen heterocyclic system.

The correctness of this interpretation was shown by Wizinger and Wenning's experimental evidence (*loc. cit.*). In the first place, the greater ease of ionization of the spirans where X = NR, compared with those where X = O, is a manifestation of the greater −*M* effect of the NR group. Those nuclei, *i.e.*, 1 : 3 : 3-trimethylindoline and 9 : 10-dihydro-10-methylacridine, which form spirans must clearly on this hypothesis possess weaker $-M$ effects than the other nuclei. Brooker (*Rev. Mod. Physics*, 1942, **14**, 275; Burk and Grummit, " Frontiers in Chemistry," Interscience Publ. Inc., Vol. III, Chap. IV) has indeed shown, by his absorption deviation method (see also Knott and Williams, *J.*, 1951, 1586), that the 1 : 3 : 3-trimethylindoline nucleus exerts a significantly weaker $-M$ effect than does the 3-ethylbenzothiazoline, 3-ethylbenzoselenazoline, 1-ethyl-1 : 2(or 1 : 4)-dihydroquinoline, or 1-ethyl-1 : 2-dihydropyridine nucleus. Application of the qualitative resonance method used by Brooker to interpret his series would also lead to a weak $-M$ effect of the dihydro-10-methylacridine nucleus (cf. Brooker, White, Sprague, Dent, and van Zandt, *Chem. Reviews*, 1947, **41**, 325).

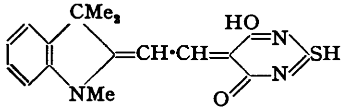
Wizinger and Wenning (*loc. cit.*) also observed that spirans containing the 5-methoxy-1 : 3 : 3-trimethylindoline nucleus were more chromotropic than the parent spirans without the methoxy-group. This is readily understood in that, whilst the introduction of this group will stabilize the spiran by contributions of such structures as (IV), it will stabilize the dye not only by analogous contributions but, in addition, by the participation of such structures as (V), *i.e.*, by effectively increasing the $-M$ effect of the indoline nucleus.

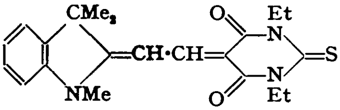
The factor (*b*). Although an increase in the $+M$ effect of the ketonic nucleus will again stabilize the dipolar extreme structure of the dye this does not necessarily mean that a resultant increase in ease of ionization of the spiran will occur. If the free-energy change on electron capture by this nucleus is negative, the resultant stabilization of the nucleus is felt both by the dye and also by the spiran since the latter contains this nucleus (as the pyran nucleus) in its reduced form. It is necessary, therefore, in determining the effect of changes in $+M$ effect, to analyse each case separately and it will be shown below that, depending on the nature of the structural change, an increase in $+M$ effect may stabilize either the spiran or the dye.

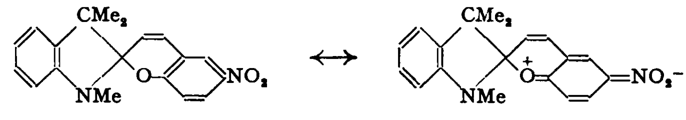

(IV)

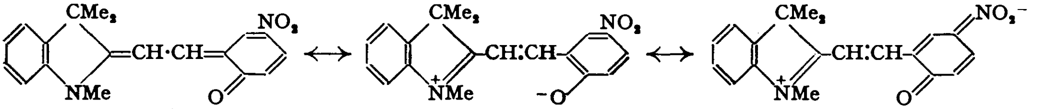

(V)

In the first place it can be shown, by employing the same empirical reasoning as was applied by Brooker (*loc. cit.*) to pyridine and quinoline, that the $+M$ effect of the 2-keto*cyclo*hexa-3 : 5-dienylidene residue is greater than that of the 1 : 2-dihydro-2-ketonaphthylidene residue (this is manifested experimentally by the lower nucleophilic activity of the 2-position in the phenoxide ion compared with the 1-position in the 2-naphthoxide ion). Reasoning similar to that used by Brooker (*loc. cit.*) shows the naphthopyran (I) (the nitrogenous heterocyclic component being neglected) to be stabilized by three major contributing (Kekulé) structures, and the dye (II*a*, *b*) (both II*a* and II*b* being assumed to be significant) by five major structures (two in II*a* and three in II*b*). The loss of the extra benzene ring reduces the number of such structures in the spiran to two and in the dye to three. On this reasoning, therefore, such a structural change would be expected to result in spiran stabilization. This is in agreement with experimental evidence (see earlier) and may be a contributory cause.


(VI)


(VII)


(VIII*a*) (VIII*b*)

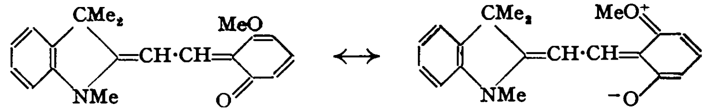

(IX*a*) (IX*b*) (IX*c*)

Further examples of this effect are provided by the fact that dimethin*mero*cyanines containing a heterocyclic ketonic nucleus show no tendency at all to spiran formation, even when the latter nucleus is six-membered. Thus, for example, [1 : 3 : 3-trimethyl-2-indolenine]-[5 : 6-dihydro-4-hydroxy-6-keto-2-mercapto-5-pyrimidine]dimethin*mero*cyanine (VI) Kendall B.P. 428,722; 428,360) or [1 : 3 : 3-trimethyl-2-indoline][1 : 3-diethylhexahydro-2-thio-5-pyrimid-4 : 6-dione]dimethin*mero*cyanine (VII) are quite stable at low temperatures, consistently with the much weaker $+M$ effect of the thiobarbituric acid residues compared with the dihydroketo-aromatic systems.

As a second type of structural change resulting in a change in the $+M$ effect of the ketonic nucleus, the introduction of substituents in the ketonic nucleus was studied. The nitro-group was selected for convenience and because of its strong $+M$ effect. 2-Hydroxy-3- and -5-nitrobenzaldehyde were condensed with a number of cyclic quaternary ammonium salts carrying a reactive methyl group. Stable dyes were obtained in all cases, except with trimethylindolenine methiodide which yielded 1 : 3 : 3-trimethyl-8′- and -6′-nitroindoline-2-*spiro*-2′-benzopyran (VIII*a, b*). The introduction of this nitro-group will stabilize the spiran by contributions by such structures as (VIII*b*).

In the dye the presence of the nitro-group will not appreciably affect the resonance energy of the non-polar extreme structure (IX*a*), but the dipolar extreme structure (IX*b*) will acquire considerable additional stabilization by important contributions of (IX*c*). It appears probable that the resonance (IX*b* $\longleftrightarrow$ IX*c*) is more significant than (VIII*a* $\longleftrightarrow$ VIII*b*) since, in the latter, energy of charge separation is involved. Consequently the increase in the $+M$ effect of the nucleus by the introduction of the nitro-group would be expected to favour ionization of the spiran. This is confirmed experimentally, both nitro-spirans, and particularly (VIII), being more readily ionized than the parent compound (Wizinger and Wenning, *loc. cit.*). Even in cold polar solvents, such as alcohol, intensely red solutions are obtained.

If, on the other hand, a $-M$ substituent is introduced into the ketonic nucleus a decrease in its $+M$ effect will result. This decrease however is not due to a rise in the energy of the

(X*a*)  (X*b*)

dipolar extreme structure relative to that of the classical structure (X*a*), but rather to a fall in the energy of the latter structure owing to contributions of such structures as (X*b*). Since such additional resonance stabilization is not enjoyed by the corresponding spiran the introduction of this $-M$ substituent can only favour ionization. This was shown to be true by Wizinger and Wenning (*loc. cit.*) who recorded that the introduction of a methoxy-group favoured dye formation.

The factor (*c*). The energy associated with the resonance responsible for colour will be at a maximum at the point of accidental degeneracy, *i.e.*, when $E_{\text{II}a} = E_{\text{II}b}$. Loss of such degeneracy may occur in four ways, by the raising or lowering of the energy level of either extreme structure. At this point it is not known whether $E_{\text{II}a}$ is greater or less than $E_{\text{II}b}$, but if, for the moment, it is assumed that $E_{\text{II}a} < E_{\text{II}b}$ then any increase in the $-M$ effect of the heterocyclic system will decrease the non-degeneracy of the resonance system until degeneracy is achieved, and any further increase in this effect will result in $E_{\text{II}a}$ becoming greater than $E_{\text{II}b}$ with a resultant increase in non-degeneracy (Förster, *Z. Elektrochem.*, 1939, **45**, 545). Although in this progression the resonance energy of the system (II*a* $\longleftrightarrow$ II*b*) rises and then falls again, this does not mean that the dye–spiran stability ratio is at a maximum at the point of degeneracy; for such changes, in general, increasingly lower the energy of the dipolar extreme structure, and hence of the hybrid relative to that of the spiran, even beyond the point of attainment of degeneracy. The degree of non-degeneracy of this system in itself is, therefore, not an essential factor which determines spiran or dye stability.

It is obvious, however, that if such a progression is assumed, the superimposition of the increasing resonance energy of the system (II*a* $\longleftrightarrow$ II*b*) will accelerate the favouring of dye formation up to the point of degeneracy, and beyond this point will decelerate the process. This may be represented by Fig. 1, in which energy is plotted against the ratio $E_{\text{II}a} : E_{\text{II}b}$, the vertical broken line representing the point $E_{\text{II}a} = E_{\text{II}b}$. The line X represents the constant decrease in $E_{\text{II}b}$ relative to E_{spiran} as the $-M$ effect of the heterocyclic nucleus increases. The shape of curve Y, and its position relative to the other curves, are purely artificial; this curve represents the resonance energy $E_{(\text{II}a \longleftrightarrow \text{II}b)}$, and curve Z is the resultant of X and Y. The point *A* represents the ratio $E_{IIa} : E_{IIb}$ at which dye formation, under the particular conditions chosen, does not occur. The minimum value of E_{spiran} will then always lie above the point *B*.

It has been pointed out above that the resonance energy of the system II*a* $\longleftrightarrow$ II*b* will favour dye formation although changes in its value brought about by changes in the $+M$ and the $-M$ effects of the two nuclei are less important. It is possible however to change its value without structural change of the nuclei and without altering their *M* effects. Suppose that the ground level of the dye lies either at a point *C* or *D* (on curve Z). If now a substituent is introduced into the chain, which causes overcrowding, the latter may be relieved by a twisting of the chain bonds which causes a loss of coplanarity of the two nuclei. The value of $E_{IIa \leftrightarrow IIb}$ will consequently fall, owing to a reduction in the overlap of the π-electron orbitals. The ground level of the dye may now be represented by points *C′* or *D′*. However, if the twisting is severe the energetic asymmetry of the dye will be affected, causing a further shift in $E_{IIa \leftrightarrow IIb}$. Unless the system II*a* $\longleftrightarrow$ II*b* is near-degenerate such twisting can only cause an increase in the energetic asymmetry of the molecule (cf. Brooker *et al.*, *loc. cit.*), so that the points *C″* or *D″* now represent the dye ground level. The diagram shows the theoretical possibility of the introduction of an overcrowding substituent causing a stable dye to revert

FIG. 1.

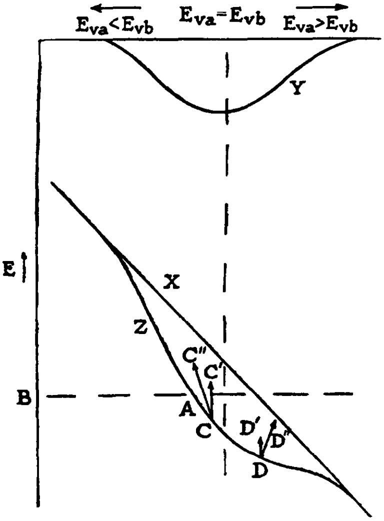


FIG. 2.

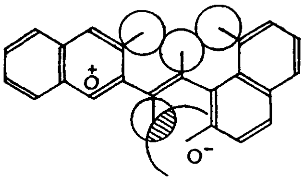


FIG. 3.

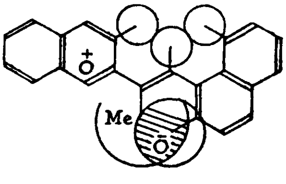


FIG. 4.

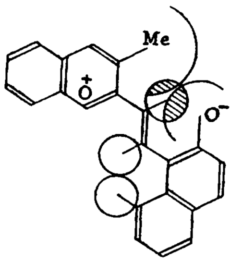
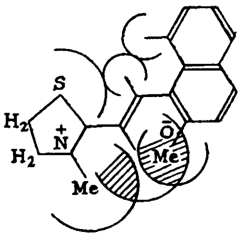


FIG. 5.

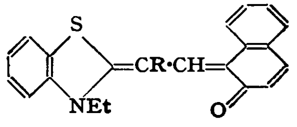


to spiran since the energy points *C′* or *C″* lie above the point *B*. It also shows that the likelihood of such an occurrence will decrease with increasing dye polarity. This explains the inhibition of thermochromotropy in *spiro*bispyrans (I; X = O) by substituents.

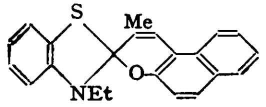
Fig. 2 shows a scale drawing of the dye obtained by the ionization of benzopyran-2-*spiro*-2′-[naphtho(2″ : 1″-2 : 3)pyran]. Although there is some overcrowding between a chain-hydrogen atom and the negatively charged oxygen atom the dye may be considered to be near-planar. The introduction of a substituent, to give 3′-methylbenzopyran-2-*spiro*-2′-[naphtho(2″ : 1″-2 : 3-pyran] (cf. I; X = O, R = Me), is known to inhibit completely its thermochromic properties. Fig. 3 represents the least overcrowded configuration of the hypothetical dye resulting from this spiran and it will be seen that the chain-methyl group will prevent the naphthyl residue from being coplanar with the rest of the molecule. On the other hand, the introduction of a methyl group to give the 3-methyl spiran is known not to inhibit ionization and, as Fig. 4 shows, the resultant dye is only slightly more overcrowded than the parent dye.

It has now also been found possible to demonstrate the effect at room temperature. Whereas the condensation of 2-methylbenzothiazole ethiodide (Wizinger and Wenning, *loc. cit.*) or 2-methylthiazoline methiodide with 1-formyl-2-naphthol, followed by treatment of the product with a base, gave the dyes (XI; R = H) and (XIII; R = H) respectively, the use of the 2-ethyl homologues led to (XII) and (XIV). Of these, (XII) is the more easily ionized, giving red solutions in polar solvents and a purple melt. The dye (XIV) gave a yellow melt, consistently with the lighter colour usually associated with the thiazolidine nucleus. The higher stability of (XIV) is also consistent with the weaker −*M* effect of the 2-thiazolidine nucleus, as found by Brooker (*loc. cit.*). The degree of overcrowding in (XIII; R = Me) (the same applies to XI) is shown in Fig. 5. Treatment of solutions of (XII) and (XIV) with gaseous hydrogen chloride readily gave the corresponding chlorides of type (III).

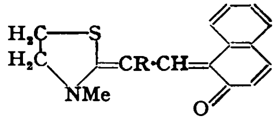
(XI)



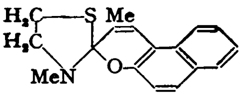
(XII)



(XIII)



(XIV)



The Effect of Polar Solvents on Spiran Stability.—It has been mentioned earlier that, apart from structural considerations, the polarity of the solvent will be of importance in determining the spiran–dye equilibrium in solution. Thus Wizinger and Wenning (*loc. cit.*) reported the development of colour on addition of water to the colourless solutions of certain of these spirans in water-miscible non-polar or weakly polar solvents such as pyridine. This effect is particularly well shown by 1 : 3 : 3-trimethylindoline-2-*spiro*-2′-[naphtho(1′ : 2′-5″ : 6″)pyran] (or its derivatives) which gives colourless solutions in light petroleum and intensely purple ones in *o*-chlorophenol. The favouring of dye formation on increase of solvent polarity may be directly ascribed to the hydrogen-bonding properties of aqueous or other polar solvents which, while affecting the ground-state level of the spiran but slightly, will decrease considerably more the energy levels of all dipolar structures contributing to the resonance hybrid of the dye. The resultant decrease in the ground-state level of the dye is thus quite analogous to the decrease occasioned by increasing the −*M* effect of the nitrogenous heterocyclic system by structural changes.*

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* [*Added*, Aug. 2nd, 1951.] Recently Schönberg, Mustafa, and Asker (*J. Amer. Chem. Soc.*, 1951, **73**, 2876) have shown that spirans (I) give deep colours when adsorbed on silica gel or alumina. Even (I; X = O, R = Me) gives the colour which it would be expected to show if it were thermochromic. They interpret this as a strong polarization effect favouring ionization of the spiran or as a shifting of the spiran–dye equilibrium by effective removal from solution of the traces of dye normally present. The first explanation seems the more likely and may be compared with the solvent effect. It is clear, however, since (I; X = O, R = Me) resists ionization in polar solvents, the polarizing electric field of the adsorbent is more powerful than that of such solvents, as might be expected. Consequently, the strong stabilization of all dipolar structures, particularly (II*b*), contributing to the hybrid of the adsorbed dye is apparently sufficient to lower the ground state level (Fig. 1) from a point lying between curves *Z* and *X* and above *B* to a point below *B*. These two points will not lie on curve *Z* since, as has been shown, the dye is non-planar and has consequently a higher energy than a similar, planar dye as a result of a decrease in the overlap of its π-orbitals.

The Energetic Asymmetry of the Dyes.—Wizinger and Wenning (*loc. cit.*) have reported that dyes of type (II; X = NR) which give red or blue solutions in solvents such as benzene or pyridine give orange or even yellow solutions in aqueous pyridine or aqueous alcohol. They explained these hypsochromic shifts by postulating that the addition of water to the dye molecule resulted in the formation of the benzostyryl dye hydroxide (III; $Y^- = OH^-$), the cations of which are all yellow or orange. They supported this thesis by the observation that the deep colour (red or blue) returned on addition of alkali to the yellow solutions, which they interpreted as an indication of the regeneration of (II*b*). Repetition of their experiments, however, failed to show the effect of alkali (either visually or on absorption measurements; see Table I). They also observed that the yellow or orange dye could be extracted completely from the aqueous solution by benzene, giving a blue solution, and explained this by postulating an equilibrium in the aqueous phase between the original dye and the yellow hydroxide, the equilibrium being largely towards the hydroxide. The high solubility of the original dye in benzene then provided a means of shifting the equilibrium completely in the other direction. Absorption measurements on the aqueous-alcoholic solutions of these dyes, however, show no indication of absorption in the region of the absorption band of the dye in benzene. From what follows it will be seen that this is not surprising. The most likely explanation of these phenomena is believed to be as follows.

Förster (*loc. cit.*) has shown that the theory, which explains the bathochromic shift exhibited by non-ionic dyes on increase of the solvent polarity, demands that this shift can only continue until the point of energetic symmetry (degeneracy) of the dye is attained. As the solvent polarity increases beyond this point the dye again loses its energetic symmetry, in that the dipolar extreme structure becomes more significant than the non-polar structure with a consequent hypsochromic shift. Examples of dyes exhibiting such an inversion were not available at that time, nor was Förster in a position to know the degree of non-degeneracy of the dyes he used as examples. The degree of degeneracy is now ascertainable by Brooker's deviation method (Brooker and Sprague, *loc. cit.*). It is now suggested that the dyes obtained by Wizinger and Wenning are examples showing such an inversion of shift and that the colour changes observed by these authors are manifestations of this inversion. Many other dyes showing this inversion have since been made by Brooker (unpublished work) and by the author.[*]

Table I.

	$\lambda_{max.}$ (mμ) in :				
Nitrogenous component in (II)	benzene	acetone	methanol	methanol–water (1 : 1)	methanol–water–NaOH
2-(3-Methylthiazolidine)	540 512	535 507	520	512	512
2-(3-Ethylbenzothiazoline)	588 551	582 545	577	565	565
2-(1-Ethyldihydroquinoline)	642 i 608	617	590	572	571
2-(1 : 3 : 3-Trimethylindoline)	—	—	570	—	—

(i = inflexion.)

Table II.

Nitrogenous component in (III)	$\lambda_{max.}$ (mμ), methanol–water (1 : 10)	$\lambda_{max.}$ (mμ), methanol–water (+ drop of acetic acid)
2-(3-Methylthiazoline)	497 412	412
2-(3-Ethylbenzothiazole)	566 440	441
2-(3-Ethylquinoline)	540 (inflexion) 433	433

To show this inversion, absorption measurements were made on three dyes of type (II) in a number of anhydrous and aqueous solvents. Table I discloses a progressive decrease in

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[*] Since this paper was written my attention has been drawn to papers by Kiprianov (with Petrun'kin, *J. Gen. Chem. U.S.S.R.*, 1940, **10**, 600, 613; with Timshenko, *ibid.*, 1947, **17**, 1468) on related dyes [see also work by Kuhn and Bär, *Annalen*, **1935**, **516**, 155, and by Brooker and Keyes (in the press) on phthalones].

$\lambda_{max.}$ on proceeding from the non-polar benzene to the highly polar aqueous methanol. This clearly precludes the explanation of the colour shift given by Wizinger and Wenning. Moreover it is readily understandable why, even if their explanation had been correct, it would not be possible for the addition of aqueous alkali to restore the colour of the solution to that given in an anhydrous solvent such as pyridine (which gives absorption figures similar to those given in benzene).

Table II shows the absorption characteristics of the hydriodides of (II), namely, (III; $Y^- = I^-$) in aqueous methanol, and in the same solvent with a drop of acetic acid. The long-wave-length peak in aqueous methanol is considered to arise by hydrolysis, resulting in the ionization of the hydroxyl group of the salt. This band would then correspond to that of the dye (II), the hypsochromic shift from the values given in Table I being due to the lower methanol–water ratio. The second peak at shorter wave-lengths is considered to be the true peak of the cation of (III), as is confirmed by the measurements under weakly acid conditions (second absorption column) where the peaks due to ionization are suppressed. This is additional evidence against the mechanism of colour change given by Wizinger and Wenning.

Even stronger hypsochromic shifts on increase of the solvent polarity were given by dimethin*mero*cyanines derived from salicylaldehyde, its 3- and 5-nitro-derivatives, and particularly from 4-hydroxy-3-nitrobenzaldehyde (see Experimental section). This is to be expected since such structural changes will increase the dye polarity and the non-degeneracy of its resonance system (II*a*, *b*) by increasing the $+M$ effect of the ketonic moiety.

EXPERIMENTAL.

Analyses are by Drs. Weiler and Strauss of Oxford. M. p.s are uncorrected.

[1 : 3 : 3-*Trimethyl-2-indolenine*][1 : 3-*diethylhexahydro-2-thio-5-pyrimid-4* : 6-*dione*]*dimethin*mero*cyanine* (VII).—2-2′-Acetanilidovinyl-3 : 3-dimethylindolenine methiodide (1·25 g., 0·0025 mol.), 1 : 3-diethylthiobarbituric acid (0·5 g., 0·0025 mol.), ethanol (10 c.c.), and triethylamine (0·5 c.c.) were refluxed together for 5 minutes on the steam-bath. The crystalline dye was collected and washed with methanol. It formed orange needles (0·7 g.), m. p. 276°, from ethanol (Found : N, 10·9; S, 8·2. $C_{21}H_{25}O_2N_3S$ requires N, 10·95; S, 8·3%).

1 : 3 : 3-*Trimethyl-6′-nitroindoline*-2-spiro-2′-*benzopyran* (VIII).—2 : 3 : 3-Trimethylindolenine methiodide (1·5 g., 0·005 mol.), 2-hydroxy-5-nitrobenzaldehyde (0·85 g., 0·005 mol.), ethanol (10 c.c.), and piperidine (0·5 c.c.) were refluxed for 15 minutes. The intensely purple solution was concentrated to half-volume and, on chilling, large purple aggregates slowly separated. They formed a pink powder when crushed. They may be recrystallized from methanol (purple solution when hot, red on cooling) but the crystals are then coloured. The *spiran* is best recrystallized from light petroleum (b. p. 80—100°) (yellow solution), forming flat, colourless needles, m. p. 147° (blue). It gives blue solutions in pyridine or nitrobenzene, red in aqueous pyridine or cold *o*-chlorophenol, the colour changing to purple, then blue, when the last solution is heated (Found : C, 70·7; H, 5·6; N, 9·0. $C_{19}H_{18}O_3N_2$ requires C, 70·8; H, 5·6; N, 8·7%). The 8-*nitro*-isomer (1·45 g.) was similarly obtained from 2-hydroxy-3-nitrobenzaldehyde (0·85 g.) as pale yellow needles, m. p. 180°, from light petroleum (b. p. 80—100°), or soft magenta needles from ethanol (Found : N, 8·8. $C_{19}H_{18}O_3N_2$ requires N, 8·7%). It gave magenta solutions in warm aqueous–pyridine or –methanol, the colour remaining on cooling. It develops a blue colour in hot diphenyl ether.

[3-*Methyl-2-thiazoline*][1 : 2-*dihydro-2-ketonaphthalene*]*dimethin*mero*cyanine* (XIII).—2-Methylthiazoline methiodide (2·33 g., 0·01 mol.), 1-formyl-2-naphthol (1·72 g., 0·01 mol.), and ethanol (20 c.c.) were warmed gently to effect dissolution, and the source of heat removed. Addition of piperidine (1 c.c.) produced a red colour, and 2-2′-(2″-*hydroxy*-1″-*naphthyl*)*vinylthiazoline methiodide* (XIII + HI; cf. III) (2·0 g.) separated. A sample formed bright yellow crystals, m. p. 226°, from acetic acid (Found : I, 31·9. $C_{18}H_{16}ONSI$ requires I, 32·0%). The crude iodide (1·9 g.) was suspended in ethanol (50 c.c.), and dissolved by addition of an excess of aqueous ammonia. Slow addition of water then caused the dye *base* (XIII) to crystallize as glittering plates. It formed red plates, m. p. 200°, from methanol (Found : N, 5·0; S, 11·85. $C_{16}H_{15}ONS$ requires N, 5·2; S, 11·9%).

3-*Methylthiazolidine*-2-spiro-2′-[3′-*methyl*-2′-*naphtho*(1′ : 2′-5″ : 6″)*pyran*] (XIV).—2-Ethylthiazoline methiodide (2·57 g., 0·01 mol.) (obtained by heating equimolar amounts of the base and methyl iodide on the steam-bath for 90 minutes), 2-hydroxy-1-naphthaldehyde (1·72 g., 0·01 mol.), ethanol (10 c.c.), and piperidine (1·0 c.c.) were warmed for 5 minutes of the steam bath. Addition of aqueous ammonia precipitated an orange oil which, after being washed with water, was extracted with hot light petroleum (b. p. 80—100°). The extract deposited colourless crystals (1·1 g.) on chilling. The *spiran* formed colourless, glassy needles, m. p. 125° from methanol. The melt became yellow at *ca.* 200° (Found : C, 72·5; H, 5·8; N, 4·6; S, 11·2. $C_{17}H_{17}ONS$ requires C, 72·1; H, 6·0; N, 4·95; S, 11·3%). Addition of 2N-hydrochloric acid to a methanol suspension gave a yellow solution (of styryl dye ?) which faded to give colourless needles. These formed glossy hairlike needles, m. p. 156°, from aqueous methanol. The same product, which is sulphur- and nitrogen-free, was obtained directly by heating 2-ethylthiazoline ethiodide and 2-hydroxy-1-naphthaldehyde in alcoholic piperidine.

3-*Ethylbenzothiazoline*-2-spiro-2′-[3-*methyl*-2-*naphtho*(1′ : 1′-5″ : 6″)*pyran*] (XII).—2-Ethylbenzothiazole ethotoluene-*p*-sulphonate (Hamer, Rathbone, and Winton, *J.*, 1947, 954) (1·85 g.), 2-hydroxy-

1-naphthaldehyde (0·85 g.), ethanol (20 c.c.), and piperidine (0·5 c.c.) were refluxed together for 30 minutes. An intense purple colour developed and crystals formed rapidly. These (1·7 g.) were collected after chilling, dissolved in hot light petroleum (b. p. 80—100°), and the solution was filtered from insoluble dark green crystals. The purple solution deposited the required *spiran* (1·0 g.) on chilling. From light petroleum it formed colourless, fluffy needles, m. p. 150° (Found: N, 3·95; S, 9·3. $C_{22}H_{19}ONS$ requires N, 4·05; S, 9·25%). The colour of the purple melt remained on cooling. It gave a weak purple colour in boiling diphenyl ether. The spiran (1·0 g.) was dissolved in ether (75 c.c.), and hydrogen chloride bubbled into the solution. The yellow oil soon crystallized and formed orange-yellow crystals, m. p. 206°, from ethanol (Found: Cl, 8·45. $C_{22}H_{20}ONSCl,C_2H_5{\cdot}OH$ requires Cl, 8·35%). It is considered to be 2-2′-(2″-*hydroxy*-1″-*naphthyl*)-1′-*methylvinylbenzothiazole ethochloride*.

[1-*Ethyl*-2-*quinoline*][4-cyclo*hexa*-2 : 4-*dienone*]*dimethin*mero*cyanine Trihydrate*.—Quinaldine ethiodide (3 g., 0·01 mol.), salicylaldehyde (2·45 g., 0·02 mol.), ethanol (15 c.c.), and piperidine (0·5 c.c.) were refluxed for 30 minutes. The styryl iodide (2·6 g.) separated rapidly. It was converted into the *base trihydrate* by boiling it for 5 minutes with aqueous 2N-sodium carbonate (100 c.c.). The green crystals (2·1 g.) were collected after chilling. It formed green-black needles, m. p. 140° (decomp.), from boiling water containing a little triethylamine. The dye was dried over phosphoric oxide at 100°/10 mm. (Found: C, 69·7; H, 7·0; N, 4·2. $C_{19}H_{17}ON,3H_2O$ requires C, 69·3; H, 7·05; N, 4·25%) and had $\lambda_{\text{max.}}$ 637 mμ in pyridine and 513 mμ in aqueous methanol.

[1-*Ethyl*-2-*pyridine*][5-cyclo*hexa*-2 : 4-*dienone*]*dimethin*mero*cyanine Pentahydrate*.—α-Picoline ethiodide (2·5 g., 0·01 mol.), salicylaldehyde (2·5 g.), ethanol (10 c.c.), and piperidine (0·5 c.c.) were refluxed for 1 hour and the styryl iodide was precipitated with ether as a yellow oil. It was well washed with ether, dissolved in ethanol (10 c.c.), and chilled. The orange powder (2·1 g.) which crystallized out was dissolved in aqueous 2N-sodium carbonate (25 c.c.), and the solution filtered and chilled. The yellow oily *pentahydrate* which separated crystallized rapidly. It formed red prisms, m. p. 170—180° (decomp.), from water. It was dried at 100°/10 mm. over phosphoric oxide (Found: C, 57·05; H, 7·9; N, 4·4. $C_{15}H_{15}ON,5H_2O$ requires C, 57·15; H, 7·95; N, 4·45%) and had $\lambda_{\text{max.}}$ 568 mμ in pyridine and 430 mμ in aqueous methanol.

[1-*Ethyl*-4-*pyridine*][5-cyclo*hexa*-2 : 4-*dienone*]*dimethin*mero*cyanine pentahydrate* was similarly obtained from γ-picoline ethiodide. From water it formed maroon needles, m. p. 180—190° (decomp.). Drying at 10 mm. over potassium hydroxide resulted in the loss of some water of crystallization, causing the crystals to break up by bubble formation (Found: C, 57·3; H, 7·8; N, 4·35. $C_{15}H_{15}ON,5H_2O$ requires C, 57·15; H, 7·95; N, 4·45%). It had $\lambda_{\text{max.}}$ 620 mμ in pyridine and 470 mμ in aqueous methanol.

[1-*Ethyl*-2-*quinoline*][6-(2-*nitro*cyclo*hexa*-2 : 4-*dienone*)]*dimethin*mero*cyanine*.—Quinaldine ethiodide (1·5 g., 0·005 mol.), 2-hydroxy-3-nitrobenzaldehyde (0·85 g., 0·005 mol.), ethanol (20 c.c.), and piperidine (0·5 c.c.) were refluxed for 5 minutes, causing solidification. The maroon powder (2·25 g.) was boiled with aqueous 2N-sodium carbonate, collected, washed with water, and air-dried. It formed a fine, brown, crystalline powder of indefinite m. p. from aniline–ether (Found: N, 8·7. $C_{19}H_{16}O_3N_2$ requires N, 8·75%); it had $\lambda_{\text{max.}}$ 573 mμ in pyridine and 480 mμ in aqueous methanol.

[1-*Ethyl*-2-*pyridine*][6-(2-*nitro*cyclo*hexa*-2 : 4-*dienone*)]*dimethin*mero*cyanine Monohydrate*.—This was similarly obtained by refluxing α-picoline ethiodide (2·5 g.) with the aldehyde (1·7 g.) in alcoholic triethylamine for 10 minutes, followed by carbonate treatment of the resulting product (2·4 g.). From water the *dye* formed flat, golden yellow platelets, m. p. 238°, after vacuum drying during which it swelled to an orange crystalline mass (Found: C, 62·6; H, 5·4; N, 9·45. $C_{15}H_{14}O_3N_2,H_2O$ requires C, 62·5; H, 5·55; N, 9·75%); it had $\lambda_{\text{max.}}$ 507 mμ in pyridine and 431 mμ in aqueous methanol.

[1-*Ethyl*-4-*pyridine*][6-(2-*nitro*cyclo*hexa*-2 : 4-*dienone*)]*dimethin*mero*cyanine dihydrate* was obtained similarly from γ-picoline ethiodide (2·5 g.) as red needles, m. p. 246° (darkens at 235°) after vacuum-drying (swells) (Found: C, 60·1; H, 5·8; N, 9·25. $C_{15}H_{14}O_3N_2,2H_2O$ requires C, 58·8; H, 5·9; N, 9·15%), and had $\lambda_{\text{max.}}$ 533 mμ in pyridine and 450 mμ in aqueous methanol.

[1-*Ethyl*-2-*quinoline*][6-(5-*nitro*cyclo*hexa*-2 : 4-*dienone*)]*dimethin*mero*cyanine* was obtained directly (1·7 g.) by refluxing for 15 minutes a solution of quinaldine ethiodide (1·5 g.), 2-hydroxy-5-nitrobenzaldehyde (0·85 g.), and piperidine (0·5 c.c.) in ethanol (20 c.c.). It formed a brownish-green crystalline powder of indefinite m. p. from ethanol (Found: N, 8·65. $C_{19}H_{16}O_3N_2$ requires N, 8·75%), having $\lambda_{\text{max.}}$ 593 mμ in pyridine and 502 mμ in aqueous methanol.

[1-*Ethyl*-2-*pyridine*][6-(5-*nitro*cyclo*hexa*-2 : 4-*dienone*)]*dimethin*mero*cyanine trihydrate* was similarly obtained from α-picoline ethiodide as red-brown crystals, m. p. 249°, after recrystallization from aqueous 2N-sodium carbonate, then from ethanol (Found: C, 55·8; H, 6·2; N, 8·4. $C_{15}H_{14}O_3N_2,3H_2O$ requires C, 55·55; H, 6·15; N, 8·6%), $\lambda_{\text{max.}}$ 545 mμ in pyridine and 468 mμ in aqueous pyridine.

[1-*Ethyl*-4-*pyridine*][6-(5-*nitro*cyclo*hexa*-2 : 4-*dienone*)]*dimethin*mero*cyanine pentahydrate*, obtained similarly, formed brown crystals, m. p. *ca.* 170°, after recrystallizing from aqueous 2N-sodium carbonate, then from ethanol (Found: C, 49·7; H, 6·7; N, 7·7. $C_{15}H_{14}O_3N_2,5H_2O$ requires C, 50·0; H, 6·65; N, 7·8%), and had $\lambda_{\text{max.}}$ 570 mμ in pyridine and 479 mμ in aqueous methanol.

[1 : 3 : 3-*Trimethyl*-2-*indolenine*][4-(2-*nitro*cyclo*hexa*-2 : 5-*dienone*)]*dimethin*mero*cyanine*.—2 : 3 : 3-Trimethylindolenine methiodide (1·5 g., 0·005 mol.), 4-hydroxy-3-nitrobenzaldehyde (0·85 g., 0·005 mol.), ethanol (10 c.c.), and piperidine (0·3 c.c.) were refluxed for 30 minutes. The solid (1·3 g.) which crystallized was boiled for 15 minutes with alcohol (250 c.c.), water (5 c.c.), and triethylamine (5 c.c.), and the crystals were collected. This was repeated and the rather insoluble dye, m. p. 252°, obtained as steel-grey crystals (Found: N, 9·0. $C_{19}H_{18}O_3N_2$ requires N, 8·7%), $\lambda_{\text{max.}}$ 558 mμ in pyridine and 505 mμ in aqueous methanol.

[3-*Ethyl*-2-*benzothiazole*][4-(2-*nitro*cyclo*hexa*-2 : 5-*dienone*)]*dimethin*mero*cyanine*, prepared similarly from 2-methylbenzothiazole ethiodide (1·5 g.), formed black crystals with a gold reflex, m. p. 270°, after being repeatedly boiled with aqueous–alcoholic triethylamine (Found : N, 8·4. $C_{17}H_{14}O_3N_2S$ requires N, 8·6%). It had $\lambda_{max.}$ 563 mμ in pyridine and 486 mμ in aqueous methanol.

[1-*Ethyl*-2-*quinoline*][4-(2-*nitro*cyclo*hexa*-2 : 5-*dienone*)]*dimethin*mero*cyanine*, similarly obtained, formed dark green crystals, m. p. 287°, from alcoholic triethylamine (Found : N, 8·4. $C_{19}H_{16}O_3N_2$ requires N, 8·75%), and had $\lambda_{max.}$ 580 mμ in pyridine and 482 mμ in aqueous methanol.

[1-*Ethyl*-2-*pyridine*][4-(2-*nitro*cyclo*hexa*-2 : 5-*dienone*)]*dimethin*mero*cyanine Heptahydrate.*—α-Picoline ethiodide (2·5 g., 0·01 mol.), 4-hydroxy-3-nitrobenzaldehyde (1·7 g., 0·01 mol.), methanol (15 c.c.), and piperidine (0·5 c.c.) were refluxed for 2 hours. The solvent was removed and the oil dissolved in a little acetone. Crystals were deposited on storage. The orange needles, m. p. *ca.* 240° (decomp.) (from water), became orange-red on vacuum-drying over potassium hydroxide (Found : C, 35·6; H, 7·3; N, 6·95. $C_{15}H_{14}O_3N_2,7H_2O$ requires C, 45·3; H, 7·05, N, 7·05%). It contained no iodide ion and had $\lambda_{max.}$ 528 mμ in pyridine and 413 mμ in aqueous methanol.

[1-*Ethyl*-4-*pyridine*][4-(2-*nitro*cyclo*hexa*-2 : 5-*dienone*)]*dimethin*mero*cyanine trihydrate* was similarly obtained as red-orange needles, m. p. *ca.* 245° (decomp.), from water, becoming deep maroon on drying in a vacuum over potassium hydroxide (Found : C, 55·7; H, 6·5; N, 8·6. $C_{15}H_{14}O_3N_2,3H_2O$ requires C, 55·55; H, 6·15; N, 8·65%) and having $\lambda_{max.}$ 549 mμ and 423 mμ in aqueous methanol.

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