Environmental Influences and the Colour of Some mero*Cyanines.*

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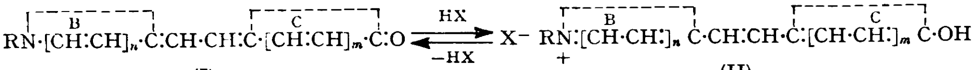
The effect of certain environmental factors on the absorption spectra of a series of dimethin*mero*cyanines has been examined. These include the degree of dilution, particularly in alcohols, the partial replacement of solvent ethanol by water, and temperature changes. It is shown that the varied behaviour of the dyes can, in general, be attributed to differences in their polarity. The most highly polar dyes exhibit two absorption bands in alcohols or aqueous alcohol, the long-wavelength band being attributed to the dye itself and the shorter-wavelength band to a quaternary cation formed between the solute and solvent. In general these bands are very sensitive to the environmental changes listed below.

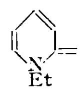
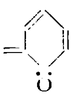
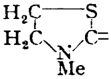
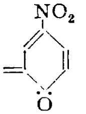
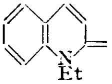
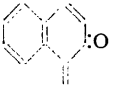
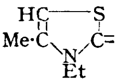
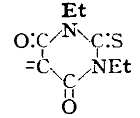
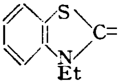
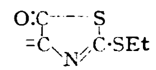
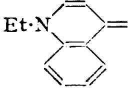
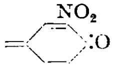
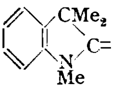
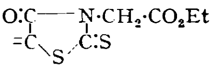
IN the course of work on the photochromism of *spiro*pyrans (Hirshberg and Fischer, *J.*, 1954, 297; 1954, 3129) an investigation was undertaken of the effect of temperature changes and other factors on the colour of some dimethin*mero*cyanine dyes (I) because the structure of these dyes is related to that postulated for the coloured form of the photochromic compounds. The colour of related *mero*cyanines has been investigated and discussed extensively by Brooker *et al.* (*J. Amer. Chem. Soc.*, 1951, **73**, 5332, 5350) and by Knott (*J.*, 1951, 3038). All the compounds now examined are combinations of basic nuclei B and carbonyl-containing nuclei C, connected by a dimethin bridge in the general form (I). For simplicity the various compounds will be denoted [B–C], where B and C stand for the numerals representing the two types of nuclei as given in Table 1, *e.g.*, (III*a*) (p. 3320) is represented by [I–3].



$$\overbrace{RN\cdot[CH{:}CH]_n\cdot C}^{B}{:}CH\cdot CH{:}\overbrace{C\cdot[CH{:}CH]_m\cdot C{:}O}^{C} \underset{-HX}{\overset{HX}{\rightleftharpoons}} X^- \overbrace{\overset{+}{RN}{:}[CH\cdot CH{:}]_n\,C}^{B}\cdot CH{:}CH\cdot\overbrace{C{:}[CH\cdot CH{:}]_m\,C\cdot OH}^{C}$$

(I) (II)

TABLE 1.

B nuclei	Designation	C nuclei	Designation	B nuclei	Designation	C nuclei	Designation
	I		1		V		5
	II		2		VI		6
	III		3		VII		7
	IV		4		VIII		8

The compounds investigated may be roughly divided into two groups according to their absorption spectra in ethanol in the visible range: (*a*) compounds possessing two bands about 100 mμ apart and (*b*) compounds possessing under all conditions only one main

TABLE 2. *Absorption spectra of group* (a) *dyes under various conditions.*

1 Compound	2 λ_1 (mμ)	3 λ_2 (mμ)[b]	4 $\varepsilon_2/\varepsilon_1$[c]	5 Concn. (mg./l.)
[VII-2]	575	470	0·05	25
,, in $COMe_2$	580, 550	—	—	8
[II-2]	600	470	0·05	35
,, in MeOH	590	460	0·1	1·7
[II-3]	560	435	0·24 2	75 1·5
,, in $COMe_2$	610, 570	425	0·22	12
[IV-3]	600	450	0·26 6·5	90 1·8
,, in $COMe_2$	660, 615	440	7	1
[II-1]	560	400 (430 + 385)[e]	0·8 6·3	80 8
,, in $COMe_2$	620	400	0·55	170
[VI-3]	510	400	0·9 3·5	120 6
[III-3]	515	400	1·1 15	130 2·6
,, in EtOH-MeOH (4 : 1)	515	—	—	15
,, in $COMe_2$	585	390	—	—
[I-3]	500	385	1·1 3·5	165 8·2
[I-1]	500	372	1·5 3·2	170 8·5
[III-1]	515	390·	1·7 7	250 12·5

1 Compound	6 Effect of cooling on ratio $\varepsilon_2/\varepsilon_1$:[g] original solution	7 with TEA added	8 Hypsochromic shift of λ_1:[d] cooling to $-100°$ (mμ)	9 EtOH-H_2O (1 : 1) (mμ)	10 EtOH-H_2O (1 : 9)[f] (mμ)	11 Hypsochromic shift of λ_2 in EtOH at $-100°$ (mμ)
[VII-2]	None	None	5	—	20	<5
,, in $COMe_2$	—	—	—	—	—	—
[II-2]	None	None	10	25	35	<5
,, in MeOH	↑↑	—	—	—	—	—
[II-3]	—	↓	—	—	—	—
	↑↑	↓	28	30	60	—
,, in $COMe_2$	—	—	—	—	—	—
[IV-3]	—	—	—	—	—	—
	↑	↓	40	35	80	−8
,, in $COMe_2$	—	—	—	—	—	—
[II-1]	—	—	—	—	—	—
	↑	↓	35	20	55	−20
,, in $COMe_2$	—	—	—	—	—	—
[VI-3]	—	—	—	—	—	—
	↑↑	None	~40	—	—	<5
[III-3]	—	—	—	—	—	—
	None	↓↓	30	30	65	<5
,, in EtOH-MeOH (4 : 1)	↑↑	—	—	—	—	—
,, in $COMe_2$	—	—	40	—	—	<5
[I-3]	—	—	—	—	—	—
	↑↑	↓	35	—	—	<5
[I-1]	—	—	—	—	—	—
	↑↑	↓	35	—	—	8
[III-1]	—	—	—	—	—	—
	↑	None	25	35	—	<5

[a] Solutions in ethanol at 26°, unless otherwise stated. [b] Identical with λ_2 in presence of excess of acid. [c] Figures in this column show the extent of the "dilution effect." No absolute data are given for ε, because of their dependence on environmental factors; however, their order of magnitude may be estimated from the fact that at the highest concentration in each case the optical density in 1-mm. cells is 0·5—1·5. [d] Unchanged by addition of triethylamine. [e] On cooling, this band is split into the two bands given, which seem to be differently affected by dilution, temperature, and pH. [f] Addition of H_2O increases the ratio $\varepsilon_2/\varepsilon_1$ in *all* cases; triethylamine annuls this effect. [g] ↑ = slight increase, ↓ = slight decrease, ↑↑ = strong increase, ↓↓ = strong decrease.

FIG. 1. *Dependence of the absorption spectra on the concentration. The optical densities were measured in* 1-*cm. cells for the medium concentration in each case, and in correspondingly shorter or longer cells at the higher or lower concentration, thus keeping constant the product of concentration and light path. The numbers in the upper left corner denote the compound, the figures accompanying the curves give the concentration in mg./l. of ethanol.*

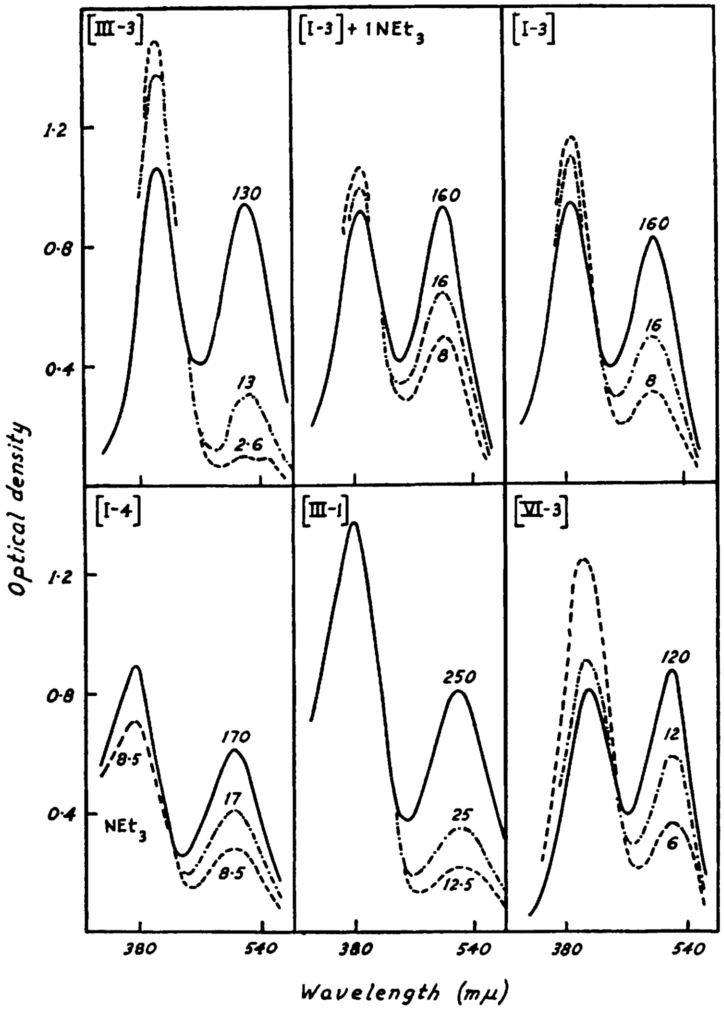


TABLE 3. *Absorption bands of nitro-derivatives in ethanol–methanol* (4 : 1) *at* 25°.

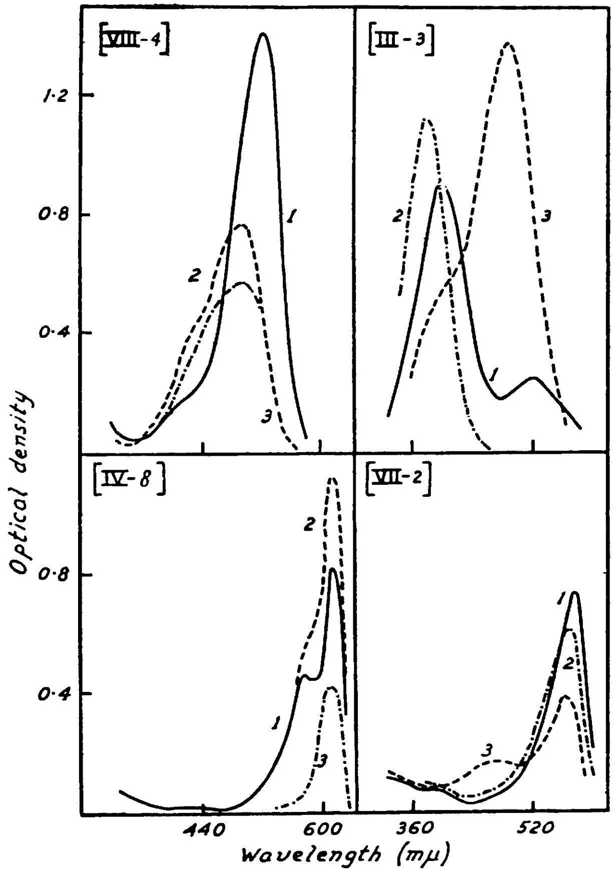
Compound	λ_1 (mμ)	$10^{-3}\,\varepsilon_1$	λ_2 (mμ)	$10^{-3}\,\varepsilon_2$	λ_3 (mμ)
[II–4]	520	175	390	116	320
[VII–4]	520	85	390	59	—
[VIII–4]	530	64	405	38	—
[II–5]	525	22	390	22	350
[III–5]	500	43	375	28	335
[VII–5]	525	30	395	26	370

Notes. In all cases neutral solutions show only a shoulder at λ_2, which increases somewhat on cooling, but forms a distinct band only with [III–5]. In presence of excess of HCl, only λ_2 is observed. No dilution effect was found with any compound. Cooling to $-100°$ little affects λ_2, but shifts λ_1 hypsochromically by 15—25 mμ. Compounds containing nucleus 5 possess a third band at λ_3, which overlaps with λ_2 to some extent; $\varepsilon_3 \ll \varepsilon_2$; λ_3 is not affected by HCl. In compounds containing nucleus 4, λ_3 is probably still shorter and does not interfere with λ_2.

band, corresponding to the long-wavelength band in group (*a*). Group (*a*) comprises compounds with c nuclei 1—5 (Tables 2 and 3) and group (*b*) those with c nuclei 6—8 (Table 4). Compounds with c nuclei containing a nitro-group (4, 5) fall between the two groups, and will be described separately (Table 3).

In ethanol solutions of compounds of group (*a*) the molar extinction coefficients ε of the two visible bands, as well as the ratio between the ε of these bands, differ from compound to compound (Table 2). Addition of excess of hydrochloric acid in all cases suppresses the band at longer wavelength and enhances the band at shorter wavelength. The quantity of acid needed to cause the long band to disappear completely varies from 1 to 10 equivalents. Compounds belonging to group (*b*) are not affected even by much larger quantities of acid.

FIG. 2. *Dependence of the absorption spectra on the water content of the solvent ethanol. The numbers in the upper left corner denote the compounds.* (1-*cm. cells.*)



Compound	Curve 1	Curve 2	Curve 3
[VIII-4]	0% H_2O	90% H_2O	90% H_2O + 10 equiv. NEt_3
[III-3]	,,	,,	,, ,,
[IV-8]	,,	60% ,,	90% H_2O
[VII-2]	,,	50% ,,	50% H_2O + 100 NEt_3

The absorption of compounds of group (*a*) is further affected by three factors—dilution, replacement of part of the solvent ethanol by water, and cooling.

The dependence of the absorption on the concentration of the solutions is shown in Fig. 1, in which the spectra for five representative compounds are given. Exact data for all compounds of this group are given in the fourth and fifth columns of Table 2. Dilution of the dye solutions is seen to result in a considerable enhancement of the short-wave band and depression of the long-wave one. The extent of this effect again differs from compound to compound. In the presence of up to 10 equivalents of triethylamine the dilution effect is somewhat less pronounced.

The effect of addition of water to solutions of some *mero*cyanines has already been

FIG. 3. *Dependence of the absorption spectra on the temperature. The numbers in the upper left corner denote the compound. Solutions in ethanol.* (2·2-*cm. cells.*)

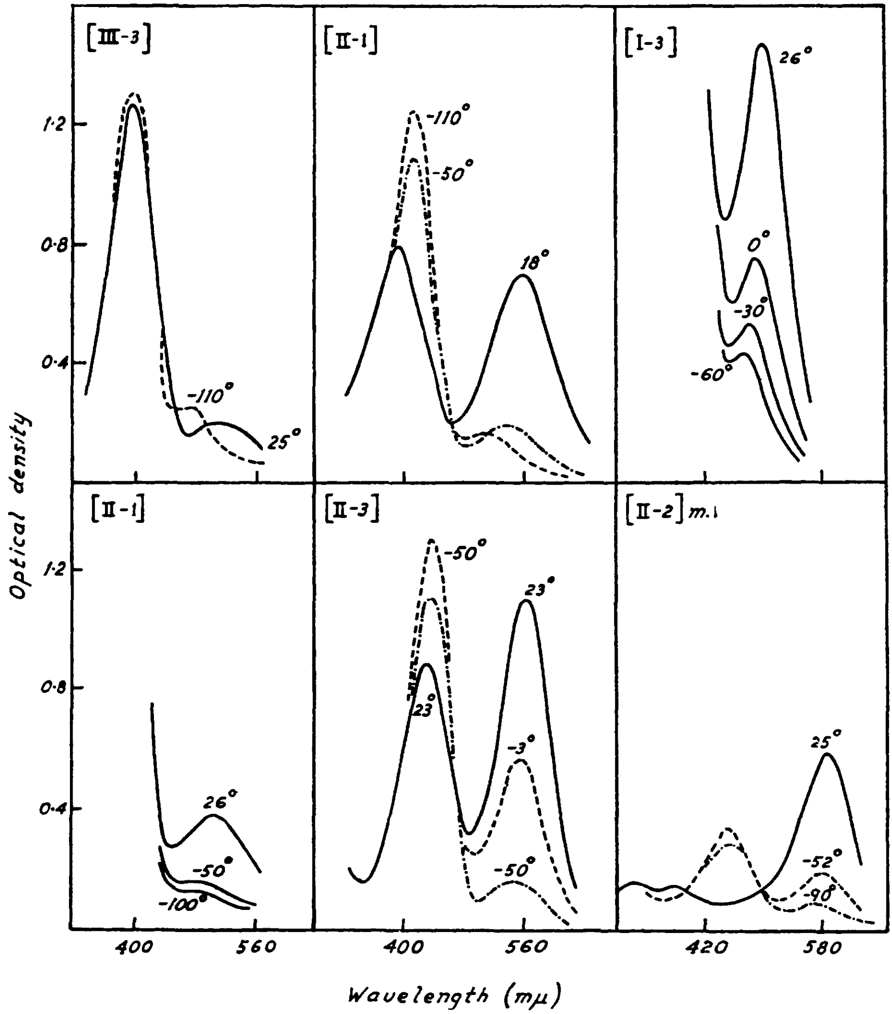


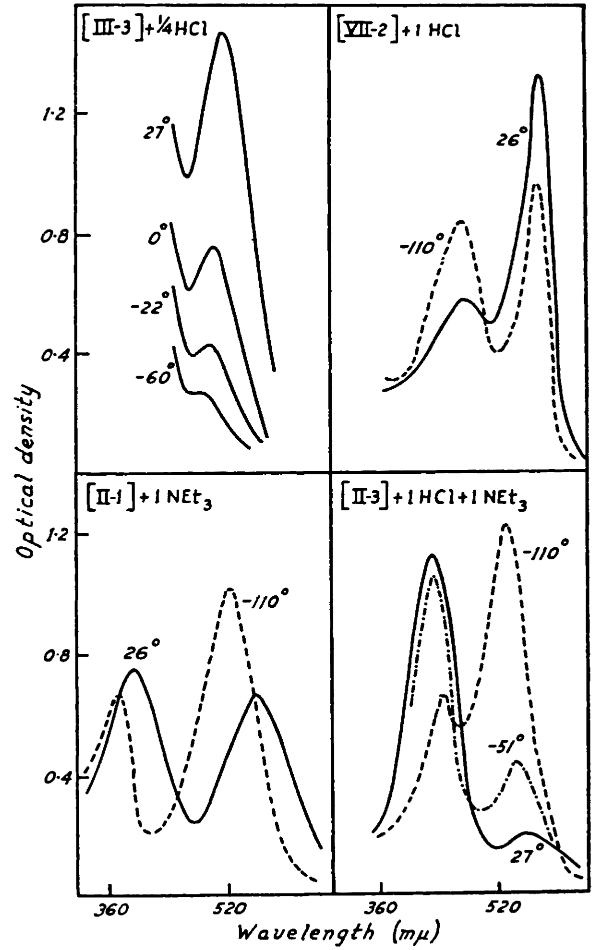
TABLE 4. *Absorption of compounds in group* (b).

Compound	$\lambda_{max.}$ (mμ) [a]	$10^{-3}\varepsilon_{max.}$	Effect of cooling : on ε	Effect of cooling : on λ (mμ)	Effect of H_2O : on ε	Effect of H_2O : on λ (mμ)
[I–8]	540 (520) [b]	85	↑	None	—	—
[II–7]	550	57	None	None	None	535
[II–8]	560, 530	164	Slight ↑	570	—	—
[III–8]	560 (530)	92	,, ↑	None	—	—
[IV–7]	630, 600, 580	109	None	None	—	—
[IV–8]	610, 470	76	Slight ↑	620	[c]	None
[VII–7]	530 (500)	38	—	—	[c]	None
[VIII–6]	490 (460)	134	None	None	↓	None

[a] Wavelength of longest visible band. [b] Wavelengths in parentheses denote inflexions. [c] With increasing percentage of H_2O, ε first rises, then falls.

reported by Brooker (*loc. cit*), who observed that the increased polarity of the solvent, resulting from an increased percentage of water, caused hypsochromic shifts of $\lambda_{\text{max.}}$ (corresponding to our long-wave band) and also changes in the extinction coefficient. Representative cases of the present observations are given in Fig. 2 and show two different phenomena : (1) For compounds of group (*a*) addition of water increases the ratio between the extinction coefficient ε_2 (of the short-wave band) and ε_1 (of the long-wave band). This effect is in all cases suppressed completely by even a small excess of triethylamine. (2) For compounds of both groups (*a*) and (*b*), a hypsochromic shift of the longer-wave band, ranging from 0 to 80 mμ, occurs when 90% of the solvent ethanol is replaced by water. This shift is not affected by addition of excess of triethylamine. A similar effect has been described by Brooker (*loc. cit.*) and is a result of the increased polarity of the solvent containing water. Brooker also described cases in which gradual addition of water at first increased and then decreased ε. A similar case is shown in Fig. 2, compound [IV–8].

FIG. 4. *Dependence of the absorption spectra on the temperature with added acid* (HCl *or* HI) *or base* (*triethylamine*). *The numbers in the upper part denote the compound, followed by the number of equivalents of acid or base added.* (2·2-*cm. cells.*)



The effect of cooling on solutions of compounds in group (*a*) runs parallel to that of water described above; with decreasing temperature both the ratio $\varepsilon_2/\varepsilon_1$ and the hypsochromic shift of λ_1 increase steadily (Fig. 3).[*] The extent of both effects is indicated in

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[*] A preliminary account of the cooling experiments has already been given (Hirshberg and Fischer, *J. Chem. Phys.*, 1954, **22**, 572).

columns 6, 8, and 11 of Table 2, again showing large variations among the compounds investigated. With compound [VII–2] there was even observed a reverse effect, ε_1 rising on cooling. This may be due to the same cause as the initial rise of ε_1 of [IV–8] on the addition of water (see Discussion). Methanol appears to be more effective than ethanol in increasing $\varepsilon_2/\varepsilon_1$ on cooling, as shown by compound [II–2]. The absorption of the latter remains unchanged when its solutions in ethanol are cooled, but is influenced strongly when a solution in a mixture of ethanol and methanol is cooled.

Since both dilution and cooling increase the ratio $\varepsilon_2/\varepsilon_1$ the two phenomena may be expected to be interdependent. The dilution effect was indeed found to be much more pronounced at higher temperatures.

The addition of acid results in occurrence of the cooling effect also for those compounds which are unaffected by cooling of their original solutions (Fig. 4: [VII–2], [III–3]. For [III–3] even $\frac{1}{4}$ equiv. of hydrochloric acid is seen to be sufficient to cause a strong cooling effect).

The influence of triethylamine on the cooling effect is analogous to its influence on the effect of water. Whereas at room temperature even a tenfold excess of triethylamine affects the absorption only slightly (Fig. 1), yet at —100° even 1 equiv. annuls the cooling effect completely and even *raises* the long band considerably in some cases (Fig. 4, compound [II–1], cf. also col. 7, Table 2). When equivalent quantities of hydrochloric acid and triethylamine are added to solutions of the dyes in ethanol, the result at room temperature resembles that of the addition of hydrochloric acid, but at —100° the result is almost equal to that obtained when triethylamine alone is added (Fig. 4, compounds [II–3]). Incidentally, these results show that a solution of the pure dye behaves differently from the same solution to which equivalent quantities of an acid and a (weak) base have been added. It is therefore impossible to liberate the free dye bases *in situ* from their hydriodides and study their properties in solution. This would have been desirable for those dyes which are unstable in the form of their free bases.

DISCUSSION

Compounds of group (*a*), unlike those of group (*b*), are fairly strong bases and readily form salts (II) with mineral acids (Kiprianov and Petrun'kin, *J. Gen. Chem., U.S.S.R.*, 1940, **10**, 600; Brooker *et al., loc. cit.*; Knott, *loc. cit.*). The equilibrium, dye + mineral acid $\rightleftharpoons$ salt, was found to shift to the right with increasing basicity of the dye, increasing total concentration of dye + acid, increasing relative concentration of acid, and decreasing temperature.

When comparing the absorption spectra of these salts, in the presence of the excess of acid, with the absorption of solutions of the free bases, one observes that in all cases the position of the only band of the salts in the visible region coincides with that of the shorter visible band of the bases. This suggests that in solutions of the dye bases the shorter-wave band should also be ascribed to a salt. In a system containing only solvent and solute, such a salt could be formed only between these two, with the solvent alcohol functioning as a very weak acid. The enhancement of the shorter-wave band and suppression of the longer-wave one resulting from the effect of various environmental factors on such solutions may then be ascribed to shifts to the right of the equilibrium, dye + solvent $\rightleftharpoons$ salt, in analogy to the equilibrium, dye + acid $\rightleftharpoons$ salt, described above.

Compound formation between dye and solvent may be expected to occur only with solvents (HX) containing an active hydrogen atom, such as water or alcohols. It was not possible to check this requirement experimentally, because of the difficulty in excluding from other solvents water and alcohols at concentrations comparable with those of the dyes in the solutions investigated.

A strong indication of the correctness of ascribing the short-wave band to the presence of the solute–solvent cation is given by the ratio $\varepsilon_2/\varepsilon_1$ (Table 2, col. 4) found for different dyes. As the basicity of the dye base increases so will the equilibrium (I) $\rightleftharpoons$ (II) be shifted to the right. If solute–solvent interaction occurs, then an increase in such basicity should lead to an increase in the ratio $\varepsilon_2/\varepsilon_1$.

As will be shown below, basicity and polarity of the dyes in general run parallel. The polarity of the dyes increases with increasing $-M$ effect of the nitrogenous nucleus (B) and with increasing $+M$ effect of the ketonic nucleus (C). The relative strengths of the $\pm M$ effects of most of the nuclei given in Table 2 have been determined by Brooker *et al.* (*loc. cit.*). Consequently, it is possible to arrange the dyes of Table 2 in a rough order of polarities. The order given in the Table is that of increasing values of $\varepsilon_2/\varepsilon_1$ in ethanol. It is found that with minor changes this same order agrees with the order of increasing polarities.

*mero*Cyanines derived from heterocyclic ketones (group *b*) are much less polar than those of group (*a*), as is known from absorption data, and indeed they show no tendency to combine with mineral acids or solvents and show no short band.

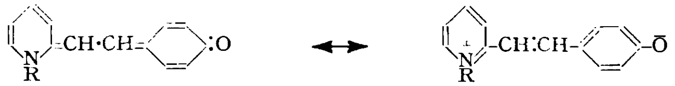
The suppression of the long-wave band of group (*a*) dye bases by dilution with water is somewhat stronger than by dilution with ethanol (cf. III-3, Figs. 1 and 2), indicating a higher stability of the cation hydroxide (II; X = OH) than of the cation ethoxide (II; X = OEt).

The hypsochromic shifts of λ_1 observed on cooling solutions of the dyes are as expected. Brooker *et al.* (1951, *loc. cit.*) have explained this on the basis of a decrease in the dielectic constant or of a stabilization of the orientation of the polar solvent molecules around the solute.

One would also expect the dielectric constant of the solvent to determine the extent to which the equilibrium solvent-solute is affected by the addition of a weak or moderately strong base. This would explain the much stronger effect of added triethylamine in suppressing the short-wave band in ethanol at —100° or in 90% water at 25°, as compared with ethanol at 25°.

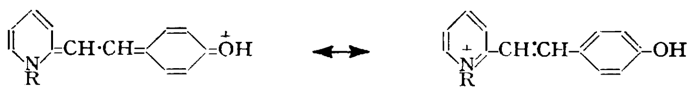
The addition of a proton to the dye molecule (III) to give the cation (IV) will convert the dipolar extreme structure (III*b*) into a more stable cation (IV*b*), and the classical structure (III*a*) into a less stable cation (IV*a*). The effect of this will be twofold. The increased separation of the energy levels of the extreme structures, as shown by the hypsochromic absorption shift, will decrease the resonance energy of the amidic resonance system. This loss of stability will be offset, however, by an increase in the resonance energy (aromatic) of the end nuclei as a result of the increased significance of (IV*b*) over (III*b*) in their respective hybrids. The net effect of proton addition to the dye base may thus either raise or lower the energy of the molecule depending upon the relative strengths of the two effects.

(III*a*)



(III*b*)

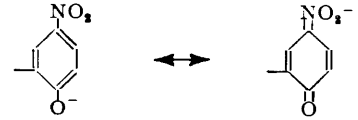
(IV*a*)



(IV*b*)

When the resonance system responsible for the long-wave band of the dyes is degenerate, the decrease of its resonance energy on proton addition will be at a maximum, falling away as the energetic symmetry of the resonance system is lost by increases or decreases in the polarity of the molecule. The greater the contributions, however, by the dipolar extreme structure in the particular solvent used, *i.e.*, the more polar the molecule, the more will the addition of a proton stabilize the molecule. Since all of the dyes of class (*a*) in polar solvents possess a dipolar extreme structure of lower energy than the classical extreme structure (Kiprianov and Petrun'kin, *loc. cit.*; *ibid.*, p. 613; Kiprianov and Timoshenko, *ibid.*, 1947, **17**, 1468; Brooker *et al.*, *loc. cit.*; Knott, *loc. cit.*), the net change in stability on proton addition will be increasingly positive with increasing dye polarity, *i.e.*, an increase in polarity results in an increase in basicity.

The nitro-derivatives described in Table 3 behave anomalously in showing no dilution effect and little fall in ε_1 on cooling. These dyes are more polar than the corresponding dyes without nitro-groups but their behaviour resembles more that of the least polar dye of group (*a*), *e.g.*, [VII-2] (cf. Table 2, col. 6). The reason for this loss of basicity on nitration is probably connected with the increased acidity of nucleus (c). The dipolar extreme structure of dyes derived say from nucleus (5) will be stabilized by the additional resonance system (V*a* ↔ V*b*) resulting in an increase in polarity of the dye over its unnitrated analogue. However, the addition of a proton to $-O^-$ will increase the energetic asymmetry of this resonance system and this loss of resonance energy will discourage proton addition.



(V*a*) (V*b*)

EXPERIMENTAL

Spectrophotometric Technique.—A Beckman model D.U. spectrophotometer was used throughout. The technique of work at reduced temperature has been described previously (Hirshberg and Fischer, *J.*, 1954, 297).

Solvents.—Great care was taken to exclude traces of acid from all the solvents used. Water, acetone, and methanol were distilled from potassium hydroxide; ethanol was refluxed over quicklime in the usual way.

Dyes and Dye Salts.—The dye [VII–2] was prepared according to the method of Witzinger and Wenning (*Helv. Chim. Acta*, 1940, **23**, 247); [II–3] and [VI–3] according to the method of Kiprianov and Petrun'kin (*loc. cit.*); [VII–5] according to the method of Kiprianov and Timoshenko (*loc. cit.*); [II–4], [VII–4], [VIII–4], [II–5], [III–5], [II–1], [I–1], [III–1], and [VIII–6] according to the method of Knott (*loc. cit.*); and [II–7], [V–7], and [VII–7] according to the method of Aubert, Knott, and Williams (*J.*, 1951, 2185). The dyes [I–8], [II–8], [III–8], and [IV–8] were prepared by condensation of the required 2(or 4)-methyl derivative of the heterocyclic quaternary salt with 3-ethoxycarbonylmethyl-5-ethoxymethylenerhodanine in alcoholic triethylamine and recrystallized from ethanol or benzene–ethanol.

1-*Ethyl*-1 : 4-*dihydro*-4-(4-*oxo*cyclo*hexadienylidene-ethylidene*)*quinoline* [IV–3].—Lepidine ethiodide (1·5 g., 0·005 mol.), *p*-hydroxybenzaldehyde (1·25 g., 0·01 ml.), methanol (10 c.c.), and piperidine (0·3 c.c.) were refluxed for 2 hr., and the mixture was chilled overnight. The styryl salt (1·55 g., 39%) which separated was heated on a steam bath with 2N-aqueous sodium carbonate until an oil separated and crystallized rapidly (1·2 g.). From water, then from methanol–ether, it formed deep blue needles of indefinite m. p., becoming bronze-coloured on drying at 95°/15 mm. (Found : C, 65·8; H, 7·4; N, 3·95. $C_{19}H_{17}ON,H_2O$ requires C, 65·7; H, 7·2; N, 4·05%).

1-*Ethyl*-1 : 2-*dihydro*-2-(4-*oxo*cyclo*hexadienylidene-ethylidene*)*pyridine* [I–3].—α-Picoline ethiodide (2·5 g., 0·01 ml.), *p*-hydroxybenzaldehyde (2·5 g., 0·02 mol.), methanol (15 c.c.), and piperidine (0·5 c.c.) were refluxed for 3 hr. The yellow crystals (2·3 g., 66%) of 2-p-*hydroxystyrylpyridine ethiodide* which separated formed yellow needles, m. p. 248°, from methanol (Found : I, 36·0. $C_{15}H_{16}ONI$ requires I, 36·1%). It (2·0 g.) was dissolved in hot 2N-aqueous sodium carbonate (25 c.c.) and the solution on chilling gave orange needles. From hot water (solution red when hot, yellow when cold) it formed yellow needles, m. p. 90°. On drying *in vacuo* over potassium hydroxide the needles became red (m. p. indefinite) but in moist air they regained their original colour (Found : C, 54·4; H, 7·9; N, 4·3. $C_{15}H_{15}ON,6H_2O$ requires C, 54·0; H, 8·1; N, 4·2%).

1-*Ethyl*-1 : 4-*dihydro*-4-(4-*oxo*cyclo*hexadienylidene-ethylidene*)*pyridine* (III–3) was obtained similarly. The red plates which separated from the sodium carbonate solution on chilling formed light purple plates from water. They formed maroon needles, m. p. 207°, from methanol–ether (Found : C, 60·6; H, 8·1; N, 4·9. $C_{15}H_{15}ON,4H_2O$ requires C, 60·6; H, 7·75; N, 4·7%).

The intermediate 4-p-*hydroxystyrylpyridine ethiodide* formed flat reddish plates, m. p. 193°, from ethanol (Found : I, 36·3. $C_{15}H_{16}ONI$ requires I, 36·1%).

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