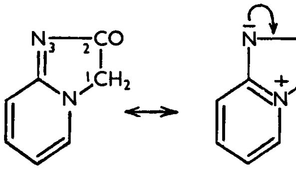
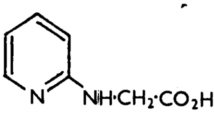
275. *The Colour of Organic Compounds. Part VIII.* A Comparison of Isomeric Dyes from 3 : 7a-Diazaindan-1-one and -2-one.*

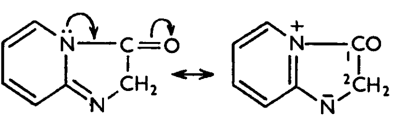
By EDWARD B. KNOTT.

N-2-Pyridylaminoacetic acid (II) has been cyclized by phosphorus trichloride to 3 : 7*a*-diazaindan-1-one (III). The latter contains a nucleophilic methylene-carbon atom and has been converted into methin and dimethin dyes. The absorptions of these dyes have been compared with those of isomeric dyes derived from 3 : 7*a*-diazaindan-2-one (I), and the differences explained on the basis of the author's colour rule.[1]

DYES derived from 3 : 7*a*-diazaindan-2-one (I) have been described [2] and it was of interest to compare their spectral properties with those of isomers derived from 3 : 7*a*-diazaindan-1-one (III). The required precursor of the amide (III) is *N*-2-pyridylaminoacetic acid (II), which has been obtained by acid hydrolysis of the readily accessible *N*-2-pyridylaminoacetonitrile.[3]


(I) (I*a*)

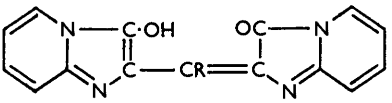

(II)


(III) (III*a*)

Whereas the diazaindan-2-one (I) is usually obtained by heating 1 : 2-dihydro-2-imino-1-pyridylacetic acid [the isomer of (II)] with mineral acid,[4] the acid (II) is less readily cyclized. With phosphorus trichloride at 95—100°, however, practically quantitative yields of the hydrochloride of the amide (III) are obtained. The hydrochloride is deliquescent and unstable towards water or alcohols. Conversion into dyes is, therefore, best carried out in a solvent such as pyridine.

In this solvent and in the presence of triethylamine, the diazaindan-1-one hydrochloride (cf. III) readily condenses with 2-2′-acetanilidovinyl- or 2-alkylthio-derivatives of cyclic quaternary ammonium salts, to yield *mero*cyanine salts or bases, with *p*-dimethylaminobenzaldehyde to give the benzylidene derivative, and with 5-ethoxymethylene-3-ethylrhodanine to give an unsymmetrical oxonol.

Attempts to cyclize the hydrochloride of the acid (II) with hot acetic anhydride gave a dye forming intensely blue solutions in neutral solvents and magenta solutions in acetic or mineral acids. This is believed to be the *meso*methyloxonol (IV; R = Me), possessing properties almost identical with those of the unsubstituted oxonol (IV; R = H) obtained by treating the diazaindan-1-one hydrochloride with ethyl orthoformate in pyridine. These dyes are strongly adsorbed by proteins.


(IV)

The Absorption of Isomeric Dyes.—The Table shows the absorption, in three solvents of differing polarities, of a series of dimethin*mero*cyanines (V) and (VI), and of the oxonol anions and of the p-dimethylaminobenzylidene derivatives of the diazaindanones (I) and (III). Both *p*-dimethylaminobenzylidene derivatives show bathochromic shifts when solvent polarity is increased. This is expected, as related dyes are known to be energetically, highly asymmetric,[5] the energy of the dipolar extreme structure being

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* Part VII, *J.* 1952, 4762.

[1] Knott, *J.*, 1951, 1024.

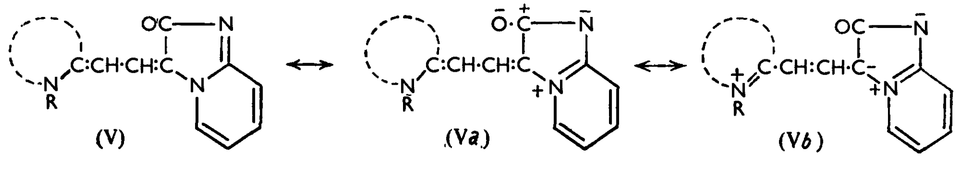
[2] (*a*) Van Dormael, *Bull. Soc. chim. France*, 1949, **58**, 167; (*b*) Knott, *J.*, 1951, 3033.

[3] Bristow, Charlton, Peak, and Short, *J.*, 1954, 616.

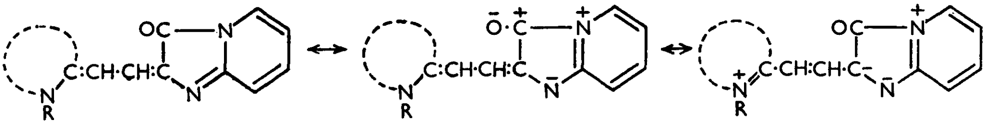
[4] Reindel, *Ber.*, 1924, **57**, 1381.

[5] Brooker, Keyes, Sprague, Van Dyke, Van Lare, Van Zandt, White, Cressman, and Dent, *J. Amer. Chem. Soc.*, 1951, **73**, 5332.

higher than that of the classical structure. Whereas the shift of the 1-ketone dye when the solvent is changed from pyridine to aqueous pyridine is only 5 mμ, that of the isomer is 31 mμ. This suggests that the former dye is much nearer to the isoenergetic point, as would be expected on the basis of the higher $+M$ effect of the 1-amide (III) compared with the isomer (I) (see below) and of the following considerations. A model of the benzylidene derivative of the 2-amide (I) shows that the two ring systems cannot be coplanar without serious bending of the bridge bond. This overcrowding can best be relieved by the rotation of the bridge bond attached to the phenylene group, which will increase still further its single-bond character and the energetic asymmetry of the molecule, with a resultant hypsochromic effect. On the other hand the deviation [6] from the calculated degenerate mean value is $+44$ mμ in both cases. This may mean that either the latter value for the 1-amide is too high or that for the isomer is too low. That the latter alternative is almost certain to be true is shown by models and by Fig. 1, a scale drawing of the 2-oxo-oxonol, the value of the absorption of which partly determines the value of the calculated degenerate value of the dye in question. The marked overcrowding of the two oxygen atoms must result in a considerable distortion of the diazaindan-2-one nuclei from coplanarity. The oxonol anion would contain a degenerate resonance system if it were a planar molecule, and it is known that small distortions of the bonds of such a system cause bathochromic shifts. When, however, large distortions occur, sufficient to weaken seriously the π-electron overlap in the system, then a loss of energetic symmetry would result, with a resultant hypsochromic shift. The 1-oxo-oxonol, on the other hand, has, as Fig. 2 shows, a planar molecule.



(V) (Va) (Vb)



(VI) (VIa) (VIb)

FIG. 1.

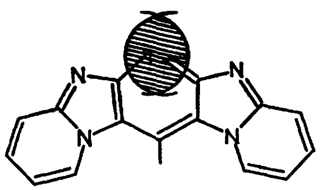
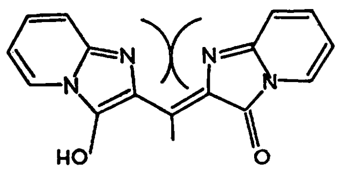


FIG. 2.



With the exception of the dye (V) derived from 3-ethylbenzoxazoline all the planar *mero*cyanines (V) and (VI) show hypsochromic shifts with increasing solvent polarity (see also Knott [2b]). In general, the shift is larger for the 1-oxo-dye. In the Table, the $-M$ effect of nuclei A and consequently the polarity of the dyes increase on proceeding down the column. The least polar of these dyes, from 3-ethylbenzoxazoline and the 2-amide, still shows a slight bathochromic shift with increasing solvent polarity but this shift is reversed to hypsochromic in its isomer from the 1-amide. This indicates that in the latter case the dipolar extreme structure of the dye is of lower energy than the classical structure and must result from the higher $+M$ effect of diazaindan-1-one (III) compared with that

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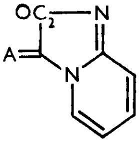
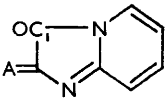
[6] Brooker and Sprague, *J. Amer. Chem. Soc.*, 1941, **63**, 3243.

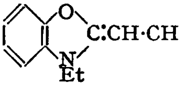
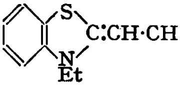
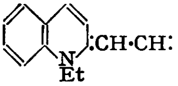
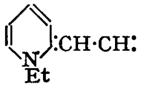
of the isomer (I). The bathochromic shift of the above dye from the 2-amide is again reversed on replacing 3-ethylbenzoxazoline by 3-ethylbenzothiazoline. This indicates that the latter nucleus has a higher $-M$ effect than the former. Brooker *et al.*,[5] from deviation studies, have shown that this is not always the case, which is more often the reverse.

Proceeding down the Table from 3-ethylbenzoxazoline in the 1-oxo-series and from 3-ethylbenzothiazoline in the 2-oxo-series the energetic asymmetry of the dyes should increase with a resultant increase in the *positive* deviation (to shorter wavelengths) from the calculated mean wavelength. As the Table shows, however, the deviation for all dyes is *negative*, the value decreasing for the 1-oxo-dyes on moving down the Table but increasing for the 2-oxo-dyes.

Absorption of the mero*cyanines* (V) *and* (VI), *etc.*





A	Position of CO	$\lambda_{max.}$ (mμ)			Calc. degenerate mean	Deviation
		Pyridine	Ethanol	Pyridine–H_2O (1 : 4)		
p-$NMe_2\cdot C_6H_4\cdot CH$:	1	520, 560	520, 562	532, 565	604	+44
	2	480	495	511	555	+44
 C:CH·CH: N Et	1	538, 575	522, 558	522, 550	545	−30
	2	497	498	505	496	−8
 C:CH·CH: N Et	1	563, 605	555, 593	555, 590	582	−23
	2	(513i), 548	538	537	532	−16
 :CH·CH: N Et	1	578, 620	600	594	606	−14
	2	557, 595	569	563	556	−39
 :CH·CH: N Et	1	592, (620i)	562	536	583	—9
	2	570	536	516	534	—36
Oxonol *	1	—	560, 606	—	—	—
(cf. IV; R = H)	2	—	507	—	—	—

* In alcoholic triethylamine. i = inflexion.

If, as discussed above, the calculated degenerate mean for the 2-oxo-*mero*cyanines is lower than the true mean because of the non-planarity of the 2-oxo-oxonol, then the true deviation in the case of the 2-oxo-dyes might well be positive in all cases. This would then lead to decreasing positive deviations on descending the Table, *i.e.* on increasing the dye polarity, which is the reverse of normal. A plausible explanation of these phenomena is lacking.

What is more easily understood is the fact that in isomeric pairs the dyes from the diazaindan-1-one in any particular solvent are deeper in colour than those from the isomer. If one considers the ketonic fragments of these dyes the most important reasonance systems will be (i) (I ⟷ I*a*) and (III ⟷ III*a*) of the amidine-type, in the dipolar form of which, aromaticity of the pyridine ring results, and (ii) the amide-type resonance denoted by the curved arrows in (I*a*) and (III). In the diazaindan-2-one (I) the operation of (ii) is dependent on the operation of (i), whilst in the isomer (III) (ii) and (i) are mutually opposed. This would be expected to endow the compound (III) with a stronger $+M$ effect than its isomer and thus give more polar dyes. The resonance (i) will also have a profound effect on the energies of the excited structures of the dyes. Important contributing structures in these *mero*cyanines in the absence of (i) are contained in (V*a*), (V*b*), and in (VI*a*), (VI*b*). The operation of (i) then increases the significance of forms (V*a* and *b*) by the stabilizing influence of adjacent atoms of unlike charge, but decreases the significance of forms (VI*a* and *b*) by virtue of the presence of atoms of like charge. According to the author's colour rule [1] the operation of (i) will cause a hypsochromic shift in the dye (V) and a bathochromic shift for the dye (VI); *i.e.*, it will result in a higher intrinsic colour value for the diazaindan-1-one than for the isomer (I), as is the case.

EXPERIMENTAL

N-2-*Pyridylaminoacetic Acid Hydrochloride.*—*N*-2-Pyridylaminoacetonitrile [3] (53 g.) and 5N-hydrochloric acid (250 c.c.) were heated on a steam-bath for 90 min. and then evaporated to dryness. The crystalline cake was ground to a powder and extracted with hot methanol. The extract was evaporated to dryness and the residue was treated with 5N-hydrochloric acid (100 c.c.) as above. The solution was concentrated until a thick meal of crystals separated. These were made into a slurry in propan-2-ol, chilled, and collected. The *hydrochloride* (57 g., 76%) formed almost colourless needles, m. p. *ca.* 190° with previous darkening, from methanol–ether or water (Found: C, 44·2; H, 5·0; N, 14·7; Cl, 18·65. $C_7H_9O_2N_2Cl$ requires C, 44·55; H, 4·75; N, 14·85; Cl, 18·85%). A solution of the hydrochloride (18·85 g.) and sodum hydrogen carbonate (8·4 g.) in boiling water (50 c.c.) solidified on chilling. The free *amino-acid* was washed with a little ice-water and recrystallized from water as colourless needles (12·8 g., 84%), softening at 120° and 165° with m. p. 175° (green), the needles breaking to a powder when washed with methanol (Found: C, 49·1; H, 5·6; N, 16·5. $C_7H_8O_2N_2,H_2O$ requires C, 49·45; H, 5·9; N, 16·45%).

3 : 7a-*Diazaindan*-1-*one Hydrochloride.*—*N*-2-Pyridylaminoacetic acid hydrochloride (10 g.) and phosphorus trichloride (50 c.c.) were heated under reflux on a steam-bath for 3 hr. The solid slowly dissolved, a transitory pink coloration occurred, and crystals slowly separated. Ether (100 c.c.) was added and the pale green grains were collected. They were difficult to purify and had m. p. *ca.* 190° (decomp.) (Found: N, 15·9; Cl, 20·3. $C_7H_7ON_2Cl$ requires N, 16·4; Cl, 20·85%).

Bis-(3 : 7a-*diaza*-2-*indan*-1-*one*)meso*methylmethinoxonol* (IV; R = Me).—*N*-2-Pyridylaminoacetic acid hydrochloride (5·0 g.) dissolved under reflux in acetic anhydride (10 c.c.) to a yellow solution which rapidly became magenta. The mixture was then allowed to cool to 40°, decomposed by water (50 c.c.), and cooled to 20°, and the dye was precipitated by addition of ammonia. The *product* (1·1 g., 28·4%) formed bronze-green needles, of indefinite m. p., from butanol (Found: C, 65·7; H, 3·85; N, 18·95. $C_{16}H_{12}O_2N_4$ requires C, 65·8; H, 4·1; N, 19·2%).

Bis-(3 : 7a-*diaza*-2-*indan*-1-*one*)*methinoxonol* (IV; R = H).—3 : 7*a*-Diazaindan-1-one hydrochloride (1·7 g.), pyridine (10 c.c.), and ethyl orthoformate (2 c.c.) were heated over a flame for 2—3 min. The dye separated from the blue solution during this time. The dye, collected from the chilled solution, was dissolved in boiling water containing a little acetic acid, and dilute aqueous ammonia was added slowly. The green flakes (0·55 g., 39·5%) which separated were recrystallized from ethanol, and the *dye* was then obtained as green needles, decomp. from 240° (Found: C, 64·8; H, 3·85; N, 19·75. $C_{15}H_{10}O_2N_4$ requires C, 64·75; H, 3·6; N, 20·15%).

[3 : 7a-*Diaza*-2-*indan*-1-*one*][3-*ethyl*-2-*thio*-5-*thiazolid*-4-*one*]*methinoxonol.*—3 : 7*a*-Diazaindan-1-one hydrochloride (0·85 g.), 5-ethoxymethylene-3-ethylrhodanine (1·1 g.), pyridine (20 c.c.), and triethylamine (0·8 c.c.) were refluxed for 30 min., then poured into water and chilled overnight. The aqueous layer was decanted from the tar, and the latter was dissolved in ethanol and acidified with acetic acid. The crystals which separated (1·0 g., 65%) were dissolved in aqueous 2N-sodium carbonate and reprecipitated with acetic acid. The *oxonol* was then dissolved in alcoholic triethylamine, and addition of alcoholic acetic acid gave green needles, m. p. indefinite (Found: N, 13·6; S, 21·15. $C_{13}H_{11}O_2N_3S_2$ requires N, 13·75; S, 21·0%).

2-(3-*Ethylbenzoxazolin*-2-*ylidene-ethylidene*)-3 : 7a-*diazaindan*-1-*one.*—The hydrochloride (1·7 g.) of the indanone (III), 2-2′-acetanilidovinylbenzoxazole ethiodide (4·35 g.), pyridine (15 c.c.), and triethylamine (1·6 c.c.) were heated on a steam-bath for 15 min. Addition of aqueous sodium carbonate precipitated the *dye base* (51%), forming brown-green threads, m. p. 237—238°, from benzene–light petroleum (b. p. 60—80°) (Found: C, 71·1; H, 5·15; N, 13·6. $C_{18}H_{15}O_2N_3$ requires C, 70·85; H, 4·9; N, 13·75%). Its *hydrochloride*, obtained by passing hydrogen chloride into a solution of the base in benzene, formed magenta needles, m. p. 259—262°, from methanol–ether (Found: Cl, 10·3. $C_{18}H_{15}O_2N_3,HCl$ requires Cl, 10·4%).

2-(3-*Ethylbenzothiazolin*-2-*ylidene-ethylidene*)-3 : 7a-*diazaindan*-1-*one.*—Obtained similarly, in 56% yield, this *dye* formed green needles, m. p. 260° (soften at 230°), from methanol (Found: C, 67·1; H, 4·9; N, 12·95. $C_{18}H_{15}ON_3S$ requires C, 67·3; H, 4·65; N, 13·1%). Its *ethiodide* was obtained in 95% yield in refluxing benzene (2 hr.) as green needles, m. p. 247° (Found : N, 8·55; I, 26·85. $C_{20}H_{20}ON_3IS$ requires N, 8·8; I, 26·6%).

2-(1-*Ethyl*-1 : 2-*dihydroquinolin*-2-*ylidene-ethylidene*)-3 : 7a-*diazaindan*-1-*one* was similarly obtained in 70% yield as green needles, m. p. 197°, from methanol (Found : C, 76·1; H, 5·2; N, 13·2. $C_{20}H_{17}ON_3$ requires C, 76·2; H, 5·4; N, 13·35%).

2-(1 : 2-*Dihydro*-1-*methylpyrid*-2-*ylidene-ethylidene*)-3 : 7a-*diazaindan*-1-*one Dihydrate.*—2-2′-Anilinovinylpyridine methiodide (3·4 g.), the hydrochloride (1·7 g.) of the amide (III), pyridine (10 c.c.), triethylamine (3 c.c.), and acetic anhydride (1 c.c.) were heated on a steam-bath for 1 hr. The solution gradually became blue. Water (25 c.c.) was added and the orange solution so formed was evaporated almost to dryness. The solid (2·0 g.) was washed with cold water, and dissolved in boiling water, the solution being then filtered and basified with aqueous sodium carbonate. The *dye base* was collected from the chilled solution as green-brown threads, m. p. 124—125° (from water) (Found: C, 62·8; H, 5·8; N, 14·45. $C_{15}H_{13}ON_3,2H_2O$ requires C, 62·75; H, 5·9; N, 14·65%).

2-(3-*Methylbenzothiazolin*-2-*ylidene*)-3 : 7a-*diazaindan*-1-*one.*—2-Ethylthiobenzothiazole ethotoluene-*p*-sulphonate (2·0 g.), the hydrochloride (0·85 g.) of the amide (III), pyridine (10 c.c.), and triethylamine (1·5 c.c.) were heated on a steam-bath for 15 min. Precipitated with aqueous sodium carbonate, the *dye base* (54% yield) formed orange needles, m. p. 256°, from benzene–ethanol (Found : C, 65·2; H, 4·2; N, 14·2. $C_{16}H_{13}ON_3S$ requires C, 65·0; H, 4·4; N, 14·25%).

2-(1 : 2-*Dihydro*-1-*methylquinolin*-2-*ylidene*)-3 : 7a-*diazaindan*-1-*one*, obtained similarly in 58% yield, formed olive-green needles, m. p. 190°, from methanol (Found : C, 74·4; H, 4·9; N, 15·15. $C_{17}H_{13}ON_3$ requires C, 74·15; H, 4·75; N, 15·3%).

2-p-*Dimethylaminobenzylidene*-3 : 7a-*diazaindan*-1-*one.*—*p*-Dimethylaminobenzaldehyde (1·5 g.), the hydrochloride (1·7 g.) of the amide (III), pyridine (10 c.c.), and triethylamine (1·5 c.c.) were heated on a steam-bath for 30 min. Addition of aqueous sodium carbonate gave 1·2 g. (45%) of *dye*, forming purple needles, m. p. 199°, from ethanol (Found : C, 72·4; H, 5·8; N, 15·65. $C_{16}H_{15}ON_3$ requires C, 72·4; H, 5·65; N, 15·85%).

The author thanks Mrs. M. E. Weston for the preparation of some of the intermediates, Mr. C. B. Dennis for microanalyses, and Mr. R. Searle for absorption measurements.

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[*Received, October 20th,* 1955.]