358. *The Colour of Organic Compounds. Part III.* A New Method of Assessing the ±M Effect of Heterocyclic Nuclei.*

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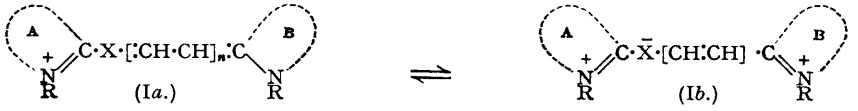
It is shown that the $\pm M$ effects of various heterocyclic nuclei found in cyanine dyes may, with certain exceptions, be assessed in order of increasing strength by a consideration of the absorption shifts resulting on replacement of methin groups by nitrogen atoms in the chromophoric chain of dyes containing these nuclei.

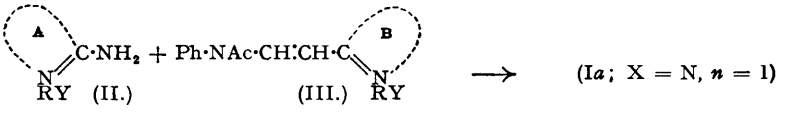
Brooker (*Rev. Mod. Physics*, 1942, **14**, 275; "Advances in Nuclear and Theoretical Organic Chemistry," Interscience Publ. Inc., New York, 1945, Chap. 4) has shown that the $\pm M$ effects of the heterocyclic nuclei contained in cyanine dyes may be set in the order of their relative strengths by his "deviation" method. A second method has now been established which uses as its basis the absorption shift resulting on the replacement of a methin group by a nitrogen atom in the chromophoric system of certain dyes and intermediates.

In Part I (*J.*, 1951, 1024) it was suggested, on the basis of a general rule, that the hypsochromic shift resulting from the replacement of X = CH by X = N in (I*a*; $n = 0$) was primarily caused by the resulting increased significance of the excited structure (I*b*; $n = 0$). In order that the



latter structure may contribute to the resonance hybrid, charge separation is required and the necessary energy involved is offset by the gain in resonance energy of the nucleus (B) on acquiring an additional double bond. Since the latter free-energy change is a function of the $-M$ effect of this nucleus it would be expected that the significance of (I*b*) and the hypsochromic shift experienced in this structural change would increase with increasing $-M$ effect of the nucleus (B).

Table I illustrates this effect in the carbocyanine series, in each set of which nucleus A is constant. The nuclei are given in the order given by Brooker (*loc. cit.*), *i.e.*, of ascending $-M$ effect ("basicity") on proceeding down the table. In general, the order is in fair agreement with that found by Brooker. The exceptions are shown by the low values of the shift for the 1-ethyl-2-quinoline and, in one case, of the 1-ethyl-2-pyridine nuclei, the high value for the 3-ethyl-4-methylthiazole nucleus in the second set, and the reversed order of benzothiazole and benzoselenazole.



The required α-azacarbocyanines were readily obtained by condensing the amino-quaternary salt (II) with the required acetanilidovinyl derivative (III).

In the cyanine series it is found that the shift in the absorption maximum of (IV) on replacing X = CH (max., 422 mμ.) by X = N (max., 368 mμ.) is less (54 mμ.) than in the case of (V) (X = CH, max. = 522 mμ.; X = N, max. = 424 mμ.; Hamer, *J.*, 1924, **125**, 1348), *i.e.*, 98 mμ. Although this is consistent with the higher $-M$ effect of the nuclei in (V) (cf. Brooker) the reverse is true in the carbocyanine series (Table I; cf. Table II). It would appear therefore that in the latter

* Part II, *J.*, 1951, 1028.

TABLE I.

(I*a*) ; $\lambda_{max.}$ (mμ.) *in methanol.*

Nucleus B.	Nucleus A, 3-Ethylbenzothiazole. No.	X = CH.	X = N.	Shift.	Nucleus A, 1-Ethyl-2-quinoline. No.	X = CH.	X = N.	Shift.
1 : 3 : 3-Trimethylindolenine	I	536	478	58	XI	550	483	67
3-Ethylthiazoline	II	502	427	75	XII	526	446	80
3-Ethylbenzoxazole	III	521 *	449	72	XIII	545 *	464	81
3-Ethylbenzoselenazole	V	562 *	466	96	XV	582 *	486	96
3-Ethylbenzothiazole	IV	557 *	465	92	XIV	578 †	489	89
3-Ethylnaphtho(1′ : 2′-4 : 5)thiazole	VI	577 *	483	94	XVI	600 *	496	104
1-Ethyl-2-quinoline	VIII	578 †	488	90	XVIII	605 *	519	86
3-Ethyl-4-methylthiazole	VII	550	448	102	XVII	583	460	123
1-Ethyl-4-quinoline	IX	630 *	513	117	XIX	656 *	555	101
1-Ethyl-2-pyridine	X	535	427	108	XX	578	468	110

Nucleus B.	Nucleus A, 3-Ethyl-4-methylthiazole. No.	X = CH.	X = N.	Shift.
1 : 3 : 3-Trimethylindolenine	XXI	516	469	47
3-Ethylthiazoline	XXII	493	427	66
3-Ethylbenzoxazole	XXIII	508	439	69
3-Ethylbenzoselenazole	XXV	554	473	81
3-Ethylbenzothiazole	XXIV	550	472	78
3-Ethylnaphtho(1′ : 2′-4 : 5)thiazole	XXVI	569	489	80
1-Ethyl-2-quinoline	XXVIII	583	500	83
3-Ethyl-4-methylthiazole	XXVII	548	449	99
1-Ethyl-4-quinoline	XXIX	645	534	111
1-Ethyl-2-pyridine	XXX	557	413	144

* Beilenson, Fisher, and Hamer, *Proc. Roy. Soc.*, 1937, **163**, 138.
† Brooker and Sprague, *J. Amer. Chem. Soc.*, 1941, **63**, 3203.

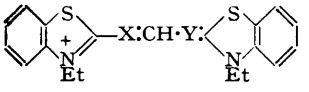
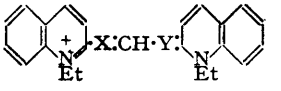
TABLE II.

$\lambda_{max.}$ (mμ.).

Dye.	X = Y = CH.	X = CH, Y = N.	X = Y = N.	Shift Y = CH → Y = N.	Shift X = CH, Y = N → X = Y = N.
VI	557	465	370	92	95
VII	605	519	430 *	86	89

* Fisher and Hamer, *J.*, 1937, 907, give $\lambda_{max.}$ = 343 mμ.

series the shift given by dyes containing a quinoline nucleus is anomalous. This is further illustrated on replacement of a second methin group by nitrogen, as in (VI) and (VII). Table II shows that the replacement shift on replacing each methin group in turn is roughly constant in each series but greater for (VI) than for (VII).

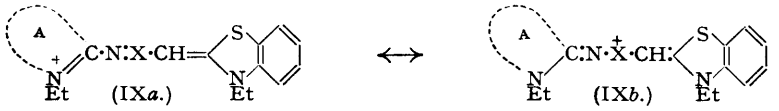
(VI.)   (VII.)

Similar considerations may be applied to the case of the β-anilinovinyl derivatives (VIII; X = CH) and the β-aza-analogues (VIII; X = N). In this case, however, the most likely excited structure (see Part I, *loc. cit.*) involves $-\overset{+}{X}-$ and not $-\overset{-}{X}=$ as in (I), so that the replacement

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

of X = CH by X = N will result in a bathochromic shift. The significance of structure (VIII*b*) will thus decrease with increasing $-M$ effect of the heterocyclic nucleus, so that the larger shift in this case should be given by the nucleus with the weaker $-M$ effect. Table III shows this to be true.

If in the molecule of (I*a*; X = N) the central chain atom is replaced by nitrogen the azo-compound (IX*a*; X = N) results. As in the case of (VIII), since structures involving $-\overset{+}{\underset{-}{X}}-$ (*i.e.*, IX*b*) will be more important than those involving $-\underset{-}{\overset{+}{X}}-$, the replacement shift will be



bathochromic. The magnitude of the shift will similarly decrease with decreasing $+M$ effect (increasing $-M$ effect) of the nucleus A. Table IV shows this to be the case.

Again it is found that the $+M$ effect of the 3-ethylbenzothiazolium nucleus is weaker than that of the selenium analogue (cf. Brooker, *loc. cit.*).

TABLE III.

(VIII); $\lambda_{max.}$ (mμ.) *in methanol.*

Nucleus A.	X = CH.	X = N.	Shift.
1 : 3 : 3-Trimethylindolenine	409	438	29
1-Ethyl-2-quinoline	443	463	20
1-Ethyl-2-pyridine	412	423	11
1-Ethyl-4-quinoline	484	490	6
1-Ethyl-4-pyridine	427	432	5

TABLE IV.

(IX); $\lambda_{max.}$ (mμ.) *in methanol.*

Nucleus A.	X = CH.	X = N.*	Shift.
3-Ethylbenzothiazole	465	495	30
3-Ethylbenzoselenazole	466	486	20
1-Ethyl-2-quinoline	488	497	9

* Fisher and Hamer, *loc. cit.*, give 480, 486, and 480 mμ. respectively.

TABLE V.

Dye (X = N; Table I).	Appearance.	M. p.	Formula.	Found, %. N.	Found, %. I.	Required, %. N.	Required, %. I.
I	Magenta plates *	225°	$C_{22}H_{24}O_4N_3ClS$ [1]	9·15	—	9·1	—
II	Yellow needles	224	$C_{16}H_{20}N_3S_2I$	9·6	28·5	9·45	28·55
III	Orange needles	232	$C_{20}H_{20}ON_3SI$	8·85	25·8	8·8	26·6
IV	Brown needles	268	$C_{20}H_{20}N_3S_2I$	—	25·5	—	25·8
V	Flat rust-coloured needles	278	$C_{20}H_{20}N_3SSeI$	—	23·2	—	23·5
VI	Green crystals	248	$C_{24}H_{22}N_3S_2I$	—	23·7	—	23·4
VII	Orange-brown prisms	257	$C_{17}H_{20}N_3S_2I$	—	28·1	—	27·8
VIII	Flat blue needles	228	$C_{22}H_{22}N_3SI$	—	26·3	—	26·1
IX	Red needles	240	$C_{22}H_{22}N_3SI$	—	26·2	—	26·1
X	Orange crystals *	215	$C_{18}H_{20}O_4N_3SCl$	10·2	—	10·3	—
XI	Red needles *	217	$C_{24}H_{26}O_4N_3Cl$	8·8	—	9·25	—
XII	Orange tablets	205	$C_{18}H_{22}N_3SI$	—	29·3	—	28·9
XIII	Orange needles	249	$C_{22}H_{22}ON_3I$	—	27·3	—	27·0
XIV	Violet needles	271	$C_{22}H_{22}N_3SI$	8·45	26·2	8·65	26·1
XV	Violet needles	267	$C_{22}H_{22}N_3SeI$ [2]	—	24·3	—	23·8
XVI	Bronze crystals	253	$C_{26}H_{24}N_3SI$	7·95	24·4	7·85	23·65
XVII	Garnet needles	230	$C_{19}H_{22}N_3SI$	—	27·8	—	28·15
XVIII	Flat blue needles	263	$C_{24}H_{24}N_3I$	7·85	25·8	7·55	26·4
XIX	Dark red needles	100—101	$C_{24}H_{24}N_3I,C_2H_5·OH$ [3]	—	23·8	—	24·1
XX	Red needles *	237	$C_{20}H_{24}O_4N_3Cl$	10·4	—	10·4	—
XXI	Blue plates *	211	$C_{19}H_{24}O_4N_3SCl$	9·65	—	9·85	—
XXII	Long orange needles	250	$C_{13}H_{20}N_3SI$	9·9	—	10·25	—
XXIII	Small orange needles	203	$C_{17}H_{20}ON_3SI,3MeOH$	7·65	—	7·80	—
XXIV	Red amorphous powder	252	$C_{17}H_{20}N_3S_2I$	9·0	—	9·25	—
XXV	Maroon needles	263 (dec.)	$C_{17}H_{20}N_3SSeI$	7·85	—	8·3	—
XXVI	Brown needles	239	$C_{21}H_{22}N_3S_2I$	8·0	—	8·3	—
XXVII	Small maroon crystals	220 (dec.)	$C_{14}H_{20}N_3S_2I$	9·6	—	10·0	—
XXVIII	Brown powder *	225	$C_{19}H_{22}O_4N_3SCl$	9·8	—	9·9	—
XXIX	Green needles	219	$C_{19}H_{22}N_3SI$	9·6	—	9·3	—
XXX	Yellow plates	161	$C_{15}H_{20}O_4N_3SCl,3EtOH$ [4]	8·0	—	8·2	—

* Perchlorates. The remainder are iodides.

[1] Found: C, 57·5; H, 5·1. Reqd.: C, 57·3; H, 5·2%. [2] Found: C, 49·2; H, 4·05. Reqd.: C, 49·5; H, 4·1%. [3] Found: C, 59·6; H, 5·4. Reqd.: C, 59·25; H, 5·7%. [4] Found: C, 49·55; H, 6·4. Reqd.: C, 50·0; H, 6·35%.

Experimental.

Microanalyses by Drs. Weiler and Strauss, Oxford.

α-Azacarbocyanines.—The general procedure adopted was to reflux the 2(or 4)-amino-quaternary salt (1 mol.) with the β-acetanilidovinyl derivative (1 mol.) in ethanol with triethylamine (1 mol.). The dye was then isolated by conversion, if necessary, into the iodide or perchlorate. Unless otherwise stated the dye was recrystallized several times from ethanol or methanol. They are all more soluble than the corresponding carbocyanines which in some cases were formed as by-products. The products are recorded in Table V.

β-Anilino-β-azavinyl Quaternary Salts (VIIIa; X = N).—Three of these compounds were obtained by Kaufmann and Valette's method (*Ber.*, 1912, **45**, 1736). A more direct method is given below.

2-*β-Anilino-β-azavinylquinoline ethiodide.* Quinaldine ethiodide (1·5 g.), diazoaminobenzene (1·0 g.), and ethanol (10 c.c.) were refluxed for 10 minutes. The required compound separated (85%) and formed orange-red needles, m. p. 252°, from ethanol (Found : I, 31·35. Calc. for $C_{18}H_{18}N_3I$: I, 31·5%). It was identical with a specimen obtained from 2-formylquinoline ethiodide and phenylhydrazine.

2-*β-Anilino-β-azavinyl*-3 : 3-*dimethylindolenine methiodide.* 2 : 3 : 3-Trimethylindolenine methiodide (1·5 g.), diazoaminobenzene (1·55 g.), and ethanol (20 c.c.) were refluxed for 2 minutes. The *dye* (1·2 g.) crystallized on cooling and formed red platelets, m. p. 237°, from ethanol (Found : N, 9·95; I, 31·55. $C_{18}H_{20}N_3I$ requires N, 10·35; I, 31·37%).

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