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Color and Constitution. VII.[1] Interpretation of Absorptions of Dyes Containing Heterocyclic Nuclei of Different Basicities

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It has been shown that it is possible to arrange certain heterocyclic nuclei in order of basicity by considering the deviations in $\lambda_{max.}$ given by unsymmetrical pyrrolocarbocyanines containing these nuclei,[1] "basicity" being rather narrowly defined. Earlier, it had been shown that a similar situation existed in the *p*-dimethylaminostyryl dyes.[2] In both series, increasing deviation is considered to indicate increasing basicity of the variable heterocyclic nucleus. It is clearly of importance to see whether the two procedures give the same order of basicity of a series of nuclei, and such a comparison is made in the present paper.

TABLE I

OPTICAL DATA[a]

Name	Nucleus no., fig. 1, 4 or 5	Dye no., Table IV	$\lambda_{max.}$ obsd., MeOH, Å.	$\lambda_{max.}$ obsd., $MeNO_2$, Å.
Symmetrical Dyes				
Michler's Hydrol Blue ClO_4[2]	..	..	..	6100
1,1'-Di-*n*-heptyl-2,2',5,5'-tetraMe-3,3'-pyrrolocy. I	..	D20	4420	..
1,1',2,2'-TetraMe-3,3'-indolocy. I[b]	1	..	4900	4900
3,3,3',3'-TetraMe-1,1'-diPh-indocarbocy. ClO_4[c]	2	D21	5550	5560
3,3'-DiEt-6,6'-dinitrothiacarbocy. I[d]	3	..	5835	5900
1,1'-DiEt-3,3,3',3'-tetraMe-indocarbocy. I[e]	4	..	5465	5480
3,3'-DiEt-5,6; 5',6'-dibenzothiacarbocy. Br[f]	5	D22	5695	5730
3,3'-DiEt-thiazolinocarbocy. I[g]	6	..	4450	4460
3,3'-DiEt-selenacarbocy. I[h]	7	..	5700	5700
3,3'-DiEt-oxacarbocy. I	8	..	4825	4850
3,3'-DiEt-thiacarbocy. I	9	..	5575	5565
3,3'-DiEt-5,5'-diMe-(1,3,4-thiadiazolo)-carbocy. I[i]	10	D23	5135	5120
3,3'-DiEt-6,7; 6',7'-dibenzothiacarbocy. I	11	..	5940	5955
1,1'-DiEt-2,2'-carbocy. Br	12	..	6040	6075
3,3'-DiEt-4,5; 4',5'-dibenzothiacarbocy. Br	13	..	5950	5990
3,3'-DiEt-4,5; 4',5'; 6,7; 6',7'-tetrabenzothiacarbocy. Br	14	..	6125	6175
3,3'-Di-(4-biphenylyl)-4,4'-diMe-thiazolocarbocy. ClO_4	15	D24	5640	5660
4,4'-DiMe-3,3'-diPh-thiazolocarbocy. ClO_4	16	D25	5610	5650
1,1'-DiEt-5,6; 5',6'-dibenzo-2,2'-carbocy. I	17	..	6340	6360
3,3'-DiEt-thiazolocarbocy. I	18	D26	5425	5410
3,3'-DiEt-4,4'-diPh-thiazolocarbocy. I	19	D27	5590	5590
3,3'-DiEt-4,4'-diMe-thiazolocarbocy. I[j]	20	..	5560	5545
3,3'-DiEt-4,5,6,7,4',5',6',7'-octahydrothiacarbocy. I[k]	21	D28	5700	5680
1,1'-DiEt-4,4'-carbocy. I	22	..	7050	7075
1,1'-DiEt-2,2'-pyridocarbocy. I[h]	23	..	5620	5620
1,1'-DiEt-4,4'-pyridocarbocy. I[l]	24	..	6030	6030
1,1',3,3'-TetraEt-benzimidazolocarbocy. I[m]	25	D29	4955	4990
3,3'-Di-*o*-nitrophenylthiacarbocy. ClO_4[d]	26	..	5695	5690
3,3'-Di-*p*-nitrophenylthiacarbocy. I	27	D30	5690	5705
3,3'-Dicarbethoxymethylthiacarbocy. I	28	D31	5600	5620
3,3'-Diphenacylthiacarbocy. I	29	D32	5620	5630
3,3'-Dibenzylthiacarbocy. I	30	D33	5620	5620
3,4,3',4'-Di-(trimethylene)-thiacarbocy. I[f]	31	..	5555	5580
3,3'-DiEt-5,5'-dinitrothiacarbocy. I	32	D34	5560	5590
6,6'-Dichloro-3,3'-diEt-thiacarbocy. I[m]	33	..	5600	5620
3,3'-DiEt-6,6'-diMe-thiacarbocy. I[n]	34	..	5610	5650
5,5'-DiEtO-3,3'-diEt-thiacarbocy. I	35	D35	5760	5780
6,6'-EtO-3,3'-diEt-thiacarbocy. I[e]	36	..	5710	5740

(1) Part VI, THIS JOURNAL, 67, 1869 (1945).

(2) Part III, *ibid.*, 63, 3203 (1941).

TABLE I (*Continued*)

Name	Nucleus no., Fig. 1, 4 or 5	Dye no., Table IV	$\lambda_{max.}$ obsd., MeOH, Å.	$\lambda_{max.}$ calcd., Å.	Deviation, Å.	Proportional deviation
Unsymmetrical Pyrrolo-Dyes						
(a) from 2,5-diMe-1-Ph-pyrrole						
1,2,2′,5′-TetraMe-1′-Ph-3-indolo-3′-pyrrolocy. ClO_4	1	D36	4650	4695	45	4.9
2′,3,3,5′-TetraMe-1,1′-diPh-indo-3′-pyrrolocarbocy. ClO_4	2	D37	4880	5020	140	15.2
3′-Et-2,5-diMe-6′-nitro-1-Ph-3-pyrrolothiacarbocy. I	3	D38	4940	5160	220	23.9
3′-Et-2,5-diMe-1-Ph-5′,6′-benzo-3-pyrrolothiacarbocy. I	5	D39	4820	5090	270	29.4
3′-Et-2,5-diMe-1-Ph-3-pyrrolothiazolinocarbocy. I	6	D40	4175	4470	295	32.1
3′-Et-2,5-diMe-1-Ph-3-pyrroloselenacarbocy. I	7	D41	4765	5095	330	35.9
3′-Et-2,5,5′-triMe-1-Ph-3-pyrrolo-(1,3,4-thiadiazolo)-carbocy. I	10	D42	4375	4810	435	47.3
3′-Et-2,5-diMe-1-Ph-6′,7′-benzo-3-pyrrolothiacarbocy. I	11	D43	4750	5215	465	50.5
1′-Et-2,5-diMe-1-Ph-3-pyrrolo-2′-carbocy. I	12	D44	4740	5265	525	57.1
3′-Et-2,5-diMe-1-Ph-4′,5′-benzo-3-pyrrolothiacarbocy. I	13	D45	4680	5220	540	58.7
3′-Et-2,5-diMe-1-Ph-4′,5′; 6′,7′-dibenzo-3-pyrrolothiacarbocy. I	14	D46	4760	5305	545	59.3
3′-(4-Biphenylyl)-2,4′,5-triMe-1-Ph-3-pyrrolothiazolocarbocy. I	15	D47	4460	5065	605	65.8
2,4′,5-TriMe-1,3′-diPh-3-pyrrolothiazolocarbocy. I	16	D48	4430	5050	620	67.4
1′-Et-2,5-diMe-1-Ph-5′,6′-benzo-3-pyrrolo-2′-carbocy. I	17	D49	4790	5415	625	68.0
3′-Et-2,5-diMe-1-Ph-3-pyrrolothiazolocarbocy. I	18	D50	4315	4955	640	69.6
3′-Et-2,5-diMe-1,4′-diPh-3-pyrrolothiazolocarbocy. I	19	D51	4390	5040	650	70.6
3′-Et-2,4′,5-triMe-1-Ph-3-pyrrolothiazolocarbocy. I	20	D52	4340	5025	685	74.5
3′-Et-2,5-diMe-1-Ph-4′,5′,6′,7′-tetrahydro-3-pyrrolothiacarbocy. I	21	D53	4390	5095	705	76.7
1-Et-2′,5′-diMe-1′-Ph-2-pyrido-3′-pyrrolocarbocy. I	23	D54	4260	5055	795	86.5
1,3-DiEt-2′,5′-diMe-1′-Ph-2-benzimidazolo-3′-pyrrolocarbocy. I	25	D55	3800	4720	920	100
2,5-DiMe-3′-*o*-nitrophenyl-1-Ph-3-pyrrolothiacarbocy. I	26	D56	4870	5090	220	23.9
2,5-DiMe-3′-*p*-nitrophenyl-1-Ph-3-pyrrolothiacarbocy. I	27	D57	4820	5090	270	29.4
3′-Carbethoxymethyl-2,5-diMe-1-Ph-3-pyrrolothiacarbocy. I	28	D58	4770	5045	275	29.9
2,5-DiMe-3′-phenacyl-1-Ph-3-pyrrolothiacarbocy. I	29	D59	4750	5055	305	33.1
3′-Benzyl-2,5-diMe-1-Ph-3-pyrrolothiacarbocy. Br	30	D60	4745	5055	310	33.7
2,5-DiMe-1-Ph-3′,4′-trimethylene-3-pyrrolocarbocy. I	31	D61	4595	5020	425	46.2
3′-Et-2,5-diMe-5′-nitro-1-Ph-3-pyrrolothiacarbocy. I	32	D62	4940	5160	220	24.5
6′-Chloro-3′-Et-2,5-diMe-1-Ph-3-pyrrolothiacarbocy. I	33	D63	4710	5045	335	36.4
3′-Et-2,5,6′-triMe-1-Ph-3-pyrrolothiacarbocy. I	34	D64	4620	5050	430	46.8
5′-EtO-3′-Et-2,5-diMe-1-Ph-3-pyrrolothiacarbocy. I	35	D65	4680	5125	445	48.4
6′-EtO-3′-Et-2,5-diMe-1-Ph-3-pyrrolothiacarbocy. I	36	D66	4600	5100	500	54.3
(b) from 1-Et-2,5-diMe-pyrrole						
1,1′-DiEt-2,5-diMe-3-pyrrolo-2′-carbocy. I	12	D67	4820	5235	415	
(c) from 1-*n*-heptyl-2,5-diMe-pyrrole						
1′-*n*-Heptyl-1,2,2′,5′-tetraMe-3-indolo-3′-pyrrolocy. I	1	D68	4560	4660	100	
1′-*n*-Heptyl-2′,3,3,5′-tetraMe-1-Ph-indo-3′-pyrrolocarbocy. ClO_4	2	D69	4930	4985	55	
1-Et-1′-*n*-heptyl-2′,3,3,5′-tetraMe-indo-3′-pyrrolocarbocy. I	4	D70	4830	4945	115	
3-Et-1′-*n*-heptyl-2′,5′-diMe-oxa-3′-pyrrolocarbocy. I	8	D71	4390	4625	235	
3′-Et-1-*n*-heptyl-2,5-diMe-3-pyrrolothiacarbocy. I	9	D72	4710	5000	290	
3′-Et-1-*n*-heptyl-2,5-diMe-6′,7′-benzo-3-pyrrolothiacarbocy. I	11	D73	4830	5180	350	
1′-Et-1-*n*-heptyl-2,5-diMe-3-pyrrolo-2′-carbocy. I	12	D74	4820	5230	410	
3′-Et-1-*n*-heptyl-2,5-diMe-4′,5′-benzo-3-pyrrolothiacarbocy. I	13	D75	4780	5185	405	
3′-Et-1-*n*-heptyl-2,5-diMe-4′-Ph-3-pyrrolothiazolocarbocy. ClO_4	19	D76	4440	5005	565	
1′-Et-1-*n*-heptyl-2,5-diMe-3-pyrrolo-4′-carbocy. I	22	D77	5120	5735	615	

Name	Nucleus no., Fig. 1, 4 or 5	Dye no., Table IV	$\lambda_{max.}$ obsd., $MeNO_2$, Å.	$\lambda_{max.}$ calcd., Å.	Deviation, Å.	Proportional deviation
Styryl Dyes						
3-*p*-Me_2N-benzylidene-1,2-diMe-pseudoindolium ClO_4[a]	1	..	5530	5500	−30	−2.1
2-*p*-Me_2N-styryl-3,3-diMe-1-Ph-pseudoindolium ClO_4[c]	2	D78	5660	5830	170	12.1
2-*p*-Me_2N-styryl-3-Et-6-nitrobenzothiazolium Cl[d]	3	..	5735	6000	265	18.8
2-*p*-Me_2N-styryl-1-Et-3,3-diMe-pseudoindolium I[b]	4	..	5500	5790	290	20.6
2-*p*-Me_2N-styryl-3-Et-naphtho[2,3]thiazolium I[f]	5	D79	5550	5915	365	26.0
2-*p*-Me_2N-styryl-3-Et-4,5-dihydrothiazolium I[g]	6	..	4815	5280	465	33.0
2-*p*-Me_2N-styryl-3-Et-benzoselenazolium I	7	D80	5410	5900	490	34.9
2-*p*-Me_2N-styryl-3-Et-benzoxazolium I[p]	8	..	5020	5475	455	32.4

TABLE I (*Concluded*)

Name	Nucleus no., Fig. 1, 4 or 5	Dye no., Table IV	$\lambda_{max.}$ obsd. $MeNO_2$, Å.	$\lambda_{max.}$ calcd., Å.	Deviation, Å.	Proportional deviation
2-*p*-Me_2N-styryl-3-Et-benzothiazolium I[p]	9	..	5280	5835	555	39.4
2-*p*-Me_2N-styryl-3-Et-5-Me-1,3,4-thiadiazolium I[t]	10	D81	4980	5610	630	44.7
2-*p*-Me_2N-styryl-3-Et-naphtho[2,1]thiazolium I[q]	11	..	5380	6030	650	46.3
2-*p*-Me_2N-styryl-1-Et-quinolinium I[r]	12	..	5270	6090	820	58.4
2-*p*-Me_2N-styryl-1-Et-naphtho[1,2]thiazolium I[q]	13	..	5325	6045	720	51.1
2-*p*-Me_2N-styryl-3-Et-phenanthro[9,10]thiazolium I	14	D82	5395	6140	745	53.0
3-(4-Biphenylyl)-2-*p*-Me_2N-styryl-4-Me-thiazolium ClO_4	15	D83	5040	5880	840	59.7
2-*p*-Me_2N-styryl-4-Me-3-Ph-thiazolium ClO_4	16	D84	5000	5875	875	62.3
3-*p*-Me_2N-styryl-4-Et-benzo[f]quinolinium I[s]	17	..	5210	6230	1020	72.5
2-*p*-Me_2N-styryl-3-Et-thiazolium I	18	D85	4830	5755	925	65.8
2-*p*-Me_2N-styryl-3-Et-4-Ph-thiazolium I	19	D86	4900	5845	945	67.3
2-*p*-Me_2N-styryl-3-Et-4-Me-thiazolium I[p]	20	..	4800	5825	1025	73.0
2-*p*-Me_2N-styryl-3-Et-4,5,6,7-tetrahydrobenzothiazolium I[u]	21	D87	4805	5890	1085	77.2
4-*p*-Me_2N-styryl-1-Et-quinolinium I[p]	22	..	5465	6590	1125	80.0
2-*p*-Me_2N-styryl-1-Et-pyridinium I[i]	23	..	4590	5860	1270	90.5
4-*p*-Me_2N-styryl-1-Et-pyridinium I[w]	24	D88	4830	6065	1235	88.0
2-*p*-Me_2N-styryl-1,3-diEt-benzimidazolium I	25	D89	4140	5545	1405	100
2-*p*-Me_2N-styryl-3-*o*-nitrophenylbenzothiazolium ClO_4[d]	26	..	5605	5895	290	20.6
2-*p*-Me_2N-styryl-3-*p*-nitrophenylbenzothiazolium I	27	D90	5580	5905	325	23.1
3-Carbethoxymethyl-2-*p*-Me_2N-styrylbenzothiazolium I	28	D91	5505	5860	355	25.2
2-*p*-Me_2N-styryl-3-phenacylbenzothiazolium I	29	D92	5445	5865	420	29.9
3-Benzyl-2-*p*-Me_2N-styrylbenzothiazolium I	30	D93	5420	5860	440	31.3
2-*p*-Me_2N-styryl-3,4-trimethylenebenzothiazolium I	31	D94	5250	5840	590	42.0
2-*p*-Me_2N-styryl-3-Et-5-nitrobenzothiazolium I	32	D95	5560	5845	285	20.3
6-Chloro-2-*p*-Me_2N-styryl-3-Et-benzothiazolium I	33	D96	5400	5860	460	32.7
2-*p*-Me_2N-styryl-3-Et-6-Me-benzothiazolium I	34	D97	5260	5875	615	43.8
2-*p*-Me_2N-styryl-5-EtO-3-Et-benzothiazolium *p*-toluenesulfonate	35	D98	5320	5940	620	44.1
2-*p*-Me_2N-styryl-6-EtO-3-Et-benzothiazolium I	36	D99	5250	5920	670	47.7

[a] Optical data for twelve of the dyes dealt with in this paper have already been given in Part VI and are not repeated here. New dyes are numbered D20 to D99, numbering being continued from the preceding paper. [b] Part I, THIS JOURNAL, **62**, 1116 (1940). [c] *Cf.* Löw, Dissertation, Dresden, 1930. [d] Part V, THIS JOURNAL, **64**, 199 (1942). [e] Hamer, *J. Chem. Soc.*, 2804 (1927). [f] I. G. Farbenindustrie A. G., British Patent 452,408. [g] Brooker, THIS JOURNAL, **58**, 662 (1936). [h] Clark, *J. Chem. Soc.*, 216 (1933). [i] Stevens and Gevaert Photo-Producten N. V., U. S. Patent 2,191,810. [j] Fisher and Hamer, *J. Chem. Soc.*, 2502 (1930). [k] Rosenhauer and Barlet, *Ber.*, **62**, 2724 (1929). [l] Brooker and Cressman, THIS JOURNAL, **67**, 2046 (1945). [m] Beilenson and Hamer, *J. Chem. Soc.*, 1229 (1936). [n] Mills, *J. Chem. Soc.*, **121**, 455 (1922). [o] Kiprianov, Suitnik and Suich, *J. Gen. Chem. U. S. S. R.*, **6**, 42 (1936). [p] Bloch and Hamer, *Phot. J.*, **70**, 374 (1930). [q] Hamer, *J. Chem. Soc.*, 2606 (1929). [r] König and Treichel, *J. prakt. Chem.*, **63**, 102 (1921). [s] Mills and Raper, *J. Chem. Soc.*, **127**, 2466 (1925). [t] Doja and Prasad, *J. Ind. Chem. Soc.*, **19**, 125 (1942). [u] Brooker and White, U. S. Patent 2,336,843. The base, 2-methyl-4,5,6,7-tetrahydrobenzothiazole, is described by Smith and Sapiro, (*Trans. Roy. Soc. S. Africa*, **18**, 229 (1930)) although it was later patented (I. G. Farbenindustrie, British Patent 497,659 [v] The 1,1',3,3'-tetramethyl dye is described by Ogata (*Proc. Imp. Acad., Tokyo*, **9**, 602 (1933)). A similar procedure was used in preparing D29. [w] The corresponding methiodide is described by Clemo and Swan, *J. Chem. Soc.*, 1454 (1938).

Twenty-five heterocyclic nuclei have been combined with the 2,5-dimethyl-1-phenylpyrrole nucleus to give a series of unsymmetrical pyrrolocarbocyanines, the formulas, absorption maxima, and deviations of which are shown in Fig. 1. The method of calculation of the deviations was that used previously.[1] The optical data for these dyes and for the others described in this paper are given in Table I. The variable nuclei are shown numbered 1 through 25 in Fig. 1.

In order to simplify comparisons between the different kinds of ring systems, the majority of these have ethyl attached to nitrogen with the exception of indole, which has a methyl group in this position. In addition to the N-ethyl derivatives, some nuclei are also shown with phenyl attached to nitrogen, and one with *p*-biphenylyl.

Once again it is striking that the deviations in $\lambda_{max.}$ of all these unsymmetrical dyes are consistently in the direction of shorter wave length, though the amount varies from 45 Å. for 1,2-dimethylindole to 920 Å. for 1,3-diethylbenzimidazole. With the exception of 1,2-dimethylindole, all the rings shown are more strongly basic than the standard 2,5-dimethyl-1-phenylpyrrole nucleus. This was proved rigorously for eleven representative nuclei using the method already described[1]; they gave smaller deviations than those shown in the figure when they were combined with 2,5-dimethyl-1-ethyl- or 2,5-dimethyl-1-*n*-heptylpyrrole.[3]

(3) In the earlier part of the investigation, the 1-*n*-heptyl-2,5-dimethylpyrrole nucleus was used because the 3-pyrrolealdehyde necessary for the dye syntheses was more readily obtainable from this base than that from 1-ethyl-2,5-dimethylpyrrole. However, the ethyl and *n*-heptyl groups would be expected to render the pyrrole nucleus more basic than the phenyl group to approximately the same

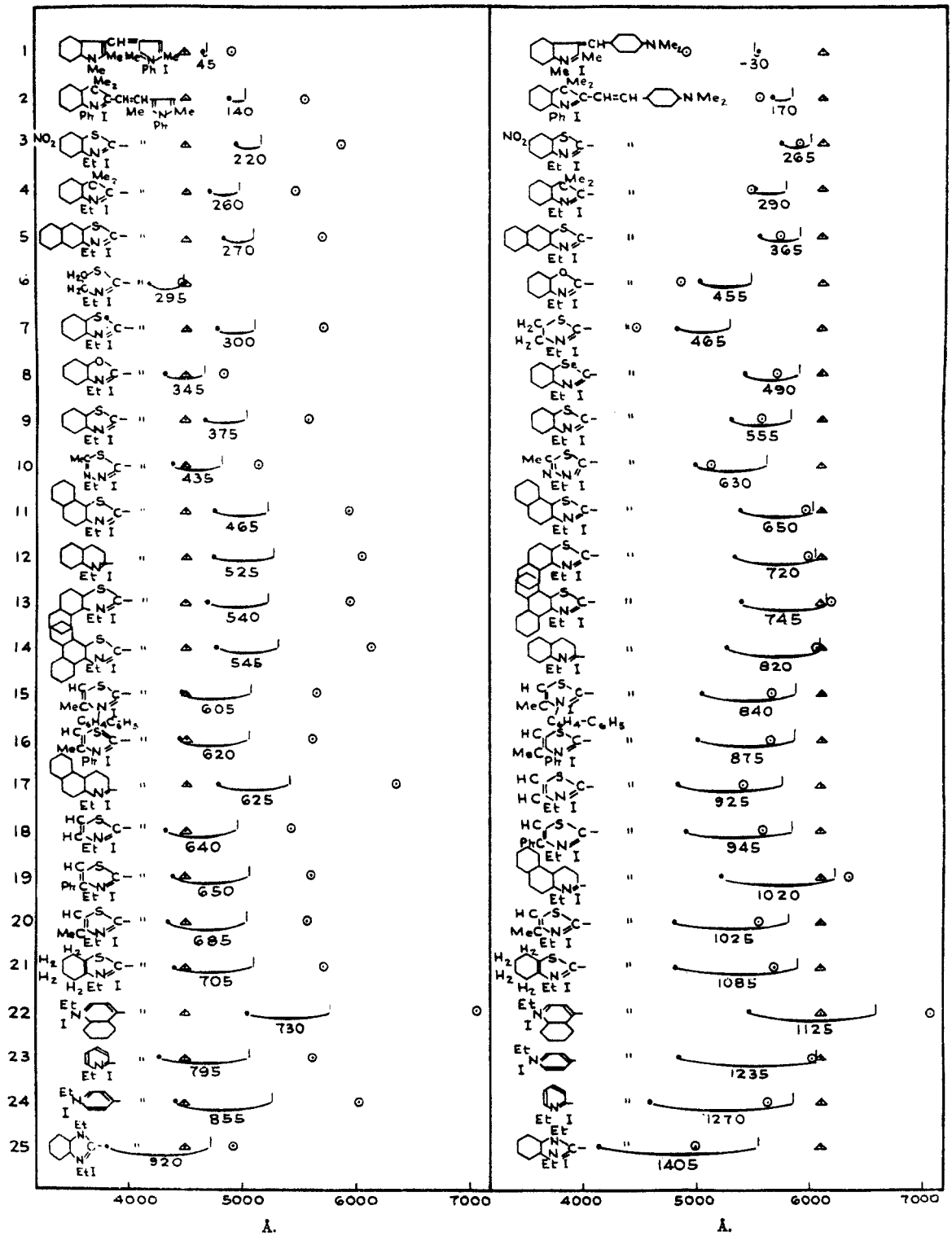


Fig. 1.—Order of basicity of twenty-five heterocyclic nuclei. Values of $\lambda_{max.}$ in methyl alcohol are shown as follows: ● unsymmetrical cyanine; △ symmetrical cyanine with two pyrrole nuclei; ⊙ second symmetrical cyanine; | arithmetic mean between △ and ⊙; ⌒ indicates deviations, the magnitudes of which are given in Å.

Fig. 2.—Order of basicity of twenty-five heterocyclic nuclei. Values of $\lambda_{max.}$ in nitromethane are shown as follows: ● styryl dye; ⊙ symmetrical cyanine; △ Michler's hydrol blue; | arithmetic mean between ⊙ and △: ⌒ indicates deviation, the magnitude of which is given in Å.

The remaining thirteen lower nuclei are more or less closely related to those tested in this way, and it is inconceivable that any of these could be less basic than the 2,5-dimethyl-1-phenylpyrrole ring. The 1,2-dimethylindole nucleus, however, gives a larger deviation when linked to 2,5-dimethyl-1-*n*-heptylpyrrole, whence it is concluded that it is even less basic than 2,5-dimethyl-1-phenylpyrrole.

The same twenty-five nuclei used in Fig. 1 have also been combined into *p*-dimethylaminostyryl dyes, the formulas, absorption maxima, and deviations of which are shown in Fig. 2.

The indole dye at the head of the column (which is strictly a benzylidene rather than a styryl derivative) absorbs at slightly longer wave length than that calculated, but the amount (30 Å.) is not considerable, and with this trifling exception it is seen that these unsymmetrical dyes similarly absorb at shorter wave lengths than the calculated. The deviations reach a maximum value of 1405 Å. for 1,3-diethylbenzimidazole.[4] This latter, then appears to be the most strongly basic nucleus of the group and the indole nucleus the least.

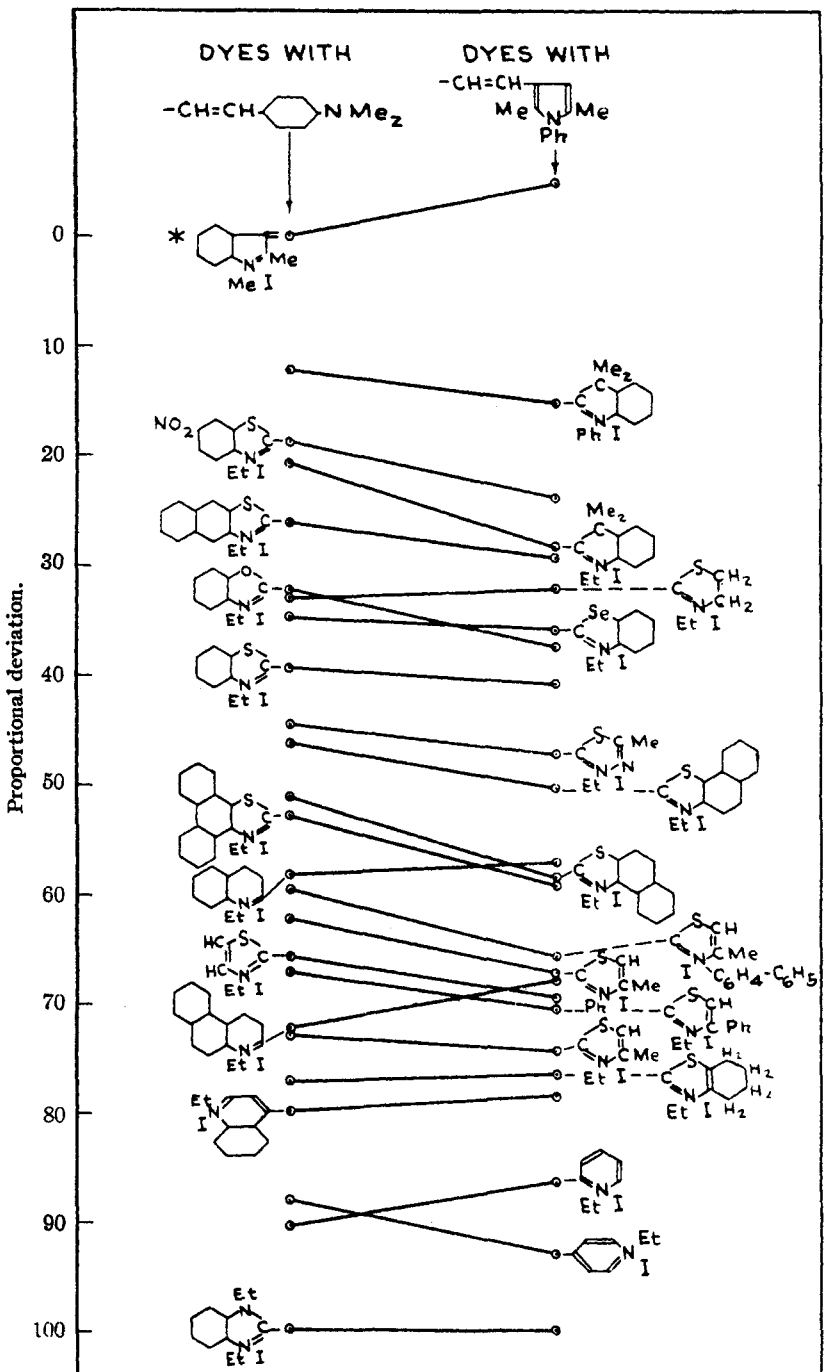


Fig. 3.—Order of basicity of nuclei, a comparison of two methods. * The indole derivatives have one —CH= group fewer in the chain between the nuclei than the remaining dyes.

The deviations obtained in the two series of dyes are compared in Fig. 3, those of the styryl series being plotted in the left-hand vertical column, those of the pyrrole series at the right.

extent, and that this assumption is justified is shown by the fact that in five cases where we have data on both the 1-ethyl- and 1-*n*-heptyl- derivatives, the deviations are practically identical (see Table I).

(4) Although it seems unlikely, it is not inconceivable that one or more of these dyes could show large deviations because they contain such extremely feebly basic nuclei that the resonance structure containing the $=N^{+}Me_2$ group is strongly dominant.[3] Let us suppose that this were true for the indolenine dye, for example. Then it should be placed above the indole dye in the column in Fig. 2, and the deviation, which is roughly zero for the indole derivative, would expand to appreciable values both above and below the zero point, according as the dominant structure were that in which the —NMe_2 nitrogen or the heterocyclic nitrogen was quaternary. Actually, this interpretation is proved to be incorrect for the indolenine dye, because replacing the N-ethyl group by phenyl results in a reduction of the deviation, whereas the above hypothesis would require it to be increased, owing to the further reduction in the basicity of the ring. This interpretation is accordingly abandoned, although it has not been proved incorrect by rigorous comparisons for all the remaining nuclei.

In order to make a comparison easier, that nucleus (1,3-diethylbenzimidazole) in each series which gives the greatest deviation has been assigned 100 arbitrary units of deviation, and those for the other nuclei have been determined proportionately. In the styryl series, one such unit equals 14.05 Å., and in the pyrrole series, one unit equals 9.2 Å.

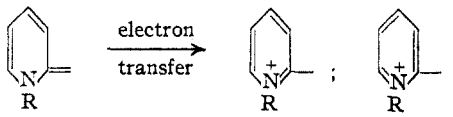
The point representing the proportional deviation for a dye with a given nucleus in one series is joined to the corresponding point in the second series by a straight line. On the whole, there is relatively little intersection of these lines, and it is seen that the order of basicity of the nuclei obtained in one series agrees remarkably well with that obtained in the other.

Two points call for comment, however, both of them having to do with the 1,2-dimethylindole nucleus. This was shown above to be less basic than the standard 2,5-dimethyl-1-phenylpyrrole ring; consequently, the deviation of its combination with this nucleus has been plotted above the zero line in the upper part of the figure. Secondly, no significance can be attached to a small deviation to longer wave length, and such must be regarded as due to small secondary effects as, for example, an abnormal displacement of the peak of the band envelope with respect to the band center. These secondary effects could mask a deviation to short waves only when the normal deviation was very small. It has, accordingly, been necessary to treat the deviation of the indole dye in Fig. 2 as indistinguishable from zero when plotting Fig. 3.

It should also be pointed out that the absorptions for the unsymmetrical cyanine column were determined in methyl alcohol and those for the styryls in nitromethane.[3]

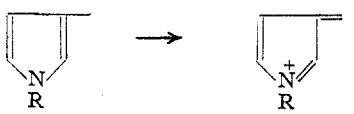
From Fig. 3 it is seen that the 1,3-diethylbenzimidazole nucleus is consistently the most strongly basic ring, and indole the least. It will be recalled that the term basicity, as used here and in the earlier papers of this series, has been defined as the relative attraction of the uncharged form of a ring for a positive charge but, thus far, no reason why one nucleus should be more basic than another has been advanced. It will now be shown that the resonance theory offers, at least in many cases, a reasonable explanation of the order of basicity actually observed in Fig. 3.

Let us first of all consider the pyridine and pyrrole rings. In the 2-pyridine nucleus, as it occurs in the cyanine and styryl dyes, the net-uncharged form of the ring containing trivalent nitrogen (which may for convenience be called the N^{III} form of the ring) contains two double bonds, and the ring will be weakly stabilized by resonance very like that present in dihydrobenzene. In the positively charged (or N^{IV}) form of the ring, however, there are three double bonds, and the stabilization is very high and comparable to that in benzene itself, corresponding to the



possibility of writing the two Kekulé structures. The stabilization is thus very much greater than in the N^{III} form, and the tendency to pass from the N^{III} to the N^{IV} form will accordingly be very great. Otherwise expressed, the pyridine nucleus will be strongly "basic," as its high deviations in Fig. 3 actually indicate.

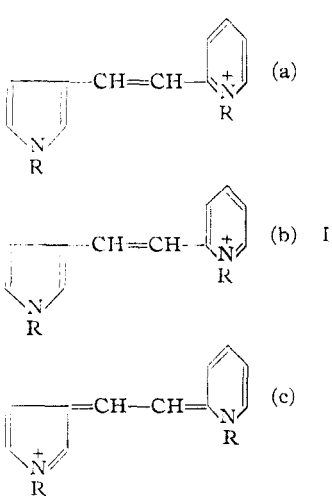
In pyrrole, on the other hand, the N^{III} and N^{IV} forms of the ring each contain the same number of double bonds, and to a first approximation the stabilization will be the same in each form. There



is thus no marked gain in stabilization as a result of acquiring a positive charge as there is for pyridine, and pyrrole will be feebly "basic."

If, now, the pyridine and pyrrole rings are linked together in a pyrido-pyrrolocyanine, where they can compete with each other for the positive charge, it is clear that the pyridine ring will tend to monopolize this charge due to the much higher stabilization which results from acquiring it. Of the two extreme resonance structures, therefore, that in which the pyridine ring is quaternary, will be of decidedly lower energy, and this dominance of a single structure is the prerequisite for a dye which shows a marked deviation.[2]

The same conclusion may be reached by a somewhat different approach. The most probable structures that it is possible to devise for a pyrido-pyrrolocarbocyanine cation are Ia, b and c of which a and b are pyridinium structures and c is a pyrrolinium structure. All three will con-

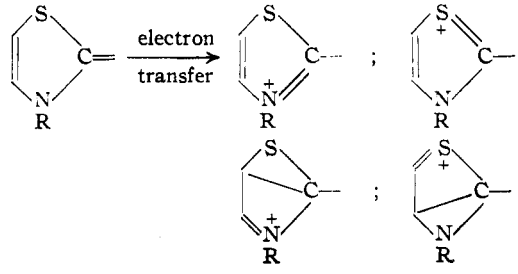


tribute to the resonance stabilization of the dye, of course, but a and b are more closely related to

each other than to c since the two may be derived one from the other without movement of charge, merely by reversing the linkages in the pyridine ring, just as with the Kekulé structures of benzene. The resonance interaction of a and b is therefore very great, and a and b together form a *closely related set of structures* which interact to give correspondingly high stability to the pyridinium type of formulation. On the other hand, Ic can only be reached from a or b through a long series of consecutive interactions of the extreme with intermediate structures.[5]

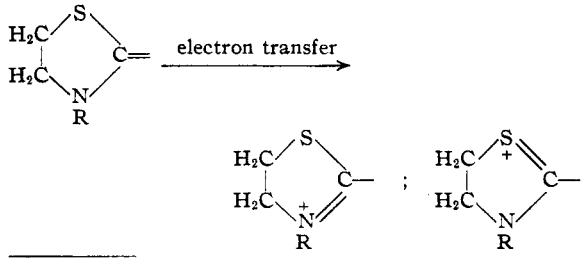
The resonance conditions of the dye may be pictured as I(a + b) ⟷ Ic. In this scheme a, b and c will have roughly the same energy, considered individually, but a and b may be imagined to interact quantum mechanically to give two new and widely separated energy levels. The lower of these, much below c in energy, will now interact with c to give a transition which determines the longest wave length absorption band of the dye ion.

Let us now consider the thiazole and thiazoline nuclei. In thiazole, the N^{III} form of the ring is stabilized by only one double bond, but additional stabilization is achieved on acquiring a positive charge corresponding to the possibility of writing not only a normal ammonium and a normal sulfonium structure, but structures of the Dewar type as well.



The charge transfer in these structures can only take place through intermediate structures, however,[5] and the reduced interaction makes it very unlikely that the gain in stabilization on acquiring a positive charge will be as high in thiazole as in pyridine, where full benzenoid stabilization is attained. Hence, thiazole will be less "basic" than pyridine, as the deviations in Fig. 3 show.

The thiazoline ring in the N^{III} form has no double bond for stabilization, but the N^{IV} form is more stabilized, corresponding to the possibility of writing both an ammonium and a sulfonium structure. However, Dewar structures are not possible here, hence thiazoline will be less "basic" than thiazole, as the deviations indicate.



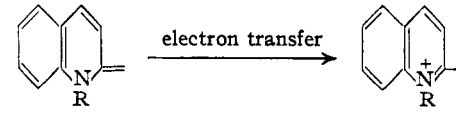
It will now be seen that it is not strictly necessary to use the term "basicity" in the preceding treatment, and it may be replaced by a term indicating the difference, usually a gain, in resonance stabilization on proceeding from the N^{III} form of the ring to the N^{IV} form. For this difference, the term "N^{IV} minus N^{III} stabilization" is convenient. It has been shown above that this quantity is especially significant if an additional double bond enters the nucleus in the N^{IV} form, but the extra stabilization resulting from this entry depends on the nature of the ring system itself. In addition, the nitrogen atom itself passes from N^{III} to N^{IV}, and an energy term will be involved here, but as a first approximation this may be taken to be the same for all nuclei, and the term will therefore cancel out when two rings are compared. The *relative* basicities of these rings are determined, then, by the N^{IV}–N^{III} stabilizations. For pyridine, N^{IV}–N^{III} stabilization is very high; it is less for thiazole, still less for thiazoline, and practically zero for pyrrole where no additional double bond enters the ring; hence, the deviations in $\lambda_{max.}$ fall in this order.

It may be noted that the N^{IV}–N^{III} stabilizations of these rings, as the term is used above, will differ from the basicities as determined by ease of proton addition. Thus, addition of a proton to pyridine cannot effect a large increase in resonance stabilization, since this is of the benzenoid type both before and after the process.

To turn now to some other nuclei. The 2-pyridine nucleus is seen to give higher deviations than 2-quinoline, but those of 5,6-benzoquinoline are intermediate. This is a rather surprising result, but it may be explained as follows:

It has already been pointed out that two structures may be written for the N^{IV} form of the pyridine ring but only one for the N^{III} form, whence the ratio of N^{IV} structures/N^{III} structures is 2/1.

If only structures of the Kekulé type are similarly considered for 2-quinoline, it will be found that two structures may be written for the N^{III}



form and three for the N^{IV} form, whence the ratio N^{IV} structures/N^{III} structures is 3/2, a lower ratio than for pyridine. It seems reasonable that this should correspond to lower N^{IV}–N^{III} stabilization for 2-quinoline, which agrees with the order of the deviations.

In 5,6-benzoquinoline, the N^{III} form of the nucleus may be written in three ways, and the

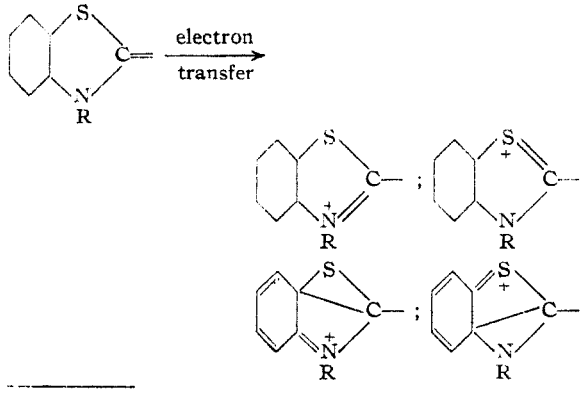
(5) (a) Sklar, *J. Chem. Phys.*, **10**, 521 (1942); (b) Herzfeld and Sklar, *Rev. Mod. Phys.*, **14**, 294 (1942).

N^{IV} form in five ways, again making the approximation of using only structures containing *o*-linkages. The ratio N^{IV}/N^{III} is accordingly 5/3, which is higher than that for 2-quinoline but lower than that for pyridine, hence the corresponding order of deviations.

It is not actually necessary, in this comparison, to make the assumption that N^{IV}–N^{III} stabilization increases in proportion to the ratio, N^{IV} structures/N^{III} structures. The resonance stabilization depends not only on the number of structures but also on how greatly they interact. However, this latter factor is often difficult to determine, and it is frequently assumed for convenience that the resonance stabilization is proportional to the number of resonating structures. This procedure needs to be used with caution, however, since it often happens that a few resonating structures of one molecule give a greater resonance energy than that shown by a molecule with more resonance structures but of smaller interaction. Thus, the two Kekulé structures of benzene provide greater stabilization than the five of fulvene, including Dewar-like structures of the latter.[6]

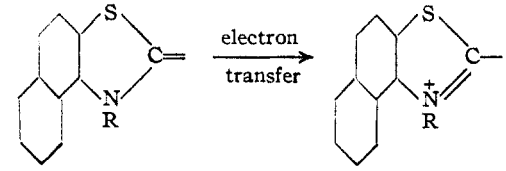
A simple comparison of this sort is permissible, however, where two closely related molecules are compared, such as benzene and cyclohexadiene. The resonance structures of benzene include all those of the kind that can be devised for cyclohexadiene and a number of others in addition, and one can be sure that benzene will have the higher resonance energy. An example of this occurred in the comparison of thiazole and thiazoline, made above, where it becomes certain that the N^{IV} form of thiazole will have a greater resonance energy than that of thiazoline.

In a comparison of several bases containing the thiazole nucleus, benzothiazole in the N^{IV} form may be assigned the normal ammonium and sulfonium structures and also structures of the Dewar type. These latter are arrived at by rearranging the linkages of those of the more conventional charged structures in which a double bond is shared between the benzene and thiazole rings. In thiazole itself, we may say that the



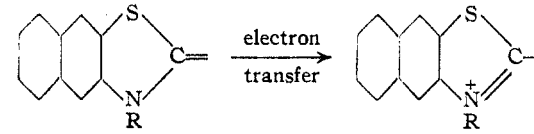
4,5-linkage is a full double bond except for its participation in the Dewar structures, but in benzothiazole this shared side has less than full double-bond character due to the Kekulé resonance within the benzene ring and, consequently, Dewar structures will have less significance in benzothiazole than in thiazole. The N^{IV}–N^{III} stabilization of benzothiazole will therefore be less than for thiazole, which accords with the order of the deviations.

In both *α*- and *β*-naphthothiazoles, on the other hand (the *β*-derivative is shown below), the side of the naphthalene residue which is shared



with thiazole is a linkage which may be said to have two-thirds double-bond character in naphthalene itself, on the grounds that it is a double bond in two of the three Kekulé arrangements.[7] This will enable the Dewar structures to be more significant than in benzothiazole, and these bases will have higher N^{IV}–N^{III} stabilizations than the latter and should show higher deviations, which is actually the case. However, the *β*-naphthothiazole derivatives give appreciably larger deviations than the *α*-isomers, and for this no explanation is yet available.

In the isomeric naphtho[2,3]thiazole, however, the side shared with thiazole has only one-third



double-bond character in naphthalene itself, and Dewar structures will contribute relatively little to the stability of the N^{IV} ring. The N^{IV}–N^{III} stabilization of this nucleus will be even less than that of benzothiazole, and with this conclusion the deviations are in agreement.

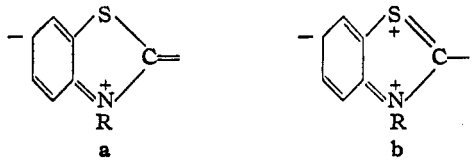
Similarly, phenanthro[9,10]thiazole should have higher N^{IV}–N^{III} stabilization than that even of the *α*- and *β*-naphthothiazoles and not greatly inferior to that of thiazole itself, for the side shared between thiazole and phenanthrene has four-fifths double-bond character in the hydrocarbon, and the deviations actually are greater than those of the naphthothiazoles.

Thiazoline, with no double bond in the 4,5-position, can have no stabilization from Dewar structures in the N^{IV} ring and should therefore be the least basic of all these sulfur-containing rings, but it is apparently anomalous in that the deviations show it to be more basic than naphtho[2,3]thiazole. However, an aromatic ring tends

(6) Sklar, *J. Chem. Phys.*, **5**, 669 (1937).

(7) Pauling, "Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, p. 142.

to attract electrons, and of the structures that this process makes possible, those such as a are more stable which are derived from the N^{III} ring than those derived from the N^{IV} form b owing to the presence of two positive charges in the same



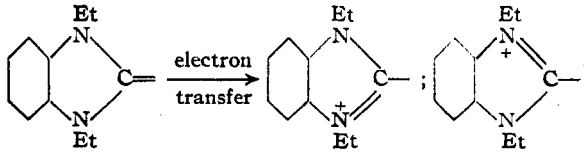
a b

ring in the latter. The result is that the N^{IV}–N^{III} stabilizations of these fused-ring hydrocarbon thiazoles are lower for this reason than they would be otherwise, thus accounting for the anomalous position of thiazoline and also for the rather wide gap in Fig. 3 between phenanthro-[9,10]thiazole and thiazole itself.

Benzoselenazole and benzoxazole have somewhat lower values of N^{IV}–N^{III} stabilization than benzothiazole, judging from the deviations, and this may be due to smaller contributions of the selenonium and oxonium structures to the N^{IV} forms of the rings compared with the sulfonium structures in benzothiazole, although it is difficult to see why this should be so. The indolenine ring is decidedly less basic than these, but this is easy to understand since there can be no carbonium structures involving the $>CMe_2$ carbon comparable to the sulfonium structures of benzothiazole.

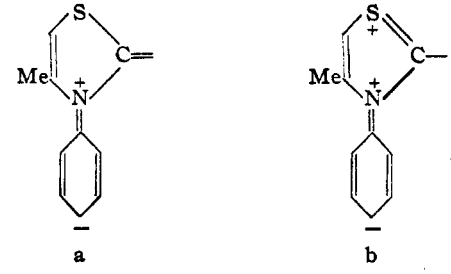
The deviations of the 4-quinoline derivatives are greater than those of the 2-quinoline isomers. This would normally be interpreted as higher N^{IV}–N^{III} stabilization of the 4-isomer, but the conjugated chains in derivatives of the latter are longer, and a direct comparison is of doubtful validity. However, it is interesting that the 2- and 4-pyridine derivatives give much the same deviations, and indeed those of the one are not consistently greater than those of the other.

It is noteworthy that the 1,3-diethylbenzimidazole nucleus should give higher deviations than either of the pyridine rings. The N^{IV}–N^{III} stabilization of this nucleus must be very high, corresponding to the possibility of writing two identical N^{IV} structures (omitting resonance in the benzene ring).



However, this is also true of the 4-pyridine ring, and it seems likely that the reason for the very high N^{IV}–N^{III} stabilization of benzimidazole is the presence of the second nitrogen atom capable of bearing the positive charge.

To turn to the matter of N-substitution. If the customary N-ethyl group in the 4-methylthiazole ring is replaced by phenyl, the deviations are reduced. This is attributed to the higher stabilization of the N^{III} ring by structures such as a, than of the N^{IV} form by structures such as b,

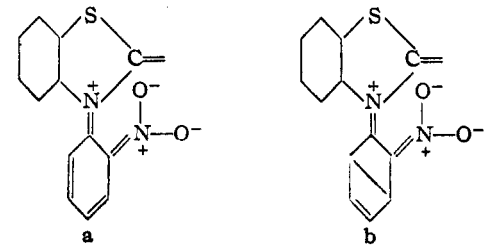


a b

which has two positive charges in close proximity. The effect is the same in the indolenine and benzothiazole[8] rings, and is doubtless a general rule. The N-*p*-biphenylyl thiazole derivative gives slightly lower deviations still; here there are even more possibilities of dipolar structures of the above a type, some of them involving carbon atoms of the second benzene ring.

In a further comparison, a number of groups have been introduced in place of the ethyl group of the benzothiazole ring in Fig. 3. The deviations of these derivatives are shown in Fig. 4, in which the new nuclei are numbered 26 through 31.

Replacement of N-ethyl by benzyl reduces the deviations. Here the electron-attracting effect of the phenyl group can operate through the $—CH_2—$ group by induction. The phenacyl group is still more effective in this respect and carbethoxymethyl still more so. In these three radicals, a negative group is attached to methylene, and the effect of these groups in reducing the N^{IV}–N^{III} stabilization of the benzothiazole ring parallels their effect in activating a reactive methylene group. The replacement most effective for reducing the basicity is that of ethyl by *o*-nitrophenyl. Here there is apparently a significant contribution to the stability of the N^{III} ring by the structure a in spite of the coplanarity of the grouping which this requires. The *p*-



a b

nitrophenyl group, surprisingly, is not quite so effective. Here coplanarity is certainly attained without difficulty, but a Dewar structure of the type of b above is not possible here, and this may be the deciding factor.

There are some other questions of nuclear substitution. In the thiazole ring, introduction of a 4-phenyl group appears to increase the basicity

(8) Part V of this series, THIS JOURNAL, 64, 199 (1942).

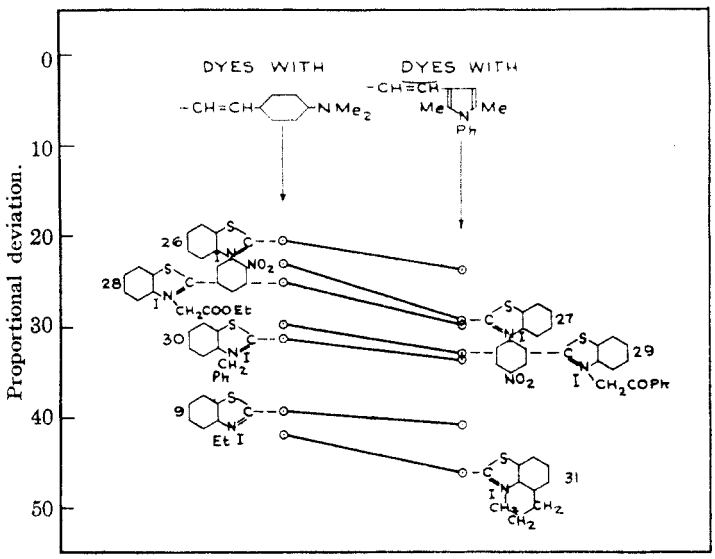
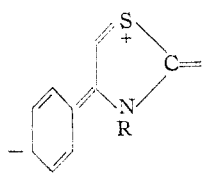


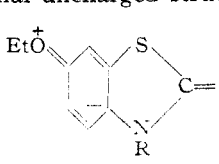
Fig. 4.—Proportional deviations of a series of N-substituted benzothiazole derivatives. The scale is that used in Fig. 3.

slightly. This is surprising, since any additional structure involving the phenyl group, such as the following, would be expected to stabilize the N^{III} form of the ring more than a corresponding structure could stabilize the N^{IV} form, and thus diminish the N^{IV}–N^{III} stabilization rather than increase it. A 4-methyl group in this ring, however, increases the basicity more strongly, and the 4,5-tetramethylene chain in tetrahydrobenzothiazole is more effective still.

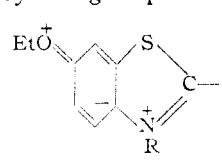


The N-ethylbenzothiazole nucleus has also been selected for a study of the effect of nuclear substitution. The substituents introduced were 5- and 6-ethoxy, 6-methyl, 6-chloro, and 5- and 6-nitro. The deviations for the two series of dyes are shown in Fig. 5, the new nuclei being numbered 32 through 36.

Of these substituents, the 6-ethoxy group increases the N^{IV}–N^{III} stabilization of the ring the most strongly. This group is strongly electron-repelling and will attract the cationic charge of the dye ion. Alternatively expressed, the N^{III} ring will be stabilized by contributions of structures such as a below, derived from the conventional uncharged structure by charge separation,

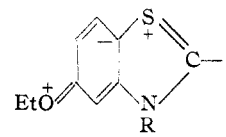


a



b

which involves an expenditure of energy. This energy term will perhaps be lower in the corresponding N^{IV} structure, b, for here the negative charge is moved in the direction in which it is attracted by the $=N^{+}R-$ atom. The ethoxy group in the 5-position is not quite so effective; here the structure below can contribute, but



since the sulfur in benzothiazole is probably not quite as strongly electropositive as the nitrogen, such a structure will not have quite the significance of b above. The electron-repelling 6-methyl group increases the N^{IV}–N^{III} stabilization of the benzothiazole ring, although not very markedly. The deviations of the 6-methyl ring are almost the same as those of the 3,4-trimethylene derivatives (Fig. 4).

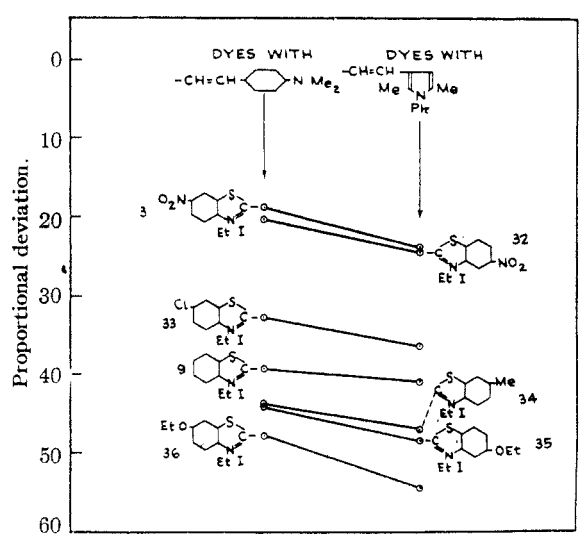
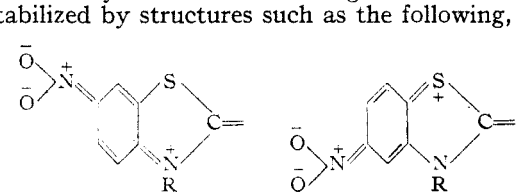


Fig. 5.—Proportional deviations of a series of nuclear substituted benzothiazole derivatives. The scale is that used in Figs. 3 and 4.

The electron-attracting chlorine atom in the 6-position diminishes the N^{IV}–N^{III} stabilization. Nitro, either in position 5 or 6, strongly reduces the basicity. Here the N^{III} rings will be heavily stabilized by structures such as the following, al-



though once again the structure involving sulfonium appears to be slightly less significant than the corresponding structure involving ammonium, judging from the deviations.

Further insight into the relation between the pyrrole and styryl dyes is provided by Fig. 6 in which the deviations of all the N-phenyl pyrrolocarbocyanines shown in the preceding figures are plotted against the deviations of the corresponding styryl dyes.

The points lie close to the gently sloping curve A, the slope of which even in the lowest portion is less than 45°, and a straight line with a slope of less than 45° or a curve of the type of A adequately fulfills the requirements of the sensitivity rule.[2] Knowing the deviation of a member of one series, it is possible with this curve to calculate with considerable accuracy the deviation, and hence $\lambda_{max.}$, of the corresponding dye in the other series.

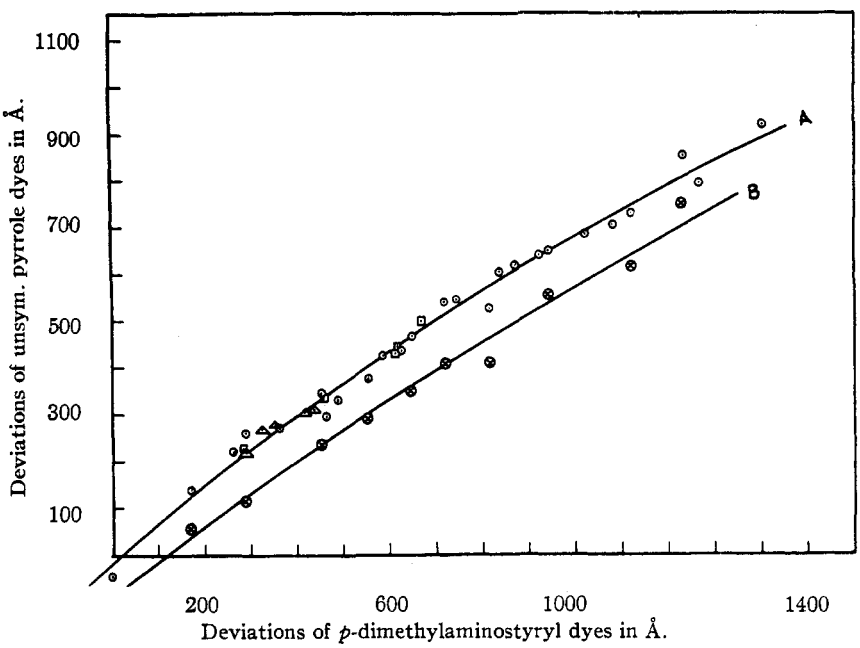


Fig. 6.—Relation between deviations in the *p*-dimethylaminostyryl and pyrrolocarbocyanine series. Points ⊙ are obtained by plotting the deviations in Fig. 1 against those in Fig. 2, ◬ are points similarly obtained from Fig. 4 and ⊡ are points obtained from Fig. 5; these points together give curve A. Points ⊗ are obtained by plotting deviations for the styryls against those of dyes containing the N-ethyl (or *n*-heptyl) 2,5-dimethylpyrrole nucleus. These give curve B.

TABLE II

REACTANTS USED IN DYE SYNTHESES

R1 1,2-Dimethyl-3-indolecarboxaldehyde
R2 2,5-Dimethyl-1-phenylpyrrole
R3 2,3,3-Trimethyl-1-phenylpseudoindolium perchlorate
R4 2,5-Dimethyl-1-phenyl-3-pyrrolecarboxaldehyde
R5 3-Ethyl-2-methyl-6-nitrobenzothiazolium iodide
R6 1-Ethyl-2,3,3-trimethylpseudoindolium iodide
R7 3-Ethyl-2-methylnaphtho[2,3]thiazolium iodide
R8 3-Ethyl-2-methyl-4,5-dihydrothiazolium iodide
R9 3-Ethyl-2-methylbenzoselenazolium iodide
R10 3-Ethyl-2,5-dimethyl-1,3,4-thiadiazolium iodide[a]
R11 3-Ethyl-2-methylnaphtho[2,1]thiazolium *p*-toluenesulfonate
R12 1-Ethyl-2-methylquinolinium iodide
R13 1-Ethyl-2-methylnaphtho[1,2]thiazolium iodide
R14 3-Ethyl-2-methylphenanthro[9,10]thiazolium iodide
R15 3-(4-Biphenylyl)-2,4-dimethylthiazolium iodide[b]
R16 2,4-Dimethyl-3-phenylthiazolium iodide[b]
R17 4-Ethyl-3-methylbenzo[f]quinolinium iodide
R18 3-Ethyl-2-methylthiazolium iodide
R19 3-Ethyl-2-methyl-4-phenylthiazolium iodide
R20 3-Ethyl-2,4-dimethylthiazolium iodide
R21 3-Ethyl-2-methyl-4,5,6,7-tetrahydrobenzothiazolium iodide
R22 1-Ethyl-2-methylpyridinium iodide
R23 1,3-Diethyl-2-methylbenzimidazolium iodide
R24 2-Methyl-3-*o*-nitrophenylbenzothiazolium iodide
R25 2-Methyl-3-*p*-nitrophenylbenzothiazolium iodide[c]
R26 3-Carbethoxymethyl-2-methylbenzothiazolium iodide
R27 2-Methyl-3-phenacylbenzothiazolium bromide
R28 3-Benzyl-2-methylbenzothiazolium bromide
R29 2-Methyl-3,4-trimethylenebenzothiazolium iodide
R30 3-Ethyl-2-methyl-5-nitrobenzothiazolium iodide[j]
R31 6-Chloro-3-ethyl-2-methylbenzothiazolium *p*-toluenesulfonate[d]
R32 3-Ethyl-2,6-dimethylbenzothiazolium *p*-toluenesulfonate[e]
R33 5-Ethoxy-3-ethyl-2-methylbenzothiazolium *p*-toluenesulfonate[e,f]
R34 6-Ethoxy-3-ethyl-2-methylbenzothiazolium *p*-toluenesulfonate[e]
R35 1-Ethyl-2,5-dimethyl-3-pyrrolecarboxaldehyde
R36 1-Ethyl-2-methylquinolinium *p*-toluenesulfonate
R37 1-*n*-Heptyl-2,5-dimethyl-3-pyrrolecarboxaldehyde[g]
R38 1-*n*-Heptyl-2,5-dimethylpyrrole[h]
R39 2-*β*-Acetanilidovinyl-3-ethylbenzoxazolium iodide
R40 3-Ethyl-2-methylbenzothiazolium iodide
R41 1-Ethyl-4-methylquinolinium iodide
R42 Ethyl orthoformate
R43 2-*β*-Acetanilidovinyl-3-ethylthiazolium iodide
R44 Triethylamine
R45 Chloral alcoholate
R46 Sodium metal
R47 2-Methyl-3-phenacylbenzothiazolium iodide

TABLE II (*Concluded*)

R48	3-Benzyl-2-methylbenzothiazolium iodide
R49	3-Ethyl-2-methyl-5-nitrobenzothiazolium *p*-toluenesulfonate[e]
R50	*p*-Dimethylaminobenzaldehyde
R51	1-Ethyl-4-methylpyridinium iodide
R52	6-Chloro-3-ethyl-2-methylbenzothiazolium iodide
R53	6-Ethoxy-3-ethyl-2-methylbenzothiazolium iodide
R54	2-Methylbenzothiazole
R55	Benzyl bromide
R56	Ethyl bromoacetate
R57	Phenacyl bromide
R58	1-Ethyl-2-methylbenzimidazole[f]
R59	Ethyl iodide
R60	Methyl isopropyl ketone *as.* diphenylhydrazone
R61	3-Ethyl-2-methylnaphtho[2,3]thiazolium *p*-toluenesulfonate[e]

[a] Stevens, U. S. Patent 2,191,810. [b] Method of H. T. Clarke and S. Gurin, THIS JOURNAL, **57**, 1881 (1935) and Todd, Bergel and Karimullah, *Ber.*, **69B**, 217 (1936). [c] Method of Evans and Smiles, *J. Chem. Soc.*, 1263 (1935). [d] Prepared by heating 6-chloro-2-methylbenzothiazole and ethyl-*p*-toluenesulfonate for five hours at 140°. [e] Prepared by heating the base with ethyl *p*-toluenesulfonate for four days at 120°. [f] Base prepared by the method of Fries, *Ann.*, **454**, 121 (1927), using 2-amino-4-ethoxythiophenol; m. p. 19–22°, b. p. 126–130° (1 mm.).

A second curve, B, is obtained by plotting deviations in the styryl series against those of dyes containing the 1-ethyl(or *n*-heptyl)-2,5-dimethylpyrrole nucleus. (It was remarked above that for all except the 1,2-dimethylindole derivatives, these deviations are smaller than those of dyes containing the 1-phenyl-2,5-dimethylpyrrole ring.) Curve B is very similar to A, although it appears to slope somewhat less.

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Experimental

The reactants used in the preparation of dyes and intermediates are numbered in Table II. Certain of these are new and methods of preparation are outlined in Table III, together with a modified method of preparation of R3.

Dyes that are new are numbered D20 to D99 in Table I, but this number includes eight (D21, 22, 23, 28, 78, 79, 81, 91) which have hitherto only been described in the patent literature or in a dissertation. Details of the dye syntheses are given in Table IV. In each case, the appropriate components were allowed to react by heating to the refluxing point in the solvent shown. The yield of crude dye is given, followed by the yield after from one to three recrystallizations from ethyl or methyl alcohol except where otherwise noted.

TABLE III

PREPARATION OF QUATERNARY SALTS

R no.	Reactants	Grams	Refluxed, hours	Yield, %	M. p., °C.	Formula	Analyses, % Calcd.	Found
R3[a]	R60	220.5	..[b]	60	194–196	.....	.....	...
	Conc. HCl	127						
R23	R58	7	15	92	200–202	$C_{12}H_{17}IN_2$	I, 40.16	40.20
	R59	10.3						
R26	R54	14.9	22[c]	44[d], 30	178–180	$C_{12}H_{14}INO_2S$	I, 34.95	34.79
	R56	16.7						
R27	R54	15	16	77[d]	189–190[e]	$C_{16}H_{14}INOS$	I, 32.12	32.33
	R57	20						
	$CHCl_3$	25						
R28	R54	7.5	15	22	231–232	$C_{15}H_{14}BrNS$	Br, 24.97	25.10
	R55	8.6						
	$CHCl_3$	25						

[a] Brunner, *Ber.*, **31**, 1948 (1898); Löw, Dissertation, Dresden, 1930, p. 106. [b] Components mixed cold, let stand one-fourth of an hour at room temperature, then heated at 100° for one hour. [c] Heated at 100°. [d] After conversion to iodide. [e] After two recrystallizations from MeOH.

TABLE IV

DETAILS OF DYE SYNTHESES

Dye no.	R	Reactants, g.	R	g.	Medium, cc.	Refluxed, min.	Yield, %	M. p., °C., dec.	Formula	Analyses, % Calcd.	Found
D20	37	2.2	38	1.9	EtOH 15	30	44,[a] 30	150–151	$C_{27}H_{45}ClN_2O_4$	C, 65.21	65.53
										H, 9.13	9.18
D21	3	1.1	42	1.0	C_5H_5N 20	45	74, 42[e]	152–155	$C_{35}H_{33}ClN_2O_4$	C, 72.33	72.34
										H, 5.73	5.70
D22	61	2.0	42	1.1	C_5H_5N 10	30	73,[c] 24	285–286	$C_{29}H_{25}BrN_2S_2$	C, 63.83	63.00
										H, 4.62	4.86
D23	10	2.7	42	0.75	C_5H_5N 10	30	36, 18	249–251	$C_{13}H_{19}IN_4S_2$	I, 30.06	30.02
D24	15	3.93	42	3.3	C_5H_5N[b] 30	20	28,[a] 6	172–176	$C_{35}H_{29}ClN_2O_4S_2$	S, 10.00	9.89
D25	16	1.6	42	1.48	C_5H_5N 25	45	40,[a] 16[f]	221–223	$C_{23}H_{21}ClN_2O_4S_2$	S, 13.12	12.85

TABLE IV (*Continued*)

Dye no.	R	Reactants, g.	R	g.	Medium, cc.	Refluxed, min.	Yield, %	M. p., °C., dec.	Formula	Analyses, % Calcd.	Found
D26	18	2.55	43	4.0	EtOH 25	10	51, 33	223–224	$C_{13}H_{17}IN_2S_2$	I, 32.36	32.36
	44	1.00									
D27	19	4.96	42	4.44	C_5H_5N 15	240	61, 16	240–241	$C_{25}H_{23}IN_2S_2$	I, 23.32	23.40
D28	21	3.53	42	2.2	C_5H_5N 10	135	12, 8	216–217	$C_{21}H_{29}IN_2S_2$	I, 25.36	25.65
D29	23	3.2	45	1.0	EtOH 60	30	23, 14	278–280	$C_{25}H_{31}IN_4$	I, 24.69	24.57
			46	0.6							
D30	25	2.0	42	3.0	Ac_2O 15	10	39, 18	>310	$C_{22}H_{19}IN_4O_4S_2$	I, 18.72	18.51
	NaOAc	0.2									
D31	26	3.63	42	2.22	C_5H_5N 25	25	82, 53	218–219	$C_{25}H_{25}IN_2O_4S_2$	I, 20.86	20.68
D32	47	3.95	42	3.0	Ac_2O 30	6	45, 33	226–228	$C_{23}H_{25}IN_2O_2S_2$	I, 18.88	18.69
	NaOAc	0.45									
D33	48	7.34	42	2.96	C_5H_5N 25	45	89, 52	246–247	$C_{31}H_{25}IN_2S_2$	I, 20.60	20.60
D34	49	3.94	42	2.22	C_5H_5N 15	30	11,[c] 3	271–272	$C_{21}H_{19}BrN_4O_4S_2$	Br, 14.93	14.60
D35	33	2.0	42	1.6	C_5H_5N 25	45	83,[d] 55	280–282	$C_{28}H_{29}IN_2O_2S_2$	I, 21.88	22.17
D36	1	1.73	2	1.71	EtOH 15	10	49,[a] 7	218–220	$C_{22}H_{23}ClN_2O_4$	C, 64.68	64.81
	HCl gas 0.45 g. in EtOH 3 cc.; $NaClO_4$ 1.2									H 5.43	5.43
D37	3	1.7	4	1.2	EtOH[b] 20	20	78, 54	219–221	$C_{30}H_{29}ClN_2O_4$	C, 69.68	69.14
										H, 5.66	5.56
D38	4	1.0	5	1.75	EtOH[b] 10	30	71, 34	250–251	$C_{23}H_{22}IN_3O_2S$	I, 23.90	23.75
D39	4	0.7	7	1.2	EtOH[b] 30	30	34, 8	281–282	$C_{27}H_{25}IN_2S$	I, 23.67	23.60
D40	4	2.0	8	2.6	EtOH[b] 15	30	35, 11	238–240	$C_{19}H_{23}IN_2S$	I, 28.96	28.65
D41	4	2.0	9	3.5	EtOH[b] 15	30	51, 17	263–265	$C_{23}H_{23}IN_2Se$	I, 23.80	23.80
D42	4	1.9	10	2.7	EtOH[b] 25	30	31, 10	205–207	$C_{19}H_{22}IN_3S$	I, 28.13	28.43
D43	4	2.0	11	3.94	EtOH[b] 25	180	54,[d] 22	277–279	$C_{27}H_{25}IN_2S$	I, 23.67	23.51
D44	4	2.0	12	3.0	EtOH[b] 15	30	56, 37	252–254	$C_{25}H_{25}IN_2$	I, 26.44	26.42
D45	4	2.0	13	3.55	EtOH[b] 15	30	41, 17	208–210	$C_{27}H_{25}IN_2S$	I, 23.67	23.54
D46	4	3.0	14	4.0	C_5H_5N[b] 30	10	7, 3	204–206	$C_{31}H_{27}IN_2S$	C, 63.46	63.10
										H, 4.64	4.86
D47	4	1.0	15	2.09	C_5H_5N[b] 15	10	24,[a] 15	213–214	$C_{30}H_{27}ClN_2O_4S$	S, 5.86	5.76
D48	4	0.5	16	0.8	C_5H_5N[b] 10	12	31,[a] 21	233–234	$C_{24}H_{23}ClN_2O_4S$	S, 6.81	6.72
D49	4	1.5	17	1.75	EtOH[b] 20	120	98, 64	260–262	$C_{29}H_{27}IN_2$	I, 23.94	23.86
D50	4	2.0	18	2.55	EtOH[b] 25	45	23, 11	215–216	$C_{19}H_{21}IN_2S$	I, 29.10	29.05
D51	4	1.86	19	3.3	EtOH[b] 25	30	35, 24	227–229	$C_{25}H_{25}IN_2S$	I, 24.77	24.51
D52	4	1.86	20	2.7	EtOH[b] 25	30	51, 30	233–235	$C_{20}H_{23}IN_2S$	I, 28.17	28.37
D53	4	1.5	21	2.3	EtOH[b] 15	30	85, 69	253–255	$C_{23}H_{27}IN_2S$	I, 25.89	25.61
D54	4	1.86	22	2.5	EtOH[b] 25	30	16, 6	253–255	$C_{21}H_{23}IN_2$	I, 29.51	29.48
D55	4	1.0	23	1.6	C_5H_5N[b] 10	60	40, 16[g]	236–238	$C_{25}H_{25}IN_2$	I, 25.53	25.39
D56	4	1.86	24	4.0	Ac_2O 25	5	36, 9	190–192	$C_{27}H_{23}IN_2O_2S$	I, 21.91	21.80
D57	4	1.0	25	2.0	EtOH[b] 15	15	86, 42	275–280	$C_{27}H_{23}IN_2O_2S$	I, 21.91	21.97
D58	4	1.86	26	3.6	EtOH[b] 25	30	74, 50	215–217	$C_{25}H_{23}IN_2O_2S$	I, 23.32	23.16
D59	4	1.86	27	3.5	EtOH[b] 25	30	43,[d] 28	186–188	$C_{29}H_{25}IN_2OS$	I, 22.03	21.77
D60	4	1.86	28	3.7	EtOH 25	30	72, 34	237–239	$C_{28}H_{25}BrN_2S$	C, 67.03	67.25
										H, 5.03	5.11
D61	4	0.67	29	1.05	EtOH[b] 25	30	67,[a] 30	264–265	$C_{24}H_{23}ClN_2O_4S$	S, 6.81	6.67
D62	4	0.28	30	0.5	EtOH[b] 10	30	40, 11	251–252	$C_{23}H_{22}IN_3O_2S$	I, 23.90	23.74
D63	4	1.0	31	1.92	EtOH[b] 10	30	38,[d] 13	256–257	$C_{23}H_{22}ClIN_2S$	C, 53.02	52.92
										H, 4.26	4.09
D64	4	1.0	32	1.82	EtOH[b] 10	30	26,[d] 10	258–260	$C_{24}H_{25}IN_2S$	I, 25.37	25.43
D65	4	1.0	33	1.97	EtOH[b] 10	30	33,[d] 28	255–259	$C_{25}H_{27}IN_2OS$	I, 23.93	23.71
D66	4	0.98	34	1.95	EtOH[b] 10	30	18,[d] 11	268–269	$C_{25}H_{27}IN_2OS$	I, 23.93	24.17
D67	35	1.5	12	3.0	EtOH[b] 25	120	39, 23	238–240	$C_{21}H_{23}IN_2$	I, 29.37	29.27
D68	1	1.6	38	1.93	EtOH 25	3	80,[d] 8[g]	168–170	$C_{24}H_{23}IN_2$	I, 26.65	27.31
	HCl gas 0.4 in EtOH 4 cc.		NaI	1.5							
D69	37	2.8	3	3.4	EtOH[b] 25	135	37, 28[g]	175–176	$C_{31}H_{29}ClN_2O_4$	C, 69.04	69.02
										H, 7.30	7.25
D70	37	2.2	6	3.2	EtOH[b] 25	30	52, 23	185–187	$C_{27}H_{29}IN_2$	I, 24.49	24.55
D71	38	4.0	39	4.34	Ac_2O 15	10	79, 73	209–210	$C_{24}H_{23}IN_2O$	I, 25.78	26.05

TABLE IV (*Concluded*)

Dye no.	Reactants, R	g.	R	g.	Medium, cc.	Refluxed, min.	Yield, %	M. p., °C. dec.	Formula	Analyses, % Calcd.	Found
D72	37	2.2	40	3.05	EtOH[b] 25	30	76, 66	215–217	$C_{24}H_{33}IN_2S$	I, 24.97	24.96
D73	37	1.1	11	1.97	EtOH[b] 15	180	18, 7	235–236	$C_{28}H_{35}IN_2S$	I, 22.73	22.67
D74	37	2.2	36	3.4	EtOH[b] 25	60	28,[d] 16	198–200	$C_{26}H_{35}IN_2$	I, 25.27	24.78
D75	37	2.2	13	3.6	EtOH[b] 25	30	66, 50	205–207	$C_{28}H_{35}IN_2S$	I, 22.73	22.57
D76	37	1.93	19	3.3	EtOH[b] 25	20	28,[a] 10	95–97	$C_{26}H_{35}ClN_2O_4S$	C, 61.58	61.22
										H, 6.96	6.95
D77	37	2.2	41	3.0	EtOH[b] 25	30	38, 20	205–206	$C_{26}H_{35}IN_2$	I, 25.27	25.14
D78	50	0.53	3	1.0	EtOH[b] 15	120	57, 20	138–140	$C_{26}H_{27}ClN_2O_4$	C, 66.83	66.02
										H, 5.84	5.59
D79	7	0.7	50	0.36	EtOH[b] 25	210	61, 35	280–281	$C_{23}H_{23}IN_2S$	S, 6.59	6.49
D80	50	1.5	9	3.5	EtOH[b] 25	240	89, 70	250–253	$C_{19}H_{21}IN_2Se$	I, 26.26	26.17
D81	10	1.35	50	0.75	Ac_2O 15	30	79, 54	231–233	$C_{15}H_{20}IN_3S$	I, 31.64	31.52
D82	50	0.55	14	1.5	EtOH[b] 20	240	15, 1	192–194	$C_{27}H_{25}IN_2S$	C, 60.40	59.84
										H, 4.70	4.62
D83	50	0.5	15	0.98	EtOH[b] 20	210	69,[a] 16	237–238	$C_{26}H_{25}ClN_2O_4S$	N, 5.64	5.74
D84	50	0.8	16	1.6	EtOH[b] 20	240	71,[a] 50	240–241	$C_{20}H_{21}ClN_2O_4S$	S, 7.62	7.88
D85	50	3.7	18	7.5	PrOH[b] 15	90	40, 23[h]	142–145	$C_{15}H_{19}IN_2S$	I, 32.87	32.57
D86	50	3.0	19	6.6	EtOH[b] 10	240	24, 17	195–198	$C_{21}H_{23}IN_2S$	I, 27.46	27.54
D87	50	1.5	21	3.1	MeOH[b] 10	135	70, 33	246–247	$C_{19}H_{25}IN_2S$	I, 28.82	28.83
D88	50	1.5	51	2.5	EtOH[b] 12	240	71, 53	257–259	$C_{17}H_{21}IN_2$	I, 33.39	33.03
D89	50	0.75	23	1.6	C_5H_5N[b] 10	60	40, 31	245–247	$C_{21}H_{26}IN_3$	I, 28.39	28.41
D90	50	1.1	25	2.0	EtOH[b] 10	20	81, 45	293–295	$C_{23}H_{20}IN_3O_2S$	I, 23.98	24.02
D91	50	1.5	26	3.63	EtOH[b] 25	240	85, 50	219–221	$C_{21}H_{23}IN_2O_2S$	I, 25.68	25.53
D92	50	0.8	47	2.0	EtOH[b] 15	180	69, 46	201–203	$C_{25}H_{23}IN_2OS$	I, 24.11	23.70
D93	50	1.5	48	3.6	EtOH[b] 15	180	83, 56	214–215	$C_{24}H_{23}IN_2S$	I, 25.47	25.43
D94	50	0.47	29	1.0	EtOH[b] 25	270	71, 20	293–294	$C_{20}H_{21}IN_2S$	N, 6.25	6.06
D95	50	0.37	30	0.88	Ac_2O 20	10	25, 17	250–251	$C_{19}H_{20}IN_3O_2S$	I, 26.38	26.10
D96	50	0.37	52	0.85	Ac_2O 10	5	38, 30	266–267	$C_{19}H_{20}ClIN_2S$	C, 48.45	48.77
										H, 4.28	4.31
D97	50	0.75	32	1.82	Ac_2O 10	5	65,[d] 27	286–287	$C_{20}H_{23}IN_2S$	I, 28.19	28.44
D98	50	0.75	33	1.97	Ac_2O 10	5	76, 50	276–279	$C_{28}H_{32}N_2O_4S_2$	C, 64.06	64.20
										H, 6.15	6.20
D99	50	0.5	53	1.16	Ac_2O 15	5	71, 41	282–283	$C_{21}H_{25}IN_2OS$	I, 26.43	26.58

The dyes appear as follows: D20, glistening orange plates; D21, green crystals; D22, green prisms with metallic reflex; D23, minute reddish crystals; D24, dark greenish crystals; D25, greenish bronze crystals; D26, dark blue needles with greenish reflex; D27, dull greenish metallic crystals; D28, greenish bronze needles; D29, orange crystals with blue reflex; D30, minute dark green crystals; D31, minute crystals with greenish metallic reflex; D32, purplish needles; D33, prisms with bright green reflex; D34, minute dark needles; D35, dark needles with metallic green reflex; D36, minute brown crystals; D37, brown prisms; D38, coppery crystals; D39, reddish brown crystals; D40, yellow crystals; D41, brownish needles; D42, orange prisms; D43, orange needles; D44, red crystals; D45, minute light brown crystals; D46, minute brownish crystals; D47, brown crystals; D48, light yellow crystals; D49, minute orange crystals with green reflex; D50, yellow-buff crystals; D51, amber crystals; D52, light yellow needles; D53, amber crystals; D54, yellow prisms; D55, light yellow crystals; D56, satiny brownish crystals; D57, amber needles with green reflex; D58, brown prisms with blue reflex; D59, orange crystals with blue reflex; D60, yellow crystals; D61, minute vermilion crystals; D62, lustrous brown crystals; D63, red crystals; D64, scarlet crystals; D65, brownish crystals; D66, minute red crystals; D67, reddish crystals; D68, golden crystals; D69, scarlet powder; D70, red crystals; D71, brown crystals with bright reflex; D72, red crystals; D73, scarlet crystals; D74, orange crystals; D75, reddish brown crystals; D76, felt of orange-red crystals; D77, minute deep red crystals; D78, dull purplish powder; D79, dark powder; D80, dark needles with blue and purplish reflex; D81, dark red needles with green reflex; D82, minute dark brown crystals; D83, lustrous dark crystals; D84, red crystals with green reflex; D85, red crystalline powder; D86, dark crystals with green reflex; D87, brownish red crystals; D88, red plates; D89, orange needles; D90, minute dark green needles; D91, minute dark crystals with blue reflex; D92, green plates; D93, leaflets with blue reflex; D94, purplish powder; D95, greenish crystals; D96, purplish crystals with blue reflex; D97, minute purplish crystals with blue reflex; D98, reddish needles; D99 reddish brown needles.

[a] After conversion to perchlorate. [b] Plus piperidine as catalyst. [c] After conversion to bromide. [d] After conversion to iodide. [e] From 50% aqueous EtOH. [f] From 80% aqueous EtOH. [g] From acetone. [h] From water.

Summary

1. The *p*-dimethylaminostyryl derivatives of quaternary salts of a wide variety of heterocyclic bases have been arranged in order of increasing deviation of $\lambda_{max.}$. This order agrees closely with that obtained with the deviations of a series of unsymmetrical pyrrolocarbocyanines.

2. Beyond a certain limit, increasing deviation in either of these two series of dyes is attributed to increasing basicity of the variable heterocyclic nucleus, and it is possible to express this "basicity" in terms of the relative stabilizations of the

(net) charged and uncharged forms of the nuclei, using the conventional arguments of the resonance theory.

3. The order of the deviations of many of the nuclei may be explained in terms of this concept, as are also many of the effects of substitution in these dyes.

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Color and Constitution. VIII.[1] Absorption of Unsymmetrical Carbocyanines

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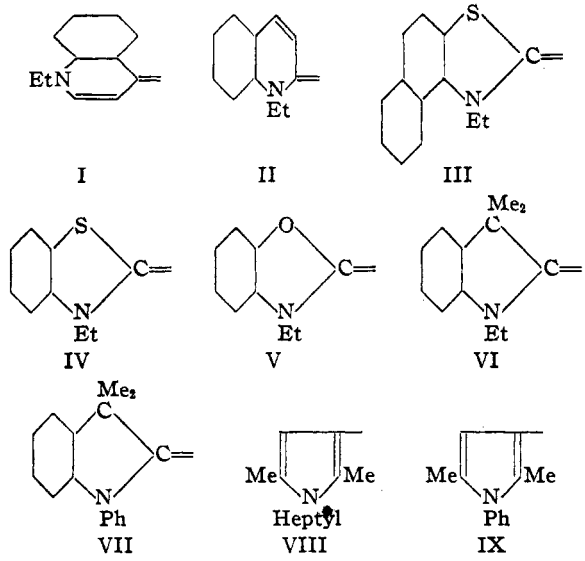
Many unsymmetrical cyanines show relatively small differences between $\lambda_{max.}$ obs. and $\lambda_{max.}$ calcd. while for others this "deviation" is considerable. In the present paper a systematic study has been made of a series of unsymmetrical carbocyanines prepared by condensing the nine nuclei I-IX with each other in all possible arrangements. The nuclei are given in order of decreasing basicity (or "N^{IV} minus N^{III} stabilization") determined for them in the preceding paper.[1] For the sake of uniformity, they are shown with a tertiary nitrogen, although in actual combination in a cyanine, the nitrogen will have partly quaternary character due to resonance.



A principal object of this survey is to determine the quantitative relation of structure to absorption and, specifically, to deviation. Carbocyanines have been selected for the comparison for several reasons. They present fewer difficulties in preparation than the dicarbocyanines, although the latter would show larger deviations. In the simple cyanines, on the other hand, the deviations will be smaller and therefore less significant than with the carbocyanines, and the two nuclei are also in such close proximity that stereochemical and similar influences can be more disturbing than with the carbocyanines.

From the nine nuclei it is theoretically possible to prepare thirty-six unsymmetrical carbocyanines, and these have all been made, using known methods. The absorption spectra of the thirty-six dyes were determined in methyl alcohol, and the observed maxima are given in Table I. Values of $\lambda_{max.}$ calcd. were obtained as the arithmetic means of the absorption maxima of the related symmetrical dyes, and the deviations, $\Delta\lambda$, are also given in the table.

The deviations are plotted in Fig. 1. Each point indicates the deviation of a carbocyanine which contains the nucleus shown at the end of the line on which the point lies, coupled to the nucleus shown vertically above the point. Some of the deviations are plotted above the zero axis and others below. The reason for this is that a nucleus of intermediate position, such as VI, shows deviations when combined with nuclei of higher and also of lower basicity. If these deviations were plotted in the same direction from zero, it is possible that the same point might have to be shared by two nuclei that differed widely in basicity, whereas this difficulty is avoided in the present method. As it now stands, a deviation in one direction from the zero axis indicates combination with a nucleus of higher basicity, and in the opposite direction, combination with a nucleus of lower basicity. It should also be pointed out that the method used is such that each deviation is plotted twice on the chart; for example, the deviation of the carbocyanine containing nuclei I and IX—this dye may be referred to as (I + IX)—is plotted in the vertical column I and also in the vertical column IX.

The greatest deviations are, of course, shown when those nuclei that differ most markedly in basicity are combined together. Less sharply contrasting nuclei give smaller deviations. Outside of the region of intersecting lines enclosed by the dotted ellipse, there is only one point in the chart where the lines intersect and, with this exception, the same order of basicity of the nuclei is maintained from series to series. This exception is that the combination (III + IX) shows a slightly greater deviation than (II + IX), thus making III more basic than II, although in combination with nuclei VI, VII, and VIII, II consistently gives higher deviations, as it does moreover in the styryl dyes.[1]

(1) Part VII, THIS JOURNAL, 67, 1875 (1945).