(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.

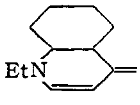
ROCHESTER 4, N. Y. RECEIVED DECEMBER 5, 1944

[COMMUNICATION NO. 1008 FROM THE KODAK RESEARCH LABORATORIES]

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

BY L. G. S. BROOKER, R. H. SPRAGUE AND H. W. J. CRESSMAN

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.



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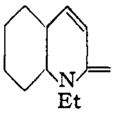

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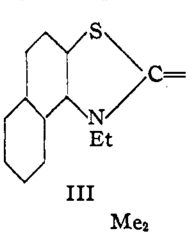

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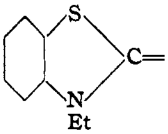

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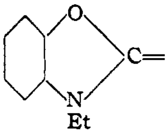

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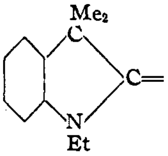

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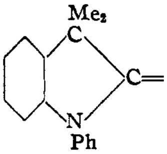

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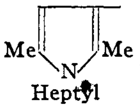

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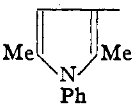

IX

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]

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

TABLE I

OPTICAL DATA[a]

Dye name	Nuclei	Dye no.[b]	$\lambda_{max.}$ obs. MeOH, Å.	$\lambda_{max.}$ calcd., Å.	Deviation, Å.
1,1′-DiEt-2,4′-carbocy.I	I + II	D100	6550(6550^c)	6545	−5
1′,3-DiEt-4,5-benzothia-4′-carbocy.I	I + III	D101	6520(6470^c)	6500	−20
1′,3-DiEt-thia-4′-carbocy.I	I + IV	D102	6300(6300^c)	6315	15
1′,3-DiEt-oxa-4′-carbocy.I	I + V	D103	5940(5960^c)	5940	0
1,1′-DiEt-3,3-diMe-indo-4′-carbocy.ClO_4	I + VI	ND104	6040	6260	220
1′-Et-3,3-diMe-1-Ph-indo-4′-carbocy.ClO_4	I + VII	ND105	5920	6300	380
1′,3-DiEt-4,5-benzothia-2′-carbocy.I	II + III	D106	5970(6000^c)	5990	20
1′,3-DiEt-thia-2′-carbocy.I	II + IV		5780^d	5810	30
1′,3-DiEt-oxa-2′-carbocy.I	II + V	D107	5420(5450^{c,e})	5435	15
1,1′-DiEt-3,3-diMe-indo-2′-carbocy.ClO_4	II + VI	ND108	5610	5755	145
1′-Et-3,3-diMe-1-Ph-indo-2′-carbocy.ClO_4	II + VII	ND109	5540	5795	255
3,3′-DiEt-4,5-benzothiacarbocy.I	III + IV	D110	5765(5770^c)	5760	−5
3,3′-DiEt-4′,5′-benzooxathiacarbocy.I	III + V	D111	5360(5370^c)	5390	30
1,3′-DiEt-3,3-diMe-4′,5′-benzoindothiacarbocy.I	III + VI	ND112	5600	5710	110
3′-Et-3,3-diMe-1-Ph-4′,5′-benzoindothiacarbocy.I	III + VII	ND113	5570	5750	180
3,3′-DiEt-oxathiacarbocy.I	IV + V	D114	5200(5200^c)	5200	0
1,3′-DiEt-3,3-diMe-indothiacarbocy.I	IV + VI	ND115	5420	5520	100
3′-Et-3,3-diMe-1-Ph-indothiacarbocy.ClO_4	IV + VII	ND116	5420	5565	145
1,3′-DiEt-3,3-diMe-indooxacarbocy.I	V + VI	ND117	5080	5145	65
3′-Et-3,3-diMe-1-Ph-indooxacarbocy.ClO_4	V + VII	ND118	5080	5190	110
1-Et-3,3,3′,3′-tetraMe-1′-Ph-indocarbocy.ClO_4	VI + VII	ND119	5480	5510	30
1-*n*-Heptyl-2,5,2′,5′-tetraMe-1′-Ph-3,3′-pyrrolocy.I	VIII + IX	ND120	4440	4455	15

[a] The optical data for fourteen of the unsymmetrical dyes and for the nine symmetrical dyes required in this paper have already been given in Part VI or VII, and are not repeated here. [b] Twenty-one of the unsymmetrical dyes in Table I are assigned numbers 100 to 120. Where a dye is new, its number is preceded by ND (for New Dye). If the number is preceded by D alone, it indicates either that the dye has been reported without preparative details, or that our method of preparation differs from that previously given. [c] Beilenson, Fisher and Hamer, *Proc. Roy. Soc.* (London), **A163**, 138 (1937). [d] Brooker and Sprague, THIS JOURNAL, **63**, 3203 (1941). [e] Ogata, *Bull. Inst. Phys. Chem. Research* (Tokyo), **13**, 557 (1934).

The crowded region of intersecting lines enclosed by the dotted ellipse is prominent in the diagram. This represents the quite insignificant deviations, none over 30 Å., obtained when the five most strongly basic nuclei, I–V, are combined with each other.

Every dye tends to achieve the highest possible resonance stabilization and, other things being equal, this reaches its maximum value in a symmetrical dye. It would appear that, up to a point at least, the effect of a small chemical change upon the deviation will vary in some inverse fashion with the resonance stabilization of the dye on which the change is carried out and, thus, a small change carried out on a symmetrical dye produces a minimum and indeed often a negligible deviation. This appears to be particularly true where the symmetrical dye contains nuclei of relatively high basicity, such as I through V, and the "small chemical change" consists of the replacement of one of these nuclei by one of the others in this group. It is thus easy to see why the early investigators who restricted themselves in general to combinations of this kind were unable to detect significant deviations among unsymmetrical carbocyanines.[2]

It is seen from Fig. 1 that the deviations of nuclei I to IV are very small when they are combined with V, but that the deviations show abrupt increases when I to V are combined with VI. This is probably due to a large *absolute* difference of basicity between nuclei V and VI, whereas in the chart the vertical columns are arbitrarily separated by equal intervals. The magnification of the differences shown by nuclei I-V when they are coupled with VI is, in general, continued when they are combined with the progressively less basic nuclei VII, VIII, and IX.

(2) (a) Beilenson, Fisher and Hamer, *Proc. Roy. Soc.* (London), **A163**, 139 (1937); (b) Yoshimura and Sakurai, *Bull. Inst. Phys. Chem. Research* (Tokyo), **16**, 1292 (1937). The latter investigators actually examined one unsymmetrical carbocyanine, the deviation of which is rather large. This is that in which IV is combined with a nucleus similar to VI but with N-Me in place of N-Et. The observed wave number of maximum absorption is given as 1818 mm.$^{-1}$ against 1811 mm.$^{-1}$ calculated, and these figures are described as making good agreement. This method of calculation lessens the deviation, however, and by our method their figures give a deviation of 80 Å., which is not inconsiderable and compares with our value of 100 Å. for the dye with nuclei IV and VI; (c) the following has been added in proof. In two articles [Kiprianov, *Dopovidi Akad. Nauk. U. R. S. R.*, No. **12**, 3–17 (1940): Kiprianov and Pilyugin, *Byull. Vsesoyuz. Khim. Obshchestva im. D. I. Mendeleeva*, No. **3-4**, 60–61 (1939)] of which only the abstracts are available to us [*C. A.*, **34**, 4663 (1940); *C. A.*, **38**, 1427 (1944)] but which had escaped our notice until recently, it was reported that certain unsymmetrical carbocyanines absorbed at shorter wave length than that calculated, particularly when the heterocyclic rings "differed greatly in their aromatic characteristics or in the basicity of the heterocyclic nitrogens." These findings are in full agreement with ours, but our results were obtained quite independently of the Russian work, of course, and in fact our first account of an unsymmetrical carbocyanine which behaved in this way was published [THIS JOURNAL, **62**, 1116 (1940)] before the appearance of the first of the two abstracts.

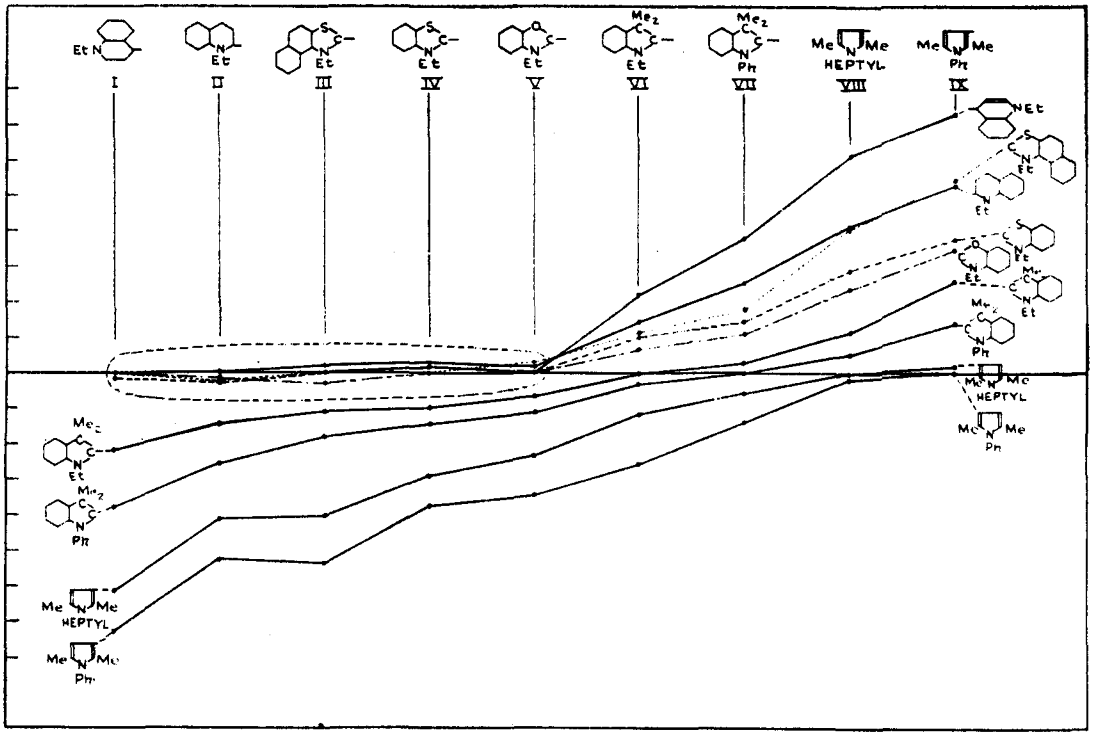

Fig. 1.—Deviations of a series of thirty-six unsymmetrical carbocyanines obtained from nuclei I to IX.

Data given in the figure may be used to test the validity of the sensitivity rule[8] that the effect on the deviation of a given small chemical change is greater the higher the asymmetry of the dye in which the change is carried out.

If the rule were followed without exception, the transverse lines of the chart would progressively diverge toward the left in the lower half of the figure and toward the right in the upper half and although many instances may be selected where this is true, there are definite exceptions.

Perhaps the best illustration of the rule is provided by a comparison of dyes containing the indolenine (or pseudoindole) nuclei, VI and VII. In each dye with VI, replacement of N-ethyl by phenyl in this nucleus gives the corresponding dye with VII, but the effect on the deviation varies from dye to dye. This effect is seen to be greatest with that derivative of VI which shows the highest deviation, namely, (I + VI). The deviation of this dye is 220 Å. and this is increased to 380 Å. in (I + VII), an increment of 160 Å. The similar chemical replacement (II + VI) → (II + VII) produces a smaller effect, the deviation being increased by 110 Å. from 145 to 255 Å., and where the same change is carried out in (III + VI), giving (III + VII) the increase in deviation is only 70 Å. The effect on the deviation thus diminishes as the dye system in which the replacement is carried out approaches energetic degeneracy of the extreme structures, and the change carried out on the symmetrical dye (VI + VI) produces a deviation of only 30 Å. The deviation increases again, however, when VI and VII are combined with the less basic pyrrole nuclei, VIII and IX, but now it is VI that gives the higher deviations.

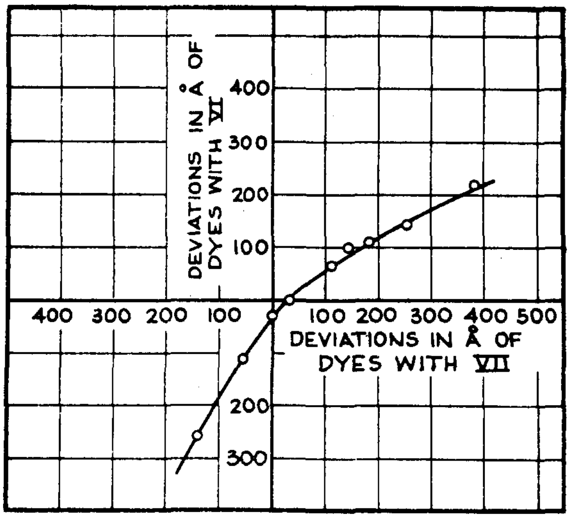

Fig. 2.—Deviations of dyes with nucleus VI plotted against those with VII.

The same rule is brought out in Fig. 2. In this figure the deviations of the unsymmetrical dyes containing VI are plotted against those of the corresponding dyes containing VII, the upper right-hand quadrant containing the deviations of those dyes in which the variable nucleus is more

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(8) Part III. This Journal, 63, 3203 (1941).

basic than VI or VII and the lower left-hand quadrant where this nucleus is less basic than VI or VII.

The points lie on a continuous curve which has an inflection point near the origin. The upper part consists of a gently sloping curve which approximates to a straight line inclined to the horizontal axis at less than an angle of 45°, and the lower part of the curve is similarly inclined to the vertical axis at less than 45°. It may be shown that these conditions satisfy the requirements of the sensitivity rule.

Divergence of the transverse lines in Fig. 1 is also well marked on passing from the set of points vertically below VII to those below VIII, and from VIII to IX it is well marked in the lower, but not in the upper, part of the column. Here it seems as if a limit in asymmetry of the molecule is approached beyond which any added asymmetry increases the deviation by a constant amount. In other words, the sensitivity rule has ceased to apply. The existence of such a limit is also indicated in the theoretical results of Herzfeld and Sklar.[4]

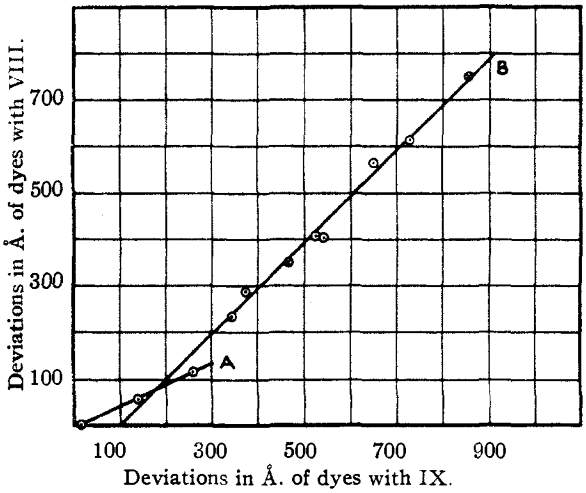

Fig. 3.—Deviations of dyes with VIII plotted against those with IX. Points ⊙ are taken from Fig. 1. Points ⊗ are additional to these.

This point is illustrated further in Fig. 3 in which the deviations of the unsymmetrical dyes with VIII as one nucleus are plotted against those with IX. Two comparisons not available from Fig. 1 are also included here; in them the constant nuclei are those of α-naphthothiazole and 4-pyridine. The three lowest points on the curve lie very close to a straight line A inclined to the horizontal axis at less than 45°, and in this region the sensitivity rule is followed, but the remainder of the points lie reasonably close to a straight line B inclined to the axes at almost exactly 45° and with an intercept on the horizontal axis of almost exactly 100 Å. In this region the deviation of one of the dyes with nucleus IX is obtained with fair accuracy simply by adding 100 Å. to that of the corresponding dye with VIII, and the sensitivity rule has ceased to hold.

It would be interesting to amplify Fig. 1 by using nuclei of intermediate basicity to those already employed, and also nuclei of different structures but of almost identical basicity as, for example, those of 3-ethyl-5-nitrobenzothiazole and 3-*o*-nitrophenylbenzothiazole. In this way irregularities in the general pattern would probably be smoothed out.

Acknowledgments.—Our thanks are due to Dr. L. T. Hallett and Mr. Donald Ketchum for the microanalyses, and to Mr. E. E. Richardson and Dr. L. A. Jones for the absorptions.

Experimental

Some of the reactants used in the preparation of the dyes are listed and numbered in Table II of the preceding paper. Additional intermediates are numbered R63 to R73 in Table II of the present paper.

TABLE II

REACTANTS USED IN DYE SYNTHESES

R63	4-β-Anilinovinyl-1-ethylquinolinium iodide
R64	2-β-Acetanilidovinyl-3-ethylbenzothiazolium iodide
R65	Sodium acetate
R66	4-β-Acetanilidovinyl-1-ethylquinolinium iodide
R67	2-β-Anilinovinyl-1-ethylquinolinium iodide
R68	2-β-Acetanilidovinyl-3,3-dimethyl-1-phenylpseudo-indolium perchlorate[a]
R69	2-β-Acetanilidovinyl-1-ethylquinolinium iodide
R70	1-Ethyl-2-methylquinolinium *p*-toluenesulfonate
R71	2-β-Acetanilidovinyl-1-ethylnaphtho[1,2]thiazolium *p*-toluenesulfonate[b]
R72	1-Ethyl-2-methylnaphtho[1,2]thiazolium *p*-toluenesulfonate
R73	3-Ethyl-2-methylbenzothiazolium *p*-toluenesulfonate

[a] 6.8 g. (1 mol) of 2,3,3-trimethyl-1-phenylpseudoindolium perchlorate and 4.8 g. (1 mol + 20% excess) of diphenylformamidine were heated together in 20 cc. of acetic anhydride at the refluxing temperature for fifteen minutes. The product was precipitated from the cold reaction mixture with 300 cc. of ether. The brown crystals were washed with a small volume of cold ethyl alcohol and used without further purification; yield 90%. [b] 10 g. (1 mol) of 1-ethyl-2-methylnaphtho[1,2]thiazolium *p*-toluenesulfonate and 9.8 g. (1 mol + 100% excess) of diphenylformamidine were heated together in 25 cc. of acetic anhydride at the refluxing temperature for twenty-two minutes. The product was precipitated from the cold reaction mixture with ether. After chilling at 0°, the brown crystals were washed with ether followed by acetone and used without further purification; yield 67%.

Details of the preparation of the dyes in Table I to which numbers have been assigned (*cf.* Table I, footnote *b*) are given in Table III. In each case the appropriate components were allowed to react by heating to the refluxing point in the solvent shown. The dye separated either on chilling or on the addition of ether. The yield of crude dye is given, followed by the yield after from one to three recrystallizations from ethyl or methyl alcohol.

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(4) Herzfeld and Sklar, *Rev. Mod. Phys.*, **14**, 297 (1942).

TABLE III

DETAILS OF DYE SYNTHESES

Dye no.	Reactants				Medium, cc.	Refluxed, min.	Yield, %	M. p., °C., dec.	Formula	Analyses, %			
	R	g.	R	g.						Calcd.	Found	Calcd.	Found
D100[a,b]	41	1.5	67	2.0	C_5H_5N 25	30	59, 12	227–231	$C_{25}H_{25}IN_2$	I, 26.43	26.60		
D101	13	1.0	63	2.0	C_5H_5N 20	15	45, 10	243–245	$C_{27}H_{25}IN_2S$	I, 23.67	23.67		
D102	41	1.5	64	2.25	C_5H_5N 25	10	55, 12	262–265	$C_{23}H_{23}IN_2S$	C, 56.76	56.40	H, 4.77	4.67
D103	41	1.5	39	2.17	EtOH 20	30	40, 9	260–262	$C_{23}H_{23}IN_2O$	C, 58.70	58.29	H, 4.93	4.75
	65	0.8											
ND104	6	3.15	66	4.44	C_5H_5N 15	15	64,[c] 34	226–227	$C_{26}H_{29}ClN_2O_4$	C, 66.58	66.55	H, 6.24	6.18
ND105	68	1.2	41	0.75	C_5H_5N 15	15	54, 23	253–255	$C_{30}H_{29}ClN_2O_4$	C, 69.68	69.37	H, 5.66	5.42
D106	13	1.8	67	2.0	C_5H_5N 25	30	50, 30	269–271	$C_{27}H_{25}IN_2S$	I, 23.67	23.56		
D107	22	1.5	39	2.17	EtOH 40	30	60, 25	248–250	$C_{23}H_{23}IN_2O$	C, 58.70	58.43	H, 4.93	4.83
	65	0.8											
ND108	6	1.6	69	2.2	C_5H_5N 25	20	64,[c] 13	247–248	$C_{26}H_{29}ClN_2O_4$	C, 66.58	66.39	H, 6.24	6.19
ND109	68	1.2	70	0.86	C_5H_5N 15	30	47, 35	230–231	$C_{30}H_{29}ClN_2O_4$	C, 69.68	69.31	H, 5.66	5.65
D110	13	1.8	64	2.25	C_5H_5N 40	10	83, 33	263–265	$C_{25}H_{23}IN_2S_2$	I, 23.41	23.27		
D111	13	1.8	39	2.17	C_5H_5N 25	10	70, 25	239–241	$C_{25}H_{23}IN_2OS$	I, 24.12	23.97		
ND112	6	1.6	71	2.7	C_5H_5N 25	15	98, 33	231–233	$C_{28}H_{29}IN_2S$	I, 22.98	23.22		
ND113	68	1.2	72	1.0	C_5H_5N 15	15	70, 21	278–279	$C_{12}H_{28}ClN_2O_4S$	C, 67.16	67.32	H, 4.93	5.00
D114[d]	40	1.5	39	2.17	C_5H_5N 25	10	88, 40	260–262	$C_{21}H_{21}IN_2OS$	C, 52.93	52.45	H, 4.45	4.46
ND115	6	1.6	64	2.25	C_5H_5N 15	10	99, 52	252–253	$C_{24}H_{27}IN_2S$	I, 25.27	25.28		
ND116	68	1.2	73	0.87	C_5H_5N 15	15	85, 31	224–225	$C_{28}H_{27}ClN_2O_4S$	C, 64.27	63.92	H, 5.21	5.05
ND117	36	3.15	39	4.34	C_5H_5N 25	5	84, 45	266–267	$C_{24}H_{27}IN_2O$	I, 26.11	26.02		
ND118	3	0.9	39	1.1	C_5H_5N 15	15	60, 32	245–246	$C_{28}H_{27}ClN_2O_5$	C, 66.30	66.50	H, 5.37	5.41
ND119	6	0.8	68	1.2	C_5H_5N 15	15	75, 41	272–273	$C_{31}H_{33}ClN_2O_4$	C, 69.82	69.48	H, 6.24	6.24
ND120	4	4.0	38	4.0	EtOH 50	3	67, 42	177–179	$C_{25}H_{35}IN_2$	I, 25.27	25.09		
	HCl gas	0.8 g. in EtOH 8 cc.	NaI	3.0									

The dyes appear as follows: D100, green crystals with golden reflex; D101, greenish grey crystals; D102, green needles; D103, blue needles with green reflex; ND104, dull crystals with greenish reflex; ND105, dark green crystals with bronze reflex; D106, greenish blue crystals; D107, dull bluish crystals; ND108, black crystals; ND109, garnet crystals with metallic green and bronze reflex; D110, dark green crystals; D111, dark blue crystals; ND112, dull brownish crystals; ND113, small needles with green reflex; D114, blue crystals; ND115, blue crystals; ND116, red and green crystals; ND117, large crystals with green reflex; ND118, red crystals; ND119, purple crystals with green reflex; ND120, orange crystals.

[a] Mills and Odams, *J. Chem. Soc.*, **125**, 1913 (1924). [b] Ogata, *Bull. Inst. Phys. Chem. Research* (Tokyo), **13**, 557 (1934). [c] after conversion to perchlorate. [d] *Cf.* Piggott and Rodd, U. S. Patent 2,071,899.

Summary

1. Nine different heterocyclic nuclei, ranging in basicity from quinoline to pyrrole, have been combined in all possible arrangements to give thirty-six unsymmetrical carbocyanines.

2. The ten unsymmetrical carbocyanines obtained by combining N-ethyl-substituted 2- and 4-quinoline, β-naphthothiazole, benzothiazole, and benzoxazole in all arrangements show negligible deviations ($\lambda_{\max.}$ calcd. minus $\lambda_{\max.}$ obs.) of 30 Å. or less. If these five nuclei are combined with N-ethyl-3,3-dimethylindolenine, however, deviations ranging from 65 to 220 Å. are obtained, and these figures are increased when the five are combined with progressively less basic nuclei. The greatest deviation obtained is 725 Å.

3. Many of the data illustrate the "sensitivity rule," but exceptions are noted.

ROCHESTER 4, N. Y. RECEIVED DECEMBER 5, 1944