

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 67

NOVEMBER 15, 1945

NUMBER 11

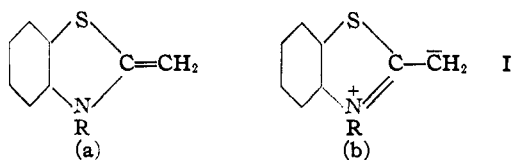
[COMMUNICATION NO. 1006 FROM THE KODAK RESEARCH LABORATORIES]

Color and Constitution. VI.¹ Pyrrolocyanines

BY L. G. S. BROOKER AND R. H. SPRAGUE

Although a wide variety of heterocyclic nuclei have been employed in cyanine dyes, the pyrrole ring has not so far been used for this purpose,^{1a} if one excepts a very large group of salts of so-called pyrro- (or dipyrrolyl-) methenes.² These have hydrogen attached to both nitrogen atoms and are therefore not strictly cyanines.

The cyanines are frequently, although not invariably, derived from quaternary salts of cyclic bases containing reactive methyl, these salts giving rise, by loss of acid, to methylene bases such as 3-alkyl-2-methylenebenzothiazoline (I). Such



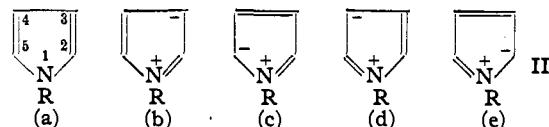
methylene bases probably constitute the reactive intermediates in many of the dye syntheses.

(1) Part V, THIS JOURNAL, 64, 199 (1942).

(1a) Note added in proof: Since this paper was submitted for publication a paper by Cook and Majer on "Pyrrole trimethine-cyanines" has appeared [*J. Chem. Soc.*, 482 (1944)] in which it is stated that "pyrrole nuclei . . . have not hitherto figured in compounds of this type (cyanine dyes) if the very numerous class of dipyrromethene salts is excepted." A 2,2'-pyrrolotrimethinecyanine with hydrogen atoms in place of the conventional N-alkyl groups was first described by König [*Z. angew. Chem.*, 38, 743 (1925)] and Cook and Majer have also overlooked our patents (Kodak Ltd., British Patent 529,440 (1940); Brooker and Sprague, U. S. Patents 2,268,798 (1942) and 2,298,731 (1942)) dealing with a wide variety of pyrrolocyanines, both symmetrical and unsymmetrical.

(2) (a) Fischer-Orth, "Die Chemie des Pyrrols," Vol. II, 1st Part, Akademische Verlagsgesellschaft m. b. H., Leipzig, 1937, p. 1, *et seq.* (b) An account of a symmetrical cyanine containing two N-alkylpyrrole rings was published by Brunings and Corwin (THIS JOURNAL, 64, 593 (1942)), when the work described in the present paper was nearing completion. They name their compound a dipyrrolylmethene salt, but this is open to certain objections, one of which is that it tends to create a distinction between pyrrole derivatives of this type and the previously studied cyanines, which seems to us to be undesirable. We have accordingly preferred to use the name pyrrolocyanines.

The 3-methylidyne (formerly called methenyl) group in N-substituted pyrroles (IIa) is somewhat similarly linked, with respect to nitrogen, to the methylene group in Ia. In both groups the hydrogen atoms are attached to carbon which is joined by a double bond to a second carbon atom which, in turn, is singly linked to nitrogen.

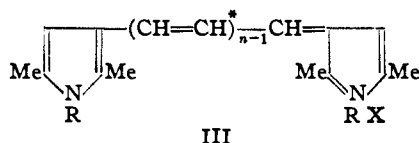


It is probable that the reactivity of I is in some way connected with the existence of the resonance structure Ib, and, since a similar structure IIb may be devised, it seemed possible that a somewhat similar reactivity in cyanine dye syntheses might be encountered in II also. There is the difference, however, that whereas there is only the one external methylene group in I, in the pyrrole ring additional resonance structures are possible (IIc, d, and e), which should result in all four of the =CH— groups being influenced, with a possible weakening of the activation at any one of the four points due to this distribution. In IIc, the 5-methylidyne group is involved, the conjugated system involved in the resonance IIa ↔ IIc extending around the periphery of the ring, so that a reactive α -position in pyrrole might be regarded more properly as a reactive δ -position. Structures II d and e, which are identical with IIb and c, respectively, should similarly confer activity on the methylidyne hydrogens in positions 4 and 2. It should be pointed out that both hydrogens of the methylene group in I are necessary for at least certain dye condensations,³ whereas only one is available in each of the pyrrole methylidyne groups, and this constitutes a further distinction between I and II.

(3) Mills and Raper, *J. Chem. Soc.*, 127, 2466 (1925).

A very wide variety of N-substituted pyrroles are known with one or more of the remaining positions unoccupied. Of these the N-substituted 2,5-dimethylpyrroles are especially readily available, being made by the Paal-Knorr synthesis from acetylacetone and primary amines.⁴ In these pyrroles, only positions 3 and 4 are unsubstituted and available for reaction, and these positions are, of course, equivalent.

That these β -positions are indeed reactive is shown by the fact that symmetrical dyes of two chain lengths (III, $n = 1, 2$) have been prepared from 1-ethyl-2,5-dimethylpyrrole and from 2,5-dimethyl-1-phenylpyrrole.⁵



* $n - 1$ is used here rather than n so that the same value of n can be used both for the dyes III and the unsymmetrical dyes V and VIII when their absorptions are compared in Figs. 1, 2 and 3.

The dye from 1-ethyl-2,5-dimethylpyrrole with the shorter chain length ($n = 1$) was satisfactorily obtained by treating the pyrrole with ethyl orthoformate in the presence of hydrochloric acid, but when applied to 2,5-dimethyl-1-phenylpyrrole, this method was greatly inferior to that in which the pyrrole was condensed with the corresponding 3-pyrrolecarboxaldehyde in the presence of acid. The 1,1'-diethyl dye (III, $n = 1$, R = Et) absorbs with its maximum at 4425 Å., and the corresponding 1,1'-diphenyl derivative is slightly deeper with λ_{\max} of 4485 Å. These dyes are, however, considerably lighter in color than a simple cyanine containing two pyridine rings, 1,1'-diethyl-2,2'-pyridocyanine iodide, which has λ_{\max} of 4825 and 4650 Å.,⁶ in spite of the fact that the shortest resonating conjugated chain between the nitrogen atoms in the latter has two carbon atoms fewer than that in the pyrrole dyes.

The dyes of the longer chain length ($n = 2$) were obtained by condensing the pyrroles with β -ethoxyacrolein acetal in the presence of acid. These absorbed with λ_{\max} of 5365 and 5410 Å. for R = Et and Ph, respectively, the vinylenes shifts therefore being 940 and 925 Å. and close to the average of about 1000 Å. observed for symmetrical cyanines in general.⁷

The reactivity of the β -methylidyne hydrogens in N-substituted 2,5-dimethylpyrroles is also demonstrated by the fact that these bases undergo condensation with certain intermediates used in the preparation of unsymmetrical cyanine dyes,⁸

(4) For a review of these syntheses, see Hazlewood, Hughes and Lions, *J. Proc. Roy. Soc. N. S. Wales*, **71**, 92 (1937).

(5) Brooker and Sprague, U. S. Patent 2,268,798; Kodak Limited, British Patent 529,440.

(6) Brooker and Keyes, *THIS JOURNAL*, **57**, 2488 (1935).

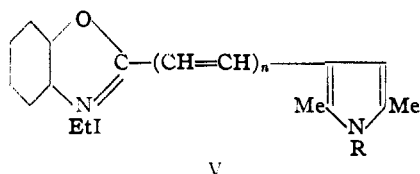
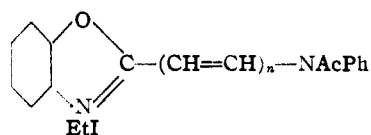
(7) Fisher and Hamer, *Proc. Roy. Soc. (London)*, **A154**, 703 (1936).

(8) Brooker and Sprague, U. S. Patent 2,298,731; Kodak Ltd., British Patent 529,440.

although under rather narrowly prescribed conditions.

Attempts to condense these pyrroles with intermediates such as 2-iodoquinoline ethiodide and 2-methylmercaptobenzothiazole methiodide, which are commonly used in the synthesis of simple cyanines, were unsuccessful, so that the simplest pyrrolocyanines in which the two nuclei are linked together directly have not been obtained.

However, the 1-ethyl- and 1-phenyl-2,5-dimethylpyrroles undergo condensation with 2- β -acetanilidovinylbenzoxazole ethiodide (IV, $n = 1$) in the presence of acetic anhydride to give the



yellow dyes V ($n = 1$; R = Et, Ph) which are unsymmetrical dimethine cyanines.⁹

Experiments with intermediates of the β -acetanilidovinyl type but derived from nuclei other than benzoxazole were not so successful. However, it was found that the desired compounds could be prepared readily by condensing a quaternary salt containing reactive methyl with the appropriate 3-pyrrolecarboxaldehyde. Thus, 2,5-dimethyl-1-phenyl-3-pyrrolecarboxaldehyde underwent condensation with lepidine ethiodide in the presence of piperidine to give VI, and the same aldehyde gave VII when condensed with γ -picoline ethiodide. Use of 2-methylbenzothiazole ethiodide and 2,3,3-trimethylindolenine ethiodide in this reaction gave VIII ($n = 1$) and IX, respectively.

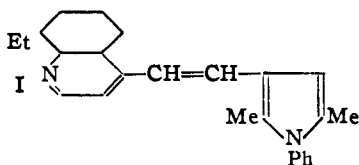
The preparation of the higher vinylenes homologs of these unsymmetrical dimethine cyanines presented difficulties at first in that condensation did not take place between 4-acetanilidobutadi-

(9) The nomenclature of the pyrrolocyanines presents certain peculiarities. Symmetrical monomethine dyes, such as III ($n = 1$), have the shortest possible connecting chain between the nuclei and may therefore be called simple pyrrolocyanines in spite of the fact that their method of preparation is similar to that which gives carbocyanines when applied to quaternary salts of bases of, for example, the quinaldine type. The trimethine dyes III ($n = 2$) may similarly be called pyrrolocarbocyanines. In unsymmetrical dyes of the type of V, linkage between the nuclei is between 0, 2, 4, etc., methine groups. The lowest conceivable homolog of this series is where $n = 0$, the nuclei being linked together directly, and the dye could be called an oxapyrrolocyanine, but it should be noted that it is not possible to select symmetrical dyes of which this unsymmetrical dye is the structural hybrid. Dimethine dyes, such as V ($n = 1$), would be called oxapyrrolocarbocyanines, bearing in mind that they are the structural crosses between oxacarbocyanines and what have been termed above simple cyanines of the pyrrole series.

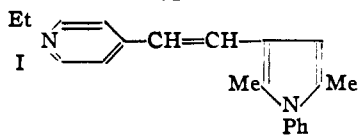
TABLE I
 OPTICAL DATA ON SYMMETRICAL AND UNSYMMETRICAL CYANINES^a

Dye name	Formula, in text	Dye no., Tables I and II	$\lambda_{\max.}$ obs., MeOH, Å.	$\lambda_{\max.}$ calcd., Å.	Deviation, Å.
Symmetrical Dyes					
3,3'-DiEt-oxacarboc. I			4825 ^b		
3,3'-DiEt-oxadiboc. I			5800 ^b		
3,3'-DiEt-thiacarboc. I			5575 ^c		
3,3'-DiEt-thiadiboc. I			6500 ^c		
1,1'-DiEt-3,3,3',3'-tetraMe-indocarboc. I			5465 ^d		
1,1'-DiEt-4,4'-carboc. I			7050 ^e		
1,1'-DiEt-4,4'-pyridocarboc. I		D1	6030		
1,1'-DiEt-2,2',5,5'-tetraMe-3,3'-pyrroloc. I	III R = Et; $n = 1$	D2	4425		
1,1'-DiEt-2,2',5,5'-tetraMe-3,3'-pyrrolocarboc. I	III R = Et; $n = 2$	D3	5365		
2,2',5,5'-TetraMe-1,1'-diPh-3,3'-pyrroloc. I	III R = Ph; $n = 1$	D4	4485		
2,2',5,5',TetraMe-1,1'-diPh-3,3'-pyrrolocarboc. I	III R = Ph; $n = 2$	D5	5410		
Unsymmetrical dyes					
1',3-DiEt-2',5'-diMe-oxa-3'-pyrrolocarboc. I	V R = Et; $n = 1$	D6	4400	4625	225
1',3-DiEt-2',5'-diMe-oxa-3'-pyrrolocarboc. I	V R = Et; $n = 2$	D7	5160	5585	425
3-Et-2',5'-diMe-1'-Ph-oxa-3'-pyrrolocarboc. I	V R = Ph; $n = 1$	D8	4310	4655	345
3-Et-2',5'-diMe-1'-Ph-oxa-3'-pyrrolocarboc. I	V R = Ph; $n = 2$	D9	4920	5605	685
1,1'-DiEt-2,5-diMe-3-pyrrolo-4'-carboc. I	VI Et replaces Ph	D10	5130	5740	610
1'-Et-2,5-diMe-1-Ph-3-pyrrolo-4'-carboc. I	VI	D11	5040	5770	730
1,1'-DiEt-2',5'-diMe-4-pyrrolo-3'-pyrrolocarboc. I	VII Et replaces Ph	D12	4480	5230	750
1-Et-2',5'-diMe-1'-Ph-4-pyrrolo-3'-pyrrolocarboc. I	VII	D13	4405	5260	855
1,3'-DiEt-2,5-diMe-3-pyrrolothiacarboc. I	VIII Et replaces Ph; $n = 1$	D14	4720	5000	280
1,3'-DiEt-2,5-diMe-3-pyrrolothiadiboc. I	VIII Et replaces Ph; $n = 2$	D15	5480	5935	455
3'-Et-2,5-diMe-1-Ph-3-pyrrolothiacarboc. I	VIII $n = 1$	D16	4655	5030	375
3'-Et-2,5-diMe-1-Ph-3-pyrrolothiadiboc. I	VIII $n = 2$	D17	5220	5955	735
1,1'-diEt-2',3,3,5'-tetraMe-indo-3'-pyrrolocarboc. I	IX Et replaces Ph	D18	4820	4945	125
1-Et-2',3,3,5'-tetraMe-1'-Ph-indo-3'-pyrrolocarboc. I	IX	D19	4710	4970	260

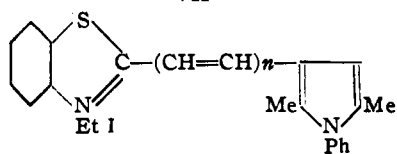
^a The optical data for the dyes required in Figs. 1 to 3 are given in this table. New dyes are assigned numbers D1 through D19 to save duplication of names in Table II. ^b Ref. 7. ^c Brooker, Sprague, Smyth and Lewis, *THIS JOURNAL*, 62, 1116 (1940). ^d Hamer, *J. Chem. Soc.*, 2804 (1927). ^e Ref. 1.



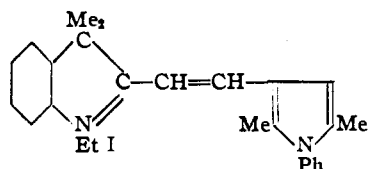
VI



VII

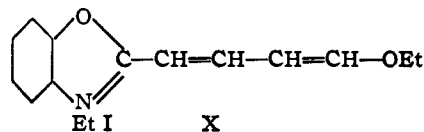


VIII



IX

enyl intermediates of the type of IV ($n = 2$) and the pyrroles, even when the second nucleus was that of benzoxazole. However, it was found that intermediates of a new type could be prepared by the interaction of quaternary salts containing reactive methyl with β -ethoxyacrolein acetal in the presence of acetic acid.¹⁰ These new intermediates reacted with the pyrroles to give the desired dyes. Thus, 2-methylbenzoxazole ethiodide and the acetal gave X, and this reacted with the 2,5-dimethyl-N-substituted pyrroles to give



the dyes V ($n = 2$), and a number of other unsymmetrical tetramethine pyrrolocyanines such as VIII ($n = 2$) were obtained similarly.

The absorptions of these unsymmetrical pyrrolocyanines present several interesting features; the optical data are summarized in Table I. It has already been shown that when the two nuclei of an unsymmetrical cyanine differ strongly in their attraction for the positive charge, or basic-

ity, the observed value of λ_{\max} lies at shorter wave length than that calculated as the arithmetic (or harmonic) mean of the values of λ_{\max} of the parent symmetrical dyes, the difference between the two values being termed the "deviation."¹ Further illustrations of this generalization occur in the present work, marked deviations being shown by all the unsymmetrical dyes V-IX.

For V ($R = Et$, $n = 1$), the deviation is 225 Å. (Fig. 1), the parent dyes being chosen as the oxycarbocyanine and the simple pyrrolocyanine, and the calculated value of λ_{\max} being taken as the arithmetic mean of the values of the symmetrical dyes. For the next higher vinylene homolog, the deviation amounts to 425 Å., thus illustrating a second general rule that in a vinylene homologous series, deviation increases with chain length.¹ The benzoxazole and pyrrole rings in V are thus shown to be of unequal basicity, although which of the two is the less basic is not evident from these results alone.

There can be little doubt, however, that pyrrole is the less basic of the two, and the point is decided in the following way. Replacement of the N-ethyl group in pyrrole by phenyl must reduce the basicity of the ring still further so that the imbalance of basicity between the nuclei of a dye where $R = Et$ should be increased by replacement of ethyl by phenyl. But the greater the imbalance of basicity between the nuclei the greater should be the deviation.¹ The replacement is actually found to have this effect, the deviation for V ($R = Ph$, $n = 1$) being 345 Å., and 685 Å. where $n = 2$ (Fig. 1). Thus, although replacement of the two N-ethyl groups by phenyl in the symmetrical dyes III brings about slight shifts of λ_{\max} to longer wave lengths (60 Å. where $n = 1$ and 45 Å. where $n = 2$), it is seen from Fig. 1 that replacement of an N-ethyl group in the pyrrole ring in V by phenyl brings about marked shifts

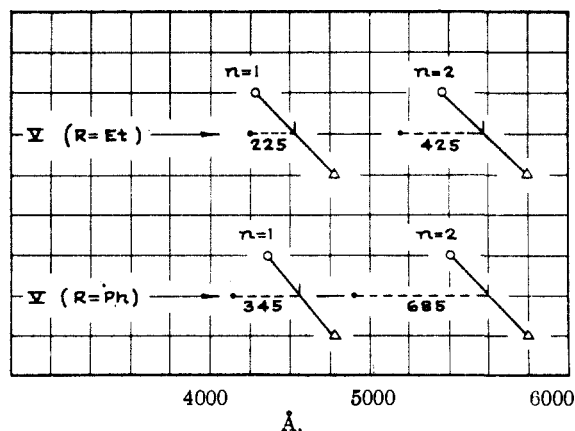


Fig. 1.—Values of λ_{\max} of unsymmetrical oxapyrrolo-cyanine dyes and related symmetrical dyes: ●, dyes V; △, related symmetrical oxacyanines; ○, dyes III; | indicates arithmetic mean between △ and ○; deviation is indicated by ---- and its magnitude is shown in Å.

to shorter wave lengths, 90 Å., where $n = 1$, and 240 Å., where $n = 2$.

It is a further striking fact that the deviations shown in Fig. 1 are sufficiently large for each of the four unsymmetrical dyes to absorb with λ_{\max} at shorter wave length than either of the related symmetrical dyes.

A similar pattern may be traced in the benzothiazole-pyrrole dyes VIII (Fig. 2). The deviations for VIII are 375 and 735 Å. for $n = 1$ and 2, respectively, the corresponding figures for the N-ethyl pyrrole series being 280 and 455 Å., so that here again pyrrole is the less basic nucleus, as would be expected.

Each of these four deviations is larger than that for the corresponding benzoxazole dye, but the pairs of symmetrical dyes in the comparisons in Fig. 2 are more widely spaced, with respect to absorption maxima, than those in Fig. 1, and only one unsymmetrical dye in Fig. 2 (VIII, $n = 2$) absorbs at shorter wave length than the lighter of the parent dyes.

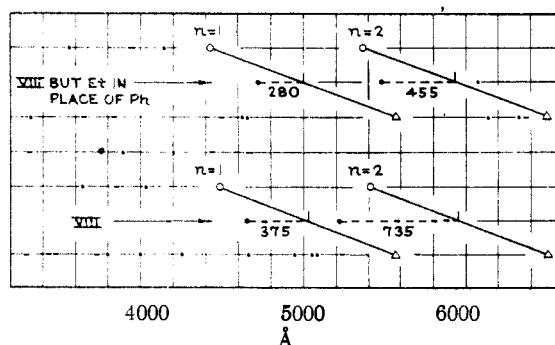


Fig. 2.—Values of λ_{\max} of unsymmetrical pyrrolothiazocyanine dyes and related symmetrical dyes: ●, dyes VIII; △, related symmetrical thiacyanines; ○, dyes III; | indicates arithmetic mean between △ and ○; deviation is indicated by ----, and its magnitude is shown in Å.

The remaining unsymmetrical dyes, VI, VII, and IX, also show deviations, so that here too the nuclei differ markedly in basicity. In these three dyes also, the deviations were reduced by replacing the N-phenyl group of the pyrrole ring by ethyl, so that pyrrole is proved to be the less basic nucleus in every case (Table I).

The postulate has been used above that for members of a series of unsymmetrical cyanines of the same chain length, the deviation is greater, the greater the imbalance of basicity between the two nuclei.¹ If, then, a comparison is made between unsymmetrical dyes of a given chain length, all of which have one 2,5-dimethyl-1-phenylpyrrole nucleus linked to a second nucleus of higher basicity, the greatest deviation will be shown by that dye in which the most strongly basic nucleus is combined with pyrrole, and the least deviation by that in which the basicity of the second nucleus most closely approximates the feeble basicity of pyrrole itself. In fact, the

order in which the deviations fall may be used to arrange the various nuclei in order of basicity.

This has been done in Fig. 3. The indolenine-pyrrole dye (IX) gives a deviation of 260 Å. which is less than that of the corresponding benzoxazole and benzothiazole dyes. The order of basicity of these nuclei is therefore indolenine < benzoxazole < benzothiazole.

The deviations of the 4-quinoline dye (VI) and the 4-pyridine dye (VII) are also shown in Fig. 3; they are 730 and 855 Å., respectively. In these dyes, however, the conjugated chain joining the nitrogens is longer by two carbon atoms than the corresponding chains in the three upper dyes in Fig. 3, so that it perhaps is scarcely valid to compare VI and VII directly with these three upper dyes. However, the deviations of VI and VII are even greater than that of the higher vinylene homolog of the benzothiazole dye (675 Å.) (Fig. 2), and it seems very likely that the 4-quinoline and 4-pyridine nuclei are of higher basicity than benzothiazole.

It is clear from these results that this method of comparing the relative basicities of nuclei could be extended to a much wider variety of ring systems than those studied here, but an extension of the subject in this direction and a deeper penetration into the nature of the basicity of these rings are reserved for the following paper.

Acknowledgments.—We take pleasure in acknowledging our gratitude to Dr. L. T. Hallett for the microanalyses, to Mr. E. E. Richardson and Dr. L. A. Jones for the absorptions, and to Mr. F. L. White for the preparation of 1,1'-diethyl-4,4'-pyridocarbocyanine perchlorate.

Experimental

All melting points given are corrected.

In the dye syntheses the following reactants were used: R1, 2- β -acetanilidovinylbenzoxazole ethioidide; R2, 1-ethyl-2,5-dimethylpyrrole; R3, 1-ethyl-2,5-dimethyl-3-pyrrolocarboxaldehyde; R4, 2,5-dimethyl-1-phenylpyrrole; R5, 2,5-dimethyl-1-phenyl-3-pyrrolocarboxaldehyde; R6, 2-(4-ethoxy-1,3-butadienyl)-benzoxazole ethioidide; R7, 2-(4-ethoxy-1,3-butadienyl)-benzothiazole ethioidide; R8, 2-methylbenzoxazole ethioidide; R9, 2-methylbenzothiazole ethioidide; R10, 2,3,3-trimethylindolenine ethioidide; R11, γ -picoline ethioidide; R12, lepidine ethioidide; R13, β -ethoxyacroleindiethylacetal; R14, ethyl orthoformate; R15, β -anilinoacroleinanilhydrochloride; R16, 2- β -acetanilidovinylbenzothiazole ethioidide. All these reactants are known with the exception of the following:

1-Ethyl-2,5-dimethyl-3-pyrrolocarboxaldehyde. R3, was prepared from 1-ethyl-2,5-dimethylpyrrole⁴ by a method of Nenitzescu and Isacescu.¹¹ The pyrrole (30.75 g., 1 mol) was dissolved in absolute ether (200 cc.), together with formamide (45 cc., 4 mols) and phosphorus oxychloride (25.5 cc., 1.1 mols) was slowly added with shaking. The mixture was allowed to stand for a day, the solvent decanted, and the solid washed with cold and then hot acetone. The solid was dissolved in hot water, filtered, and the filtrate chilled to 10° and made alkaline. The product separated as an oil which was extracted with ether and purified by recrystallization from absolute ethyl alcohol. The nearly colorless crystals (16% yield) had m. p. 88–89°.

(11) Nenitzescu and Isacescu, *Bull. Soc. Chim. Romania*, **11**, 135 (1929).

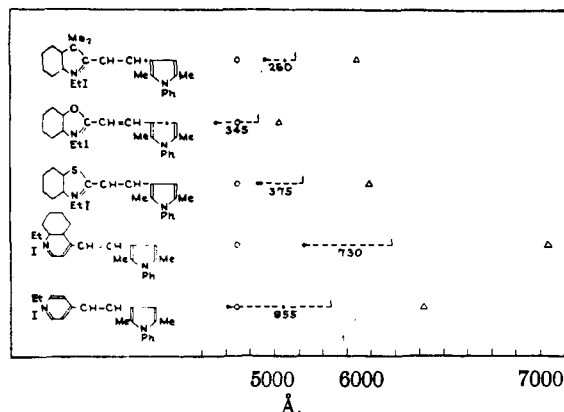


Fig. 3.—Values of λ_{max} of unsymmetrical pyrrolocyanines and related symmetrical dyes: ●, unsymmetrical dye; ⊙, III, $n = 1$; Δ, second related symmetrical dye; | indicates arithmetic mean between ⊙ and Δ; deviation is indicated by ---- and its magnitude is shown in Å.

Anal. Calcd. for $C_9H_{10}NO$: N, 9.27. Found: N, 9.17.

2,5-Dimethyl-1-phenyl-3-pyrrolocarboxaldehyde, R5, was prepared similarly. The cream-colored crystals (25% yield) melted at 89–90°.

Anal. Calcd. for $C_{13}H_{13}NO$: N, 7.04. Found: N, 6.93.

2-(4-Ethoxy-1,3-butadienyl)-benzoxazole Ethioidide, R6, (X).—2-Methylbenzoxazole ethioidide (28.9 g.; 1 mol), β -ethoxyacroleinacetal (34.8 g.; 2 mols, *i. e.*, 100% excess) and acetic acid (75 cc.) were heated together at 100° for five minutes with shaking, and then chilled. Ether (600 cc.) was added, and the insoluble precipitate washed with several fresh portions of ether until the product became crystalline. At this stage the product weighed 24.4 g. (86% yield) and consisted of dull blue crystals with m. p. 148–149°, dec. It gave a reasonably good analysis (below) but attempts at recrystallization resulted in extensive decomposition with dye formation, and the product was used without purification.

Anal. Calcd. for $C_{15}H_{18}INO_2$: I, 34.21. Found: I, 34.80.

2-(4-Ethoxy-1,3-butadienyl)-benzothiazole Ethioidide, R7, was prepared similarly. The crude compound (56% yield) consisted of green crystals with m. p. 177–178°, dec., and was used without purification.

Details of the dye syntheses are given in Table II, together with the appearance of the crystals. For each synthesis the necessary components were heated together in the medium indicated; the product separated on cooling. The percentage yields given are those before and, in general, after two recrystallizations from the solvent shown in the sixth column.

1,1'-Diethyl-4,4'-pyridocarbocyanine perchlorate, D1, requires special mention. Neither this compound nor other salts of the dye have hitherto been described, and we are indebted to Mr. F. L. White for the following details:

Attempts to prepare the dye using the method adopted for the 1,1'-dimethyl compound by Rosenhauer and Barlet¹² were found by him to be unsuccessful as was also the method of Ogata.¹³ The best method was a modification of that employed by Ogata and Suzuki.¹⁴ 4-Picoline ethioidide (5 g., 2 mols), chloral alcoholate (1.95 g., 1 mol), and potassium hydroxide (85% purity, 3.3 g., 5 mols) were heated to the refluxing point in absolute ethyl alcohol solution (45 cc.) for one-half hour, and the hot bluish mix-

(12) Rosenhauer and Barlet, *Ber.*, **62**, 2729 (1929).

(13) Ogata, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **16**, 583 (1937).

(14) Ogata and Suzuki, *ibid.*, **13**, 488 (1934).

TABLE II
 DETAILS OF DYE SYNTHESSES

Dye no.	Reactants, g.	Medium, cc.	Re-fluxed, min.	Yield, %	Solvent, cc./g.	M. p., °C., dec.	Formula	Analyses, % I,	
								Calcd.	Found
D2	R2 7.4; R14 3.0; HCl (35%) 2.2; NaI 6.0	EtOH 25	30	16, 10, 9	EtOH 50	220-222	C ₁₇ H ₂₁ IN ₂	33.05	32.95
D3	R2 4.9; R15 5.2 NaI 6.0	AcOH 10 Ac ₂ O 40	1	26, 21, 17	MeOH 73	232-233	C ₁₉ H ₂₇ IN ₂	30.94	30.64
D4	R4 3.4; R5 4.0; HCl (35%) 2.2; NaI 6.0	EtOH 30	5	89, 75, 59	EtOH 28	252-254	C ₂₁ H ₂₅ IN ₂	26.44	26.18
D5	R4 6.8; R13 3.5; NaI 6.0	AcOH 30	1	18, 11, 7	EtOH 34	173-174	C ₂₇ H ₂₇ IN ₂	25.07	24.96
D6	R1 4.34; R2 1.23	Ac ₂ O 25	5	69, 55, 43	EtOH 55	231-233	C ₁₆ H ₂₁ IN ₂ O	30.07	29.97
D6 ^a	R8 2.9; R3 1.5	EtOH 25 ^b	45	31, 21	MeOH 38	231-233			
D7	R6 3.7; R2 2.5	Ac ₂ O 25	5	71, 36, 33	EtOH 25	221-222	C ₂₁ H ₂₁ IN ₂ O	28.32	28.59
D8	R1 4.35; R4 6.0	Ac ₂ O 25	15	57, 34, 26	EtOH 50	249-251	C ₂₂ H ₂₁ IN ₂ O	27.00	26.81
D9	R6 3.7; R4 3.2	Ac ₂ O 25	5	36, 22, 16	MeOH 23	244-246	C ₂₀ H ₂₁ IN ₂ O	25.58	25.37
D10	R12 6.0; R3 3.0	EtOH 10 ^b	240	56, 42, 39	EtOH 40	252-253	C ₂₁ H ₂₁ IN ₂ O	29.37	29.33
D11	R12 3.0; R5 2.0	EtOH 15 ^b	30	40, 31, 25	EtOH 7	204-206	C ₁₆ H ₂₁ IN ₂	26.44	26.27
D12	R11 5.0; R3 3.0	EtOH 15 ^b	240	37, 34, 32	EtOH 5	204-206	C ₁₇ H ₂₁ IN ₂	33.21	33.18
D13	R11 5.0; R5 3.7	EtOH 35 ^b	30	9, 7, 5	MeOH 25	280-282	C ₂₁ H ₂₁ IN ₂	29.51	29.21
D14	R16 4.5; R2 2.5	Ac ₂ O 25	30	9, 8, 6	EtOH 100	243-244	C ₁₉ H ₂₁ IN ₂ S	28.96	28.62
D14 ^a	R9 3.05; R3 1.5	EtOH 25 ^b	45	41, 32	MeOH 50	243-244			
D15	R7 3.9; R2 2.5	Ac ₂ O 15	2	95, 80, 71	MeOH 80	248-249	C ₂₁ H ₂₁ IN ₂ S	27.34	27.15
D16	R9 6.1; R5 4.0	EtOH 25 ^b	30	47, 36, 32	EtOH 135	258-260	C ₂₁ H ₂₁ IN ₂ S	26.11	26.05
D17	R7 3.9; R4 3.4	Ac ₂ O 15	2	36, 22, 16	MeOH 137	248-249	C ₂₅ H ₂₁ IN ₂ S	24.77	24.82
D18	R10 6.3; R3 3.0	EtOH 15 ^b	240	60, 53, 50	EtOH 3	234-235	C ₂₂ H ₂₁ IN ₂	28.32	28.19
D19	R10 2.4; R5 1.5	Ac ₂ O 15	5	57, 29, 16	EtOH 18	251-252	C ₂₅ H ₂₁ IN ₂	25.57	25.52

The dyes appear as follows: D2, red crystals with silvery reflex; D3, green crystals with green reflex; D4, yellow crystals; D5, green crystals with golden reflex; D6, orange crystals; D7, steel blue crystals; D8, brown crystals with bright reflex; D9, red needles with green reflex; D10, maroon crystals; D11, red crystals with green reflex; D12, orange needles; D13, orange needles; D14, red crystals; D15, green needles with bright reflex; D16, red crystals with bright reflex; D17, green crystals; D18, brown plates; D19, brown needles.

^a Alternative method of preparation. ^b Piperidine added as catalyst.

ture was treated with sodium perchlorate (4 g.) in solution. The solid separated on chilling, from which the dye was extracted with ethyl alcohol and purified by several recrystallizations. The yield was very poor (0.04 g.). The blue and green crystals had m. p. 155-156° dec.

Anal. Calcd. for C₁₇H₂₁ClN₂O: C, 57.86; H, 6.00. Found: C, 56.96; H, 5.86.

Our figure of λ_{\max} of 6030 Å. differs somewhat from that given by Ogata¹³ (6100 Å.) for the 1,1'-dimethyl dye.

Summary

1. Symmetrical and unsymmetrical cyanines have been prepared from 1-ethyl- and 1-phenyl-

2,5-dimethylpyrrole, linkage being effected through the β -position of the pyrrole ring.

2. The unsymmetrical pyrrolocyanines examined absorb at considerably shorter wave length than that calculated as the mean of the values of λ_{\max} of the related symmetrical dyes. This deviation in λ_{\max} is the larger the greater the imbalance of basicity between the nuclei linked together in the dye. Also, the deviation is the greater, the longer the polymethine chain joining the nuclei.

ROCHESTER, NEW YORK RECEIVED DECEMBER 5, 1944