dried *in vacuo* over P_2O_5, and extracted with boiling petroleum ether (3000 ml) (bp 80–110°). The product that crystallized from the cooled extract was collected by filtration, and the filtrate was used to again extract the insoluble material from the first extract. This procedure was repeated four times. The recrystallized crops were combined and dried *in vacuo* over P_2O_5, yield 2.6 g (47%). The pmr spectrum and tlc data indicated that this material was homogeneous; however, the melting point was indefinite. This sample solidified after melting at 208° on the Kofler Heizbank apparatus and melted at >350° on the Mel-Temp apparatus. In another experiment the homogeneous material (tlc) melted in these apparatus at 132 and 145–147°, respectively.

Anal. Calcd for $C_{21}H_{20}N_6O_2$: C, 64.93; H, 5.19; N, 21.64. Found: C, 65.14; H, 5.33; N, 21.50.

The petroleum ether insoluble material was homogeneous on tlc and analyzed correctly for ethyl 4-[(diphenylmethyl)amino]-1*H*-*v*-triazolo[4,5-c]pyridine-6-carbamate (**19**), yield 1.5 g (27%), mp ~315° dec. The insolubility of this product in deuterated DMSO precluded the determination of its pmr spectrum. However, after 3 years tlc indicated that this product was a mixture containing **18**, suggesting that the original material was an unstable polymeric product and not **19**.

Anal. Calcd for $C_{21}H_{20}N_6O_2$: C, 64.93; H, 5.19; N, 21.64. Found: C, 64.76; H, 4.99; N, 21.84.

5,7-Diamino-3-(diphenylmethyl)-3*H*-*v*-triazolo[4,5-*b*]pyridine (20).—A mixture of **18** (0.50 g) and $NaOCH_3$ (0.35 g) in PrOH (20 ml) was refluxed for 20 hr and evaporated to dryness *in vacuo*. The residue was heated in 0.1 *N* HCl at 50° for 15 min, cooled, and adjusted to pH 8 (paper) with dilute NaOH. The precipitate was collected by filtration, recrystallized from C_6H_6, and dried *in vacuo* over P_2O_5 at 56°, yield 0.28 g (69%), mp 115° (Kofler Heizbank).

Anal. Calcd for $C_{18}H_6N_6$: C, 68.34; H, 5.10; N, 26.57. Found: C, 68.38; H, 5.16; N, 26.37.

Registry No.—**1**, 38359-68-1; **3**, 38359-69-2; **6**, 38359-70-5; **7**, 38359-71-6; **8**, 37437-06-2; **9**, 38359-73-8; **10**, 38359-74-9; **11**, 38359-75-0; **12**, 38359-76-1; **13**, 38359-77-2; **14**, 38359-78-3; **15**, 6502-04-1; **16**, 38359-79-4; **17** 2HCl, 38359-80-7; **18**, 38359-81-8; **20**, 38359-82-9.

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Synthesis and Properties of Pyrido- and Azapyridocyanines

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A summary of the synthesis of 2,2′-, 2,4′-, and 4,4′-pyrido- and -azapyridocyanines, including the *N*,*N*′-(1,ω-alkylene)-2,2′-cyanines is given. Several new dyes of those classes are described, and it is shown that some previous results reported in the literature must be corrected.

Pyridocyanines have been proposed recently for coupling to the conjugated backbone in a proposed model for superconducting polymers.[2] This renewed interest in this dye class promoted us to report on a comprehensive study of the syntheses of pyridocyanines and the related class of azapyridocyanines, which were prepared for an investigation of their stereoisomerism and molecular spectra.[3,4]

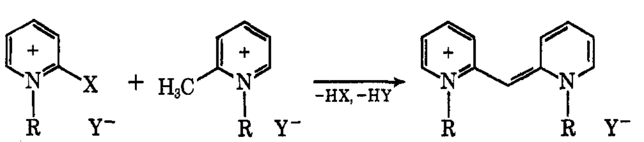
Although the syntheses of these dyes often *appear* to be straightforward, it became apparent during this work that syntheses and structures of several previously reported dyes needed revision. In addition, syntheses and properties of many new dyes of these classes will be reported. An earlier compilation of the syntheses and properties of cyanine dyes has been given by Hamer.[5]

Discussion

A. Pyridocyanines.—To synthesize pyridocyanines one can either quaternize the corresponding dipyridylmethanes or use condensation procedures. The first procedure is often useful for structure determination and the latter one is advantageous for the synthesis of large quantities of the dyes, because the starting materials can be obtained with less effort.

1. 2,2′-Pyridocyanines. a. *N*,*N*′-Dialkyl-2,2′-pyridocyanines (I).—The principle of synthesis of pyridocyanine dyes is well demonstrated by the various syntheses of the *N*,*N*′-dialkyl-2,2′-pyridocyanines (I).

Most commonly these dyes are synthesized by condensation from *N*-alkyl-2-X-pyridinium (1) [X = -I,[6] -Cl,[7,8] -SR[9] (R = CH_3, C_2H_5)] and *N*-alkyl-2-methylpyridinium salts (2) in the presence of suitable organic bases, *e.g.*, triethylamine.



1 2 I

An alternative synthesis is from di(2-pyridyl)methane[10] (3) and alkyl iodide, which may proceed *via* two different routes.[11-13] With methyl iodide the reaction proceeds *via* the intermediate **6**,

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[1] Correspondence should be addressed to Research Laboratories, Eastman Kodak Co., Rochester, N. Y. 14650.

[2] R. Liepins and C. Walker, *Ind. Eng. Chem., Prod. Res. Develop.*, **10**, 401 (1971).

[3] (a) I. Leubner, J. Dehler, and G. Hohlneicher, *Ber. Bunsenges. Phys. Chem.*, **71**, 560 (1967); (b) I. Leubner, J. Dehler, and G. Scheibe, *ibid.*, **72**, 1133 (1968).

[4] I. H. Leubner, "Determination of the Structure of Pyrido- and Azapyridocyanines by Nuclear Magnetic Resonance," to be submitted for publication.

[5] F. Hamer in "The Chemistry of Heterocyclic Compounds," A. Weissberger, Ed., Interscience, New York, N. Y., 1964.

[6] L. G. S. Brooker and G. H. Keyes, *J. Amer. Chem. Soc.*, **57**, 2488 (1935).

[7] H. Larivé and J. Dennilauler, French Patent 1,274,963; *Chem. Abstr.*, **57**, 3015 (1962).

[8] I. Leubner, Ph.D. Dissertation, Technische Universitaet, Munich (1966).

[9] J. P. Kendall and J. Saggate, *J. Chem. Soc.*, 1503 (1949).

[10] E. Leete and L. Marion, *Can. J. Chem.*, **30**, 563 (1952).

[11] H. J. Friedrich, W. Gueckel, and G. Scheibe, *Chem. Ber.*, **95**, 1378 (1962); G. Scheibe and W. Fischer, *ibid.*, **59**, 502 (1926).

[12] W. Gueckel, Ph.D. Dissertation, Technische Universitaet, Munich (1962).

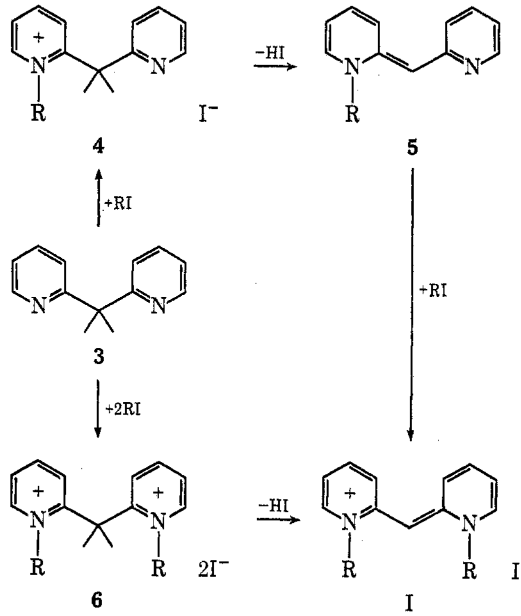
[13] I. Leubner, Diplomarbeit, Technische Universitaet, Munich (1963).

TABLE I

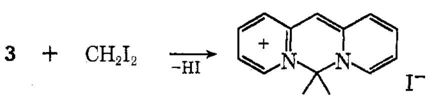
Dye	Anion	γ, cm^{-1}	$\epsilon_0 \times 10^{-3}$	Mp, °C[a]	Crystal form and color	Reference
I (R = C_2H_5)	I	20,700	31.0	235–237[b]	Brown needles	6, 7, 11
I (R = CH_3)	I	20,900	31.0	315–317[c]	Brown and green dichroic platelets	6, 11, 12
II	I	20,100	15.0	228–230		
IIa	I	19,800	12.0	195	Dark red crystals	11, 12, 14
IIb	I	19,600	9.0	257–259		
III	Br	20,600	28.0	200	Orange crystals	
	I			223–224	Yellowish brown crystals	
IV	I	20,800	53.0	218–219[d]	Violet shining crystals	6
V	I	20,700	125.5	174–176	Reddish brown crystals	12
VI	2I	19,800	55.5	320–322	Dark red and green dichroic crystals	16
VII (R = C_2H_5)	I	25,550	28.4	243–244	Nearly colorless platelets	3b, 18, 19
VII (R = CH_3)	I	25,750	28.4	290–292[e]	Nearly colorless needles	18, 19
VIII	I	24,200	15.8	258–260	Yellow needles	
IXa,b (R = C_2H_5)	I	31,000	30.0	148	Colorless needles	
IXa,b (R = CH_3)	I	31,000	30.6	242–243	Colorless, sturdy crystals	
X	I	25,900–26,600	36.2	213	Nearly colorless needles	
XI	I	25,500	66.6	204	Light yellow needles	

[a] All dyes decomposed on melting. [b] Lit.[11] mp 223–224°; lit.[6] mp 237–239°. [c] Lit.[11] mp 314–315°; lit.[6] mp 315–317°. [d] Lit.[6] mp 214–217°. [e] Lit.[18] mp 288–291°; lit.[19] mp 290°. [f] γ = long wavelength absorption in ethanol, 20°.

and with ethyl iodide *via* the intermediates **4** and **5**. The reaction path cannot be predicted but may be influenced by steric factors.



b. Di Cis Forms of the 2,2′-Pyridocyanine. i. *N*,*N*′-Methylene-2,2′-pyridocyanine Iodide (II).—The synthesis of dye II was accomplished by refluxing di(2-pyridyl)methane (**3**) with diiodomethane corresponding to the synthesis of *N*,*N*′-methylene-2,2′-cyanine.[8,11–14]



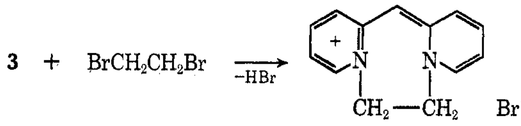
II

Although this reaction appears straightforward, three different products (II,[2] IIa,[11,12] IIb[13,14]) were reported as having structure II. All three have similar absorption spectra in the region up to 35,000 cm^{-1} so that one can assume that they have the same chromophore II.

These dyes differ slightly in the position of their long wavelength absorption maxima (γ) and significantly in their molar extinction coefficient ϵ_0 (referred to structure II), melting point, and nmr spectra.[4] Their properties are reported in Table I.

Dye IIa was reported to contain 2 mol of methanol per molecule in the crystal;[11,12] however, we were unable to repeat these results. Neither dye II nor dye IIb could be purified further by recrystallization and column chromatography. It was not possible to convert the dyes into each other. The dye which by its nmr spectrum[4,8] and analysis has structure II is listed in Table I as II. The structure of IIb could not be elucidated; however, additional bands in the shortwave region of the absorption spectrum, extinction coefficient, analysis, and additional signals in the nmr spectrum indicate that it probably has structure II with additional substituents (pyridyl?).

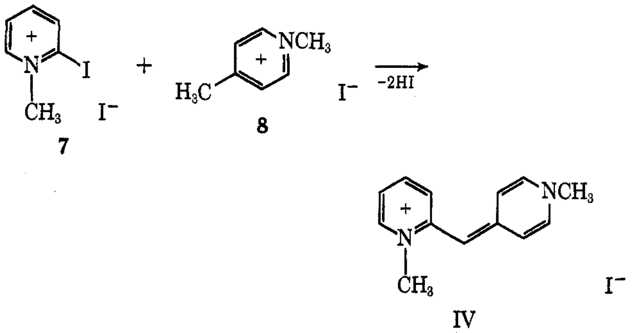
ii. *N*,*N*′-Ethylene-2,2′-pyridocyanine Bromide (III).—This dye was obtained by refluxing di(2-pyridyl)methane (**3**) and 1,2-dibromoethane. No complications, such as those arising in the synthesis of dye II, were encountered. This dye shows intense green fluorescence in ethanol solution at room temperature.



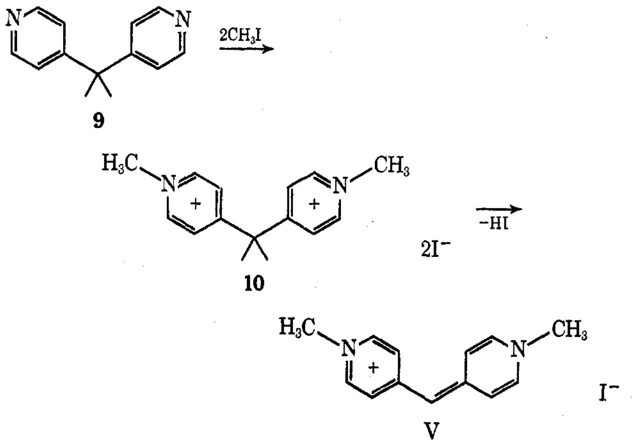
III

2. 2,4′-Pyridocyanines. *N*,*N*′-Dimethyl-2,4′-pyridocyanine Iodide (IV).—According to Brooker and Keyes,[6] this dye was obtained by condensation of *N*-methyl-2-iodopyridinium iodide (**7**) and 1,4-dimethylpyridinium iodide (**8**) in the presence of triethylamine. At present there is no synthesis known for 2,4′-dipyridylmethane and thus this dye could not be synthesized by quaternization of this base. Dye IV is yellow in solution but crystallizes from ethanol as deep violet platelets.

(14) E. Daltrozzo, G. Scheibe, and J. Smits, *Chimia*, **19**, 325 (1965).



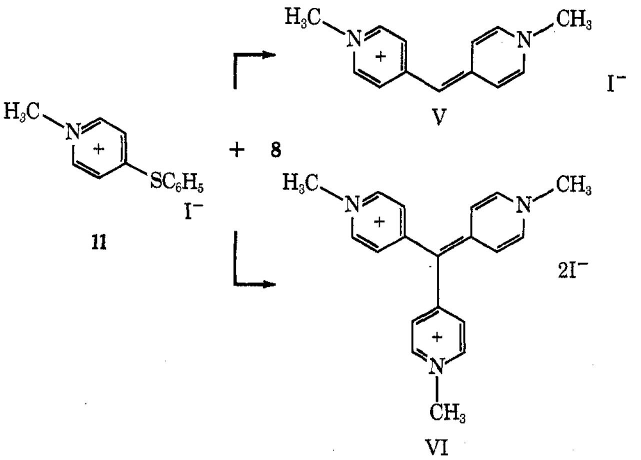
3. **4,4′-Pyridocyanines.** a. ***N,N′*-Dimethyl-4,4′-pyridocyanine Iodide (V).**—This dye (V) has been obtained by quaternization of di(4-pyridyl)methane (**9**) with methyl iodide.[12]



Proof of structure for V is provided by the synthesis itself and analysis. The base (**9**) was obtained from cyanodi(4-pyridyl)methane,[11,12] which was synthesized by the method of Sperber[15] from 4-chloropyridine and acetonitrile.

The properties of this dye are distinctly different from those of the dye to which Sprague and Brooker[16] attributed this structure.

b. ***N,N′,N″*-Trimethyl-4,4′,4″-tripyridocyanine Iodide (VI).**—To synthesize dye V, Sprague and Brooker[16] condensed *N*-methyl-4-phenylmercaptopyridinium iodide (**11**) and 1,4-dimethylpyridinium iodide (**8**) with triethylamine.

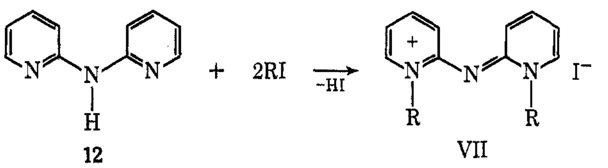


Our experiments showed, however, that they had isolated dye VI instead of dye V. Dye VI is considerably less soluble in ethanol than dye V and can thus be purified easily by recrystallization in this solvent. A small amount of dye V was obtained from the mother liquors by column chromatography. The structures of V and VI have been confirmed by their analysis, nmr,[4,8] and electronic spectra.[2,8]

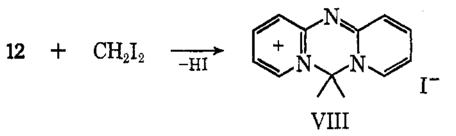
In their work on the absorption spectra of pyridocyanines, Levinson, *et al.*,[17] used dye VI; however, they based their discussion erroneously on structure V. The implications have been discussed previously.[2]

B. **Azapyridocyanines.**—For the synthesis of the azapyridocyanines no condensation procedures are known at present. Thus the corresponding dipyridylamines were quaternized with suitable agents. Dipyridylamines can generally be obtained in better yields and with less effort than the corresponding dipyridylmethanes.

1. **2,2′-Azopyridocyanines.** a. ***N,N′*-Dialkyl-2,2′-azapyridocyanine Iodide (VII).**—Dyes of structure VII are obtained by reaction of di(2-pyridyl)amine (**12**) with alkyl iodide (alkyl = CH_3, C_2H_5) at elevated temperatures.[18,19] The doubly quaternized dye is formed immediately for both methyl and ethyl substitution (compare 2,2′-pyridocyanines above). Synthesis and properties of dye VII (R = C_2H_5) have not been reported previously.



b. ***N,N′*-Methylene-2,2′-azapyridocyanine Iodide (VIII).**—This di cis isomer of dye VII was obtained by reaction of di(2-pyridyl)amine (**12**) with diiodomethane without the complications encountered for the homolog dye II. Dye VII was separated from the slightly soluble by-products by column chromatography on alumina. Its structure is supported by its analysis, model calculations, and electronic spectra.[3]



The aza analog of dye III, *N,N′*-ethylene-2,2′-azapyridocyanine, could not be obtained by reaction of di(2-pyridyl)amine (**12**) with 1,2-dibromo-, -dichloro-, or -diiodoethane.

2. **2,4′-Azapyridocyanines.** a. **Monoalkylation Product of 2,4′-Dipyridylamine (IX).**—Reaction of 2,4′-dipyridylamine (**13**) with alkyl iodide (alkyl = CH_3, C_2H_5) at elevated temperatures yielded only a monoalkylated product IX, which can have either structure IXa or IXb. Its molecular composition is supported by its analysis.

A distinction between structures IXa and IXb was not possible. However, structure IXa has a some-

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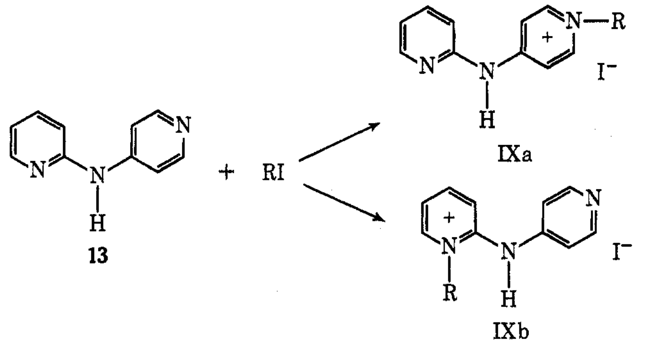
[15] N. Sperber, D. Papa, E. Schenk, and M. Sherlock, *J. Amer. Chem. Soc.*, **73**, 3856 (1951).

[16] R. H. Sprague and L. G. S. Brooker, *ibid.*, **59**, 2697 (1937).

[17] G. S. Levinson, W. T. Simpson, and W. Curtis, *ibid.*, **79**, 4314 (1957).

[18] E. Diepolder, *J. Prakt. Chem.*, **106**, 41 (1923).

[19] H. H. Credner, H. J. Friedrich, and G. Scheibe, *Chem. Ber.*, **95**, 1881 (1962).



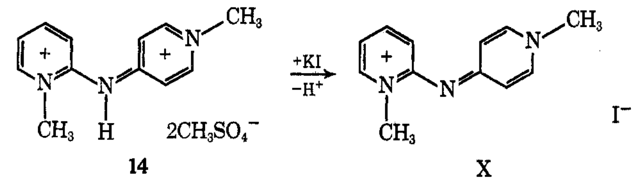
what higher probability than formula IXb, since 4-substituted pyridines are generally more easily quaternized than 2-substituted pyridines.

Compound IX reacted with alkyl iodide in the presence of barium oxide in methanol to yield a small amount of *N,N'*-dialkyl-2,4'-azapyridocyanine (X).

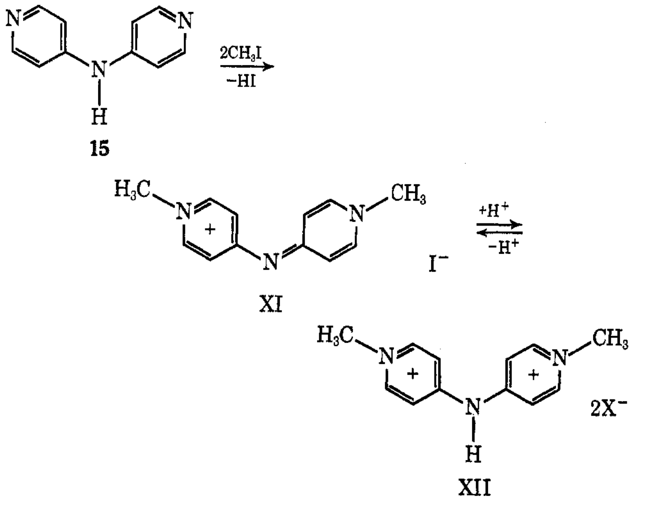
The 2,4'-dipyridylamine (**13**)[20,21] was synthesized according to Zwart and Wibaut[20] from 2-aminopyridine and 4-hydroxypyridine.

b. *N,N'*-Dimethyl-2,4'-azapyridocyanine Iodide (X).—Reaction of 2,4'-dipyridylamine (**13**) with dimethyl sulfate leads at once to the doubly quaternized intermediate **14**, which was not isolated, and further to the dye X. Its structure is supported by its absorption spectrum[3] and analysis.

13 + $2(CH_3)_2SO_4$ $\longrightarrow$



3. *N,N'*-Dimethyl-4,4'-azapyridocyanine Iodide (XI).—This dye was synthesized from di(4-pyridyl)amine (**15**) and methyl iodide.



A striking property of XI is its high basicity, so that a mixture of XI and XII is always obtained from the synthesis. Both compounds can be readily distinguished by their absorption spectra, because XII has its absorption peak at a wavelength (30,500 cm^{-1}) where XI has an absorption minimum (absorption peak 25,500 cm^{-1}). Dye XI can be obtained pure if the reaction mixture is dissolved in little aqueous ammonia and then chromatographed with acetonitrile on alumina. The equilibrium between XI and XII can be influenced arbitrarily by addition of acid or base. However, XII is unstable and decomposes in solution.

For the synthesis of di(4-pyridyl)amine (**15**)[22-24] the method of Koenigs and Jung[22] was preferred.

Experimental Section

The dyes are characterized by color, crystal form, melting point, absorption maxima (cm^{-1}), and molar extinction coefficient (ϵ_0) at room temperature (Table I). For all newly synthesized compounds the structures are supported by their analysis. The absorption, emission, and polarization spectra of these dyes were published previously and were found to be in excellent agreement with molecular orbital calculations (pyridocyanines,[3a] azapyridocyanines[3b]). The structures of all dyes are supported by their nmr spectra, which will be published in a separate report.[4] Where melting points were reported previously in the literature they are listed in Table I.

The following dyes have been synthesized according to published procedures: *N,N'*-dimethyl-(diethyl-, respectively) 2,2'-pyridocyanine (I),[6,11-13] *N,N'*-methylene-2,2'-pyridocyanine (II),[8,11-13] *N,N'*-dimethyl-2,4'-pyridocyanine (IV),[6] and *N,N'*-dimethyl-2,2'-azapyridocyanine iodide (VII, R = CH_3).[18,19] The synthesis of *N,N'*-dimethyl-4,4'-pyridocyanine (V) *via* di(4-pyridyl)methane (**9**) was reported elsewhere.[11,12] Novel observations in these syntheses and discrepancies with previously reported results are discussed in the previous sections.

The starting materials for the synthesis of the dyes were either commercially available or were synthesized following the published procedures mentioned in the text.

***N,N'*-Methylene-2,2'-pyridocyanine Iodide (II).**—Di(2-pyridyl)methane (**3**) (3.0 g, 0.018 mol) and 4.8 g (0.018 mol) of diiodomethane were heated until reaction began. After the reaction subsided, the reaction mixture was dissolved in 10 ml ethanol and then precipitated with ether to remove unreacted starting material. The precipitate was dissolved in a little methanol and twice chromatographed on alumina with acetone–methanol (9:1). The orange-green fluorescing zone was collected and evaporated to dryness *in vacuo*. The dark red residue was treated with a little absolute ethanol, whereupon it crystallized, yield *ca.* 0.80 g of II or IIb (15% referred to structure II).

In 11 of 12 repeats of this synthesis product IIb was isolated; only once was II isolated. In no case were both compounds isolated from the same reaction nor was the previously reported compound IIa.

The following variations were tried, but led to IIb: use of acetonitrile or nitromethane as reaction solvent, and addition of pyridine.[11] The di(2-pyridyl)methane (**3**) was synthesized according to Leete and Marion[10,11] as well as by saponification of cyanodi(2-pyridyl)methane[15] with sulfuric acid.[11,12] The base **3** was purified by distillation and by precipitation as the $ZnCl_2$ complex from methanol.[11] It was checked routinely for its purity and identity by nmr. At present it cannot be predicted under which conditions II or IIb will be obtained by this route.

Anal. Calcd for $C_{12}H_{11}N_2I$: C, 46.45; H, 3.55; N, 9.03. Found for II: C, 46.66; H, 3.71; N, 8.75. Found for IIb: C, 57.40; H, 4.68; N, 10.39.

***N,N'*-Ethylene-2,2'-pyridocyanine Bromide and Iodide (III).**—Di(2-pyridyl)methane (**3**) (3.0 g, 0.018 mol) and 6.5 g (0.036 mol) of ethylene bromide were heated to reflux for 15 min. The reaction product was washed with ether to remove unreacted starting materials, dissolved in a little ethanol, and chromatographed on alumina with acetone–methanol (9:1). The yellow, intensely green fluorescing zone was collected, concentrated, and the product precipitated with ether. The chromatography was repeated once, yield 1.1 g (22%). In a similar experiment the crude reaction product was treated with ammoniacal potassium iodide solution and twice chromatographed on alumina with acetonitrile to yield the dye iodide.

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[20] C. Zwart and J. P. Wibaut, *Recl. Trav. Chim. Pays-Bas*, **74**, 1081 (1955).

[21] D. Jerchel and L. Jakob, *Chem. Ber.*, **91**, 1266 (1958).

[22] E. Koenigs and G. Jung, *J. Prakt. Chem.*, **137**, 141 (1933).

[23] M. J. Pieterse and H. J. den Hertog, *Recl. Trav. Chim. Pays-Bas*, **80**, 1376 (1961).

[24] E. Koenigs, H. Friedrich, and H. Jurany, *Chem. Ber.*, **58**, 2571 (1925).

Anal. Calcd for $C_{13}H_{13}N_2I$: C, 48.20; H, 4.01; N, 8.65. Found: C, 48.12; H, 4.16; N, 8.52.

***N,N'*-Dimethyl-4,4'-pyridocyanine iodide (V) and *N,N',N''*-trimethyl-4,4',4''-tripyridocyanine (VI)** were synthesized following the procedure of Sprague and Brooker.[16] After two recrystallizations from ethanol dye VI was obtained as dark red crystals which showed green dichroism, yield 41%. The mother liquors were concentrated and filtered from a second crop of VI. The filtrate was chromatographed with acetone–methanol (9:1) on alumina and dye V was eluted in a yellow zone. After concentration of the solution, V was precipitated with ether and recrystallized from a little ethanol, yield *ca.* 5%.

Anal. Calcd for $C_{13}H_{15}N_2I$ (V): C, 47.85; H, 4.60; N, 8.59. Found: C, 47.76; H, 4.99; N, 8.52. Calcd for $C_{19}H_{21}N_3I$ (VI): C, 41.83; H, 3.85; N, 7.71. Found: C, 41.75; H, 4.05; N, 7.62.

***N,N'*-Diethyl-2,2'-azapyridocyanine Iodide (VII, R = C_2H_5).**—Di(2-pyridyl)amine (12) (2.0 g, 0.012 mol) and 5.5 g (0.036 mol) of iodoethane were heated to 100° for 4 hr in a sealed glass tube. The product was washed with ether and twice recrystallized from ethanol, yield 2.9 g (70%).

Anal. Calcd for $C_{14}H_{18}N_3I$: C, 47.30; H, 5.07; N, 11.83. Found: C, 47.20; H, 5.10; N, 11.70.

***N,N'*-Methylene-2,2'-azapyridocyanine Iodide (VIII).**—A mixture of 3.0 g (0.018 mol) of di(2-pyridyl)amine (**12**) and 7.0 g (0.026 mol) of diiodomethane was heated to 100° for 4 hr in a sealed glass tube. The reaction product was washed with ether, then extracted with methanol, and chromatographed on alumina, first with acetone–methanol (9:1). The blue fluorescing zone was collected, concentrated, precipitated with ether, and once more chromatographed with acetonitrile, yield 0.6 g (10%).

Anal. Calcd for $C_{11}H_{10}N_3I \cdot H_2O$: C, 40.12; H, 3.65; N, 12.80. Found: C, 40.45; H, 3.50; N, 12.89.

Monoalkylation Product of 2,4'-Dipyridylamine (IX, R = CH_3).—A mixture of 1.0 g (0.006 mol) of 2,4'-dipyridylamine (**13**) and 2.5 g (0.018 mol) of iodomethane was heated to 100° for 3 hr in a sealed glass tube. The reaction product was washed with ether and recrystallized from ethanol, yield 1.5 g (80%). A similar reaction using 2.8 g (0.018 mol) of iodoethane in place of iodomethane yielded 1.5 g (80%) of IX (R = C_2H_5).

Anal. Calcd for $C_{11}H_{12}N_3I$ (R = CH_3): C, 42.17; H, 3.83; N, 13.42. Found: C, 42.15; H, 3.95; N, 13.30.

***N,N'*-Dimethyl-2,4'-azapyridocyanine Iodide (X).**—2,4'-Dipyridylamine (**13**) (1.0 g, 0.006 mol) and 2.2 g (0.018 mol) of dimethyl sulfate were heated until reaction began. After it had subsided, the reaction mixture was dissolved in a little ammonia containing potassium iodide and then chromatographed on alumina with acetone–methanol (1:1). The blue fluorescing zone was collected and concentrated, and the product was precipitated with ether. It was again chromatographed as above, and once more with acetonitrile, yield 0.6 g (30%).

Anal. Calcd for $C_{12}H_{14}N_3I$: C, 44.03; H, 4.28; N, 12.84. Found: C, 44.03; H, 4.44; N, 12.81.

***N,N'*-Dimethyl-4,4'-azapyridocyanine Iodide (XI).**—A mixture containing 1.0 g (0.006 mol) of di(4-pyridyl)amine (**15**) and 2.5 g (0.018 mol) of iodomethane was heated to 100° for 2 hr in a sealed glass tube. The reaction product was washed with ether, dissolved in a little concentrated ammonia, and chromatographed on alumina with acetonitrile. The blue fluorescing zone was collected and concentrated, and the product precipitated with ether. It was then dried *in vacuo* for 12 hr at 100° where it lost acetonitrile that was enclosed in the crystals, yield 1.5 g (80%).

Anal. Calcd for $C_{12}H_{14}N_3I$: C, 44.03; H, 4.28; N, 12.84. Found: C, 43.99; H, 4.32; N, 12.81.

Registry No.—**3**, 1132-37-2; **12**, 1202-34-2; **13**, 33932-96-6; **15**, 1915-42-0; II, 38222-62-7; III bromide, 16521-09-8; III iodide, 38222-64-9; V, 16521-11-2; VI, 16610-36-9; VII (R = Et), 22013-57-6; VIII, 22013-58-7; IXa (R = Me), 38222-69-4; IXa (R = Et), 38222-70-7; IXb (R = Me), 38222-71-8; IXb (R = Et), 38222-72-9; X, 38222-73-0; XI, 22013-60-1.

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Synthesis and Structure of a Trimer of 4,5-Dihydropyridazine

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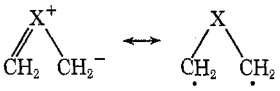
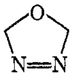
The synthesis and X-ray structure of the trimer of 4,5-dihydropyridazine (11), 4,4a,9,9a,14,14a-hexahydro-3*H*,8*H*,13*H*-tripyridazino[1,6-*a*:1',6'-*c*:1'',6''-*e*]-*s*-triazine (13), is described.

Dipolar structures or ylides (**1**) have been assigned to a number of "1,3-diradical" (**2**) systems. These intermediates have been examined theoretically,[1] observed spectroscopically,[2,3] trapped with dipolarophiles,[4,5] and studied kinetically.[4-6]

We were interested in preparing the oxadiazole ring system, (**3**), in an attempt to evaluate ylide character



1 **2**



3

(**1**, X = O) in the intermediate formed from thermolysis of **3**.[7]

Results and Discussion

The most likely entry into the oxadiazole ring system appeared to be through the Diels–Alder addition of furan (**4**) and an azodicarboxylate (**5**). This reaction with diethyl azodicarboxylate has been reported, although the adduct **6a** was only poorly characterized because of its instability.[8-12] Critical factors in its formation seem to be temperature, stoichiometry, and length of time allowed for formation of adduct. Apparently, once formed, the adduct undergoes additional

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