however, did not result in the desired Nb/Ti separation; multiple extractions (up to 10) also failed to give the desired Nb/Ti separation. The starting ilmenite solutions contained similar Nb/Ti ratios but the high iron content of 0.6 g of Fe per g of Ti apparently interfered with efficient Nb extraction.

The data in Table IV indicate that TiO_2 precipitated from most of these extracted solutions would contain less than 0.003 wt % Nb.

Conclusions

The Nb impurity in TiO_2 can be reduced from the 0.1 wt % range to less than 0.003 wt % by a single extraction of concentrated titanium solutions containing 50 to 120 grams of TiO_2 per liter. Since the Nb impurity in TiO_2 is reduced to less than 0.01 wt %, it will no longer have an adverse effect on the electrical properties of high purity, barium titanate ceramic capacitors. This technique is simpler, faster, and more direct than a previously reported (Bonsack, 1969) ion-exchange method for removing niobium from titanium sulfate solutions which required electrolytic reduction of Ti(IV) to Ti(III) and dilution to a TiO_2 concentration of about 10 grams per liter.

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Azo, Cyanine, and Merocyanine Dyes with 1,2-Dinitrile Groups

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Four new dyes with pendent 1,2-dinitrile groups have been synthesized and polymerized. The following dyes: 4-(2,4-dinitrophenylazo)-N-methyl-N-tricyanovinylmethyleneaniline, 4-(2,4-dinitrophenylazo)-N-methyl-N-tricyanovinylmethyleneaniline hydrobromide, 1-methyl-1′-(1,2-dicyanoethene)-4,4′-pyridocyanine bromide, and 3-ethyl-5-[1-(1,2-dicyanovinyl)-4(1H)-pyridylidene]rhodanine were isolated as dark brown-red to black microcrystalline solids in 9–36% overall yields. Such dyes are considered to be appropriate for coupling to the conjugated backbone in a proposed model for superconducting polymers.

The purpose of this work is to prepare monomers which when polymerized will yield polymeric structures of the type discussed by Little (1964) and as modified by Salem (1966). Synthetically difficult problems exist and the synthesis of the exact Little model has not been accomplished yet. In the past a simplified Little model approach to possible high temperature superconductors had been taken. In those attempts (Lupinski et al., 1967; Yagubskii et al., 1968; Klanderman et al., 1969) 7,7,8,8-tetracyanoquinodimethane salt-like derivatives of various cyanine, merocyanine, and phenothiazine dyes, instead of polymers, were prepared and tested for electrical properties. We have synthesized four new dyes with pendent 1,2-dinitrile groups for subsequent polymerization work (Liepins et al., 1970). The dyes were selected with a view of varying the polarizability in the pendent groups of the polymeric chains.

Experimental

Synthesis of 4-(2,4-dinitrophenylazo)-*N*-methyl-*N*-tricyanovinylmethyleneaniline. *4-(2,4-Dinitrophenylazo)-N,N-dimethylaniline.* DIAZOTIZATION. Dry sodium nitrite (3.5 grams) was slowly added with stirring to concentrated sulfuric acid (75 ml), and the temperature was allowed to

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rise to 50°C. 2,4-Dinitroaniline (8.35 grams, 0.05 mole) was added at 34°C over a 15-min period, and the solution was then stirred at room temperature for 3 hr. The solution was filtered through a sintered glass funnel and poured onto crushed ice (about 400 grams).

Coupling. To the filtered and stirred diazonium salt was added next a solution of *N*,*N*-dimethylaniline in glacial acetic acid (6.33 grams, 0.05 mole in 5 ml). The reaction mixture was stirred at room temperature for about 20 min and then placed in an ice bath as considerable warming and foaming developed. A dark brown-red solid separated and additional water (100 ml) was added before the reaction mixture was filtered. The collected solid was washed with distilled water until neutral (litmus). The solid was dissolved in tetrahydrofuran, methanol added, and the solution was cooled to −20°C. The collected material was reprecipitated from boiling methanol. The material was dried in a vacuum oven at 90°C for 16 hr. Approximately 8.82 grams (56%) of dark purple/black microcrystalline solid melting point (mp) 207–8°C was collected.

Anal. calcd. for $C_{14}H_{13}N_5O_4$: 53.32% C, 4.16% H, 22.21% N. Found: 53.25% C, 4.13% H, 22.09% N.

4-(2,4-Dinitrophenylazo)-N-methyl-N-tricyanovinylmethyleneaniline. The diazo dye (0.31 gram, 0.00098 mole) was dissolved in dimethylformamide (2.0 ml, Baker analyzed, H_2O 0.02%) followed by tetracyanoethylene (0.13 gram, 0.001 mole) and heating at 125°C for 19 hr. The resulting deep red solution was poured onto 15 ml of ice and water. The precipitated black solid was filtered and dried in a vacuum oven at room temperature for 13 hr. The dried material, taken up in a minimum amount of acetone and fractional crystallization from acetone/benzene mixtures, yielded the following materials: polymeric dye, 0.053 gram (13%); unreacted tetracyanoethylene (TCNE), 0.025 gram (19%); and the reaction product, mp 130–3°C, 0.160 gram (38%). Concentration of the filtrate yielded a black semisolid residue which contained a mixture of materials.

The uv (methanol) and nmr (deuterated dimethylsulfoxide) absorptions on the reaction product were as follows: 217 mμ (16,660), 297 mμ (11,320), 518 mμ (14,710); and nmr 3.47 ppm N—CH_3 (TMS std. in capillary), 3.75 ppm N—CH_2—C, 7.13, 7.29, 8.04, 8.18, 8.30, 8.77, 8.94, 9.18 ppm, 7 aromatic protons.

Anal. calcd. for $C_{19}H_{12}O_4N_8$: 54.80% C, 2.91% H, 26.91% N. Found: 55.00% C, 3.20% H, 26.93% N.

Synthesis of 4-(2,4-dinitrophenylazo)-*N*-methyl-*N*-tricyanovinylmethyleneaniline Hydrobromide. The hydrobromide of the "aniline" was prepared by combining at room temperature a tetrahydrofuran solution of "aniline" compound (0.48 gram, 0.0012 mole in 5 ml of tetrahydrofuran) with an anhydrous diethyl ether solution of hydrogen bromide (0.093 gram, 0.0012 mole in 2 ml of ether). Instantaneously, a dark red-black precipitate formed upon combining of the solutions. Next, the mixture was placed in a vacuum oven, the solvent was stripped at room temperature, and the sample dried until the theoretical weight (0.573 gram) of the dried sample was achieved. The material was extremely hygroscopic, and no easy determination of the melting point could be made (giving a different point each time a determination was attempted).

Synthesis of 1-Methyl-1′-(1,2-dicyanoethane)-4,4′-pyridocyanine Bromide. *Method A.* Acetylene Dicarboxylic Acid Diamide. The procedure used was a slight modification of that reported by Byrd et al. (1967). In absolute ethanol, the solution was cooled −25°C before addition of the acetylene dicarboxylic acid diester. The temperature was maintained at about −20°C while stirring the reaction mixture. Yield of the dried product was always above 90%, mp 200°C (dec).

Acetylene Dinitrile. The procedure used was essentially that of Byrd et al. (1967). We used washed sea sand (Fisher) as received. The material was isolated as glistening white platelets, mp +18°C (sublimed), in about 32% yield, which melted into water clear liquid at room temperature. The product is an extremely strong lachrimator and not stable above the temperatures of a Dry Ice/acetone bath. Acetylene dinitrile is also a potentially **explosive substance** both in pure state and in concentrated solutions.

Bromo-1,2-dicyanoethane. The procedure of Moureu and Bongrand (1909, 1920a,b) was used. The product was recrystallized from ethyl ether/hexane mixture and was isolated as pale cream platelets, mp 49°C (lit. 48.5–49.0°C). The yield was usually over 70%.

Bromo-1,2-dicyanoethene Quaternary Salt of 4-Methylthiopyridine. Bromo-1,2-dicyanoethene (0.110 gram, 0.0007 mole) was combined with 0.75 ml of absolute ethanol, and then 4-methylthiopyridine (0.088 gram, 0.0007 mole) was added to it. The reaction mixture was then allowed to stand at room temperature in the dark for 48 hr. Addition of anhydrous ether and cooling of the reaction mixture to −20°C yielded 0.108 gram (55%) of black solid. The recrystallized material from dimethylformamide/ether mixture yielded black needles with a melting point of 168–70°C.

Anal. Calcd. for $C_{10}H_8N_3SBr$: 42.55% C, 2.86% H, 14.88% N. Found: 42.37% C, 2.96% H, 14.81% N.

1-Methyl-1′-(1,2-dicyanoethene)-4,4′-pyridocyanine Bromide. The 4-methylpyridine salt was prepared by combining methyl-*p*-toluenesulfonate (0.026 gram, 0.00014 mole) with 4-methylpyridine (0.013 gram, 0.00014 mole) at room temperature. In a few minutes the solid salt had formed with considerable heating of the reaction mixture. The solid was placed in a 100°C bath for 1 hr and used directly in the next reaction.

To the above prepared salt (0.039 gram, 0.00014 mole) were added the bromo-1,2-dicyanoethene quaternary salt of 4-methylthiopyridine (0.041 gram, 0.00014 mole) and absolute ethanol (0.20 ml), and the contents were thoroughly mixed. This was followed by the addition of triethylamine (0.031 gram, 2.2 × 0.00014 mole). As soon as the amine was added, the reaction mixture became dark colored. The solution was then kept in a 100 ± 2°C bath for 50 min. At the end of this period, a dark red viscous oil was produced. The oil was triturated with anhydrous ether, leaving a black semisolid material. It was dissolved in dimethylformamide and then diluted with ether and kept at −20°C. After several recrystallizations from dimethylformamide/ether mixture, we isolated 0.007 gram (15%) of black crystals with a mp 135–40°C. The uv spectrum in dimethylformamide possessed two major absorptions: 273 mμ (14,500) and 516 mμ (8,170).

Anal. Calcd. for $C_{16}H_{13}N_4Br$: 16.41% N. Found: 16.18% N.

Method B. Bis(1-methyl-4-pyridine)-methinecyanine Iodide. Methyl-*p*-toluenesulfonate quaternary salt of 4-methylpyridine was prepared by combining 4-methylpyridine (0.093 gram, 0.001 mole) with methyl-*p*-toluenesulfonate (0.186 gram, 0.001 mole) at room temperature. In a few minutes the solution solidified, giving the quaternary salt.

The other quaternary salt was prepared by combining 4-methylthiopyridine (0.125 gram, 0.001 mole) with methyl iodide (0.142 gram, 0.001 mole) at room temperature, giving the solid quaternary salt in a few minutes.

Both quaternary salts were then combined without purification and were dissolved in absolute ethanol (1.0 ml). Next triethyl amine (0.222 gram, 2.2 × 0.001 mole) was added, and an immediate discoloration of the solution occurred. The reaction mixture was placed in a 100°C bath for 30 min. Dark red–brown viscous liquid had formed which was allowed to stand at room temperature for 16 hr. Dark red needles had precipitated out which were filtered and dried in a vacuum oven at room temperature for 18 hr. Isolated was 0.182 gram (56%) of the dye, mp 174–5°C. A portion of this material was dissolved in the minimum quantity of hot methanol and converted into perchlorate, mp 262–4°C; literature (Sprague and Brooker, 1937) mp 263–5°C. The uv spectrum of the iodide in dimethylformamide has two major absorptions: 306 $m\mu$ (10,600) and 490 $m\mu$ (2880).

1-Methyl-4,4′-pyridocyanine. Bis(1-methyl-4-pyridine)-methinecyanine iodide (0.20 gram, 0.0006 mole) was combined with 40% aq KOH (5 ml) and warmed until complete solution was obtained. The solution was then extracted with chloroform (3 × 10 ml), the extracts were dried over anhydrous $MgSO_4$, and the solvent was stripped at room temperature under high vacuum (0.001 mm). A dark red oil, 0.085 gram (77%), the expected product according to the ir spectrum, was isolated and immediately used in the next reaction step.

1 - Methyl - 1′ - (1,2 - dicyanoethene) - 4,4′ - pyridocyanine Bromide. 1-Methyl-4,4′-pyridocyanine (0.063 gram, 0.00034 mole) was dissolved in 0.70 ml of absolute ethanol and then combined with bromofumaronitrile (0.054 gram, 0.00034 mole). The reaction mixture was kept at room temperature in the dark for 48 hr. It was then placed in a vacuum oven at room temperature, and the solvent and any unreacted material were removed. The work-up of the reaction mixture was the same as described in Method A. This procedure gave at least a 45% yield of the dye, mp 136–40°C.

Synthesis of 3-ethyl-5-[1-(1,2-dicyanovinyl)-4(1*H*)-pyridylidene]rhodanine. In the synthesis of the merocyanine dye the following procedure was developed. The 4-methylthiopyridine/bromo-1,2-dicyanoethane quaternary salt (0.089 gram, 0.0003 mole) was combined with absolute ethanol (1.0 ml) and then to it were added rhodanine (0.049 gram, 0.00036 mole) and triethylamine (0.037 gram, 0.00036 mole), and the mixture was heated at 82°C/10 min and kept at room temperature in the dark for 23 hr. As soon as the reaction mixture was warmed, it began to turn red and later dark red to dark brown. The solvent was stripped under vacuum, and the black residue was recrystallized from methanol giving 0.056 gram (60%) of dark brown solid with an mp 138–40°C. Infrared spectrum (KBr pellet) showed absorptions for the expected product including the characteristic rhodanine ring absorptions at 1720, 1450, and 1185 cm^{-1}.

Anal. Calcd. for $C_{14}H_{10}N_4S_2O$: 17.81% N. Found: 16.70% N.

Synthesis of Bromosuccinonitrile. Fumaronitrile (0.5 gram, 0.0065 mole) and hydroquinone (15 mg) were dissolved in anhydrous ether (10.5 ml) and combined with a glacial acetic acid solution of anhydrous hydrogen bromide (3.5 ml of 1.88 mole solution, 0.0065 mole). The reaction mixture was placed in a water bath at 9°C and maintained for 6 hr while the temperature rose to 18°C. Next, water was added (90 ml) to the reaction mixture and then neutralized with $NaHCO_3$ to a pH of 6. The solution was extracted with chloroform (3 × 50 ml), dried, and stripped in a Rotovac yielding light yellow colored oil, 0.96 gram (92%). The purification of the product could be accomplished only by a multiple high-vacuum (0.001 mm or better) distillation. After the purification step, we isolated a clear liquid, bp 90–5°C/0.001 mm, $n^{31} = 1.4935$, in about a 50% yield. Nmr absorptions (neat): 3.92 ppm, doublet, $—CH_2—$, (TMS std. in capillary); 5.32 ppm, triplet, —CH—.

Anal. Calcd. for $C_4H_3N_2Br$: 30.20% C, 1.89% H, 17.62% N. Found: 30.72% C, 1.87% H, 17.86% N.

Reaction between Bromosuccinonitrile and 4-Methylthiopyridine. Bromosuccinonitrile (0.271 gram, 0.0017 mole) was combined with absolute ethanol (0.5 ml) and 4-methylthiopyridine (0.213 gram, 0.0017 mole) and refluxed for 12.5 hr. At the end of this period the solution had turned black and contained solid material. To this suspension was added 1 ml of anhydrous ether, and the mixture was filtered. The collected solid was recrystallized from dimethylformamide/ether mixture twice yielding white needles, mp 192–3°C, in about 44% yield. The nmr in deuterated dimethylfulfoxide, 2.75 ppm, $—S—CH_3$, (TMS std., capillary) 7.99 ppm and 8.93 ppm, 4 aromatic protons (12.57 ppm, $H—N\equiv$), and analytical data indicated the material to be the HBr salt of 4-methylthiopyridine.

Anal. Calcd. for C_6H_8NSBr: 34.96% C, 3.92% H, 6.79% N, 15.56% S. Found: 35.06% C, 3.88% H, 6.92% N, 14.13% S.

Synthesis of Iodotricyanoethene. Dicyanoacetylene (0.30 gram, 0.0039 mole) was dissolved in 1 ml of anhydrous ether and then combined with an ether solution of cyanogen iodide (0.60 gram, 0.0039 mole in 4 ml ether). The solution was kept at room temperature in the dark for 14 hr. Stripping of solvent under high vacuum (0.001 mm) at room temperature left behind a dark red solid. The material was kept under high vacuum for several hours to sublime out unreacted starting materials. Further purification of the product was attempted by dissolving the residue from the sublimation step in a minimum amount of anhydrous ether and then diluting with hexane and cooling to −20°C. We isolated 0.10 gram (11%) of dark red solid with an mp of about 155°C (sealed tube), although it started subliming at a lower temperature.

Anal. Calcd. for C_5N_3I: 26.29% C, 18.34% N, 55.41% I. Found: 26.61% C, 14.61% N, 53.29% I.

Results and Discussion

Synthesis of 4-(2,4-Dinitrophenylazo)-*N*-methyl-*N*-tricyanovinylmethyleneaniline and Its Hydrobromide. The reaction scheme shown in Figure 1 was used in the synthesis of these monomers. The synthesis of 4(2,4-dinitrophenylazo)-*N*,*N*-dimethylaniline has not been reported.

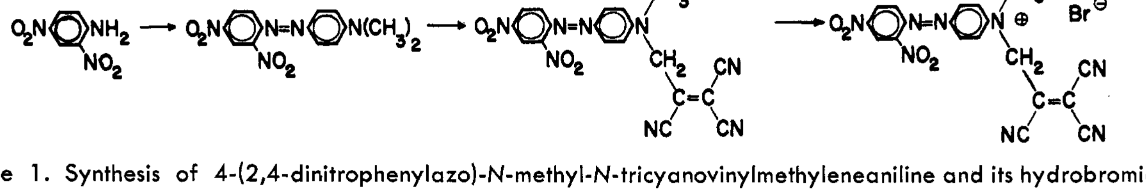
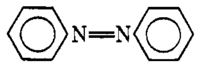
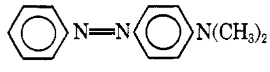
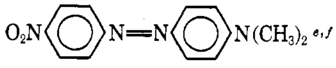
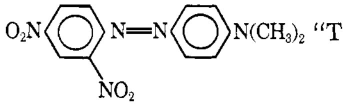


Figure 1. Synthesis of 4-(2,4-dinitrophenylazo)-N-methyl-N-tricyanovinylmethyleneaniline and its hydrobromide

Table I. Ultraviolet Data

	Assignment and position of bands					
	$n \rightarrow \pi^*$		$\pi \rightarrow \pi^*$		Other bands	
	λ	ϵ	λ	ϵ	λ	ϵ
 Trans[a]	443	510	319	22,000	228	14,000
Cis[a]	432	1518	280	5,260	242	10,480
 Trans[b]	[c]	[c]	410	30,400	260	10,500
Cis[d]	460	4300	362	12,000	<290	. . .
 [e,f]	[c]	[c]	480	33,000	280	12,600
 "Trans"	[c]	[c]	518	42,250	290 207	12,250 27,090

[a] Birnbaum et al. (1953). [b] Lewis (1960). [c] Overlain by $\pi \rightarrow \pi^*$ band. [d] Brode et al. (1952). [e] Pongratz et al. (1938). [f] Not specified.

From the melting point and ultraviolet absorption data, we are tentatively assigning the transconfiguration to this product. The ultraviolet data (in methanol) on this compound along with that of the other compounds in this series, taken from the literature, are given in Table I. The introduction of the second auxochrome (NO_2) in *o*-position shifts the $\pi \rightarrow \pi^*$ band further into the visible region (480 → 518 mμ) as well as providing for a further increase in the extinction coefficient (33,000 → 42,250) as compared to *N*,*N*-dimethyl-*p*-(*p*-nitrophenylazo)aniline.

The alkylation of an aromatic or heterocyclic nucleus by tetracyanoethylene (TCNE) will take place only if the ring is sufficiently activated (McKusick et al., 1958; Sausen et al., 1958; Rappoport, 1963; Dhar, 1967; Sulzberg and Cotter, 1969). However, a para-substituted dimethylaniline has not been found to react with TCNE (McKusick et al., 1958; Sulzberg and Cotter, 1969). We find that a reaction between 4-(2,4-dinitrophenylazo)-*N*,*N*-dimethylaniline and TCNE at 125°C does take place with the apparent elimination of the elements of HCN. We are basing this conclusion on our analytical, nmr, and uv data. A concurrent polymeric material formation of the reaction product also takes place. The hydrobromide of 4-(2,4-dinitrophenylazo)-*N*,*N*-dimethylaniline and TCNE reaction product, because of its extreme hygroscopicity, proved difficult to handle, and no reliable physical constants could be determined on it.

Synthesis of 1-Methyl-1′-(1,2-dicyanoethene)-4,4′-pyridocyanine Bromide. The reaction schemes shown in Figure 2 were used in the synthesis of this monomer. The synthesis of 1-methyl-1′-(1,2-dicyanoethene)-4,4′-pyridocyanine bromide has not been reported. We have synthesized it in two different ways. The synthetic sequence involving the intermediate dicyanoacetylene was of much interest to us because of the potential in the preparation of many different derivatives from dicyanoacetylene. However, the method involving the quaternary salt formation between 1-methyl-4,4′-

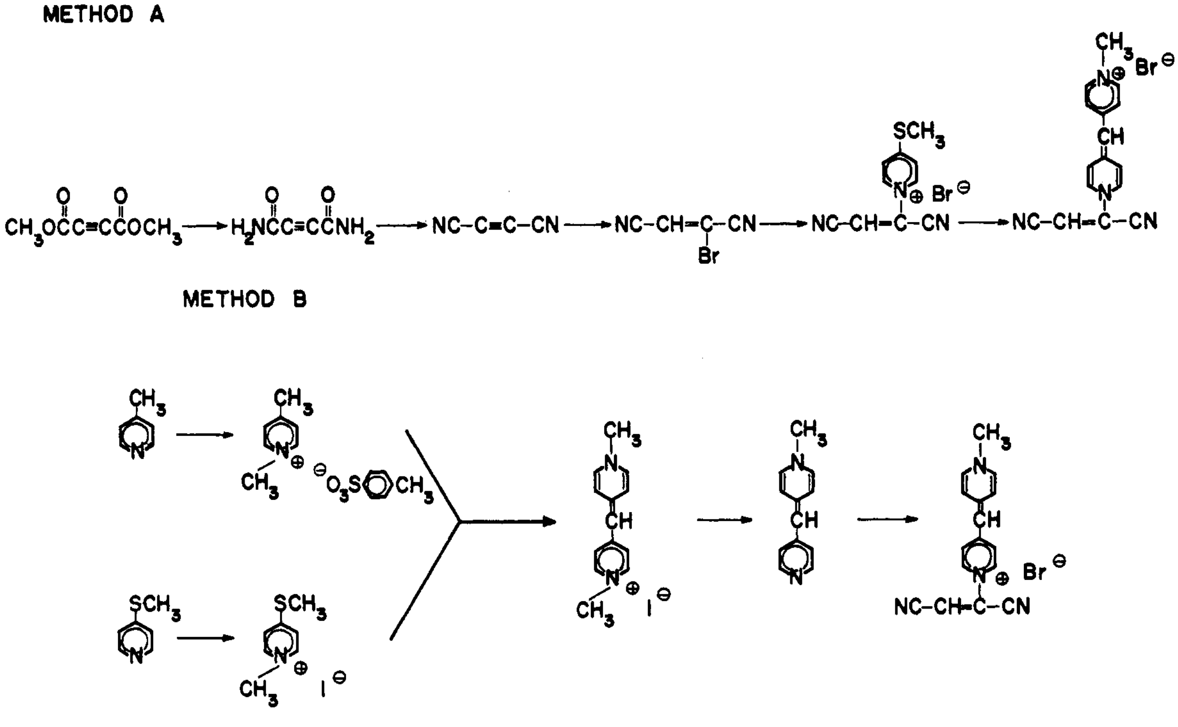


Figure 2. Synthesis of 1-methyl-1′-(1,2-dicyanoethene)-4,4′-pyridocyanine bromide

pyridocyanine and bromofumaronitrile was an easier synthetic approach to this product. Although dicyanoacetylene is a **potentially explosive substance** both in the pure state and in concentrated solutions (Ciganek and Krespan, 1968), we experienced no explosions. We did find that the highly purified material was not stable above Dry Ice/acetone temperatures. While the formation of the quaternary salt between 4-methylthiopyridine and bromofumaronitrile takes place readily at room temperature in good yield (77%), the conversion of the quaternary salt into the cyanine dye yields dark red/black viscous oil which is not easily purified. Trituration of it with anhydrous ether converted it into a semicrystalline material which upon several recrystallizations from dimethylformamide/ether yielded the cyanine dye in 15% yield. The reactions in the other synthetic approach are all high yield reactions, and the product was isolated in a 45% yield. Two broad absorptions in the uv spectra (dimethylformamide) of bis(1-methyl-4-pyridine)-methinecyanine iodide at 306 mμ (ϵ = 10,600) and 490 mμ (ϵ = 2,880) and 1-methyl-1'-(1,2,2-tricyanoethene)-4,4'-pyridocyanine bromide at 273 mμ (ϵ = 14,500) and 516 mμ (ϵ = 8,170) were observed. The shift in the $\pi \rightarrow \pi^*$ from 490 mμ for the iodide to 516 mμ for the bromide along with the higher extinction coefficients for the latter is in agreement with the longer conjugated system in the bromide.

In the unsuccessful attempts to prepare other cyanine dye derivatives the following new compounds were made: iodotricyanoethane, bromosuccinonitrile, and the hydrobromide salt of 4-methylthiopyridine.

Synthesis of 3-Ethyl-5-[1-(1,2-dicyanovinyl)-4(1*H*)-pyridylidene]rhodanine. In the synthesis of the rhodanine dye the same synthetic sequence (Method A) as for the cyanine dye was used with the exception of the last reaction step in which rhodanine instead of 4-methylpyridine was utilized. The rhodanine product was isolated as a dark brown solid in 60% yield. The ir spectrum of the product contained the characteristic absorptions for C≡N at 2230 cm^{-1} and rhodanine ring at 1720, 1450, and 1185 cm^{-1}.

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