ethyl alcohol or acetone, but was very soluble in 5% sodium bicarbonate solution.

Anal. Calcd. for $C_7H_4N_4O_2{\cdot}2H_2O$: C, 39.63; H, 3.80; N, 26.40. Found: C, 39.72; H, 3.91; N, 26.50.

2,2-Dicyano-1-alkoxyethenolate Inner-salts.[12]—The inner-salts listed in Table I were all prepared by the same general procedure. The base (amine, sulfide, thiourea or thioamide) and the dicyanoketene cyclic acetal were dissolved in a mutual solvent and allowed to react spontaneously. In many cases, crystals of the inner-salt precipitated from the solution after standing only a few minutes. The more basic reagents, such as the trialkylamines, reacted almost instantaneously with the cyclic acetal, whereas less basic reagents such as the sulfides required a longer period of time (1 or 2 days).

In a typical example, a solution of 10.1 g. (0.1 mole) of triethylamine and 13.6 g. (0.1 mole) of dicyanoketene ethylene acetal in 50 ml. of tetrahydrofuran was allowed to stand at room temperature for 10 minutes. The white precipitate that formed was collected on a filter, washed with ether, and recrystallized from water. There was obtained 23.0 g. of 2,2-dicyano-1-[2-(triethylammonio)-ethoxy]-ethenolate in the form of white needles, m.p. 184–186° (see Table I).

1-(2-Hydroxyethyl)-pyridinium Reineckate.—A solution of 3.54 g. (0.01 mole) of the reinecke salt in 50 ml. of water was mixed with a solution of 1.6 g. (0.01 mole) of 1-(2-hydroxyethyl)-pyridinium chloride[13] in 10 ml. of water. The pink precipitate which formed was collected on a filter, washed with water, and recrystallized from acetone–water. There was obtained 5.0 g. of 1-(2-hydroxyethyl)-pyridinium reineckate in the form of lavender flakes, m.p. 186–192° dec.

Anal. Calcd. for $C_{11}H_{16}N_7S_4OCr$: C, 29.85; H, 3.66; N, 22.15. Found: C, 30.14; H, 3.82; N, 22.20.

Hydrolysis of 2,2-Dicyano-1-[2-(1-pyridinio)-ethoxy]-ethenolate.—2,2-Dicyano-1-[2-(1-pyridinio)-ethoxy]-ethenolate (2.15 g., 0.01 mole) was dissolved in 20 ml. of 5 *N* hydrochloric acid and the solution was heated under reflux for 30 minutes. The solution was cooled and mixed with a filtered solution of 3.54 g. (0.01 mole) of the reinecke salt in 50 ml. of water. The pink precipitate which formed was collected on a filter, washed with water, and recrystallized from acetone–water. There was obtained 4.0 g. of a reineckate salt in the form of lavender flakes, m.p. 186–189° dec. The X-ray diffraction pattern and infrared absorption spectrum of this product are identical with those of 1-(2-hydroxyethyl)-pyridinium reineckate.

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[12] W. J. Middleton, U. S. Patent 2,721,206 (1955); and V. A. Engelhardt and W. J. Middleton, U. S. Patent 2,766,270 (1956).

[13] O. A. Barns and R. Adams, THIS JOURNAL, 49, 1311 (1927).

WILMINGTON, DELAWARE

[CONTRIBUTION NO. 439 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

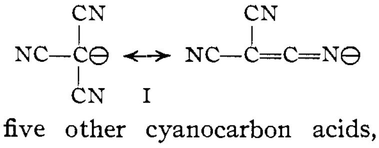
Cyanocarbon Chemistry. V.[1] Cyanocarbon Acids and their Salts

BY W. J. MIDDLETON, E. L. LITTLE, D. D. COFFMAN AND V. A. ENGELHARDT

RECEIVED NOVEMBER 14, 1957

A number of new cyanocarbon acids and their salts have been prepared from tetracyanoethylene. 1,1,2,3,3-Pentacyanopropene was prepared by the basic hydrolysis of tetracyanoethylene, 1,1,2,4,5,5-hexacyano-3-azapentadiene was prepared from tetracyanoethylene and ammonia, and salts of the dibasic acid 1,1,2,5,6,6-hexacyano-3,4-diazahexadiene were prepared from tetracyanoethylene and hydrazine. 2-Dicyanomethylene-1,1,3,3-tetracyanopropane, another dibasic acid, was prepared by the reaction of dicyanoketene acetals with malononitrile. These four strongly acidic compounds ionize to give resonance-stabilized anions that are comprised entirely of carbon and nitrogen. Several strongly acidic tetracyanopropenes have been prepared from the dicyanoketene acetals derived from tetracyanoethylene. 2-Alkoxy-1,1,3,3-tetracyanopropenes were obtained from the reaction of these acetals with one equivalent of malononitrile. Reaction of the alkoxypropenes with ammonia, methylamine or dimethylamine resulted in the preparation of 2-amino-1,1,3,3-tetracyanopropenes. Diazotization of 2-amino-1,1,3,3-tetracyanopropene with nitrous acid in the presence of chloride or bromide ion produced 2-chloro- or 2-bromo-1,1,3,3-tetracyanopropene.

Cyanocarbon acids are a relatively unknown class of strong organic acids whose acidic strengths rival those of the mineral acids. Cyanocarbon acids can be defined as organic compounds that contain a plurality of cyano groups and are easily ionized to hydrogen ions and anions of high resonance stability. The structure of these anions can be represented by a number of resonance forms, all of which contain the negative charges on either carbon or nitrogen. Of the known cyanocarbon acids, tricyanomethane (cyanoform)[2] is of interest since its anion I contains only carbon and nitrogen.



$$NC{-}C(CN)_2^{\ominus} \longleftrightarrow NC{-}C(CN){=}C{=}N^{\ominus}$$

I

Salts of five other cyanocarbon acids, 1,1,3,3-tetracyanopropene,[3] 2-methyl-1,1,3,3-tetracyanopropene,[4] 1,1,5,5-tetracyanopentadiene, 1,1,7,7-tetracyanoheptatriene and 1,1,9,9-tetracyanononatetraene,[5] have been reported but have not been extensively studied. A number of new cyanocarbon acids and their salts have been synthesized from tetracyanoethylene, and this paper describes their preparation and some of their physical and chemical properties.

1,1,2,3,3-Pentacyanopropene.—Salts of 1,1,2,3,3-pentacyanopropene were formed by the reaction of tetracyanoethylene with water in the presence of a base. Thus, pyridinium pentacyanopropenide[6] was formed in 81% yield when a solution of

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[1] Paper IV, W. J. Middleton and V. A. Engelhardt, THIS JOURNAL, 80, 2788 (1958).

[2] (a) A. Hantzsch and G. Oswald, *Ber.*, 32, 641 (1899); H. Schmidtmann, *ibid.*, 29, 1171 (1896); L. Birkenbach and K. Huttner, *ibid.*, 64B, 153 (1929); L. Birkenbach, K. Huttner and W. Stein, *ibid.*, 62B, 2065 (1929); (b) E. Cox and A. Fontaine, *Bull. soc. chim. France*, 948 (1954).

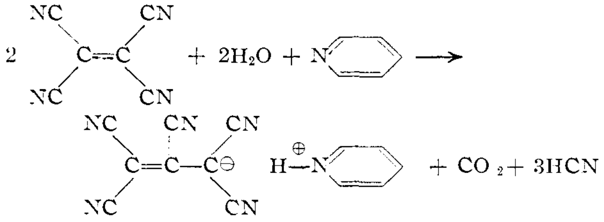
[3] Y. Urushibara, *Bull. Chem. Japan*, 2, 278 (1927); *C. A.*, 22, 579 (1928).

[4] Y. Urushibara and M. Takebayashi, *Bull. Chem. Soc. Japan*, 11, 557 (1936); *C. A.*, 31, 1769 (1937).

[5] M. Strell, *et al.*, *Ann.*, 587, 177 (1954).

[6] There appears to be no widely used general method for naming salts of non-carboxylic organic acids. This problem is usually overcome by merely specifying the "salt of" a given acid. However, this method can be ambiguous in cases where there is more than one type of hydrogen present in the acid molecule, *e.g.*, $C(CN)_2{=}C(CH_2CH_2OH){-}C(CN)_2H$. There is a need for a systematic method of nomenclature for the salts of non-carboxylic organic acids whose acidic hydrogens

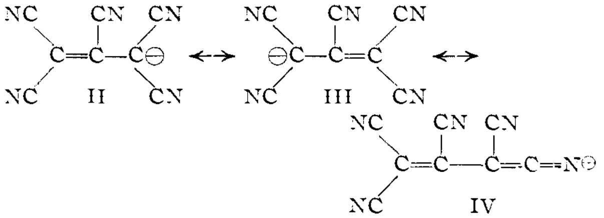
pyridine in water was added to a cold solution of tetracyanoethylene in acetone. Similarly, the quinolinium salt was formed when quinoline was substituted for pyridine, and sodium pentacyanopropenide was formed by the reaction of tetracyanoethylene with aqueous sodium bicarbonate.



Both the pyridinium and quinolinium salts of pentacyanopropene are quite acidic and will liberate carbon dioxide when dissolved in aqueous sodium bicarbonate. A crystalline adduct containing two moles of quinoline for each mole of pentacyanopropene will precipitate from solution when an excess of quinoline is present. These facts indicate that pentacyanopropene is a strongly acidic compound.

Pyridinium pentacyanopropenide is soluble in water. Other less soluble salts, including the N,N-dimethylanilinium, trimethylsulfonium, tetraethyl- and tetramethylammonium and quinolinium salts were prepared from the pyridinium salt by simple metathetical reactions. Many of the cyanocarbon acids form quaternary ammonium salts that are insoluble in cold water, but can be recrystallized from hot water. Therefore, the preparation of quaternary ammonium salts was found to be a convenient method for the isolation of these acids. For example, an aqueous solution of pyridinium pentacyanopropenide was prepared by dissolving tetracyanoethylene in aqueous pyridine, and then the tetramethylammonium salt was precipitated from this solution by adding tetramethylammonium chloride. The tetramethylammonium pentacyanopropenide was then purified by recrystallization from hot water.

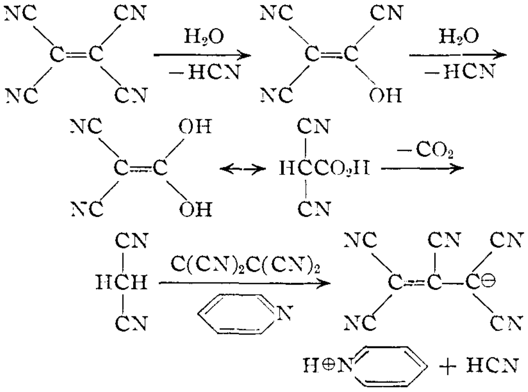
The hydrate of the free acid, 1,1,2,3,3-pentacyanopropene, was obtained as a somewhat unstable yellow-brown crystalline material by the acidification of the pyridinium salt with an acidic ion exchange resin. 1,1,2,3,3-Pentacyanopropene dihydrate is a strong acid with a pK_a of 1.9. It is very soluble in both ether and water. Neutralization of ethereal or aqueous solutions with amines produced stable amine salts. Some of the resonance forms of the pentacyanopropene anion are illustrated by structures II, III and IV.



Hydrolysis of tetracyanoethylene in neutral or acidic solutions did not produce pentacyanopropene. Instead, a single cyano group was replaced with hydroxyl to form tricyanoethenol (tricyanovinyl alcohol). An aqueous solution of tricyanoethenol was formed by boiling a suspension of finely-ground tetracyanoethylene in water until solution was complete, and then removing the dissolved hydrogen cyanide under reduced pressure. Solutions of tricyanoethenol prepared in this manner were strongly acidic, possessing a pK_a of about 1.9. A number of solid, crystalline amine salts of tricyanoethenol were prepared. These amine salts were relatively insoluble in cold water but could be recrystallized from hot water. An insoluble silver salt of tricyanoethenol was prepared from the tetramethylammonium salt of tricyanoethenol and silver nitrate.

Salts of tricyanoethenol are surprisingly stable toward hydrolysis. They can be boiled with dilute acids and bases for short periods of time and remain unaffected. They are also resistant to prolonged boiling in ethyl alcohol and ethyl alcohol–pyridine mixtures. These facts are at variance with the report of Schenck and Finken[7] who have postulated potassium tricyanoethenolate as a hydrolytically unstable intermediate in the condensation of malononitrile and ethyl cyanoformate in the presence of potassium ethoxide. They did not identify the postulated intermediate but assumed that in an attempted recrystallization from ethyl alcohol it reacted with alcohol to yield the potassium salt of ethyl dicyanoacetate, which is the only product they identified. The assumed reaction with alcohol during recrystallization appears unlikely when it is considered that an excess of alcohol was present during the original condensation. A repetition of their work indicated that the potassium salt of ethyl dicyanoacetate is the direct and only product from this condensation. Attempts to prepare salts of ethyl dicyanoacetate by ethanolysis of the salts of tricyanoethenol prepared from tetracyanoethylene were unsuccessful. This may be due to the fact that the tricyanoethenolate ion possesses a negative charge and repels the ethoxide ion.

At first, it was considered likely that tricyanoethenol was formed in the first step of the base-catalyzed hydrolysis of tetracyanoethylene to pentacyanopropene (equation 1).



(1)

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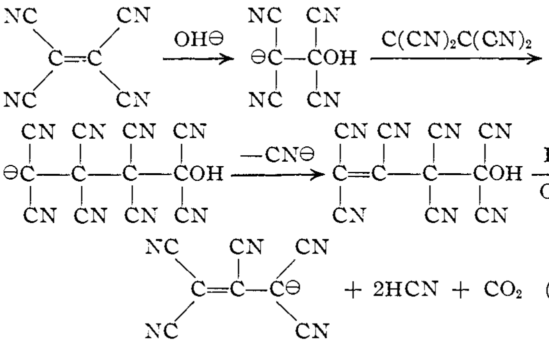
are bonded to carbon or nitrogen. We propose that the electron which is left on the anion derived from the acid be given the functional suffix *ide*. The salts can then be named in accordance with the "Chemical Abstracts" type of nomenclature following the rules governing functional groups. The salts of cyanocarbon acids described in this paper have been named in this manner.

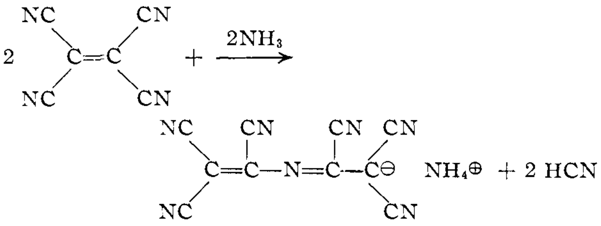
[7] R. Schenck and H. Finken, *Ann.*, **462**, 158 (1928).

However, this appears unlikely, for attempts to prepare pentacyanopropene by the basic hydrolysis of a mixture of tetracyanoethylene and tricyanoethenol resulted in only the amount of pentacyanopropene that would be expected from the tetracyanoethylene. The tricyanoethenol remained unchanged. Also, attempts to prepare pentacyanopropene from the reaction of tetracyanoethylene with malononitrile were unsuccessful. Thus it appears that tricyanoethenol is not an intermediate to pentacyanopropene. The series of reactions represented in equation 2 is suggested as the course of the basic hydrolysis.



(2)

1,1,2,4,5,5-Hexacyano-3-azapentadiene.—This acid, whose anion also contains only carbon and nitrogen, was prepared by the reaction of tetracyanoethylene with ammonia. A solution of ammonium 1,1,2,4,5,5-hexacyano-3-azapentadienide was prepared by passing anhydrous ammonia over a solid solution of tetracyanoethylene in acetone.

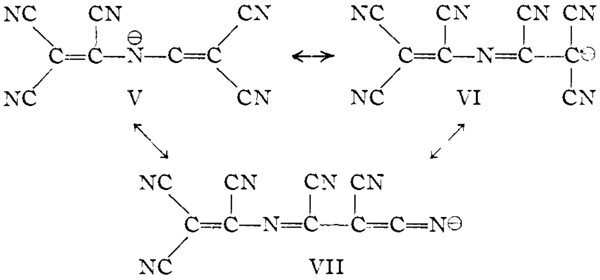


Stable orange or red quaternary ammonium salts of hexacyanoazapentadiene were precipitated from this solution by the addition of suitable quaternary ammonium halides. An orange trimethylsulfonium salt and a deep-red crystalline silver salt were also prepared by metathesis.

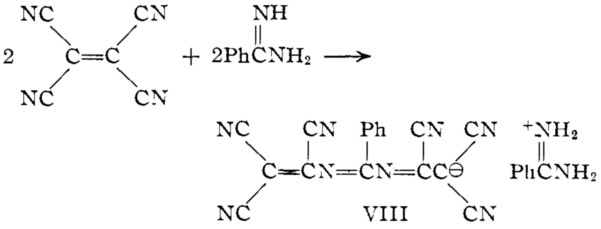
The action of aqueous ammonium hydroxide on a cold solution of tetracyanoethylene in acetone resulted in the formation of salts of both hexacyanoazapentadiene (83%) and pentacyanopropene (17%). This indicates that both condensation with ammonia and hydrolysis can proceed concurrently.

The free acid, 1,1,2,4,5,5-hexacyano-3-azapentadiene, was isolated in a hydrated form from the percolate obtained by passing a solution of the tetramethylammonium salt through an acidic ion exchange column. The hydrated acid was obtained as large, dark maroon crystals. It possesses a pK_a of 2.1. The infrared spectrum of the hydrated acid indicates that it is in an ionized form. The quinolinium and triphenylphosphonium salts of hexacyanoazapentadiene were prepared by neutralization of an ethereal solution of the acid with quinoline and triphenylphosphine, respectively. Benzamidinium and acetamidinium salts were also prepared from the free acid.

Some of the resonance forms of the hexacyanoazapentadiene anion are represented by V, VI and VII.

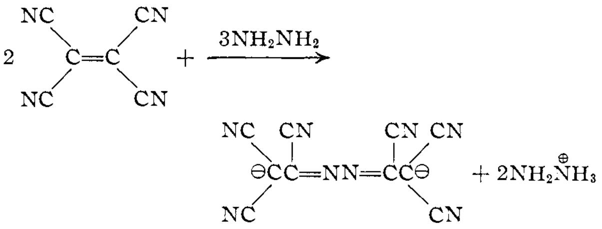


An attempt was made to prepare a cyanocarbon acid in which the conjugated chain would be extended even further. Tetracyanoethylene was treated with anhydrous benzamidine under the same conditions that were successful with ammonia.

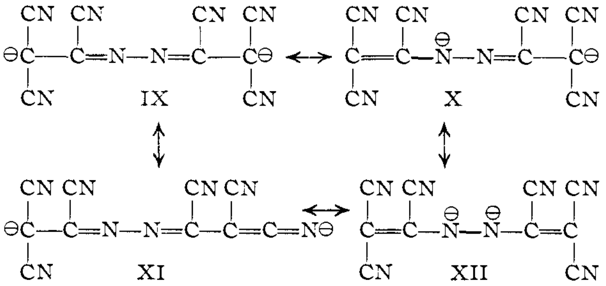


A dark green crystalline product was formed that possessed the desired elemental analysis and the expected spectrum for VIII, but complete identification was not made because of its extreme susceptibility to hydrolysis.

1,1,2,5,6,6-Hexacyano-3,4-diazahexadiene.—Salts of this dibasic cyanocarbon acid were prepared from the reaction of tetracyanoethylene with hydrazine.

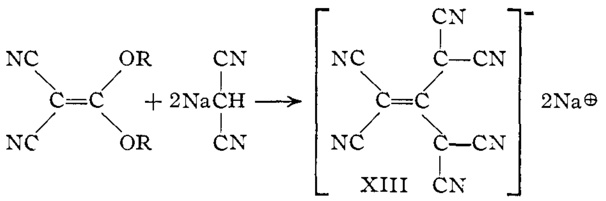


The reaction was accomplished by adding powdered tetracyanoethylene to a cold aqueous solution of hydrazine. A crystalline red-orange tetraethylammonium salt of 1,1,2,5,6,6-hexacyano-3,4-diazahexadiene was precipitated from this solution by the addition of tetraethylammonium bromide. A red silver salt and an orange benzyltrimethylammonium salt were prepared from the tetraethylammonium salt by conventional metathetical reactions. These salts are unstable in acidic solutions; therefore, attempts to prepare the free acid were unsuccessful. The pK_a of this acid was not determined; however, it must be a strong acid for aqueous solutions of its quaternary ammonium salts are essentially neutral. A few of the resonance forms of the hexacyanodiazahexadiene anion are illustrated by IX through XII.



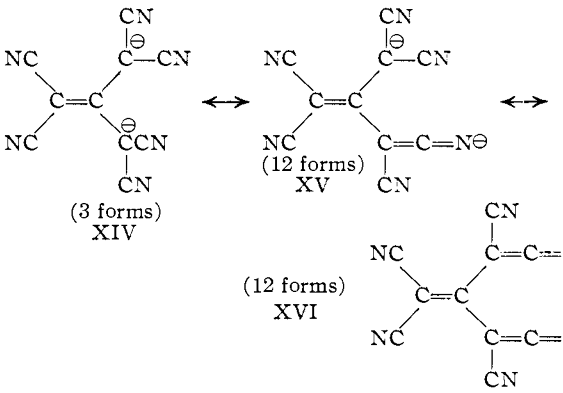
2-Dicyanomethylene-1,1,3,3-tetracyanopropane.—Another dibasic cyanocarbon acid, 2-dicyanomethylene-1,1,3,3-tetracyanopropane, was prepared by the reaction of a dicyanoketene acetal[8] with two equivalents of malononitrile. This acid is of considerable interest because its anion, which is comprised entirely of carbon and nitrogen, is a planar, symmetrical, highly resonating system. In this respect, it resembles sulfuric and nitric acids.

Sodium 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide (XIII) was prepared by the direct reaction of two equivalents of sodiomalononitrile with dicyanoketene diethyl or ethylene acetal.

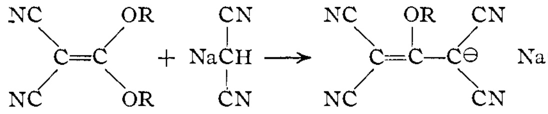


Other less soluble metal and quaternary ammonium salts were prepared from the sodium salt XIII by conventional metathetical reactions. For example, barium 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide was precipitated when barium chloride was added to an aqueous solution of the sodium salt XIII. This barium salt, obtained as a hexahydrate, could be purified by recrystallization from water. Its solubility characteristics were such that it was a convenient intermediate to other salts. A wide variety of metal and amine salts of 2-dicyanomethylene-1,1,3,3-tetracyanopropane were prepared by adding aqueous solutions of the corresponding sulfates to aqueous barium 2-dicyanomethylene - 1,1,3,3 - tetracyanopropanediide. The barium salt was exceedingly soluble in methanol, and advantage was taken of this property to prepare the methanol-insoluble potassium salt.

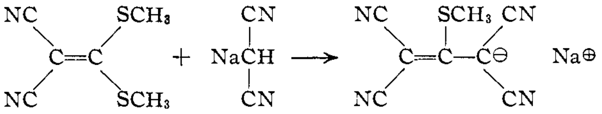
An aqueous solution of the free acid, 2-dicyanomethylene-1,1,3,3-tetracyanopropane, was also prepared from the barium salt. An exact equivalent of sulfuric acid was added to an aqueous solution of barium 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide, and the precipitated barium sulfate was removed by filtration. The pK_a of the second hydrogen of 2-dicyanomethylene-1,1,3,3-tetracyanopropane was determined to be 2.25. The first hydrogen of this acid is so strongly ionized that its pK_a could not be determined by conventional means. Dilute aqueous solutions of 2-dicyanomethylene-1,1,3,3-tetracyanopropane possess a pH approximately equal to solutions of sulfuric acid of the same molar concentration. This extreme acidity probably is due both to the inductive effects of the six cyano groups and to the high order of resonance stabilization of the 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide ion, as indicated by the large number of resonance forms that can be written for this ion (XIV, XV and XVI).



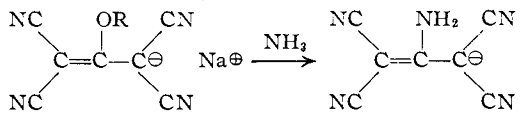
2-Alkoxy-1,1,3,3-tetracyanopropenes.—When only one equivalent of malononitrile was allowed to react with a dicyanoketene acetal, a new class of cyanocarbon acids, the 2-alkoxy-1,1,3,3-tetracyanopropenes, were formed. Thus, sodium 2-ethoxy-1,1,3,3-tetracyanopropenide was prepared from dicyanoketene diethyl acetal and sodiomalononitrile, and sodium 2-(2-hydroxyethoxy)-1,1,3,3-tetracyanopropenide was prepared from the ethylene acetal.



Other salts of these acids were prepared by metathetical reactions. Sodium 2-methylthio-1,1,3,3-tetracyanopropenide also was prepared by an analogous reaction of sodiomalononitrile with dicyanoketene dimethyl thioacetal.[9] Other salts of this acid also were prepared by metathesis.



2-Amino-1,1,3,3-tetracyanopropenes.—Salts of 2-alkoxy-1,1,3,3-tetracyanopropenes undergo aminolysis with ammonia and primary and secondary amines to form salts of 2-amino-1,1,3,3-tetracyanopropenes. An aqueous solution of sodium 2-amino-1,1,3,3-tetracyanopropenide was prepared by boiling a solution of sodium 2-ethoxy- or 2-(2-hydroxyethoxy)-1,1,3,3-tetracyanopropenide in concentrated ammonium hydroxide.



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[8] Paper IV. W. J. Middleton and V. A. Engelhardt, THIS JOURNAL, 80, 2788 (1958).

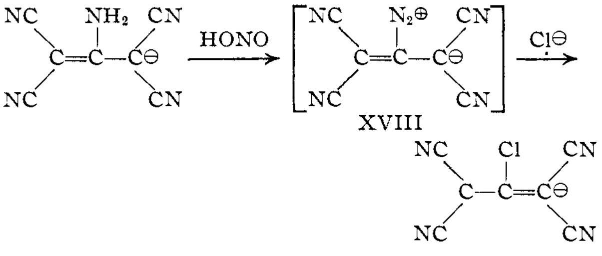
[9] H. D. Edwards and J. D. Kendall, U. S. Patent 2,533,233 (1950).

Crystalline quaternary ammonium salts of 2-amino-1,1,3,3-tetracyanopropene were then isolated after metathetical reactions of the sodium salt with the appropriate quaternary ammonium halides.

The free acid, 2-amino-1,1,3,3-tetracyanopropene, was prepared by acidification of the tetraethylammonium salt with an acidic ion exchange resin. This compound was determined to be a very strong organic acid (pK_a 2.58) in spite of the free amino group present in the molecule. The pyridinium salt, prepared by neutralization of the acid with pyridine, still exhibited an acidic pH when dissolved in water. The amino group of 2-amino-1,1,3,3-tetracyanopropene apparently has lost much of its basicity because of the resonating system of electrons in the propene anion.

N-Substituted 2-amino-1,1,3,3-tetracyanopropenes were prepared by treating 2-alkoxy-1,1,3,3-tetracyanopropenes with amines. Thus, the sodium salts of 2-methylamino- and 2-dimethylamino-1,1,3,3-tetracyanopropenes were prepared by the reaction of sodium 2-(2-hydroxyethoxy)-1,1,3,3-tetracyanopropenide with alcoholic solutions of methylamine and dimethylamine, respectively. Both of these sodium salts were obtained as white crystalline compounds that could be recrystallized from water. Other salts of these acids were prepared from the sodium salts by metathetical reactions.

2-Halo-1,1,3,3-tetracyanopropenes.—Nitrosation of 2-amino-1,1,3,3-tetracyanopropene appeared to be a possible route to a number of new and interesting compounds. However, attempts to isolate the inner salt XVIII were unsuccessful. Instead, tetraethylammonium 2-chloro-1,1,3,3-tetracyanopropenide was isolated when tetraethylammonium 2-amino-1,1,3,3-tetracyanopropenide was treated with nitrous acid generated from sodium nitrite and hydrochloric acid. Also, N-methylquinolinium 2-bromo-1,1,3,3-tetracyanopropenide was formed from the reaction of the corresponding salt of the aminopropene with sodium nitrite and hydrobromic acid.

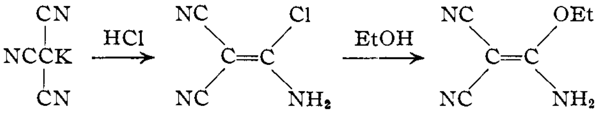


The mechanism of this reaction is not fully understood, but it probably involves the transitory formation of the diazonium inner-salt XVIII which then reacts with the halide ion to give the 2-halo-1,1,3,3-tetracyanopropene. Simple displacement of the amino group with a halide ion seems unlikely, for treatment of the aminopropene with hydrogen bromide in the absence of sodium nitrite resulted in other products.[10] Nitrosation of 2-methylamino-1,1,3,3-tetracyanopropene resulted in the formation of 2-(N-nitrosomethylamino)-1,1,3,3-tetracyanopropene. This fact also lends support to the theory that XVIII is an intermediate in the formation of the halopropenes.

Several salts of 2-chloro- and 2-bromo-1,1,3,3-tetracyanopropenes were prepared as described in the Experimental section. The free acid, 2-bromo-1,1,3,3-tetracyanopropene, was prepared by acidification of the N-methylquinolinium salt with an acidic ion exchange resin. It was found to be a strong acid (pK_a 2.60).

Tricyanomethane.—Reactions of tricyanomethane, the simplest cyanocarbon acid, were investigated briefly. Potassium tricyanomethanide (potassium salt of cyanoform) was prepared as described by Cox and Fontaine,[2b] and a barium salt was prepared from the potassium salt and barium chloride. An aqueous solution of free tricyanomethane was prepared by the addition of an equivalent amount of sulfuric acid to an aqueous solution of the barium salt. The pK_a of tricyanomethane prepared in this manner was determined to be 2.04.

Salts of tricyanomethane reacted with hydrogen halides to form adducts of tricyanomethane with the hydrogen halide. These adducts were identified as 1-halo-1-amino-2,2-dicyanoethylenes. The adducts prepared from hydrogen chloride and hydrogen bromide both contained a doublet in the 3 μ region of their infrared spectra that was assigned to the NH_2 absorption. These compounds also contain active halogens which resemble those of acyl halides. 1-Amino-1-bromo-2,2-dicyanoethylene reacted spontaneously with cold ethyl alcohol to produce 1-amino-1-ethoxy-2,2-dicyanoethylene, a compound that can also be prepared from dicyanoketene diethyl acetal and ammonia.[8]



Experimental

Table I contains a list of the salts of new cyanocarbon acids that have been prepared, together with their analyses and some of their properties.

Pyridinium 1,1,2,3,3-Pentacyanopropenide.[11]—A solution of 12.8 g. (0.01 mole) of tetracyanoethylene in 100 ml. of acetone was cooled to −50° in a flask which contained a dropping funnel and a gas inlet and outlet tube. Nitrogen was bubbled through the solution until all of the air in the system was displaced. The gas from the outlet tube was bubbled through a train of two traps containing saturated solutions of barium hydroxide. A mixture of 3.95 g. (0.05 mole) of pyridine and 10 ml. of water was added dropwise over a period of 10 minutes to the cold solution. The resulting intensely purple colored solution was then allowed to warm to room temperature. As the solution became warm, the color changed to yellow-brown, and gas was evolved. A white precipitate of barium carbonate formed in the traps that contained barium hydroxide. The solution was purged with nitrogen, and the barium carbonate in the traps was collected, washed with water and dried. There was obtained 7.62 g. (0.0387 mole) of barium carbonate.

The acetone solution was evaporated to near dryness, and the residue was collected on a filter, washed with a little water and dried. There was obtained 10.0 g. of crude pyridinium 1,1,2,3,3-pentacyanopropenide in the form of a brown solid. The solid was recrystallized from water to give yellow plates, m.p. 167–168°.

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[10] Paper X, E. L. Little, W. J. Middleton, D. D. Coffman, V. A. Engelhardt and G. N. Sausen, THIS JOURNAL, 80, 2832 (1958).

[11] W. J. Middleton, U. S. Patent 2,766,243 (1956).

Table I

Cyanocarbon Acid Salts

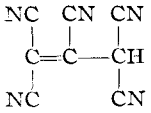
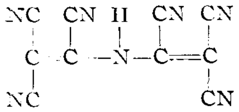
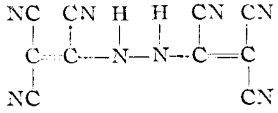
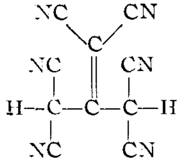
Acid	Salt	M.p., °C.	Color	Yield, %	Recrystn. solvent[a]	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Metal, %	
							Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
	Pyridinium	167–168	Yellow	81	A	$C_{13}H_6N_6$	63.41	63.36	2.45	2.27	34.14	34.21		
	Quinolinium	165–166	Yellow	55	A	$C_{17}H_8N_6$	68.91	69.15	2.72	2.73	28.37	28.59		
	Quinoline quinolinium	148–150	Yellow	74	A	$C_{26}H_{15}N_7$	73.40	73.27	3.55	3.60	23.06	23.15		
	Tetramethylammonium	314	Yellow	95	A	$C_{12}H_{12}N_6$	59.98	60.15	5.04	5.06	34.98	35.10		
	Anilinium	145–146	Yellow	75	A	$C_{14}H_8N_6$	64.61	65.01	3.10	3.27	32.30	32.36		
	Piperidinium	165–167	Yellow	95	A	$C_{13}H_{12}N_6$	61.89	62.02	4.80	4.55	33.32	32.94		
	Triethylammonium	126–128	Yellow	90	A	$C_{14}H_{16}N_6$	62.66	62.60	6.01	5.72	31.32	31.37		
	α-Picolinium	85–87	Yellow	75	A	$C_{14}H_8N_6$	64.61	64.31	3.10	3.11	32.30	32.33		
	N-Methylpyridinium	160–161	Yellow	70	A	$C_{14}H_8N_6$	64.61	64.98	3.10	3.21	32.30	32.27		
	Silver	d. 261	Yellow	100	B	AgC_8N_5	35.47	35.66			25.56	25.55	39.37	39.48
	N,N-Dimethylanilinium	124–125	Yellow	73	A	$C_{16}H_{12}N_6$	66.65	66.49	4.19	4.10	29.15	29.45		
	Cuprictetrapyridyl		Dark green	80	A	$CuC_{36}H_{20}N_{14}$	60.58	60.84	2.83	3.11	27.54	27.49	8.93	8.96
	Trimethylsulfonium	239–241	Yellow	93	A	$C_{11}H_9N_5S$	54.30	54.76	3.73	3.57	28.79	28.77	13.18[b]	13.05[b]
	Tetraethylammonium	220–221	Yellow	61	A	$C_{16}H_{20}N_6$	64.90	65.00	6.75	6.81	28.35	28.39		
	Tris-(*p*-dimethylaminophenyl)-carbonium	223–224	Bronze	86	C	$C_{33}H_{30}N_8$	73.58	74.00	5.61	5.63	20.81	21.06		
	Tetraethylammonium	203–205	Orange	55	C	$C_{18}H_{20}N_8$	62.05	62.27	5.79	5.83	32.16	32.18		
	Tetramethylammonium	252–254	Orange-red	35	A	$C_{14}H_{12}N_8$	57.52	57.32	4.14	4.16	38.34	38.30		
	Trimethylsulfonium	150–151	Orange	40	A	$C_{13}H_9N_7S$	52.87	52.67	3.07	3.00	33.20	33.25	10.86[b]	10.56[b]
	Silver	270 d.	Deep red	74	D	$AgC_{10}N_7$	37.18	37.10			29.74	30.16	33.08	33.17
	Quinolinium	199–201	Ruby red	90	C	$C_{19}H_8N_8$	65.51	65.53	2.32	2.31	32.18	32.13		
	Triphenylphosphonium	85–87	Red	50	B	$C_{28}H_{16}N_7P$	69.85	69.54	3.35	3.50	20.37	20.40	6.43	6.54[c]
	Benzamidinium	152–153	Orange	92	A	$C_{17}H_9N_9$	60.17	60.25	2.67	2.70	37.15	37.17		
	Acetamidinium	151–152	Orange	87	A	$C_{12}H_7N_9$	51.98	51.97	2.55	2.58	45.46	45.13		
	Tetraethylammonium	137–138	Orange-red	35	C	$C_{26}H_{40}N_{10}$	63.38	63.47	8.18	8.11	28.43	28.24		
	Benzyltrimethylammonium	175–178	Orange	60	A	$C_{30}H_{32}N_{10}$	67.64	67.55	6.06	6.02	26.30	26.23		
	Silver	d. 250	Red	97	B	$Ag_2C_{10}N_8$	26.81	27.06			25.02	24.67	48.17	48.27
	Sodium	>300	White	72	E	$Na_2C_{10}N_6$	48.02	48.28			33.61	33.35	18.39	17.43
	Barium	>300	White	89	A	$BaC_{10}N_6 \cdot 6H_2O$	26.71	27.01	2.69	2.79	18.69	18.59	30.55	30.31
	Potassium	>300	White	97	B	$K_2C_{10}N_6$	42.54	42.65			29.77	30.08	27.70	27.30
	Aluminum	d. 250	White		A	$Al_2C_{30}N_{18} \cdot 25H_2O$	32.26	32.20	4.51	4.35	22.58	22.71	4.83	5.27
	Magnesium		White		A	$MgC_{10}N_6 \cdot 6^1/_2H_2O$	34.75	34.93	3.79	3.66	24.32	24.30	7.04	6.69
	Silver		White	100	B	$Ag_2C_{10}N_6$	28.60	28.92			20.00	19.95	51.40	51.72
	Cadmium		White		A	$CdC_{10}N_6 \cdot 2H_2O$	34.06	34.50	1.14	1.23	23.84	23.82	31.88	31.22
	Uranyl	>300	White		A	$UO_2C_{10}N_6 \cdot 2H_2O$	23.54	23.34	0.79	1.27	16.47	16.01		
	Ferrous	>300	Yellow		A	$FeC_{10}N_6 \cdot 2^1/_2H_2O$	39.37	39.91	1.65	1.79	27.55	27.51	18.31	18.59
	Vanadyl		White		A	$VOC_{10}N_6 \cdot 3^1/_2H_2O$	35.94	36.18	2.11	2.15	25.15	24.26	15.25	16.20
	Cupric	d. 300	Black		A	$CuC_{10}N_6 \cdot {}^1/_2H_2O$	43.40	43.27	0.36	0.86	29.52	29.32	22.97	22.75

TABLE I (*Continued*)

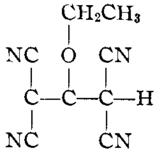
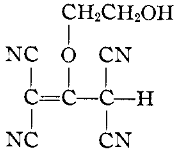
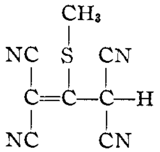
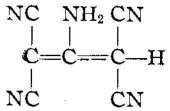
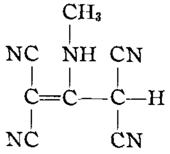
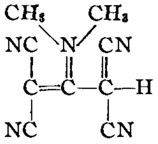
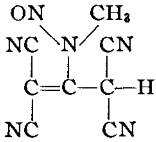
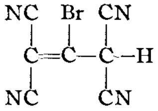
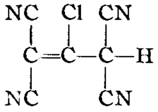
Acid	Salt	M.p., °C.	Color	Yield, %	Recrystn. solvent[a]	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Metal, %	
							Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
	Nickel	>300	Green		A	$NiC_{10}N_6 \cdot 4H_2O$	35.86	35.93	2.39	2.01			17.50	17.16
	Cobaltous		Orange		A	$CoC_{10}N_6 \cdot 2H_2O$	40.15	40.23	1.35	1.47	28.10	27.60	19.70	19.45
	Strontium		White		A	$SrC_{10}N_6 \cdot 7H_2O$	28.14	28.17	3.38	3.17			20.96	20.60
	Zinc	>300	White		A	$ZnC_{10}N_6 \cdot 2^1/_2H_2O$	38.30	38.65	1.60	1.44	26.72	27.14		
	Manganous		White		A	$MnC_{10}N_6 \cdot 2H_2O$	40.70	41.48	1.37	1.04	28.48	28.93		
	Mercuric		Yellow		B	$HgC_{10}N_6$							49.56	50.12
	Ammonium	d. 305	White		A	$C_{10}H_8N_8$	50.00	50.15	3.36	3.20	46.65	46.28		
	Anilinium		White		A	$C_{22}H_{16}N_8$	67.33	67.48	4.11	4.13	28.56	28.46		
	Quinolinium	206–208	Yellow		A	$C_{28}H_{16}N_8$	72.40	72.53	3.47	3.62	24.13	24.12		
	Tetrapropylammonium	296–298	White		C	$C_{34}H_{56}N_8$	70.79	70.05	9.78	9.50	19.43	19.45		
	Sodium	>300	White	85	C	$NaC_9H_5N_4O$	51.93	52.24	2.42	2.50	26.92	27.02	11.05	11.00
	N-Methylquinolinium	131–132	Yellow	83	A	$C_{19}H_{15}N_5O$	69.28	69.22	4.59	4.59	21.27	21.40		
	Tetraethylammonium	63–64	White	75	A	$C_{17}H_{25}N_5O$	64.73	64.63	7.99	7.81	22.21	22.26		
	Cobaltous	d. 215	Orange		A	$CoC_{18}H_{10}N_8O_2 \cdot 2H_2O$	46.46	46.78	3.04	3.10	24.08	24.05	12.67	12.82
	Cupric		Red-brown		A	$CuC_{18}H_{10}N_8O_2 \cdot 2^1/_2H_2O$	45.14	45.61	3.15	3.19	23.40	23.49	13.27	13.15
	Nickelous	d. 235	Blue		A	$NiC_{18}H_{10}N_8O_2 \cdot 3H_2O$	44.75	46.75	3.34	3.06	23.20	24.05		
	Sodium	300	White	87	C	$NaC_9H_5N_4O_2$	48.22	48.61	2.25	2.43	25.00	25.00	10.26	10.08
	Cobaltous		Orange		A	$CoC_{18}H_{10}N_8O_2 \cdot 4H_2O$	43.12	43.18	3.62	2.97	22.35	21.17		
	Tetramethylammonium	113–114	White	70	F	$C_{12}H_{15}N_5S$	55.15	55.34	5.78	5.82	26.80	26.44	12.27[b]	11.93[b]
	N-Methylquinolinium	133–143	Yellow	98	A	$C_{18}H_{13}N_5S$	65.24	64.84	3.96	3.66	21.14	21.17	9.67	9.58
	Tetraethylammonium	140–141	White	73	A	$C_{15}H_{20}N_6$	63.35	63.08	7.90	7.25	29.56	29.39		
	N-Methylquinolinium	180–181	Light yellow	82	A	$C_{17}H_{12}N_6$	67.98	68.02	4.03	4.07	27.99	28.11		
	Silver	>300	White	59	B	$AgC_7H_2N_5$	31.84	32.20	0.76	0.84	26.53	26.71	40.86	40.43
	Pyridinium	200–203	White	74	C	$C_{12}H_8N_6$	61.01	61.05	3.41	3.33	35.58	35.62		
	Sodium	>300	White	87	A	$NaC_8H_4N_5$	49.74	49.90	2.09	2.11	36.26	36.09	11.91	11.97
	N-Methylquinolinium	129–130	Light yellow	85	A	$C_{18}H_{14}N_6$	68.80	69.08	4.99	4.52	26.73	26.82		

TABLE I (*Continued*)

Acid	Salt	M.p., °C.	Color	Yield, %	Re-crystn. sol-vent[a]	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Metal, %	
							Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
	Sodium	>300	White	44	A	$NaC_9H_6N_6$	52.17	52.37	2.92	3.02	33.81	33.82	11.10	11.24
	Tetraethylammonium	110-111	Yellow	70	A	$C_{12}H_{15}N_7O$	52.73	52.98	5.53	5.53	35.88	35.77		
	Tetraethylammonium	104-107	Orange	43	A	$C_{16}H_{20}BrN_5$	51.43	51.42	5.76	5.88	20.00	19.70	22.82[d]	22.49[d]
	N-Methylquinolinium	170-171	Yellow-brown	90	A	$C_{17}H_{10}BrN_5$	56.06	56.05	2.77	2.95	19.23	19.20	21.94[d]	21.83[d]
	Silver	<300	Cream	86	D	AgC_7BrN_4	25.64	25.46	24.37[d]	23.58[d]	17.09	17.07	32.90	33.34
	Pyridinium	180-181	White	93	A	$C_{12}H_6BrN_5$	48.02	48.32	2.02	2.13	23.34	23.12	26.63[d]	26.39[d]
	Barium	<300	Cream	62	A	$BaC_{14}N_8Br_2 \cdot 4H_2O$[e]	25.89	26.03	1.24	1.52	17.25	17.28	21.15	20.65
	N-Methylquinolinium	136-138	Yellow-brown	63	A	$C_{17}H_{10}ClN_5$	63.85	63.90	3.15	3.14	21.91	21.96	11.09[f]	10.99[f]
	Tetraethylammonium	180-181	Orange	67	A	$C_{15}H_{20}ClN_5$	58.91	59.17	6.59	6.63	22.90	22.54	11.60[f]	11.30[f]
	Tetramethylammonium	211-213	White	30	A	$C_{11}H_{12}ClN_5$	52.91	52.95	4.85	5.04	28.05	28.28	13.77[f]	14.20[f]

[a] A = water, B = product not recrystallized, C = ethanol, D = acetonitrile-water, E = acetone-ether, F = ethanol-ether. [b] Sulfur analysis. [c] Phosphorus analysis. [d] Bromine analysis. [e] Calcd.: Br, 24.61. Found: Br, 24.67. [f] Chlorine analysis.

Quinolinium 1,1,2,3,3-pentacyanopropenide was prepared in a similar manner from 0.1 mole of tetracyanoethylene, 10 ml. water and 0.05 mole of quinoline. When this reaction was repeated using only 0.05 mole of tetracyanoethylene, **quinolinequinolinium 1,1,2,3,3-pentacyanopropenide** was obtained as the only product.

Quinolinium 1,1,2,3,3-pentacyanopropenide also was prepared from the pyridinium salt. Quinoline was added to a solution of pyridinium 1,1,2,3,3-pentacyanopropenide in 5% sodium bicarbonate. The solution was stirred, and then acidified with 5% hydrochloric acid. The quinolinium salt was obtained as a yellow precipitate.

N,N-Dimethylanilinium 1,1,2,3,3-Pentacyanopropenide.—A solution of 1.5 g. of pyridinium 1,1,2,3,3-pentacyanopropenide in 10 ml. of N,N-dimethylaniline was allowed to remain at room temperature for 10 minutes. A yellow precipitate formed slowly. The solution was diluted with 50 ml. of ether, and the precipitate that formed was collected on a filter, washed with ether and recrystallized from water. There was obtained 1.1 g. of N,N-dimethylanilinium 1,1,2,3,3-pentacyanopropenide in the form of yellow prisms.

Cuprictetrapyridyl 1,1,2,3,3-Pentacyanopropenide.—A solution of 2.0 g. of cupric acetate monohydrate in 50 ml. of hot water was mixed with a solution of 2.07 g. of pyridinium 1,1,2,3,3-pentacyanopropenide in 25 ml. of hot water. The hot solution was filtered and the filtrate was cooled. The long, dark green crystals that separated were collected on a filter, washed with water, and dried. There was obtained 1.6 g. of cuprictetrapyridyl 1,1,2,3,3-pentacyanopropenide.

Trimethylsulfonium 1,1,2,3,3-Pentacyanopropenide.—A solution of 1.0 g. of pyridinium pentacyanopropenide in 10 ml. of hot water was mixed with a solution of 1.0 g. of trimethylsulfonium iodide in 10 ml. of water. The solution was cooled, and the yellow precipitate that formed was collected on a filter, washed with water, and recrystallized from water to give 1.0 g. of trimethylsulfonium pentacyanopropenide in the form of long yellow needles.

Tetramethylammonium 1,1,2,3,3-Pentacyanopropenide.—A mixture of 5.0 g. (0.039 mole) of tetracyanoethylene and 100 ml. of 5% sodium bicarbonate solution was stirred at room temperature until all of the solid had dissolved. The solution was filtered, and a solution of 5 g. of tetramethylammonium chloride in 5 ml. of water was added to the filtrate. The brown precipitate that formed was collected on a filter, washed with water, and recrystallized from water. There was obtained 2.0 g. (43% yield) of tetramethylammonium 1,1,2,3,3-pentacyanopropenide in the form of yellow needles. This same salt was prepared in improved yield by the following procedure. A solution of 7.9 g. (0.1 mole) of pyridine in 10 ml. of water and 10 ml. of acetone was added to a solution of 12.8 g. (0.1 mole) of tetracyanoethylene in 90 ml. of acetone cooled to −50°. The mixture was allowed to warm to room temperature and then mixed with a solution of 11.0 g. (0.1 mole) of tetramethylammonium chloride in 600 ml. of water. The precipitate that formed (10.0 g.) was collected on a filter, washed with water, and recrystallized from water. There was obtained 7.8 g. of tetramethylammonium 1,1,2,3,3-pentacyanopropenide. **Tetraethylammonium 1,1,2,3,3-pentacyanopropenide** was prepared in a similar manner by substituting tetraethylammonium bromide for tetramethylammonium chloride. **Tris-(*p*-dimethylaminophenyl)-carbonium 1,1,2,3,3-pentacyanopropenide**[12] was prepared by mixing hot methanol solutions of equimolar amounts of crystal violet and tetramethylammonium pentacyanopropenide.

1,1,2,3,3-Pentacyanopropene Dihydrate.—A solution of 20 g. of pyridinium 1,1,2,3,3-pentacyanopropenide in 50 ml. of acetone was passed through an acidic ion-exchange column (Amberlite IR-120-H) which had been rendered acid with aqueous hydrochloric acid, washed thoroughly with water, and flushed with acetone to remove most of the water. The solution was washed through with additional quantities of acetone. The acetone percolate was evaporated to dryness under a stream of nitrogen. There was obtained 15.0 g. of 1,1,2,3,3-pentacyanopropene dihydrate in the form of a yellow-brown solid, m.p. 65–70°, pK_a 1.90. 1,1,2,3,3-Pentacyanopropene dihydrate was also prepared in a similar manner from quinoline-quinolinium 1,1,2,3,3-tetracyanopropenide.

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[12] We wish to thank Dr. B. C. McKusick for the preparation of this salt.

Anal. Calcd. for $C_8HN_5 \cdot 2H_2O$: C, 47.29; H, 2.48; N, 34.48; neut. equiv., 203. Found: C, 47.56; H, 2.63; N, 34.13; neut. equiv., 207.

Anilinium 1,1,2,3,3-Pentacyanopropenide.—One ml. of aniline was added to a solution of 2.0 g. of 1,1,2,3,3-pentacyanopropene dihydrate in 20 ml. of water. The solution was cooled, and the yellow crystals that separated were collected on a filter, washed with water, and recrystallized from water. There was obtained 1.5 g. of anilinium 1,1,2,-3,3-pentacyanopropenide in the form of yellow needles. Other amine salts (see Table I) were prepared in a similar manner by neutralization of 1,1,2,3,3-pentacyanopropene with triethylamine, α-picoline and piperidine. **Silver 1,1,2,-3,3-pentacyanopropenide** was precipitated when silver nitrate was added to an aqueous solution of 1,1,2,3,3-pentacyanopropene, and **N-methylpyridinium 1,1,2,3,3-pentacyanopropenide** was precipitated when N-methylpyridinium chloride was added to an aqueous solution of 1,1,2,3,3-pentacyanopropene.

Tricyanoethenol.[13]—To 60 ml. of distilled water was added 6.4 g. of powdered tetracyanoethylene. The mixture was boiled until evolution of gas ceased and all the solid had dissolved. The resulting aqueous solution was cooled and most of the hydrogen cyanide was removed under reduced pressure. Aqueous tricyanothenol prepared in this manner possessed a pK_a of 1.9.

Tetramethylammonium Tricyanoethenolate.—A mixture of 25.6 g. (0.2 mole) of tetracyanoethylene and 100 ml. of water was heated to reflux and stirred vigorously until all of the solid had gone into solution. Twenty-two grams of tetramethylammonium chloride was dissolved directly in the reaction mixture, and the resulting solution was filtered and cooled. The crystalline precipitate that formed was collected on a filter, washed with a small amount of cold water and then alcohol. There was obtained 30.6 g. (80% yield) of tetramethylammonium tricyanoethenolate as long, light yellow needles, m.p. 210–211°. Additional recrystallizations from ethyl alcohol or water did not change the melting point. The yellow color of the salt was removed by recrystallizing it from ethyl alcohol containing a little ethylenediamine.

Anal. Calcd. for $C_9H_{12}N_4O$: C, 56.23; H, 6.29; N, 29.15. Found: C, 56.04; H, 6.24; N, 29.16.

N-Methylquinolinium tricyanoethenolate, light yellow needles, m.p. 134–136°, was prepared in a similar manner from tetracyanoethylene, water and N-methylquinolinium iodide.

Anal. Calcd. for $C_{15}H_{10}N_4O$: N, 21.36. Found: N, 21.37.

Quinolinium tetracyanoethenolate, light yellow prisms, m.p. 131–132°, was prepared in a similar manner from tetracyanoethylene, water and aqueous quinoline hydrochloride.

Anal. Calcd. for $C_{14}H_8N_4O$: C, 67.74; H, 3.25; N, 22.57. Found: C, 67.67; H, 3.43; N, 22.61.

Silver Tricyanoethenolate.—A solution of 2.0 g. of tetramethylammonium tricyanoethenolate in 25 ml. of warm water was mixed with a solution of 5.0 g. of silver nitrate in 100 ml. of water. The precipitate that formed was collected on a filter and washed with water. There was obtained 2.2 g. of silver tricyanoethenolate as a white powder, m.p. > 300°.

Anal. Calcd. for C_5H_3OAg: C, 26.58; N, 18.60; Ag, 47.75. Found: C, 26.88; N, 18.68; Ag, 47.94.

Potassium 2,2-Dicyano-1-ethoxyethenolate.—A solution prepared by dissolving 7.8 g. (0.2 gram atom) of potassium in 100 ml. of absolute ethyl alcohol was added dropwise to a cooled, stirred solution of 13.2 g. (0.2 mole) of malononitrile and 20.0 g. (0.2 mole) of ethyl cyanoformate in 200 ml. of absolute ethyl alcohol. The white solid that precipitated was collected on a filter and washed with a little cold alcohol, and then ether, and recrystallized twice from water. There was obtained 10.0 g. of potassium 2,2-dicyano-1-ethoxyethenolate in the form of white needles, m.p. 302–305°.

Anal. Calcd. for $C_6H_5N_2O_2K$: C, 40.89; H, 2.86; N, 15.90; K, 22.19. Found: C, 40.75; H, 3.06; N, 16.01; K, 21.94.

An aqueous solution of this potassium salt was mixed with an aqueous solution of bisethylenediaminecopper(II) acetate. The purple solid that precipitated was collected on a filter, washed with water and recrystallized from water. **Bisethylenediaminecopper(II) 2,2-dicyano-1-ethoxyethenolate** was obtained as long purple needles, m.p. 257–260°.

Anal. Calcd. for $C_{16}H_{26}N_8O_4Cu$: Cu, 13.88; N, 24.47. Found: Cu, 13.80; N, 24.37.

Tetraethylammonium 1,1,2,4,5,5-Hexacyano-3-azapentadiene.[14]—A vigorously stirred solution of 64.0 g. (0.5 mole) of tetracyanoethylene in 500 ml. of acetone was cooled to −40°, and anhydrous ammonia was passed very slowly into the solution until the initial blue color faded to yellow. This addition required about 30 minutes. The cold solution was mixed with a solution of 57.5 g. (0.25 mole) of tetraethylammonium bromide in 250 ml. of water, and the mixture was allowed to stand in an ice-bath for 30 minutes. The orange precipitate that formed was collected on a filter, washed with water, and recrystallized from ethyl alcohol. There was obtained 48 g. of tetraethylammonium 1,1,2,4,-5,5-hexacyano-3-azapentadienide in the form of orange needles. The corresponding tetramethylammonium and trimethylsulfonium salts of 1,1,2,4,5,5-hexacyano-3-azapentadiene were prepared in a similar manner by substituting tetramethylammonium chloride and trimethylsulfonium iodide, respectively, for the tetraethylammonium bromide in this procedure (see Table I).

Reaction of Aqueous Ammonium Hydroxide with Tetracyanoethylene.—A solution of 6.4 g. (0.05 mole) of tetracyanoethylene in 50 ml. of acetone was stirred and cooled to −40°, and 3.33 ml. (0.05 mole) of concentrated ammonium hydroxide was added in two equal portions. A solution of 5.75 g. (0.025 mole) of tetraethylammonium bromide in 25 ml. of water was added to the mixture, and the orange precipitate that formed was collected on a filter, washed with water, and recrystallized from ethyl alcohol. There was obtained 3.5 g. of light orange needles, m.p. 40–190°. Ultraviolet spectral data indicate that this product is a mixture of tetraethylammonium 1,1,2,4,5,5-hexacyano-3-azapentadienide (83%) and tetraethylammonium 1,1,2,3,3-pentacyanopropenide (17%).

Silver 1,1,2,4,5,5-Hexacyano-3-azapentadienide.—A solution of 5.0 g. (0.017 mole) of tetramethylammonium 1,1,2,4,5,5-hexacyano-3-azapentadienide in 50 ml. of acetone was mixed with 50 ml. of aqueous 5% silver nitrate solution. The red precipitate that formed was collected on a filter, washed with water, and recrystallized from acetonitrile–acetone–water (1:10:50). There was obtained 4.1 g. of the silver salt as deep-red prisms which melted with decomposition at 220° when dropped on a preheated block.

1,1,2,4,5,5-Hexacyano-3-azapentadiene.—A solution of 5.0 g. (0.017 mole) of tetramethylammonium 1,1,2,4,5,5-hexacyano-3-azapentadienide in 25 ml. of acetone was passed through an acidic ion-exchange column (Amberlite IR-120-H) which had been rendered acid with aqueous hydrochloric acid, washed thoroughly with water and flushed with acetone to remove most of the water. The percolate was allowed to evaporate to dryness. There was obtained 4.6 g. of 1,1,2,4,5,5-hexacyano-3-azapentadiene·$3^1/_2H_2O$ in the form of large dark maroon crystals, m.p. 47–52°, pK_a 2.1.

Anal. Calcd. for $C_{10}HN_7 \cdot 3^1/_2H_2O$: C, 42.55; H, 2.86; N, 34.75. Found: C, 42.50; H, 3.16; N, 34.66.

The quinolinium and triphenylphosphonium salts of 1,1,2,4,5,5-hexacyano-3-azapentadiene were prepared by neutralization of an ethereal solution of the acid with quinoline and triphenylphosphine, respectively.

Benzamidinium 1,1,2,4,5,5-Hexacyano-3-azapentadienide.—A solution of 1.0 g. of 1,1,2,4,5,5-hexacyano-3-azapentadienide·$3^1/_2H_2O$ in 3 ml. of water was mixed with a solution of 5.0 g. of benzamidine hydrochloride in 5 ml. of water. The orange precipitate that formed was collected on a filter, washed with water, and recrystallized from water. There was obtained 1.3 g. of benzamidinium 1,1,2,-4,5,5-hexacyano-3-azapentadienide in the form of orange needles. The acetamidinium salt was prepared in a similar manner from the acid and acetamidine hydrochloride.

Reaction of Tetracyanoethylene with Benzamidine.—Fifteen grams of benzamidine hydrochloride was mixed with 15 ml. of saturated aqueous sodium hydroxide solution, and the mixture was extracted with 15 ml. of acetone. The

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(13) W. J. Middleton, U. S. Patent 2,766,135 (1956).

(14) W. J. Middleton, U. S. Patent 2,762,811 (1956).

acetone extract, containing free benzamidine, was dried over solid sodium hydroxide. This benzamidine solution was then added dropwise to a solution of 6.4 g. (0.05 mole) of tetracyanoethylene in 50 ml. of acetone cooled to −50° until the initial blue color changed to red. The solution was mixed with 500 ml. of water, and the near-black precipitate that formed was collected on a filter, washed with water, redissolved in acetone, and reprecipitated with water. There was obtained 3.3 g. of a very dark green crystalline material, $\lambda_{\max}^{\text{Acetone}}$ 598 mμ, 375 mμ, which decomposed when heated above 200°. An acetone solution of this material was dark green, and was decolorized irreversibly by trace quantities of aqueous acid or base.

Anal. Calcd. for $C_{24}H_{14}N_{10}$: C, 65.15; H, 3.19; N, 31.66. Found: C, 64.48; H, 3.32; N, 31.60.

Tetraethylammonium 1,1,2,5,6,6-Hexacyano-3,4-diazahexadienediide.—A solution of 10 ml. of hydrazine hydrate in 100 ml. of water was mixed rapidly with cooling with 12.8 g. (0.1 mole) of powdered tetracyanoethylene. Tetraethylammonium bromide (21 g., 0.1 mole) was added and the mixture was stirred. The orange-brown precipitate that formed was collected on a filter, washed with water and recrystallized from alcohol. There was obtained 8.5 g. of tetraethylammonium 1,1,2,5,6,6-hexacyano-3,4-diazahexadienediide in the form of orange needles. The less soluble **silver and benzyltrimethylammonium** salts of 1,1,2,5,6,6-hexacyano-3,4-diazahexadiene were prepared by simple metathetical reactions of the tetraethylammonium salt with silver nitrate and benzyltrimethylammonium chloride, respectively, in water.

Sodium 2-Dicyanomethylene-1,1,3,3-tetracyanopropanediide.[15]—A solution of 6.8 g. (0.05 mole) of dicyanoketene ethylene acetal in 25 ml. of hot ethyl alcohol was added to an alcoholic solution of sodiomalononitrile prepared by adding 6.6 g. (0.1 mole) of malononitrile and 2.3 g. (0.1 g. atom) of sodium to 50 ml. of ethyl alcohol. An exothermic reaction ensued, and the reaction mixture was cooled in ice. The clear reaction mixture was filtered, and the filtrate was mixed with 400 ml. of ether. The white precipitate that formed was collected on a filter, washed with ether and dried. There was obtained 9.0 g. of sodium 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide. The less soluble barium, strontium, cupric, cobaltous, tetra-*n*-butylammonium and tetra-*n*-propylammonium salts of 2-dicyanomethylene-1,1,3,3-tetracyanopropane were prepared by simple metathetical reactions of the sodium salt with barium chloride, strontium chloride, cupric nitrate, cobaltous sulfate, tetra-*n*-butylammonium iodide and tetra-*n*-propylammonium iodide, respectively, in water.

Barium 2-Dicyanomethylene-1,1,3,3-tetracyanopropanediide.—A solution of 16.6 g. (0.01 mole) of dicyanoketene diethyl acetal in 100 ml. of tetrahydrofuran was added slowly to an alcoholic solution of sodiomalonitrile prepared by dissolving 13.2 g. (0.2 mole) of malononitrile and 4.6 g. (0.2 g. atom) of sodium in 200 ml. of ethyl alcohol. The reaction mixture was stirred at 0° for 2 hours and then at room temperature for 2 hours. Ether was added to the solution, and the white precipitate that formed was collected on a filter and then dissolved in 100 ml. of water. A solution of 25 g. of barium chloride in 100 ml. of water was mixed with this solution. A precipitate of 41 g. of barium 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide hexahydrate, as long colorless needles, was obtained.

The barium salt was also prepared by a similar procedure when dicyanoketene dimethyl thioacetal was substituted for the dicyanoketene diethyl acetal. The less soluble mercuric and silver salts of 2-dicyanomethylene-1,1,3.3-tetracyanopropene were prepared by simple metathetical reactions of the barium salt with mercuric acetate and silver nitrate, respectively, in hot water.

Potassium 2-Dicyanomethylene-1,1,3,3-tetracyanopropanediide.—A solution of 2.25 g. (0.005 mole) of barium 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide hexahydrate in 25 ml. of methanol was mixed with a solution of 1.66 g. (0.01 mole) of potassium iodide in 25 ml. of methanol. The white crystalline precipitate that formed was collected on a filter, washed with methanol and dried. There was obtained 2.1 g. of potassium 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide.

Preparation of Metal Salts of 2-Dicyanomethylene-1,1,3.3-tetracyanopropane from the Barium Salt and Metal Sulfates.—A number of metal salts of 2-dicyanomethylene-1,1,3,3-tetracyanopropane were prepared by treating a solution of the barium salt in hot water with various metal sulfates. The precipitated barium sulfate was removed by filtration, and the filtrate was evaporated to obtain the new salt. For example, a hot solution of 2.50 g. (0.01 mole) of cupric sulfate pentahydrate in 60 ml. of water was added to a hot solution of 4.49 g. (0.01 mole) of barium 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide hexahydrate in 75 ml. of water. The mixture was stirred and boiled for 0.5 hour, and the precipitated barium sulfate was removed by filtration. Evaporation of the filtrate yielded 4.0 g. of lustrous black crystals of cupric 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide. The aluminum, magnesium, cadmium, uranyl, ferrous, vanadyl, nickelous, zinc, manganous, ammonium and anilinium salts of 2-dicyanomethylene-1,1,3,3-tetracyanopropane were prepared in a similar manner from the corresponding sulfates.

Preparation of Aqueous 2-Dicyanomethylene-1,1,3,3-tetracyanopropane.—A solution of 4.496 g. (0.01 mole) of barium 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide hexahydrate in 50 ml. of warm water was mixed with 30.00 ml. of 0.3329 molar sulfuric acid. The mixture was cooled, and the barium sulfate was removed by filtration. Water was added to the filtrate to bring the volume up to 100 ml., and the resulting solution of 2-dicyanomethylene-1,1,3,3-tetracyanopropane was standardized with sodium hydroxide, using phenolphthalein as the indicator, and was found to be 0.0993 molar (0.1986 normal). The second pK_a of this acid was determined to be 2.25. The first hydrogen of this acid is so strongly ionized that it was difficult to determine its pK_a. The *p*H of solutions of 2-dicyanomethylene-1,1,3,3-tetracyanopropane over a wide range of concentrations, as measured by a Beckman *p*H meter, were equivalent to those of aqueous sulfuric acid of the same concentrations.

Quinolinium 2-Dicyanomethylene-1,1,3,3-tetracyanopropanediide.—A mixture of 10 ml. of 0.1986 *N* 2-dicyanomethylene-1,1,3,3-tetracyanopropane, 0.5 g. of quinoline and 10 ml. of 5% hydrochloric acid was allowed to stand at room temperature for 10 minutes and then cooled. The orange precipitate that formed was collected on a filter and recrystallized from water to give 0.6 g. of quinolinium 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide as light yellow needles, m.p. 206–208°.

Sodium 2-Ethoxy-1,1,3,3-tetracyanopropenide.[16]—Dicyanoketene diethyl acetal (5.54 g., 0.033 mole) was added to an alcoholic solution of sodiomalononitrile prepared by dissolving 0.77 g. (0.033 g. atom) of sodium and 2.2 g. (0.033 mole) of malononitrile in 50 ml. of ethyl alcohol. As the solid dissolved, the solution became warm. The solution was cooled, and the white precipitate that formed was collected on a filter, washed with ether, and recrystallized from ethyl alcohol. There was obtained 4.5 g. of sodium 2-ethoxy-1,1,3,3-tetracyanopropenide as white needles. Sodium **2-(2-hydroxyethoxy)-1,1,3,3-tetracyanopropenide** was prepared in a similar manner from sodiomalononitrile and dicyanoketene ethylene acetal.

The N-methylquinolinium, tetraethylammonium, cobaltic, cupric and nickelous salts of 2-ethoxy-1,1,3,3-tetracyanopropene were prepared by simple metathetical reactions of the more soluble sodium salt with N-methylquinolinium iodide, tetraethylammonium bromide, cobaltic sulfate, cupric sulfate and nickelous sulfate, respectively, in water. The cobaltous salt of 2-(2-hydroxyethoxy)-1,1.3.3-tetracyanopropene was prepared by a metathetical reaction between the more soluble sodium salt and cobaltous sulfate.

Salts of 2-Methylthio-1,1,3,3-tetracyanopropene.—A solution of sodiomalononitrile prepared from 0.46 g. of sodium and 1.32 g. of malononitrile in 40 ml. of ethyl alcohol was mixed with a warm solution of 3.4 g. of dicyanoketene dimethyl thioacetal in 50 ml. of ethyl alcohol. The solution was allowed to stand at room temperature for one hour, and then drowned in 1 l. of ether. There was obtained 3.1 g. of sodium **2-methylthio-1,1,3,3-tetracyanopropenide** in the form of a white powder.

A solution of 1.5 g. of this sodium salt in 10 ml. of water was mixed with a solution of 3.0 g. of tetramethylammonium chloride in 5 ml. of water. The white precipitate that formed was collected on a filter, washed with a small amount of water, and recrystallized from ethyl alcohol–ether.

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(15) W. J. Middleton, U. S. Patent 2,766,135 (1956).

(16) W. J. Middleton, U. S. Patent 2,766,247 (1956)

There was obtained 1.1 g. of **tetramethylammonium 2-methylthio-1,1,3,3-tetracyanopropenide** in the form of white needles, m.p. 113–114°. **N-Methylquinolinium 2-methylthio-1,1,3,3-tetracyanopropenide** was obtained in a similar manner from the sodium salt and N-methylquinolinium iodide as long yellow needles, m.p. 133–134°.

Tetraethylammonium 2-amino-1,1,3,3-tetracyanopropenide.—A solution of 100 g. (0.45 mole) of sodium 2-(2-hydroxyethoxy)-1,1,3,3-tetracyanopropenide in 1 liter of concentrated ammonium hydroxide was heated under reflux for 2 hours, cooled to 10° and saturated with anhydrous ammonia, and again heated under reflux for 16 hours. The solution was filtered, and the filtrate was mixed with a solution of 100 g. (0.48 mole) of tetraethylammonium bromide in 300 ml. of water. The long white needles that separated upon cooling were collected on a filter and recrystallized from water to give 93.1 g. of tetraethylammonium 2-amino-1,1,3,3-tetracyanopropenide. **N-Methylquinolinium 2-amino-1,1,3,3-tetracyanopropenide** was prepared by a similar procedure, except that N-methylquinolinium iodide was substituted for tetraethylammonium bromide. This salt also was prepared by the reaction of sodium 2-ethoxy-1,1,3,3-tetracyanopropenide with ammonia, following an analogous procedure.

Silver 2-Amino-1,1,3,3-tetracyanopropenide.—A solution of 0.5 g. of N-methylquinolinium 1,1,3,3-tetracyanopropenide in 25 ml. of hot water was mixed with 10 ml. of 5% silver nitrate solution. The white precipitate that formed was collected on a filter, washed with water and dried. There was obtained 0.43 g. of the silver salt.

2-Amino-1,1,3,3-tetracyanopropene Dihydrate.—A solution of 5.0 g. of tetramethylammonium 2-amino-1,1,3,3-tetracyanopropenide in 50 ml. of acetone was passed through an ion-exchange column (Amberlite-IR-120-H) which had been flushed with acetone to remove most of the water. The percolate was evaporated to dryness at room temperature. There was obtained 2.4 g. of a residue which consisted of colorless needles covered with a light brown deposit. Further attempts to purify this product failed. The pK_a was 2.58.

Anal. Calcd. for $C_7H_3N_7 \cdot 2H_2O$: C, 43.52; H, 3.65; N, 36.26; neut. equiv., 193. Found: C, 44.11; H, 3.12; N, 35.78; neut. equiv., 207.

A solution of this acid in acetone was neutralized with pyridine, the acetone removed by evaporation, and the residue recrystallized from ethyl alcohol. **Pyridinium 2-amino-1,1,3,3-tetracyanopropenide** was obtained as white plates, m.p. 200–203°.

Sodium 2-Methylamino-1,1,3,3-tetracyanopropenide.—A solution of 10 g. of sodium 2-(2-hydroxyethoxy)-1,1,3,3-tetracyanopropenide in 100 ml. of ethyl alcohol was saturated with anhydrous methylamine and heated to reflux for 2 hours. The clear solution became milky after about 30 minutes. The solution was cooled and the white precipitate that formed was collected on a filter and recrystallized from water. There was obtained 7.5 g. of sodium 2-methylamino-1,1,3,3-tetracyanopropenide as white prisms. The less soluble N-methylquinolinium 2-methylamino-1,1,3,3-tetracyanopropenide was prepared by metathesis of the more soluble sodium salt with N-methylquinolinium iodide.

Sodium 2-Dimethylamino-1,1,3,3-tetracyanopropenide.—A stirred solution of 7.5 g. (0.033 mole) of sodium 2-(2-hydroxyethoxy)-1,1,3,3-tetracyanopropenide in 75 ml. of ethyl alcohol and 50 ml. of dimethylamine was heated under reflux for 2 hours and then allowed to cool in an ice-bath to 10°. The white solid was collected on a filter, washed with water, and recrystallized from water. There was obtained 3.0 g. of sodium 2-dimethylamino-1,1,3,3-tetracyanopropenide in the form of a white crystalline powder.

Tetramethylammonium 2-N-nitrosomethylamino-1,1,3,3-tetracyanopropenide.—A solution of 6.5 g. (0.1 mole) of sodium nitrite in 25 ml. of water was added dropwise to a stirred solution of 6.5 g. (0.034 mole) of sodium 2-methylamino-1,1,3,3-tetracyanopropenide in 140 ml. of 2.5% hydrochloric acid. When the evolution of gas ceased, a solution of 6.5 g. of tetramethylammonium chloride in 20 ml. of water was added, and the large yellow needles that separated upon cooling were collected on a filter (8.2 g.), washed with water and recrystallized from water. There was obtained 6.5 g. of tetramethylammonium 2-N-nitrosomethylamino-1,1,3,3-tetracyanopropenide in the form of long, flat, yellow needles, m.p. 110–111°.

Tetraethylammonium 2-Bromo-1,1,3,3-tetracyanopropenide.—A solution of 3.0 g. (0.043 mole) of sodium nitrite in 10 ml. of water was added dropwise with stirring to a hot solution of 3.0 g. (0.014 mole) of tetraethylammonium 2-amino-1,1,3,3-tetracyanopropenide in 25 ml. of water and 6 ml. of 45% hydrobromic acid. Fifty ml. of boiling water was added to the reaction mixture to bring into solution the oil that separated, and the solution was boiled with carbon-black for 10 minutes and then filtered. The filtrate was cooled, and the orange needles that separated were collected on a filter, washed with water and recrystallized from water. There was obtained 2.1 g. of tetraethylammonium 2-bromo-1,1,3,3-tetracyanopropenide in the form of orange needles, m.p. 104–107°. **N-Methylquinolinium 2-bromo-1,1,3,3-tetracyanopropenide** was prepared by a similar procedure from N-methylquinolinium 2-amino-1,1,3,3-tetracyanopropenide. **Silver 2-bromo-1,1,3,3-tetracyanopropenide** was prepared by metathesis of the more soluble N-methylquinolinium salt with silver nitrate in water.

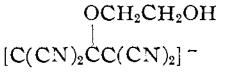
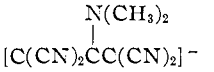
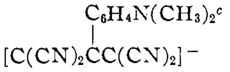
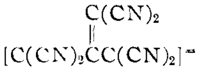
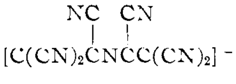
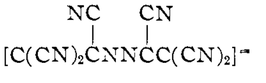
2-Bromo-1,1,3,3-tetracyanopropene.—A solution of 5.0 g. of N-methylquinolinium 2-bromo-1,1,3,3-tetracyanopropenide in 100 ml. of acetone was passed through an acidic ion-exchange column (Amberlite IR-120-H) which had been flushed with acetone to remove most of the water. The percolate was evaporated to dryness. There was obtained 3.3 g. of hydrated 2-bromo-1,1,3,3-tetracyanopropene as a light tan crystalline solid, m.p. 70–100°, pK_a 2.60.

Anal. Calcd. for $C_7HBr_4 \cdot 3^1/_2H_2O$: C, 31.60; H, 2.27; Br, 30.04; N, 21.05; neut. equiv., 266. Found: C, 31.70; H, 2.57; Br, 29.78; N, 20.75; neut. equiv., 260.

A solution of this acid in water was neutralized with pyridine, and the precipitate was recrystallized from water to give matted white needles of **pyridinium 2-bromo-1,1,3,3-tetracyanopropenide.** Barium chloride was mixed with a

TABLE II

ULTRAVIOLET SPECTRA FOR CYANOCARBON ACID ANIONS

Anion	Solvent[a]	$\lambda_{max.}$ mμ	ε
$[C(CN)_3]^-$	A	211	37,400
$[C(CN)_2CHC(CH)_2]^{-b}$		344	
$[C(CN)_2C(CN)C(CN)_2]^-$	A	412	22,100
		393	22,600
$[C(CN)_2C(OEt)C(CN)_2]^-$	A	327	29,700
 $[C(CN)_2\overset{\overset{OCH_2CH_2OH}{\vert}}{C}C(CN)_2]^-$	A	327	30,700
$[C(CN)_2C(SCH_3)C(CN)_2]^-$	A	361	26,100
$[C(CN)_2C(NH_2)C(CN)_2]^-$	B	310	30,500
$[C(CN)_2C(NHCH_3)C(CN)_2]^-$	A	306	22,800
 $[C(CN)_2\overset{\overset{N(CH_3)_2}{\vert}}{C}C(CN)_2]^-$	A	310	22,000
$[C(CN)_2C(NHNO)C(CN)_2]^-$	C	362	19,100
$[C(CN)_2C(C_6H_5)C(CN)_2]^{-c}$	B	357	22,800
 $[C(CN)_2\overset{\overset{C_6H_4N(CH_3)_2{}^c}{\vert}}{C}C(CN)_2]^-$	B	360	32,300
$[C(CN)_2C(Cl)C(CN)_2]^-$	A	353	32,000
$[C(CN)_2C(Br)C(CN)_2]^-$	A	356	28,300
 $[C(CN)_2\overset{\overset{C(CN)_2}{\Vert}}{C}C(CN)_2]^{=}$	A	335	32,700
 $[C(CN)_2\overset{\overset{NC}{\vert}}{C}N\overset{\overset{CN}{\vert}}{C}C(CN)_2]^-$	C	464	45,300
		440	38,000
 $[C(CN)_2\overset{\overset{NC}{\vert}}{C}NN\overset{\overset{CN}{\vert}}{C}C(CN)_2]^{=}$	C	456	15,300
		478	14,500

[a] A = water, B = ethyl alcohol, C = acetone. [b] Sodium 1,1,3,3-tetracyanopropenide was prepared according to the directions of Y. Urushibara, *Bull. Chem. Soc. Japan*, **2**, 278 (1927). [c] The preparation of these cyanocarbon acids is described by G. N. Sausen, V. A. Engelhardt and W. J. Middleton, THIS JOURNAL, **80**, 2815 (1958).

solution of the acid in water, and **barium 2-bromo-1,1,3,3-tetracyanopropenide** precipitated.

Tetraethylammonium 2-Chloro-1,1,3,3-tetracyanopropenide.—A solution of 6.9 g. (0.1 mole) of sodium nitrite in 25 ml. of water was added dropwise with stirring to a solution of 14.2 g. (0.05 mole) of tetraethylammonium 2-amino-1,1,-3,3-tetracyanopropenide in 500 ml. of water and 25 ml. of hydrochloric acid. The resulting solution was heated to boiling, treated with carbon-black, and filtered. The precipitate that formed when the filtrate was cooled was collected on a filter, washed with water and dried (10.2 g.). This material was recrystallized from water to give 6.3 g. of orange needles of tetraethylammonium 2-chloro-1,1,3,3-tetracyanopropenide. **N-Methylquinolinium 2-chloro-1,1,3,-3-tetracyanopropenide** was prepared by a similar procedure from N-methylquinolinium 2-amino-1,1,3,3-tetracyanopropenide.

Tetramethylammonium 2-Chloro-1,1,3,3-tetracyanopropenide.—A solution of 5.0 g. of N-methylquinolinium 2-amino-1,1,3,3-tetracyanopropenide in 50 ml. of hot water was passed through an acidic ion-exchange column (Amberlite IR-120-H). Concentrated hydrochloric acid, 10 ml., and then a solution of 5.0 g. of sodium nitrite in 25 ml. of water was added to the cooled percolate. The resulting solution was boiled for 5 minutes, cooled and then mixed with 10 ml. of aqueous 30% tetramethylammonium chloride solution. The precipitate that formed was collected on a filter, washed with water, and recrystallized from water. There was obtained 1.2 g. of tetramethylammonium 2-chloro-1,1,3,3-tetracyanopropenide as long colorless needles, m.p. 211–213°.

Barium Tricyanomethanide.—A hot aqueous solution (50 ml.) of barium chloride dihydrate was added with stirring to a hot solution of 33.9 g. of sodium tricyanomethanide in 50 ml. of water. The resulting solution was stored in a cold room at 4° for one week. The large crystals that formed were collected on a filter and recrystallized from water. There was obtained 17.5 g. of barium tricyanomethanide as colorless crystals, m.p. >300°.

Anal. Calcd. for BaC_8N_6: C, 30.26; N, 26.47. Found: C, 29.80; N, 26.30.

1-Amino-1-chloro-2,2-dicyanoethylene.[17]—Dry hydrogen chloride was passed into a solution of 6.4 g. of potassium tricyanomethanide in 200 ml. of acetone for 10 minutes. The precipitate of potassium chloride (3.5 g.) was separated by filtration, and the filtrate was allowed to stand at solid carbon dioxide temperature overnight and was then poured into *n*-heptane. The oil that separated was extracted with ethyl ether. On evaporation, the ether extract yielded 4 g. (63% yield) of 1-amino-1-chloro-2,2-dicyanoethylene as a light yellow solid.

Anal. Calcd. for $C_4H_2ClN_3$: C, 37.67; H, 1.57; Cl, 27.80; N, 32.95. Found: C, 37.99; H, 1.73; Cl, 27.46; N, 32.89.

1-Amino-2-bromo-2,2-dicyanoethylene was obtained as a sublimable white solid in a similar manner by the reaction of dry hydrogen bromide with potassium tricyanomethanide.

Anal. Calcd. for $C_4H_2BrN_3$: N, 24.43. Found: N, 24.82.

1-Amino-2-bromo-2,2-dicyanoethylene reacted at 20–30° with ethyl alcohol to form 1-amino-1-ethoxy-2,2-dicyanoethylene (m.p. 218–219°) and with methyl alcohol to yield 1-amino-1-methoxy-2,2-dicyanoethylene (m.p. 213–214°).

Ultraviolet Spectra.—The ultraviolet absorption spectra of a number of free cyanocarbon acids and their salts were determined. The absorption maxima and extinction coefficients for a given free acid and any of its salts were essentially identical, so only the anions are listed in Table II.

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[17] E. L. Little, U. S. Patent 2,773,892 (1956).

Wilmington, Delaware

[Contribution No. 440 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co.]

Cyanocarbon Chemistry. VI.[1] Tricyanovinylamines

By B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower

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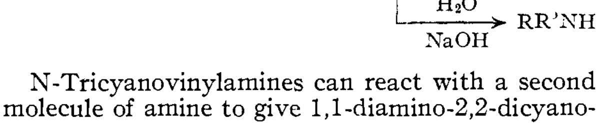
Tetracyanoethylene reacts with primary amines and some secondary amines to give N-tricyanovinylamines (I). It generally reacts with secondary and tertiary arylamines by attacking the aromatic ring to give 4-tricyanovinylarylamines such as II. The 4-tricyanovinylarylamines are a new class of dyes with strong affinity for hydrophobic fibers. Some of their analogs have similar dyeing characteristics.

Tetracyanoethylene reacts with ammonia and hydrazine with elimination of hydrogen cyanide to give, respectively, bis-(tricyanovinyl)-amine and 1,2-bis-(tricyanovinyl)-hydrazine.[1] The present paper describes the related reactions of tetracyanoethylene with amines.

N-Tricyanovinylamines.—Tetracyanoethylene reacts readily with primary or secondary aliphatic amines and with most primary and some secondary aromatic amines to give N-tricyanovinylamines (I) and hydrogen cyanide.

$$RR'NH + C(CN)_2{=}C(CN)_2 \longrightarrow \underset{\text{I}}{RR'NC(CN){=}C(CN)_2} + HCN$$

Sixteen such N-tricyanovinylamines, all solids ranging in color from white to yellow, have been prepared (Table I). The N-tricyanovinylamine structure is assigned partly on the basis of absorption spectra. Thus, N-tricyanovinyl derivatives of primary amines (*e.g.*, aniline, *n*-butylamine) absorb strongly in the N–H stretching region of the infrared, whereas N-tricyanovinyl derivatives of secondary amines (*e.g.*, N-methyl-*p*-toluidine, piperidine) do not. The compounds are hydrolyzed by base to give the parent amine in good yield, which is evidence that the tricyanovinyl group is attached to nitrogen rather than carbon. Acid hydrolysis of N-tricyanovinyl-*n*-butylamine gave α-*n*-butylamino-β-cyanomaleimide.



N-Tricyanovinylamines can react with a second molecule of amine to give 1,1-diamino-2,2-dicyanoethylenes.

$$BuNHC(CN){=}C(CN)_2 + Me_2NH \longrightarrow BuNHC(NMe_2){=}C(CN)_2$$

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[1] Paper V. W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, This Journal, 80, 2795 (1958).