nium bromide in 50 ml. of water. The orange precipitate which formed was collected on a filter, washed with water and recrystallized from water. There was obtained 6.5 g. of the tetraethylammonium salt of 2-amino-6-dicyanomethyl-3,4,5-tricyanopyridine in the form of orange, matted needles, m.p. 190–191°.

2-Amino-6-dicyanomethyl-3,4,5-tricyanopyridine.—A solution of 30 g. of the tetraethylammonium salt of 2-amino-6-dicyanomethyl-3,4,5-tricyanopyridine in 500 ml. of acetone was passed slowly through a column packed with a sulfonic acid ion exchange resin. Evaporation of the effluent yielded 20 g. of 2-amino-6-dicyanomethyl-3,4,5-tricyanopyridine in the form of a light yellow solid which melted above 300°.

Anal. Calcd. for $C_{11}H_3N_7$: C, 56.70; N, 42.00; neut. equiv., 233. Found: C, 56.95; N, 41.80; neut. equiv., 240.

2-Amino-6-benzenesulfonyl-3,4,5-tricyanopyridine.—To a solution of 3.28 g. (0.02 mole) of sodium benzenesulfinate in 20 ml. of 50% ethyl alcohol was added a hot solution of 4.07 g. (0.02 mole) of 2-amino-6-chloro-3,4,5-tricyanopyridine in 100 ml. of ethyl alcohol. The solution was heated under reflux for 5 minutes and then cooled. The precipitated salt was removed by filtration, and the filtrate was mixed with 300 ml. of cold water. The yellow precipitate which formed was collected on a filter, washed with water, and recrystallized from ethyl alcohol. There was obtained 3.5 g. of 2-amino-6-benzenesulfonyl-3,4,5-tricyanopyridine in the form of yellow needles, m.p. 254–256° dec.

Anal. Calcd. for $C_{14}H_7N_5SO_2$: C, 54.36; H, 2.29; N, 22.64; S, 10.36. Found: C, 54.24; H, 2.59; N, 22.59; S, 10.27.

Bromodiaminocyanomethylnaphthyridine.—A solution of 3.0 g. (0.01 mole) of N-methylquinolinium 2-amino-1,1,3,3-tetracyanopropenide in 50 ml. of acetone was saturated with anhydrous hydrogen bromide. The solution was cooled and mixed with 150 ml. of water. The precipitate which formed was collected on a filter, washed with water and then alcohol, and dried. There was obtained 2.0 g. (72%) of a very light yellow crystalline solid which sublimed above 235° and decomposed slowly above 250°.

Anal. Calcd. for $C_{10}H_8N_5Br$: C, 43.19; H, 2.90; N, 25.18; Br, 28.74. Found: C, 43.18; H, 2.97; N, 25.07; Br, 28.19.

Aminobromocyanomethyl-(methylamino)-naphthyridine.—A mixture of 2.0 g. of sodium 2-methylamino-1,1,3,3-tetracyanopropenide in 50 ml. of acetone was saturated with anhydrous hydrogen bromide. The reaction was exothermic. The hot solution was filtered, and the filtrate was cooled to 0°, and mixed with 100 ml. of water. The solid which separated was collected on a filter, washed with alcohol, and dried. There was obtained 0.93 g. (33%) of aminobromocyanomethyl-(methylamino)-naphthyridine in the form of light yellow crystalline solid, m.p. 207–208°.

Anal. Calcd. for $C_{11}H_{10}N_5Br$: C. 45.22; H, 3.45; N, 23.97; Br, 27.36. Found: C, 45.25; H, 3.35; N, 24.08; Br, 27.59.

Chlorocyanodiaminomethylnaphthyridine.—A solution of 5.0 g. of tetraethylammonium 2-amino-1,1,3,3-tetracyanopropenide in 25 ml. of acetone was saturated with anhydrous hydrogen chloride, and then mixed with 100 ml. of ice-water. The crystals which formed upon standing were collected on a filter and washed with water. There was obtained 3.0 g. (70%) of chlorocyanodiaminomethylnaphthyridine in the form of white needles which sublimed above 240° and decomposed slowly above 260°.

Anal. Calcd. for $C_{10}H_8N_5Cl$: C, 51.40; H, 3.45; N, 29.98; Cl, 15.17. Found: C, 51.18; H, 3.62; N, 30.05; Cl, 15.18.

Wilmington, Delaware

[Contribution No. 445 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co.]

Cyanocarbon Chemistry. XI.[1] Malononitrile Dimer

By R. A. Carboni, D. D. Coffman and E. G. Howard

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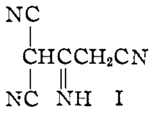
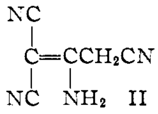
Malononitrile dimer, 2-amino-1,1,3-tricyanopropene, has been prepared by several routes, including dimerization of malononitrile in the presence of bases and acids. Some reactions of the dimer are described.

A variety of nitriles have been converted to dimers and trimers by means of alkaline or acidic reagents. For example, mononitriles such as acetonitrile and propionitrile have been dimerized to 3-iminobutyronitrile and 2-methyl-3-iminovaleronitrile, respectively, by treatment with sodium followed by hydrolysis of the resulting sodium derivatives with water.[2] Cyclic trimers of acetonitrile and propionitrile[3] and of malononitrile[4] have been formed by treatment of the monomers with sodium alkoxides and other bases. This paper describes the preparation and some of the properties of 2-amino-1,1,3-tricyanopropene (hereafter called "malononitrile dimer") under both acidic and alkaline conditions.

The dimer was obtained conveniently by treating a solution of malononitrile in an inert solvent such as ether or tetrahydrofuran with sodium and hydrolyzing the resulting solid with a strong mineral acid at 5°. Elemental analyses and molecular weight determinations are in accord with the formula $C_6H_4N_4$. The product, m.p. 172–173°, which presumably forms through a Thorpe type reaction between two molecules of the dinitrile may be formulated as I or II. The spectral evidence favors


$NC-CH(CN)-C(=NH)-CH_2CN$ I


$NC-C(CN)=C(NH_2)-CH_2CN$ II

the ene–amine structure II as the predominant form. The infrared spectrum shows three bands at 4.22, 4.51 and 4.55 μ which are associated with the unconjugated and conjugated nitrile groups, respectively. A pair of bands at 2.98 and 3.10 μ are attributed to the amino function.

The dimer also was formed when dry hydrogen chloride was passed through a benzene solution of malononitrile. When hydrogen bromide was employed, the reaction proceeded vigorously to give a nitrile-substituted 2,4-diamino-6-bromopyridine (III).[1] Since the same product resulted when the dimer was used rather than malononitrile, the re-

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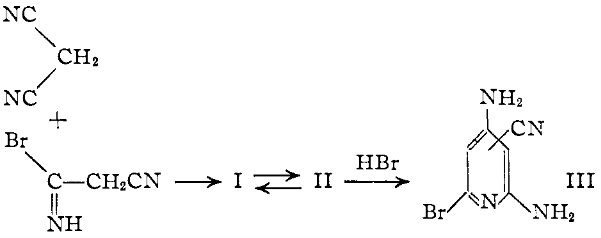
[1] Paper X, E. L. Little, W. J. Middleton, D. D. Coffman, V. A. Engelhardt and G. N. Sausen, This Journal, 80, 2832 (1958).

[2] R. J. Holtzwart, *J. prakt. Chem.*, [2] 39, 230 (1889); H. Adkins and G. M. Whitman, This Journal, 64, 150 (1942).

[3] R. Schwarze, *J. prakt. Chem.*, [2] 42, 1 (1890).

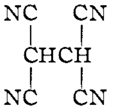
[4] R. Schenck and H. Finken, *Ann.*, 462, 267 (1928).

action may be represented as proceeding by the scheme



Finally, the tricyanopropene was obtained by adding a solution of malononitrile in an equivalent of aqueous alkali to a warm solution of copper sulfate and filtering. The crystalline product which separated from the cooled filtrate was identical to the dimer formed by the methods described above.

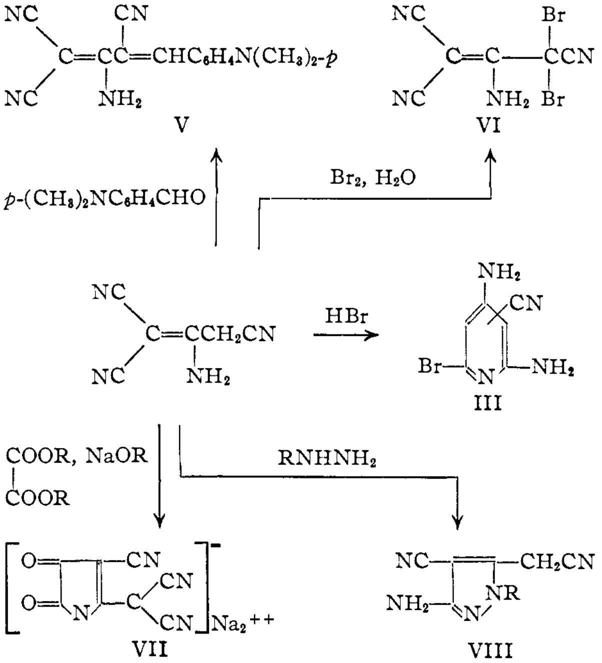
Meier[5] has reported that the low temperature reaction of nitrous oxide with sodiomalononitrile in absolute alcohol yields a crystalline product, m.p. 170–172°, which was assumed to be tetracyanoethane (IV) but which was not analyzed. The


IV

$$\mathrm{(NC)_2CHCH(CN)_2}$$

latter substance, which has been prepared by the reduction of tetracyanoethylene,[6] does indeed have a melting point of 170–172°, though with decomposition. In repeating the Meier procedure to assess its value as a route to tetracyanoethane, two products were isolated, neither of which proved to be the tetranitrile. The first was a liquid whose infrared spectrum coincided with that of ethyl cyanoacetate. The second product, m.p. 170–172°, could not be oxidized to tetracyanoethylene. Instead its infrared and X-ray patterns agreed with those of malononitrile dimer II. No depression of the melting point was obtained on admixture with a sample of the dimer prepared by the present methods.

The interesting structural features of the dimer II have been utilized in a number of transformations. For example, condensation with *p*-dimethylaminobenzaldehyde in the presence of a trace of amine yielded a yellow benzylidene dye V. The presence of the amino bands at 2.9, 3.0 and 3.1 μ in the infrared spectrum of the product indicated that the condensation had occurred through the activated methylene group rather than through the amide-like amino group in II. An aqueous suspension of one mole of malononitrile dimer reacted readily with two moles of bromine to yield the substitution product, 2-amino-1,1,3-tricyano-3,3-dibromopropene (VI). The labilizing influence of the vinylogous dicyanomethylene group as well as of the adjacent nitrile on the carbon–bromine bonds is manifested by the "positive" nature of the bromines. A disodium dioxopyrrolidine (VII) was obtained when the dimer II and diethyl oxalate were added to two molecules of sodium ethoxide in ethyl alcohol.[7] Acidification of the bright yellow disodium derivative with excess concentrated hydrochloric acid caused replacement of only one sodium atom, demonstrating the highly acidic nature of the tricyanodioxopyrrolidine derivative. When the dimer was heated with an equivalent amount of hydrazine hydrate or phenylhydrazine, products believed to be 3-amino-4-cyano-5-pyrazoleacetonitriles (VIII) formed with the liberation of one molecule of ammonia. However, the isomeric 5-amino-4-cyano-3-pyrazoleacetonitrile structure cannot be eliminated as a possibility in the case of monosubstituted hydrazines. The formation of pyridines III was described above.



Experimental

Malononitrile Dimer II. Method A.[8]—To a stirred mixture of 33 g. (0.50 mole) of malononitrile in 200 ml. of tetrahydrofuran and 100 ml. of diethyl ether was gradually added 6 g. (0.25 mole) of sodium sand. The reaction mixture was allowed to stir at room temperature for one hour then at reflux for 24 hours. The solid which formed was filtered, dried at room temperature, and cautiously dissolved in 300 ml. of ice-cold water to decompose the remaining unreacted sodium. The solution was treated slowly with 15 ml. of concentrated hydrochloric acid, whereupon 25 g. (75%) of crude dimer II separated. Recrystallization from water yielded almost colorless rodlets, m.p. 170–173°. The yield was lower when the mixture was heated for only 6 hours.

Anal. Calcd. for $C_6H_4N_4$: C, 54.54; H, 3.05; N, 42.41; mol. wt., 132. Found: C, 54.49; H, 3.15; N, 42.20; mol. wt., 126.

Method B.—Dry hydrogen chloride was passed through a solution of 13.2 g. (0.2 mole) of malononitrile in 150 ml. of dry benzene at 35°. After the solution was saturated, the addition was continued very slowly for an additional two hours, at which time the original oily precipitate slowly solidified to yield 7 g. (53%) of the dimer. Recrystallization from ethyl alcohol yielded crystals melting at 168–169°.

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(5) R. Meier, *Ber.*, **86**, 1491 (1953).

(6) Paper III, W. J. Middleton, R. E. Heckert, E. L. Little and C. G. Krespan, THIS JOURNAL, **80**, 2783 (1958).

(7) P. L. Southwick and L. L. Seivard, THIS JOURNAL, **71**, 2532 (1949); P. L. Southwick and R. T. Crouch, *ibid.*, **75**, 3413 (1953). These authors prepared a series of 4-carboalkoxy-2,3-dioxopyrrolidines by the condensation of methyl or ethyl oxalate with a series of N-substituted β-aminopropionic esters in the presence of sodium alkoxides.

(8) R. A. Carboni, U. S. Patent 2,719,861 (1955).

No depression of the melting point was observed on admixture with a sample obtained from method A. The infrared spectra were identical.

Method C.—A solution of 13.2 g. (0.2 mole) of malononitrile and 8 g. (0.2 mole) of sodium hydroxide in 50 ml. of water was added to 50 g. of cupric sulfate pentahydrate in 100 ml. of warm water. The mixture was heated to 90° and filtered to remove the insoluble inorganic salts. On cooling, the crude dimer separated (5.5 g., 42%) and was recrystallized from water, m.p. 170–171°. A mixture of this material and a sample from method A gave no depression of the melting point.

Reactions of Malononitrile Dimer. A. With Bromine.—To a suspension of 13.2 g. (0.1 mole) of malononitrile dimer in 150 ml. of water was added slowly 32 g. (10.3 ml., 0.2 mole) of bromine with shaking. The solid was collected by filtration, washed with water and dried. The yield was 26.9 g. (93%). Crystallization from 50% aqueous ethyl alcohol yielded an almost colorless crystalline solid, m.p. 155° dec.

Anal. Calcd. for $C_6H_2Br_2N_4$: N, 19.32; Br, 55.14. Found: N, 19.40; Br, 55.39.

B. **With *p*-Dimethylaminobenzaldehyde.**—A solution of 0.53 g. (0.004 mole) of the dimer and 1.2 g. (0.008 mole) of *p*-dimethylaminobenzaldehyde in 10 ml. of methanol containing a trace of piperidinium acetate was heated at reflux for 30 minutes. The color of the reaction mixture deepened to orange. On cooling, yellow-orange crystals of the benzylidene dye were obtained in 85% yield, m.p. 270–272° dec. The infrared spectrum of this compound showed bands at 2.9, 3.0 and 3.1 μ, indicating that the condensation occurred through the methylene rather than through the amino group. The ultraviolet spectrum in acetone gave a maximum at 434 mμ (ϵ 33,400).

Anal. Calcd. for $C_{15}H_{13}N_5$: C, 68.42; H, 4.98; N, 26.60. Found: C, 68.63; H, 4.99; N, 26.56.

C. **With Diethyl Oxalate.**—A mixture of 13.2 g. (0.1 mole) of the dimer and 16 g. (0.11 mole) of diethyl oxalate was added quickly to 75 ml. of an ethyl alcohol solution containing 0.2 mole of sodium ethoxide. The mixture was stirred for two hours, diluted with two volumes of benzene and filtered. Crystallization of the solid from 90% aqueous *n*-propyl alcohol yielded bright yellow crystals of disodium-4-cyano-5-dicyanomethylene-2,3-dioxopyrrolidine.

Anal. Calcd. for $C_8N_4O_2Na_2$: Na, 19.99. Found: Na, 19.60.

The disodium derivative was dissolved in a minimum of water and treated with excess hydrochloric acid. However, one sodium atom was retained, demonstrating the strongly acidic nature of this substance. Crystallization from 90% aqueous *n*-propyl alcohol yielded yellow, hair-like crystals of the monosodium derivative.

Anal. Calcd. for $C_8HN_4O_2Na\cdot 2H_2O$: C, 39.35; H, 2.06; N, 22.94; Na, 9.42. Found: C, 39.69; H, 2.28; N, 22.81; Na, 8.82.

D. **With Hydrazines.** 1. **Hydrazine Hydrate.**—To a suspension of 6.6 g. (0.05 mole) of malononitrile dimer in 65 ml. of water was added 2.8 g. (0.056 mole) of hydrazine hydrate with stirring. When the exothermic reaction had subsided, the mixture was heated at 90° for 15 minutes. On cooling, 5.0 g. (68%) of the pyrazole derivative separated as rodlets. Recrystallization from water yielded a product melting at 197–198°.

Anal. Calcd. for $C_6H_5N_5$: C, 48.97; H, 3.43; N, 47.60; mol. wt., 147. Found: C, 49.23; H, 3.47; N, 47.69; mol. wt., 141.

2. **Phenylhydrazine.**—A mixture of the dimer (9.5 g., 0.072 mole) and 50 ml. of methanol was heated at reflux for one hour with 8.2 g. (0.075 mole) of phenylhydrazine. From the cooled mixture was obtained 7.7 g. (48%) of 1-phenyl-3-amino-4-cyano-5-pyrazoleacetonitrile, m.p. 166–167°.

Anal. Calcd. for $C_{12}H_9N_5$: C, 64.56; H, 4.06; N, 31.38. Found: C, 64.70; H, 4.21; N, 31.49.

E. **With Hydrogen Bromide.**[9]—Dry hydrogen bromide was passed through a solution of 3.96 g. (0.03 mole) of the dimer in 50 ml. of tetrahydrofuran while the mixture was cooled in an ice-bath. The solid (3.2 g.) which formed was collected by filtration, dissolved in a minimum amount of boiling water, and the solution made alkaline with dilute sodium hydroxide. The resulting solid was filtered, washed with water and dried. The infrared spectrum of this product indicated the presence of amino and conjugated nitrile groups. An identical product was obtained in 72% yield starting with malononitrile, m.p. 260–265° dec.

Anal. Calcd. for $C_6H_5BrN_4$: N, 26.30; Br, 37.51; mol. wt., 213. Found: N, 26.26; Br, 37.38; mol. wt., 214.

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(9) W. J. Middleton, U. S. Patent 2,790,806 (1957).

WILMINGTON, DELAWARE

[CONTRIBUTION NO. 342B FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Cyanocarbon Chemistry. XII.[1] Some Physical Characteristics of Cyanocarbon Derivatives

BY CATHARINE E. LOONEY AND J. R. DOWNING

RECEIVED NOVEMBER 14, 1957

A study has been made of molecular spectra and thermal properties of some cyanocarbons and their salts. Infrared and Raman spectra showed that the —$C\equiv N$ and —$C{=}C$— stretching frequencies of these compounds are highly dependent upon charge and resonance effects. The degree of conjugation also has a pronounced effect on ultraviolet spectra. Heats of combustion and sublimation of tetracyanoethylene were found to be 722 and 18.65 kcal. per mole. A spontaneous exothermic rearrangement of cyano groups was observed to occur in some of these compounds at elevated temperatures.

Introduction

A new class of chemical compounds has been made available by the synthesis in this Laboratory of tetracyanoethylene (TCNE), highly cyano-substituted hydrocarbons (cyanocarbons) and cyanocarbon salts. Spectroscopic and thermal properties determined in the course of a physical study of these materials are presented in this paper.

Infrared and Raman Spectra.—Of primary interest in the infrared and Raman spectra of cyanocarbons are the positions of the $C\equiv N$ and $C{=}C$ stretching frequencies. The $C\equiv N$ frequency in simple aliphatic nitriles is found at wave lengths between 4.40 and 4.45 μ. The effect of conjugation on the position of the nitrile absorption is to shift this band to slightly longer wave lengths (near 4.5 μ in acrylonitrile, 1,1-dimethyl-2,2-dicyanoethylene and benzonitrile). The CN^- group in such inorganic cyanides as KCN and the ferri- and ferrocyanides is shifted to about 4.8 μ because of the ionic character of these compounds. The stretching frequency of an isolated $C{=}C$ bond is

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(1) Paper XI, R. A. Carboni, D. D. Coffman and E. G. Howard, THIS JOURNAL, **80**, 2838 (1958).