Kirk-Othmer Encyclopedia of Chemical Technology.

CYANOCARBONS

Cyanocarbons are compounds having such a large number of cyano groups that the chemical reactions of the class are essentially new in kind and not shared by analogous compounds free of such groups. The unique reactivity of cyanocarbons was first recognized with the synthesis of tetracyanoethylene [670-54-2] (TCNE) (1, 2). Previously, dicyanoacetylene [1071-98-3] (3) and dicyanodiacetylene [16419-78-6] (4) were the only known "per" cyanocarbons, and cyanoform [454-50-2] (5), $CH(CN)_3$, was the best known compound whose properties were exceptional as the consequence of a large number of cyano groups.

The cyano group is a powerful electron-withdrawing group. It is sufficiently small to present no great steric problem. Tetracyanoethylene must be regarded as a highly electron-deficient olefin that should be a strongly electrophilic reagent. This characteristic is reflected in the ease with which TCNE is attacked by electron-rich olefins, eg, in Diels-Alder additions and cyclobutane formation, and other nucleophiles, eg, methanol and dimethylaniline. Moreover, the affinity of TCNE for electrons is so great that the stable anion radical, $\text{TCNE}^{\cdot-}$, is formed by treatment with many mild reducing agents, such as I^-. For similar reasons, a compound with a hydrogen atom on a saturated carbon atom bearing cyanocarbon groups is highly ionized and is a very strong acid, eg, cyanoform and 1,1,2,3,3-pentacyanopropene [45078-17-9].

The most important members of the cyanocarbon class are the alkenes: tetracyanoethylene, hexacyanobutadiene, and tetracyanoquinodimethan; the alkanes: tetracyanomethane and hexacyanoethane; dicyanoacetylene; hexacyanobenzene; tetracyanoquinone; cyanocarbon acids; oxacyanocarbons; thiacyanocarbons; and azacyanocarbons. Tetracyanoethylene is described first because its chemical versatility makes it a rich source of other polycyano compounds. Moreover, an understanding of its chemistry is helpful in understanding the chemistry of other cyanocarbons.

1. Tetracyanoethylene

Tetracyanoethylene, ethenetetracarbonitrile (TCNE) (2) has a high positive heat of formation (Table 1), but is stable to shock. It has good thermal stability and can thus be sublimed unchanged through a tube at 600°C. Tetracyanoethylene resists oxidation, but once ignited in oxygen it burns with an intensely hot flame that may be above 4000 K and is, at any rate, hotter than the oxygen–acetylene flame.

Tetracyanoethylene is colorless but forms intensely colored complexes with olefins or aromatic hydrocarbons, eg, benzene solutions are yellow, xylene solutions are orange, and mesitylene solutions are red. The colors arise from complexes of a Lewis acid–base type, with partial transfer of a π-electron from the aromatic hydrocarbon to TCNE (8). TCNE is conveniently prepared in the laboratory from malononitrile [109-77-3] (1) by debromination of dibromomalononitrile [1855-23-0] (2) with copper powder (9). The debromination can also be done by pyrolysis at ca 500°C (10).

$$CH_2(CN)_2 + Br_2 \longrightarrow Br_2C(CN)_2 \longrightarrow (NC)_2C{=}C(CN)_2$$

(1) (2) TCNE

Table 1. Physical Properties of Tetracyanoethylene[a]

Property	Value
mol wt	128.1
mp, °C	200–202
bp, °C	223
density[b], g/mL	1.318
λ_{max}, nm(ϵ)[c]	267 (13,600) 277 (12,050)
heat of combustion, kJ/mol[d]	−3022
heat of formation, kJ/mol[d]	628

[a] Ref. 6.
[b] Ref. 7.
[c] In methylene chloride.
[d] To convert kJ/mol to kcal/mol, divide by 4.184.

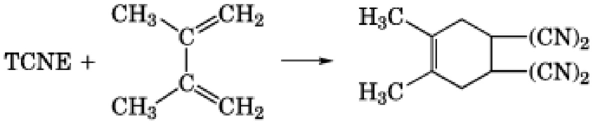
With substances that give up an electron more readily than aromatic hydrocarbons, such as potassium, nickel carbonyl, cyanide ion, or iodide ion, complete transfer of an electron occurs and the TCNE anion radical is formed (11). Potassium iodide is a particularly useful reagent for this purpose, and merely dissolving potassium iodide in an acetonitrile solution of TCNE causes the potassium salt of the anion radical to precipitate as bronze-colored crystals.

$$2\,KI + 2\,(NC)_2C{=}C(CN)_2 \longrightarrow 2\,K^+\,[(NC)_2C{=}C(CN)_2]^{\dot{-}} + I_2$$

The reaction of bis(benzene)vanadium [12129-72-5] with TCNE affords an insoluble amorphous black solid that exhibits field-dependent magnetization and hysteresis at room temperature, an organic-based magnet (12). The anion radical is quite stable in the solid state. It is paramagnetic, and its intense electron paramagnetic resonance (epr) spectrum has nine principal lines with the intensity ratios expected for four equivalent ^{14}N nuclei (13) and may be used as an internal reference in epr work (see Magnetic spin resonance).

Tetracyanoethylene undergoes two principal types of reactions, addition to the double bond and replacement of a cyano group. Addition of hydrogen catalyzed by Pd gives 1,1,2,2,-tetracyanoethane [14778-29-1] (14).

The Diels-Alder addition to 1,3-dienes is particularly interesting because of the exceptional ease with which it takes place, eg, see equation **1** in which 1,2-dimethyl-4,4,5,5-tetracyanocyclohexene [69155-29-9] is formed.

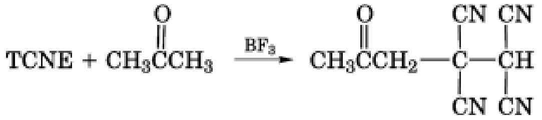


(1)

In a study of the relative rates of addition of 20 dienophiles to cyclopentadiene, TCNE was at the head of the list, eg, it added 7700 times as rapidly as maleic anhydride (15). Reaction with most 1,3-dienes takes place rapidly and in high yield at room temperature. TCNE has often been used to characterize 1,3-dienes, including those that are unstable and difficult to isolate (16).

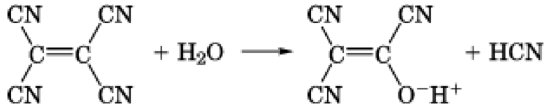
Electron-rich alkenes (eq. **2**) (17), and ketones (eq. **3**) (14) add readily to TCNE, as do nucleophilic radicals (14). The product in equation **2** is 1,1,2,2,-tetracyano-3-methoxycyclobutane [69155-30-2]. Addition of acetone yields 4,4,5,5-tetracyano-2-pentanone [69155-31-3].

(2)

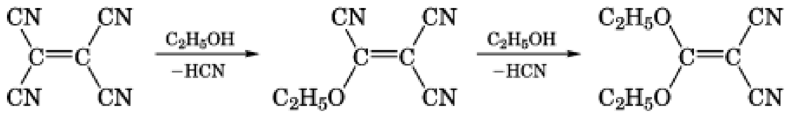


(3)

Although a C–CN bond is normally strong, one or two cyano groups in TCNE can be replaced easily, about as easily as the one in an acyl cyanide. The replacing group can be hydroxyl, alkoxyl, amino, or a nucleophilic aryl group. Thus hydrolysis of TCNE under neutral or mildly acidic conditions leads to tricyanoethenol [27062-39-1], a strong acid isolated only in the form of salts (18).



Heating TCNE with an alcohol in the presence of a mild base such as urea causes replacement of either one (19) or two (20) cyano groups by alkoxyl. The products with ethanol are 1-ethoxy-1,2,2-tricyanoethylene [69155-32-4] and 1,1-bisethoxy-2,2-dicyanoethylene [17618-65-4].



Aromatic compounds that are sufficiently nucleophilic to condense with benzenediazonium chloride and form azo compounds generally condense with TCNE, eg, the reaction of *N,N*-dimethylaniline proceeds stepwise (21, 22).

The *p*-tricyanovinylarylamines such as *p*-tricyanovinyl-*N,N*-dimethylaniline [6673-15-0] (**3**) are highly colored substances that give bright orange, red, or blue dyeings on poly(ethylene terephthalate) and other hydrophobic fibers.

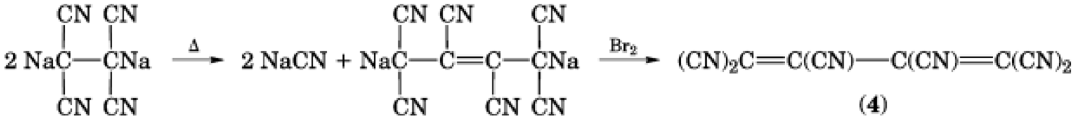
(**3**)

Among other aromatic compounds that have been tricyanovinylated are phenanthrene (23), *o*-alkylphenols (24), pyrrole (23), indoles (23, 25), 2-methylfuran (26), azulenes (26, 27), diazocyclopentadiene (28), and a variety of phenylhydrazones (26).

A few percent TCNE added during formation of urethane foams imparts enough conductivity to dissipate electrostatic charges. Airplane fuel tanks filled with this foam still have about the same volume for fuel but do not build up static charges (29).

2. Hexacyanobutadiene

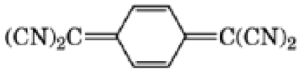
Hexacyanobutadiene [5104-27-4] (**4**), 1,3-butadiene-1,1,2,3,4,4-hexacarbonitrile, is prepared in good yield by a two-step process from the disodium salt of tetracyanoethane (30). It is like TCNE in forming colored π-complexes and an anion radical.



(4)

3. Tetracyanoquinodimethane

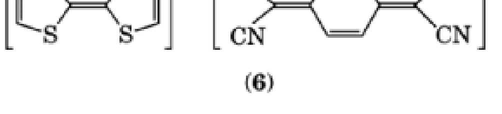
Tetracyanoquinodimethane [1518-16-7] (**5**), 2,2′-(2,5-cyclohexadiene-1,4-diylidene)bispropanedinitrile (TCNQ), is prepared by condensation of 1,4-cyclohexanedione with malononitrile to give 1,4-bis(dicyanomethylene)cyclohexane [1518-15-6], which is oxidized with bromine (31).



(5)

It resembles tetracyanoethylene in that it adds reagents such as hydrogen (31), sulfurous acid (31), and tetrahydrofuran (32) to the ends of the conjugated system of carbon atoms; suffers displacement of one or two cyano groups by nucleophilic reagents such as amines (33) or sodiomalononitrile (34); forms π-complexes with aromatic compounds (35); and takes an electron from iodide ion, copper, or tertiary amines to form an anion radical (35, 36). The anion radical has been isolated as salts of the formula $M^+(TCNQ)_n^{\dot{-}}$ where M^+ is a metal or ammonium cation, and $n = 1$, 1.5, or 2. Some of these salts have unusual electrical properties; their conductivities are in the remarkably high range 0.01–100 S/cm and differ by several orders of magnitude along the three principal crystal axes (35, 37).

The most remarkable substance of this kind is tetrathiafulvalenium tetracyanoquinodimethanide [40210-84-2] (**6**) (TTF–TCNQ). It is the most highly conducting organic compound known (10^4S/cm at 70 K) (38, 39) (see Semiconductors, organic). Moreover, the conduction is metalliclike in that it increases as temperature decreases. Superconduction properties for highly purified crystals of TTF–TCNQ at 60 K are reported (40, 41) (see SUPERCONDUCTING MATERIALS).



(6)

4. Tetracyanomethane

Tetracyanomethane [24331-09-7], methanetetracarbonitrile, is prepared by heating silver tricyanomethanide [36603-81-3] in liquid cyanogen chloride (42).

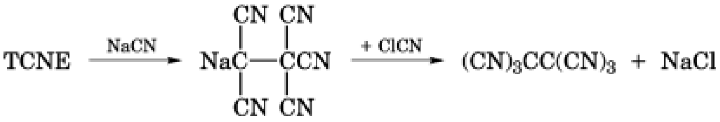
$$\mathrm{AgC\,(CN)_3 + ClCN \longrightarrow C\,(CN)_4 + AgCl}$$

It is a very strong cyanating agent; eg, it converts chloride ion to cyanogen chloride [506-77-4].

$$\mathrm{C\,(CN)_4 + Cl^- \longrightarrow ClCN + {}^-\,C\,(CN)_3}$$

5. Hexacyanoethane

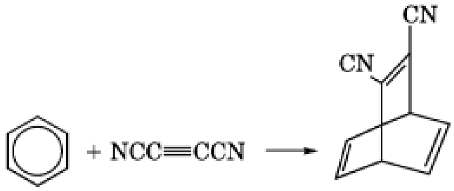
Hexacyanoethane [4383-67-9], ethanehexacarbonitrile, is quite unstable and readily decomposes to TCNE and cyanogen [460-19-5] (NC–CN) (43). It is prepared as follows:



$$\mathrm{TCNE} \xrightarrow{\mathrm{NaCN}} \mathrm{Na}\overset{\mathrm{CN}}{\underset{\mathrm{CN}}{\mathrm{C}}}-\overset{\mathrm{CN}}{\underset{\mathrm{CN}}{\mathrm{C}}}\mathrm{CN} \xrightarrow{+\,\mathrm{ClCN}} \mathrm{(CN)_3CC(CN)_3 + NaCl}$$

6. Dicyanoacetylene

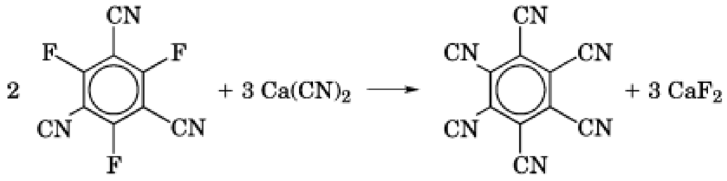
Dicyanoacetylene, 2-butynedinitrile, is obtained from dimethyl acetylenedicarboxylate by ammonolysis to the diamide, which is dehydrated with phosphorus pentoxide (44). It burns in oxygen to give a flame with a temperature of 5260 K, the hottest flame temperature known (45). Alcohols and amines add readily to its acetylenic bond (46). It is a powerful dienophile in the Diels-Alder reaction; it adds to many dienes at room temperature, and at 180°C actually adds 1,4- to benzene to give the bicyclo adduct (**7**) [18341-68-9], $C_{10}H_6N_2$ (47).



(**7**)

7. Hexacyanobenzene

Hexacyanobenzene [1217-44-33], benzenehexacarbonitrile, is prepared from 2,4,6-trifluorobenzene-1,3,5-tricarbonitrile [3638-97-9] by substitution with calcium cyanide (48, 49). It forms colored π-complexes with aromatic hydrocarbons.



8. Tetracyanobenzoquinone

Tetracyanobenzoquinone [4032-03-5], 3,6-dioxo-1,4-cyclohexadiene-1,2,4,5-tetracarbonitrile, is a remarkably strong oxidizing agent for a quinone; it abstracts hydrogen from tetralin or ethanol even at room temperature (50). It is a stronger π-acid than TCNE because it forms more deeply colored π-complexes with aromatic hydrocarbons.

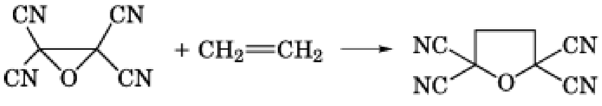
9. Cyanocarbon Acids

These acids (51) are organic molecules that contain a plurality of cyano groups and are readily ionized to hydrogen ions and resonance-stabilized anions. Typical cyanocarbon acids are cyanoform, methanetricarbonitrile (5); 1,1,3,3-tetracyanopropene [32019-26-4], 1-propene-1,1,3,3-tetracarbonitrile (52); 1,1,2,3,3-pentacyanopropene [45078-17-9], 1-propene-1,1,2,3,3-pentacarbonitrile (51); 1,1,2,6,7,7-hexacyano-1,3,5-heptatriene [69239-39-0] (53); 2-dicyanomethylene-1,1,3,3-tetracyanopropane [32019-27-5] (51); and 1,3-cyclopentadiene-1,2,3,4,5-pentacarbonitrile [69239-40-3] (54, 55). Many of these acids rival mineral acids in strength (56) and are usually isolable only as salts with metal or ammonium ions. The remarkable strength of these acids results from resonance stabilization in the anions that is not possible in the protonated forms.

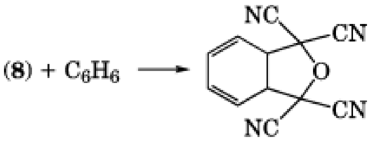
Some of the cyanocarbon anions are highly colored, eg, salts of 1,1,2,6,7,7-hexacyano-1,3,5-heptatriene are deep blue, $\log_{10}\epsilon = 4.22$ at 635 nm (53).

10. Oxacyanocarbons

Tetracyanoethylene oxide [3189-43-3] (**8**), oxiranetetracarbonitrile, is the most notable member of the class of oxacyanocarbons (57). It is made by treating TCNE with hydrogen peroxide in acetonitrile. In reactions unprecedented for olefin oxides, it adds to olefins to form 2,2,5,5-tetracyanotetrahydrofuran [3041-31-4] in the case of ethylene, acetylenes, and aromatic hydrocarbons via cleavage of the ring C—C bond. The benzene adduct (**9**) is 3*a*,7*a*-dihydro-1,1,3,3-phthalantetracarbonitrile [3041-36-9], $C_{12}H_6N_4O$.



(**8**)



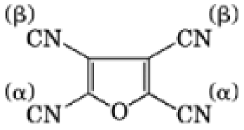
(9)

With pyridine, reaction takes place at the nitrogen rather than at a double bond, and an ylid [27032-01-5] is formed (57, 58). Sulfides react similarly to give sulfilidenes and carbonyl cyanide (59).

This is the most convenient synthesis of carbonyl cyanide [1115-12-4]. The product of (**8**) and dimethyl sulfide is dimethyl sulfonium dicyanomethylide [5362-78-7].

$$(\mathbf{8}) + (CH_3)_2S \longrightarrow (CH_3)_2\overset{+}{S}{-}\overset{-}{C}(CN)_2 + CO(CN)_2$$

Tetracyanofuran [17989-87-6] 2,3,4,5-furantetracarbonitrile, has been obtained by dehydration of the corresponding tetracarboxamide (60). The α-cyano groups are more reactive, preferentially adding water, hydroxylamine, or phenylhydrazine.

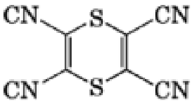


11. Thiacyanocarbons

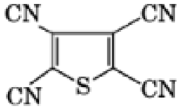
For the most part, thiacyanocarbons are derived from “Bähr’s Salt” [18820-77-4] (**10**), prepared from carbon disulfide and sodium cyanide (61) through the intermediacy of the sodium salt of carbonocyanidodithione acid [33498-03-2], C_2NS_2Na.

(10)

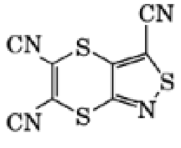
Oxidation of Bähr’s Salt with iodine or thionyl chloride gives tetracyano-1,4-dithiin [2448-55-7] (**11**), 1,4-dithiin-2,3,5,6-tetracarbonitrile (62, 63). The dithiin loses sulfur at 210°C to give tetracyanothiophene [4506-96-1] (**12**), 2,3,4,5-thio-phenetetracarbonitrile, and adds sulfur under the influence of sodium ethoxide to give the isothiazole [4656-27-3] (**13**) (63).



(**11**)



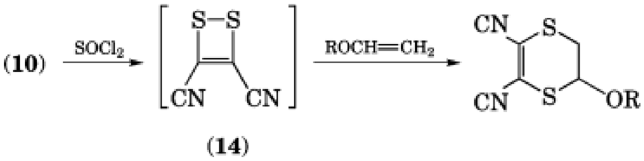
(**12**)



(**13**)

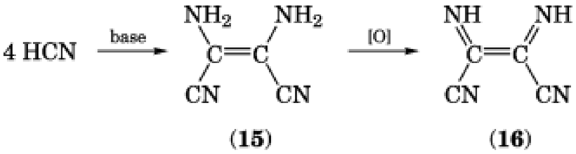
The nitrile groups of these three heterocyclic thiacyanocarbons behave normally and are convertible to amide, imide, or carboxylic acid groups.

Dicyano-1,2-dithiete [53562-16-6] (**14**) is thought to be an intermediate when Bähr's Salt is oxidized (64, 65). If the oxidation is carried out in the presence of vinyl ethers, dihydrodithiins can be obtained in yields up to 60%.



12. Azacyanocarbons

Hydrogen cyanide tetramer (*Z*-) 2,3-diamino-2-butenedinitrile [1187-42-4] (**15**), an azacyanocarbon, is produced by Nippon Soda in pilot-plant quantities for development as a chemical intermediate (66, 67). On oxidation it forms 2,3-diiminobutanedinitrile [28321-79-7] (**16**) (68). These two, in turn, combine to give pyrazine–tetracarbonitrile [33420-37-0] (69).



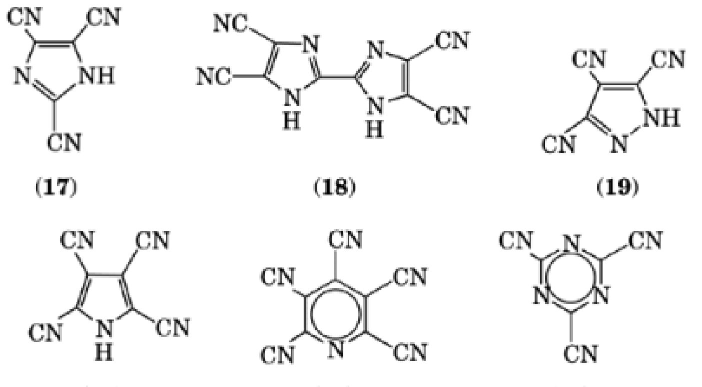
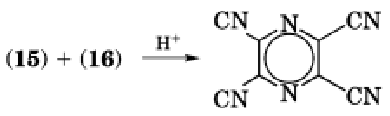
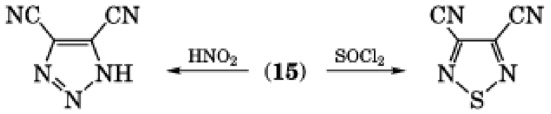


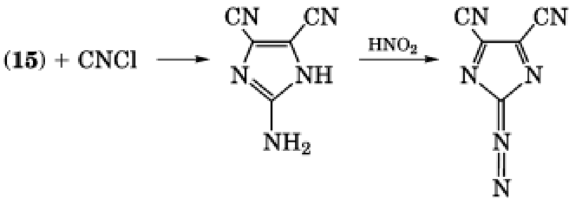
Fig. 1. Azacyanocarbons: 1*H*-imidazole-2,4,5-tricarbonitrile [69239-41-4] (**17**) (74, 75); 4,4′,5,5′-tetracyanobiimidazole [83312-48-7] (**18**) (76); 1*H*-pyrazole-3,4,5-tricarbonitrile [69239-42-5] (**19**) (77); 1*H*-pyrrole-2,3,4,5-tetracarbonitrile [5231-17-4] (**20**) (78); 2,3,4,5,6-pyridinepentacarbonitrile [69239-43-6] (**21**) (79); and 1,3,5-triazine-2,4,6-tricarbonitrile [7615-57-8] (**22**) (80).



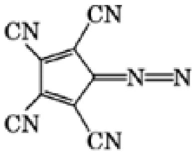
Treatment of (**15**) with nitrous acid gives 1*H*-1,2,3-triazole-4,5-dicarbonitrile [53817-16-6] (70). The action of thionyl chloride on (**15**) gives 1,2,5-thiadiazole-3,4-dicarbonitrile [23347-22-0] (71).

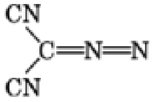


Reaction of (**15**) with cyanogen chloride gives 2-amino-1*H*-imidazole-4,5-dicarbonitrile [40953-34-2] (72). This amino compound reacts with nitrous acid to form 2-diazo-1*H*-imidazole-4,5-dicarbonitrile [51285-29-1] (72). Thermolysis of this diazo compound generates an extremely electrophilic carbene (72).



5-Diazo-1,3-cyclopentadiene-1,2,3,4-tetracarbonitrile [54747-37-4] (54) and 2-diazopropanedinitrile [1618-08-2] (73) also possess reactive diazo groups.





Other azacyanocarbons are shown in Figure 1.

13. Health and Safety Factors (Toxicology)

Unless specifically tested, all cyanocarbons should be considered as toxic as sodium cyanide or hydrogen cyanide (see Cyanides). They should be used only in a fume hood, and rubber gloves should be worn.

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