Alkyl- and Aryltricyanomethanes. Synthesis and Properties

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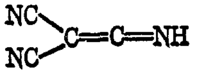
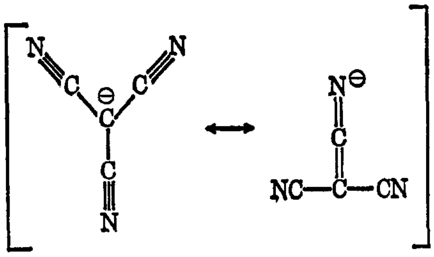
The reaction of sodium salts of substituted malononitriles with cyanogen chloride provides a new, general synthesis of alkyl- and aryltricyanomethanes. As a modified method, benzotricyanides are prepared directly from arylacetonitriles, sodium hydride, and cyanogen chloride. The tricyanomethyl group is *meta* directing to electrophilic substitution reactions on the aromatic ring and inductively withdraws electrons much more strongly than nitro or cyano but shows no significant resonance effect.

Tricyanomethane (cyanoform) is a strong acid ($pK_a = -5$) that is unstable in the free form except in solution.[2,3] By rapid manipulation, the pure acid was isolated and shown to be dicyanoketenimine (1) with the proton bound to nitrogen.[3] However, in solution, spectral evidence suggests that the protonated form has the tricyanomethane structure (2).[2] In contrast, salts of tricyanomethane are quite stable because of the large delocalization energy of the tricyanomethide anion (3) in which the negative charge is distributed symmetrically into the three cyano groups.


1

$HC(CN)_3$

2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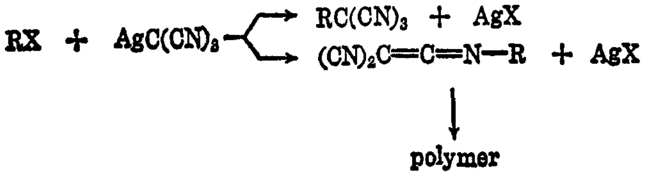
As part of a general program on cyanocarbons,[4] we undertook a study of tricyanomethyl groups by examining the properties of compounds in which a substituent was covalently bound to the central carbon of the tricyanomethyl group. Two members of this series, the benzyl and methyl compounds, have been reported as the products of the reaction of silver tricyanomethide with benzyl or methyl iodide.[5] We have reexamined this reaction and found that the substituted tricyanomethanes are formed in consistently low yields (10–15%) along with large amounts of intractable, orange material. The competing reaction probably is N-alkylation followed by polymerization of the N-alkyldicyanoketenimine.



$$RX + AgC(CN)_3 \rightarrow RC(CN)_3 + AgX \quad\text{or}\quad (CN)_2C{=}C{=}N{-}R + AgX \rightarrow \text{polymer}$$

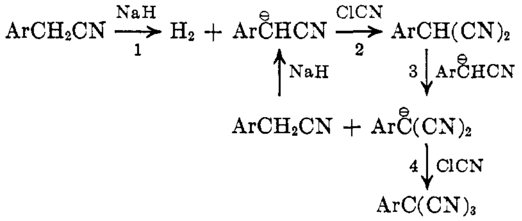
Preparation of Tricyanomethanes.—In order to make a variety of compounds containing the tricyanomethyl group, a synthesis was required that could provide not only alkyl- but also aryl-substituted tricyanomethanes. A new, general synthesis[6] is the reaction of cyanogen chloride with the sodium salts of substituted malononitriles and is useful in preparing substituted tricyanomethanes in yields of 36 to 94%.

$$R\overset{\ominus}{C}(CN)_2Na^{\oplus} + ClCN \longrightarrow RC(CN)_3$$

The sodium salts are prepared in inert solvents, such as benzene or dimethoxyethane, by treating the substituted malononitrile with an equivalent of base. Gaseous cyanogen chloride reacts rapidly when it is passed into the solution or suspension of sodium salt, and sodium chloride precipitates. Excess cyanogen chloride can be used to assure complete reaction and is easily removed by volatilization during work-up of the substituted tricyanomethane. Sodium hydride dispersion in mineral oil is a convenient base for preparing the sodium salts of malononitriles, and contamination of the product by mineral oil can be avoided by washing the sodium hydride with solvent before addition of the malononitriles. Sodium methoxide can also be used to prepare the sodium salts of arylmalononitriles but gives poor results with alkylmalononitriles; the major products are high-boiling, oxygen-containing substances.

The reaction has been extended to prepare aryltricyanomethanes directly from arylacetonitriles without isolating the arylmalononitrile intermediate by taking advantage of the slow reaction between sodium hydride and cyanogen chloride under moderate conditions. The reaction of arylacetonitriles with 2 moles each of sodium hydride and cyanogen chloride is conveniently run in dimethoxyethane solvent as shown in Scheme I. To initiate step 1, the sodium hydride (preferably washed free of mineral oil) is activated by

SCHEME I



$$\begin{tikzcd} ArCH_2CN \arrow[r, "NaH", "1"'] & H_2 + Ar\overset{\ominus}{C}HCN \arrow[r, "ClCN", "2"'] & ArCH(CN)_2 \arrow[d, "3", "Ar\overset{\ominus}{C}HCN"'] \\ & ArCH_2CN \arrow[u, "NaH"'] + & Ar\overset{\ominus}{C}(CN)_2 \arrow[d, "4", "ClCN"'] \\ & & ArC(CN)_3 \end{tikzcd}$$

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[1] To whom correspondence should be addressed.

[2] R. H. Boyd, *J. Phys. Chem.*, **67**, 737 (1963).

[3] S. Trofimenko, *J. Org. Chem.*, **28**, 217 (1963).

[4] T. L. Cairns and B. C. McKusick, *Angew. Chem.*, **73**, 520 (1961).

[5] A. Hantzsch and G. Osswald, *Ber.*, **32**, 641 (1899).

[6] This reaction was first described by J. K. Williams [U. S. Patent 2,995,597 (1961)] and by E. L. Martin and J. K. Williams [U. S. Patent 3,166,583 (1965)] for the preparation of selected arylalkylcyanoforms, which were reported to decompose to cyanoform. See also H. D. Hartzler, *J. Am. Chem. Soc.*, **86**, 2174 (1964), for the reaction of *p*-nitrophenylacetonitrile anion with cyanogen chloride.

TABLE I

SUBSTITUTED TRICYANOMETHYL COMPOUNDS, $RC(CN)_3$. PREPARATION AND PROPERTIES

R	Method of prepn[a]	Yield, %	Bp, °C (mm)	n^{25}_{D} (mp, °C)	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
C_2H_5–	A[b]	66	115–116 (100)	1.4193	$C_6H_5N_3$	60.5	4.23	35.3	60.7	4.31	34.9
$CH_2{=}CHCH_2$–	A[c]	36	90.0–90.2 (100)	1.4400	$C_7H_5N_3$			32.1			32.0
$C_6H_5CH_2CH_2$–	A[d]	72		(47–49)	$C_{12}H_9N_3$	73.8	4.65	21.5	73.9	4.65	21.7
$C_6H_5C(CH_3)_2$–	A[e]	52		(106–107)	$C_{13}H_{11}N_3$	74.7	5.30	20.1	73.9	5.25	20.2
$C_6H_5CH_2$–[f]	A[g]	94		(139–140)							
C_6H_5–	C[h]	78	87–88 (3.3)	1.5087	$C_{10}H_5N_3$	71.8	3.01	25.2	72.2	3.03	25.6
	B	39									
m-$CH_3C_6H_4$–	B[i]	34	78 (0.8)	1.5074	$C_{11}H_7N_3$	73.0	3.90	23.2	73.3	4.55	23.0
m-FC_6H_4–	B[j]	30	92 (3.5)	1.4954	$C_{10}H_4FN_3$			22.7			22.6[k]
p-FC_6H_4–	B[j]	19	91–92 (3.3)	1.4958 (35–36)	$C_{10}H_4FN_3$	64.9	2.18	22.7	65.5	2.25	22.6[l]
α-$C_{10}H_7$–	C[d]	69		(109–110)	$C_{14}H_7N_3$	77.4	3.25	19.3	77.7	3.56	19.5
1,4-C_6H_4–	C[m]	94		(261.0–261.5)	$C_{14}H_4N_6$	65.6	1.56	32.8	65.6	1.66	32.6

[a] The sources of starting materials are given as footnotes. Capital letters refer to method described in Experimental Section under synthesis. [b] P. Henry, *Jahresber. Fortschr. Chem.*, **42**, 639 (1889); J. C. Hessler, *Am. Chem. J.*, **22**, 185 (1899). [c] P. Henry, *Jahresber. Fortschr. Chem.*, **42**, 640 (1889). [d] See Experimental Section on preparation of starting materials. [e] F. S. Prout, E. P.-Y. Huang, R. J. Hartman, and C. J. Korpics, *J. Am. Chem. Soc.*, **76**, 1911 (1954). [f] See ref 5. [g] See ref 16. [h] J. C. Hessler, *Am. Chem. J.*, **32**, 123 (1904). [i] B. Radziszewski and P. Wispech, *Ber.*, **18**, 1282 (1885). [j] Pierce Chemical Co., Rockfort, Ill. [k] *Anal.* Calcd: F, 10.3. Found: F, 10.1. [l] *Anal.* Calcd: F, 10.3. Found: F, 10.2. [m] D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, **84**, 3370 (1962).

TABLE II

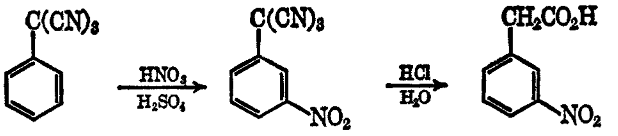
F^{19} NMR CHEMICAL SHIFTS FOR FC_6H_4X AND SUBSTITUENT PARAMETERS

X		Chemical shift, cps relative to CCl_3F at infinite dilution (56.4 Mc/sec)	Chemical shift δ, ppm relative C_6H_5F	σ_I	σ_R°	σ_m°	σ_p°
H		6382	0				
$C(CN)_3$	*meta*	6018	−6.46	1.00	0.01	1.00	1.01
	para	6003	−6.71				
NO_2	*meta*	...	−3.45[a]	0.57	0.20	0.67	0.77
	para	...	−9.45[a]				
CN	*meta*	...	−2.75[a]	0.47	0.22	0.58	0.69
	para	...	−9.20[a]				
SO_2CF_3	*meta*	...	−4.93[a]	0.75	0.31	0.90	1.06
	para	...	−14.01[a]				

[a] Values from ref 8 at 5% concentration in CCl_4.

the addition of a small quantity of ethanol, and the mixture is heated to 60–70°. When step 1 is complete, as indicated by cessation of hydrogen evolution, cyanogen chloride is passed into the mixture. Step 2 is exothermic, and the reaction can be maintained at 60–70° by adjusting the rate of addition of cyanogen chloride. Step 3 is very rapid, and the reaction must be kept at 60–70° during the addition of cyanogen chloride so that the $Ar\overset{\ominus}{C}HCN$ ion can be regenerated from the second mole of sodium hydride and the $ArCH_2CN$ that is formed. The results are summarized in Table I. The yields were 30 to 40%, and this method is advantageous because considerable time is saved over preparing the arylmalononitrile by literature methods.

Electronic Effects of Tricyanomethyl Group.—A qualitative evaluation of the electronic effect of the tricyanomethyl group as electron withdrawing was obtained by examination of its orienting effect on an electrophilic substitution reaction. When phenyltricyanomethane was nitrated, a 78% yield of m-nitrophenyltricyanomethane was obtained. The structure of the nitration product was proved by hydrolysis and decarboxylation to the known m-nitrophenylacetic acid.



Because the tricyanomethyl group is susceptible to hydrolysis by base[7] or hydrogen halide acids, the preparation of derivatives, such as benzoic acids, phenols, or anilines, containing the tricyanomethane group was not readily accomplished, and quantitative evaluation of the inductive and resonance effects of the $C(CN)_3$ groups by classical pK_a or rate measurements appeared impractical. Recently Taft and co-workers[8] have described the use of F^{19} nmr chemical shifts of aryl fluorides as an effective method for determining inductive and resonance parameters for substituents, particularly those that are hydrolytically unstable. The F^{19} chemical shifts for the m- and p-fluorobenzotricyanides are reported in Table II along with the calculated substituent parameters. For comparison, data for three other very strong electron-withdrawing groups, CN, NO_2, and SO_2CF_3, are also given. Inductively the $C(CN)_3$ group is one of the strongest electron-

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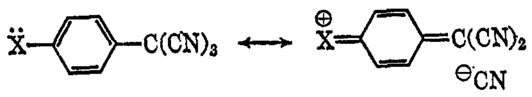
(7) O. W. Webster, W. Mahler, and R. E. Benson [*ibid.*, **84**, 3678 (1962)] reported that benzotricyanide reacted with cyanide ion at −60° in acetonitrile to give phenylmalononitrile anion in 60% yield.

(8) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 709, 3146 (1963).

withdrawing groups (σ_I of 1.00) that has been reported[9] and is significantly stronger than the SO_2CF_3 group which was previously pointed out as the strongest neutral electron-withdrawing group.[10] However, the resonance effect for the $C(CN)_3$ is almost negligible since the chemical shift for the fluorine in the *para* position is only slightly downfield from that for the *meta*. However, a small resonance deactivation (+R effect) is present, and no mutual interactions of the nitro or cyano type are possible. This small resonance effect may originate in contributions from hyperconjugation structures involving cyanide ion, such as



(in analogy to fluoride ion hyperconjugation proposed for the CF_3 group), or by a π-inductive mechanism or through p–π interaction.[11] An interesting point is that the inductive effect of the tricyanomethyl group is larger than predicted. Normally a transmission factor of 0.3–0.5/carbon[12] is assigned to the inductive effect and, based upon the inductive parameter for a cyano group, the tricyanomethyl should have a σ value of 0.5–0.8 instead of 1.00 which was found. A possible explanation is through space interaction (field effect), since the cyano groups on a tetrahedral carbon are oriented in a different direction and thus are effectively closer than a cyano group attached directly to the aromatic ring. Further discussion of these effects will be made in subsequent publication of data on electronic effects for a series of CX_3 groups.

The dipole moment of 4.22 D for benzotricyanide (see Table III) is significantly larger than that for nitrobenzene (3.95 D) or benzonitrile (4.0 D) and again reflects the stronger electron-withdrawing power of the tricyanomethyl group compared to nitro or cyano.

TABLE III

PROPERTIES OF BENZOTRICYANIDE

Dielectric Constants, Densities, and Polarizations in Benzene at 25°

f_2	ϵ	d	P_2
0.0000	2.2740	0.80100	266.94
0.01128	2.5600	0.8770	396.19
0.02134	2.8160	0.8807	381.02
0.03808	3.2196	0.8869	351.92

Molar Refractions, Polarization, and Dipole Moments

MR_D	P_∞ (25°)	μ, D
50.598	415.52	4.22

Experimental Section

Preparation of Starting Materials. 1. γ-Phenyl-α-cyanobutyramide.—A mixture of 182 g of ethyl γ-phenyl-α-cyanobutyrate[13] and 450 ml of concentrated ammonium hydroxide was stirred for 15 hr at 25°. Crystals of the cyanoamide began to separate in a few minutes and a thick reaction mixture was obtained after about 1 hr. The solid material was collected, washed with three 100-ml portions of ice–water, and, after air drying, was dried at 40–50° over phosphorus pentoxide at 15-mm pressure. The yield of colorless, crystalline γ-phenyl-α-cyanobutyramide, mp 152–154°, was 122 g (87%). Crystallization of a sample for analysis from methanol–methylene chloride gave colorless crystals, mp 152–154°.

Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.2; H, 6.43; N, 14.9. Found: C, 70.2; H, 6.30; N, 14.9.

2. **2-Phenylethylmalononitrile.**—A mixture of 150 g of γ-phenyl-α-cyanobutyramide, 50 g of sodium chloride, and 300 ml of 1,2-dichloroethane was stirred at room temperature for 5 min; then 80 g of phosphorus oxychloride was added. The mixture was heated at reflux with vigorous mechanical stirring for 8 hr. The mixture tended to gum, and stirring was not efficient. The mixture was filtered, and the filter cake was washed with 1,2-dichloroethane. Ice–water was added to the filtrate and the mixture was stirred to hydrolyze the excess phosphorus oxychloride. Solid sodium bicarbonate was added in small portions until the aqueous layer was neutral. The organic layer was separated and washed with aqueous sodium bicarbonate. After drying with anhydrous magnesium sulfate, the organic layer was concentrated, and the residue was distilled. The yield of 2-phenylethylmalononitrile, bp 109–110° (0.2 mm), was 116 g (78%). The compound solidified on standing at room temperature and melted at 44–46°.

Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.6; H, 5.92; N, 16.5. Found: C, 78.0; H, 6.09; N, 16.5.

3. **α-Naphthylmalononitrile.**—A mixture of 126 g of α-naphthylcyanoacetamide,[14] 50 ml of phosphorus oxychloride, 90 g of sodium chloride, and 600 ml of acetonitrile was heated at reflux with stirring for 19.5 hr. The mixture was filtered while hot and allowed to cool. The solid that deposited weighed 83 g. A second 22-g portion of material was obtained by pouring the liquors into 1.5 l. of water and recrystallizing the precipitate from acetonitrile. The combined solids were recrystallized from ethanol to give 98 g of α-naphthylmalononitrile, mp 166–167°.

Anal. Calcd for $C_{13}H_8N_2$: C, 81.2; H, 4.20; N, 14.6. Found: C, 81.1; H, 4.34; N, 14.6.

Alkyl- and Aryltricyanomethanes. 1. Synthesis.—The three methods used to prepare the substituted tricyanomethyl compounds described in Table I are illustrated by the following three typical experimental procedures.

Method A. 1,1,1-Tricyano-2-phenylethane.—To a mixture of 24 g of 50% sodium hydride dispersion in mineral oil[15] and 500 ml of tetrahydrofuran was added, in the course of 0.5 hr, a solution of 78 g of benzylmalononitrile[16] in 800 ml of tetrahydrofuran. The mixture was stirred for an additional 0.5 hr and then cooled in an ice bath while 40 g of cyanogen chloride was passed in. The mixture was stirred for an additional 1 hr and then poured into 4 l. of cold water. The oil that separated crystallized and was collected by filtration. The crude product was sublimed to give 85 g (94%) of almost white 1,1,1-tricyano-2-phenylethane. When 81 g of sublimed material was recrystallized from a mixture of 100 ml of 1,2-dichloroethane and 150 ml of petroleum ether (bp 39–52°), 66 g (82% recovery, 77% yield) of pure 1,1,1-tricyano-2-phenylethane, mp 138°, was obtained.

Method B. *m*-Fluorobenzotricyanide.—A mixture of 13.5 g of *m*-fluorobenzylnitrile, 100 ml of 1,2-dimethoxyethane, 10 g of sodium hydride as a 58% suspension in mineral oil,[17] and a few drops of anhydrous ethanol in a three-necked flask fitted with thermometer, magnetic stirrer, and ice condenser connected to a wet-test meter (to measure gas evolution) was heated in an oil bath. At approximately 65°, an exothermic reaction started and 2700 cc of gas was evolved. Cyanogen chloride was bubbled into the solution, a vigorous exothermic reaction occurred, and the oil bath had to be removed. Gas evolution continued while approximately 7 g of cyanogen chloride was added and an exothermic reaction continued until about 14 g of cyanogen chloride had been added (theoretical 12.3 g); total gas evolution was approximately 6000 cc. External heating was resumed, and cyanogen chloride addition was continued until approximately 23 g had been added. The reaction mixture changed

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[9] The trinitromethyl group, $C(NO_2)_3$, has been reported to have σ_p of 0.82: J. Hine and W. C. Bailey, *J. Org. Chem.*, **26**, 2098 (1961). The substituent parameters for the ICl_2 group were reported as σ_m and σ_p both equal to 1.3: G. E. Maciel, *J. Am. Chem. Soc.*, **86**, 1269 (1963).

[10] W. A. Sheppard, *ibid.*, **85**, 1314 (1963).

[11] W. A. Sheppard, *ibid.*, **86**, 2410 (1965).

[12] M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962, p 154.

[13] S. Windeqvist, *Arkiv Kemi, Mineral. Geol.*, **26A**, 13 (1948); *Chem. Abstr.*, **43**, 2168 (1949).

[14] S. Wideqvist, *Arkiv Kemi, Mineral. Geol.*, **24B**, 7 (1947); *Chem. Abstr.*, **42**, 6349 (1948).

[15] Metal Hydrides, Inc., Beverly, Mass.

[16] J. C. Hessler, *Am. Chem. J.*, **22**, 169 (1899).

[17] Because the mineral oil is difficult to separate from the product, we recommend the modified procedure of washing the hydride suspension with three 100-ml portions of 1,2-dimethoxyethane.

TABLE IV

ULTRAVIOLET SPECTRA

Compd	λ_{max}, mμ (log ϵ)				
$C_6H_5C(CN)_3$[a]	268 (2.4)	262 (2.5)	255 (2.4)	248 (2.2)	
$C_6H_5CH_3$[b]	268 (1.9)	261.5 (2.5)	257 (2.0)	251 (1.4)	
α-$C_{10}H_7C(CN)_3$[c]	319 (2.9)	314 (2.8)	286.5 (3.8)	277 (3.9)	228 (4.7)
α-$C_{10}H_7CH_3$[b]	314 (2.5)	308 (2.5)	281.5 (3.8)	271 (3.8)	224 (5.0)

[a] Solvent, isooctane. [b] Reference spectra from American Petroleum Institute, Research Project No. 44. [c] Solvent, cyclohexane.

from an initial dark orange-red to yellow. The mixture was cooled and filtered (14.1 g of salt separated), and the solvent was removed by distillation. The *m*-fluorobenzotricyanide, bp 90–93° (3.8 mm), $n^{25}D$ 1.4925–1.4950, was obtained in a yield of 5.51 g (30%). This product contained a few per cent mineral oil as detected by infrared and proton nmr spectroscopy. Purification was accomplished by recrystallization from pentane: mp 39.0–40.5°.

Method C. 1,4-Bis(tricyanomethyl)benzene.—A mixture of 4.1 g of 1,4-phenylenebismalononitrile, 2.5 g of sodium methoxide, and 200 ml of 1,2-dimethoxyethane was heated at reflux under an atmosphere of nitrogen for 7 hr. The mixture was then cooled to 10°, and 10 g of cyanogen chloride was passed in with vigorous stirring over the course of 10 min. The mixture was alowed to warm to 25° and stirred for 20 hr. The inorganic solid was removed by filtration, and the filtrate was evaporated to dryness to give 5.0 g of 1,4-bis(tricyanomethyl)benzene, mp 255°. The product was purified to mp 261–261.5° by four recrystallizations from acetonitrile and two from methyl ethyl ketone.

When a sample of this material was heated under reflux with concentrated hydrochloric acid, it was converted to 1,4-phenylenebisacetic acid, mp 251–253°. A mixture melting point with an authentic sample[18] was undepressed.

2. **Reactions. A. *m*-Nitrobenzotricyanide.**—Throughout the course of 5 min 33.4 g of benzotricyanide was added to a stirred mixture of 50 ml of fuming nitric acid and 150 ml of concentrated sulfuric acid maintained at 0–15°. A solid precipitated during the addition. The reaction mixture was poured into 1 l. of ice-water as soon as the addition of benzotricyanide was complete. The cream-colored, crystalline solid was collected by filtration and washed with water. The moist product was dissolved in boiling toluene. The toluene solution was decanted while hot from a small amount of water, and the hot solution was dried by distillation of a small quantity of toluene, filtered, and allowed to cool. The *m*-nitrobenzotricyanide crystallized in massive prisms, 32.2 g (78%), mp 127.5–128.5°.

Anal. Calcd for $C_{10}H_4N_4O_2$: C, 56.6; H, 1.90; N, 26.4. Found: C, 57.0; H, 2.16; N, 26.7.

B. Hydrolysis and Decarboxylation.—A mixture of 5 g of *m*-nitrobenzotricyanide and 75 ml of concentrated hydrochloric acid was heated under reflux overnight. The hot reaction mixture was filtered and allowed to cool. The crystalline material that precipitated on cooling was collected and recrystallized from aqueous ethanol to give 3.1 g of long prisms, mp 116–117°. An additional crystallization gave material, mp 118–119°; the reported melting point for *m*-nitrophenylacetic acid is 117°.[19]

The amide was prepared by heating together 1 g of the acid with 10 ml of thionyl chloride under reflux for 1 hr, removing the excess thionyl chloride under vacuum, and adding a solution of the acid chloride so obtained in 15 ml of benzene to 25 ml of concentrated aqueous ammonia. The amide was collected by filtration and washed with water. After two crystallizations from ethanol, it melted at 139–140°. The reported melting point for *m*-nitrophenylacetamide is 109–110°.[20]

Because of the apparent discrepancy in the melting point of amide prepared in this way with that reported for the amide, this derivative was characterized by elemental analysis.

Anal. Calcd for $C_8H_8N_2O_3$: C, 53.3; H, 4.48; N, 15.6. Found: C, 53.3; H, 4.30; N, 15.8.

To characterize the hydrolysis product of *m*-nitrobenzotricyanide further, a small sample of the acid was oxidized with sodium dichromate in aqueous sulfuric acid. Recrystallization of the oxidation product twice from methanol–water mixture gave material, mp 134–135°, which showed no depression in melting point upon admixture with an authentic sample of *m*-nitrobenzoic acid.

3. **Nmr Measurements and Substituent Parameters.**—F^{19} nmr calibrations were carried out on *m*- and *p*-fluorobenzotricyanides at 40, 20, 10, and 5% concentration in trichlorofluoromethane as solvent and internal calibrant, and the chemical shifts were obtained by extrapolation to infinite dilution.[11] The substituent parameters were calculated from these chemical shifts by the method of Taft[7,21,22] using the following equations.

$$\delta_H{}^{m-X} = -7.10\sigma_I + 0.60$$

$$\sigma_R{}^\circ = -0.0339(\delta_H{}^{p-X} - \delta_H{}^{m-X})$$

$$\sigma_m{}^\circ = \sigma_I + 0.50\sigma_R{}^\circ$$

$$\sigma_p{}^\circ = \sigma_I + \sigma_R{}^\circ$$

The nmr chemical shift and calculated substituent parameters are given in Table II.

4. **Dipole Moment.**—The dipole moment was determined by literature methods[23] employing Wissenschaftlich Technische Werkstatten Dipolmeter, Type DM 01, Cell DFL 1 (20-ml volume). The data are given in Table III. A precision of ±0.02 D is ascribed to the dipole moment of 4.22 D reported for benzotricyanide.

5. **Spectral Properties.**—The tricyanomethyl group does not significantly perturb the normal aromatic electronic spectra; the absorption for benzotricyanide was almost identical with that of toluene (see Table IV). α-Naphthotricyanide also had a spectrum essentially identical with that of α-methylnaphthalene, except that all the bands observed were shifted 5 mμ toward the longer wavelength. Intramolecular charge transfer was expected to be observed, and the small shift to longer wavelength suggests that such interaction must be very small.

The infrared spectra of the tricyanomethanes are normal with a medium to weak CN absorption at approximately 2250 cm^{-1}.

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