138. Synthesis and Structure of Fluorotricyanomethane

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Summary

Fluorotricyanomethane is prepared from potassium tricyanomethanide and perchlorylfluoride. The crystal structure of this compound (orthorhombic, space group $P2_12_12_1$, with $a = 6.270$, $b = 6.734$, $c = 11.776$ Å) has been determined by X-ray analysis. The results are discussed in relation to those of $(NC)_3C{-}X$ ($X = {-}CH_3$, $-Cl$, $-Br$ or $-CN$).

Introduction. – It is generally assumed that a S_N2-reaction at a tetrahedral carbon atom proceeds *via* a transition state in which the three atoms covalently bound to the carbon are coplanar with it, and that the entering nucleophile and the leaving group are essentially colinear [1] with it. This mechanistic description usually implies that the reaction profile contains but a single maximum. Although a stable intermediate in a S_N2-reaction has not been detected, the possibility remains that under favorable conditions a short-lived intermediate might be detectable.

It has been recognized that π-acceptor groups, attached to the central carbon atom, enhance the rate of nucleophilic substitution [2]. In order to enhance the rate of the S_N2-reaction, however, the π-system axis of such π-acceptor groups has to be parallel with the linear arrangement: entering nucleophile – central carbon-atom – leaving group [3].

Three good π-acceptor groups, bonded to the carbon atom at which a nucleophilic substitution is to take place, should either lead to an enormous rate enhancement, or else enhance a reaction in which the central carbon atom with its π-acceptor substituents acts as a leaving group. However, a compound containing a carbon atom to which three good π-acceptor substituents and a specific leaving group are attached might be prone to yield a detectable intermediate during its S_N2-reaction. A compound, suggested by *A. Eschenmoser*[3], which potentially incorporates these features, is fluorotricyanomethane.

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As a first report of our investigation of the properties of fluorotricyanomethane, we describe here its synthesis and its crystal structure. The structure of fluorotricyanomethane in itself is of interest for comparison with those of X–C(CN)$_3$, where X is CH$_3$, Cl, Br[4] or NC[5], because in these latter compounds intermolecular distances shorter than *van der Waals* distances and, therefore, presumably, interactions stronger than *van der Waals* interactions, have been found.

Experimental Part

Preparation of F-C(CN)$_3$[6]. – To a two-necked cylinder flask, equipped with a fritted-glass gas-dispersion tube, are added 1.04 g (8.5 mmol) of potassium tricyanomethanide [7] and 15 ml of triglyme [distilled twice over lithium aluminium hydride]. The stirred solution is cooled in an ice-salt bath to −15°, and perchloryl fluoride [8] is passed through the solution during 90 min (~2 g, ~19.5 mmol). After stirring for another 30 min at −15°, the white precipitate is filtered off and the product sublimated out of the light yellow solution at RT. i.V. (15 Torr). The yield of the white solid is 0.752 g (81%), m.p. 37–39°. – IR.(CHCl$_3$, cm^{-1}): 2260*vs*, 1085*vs*, 1050*s*. – ^{19}F-NMR.(CH$_3$CN, int. ref. C$_6$H$_5$CF$_3$); 75,5 ppm. – MS. (m/e, % of base peak): 109 (0.4, *M*$^+$), 90 (3), 83 (14), 64 (13), 57 (*100*), 38 (40), 32 (37), 31 (25), 26 (14). –

C$_4$FN$_3$ (109.06) Calc. C 44.08 F 17.42% Found C 44.96 F 17.15%

Data collecting for X-ray studies. – The crystals were colorless, thick prisms, which showed extinction parallel to the longest direction in the crystal. The crystals sublimed or decomposed at RT. slowly in an inert atmosphere and rapidly (2–3 min) in air. They could be stored several months at −25° in an inert atmosphere. All crystals used for X-ray studies were mounted as follows: a 1.0 mm diameter thinwalled glass capillary sealed at one end was filled at the sealed end for about 3 mm with Apiezon L grease, a crystal 0.4–0.7 mm in diameter and 0.6–1.0 mm in length was pushed into the grease, another layer of about 3 mm of grease was added, and the capillary was sealed. Crystals so mounted remained good indefinitely in the refrigerator, but in actual use, which included mounting a crystal in a cold nitrogen stream, taking pictures, returning the crystal to the refrigerator overnight, remounting the crystal *etc.*, the crystal began to fragment or sublime after about ten days and was useless for further X-ray work. The X-ray data consisted exclusively of precession photographs taken on a *Stoe* precession camera using the *Stoe* low-temperature apparatus to cool the crystal. The crystals were cooled to −10° for data collection; the temperature fluctuated about ±5° as estimated from a thermocouple mounted directly in the stream of cold nitrogen about 3 mm beyond the crystal.

The precession photographs showed the crystal to be orthorhombic with systematic extinctions (h00, h≠ 2n; 0k0, k≠ 2n; 001, 1≠ 2n) that indicate the space group to be $P2_12_12_1$. The cell dimensions are a = 6.270, b = 6.734, c = 11.776 Å, determined from precession photographs (MoK_α radiation, λ = 0.7107 Å); we estimate the error to be approximately 1 part in 500 for the method. For Z = 4 the molecular volume is 124.3 Å^3/molecule and the calculated density is 1.456 gm/cm^3; the density was estimated by flotation of the dissolving crystals in chloroform/carbon tetrachloride to be 1.40±0.01 gm/cm^3. The linear absorption coefficient (MoK_α) is 1.37 cm^{-1}; no absorption corrections were made. Intensity photographs were collected for 0kl−1kl, hk0−hk2, hkh−hk · h+3, hk · 2h−hk · 2h+2, hk · 3h−hk· 3h+2. The intensities were measured on a *Joyce-Loebel* recording microdensitometer and reduced to a single scale by comparison of reflections common to various sets of films.

Solution and Refinement. – The approximate orientation of the molecule was found from a sharpened *Patterson* map, and the approximate location of the center of the molecule was found from packing considerations. After several attempts, a successful trial structure was found. Refinement with all atoms with isotropic temperature factors converged at R = 0.116, r = 0.062[4]). Further refinement with all atoms with anisotropic thermal parameters converged at R = 0.092, r = 0.033. The largest peaks and troughs on a difference *Fourier* map at this point were 0.3 e/Å^3 compared with

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[4]) $r = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
The numerator of r was the function minimized.
$w = 1$ for $F_o < 6.2$; $w = (6.2/F_o)^4$ for $F_o > 6.2$.

Table 1. *Positional and thermal parameters*
Anisotropic temperature factors are of the form exp $[-1/4\ (B_{11}h^2a^{*2}+\ldots+2B_{12}hka^*b^*+\ldots)]$. Estimated standard deviations for the final significant figures are given in parentheses. The positional parameters are multiplied by 10^4.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{14}
C(O)	1900(8)	188(8)	1397(5)	2.7(2)	2.7(2)	3.5(2)	0.0(2)	0.5(2)	0.4(2)
C(1)	3087(10)	1825(10)	1938(5)	2.7(2)	4.6(3)	2.9(3)	0.3(2)	−0.2(2)	0.3(3)
N(1)	3966(9)	3081(10)	2361(5)	4.5(3)	6.0(3)	5.4(3)	−0.9(3)	−0.3(3)	−1.9(3)
C(2)	3180(9)	− 831(8)	531(5)	2.8(2)	3.0(2)	4.0(3)	−0.3(2)	−0.3(3)	0.2(2)
N(2)	4195(9)	−1571(8)	− 162(6)	3.7(2)	4.1(3)	7.0(3)	0.5(2)	0.4(3)	1.5(3)
C(3)	− 108(9)	980(8)	862(5)	3.0(2)	2.7(2)	3.0(2)	−0.2(2)	0.2(2)	0.1(2)
N(3)	−1610(9)	1617(7)	496(5)	3.8(2)	3.8(2)	4.8(3)	0.7(2)	−0.7(2)	0.1(2)
F	1312(6)	−1160(6)	2203(3)	4.0(2)	5.0(2)	4.5(2)	−0.4(2)	−0.5(2)	1.9(2)

peak heights of 7–12 e/Å^3 on the *Fourier* map. The final parameters are given in *Table 1*. A table of observed and calculated structure factors may be obtained on request from *D.B.*

Results and discussion. – The bond lengths and angles are given in *Table 2*. The bond lengths, C–F, 1.364(7) Å; C–C(avg.), 1.483(11) Å; and C–N(avg.), 1.132(8) Å agree with those for similar bonds in comparable molecules. The bond angles about the central carbon atom, F–C–C(avg.), 108.6(6)°, and C–C–C(avg.), 110.3(8)° are not significantly different from tetrahedral; the differences from tetrahedral, such as they are, are in the normal direction of putting the smaller angles adjacent to the more electronegative fluorine atom.

Table 2. *Bond lengths and angles in* $FC(CN)_3$

C(0)–F	1.364(7) Å	F–C(0)–C(1)	109.5(5)°
		F–C(0)–C(2)	108.7(5)
		F–C(0)–C(3)	107.5(4)
C(0)–C(1)	1.474(8)	C(1)–C(0)–C(2)	111.9(5)
C(0)–C(2)	1.468(8)	C(2)–C(0)–C(3)	109.4(5)
C(0)–C(3)	1.506(8)	C(3)–C(0)–C(1)	109.7(5)
C(1)–N(1)	1.127(9)	C(0)–C(1)–N(1)	178.9(7)
C(2)–N(2)	1.148(9)	C(0)–C(2)–N(2)	177.9(6)
C(3)–N(3)	1.121(8)	C(0)–C(3)–N(3)	177.5(5)

The packing in the crystal is shown in *Fig. 1*. As is the case for $C(CN)_4$ [5], the structure can be regarded as a distortion of the structure of SiF_4 [9] [10], which has SiF_4 molecules at the corners and body center of a cubic cell such that each Si–F bond points directly toward the silicon atom in an adjacent molecule. In the $FC(CN)_3$ structure neither the C–F nor C–C–N bonds are colinear with the central carbon atom of the next molecule, but each terminal nitrogen atom makes intermolecular contacts such that it is in the pocket formed on an adjacent molecule by the central carbon atom and three of its bonded neighbors. Thus the nitrogen atom N(3) fits into the pocket opposite the fluorine atom. This is shown in the *Figur* and is also summarized in *Table 3*. The fluorine atom does not fit as well into the remaining pocket,

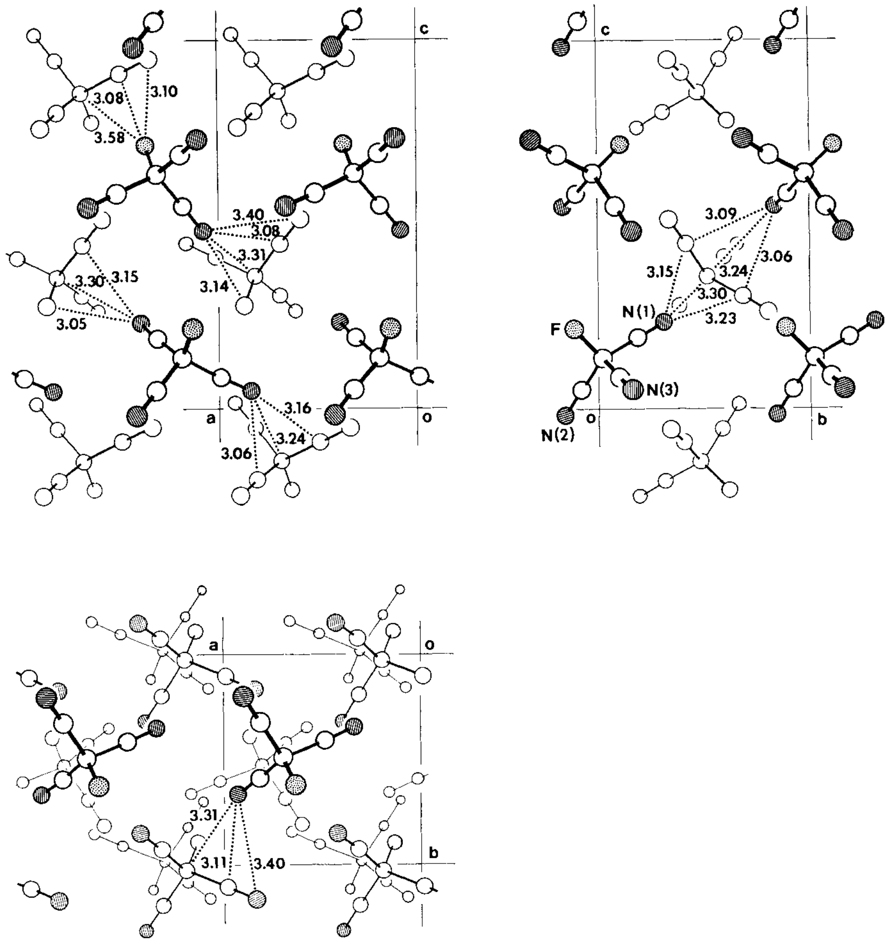

Fig. *The structure of FC* (*CN*)$_3$. The short intermolecular contact distances are shown (in Å). Most of the distances are shown in more than one view.

Table 3. *Intermolecular contacts in FC* (*CN*)$_3$

Atom	Fits into the pocket opposite	Makes contact with	(Å)	Atom	Fits into the pocket opposite	Makes contact with	(Å)
N(1)	C(3)	C(0)	3.30	N(3)	F	C(0)	3.24
		C(1)	3.23			C(1)	3.06
		C(2)	3.15			C(2)	3.09
		F	3.05			C(3)	3.16
N(2)	C(1)	C(0)	3.31	F	C(2)	C(0)	3.58
		C(2)	3.08			C(1)	3.24
		C(3)	3.11			C(3)	3.08
		F	3.14			N(3)	3.10
						F	3.81

which is opposite C(2), being pointed more at one of the nitrile groups, but it is in that neighborhood so that the overall analogy with the structure of SiF_4 and $C(CN)_4$ holds. The *van der Waals* radius of F is usually regarded as 0.15–0.2 Å smaller than that of N so that, while the intermolecular contacts made by the fluorine are at about the same distance as those made by the nitrogen atoms, relatively speaking they are longer and presumably weaker. The short intermolecular distances between the nitrogen atoms and the carbon atoms of the nitrile groups in *Table 3* should be compared with those found in $C(CN)_4$, 3.00 and 3.05 Å, those found in $CH_3C(CH)_3$, 3.09 and 3.11 Å, and those found in $ClC(CN)_3$, 3.09 and 3.09 Å [4].

It is noteworthy that the shortest distance between a nitrogen atom and the central carbon atom of an adjacent molecule is found for N(2), which points into the pocket opposite the fluorine atom. The N ... C distance of 3.24 Å is significantly shorter than the sum of the *van der Waals* radii (3.4 Å [4]) and hence just suggestive of an incipient nucleophilic substitution reaction.

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