Triethylamine-assisted reaction between 2,4-dinitrofluorobenzene and malononitrile

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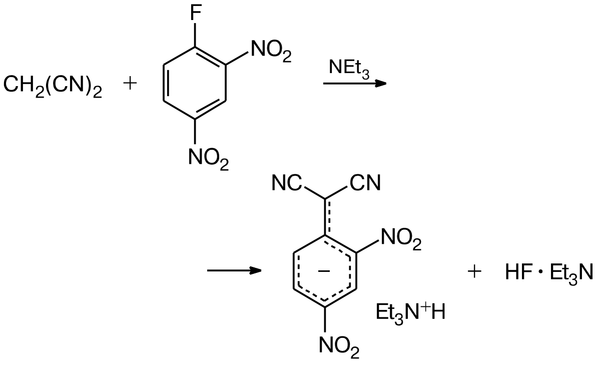
The reaction of malononitrile with 2,4-dinitrofluorobenzene in the presence of triethylamine on contact with glass or silicon dioxide affords the triethylammonium salt of 2,4-dinitrophenylmalononitrile along with the related salt containing hexafluorosilicate anion.

Key words: 2,4-dinitrofluorobenzene, malononitrile, hexafluorosilicates, silicon dioxide.

As shown earlier,[1] triethylammonium salts of CH acids of type **1** are formed during the reaction between malononitrile or methyl cyanoacetate and 2,4-dinitrofluorobenzene (DNFB) in the presence of triethylamine (Scheme 1).

Scheme 1



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Such salts can be promising as electroactive materials[2] or used in synthesis of physiologically active compounds.[3] Unusual reactions of 2,4,6-trinitrofluorobenzene with cyano-containing carbanions proceeding at the N atoms of the cyano group have recently been described.[4,5] In the present work, we studied these transformations in more detail. It turned out that the reaction of malononitrile with DNFB in the presence of triethylamine (TEA) performed by a known procedure[1] (see Experimental) affords the expected salt **1** and also a small amount of salt **2** containing the SiF_6 fragment according to the X-ray structure data (Scheme 2).

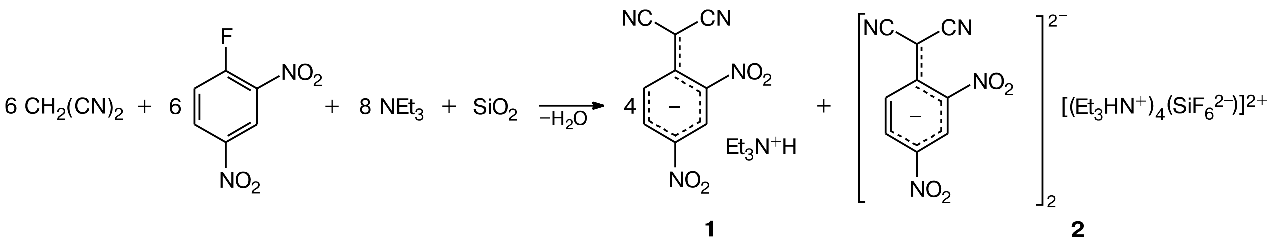
This unexpected result can be explained assuming that one of the reaction products (triethylamine fluorohydrate) reacts with the SiO_2 component of glass of the reaction vessel to form triethylammonium hexafluorosilicate **3** *via* Scheme 3.

A similar reaction of pyridine fluorohydrate with silica affording pyridinium hexafluorosilicate has been described.[6] The combining of salts **1** and **3** at the ratio 2 : 1 gives compound **2**.

To confirm these concepts, we carried out the model experiment (see Experimental) by introducing highly active silicon oxide (Aerosil 380) into the reaction mixture. Indeed, under these conditions, the yield of salt **2** increased to 23%, and the yield of product **1** was 53% (see Scheme 2).

The structure of salt **2** was determined by X-ray structure analysis. The spectral characteristics of salt **2** corre-

Scheme 2



1 **2**

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Table 1. Bond lengths and selected bond angles in the carbanionic part of salt **2**

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
C(1)—C(4)	1.423(5)	N(2)—O(3)	1.219(5)	C(3)—C(1)—C(4)	118.7(4)
C(4)—C(5)	1.400(5)	C(1)—C(2)	1.397(6)	C(5)—C(4)—C(9)	113.1(3)
C(4)—C(9)	1.438(5)	N(2)—O(4)	1.234(5)	C(6)—C(7)—C(8)	120.0(4)
C(9)—C(8)	1.337(6)	C(1)—C(3)	1.418(6)	C(2)—C(1)—C(4)	126.2(4)
C(8)—C(7)	1.398(6)	C(3)—N(4)	1.135(6)	C(4)—C(5)—C(6)	123.6(4)
C(2)—N(3)	1.144(6)	C(5)—N(1)	1.468(5)	C(9)—C(8)—C(7)	119.7(4)
C(7)—C(6)	1.358(5)	N(1)—O(1)	1.214(5)	C(2)—C(1)—C(3)	114.9(4)
C(6)—C(5)	1.388(5)	N(1)—O(2)	1.233(5)	C(5)—C(6)—C(7)	119.5(4)
C(7)—N(2)	1.439(5)			C(4)—C(9)—C(8)	123.9(4)

Scheme 3

$$6\ \mathrm{Et_3N \cdot HF} + \mathrm{SiO_2} \longrightarrow$$

$$\longrightarrow \underset{\mathbf{3}}{\mathrm{(Et_3NH)_2SiF_6}} + 4\ \mathrm{Et_3N} + 2\ \mathrm{H_2O}$$

spond to the spectra of triethylammonium salts of CH acids, whose anion has a system of conjugated bonds.[1,7] The structure of salt **2** consists of four triethylammonium cations, two 6-dicyanomethylidene-2,4-dinitrocyclohexadienide anions, and $\mathrm{SiF_6}^{2-}$ dianion.

The structure of the carbanionic part of salt **2** is shown in Fig. 1. The bond lengths and bond angles are given in Table 1. In similar salts, the negative charge of the carbanion is usually delocalized in the C_6 cycle,[1,7] resulting in the dearomatization of the benzene ring.

In this case, the C_6 cycle is distorted: the C(8)—C(9) double bond is localized (1.337(6) Å), the C(9)—C(4) bond is strongly elongated (1.438(5) Å), and the C(6)—C(7) bond is somewhat shortened (1.358(5) Å) compared to standard delocalized bonds in the benzene ring (1.40 Å). The intracyclic bond angles are also strongly distorted, especially those at the C(4), C(5), and C(9) atoms, which substantially differ from the standard values (120°). These data indicate the absence of full delocalization of bonds in the cycle, and delocalization is retained only in the C(4)—C(5)—C(6)—C(7) fragment.

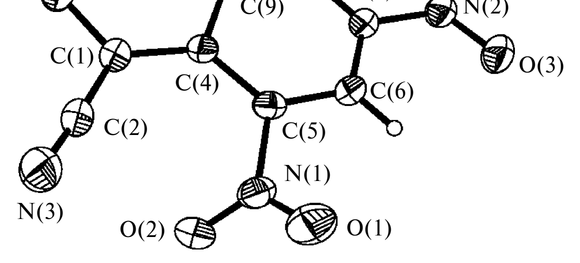

Fig. 1. Geometry of the carbanionic part in the crystal structure of salt **2**.

The C(1)—C(4) exocyclic bond ((1.423(5) Å)) is somewhat shorter than the standard C_{sp^2}—C_{sp^2} bond length (1.455 Å). The C—NO_2 bond lengths differ: the C(7)—N(2) bond is shortened compared to the C(5)—N(1) bond (1.439(5) and 1.468(5) Å, respectively). The nitro group just at the C(5) atom is withdrawn from conjugation with the cycle (turned at the C(5)—N(1) bond by an angle of 46.7°), unlike the nitro group at the C(7) atom, which is turned by 8.7° only. The $C(CN)_2$ group is nearly coplanar to the plane of the C_6 ring (turning angle 5.7°).

Thus, it can be concluded that distortions in a carbanion molecule involve predominantly the C(1)—C(4)—C(9)—C(8)—C(7)—C(6)—N(2) fragment are related, most likely, to the negative charge delocalization. This fragment is planar (deviations of the atoms ±0.02 Å), and the C(5) and N(1) atoms deviate from this plane by 0.11 and 0.38 Å, respectively.

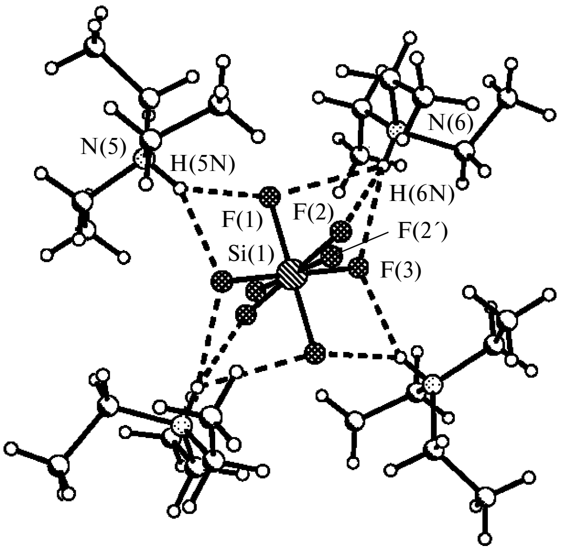

Fig. 2. Cation-anionic associates $\{\mathrm{SiF_6...(NHEt_3)_4}\}^{2+}$ formed by hydrogen bonds H...F (one fluorine atom is disordered over two positions F(2) and F(2′) with the site occupancy 0.5).

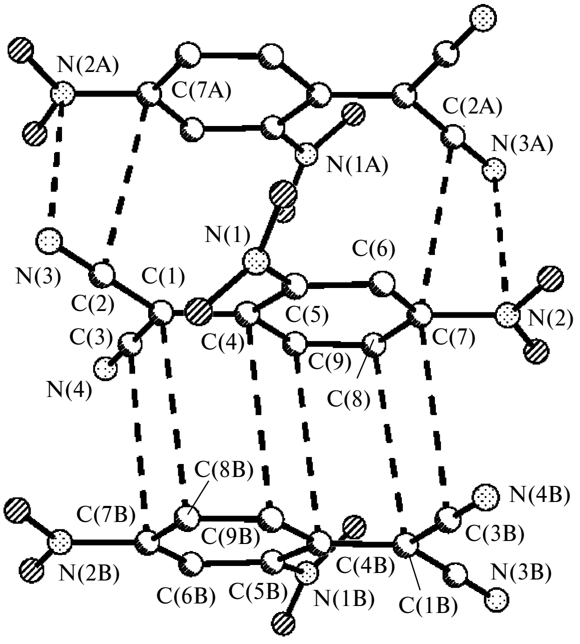

Fig. 3. Structure of carbanion stacks formed due to the π—π-stacking interaction.

In the crystal structure of salt **2**, the SiF_6^{2-} anion and Et_3N^+H cations form isolated centrosymmetric cation-anionic associates (Fig. 2) due to hydrogen bonds H...F (2.04(4)—2.42(4) Å).

Carbanions in the crystal structure of salt **2** are joined into negatively charged stacks due to the π—π-stacking interaction (Fig. 3). Dimerization is observed in the stacks, and the interplanar spacings in the "dimers" (3.37 Å) are substantially shorter than the distance between the "dimers" (3.61 Å).

The C_6 cycles in a stack are parallel to each other. Interestingly, the C(1)—C(4)—C(9)—C(8)—C(7)—N(2) fragment and both cyano groups (interplanar spacings C...C are 3.42 — 3.48 Å) predominantly participate in this interaction.

As a whole, the crystal structure of compound **2** is a packing of isolated anionic stacks and cation-anionic associates (Fig. 4).

In summary, the possibility of occurrence of side processes should be taken into account in the cases where fluorohydrates of tertiary amines, which are efficient fluorinating agents, are formed in the course of the main reaction.[8,9]

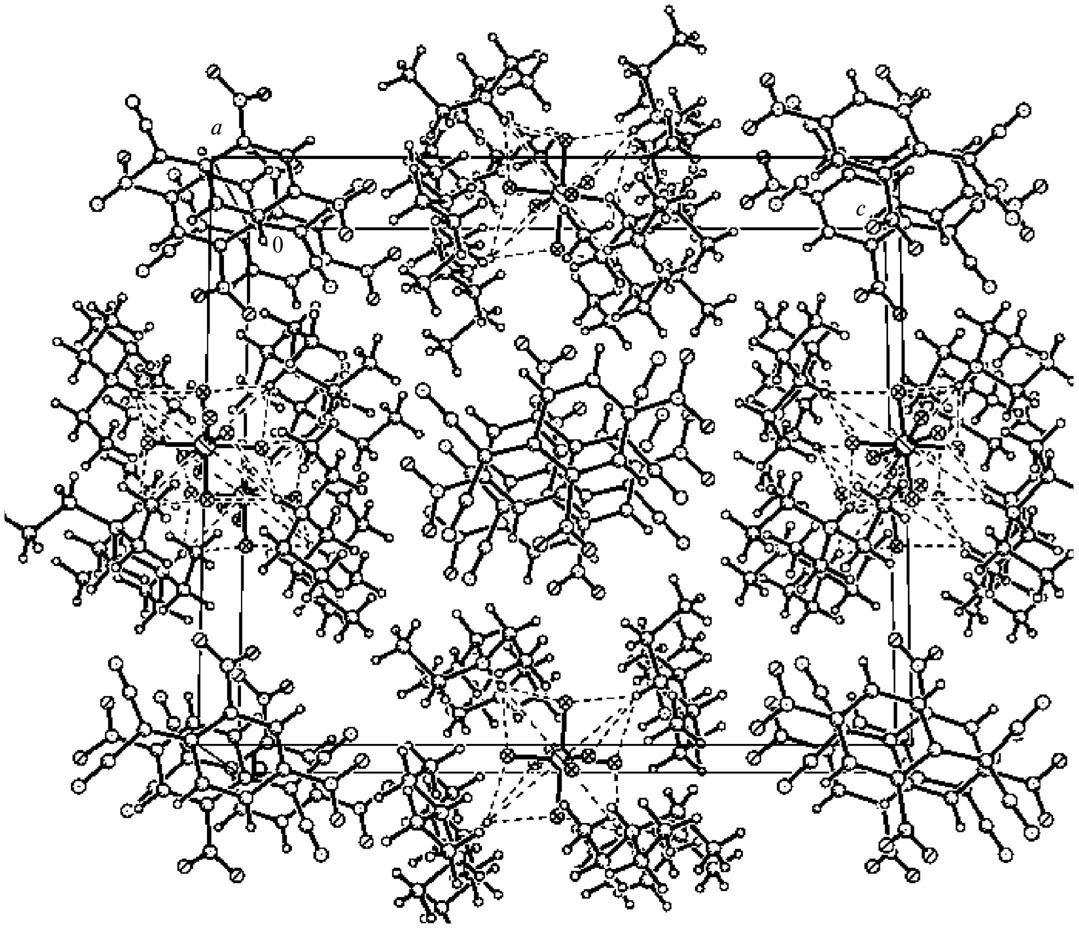

Fig. 4. Crystal structure of compound **2**.

Experimental

^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker Avance TM-400 spectrometer (working frequencies 400.1 (^{1}H), 100.68 (^{13}C), and 282.4 MHz (^{19}F)). IR spectra were measured on a Magna-IR-750 FTIR spectrometer (Nicolet). The reactions were carried out under an atmosphere of anhydrous nitrogen.

Compounds 1 and 2. ***A.*** A solution of TEA (1.45 g, 14 mmol) in diethyl ether (15 mL) was added dropwise to a solution of malononitrile (0.61 g, 9 mmol) and DNFB (1.71 g, 9 mmol) in diethyl ether (25 mL), and the mixture was kept for 2 days at 20 °C. The solvent was removed *in vacuo*, and the residue was dissolved in ethyl acetate. A diethyl ether—petroleum ether (1 : 1) mixture was added to the solution. After the solution was kept at 5 °C for 1 day, a copper-golden precipitate of compound **1** was formed in an amount of 0.96 g (32% yield), m.p. 84—86 °C (*cf.* Ref. 1: m.p. 84—86 °C). The filtrate was evaporated, the residue was dissolved in chloroform, and diethyl ether was added. As the solution was cooled, 4 mg of beet-red plates of compound **2** precipitated (m.p. 65—66 °C; according to the X-ray structure analysis data, the empirical formula is $C_{42}H_{70}F_6N_{12}O_8Si$).

B. Aerosil 380 (2.4 g, 40 mmol) and a solution of TEA (1 mL, 7 mmol) in acetonitrile (4 mL) were added to a solution of DNFB (0.81 g, 4.3 mmol) and malononitrile (0.29 g, 4.4 mmol) in anhydrous acetonitrile (6 mL), and the mixture was stirred for 3 h at 20 °C and kept at this temperature for 2.5 days. The mixture turned dark red. The precipitate was separated, the solvent was removed *in vacuo* from the filtrate, and the residue was treated as in entry ***A***. Compound **1** with m.p. 85—86 °C (0.51 g, 53%) and beet-red plates of compound **2b** with m.p. 64—66 °C (0.17 g, 23%) were obtained.

Triethylammonium 6-dicyanomethylidene-1,3-dinitrohexa-2,4-dien-1-ide (1). ^{13}C NMR, δ: 142.2, 138.6, 137.0 (C, C_6 cycle); 125.3, 123.6, 122.7 (C(H), C_6 cycle); 121.3 (CN); 40.0 ($\underline{C}(CN)_2$); 46.8 (CH_2); 8.6 (CH_3). The ^{1}H NMR spectrum is identical to that described earlier.[1]

Tetrakis(triethylammonium) bis(6-dicyanomethylidene-1,3-dinitrohexa-2,4-dien-1-ide) hexafluorosilicate (2). Found (%): C, 49.81; H, 6.91; N, 16,56; F, 11.07; Si, 2.54. $C_{42}H_{70}N_{12}F_6O_8Si$. Calculated (%): C, 49.74; H, 6.98; N, 16.57; F, 11.24; Si, 2.87. IR, ν/cm^{-1}: 2787 (NH$^+$); 2185, 2156 (CN); 1599, 1568 (C=C); 1310, 1270 (NO_2); 743 (SiF). ^{1}H NMR, δ: 8.42 (d, 1 H, H(6), J = 2.4 Hz); 7.84 (dd, 1 H, H(8), J = 2.4 Hz, J = 9.3 Hz); 7.25 (d, 1 H, H(9), J = 9.3 Hz); 3.13 (q, 12 H, CH_2, Et_3NH^+, J = 7.2 Hz), 1.31 (t, 18 H, Me, Et_3NH^+, J = 7.2 Hz). ^{13}C NMR, δ: 142.6, 138.4, 136.5 (C, C_6 cycle); 125.1, 123.5, 122.8 (C(H), C_6 cycle); 120.9 (CN); 41.1 ($\underline{C}(CN)_2$); 46.5 (CH_2), 8.3 (CH_3). ^{19}F NMR, δ: −126.2 (s, $J_{^{19}F-^{29}Si}$ = 112.3 Hz). Numbering of the protons is given according to Fig. 1.

X-ray diffraction study of compound 2. Plate-like crystals of compound **2**, $C_{42}H_{70}F_6N_{12}O_8Si$ (M = 1013.19) are red, monoclinic, at 295 K: a = 7.441(2) Å, b = 17.304(4) Å, c = 20.213(4) Å, β = 92.791(5)°, V = 2600(1) Å^3, space group $P2_1/n$, Z = 2, d_{calc} = 1.294 g cm^{-3}. An experimental array of 20 307 reflections was obtained on a Bruker SMART CCD area detector diffractometer at 295 K (Mo-Kα radiation, $2\theta_{max}$ = 63.84°) with a single crystal 0.55×0.40×0.20 mm in size. After averaging equivalent reflections, 5042 independent reflections (R_{int} = 0.0531) were obtained, which were used for structure determination and refinement. An absorption correction (μ = 0.126 mm^{-1}) was applied using the SADABS program,[10] and the transmission coefficients T_{max} and T_{min} were 0.975 and 0.945, respectively. The structure was solved by a direct method. All non-hydrogen atoms were localized in difference electron density syntheses and refined for F^2_{hkl} in the anisotropic approximation, and the hydrogen atoms of the NH groups were found in difference synthesis and refined in the isotropic approximation. Other hydrogen atoms were placed in geometrically calculated positions and refined by the riding model with U(H) = 1.2 U(C) (for methylene groups) and 1.5 (for methyl groups), where U(C) is the equivalent temperature factor of the carbon atom to which the corresponding H atom is bonded. The final values of the R factors are R_1 = 0.0752 (calculated by F_{hkl} for 3131 reflections with $I > 2\sigma(I)$), wR_2 = 0.1469 (calculated by F^2_{hkl} for all 5042 reflections), GOOF = 1.005, 330 refined parameters.

All calculations were performed using the SHELXTL PLUS 5 program package.[11]

The coordinates of atoms, bond lengths, bond and torsional angles, and anisotropic temperature parameters were deposited with the Cambridge Crystallographic Data Centre (CCDC 727566) and are available free of charge at www.ccdc.cam.uk/conts/retrieving.html.

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