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Structure of 1-Methylhydrazinium Trifluoroacetate, $CH_7N_2^+.C_2F_3O_2^-$

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Abstract. $M_r = 160.1$, monoclinic, $P2_1/c$, $a = 7.841$ (1), $b = 13.191$ (2), $c = 6.149$ (1) Å, $\beta = 92.80$ (1)°, $V = 635.2$ (2) Å^3, $Z = 4$, $D_x = 1.674$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 2.03$ cm^{-1}, $F(000) = 328$, $T = 150$ K, $R = 0.049$ for 1308 reflections. The crystal is built up of $[F_3CCOO]^-$ anions and $[H_2NN(H_2)CH_3]^+$ cations, linked by N—H···O hydrogen bonds to form zigzag chains along the c axis. Several interionic contacts are less than the sum of the van der Waals radii. The bond lengths and angles of both ions differ slightly from those of the uncharged compounds in the manner expected.

Introduction. An X-ray study of 1-methylhydrazinium trifluoroacetate (I) was carried out in order to investigate the peculiarities of crystal packing and the hydrogen-bond system in the crystal of this salt.

Experimental. Transparent plate-shaped single crystal, $0.4 \times 0.4 \times 0.1$ mm. Unit-cell parameters from 24 reflections with $32 \le 2\theta \le 34°$. 1607 reflections measured ($0 \le h \le 8$, $0 \le k \le 17$, $-10 \le l \le 10$). Syntex $P2_1$ diffractometer (graphite monochromator, $\theta/2\theta$

scan, $2\theta_{max} = 55°$). No significant variation in intensities of 2 standard reflections (400, 080) measured every 100 reflections. No absorption or secondary-extinction corrections. Structure solved by direct methods (MULTAN; Germain, Main & Woolfson, 1971), revealing all nonhydrogen atoms. Refinement by full-matrix least squares with anisotropic thermal parameters for nonhydrogen atoms. 1308 independent reflections with $I \ge 2\sigma(I)$. $\sum w(|F_o|-|F_c|)^2$ minimized; $w = 1/[\sigma^2(F_o) + |F_o|^2]$. Scattering factors from International Tables for X-ray Crystallography (1974). Hydrogen atoms located by difference synthesis, refined isotropically. Final $R = 0.049$, $wR = 0.044$, max. $(\Delta/\sigma) = 0.5$, final electron density fluctuations ± 0.4 e Å^{-3}. All calculations carried out with Eclipse S/200 computer using INEXTL programs (Gerr, Yanovsky & Struchkov, 1983).*

Discussion. The positional and thermal atomic parameters are listed in Table 1 and the atom numbering is given in Fig. 1, which shows the crystal structure of (I). Bond lengths, bond angles and torsion angles are given in Table 2. Table 3 lists non-bonded interatomic distances in the anion, short interionic distances and hydrogen-bond parameters.

The crystal is built up of $[F_3CCOO]^-$ anions and $[H_2NN(H_2)CH_3]^+$ cations. The trifluoroacetate anion has approximate C_s symmetry with the F(2), C(1) and C(2) atoms situated on the non-crystallographic mirror plane. The F—C distances of 1·319 (2), 1·347 (2) and 1·326 (2) Å are close to those observed in trifluoro-acetic acid [(II): 1·324 (4), 1·331 (4) and 1·340 (4) Å (Nahringbauer, Lundgren & Andersen, 1979)]. The FCF bond angles of 105·7 (1), 107·6 (3) and 105·9 (1)° are decreased in comparison with the tetrahedral value. In (II) the mean value of the FCF bond angles is also somewhat decreased (to 108·3°). Accordingly, the FCC bond angles of 113·6 (1), 109·8 (1) and 113·5 (1)° in (I) exceed the tetrahedral value [in (II) the mean FCC bond angle is 110·7°] and the smallest increase [to 109·8 (1)°] is observed for the F(2)-C(1)C(2) bond angle, involving F(2), which forms the longest bond with C(1). Such characteristic distortions of the C(1) coordination are a result of intramolecular non-bonded F···O interactions, which in the observed anion conformation (Table 3) least affect the F(2) atom.

The C(1)—C(2) bond length of 1·545 (2) Å is somewhat larger than 1·526 (4) Å in (II) and the standard value for the $C(sp^2)$—$C(sp^3)$ bond length of 1·510 (5) Å (Sutton, 1965). The C(2)—O(1) and C(2)—O(2) bond lengths of 1·245 (2) and 1·238 (2) Å are somewhat less than the standard value of the C—O distance 1·26 (1) Å in $[RCO_2]^-$ anions (Sutton, 1965) and intermediate between the greater and smaller C—O distances in non-ionized carboxylic groups, e.g. 1·303 (4) and 1·213 (4) Å in (II).
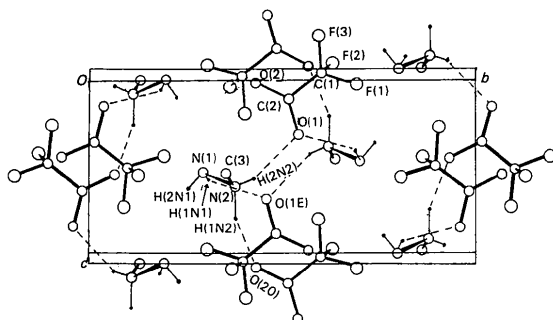

Fig. 1. *bc* projection of the crystal structure of (I). H atoms of the CH₃ groups are omitted. The N—H···O hydrogen bonds linking anions and cations into ribbons are shown by the dashed lines.

Table 1. *Atomic coordinates* ($\times 10^4$ *for nonhydrogen atoms,* $\times 10^3$ *for* H *atoms) and equivalent isotropic (for* H *atoms isotropic) temperature factors* ($Å^2$)

$$B_{eq} = \frac{1}{3}\sum_i\sum_j B_{ij}a_i^* a_j^* (\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	B_{iso}/B_{eq}
F(1)	2855 (2)	6932 (1)	430 (2)	3·16 (3)
F(2)	678 (2)	6019 (1)	−357 (2)	3·38 (3)
F(3)	2853 (2)	5935 (1)	−2307 (2)	2·95 (3)
O(1)	3335 (2)	5402 (1)	3172 (2)	2·04 (3)
O(2)	3244 (2)	4318 (1)	353 (2)	1·71 (3)
N(1)	4022 (2)	2976 (1)	5219 (2)	2·08 (4)
N(2)	2991 (2)	3805 (1)	5948 (2)	1·82 (3)
C(1)	2399 (2)	6021 (1)	−265 (3)	1·49 (4)
C(2)	3082 (2)	5155 (1)	1228 (2)	1·35 (3)
C(3)	1167 (3)	3562 (2)	5547 (2)	2·57 (5)
H(1N1)	514 (4)	330 (2)	553 (5)	4·9 (7)
H(2N1)	401 (4)	246 (2)	623 (5)	3·3 (7)
H(1N2)	313 (3)	395 (2)	738 (3)	2·1 (4)
H(2N2)	311 (3)	431 (2)	519 (4)	2·3 (5)
H(1C3)	83 (3)	351 (2)	410 (4)	3·1 (5)
H(2C3)	89 (5)	297 (3)	624 (6)	5·3 (8)
H(3C3)	43 (5)	411 (3)	604 (6)	4·9 (8)

Table 2. *Bond distances* (Å), *bond angles* (°) *and torsion angles* (°)

C(1)—F(1)	1·319 (2)	C(2)—O(1)	1·245 (2)
C(1)—F(2)	1·347 (2)	C(2)—O(2)	1·238 (2)
C(1)—F(3)	1·326 (2)	N(1)—N(2)	1·444 (2)
C(1)—C(2)	1·545 (2)	N(2)—C(3)	1·475 (3)

F(1)C(1)F(2)	105·7 (1)	F(3)C(1)C(2)	113·5 (1)
F(1)C(1)F(3)	107·6 (3)	O(1)C(2)O(2)	129·5 (2)
F(2)C(1)F(3)	105·9 (1)	O(1)C(2)C(1)	114·3 (1)
F(1)C(1)C(2)	113·6 (1)	O(2)C(2)C(1)	116·2 (1)
F(2)C(1)C(2)	109·8 (1)	N(1)N(2)C(3)	109·7 (1)

F(1)C(1)C(2)O(1)	−27·4 (2)
F(2)C(1)C(2)O(1)	90·8 (2)
F(3)C(1)C(2)O(1)	−150·7 (2)

Table 3. *Non-bonded distances in the anion* (Å), *short interionic distances* (Å) *and hydrogen-bond parameters* (Å, °)

F(1)···O(1)	2·645 (2)*	F(2)···O(2)	3·031 (2)
F(1)···O(2)	3·462 (2)	F(3)···O(1)	3·444 (2)
F(2)···O(1)	3·044 (2)	F(3)···O(2)	2·697 (2)*

F(1)···N(1ⁱ)	2·854 (2)	F(3)···N(2ⁱⁱ)	3·012 (2)
F(1)···H(1N1ⁱ)	2·48 (3)	F(3)···H(1N2ⁱⁱ)	2·64 (3)
F(3)···O(1ⁱⁱ)	2·910 (2)	F(3)···H(2N2ⁱⁱ)	2·65 (3)
O(2)···H(2N1ⁱⁱⁱ)	2·47 (3)		

N(2)···O(1)	2·733 (2)	N(2)···O(2ⁱᵛ)	2·790 (2)
H(2N2)···O(1)	1·91 (2)	H(1N2)···O(2ⁱᵛ)	1·89 (2)
N(2)H(2N2)O(1)	175 (2)	N(2)H(1N2)O(2ⁱᵛ)	176 (3)

N(1)···O(1ᵛ)	3·107 (2)		
H(1N1)···O(1ᵛ)	2·22 (3)		
N(1)H(1N1)O(1ᵛ)	150 (2)		

Symmetry transformations: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $x, y, z - 1$; (iii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $x, y, z + 1$; (v) $1 - x, 1 - y, 1 - z$.

* Short compared with the sum of van der Waals radii of 2·99 Å (Bondi, 1964).

The N—N ordinary bond length of 1·444 (2) Å in the 1-methylhydrazinium cation in (I) is shorter than the corresponding distance of 1·463 (3) Å in 1,1,1-trimethylhydrazinium chloride [(III), Giordano, Palenik & Sisler, 1976]. The C—N bond length of 1·475 (3) Å is shorter than the average C—N bond length of 1·494 (4) Å in (III), but coincides with the standard value of 1·479 (5) Å (Sutton, 1965).

The N(2)—H(2N2)···O(1) and N(2)—H(1N2)··· O(2^{iv}) hydrogen bonds (Table 3) link alternating anions and cations in infinite zigzag chains along the c axis. These chains are joined pairwise into ribbons via the weaker N(1)—H(1N1)···O(1^v) hydrogen bonds (Fig. 1). The fourth active hydrogen atom H(2N1) of the cation forms a close contact with the O(2^{iii}) atom in the adjacent ribbon. However, the angle N(1)H(2N1)-O(2^{iii}) of 124 (2)° is unfavourable for an N(1)—H(2N1)···O(2^{iii}) hydrogen bond, although the H(2N1)···O(2^{iii}) distance of 2·47 (3) Å allows such interaction.

In the crystal of (I) there are also a number of F···N and F···H interionic contacts (Table 3) shorter than the sums of the van der Waals radii of 3·02 and 2·67 Å, respectively (Bondi, 1964). However, the values of the angles N(1)H(1N1)F(1), 104 (1)°, N(2)-H(1N2)F(3), 107 (1)°, and N(2)H(2N2)F(3), 108 (1)°, do not suggest the presence of N—H···F hydrogen bonding.

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Détermination Structurale à 205 K du Monomère Bis[(o-méthoxyphényl)carbamate] de Hexadiyne-2,4 Diyle-1,6, C22H20N2O6

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Abstract. $M_r = 408·4$, orthorhombic, Pbca, $a = 21·051$ (3), $b = 8·281$ (3), $c = 11·364$ (1) Å, $V = 1981$ (1) Å^3, $Z = 4$, $D_x = 1·37$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1·54178$ Å, $\mu = 0·82$ mm^{-1}, $F(000) = 856$, $T = 205$ K, $R = 0·050$ for 1225 hkl with $F_o \geq \sigma(F_o)$. There are no unusual bond distances or angles. The absence of solid-state reactivity in this compound is clearly explained by the crystal packing. The intermolecular cohesion is assured only by van der Waals contacts.

Introduction. La plupart des composés diacétyléniques R—C≡C—C≡C—R ont la propriété de se polymériser à l'état cristallin, soit thermiquement, soit sous irradiation (γ, UV, X) par 1,4 trans–trans addition (Wegner, 1972). Des problèmes stériques liés à la nature du radical R ou à l'empilement des chaînes diacétyléniques peuvent faire obstacle à cette polymérisation. Il semble que ce soit le cas du bis[(o-méthoxyphényl)-carbamate] de hexadiyne-2,4 diyle-1,6 ($R = -CH_2-O-CONHC_6H_4OCH_3$). En effet, ce composé, appelé également HDoMPU [soit hexadiyne-2,4 bis(o-methoxyphényluréthane)-1,6] est inactif puisque ses cristaux restent incolores sous irradiation X (Patel, Duesler, Curtin & Paul, 1980). La détermination structurale doit permettre d'expliquer son inactivité; cette étude a été effectuée à 205 K uniquement pour limiter les effets de l'agitation thermique.

Partie expérimentale. Composé préparé par G. N. Patel,* recristallisation dans éthanol, plaquette 0,03 × 0,15 × 0,18 mm; étude à 205 K; diffractomètre Philips PW 1100, monochromateur graphite; refroidissement par jet d'azote gazeux; méthode 'flying step-scan'; 1320

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