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Sarcosinium trifluoroacetate

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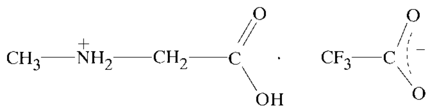
The title compound, $C_3H_8NO_2^+\cdot C_2F_3O_2^-$, crystallizes in space group *C*2/*c*. The main N—C—COOH skeleton of the protonated sarcosine molecule is almost perfectly planar. The trifluoroacetate anion has a staggered conformation and typical bond distances and angles. The CF_3 group is probably slightly disordered. The structure is stabilized by an extensive network of strong O—H···O hydrogen bonds and weaker N—H···O bonds.

Comment

Sarcosine (*N*-methylglycine, $CH_3NH_2^+CH_2COO^-$) is an α-amino acid found in many biological materials and also used in cosmetics (Meister, 1965).

In its pure form, sarcosine exists as a zwitterion, where the carboxylic acid proton has been transferred to the amino group. Like most amino acids, sarcosine has an amphoteric character, being able to accept a proton at the carboxylate group from even moderately weak acids, and to donate the amino proton in basic environments. The anionic form of sarcosine is a well known chelating agent of 3*d* and 4*d* transition metals (Guha, 1973; Krishnakumar *et al.*, 1994; Darensbourg *et al.*, 1994). On the other hand, structural data for compounds where sarcosine is in the cationic form are rather scarce.

Our main interest in sarcosine compounds relates to their physical properties. The best known sarcosine compound, tris(sarcosine) calcium chloride (TSCC), undergoes a ferroelectric transition at T_c = 127 K (Pepinsky & Makita, 1962). Its crystal structure both in the paraelectric phase at room temperature (Ashida *et al.*, 1972) and in the ferroelectric phase (Mishima *et al.*, 1984) has been reported. Another closely related compound which also shows a 'devil stair' series of phase transitions is betaine (trimethylglycine) calcium chloride (BCCD) (Almeida *et al.*, 1992). A number of simple salts of betaine show ferroelectric or antiferroelectric phase transitions at low temperature, as well as ferroelastic behaviour inducing phase transitions to both commensurate and incommensurate superstructures (Shildkamp & Spilker, 1984; Haussül, 1984, 1988). Therefore, it is reasonable to expect that simple salts of sarcosine also show interesting properties at low temperature. Trifluoroacetic acid is a very strong carboxylic acid due to the charge-withdrawing effect of the F atoms on the C_α atom. Its dissociation constant is K = 0.66 mol dm^{-3} (Strehlow & Hildebrandt, 1990), as determined by Raman spectroscopy. Phase transitions at low temperature in crystalline trifluoroacetic acid tetrahydrate have been recently discovered for undeuterated and deuterated samples (Mootz & Schilling, 1992). Thus, sarcosinium trifluoroacetate, (I) (Fig. 1), is expected to be a good candidate to exhibit phase transitions and superstructures at low temperature. This is the first report of a research project on a systematic study of the structural and physical properties of sarcosine compounds. The present study, performed at room temperature, will be completed by other low-temperature structural and spectroscopic studies.



(I)

The ionization states of the sarcosine and trifluoroacetic acid molecules were determined from the objective localization of the H atoms bonded to the carboxylic acid groups but could easily be inferred from the bond distances within these groups. The sarcosine molecule exists in a cationic form with a mono-positively charged amino group and a neutral carboxylic group, in agreement with the large asymmetry between the C—O bond lengths of this functional group. The trifluoroacetate molecules are found in the ionized state, as expected from the strength of the acid and the required charge neutrality of the salt.

The sarcosine carboxy skeleton, which includes atoms O1, O2, C1 and C2, is planar within 0.0015 (13) Å. The N atom is slightly displaced out of this plane by −0.0557 (30) Å, corresponding to a small rotation around the single C1—C2 bond.

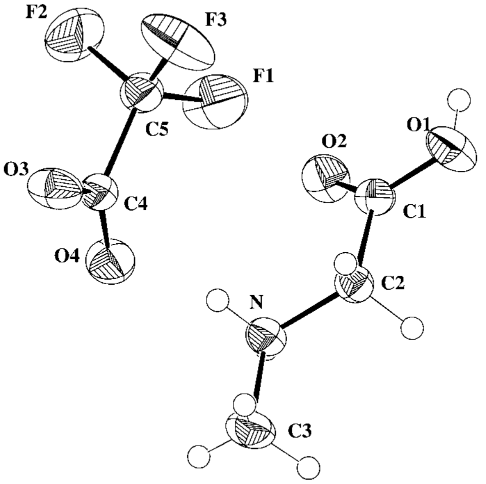


Figure 1
*ORTEP*II (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

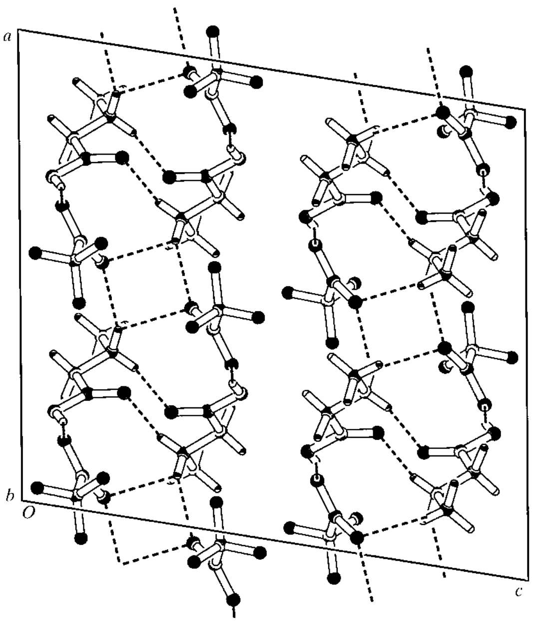


Figure 2
Projection of the structure along the *b* axis showing the hydrogen bonds as dashed lines.

The relevant torsion angles are O1—C1—C2—N [177.75 (14)°] and O2—C1—C2—N [−2.5 (2)°]. These values can be compared with the corresponding ones in pure sarcosine, 173.7 (2) and −6.8 (2)°, respectively (Mostad & Natarajan, 1989), which is more distorted from planarity. The methyl group breaks the almost perfect planarity of the main chain. The torsion angle C1—C2—N—C3 is 172.39 (14)° and the C3 atom is 0.1256 (46) Å away from the plane, in the opposite direction to the N atom. This deviation of the methyl group from the plane of the main skeleton is, however, smaller than that observed in pure sarcosine for which the torsion angle is −166.3° (Mostad & Natarajan, 1989).

The trifluoroacetate anion has a staggered conformation, as indicated by the torsion angle O4—C4—C5—F1 of −24.4 (3)°. The geometry of the CF_3 group is similar to that found in other structures (Nahringbauer *et al.*, 1979), with an average C—F bond length and an F—C—F angle of 1.32 (12) Å and 106 (2)°, respectively. The average F—C—C angle is 112 (1)°. The carboxylate group of the anion is planar within 0.0065 (14) Å; the C4—C5 bond length [1.539 (2) Å] is longer than the average C*sp*^{3}—C*sp*^{2} bond, but is within the normal range of values found in trifluoroacetic acid and trifluoroacetate compounds (Lundgren, 1978).

It should be pointed out that the atomic displacement tensors of the F atoms have a strong anisotropic character which indicates some disorder, probably of dynamic nature, of these atoms. As is often found in trifluoroacetate compounds, it is plausible that at room temperature the CF_3 groups rotate undergoing angular oscillations around the single C—C bond. Such a minor disorder may account for the relatively large final *R* and *wR* values.

The sarcosine cations interact directly, *via* hydrogen bonds, with two neighbouring sarcosine molecules and three trifluoroacetate anions (Fig. 2). The N atom is only bonded to two H atoms but is engaged in three hydrogen bonds as a donor. One of the two H atoms is shared between two carboxylate O atoms of two distinct trifluoroacetate anions in a bifurcated hydrogen bond. The other H atom is shared with the unprotonated O atom of another sarcosine molecule. The N—H···O distances and angles are in the ranges 2.880 (2)–2.919 (2) Å and 121 (3)–146 (3)°, respectively, which allows a classification of these hydrogen bonds as relatively weak.

The strongest hydrogen bond in the title compound involves the carboxylic O atom of the cation as a donor and a carboxylate O atom of the anion as an acceptor [O—H···O 2.575 (2) Å and O—H—O 163 (4)°].

Like other carboxylic acid complexes *viz.* D-tryptophan hydrogen oxalate (Bakke & Mostad, 1980), and L-histidine oxalate and DL-histidine oxalate (Prabu *et al.*, 1996), the present compound has no solvate molecules, in contrast with the more closely related complex sarcosine hydrogen oxalate (Krishnakumar *et al.*, 1998).

Experimental

Large colourless crystals of tabular form were obtained after one-day evaporation of the solution obtained from adding an excess of trifluoroacetic acid (Aldrich, 99%) directly to pure sarcosine (1 g), as purchased from Aldrich (98%). Most of these crystals were too big to be used on the X-ray diffractometer and had to be cut. However, twinned crystals were systematically obtained under application of pressure. Therefore, a small single-crystal cast as grown from the solution was used and checked prior to data collection by photographic methods.

Crystal data

$C_3H_8NO_2^+\cdot C_2F_3O_2^-$
$M_r = 203.118$
Monoclinic, $C2/c$
$a = 14.5912$ (19) Å
$b = 7.0951$ (11) Å
$c = 15.8414$ (13) Å
$\beta = 99.138$ (8)°
$V = 1619.2$ (4) Å^3
$Z = 8$
$D_x = 1.666$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.08$–18.00°
$\mu = 0.181$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.45 × 0.40 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
2462 measured reflections
2350 independent reflections
1883 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.011$
$\theta_{\rm max} = 30.01°$
$h = 0 \rightarrow 20$
$k = 0 \rightarrow 9$
$l = -22 \rightarrow 22$
3 standard reflections
frequency: 180 min
intensity decay: 10%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.179$
$S = 1.038$
2350 reflections
150 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.1088P)^2 + 1.4397P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.63$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.38$ e Å^{-3}

All H atoms were located on a difference Fourier map and refined isotropically [C—H 0.87 (4)–1.00 (3) Å]. Examination of the crystal structure with *PLATON* (Spek, 1995) showed that there are no solvent-accessible voids in the crystal lattice.

Table 1
Selected geometric parameters (Å, °).

C1—O2	1.204 (2)	C4—O3	1.245 (2)
C1—O1	1.300 (2)	C4—C5	1.538 (2)
C1—C2	1.512 (2)	C5—F2	1.314 (2)
C2—N	1.470 (2)	C5—F1	1.319 (2)
N—C3	1.484 (2)	C5—F3	1.331 (3)
C4—O4	1.227 (2)		
O2—C1—O1	126.80 (16)	O4—C4—O3	129.71 (16)
O2—C1—C2—N	−2.5 (2)	C1—C2—N—C3	172.39 (14)
O1—C1—C2—N	177.75 (14)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1—H1⋯O3^{i}	0.84 (4)	1.76 (4)	2.575 (2)	163 (4)
N—H4⋯O2^{ii}	0.85 (3)	2.14 (3)	2.880 (2)	146 (3)
N—H5⋯O4^{iii}	0.84 (3)	2.40 (3)	2.918 (2)	121 (3)
N—H5⋯O4	0.84 (3)	2.18 (3)	2.885 (2)	141 (3)

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

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1378). Services for accessing these data are described at the back of the journal.

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