Betainium trifluoroacetate

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The title compound, $C_5H_{12}NO_2^+ \cdot C_2F_3O_2^-$ or $BET^+ \cdot CF_3COO^-$ [BET is trimethylglycine (betaine); IUPAC: 1-carboxy-N,N,N-trimethylmethanaminium inner salt], contains pairs of betainium and trifluoroacetate ions forming a dimer bridged by a strong hydrogen bond between the carboxyl and carboxylate groups of the two ions. The molecular symmetry of the cation is close to C_s, with protonation occurring at the carboxy O atom positioned *anti* to the N atom. The trifluoroacetate anions are disordered over two positions. In one, the conformation of the CF_3 group is staggered with respect to the carboxylate group, in the other, it is close to an eclipsed conformation. The sole hydrogen bond present in the structure is the strong $O-H \cdots O$ bond between the anion and the cation.

Comment

Betaine (trimethylglycine) is a naturally occurring compound present in many biological systems, where it acts as a *trans*-methylating agent in the synthesis of lipids and also as an osmoprotector and osmoregulator. It can be obtained in large concentrations as a by-product of sugar processing. The betaine molecule is an inner salt (zwitterion) where the carboxylate and trimethylammonium groups carry a negative and positive charge, respectively. The molecule has a large proton affinity and can be easily combined with even weak acids to form 1:1 and 2:1 betainium salts. Several adducts of betaine with inorganic salts, *e.g.* KBr, have also been synthesized. Betaine can act as a chelating agent, *via* the carboxy group, of many *d* and *f* metals. Several betaine salts and adducts exhibit low-temperature phase transitions associated with ferroelectric, antiferroelectric and ferroelastic behaviour, as well as commensurate and incommensurate superstructures (Shildkamp & Spilker, 1984; Haussühl, 1984, 1988). The betaine compound known as BCCD (betaine calcium chloride dihydrate) has been much studied because it exhibits a series of phase transitions chained in a 'devil stair' sequence (Almeida *et al.*, 1992). Other compounds attracting much attention are the isostructural ferroelectric betaine phosphite and antiferroelectric betaine phosphate which form solid solutions over an extended composition range (Andrade *et al.*,

1999; Banys *et al.*, 2000). The crystal structures of betaine hydrate (Mak, 1990) and its salts of hydrogen chloride (Fischer *et al.*, 1970; Mak & Chen, 1990), and phosphoric (Shildkamp & Spilker, 1984), sulfuric (Ratajczak *et al.*, 1994), arsenic (Shildkamp *et al.*, 1984), boric (Zobetz & Preisinger, 1989), telluric (Ilczyszyn *et al.*, 1992), maleic (Ilczyszyn *et al.*, 1995), nitric (Baran, Drozd, Glowiak *et al.*, 1995), selenic (Baran, Drozd, Lis *et al.*, 1995; Baran *et al.*, 1997) and selenous acids (Paixão *et al.*, 1997) are reported in the October 2000 release of the Cambridge Structural Database (Allen & Kennard, 1993).

Very recently the crystal structures of anhydrous betaine (Viertorinne *et al.*, 1999), betainium trichloroacetate (Baran *et al.*, 2000), perchlorate (Matos Beja *et al.*, 2000) and betaine-betainium hydrogen oxalate hydrate (Rodrigues *et al.*, 2001a) have been reported. In the trichloroacetate salt, two reversible low-temperature phase transitions at 177 and 187 K were resolved in both differential scanning calorimetry (DSC) and temperature-dependent FT–IR measurements, one of them having been also detected by powder diffraction. Furthermore, the FT–IR data suggest that a further transition below 100 K possibly exists (Baran *et al.*, 2000).

The present work represents an effort to find other compounds of N-methylated glycine derivatives which may feature similar interesting physical properties. Motivated by the results reported for betainium trichloroacetate, we have decided to synthesize and investigate the structure and physical properties of the trifluoroacetate salts. Trifluoroacetic acid (TFA) 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 on crystalline trifluoroacetic acid tetrahydrate itself have been discovered for undeuterated and deuterated samples (Mootz & Schilling, 1992). Thus, betainium trifluoroacetate is expected to be a good candidate to exhibit phase transitions and, possibly, superstructures at low temperature. We have already determined the crystal structures of sarcosinium trifluoroacetate (Rodrigues *et al.*, 2000) and dimethylglycinium trifluoroacetate (Rodrigues *et al.*, 2001b). Further studies of these trifluoroacetate salts including dielectric measurements, DSC calorimetry, low-temperature X-ray diffraction and spectroscopic measurements will be reported elsewhere.


(I)
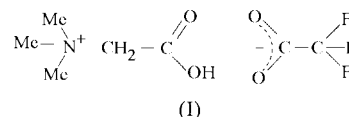
The title compound, (I), contains a protonated betaine molecule counterbalanced by a disordered trifluoroacetate anion (Fig. 1). The ionization states of both betaine and TFA acid molecules were determined from the localization of the H atom bonded to the carboxyl group of betaine, which was clearly seen on a difference Fourier map, but could also be inferred from an inspection of the $C-O$ bond distances. These are highly asymmetric [1.193 (2) and 1.299 (2) Å], corre-

sponding to a well ordered carboxylic acid group. It is interesting to note that protonation occurs at the carboxy O atom which is in the *anti* position with respect to the N atom. In a recently reported *ab initio* study of betainium dimer complexes (Zhu & Lifshitz, 2000), protonation at the *anti* position of an isolated betaine molecule was found to be more stable by 16.2 kJ mol^{-1} than at the *syn* position. For the betainium/NH$_3$ complex, protonation at the *anti* position is 12.1 kJ mol^{-1} lower in energy than at the *syn* position, the *anti*- and *syn*-isomers being separated by a transition state with an energy barrier of 17.2 kJ mol^{-1}.

Previous studies have shown that the betaine molecule has some degree of conformational flexibility depending on the crystalline environment. However, in the title compound, the symmetry does not deviate much from the ideal C_s symmetry of an isolated molecule. The main carboxy skeleton of the protonated betaine molecule is planar within 0.002 (2) Å. The C3 and C4 methyl groups are placed in almost symmetrical positions with respect to the least-squares plane passing through the molecule backbone. Atoms N and C5 are not strictly coplanar with the carboxyl group; they deviate from the least-squares plane by 0.076 (3) and 0.143 (5) Å, respectively. These small displacements arise from a small rotation of the carboxyl and trimethylammonium groups around bonds C1—C2 and C2—N of −2.7 (3) and 3.07 (16)°, respectively, as shown by inspection of the appropriate torsion angles. These twist angles are comparable with those of betaine monohydrate; in the anhydrous crystalline form, the molecule has perfect crystallographically imposed C_s symmetry (Viertorinne *et al.*, 1999). Larger twist angles, exceeding 20° for the carboxyl and 7° for the trimethylammonium group, were found in other betainium compounds (Matos Beja *et al.*, 2000; Rodrigues *et al.*, 2001a). The N—C2—C1 angle [116.12 (13)°] is larger than the expected tetrahedral angle of 109.5°, a feature also observed in other betainium compounds as well as in the neutral molecule.

The trifluoroacetate anions are disordered over two positions with an occupancy ratio of 0.62:0.38 (2). The two disordered ions are related by a rotation of the CF$_3$ group by 18 (2)° and a counter-rotation of the carboxylate group around the central C6—C7 bond by −25 (2)°. In the major fraction, the conformation of the CF$_3$ group is staggered, whereas in the minor fraction, one of the F atoms almost eclipses the carboxylate group, as can be seen by an inspection of the torsion angles. In both cases, the anion establishes a strong hydrogen bond with the carboxylate group of the same neighbour betainium
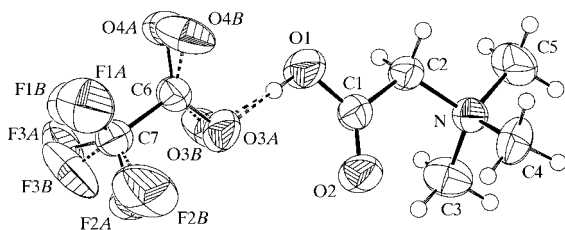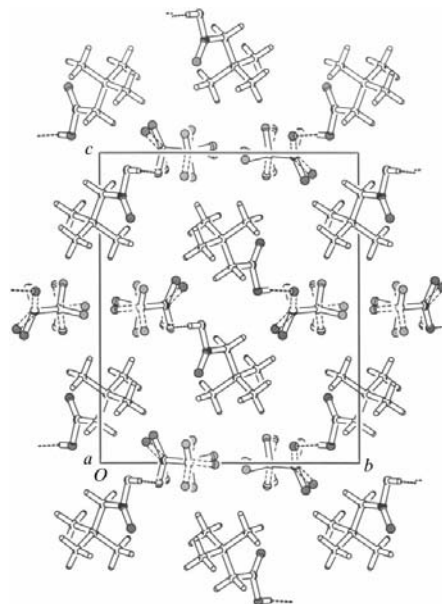
cation, as shown in Fig. 1, with O1···O3A and O1···O3B distances of 2.565 (8) and 2.488 (14) Å. It is not unusual for the trifluoroacetate anion to be disordered over two rotational conformers, and such a disorder also occurs in the structure of perdeuterated trifluoroacetic acid tetrahydrate. However, when the carboxylate group is engaged in strong hydrogen bonding, such as in the present case, this disorder usually affects the CF$_3$ groups only, the carboxylate group remaining undisordered, anchored by the hydrogen bonds. It is an interesting feature of the title compound that interconversion between the two rotamers is accomplished by a concerted rotation of the carboxylate and CF$_3$ groups. In the trichloroacetate compound, the anions are also found to be disordered and such disorder was found to play a major role in the phase transitions occurring at low temperature (Baran *et al.*, 2000). Therefore, similar phase transitions are likely to occur in the trifluoroacetate salt as well. In the closely related compounds sarcosinium and dimethylglycinium trifluoroacetate, the anions were not found to be disordered as a whole, although the anisotropy of the displacement tensors of the F atoms pointed to some minor static disorder of the CF$_3$ groups or that these groups are rotating, undergoing small angular oscillations around the single C—C bond at room temperature. It should be remarked that although the C6—C7 bond length [1.529 (2) Å] is longer than average for a Csp^3—Csp^2 bond, it is nevertheless within the range of values normally found in trifluoroacetate salts (Lundgren, 1978).

The packing diagram of the structure is shown in Fig. 2. The sole hydrogen bond present in the structure is the strong bond linking the betainium–trifluoroacetate dimers. Inspection of the intermolecular distances shows that there are no C···O close contacts with appropriate geometry to be classified as weak hydrogen bonds. As usual, the F atoms are not actively engaged in hydrogen bonding and no relevant short contacts involving these atoms were found in the structure. This is in agreement with a recent study based on a statistical survey of

Figure 1
*ORTEP*II (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

Figure 2
Packing diagram viewed along the *a* axis.

the Cambridge Structural Database (Dunitz & Taylor, 1997), which shows that the neutral F atom seldom participates in hydrogen bonding, in contrast with the fluorine anion, which often acts as a hydrogen-bond acceptor.

Experimental

Small colourless crystals of block form were obtained after one day on evaporation of the solution obtained from adding an excess of trifluoroacetic acid (Aldrich, 99%) directly to pure betaine (1 g) as purchased from Aldrich (98%). A suitable crystal was selected and checked by photographic methods before the data collection.

Crystal data

$C_5H_{12}NO_2^+\cdot C_2F_3O_2^-$
$M_r = 231.18$
Monoclinic, $P2_1/c$
$a = 6.088 (2)$ Å
$b = 11.9486 (15)$ Å
$c = 15.022 (12)$ Å
$\beta = 107.54 (4)°$
$V = 1041.9 (9)$ Å^3
$Z = 4$

$D_x = 1.474$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.8–15.2°$
$\mu = 0.15$ mm^{-1}
$T = 293 (2)$ K
Block, colourless
$0.33 \times 0.27 \times 0.25$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω–2θ scans
2588 measured reflections
2371 independent reflections
1735 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$

$\theta_{max} = 27.5°$
$h = 0 \rightarrow 7$
$k = -15 \rightarrow 0$
$l = -19 \rightarrow 18$
3 standard reflections
  frequency: 180 min
  intensity decay: 4.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.124$
$S = 1.03$
2371 reflections
190 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2 + 0.3392P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.14$ e Å^{-3}
Extinction correction: SHELXL97
Extinction coefficient: 0.017 (4)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.298 (2)	C6—C7	1.529 (2)
O2—C1	1.193 (2)		
N—C2—C1	116.12 (13)		
C4—N—C2—C1	−58.52 (19)	C5—N—C2—C1	−176.96 (16)
C3—N—C2—C1	64.70 (19)	O2—C1—C2—N	−2.7 (3)

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O1—H1$\cdots$O3A	0.88 (4)	1.68 (4)	2.565 (8)	175 (3)
O1—H1$\cdots$O3B	0.88 (4)	1.62 (4)	2.488 (14)	168 (3)

All H atoms were located on a difference Fourier map; those bonded to C atoms were placed at idealized positions and refined as riding. The H atom attached to the betaine carboxyl group involved in the intra-dimer hydrogen bond was freely refined isotropically. The anisotropic displacement parameters of the F atoms were restrained with a DELU instruction.

Data collection: CAD-4 Software (Enraf–Nonius, 1989); cell refinement: CAD-4 Software; data reduction: HELENA (Spek, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976).

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