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Glycinium trifluoroacetate

V. H. Rodrigues,* J. A. Paixão, M. M. R. R. Costa and A. Matos Beja

Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, P-3000 Coimbra, Portugal
Correspondence e-mail: vhugo@pollux.fis.uc.pt

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In the title compound, $C_2H_6NO_2^+\cdot C_2F_3O_2^-$, the main N—C—COOH skeleton of the glycinium cation is almost perfectly planar. The trifluoroacetate anion has a staggered conformation with typical bond distances and angles. The CF_3 group is slightly disordered. The structure is stabilized by an extensive network of strong O—H···O hydrogen bonds and weaker N—H···O bonds.

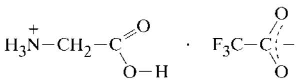
Comment

Glycine (aminoethanoic acid) is the simplest amino acid and is the only amino acid that is not optically active (it has no stereoisomers). This amino acid is essential for the biosynthesis of nucleic acids, as well as the biosynthesis of bile acids, porphyrins, creatine phosphate and other amino acids. On a molar basis, glycine is the second most common amino acid found in proteins and enzymes, being incorporated at a rate of 7.5% compared with the other amino acids. Glycine is also similar to γ-aminobutyric acid and glutamic acid in its ability to inhibit neurotransmitter signals in the central nervous system. Glycine systems may be important in controlling epilepsy and other central nervous system disorders.

In its pure form, glycine exists as a zwitterion, with the carboxyl H atom transferred to the amino group. In common with most amino acids, glycine has an amphoteric character, being able to accept an H atom at the carboxylate group from even moderately weak acids and donate the amino H atom in basic environments. Anionic glycine chelates 3*d* and 4*d* transition metals.

Our main interest in glycine compounds relates to their physical properties. The most well known glycine compounds are those that undergo ferroelectric transitions. Other closely related compounds, which also show phase transitions, are simple salts of sarcosine (*N*-methylglycine) and betaine (*N*,*N*,*N*-trimethylglycine). Therefore, it would be reasonable to expect that simple salts of glycine, sarcosine or betaine also show interesting properties at low temperature; however, many of them do not.

Trifluoroacetic acid is a very strong carboxylic acid, due to the charge-withdrawing effect of the F atoms on the C_α carbon. Its dissociation constant is $K = 0.66\ \mathrm{mol\ dm^{-3}}$ (Strehlow & Hildebrandt, 1990), as determined by Raman spectroscopy. Phase transitions in crystalline trifluoroacetic acid tetrahydrate at low temperature have recently been observed for both deuterated and non-deuterated samples (Mootz & Schilling, 1992).



$$\mathrm{H_3\overset{+}{N}-CH_2-C(=O)-O-H}\ \cdot\ \mathrm{F_3C-C(\overset{\cdots}{O})(\overset{\cdots}{O})^{-}}$$

(I)

The present study of glycinium trifluoroacetate, (I), performed at room temperature, completes a series of structural investigations. The crystal structures of sarcosine, dimethylglycine and betaine trifluoroacetates have already been determined (Rodrigues *et al.*, 2000, 2001*a*,*b*). Complementary differential scanning calorimetry and low-temperature X-ray diffraction have not revealed any phase transitions of an electrical nature in these substances; nevertheless, the true significance of these results has not yet been discussed.

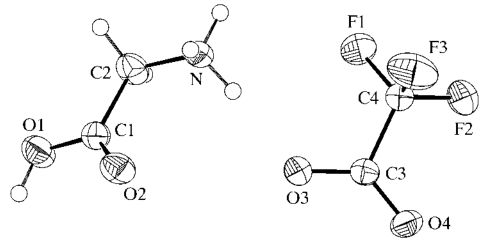


Figure 1
A view of the cation and anion of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

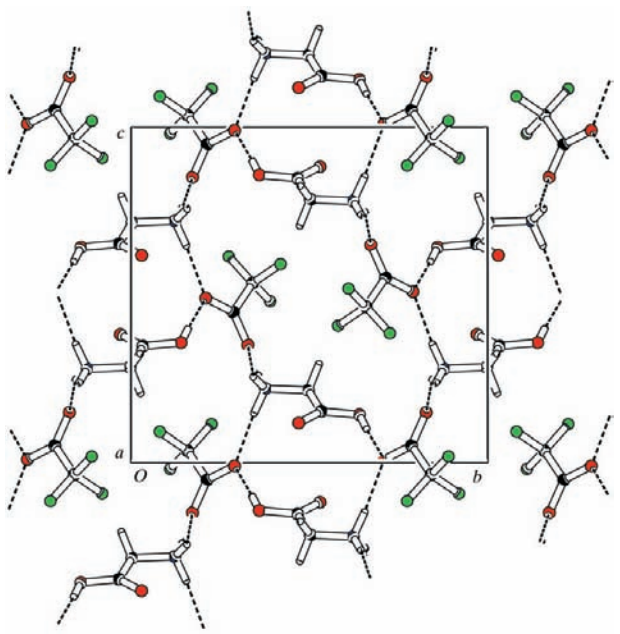


Figure 2
A projection of the structure of (I) along the *bc* plane, showing the four-molecule hydrogen-bonded rings.

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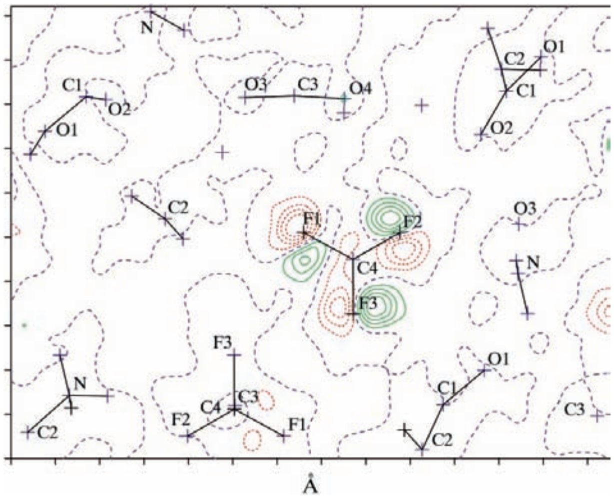

Figure 3
A projection of the difference Fourier map for (I) in the plane of the main F atoms, showing the disordered charge (when disorder is not accounted for).

The ionization states of the glycine and trifluoroacetic acid molecules in (I) 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 glycine molecule exists in the cationic form, with a mono-positively charged amino group and a neutral carboxylic acid group, in agreement with the large asymmetry between the C—O bond lengths of this functional group. The trifluoroacetate molecules are in the ionized state, as expected from the strength of the acid and the required charge neutrality of the salt.

The glycine carboxyl skeleton, which includes atoms O1, O2, C1 and C2, is planar to within 0.0010 (4) Å. The N atom is slightly displaced out of this plane, by −0.072 (3) Å, corresponding to a small rotation around the C1—C2 single bond. The relevant torsion angles are O1—C1—C2—N of 3.3 (2)° and O2—C1—C2—N of −177.09 (13)°. These can be compared with the corresponding values in pure γ-glycine [167.1 (1) and −15.4 (1)°, respectively; Kvick *et al.*, 1980], which is more distorted from planarity.

The trifluoroacetate anion in (I) has a staggered conformation, as indicated by the O—C4—C5—F torsion angles. 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 F—C—F angle of 1.327 (7) Å and 106.8 (2)°, respectively. The average F—C—C angle is 112 (2)°. The carboxylate group of the anion is planar to within 0.0089 (4) Å; the C4—C5 bond length of 1.541 (2) Å is longer than the average value for a Csp^3—Csp^2 bond (Allen *et al.*, 1987), but is within the normal range of values found in trifluoroacetic acid and trifluoroacetate compounds (Lundgren, 1978). The CF_3 group is disordered over two very close positions, the most probable occurring with roughly 0.75 probability. Low-temperature measurements seem to support the possible dynamic nature of this disorder, as no refinement of two different positions for each F atom is then necessary.

The glycine cations in (I) interact directly, *via* hydrogen bonds, with two neighbouring trifluoroacetate anions, forming cation–anion–cation–anion rings lying in the *bc* plane. The glycine cation acts as a donor in four hydrogen bonds; the N atom is engaged in three hydrogen bonds as a donor, and the O atom of the carboxylic acid group is also the donor of the strongest hydrogen bond found in this structure. Both O atoms of the carboxylate group of the anion act as acceptors of hydrogen bonds. The above-mentioned ring is formed *via* two very strong O—H···O and two weaker N—H···O hydrogen bonds. The N—H···O distances and angles are in the ranges 2.856 (2)–2.984 (2) Å and 159.2 (18)–175.5 (17)°, respectively, which allows a classification of these hydrogen bonds as relatively weak (Desiraju & Steiner, 1999). The strongest hydrogen bond in (I) involves the carboxylic acid O atom of the cation as a donor and a carboxylate O atom of the anion as an acceptor [O—H···O = 2.597 (2) Å and O—H—O = 175 (2)°].

Experimental

Colourless prismatic crystals of (I) were obtained by evaporation of the solvent from a solution of glycine in trifluoroacetic acid. Good quality single crystals recrystallized after a few hours at room temperature. A small single crystal was cast and checked by photographic methods prior to data collection.

Crystal data

$C_2H_6NO_2^+\cdot C_2F_3O_2^-$	D_x = 1.798 Mg m^{-3}
M_r = 189.10	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
a = 4.9598 (6) Å	θ = 9.6–15.4°
b = 12.239 (2) Å	μ = 0.20 mm^{-1}
c = 12.015 (8) Å	T = 293 (2) K
β = 106.67 (7)°	Prismatic, colourless
V = 698.7 (5) Å^3	0.47 × 0.40 × 0.15 mm
Z = 4	

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.3127 (17)	F2—C4	1.313 (6)
O2—C1	1.1997 (17)	F3—C4	1.323 (7)
N—C2	1.4736 (18)	O4—C3	1.2446 (17)
C1—C2	1.5084 (18)	O3—C3	1.2317 (17)
F1—C4	1.361 (7)	C3—C4	1.5430 (19)
O2—C1—O1	126.11 (12)	O4—C3—C4	114.21 (11)
O2—C1—C2	122.61 (12)	F2—C4—C3	114.0 (3)
O1—C1—C2	111.28 (11)	F3—C4—C3	109.0 (4)
O3—C3—O4	129.44 (12)	F1—C4—C3	112.2 (3)
O3—C3—C4	116.28 (12)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O4^{i}	0.86 (2)	1.74 (3)	2.597 (2)	175 (2)
N—H5···O4^{ii}	0.93 (2)	1.93 (2)	2.856 (2)	175.5 (17)
N—H4···O3^{iii}	0.91 (2)	2.04 (2)	2.941 (2)	173.0 (16)
N—H6···O3^{iv}	0.93 (2)	2.09 (2)	2.984 (2)	159.2 (18)

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

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from $\omega/2\theta$ scans
1772 measured reflections
1599 independent reflections
1285 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.021$

$\theta_{\rm max} = 27.5°$
$h = -6 \rightarrow 0$
$k = -15 \rightarrow 0$
$l = -14 \rightarrow 15$
25 standard reflections
frequency: 180 min
intensity decay: 7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.092$
$S = 1.02$
1599 reflections
154 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0538P)^2 + 0.1642P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.32$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.197 (10)

All H atoms could be located in a difference Fourier map; those attached to atom C2 were placed in idealized positions and refined as riding, while the remaining H atoms were refined isotropically [O—H = 0.86 (2) Å and N—H = 0.91 (2)–0.93 (2) Å]. Examination of the structure with *PLATON* (Spek, 2001) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *PLATON* (Spek, 2001); 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: SK1592). Services for accessing these data are described at the back of the journal.

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