

Glycinium trichloroacetate

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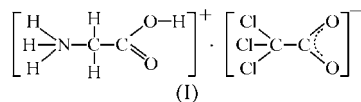
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The title compound, $C_2H_6NO_2^+ \cdot C_2Cl_3O_2^-$, crystallizes in the $P4_1$ space group with two glycinium cations and two trichloroacetate anions in the asymmetric unit. The glycinium cations have nearly C_s point-group symmetry which is only broken by the H atoms of the amine group. The trichloroacetate anions show typical bond lengths and angles, one of the trichloromethyl groups being disordered. Chains of alternating anions and cations run along the c axis. Within these chains, consecutive anion–cation pairs are bound *via* strong hydrogen bonds involving the carboxylate anions and the carboxyl or amine groups of the cations. Weaker hydrogen bonds bind neighbouring chains together.

Comment

Glycine is a non-essential genetically coded amino acid and the second most abundant amino acid found in proteins and enzymes. It is similar to γ -aminobutyric and glutamic acids in inhibiting neurotransmitter signals in the nervous system. Hence, glycine systems are potential drugs to control some disorders of the nervous system. Glycine is also the only protein-forming amino acid without a centre of chirality (Meister, 1965). However, 103 chiral glycine compounds have



been reported so far to the Cambridge Structural Database (CSD, Version 5.26; Allen, 2002). This large and rapidly increasing number [by February 2004, only about 65 entries of this kind existed in the CSD (Fleck & Bohatý, 2004)] is indicative of active ongoing investigation regarding chiral glycine systems. Some examples of chiral structures involving glycine and other light non-chiral molecules are triglycine sulfate (TGS; Matthias *et al.*, 1956), selenate (TGSe; Fugiel & Mierzwa, 1998), tetrafluoroberylate (TGFBer; Hoshino *et al.*, 1957), diglycine nitrate (DGN; Pepinsky *et al.*, 1958) and glycine phosphite (GPI; Tchukvinsky *et al.*, 1998), all of which exhibit ferroelectricity within a particular temperature range. It is believed that the conformational variability of the glycine

molecule in a crystalline environment is crucial for the mechanisms that lead to the observed ferroelectricity in these compounds.

In addition to glycine, for which 394 entries in the CSD have been reported so far, closely related *N*-methylated glycine derivatives, such as sarcosine (*N*-methylglycine), dimethylglycine and betaine (*N,N,N*-trimethylglycine), have also aroused much interest (Rodrigues *et al.*, 2001).

Because of its amphoteric character, the glycine molecule can assume four possible forms: a neutral form stable in the gas phase, $\text{NH}_2\text{-CH}_2\text{-COOH}$, a neutral zwitterionic phase unstable in the gas phase but found in solids and in solutions, $^+\text{NH}_3\text{-CH}_2\text{-COO}^-$, an anionic form, $\text{NH}_2\text{-CH}_2\text{-COO}^-$, and finally, a cationic form, $^+\text{NH}_3\text{-CH}_2\text{-COOH}$. The up-to-date occurrences of each of these forms in the CSD is: $\text{NH}_2\text{-CH}_2\text{-COOH}$ 33, $^+\text{NH}_3\text{-CH}_2\text{-COO}^-$ 141, $\text{NH}_2\text{-CH}_2\text{-COO}^-$ 137 and $^+\text{NH}_3\text{-CH}_2\text{-COOH}$ 83.

In the title compound, (I), both crystallographically independent glycine molecules, *A* and *B*, are found in the cationic form with a neutral carboxylic acid group. The bond lengths C2–N1 [1.466 (8) Å in cation *A* and 1.477 (8) Å in cation *B*] and C1–C2 [1.522 (8) Å in cation *A* and 1.503 (8) Å in cation *B*], and angles N–C2–C1 [110.7 (5)° in cation *A* and 110.4 (5)° in cation *B*] and N–C2–C1–O2 [−2.6 (9)° in cation *A* and −2.2 (10)° in cation *B*] are within typical ranges for the glycinium cation. A *cis* conformation is observed for the carboxylic acid groups of both *A* and *B* cations.

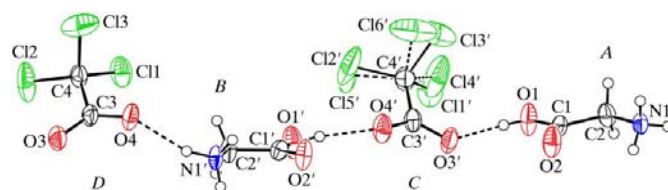


Figure 1

A plot of (I), showing the four ions (*A–D*) of the asymmetric unit and the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

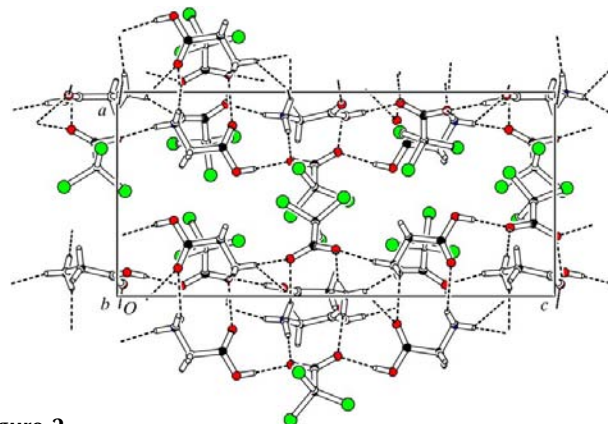


Figure 2

The packing of the molecules of (I), showing the building pattern in the chains running along the c direction. A trichloroacetate anion (disordered) is bonded *via* two hydrogen bonds to the carboxylic acid groups of two neighbouring cations. The next trichloroacetate anion in the chain bonds to its cation neighbours *via* hydrogen bonds with the amine N atoms of the cations.

The trichloroacetate anions, *C* and *D*, have typical geometries, with average C–O and C–Cl distances [C3–O = 1.236 (6) Å in anion *C* and 1.233 (5) Å in anion *D*, and C4–Cl = 1.76 (2) Å in anion *C* and 1.75 (6) Å in anion *D*]. The C3–C4 distances [1.572 (9) Å in anion *C* and 1.560 (9) Å in anion *D*] and O1–Cl–O2 angles [131.0 (6)° in anion *C* and 127.3 (6)° in anion *D*] are also within typical ranges. One of the trichloroacetate anions is disordered. This disorder was assumed and modelled as static according to a prior difference Fourier map, which showed unassigned peaks of charge close to the terminal Cl atoms. Disordered terminal halogens are rather common and the disorder is frequently found to be of a dynamic nature, corresponding to a rotation of the halogenated methyl group. In (I), this type of disorder is probably also present, this assumption being reinforced by the somewhat large and highly anisotropic vibration tensors of both anions.

The intermolecular bonds present in (I) are of two types, hydrogen bonding and van der Waals contacts. There are chains of alternating cations and anions running along the *c* axis. Within these chains, a disordered trichloroacetate ion is bonded *via* two hydrogen bonds to the carboxylic acid groups of two neighbouring cations, whereas the next trichloroacetate anion in the chain bonds to its cation neighbours *via* hydrogen bonds with the amine N atoms of the cation (Fig. 2). This pattern is then infinitely repeated along the chain. The chains are also interconnected through weaker hydrogen bonds and van der Waals interactions between the Cl atoms of the anions.

Experimental

Colourless block-shaped crystals of (I) were obtained by recrystallization of an equimolar solution of glycine and trichloroacetic acid (from Aldrich, 98%) in water.

Crystal data

C ₂ H ₆ NO ₂ ⁺ ·C ₂ Cl ₃ O ₂ [−]	Mo Kα radiation
<i>M_r</i> = 238.45	Cell parameters from 25 reflections
Tetragonal, <i>P</i> 4 ₁	<i>a</i> = 9.4416 (9) Å
<i>a</i> = 9.4416 (9) Å	<i>c</i> = 20.213 (4) Å
<i>c</i> = 20.213 (4) Å	<i>V</i> = 1801.9 (4) Å ³
<i>Z</i> = 8	<i>D_x</i> = 1.758 Mg m ^{−3}
<i>D_x</i> = 1.758 Mg m ^{−3}	Block, colourless
	0.34 × 0.30 × 0.20 mm

Table 1
Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O1–H1...O3 ⁱ	0.82	1.83	2.644 (7)	176
N1–H1A...O3 ⁱⁱ	0.89	1.97	2.852 (7)	170
N1–H1B...O3 ⁱⁱⁱ	0.89	1.96	2.832 (7)	168
N1–H1C...O4 ⁱⁱⁱⁱ	0.89	2.11	2.862 (7)	142
N1–H1C...O2 ^{iv}	0.89	2.41	3.021 (7)	126
O1'–H1'...O4'	0.82	1.87	2.689 (7)	173
N1'–H1A'...O4 ^v	0.89	2.00	2.877 (8)	167
N1'–H1B'...O4	0.89	1.94	2.797 (7)	161
N1'–H1B'...O2 ^v	0.89	2.52	2.982 (7)	113
N1'–H1C'...O3 ⁱ	0.89	2.02	2.862 (7)	158

Symmetry codes: (i) *y*, *−x*, *z* − ½; (ii) *x*, *y*, *z* − 1; (iii) *−y*, *x*, *z* − ¾; (iv) *−x*, *−y*, *−z* − ½; (v) *−y*, *x*, *z* + ¼.

Data collection

Enraf–Nonius CAD-4 diffractometer	<i>R</i> _{int} = 0.024
Profile data from ω/2θ scans	θ _{max} = 27.6°
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	<i>h</i> = 0 → 11
<i>T</i> _{min} = 0.722, <i>T</i> _{max} = 0.817	<i>k</i> = 0 → 11
2596 measured reflections	<i>l</i> = −24 → 24
2106 independent reflections	3 standard reflections
1493 reflections with <i>I</i> > 2σ(<i>I</i>)	frequency: 120 min
	intensity decay: 59%

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0777 <i>P</i>) ² + 0.9874 <i>P</i>]
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.045	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>wR</i> (<i>F</i> ²) = 0.145	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.09	Δρ _{max} = 0.33 e Å ^{−3}
2106 reflections	Δρ _{min} = −0.32 e Å ^{−3}
249 parameters	Absolute structure: Flack (1983), with 24 Friedel pairs
H-atom parameters constrained	Flack parameter: 0.03 (13)

All H-atom positions were generated geometrically and subsequently refined as riding, with C–H = 0.97 Å, N–H = 0.89 Å and O–H = 0.89 Å, and *U*_{iso}(H) = 1.2*U*_{eq}(C) or 1.5*U*_{eq}(N,O).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *PLATON* (Spek, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1890). Services for accessing these data are described at the back of the journal.

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