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Betaine betainium hydrogen oxalate

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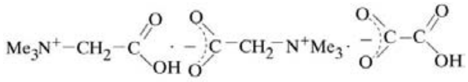
The title compound, $C_5H_{12}NO_2^+\cdot C_2HO_4^-\cdot C_5H_{11}NO_2$ or $HC_2O_4^-\cdot(HBET\cdot BET)^+$ [BET is trimethylglycine (betaine); IUPAC name: 1-carboxy-*N*,*N*,*N*-trimethylmethanaminium hydroxide inner salt], contains pairs of betaine molecules bridged by an H atom, forming dimers linked by a strong hydrogen bond. The hydrogen oxalate anions have a rather unusual star conformation, with an internal torsion angle of 70.1 (4)°. The betaine–betainium dimers are anchored between two zigzag chains of hydrogen oxalate molecules hydrogen bonded head-to-tail running parallel to the *b* axis. An extended network of C—H···O interactions links the anionic chains to the cationic dimers.

Comment

Betaine compounds are of importance in biological systems as components of complex lipids and as *trans*-methylating agents. Pure betaine is an inner salt (zwitterion) where the H atom of the carboxylic acid group has been transferred to the amino group. It may be combined with a variety of acids and inorganic salts to form 1:1 and 2:1 betainium salts and adducts and it is also a good chelating agent, *via* the carboxy group, of *d* and *f* metals. Many of these salts and adducts exhibit phase transitions associated with ferroelectric, antiferroelectric and ferroelastic behaviour, as well as commensurate and incommensurate superstructures (Shildkamp & Spilker, 1984; Haussühl, 1984, 1988). The most famous betaine compound is BCCD (betaine calcium chloride dihydrate), which exhibits a series of low-temperature phase transitions in a 'devil chair' sequence (Almeida *et al.*, 1992). Recently, the system of isostructural ferroelectric betaine phosphite and antiferroelectric betaine phosphate, which forms solid solutions over the entire composition range, has been much studied (Andrade *et al.*, 1999; Banys *et al.*, 2000). The crystal structures of betaine monohydrate (Mak, 1990) and its salts of hydrogen chloride (Fischer *et al.*, 1970; Mak & Chen, 1990), phosphoric (Shildkamp & Spilker, 1984), sulfuric (Ratajczak *et al.*, 1994), arsenic (Shildkamp *et al.*, 1984), boric (Zobetz & Preisinger, 1989), telluric (Ilczysczyn *et al.*, 1992), maleic (Ilczysczyn *et al.*, 1995), selenic (Baran, Drozd, Lis *et al.*, 1995), nitric (Baran, Drozd, Glowiak *et al.*, 1995) and selenous (Paixão *et al.*, 1997) acids have already been determined. The present work represents an effort to find other betaine compounds which may have similar interesting physical properties.



(I)

The title compound, (I), contains a protonated betaine molecule with a charge counterbalanced by a hydrogen oxalate anion and an additional neutral molecule of betaine (Fig. 1). The ionization states of both the betaine and oxalic acid molecules were determined from the objective localization on difference Fourier maps of the H atoms bonded to the carboxylic acid groups, but could also be inferred from an inspection of the C—O bond distances. One of the betaine molecules exists in the cationic form with a monopositively charged trimethylammonium group and a neutral carboxylic acid group. The other betaine molecule retains the zwitterionic form with its large internal dipole moment due to the trimethylammonium and carboxylate groups carrying a positive and a negative charge, respectively. The oxalic acid molecule is found in a single-ionized state, as necessary to maintain the overall charge neutrality of the structure. The related HBET–BET–selenic acid structure was reported by Baran *et al.* (1997).

Previous studies have shown that the betaine molecule has some degree of conformational flexibility depending on the crystalline environment. The carboxy groups of both protonated and neutral betaine molecules are planar within 0.003 (4) Å. The main backbone of the unprotonated betaine molecule is practically planar, the N1 atom lying within one s.u.'s in the carboxy plane and atom C5 being displaced out of this plane by 0.050 (8) Å. These small displacements arise from a small rotation of the carboxy and trimethylammonium groups around bonds C3—C4 and C4—N1 of 0.9 (5) and 1.9 (3)°, respectively, as shown by inspection of the appropriate torsion angles. Accordingly, the methyl groups C6 and C7 are placed in almost symmetrical positions with respect to the least-squares plane passing through the molecular backbone. The geometry of the protonated betaine molecule differs slightly from that of the neutral molecule. The torsion around C9—N2 is small and comparable to that of the neutral molecule, but in the protonated species there is a significant twist by 6.5 (5)° of the carboxy group around the C8—C9 bond. As a result of this twist, the N2 atom is displaced out of the carboxy plane by −0.1261 (58) Å and the distances of the C10 and C12 atoms to this plane show a larger asymmetry [−1.407 (5) and 1.044 (6) Å] compared with that of the neutral molecule.

The most interesting feature of the structure is the strong hydrogen bond linking together the protonated and unprotonated betaine molecules, with an O7···O6 distance of 2.457 (3) Å and a rather short H2···O6 distance of 1.39 (4) Å. The O7—H2 distance [1.07 (4) Å] is, accordingly, somewhat longer than the typical O—H bond distance found in weaker

O—H···O hydrogen bonds such as those interlinking the anions in the present compound (see below). It is characteristic of betainium compounds that the H atom is loosely bound to the cation and in the presence of even a moderately strong acid, the H atom is often found to be located in a double potential minimum between the donor and the acceptor. This feature is considered responsible for the phase transitions often occurring in these compounds and for their peculiar dielectric properties. In such cases, and when the structure crystallizes in a polar space group, a small applied electric field may overcome the double potential barrier and switch the position of the H atom between donor and acceptor. The angle defined by the planes containing the backbones of the two betaines is 11.07 (11)°, but they are not facing each other in a herring-bone fashion, the two molecules being practically inverted with respect to the hydrogen-bond centre so that the bare O atoms not involved in the intramolecular hydrogen bonding of the dimer are positioned farther away from each other.

The hydrogen oxalate anion is a relatively weak acid and has a large range of pK_a values in solution (1.37–3.81) due to interaction between the carboxylic acid groups (McAuley & Nancollas, 1960). In the many reports of structures including the hydrogen oxalate ion, it usually has a near planar geometry and the anions are often found to be interconnected in chains by relatively short (2.49–2.57 Å) hydrogen bonds, with a typical H···O distance of 1.63 (3) Å (Küppers, 1973). The conformation of this anion is determined by the torsion angle around the central C—C bond that connects the two carboxylic acid groups. This angle rarely exceeds 35°, and it can be stated that the ion has a clear preference to remain planar. However, important deviations from planarity have been reported in some hydrogen oxalate salts (Chandra *et al.*, 1998). In the present compound, the hydrogen oxalate anions assume the more rare star conformation, with an O1—C1—C2—O4 torsion angle of 70.1 (4) Å. The rather long Csp^2—Csp^2 bond [1.531 (4) Å] is within the reported range of values for the hydrogen oxalate anion (1.546–1.553 Å; Allen *et al.*, 1987; Barnes *et al.*, 1998) and reflects the charge-withdrawing effect of the electronegative carboxy groups. There is a clear asymmetry between the C—O bond lengths of the unionized carboxylic acid group, which shows that the H atom is not disordered. The angle H1—O1—C1—O2 is close to 0°, corresponding to the usual *syn* conformation (Chandra *et al.*, 1998). The C1—O2 and C2—O4 bonds are short and approach the typical value of a Csp^2=O bond. The C2—O3 bond is significantly larger than these two bonds, as expected from the fact that O3 is an acceptor of a relatively strong hydrogen bond (see Table 1).

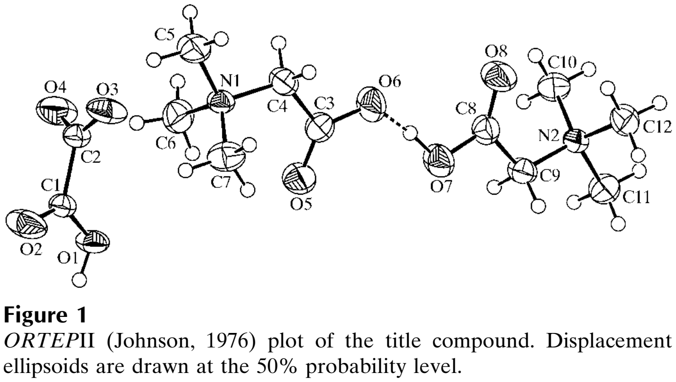


Figure 1
*ORTEP*II (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

The hydrogen oxalate ions are interlinked head-to-tail through hydrogen bonds, forming infinite chains running along the *b* axis. As a result of the hydrogen bonding, the O1 and O3 atoms are not able to vibrate as freely as the O2 and O4 atoms, which have slightly larger and, in the case of O2, more anisotropic atomic displacement parameters. These latter atoms are only involved as acceptors in weaker C—H···O interactions that connect the hydrogen oxalate chains with the betaine dimers as shown in Fig. 2.

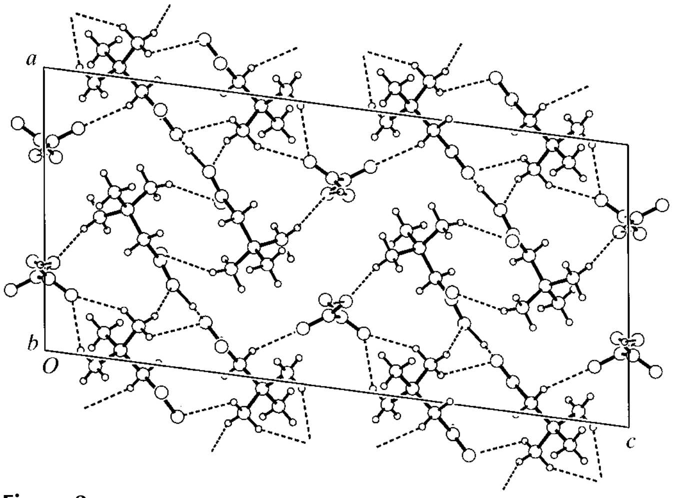


Figure 2
Packing diagram viewed along the *b* axis showing the intermolecular hydrogen-bonding network.

Experimental

Small needle-shaped colourless crystals were obtained after a few weeks of slow evaporation from an aqueous solution containing betaine and oxalic acid in a 2:1 ratio. A suitable crystal was cut and checked by photographic methods before the data collection.

Crystal data

$C_5H_{12}NO_2^+\cdot C_2HO_4^-\cdot C_5H_{11}NO_2$
$M_r = 324.33$
Monoclinic, $P2_1/c$
$a = 11.7729$ (7) Å
$b = 5.5841$ (4) Å
$c = 24.549$ (3) Å
$\beta = 97.520$ (7)°
$V = 1600.0$ (2) Å^3
$Z = 4$
$D_x = 1.346$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 8.07$–15.49°
$\mu = 0.113$ mm^{-1}
$T = 293$ (2) K
Needle, colourless
0.50 × 0.20 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω–2θ scans
3044 measured reflections
2845 independent reflections
1634 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.026$
$\theta_{\max} = 25.06$°
$h = -14 \rightarrow 13$
$k = -7 \rightarrow 7$
$l = 0 \rightarrow 29$
3 standard reflections every 180 reflections intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.137$
$S = 1.003$
2844 reflections
214 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0569P)^2 + 1.1216P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0094 (13)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.304 (3)	O5—C3	1.223 (3)
O2—C1	1.193 (3)	O6—C3	1.264 (3)
O3—C2	1.248 (3)	O7—C8	1.290 (3)
O4—C2	1.220 (3)	O8—C8	1.209 (3)
C1—C2	1.531 (4)		
O1—C1—C2—O4	70.1 (4)	C11—N2—C9—C8	−178.2 (2)
C5—N1—C4—C3	−178.1 (3)	O8—C8—C9—N2	−6.5 (5)
O5—C3—C4—N1	0.9 (5)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O3^{i}	0.87 (4)	1.76 (4)	2.614 (3)	167 (4)
O7—H2···O6	1.07 (4)	1.39 (4)	2.457 (3)	172 (4)
C5—H5*A*···O4	0.96	2.44	3.383 (4)	168
C6—H6*A*···O5	0.96	2.36	2.971 (4)	121
C6—H6*B*···O5^{ii}	0.96	2.59	3.472 (4)	153
C7—H7*B*···O3^{iii}	0.96	2.59	3.528 (4)	165
C7—H7*C*···O5	0.96	2.42	3.066 (4)	124
C9—H9*B*···O4^{iv}	0.97	2.46	3.356 (4)	153
C10—H10*B*···O2^{v}	0.96	2.55	3.409 (4)	150
C10—H10*C*···O8	0.96	2.41	3.043 (4)	123
C12—H12*A*···O2^{v}	0.96	2.50	3.366 (4)	151
C12—H12*B*···O6^{vi}	0.96	2.53	3.409 (4)	153
C12—H12*C*···O8	0.96	2.38	3.019 (4)	123

Symmetry codes: (i) $x, y-1, z$; (ii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $1-x, 2-y, 1-z$; (iv) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (v) $1+x, \frac{3}{2}-y, z-\frac{1}{2}$; (vi) $2-x, y-\frac{1}{2}, \frac{1}{2}-z$.

All H atoms could be located on a difference Fourier map; those bonded to C atoms were placed at idealized positions and refined as riding using suitable *AFIX* instructions with *SHELXL*97 (Sheldrick, 1997) defaults. The H atoms attached to O atoms and involved in hydrogen bonding were freely refined isotropically. Examination of the crystal structure with *PLATON* (Spek, 1995) 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: *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: SK1441). Services for accessing these data are described at the back of the journal.

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