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Investigation of hydrogen-bond network in bis(glycinium) oxalate using single-crystal neutron diffraction and spectroscopic studies

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Single-crystal neutron diffraction investigation of bis(glycinium) oxalate was undertaken in order to study its hydrogen-bonding network, particularly the very short hydrogen bond between the glycinum and oxalate ions, indicated by the X-ray diffraction study. The non-existence of any phase transition in these crystals was attributed to the fact that the short hydrogen bond in bis(glycinium) oxalate is asymmetric in nature, with no hydrogen disorder. The potential energy landscape for the above-mentioned H atom was found to have a single minimum closer to the glycinium ion. IR and Raman investigations of the title complex supported the above result.

1. Introduction

Glycine is the simplest and only optically inactive amino acid. It has important applications in the field of biology, *i.e.* it is essential for the biosynthesis of bile acids, porphyrins and creatine, and many of the glycine complexes with inorganic acids and salts are known to exhibit ferroelectricity (Matthias *et al.*, 1956; Pepinsky *et al.*, 1957; Pepinsky, Vedam, Hoshino & Okaya, 1958; Shikanai *et al.*, 2002) and hence have a great technological relevance. Apart from glycine, there are other complexes of amino acids that exhibit nonlinear optical properties (Petrosyan, Karapetyan *et al.*, 2005; Petrosyan, Sukiasyan *et al.*, 2005). In its pure form, glycine exists as a zwitterion, with the carboxyl H atom transferred to the amino group. When complexed with an H-atom donor such as the inorganic acids, it can exist in cationic form (glycinium ion), with a net positive charge on the amino group and a neutral carboxyl group. Oxalic acid is the simplest dicarboxylic acid, and it can exist as the oxalate, semioxalate or oxalic acid. The structure of a complex of glycine and oxalic acid in a 1:1 ratio has already been reported (Subha Nandini *et al.*, 2001). The X-ray single-crystal structure of bis(glycinium) oxalate was recently published (Chitra *et al.*, 2006) by our laboratory. This X-ray study carried out at room temperature indicated the existence of a very strong and short hydrogen bond, like those observed in the glycine complexes triglycine sulfate (Matthias *et al.*, 1956) and diglycine nitrate (Pepinsky, Vedam & Okaya, 1958), which exhibit ferroelectricity. This encouraged us to carry out neutron diffraction on these crystals in order to explore the possibility of any kind of phase transition due to hydrogen disorder in these crystals. In very short hydrogen bonds (2.40–2.55 Å), the hydrogen bond could be asymmetric (H atom closer to one of the O atoms) or symmetric (H atom precisely at the center) or dynamically disordered between two positions on either sides of the bond center. Neutron diffraction is a tool that can be used to obtain accurate posi-

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Table 1
Experimental details.

Crystal data	
Chemical formula	$C_2H_6NO_2 \cdot 0.5C_2O_4$
M_r	120.08
Cell setting, space group	Monoclinic, $P2_1/n$
Temperature (K)	300
a, b, c (Å)	4.934 (3), 9.955 (6), 10.854 (9)
β (°)	97.440 (10)
V (Å^3)	528.6 (6)
Z	4
D_x (Mg m^{-3})	1.509
Radiation type	Neutron
μ (mm^{-1})	0.18
Crystal form, color	Needle with six faces, colorless
Crystal size (mm)	6 × 2.12 × 1.06
Data collection	
Diffractometer	Indigenously made four-circle diffractometer
Data collection method	θ–2θ
Absorption correction	Integration
$T_{\min}$	0.409
$T_{\max}$	0.831
No. of measured, independent and observed reflections	1298, 1298, 894
Criterion for observed reflections	$I > 2\sigma(I)$
$R_{\rm int}$	0.000
$\theta_{\max}$ (°)	41.8
No. and frequency of standard reflections	2 every 25 reflections
Intensity decay (%)	< 3%
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.057, 0.180, 1.09
No. of reflections	1298
No. of parameters	128
H-atom treatment	Mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0841P)^2 + 3.773P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	<0.0001
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	1.06, −0.82
Extinction method	*SHELXL97*
Extinction coefficient	0.071 (9)

Computer programs used: *SCAD* (Rajagopal *et al.*, 1992), *REFINE* (Srikanta & Sequeira, 1968), *DATRED* (Srikanta, 1968), *SHELXL*97 (Sheldrick, 1997), *ORTEP*3 (Farrugia, 1997).

tions of H atoms and hence classify the symmetric or asymmetric hydrogen bonds. Using the Cambridge Structural Database (CSD; Version 5.26 of 2005; Allen, 2002) an analysis of the geometry and hydrogen bonding in all the neutron structures containing the glycine molecule has also been carried out.

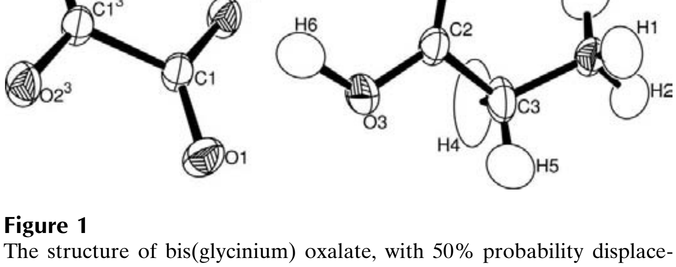

Figure 1
The structure of bis(glycinium) oxalate, with 50% probability displacement ellipsoids [symmetry code: (3) $-x, -y, -z$].

Spectroscopic investigations and hydrogen-bond energy calculations were also undertaken to obtain the complete picture of the hydrogen bonding in bis(glycinium) oxalate.

2. Structural investigation

Colorless three-dimensional transparent single crystals of bis(glycinium) oxalate were grown by mixing α-glycine and oxalic acid dihydrate in a 2:1 stoichiometric ratio in water. A clear crystal of approximately 6 × 2 × 1 mm was selected for the neutron measurement.

2.1. Neutron diffraction

A four-circle single-crystal diffractometer with BF_3 point detector located at Dhruva Reactor (Rajagopal *et al.*, 1992; Naik *et al.*, 2004) at Trombay was used to collect the single-crystal diffraction data of bis(glycinium) oxalate at room temperature. The neutron wavelength used was 0.995 Å, obtained from a Cu(220) monochromator crystal. The cell constants and orientation matrix were refined by least-squares techniques from optimized 2θ angles of 50 reflections using the *REFINE* program (Srikanta & Sequeira, 1968). The reflections were chosen to represent the randomly distributed reciprocal space. Crystallographic details are summarized in Table 1.[1]

The integrated neutron counts for 1298 Bragg reflections were measured in the symmetrical setting of the diffractometer using the θ–2θ coupled step scan mode (0.1° step in 2θ). The background was scanned for a minimum of 1° on either side. The standard reflections were measured after every 25 reflections. The variation of the standard reflection intensity was within 3%. Squared observed structure factors were obtained from integrated intensities using the program *DATRED* (Srikanta, 1968). These were corrected for absorption. The data collection details are summarized in Table 1.

The structural parameters obtained using X-rays were used as the starting parameters and were subjected to a series of isotropic and anisotropic full-matrix least-squares refinement using *SHELXL*97 (Sheldrick, 1997). The nuclear scattering lengths used are $b_{\rm N} = 0.936$, $b_{\rm C} = 0.6646$, $b_{\rm H} = -0.3739$, $b_{\rm O} = 0.5803 \times 10^{-12}$ cm. All the reflections including negative F_o^2 were used for refinement. In the initial stages of refinement the weight (w) was taken to be $1/\sigma(F_o^2)$, which was derived using counting statistics. From the difference Fourier map all the H atoms were located and refined anisotropically. The refinement details are given in Table 1. The $\Delta\rho_{\max}$ of 1.06 e Å^{-3} is 0.86 Å from atom N1. The $\Delta\rho_{\min}$ of −0.82 e Å^{-3} is 0.73 Å from atom O3.

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV5084). Services for accessing these data are described at the back of the journal.

Table 2
Comparison of bond lengths between single-crystal X-ray and neutron diffraction in (Å).

Atoms	Neutron	X-ray	Atoms	Neutron	X-ray
O1—C1	1.236 (4)	1.236 (2)	C2—C3	1.520 (4)	1.506 (2)
O2—C1	1.272 (3)	1.270 (2)	N1—C3	1.467 (3)	1.467 (2)
O2—H6	1.300 (7)	1.34 (3)	N1—H1	1.025 (7)	0.93 (2)
C1—C1^{i}	1.550 (4)	1.551 (3)	N1—H2	1.040 (6)	0.93 (2)
O3—C2	1.286 (4)	1.284 (2)	N1—H3	1.009 (6)	0.93 (2)
O3—H6	1.165 (7)	1.11 (3)	C3—H4	1.075 (9)	0.91
O4—C2	1.214 (4)	1.219 (2)	C3—H5	1.056 (10)	0.93

Symmetry code: (i) $-x, 1-y, -z$.

Table 3
Comparison of bond angles between single-crystal X-ray and neutron diffraction in (Å).

Atoms	Neutron	X-ray	Atoms	Neutron	X-ray
C1—O2—H6	114.0 (4)	113.3 (12)	H1—N1—H2	108.3 (6)	109.1 (17)
O1—C1—O2	125.8 (2)	126.0 (1)	C3—N1—H3	113.1 (4)	113.4 (13)
O1—C1—C1^{i}	119.5 (2)	119.4 (2)	H1—N1—H3	110.2 (6)	110.8 (17)
O2—C1—C1^{i}	114.7 (3)	114.6 (2)	H2—N1—H3	107.9 (5)	107.2 (17)
C2—O3—H6	116.5 (4)	118.2 (14)	N1—C3—C2	112.3 (2)	112.7 (1)
O4—C2—O3	125.9 (3)	125.9 (1)	N1—C3—H4	108.4 (6)	108.1
O4—C2—C3	121.9 (2)	121.7 (1)	C2—C3—H4	107.2 (5)	108.0
O3—C2—C3	112.2 (2)	112.4 (1)	N1—C3—H5	108.4 (5)	107.4
C3—N1—H1	108.6 (4)	107.3 (12)	C2—C3—H5	110.4 (5)	110.5
C3—N1—H2	108.6 (4)	108.9 (11)	H4—C3—H5	110.1 (10)	110.2

Symmetry code: (i) $-x, 1-y, -z$.

Table 4
Torsion angles (°) involving methyl and ammonium groups of glycinium.

H3—N1—C3—C2	−60.9 (5)
C2—C3—N1—H1	61.8 (5)
H1—N1—C3—H5	−60.4 (8)
H5—C3—N1—H2	57.1 (8)
H2—N1—C3—H4	−62.4 (8)
H4—C3—N1—H3	57.4 (9)

Table 5
Deviation (Å) of atoms from the least-squares plane.

C2	0.025 (2)
C3	0.137 (2)
N1	−0.109 (2)
O4	0.037 (1)
O3	−0.090 (2)

Table 6
Hydrogen-bond parameters (Å, °).

	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H1$\cdots$O1^{i}	1.025 (7)	1.937 (7)	2.910 (5)	157.3 (5)
N1—H1$\cdots$O3^{i}	1.025 (7)	2.556 (7)	3.062 (5)	110.0 (5)
N1—H2$\cdots$O1^{ii}	1.040 (6)	1.810 (7)	2.848 (5)	175.1 (6)
N1—H2$\cdots$O2^{iii}	1.040 (6)	2.445 (7)	2.925 (5)	107.1 (4)
N1—H3$\cdots$O4^{iv}	1.009 (6)	1.885 (7)	2.874 (5)	166.3 (6)
O3—H6$\cdots$O2	1.165 (7)	1.300 (7)	2.461 (5)	174.2 (6)
O3—H6$\cdots$O1	1.165 (7)	2.531 (7)	3.203 (6)	115.0 (4)
C3—H4$\cdots$O2^{v}	1.075 (9)	2.566 (8)	3.460 (5)	140.2 (6)
C3—H5$\cdots$O2^{iii}	1.056 (10)	2.392 (9)	3.099 (6)	123.1 (5)

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

The asymmetric unit consists of one glycine molecule in the cationic form with a positively charged amino group and an uncharged carboxylic acid group. The oxalic acid molecule exists as a doubly charged oxalate anion and lies across an inversion center in the crystal (Fig. 1). In the extended crystal structure, a given oxalate ion interacts with two glycinium ions.

The bond lengths and bond angles obtained using the X-ray and neutron studies are tabulated in Tables 2 and 3, respectively. The bond distance agree to within 3σ. The methyl and ammonium groups are almost in a staggered conformation with a departure of only 3° from the mean value of 60° (Table 4).

The non-H-atom backbone of the glycinium ion is not very planar, the equation of the plane being

$$3.0978\,(89)\,x + 7.5488\,(202)\,y - 2.7718\,(209)\,z = 4.6601\,(120).$$

Table 5 gives the deviation of the atoms from this least-squares plane. The maximum deviation occurs for atom C3.

Table 6 gives the hydrogen-bond parameters observed in the present complex. The carboxylic OH group of glycinium makes a very strong hydrogen bond with an O atom of the doubly ionized oxalate molecule. It is also seen that this hydrogen bond is asymmetric, *i.e.* the H atom is closer to the glycinium ion. Two of the amino H atoms (H1 and H2) of glycine form a three-centered or bifurcated hydrogen bond (Table 6). The three-center bond is defined as one in which the H atom forms two contacts to hydrogen-bond acceptor atoms, such that both are in the forward direction and shorter than the sum of the van der Waals radii of the atoms involved (Taylor *et al.*, 1984). For the three-centerd bond the sum of the three angles at H (*i.e.* $A1\cdots$H$\cdots A2$, D—H$\cdots A1$ and D—H$\cdots A2$) should be ~360° (Jeffrey & Mitra, 1984). It is observed that these sum to 357.1 (7) and 359.0 (7)° for the two bifurcated bonds involving the N1/H1 and N1/H2 atoms, respectively. The amino H1 atom forms a hydrogen bond to the hydroxyl O3 atom of glycine and the carbonyl O1 atom of the oxalate anion. Similarly, the amino H2 atom forms hydrogen bonds with the carbonyl O1 atom and the O2 atom of the oxalate anion. The third amino H atom, H3, hydrogen bonds to the carbonyl O4 atom of the glycine cation. In turn each O atom of the oxalate anion becomes an acceptor of two hydrogen bonds. Hence the protonated glycine molecules are linked by N—H$\cdots$O hydrogen bonds, forming a three-dimensional network along all three principal axes, as shown in Fig. 2. Apart from these, C—H$\cdots$O bonds also have been observed for both C$_{\alpha}$ H atoms of the glycinium ion; these bonds fall in the normal category of C—H$\cdots$O interactions.

2.2. Database analysis

The CSD was used to retrieve data of all the structures containing the glycine molecule studied using neutron diffraction. A subset was created containing five good quality crystal structures: glycinium ammonium sulfate (Vilminot *et* *al.*, 1976), bis(glycine) telluric acid monohydrate (Qui *et al.*, 1987), α-glycine (Kvick *et al.*, 1980), β-glycine (Langan *et al.*, 2002) and triglycine sulfate (Kay & Kleinberg, 1973), with CSD refcodes AGLYSL01, BINFAF02, GLYCIN15, GLYCIN19 and TGSLYU11, respectively. Among these, four structures had glycine in the cationic form, *i.e.* glycinium, and four in the zwitterionic form. Average values for various structural parameters involving the glycine unit were computed.

A comparison of the bond parameters of the glycine molecule in the present structure (Tables 2 and 3) with the average values obtained from other neutron structures (Table 7) shows that the distances fall within the minimum and maximum values observed, except for the O3—H6 distance. This is due to the fact that O3/H6 forms a very strong hydrogen bond with the oxalate O atom.

The N—H bond distances range from 0.95 to 1.07 Å, with the hydrogen-bonding distance H$\cdots$*A* ranging between 1.7 and 2.6 Å (Fig. 3). As observed in Fig. 4, which shows the distribution of the H$\cdots$*A* hydrogen-bond distance with the N—H$\cdots$*A* angle, there are two clusters of data, indicating the involvement of the amino group in three-centered hydrogen bonds. However, it is observed that in BINFA02 there are no three-centered bonds, because the number of donors is more than the number of acceptors in this structure.

The crystal structures of various amino acids containing C—H$\cdots$O interactions (Jeffrey & Maluszynska, 1982) have been studied, and the importance of the C—H$\cdots$O hydrogen bond in determining the interbilayer arrangement in α-glycine was also revealed (Berkovitch-Yellin & Leiserowitz, 1984). In amino acids, the C_αH group is activated by the neighboring N atom and the side chain *R*. In the case of glycine additional activation by the side chain does not exist; as a result, its C_αH group is a weaker donor (Desiraju & Steiner, 1999). It is observed that in almost all of the structures except AGLYSL01 there are C—H$\cdots$O interactions (Figs. 5 and 6) with H$\cdots$*A* distances ranging from 2.2 to 2.6 Å and C—H$\cdots$*A* angles ranging between 137 and 170°.

Table 7
Mean, minimum and maximum values of the geometric parameters of the glycine molecule in various neutron structures (Å, °).

	Mean	Minimum	Maximum
N1—H1	1.036	0.969	1.066
N1—H3	1.017	0.975	1.054
N1—H2	1.026	0.944	1.056
N1—C3	1.474	1.450	1.509
C3—C2	1.515	1.501	1.536
C3—H4	1.093	1.014	1.197
C3—H5	1.055	0.973	1.102
C2═O4	1.230	1.182	1.271
C2—O3	1.285	1.254	1.313
O3—H6	1.027	0.996	1.096
H1—N1—H3	109.0	104.95	113.13
H1—N1—H2	107.79	99.33	112.12
H2—N1—H3	108.40	106.81	111.08
H1—N1—C3	110.93	107.43	113.37
H1—N1—C3	109.76	104.06	112.57
H2—N1—C3	110.59	107.35	115.83
N1—C3—C2	111.56	110.25	113.01
N1—C3—H4	108.77	103.49	111.83
N1—C3—H5	109.37	105.26	109.89
H4—C3—H5	107.68	108.13	111.73
H4—C3—C2	109.32	108.69	111.15
H5—C3—C2	109.85	108.10	114.25
C3—C2—O4	120.51	117.09	123.34
C3—C2—O3	114.18	110.48	117.11
O3—C2—O4	125.22	121.98	127.48
C2—O3—H6	111.97	110.08	114.24

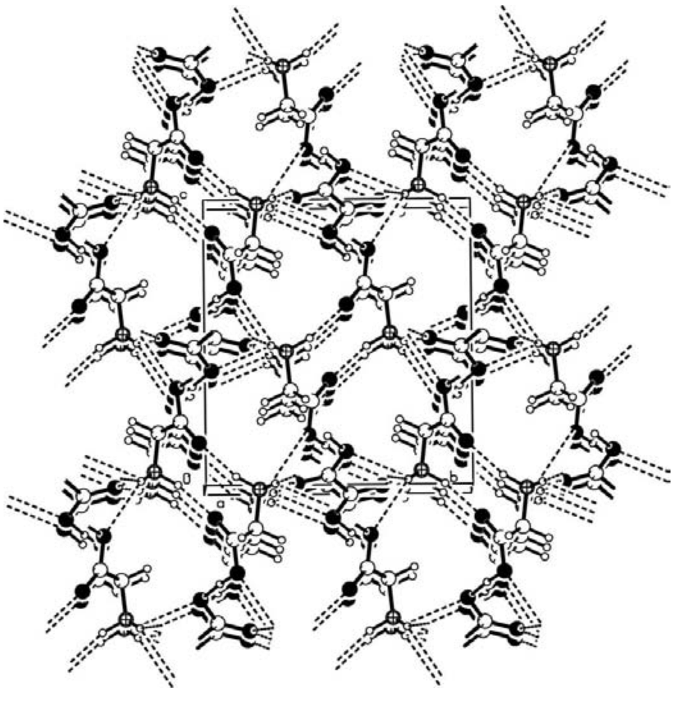

Figure 2
Packing diagram of bis(glycinium) oxalate viewed down the *a* axis showing the three-dimensional hydrogen-bonding network.

2.3. DSC measurement

A differential scanning calorimetry (DSC) measurement on the crystals of bis(glycinium) oxalate in the temperature range 173–473 K with a heating rate of 10 K min^{-1} was performed using a Mettler Toledo differential scanning calorimeter in order to ascertain whether the crystal undergoes a phase transition (Fig. 7). It was found that the crystal does not undergo any phase transition in the above-stated temperature range. This is consistent with the observation that no hydrogen disorder is observed in the short hydrogen bond of these crystals, since most of the glycine complexes that undergo a ferroelectric phase transition, such as triglycine selenate (Matthias *et al.*, 1956), diglycine nitrate (Pepinsky, Vedam & Okaya, 1958) and glycinium phosphite (Shikanai *et al.*, 2002), have a disordered short hydrogen bond at room temperature.

3. Spectroscopic investigations

Small single crystals grown by the solution method described above were used to record IR as well as Raman spectra.

3.1. Raman investigations

The Raman spectrum of bis(glycinium) oxalate in the internal mode region was excited using the 514.5 nm line of an Ar^+ laser (Model Innova-70, Coherent Inc., USA). Power on the sample was kept at 100 mW. The scattered radiation, collected in the back-scattering geometry, was analyzed using a home-built double monochromator. The spectrometer slits were kept at 250-400-250, which gives a spectral band pass of 3 cm^{-1}. The analyzed signal was detected using a cooled GaAs photomultiplier tube operated in the photon counting mode. Scanning of the spectra was carried out in steps of 0.5 cm^{-1}.

The assignment of the internal modes (Table 8) was achieved by comparing the Raman frequencies of the title compound with those observed in the parent molecules, *i.e.* α-glycine (Stenback, 1976) and oxalic acid dihydrate (Ebisuzaki & Angel, 1981), as one expects close correspondence between the internal frequencies of these molecules. The frequency shifts as indicated in Table 8 could be attributed to the influence of hydrogen bonds of different strengths in these compounds.

It is observed that there is a significant upward shift in the C—H stretch frequency in bis(glycinium) oxalate as compared with that in α-glycine. There is a downward shift in the C═O frequency in bis(glycinium) oxalate as compared with that in

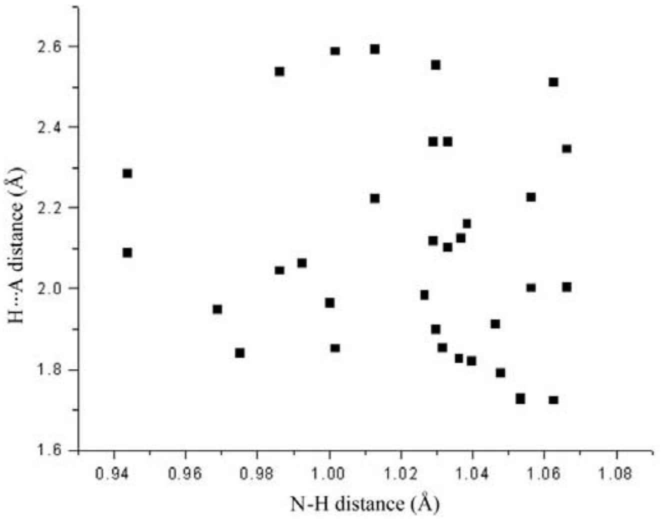

Figure 3
Distribution of N—H distance with H···*A* distance of neutron structures involving the glycine molecule or glycinium ion.

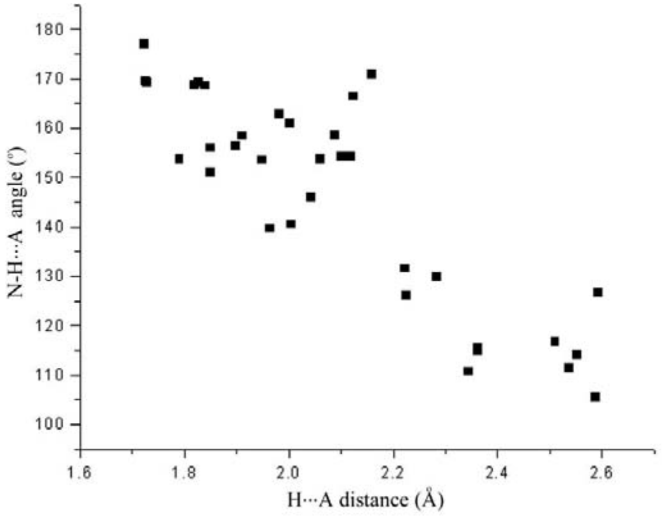

Figure 4
Distribution of H···*A* distance with N—H···*A* of neutron structures involving the glycine molecule or glycinium ion.

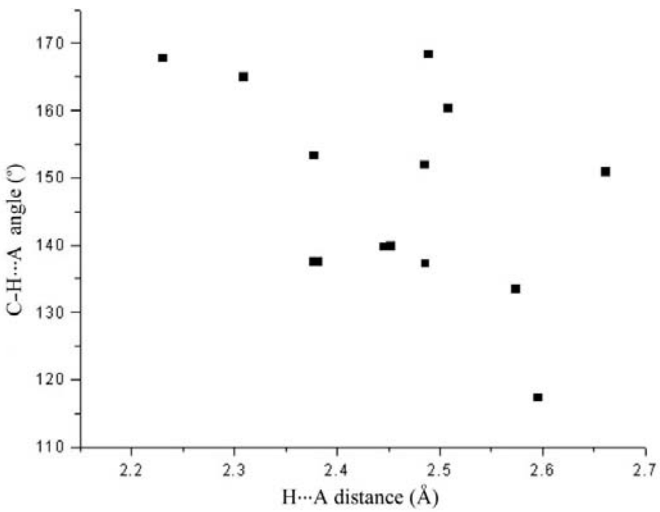

Figure 5
Distribution of H···*A* distance with C—H···*A* of neutron structures involving the glycine molecule or glycinium ion.

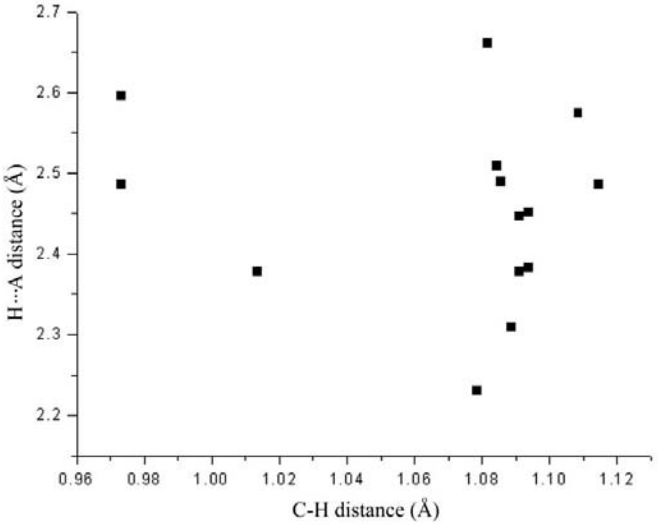

Figure 6
Distribution of C—H distance with H···*A* distance of neutron structures involving the glycine molecule.

oxalic acid dihydrate and there is an extra C═O mode at 1690 cm^{-1} (Fig. 8) in bis(glycinium) oxalate.

The upward shift in the C−H stretch frequency of bis(glycinium) oxalate indicates that the C−H···O bonds are much weaker than those observed in α-glycine. This conclusion is supported by the fact that the C−H bonds in α-glycine (C−H = 1.091 and 1.086 Å) are much more stretched than those in the title compound (C−H = 1.075 and 1.056 Å).

The downward shift of the C═O stretch frequency from 1738 cm^{-1} in oxalic acid dihydrate to 1717 cm^{-1} in bis(glycinium) oxalate indicates the existence of stronger hydrogen bonds involving this group. The mode at 1690 cm^{-1} (Fig. 7) was assigned to the highly stretched C═O bond of the oxalate ion (C═O = 1.272 Å) involved in the very short asymmetric hydrogen bond of bis(glycinium) oxalate. The following empirical relation between the bond strength and stretching frequency (Finkelshtein, 2003) was used to calculate the strength of the two C═O bonds of the oxalate ions: $D(\text{C═O}) = -246.7 + 0.5582\nu(\text{C═O})$.

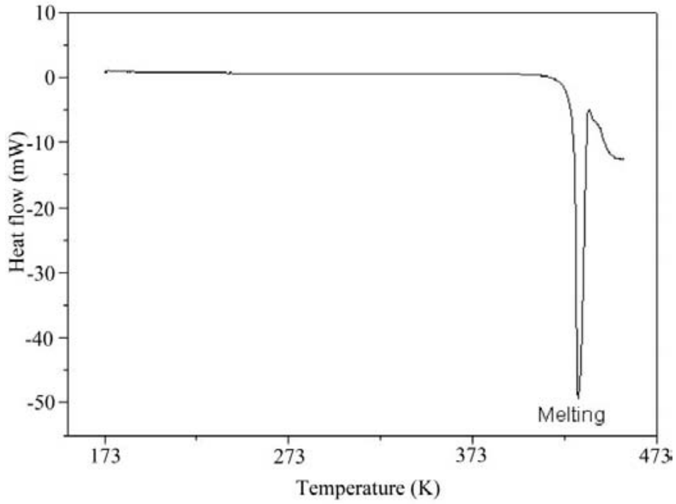

Figure 7
DSC curve of bis(glycinium) oxalate.

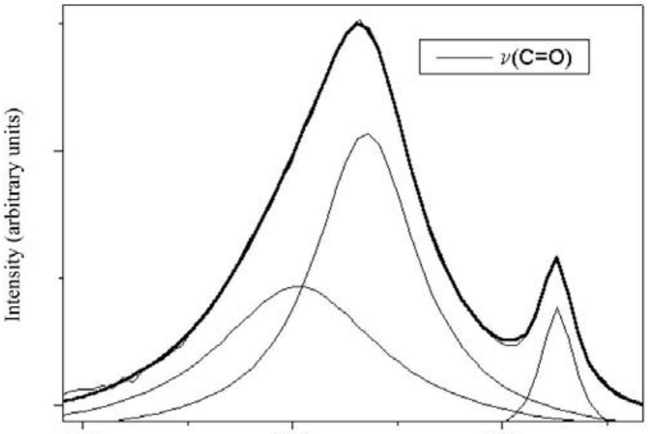

Figure 8
Raman spectrum of the C···O mode.

Table 8
Assignment of internal modes of Raman spectra of bis(glycinium) oxalate.

S. No.	Bis(glycinium) oxalate (cm^{-1})	α-glycine (cm^{-1})	Oxalic acid dihydrate (cm^{-1})	Tentative assignment
1	288			
2	321	358		C−C torsion
3	423			
4	475	493	480	CO_2 rock
5	533			
6	582	602		CO_2 wagging
7	672	698		CO_2 bending
8	859 901	892	856	C−C stretch
9	921	922		CH_2 rock
10	1052	1035		C−N stretch
11	1128	1109		NH_3 rock
12	1146	1139		
13	1315	1314		CH_2 wagging
14	1326	1334		Twisting
15	1419	1411		CO_2 sym. stretch
16	1440	1440		CH_2 scissoring
17	1455	1456		
18	1516	1515		NH_3 deformation
19	1612	1630		C−C stretch + CH_2 wagging
20	1670	1671		CO_2 asym. stretch
21	1690			C═O stretch
22	1717		1738	C═O stretch
23	2992	2972		CH_2 symm. stretch
24	3036	3007		CH_2 asym. stretch
25	3114	3127		N−H stretch

The values thus obtained are 2976.8 and 2914.0 kJ mol^{-1}; it is clear from these values that the short hydrogen bond of bis(glycinium) oxalate is very strong, causing a significant weakening of the acceptor C═O bond.

3.2. IR investigation

The IR absorption measurements were carried out on bis(glycinium) oxalate samples dispersed in CsI using a BOMEM DA8 FT–IR spectrometer operating at a resolution of 4 cm^{-1}. The far-IR spectrum was recorded in the range 30–600 cm^{-1} using a globar source, an extended Mylar beamsplitter and a DTGS detector. For recording the mid-IR spectrum, a Ge-coated KBr beamsplitter and MCT detector were used.

Using the well established correlation between the O···O distance in an O−H···O hydrogen bond and O−H stretch frequency (Nakamoto *et al.*, 1955), the broad band at 1750 cm^{-1} in the IR spectrum (Fig. 9) was assigned to the O−H bond involved in the short asymmetric hydrogen bond of bis(glycinium) oxalate. There is a very large shift in the O−H stretch frequency from the unperturbed value of 3700 cm^{-1}, indicating a very strong O−H···O hydrogen bond

4. Hydrogen-bond energy calculation

The Lippincott & Schroeder (1955) semi-empirical potential function for linear hydrogen bonds described below was used to estimate the bond energy of the very short O—H···O bond

$$\begin{aligned} V_{\rm HB} = {} & D_1\{1-\exp[-n_1(r-r_{01})^2/2r]\} \\ & - CD_2\{\exp[-n_2(R-r-r_{02})^2/2C(R-r-r_{02})]\} \\ & + A\exp[-b(R)] - B/R^6. \end{aligned}$$

The energy calculated using the potential parameters A, B, b, D_1, D_2, n_1, n_2, r_{01}, r_{02} and C taken from the literature (Reid, 1959) was -247.36 kJ mol^{-1}. This value indicates that this bond between the H atom and the acceptor O atom of the oxalate ion has partial covalent nature. Fig. 10 shows the potential energy contour of the O—H···O bond for the experimentally obtained O···O distance. Since there is no second minima in the potential energy near the acceptor O atom there is no disorder in the hydrogen bond.

One can explain the asymmetry of this short hydrogen bond by the fact that it is between two molecules having different proton-donating power. It is known that the proton-donating powder of oxalic acid (pK_a = 1.23) is higher than that of glycine (pK_a = 2.35). This fact is taken into account in the energy calculation by the potential parameter C. C is taken as 1 only for the cases where donor and acceptor groups are identical in all respects (Reid, 1959), making the potential symmetric; such homonuclear symmetric hydrogen bonds are the strongest known hydrogen bonds (Gilli & Gilli, 2000). For all other cases, C is less than 1, resulting in an asymmetric potential.

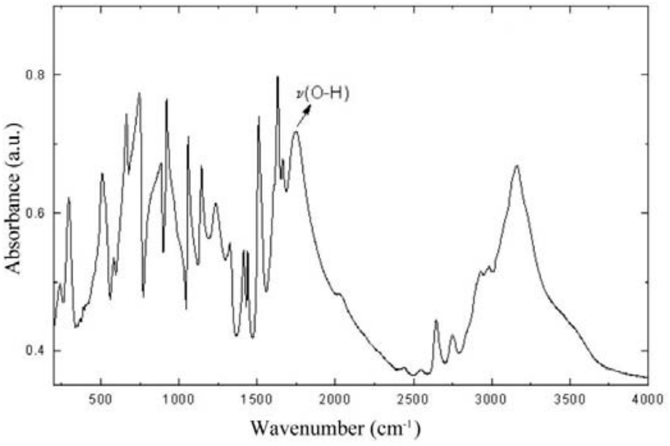

Figure 9
IR spectra of bis(glycinium) oxalate.

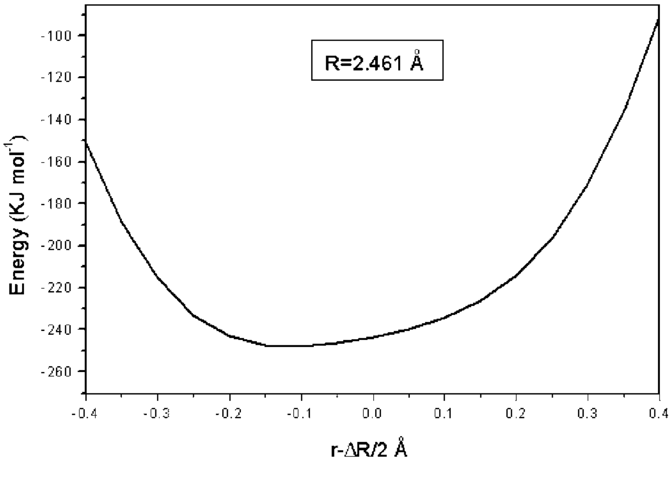

Figure 10
Potential energy contour of the O—H···O bond for the experimentally obtained O···O distance.

5. Conclusions

The most significant conclusion that one arrives at from this study is that the very short O—H···O bond between the glycinium and oxalate ions of bis(glycinium) oxalate is asymmetric in nature owing to the difference in the proton affinity of the two hydrogen-bonded molecules (Gilli & Gilli, 2000). The non-existence of any phase transition in these crystals can be rationalized by the fact that there is no disorder in the short O—H···O bond at room temperature. This lack of disorder is due to the fact that there is no secondary minimum in the hydrogen-bond energy, which can become prominent at some temperature. The spectroscopic measurements as well as the hydrogen-bond energy calculation indicated that the hydrogen bond is very strong with partial covalent nature. C—H···O interactions for both the Cα H atoms of the glycinium ion have been observed. A database study of various room-temperature neutron structures of compounds involving glycine showed that the $\rm NH_3^+$ group predominantly forms a three-centered hydrogen bond. This behavior is due to the fact that there are more acceptors than donors.

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