

Crystal structure of *bis*glycine hydrobromide – A reinvestigation

S NATARAJAN^{a*} and E ZANGRANDO^b

^aSchool of Physics, Madurai Kamaraj University, Madurai 625 021, India

^bDepartment of Chemistry, University of Trieste, 34127 Trieste, Italy

MS received 19 September 1991; revised 10 March 1992

Abstract. A reinvestigation of the crystal structure of *bis*glycine hydrobromide was carried out. The structure is orthorhombic, space group $P2_12_12_1$, with $a = 5.385(1)$, $b = 8.199(2)$, $c = 18.402(3)$ Å and $Z = 4$. Three-dimensional X-ray intensity data were collected on a CAD 4 diffractometer using $\text{MoK}\alpha$ radiation for the structure elucidation and refinement. The final R value is 0.019 for 1020 reflections. The structural parameters obtained are more accurate than those reported earlier. All the hydrogen atoms have been located in the present study. The glycine molecules are held together by a network of $\text{N-H}\dots\text{Br}^-$, $\text{N-H}\dots\text{O}$ and $\text{O-H}\dots\text{O}$ hydrogen bonds. One of the glycine molecules exists as a zwitterion whereas the other is in the cationic form.

Keywords. Glycine; amino acid adduct; crystal structure.

1. Introduction

Amino acids and their complexes are of considerable chemical and biological interest. Also, *bis*glycine compounds are reported to have some therapeutic values (Frost 1942). Hence, we have taken up a systematic investigation of several complexes of glycine with inorganic acids and salts and elucidated their crystal structures (Natarajan *et al* 1984). The crystal structure of a complex of glycine with hydrobromic acid was reinvestigated and reported here. The structure of this complex has been known for some time (Buerger *et al* 1956; Hahn 1959) and the final value of the R factor is only of the order of 0.11 in the three projections. These authors had used the intensity data collected using Weissenberg and precession photographs. The present study was aimed at providing accurate structural parameters including the positions of the hydrogen atoms, for this important amino acid derivative.

2. Experimental

Single crystals of *bis*glycine hydrobromide in the form of transparent colourless needles were obtained from a saturated aqueous solution containing glycine and hydrobromic acid. Preliminary cell dimensions were obtained from Weissenberg photographs. Final unit cell dimensions were determined by least-squares refinement of the setting angles

*For correspondence

Table 1. Crystal data for bisglycine hydrobromide.

	Present work	Earlier work*
Molecular formula	: (NH ₂ CH ₂ COOH) ₂ HBr	
Molecular weight	: 231.05	
Crystal system	: Orthorhombic	
<i>a</i>	: 5.385(1) Å	5.40 Å
<i>b</i>	: 8.199(2)	8.21
<i>c</i>	: 18.402(3)	18.42
Volume of the unit cell	: 812.5 Å ³	816.6 Å ³
Number of molecules in the unit cell	: 4	4
Density (experiment)	: 1.90 g cm ⁻³	1.94 g cm ⁻³
Density (calculated)	: 1.89	1.88
Linear absorption coefficient (for MoKα)	: 49.8 mm ⁻¹	
Space group	: P2 ₁ 2 ₁ 2 ₁	

* Burger, Barney and Hahn, 1956.

for 25 reflections collected using a CAD 4 diffractometer. The density of the crystals was determined by the flotation method using a liquid-mixture of bromoform and xylene. The crystal data are given in table 1. The cell parameters reported by Burger *et al* (1956) are also given in the same table for comparison.

The three-dimensional intensity data were collected using MoKα radiation in the $\omega - 2\theta$ scan mode in the range $3 \leq \theta \leq 28^\circ$, $0 < h < 7$, $0 < k < 10$, $0 < l < 24$. Out of the 1179 reflections measured, 1020 reflections with $I > 3\sigma(I)$ were used for structure determination and refinement. Three monitor reflections, measured every three hours, showed no significant intensity decay. Intensities were corrected for Lorentz and polarization effects and for anomalous dispersions. Transmission factors varied from a maximum of 99.9% to a minimum of 93.8%. An empirical absorption correction was applied.

The structure was determined using the Patterson and Fourier methods with the programs in the *Structure determination package* (1981) and refined using full-matrix least-squares calculations. All the hydrogen atoms were located from a difference Fourier map and included in the refinement. The function minimized was $\Sigma w(|Fo| - |Fc|)^2$ where $w = 1/[\sigma^2(Fo) + (0.02 * Fo)^2 + 1.0]$. The final *R* index was 0.019 and $R_w = 0.022$. Refinement with inverted coordinates gave $R^- = 0.035$ and $R_w^- = 0.045$, confirming the correct assignment of absolute configuration. The atomic scattering factors used were from the *International tables for X-ray crystallography* (1974). Calculations were carried out using a MICROVAX 2000 computer. The maximum and minimum electron densities in the final difference Fourier map were 0.27 and $-0.27 e/\text{\AA}^3$ respectively, adjacent to the bromine atom.

Lists of structure factors and anisotropic thermal parameters for the non-hydrogen atoms are available from the authors.

3. Results and discussion

An ORTEP (Johnson 1965) drawing of the asymmetric unit with the atom numbering scheme (thermal ellipsoids 50%) is shown in figure 1, in which hydrogen atoms are

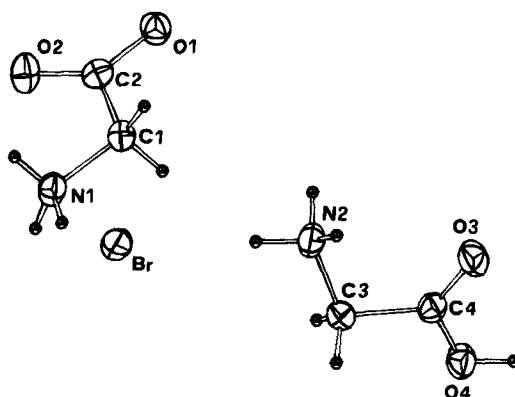


Figure 1. ORTEP drawing of the asymmetric unit with the atom numbering scheme (thermal ellipsoids 50%). Hydrogen atoms are represented as spheres of radius 0.10 Å.

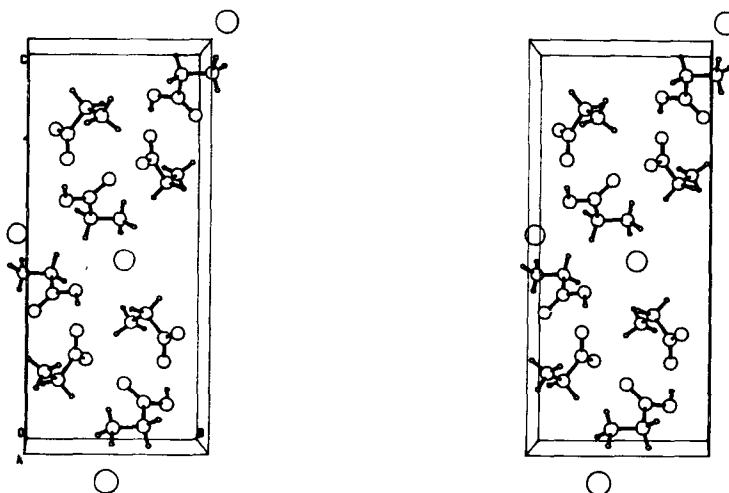


Figure 2. Stereo PLUTO diagram of molecular packing.

represented as spheres of radius 0.10 Å. A stereo PLUTO (Motherwell and Clegg 1978) diagram of the molecular packing is given in figure 2. The final positional and equivalent isotropic thermal parameters for non-hydrogen atoms are given in table 2. The positional and isotropic thermal parameters of the hydrogen atoms are also given in table 2.

The main new features of the present investigation are the precision of the structural parameters and the accurate determination of the positions of the hydrogen atoms. The bond lengths and angles of the glycine molecules are given in table 3. The esd's are much smaller in this investigation in comparison with the earlier study (Buerger *et al* 1956; Hahn 1959). The glycine molecule 1 exists as a zwitterion, i.e., $\text{NH}_3^+ \text{CH}_2\text{COO}^-$, whereas glycine molecule 2 exists in the cationic form, i.e., $\text{NH}_3^+ \text{CH}_2\text{COOH}$ in this structure. This is evident from the fact that the C–O distances and the bond angles around the carbon atom of the carboxylic group have values

Table 2. Fractional atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms.

Atom	x	y	z	* B_{eq} (\AA^2)
(a) <i>Non-hydrogen atoms</i>				
Br	-0.66875(6)	-0.07315(4)	0.53487(2)	2.143(4)
O1	0.3034(5)	0.3413(3)	0.2129(1)	2.24(4)
O2	0.6104(4)	0.2821(3)	0.2905(1)	2.40(5)
C1	0.6399(7)	0.1835(4)	0.1694(2)	2.04(6)
C2	0.5096(6)	0.2774(4)	0.2290(2)	1.74(5)
N1	0.8721(5)	0.1060(3)	0.1948(1)	2.10(5)
O3	0.1715(6)	0.0442(3)	0.3335(1)	2.82(5)
O4	0.2682(5)	0.2808(3)	0.3874(1)	2.46(5)
C3	-0.0860(6)	0.1409(4)	0.4296(2)	1.91(6)
C4	0.1331(7)	0.1487(4)	0.3789(2)	1.94(6)
N2	-0.1860(6)	-0.0274(3)	0.4295(1)	2.26(5)
(b) <i>Hydrogen atoms</i>				
H1	0.52(1)	0.097(6)	0.157(2)	2.64
H2	0.67(1)	0.257(6)	0.130(2)	2.64
H3	-0.02(1)	0.171(6)	0.479(2)	2.38
H4	-0.20(1)	0.217(6)	0.409(2)	2.38
H5	0.97(1)	0.061(6)	0.158(2)	2.74
H6	0.96(1)	0.182(6)	0.213(2)	2.74
H7	0.85(1)	0.017(6)	0.225(2)	2.74
H8	-0.32(1)	-0.038(6)	0.463(3)	2.90
H9	-0.23(1)	-0.053(6)	0.386(2)	2.90
H10	-0.09(1)	-0.105(6)	0.451(3)	2.90
H11	0.38(1)	0.292(6)	0.355(3)	3.15

$$*B_{eq} = (4/3) \sum_i \sum_j a_i a_j \beta_{ij}$$

Table 3. Bond lengths (\AA) and angles ($^\circ$). The esd's are given in parentheses.

Bond lengths		Bond angles	
C1-C2	1.512(8)	O1-C2-O2	125.3(5)
C2-C1	1.263(7)	C1-C2-O1	116.7(5)
C2-O2	1.257(7)	C1-C2-O2	118.0(5)
C1-N1	1.478(8)	N1-C1-C2	112.4(5)
C1-H1	0.975(6)	H1-C1-H2	112.6(5)
C1-H2	0.954(6)	H5-N1-H6	104.7(5)
N1-H5	0.947(5)	H5-N1-H7	101.1(5)
N1-H6	0.855(5)	H6-N1-H7	113.3(5)
N1-H7	0.927(5)	O3-C4-O4	124.7(6)
C3-C4	1.506(9)	C3-C4-O3	122.0(6)
C4-O3	1.214(7)	C3-C4-O4	113.2(5)
C4-O4	1.314(7)	N2-C3-C4	108.9(5)
C3-N2	1.481(7)	H3-C3-H4	114.6(6)
O4-H11	0.859(4)	H8-N2-H9	113.8(6)
C3-H3	0.998(6)	H8-N2-H10	94.6(4)
C3-H4	0.934(6)	H9-N2-H10	112.3(5)
N2-H8	0.934(5)	H11-O4-C4	113.4(5)
N2-H9	0.858(5)		
N2-H10	0.916(5)		

Table 4. Hydrogen bond parameters.

X-H...Y	X...Y(Å)	H...Y(Å)	X-H...Y(°)
N1-H5...Br ^I	3.359(5)	2.496	151.5
N1-H6...O1 ^{II}	3.038(7)	2.263	150.8
N1-H7...O1 ^{III}	2.913(7)	2.018	161.8
N2-H8...Br	3.265(6)	2.335	173.7
N2-H9...O1 ^{IV}	2.902(6)	2.056	168.6
N2-H10...Br ^V	3.341(5)	2.686	123.3
O4-H11...O2	2.564(6)	1.711	171.0

Symmetry code: I $\frac{1}{2}-x, -y, \frac{1}{2}+z$, II $1+x, y, z$, III $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$, IV $-x, \frac{1}{2}+y, \frac{1}{2}-z$, V $\frac{1}{2}+x, \frac{1}{2}-y, -z+1$.

expected for such configurations. The molecular parameters of the glycine molecules are normal as found in other similar structures (Natarajan 1979).

The glycine molecules are held together by a network of N-H...Br, N-H...O and O-H...O hydrogen bonds. There is a strong hydrogen bond between O4 and O2, the O4...O2 distance being 2.564 Å, which also connects the two glycine molecules.

The geometry of the hydrogen bonds is given in table 4. The C^α-C' groups are planar, the nitrogen atom is shifted from the plane of the C^α-C' group by 0.062 and 0.368 Å, respectively, in glycine 1 and 2. The dihedral angles between the C^α-C' and the C'-C^α-N planes are 2.3° and 15.6°, respectively, in the two glycine molecules. The bromine anion participates in hydrogen bonding and fills up the empty spaces, providing the necessary charge balance.

References

- Buerger M J, Barney E and Hahn T 1956 *Z. Kristallogr.* **108** 130 *structure determination package* 1981 (Delft: Enraf-Nonius)
- Frost W S 1943 *J. Am. Chem. Soc.* **64** 1286
- Hahn T 1959 *Z. Kristallogr.* **111** 161
- International tables for X-ray crystallography* 1974 (Birmingham: Kynoch) vol. 4
- Johnson C K 1956 ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, USA
- Motherwell W D S and Clegg W 1978 PLUTO, Program for plotting molecular and crystal structures, University of Cambridge, England
- Natarajan S 1979 *Studies in crystal structure analysis*, PhD Thesis, Madurai Kamaraj University, Madurai, p. 96
- Natarajan S, Ravikumar K and Rajan S S 1984 *Z. Kristallogr.* **168** 75