

# The Crystal and Molecular Structure of *N*-(Phosphonomethyl)-glycine (Glyphosate)

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*N*-(Phosphonomethyl)glycine (glyphosate) was isolated from the commercial product Roundup® and recrystallized from hot water. The compound was identified by IR and <sup>13</sup>C NMR spectra. The crystal and molecular structure was determined from three dimensional X-ray diffraction data. The white crystals belong to the monoclinic space group *P*2<sub>1</sub>/*c* (No. 14). The cell parameters are *a* = 8.682(5), *b* = 7.973(8), *c* = 9.875(5) Å, β = 105.74(4)°, *V* = 675.9(8) Å<sup>3</sup> and *Z* = 4. The structure was refined to a final *R*-value of 3.0 %. The molecules are zwitterions <sup>-</sup>HO<sub>3</sub>PCH<sub>2</sub>NH<sub>3</sub><sup>+</sup>CH<sub>2</sub>COOH. The molecules are connected by a network of hydrogen bonds.

A study of *N*-(phosphonomethyl)glycine and its metal complexes is essential to understand its behaviour as a herbicide and its metabolic decomposition. Our interest in crystalline metal complexes of glyphosate led us to study its crystal and molecular structure.

## EXPERIMENTAL

**Crystal preparation.** Glyphosate was isolated from the commercial herbicide Roundup® by ion-exchange chromatography using Amberlit IRA-400<sup>1</sup> followed by recrystallization from hot water. The IR and <sup>13</sup>C NMR spectra of recrystallized glyphosate was compared to those of a glyphosate sample (96 %) supplied by Monsanto Co., St. Louis, Missouri, U.S.A.; the spectra were found to be identical.

**Structure determination.** The X-ray intensities were recorded with a Syntex *P*2<sub>1</sub> automatic four circle diffractometer employing graphite monochromatized MoKα-radiation. The unit cell parameters were calculated by least squares refinement of 15 reflections. The intensities of 2056 independent reflections were collected (5 ≤ 2θ ≤ 50°) at room temperature using θ/2θ-scan technique and the scan rate varying from 1.00 to 29.3° min<sup>-1</sup> depending upon the

peak intensity. The intensity of one standard reflection, recorded after every 50 measurements to monitor the crystal stability, remained essentially constant throughout the data collection.

Out of 2056 measured reflections 1542 were observed on the basis of *I* > 3δ(*I*). The data were corrected for Lorentz and polarisation factors but not for absorption. The intensity, *I*, and standard deviation of each reflection was calculated by using the following equations:

$$I = [\text{SC} - \text{BC}] \text{SR} \text{ and}$$

$$\delta = [\text{SC} + \text{BC}]^{1/2} \text{SR}$$

where SC is the total scan count  
BC is the total background count  
SR is the scan rate

The structure was solved by direct methods using the X-Ray System.<sup>2</sup> The phases of the 352 *E*-values larger than 1.2 were calculated. Refinement was carried out with programs of the X-Ray System. The scattering factors for C, P, O and N were those of Cromer and Mann<sup>3</sup> and for H atoms those of Stewart Davidson and Simpson.<sup>4</sup>

Refinement of all non-hydrogen atoms with isotropic thermal parameters led to an *R*-value of 0.083 and subsequent block-diagonal refinement with anisotropic temperature factors led to an *R*-value of 0.049. At this point all hydrogen atoms were located from a difference Fourier map. Three least squares cycles were then computed, in which non-hydrogen atoms were assigned anisotropic and hydrogen atoms isotropic thermal parameters. After the last cycle the final *R*-value was 0.030. No weighting scheme was used. The final difference Fourier map showed no significant features. The calculations were carried out on a UNIVAC 1100 computer. The final positional and thermal parameters of the atoms are given in Tables 1 and 2. A table of the calculated and observed structure factors is available from the authors.

Table 1. Fractional atomic coordinates and anisotropic thermal parameters ( $\times 10^3$ ) for non-hydrogen atoms with their standard deviations. The anisotropic thermal parameters are of the form  $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$ .

Atom	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
P1	.94899(1)	.27559(1)	.07465(1)	16.57(3)	16.04(5)	19.00(6)	-.10(3)	8.90(3)	-1.28(4)
O1	.04375(3)	.71869(4)	.08303(3)	36.3(1)	24.4(2)	20.2(2)	-.4(1)	13.5(1)	-.4(1)
O2	.90047(3)	.44165(4)	.12153(3)	30.1(1)	20.2(2)	26.5(2)	3.1(1)	15.4(1)	-1.9(1)
O3	.85233(3)	.12301(4)	.08678(3)	19.2(1)	22.1(2)	30.1(2)	-4.8(1)	11.5(1)	-1.9(1)
O4	.56500(3)	.67680(4)	.46322(4)	27.7(1)	38.5(2)	33.0(2)	-2.5(1)	13.8(1)	-10.8(1)
O5	.36448(3)	.58338(4)	.28341(3)	16.4(1)	46.5(2)	33.1(2)	-.8(1)	9.9(1)	-4.6(2)
C1	.15631(4)	.24194(5)	.17485(5)	17.1(1)	19.0(2)	29.1(3)	-1.9(1)	8.0(1)	-2.0(2)
C2	.37871(4)	.03577(6)	.23287(5)	17.5(1)	33.5(2)	35.9(3)	3.3(1)	10.6(2)	1.3(2)
C3	.51482(4)	.60760(5)	.35134(5)	19.6(1)	20.5(2)	28.5(3)	-.3(1)	10.3(1)	1.6(2)
N1	.79313(3)	.56575(4)	.33676(4)	16.8(1)	18.4(2)	26.0(2)	1.7(1)	9.2(1)	-1.7(1)

Table 2. Final positional parameters and isotropic thermal parameters ( $\times 10^3$ ) for hydrogen atoms with their standard deviations.

Atom	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>	<i>U</i>
H1	-.0196(8)	.1462(9)	.3861(7)	8.0(2)
H2	.8282(6)	.7669(8)	.2109(6)	4.2(2)
H3	.2218(4)	.3184(4)	.1368(4)	1.6(1)
H4	.1785(6)	.4873(7)	.5723(5)	3.8(1)
H5	.8449(6)	.4915(7)	.2939(6)	3.7(2)
H6	.4051(5)	.0927(6)	.3282(5)	3.2(1)
H7	.3954(6)	.9095(7)	.2412(6)	3.8(1)
H8	.6959(8)	.4014(8)	.6771(7)	6.5(2)

## RESULTS

The molecular structure of the *N*-(phosphonomethyl)glycine is shown in Fig. 1.

The backbone of the molecule forms a non-planar zig-zag chain. Atoms P1-C1-N1-C2 and N1-C2-C3-O5 in the zig-zag chain form an almost planar group at an angle of 75° to each other. Some selected torsional angles are given in Table 3.

Intramolecular distances and angles with their standard deviations are shown in Table 4. The C1-P1 bond length of 1.823 Å is in good agreement with the values given in the litera-

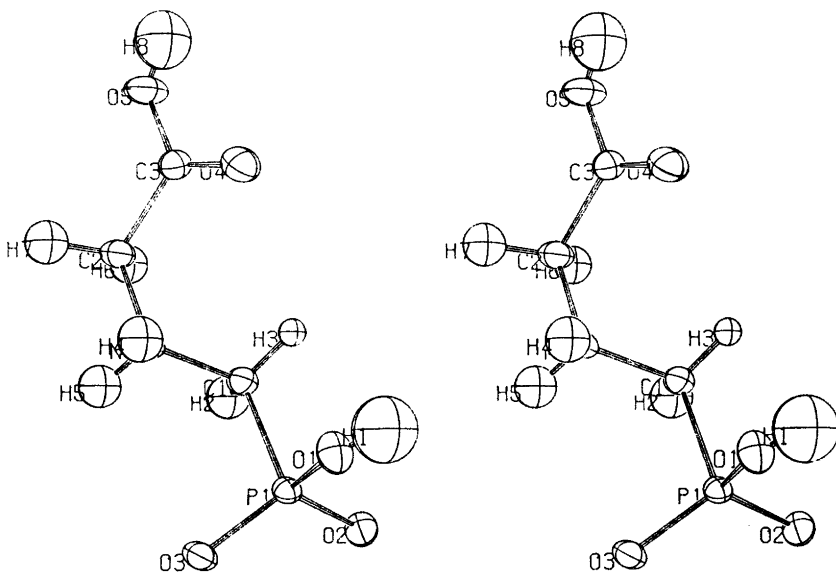


Fig. 1. A stereo view of glyposate molecule.

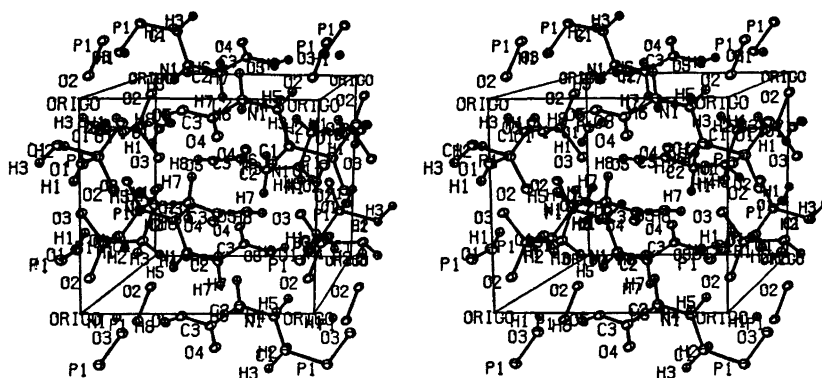


Fig. 2. Stereo view of the molecule packing of glyphosate.

ture.<sup>5</sup> One hydrogen atom has transferred from the phosphono group to the amino group. The C–H and N–H bond lengths vary from 0.914 to 1.118 Å. The O–H bond lengths in the phosphono and carboxyl groups are 0.711 and 0.743 Å, respectively. Two oxygens of the phosphono group are in resonance with each other as indicated by the lengths of the bonds P1–O2 and P1–O3, which are 1.500 and 1.501 Å, respectively. The P1–O1 bond length of 1.576 Å indicates a single bond.

The molecules are hydrogen bonded to their neighbours, forming a hydrogen bonded lattice via O–H...O and N–H...O bonds between the

Table 5. Hydrogen bonds.

Symmetry code:  
 (a)  $1-x, y-1/2, 1/2-z$  (c)  $x, y, z$   
 (b)  $1-x, 1/2+y, 1/2-z$  (d)  $x, 1/2-y, 1/2+z$

A–H...B	H...B	∠AHB	A–B
O1–H1...O2 <sup>a</sup>	1.944(69)	157.0(66)	2.613(4)
N1–H4...O3 <sup>b</sup>	1.866(53)	169.3(44)	2.817(5)
N1–H5...O2 <sup>c</sup>	1.932(60)	144.4(47)	2.728(5)
O5–H8...O3 <sup>d</sup>	1.826(75)	175.8(69)	2.568(5)

phosphono, amino and carboxyl groups. Data for the hydrogen bonds are given in Table 5 and the packing of the molecules is shown in Fig. 2.

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Table 3. Torsion angles (°).

O1–P1–C1–N1	± 75.2(7)
P1–C1–N1–C2	± 175.0(3)
C1–N1–C2–C3	± 74.6(1)
N1–C2–C3–O5	± 177.7(6)

Table 4. Interatomic distances (Å) and angles (°) with their standard deviations.

O1–P1	1.576(3)	O1–H1	0.711(71)	O1–P1–O2	111.7(2)
O2–P1	1.500(3)	C1–H2	1.118(61)	O1–P1–O2	106.0(2)
O3–P1	1.501(3)	C1–H3	0.975(38)	O2–P1–O3	118.7(2)
P1–C1	1.823(3)	N1–H4	0.962(52)	C1–P1–O1	104.0(2)
C1–N1	1.485(5)	N1–H5	0.914(59)	C1–P1–O2	106.3(2)
N1–C2	1.483(4)	C2–H6	1.014(50)	C1–P1–O3	109.2(2)
C2–C3	1.514(7)	C2–H7	1.017(53)	N1–C1–P1	111.5(2)
C3–O4	1.206(5)	O5–H8	0.743(75)	C2–N1–C1	113.4(3)
C3–O5	1.310(4)			C3–C2–N1	111.8(4)
				O5–C3–C2	109.6(4)
				O4–C3–C2	123.6(3)

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