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The Crystal and Molecular Structure of β-Guanidinopropionic Acid

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β-Guanidinopropionic acid (βGP), $C_4H_9N_3O_2$, m.p. 215–220°C, is monoclinic, with the following space group and cell dimensions at room temperature: $P2_1/a$; $a=11{\cdot}818$ (4), $b=7{\cdot}247$ (4), $c=7{\cdot}311$ (4) Å, $\beta=98{\cdot}22$ (4)°; $Z=4$, $\varrho_{\text{calc}}=1{\cdot}403$, $\varrho_{\text{meas}}=1{\cdot}403$ g cm^{-3}. Sphenoidal crystals were grown from aqueous solution. Final $R=0{\cdot}061$ on 885 observed reflexions. The molecules are folded zwitterions held by hydrogen bonds in planar sheets perpendicular to **c**. An intramolecular hydrogen bond is found.

Experimental

Weissenberg photographs showed systematic absences for $0k0$, k odd and $h0l$, l odd, uniquely defining the space group as $P2_1/a$. A tape-controlled Stoe-Güttinger diffractometer was used for data collection. Accurate cell dimensions were obtained from a least-squares refinement using the 2θ values of 43 reflexions. Intensity data were collected from hnl and hkn layers ($n=0,1,2,3$) up to $\sin\theta/\lambda=0{\cdot}622$ using Ni-filtered Cu $K\alpha$ radiation (1·5418 Å) and a pulse-height analyser. 1131 reflexions were measured of which 106 were systematically extinct, and 85 designated as 'unobserved', *i.e.* with integrated intensity less than 100 counts above background. The remaining reflexions were regarded as 'observed'.

The X-RAY 70 suite of programs (Stewart, Kundell & Baldwin, 1970), implemented on the CDC 7600 computer at the University of London Computer Centre, was used for data processing and structure determination. Atomic scattering factor data were taken from *International Tables for X-ray Crystallography* (1962).

The positions of the heavy atoms were found from a Fourier synthesis employing an initial set of 163 phases obtained by the conventional symbolic addition procedure of Karle & Karle. However, it was not immediately possible to distinguish between the guanidino and carboxyl ends of the molecule from this Fourier map. The two possible models gave initial residual indices $[R=\sum||F_o|-|F_c||/\sum|F_o|]$ of 0·428 and 0·403. Three cycles of full-matrix least-squares refinement, mini-

Table 1. *Fractional atomic coordinates*

	x	y	z		x	y	z
C(1)	0·5226 (2)	0·0511 (5)	0·7714 (4)	H(1)	0·390 (3)	−0·049 (7)	0·585 (6)
C(2)	0·3982 (2)	0·0492 (5)	0·6783 (5)	H(2)	0·352 (4)	0·002 (6)	0·755 (5)
C(3)	0·3506 (2)	0·2297 (5)	0·5955 (4)	H(3)	0·281 (3)	0·202 (6)	0·502 (5)
C(4)	0·3626 (2)	0·5083 (5)	0·7935 (4)	H(4)	0·411 (3)	0·294 (6)	0·534 (5)
O(1)	0·5628 (2)	−0·0982 (4)	0·8367 (4)	H(5)	0·235 (3)	0·337 (6)	0·748 (5)
O(2)	0·5789 (2)	0·1987 (3)	0·7718 (4)	H(6)	0·223 (3)	0·604 (6)	0·877 (5)
N(1)	0·3100 (2)	0·3563 (4)	0·7267 (4)	H(7)	0·346 (3)	0·711 (6)	0·953 (6)
N(2)	0·3054 (2)	0·6286 (5)	0·8834 (4)	H(8)	0·491 (3)	0·656 (7)	0·793 (6)
N(3)	0·4696 (2)	0·5431 (5)	0·7711 (5)	H(9)	0·510 (4)	0·453 (7)	0·740 (6)

Table 2. *Final thermal parameters* × 100 Å^2

The temperature factor is of the form:

$$T=\exp\{-2\pi^2[(ha^*)^2U_{11}+(kb^*)^2U_{22}+(lc^*)^2U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23}]\}.$$

The overall temperature factor for the hydrogens, $U_{\text{Hyd}}=1{\cdot}5$ (3).

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2·4 (4)	2·1 (4)	3·6 (4)	−0·1 (1)	+0·2 (1)	−0·5 (2)
C(2)	2·7 (4)	2·6 (4)	4·6 (4)	−0·3 (1)	−0·5 (1)	−0·8 (2)
C(3)	3·0 (4)	3·3 (4)	3·4 (4)	−0·3 (1)	−0·5 (1)	−0·5 (2)
C(4)	2·7 (4)	2·3 (4)	2·9 (4)	+0·1 (1)	−0·5 (1)	+0·2 (2)
O(1)	3·1 (3)	2·6 (4)	6·1 (4)	+0·2 (1)	−0·4 (1)	+0·4 (2)
O(2)	2·4 (3)	2·5 (4)	6·1 (4)	−0·3 (1)	−0·1 (1)	−0·2 (1)
N(1)	2·4 (3)	2·5 (4)	3·9 (4)	−0·2 (1)	0·0 (1)	−0·8 (2)
N(2)	3·0 (4)	3·2 (4)	4·8 (4)	+0·2 (1)	−0·2 (1)	−1·0 (2)
N(3)	2·6 (4)	2·5 (4)	6·0 (4)	−0·3 (1)	+0·2 (1)	−0·2 (2)

mizing the function $\sum[\omega(|F_o|-|F_c|)^2]$, with an overall temperature factor and unit weights for all reflexions, were therefore carried out on each model, and gave residual indices of 0·244 and 0·172. It was found, moreover, that the bond lengths and angles from the latter structure were in good agreement with expected values and hence this was adopted as the correct alternative. Two cycles of least-squares refinement using isotropic temperature factors reduced R to 0·162. A further three cycles of refinement with anisotropic temperature factors and a weighting scheme then gave $R=0{\cdot}126$. Weights were assigned according to the following scheme:

$$\omega=XY$$

where

if $\sin\theta>0{\cdot}45$, $X=1$, otherwise $X=\sin\theta/0{\cdot}45$

if $F_o<6$, $Y=1$, otherwise $Y=6/F_o$.

A difference Fourier map was then prepared which revealed the positions of eight of the hydrogen atoms. The ninth hydrogen atom, however, could not be discerned. Examination of the observed and calculated structure factors (computed using non-hydrogen atoms only) showed considerable disagreement for the $hk3$ layer. Upon further investigation the residual index for this layer alone was found to be 0·362, as compared with the overall R of 0·126. It seemed likely that this was due to an error at the data collection stage, and detailed examination of the original data tape from the diffractometer showed this to be the case. Accordingly this group of data (55 'observed' and 34 'unobserved' reflexions) was discarded. The overall R index then became 0·089. A ΔF map now clearly revealed the positions of the nine hydrogen atoms. At this stage it was noted that 11 of the strongest reflexions (all with $\sin\theta/\lambda<0{\cdot}2$) had F_o considerably less than F_c. These re-

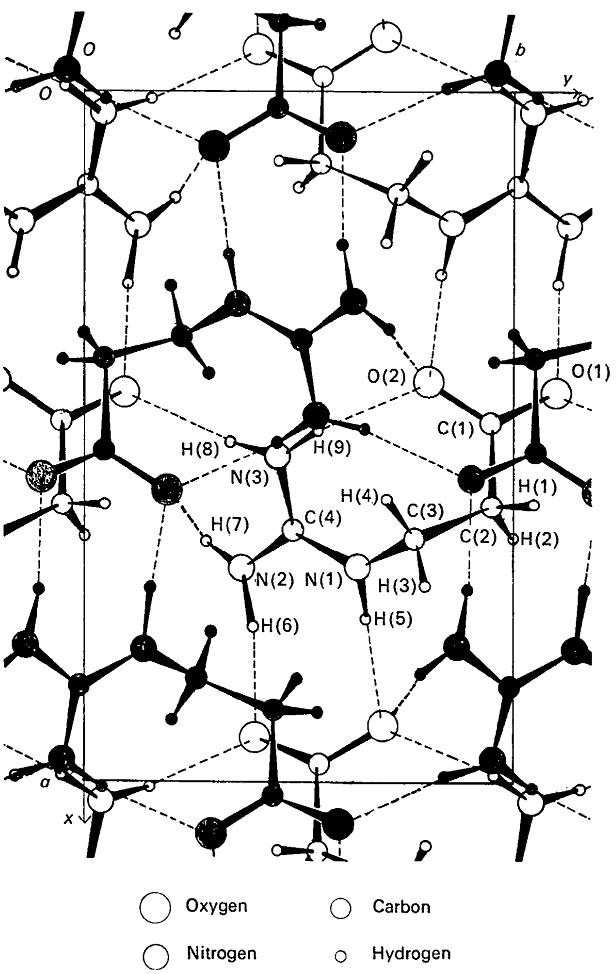

Fig. 1. z projection of the unit cell of βGP. ------ hydrogen bonds. Atoms on upper level are shaded.

Table 3. *Bond lengths* (Å)

C(1)	O(1) 1·249 (4)	O(2) 1·259 (4)	C(2) 1·529 (3)
C(2)	C(3) 1·515 (5)	H(3) 0·98 (5)	H(2) 0·95 (4)
C(3)	N(1) 1·457 (4)	H(3) 1·01 (3)	H(4) 1·01 (4)
C(4)	N(1) 1·323 (4)	N(2) 1·333 (5)	N(3) 1·322 (4)

N(1)	H(5) 0·93 (4)	
N(2)	H(6) 0·98 (4)	H(7) 0·88 (4)
N(3)	H(8) 0·87 (5)	H(9) 0·86 (5)

Hydrogen bonds (Å)

N(1)	—H(5)···O(2)	2·826 (4)	H(5)···O(2)	1·89 (4)
N(2)	H(6)···O(1)	2·847 (3)	H(6)···O(1)	1·88 (4)
	H(7)···O(2)	2·967 (4)	H(7)···O(2)	2·18 (4)
N(3)	H(8)···O(1)	2·837 (5)	H(8)···O(1)	1·98 (5)
	H(9)···O(2)	2·810 (4)	H(9)···O(2)	2·02 (5)

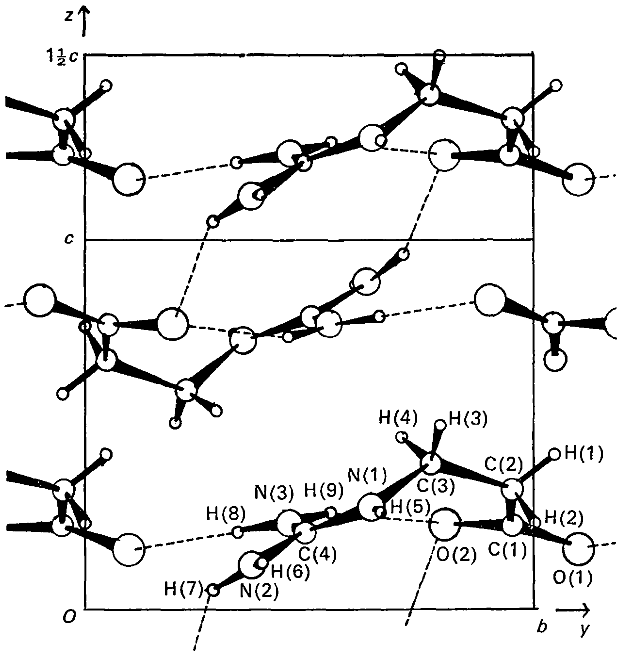

Fig. 2. *x* projection of part of the unit cell of *β*GP showing hydrogen-bonding scheme in the *yz* plane. For clarity, only a half of the contents of the unit cell in the x direction is shown.

flexions were thought to be affected by extinction and were assigned zero weight. An overall temperature factor was then assigned to the hydrogen atoms and all positional and thermal parameters further refined. The refinement was completed after four cycles, the final *R* indices being 0·061 for the observed reflexions and 0·064 for all measured reflexions. The average shift/error of the parameters in the final cycle of least-squares refinement was 0·1.

Final fractional coordinates are given in Table 1, temperature factors in Table 2, bond lengths in Table 3, and bond angles for the heavy atoms in Table 4. Table 5 gives some torsion angles for the molecule.[*]

Table 4. *Bond angles* (°)

O(1)–C(1)–O(2)	124·3 (2)	N(1)–C(4)–N(2)	118·8 (3)
O(1)–C(1)–C(2)	116·8 (3)	N(1)–C(4)–N(3)	121·3 (3)
O(2)–C(1)–C(2)	118·8 (3)	N(2)–C(4)–N(3)	119·8 (3)
C(1)–C(2)–C(3)	116·6 (3)	C(3)–N(1)–C(4)	125·8 (3)
C(2)–C(3)–N(1)	114·8 (3)		

The arrangement of the four molecules in the unit cell is shown in Fig. 1 and the *yz* plane hydrogen-bonding scheme in Fig. 2.

Table 5. *Torsion angles* (°)

The torsion angle *ABCD* is defined as the angle from *AB* to *CD* when viewed along the *BC* direction. The anticlockwise direction is defined as positive.

A	*B*	*C*	*D*	
O(1)	C(1)	C(2)	C(3)	+181
C(1)	C(2)	C(3)	N(1)	+83
C(2)	C(3)	N(1)	C(4)	+254
C(3)	N(1)	C(4)	N(3)	+192

Discussion

There is evidence that *β*GP gives rise to inhibitory effects at the crayfish neuromuscular junction which are indistinguishable from the effects of the natural inhibitory transmitter (Dudel, 1965). Its molecular structure and conformation may be of importance in elucidating its mode of action.

The molecule, in the crystal, is found to exist as a folded zwitterion, each terminal nitrogen atom being bonded to two hydrogen atoms. The five guanidyl hydrogen atoms are suitably placed for the formation of hydrogen bonds (Table 3). Three of these hold the molecules in sheets perpendicular to the **c** direction (Fig. 1), the fourth provides a link between pairs of adjacent sheets forming bilayers which are connected to each other purely by non-bonded interactions (Fig. 2). The fifth is an intramolecular bond between N(3) and O(2) (Fig. 1). This heterodesmic bonding pattern may, in part, explain the range in melting point which is observed.

The bond lengths obtained (Table 3) are in good agreement with usual values. The C(1)–O(1) and C(1)–O(2) bond lengths are effectively equal as are the C–N distances in the guanidyl group. This is as expected for the zwitterion. The bond angles about C(2) and C(3) (Table 4) deviate from the tetrahedral value by about 6°, but the remaining angles are not remarkable.

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References

Dudel, J. (1965). *Pflügers Arch.* **284**, 81–94.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 201–207. Birmingham: Kynoch Press.
Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1970). The X-RAY system, version of 1970.

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[*] The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30301 (10 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.