

Structure of γ -Guanidino- β -hydroxybutyric Acid, $C_5H_{11}N_3O_3$

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Abstract. $M_r = 161.16$, triclinic, $P\bar{1}$, $a = 8.519$ (3), $b = 9.909$ (2), $c = 4.879$ (6) Å, $\alpha = 92.69$ (5), $\beta = 112.00$ (5), $\gamma = 69.90$ (5)°, $V = 354.02$ Å³, $Z = 2$, $D_m = 1.494$, $D_x = 1.499$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.70924$ Å, $\mu = 1.3$ mm⁻¹, $F(000) = 172$, $T = 293$ K, $R = 0.091$ for 1622 observed reflections. The molecule occurs as a zwitterion, with the carboxyl group H transferred to the guanidyl group N, in the fully extended *trans*-zigzag form. All of the non-H atoms except the hydroxyl O are essentially coplanar. The molecules are held together by a three-dimensional network of N–H...O and O–H...N hydrogen bonds.

Introduction. γ -Guanidino- β -hydroxybutyric acid (GGBOPA) is a guanidyl and β -hydroxy derivative of γ -aminobutyric acid, GABA (Tomita, Higashi & Fujiwara, 1973), which is a nervous inhibitory transmitter of the central nervous system. The structural investigations of the GABA-related compounds are of interest for elucidation of the relationship between molecular conformations and their physiological functions. This paper deals with the molecular and crystal structure of the title compound and discusses some structural similarities between the related compounds.

Experimental. Title compound crystallized from aqueous ethanol solution as colorless, transparent prisms; space group from Weissenberg and precession photographs; unit-cell dimensions determined by least-squares refinement of the angular values of 25 diffractometer-measured reflections; density measured by flotation in C_6H_6 – CCl_4 mixture; intensities of 1637 independent reflections with $\sin\theta/\lambda < 0.65$ Å⁻¹ ($-10 \leq h \leq 10$, $-12 \leq k \leq 12$, $0 \leq l \leq 6$) collected from a crystal $0.24 \times 0.42 \times 0.18$ mm; Rigaku computer-controlled four-circle diffractometer, Mo $K\alpha$ radiation (Zr-filtered), ω - 2θ scan technique; 1622 reflections had $|F_o| > 2\sigma(F_o)$; three standard reflections (700, 0,10,0 and 005) monitored after every 50 reflections showed $< 3.1\%$ intensity fluctuation throughout data collection; intensities corrected for Lorentz and polarization factors but not for absorption;

direct methods using *SHELX75* (Sheldrick, 1975); block-diagonal least-squares procedure on F with unit weights; all H atoms located on a difference Fourier map; their positional and isotropic thermal parameters (fixed to 2.26 Å²) were included in the final refinement; final $R = 0.091$ ($R_w = 0.094$, $S = 0.749$); absolute max. height in final difference Fourier synthesis 0.9 e Å⁻³; average and max. Δ/σ after refinement 0.12 and 0.51 respectively for non-H atoms; all numerical calculations carried out on IBM 370 at Seoul National University; atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The final atomic parameters with their e.s.d.'s are given in Table 1.* The H atom of the carboxyl group is transferred to the N atom of the guanidyl group, and the molecule occurs as a zwitterion, $(\text{NH}_2)_2^+\text{CNHCH}_2\text{CH}(\text{OH})\text{CH}_2\text{COO}^-$, as in the cases of γ -guanidino- β -hydroxypropanesulfonic acid, GGBOPSA (Kim, Wakahara, Fujiwara & Tomita, 1973a), L-arginine dihydrate (Karle & Karle, 1964), GABA (Tomita *et al.*, 1973), taurine (Sutherland & Young, 1963; Okaya, 1966), homotaurine (Ueoka, Fujiwara & Tomita, 1972), γ -guanidinopropanesulfonic acid, GGPSA (Kim, Wakahara, Fujiwara & Tomita, 1973b), γ -amino- β -hydroxypropanesulfonic acid, GABOPSA (Kim, Bando, Hombo, Fujiwara & Tomita, 1979) and γ -hydroxy- β -aminobutyric acid, GOBAB (Kim & Park, 1979).

The bond distances and angles are listed in Table 2, and together with the intermolecular hydrogen-bond distances (deposited) these are acceptable values as a whole. In the guanidyl group, the three C–N distances and angles are also similar to those of guanidyl derivatives such as GGBOPSA, GGPSA and L-

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, hydrogen-bond distances and angles and planarities of the backbone and guanidyl group have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39707 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final positional ($\times 10^4$) and equivalent isotropic thermal parameters (\AA^2) for non-H atoms with their e.s.d.'s in parentheses

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_i a_i a_j$$

| | x | y | z | B_{eq} |
|------|-----------|----------|-----------|-----------|
| C(1) | 2531 (5) | 8015 (4) | 5991 (7) | 1.92 (10) |
| C(2) | 1131 (5) | 8381 (4) | 2800 (8) | 2.14 (10) |
| C(3) | 269 (5) | 7261 (4) | 1457 (7) | 1.86 (10) |
| C(4) | -1323 (5) | 7963 (4) | -1462 (8) | 2.11 (10) |
| C(5) | -3454 (5) | 7215 (4) | -5607 (8) | 2.01 (10) |
| N(1) | -2156 (4) | 6925 (3) | -2915 (7) | 2.36 (9) |
| N(2) | -4138 (5) | 6207 (3) | -6854 (8) | 2.81 (11) |
| N(3) | -4110 (5) | 8511 (3) | -7145 (7) | 3.18 (10) |
| O(1) | 2896 (4) | 6841 (3) | 7384 (6) | 2.41 (8) |
| O(2) | 3203 (4) | 8958 (3) | 7060 (6) | 3.36 (10) |
| O(3) | 1519 (4) | 5974 (3) | 976 (6) | 2.26 (8) |

Table 2. Bond distances (\AA) and angles ($^\circ$) of GGBOPA

| | | | |
|----------------|-----------|----------------|-----------|
| C(1)—C(2) | 1.530 (6) | C(3)—O(2) | 1.429 (5) |
| C(1)—O(1) | 1.257 (5) | C(4)—N(1) | 1.456 (6) |
| C(1)—O(2) | 1.253 (6) | C(5)—N(1) | 1.326 (6) |
| C(2)—C(3) | 1.527 (6) | C(5)—N(2) | 1.336 (6) |
| C(3)—C(4) | 1.533 (5) | C(5)—N(3) | 1.344 (6) |
| C(2)—C(1)—O(1) | 119.5 (4) | C(4)—C(3)—O(3) | 110.8 (3) |
| C(2)—C(1)—O(2) | 116.0 (4) | C(3)—C(4)—N(1) | 110.5 (3) |
| O(1)—C(1)—O(2) | 124.5 (4) | N(1)—C(5)—N(2) | 120.0 (4) |
| C(1)—C(2)—C(3) | 117.1 (4) | N(1)—C(5)—N(3) | 121.5 (4) |
| C(2)—C(3)—C(4) | 108.0 (3) | N(2)—C(5)—N(3) | 118.4 (4) |
| C(2)—C(3)—O(3) | 112.9 (3) | C(4)—N(1)—C(5) | 122.7 (4) |

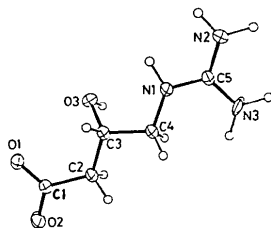


Fig. 1. Molecular conformation (Johnson, 1976) with atom numbering.

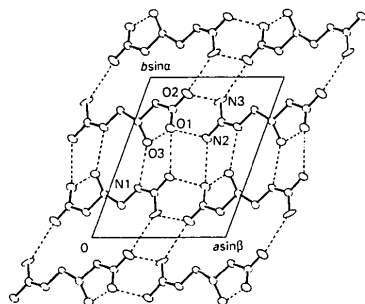


Fig. 2. The crystal structure projected along the c axis. Dotted lines indicate the hydrogen bonds.

arginine dihydrate. The C(5)—N distances in the guanidyl group average to 1.335 \AA , indicating that they have some double-bond character. The amounts of double-bond character (Pauling, 1960) of C(5)—N(1), C(5)—N(2) and C(5)—N(3) bonds are approximately 36, 33 and 31%, respectively.

As shown in Fig. 1, the molecular conformation is the fully extended *trans*-zigzag form; the torsion angle around C(4)—N(1) is $186.4 (4)^\circ$, which means roughly a *trans* conformation similar to those of GGBOPSA (Kim *et al.*, 1973a), L-arginine dihydrate (Karle & Karle, 1964) and GGPSA (Kim *et al.*, 1973b). The torsion angles around C(1)—C(2), C(2)—C(3) and C(3)—C(4) bonds are $180.9 (4)$, $169.2 (3)$ and $177.6 (3)^\circ$, respectively. Therefore, all of the non-H atoms except β -OH are essentially coplanar. The guanidyl group is planar with a maximum displacement of $0.010 (6) \text{ \AA}$. The dihedral angle between the plane of the guanidyl group and that passing through C(1)—C(2)—C(3)—C(4)—N(1)—C(5) is $2.5 (3)^\circ$.

In the crystal structure, all feasible H atoms of the molecule are utilized to form the hydrogen bonds, the molecule being held together by a three-dimensional network of N—H \cdots O and O—H \cdots N hydrogen bonds (Fig. 2).

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