

Table 4. Geometry of the internal H bond of H_3O_2^+ as determined by neutron diffraction

Compound	Symmetry at bond centre	O...O (Å)	O—H (Å)	H...O (Å)	O—H...O (°)	Reference
$o\text{-C}_6\text{H}_4(\text{COOH})\text{SO}_3\text{H}\cdot 3\text{H}_2\text{O}$	—	2.414 (3)	1.201 (5)	1.219 (5)	172.5 (3)	Attig & Williams (1976)
$\text{Co}(\text{en})_2\text{Cl}_3\cdot \text{HCl}\cdot 2\text{H}_2\text{O}$	1	2.431 (6)	1.215		180	Rozière & Williams (1976)
$\text{C}_6\text{H}_2(\text{NO}_2)_3\text{SO}_3\text{H}\cdot 4\text{H}_2\text{O}$	—	2.436 (2)	1.128 (4)	1.310 (4)	175.0 (3)	Lundgren & Tellgren (1974)
$\text{C}_6\text{H}_3(\text{COOD})(\text{OD})\text{SO}_3\text{D}\cdot 2\text{D}_2\text{O}$	1	2.435 (3)	1.217		180	Attig & Williams (1977)
$\text{YH}(\text{C}_2\text{O}_4)_2\cdot 3\text{H}_2\text{O}$	1	2.442 (3)	1.221		180	
$\text{YH}(\text{C}_2\text{O}_4)_2\cdot 3\text{H}_2\text{O}$	2	2.442 (2)	1.221		178.2 (3)	Brunton & Johnson (1975)
$\text{C}_6\text{H}_5\text{O}_2\text{NO}_2\cdot 2\text{H}_2\text{O}$	—	2.477 (2)	1.087 (3)	1.390 (3)	179.2 (2)	This work

H(11), H(12) and H(13). The long O—H distance, 1.087 (3) Å, and the short O...O distance, 2.477 (2) Å, fit well into the plot of O—H vs O...O distances given by Olovsson & Jönsson (1976). $Z_{\text{H}(13)}^2 - Z_{\text{O}(w)}^2$ is large, 0.0277 Å², in accordance with a broad, flat potential well. The corresponding values for the remaining four H atoms of the H_3O_2^+ complex are 0.0086, 0.0128, 0.0088 and 0.0069 Å² for H(11), H(12), H(21) and H(22) respectively. The conformation of the H_3O_2^+ complex is *gauche*. The angle between the planes defined by the central O...O bond and the bisectors of the outer H—O—H angles is 60.7°.

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Structure of DL- α -Amino-*n*-butyric Acid (Modification A): A Reinvestigation

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Abstract. $\text{C}_4\text{H}_9\text{NO}_2$, monoclinic, $P2_1/a$, $a = 9.829$ (4), $b = 4.78$ (2), $c = 11.908$ (5) Å, $\beta = 101.02$ (4)°, $V = 549.2$ Å³, $Z = 4$, $D_c = 1.247$ Mg m⁻³. Modification A shows disorder with regard to the position of the

terminal methyl group. The structure was refined both with and without constraints for the geometry of this terminal methyl group, and yielded final R values of 0.052 and 0.077, respectively, for 675 reflexions.

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Introduction. This work is part of a programme on intermolecular interactions in hydrogen-bonded molecular crystals (in particular, amino acids). DL- α -Amino-*n*-butyric acid has several crystalline modifications. Modification *A* was solved by Ichikawa & Iitaka (1968). They found the structure to be disordered with the terminal methyl group distributed over three orientations, corresponding to *trans*, *gauche* I and *gauche* II with respect to the N atom. The bond lengths belonging to the three terminal C—C distances appear to be much too short (1.42, 1.08 and 1.30 Å respectively); the other bond lengths and bond angles are normal. At lower temperature, ordering of the terminal methyl group might occur. Differential thermal analysis, however, indicated a phase transition to the low-temperature *C* modification at 201 K (Akimoto & Iitaka, 1972). Short bond lengths also appear in the refinement of the high-temperature *D* modification (Nakata, Takaki & Sakurai, 1980); here the terminal methyl group is distributed over two orientations, *trans* and *gauche* II with respect to the N atom. Molecular geometries with such extremely short C—C distances are not satisfactory. We therefore decided to reinvestigate the crystal structure of modification *A*, both with and without geometry constraints for the terminal methyl group.

Crystals of modification *A* were obtained by evaporation of an aqueous solution. Systematic absences determine the space group $P2_1/a$. Cell dimensions and intensities were measured with a θ - 2θ scan technique, up to 27.5° , on a computer-controlled CAD-4 diffractometer (Nonius), with Zr-filtered Mo $K\alpha$ radiation and a scintillation counter. Of the 964 independent reflexions, 675 with $I \geq 2.5\sigma(I)$ were measured, where $\sigma(I)$ is the variance of the intensity on the basis of counting statistics. No corrections for absorption and extinction were made. The structure was solved with *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Scattering factors were from Cromer & Mann (1968) for C, O and N and from Stewart, Davidson & Simpson (1965) for H. Full-matrix refinement without constraints gave results similar to those of Ichikawa & Iitaka (1968). The function minimized was $\sum w_i(|F_o| - |F_c|)^2$ with weights based on $\sigma^{-2}(F_o)$; in this case our final R ($= \sum |F_o| - |F_c| / \sum |F_o|$) was 0.052. The three bond lengths for *trans*, *gauche* I and *gauche* II were 1.454, 1.059 and 1.245 Å, respectively. In order to obtain a molecular structure with normal intramolecular bond lengths and angles, we constrained the terminal C(4) at expected positions, as only this atom could not be located uniquely. We placed three C(4) atoms, corresponding to *trans*, *gauche* I and *gauche* II with respect to the N atom, at fixed distances of 1.52 Å with regard to C(3) and 2.55 Å with regard to C(2) [this corresponds to a C(2)—C(3)—C(4) angle of 114°]. The H atoms on C(3) and C(4) were placed staggered,

at 1.00 Å, with populations proportional to the populations of the corresponding C atoms. Full-matrix refinement gave a final R of 0.077. The positional parameters are listed in Table 1, the bond lengths and angles in Table 2 and the hydrogen bonds in Table 3.* All calculations were performed with *SHELX* 76 (Sheldrick, 1976).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35567 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates for C, N, O ($\times 10^4$) and H ($\times 10^3$), the populations for the three C(4) atoms and the equivalent isotropic temperature factors (Å^2) for the non-hydrogen atoms

The e.s.d.'s in parentheses refer to the least significant digit.

$$B_{\text{eq}} = \frac{1}{3} \text{trace } \tilde{B} = 8\pi^2 U_{\text{eq}}$$

	x	y	z	Population	B_{eq}
O(1)	5100 (3)	4511 (7)	1765 (3)		4.0 (2)
O(2)	3328 (3)	1899 (7)	931 (2)		5.1 (2)
N(1)	1446 (3)	5549 (8)	1302 (3)		4.6 (2)
C(1)	3845 (4)	3921 (9)	1496 (4)		3.9 (2)
C(2)	2867 (4)	5855 (9)	1975 (3)		4.2 (2)
C(3)	2842 (5)	5224 (13)	3222 (3)		10.9 (4)
C(4) ^T	4239 (8)	5550 (32)	4019 (5)	0.49 (4)	12.0 (5)
C(4) ^{GI}	2996 (23)	2137 (16)	3528 (8)	0.28 (3)	18.5 (6)
C(4) ^{GII}	1803 (19)	6965 (38)	3716 (8)	0.23 (3)	14.5 (6)
H(1)	314 (4)	784 (6)	170 (3)		
H(7)	81 (4)	687 (6)	154 (3)		
H(8)	151 (4)	564 (6)	66 (4)		
H(9)	94 (4)	376 (6)	146 (3)		

Table 2. Bond lengths (Å) and angles ($^\circ$)

The e.s.d.'s are in parentheses.

C(1)—O(1)	1.246 (5)	C(2)—C(1)—O(1)	115.6 (4)
C(1)—O(2)	1.231 (5)	C(2)—C(1)—O(2)	117.3 (4)
C(1)—C(2)	1.521 (6)	O(1)—C(1)—O(2)	127.1 (4)
C(2)—N(1)	1.479 (5)	C(1)—C(2)—N(1)	109.6 (3)
C(2)—C(3)*	1.520	C(1)—C(2)—C(3)	112.1 (3)
C(3)—C(4)*	1.520	C(2)—C(3)—C(4)*	114
C(2)—H(1)	1.06 (3)	C(3)—C(2)—N(1)	108.6 (3)
N(1)—H(7)	0.97 (4)	C(1)—C(2)—H(1)	103 (2)
N(1)—H(8)	0.78 (4)	N(1)—C(2)—H(1)	101 (2)
N(1)—H(9)	1.02 (3)	C(3)—C(2)—H(1)	122 (2)
		C(2)—N(1)—H(7)	112 (2)
		C(2)—N(1)—H(8)	106 (3)
		C(2)—N(1)—H(9)	115 (2)

* These values were constrained.

Table 3. Hydrogen-bond lengths (Å) and angles ($^\circ$)

The e.s.d.'s are in parentheses.

N—H...O	N...O	H...O	N—H	\angle N—H...O
N(1)—H(7)...O(1)	2.812 (4)	1.90 (4)	0.97 (4)	155 (3)
N(1)—H(8)...O(2)	2.786 (4)	2.02 (4)	0.78 (4)	166 (3)
N(1)—H(9)...O(1)	2.861 (4)	1.84 (4)	1.02 (3)	178 (3)

Discussion. The crystal structure of modification *A* shows a distribution of the terminal methyl group among three positions, roughly corresponding to *trans*, *gauche* I and *gauche* II. The strongly related *D* modification shows a similar distribution among two positions, *trans* and *gauche* II. For a detailed description of the crystal structures we refer to the work of Ichikawa & Iitaka (1968) and Nakata, Takaki & Sakurai (1980).

In modification *A* the populations of the three positions are about 50% *trans*, and the remaining 50% almost evenly distributed over *gauche* I and *gauche* II. The packing of the layers, which have their closest contact through the terminal CH₃ groups, must be so that only *trans-gauche* I or *trans-gauche* II contacts between neighbouring molecules occur, as contacts of the other combinations yield intermolecular distances which are too short. The imperfect ordering of the stacking of the molecular layers, as suggested by Ichikawa & Iitaka (1968), may consist of domains of ordered arrangements of layers *GI/GI--T/T* or *GII/GII--T/T* (here / refers to contacts through hydrogen bonds within one layer). Such a structure would consist of 50% *trans* and 50% of *gauche* I + *gauche* II. We calculated the lattice energies for the completely ordered crystals with layers *GI/GI--T/T* and *GII/GII--T/T* and also for *T/T--T/T* by means of the atom-atom potential method (Derissen & Smit, 1978), and added the energy for the internal rotation around C(3)-C(4), calculated by means of the LCAO-MO-SCF method, with a Gaussian minimal basis set (Table 4). The sum of the lattice energy and the

Table 4. The lattice energies ΔU (kJ mol⁻¹) for the completely ordered crystals *T--T*, *GI--T* and *GII--T*, and the relative intramolecular energies ΔE (kJ mol⁻¹)

	ΔU	ΔE	Sum
<i>T--T</i>	-169	0	-169
<i>GI--T</i>	-280	8	-272
<i>GII--T</i>	-283	3	-280

conformational energy shows that the ordered *GI--T* and *GII--T* crystals have crystal energies comparable to that of the ordered *B* modification, which was calculated with the same method as -270 kJ mol⁻¹. Modification *A* is about 5 kJ mol⁻¹ less stable than modification *B* (Abraham, Ah-Sing, Marks, Schulz & Stace, 1977).

Concluding, we see that the advantage of the constrained refinement is that one obtains a molecular geometry with normal C-C distances. The populations of the disordered terminal methyl group strongly depend on whether the structure is refined with or without constraints. With the populations of the constrained refinement it is possible to give an acceptable explanation for the crystal structure.

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