

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

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Abstract. C₄H₉NO₂, tetragonal, $P4_2/n$, $a = 13.354$ (5), $c = 5.806$ (2) Å, $V = 1035.4$ Å³, $D_c = 1.322$ Mg m⁻³, $Z = 8$. The final $R = 0.040$ for 532 reflexions and 91 variables. An earlier determination is corrected.

Introduction. As part of a programme on intermolecular interactions in hydrogen-bonded crystals (in particular, amino acids) it is of special interest to study compounds for which several crystalline modifications exist and whose structures must be accurately known. DL- α -Amino-*n*-butyric acid is such a compound. Of the four known modifications, modification *A* (Ichikawa & Iitaka, 1968), modification *C* (Akimoto & Iitaka, 1972) and modification *D* (Nakata, Takaki & Sakurai, 1980) show statistical disorder of the terminal methyl group. Only the modification *B*, the structure of which was solved by Ichikawa & Iitaka (1968), has no statistical disorder. However, with the crystal coordinates given, we were unable to reproduce some intermolecular distances, among which a hydrogen bond, as given in Table 11 of their paper. We therefore decided to reinvestigate modification *B*.

Small square-pyramidal crystals were obtained by evaporation of an aqueous ethanol solution. Systematic absences determine uniquely the space group $P4_2/n$. Cell dimensions and intensities were measured with a θ - 2θ scan, up to $\theta = 25^\circ$, on a computer-controlled CAD-4 diffractometer (Nonius), with Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) and a scintillation counter. Of the 859 independent reflexions, 532 with $I \geq 2\sigma(I)$ were measured, where $\sigma(I)$ is the variance of the intensity on the basis of counting statistics. No corrections for absorption or extinction were made. The structure was solved with *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Scattering factors were taken from Cromer & Mann (1968) for C, O and N and from Stewart, Davidson & Simpson (1965) for H. Refinement was by full-matrix least-squares minimization of $\sum w_i(|F_o| - |F_c|)^2$, with weights based on $\sigma^{-2}(F_o)$. The final R ($= \sum ||F_o| - |F_c|| / \sum |F_o|$) was 0.040; R_w was 0.029. A final difference synthesis showed no peaks higher than $0.20 \text{ e } \text{Å}^{-3}$. * Positional parameters are listed in Table

1, bond lengths and angles in Table 2, the hydrogen bonds in Table 3, and the atom numbering is in Fig. 1. All calculations were performed with the XRAY system (1976).

Table 1. Fractional coordinates for C, N, O ($\times 10^4$) and H ($\times 10^3$) (with respect to the origin at $\bar{1}$ at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ from $\bar{4}$) and the equivalent isotropic temperature factors (Å²) for the non-hydrogen atoms

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
O(1)	-2098 (2)	814 (2)	-3604 (3)	2.8 (1)
O(2)	-553 (2)	552 (2)	-2331 (3)	2.8 (1)
N(1)	-1113 (2)	842 (2)	2096 (4)	2.0 (1)
C(1)	-1468 (2)	643 (2)	-2038 (4)	1.9 (1)
C(2)	-1879 (2)	510 (2)	393 (4)	1.9 (1)
C(3)	-2135 (3)	-581 (3)	903 (5)	2.6 (1)
C(4)	-2958 (3)	-1005 (3)	-583 (5)	3.1 (1)
H(1)	-245 (2)	96 (2)	61 (4)	
H(2)	-154 (2)	-101 (2)	68 (4)	
H(3)	-237 (2)	-64 (2)	259 (4)	
H(4)	-306 (2)	-178 (2)	-23 (4)	
H(5)	-280 (2)	-91 (2)	-220 (4)	
H(6)	-357 (2)	-63 (2)	-24 (4)	
H(7)	-137 (2)	80 (2)	373 (4)	
H(8)	-96 (2)	151 (2)	188 (4)	
H(9)	-56 (2)	44 (2)	190 (4)	

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

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

C(1)–O(1)	1.260 (3)	C(2)–C(1)–O(1)	116.7 (3)
C(1)–O(2)	1.239 (3)	C(2)–C(1)–O(2)	118.1 (2)
C(1)–C(2)	1.525 (4)	O(1)–C(1)–O(2)	125.2 (3)
C(2)–N(1)	1.490 (4)	C(1)–C(2)–N(1)	109.4 (2)
C(2)–C(3)	1.525 (4)	C(1)–C(2)–C(3)	111.8 (2)
C(3)–C(4)	1.507 (4)	C(2)–C(3)–C(4)	114.3 (3)
C(2)–H(1)	0.98 (3)	C(3)–C(2)–N(1)	108.0 (2)
C(3)–H(2)	0.99 (3)	C(1)–C(2)–H(1)	109 (1)
C(3)–H(3)	1.03 (3)	N(1)–C(2)–H(1)	106 (2)
C(4)–H(4)	1.06 (3)	C(3)–C(2)–H(1)	112 (2)
C(4)–H(5)	0.97 (3)	C(2)–C(3)–H(2)	111 (2)
C(4)–H(6)	0.98 (3)	C(4)–C(3)–H(2)	107 (2)
N(1)–H(7)	1.01 (3)	C(2)–C(3)–H(3)	109 (2)
N(1)–H(8)	0.92 (3)	C(4)–C(3)–H(3)	107 (2)
N(1)–H(9)	0.92 (3)	C(3)–C(4)–H(4)	111 (2)
		C(3)–C(4)–H(5)	110 (2)
		C(3)–C(4)–H(6)	107 (2)
		C(2)–N(1)–H(7)	112 (2)
		C(2)–N(1)–H(8)	111 (2)
		C(2)–N(1)–H(9)	107 (2)

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35568 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Hydrogen-bond lengths (\AA) 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)	2.822 (3)	1.83 (3)	1.01 (3)	166 (2)
N(1)—H(8)...O(1)	2.810 (3)	1.89 (3)	0.92 (3)	173 (2)
N(1)—H(9)...O(2)	2.904 (3)	2.01 (3)	0.92 (3)	165 (2)

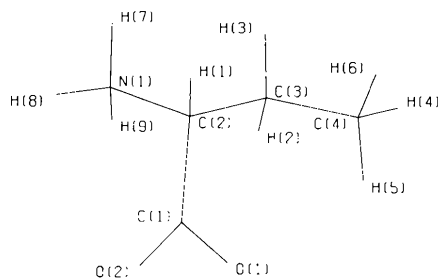


Fig. 1. Numbering of the atoms.

Discussion. The structure of the title compound was first reported by Ichikawa & Iitaka (1968). It was based on 630 reflexions from Weissenberg photographs, and yielded a final R of 0.12. The present structure determination is more accurate. The main difference between the atomic coordinates given in this paper and those of Ichikawa & Iitaka is that all the y coordinates have opposite signs. With our coordinates

we can reproduce all interatomic distances and hydrogen bonds as given by Ichikawa & Iitaka. The cell dimensions, bond lengths and bond angles differ only slightly. For a detailed description of the structure we refer to their paper.

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Methyl (Z)-4-Oxo-1,3-diphenyl-2-phenylimino-5-imidazolidinylideneacetate

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Abstract. $C_{24}H_{19}N_3O_3$, orthorhombic, $Pcab$, $a = 10.97$ (1), $b = 14.99$ (1), $c = 25.66$ (1) \AA , $Z = 8$, $\mu = 0.093$ mm^{-1} (Mo $K\alpha$ radiation), $D_m = 1.28$, $D_c = 1.25$ Mg m^{-3} , final $R = 0.054$. The product from 1,2,3-triphenylguanidine and dimethyl acetylenedicarboxylate possesses a five-membered-ring structure and not the six-membered-ring structure previously assigned.

Introduction. The 1:1 molar MeOH adducts produced by the reaction of acyclic guanidines with dimethyl

acetylenedicarboxylate (DMAD) have been given both the imidazolidin-4-one structure (1) (Sasaki, Sakata & Iwanami, 1964) and the pyrimid-4-one structure (2) (Ruhemann & Stapleton, 1900), although the structural assignments were often unsupported. Some chemical degradative evidence favours the five-membered-ring structure (3) for the adduct from guanidine itself and DMAD (Katner & Zeige, 1971) but, in contrast, the adduct from 1,2,3-triphenylguanidine has been assigned the six-membered-ring structure (4), principally from its high-resolution mass