Rotational Isomers in the Crystals of DL-α-Amino-*n*-butyric Acid

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For DL-α-amino-*n*-butyric acid, two crystalline modifications were previously found.[1] They were called as A- and B-forms. A-form is monoclinic, with the space group of $P2_1/a$, and with the unit cell dimensions: $a=9.85$ Å, $b=4.77$ Å, $c=11.94$ Å, $\beta=101°$, $Z=4$. B-form is tetragonal, with $P4_2/n$, $a=13.40$ Å, $c=5.82$ Å, and $Z=8$. By our recent X-ray analyses, it has now been established that all of the three rotational isomers (I, II, and III) shown in Fig. 1 are coexisting in the A-form crystal, whereas only one conformation (II in Fig. 1) is found in the B-form crystal.

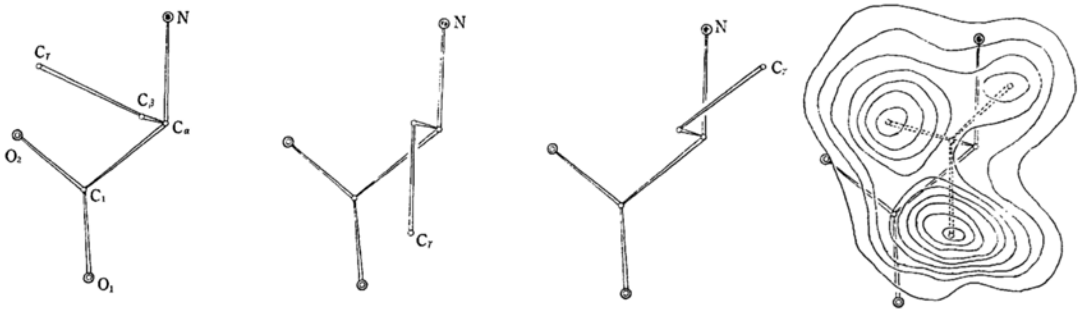
Three-dimensional intensity data were collected from multiple-film equi-inclination Weissenberg photographs taken with filtered Cu*K*α radiation. For the A-form crystal, data of 809 reflections were used. First, the sharpened three-dimensional Patterson function was calculated. From this function, approximate coordinates of two oxygen atoms were estimated. The signs based upon these coordinates were used in the first three-dimensional Fourier synthesis. The coordinates of all the heavy atoms except those of the γ-carbon could be obtained in the Fourier map. In the course of the refinement, the γ-carbon atom was found to be distributed over the three positions corresponding to the three rotational isomers shown in Fig. 1. Therefore, the site occupancy factors of the γ-C in the three positions were set as parameters in the least squares refinement. After two cycles of full matrix least squares calculation with anisotropic temperature factors, the R factor dropped to 0.13. At the right end of Fig. 1, an electron density map of a section through the centers of the three possible methyl groups is given, which is obtained from the difference Fourier synthesis. This map shows how the methyl group (and two hydrogen atoms) on the β-carbon are distributed among the possible sites in the internal rotation around the C_α–C_β axis. The dihedral angles $C_\gamma C_\beta C_\alpha N$ determined are given in Table 1.

TABLE 1. DIHEDRAL ANGLES[a] $C_\gamma C_\beta C_\alpha N$ IN α-AMINO-*n*-BUTYRIC ACID

A-form	I	72.4°	(36%[b])
	II	−174.6	(40%)
	III	−53.8	(24%)
B-form		−176.0	

a) This angle is defined so that it is zero when C_β–C_γ bond comes at the eclipsed position with respect to the C_α–N bond. The positive direction is defined as that of the anticlockwise rotation of the C_β–C_γ bond, when viewed along the $C_\beta \rightarrow C_\alpha$ bond as shown in Fig. 1.

b) Normalized site occupancy factors as determined by the least squares calculation.



I II III Observed (A-form)

Fig. 1. Rotational isomers I, II, and III expected for α-amino-*n*-butyric acid. What is given at the right end is a section of the electron density map at the CH_3 group of A-form. This was obtained by a difference Fourier synthesis by the use of the structure factors calculated on the basis of all the heavy atoms except the γ-carbon. In this synthesis, there appeared three maxima corresponding to the three stable positions of C_γ, and this section was prepared through the plane determined by these three points. The figure is the projection along the c-axis of this section. Contours are drawn at 0.1, 0.2,···, 0.9 electron Å^{-3}.

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1) M. Tsuboi, Y. Iitaka, S. Suzuki and S. Mizushima, This Bulletin, **32**, 529 (1959).

For the B-form crystal, intensities of 630 reflections were measured. The Harker section at $w=1/2$ allowed us to estimate only two-dimensional (x and y) coordinates of oxygen atoms and it was not possible to estimate the z parameters from the Patterson function. Accordingly, the analysis was started with two dimensional Fourier methods. After the x and y coordinates of all the heavy atoms (except C_γ) were determined, the approximate z coordinates of these atoms were estimated on the basis of a model-building. The first three-dimensional Fourier synthesis was made on the basis of the estimated coordinates of the two oxygen and one nitrogen atoms. All the carbon atoms including C_γ appeared at reasonable positions. C_γ appeared at the trans position to the NH_3^+ group, with the dihedral angle of $-176°$ (II of Fig. 1). It was ascertained that C_γ takes only this site by a three-dimensional difference Fourier synthesis based upon the coordinates of the heavy atoms except C_γ. After three cycles of least squares refinement with isotropic temperature factors, the R value reached 0.12.

More detailed crystallographic data as well as a full account of the crystal structures of the A- and B-forms of this amino acid will be given elsewhere.

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