Coexistence of Two Different Molecular Forms within a Single Crystal of L-Valine

By Masamichi Tsuboi, Tadao Takenishi[*] and Yoichi Iitaka

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In the course of our work on the infrared absorption spectra of amino acids, we found that a crystal of L-valine gives a spectrum quite different from that of a crystal of DL-valine (Fig. 1). The number of the bands observed for the DL-valine crystal is that expected from one valine molecule[1], and almost every band has been assigned to one of the vibrational modes expected for the molecule[2]. While, the L-valine crystal shows much more bands than the DL-valine crystal does. For example, instead of the band at 680 cm^{-1} of the DL-crystal, which is assigned to the COO$^-$ scissoring mode, the L-crystal shows two bands at 715 and 663 cm^{-1}. These are situated too far apart to be considered as arising from one molecular vibration due to the splitting in the crystalline force field. A pair of bands is also observed in the spectrum of the L-crystal, instead of each of the bands of the DL-crystal at 774, 818, 890, 925, 948, 1035, 1105, 1181, 1320, 1355, 1406, 1593 and 1629 cm^{-1}. These observations may lead us to a view that the L-valine crystal belongs to an unusual type of crystal composed of molecules of one species of two different forms.

This view is supported by an X-ray examination. From the oscillation- and Weissenberg-photographs of the L-valine crystal the following data were obtained: monoclinic, $a=9.71$ Å, $b=5.32$ Å, $c=12.08$ Å, $\beta=90.8°$. Its density was reported by Cohn et al.[3] to be 1.230 g. cm^{-3}, which shows that there are four molecules per one unit cell, its density calculated being 1.247 g. cm^{-3}. Systematic extinctions on the photographs indicate the space group to be either $C_2^2–P2_1$ or $C_{2h}^2–P2_1/m$. The piezoelectricity is detected of this crystal; accordingly, the possibility of $C_{2h}^2–P2_1/m$ is eliminated, and the space group is determined to be $C_2^2–P2_1$. This space group requires only two crystallographically similar units (related by the twofold screw axis) within one unit cell. This requirement is fulfilled by supposing that the four molecules in one unit cell are in two sets of two molecules of different forms[1].

The question may now be raised, what is the difference between these two forms. Considered on the basis of what are at present known on the internal rotation around the C–C single bond[4], three rotational isomers are possible for the valine molecule, i. e., *trans*, *gauche I*, and *gauche II* isomers (Fig. 2; A, B, and C). The energy differences among these three isomers may be very small as are the energy differences between the *trans* and *gauche* isomers of symmetric tetrachloroethane[5] and between those of symmetric tetrabromoethane[6,7] (Fig. 2; D and E). The two molecules of different forms, composing the L-valine crystal, are probably two of these three isomers.

Similar rotational isomers with the small energy differences are also possible for the isoleucine molecule, in which one of the two methyl groups of the valine molecule is substituted by the ethyl group. Then, the existence of isoleucine crystals composed of two rotational isomers may

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[*] Central Research Laboratory, Ajinomoto Co., Inc. Kawasaki, Kanagawa.

[1] That the DL-valine crystal is composed of molecules of one form is evident from the space group ($C_i^1-P\bar{1}$), the unit cell dimensions ($a=5.25$Å, $b=5.43$Å, $c=11.05$Å, $\alpha=91°$, $\beta=92.4°$, $\gamma=109.4°$), and the the density (1.315 g. cm.$^{-3}$) of this crystal; this space group requiring two crystallographically similar units within one unit cell, and the unit cell dimensions and the density requiring two molecules (D and L) in each unit cell. Details will be shown elsewhere (M. Tsuboi, T. Takenishi and Y. Iitaka, to be published).

[2] M. Tsuboi and T. Takenishi, to be published.

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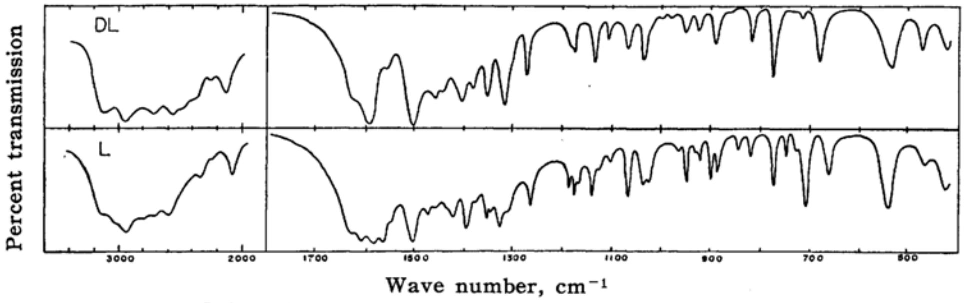

Fig. 1. Infrared absorption spectra of DL-valine and L-valine crystals.

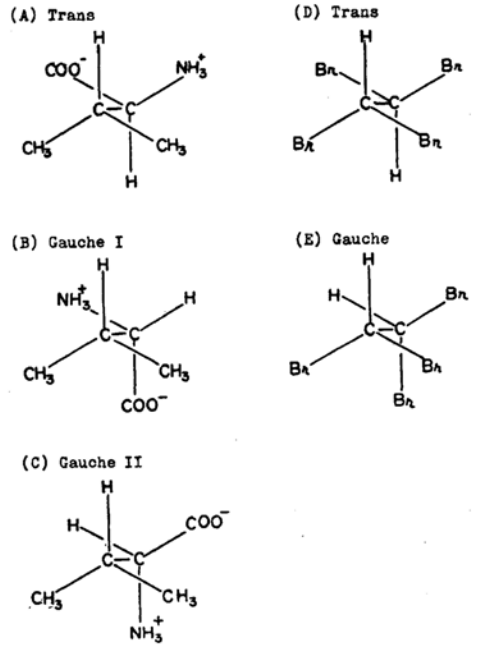

Fig. 2. Rotational isomers of L-valine and symmetric tetrabromoethane.

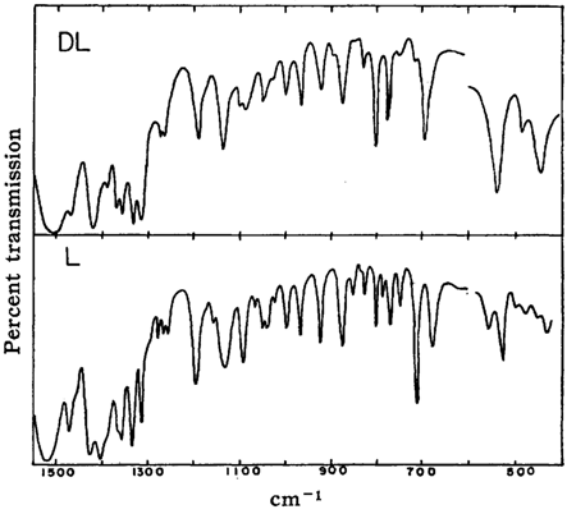

Fig. 3. Infrared absorption spectra of DL-isoleucine and L-isoleucine crystals.

be conjectured. As a matter of fact, there is an L-isoleucine crystal which shows much more bands than a DL-isoleucine crystal (Fig. 3). This may correspond to one of what have been above conjectured.

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Faculty of Science
The University of Tokyo
Hongo, Tokyo