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Structure of α Form of L-Glutamic Acid. α-β Transition

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An X-ray analysis of the α form of L-glutamic acid, $C_5H_9NO_4$, has been carried out. The space group is $P2_12_12_1$ with $a=7.068(1)$, $b=10.277(1)$, $c=8.755(1)$ Å and $Z=4$. The structure was solved by the direct method, and least-squares refinement using 855 reflexions led to the final R value of 0.034. The molecule is in a zwitter ion form, and there is a strong OH···O intermolecular hydrogen bond with the O···O distance of 2.578(2) Å. The conformation of L-glutamic acid in the α form is quite different from that in the β form. The occurence frequency in various crystal structures containing glutamic acid residues shows that the conformation in the β crystal is more stable and favourable than that in the α crystal. The transition of the α form to the β form of L-glutamic acid in the mother liquor and the conditions for obtaining the α crystals are discussed based on the crystal and molecular structures of the two polymorphs.

L-Glutamic acid crystallizes in two polymorphic forms; they are designated α and β forms by Hirokawa.[1)] In industrial processes, the α form is more advantageous to handle. The α crystal, however, is converted to the β when the α crystal is placed in solution for a long time. The β crystal is also obtained when it is grown slowly. Consequently, various kinds of investigations have been undertaken to find the conditions for crystallization of L-glutamic acid in the α form and to elucidate the mechanism of the α-β transition.[2—5)] It was found empirically that addition of trace amount of some amino acids or other special compounds causes formation of the α form.[2,4,5)] To clarify these problems, however, it is inevitable to know the difference in the crystal and molecular structure between the two polymorphs. While the refined crystal structure of the β form was obtained from neutron diffraction,[6)] only crystal data for the α form has been reported by Bernal.[7)] We have, therefore, undertaken an X-ray analysis of the α form of L-glutamic acid.

Experimental and Structure Determination

Prismatic crystals were obtained from an aqueous solution. A crystal, 0.5×0.4×0.3 mm in size, was used for data collection on a Rigaku four-circle automated diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.71069$ Å). Preliminary unit cell dimensions and space group were obtained from photographs. The space group was determined from the systematic absences ($h00$, $2n+1$; $0k0$, $2n+1$; $00l$, $2n+1$). Accurate cell dimensions were determined by the least-squares method using the 2θ values of 15 high angle reflexions, measured on the diffractometer. Crystal data are summarized in Table 1. All reflexions within the range of $2\theta \leqq 55°$ were collected by the use of the ω-2θ scan mode with a scanning rate of $4°(2\theta)$ min^{-1}. Stationary background counts were accumulated for 10 s before and after each scan. A total of 874 independent reflexions were obtained, of which 17 ($|F_o|<3.0\sigma(|F_o|)$) were considered as unobserved. A Lorentz-polarization correction was made as usual but absorption effect was neglected.

The phases for 191 reflexions with $|E_o|\geqq 1.2$ were assigned with MULTAN.[8)] An E map computed with the phase set of the lowest R_K revealed the positions of 10 non-hydrogen atoms.** All hydrogen atoms were located from the difference synthesis. The structural parameters were refined by the block-diagonal least-squares method. The function minimized was $\sum w(|F_o|-|F_c|)^2$ with unit weight.

Table 1. Crystal data

$C_5H_9NO_4$	$V=637.5$ Å^3
$M.W.=147.13$	$D_x=1.533$ g·cm^{-3}
Orthorhombic	$Z=4$
$P2_12_12_1$	$\mu(\text{Mo }K\alpha)=3.426$ cm^{-1}
$a=7.068(1)$ Å	
$b=10.277(1)$	
$c=8.775(1)$	

Table 2a. Final positional parameters multiplied by 10^4 for non-hydrogen atoms and by 10^3 for hydrogen atoms

Estimated standard deviations are given in parentheses.

Atom	x	y	z
O(1)	4566(3)	2360(2)	5129(2)
O(2)	4232(3)	3718(1)	3154(2)
C(1)	4180(3)	3438(2)	4568(2)
C(2)	3607(3)	4528(2)	5657(2)
N	2088(3)	4018(2)	6681(2)
C(3)	5261(3)	4991(2)	6650(3)
C(4)	6956(3)	5509(2)	5742(3)
C(5)	6509(3)	6768(2)	4957(2)
O(3)	6244(3)	6651(2)	3467(2)
O(4)	6368(3)	7805(2)	5610(2)
HC(2)	306(4)	528(3)	502(3)
HN1	112(3)	357(2)	610(2)
HN2	253(4)	349(2)	720(3)
HN3	165(4)	465(3)	736(3)
H1C(3)	565(4)	420(2)	730(3)
H2C(3)	478(4)	572(2)	743(3)
H1C(4)	740(5)	481(3)	492(3)
H2C(4)	807(4)	583(3)	647(3)
HO(3)	582(5)	751(3)	292(4)

** It was informed that Matsuzaki reported in his Ms thesis[9)] the structure analysis of the α form as one example of successful applications of the symbolic addition method.

Table 2b. Final thermal parameters multiplied by 10^4 for non-hydrogen atoms and by 10^3 for hydrogen atoms

Estimated standard deviations are given in parentheses.

Atom	U_{11} or U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	417(9)	191(7)	234(8)	98(8)	47(8)	34(6)
O(2)	394(9)	211(7)	152(7)	9(7)	19(8)	−1(6)
C(1)	183(9)	189(9)	184(9)	−9(8)	10(8)	−23(8)
C(2)	208(9)	159(8)	158(8)	9(8)	15(9)	4(8)
N	239(8)	179(8)	175(8)	−12(8)	31(8)	−4(7)
C(3)	285(11)	240(10)	178(9)	−58(9)	−31(9)	18(9)
C(4)	225(10)	252(10)	282(11)	−31(9)	−34(9)	39(10)
C(5)	221(10)	224(10)	212(9)	−64(9)	11(9)	0(9)
O(3)	446(10)	228(7)	201(7)	−12(8)	−53(8)	−6(6)
O(4)	618(12)	237(7)	247(8)	−51(9)	−18(10)	−35(7)
HC(2)	38(8)					
HN1	18(6)					
HN2	29(7)					
HN3	58(10)					
H1C(3)	38(8)					
H2C(3)	27(7)					
H1C(4)	48(9)					
H2C(4)	47(9)					
HO(3)	67(10)					

Two strong reflexions, (2 1 0) and (1 2 1) were excluded because they seemed to suffer from secondary extinction. The final R value was 0.034 for 855 reflexions. Atomic scattering factors were taken from "International Tables for X-Ray Crystallography."[10] The final positional and thermal parameters are given in Table 2.***

Description of the Structure

Hydrogen Bond. The crystal structure viewed along the a axis is drawn in Fig. 1, where the numbering of the atoms are shown. Here O(1) of α-carboxylate group is denoted to the oxygen atom whose torsional angle of O(1)–C(1)–C(2)–C(3) is negative. All of the hydrogen donors, OH and NH_3, participate in hydrogen bonds. The distances and angles of the hydrogen bonds are given in Table 3. A strong OH···O bond between the α- and γ-carboxyl groups links the molecules to form a chain along the b axis. The chains are interlinked by the three NH···O hydrogen bonds to make a three-dimensional network. This scheme is similar, in general, to that of the β crystal. The difference is that in α O(2) accepts the hydrogen bonds from the γ-carboxyl and the NH_3^+ group and O(1) links to another NH_3^+ group while in β O(2) is the hydrogen bond acceptor from two NH_3^+'s and O(1) links to OH. The OH···O distance in α is 0.06 Å longer than that in β, whereas the average of three NH···O distance in the former are 0.06 Å shorter than those of the latter.

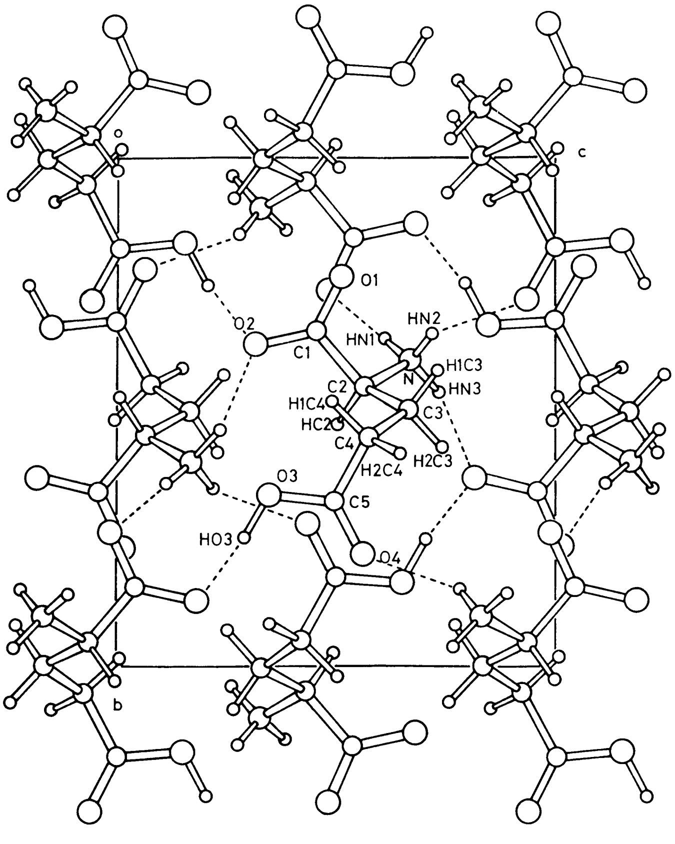

Fig. 1. A crystal structure viewed along the a axis with the numbering system of L-glutamic acid molecule.

Conformation. Figure 2 shows a stereoscopic drawing of the present molecule. The torsional angles are listed in Table 4. The conformations around the C(2)–C(3) and C(3)–C(4) bonds in the α form are both *gauche*, whereas those in the β form are *trans-gauche*. Such folded conformation of the molecule has

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***Lists of the observed and calculated structure factors are kept as Document No. 8002 at the Chemical Society of Japan.

not been observed in the crystal structures of the related compounds so far determined. Some torsional angles are compared with those of the related compounds in Table 5, in which the torsional angle nomenclature of IUPAC-IUB commission[11] are also given.

The conformation around the C(1)–C(2) bond in the α form is similar to that of the β form; the O(1)–C(1)–C(2)–N torsional angles for α and β are −50.3 and −42.3°, respectively. Similar negative values are usually observed in L-amino acids.[21] This would be brought about by the fact that both oxygen atoms of the α-carboxylate group should avoid C(3) and N which are bulky substituents. The torsional angles, χ^{31} and χ^{32}, in α are different from those in β, although the values in β are similar to those of the other compounds.

Table 3. Intermolecular hydrogen bond lengths (l/Å) and angles (ϕ/°)

A-H···B	H···B	A···B	∠A-H···B
O(3)-HO(3)···O(2)$^{\mathrm{I}}$	1.56(3)	2.578(2)	163(3)
N-HN3···O(2)$^{\mathrm{II}}$	1.93(3)	2.820(2)	161(3)
N-HN2···O(4)$^{\mathrm{III}}$	2.19(3)	2.898(3)	152(3)
N-HN3···O(1)$^{\mathrm{IV}}$	1.82(2)	2.776(3)	172(2)
I. (1.0−x	0.5+y	0.5−z)	
II. (0.5−x	1.0−y	0.5+z)	
III. (1.0−x	−0.5+y	1.5−z)	
IV. (−0.5+x	0.5−y	1.0−z)	

Bond Lengths and Angles. Bond lengths and angles are listed in Table 6, in which the corresponding values of the related compounds are also shown. As found in the β form, L-glutamic acid in the α form exists as a zwitter ion; a proton transfers from the α-carboxyl group to the amino group. The C(1)–O(1) and C(1)–O(2) distances of 1.242(3) and 1.275(3) Å, respectively, are the values of the ionized carboxyl group. The discrepancy of 0.03 Å between them can be attributed to differences of their intermolecular hydrogen bonds. As mentioned above, O(2) makes a very short hydrogen bond with the OH group and a NH···O hydrogen bond with the NH_3^+ group, while O(1) makes one NH···O bond with NH_3^+.

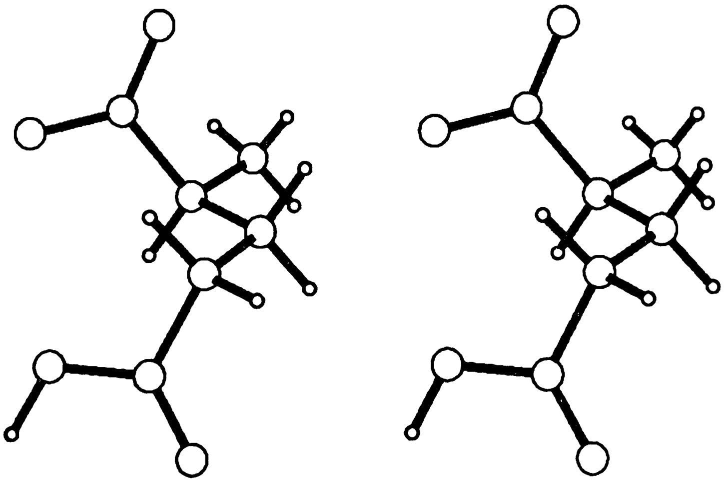

Fig. 2. A stereoscopic drawing of L-glutamic acid in the α form.

Table 4. Torsional angles (ϕ/°)

O(1)-C(1)-C(2)-C(3)	69.0	HC(2)-C(2)-C(3)-H1C(3)	175.8
O(2)-C(1)-C(2)-C(3)	−110.6	HC(2)-C(2)-C(3)-H2C(3)	61.5
O(1)-C(1)-C(2)-N	−50.3	N-C(2)-C(3)-H1C(3)	56.4
O(2)-C(1)-C(2)-N	130.0	N-C(2)-C(3)-H2C(3)	−57.9
O(1)-C(1)-C(2)-HC(2)	−167.9	C(2)-C(3)-C(4)-C(5)	68.8
O(2)-C(1)-C(2)-HC(2)	12.4	H1C(3)-C(3)-C(4)-H1C(4)	66.2
C(1)-C(2)-N-HN1	−47.4	H1C(3)-C(3)-C(4)-H2C(4)	−61.2
C(1)-C(2)-N-HN2	67.2	H2C(3)-C(3)-C(4)-H1C(4)	−176.7
C(1)-C(2)-N-HN3	178.6	H2C(3)-C(3)-C(4)-H2C(4)	55.9
HC(2)-C(2)-N-HN1	69.8	C(3)-C(4)-C(5)-O(4)	−105.0
HC(2)-C(2)-N-HN2	−175.6	C(3)-C(4)-C(5)-O(3)	73.9
HC(2)-C(2)-N-HN3	−61.4	H1C(4)-C(4)-C(5)-O(3)	17.6
C(3)-C(2)-N-HN1	−170.3	H1C(4)-C(4)-C(5)-O(4)	−163.5
C(3)-C(2)-N-HN2	−54.7	H2C(4)-C(4)-C(5)-O(3)	136.9
C(3)-C(2)-N-HN3	59.5	H2C(4)-C(4)-C(5)-O(4)	−44.2
C(1)-C(2)-C(3)-C(4)	59.1	O(4)-C(5)-O(3)-HO(3)	−3.7
N-C(2)-C(3)-C(4)	178.4	C(4)-C(5)-O(3)-HO(3)	175.2
HC(2)-C(2)-C(3)-C(4)	−62.2		

TABLE 5. SELECTED TORSIONAL ANAGLES (ϕ/°) IN THE α FORM L-GLUTAMIC ACID AND OTHER RELATED CRYSTAL STRUCTURES

IUPAC-IUB nomenclature	N-C2-C3-C4 χ^1	C2-C3-C4-C5 χ^2	C3-C4-C5-O3 χ^{32}	C3-C4-C5-O4 χ^{31}	Ref. 11
L-Glutamic acid α form	178.4	68.8	−105.0	73.9	present work
L-Glutamic acid β form	−51.8	−73.1	−160.7	18.8	6
L-Glutamic acid·HCl	−68.9	−173.1	−167.0	15.0	12
L-Arginine L-glutamate	−57	−172	180	−3	13
1:1 Mixed crystal of L-glutamic acid and L-pyroglutamic acid	−55.9	−65.2	−173.3	3.8	14
N-Tosyl-L-glutamic acid					15
A molecule	−51.9	−164.1	176.2	−3.2	
B molecule	−55.6	174.0	−174.2	7.5	
Phthaloyl-DL-glutamic acid					16
A molecule	−144.8	69.0	−162.4	16.9	
B molecule	−61.3	−65.5	154.3	−25.4	
Cu L-Glutamate·H_2O	67.8	−177.1	−171.2	6.7	17
Zn L-Glutamate·H_2O	67.0	−176.6	−170.1	7.8	18
Ca L-Glutamate·$3H_2O$	179.4	174.6	−169.1	12.3	19
L-glutamatobis(ethylenediamine) cobalt(III) perchlorate	70.6	−92.3	−122.7	54.8	20

TABLE 6. BOND LENGTHS (l/Å) AND ANGLES (ϕ/°)
Estimated standard deviations are given in parentheses.

	α form	β form[10]	HCl salt[11]		α form	β form[10]	HCl salt[11]
C(1)-O(1)	1.242(3)	1.263(2)	1.221(9)	C(3)-C(4)-C(5)	111.9(2)	116.1(1)	112.0(4)
C(1)-O(2)	1.275(3)	1.243(2)	1.296(8)	C(4)-C(5)-O(3)	113.9(2)	112.2(1)	114.9(5)
C(1)-C(2)	1.527(3)	1.533(2)	1.535(7)	C(4)-C(5)-O(4)	123.9(2)	124.1(1)	122.7(5)
C(2)-N	1.495(3)	1.490(2)	1.482(6)	O(3)-C(5)-O(4)	122.3(2)	123.7(2)	122.4(5)
C(2)-C(3)	1.534(3)	1.530(2)	1.537(6)	C(5)-O(3)-HO(3)	115(2)	115.1(2)	114.7(9)
C(3)-C(4)	1.534(3)	1.523(2)	1.526(7)	C(2)-N-HN1	111(1)	110.8(2)	109.8(7)
C(4)-C(5)	1.500(3)	1.501(2)	1.476(7)	C(2)-N-HN2	108(2)	110.1(2)	110.0(8)
C(5)-O(4)	1.214(3)	1.219(2)	1.225(9)	C(2)-N-HN3	112(2)	112.3(2)	108.9(6)
C(5)-O(3)	1.327(3)	1.312(2)	1.315(8)	HN1-N-HN2	105(2)	108.6(3)	109.5(10)
N-HN1	0.97(2)	1.038(3)	1.04(1)	HN2-N-HN3	116(2)	107.1(2)	107.2(9)
N-HN2	0.77(3)	1.038(4)	1.06(1)	HN2-N-HN3	104(3)	107.8(3)	110.4(9)
N-HN3	0.93(3)	1.027(3)	1.08(1)	HC(2)-C(2)-N	109(1)	107.5(2)	108.2(7)
C(2)-HC(2)	1.03(3)	1.091(3)	1.085(10)	HC(2)-C(2)-C(1)	108(1)	110.5(2)	108.4(7)
C(3)-H1C(3)	1.03(3)	1.102(4)	1.08(1)	HC(2)-C(2)-C(3)	111(1)	110.9(2)	110.9(7)
C(3)-H2C(3)	1.07(3)	1.079(4)	1.07(1)	H1C(3)-C(3)-C(2)	106(1)	107.9(2)	108.4(8)
C(4)-H1C(4)	1.07(3)	1.080(4)	1.10(1)	H1C(3)-C(3)-C(4)	111(1)	107.0(2)	109.1(8)
C(4)-H2C(4)	1.06(3)	1.086(4)	1.11(1)	H2C(3)-C(3)-C(2)	110(1)	107.1(3)	108.0(7)
O(3)-HO(3)	1.04(3)	1.050(2)	0.98(1)	H2C(3)-C(3)-C(4)	110(1)	109.9(2)	108.4(8)
O(1)-C(1)-O(2)	125.5(2)	126.0(2)	125.4(6)	H1C(3)-C(3)-H2C(3)	106(2)	106.5(3)	106.7(12)
O(1)-C(1)-C(2)	117.7(2)	115.6(1)	122.0(5)	H1C(4)-C(4)-C(3)	110(2)	108.0(2)	112.7(8)
O(2)-C(1)-C(2)	116.8(2)	118.3(1)	112.6(5)	H1C(4)-C(4)-C(5)	109(2)	106.6(2)	109.0(7)
C(1)-C(2)-N	108.1(2)	109.3(1)	108.8(4)	H2C(4)-C(4)-C(3)	112(1)	112.8(2)	108.5(7)
C(1)-C(2)-C(3)	112.4(2)	107.3(1)	107.7(4)	H2C(4)-C(4)-C(5)	96(1)	106.8(2)	109.2(8)
N-C(2)-C(3)	108.3(2)	111.5(1)	112.6(3)	H1C(4)-C(4)-H2C(4)	114(2)	105.9(4)	105.2(13)
C(2)-C(3)-C(4)	114.1(2)	117.8(1)	115.8(4)				

Such a discrepancy is also found in the β form. The O(1) atom forms one OH···O hydrogen bond, whereas O(2) participates in two NH···O hydrogen bonds. The C(1)–O(1) bond is 0.02 Å longer than C(1)–O(2). This seems to indicate that the OH···O hydrogen bond is predominant in the L-glutamic acid crystals.

In the γ-carboxyl group, the lengths of C(5)–O(4) and C(5)–O(3), 1.214(3) and 1.327(3) Å, respectively, indicate that it is unionized. Other bond lengths and angles are normal.

The bond angles around C(2), C(3), and C(4) in the α form are significantly different from the corresponding ones in the β form. Such discrepancies may be resulted from the steric repulsions which are due to the conformational difference.

Discussion

In glutamic acid, χ^1 and χ^2 represent rotation about C(sp^3)–C(sp^3) bonds. Each of them is likely to have values in the neighbourhood of 60, 180, and −60° which are designated by g, t, and $\bar{g}$, respectively. According to the conformational energy calculation,[22] favourable combinations χ^1 and χ^2 should be ($\bar{g}$, $\bar{g}$), (g, t), ($\bar{g}$, t), (t, t), and (t, g). The corresponding minimum conformational energies are 0.00, 0.21, 0.23, 0.40, and 0.43 kcal/mol. Judging from these values, glutamic acid in the β form is of the ($\bar{g}$, $\bar{g}$) conformer with the lowest energy, whereas that of the α form is of the (t, g) conformer with the highest energy. From the NMR study, Ham suggested that six conformers of L-glutamic acid can exist in solution.[23,24] Their populations are 0.27, 0.27, 0.18, 0.18, 0.06, and 0.04 for ($\bar{g}$, t), (g, t), ($\bar{g}$, g), (g, g), (t, t), and (t, g), respectively.

Six distinct conformations have been observed in the crystal structures so far reported as seen from Table 5. There are four, three, two, two, one, and one crystal structures containing conformers of ($\bar{g}$, t), ($\bar{g}$, $\bar{g}$), (g, t), (t, g), (g, $\bar{g}$), and (t, t), respectively. The occurence frequency in the crystal structures is in qualitative correspondence to the minimum conformational energy and the population in solution. This coincidence seems to indicate that the occurence frequency of each conformer is not biased to much extent by different crystalline fields or different substituents. Therefore, the occurence frequency may reflect the inherent relative stability of the conformations, and be used as a measure of the stability of the conformers if the considerable number of the related crystal structures can be obtained. These three measures suggest that the conformation in the β crystal is more stable and favourable than in the α crystal. The difference in conformational energy should be responsible for the transition from the α to β form.

Two types of chains or molecular arrangements, which are observed in the α and β crystals, are shown in Fig. 3, a and b, respectively. As mentioned above, the OH···O bond seems to be most predominant among the four hydrogen bonds. Therefore, it is reasonable to assume that the considerable amounts of molecules are connected by the OH···O hydrogen bond to form chains in solution. The neighbouring chains can be connected by the NH···O hydrogen bonds and the conformation and the arrangement of the molecules are stabilized by these hydrogen bonds.

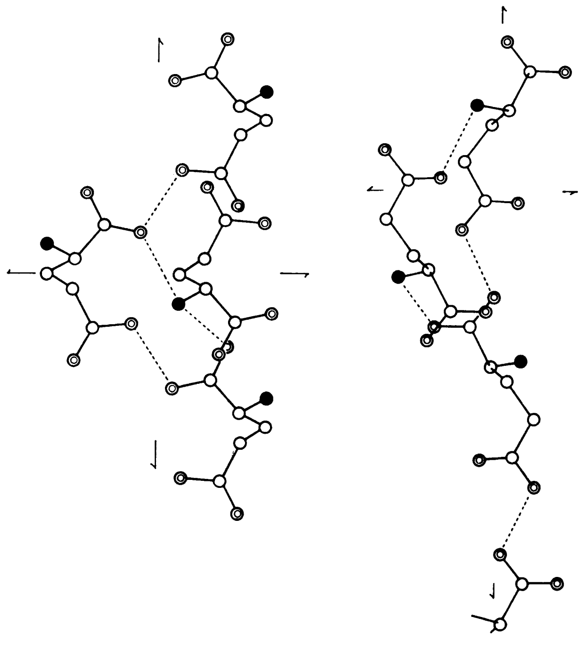
a b

Fig. 3. A comparison of the hydrogen bond systems and the molecular arrangements in the α form (a) and the β form (b) crystals.

The α to β transition can be explained as shown in Fig. 4, in which the OH···O hydrogen bond is conserved. Here a and e correspond, respectively, to the initial α and the final β conformation. The b, c, and d conformers are hypothetical intermediates rotated stepwisely around the C–C single bonds. The

a b c d e

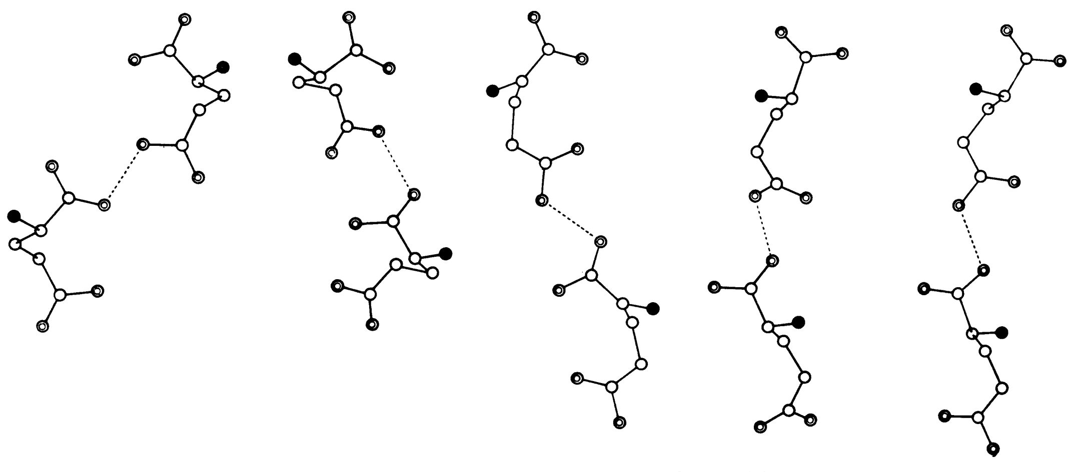

Fig. 4. A schematic drawing of the α to β transition.

actual conformational change might occur cooperatively. The α conformation would change to the β conformation, from a to e spontaneously rearranging the NH···O hydrogen bonds in solution.

Figure 4 also gives us an idea how the trace amount of the specific amino acids facilitates the crystallization of L-glutamic acid in the α form. Conformation of such amino acids would be suitable to make the NH···O hydrogen bonds with OH···O hydrogen bonded L-glutamic acid chains in the state a, and the nuclei generated in this way may trigger the initial stage of the crystallization to grow the α crystal.

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24) It seems that Ham assumed the conformers with $\chi^2=-60°$ are identical to those with $\chi^2=60°$. Therefore, the ($\bar{g}$, g) conformer is essentially equal to the ($\bar{g}$, $\bar{g}$) conformer in this discussion.