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A New Modification of L-Glutamic Acid and its Crystal Structure

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A new modification of L-glutamic acid has been found. Its unit cell has a close relationship in dimensions to the other modification reported by Bernal. The crystal structure of this new form has been determined by means of electron-density projections on (100) and (001). Three N-H...O and one O-H...O hydrogen bonds link molecules in three dimensions. An indication of the configuration of the zwitterion is obtained from the dimensions of the carboxylic groups and also from the projected maps of difference series. The carbon-chain configuration is compared with those of two similar compounds, L-glutamine and DL-glutamic acid hydrochloride.

Introduction

In the course of preparing monosodium glutamate, the present author found crystals which had not hitherto been reported. Though the result of chemical analysis and the measurement of specific rotation* showed that they were glutamic acid, the preliminary X-ray test revealed that the dimensions of the unit cell were different from those for L-glutamic acid investigated by Bernal (1931). We shall call Bernal's modification the α -form and the present modification the β -form. As the β -form has one rather short axis it seemed to be promising for the structure determination, and so it was decided to analyse this newly found form as a part of a current program of research in this laboratory on the crystal structures of the fundamental substances composing high polymers.

Crystallographic data

While the α -form reported by Bernal (1931) has $a = 7.06$, $b = 10.3$ and $c = 8.75$ kX., space group $P2_12_12_1$, $Z = 4$, the present form is also orthorhombic but has

$$a = 5.17, b = 17.34 \text{ and } c = 6.95 \text{ \AA} \quad (\text{all } \pm 0.2\%), \\ Z = 4.$$

From the systematic absences $h00$, $0k0$ and $00l$ for h, k, l odd, the space group was found to be $P2_12_12_1$. The calculated density (1.56 g.cm.^{-3}) is in agreement with that observed (1.57 g.cm.^{-3}). Thus there is seen a simple relation between the dimensions of the two unit cells:

* $[\alpha]_D^{20} = +31.7^\circ$ (2N HCl solution).

$$a (\beta\text{-form}) \cong \frac{1}{2}b (\alpha\text{-form}), \quad b (\beta\text{-form}) \cong 2c (\alpha\text{-form}), \\ c (\beta\text{-form}) \cong a (\alpha\text{-form}).$$

Cu $K\alpha$ radiation was used throughout the investigation, and intensity data for $0kl$, $h0l$ and $hk0$ reflexions, which were recorded on zero-level Weissenberg and oscillation photographs about the three principal axes, were estimated visually. Correction for absorption was neglected because crystals were cut and ground carefully into rods of cross-sections less than 0.2 mm. After being corrected for Lorentz and polarization factors the intensities were roughly converted to an absolute scale by comparing the calculated average values with those observed (Wilson, 1942).

Determination of the structure

The Patterson projections along the three principal axes were computed from the $0kl$, $h0l$ and $hk0$ intensity data. As we were not successful in deriving atomic coordinates from these projections, the minimum-function method (Buerger, 1951) was applied. The M_2 and M_4 maps showed up a number of possible atomic positions, from which several reasonable structures were derived. Inequality relations (Harker & Kasper, 1948; Okaya & Nitta, 1952) gave signs of 26 $F_{(0kl)}$'s and 35 $F_{(hko)}$'s, from which preliminary Fourier series were synthesized. Comparing M_2 and M_4 maps with these Fourier projections, an approximate disposition of the molecule was obtained. The locations of atoms were checked by the trial-and-error method on the assumption of a plausible molecular model for glutamic acid. The atomic coordinates were refined in the usual manner by successive two-dimensional Fourier

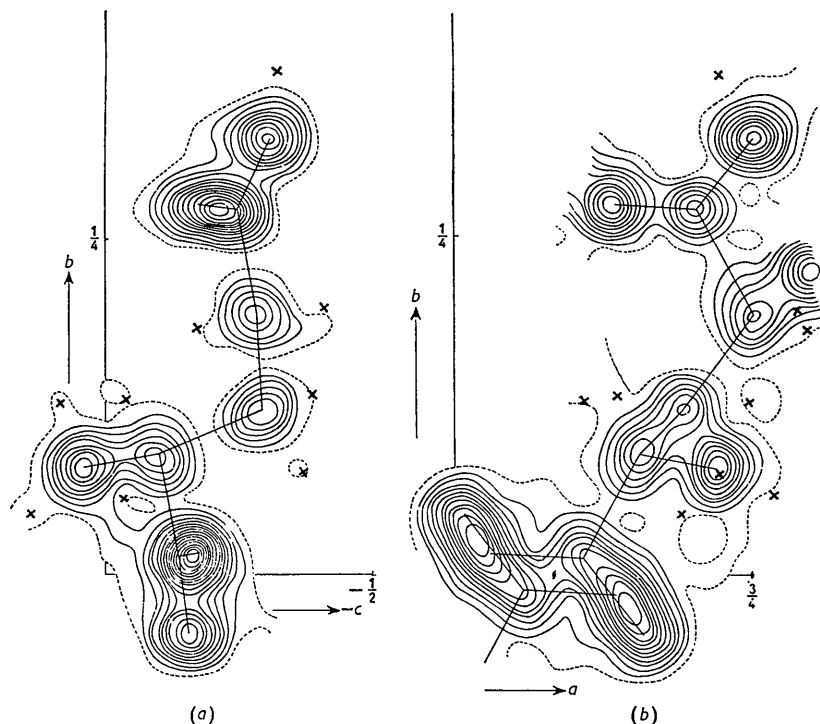


Fig. 1. Electron-density projection of one molecule (a) on (100), (b) on (001). Contours at an interval of $1.0 \text{ e.}\text{\AA}^{-2}$, starting at $2.0 \text{ e.}\text{\AA}^{-2}$ (broken lines). Crosses show the postulated locations of hydrogen atoms. Scale: $1 \text{ cm.} = 1 \text{ \AA}$.

syntheses at intervals of $a/30$, $b/120$ and $c/60$. Further refinement was continued by the calculation of successive difference-syntheses. The coordinate values of the resolved Fourier peaks were determined by the Carpenter-Donohue method (1950). As the positions of the atoms 3, 1, 7 and 9 (see Fig. 2) remained unresolved in $\rho(y, z)$ and also of atoms 3, 1 and 2 in $\rho(x, y)$, their coordinates were determined by repeated structure-factor calculations in which these values were varied so as to reduce the reliability indices as far as possible, partial configurations of the molecule being so chosen that the α -carbon atoms did not depart from the planes of the carboxylic groups.

The locations of hydrogen atoms were assumed to be at 1.09 , 1.01 and 0.97 \AA from the carbon, nitrogen and oxygen atoms, respectively, in the required directions. For the calculation of the structure factors, atomic scattering curves for H, C, N and O atoms given in *Internationale Tabellen* were corrected, using temperature factors which were assumed to have $B = 2.25 \text{ \AA}^2$ for heavy atoms and $B = 3.00 \text{ \AA}^2$ for the hydrogen atom from the comparison of F_c/F_o values against $\sin \theta$. Reliability indices, R , were calculated to be 0.160 for $0kl$, 0.153 for $h0l$ and 0.154 for $hk0$ reflexions, including all reflexions up to $\sin \theta = 0.98$, except for those not observed. A comparison of F_o and F_c is listed in Table 1.*

* Table 1 has been deposited as Document No. 4610 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., U.S.A.

The atomic coordinates (to ± 0.003) are collected in Table 2. The final electron-density projections on (100) and on (001) are shown in Fig. 1.

Table 2. Atomic coordinates

	x	y	z		x	y	z
O(1)	0.092	0.016	0.820	H ₁	0.808	0.058	0.967
O(2)	0.475	-0.045	0.842	H ₂	0.757	0.128	0.085
C(3)	0.325	0.013	0.863	H ₃	0.570	0.046	0.138
C(4)	0.463	0.091	0.899	H ₄	0.667	0.373	0.677
C(5)	0.571	0.123	0.706	H ₅	0.323	0.130	0.961
C(6)	0.750	0.194	0.719	H ₆	0.667	0.075	0.628
C(7)	0.607	0.273	0.754	H ₇	0.411	0.133	0.613
O(8)	0.746	0.325	0.692	H ₈	0.888	0.184	0.832
O(9)	0.400	0.276	0.830	H ₉	0.862	0.197	0.590
N(10)	0.663	0.079	0.043				

Discussion

The general features of the structure can be seen in Figs. 1 and 3, where one can see that the carbon-chain configuration is not coplanar. A discussion of this configuration compared with other similar substances will be given later. The structure consists of molecules tied into infinite chains along the direction of the b axis by $\text{O-H} \cdots \text{O}$ hydrogen bonds, and these chains are linked together in other directions by $\text{N-H} \cdots \text{O}$ hydrogen bonds.

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The interatomic distances and bond angles calculated from the atomic coordinates are given in Fig. 2.

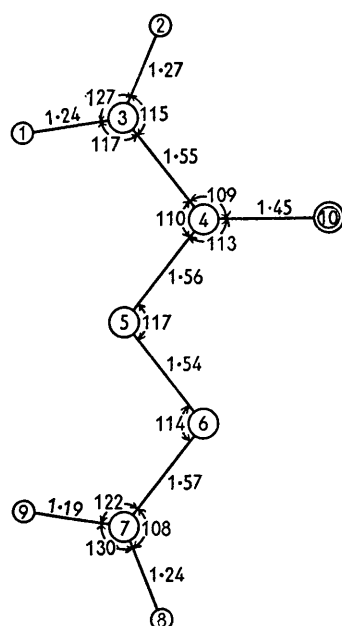


Fig. 2. Interatomic distances (± 0.05 Å) and bond angles ($\pm 5^\circ$) in *L*-glutamic acid.

The C-N distance (1.45 Å) is in agreement with that found in *N*-acetylglucine (Carpenter & Donohue, 1950). In other investigations by three-dimensional Fourier series the same bond was reported to be of the length 1.49 ~ 1.50 Å (DL-alanine (Donohue, 1950), hydroxy-L-proline (Donohue & Trueblood, 1952), L-threonine (Shoemaker, Donohue, Schomaker & Corey, 1950), α -amino isobutyric acid (Hirokawa, Kuribayashi & Nitta, 1952) and DL-serine (Shoemaker, Borieau, Donohue & Lu, 1953)).

The average C-C bond distance of 1.55 Å and the average C-C-C angle of 114° may be compared with the corresponding values in the other compounds given above. The dimensions of the two carboxylic groups are also reasonable, as will be discussed later.

The molecular arrangement viewed along the *c* axis is shown in Fig. 3, where four short N...O separations, shown as broken lines and a chain line, can be seen. These separations are 2.86, 2.92, 2.94 and 2.86 Å, making angles of 102, 103, 113 and 174° , respectively, with the C-N bond. Of these separations the last cannot be considered as a hydrogen bond because its bond angle (174°) is too large. Thus the nitrogen atom is regarded as connected to three oxygen atoms by hydrogen bonds. Though at least the two hydrogen atoms in these bonds are evidently attached to the nitrogen atom, it is rather difficult to give a decisive conclusion as to whether the third is also attached to the same atom or not. As three hydrogen atoms are attached to the amino nitrogen surrounded by three oxygen atoms in all the structures of amino acids so

far reported (just as in the present case), it is also likely that in the present case the same situation oc-

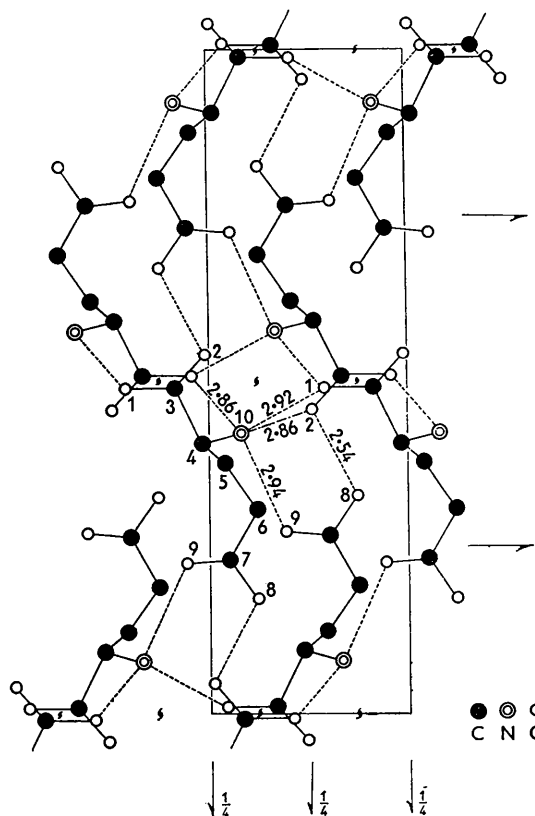
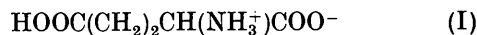


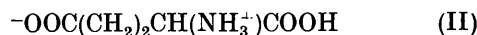
Fig. 3. Molecular arrangement viewed along [001] showing hydrogen bonds (broken lines). Scale: 1 cm. = 2 Å.

occurs and that the molecule as a whole forms a zwitterion. The difference Fourier maps (Fig. 4) favour this view. A short O...O separation of 2.54 Å is seen between atoms 2 and 8. This is in agreement with the corresponding distances in *N*-acetylglucine (2.56 Å) and in DL-glutamic acid hydrochloride (2.57 Å).

Here arises an interesting question: Which of the two forms,



and



is found in this structure? Although within the limit of error in the present determination it is rather difficult to discriminate decisively, it may still be said that the structural features favour (I) for the following reasons. The two C-O bonds in the γ -carboxylic group are 1.19 Å for atoms 7-9 and 1.24 Å for atoms 7-8. The former (1.19 Å) is the value proposed by Goldschmidt & Llewellyn (1950) for the pure C-O double bond, and moreover the angle 6-7-9 (122°) is very close to 120° ; the latter (1.24 Å) is not so short, and the angle 6-7-8 (108°) is very close to the tetrahedral angle. On the other hand in the α -carboxylic group corresponding distances are 1.24 Å for 3-1 and 1.27 Å

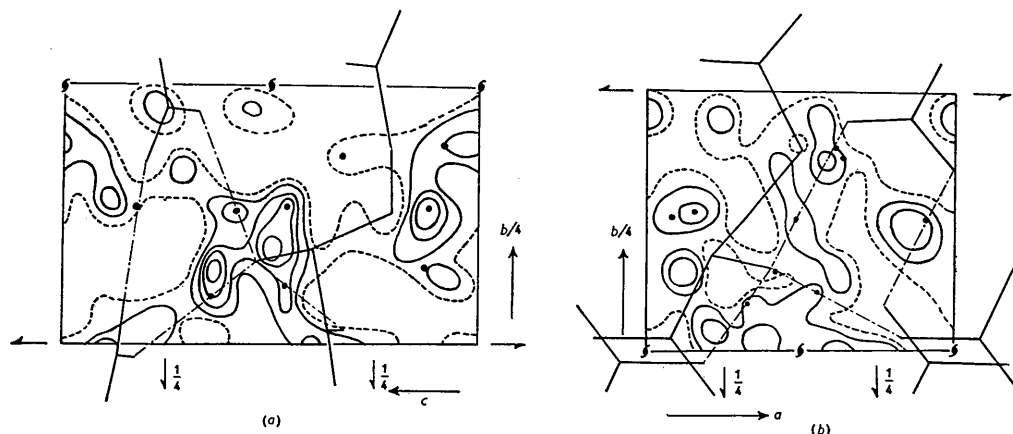


Fig. 4. Projection of electron density (a) on (100), (b) on (001) from which the contributions of C, N and O atoms have been subtracted. Postulated locations of hydrogen atoms are indicated by dots. Contours at approximately $0, \frac{1}{2}, 1, \frac{3}{2} \text{ e.}\text{\AA}^{-2}$, lowest contours being drawn in broken lines. Scale: $1 \text{ cm.} = 1.25 \text{ \AA}$.

for 3-2 and angles are 117° for 4-3-1 and 115° for 4-3-2. The projected difference syntheses seem to support the above conclusion. It may be added that for the free zwitterion the charge distribution corresponding to (I) is considered to be electrostatically more stable than that corresponding to (II).

It is of some significance to compare carbon-chain

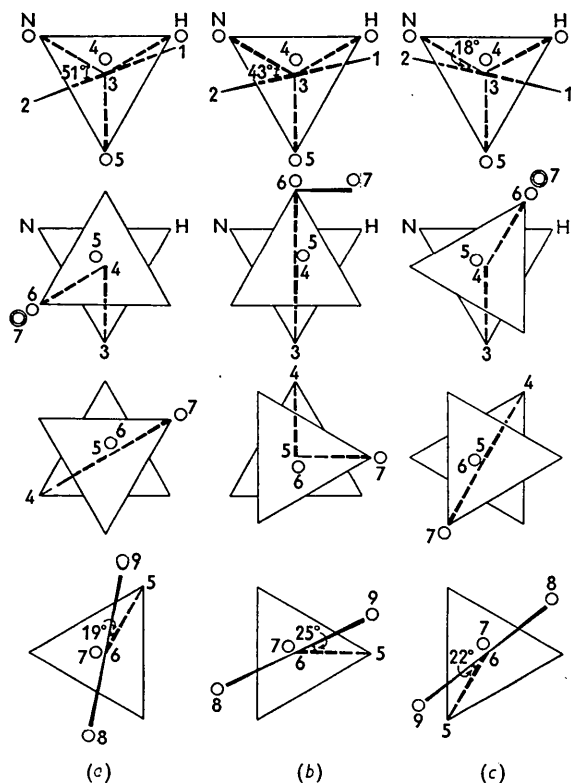


Fig. 5. Carbon-chain configurations of (a) L-glutamine, (b) L-glutamic acid and (c) L-glutamic acid hydrochloride viewed along each C-C bond.

configurations among the three structures of L-glutamine, L-glutamic acid and DL-glutamic acid hydrochloride. The comparison is shown in Fig. 5, in which the configurations are given in a somewhat idealized tetrahedral representation. In the first column they are viewed from the bond direction 4-3, in the second from 5-4, in the third from 6-5 and in the fourth from 7-6. The atoms on the upper side are indicated by circles, and double circles mean the atoms lying at a still higher level. In this figure the configuration of glutamic acid hydrochloride is so chosen as to enable mutual comparison by changing the signs of the α parameter given by Dawson (1953).

From the comparison we can summarize the following features:

(1) The α -carboxylic and the amino groups are not coplanar in all the three structures; the angles of rotation of the C-N bond from the plane of the α -carboxylic group are 51° for L-glutamine, 43° for L-glutamic acid and 18° for L-glutamic acid hydrochloride.

(2) In L-glutamine the carbon-chain configuration is of the *gauche* form with respect to the central 5-4 bond, the actual deviation from the idealized position being 5° , and of the *trans* form with respect to the 6-5 bond. In L-glutamic acid it is of the *trans* form for the 5-4 bond, the angular deviation being 9° , and of the *gauche* form for the 6-5 bond, the plane 5-6-7 making an angle of 85° with the plane 4-5-6. In L-glutamic acid hydrochloride it is of the *trans* form for the 5-4 bond, with an angular deviation of 23° with respect to the idealized form, and again of the *trans* form for the 6-5 bond.

(3) Interplanar angles between the two planes 7-8-9 (γ -carboxylic group) and 5-6-7 are approximately of the same magnitude in the three cases.

The arguments given above show that though the present form of L-glutamic acid has a hydrogen-bonded structure similar to those of other amino acids,

it has a different configuration from other related compounds with respect to the carbon chain. The present investigation is another example of the fact that while the bond distances and valency angles in the carbon chain of different amino acids remain unchanged, each amino acid assumes a different configuration referring to a particular C-C bond. It seems that the rotation about the C-C bond depends more or less on the effect of surrounding molecules, while otherwise keeping the chain approximately in the *trans* or *gauche* configuration. In this connexion, it is highly desirable to determine the structure of the α -form in order to see if the molecule in this form assumes another configuration as in the cases of methionine (Mathieson, 1952) and D-(-)-isoleucine salts (Trommel & Bijvoet, 1954).

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Inégalités de Karle-Hauptman et Géométrie Euclidienne

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Structure-factor inequalities are formulated which are simpler than those of Karle & Hauptman but which are nevertheless rigorously equivalent to them for centro-symmetrical structures. Furthermore, the condensation of the general determinant facilitates the establishment of inequalities of higher order.

1. Introduction

Les dernières années ont vu se développer un nombre considérable de techniques, et surtout de théories, tendant à permettre de déterminer les phases des facteurs de structure. Le volume de ces recherches atteste de l'importance du problème, et, en même temps, de la grande difficulté que présente sa résolution. Les inégalités de Harker & Kasper (1948) ont manifestement été utilisées le plus souvent; cependant, grâce à des travaux systématiques (Grisson, 1951; Sakurai, 1952), l'outil qu'elles constituent semble avoir atteint son maximum d'efficacité. Par ailleurs, il appartient encore à l'avenir de réserver aux méthodes statistiques la place qui leur est due.

Mais il est surprenant que, parmi les théories analytiques, l'une des plus élégantes et des plus complètes soit jusqu'à présent restée sans écho dans le domaine de la pratique: en effet nous ne connaissons pas

d'exemple de structure ayant été résolue grâce aux inégalités de Karle & Hauptman (1950). La responsabilité de cet insuccès incombe évidemment à l'aspect rébarbatif de ces inégalités, qui fait reculer devant leur emploi, plutôt qu'à une éventuelle inaptitude à résoudre le problème des phases.

Or il est possible, et de façon naturelle, de substituer aux déterminants de Karle & Hauptman des relations plus simples quoique rigoureusement équivalentes: ainsi l'étude des déterminants positifs d'ordre 3 se ramène à celle d'inégalités linéaires. D'autre part il existe un procédé mathématique commode permettant d'obtenir systématiquement l'ensemble des inégalités de chaque catégorie.

2. Géométrie et positivité

Convenons d'abord d'étudier une structure cristalline centrée et unidimensionnelle. La généralisation à 3