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A refinement of the structure of allokainic acid.

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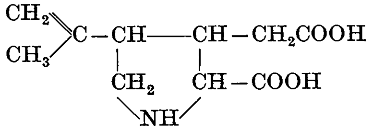
The crystal structure of allokainic acid (I) has



(I)

recently been determined by Watase (1958) for stereochemical purposes from electron-density maps of two projections, with final discrepancy factors of 17·8 and 19·2%. An unusual feature of the reported dimensions was the length of 1·40 Å found for the distance C_7–O_3 in one of the carboxyl groups, which is almost the length of 1·43 Å for the ordinary C–O single bond and is much longer than the distances of 1·29–1·32 Å commonly found for C–O(H) distances in carboxylic acids. Since only the oxygen O_3 of this carboxyl group is involved in hydrogen bonding, whereas usually both oxygens of a group are involved, it seemed worthwhile refining Watase's data by least-squares on the Leeds University electronic computer to see if the unusual C_7–O_3 distance could be confirmed.

After 7 cycles of least-squares refinement the molecular dimensions were recalculated and the C_7–O_3 length was found to be 1·32 Å with an e.s.d. of approximately 0·03 Å; the revised C_7–O_4 distance is 1·20 Å. There is thus no evidence that the lack of a hydrogen bond to O_4 causes any departure from the dimensions expected for a carboxyl group.

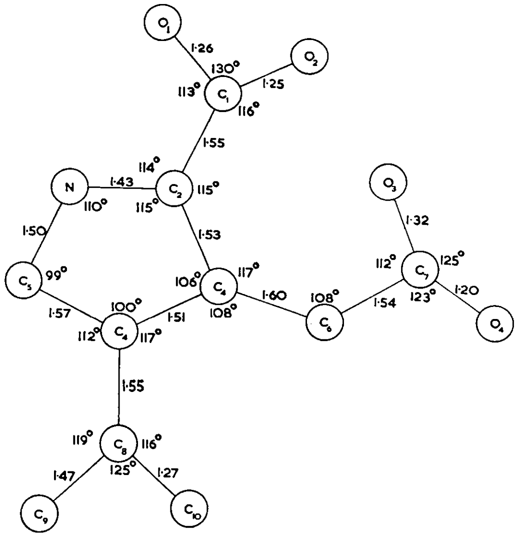


Fig. 1. Bond lengths (Å) and bond angles (°).

The details of the refinement were as follows. The data for the two projections were combined and were weighted according to Hughes' (1941) scheme. The first three cycles were carried out isotropically and the last four with individual atomic anisotropic vibrations; the hydrogens were neglected. The revised bond lengths and angles are shown in Fig. 1, the maximum differences from Watase's values being 0·08 Å and 5° respectively. Including allowance for off-diagonal terms in the normal equations due to atomic overlaps in the projections, the e.s.d.'s are approximately 0·03–0·04 Å and 2° respectively. As the atomic vibrations did not prove markedly anisotropic only the mean square amplitudes U are recorded here and these are shown in Table 1 along with the revised co-ordinates. The atoms at the ends of the side chains evidently vibrate more than those near the centre of the molecule. The F_o scale was increased by a factor of 1·155 during the refinement, which explains why the average U of 0·044 Å² is a little lower than the overall value of 0·051 Å² used by Watase. The discrepancy factor improved only to 15·6% during the refinement, but the sum of the weighted residuals dropped to a third of its initial value. The revised hydrogen bond distances are 2·86 Å for N–H · · · O_1, 2·69 Å for N–H · · · O_2 and 2·71 Å for O_3–H · · · O_1. The revised co-ordinates do not affect the discussion of the molecular stereochemistry and the crystal structure given by Watase.

Table 1. *Atomic parameters*

Atom	x/a	y/b	z/c	U (Å²)
C_1	0·2237	0·1822	0·2679	0·031
C_2	0·1950	0·4019	0·3316	0·036
C_3	0·1390	0·3639	0·3873	0·030
C_4	0·1093	0·5622	0·3015	0·041
C_5	0·1401	0·6014	0·1110	0·048
C_6	0·1263	0·3526	0·6118	0·041
C_7	0·1435	0·1177	0·6879	0·039
C_8	0·0513	0·5232	0·2639	0·043
C_9	0·0360	0·3426	0·1282	0·069
C_{10}	0·0205	0·6586	0·3497	0·056
N	0·1936	0·5788	0·1891	0·035
O_1	0·2366	0·7229	0·8299	0·046
O_2	0·2081	0·9983	0·3402	0·045
O_3	0·1895	0·1256	0·7681	0·047
O_4	0·1164	0·9515	0·6854	0·055

I am very grateful to Dr A. M. B. Douglas for her help with the calculations and to the Leeds University Electronic Computing Laboratory for the use of their Ferranti Pegasus Computer.

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Crystal structure of silver fulminate.

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The present note describes attempts which have been made to determine the crystal structure of silver fulminate. For preparation of this compound 30 c.c. of absolute alcohol were added to 19 c.c. of 21·5% solution of silver nitrate in nitric acid. Chemical reaction was carried at a temperature range of 60 to 80 °C. Well formed crystals of the compound were obtained by dissolving the freshly precipitated product in a 20% solution of ammonium acetate at a temperature of 50 °C. This saturated solution was cooled very slowly from 50 °C. to room temperature when glistening needle-shaped crystals of silver fulminate were obtained. The average length of the crystals was 4 to 5 mm. Chemical analysis gave 71·87% silver (theoretical 71·94).

The refractive indices of the crystal were determined by the Becke line method using as immersion media liquids such as carbon disulphide and mixtures of methylene iodide and arsenous sulphide. The refractive index of the crystal for sodium light polarized along the needle axis (or a-axis) is found to be 1·630 and for the light polarized perpendicular to the needle axis (or parallel to the b-axis) is found to be 1·831. The density of the crystals determined with the help of a pycnometer is 3·938 g.cm.$^{-3}$.

Study of oscillation and Weissenberg X-ray photographs reveals that the crystal is orthorhombic. The dimensions of the unit cell are found to be $a=6·04$, $b=3·88$ and $c=11·20$ Å. All observed reflections obey the relationship that the sum $(h+k+l)$ is even; the unit cell is, therefore, body centred. Further it is found that for the $0kl$ reflexions $h+l$ is even, for $h0l$ both h and l are even, and for $hk0$ both h and k are even. These observations suggest that the space group probably is *Imca*. The value of the density of the crystal calculated by assuming four molecules in the unit cell is 3·936 g.cm.$^{-3}$ which agrees reasonably well with the experimental results.

Sincere thanks are due to Prof. D. S. Kothari and Dr A. R. Varma of the Delhi University for kind help and useful discussions.

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Structure de $SP(C_2H_5)_3$ et $SeP(C_2H_5)_3$.

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$SP(C_2H_5)_3$ (I) et $SeP(C_2H_5)_3$ (II) sont isomorphes. L'étude de la projection (001) de I a fait l'objet d'une note antérieure (Van Meerssche, 1954). Le présent travail est une détermination de la structure tridimensionnelle de $SP(C_2H_5)_3$ et de $SeP(C_2H_5)_3$. Ces substances cristallisent sous forme de longues aiguilles hexagonales. Les paramètres de la maille-unité valent:

	a	*c*
I	8,98 ± 0,01 Å	6,32 ± 0,01 Å
II	9,06 ± 0,01	6,54 ± 0,01

2 molécules par maille.

Données expérimentales utilisées dans l'analyse des structures:

I	$hk0$, $0kl$, hkl, $hk2$
II	$hk0$, —, hkl, $hk2$, $hk3$, $hk4$

Les intensités ont été lues visuellement sur des films de Weissenberg intégrés et corrigées pour l'absorption et l'extinction secondaire (F. Jellinek, 1958). Rayonnement incident: Cu $K\alpha$.

Les molécules possèdent la symétrie ponctuelle 3 et réalisent deux configurations énantiomorphes (A et B de la Fig. 1).

Selon le mode de répartition de ces deux formes, le groupe spatial serait $P6_3mc$ (répartition statistique représentée à la Fig. 1) ou $P31c$ (macle de cristaux à structure ordonnée, où chaque molécule A est entourée de $3B$ et inversément).

Bien qu'il ne nous ait pas été possible de décider avec certitude de la symétrie spatiale, $P6_3mc$ semble probable. La maille contiendrait alors des molécules 'statistiques', superposition de A et B, de symétrie $3m$.

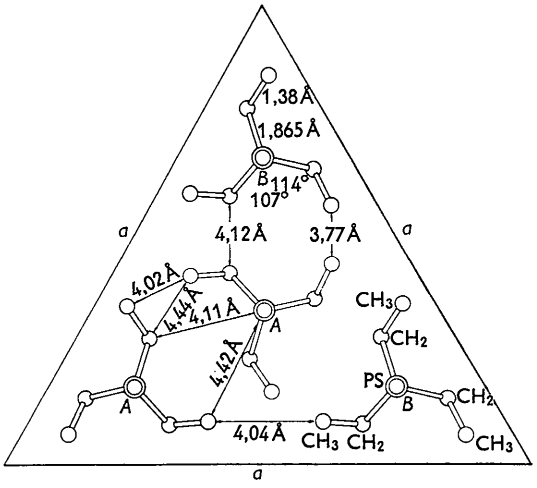

Fig. 1. $SP(C_2H_5)_3$. Projection sur le plan (001). Maille double. Répartition statistique des formes énantiomorphes A et B. Quelques distances intermoléculaires sont indiquées. Les distances entre CH_2 et S de la molécule située en dessous, sont de 4,15 Å. La molécule centrale est à $c/2$ en dessous des autres.