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The Crystal Structure of β-Nitropropionic Acid

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β-Nitropropionic acid is monoclinic, $A2/a$–C_{2h}^6 with eight molecules of $C_3H_5NO_4$ in a unit cell of dimensions $[a] = 20{\cdot}02$, $[b] = 5{\cdot}20$, $[c] = 9{\cdot}57$ Å, $\beta = 92^\circ\ 26'$. Two molecules are linked through the carboxyl groups by hydrogen bonds of length 2·66 Å across a centre of symmetry, and adjacent pairs are further linked by a zigzag arrangement of weak contacts of length 3·06 Å.

Introduction

The identity of β-nitropropionic acid and hiptagenic acid has been established by means of mixed melting points, dissociation constants, optical properties and X-ray powder photographs. Because of the unusual reactions given by hiptagenic acid, a naturally occurring product, many workers have regarded it as a 1:2-disubstituted propionic acid; in order to determine its constitution, the crystal structure has been investigated.

Experimental

β-Nitropropionic acid was prepared by a variation of the method of Lewkowitsch (1879) by the action of silver nitrite on 2-iodopropionic acid.

The crystals obtained from chloroform solution are very thin monoclinic plates elongated along [*b*] with {100} predominant and {001} and {101} occasionally developed. When carefully cut the crystals cleave along {101}. They are optically positive and biaxial with the optic axes lying in the (*ac*) plane and with γ vibrating 25° away from [*c*] in the acute angle β. The refractive indices, using the NaD line, are

$$\alpha = 1{\cdot}463,\ \beta = 1{\cdot}499,\ \gamma = 1{\cdot}558\ .$$
$$2V = 78^\circ\ 46'.$$

The unit-cell dimensions and space group were obtained from rotation and oscillation photographs:

$$[a] = 20{\cdot}02,\ [b] = 5{\cdot}20,\ [c] = 9{\cdot}57\ \text{Å};\ \beta = 92^\circ\ 26'.$$

Systematic absences are $\{hkl\}$ when $k+l \neq 2n$ and $\{h0l\}$ when $h \neq 2n$ and $l \neq 2n$. The space group is therefore either $A2/a$–C_{2h}^6 or Aa–C_s^4; these can accommodate eight and four molecules respectively in general positions. The density measured by flotation is 1·59 g.cm.$^{-3}$; the value calculated for eight molecules of $C_3H_5NO_4$ per cell is 1·589 g.cm.$^{-3}$. The space group was therefore taken as $A2/a$. Absorption coefficient for Cu $K\alpha$ X-rays, $\mu = 15{\cdot}0$ cm.$^{-1}$.

The intensities of all $\{hkl\}$ reflexions obtainable with Cu $K\alpha$ radiation were recorded on equi-inclination Weissenberg photographs, using the multiple-film technique. The crystals, which are deliquescent and volatile, were enclosed in perspex capsules (Llewellyn, 1951). The intensities were measured visually, a total of 512 planes out of a possible 1148 being observed, and then converted to structure amplitudes; these were placed on an approximately absolute scale, first by a photographic method in which a few planes from β-nitropropionic acid were compared with planes from *p*-dinitrobenzene (Llewellyn, 1947) and secondly by the method of Harker (1948).

Later, when the crystal structure would not refine, the $\{h0l\}$ and $\{hk0\}$ planes were corrected for absorption, using the intensities from the [*b*] and [*c*] axes zero-layer-line Weissenberg photographs, by a modification of the method of Albrecht (1939); only one value of the path length of the X-rays through the crystal was calculated, by taking one measurement through the geometric centre of the crystal. This was considered justifiable as the differences between this method and the more laborious Albrecht method were found to be small for the planes tried. The dimensions of the crystals were $0{\cdot}05\times0{\cdot}76\times0{\cdot}20$ mm. for [*b*]- and $0{\cdot}06\times0{\cdot}34\times0{\cdot}35$ mm. for [*c*]-axis photographs.

The Fourier series were summed at intervals of 1/120 along [a] and 1/60 along [b] and [c], using Robertson's strips.

Determination of the structure

Attempts were first made to solve the crystal structure by trial-and-error methods using a model containing a primary nitro group, but the difficulty lay in the flexibility of the model along the three bonds of the chain. Numerous models were postulated and tested without success and at one stage, when the molecule appeared approximately planar, the Fourier transform theory was applied; an analysis of the resulting contour diagram was not successful, however, though many variations were attempted. Finally an (010) Fourier projection was obtained which resolved eight atoms, but no three-dimensional model could be fitted to this projection. The signs of the ($h00$) planes used were confirmed by Banerjee's method (1933).

It became necessary, therefore, to determine the structure in a way which did not involve any assumptions about the chemical formulation of the molecule. As no information could be obtained from the Harker–Kasper inequalities (Harker & Kasper, 1948), the method described by Zachariasen (1952) was investigated. In a primitive monoclinic lattice three phases, $\alpha(h_1k_1l_1)$, $\alpha(h_2k_2l_2)$, $\alpha(h_3k_3l_3)$ may be chosen arbitrarily, provided the indices satisfy the selection rules (Lonsdale & Grenville-Wells, 1954). Since there is a known relationship, dependent on the particular space group, between $\alpha(h_1k_1l_1)$, $\alpha(h_1\bar{k}_1l_1)$, $\alpha(\bar{h}_1\bar{k}_1\bar{l}_1)$, $\alpha(\bar{h}_1k_1\bar{l}_1)$ etc., there are twelve phases in all which may be used in the Zachariasen calculations. In an A-centred monoclinic lattice the eight symmetry centres not related by a lattice translation occur in two sets with four centres in each:

$$\begin{array}{lllll} (1) & 0, 0, 0 & 0, \tfrac{1}{2}, 0 & \tfrac{1}{2}, 0, 0 & \tfrac{1}{2}, \tfrac{1}{2}, 0 \\ (2) & 0, \tfrac{1}{4}, \tfrac{1}{4} & 0, \tfrac{3}{4}, \tfrac{1}{4} & \tfrac{1}{2}, \tfrac{1}{4}, \tfrac{1}{4} & \tfrac{1}{2}, \tfrac{3}{4}, \tfrac{1}{4} \end{array}$$

The phase relationships for the two sets are different and this reduces to eight the number of known phases available for the Zachariasen calculations. The planes 511, $45\bar{3}$ and $74\bar{2}$ satisfy the selection rules for an A-centred lattice (Lonsdale & Grenville-Wells, 1954) and were chosen as positive. It was further assumed that the origin centre (which is determined by the choice of phase for the three planes, but remains unknown) belonged to the $0, 0, 0$; $0, \tfrac{1}{2}, 0$; $\tfrac{1}{2}, 0, 0$; $\tfrac{1}{2}, \tfrac{1}{2}, 0$ set.

Application of Zachariasen's method gave the signs of 58 $\{h0l\}$ planes and the resulting Fourier synthesis is shown in Fig. 1. From this projection it can be seen that β-nitropropionic acid contains a primary nitro group, though, owing to the symmetry of the molecule, the nitrogen atom could not be distinguished at this early stage. The projection was refined by Fourier syntheses. The y coordinates were obtained from a set of three-dimensional Fourier lines, using 310 $\{hkl\}$ phases determined by Zachariasen's method.

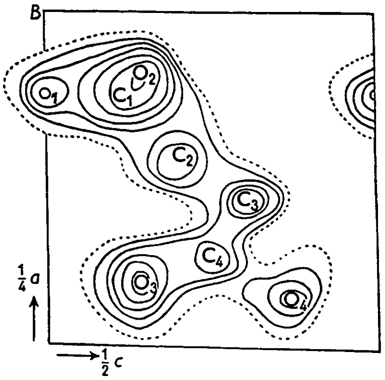


Fig. 1. $\{h0l\}$ Fourier projection calculated from the 58 planes whose signs were determined by Zachariasen's method. The true origin of this projection was later shown to be the point B. Contours are drawn at equal intervals; zero contour broken.

Agreement between observed and calculated structure amplitudes was poor for all planes excepting those with $h = 2n$, $k = 2n$, $l = 2n$. Trial calculations showed that the agreement was considerably improved when the origin was removed to a point $\tfrac{1}{4}, \tfrac{1}{4}, 0$. It was evident, therefore, that the assumptions made concerning the phase relationships were incorrect; a redetermination of phases by Zachariasen's method using the postulated 511 (+), $45\bar{3}$ (−) and $74\bar{2}$ (+) and the same phase relationships as before produced a phase pattern substantially in agreement with that obtained following the arbitrary origin shift. The true origin of the $\{h0l\}$ projection is the point B (Fig. 1).

The coordinates were refined by $\{h0l\}$ and $\{hk0\}$ difference syntheses (Booth, 1948; Cochran, 1951).

F_c was evaluated using a scattering curve constructed in the same way as for dipotassium nitroacetate (Sutor, Llewellyn & Maslen, 1954). The reliability factor was reduced to 0·310 for the $\{h0l\}$ projection and 0·299 for the $\{hk0\}$ projection. Refinement beyond this stage was very slow and it was assumed that the experimental structure amplitudes were considerably in error because of absorption, the ratio

maximum dimension/minimum dimension

in the crystals used being 15 and 6 respectively. The $\{h0l\}$ and $\{hk0\}$ planes were corrected for absorption

Table 1. *Scattering curves.*

$\sin\theta$	$f(\{h0l\}$ projection)	$f(\{hk0\}$ projection)
0	6·00	6·00
0·1	5·33	5·33
0·2	4·13	4·13
0·3	2·93	2·93
0·4	2·06	2·00
0·5	1·33	1·28
0·6	0·86	0·90
0·7	0·60	0·80
0·8	0·34	0·78
0·9	0·19	0·68
1·0	0·08	0·41

and thereafter refinement proceeded more rapidly to 0·188 for $\{h0l\}$ planes and 0·199 for $\{hk0\}$ planes.

The scattering curves for the two projections are shown in Table 1.

These two sets of f values represent the best experimental curves for the two projections. It is doubtful whether the difference between them is significant as the number of planes of measurable intensity with $\sin\theta > 0·7$ is extremely small.

The atom C_4 was identified as the nitrogen atom from a consideration of reliability factors, hydrogen bonding which should occur in the carboxyl group, and bond lengths.

Because the positions of the hydrogen atoms could not be obtained, parameters were calculated assuming tetrahedral bond angles and a C–H bond length of 1·09 Å. Four atoms were placed in this way, two on C_2 and two on C_3. The hydrogen of the carboxyl group was placed in the plane of this group and at a distance of 0·96 Å from O_1 along the line of the hydrogen bond between O_1 and the atom O_2 of the neighbouring molecule. Inclusion of their contribution in F_c using the scattering curve for hydrogen given by Viervoll & Ögrim (1949) reduced the reliability factor to 0·179 for the $\{h0l\}$ projection but did not alter the reliability factor for the $\{hk0\}$ projection.

In order to confirm the coordinates obtained from the two projections, the structure amplitudes of some $\{hkl\}$ planes were calculated. Planes in the range $\sin\theta \leqslant 0·35$ were chosen from the $[a]$ axis as these were less likely to have suffered from serious absorption effects. The reliability factor for these planes is 0·164, thus confirming the correctness of the coordinates.*

Discussion of the structure

The fractional coordinates referred to the monoclinic crystals axes are

	x/a	y/b	z/c
O_1	0·050	0·217	0·531
O_2	0·040	0·485	0·352
O_3	0·192	0·558	0·371
O_4	0·205	0·612	0·148
C_1	0·066	0·292	0·403
C_2	0·116	0·109	0·330
C_3	0·146	0·255	0·209
$N(C_4)$	0·181	0·494	0·246

The bond lengths and bond angles within the molecule are shown in Fig. 2.

The standard deviation in bond length calculated by the method of Cruickshank (1949) is 0·03 Å, taking p as 4·9. The standard deviation in a bond angle was found to be 2°.

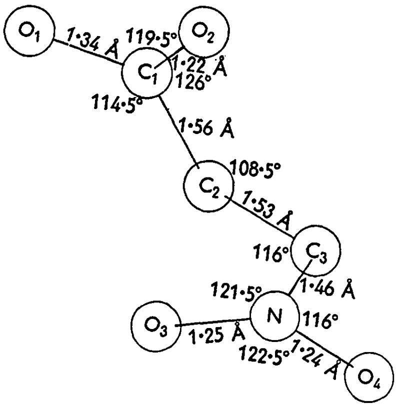


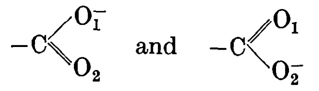
Fig. 2. The interatomic distances and bond angles.

The C–C bond lengths of 1·56 and 1·53 Å and the C–N bond of 1·46 Å are all, within experimental error, equivalent to the expected values of 1·54 and 1·47 Å from the sum of the covalent radii. It is doubtful whether the lengthening of the C_1–C_2 bond is at all significant, but the values are longer than in the dicarboxylic acids β-succinic acid, adipic acid, sebacic acid and β-glutaric acid, where the average C–C distance is 1·51 Å (Morrison & Robertson, 1949).

The inequality of bonds in the carboxyl group is similar to that in dipotassium nitroacetate (Sutor, Llewellyn & Maslen, 1954) and in other dicarboxylic acids, though in this case the asymmetry is greater:

	C–O	C–O
β-Succinic acid	1·25 Å	1·30 Å
Adipic acid	1·23	1·29
Sebacic acid	1·24	1·27
β-Glutaric acid	1·23	1·30
Dipotassium nitroacetate	1·27	1·33
β-Nitropropionic acid	1·22	1·34

In carboxylic acids there is resonance between the forms



$$-\mathrm{C}\begin{matrix}\diagup O_1^- \\ \diagdown\!\!\diagdown O_2\end{matrix} \quad \text{and} \quad -\mathrm{C}\begin{matrix}\diagup\!\!\diagup O_1 \\ \diagdown O_2^-\end{matrix}$$

and the relative contributions of each may be calculated. The C–O single and double bonds of 1·42 and 1·20 Å, which had given satisfactory results for other acids (Vaughan & Donohue, 1952), were used. Excellent agreement was obtained between observed and calculated bond distances:

Double bond character	C–O (obs.)	C–O (calc.)
0·20	1·34 Å	1·33 Å
0·80	1·22	1·22

Levy & Corey (1941) suggest that this inequality in the carboxyl group is due to the oxygen atom of the longer C–O bond taking part in two hydrogen bonds, and this should tend to stabilize the form in which

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* *Editorial note.*—A list of observed and calculated structure factors has been deposited as Document No. 4309 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., U.S.A. A copy may be secured by citing the Document number and by remitting \$1·25 for photoprints, or \$1·25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

this atom carries a formal negative charge. In β-nitropropionic acid, two molecules are linked together by hydrogen bonds of length 2·66 Å between oxygen atoms of the carboxyl groups, and these pairs are further linked by a weak bond of 3·06 Å between O_1 atoms of adjacent pairs (see Fig. 3).

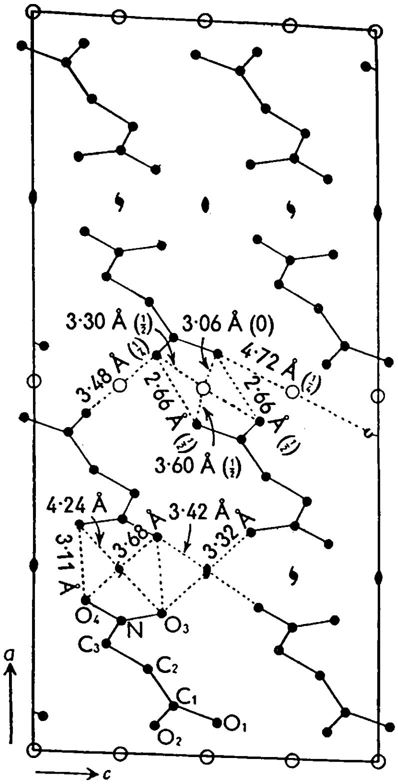

Fig. 3. Projection of the unit cell on to (010), showing hydrogen bonds and some intermolecular distances. The height of the centre to which each distance refers is given in brackets.

The equation of the plane containing the atoms C_2, C_1, O_1 and O_2 is

$$1{\cdot}038x' + 0{\cdot}793y + 0{\cdot}569z' - 4{\cdot}597 = 0\,,$$

where x', y, z' are the orthogonal coordinates expressed in Ångstrom units. The deviation of an atom from this plane is not greater than 0·03 Å. The O_1–C_1–O_2 bond angle of 119·5° is considerably different from the predicted value of 125°, assuming complete resonance in the carboxyl group, and is closer to that of 117° found in dipotassium nitroacetate. The two values of 114·5° and 126° for the O_1–C_1–C_2 and O_2–C_1–C_2 angles are consistent with the notion that the resonating double bond tends to be stabilized in the C_1–O_2 position. The N–O bonds of 1·25 and 1·24 Å are equal within experimental error. The atoms C_3, N, O_3 and O_4 are planar, and the equation of the plane is

$$3{\cdot}795x' - 2{\cdot}367y + 0{\cdot}313z' - 8{\cdot}256 = 0\,,$$

where x', y, z' are orthogonal coordinates in Ångström units. The calculated deviation of an atom from this plane does not exceed 0·04 Å.

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