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The Crystal Structure of 2,3:4,5-Dimethano-2,4-dinitro-1-hydroxycyclohexane-1-carboxylic Acid

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$C_9H_{10}N_2O_7$ crystallizes as monoclinic needles, space group $P2_1/a$, with $a = 13{\cdot}938$, $b = 6{\cdot}922$, $c = 10{\cdot}800$ Å, $\beta = 95{\cdot}63°$, $Z = 4$. The two cyclopropane rings are on opposite sides of the cyclohexane ring. The carboxyl group is on the same side as the nearer nitro group. An intramolecular hydrogen bond joins an O atom of this nitro group and the hydroxyl group. The arrangement of the molecules in the crystal is essentially that of a pseudo-cubic close packing of distorted spheres.

Introduction

Stam & Evers (1965) published the crystal structure of 6,6-dibromo-2,3:4,5-dimethano-2,4-dinitrocyclohexanone which was obtained in a study by de Boer & van Velzen (1964, 1971) of trismethylenetrinitrobenzene (1,3,5-trinitro-3,4:5,6-dimethano-1-cycloheptane) and its reactions. The latter authors were unable to determine whether the two three-membered rings are located on the same side of the six-membered ring, or on different sides. In order to solve this problem the related dibromo compound was investigated by X-ray diffraction. As a result the general configuration of the molecule was found, but the interatomic distances and interbond angles could not be derived with high precision, due to the presence of the heavy Br atoms.

In the present work an X-ray investigation of 2,3:4,5-dimethano-2,4-dinitro-1-hydroxycyclohexane-1-carboxylic acid was undertaken. This α-hydroxy acid was isolated by de Boer & van Velzen (1964) from the oxidative rearrangement of trismethylenetrinitrobenzene, together with an enantiomeric α-hydroxy acid.

As the relative positions of the hydroxyl and the carboxyl group could not be determined by spectroscopic methods, an investigation of one of these isomers was undertaken. The absence of Br atoms led us to expect more accurate values for interatomic distances and angles.

Experimental

The compound crystallizes in monoclinic needles along [010] with space group $P2_1/a$. The cell constants, derived from Weissenberg diagrams (Cu $K\alpha$: 1·5418, α_1: 1·5405, α_2: 1·5443 Å), calibrated with Al-powder lines are $a = 13{\cdot}938$ (3), $b = 6{\cdot}922$ (4), $c = 10{\cdot}800$ (2) Å $V = 1037{\cdot}0$ Å^3, $\beta = 95{\cdot}63$ (2)°, $d_x = 0{\cdot}9460$ g cm^{-3}, $Z = 4$. 1865 independent reflexions (including those with intensities too low to be observed) were obtained from 9 Rimsky retigrams about [020] with k from 0 to 8 respectively and 3 about [100] with h from 0 to 2 taken with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). The entire intensity range could be covered in one exposure using the multiple-film technique. The intensities were measured photometrically.

Because of the oblique direction of the diffracted beams in the Rimsky retigraph the intensity ratio between successive films is rather high (about a factor of 10). If the intensity measurements had been confined to the linear part of the film, only a limited number of reflexions would have been measured with sufficient accuracy on more than one film. We therefore also used the non-linear part of the characteristic curve for higher densities. A special calibration method was developed for this purpose. No absorption correction was applied [μ(Cu $K\alpha$) = 1·28 cm^{-1}].

Structure determination and refinement

The structure was solved by direct methods (Karle & Karle, 1966) with semi-automatic programs (Schenk, 1969). The signs of 227 reflexions with $|E| > 0{\cdot}6$ could be expressed in terms of 4 unknown symbols. A Fourier synthesis based on the solution with highest $\sum_2$-consistency revealed the complete structure.

The structure was refined by block-diagonal least squares. The H atoms were located from a difference synthesis and included in the refinement with isotropic temperature parameters. The final R was 8·2%. The final parameters are listed in Table 1 and the average standard deviations in Table 2.*

A rigid-body calculation was performed for the six-membered ring with the adjacent C, O and N atoms (Schomaker & Trueblood, 1968). The resulting libration ellipsoid is described in Table 3. All bond lengths, except those involving H atoms, were corrected for this libration (Busing & Levy, 1964). The corrections are of the same order of magnitude as the standard deviations.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31503 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

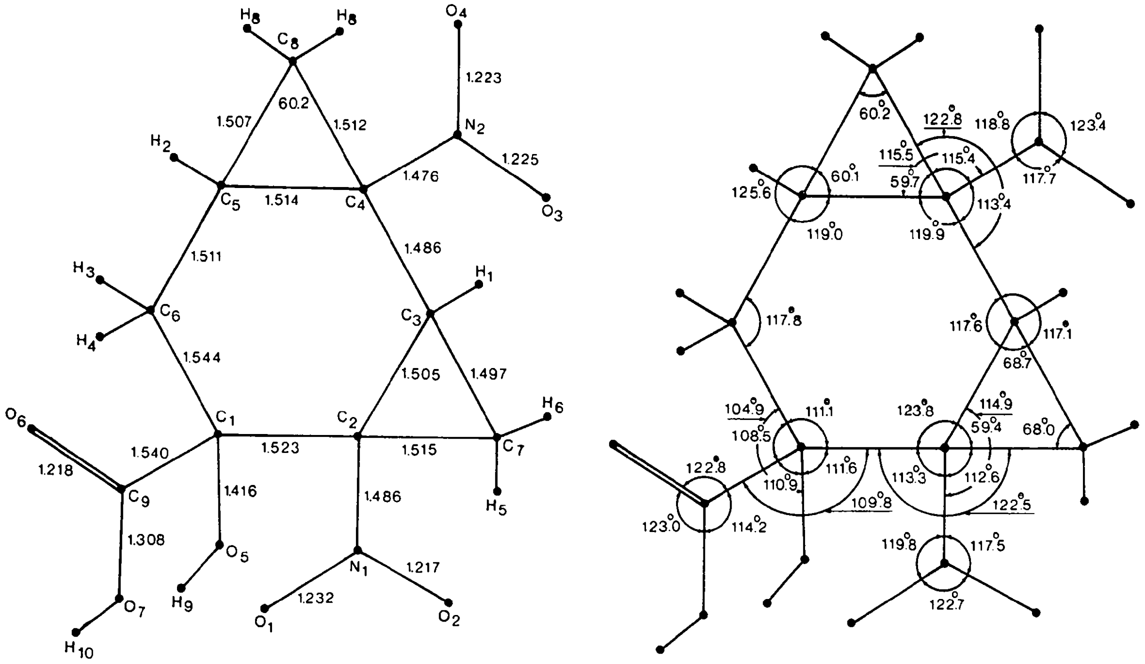

Fig. 1. Schematic representation of the molecule with bond lengths (Å) and bond angles.

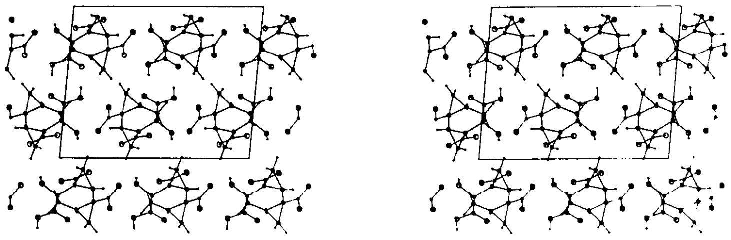

Fig. 2. Stereoscopic view along [010] of a part of the crystal structure.

Table 1. *Atomic coordinates* ($\times 10^4$ *for* C,O,N *and* $\times$ 10^3 *for* H) *and temperature parameters* ($\times 10^5$) (*except* B_{iso})

Anisotropic temperature factor: $\exp[-2\pi^2\{h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+hka^*b^*(2U_{12})+klb^*c^*(2U_{23})+lhc^*a^*(2U_{13})\}]$.

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
C(1)	5008	2082	2389	2930	3177	3026	200	−1031	956
C(2)	5876	2533	1689	3675	2390	2757	−234	−340	826
C(3)	6831	1526	1921	3151	3233	3297	−52	−493	1446
C(4)	6907	−75	2838	3560	3062	2969	678	−224	1041
C(5)	6012	−828	3356	4583	2916	3269	−192	163	2170
C(6)	5043	−16	2869	3734	2766	3964	−825	−405	1639
C(7)	6222	1182	726	4043	3702	2633	768	−498	1466
C(8)	6767	212	4193	4954	4445	2842	1002	−430	1060
C(9)	4993	3445	3508	4068	2613	3117	102	−312	2061
O(1)	5229	5619	4153	5746	3215	5981	2336	278	2417
O(2)	6646	5189	892	5590	4220	6555	−2137	1977	4397
O(3)	8109	−1258	1715	5257	5347	5198	1402	−1606	4459
O(4)	7715	−2976	3245	8496	6016	5026	7080	3196	1745
O(5)	4137	2207	1604	2921	4218	4186	100	−1089	89
O(6)	5717	4182	4021	3976	4246	4113	−771	−3355	1593
O(7)	4139	3686	3888	3576	5372	4174	492	−2652	2537
N(1)	5933	4592	1326	4824	3045	3430	−472	112	2095
N(2)	7624	−1551	2579	4278	3902	3513	1411	−665	−133

Table 1 (*cont.*)

	x	y	z	B_{iso}
H(1)	740	239	190	0·72
H(2)	603	−228	353	0·27
H(3)	460	−14	360	0·66
H(4)	477	−76	212	1·36
H(5)	587	−15	61	1·71
H(6)	642	184	−6	0·38
H(7)	720	−61	483	2·02
H(8)	663	155	449	2·01
H(9)	407	349	124	10·35
H(10)	418	458	458	4·02

Table 2. *Mean values of the estimated standard deviations of the atomic coordinates* ($\times 10^5$ *for* C,O,N *and* $\times 10^4$ *for* H)

The e.s.d.'s reduced to Å ($\times 10^4$ for C, O, N and $\times 10^3$ for H) are given in parentheses.

	x	y	z
C	24 (33)	47 (32)	29 (31)
O	20 (28)	40 (28)	25 (27)
N	22 (31)	42 (29)	26 (29)
H(CH)	24 (34)	52 (36)	32 (35)
H(CO.OH)	30 (42)	65 (45)	41 (44)
H(OH)	52 (68)	112 (78)	69 (75)

Table 3. *Libration tensor of the assumed rigid body*

	Direction cosines with respect to orthogonal axes		
Principal axes (°)^2	x'	y'	z'
14·755	−0·6083	+0·7302	+0·3109
6·227	−0·0718	+0·3395	−0·9379
3·091	+0·7904	+0·5929	+0·1541

In Fig. 1 the corrected values of the bond lengths are shown with the interbond angles. The mean estimated standard deviations in the lengths are: C–C, 0·005; C–O, C–N, N–O, 0·004 Å. Those in the angles vary from 0·2° for angles of about 60° to 0·3° for angles of about 120°.

Discussion

The shape and the arrangement of the molecules in the crystal are shown in Fig. 2, a stereoscopic view along [010]. The general arrangement of the rings with the attached nitro groups is the same as in the dibromo compound. Again the two CH_2 groups of the cyclopropane rings are on opposite sides of the cyclohexane ring. The angles between the best plane through the latter ring and the planes of the three-membered rings are 99·5° and 105·0°, practically the same as those in the dibromo compound. The carboxyl and the nearer nitro group are situated on the same side of the six-membered ring.

In the dibromo compound the C–C bonds are shorter (about 1·50 Å) than the normal single bond. In the present study the higher precision justifies a discussion of the various C–C distances. The shortest C–C bond is the one between the two cyclopropane rings, 1·486 Å (*i.e.* 0·06 Å shorter than a normal single bond). According to Pauling (1960), who discusses the shortening of the central bond in 1,3-butadiene, this may be explained by the fact that the other C–C bonds are bent away from their tetrahedral directions, which reduces the repulsion between the C atoms. In 1,3-butadiene this effect is superposed by that of the partial multiple-bond character of the bond, resulting in a still shorter distance, 1·46 Å. The shortening of the two bonds which share one atom with a three-membered ring may be expected to be about half that of one that shares both atoms with such a ring. These bonds are actually about 0·02 and 0·03 Å shorter than a normal bond, while the bond furthest from both cyclopropane rings does not differ from a normal single bond. The bond lengths within the cyclopropane rings do not differ significantly and their average is in good agreement with the usual value of 1·51 Å. The C–H bonds vary from 1·00 to 1·05 Å.

The widening of the bond angles in the cyclohexane ring of the C atoms shared with cyclopropane rings causes a flattening of the former ring. The sum of the squares of the distances of the atoms from their best plane is 0·106, compared with 0·15 in cyclohexane itself and 0·08 Å^2 in the dibromo compound. In particular the four atoms shared with one of the three-membered rings are nearly coplanar. The root mean square distance from their best plane is only 0·033 Å. The flattening of the six-membered ring prohibits the remaining C atoms from forming the normal tetrahedral angles. For C(1) the effect is partly compensated by the mutual repulsion of the COOH group and the OH group, resulting in only a slightly widened bond angle (111·1°) but C(6), which carries two H atoms, shows an interbond angle of 117·8°. There is an intramolecular hydrogen bond between the hydroxyl group and the adjacent nitro group with H(9)···O(1), 2·19; O(1)···O(5), 2·822; O(5)–H(9), 0·97 Å. This hydrogen bond might be responsible for the possibly significant difference between the bonds N(1)–O(1) and N(1)–O(2). Similar results were reported for dilituric acid (Bolton, 1963).

The packing of the molecules in the crystal

Two of the molecules in the cell, related by a glide plane, are situated essentially within the half of the cell with $y < \frac{1}{2}b$ (Fig. 2). The molecules are paired by means of hydrogen bonds between the carboxyl groups around centres of symmetry with O···O, 2·688 Å.

Every molecule appears to have points of contact with 12 adjacent molecules. This suggests close packing. In fact, when a sphere centred at (0·625, 0·750, 0·250) is substituted for the molecule of Table 1, the application of the symmetry operations results in a slightly distorted cubic face-centred lattice. The primitive vectors of this pseudo-cubic cell are [110], [110], and [001]. The cell dimensions are: $a' = b' = 9{\cdot}827$, $c' = 10{\cdot}800$ Å; $\alpha' = 95{\cdot}65$, $\beta' = 84{\cdot}33$, $\gamma' = 90{\cdot}38°$.

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References

Boer, T. J. de & van Velzen, J. C. (1964). *Rec. Trav. Chim. Pays-Bas*, **83**, 477–486.

Boer, T. J. de & van Velzen, J. C. (1971). *Rec. Trav. Chim. Pays-Bas*, **90**, 842–848.

Bolton, W. (1963). *Acta Cryst.* **16**, 950–956.

Busing, W. R. & Levy, H. A. (1964). *Acta Cryst.* **17**, 142–146.

Karle, J. & Karle, I. L. (1966). *Acta Cryst.* **21**, 849–859.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 233. Ithaca: Cornell Univ. Press.

Schenk, H. (1969). Dissertation, Amsterdam.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* **B24**, 63–76.

Stam, C. H. & Evers, H. (1965). *Rec. Trav. Chim. Pays-Bas*, **84**, 1496–1502.

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The Crystal Structure of Bis-(β-alaninato)copper(II) Tetrahydrate

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Crystals of bis-(β-alaninato)copper(II) tetrahydrate ($CuC_6N_2O_8H_{20}$) belong to the space group $P\bar{1}$ with the unit-cell dimensions, a=9·164 (7), b=10·000 (7), c=7·041 (7) Å, α=99·89 (9), β=102·21 (9) and γ=91·42 (9)°. The atomic parameters were refined to a final R value of 0·061 for 2092 reflexions. The crystal contains two different complex molecules A and B. Both complexes assume a distorted octahedron with the copper ion at the centre of symmetry as found in bis-(β-alaninato)copper(II) hexahydrate. The two β-alanine residues are coordinated *trans* to each other forming an equatorial square. The apical coordination sites are occupied by water molecules in complex B, while in complex A they are occupied by carbonyl oxygen atoms of the β-alanine residues belonging to the adjacent complex B.

Introduction

While crystal structures of many metal–amino acid complexes have been elucidated so far, few data are available for the complexes with β-alanine, that is, bis-(β-alaninato)copper(II) hexahydrate (Tomita, 1961) and bis-(β-alaninato)nickel(II) dihydrate (Jose, Pant & Biswas, 1964). The conclusions derived from these earlier studies are: (1) β-alanine behaves as a bidentate chelating agent, the two β-alanine residues being *trans* to each other, (2) the four donor atoms (probably in the forms of NH_2 and COO^-) form an approximate square about the metal, and octahedral coordination is completed by two water molecules, (3) characteristic for Cu^{II}, the bonds to the two apical oxygen atoms of water molecules are longer than those to the donor atoms in the coordination square. These studies, however, are based on two-dimensional intensity data visually estimated from the Weissenberg photographs. We report here a structure analysis of the title compound which seems to be precise enough to allow one to discuss the details of the structure. Like Cu^{II} complexes with histamine or histidine (Asato, Komano, Okuyama & Satake, 1967) the bis-(β-alaninato)copper(II) complex has been shown to have a peroxidase activity as indicated by hypochromism of indigo disodium sulphonate (Sakaguchi, unpublished result).

Experimental

Deep blue crystals of the complex were obtained by: (1) mixing an aqueous solution of β-alanine (0·01 M) with copper nitrate (0·005 M), (2) warming the solution at 40°C for 30 min after adjusting the pH to 8 with ammonia, (3) adding isopropyl alcohol after cooling to room temperature and (4) drying the precipitate *in vacuo*. The melting point of the crystals recrystallized from water was 225°C (dec.) (Sakaguchi, 1976).

A block of the crystal with irregularly cleaved surfaces was shaped to a roughly spherical specimen, with a diameter of about 0·15 mm, by soaking in water and methanol for a few minutes. The space group and the lattice constants were determined by Weissenberg photographs, the latter being refined later by mea-