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The Crystal Structure of Ninhydrin

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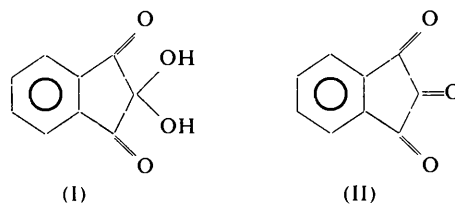
The crystal structure of ninhydrin, $C_9H_6O_4$, has been determined using filtered $Cu K\alpha$ radiation and a Nonius integrating Weissenberg camera. The crystals are monoclinic, $P2_1$, with $a=11.24$, $b=6.06$, $c=5.77$ Å, $\beta=99.1^\circ$, and $Z=2$. The intensities of 849 independent reflections were measured with a densitometer. The structure was solved using Patterson and Fourier methods and refined by the anisotropic full-matrix least-squares method to an R value of 0.062. The molecules are connected in layers parallel to (100) by two types of hydrogen bonds. Each molecule is linked along c by two hydroxyl-carbonyl bonds and about a screw axis in the b direction by two hydroxyl-hydroxyl bonds. The oxygen-oxygen distance is 2.80 Å for both types. One carbonyl oxygen is not involved in the hydrogen bonding scheme.

Introduction

Interest in ninhydrin, $C_9H_6O_4$, was originally stimulated by its rather high melting point and its resistance to dehydration in air which is unusual for a *gem*-dihydroxy compound; that is, a compound with two hydroxyl groups attached to the same carbon atom. It is a valuable reagent in the qualitative and quantitative determination of α -amino acids, proteins, and some of their degradation products because the reaction produces a deep blue color and also causes a stoichiometric amount of carbon dioxide to be evolved. Since this work began, reference has been made (Tollin & Cochran, 1964) to an unpublished thesis (Tollin, 1963) concerning this crystal structure. An account of the initial synthesis of ninhydrin by Ruhemann in 1910 and his subsequent study of its reactions, including the one cited above, has recently appeared (West, 1965).

Ninhydrin(I) is also referred to as triketoindane monohydrate or 1,2,3-indantrione monohydrate, which are, as are chloral hydrate and alloxan monohydrate, misnomers because there are no water molecules as

such in any of the structures. The structure of the anhydrous form of ninhydrin, triketoindane(II), has also been reported (Bolton, 1965).



Other structure determinations of *gem*-dihydroxy compounds are chloral hydrate (Brown & Levy, 1962), alloxan monohydrate or 5,5-dihydroxybarbituric acid (Singh, 1965), alloxan tetrahydrate or 5,5-dihydroxybarbituric acid trihydrate (Mootz & Jeffrey, 1965), and 3,3,4,4-tetrahydrofuran-tetrol (Mighell & Jacobson, 1964). In these structures all groups of the type OH, NH, or CO, when present, form at least one hydrogen bond.

Experimental

Crystals of commercially obtained ninhydrin were grown by slow cooling of an aqueous solution which had been saturated at a temperature slightly above am-

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bient. The composition of the crystals was checked by a carbon-hydrogen analysis (Carbon: 60.67% observed and 60.68% calculated from formula. Hydrogen: 3.66% observed and 3.39% calculated). The crystals were monoclinic prisms, elongated along **b** and bounded by {001} and {101}. The experimental density was determined by flotation in a chloroform-methylene iodide mixture. The cell constant *b* was determined from a precession photograph of the *Ok*l zone; *a*, *c* and β from an *h*0*l* back reflection Weissenberg film. Crystal data are given in Table 1.

Since the unit cell contains only two molecules and the ninhydrin molecule has no inversion center, the molecule must possess a mirror plane if the space group is to be $P2_1/m$. A reasonable packing arrangement could not be deduced with such a restriction, so $P2_1$ was tentatively chosen. The asymmetric unit is one molecule.

The data were obtained from a crystal which was 1.6 mm in length and 0.35 by 0.45 mm. in cross section. The crystal was small enough to be completely immersed in the X-ray beam. Equi-inclination Weissenberg photographs using Ni filtered Cu $K\alpha$ radiation were taken about the *b* axis for levels zero through five with a Nonius camera, integrating in one direction and using the multiple film technique. Of the 946 reflections within the Cu sphere, 849 were accessible with this camera and crystal setting and, of these, 15 were below the minimum observable intensity. Two reflections, 100 and 110, occurred at such a low scattering angle that they were obscured by the beam stop.

Intensities were measured with a microdensitometer-recorder system by scanning each spot perpendicular to the direction of camera integration and using a computer program for processing the recorder output. A film transmission factor for each film pack was determined using reflections common to more than one film of the pack. The range of intensity covered was 17,000 to 1. An effort was made to take all data under as close to identical experimental conditions as possible because the levels were scaled together initially by their exposure times.

The intensities of the weak reflections were estimated visually by comparison with a series of timed exposures of the 701 reflection from the same crystal that was used to obtain all the data. These values were then scaled together with the rest of the data using reflections common to both groups.

Lorentz and polarization corrections were applied but no absorption correction was made. The scattering factors for C, O, and H used in all calculations were taken from *International Tables for X-ray Crystallography* (1962). No anomalous dispersion or extinction corrections were applied.

All calculations were performed on an IBM 7090 computer using the X-ray 63 system of computer programs (Stewart, 1964).

Structure determination

The first step was the conversion of the intensity data to a set of normalized structure factors (Hauptman & Karle, 1953) using the following formula:

$$E(hkl) = \{KF(hkl) \exp [B(\sin \theta (hkl)/\lambda)^x]\} / \left[\varepsilon \sum_{j=1}^N n(j)f^2(j) \right]^{1/2}$$

where *K*=scale constant; *F*(*hkl*)=relative structure factor; *B*=overall temperature factor; θ (*hkl*)=Bragg angle; λ =X-ray wavelength; *x*=temperature factor exponent (assumed = 2); ε =systematic extinction compensation weight; *f*(*j*)=atomic scattering factor for atom *j*; *n*(*j*)=number of atoms of type *j* in the unit cell; *N*=number of atom types in the unit cell. Values of *K* and *B* were obtained from the conversion program. In this program, for each value of *B* the value of *K* is set so that $|E|^2 = 1.00$. The value of *B* is then adjusted by trial and error to minimize the sum of $| |E|^2 - 1 |$. The values of *K* and *B* obtained in this manner were used for all calculations until least-squares refinement was begun.

Some statistical averages (Dragonette & Karle, 1965) were also calculated for the normalized structure factors. Averages for 681 reflections, excluding those of the zone [010], are:

	Observed	Theoretical
$\overline{ E ^2}$	1.000	1.000
$\overline{ E }$	0.885	0.886
$\overline{ E ^2 - 1 }$	0.744	0.736

These values further substantiate the choice of $P2_1$ as the proper space group.

The first step in the structure solution was to use the spherical Patterson function with $\varepsilon \overline{| |E|^2 - 1 |}$ as the coefficients which correspond to a sharpened, origin-

Table 1. *Crystal data for ninhydrin*

Monoclinic	$C_9H_6O_4$
$a = 11.42 \pm 0.02 \text{ \AA}$	m.p. 253°C (dec.)
$b = 6.06 \pm 0.02$	M.W. 178.0
$c = 5.77 \pm 0.01$	$D_m = 1.52 \text{ g.cm}^{-3}$
$\beta = 99.1 \pm 0.3^\circ$	$D_x = 1.50$
Absent spectra: <i>Ok</i> 0 for <i>k</i> odd	$Z = 2$
Possible space groups: $P2_1$ (No. 4) or $P2_1/m$ (No. 11)	$F(000) = 184$
Absorption coefficient for Cu $K\alpha$ ($\lambda = 1.5418 \text{ \AA}$), $\mu = 12.4 \text{ cm}^{-1}$	λ (Cu $K\alpha_1$) = 1.5405 Å
	λ (Cu $K\alpha_2$) = 1.5443

removed Patterson function. Since the distances 1.4, 2.4 and 2.8 Å occur frequently in organic compounds containing five- and six-membered rings, three spherical shells in Patterson space with the above radii were calculated. An idealized ninhydrin molecule with *mm* symmetry was assumed and spherical Patterson shells with the above three radii were calculated on a grid for all possible orientations. Each of the calculated shells was compared with the corresponding observed shell and an index of agreement was calculated. The Patterson function for more than one molecular orientation showed good coincidence with each observed shell but only one orientation agreed well with all three observed shells. This molecular orientation was found later to be the correct one.

The remaining task was to position the molecule in its proper location in the unit cell and, since the *y* coordinate of the origin in space group *P2*₁ is arbitrary, only the increments Δx and Δz were needed. Using the set of atomic coordinates obtained from the spherical Patterson, values of Δx in increments of 0.02 *a* were added to the *x* coordinate of each atom, followed by an *hk0* structure factor and an *R* value calculation. A similar procedure was followed for determining *z* atomic coordinates by adding increments of 0.01 *c* and using *0kl* data. Six values of Δx and two of Δz gave the lowest *R* values which were clustered about 0.40.

Each of the twelve sets of coordinates was used in a Fourier refinement program which calculates electron density for a 27-point block about each atom position, finds the point of maximum electron density in the block, and changes the atom coordinates to coincide with this maximum. After five cycles of refinement using all data, one set of Δx and Δz gave an *R* value of 0.39 while all other sets gave 0.45 or higher.

It was noted that the *0kl* data had a considerably lower *R* value of 0.26. This was quickly reduced to 0.13 using the standard Fourier method. Again the Fourier refinement program with all data was used and the overall *R* dropped to 0.16.

Structure refinement

Full-matrix least-squares refinement was used to bring the parameters to their final values. The function minimized was $\sum_i w_i (\Delta F)^2$. The origin of the unit cell

was established by fixing the *y* coordinate of O(12) at 0.0500. Unless mentioned otherwise, two cycles of least-squares were run with each set of conditions.

An overall scale factor with individual isotropic temperature factors for each atom gave an *R* value defined in the conventional manner of 0.130. A scale factor assigned to each level and refined gave 0.110. Anisotropic temperature factors for each atom defined by the following expression reduced *R* to 0.077.

$$\text{T.F.} = \exp \left[-\frac{1}{4}(h^2 a^{*2} B_{11} + k^2 b^{*2} B_{22} + l^2 c^{*2} B_{33} + 2hka^* b^* B_{12} + 2hla^* c^* B_{13} + 2klb^* c^* B_{23}) \right]$$

Instead of unit weight for all reflections the following weighting scheme was now introduced:

$$\begin{cases} |W \propto 1/|F_o| & \text{for } |F_o| > F^* \text{ and} \\ |W \propto 1/F^* & \text{for } |F_o| \leq F^* \end{cases}$$

where *F** equals 4.4. The *R* value now became 0.074.

Hydrogen atoms were then added to the calculations. The four attached to the benzene ring were placed in the plane of the ring at a distance of 1.07 Å from the respective carbon atom and held there during subsequent refinement. The two hydroxyl hydrogen atoms, H(11) and H(12), were located using a difference Fourier synthesis. All hydrogen atoms were assigned temperature factors of 3.0 which were also fixed. The addition of hydrogen atoms lowered *R* to 0.068.

The five most intense reflections, 10 $\bar{1}$, 200, 111, 210, and 211, were given zero weight because of good evidence that they were affected by extinction. After further least-squares refinement, another difference Fourier synthesis was calculated using structure factors with no hydrogen contribution. Slight corrections in the positions of H(11) and H(12) were indicated.

Least-squares refinement was continued until all parameter shifts were less than 0.1 times their respective estimated standard deviation (e.s.d.). There were no significant differences in atomic positions between the isotropic and the anisotropic refinements. The final *R* values were 0.061 for observed reflections only and 0.062 when the unobserved reflections for which

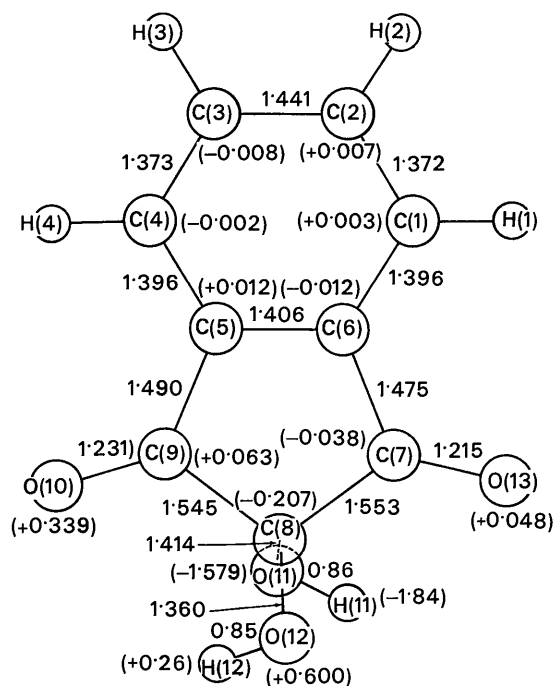


Fig. 1. Bond lengths in ninhydrin with distances from the least-squares plane (in parentheses). A positive deviation from the least-squares plane means that the atom is closer to the origin than the plane is.

$|F_c| > |F_{\min}|$ were included (6 of 15). Reflection multiplicity was one for all calculations. All errors cited are those calculated from the inverse-matrix of the least-squares normal equations. The average position e.s.d. for a carbon atom is 0.006 Å and for an oxygen atom it is 0.004 Å. To that accuracy they agree with estimates from the formula of Cruickshank (1960).

A final three-dimensional difference Fourier synthesis was calculated. The maximum deviation from zero was $\pm 0.30 \text{ e.}\text{Å}^{-3}$. The following formula for the e.s.d. of electron density (Cruickshank, 1949),

$$\sigma(\rho) = (1/V) [\sum (\Delta F)^2]^{\frac{1}{2}}$$

gives the value $0.07 \text{ e.}\text{Å}^{-3}$.

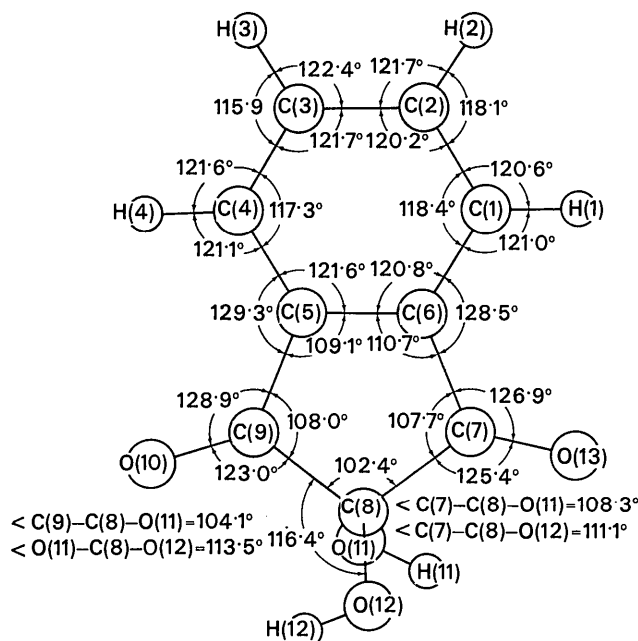


Fig. 2. Bond angles in ninhydrin.

The final values of observed and calculated structure factors are shown in Table 2. They were calculated using the atomic parameters shown in Table 3.

The treatment of the scale factors was done in the same manner as outlined previously (Dickinson, Stewart & Holden, 1966). Data were taken only along **b** with an effort to take all film packs in the same manner with regard to length of exposure, current and voltage settings, and method of developing. An overall scale factor was determined as described above from the quasi-normalized structure factors. This value was used until least-squares refinement began when a scale factor for each level was refined together with an isotropic temperature factor for each atom. These scale factors were fixed during the rest of the refinement because of the complete correlation between them and the B_{22} temperature factor for each atom (Lingafelter & Donohue, 1966). This method of taking data probably accounts for the higher e.s.d.'s of the parameters in the **b** direction, but all the parameters have reasonable values.

Discussion

The ninhydrin molecule

Bond lengths are shown in Fig. 1 together with deviations from a least-squares plane passed through the six carbon atoms of the benzene ring. The method of determining the plane is that of Schomaker, Waser, Marsh & Bergman (1959) and the equation of the plane with respect to the *a*, *b*, and *c* axes is:

$$5.616x + 3.787y + 3.006z = 4.179 \text{ Å}.$$

The root mean square deviation of the six defining atoms from the plane is 0.009 Å. Table 4 contains bond lengths of ninhydrin compared with corresponding lengths in triketoindane (Bolton, 1965) and Table 5 gives bond angles for both molecules. The triketoindane column in Tables 4 and 5 has fewer entries than does the ninhydrin column because the triketoindane mole-

Table 3. Final atomic parameters and estimated standard deviations for one discrete molecule

	<i>x</i>	<i>y</i>	<i>z</i>	B_{11} or <i>B</i>	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0.1035 (4)	0.7005 (13)	0.3133 (10)	2.1 (2)	1.3 (3)	4.0 (2)	0.5 (2)	0.0 (2)	-0.1 (2)
C(2)	0.0927 (5)	0.8551 (12)	0.1372 (10)	3.5 (2)	1.3 (3)	4.1 (2)	0.8 (2)	-0.4 (2)	0.6 (2)
C(3)	0.1771 (5)	0.8616 (12)	-0.0237 (09)	5.0 (3)	1.0 (3)	3.1 (2)	-0.1 (2)	-0.3 (2)	1.1 (2)
C(4)	0.2686 (5)	0.7131 (12)	-0.0095 (08)	3.8 (2)	0.8 (3)	2.5 (2)	-0.7 (2)	0.4 (2)	0.8 (2)
C(5)	0.2772 (3)	0.5552 (11)	0.1687 (07)	2.2 (1)	0.7 (2)	1.9 (1)	-0.3 (1)	0.2 (1)	0.4 (2)
C(6)	0.1975 (3)	0.5511 (11)	0.3310 (07)	1.9 (1)	0.8 (2)	2.5 (1)	-0.1 (1)	0.5 (1)	0.1 (2)
C(7)	0.2287 (3)	0.3738 (10)	0.5048 (07)	1.7 (1)	0.5 (2)	2.0 (1)	-0.2 (1)	0.5 (1)	0.1 (1)
C(8)	0.3487 (3)	0.2736 (14)	0.4632 (06)	1.5 (1)	0.7 (3)	1.4 (1)	-0.3 (1)	0.4 (1)	0.1 (1)
C(9)	0.3637 (3)	0.3712 (11)	0.2221 (07)	1.9 (1)	1.5 (2)	1.7 (1)	0.0 (1)	0.2 (1)	0.4 (1)
O(10)	0.4323 (3)	0.2940 (10)	0.0988 (05)	2.9 (1)	3.7 (2)	1.5 (1)	1.0 (1)	1.2 (1)	0.3 (1)
O(11)	0.4404 (2)	0.3731 (09)	0.6225 (05)	1.9 (1)	2.8 (2)	1.3 (1)	-0.9 (1)	0.1 (1)	0.0 (1)
O(12)	0.3472 (3)	0.0500	0.4787 (06)	2.4 (1)	0.8 (2)	2.9 (1)	0.3 (1)	1.0 (1)	0.4 (1)
O(13)	0.1721 (3)	0.3154 (10)	0.6555 (06)	2.6 (1)	2.0 (2)	3.7 (1)	0.3 (1)	1.7 (1)	1.3 (1)
H(1)	0.042*	0.696*	0.434*	3.0*					
H(2)	0.021*	0.971*	0.126*	3.0*					
H(3)	0.175*	0.985*	-0.155*	3.0*					
H(4)	0.331*	0.717*	-0.130*	3.0*					
H(11)	0.436*	0.336*	0.765*	3.0*					
H(12)	0.420*	0.045*	0.461*	3.0*					

* Parameters fixed during least-squares refinement.

cule has *mm* symmetry in the crystal while the ninhydrin molecule has none. Fig. 2 shows bond angles for ninhydrin.

Table 4. Bond lengths in ninhydrin with corresponding lengths in triketointhane

Bond	Ninhydrin	Triketointhane
C(2)—C(3)	1.441 (9) Å	1.414 (14) Å
C(2)—C(1)	1.373 (9)	1.363 (10)
C(3)—C(4)	1.372 (9)	
C(1)—C(6)	1.396 (7)	1.390 (09)
C(4)—C(5)	1.396 (7)	
C(5)—C(6)	1.406 (6)	1.392 (12)
C(6)—C(7)	1.475 (7)	1.478 (09)
C(5)—C(9)	1.490 (7)	
C(7)—C(8)	1.553 (5)	1.526 (11)
C(9)—C(8)	1.545 (5)	
C(7)—O(13)	1.215 (5)	1.227 (09)
C(9)—O(10)	1.231 (5)	
C(8)—O(11)	1.414 (5)	
C(8)—O(12)	1.360 (7)	
O(11)—H(11)	0.86	
O(12)—H(12)	0.85	

Table 5. Bond angles in ninhydrin with corresponding angles in triketointhane

Angle	Ninhydrin	Triketointhane
C(3)—C(2)—C(1)	120.2 (5)°	120.8 (9)°
C(2)—C(3)—C(4)	121.7 (5)	
C(2)—C(1)—C(6)	118.4 (5)	118.3 (6)
C(3)—C(4)—C(5)	117.3 (5)	
C(1)—C(6)—C(5)	120.8 (5)	120.9 (9)
C(4)—C(5)—C(6)	121.6 (5)	
C(5)—C(6)—C(7)	110.7 (4)	
C(6)—C(5)—C(9)	109.1 (4)	109.2 (8)
C(6)—C(7)—C(8)	107.7 (3)	108.1 (6)
C(5)—C(9)—C(8)	108.0 (3)	
C(7)—C(8)—C(9)	102.4 (3)	105.2 (9)
C(8)—C(7)—O(13)	125.4 (4)	124.3 (7)
C(8)—C(9)—O(10)	123.0 (4)	
C(7)—C(8)—O(11)	108.3 (3)	
C(9)—C(8)—O(11)	104.1 (3)	
C(7)—C(8)—O(12)	111.1 (4)	
C(9)—C(8)—O(12)	116.4 (4)	
O(11)—C(8)—O(12)	113.5 (4)	
C(8)—O(11)—H(11)	111	
C(8)—O(12)—H(12)	90	

As seen from Tables 4 and 5, corresponding bond lengths and bond angles in ninhydrin and triketointhane are similar. Bond C(2)—C(3) in ninhydrin at 1.441(9) Å is considerably longer than the benzene bond length of 1.397(1) Å (Langseth & Stoicheff, 1956). Bonds C(7)—C(8) and C(9)—C(8) at 1.553(5) and 1.545(5) Å are longer than expected for an sp^2-sp^3 carbon-carbon bond, but corresponding values for related compounds are similarly long. Chloral hydrate (Brown & Levy, 1962) has 1.549(2) Å, alloxan monohydrate (Singh, 1965) has two of 1.539(5) Å, and alloxan tetrahydrate (Mootz & Jeffrey, 1965) has two of 1.526(5) Å. Bond C(8)—O(12) at 1.360(7) Å is considerably shorter than the usual C—O single bond distance of 1.43 Å (Pauling, 1960). The short C—O(H) single bond has also been found in chloral hydrate

where the distances are 1.392(2) and 1.385(2) Å, in alloxan monohydrate where the distances are 1.394(5) and 1.389(5) Å, and in alloxan tetrahydrate where the distances are 1.407(5) and 1.384(5) Å. A similar decrease has also been noted in C—F bonds of *gem*-difluoro compounds as compared with the corresponding monofluoro compound (Pauling, 1960).

As shown in Fig. 1, there are atoms whose positions deviate considerably from the least-squares plane; particularly O(10), C(8), C(9), O(13), and C(7). The triketointhane molecule, on the other hand, was found to be planar within experimental error (Bolton, 1965). Accommodation to the hydrogen-bonding network is very likely a major cause for these deviations in ninhydrin.

Hydrogen-bonding network

Figs. 3 and 4 show the ninhydrin hydrogen-bonding network which connects the molecules in layers parallel to (100). This bonding scheme is very similar to that of chloral hydrate, particularly when both structures are viewed along the *b* axis. Two types of hydrogen bonds occur in ninhydrin. The first is between two hydroxyl groups, O(11ⁱ)...H(12^v)-O(12^v), with an O...O distance of 2.798 Å. This type of bond occurs about the screw axes along *b*. The second type is a hydroxyl-carbonyl bond, O(10ⁱ)...H(11^{vii})-O(11^{vii}), 2.805 Å in length, which links the molecules along *c*. This type bond can only be seen in Fig. 3. This molecular arrangement means that O(11) is both a hydrogen donor and an acceptor, O(12) is a donor, O(10) is an acceptor, and O(13) does not participate at all. The latter feature is in contrast to the other reported structures of *gem*-dihydroxy compounds in which OH, CO, and NH groups, when present, all form hydrogen

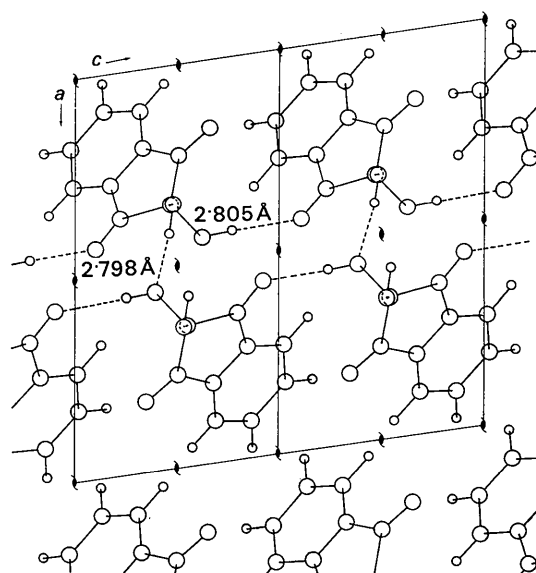


Fig. 3. The structure viewed along the *b* axis showing the two types of hydrogen bonds.

bonds. Chloral hydrate has O...O bond lengths of 2.898 and 2.842 Å and the two oxygens are both hydrogen donors and acceptors. In alloxan monohydrate, the hydroxyl oxygens are donors only and the corresponding O...O distances are 2.778 and 2.731 Å. In alloxan tetrahydrate the O...O distances are 2.750 and 2.749 Å, but the attached hydrogen atoms were not located. In the structure of 3,3,4,4-tetrahydrofuran-tetrol, which has two adjacent *gem*-dihydroxy carbon atoms, three of the four hydroxyl oxygens are both hydrogen donors and acceptors, the remaining hydroxyl oxygen is a donor only, and the ring oxygen atom is an acceptor. The O...O distances are 2.82, 2.74, 2.72 and 2.65 Å.

Other intermolecular contacts

Aside from the hydrogen bonds, there are no intermolecular contacts at less than normal van der Waals distances. Table 6 gives a list of these distances in ninhydrin. The surroundings of O(13), which does not participate in the hydrogen bonding scheme, were examined closely in view of the short distances reported involving carbonyl groups in similar compounds (Bolton, 1964 and 1965). The shortest distances found were 3.18 Å between C(4ⁱ) and O(13^{vii}) and 3.26 Å between C(1ⁱ) and O(13^{iv}). The sum of the van der Waals radii for C and O is given as 3.1 Å (Pauling, 1960). There are no distances involving a hydroxyl oxygen as short as the 2.90 Å value found in alloxan monohydrate. The shortest distance of this type in ninhydrin is 3.24 Å between O(11ⁱ) and O(10^v).

Table 6. Intermolecular distances less than 3.7 Å or less than 3.0 Å if hydrogen is involved

From	To	At	Distance
C(1)	O(13)	IV	3.26 Å
C(2)	O(13)	IV	3.43

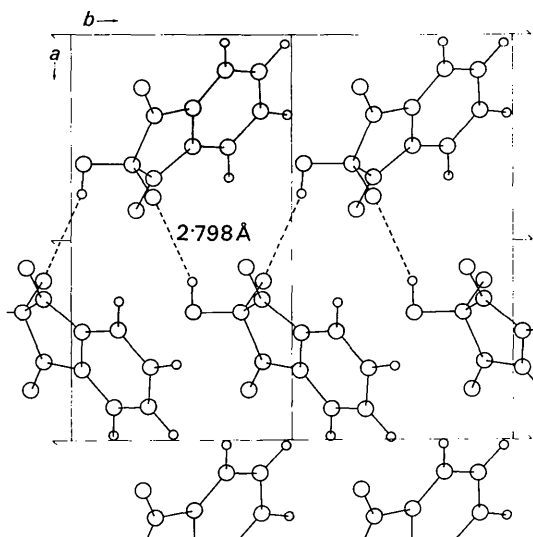


Fig. 4. The structure viewed along the *c* axis.

Table 6 (cont.)

From	To	At	Distance
C(4)	C(7)	VII	3.45
	O(10)	III	3.57
	O(13)	VII	3.18
C(5)	O(13)	VII	3.35
	O(12)	V	3.64
C(9)	O(13)	VII	3.65
	H(11)	VII	2.89
	C(8)	VII	3.64
	O(10)	III	3.67
	O(11)	VII	2.80*
	H(11)	VII	1.95*
O(10)	O(12)	V	3.57
	O(13)	VII	3.60
	C(8)	V	3.51
	O(10)	V	3.24
	O(11)	V	3.69
	O(12)	V	2.80*
O(11)	H(12')	V	2.03*
	C(1)	VI	3.51
	C(2)	VI	3.45
	C(3)	VI	3.42
	C(4)	VI	3.48
	C(5)	VI	3.52
H(1)	C(6)	VI	3.51
	O(13)	IV	2.52
H(2)	C(2)	II	2.97
	O(13)	IV	2.87
H(4)	O(10)	III	2.72
	O(11)	VII	2.92
H(11)	H(12)	V	2.59

I	<i>x</i>	<i>y</i>	<i>z</i>
II	- <i>x</i>	$\frac{1}{2} + y$	- <i>z</i>
III	1 - <i>x</i>	$\frac{1}{2} + y$	- <i>z</i>
IV	- <i>x</i>	$\frac{1}{2} + y$	1 - <i>z</i>
V	1 - <i>x</i>	$\frac{1}{2} + y$	1 - <i>z</i>
VI	<i>x</i>	<i>y</i> - 1	<i>z</i>
VII	<i>x</i>	<i>y</i>	<i>z</i> - 1

* Hydrogen bonds.

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Crystal Structure of L-Threonyl-L-phenylalanine-*p*-nitrobenzyl Ester Hydrobromide*

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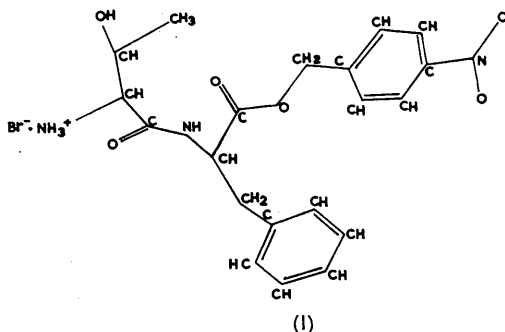
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The crystal structure of L-threonyl-L-phenylalanine-*p*-nitrobenzyl ester hydrobromide, $C_{20}N_3O_6H_{24}Br$, has been determined using three-dimensional data. The crystals are orthorhombic with space group $P2_12_12_1$, and $a = 8.93 \pm 0.02$; $b = 45.75 \pm 0.06$ and $c = 5.05 \pm 0.03$ Å. The final R value at the end of three-dimensional refinement is 0.089. A brief discussion of the backbone and side chain conformations is given. All five protons in the structure available for the formation of hydrogen bonds are utilized in forming a three-dimensional network of hydrogen bonds stabilizing the structure.

The X-ray crystallographic investigation of the structure of L-threonyl-L-phenylalanine-*p*-nitrobenzyl ester hydrobromide(I) was undertaken as a part of the project on the determination of the structures of organic compounds of biological importance, being carried out in this laboratory. The material was obtained from Professor S. Akabori, Institute for Protein Research, Osaka, Japan.



Experimental

The crystals, in the form of long thin needles elongated along the c axis, were obtained by slow evaporation of an aqueous solution at 45°C . Rotation, Weissenberg and precession photographs were taken with $\text{Cu } K\alpha$ radiation and the crystal data are given below:

Crystal system:	Orthorhombic
Cell dimensions:	$a = 8.93 \pm 0.02$, $b = 45.75 \pm 0.06$ and $c = 5.05 \pm 0.03$ Å
Space group:	$P2_12_12_1$ ($h00$, $0k0$, $00l$ absent for h , k or l odd)
Molecular formula:	$C_{20}N_3O_6H_{24}Br$
Number of formula units:	$Z = 4$
Measured density by flotation:	1.59 g.cm^{-3}
Calculated density:	1.56 g.cm^{-3} .

A preliminary Weissenberg photograph of the $hk0$ reflexions with $\text{Cu } K\alpha$ radiation showed that, as a result of the large thermal vibration, the effective range could be covered with $\text{Fe } K\alpha$ radiation. Further, use of $\text{Fe } K\alpha$ radiation would make indexing of the spots at high angles relatively easy since with $\text{Cu } K\alpha$ radiation, the spots tended to coalesce owing to the long b axis. Consequently, intensity data were collected with $\text{Fe } K\alpha$

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