The Crystal Structure of a Photodimer of 1,4-Epoxy-1,4-dihydronaphthalene

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The crystal structure of a photodimer of 1,4-epoxy-1,4-dihydronaphthalene, with empirical formula $C_{20}H_{16}O_2$, has been determined by the application of direct methods. Three-dimensional data were collected on a Datex-automated General Electric diffractometer to a minimum spacing of 1·0 Å. The coordinates of all atoms in the molecule, the isotropic temperature factors for the hydrogen atoms, and the anisotropic temperature factors for the other atoms were refined by the method of least squares. The final R index was 0·027. The crystals are orthorhombic, space group $Pca2_1$ with $a = 16·52$, $b = 7·975$ and $c = 10·58$ Å. Of four possible configurations, the molecule of the photodimer has the *exo–trans–exo* configuration. Despite the lack of a center of symmetry in the space group, the molecule is centrosymmetric almost within experimental error.

Introduction

The photodimer, $C_{20}H_{16}O_2$, was obtained during a study in these laboratories of the photorearrangement of 1,4-epoxy-1,4-dihydronaphthalene (Ziegler, 1969). Study of the nuclear magnetic resonance spectrum showed that the molecule must have either the *endo–endo* or the *exo–exo* configuration. This structure determination was undertaken to find the true configuration.

Experimental

Crystals, in the form of large, thin plates, were obtained by slow evaporation of an ethanol solution of the photodimer. Unit-cell parameters were determined from measurements of precession photographs which were calibrated by lines diffracted from a powdered sample of sodium chloride ($a_0 = 5·6402$ Å). The resulting values for the unit-cell dimensions are:

$$a = 16·520 \ (2) \ \text{Å}$$
$$b = 7·795 \ (7)$$
$$c = 10·58 \ (1)$$

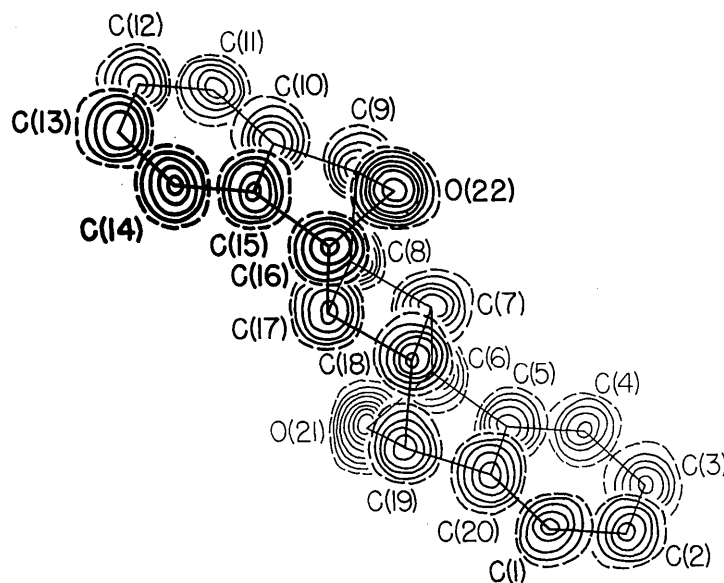The absence of $0kl$ reflections with l odd and the

Fig. 1. A composite of sections of a three-dimensional electron density map through each of the heavy atoms, viewed down the c axis. The dashed contour is at 2 e.Å^{-3}. The successive contours are at 3, 4, 5, ... e.Å^{-3}.

absence of $h0l$ reflections with h odd indicate that the space group is either $Pca2_1$ or $Pcam$.

The density of the crystals measured by the flotation method and the density calculated for the photodimer, assuming four molecules per unit cell, is 1·374 g. cm^{-3}.

The intensity data used for final refinement of the structure were collected from a crystal cut from one of the large, thin plates with a razor blade. It had a thickness of approximately 0·1 mm and had a trape-

Table 1. *Distribution of normalized structure factors*

	Observed	Theoretical Centric	Acentric
$\langle|E|\rangle$	0·881	0·798	0·886
$\langle||E|^2-1|\rangle$	0·720	0·968	0·736
$\langle|E|^2-1\rangle$	0·005	0·000	0·000

zoidal face with an altitude of 0·3 mm and bases of 0·5 and 0·2 mm.

Intensity data were collected by the θ–2θ scan method on a Datex-automated General Electric diffractometer using Cu $K\alpha$ radiation. An initial set of data was collected from a small crystal with a scan speed of two degrees per minute and a background count was collected for ten seconds at both the beginning and the end of the scan. These data proved to be inadequate for satisfactory refinement of the structure. A second set of data was collected using the new crystal described above. This set was collected with a scan speed of one degree per minute and background count was collected for thirty seconds at both ends of the scan. All reflections were collected to a minimum spacing of 1 Å. These numbered a total of 774, of which 9 were observed to have intensities less than background and were assigned intensities of zero. No correction for absorption was made ($\mu = 7\cdot0$ cm^{-1}).

The determination and initial refinement of the structure were based on the first set of data. They were placed on an absolute scale by Wilson's (1942) statistical method. A Howells, Phillips & Rogers (1950) plot indicated that the crystal was probably
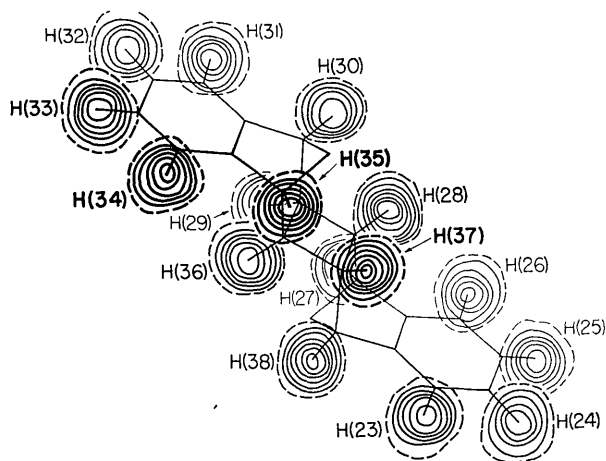
Fig. 2. A composite of sections of a three-dimensional difference electron density map through each of the hydrogen atoms, viewed down the c axis. The dashed contour is at 0·1 e.Å^{-3}. The successive contours are at 0·2, 0·3, 0·4, ... e.Å^{-3}.

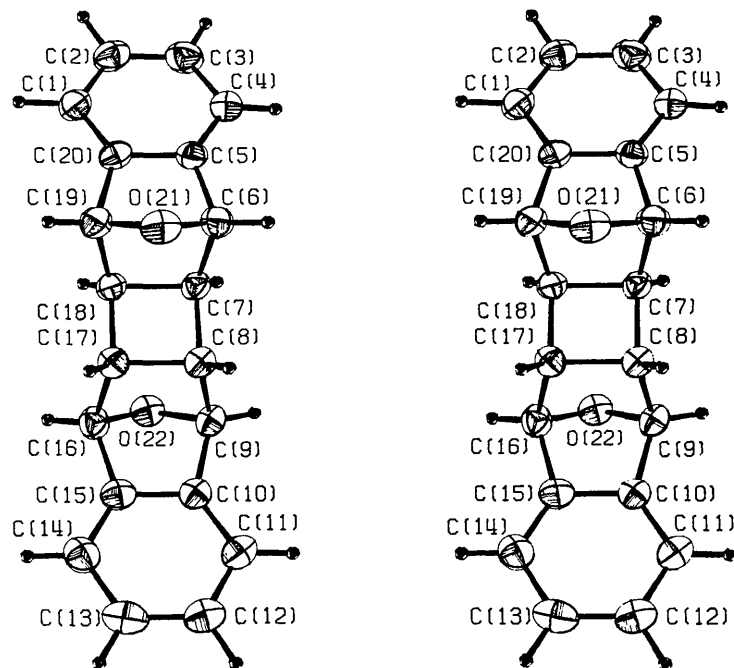Fig. 3. Stereoscopic view of the photodimer.

noncentrosymmetric; therefore, the space group should be $Pca2_1$.

The normalized structure factors $|E|$ (Karle & Karle, 1966) were then calculated using an overall temperature parameter of 1·50 Å². The observed and theoretical values for certain statistical averages and distributions of the normalized structure factors are shown in Table 1. A comparison of the observed values with those calculated for centrosymmetric and noncentrosymmetric structures confirms that the space group is the noncentrosymmetric $Pca2_1$.

Phase determination

A general description of the normal phase determination procedure has been given by Karle & Karle (1966).

Table 2. *Observed and calculated structure factors*

Within each group the columns contain k, $100F_o$, $100F_c$, and $\varphi_c(°)$, the phase angle. Reflections marked with an asterisk were assigned zero weight in the final least-squares cycles.

[Table of observed and calculated structure factors — numerical data in multiple column groups]

The method used in this case, however, is somewhat unconventional. The phases of three reflections were assigned to specify the origin in space group $Pca2_1$ (Hauptman & Karle, 1956). These reflections were chosen on the basis of their large E values and the large number of relationships which they formed with other reflections with large E values. The reflections chosen were 14,1,3, 7,5,5 and 10,2,1 and their assigned phases were $\pi/4$, $\pi/2$, and $-\pi/4$, respectively. The application of the phase determining formula

$$\varphi_h \simeq \langle \varphi_k + \varphi_{h-k} \rangle_{k_r}$$

to the reflection 14,0,0 gives a strong indication of its sign. The right-hand side contains nine terms of the type $\varphi(7kl) + \varphi(7\bar{k}\bar{l})$; eight of these terms indicate a phase of 0 and one a phase of π. The phase of the 14,0,0 reflection was therefore assumed to be 0.

At this time a program for the iterative application of the tangent formula (Karle & Hauptman, 1956),

$$\tan\varphi_h = \frac{\sum_k |E_k E_{h-k}| \sin(\varphi_k + \varphi_{h-k})}{\sum_k |E_k E_{h-k}| \cos(\varphi_k + \varphi_{h-k})},$$

was being written and tested. While testing the program with the three origin-determining reflections and the 14,0,0 reflection, it was evident that just these four reflections generated very many relationships with other reflections. By introducing the phases determined in this way into the list of known phases, it was possible by cyclic application of the tangent formula to determine eventually the phases for 274 reflections with E values greater than 1·0.

The reflections whose phases had been determined in the method described above were used to calculate an E map, the normalized structure factors, E_h, being used as Fourier coefficients. Twelve of the carbon atoms and both of the oxygen atoms were easily located in this map. The alternate calculation of structure factors and electron density maps led quickly to the complete elucidation of the structure.

Two phenomena observed during this structure determination bear special notice. First, the application of direct methods led to the correct structure in spite of the rather poor quality of the data; second, the distribution of the E values (Table 1) gave no indication of the pseudo-centrosymmetric nature of the molecule.

Refinement of the structure

All calculations below were carried out on an IBM 7094 computer with subprograms operating under the

Table 3. *Heavy-atom parameters and their standard deviations*

The values have been multiplied by 10^4. The temperature factor is in the form

$$T = \exp\{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)\}.$$

|	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	-1969(2)	7107(4)	7847(4)	36(2)	104(7)	65(4)	12(6)	8(4)	0(9)
C(2)	-2738(2)	7219(4)	7269(5)	32(2)	126(7)	84(4)	28(5)	18(5)	10(10)
C(3)	-2902(2)	6245(5)	6231(4)	28(2)	166(8)	92(5)	28(6)	-14(5)	14(11)
C(4)	-2338(2)	5148(4)	5718(4)	33(2)	130(6)	71(4)	28(6)	-15(5)	-16(9)
C(5)	-1589(2)	5063(4)	6278(4)	27(2)	100(6)	53(4)	17(5)	-1(4)	17(9)
C(6)	-851(2)	3989(5)	6079(4)	30(2)	135(7)	55(4)	24(6)	5(4)	1(9)
C(7)	-856(2)	2648(4)	7109(4)	22(1)	81(6)	64(4)	-1(5)	-4(4)	-11(9)
C(8)	-62(2)	1671(4)	7271(4)	23(1)	93(6)	58(4)	-6(5)	10(4)	5(9)
C(9)	-160(2)	-81(4)	7855(4)	27(2)	97(6)	60(4)	-2(5)	13(4)	-13(9)
C(10)	676(2)	-662(4)	8234(4)	25(1)	84(6)	57(4)	-11(5)	8(4)	25(9)
C(11)	1229(2)	-1752(4)	7722(4)	32(2)	105(7)	80(4)	14(5)	12(4)	-5(10)
C(12)	1979(2)	-1883(5)	8287(5)	29(2)	134(7)	95(5)	22(6)	11(5)	10(10)
C(13)	2176(2)	-918(5)	9326(5)	25(2)	138(8)	107(5)	1(5)	-8(5)	75(11)
C(14)	1623(2)	211(4)	9832(4)	35(2)	112(7)	72(4)	-15(6)	-13(5)	36(10)
C(15)	868(2)	314(4)	9288(4)	28(2)	96(6)	64(4)	-1(5)	7(5)	40(9)
C(16)	142(2)	1410(5)	9491(4)	30(2)	121(7)	52(4)	-1(5)	3(4)	-4(8)
C(17)	146(2)	2750(4)	8456(4)	24(1)	96(6)	60(4)	-15(5)	-4(4)	10(9)
C(18)	-652(2)	3714(4)	8292(4)	24(1)	90(7)	54(3)	11(5)	3(4)	5(8)
C(19)	-573(2)	5472(4)	7730(4)	30(2)	96(7)	73(4)	-4(5)	-15(4)	-2(9)
C(20)	-1410(2)	6025(4)	7336(4)	27(1)	81(6)	67(4)	-1(5)	4(4)	17(9)
O(21)	-212(1)	5104(3)	6513	27(1)	125(4)	86(3)	2(4)	15(3)	38(6)
C(22)	-509(1)	326(3)	9082(3)	28(1)	114(4)	70(3)	-5(4)	10(3)	24(6)
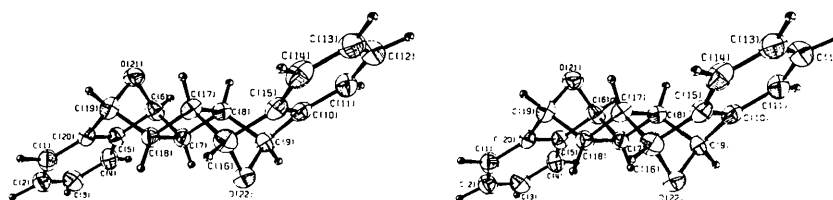
Fig. 4. Stereoscopic view of the photodimer.

Table 4. *Hydrogen atom parameters and their standard deviations*

The values for the coordinates have been multiplied by 10^3. The values for the isotropic temperature factors have been multipied by 10.

	x	y	z	B
H(23)	− 181 (1)	790 (4)	859 (3)	37 (8)
H(24)	− 314 (2)	813 (4)	.759 (4)	50 (8)
H(25)	− 340 (2)	640 (4)	585 (3)	39 (8)
H(26)	− 246 (2)	444 (3)	505 (4)	45 (8)
H(27)	− 74 (1)	359 (3)	525 (3)	16 (6)
H(28)	− 133 (1)	198 (3)	709 (2)	16 (6)
H(29)	31 (2)	175 (4)	658 (3)	30 (7)
H(30)	− 57 (2)	− 89 (4)	740 (3)	42 (8)
H(31)	113 (2)	− 242 (4)	699 (3)	38 (8)
H(32)	235 (2)	− 275 (4)	798 (3)	52 (9)
H(33)	271 (2)	− 99 (4)	969 (3)	35 (8)
H(34)	178 (2)	88 (4)	1054 (3)	45 (9)
H(35)	6 (2)	182 (4)	1031 (3)	34 (8)
H(36)	64 (2)	339 (4)	846 (3)	26 (7)
H(37)	− 102 (2)	367 (4)	903 (3)	29 (7)
H(38)	− 24 (1)	627 (4)	818 (3)	24 (7)

CRYRM system (Duchamp, 1964). The atomic scattering factors for C and O were taken from *International Tables for X-ray Crystallography* (1962). The atomic

scattering factor for H is that given by Stewart, Davidson & Simpson (1965). The least-squares routine minimizes the quantity $\sum w(F_o^2 - F_c^2)^2$. The weights, w, used throughout the refinement of the structure, were set equal to $1/\sigma^2(F_o^2)$ which were derived from counting statistics. The variance of the intensity was calculated by the formula:

$$\sigma^2(I) = S + \alpha^2(B_1 + B_2) + (dS)^2,$$

where S is the total counts collected during the scan; B_1 and B_2 are the numbers of counts collected for each background; α is the scan time to total background time ratio; d is an empirical constant of 0·02.

Approximate coordinates for all twenty-two heavier atoms were obtained by the Fourier technique described above. In space group $Pca2_1$ the location of the origin in the z direction is arbitrary. Accordingly, the z coordinate of atom O(21) was held constant throughout the refinement of the structure. The proposed structure was put through several cycles of least-squares refinement, but the R index could not be reduced below 18%. A careful survey of the data indicated that this was probably the best fit that could be obtained with the first set of data that had
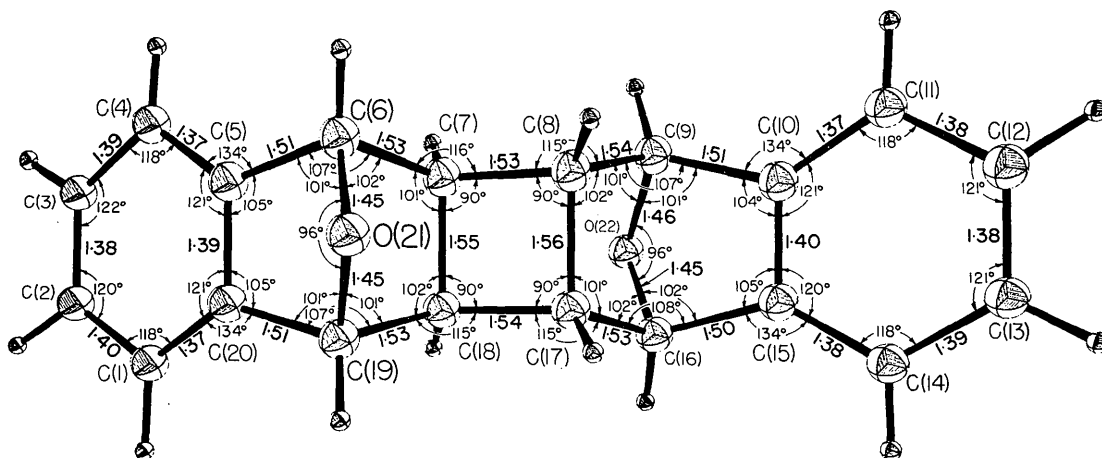

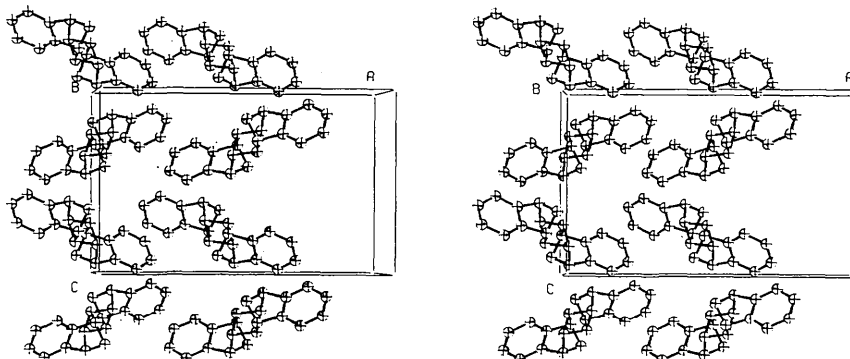Fig. 5. Bond distances and angles for the heavy atoms of the photodimer.

Fig. 6. A stereoscopic view down the *b* axis showing the packing of the photodimer.

been collected. The second set of more carefully collected data was then obtained and was used in final and complete refinement of the structure.

After several cycles of refinement with anisotropic temperature factors, hydrogen atoms were introduced at their expected positions. Both the coordinates and isotropic temperature factors for the hydrogen atoms were included in the refinement. In the later stages of refinement a secondary extinction factor was also included; the expression used is $F^2_{corrected} = (F_{cal})^2/(1 + g\beta(F_{cal})^2)$ (Larson, 1967). During the final cycles of refinement the atomic coordinates for all atoms were contained in one matrix and the temperature factors, scale factor, and secondary extinction factor were included in a second matrix. The final value obtained for the secondary extinction factor g is 17·6 $(\pm 0·7) \times 10^{-6}$. The final R index is 0·027. The observed and calculated structure factors, F_o and F_c, and the phase angles, φ, are listed in Table 2.

The final coordinates and anisotropic temperature factors for the heavy atoms and their standard deviations are given in Table 3. The positional parameters and isotropic temperature factors for the hydrogen atoms and their standard deviations are given in Table 4. The shifts calculated for the parameters in the final cycle of least squares were all less than one-tenth of the standard deviations.

Description of the structure

A composite of the final electron density map viewed along the c axis is shown in Fig. 1. An analogous composite of a difference synthesis for which the contributions of the hydrogen atoms were omitted from F_c is shown in Fig. 2. No other significant features appeared in the difference map. Two stereoscopic views of the molecule are shown in Figs. 3 and 4. [Figs. 3, 4, 5 and 6 were drawn on a CALCOMP plotter controlled by an IBM 360/75 computer using the ORTEP program (Johnson, 1965).]

The bond distances and angles involving the heavy atoms are shown in Fig. 5. The standard deviations in the atomic coordinates (Tables 3 and 4) correspond to positional uncertainties of approximately 0·004 Å for the carbon atoms, 0·002 Å for the oxygen atoms and 0·03 Å for the hydrogen atoms. The standard deviations are expected to be about 0·006 Å for C–C distances, 0·005 Å for C–O distances and 0·03 Å for C–H distances The standard deviations in the bond angles between heavy atoms are about 15′ and about 2° in angles involving hydrogen atoms; the agreement among chemically equivalent bonds suggests that these standard deviations are reasonable. Distances and angles involving hydrogen atoms are listed in Table 5.

The molecule, within a close approximation, possesses the symmetry $2/m$. The position of the center of symmetry, obtained by averaging the positions of

the heavy atoms, is $x = -0·0362$, $y = 0·2687$, and $z = 0·7784$. The root-mean-square deviation from this center of the midpoints of lines joining centrosymmetrically related atoms is 0·016 Å; the average deviation is 0·015 Å. The equation for the mirror plane, obtained by a least-squares fit to the midpoints of lines joining atoms symmetrically related by the mirror plane, is

$$0·2211X + 0·5469Y + 0·8075Z - 7·6916 = 0,$$

where X, Y, and Z are the coordinates in Ångstrom units. The root-mean-square deviation of the midpoints from this plane is 0·013 Å and the average deviation is 0·011 Å.

Table 5. *Bond distances and angles involving hydrogen atoms*

Table 6. *Least-squares planes of the benzene and cyclobutane rings and atomic deviations from the plane*

Coefficients are directions cosines relative to the crystallographic axes.

Plane through atoms C(7), C(8), C(17) and C(18)
$$-0·4679X - 0·6655Y - 0·5815Z = 3·632$$

	Deviation
C(7)	−0·002 Å
C(8)	0·002
C(17)	−0·002
C(18)	0·002

Plane through atoms C(1), C(2), C(3), C(4), C(5), and C(20)
$$-0·3347X - 0·7296Y + 0·5964Z = 1·901$$

	Deviation
C(1)	0·004
C(2)	−0·006
C(3)	0·002
C(4)	0·005
C(5)	−0·007
C(20)	0·002

Plane through atoms C(10), C(11), C(12), C(13), C(14), and C(15)
$$-0·3404X - 0·7207Y + 0·6040Z = 5·259$$

	Deviation
C(10)	0·003
C(11)	−0·009
C(12)	0·006
C(13)	0·004
C(14)	−0·011
C(15)	0·007

This structure is an example of the unusual situation of a nearly centrosymmetric molecule which crystallizes in a non-centrosymmetric space group. Another molecule which has a center of symmetry, but crystallizes in a non-centrosymmetric space group, is β-1:2-5:6-dibenzanthracene (Robertson & White, 1956). Biphenylene (Waser & Lu, 1944; Fawcett & Trotter, 1966) crystallizes in space group $P2_1/a$ with six molecules per unit cell. Two of the molecular centers fall on centers of symmetry, but the other four molecules are in general positions despite their apparent center of symmetry.

The equations of the least-squares planes through the benzene and cyclobutane rings and the deviations of the individual atoms from their respective planes are given in Table 6. The second benzene ring shows a slight degree of non-planarity.

A stereoscopic view down the b axis showing the packing of the molecules is given in Fig. 6. There are no short contacts between molecules. The shortest heavy-atom-to-hydrogen intermolecular distance is 2·73 Å between H(24) of the base molecule and C(15) of the molecule in equivalent position $x-\frac{1}{2}, -y+1, z$. The shortest hydrogen-to-hydrogen intermolecular

distance is 2·45 Å between H(32) of the base molecule and H(28) of the molecule in the equivalent position $x+\frac{1}{2}, -y, z$.

We wish to express our thanks to Dr Richard E. Marsh for advice and guidance throughout this project. The preparation of drawings by Miss Lillian Casler and of the manuscript by Miss Allison Kimball is gratefully acknowledged.

References

International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* 9, 635.

KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* 21, 849.

LARSON, A. C. (1967). *Acta Cryst.* 23, 664.

ROBERTSON, J. M. & WHITE, J. G. (1956). *J. Chem. Soc.* p. 925.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175.

WASER, J. & LU, C.-S. (1944). *J. Amer. Chem. Soc.* 66, 2035.

WILSON, A. J. C. (1942). *Nature, Lond.* 150, 151.

ZIEGLER, G. R. (1969). *J. Amer. Chem. Soc.* 91, 446.

The Crystal Structure of Bis(L-serinato)zinc*

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The crystal structure of bis(L-serinato)zinc, $ZnC_6H_{12}O_6N_2$, has been determined and refined by three-dimensional least-squares techniques. The crystals are monoclinic, space group $P2_1$, with $a=9·542$, $b=8·818$, $c=5·666$ Å and $\beta=96·7°$. The final R value for 950 reflections is 0·036; the standard deviations are about 0·006 Å for the C, N and O atom positions. The compound is not isostructural with either the Ni or Cu complex of L-serine. The zinc coordination is intermediate between a square pyramid and a trigonal bipyramid with the first one being slightly favored. The two serine molecules have different conformations for the hydroxyl group; one serine molecule having the unusual *anti-gauche* conformation.

Introduction

The structure of the Zn chelate of L-serine was determined as one of a series of L-serine chelates (van der Helm & Franks, 1969; Van der Helm & Hossain, 1969) to obtain information about the relative influence of transition metal ions on the configuration of an amino acid. No two of the three complexes of serine thus far

determined are isomorphous. Zinc was chosen as one of the transition metal ions because its role in biological reactions has long been known.

Experimental

The compound bis(L-serinato)zinc was prepared by reacting two moles of L-serine with one mole each of zinc sulfate and barium hydroxide in a minimal amount of water. The barium sulfate produced was removed by centrifugation. The solution produced, which tended to become supersaturated, was then diluted about fifty times with absolute ethanol in order to ob-