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The Crystal Structure of 1, 2-Diphenoxyethane

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1, 2-Diphenoxyethane crystallizes in two forms, flake-shaped and prismatic. The crystal and molecular structures of the prismatic crystals were determined and described. The orthorhombic unit cell dimensions are: a=34.74, b=12.04, and c=5.58 Å. The space group is *Fdd*2. The molecule has the symmetry of a two-fold axis, and the OCH_2CH_2O group exists in a gauche conformation with an internal rotation angle of 66.9°.

Two different molecular structures of *p, p'*-dichlorodiphenoxy-1, 2-ethane were found by the authors and described in a preceding paper.1) The reason why this substance takes different structures in the same crystal is not clear. It may, however, be possible that the chlorine atoms introduced for convenience of structure analysis affect the molecular and crystal structure of this substance. Therefore, we undertook a crystal structure analysis of 1, 2-diphenoxyethane. This substance will be cited below as DPOE, while *p, p'*-dichlorodiphenoxy-1, 2-ethane as Cl-DPOE.

TABLE 1. CRYSTAL AND PHYSICAL DATA

mp	97—97.5°C
a	34.74 Å
b	12.04
c	5.58
Space group	*Fdd* 2
Z	8
$\rho_{\text{obs.}}$	1.2 g cm^{-3}
$\rho_{\text{cald.}}$	1.22

Experimental

Crystal of a flake shape were obtained by slowly cooling an ethanol solution saturated with this substance; mp 96—96.5°C (97—98°C2); 98—98.5°C3)). After these crystals had been filtered off, the filtrate gave prismatic crystals when the solvent was slowly evaporated; mp 97—97.5°C (95°C4)). These two types of crystals gave different X-ray powder patterns, and their infrared spectra were slightly different from each other, as is shown in Fig. 5.[*2] It was not possible to obtain flake-shaped crystals large enough to be submitted to an X-ray structure analysis. Therefore, the prismatic crystals were used in this X-ray work.

From oscillation and Weissenberg photographs of these crystals, the unit-cell dimensions and the space group were determined. The crystal and physical data are summarised in Table 1. The observed density was measured by the floatation method.

The intensity data were collected by the photographic method. Equi-inclination Weissenberg photographs around the c and b axes were taken with nickel-filtered copper $K\alpha$ radiation, for l values from 0 to 4 and for k values from 0 to 9 respectively. The crystals used had a cross-section of 0.2×0.2 mm for the c axis and of 0.3×0.3 mm for the b axis. Independent reflections from 630 planes were observed out of 682 possible (hkl)'s. In order to correlate strong and weak reflections, a multiple-film technique was applied, the relative intensities ranging between 1 to 6×10^3. The intensities were measured by a visual comparison with a standard intensity scale prepared with the same crystal. No correction was made for the absorption, while the corrections for the Lorentz and polarization factors were made in the usual way; corrections for the shape factors were made according to the method of Lonsdale.5)

Structure Determination

Since the number of general points of the space group *Fdd*2 is sixteen and since a unit cell contains eight molecules, the molecule must be on a special position, that is, on the two-fold axis parallel to the c axis. Therefore, a half molecule is in an asymmetric unit.

The two-dimensional Patterson function along the c axis was computed. Then several trial structures which could account for the Patterson map were deduced, and the structure factors were calculated on each trial structure. The one that gave the best agreement between the calculated and the observed structure factors was then chosen and refined by a least-squares method. Five cycles of the calculations reduced the discrepancy index,

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1) Preceding paper

2) A. Solonia, *J. Russ. Phys. Chem. Soc.*, **30**, 607 (1898); *Chem. Centr.*, **1899**, **I**, 25.

3) A. C. Cope, *J. Am. Chem. Soc.*, **57**, 572 (1935).

4) G. Gilta, *Bull. Soc. Chem. Belges.*, **31**, 245 (1922); *Chem. Centr.*, **1923**, **I**, 241.

[*2] These two types of crystals have already been described as "*Blättchen*" in Ref. 2 and as "*rhombisch*" in Ref. 3.

5) K. Lonsdale, *Acta Cryst.*, **17**, 308 (1964).

TABLE 2. ATOMIC COORDINATES AND TEMPERATURE FACTORS

Atom	x/a	y/b	z/c	B
O	−0.0311	0.0782	−0.003	3.3
C_1	−0.0923	0.3731	0.935	4.1
C_2	−0.0953	0.2905	0.762	3.9
C_3	−0.0737	0.1932	0.786	3.5
C_4	−0.0499	0.1783	0.985	3.0
C_5	−0.0456	0.2630	0.154	3.3
C_6	−0.0678	0.3602	0.129	4.0
C_7	−0.0064	0.0607	0.203	5.4

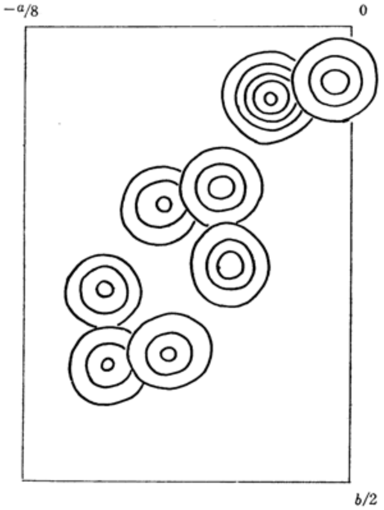

Fig. 1. The final electron density distribution. Composite diagram of sections parallel to (001). Contours are drawn at equal intervals on an arbitary scale.

$R=\sum||F_o|-|F_c||/\sum|F_o|$, from 0.36 to 0.18. Thus the x and y coordinates of all atoms except hydrogens were obtained. The remaining z coordinates were deduced assuming the normal bond distances. Then the three-dimensional least-squares refinement was carried out. After six cycles the R factor decreased to 0.153.

The final atomic coordinates and temperature factors are listed in Table 2. Tables of the observed and calculated structure factors are preserved by

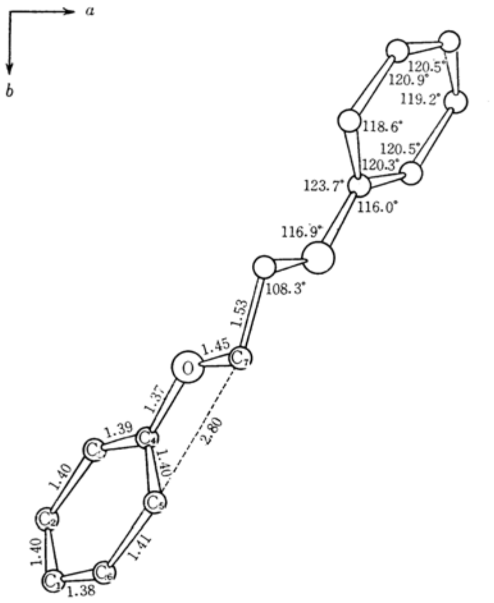

Fig. 2. The molecular shape viewd along the c axis, and the bond lengths (Å) and bond angles (°) in the molecule of 1,2-diphenoxyethane.

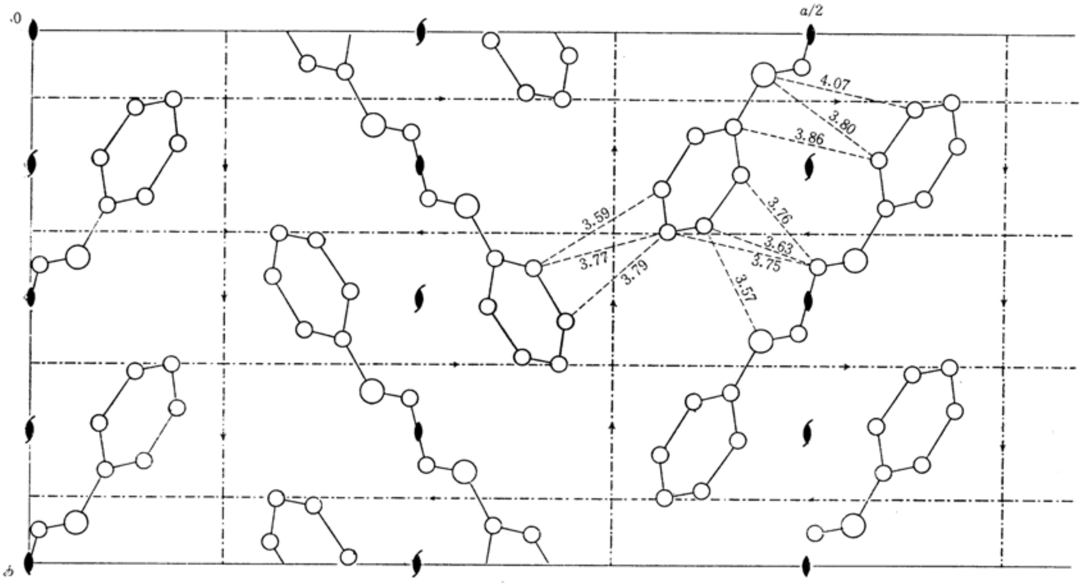

Fig. 3. Arrangement of the molecules in the unit cell viewed along the c axis with some short intermolecular distances (Å).

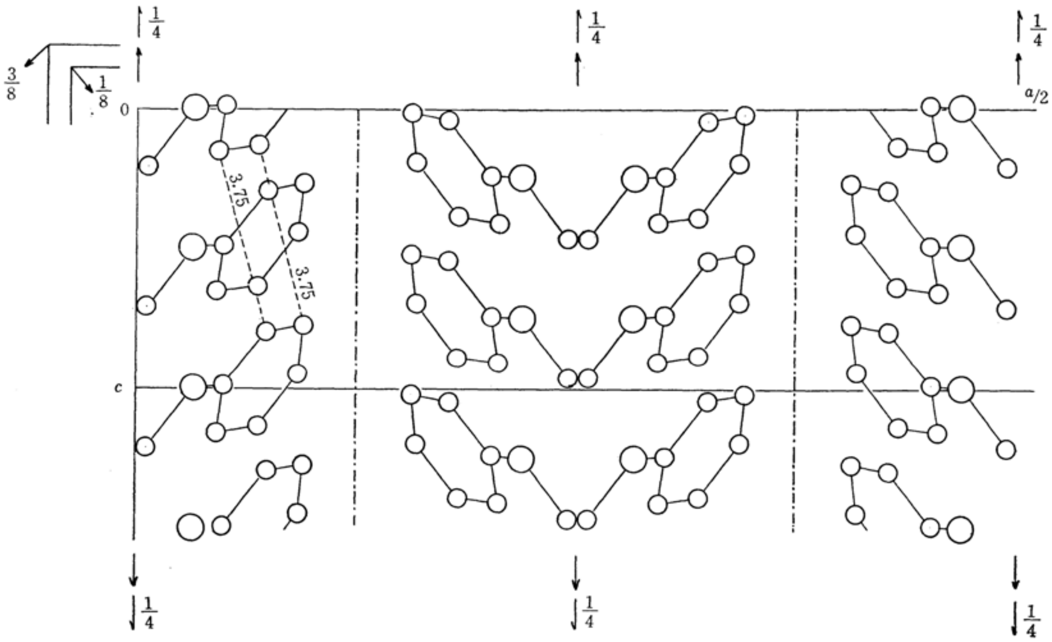

Fig. 4. Arrangement of the molecules viewed along the *b* axis.

the Chemical Society of Japan.*3 Figure 1 gives the superimposed (001) sections of final electron density distribution.

A Description and Discussion of the Structure

The molecular shape viewed along the c axis, and the bond lengths and angles are illustrated in Fig. 2. The average estimated standard deviations of the coordinates are 0.0057 and 0.0086 Å for oxygen and carbon atoms respectively. Therefore, the estimated standard deviations of the bond lengths are 0.010 for C–O, 0.012 for C–C in the benzene ring, and 0.013 Å for CH_2–CH_2 in the center of molecule, while those of the bond angles are 0.8° for ∠CCC and 0.6° for ∠COC.

The benzene ring is approximately planar, the best plane being represented by the equation:

$$y = -1.8063x + 1.2602z - 0.8224$$

The coefficients were determined by a least-squares methods with a program written by Yoshiko Tsukuda. The departures of the atoms from this plane are less than 0.02 Å. The plane makes an angles of 58.6° with the (001) plane. C_7 lies almost on the plane of the benzene ring, the displacement being only 0.11 Å. The internal rotation angle around the C–C bond at the center of the molecule is 66.9° and has a gauche form. Judging from these values, the molecule resembles in shape the B type of Cl-DPOE1).

Figures 3 and 4 show the crystal structures

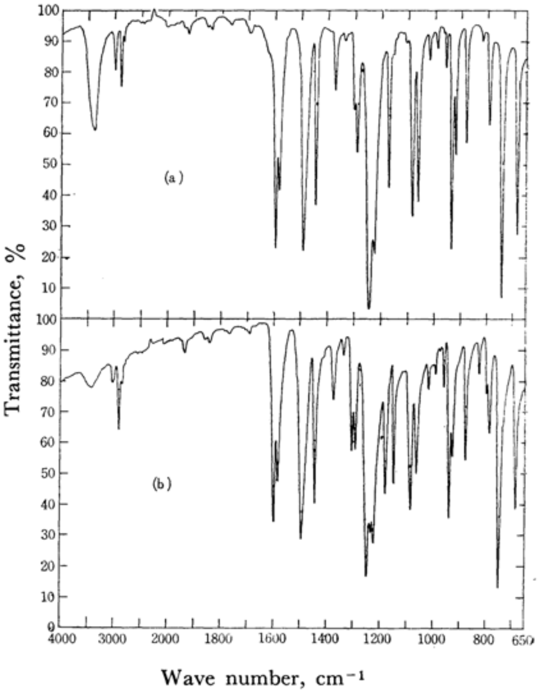

Fig. 5. Infrared spectra of 1, 2-diphenoxyethane.
(a) Flake-shaped crystals.
(b) Prismatic crystals.

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6) A. Miyake, *J. Am. Chem. Soc.*, **82**, 3040 (1960).

*3 The complete data of the $F_o - F_c$ table are kept as Document No. 6702 at the office of the Bulletin of the Chemical Society of Japan. A copy may be secured by citing the document number and by remitting, in advance, ¥350 for photoprints. Pay by check or money order payable to: Chemical Society of Japan.

projected along the c and b axes respectively. The benzene rings, which are apart by one period in the direction of the c axis, are packed side by side, the nearest interatomic distance concerned with the rings being 3.75 Å, which is slightly longer than that in the case of Cl-DPOE.

Miyake investigated the CH_2 rocking frequencies of ethylene glycol and its derivatives, including DPOE. He assigned two absorption bands, at 928 cm^{-1} and 941 cm^{-1}, to the CH_2 rocking vibrations of a gauche OCH_2CH_2O group. The infrared absorption spectra shown in his paper resemble those of flake-shaped DPOE, as is shown in Fig. 5(a). Since the absorption bands in the range of 920—950 cm^{-1} show little difference in these two types of crystals, his conclusion seems to be correct in the light of the results of our X-ray crystal structure analysis, though the crystal used in the present work was of a prismatic shape, as has been mentioned above.

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