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The Crystal Structure of p,p'-Dichlorodiphenoxy-1, 2-ethane

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Crystals of p,p'-dichlorodiphenoxy-1, 2-ethane are monoclinic; their space group is $P2/c$, and they have 4 molecules in the cell with dimensions of:

$$a = 12.79, \quad b = 9.89, \quad c = 10.37\text{Å}; \quad \beta = 98.2°.$$

Two crystallographically-independent molecules, which are slightly different in conformation, are located on the two-fold axis of the crystal. The OCH_2CH_2O groups are of the gauche form.

It has been reported that the polyamide obtained by the condensation of 1, 2-bis-[p-(3-aminopropyl)phenoxy]ethane and adipic acid and its homologues show "shortening" of the fiber periods.[1] Here "shortening" means that the observed fiber periods of these polyamides are shorter by 3—4 Å than the calculated values, assuming that all the single bonds along the chains take trans conformations.

This suggests that one or more single bonds, especially carbon-carbon single bonds along the chains, take conformations other than the trans.

There are three different sorts of methylene groups in the repeating unit of the chain. The first is the residue from adipic acid; the second, the aminopropyl group, and the third, the methylene groups between phenoxy groups. The evidence that the residue from adipic acid has the trans zig-zag conformation has been reported.[1] However, it has remained unknown in what conformation the two remaining parts exist. Therefore, we first attempted to clarify the conformation of methylene groups between two phenoxy groups, and so undertook a crystal structure analysis of p,p'-dichlorodiphenoxy-1, 2-ethane by means of X-rays. This substance can be regarded as a model of the 1, 2-diphenoxyethane group in the chain; the X-ray work would also give information about the details of the molecular structure and the situation of the packing of this group in the crystalline state of the polyamide.

Experimental

Crystals of p,p'-dichlorodiphenoxy-1, 2-ethane were obtained by slowly evaporating the solvent from a methanol solution.

From oscillation and Weissenberg photographs of one of these crystals, the unit-cell dimensions were determined. The crystal belongs to the monoclinic system. The missing rule indicates that the cell is primitive and that c glide planes are present. Therefore, the space group must be $P2/c$ or Pc. The results of the crystal structure analysis revealed that the space group is $P2/c$. The crystal and physical data are summarized in Table 1. Although the density was not measured, the calculated density given in Table 1 may reasonably be considered to be adequate.[2]

TABLE 1. CRYSTAL AND PHYSICAL DATA

Mp	132—133°C
a	12.79 Å
b	9.89
c	10.37
β	98.2°
Space group	$P2/c$
Z	4
$\rho_{\text{cald.}}$	1.45 g cm^{-3}

Intensity data were collected by the photographic method. Equi-inclination Weissenberg photographs around the c axis were taken with nickel-filtered copper $K\alpha$ radiation for l values from 0 to 7. The crystal used had a cross section of 0.2×0.2 mm. Similarly, the photographs around the b axis were taken for k values from 0 to 6. In this case, the cross section of the crystal was 0.1×0.2 mm. Independent reflections from 1350 planes were observed. 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.[3]

Structure Determination

As has been mentioned above, the possible space groups of this crystal were $P2/c$ and Pc. Since the

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1) T. Ando, N. Yasuoka and S. Kuribayashi, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **87**, 536 (1966).

2) Subsequent paper.

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

unit-cell contains four molecules, one molecule would exist in the asymmetric unit if the space group is $P2/c$, and two molecules, if it is Pc. We first considered the simpler case, that the space group is $P2/c$; fortunately, this proved to be the correct structure.

This space group contains centers of symmetry and two-fold axes. The structural formula of this substance would seem to allow for the existence of molecular symmetry, a center of symmetry, or a two-fold axis, the former corresponding to the trans form of the methylene groups between phenoxy groups, and the latter, to the trans or gauche form. Since the number of general points in the $P2/c$ space group is four, two possible cases can be considered. First, the whole molecules lies in the asymmetric unit. This need not imply any symmetry element for the molecules. Secondly, the molecule has the center of symmetry or the two-fold axis which coincides with the crystallographic symmetry of $P2/c$. In this case, two of the half molecules, which are crystallographically independent, are in the asymmetric unit.

The $F(hkl)$'s intensity distribution seemed to be remarkable. $F(h0l)$'s are strong if $h=2n$; otherwise they are weak or absent. On the other hand, $F(h2l)$'s are stronger when $h=2n+1$ than $h=2n$. Similarly, $F(h4l)_{h=2n}$'s are stronger, $F(h6l)_{h=2n+1}$'s are stronger, and so on. After all, $F(hkl)$'s have larger intensities when $k=4n$ and $h=2n$, or when $k=4n+2$ and $h=2n+1$.

Therefore, the very high peak (7734 in an arbitary scale), comparable to the peak in the origin (12920 in the same scale), was observed at the coordinate (1/2, 1/4, 0) in the three-dimensional Patterson function. This fact indicated that two of the half molecules exist ($\boldsymbol{a}/2+\boldsymbol{b}/4$) apart, and so the second case mensioned above seems to be favored. Therefore, two chlorine atoms in the asymmetric unit would also lie at a distance of about ($\boldsymbol{a}/2+\boldsymbol{b}/4$). According to these presumptions, peaks indicating chlorine-chlorine vectors were searched for in the $P(U\,V\,W)$; some of them were found at the special points, for instance, at (0, V, 1/2). Thus, the approximate atomic coordinates of the two chlorine atoms were obtained as ($\overline{0.09}$, 0.09, 0.37) for Cl_1 and (0.41, 0.34, 0.37) for Cl_2.

The Fourier syntheses of the electron-density projections along the b axis and the c axis were carried out with signs based on the two chlorine atoms only, and their atomic coordinates were refined. Then the Fourier synthesis of the three-dimensional electron density distribution was carried out. Significant peaks appearing in the Fourier map gave a reasonable molecular shape, and the coordinates of all the atoms except those of hydrogen could be read off from it. Structure factors were computed with these atoms and $B=5.0$ Å^2, the discrepancy factor $R=\sum||F_o|-|F_c||/$

TABLE 2. ATOMIC COORDINATES AND TEMPERATURE FACTORS

Atom	x/a	y/b	z/c	β
Cl_1	0.0876	0.0866	0.1455	5.0
Cl_2	0.4169	0.3385	0.3635	5.7
O_1	0.4438	0.1536	−0.1364	4.7
O_2	0.0591	0.3980	0.6464	3.8
C_1	0.1911	0.1151	0.0575	3.9
C_2	0.2898	0.0645	0.1160	4.1
C_3	0.3725	0.0848	0.0462	4.3
C_4	0.3555	0.1477	−0.0780	3.5
C_5	0.2582	0.1914	−0.1328	4.6
C_6	0.1750	0.1745	−0.0620	4.4
C_7	0.4482	0.2620	−0.2331	5.0
C_8	0.3117	0.3614	0.4495	4.1
C_9	0.2358	0.2579	0.4416	4.4
C_{10}	0.1531	0.2739	0.5099	3.7
C_{11}	0.1459	0.3909	0.5864	3.3
C_{12}	0.2219	0.4923	0.5959	3.9
C_{13}	0.3061	0.4751	0.5223	4.5
C_{14}	0.0524	0.5145	0.7289	4.2

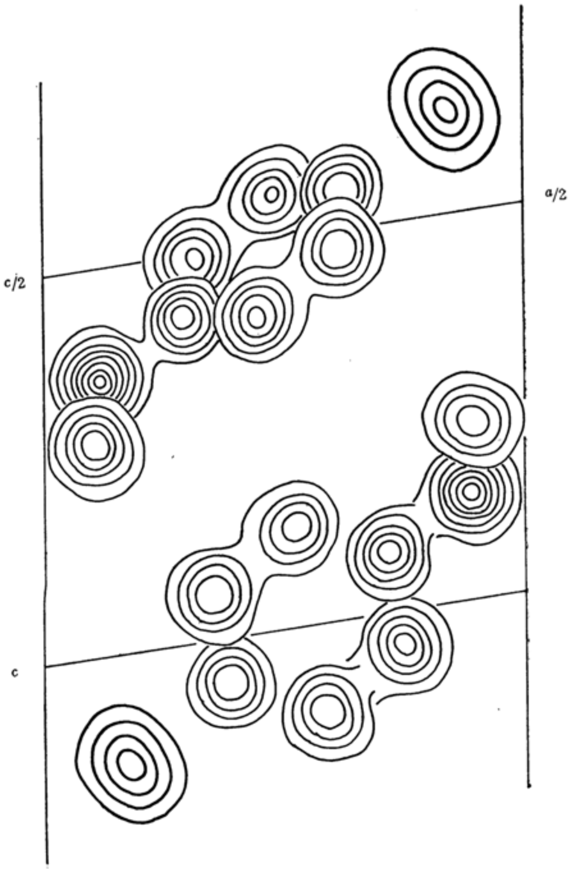

Fig. 1. The final electron density distribution. Composite diagram of sections parallel to (010). Contours are drawn at equal intervals on an arbitary scale. Those of chlorine atoms are partly omitted.

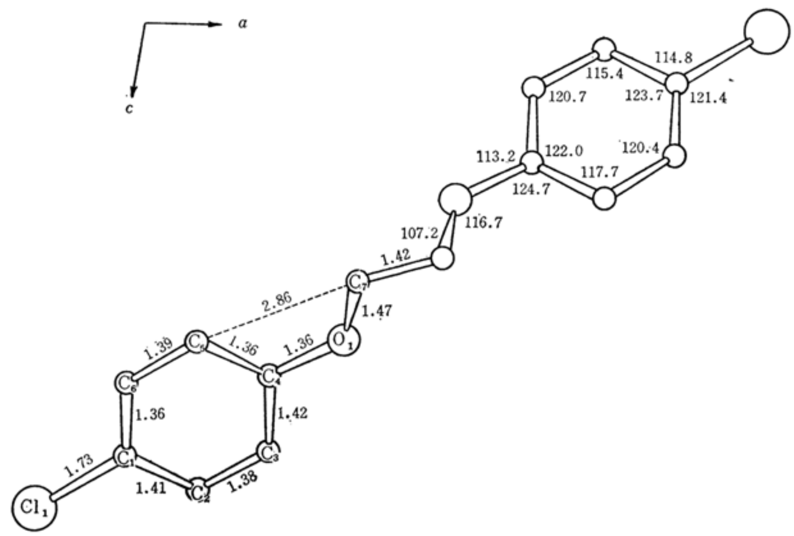

Fig. 2. The molecular shape viewed along the b axis, and bond lengths (Å) and bond angles (°) in the molecule of *p, p'*-dichlorodiphenoxy-1, 2-ethane; the molecule of the type A.

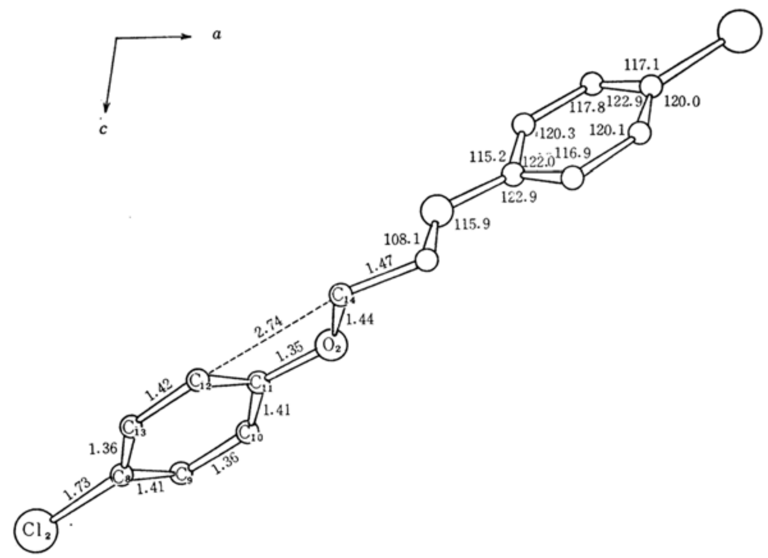

Fig. 3. The molecule of the type B.

$\sum|F_o|$ being 0.59. The second Fourier synthesis looked very refined, and the calculation of the structure factors based on the coordinates from this Fourier map resulted in an R factor of 0.37.

The atomic coordinates and isotropic temperature factors were refined by the least-squares method. After six cycles, the R factor decreased to 0.182, non-observed reflections being omitted. All the calculations in this work were carried on an OKITAC 5090 C electronic computer of this Institute, using programs written by the authors.[4]

The final atomic coordinates and temperature factors are listed in Table 2. Tables of the observed and calculated structre factors are preserved by the Chemical Society of Japan.*2 Figure 1 gives the superimposed (010) sections of final electron-density distribution.

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4) Some of them were published: N. Yasuoka and T. Mitsui, *Bull. Gov. Ind. Res. Inst., Osaka,* **16**, 37 (1965); N. Yasuoka, *ibid.,* **16**, 194 (1965); S. Kuribayashi, *ibid.,* **16**, 200 (1965).

*2 The complete data of the F_o—F_c table are kept as Document No. 6701 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, ¥600 for photoprints. Pay by check or money order payable to: Chemical Society of Japan.

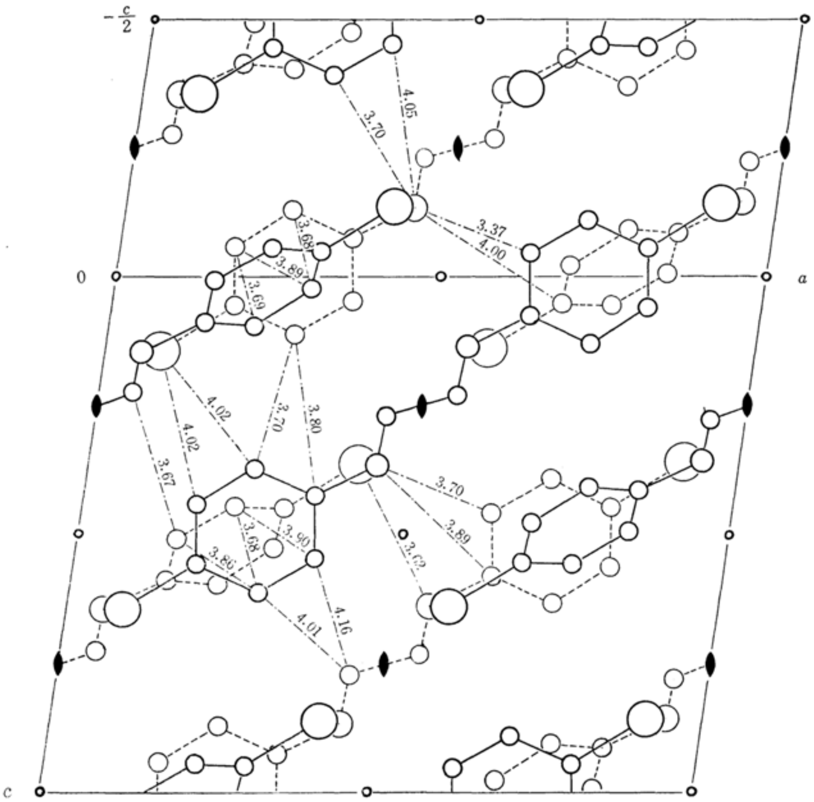

Fig. 4. Arrangement of the molecules in the unit cell viewed along the b axis, with some short intermolecular distances (Å).

A Description and Discussion of the Structure

The molecular shape viewed along the b axis and the bond lengths and angles are illustrated in Figs. 2 and 3. It is clear that the conformation of the methylene group between phenoxy groups has the gauche form. The average estimated standard deviations of the coordinates are 0.0046, 0.010 and 0.015 Å for chlorine, oxygen and carbon atoms respectively. Therefore, the estimated standard deviations of the bond lengths are 0.016 for C–Cl, 0.18 for C–O, and 0.021 Å for C–C except for CH_2–CH_2 in the center of the molecule, for which 0.030 Å. The estimated standard deviations of the bond angles are 1.4°, 1.2° and 1.1° for ∠CCC, ∠ClCC and ∠COC, respectively. The bond lengths and angles are quite consistent in two independent molecules.

The benzene rings are approximately planar, the best planes being represented by the equations:

$$Y = -0.2180X - 0.4599Z + 1.7657$$

for the A molecule, and

$$Y = 1.1427X + 1.5558Z - 7.3036$$

for the B molecule, where $X = x \sin \beta$, $Y = y$ and $Z = z + x \cos \beta$. the coefficients were determined by a least-squares method with a program written by Yoshiko Tsukuda. The departures of the atoms from these planes are less than 0.016 Å.

The shapes of the two independent molecules are slightly different from each other. First, the internal rotation angles around the CH_2–CH_2 bonds at the centers of the molecules are 81° in the molecule of type A, and 66° in the molecule of type B (see Figs. 2 and 3 for the notation).*3 Secondly, the planes of the benzene rings make angles of 27.0° (molecule A) and 62.6° (molecule B) with the (010) plane. Thirdly, C_7 almost lies on the plane of the benzene ring, the displacement being only 0.01 Å, while C_{14} deviates by 0.51 Å from the plane of the benzene ring.

Figures 4 and 5 show the crystal structure projected along the b and c axes respectively. Two benzene rings, which are crystallographically independent, incline in the same direction, though they make different angles with the (010) plane and are mutually piled up in the direction of the b axis.

The chlorine-chlorine contacts between the

*3 The standard deviations of these internal rotation angles have not been estimated, but it is possible that they are considerably larger than those of bond angles.

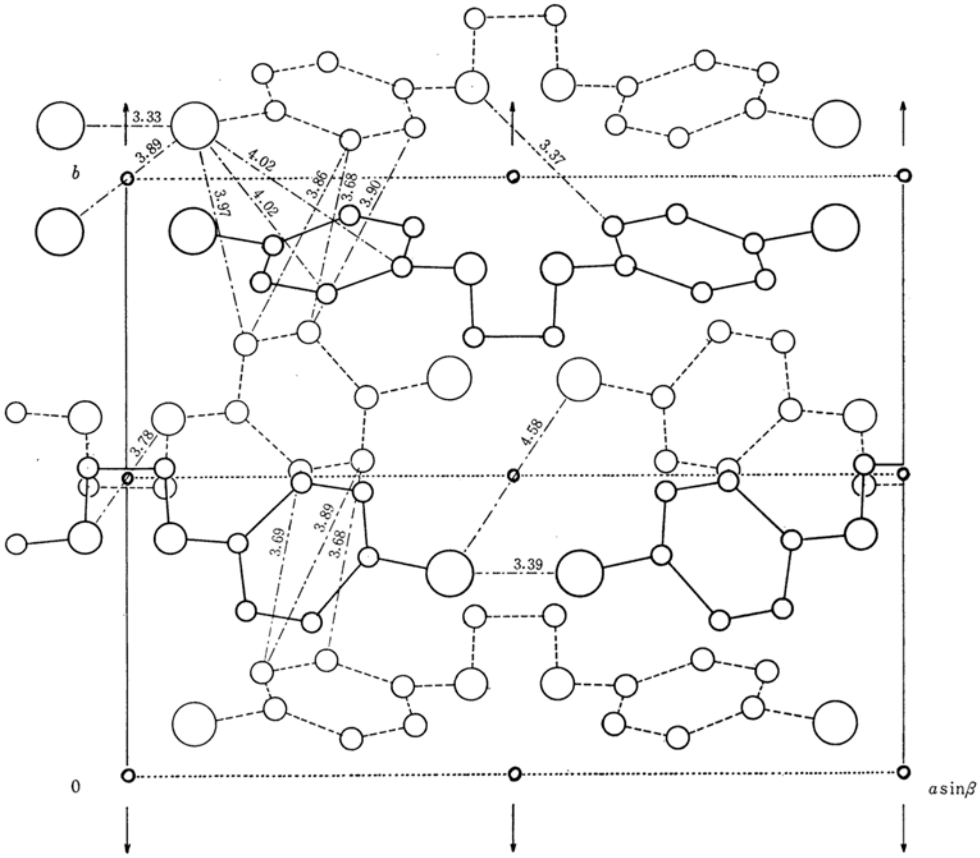

Fig. 5. Arrangement of the molecules viewed along the c axis.

chlorine atoms which are related to each other by the two-fold axis are 3.33 and 3.39 Å, slightly shorter than the usually accepted value of the van der Waals radius of the chlorine atom (1.80 Å).

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