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The Crystal Structure of *dl*-Bi-1,4-dioxanyl

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Synopsis. The two forms of bi-1,4-dioxanyl (mp 157.5—158.0 °C and 133.5—134.0 °C), obtained by the photochemical reaction of 1,4-dioxane with acetophenone, have been assigned unequivocally to the *meso* and *dl* forms respectively by the X-ray method.

In the absence of copper ions, the photochemical reaction of 1,4-dioxane with *t*-butyl peracetate yielded two isomeric products ($C_8H_{14}O_4$), mp 157 °C and 132 °C.[1] From the results of microanalyses and molecular-weight determinations, it was inferred that one product was the *meso* form of bi-1,4-dioxanyl and the other was the *dl* form. It has recently been found in this laboratory that the same products, mp 157.5—158.0 °C and 133.5—134.0 °C, are obtained also by the photochemical reaction of 1,4-dioxane with acetophenone.[2] In order to assign unambiguously the configurations of these two products, an X-ray crystallographic analysis has been made on the product with the lower melting point.

The crystals are monoclinic, with four molecules in a unit cell of the dimensions; $a=12.198\pm0.004$, $b=4.645\pm0.002$, $c=14.660\pm0.004$ Å, and $\beta=93.56\pm0.07°$. These dimensions were measured on a single-crystal diffractometer using Cu$K\alpha$ radiation ($\lambda=1.54178$ Å). The calculated density is 1.395 g/cm³. The systematic absences, hkl for $h+k=2n+1$ and $h0l$ for $l=2n+1$, showed that the space group was either Cc or C2/c. At the beginning of the study, the latter was assumed; this choice was confirmed later by successful refinement. A crystal with dimensions of about 0.1×0.2×0.5 mm was used, and the intensity data were collected on a Rigaku automatic four-circle diffractometer using Cu$K\alpha$ radiation monochromatized with a LiF crystal. The intensities were corrected for the usual Lorentz and polarization factors, but not for either the absorption or the extinction effect. In the range of 2θ values up to 140°, 693 structure factor magnitudes above $2\sigma(F)$ were selected for the structural study.

The structure was solved by the symbolic addition procedure using 148 $|E|$ values above 1.30. Approximate positions of all non-hydrogen atoms were obtained from an E-map based on 143 phases. These atomic coordinates were refined by the block-diagonal-matrix least-squares method, at first with isotropic and then with anisotropic thermal parameters. A difference Fourier map yielded the locations of all 7 hydrogen atoms. Further least-squares refinement including these hydrogen atoms with isotropic temperature factors was carried out. In this refinement, the following weighting scheme was introduced:

$$W = 1/\{\sigma(F)^2 \exp(AX^2 + BY^2 + CXY + DX + EY)\}$$

where $X=|F_o|$ and $Y=\sin\theta/\lambda$. The coefficients, A, B, C, D, and E, are constants which have been determined from $(\Delta F)^2$ values. The R value reached 4.9%. The atomic parameters are listed in Table 1. The tables of the observed and calculated structure factors are preserved by the Chemical Society of Japan (Document No. 7422). The atomic scattering factors were taken from International Tables for X-ray Crystallography, Vol. III. All calculations were performed on a FACOM 230—60 computer at the Computer Center of Hokkaido University.

TABLE 1. THE FINAL ATOMIC PARAMETERS AND ESTIMATED STANDARD DEVIATIONS

(a) The non-hydrogen atoms

The parameters are multiplied by 10^5. The anisotropic temperature factors are defined as $\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-\beta_{12}hk-\beta_{23}kl-\beta_{31}lh)$.

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{31}
O(1)	40912(8)	25075(23)	4892(6)	576(6)	3719(40)	277(3)	−398(27)	515(21)	−140(7)
O(2)	38420(7)	1914(20)	22488(6)	384(4)	3428(36)	290(3)	−533(23)	278(20)	−15(6)
C(1)	45399(8)	26213(23)	21255(7)	375(6)	2466(41)	290(4)	−14(30)	48(24)	−6(8)
C(2)	49771(10)	25617(31)	11740(8)	436(7)	4023(56)	279(4)	−389(35)	332(28)	−14(9)
C(3)	34243(11)	348(30)	6160(8)	574(7)	3216(48)	316(5)	−137(34)	−24(27)	−167(9)
C(4)	29696(10)	1087(32)	15516(9)	396(6)	4037(57)	374(5)	−360(36)	103(30)	−79(9)

(b) The hydrogen atoms

The positional parameters are multiplied by 10^3.

Atom	x/a	y/b	z/c	B(Å²)	Atom	x/a	y/b	z/c	B(Å²)
H(1)	414(2)	431(4)	220(1)	1.2(3)	H(3-2)	283(2)	5(5)	14(1)	1.8(3)
H(2-1)	543(2)	89(5)	110(1)	1.6(3)	H(4-1)	250(2)	180(5)	159(2)	1.8(4)
H(2-2)	539(2)	426(5)	106(2)	2.2(4)	H(4-2)	256(2)	−158(6)	166(2)	2.2(4)
H(3-1)	386(2)	−174(5)	57(1)	1.5(3)					

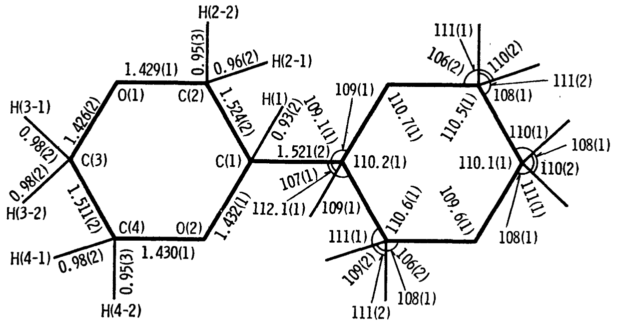

Fig. 1. The bond distances (Å) and angles (°).

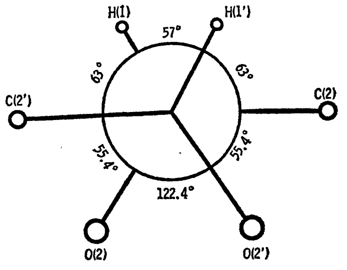

Fig. 2. The Newman projection along the C(1)-C(1') bond.

As is shown in Fig. 3, the present molecule has the C_2 symmetry. Thus, out of the two crystalline forms of bi-1,4-dioxanyl, the one with the melting point of 133.5—134.0 °C is assigned to the *dl* form.

The bond distances and angles are given in Fig. 1. The dioxane rings in a molecule have normal chair-forms, with the C(1)–C(1') bond oriented equatorially, and the molecule takes such a staggered conformation around the C(1)–C(1') bond as is shown in Fig. 2. This conformation, in which the largest groups, $C(2)H_2$ and $C(2')H_2$, are farthest from each other, is probably the most stable of the three possible staggered ones. The average of three independent C–C bond distances, 1.519 Å, is somewhat smaller than the normal distance for C–C, while the average of four C–O distances, 1.429 Å, is in good agreement with the standard value, 1.43 Å.

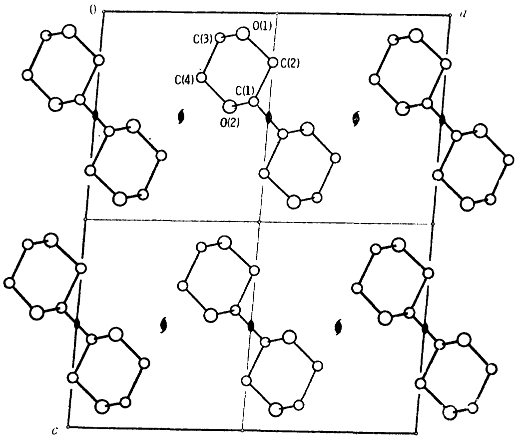

Fig. 3. The molecular arrangement viewed along the *b* axis.

The crystal structure viewed along the *b* axis is shown in Fig. 3. The molecules are held together mainly by the van der Waals interactions.

References

1) G. Sosnovsky, *J. Org. Chem.*, **28**, 2934 (1963).
2) S. Misumi and T. Matsumoto, The 28th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1973; Preprint, Vol. III, p. 1559 (1973).