Crystal and Molecular Structure of 1,2-Dimethoxyethane Crystallized on a New Diffractometer

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Crystal and molecular structure of 1,2-dimethoxyethane (DME) with low melting point (-58 °C) was investigated by crystallization on a new imaging plate-Weissenberg type diffractometer with a new low temperature equipment. The crystal belongs to the monoclinic system and the space group is *C2/c*. There are four molecules in a unit cell. The DME molecule lies on a two-fold axis and has a TGT conformation in the crystalline state.

1,2-Dimethoxyethane (DME), which is a low-melting-point material, has long been a subject of interest for conformation studies as a monomer model of poly(oxyethylene) and there are 10 possible conformers. The conformational studies of this compound in the crystalline state as well as in the gaseous, liquid, solution and amorphous states were investigated by infrared and Raman spectroscopies[1] and molecular dynamics.[2] In addition, the crystal structure has been estimated based on the lattice variable molecular dynamics.[2] However, the crystal structure has not been analyzed because of the difficulty in getting the single crystal at low temperatures.

Recently a new imaging plate-Weissenberg type diffractometer was designed and made to perform the rapid intensity data collection.[3] The diffractometer is very advantageous to the low temperature X-ray analysis since the intensity data can be collected before ice is formed on the surface of the crystal. Moreover, a new cooling system without using liquid nitrogen has been designed and constructed. Nitrogen gas is separated from the air and cooled to the desired temperature with liquid helium cooling system. This equipment enables us to perform low temperature experiments very easily. The crystallization of liquid DME was attempted on the diffractometer avoiding the ice forming. Such a crystallizing method is called '*in situ*' crystallization technique.[4]

DME (Tokyo Kasei Kogyo Co., Ltd.) was filled in a 0.7 mm glass capillary, which was mounted on the diffractometer. The sample was cooled down to 10°C below the melting point at 0.3 °C/min until polycrystals appeared and then the polycrystalline sample was warmed up to the melting point at 10 °C/min. During this process, an attention was paid not to melt the crystalline sample completely. After several cycles of the heating-up and cooling-down processes a cylindrical single crystal was obtained in the glass capillary. The oscillation photograph showed sharp diffraction peaks. After an oscillation photograph was taken for determination of cell dimensions and orientation matrix, no-screen Weissenberg measurement was performed at -90 °C.

The crystal data are as follows; $C_4H_{10}O_2$, F.W.=90.12, monoclinic, space group *C2/c*, $a = 11.826(9)$, $b = 4.603(3)$, $c = 10.290(7)$ Å, $\beta = 106.32(3)°$, $V = 537.6(6)$ Å^3, $Z = 4$, $D_x = 1.113$ g cm^{-3}, $\mu = 0.08$ mm^{-1}, $R = 0.0459$, $wR(F^2) = 0.112$. The data were merged with 15 Weissenberg photographs. Since 20 min are necessary to take a Weissenberg photograph, 5 h are necessary for the data collection. A total of 1962 reflections, of which 599 reflections were independent, were measured. The structure was solved by the direct method and refined by the full-matrix least-squares with SHELXL-93,[5] based on the 487 observed reflection ($I>2\sigma(I)$) and 29 variable parameters.

Table 1. Geometric parameters (Å or °)

O1-C1	1.4188(12)	C1-C1^i	1.496(2)
O1-C2	1.4196(14)		
C1-O1-C2	111.26(8)	O1-C1-C1^i	109.76(8)
C2-O1-C1-C1^i	175.95(7)	O1-C1-C1^i-O1^i	69.10(15)

Symmetry codes; (i)1-*x*,*y*,1/2-*z*

The bond distances, bond angles and torsion angles are shown in Table 1.[6] Since the center of the C-C bond of the DME molecule is situated on the two-fold axis, a half of the molecule is crystallographically independent. The torsion angles indicate that the DME molecule has a TGT form (tg^+t or tg^-t) in the crystalline state. This is consistent with the results of the infrared and Raman spectroscopies[1] and molecular dynamics.[2] The molecular structure is shown in Figure 1.

As shown in Figure 2, the tg^+t and tg^-t conformers are closely packed as sheets parallel to the *ab* plane, respectively. The short contacts such as O...CH_3 = 3.639 and 3.666 Å, and O...CH_2 = 3.616 Å along the *b* axis (not shown in Figure 2) may be responsible to the sheet formation. The sheets are

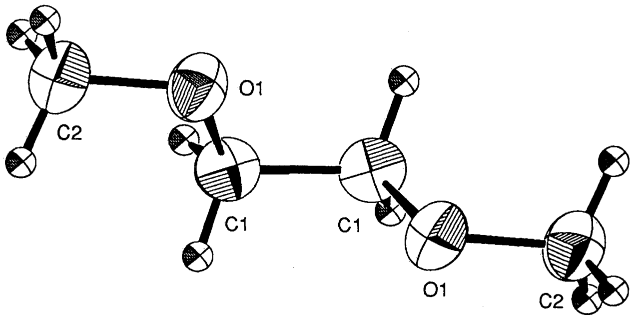

Figure 1. Perspective view of a DME molecule.

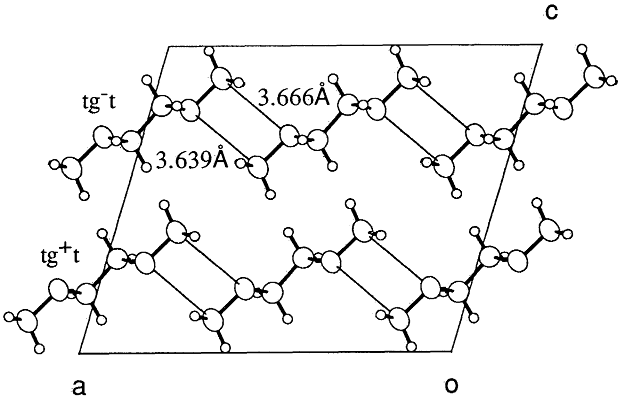

Figure 2. Crystal structure viewed along the *b* axis.

stacked along the *c* axis.

The observed crystal structure is not in agreement with that obtained by the molecular dynamics calculation,[2] in which the sheet was constructed by the short contacts between the different conformers. Although the observed O...C distances are longer than those of the calculated structure, the crystal structure is more closely packed than the calculated one (the density of the calculated structure is 1.019 g cm^{-3}).[2]

No phase transition was observed when the crystal was cooled at a constant rate of 0.1 °C/min from the room temperature to -175 °C.

References and Notes

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6 The atomic parameters and a table of F_o-F_c are deposited to the Office of the Chemical Society of Japan.