

09.2-27 STRUCTURAL PROPERTIES OF MODIFIED β -CYCLODEXTRINS: per-2,6-O-METHYL DERIVATIVES
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β -cyclodextrin can be methylated to the extent that all primary (O6) and half of the secondary (O2) hydroxyl groups are substituted (per-2,6-O-Me- β -CD, I). This derivative displays surprisingly different physical properties from the parent. For example, it is approximately an order of magnitude more soluble in cold water even though it contains 14 ether moieties per molecule in place of the hydroxyl groups of the parent. The adduct can easily be crystallized from hot water (a negative thermal solubility coefficient) whereas the parent displays increased solubility at elevated temperature. Also in contrast to the parent cyclodextrin, I is not expected to catalyze the cleavage of phenylester bonds. These observations have prompted us to examine the structures of a number of crystals containing I.

We report a crystal structure determination for I crystallized from hot water, Ia, from cold water, Ib, and in an inclusion complex with meta-cresoleacetate (phenylester substrate), Ic. A data set for what is apparently is a second modification of I crystallized from cold water, Id, is presently being collected.

Crystallographic Data

	<u>Ia</u>	<u>Ib</u>	<u>Ic</u>	<u>Id</u>
Space Group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁
a	13.585 ₁	13.976 ₇	11.080 ₃	13.682 ₃ *
b	17.653 ₁	20.763 ₇	14.932 ₄	22.606 ₆
c	29.766 ₁	28.807 ₆	44.906 ₁₀	27.562 ₉
T	300 K	~120	~120	~120
Formula asym. unit	$n_1 \text{H}_2\text{O}$	$(\text{C}_8\text{H}_{14}\text{O}_5)_7 \cdot 15\text{H}_2\text{O}$	$\text{C}_9\text{H}_{10}\text{O}_2$	$n_j \text{H}_2\text{O}$
R*	.158	.129	.081	-
No. hkl's	4640	8460	4796	-

* The crystal structure models are still under refinement. A rough model for Id has been determined and will be refined with the full low temperature data set.

09.2-28 THE OXETANE AND OXEPANE X-RAY STRUCTURES. By J. Buschmann, E. Müller, and P. Luger. Institut für Kristallographie, Fachbereich Chemie, Freie Universität Berlin, D-1000 Berlin 33 (Dahlem), Germany.

In a series of x-ray investigations on small cyclic ethers we have previously reported on structures with ring size n=5 (tetrahydrofuran, Luger & Buschmann, Angew. Chem. 22 (1983) 410) and n=6 (dioxane, Buschmann, Luger and Müller, ECM-8, abstract collection, Liège, 1983).

Oxetane (n=4) was crystallized on the x-ray diffractometer at a temperature below 174 K, space group orthorhombic Pnam, 4 molecules per cell. Structure determination revealed the ring molecule (Fig. 1) as lying on the mirror plane with an angle of pucker of 8°.

The first phase of oxepane (n=7) below the melting point is plastic having cubic crystal symmetry (space group P43n (most probably)). We were able to obtain good single crystals of the second (ordered) phase below the transition point at 175 K. For this phase the lattice is monoclinic, space group C2/m, 4 molecules per cell. Threedimensional x-ray intensity data were measured; structure determination is in progress.

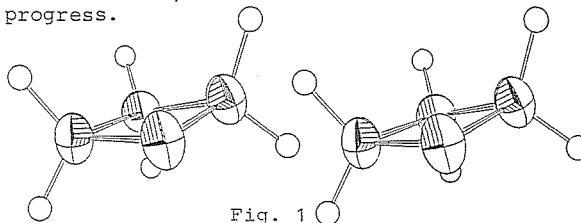


Fig. 1

09.2-29 THE LOW AND HIGH TEMPERATURE PHASES OF TRIS(ETHYLENE TEREPHTHALATE). By R.H. Vyas, Preston Polytechnic, Preston and C.J.E. Kempster, UMIST, Manchester, England.

Tris(Ethylene Terephthalate) is an oligomer of polyethylene terephthalate with two phases, first reported by Binns, Frost, Smith & Yeadon [Polymer (1966) 7, 583]: a low temperature phase (LTP) stable below 80°C and a high temperature phase (HTP) stable from 80°C to the melting point (320°C). The crystal structures have been determined by X-ray diffraction, confirming the structural formula $[-O.O.C_6H_4.COOCH_2.CH_2-]_3$.

The LTP structure is monoclinic, space group Cc, with $a=16.87(3)\text{Å}$, $b=19.56(2)\text{Å}$, $c=8.54(5)\text{Å}$, $\beta=96.24(3)^\circ$, $Z=4$, $D(\text{meas})=1.375$, $D(\text{calc})=1.370 \text{ g cm}^{-3}$.

The HTP crystals, grown from Dekalin solution above 120°C, were hexagonal in shape. The structure is hexagonal, space group P6₁, with

$$a=15.37(1)\text{Å}, c=20.78(5)\text{Å}, Z=6, \quad -3 \\ D(\text{meas})=1.322, C(\text{calc})=1.358 \text{ g cm}^{-3}.$$

The structures were refined to R-factors of 0.097 and 0.149 from Weissenberg data. The molecular conformations in the two phases are similar: the double-bonded oxygens point outwards and the glycol residue links are in 'gauche' conformation, disordered in the HTP between two possible configurations for each link.

The trimer molecules in the LTP structure are associated in pairs, stacked in columns parallel to the c-axis. In the HTP structure the molecules are arranged in six-fold helical stacks meshing with neighbouring stacks. The benzene rings are closely associated in the c-direction, while the glycol residue links are in more open regions of the structure, enabling their disorder to be more easily accommodated.