09.2–27 STRUCTURAL PROPERTIES OF MODIFIED 8-CYCLODEXTRINS: per-2,6-O-METHYL DERIVATIVES
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8-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-8-CD, 1). This derivative displays surprisingly different physical properties from the parent. For example, it is approximately an order of magnitude more soluble in cold water (a negative thermal solubility coefficient) whereas the parent displays increased solubility at elevated temperature. Also in contrast to the parent cyclodextrin, 1 is not expected to hydrogen bond in place of the hydroxyl groups of the parent.

These observations have prompted us to examine the structures of a number of crystals containing 1. For example, it is approximately an order of magnitude more soluble in cold water even though it contains 14 ether moieties per molecule. 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, 1 is not expected to hydrogen bond in place of the hydroxyl groups of the parent.

We report a crystal structure determination for 1 crystallized from hot water, 1a, from cold water, 1b, and in an inclusion complex with meta- cresoleacetate (phenylester substrate), 1c. A data set for what is apparently is a second (ordered) phase below the melting point at 175 K. For this phase the lattice is monoclinic, space group P21/n, 4 molecules per cell. Structure determination revealed the structure the molecules are arranged in six pairs, stacked in columns parallel to the c-axis. In the crystal 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.

09.2–28 THE OXEPANE AND OXEPANE X-RAY STRUCTURES.
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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, ECH-8, abstract collection, Liège, 1983).

Oxepane (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 puckering of 8°.

The first phase of oxepane (n=7) below the melting point is plastic having cubic crystal symmetry (space group Pm3n (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. Three-dimensional x-ray intensity data were measured; structure determination is in progress.

The crystal structure models are still under refinement. A rough model for 1d has been determined and will be refined with the full low temperature data set.