06-Crystallography of Organic Compounds

There are the following intramolecular hydrogen bonds (including weak interactions) in crystals of I and II:

- (I) C1 - H11B ... O221 2.070(3)Å 143.6(3)°
- (II) C1 - H11B ... O421 2.09(2)Å 155.0(1)°
- (I) C1 - H11C ... O221 1.947(3)Å 171.6(4)°
- (II) O1 - H11B ... N11 2.695(3)Å 107.5(4)°
- (II) O1 - H11C ... S22 2.721(3)Å 143.0(4)°

06.03 - Molecular Recognition, Chirality

**PS-06.03.01 DEHYDRATION OF β-CYCLODEXTRIN-HEXAHYDRATE AT DIFFERENT AMBIENT HUMIDITIES.**

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Crystalline β-cyclodextrin hydrate is an important model system to explore structural and dynamic properties of inclusion complexes and of hydrogen bond networks. Even though it was early known that the substance suffers some dehydration at ambient conditions, this was never quantitatively described. Only recently, an X-ray crystal structure analysis showed that the dehydration does not affect the crystalline order, and it is completely reversible (Steiner, Th., Koelner, G., Ali, S., Zakin, D. & Saenger, W. Biochim. Biophys. Res. Commun., 1992; 188, 1060-1066).

To quantify these observations, crystal structural analyses were performed on β-CD hydrate at five atmospheric humidities between 15% and 100%. To obtain defined and constant humidities, crystals were sealed in capillaries together with various saturated aqueous salt solutions. The unit cell volume continuously decreases with decreasing humidity, with no sign of a phase transition. Preliminary results of the structure analyses indicate that the water content continuously decreases from ~ β-CD - 12 H2O to ~ β-CD - 10 H2O in the chosen humidity range. The location of the water sites does not change upon the dehydration, but the occupancies gradually lower. This mainly affects the water molecules that are enclosed in the β-CD cavity.

**PS-06.03.02 CRYSTAL AND MOLECULAR STRUCTURES OF TWO DIESTEROISOMERIC 2-HENZENESULFONYLAMINO-N02-(ISOxoXYNYL)BENZENESULFONAMIDES.**

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The structures and configurations of two disteroisomers of the title compound were determined. The compounds were synthesized by O. Szmolakowicz and B. Szczepaniak at the Pharmaceutical Research Institute in Warsaw and crystallized in the orthorhombic space group P212121 with Z = 4. The lattice constants are:

| compound | a(Å) | b(Å) | c(Å) | used
|----------|------|------|------|------|
| II       | 7.854(2) | 11.394(2) | 19.500(4) | CuKα
| II       | 7.821(2) | 11.397(2) | 19.504(4) | MoKα

X-ray data were collected on a KM-4 diffractometer for compound I and on a P3 STEDUS diffractometer for compound II. The structures were solved by direct methods and refined by full-matrix least-squares using SHELXL-PC. The final R factors were:

| compound | R | GOF | Observed reflections with F > 4σ(F)
|----------|---|-----|---------------------------------|
| I        | 0.0254 | 0.043 | 1.36 | 1686
| II       | 0.0249 | 0.045 | 1.61 | 1623

The configuration of (I) is (S)(C), (S)(C) and for compound (II) (S)(C), (S)(C).

06.03.03 CYCLODEXTRIN HYDRATES CONTINUE TO GIVE INSIGHT INTO O-H...O AND C-H...O HYDROGEN BONDING.

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In our laboratory, cyclodextrin complexes are used as a biologically relevant model system for general studies of hydrogen bonding. In particular, a series of neutron diffraction studies was performed over a period of over 10 years (1 and references therein). As an ensemble, these neutron studies supply accurate structure data for analysis of various hydrogen bond properties, which were not considered in the original publications. Some of the recent results, which also show the unique power of high resolution neutron diffraction, are briefly summarized (further related studies are in progress).

Due to the high density of O-H...O and C-H...O donor and acceptor groups, the cyclodextrins hydrates exhibit an exceptionally high number of three-center hydrogen bonds and also of short O-H...H-O contacts. The numerous three-center bonds give the possibility to observe a lengthening of the bonding O-H bond due to long-distance H...O interactions (H...O > 2.5 Å). This is not possible with 'normal' two-center bonds, which are usually longer than 2.5 Å. From the O-H...O contacts, the shortest possible H...H approach (van der Waals distance) in core-hygroscopic hydrogen bonds could be determined.

Only recently, it became clear that the cyclodextrin (and also the carbohydrates in general) absorbed C-H...O hydrogen bonds (1). In cyclodextrins, in less than 70% of all C-H groups form such interactions with H...O < 2.7 Å; the shortest H...O separations are slightly below 2.3 Å. Numerous types of intra- and intermolecular O-H...O hydrogen bonds could be classified, of particular interest are the guest C-H...O interactions.


06.03.04 RESONANCE ASSISTED HYDROGEN BONDS BETWEEN OXIME AND CARBOXYL GROUP. THE COMPARISON OF TETRAMERIC STRUCTURES OF 4-METHYL-2-OXOPANTANOIC ACID OXIME AND LEVULINIC ACID OXIME.


Several structures of compounds containing both carboxyl and oxime groups have been studied (Pandamabalan, Paul, Curin, 1989; Maurin, Paul, Curin, 1992-93, 1995). All of them consist of infinite polar chains of molecules held together by pairs of strong intramolecular hydrogen bonds O-H...O and N-H...O between carboxyl and oxime groups. This leads to tail arrangement of molecules suggested the strong-priority of oxime-carboxyl interaction comparing to the usual antiparallelism oxime-oxime or carboxyl-carboxyl hydrogen bonds. What was also proved by the studies on the reaction between benzoic acid and acetylperoxide oxime in solid state and solutions.