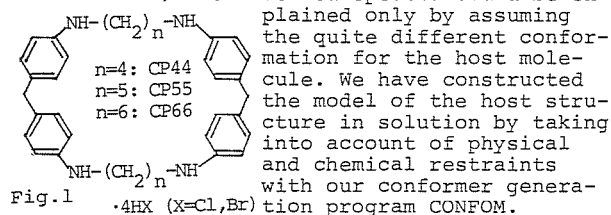


04.5-6 THE STRUCTURAL STUDY ON POLYMERIC INCLUSION COMPOUND, MONOSUBSTITUTED  $\beta$ -CYCLODEXTRIN. By K. Hirotsu, S. Kamitori and T. Higuchi, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan.

In order to clear the molecular interaction (host-guest interaction) of monosubstituted  $\beta$ -cyclodextrin compounds, with a mimic of enzyme, structures of them have been crystallographically studied. We present the results in the cases of 6-deoxy-6-(tert-butylthio)- (I), 6-deoxy-6-(neopentylthio)- (II), and 6-deoxy-6-(phenylthio)- $\beta$ -cyclodextrin (III). (I): orthorhombic, space group  $P2_12_12_1$ , (II): orthorhombic,  $P2_12_12_1$ , (III): tetragonal,  $P4_12_12_1$ . Intensity data was collected at  $-100^\circ\text{C}$  for (I), at room temperature for (II) and (III) respectively, by using a crystal sealed together with its mother liquor in a glass tube. The structures were solved by the rotation function, R maps, and rigid-body least-squares methods. In the lattice of each  $\beta$ -cyclodextrin derivative, molecules are located around the  $2_1$  screw axis for (I) (Hirotsu, Higuchi et al., J. Org. Chem. (1982) 47, 1143) and (II) and the  $4_1$  screw axis for (III) respectively, and thus they make a column structure. Molecules are kept with several hydrogen bonds and van der Waals contacts to give an interesting polymeric structure where the substituent group (guest) is intermolecularly included in the hydrophobic cavity of the neighbor cyclodextrin moiety (host).

04.5-7 THE STRUCTURES OF THE PARACYCLOPHANE HOST-GUEST INCLUSION COMPOUNDS WITH VARIOUS RING SIZES. by A. Itai, N. Tomioka, Y. Kato, Y. Ikeda, K. Odashima, K. Koga and Y. Iitaka, Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Tokyo, Japan.

The water-soluble paracyclophane with different ring size ( $n=4,5$  and  $6$  in Fig.1) include various aromatic compounds to form stable complexes in the solid as well as in solution. We have elucidated the crystal structures of six complexes and four guest-free paracyclophanes. The guest molecules are included in the cavity of the host molecules adopting the 'face conformation' with the four benzene rings facing each other. The complexes seem to be stabilized mainly by the hydrophobic interactions. In some cases, the structures suggested by nmr spectra do not agree with those obtained by X-ray. This tempted us to determine the inclusion structure in solution by means of the energy calculation and nmr data. The chemical shift of the guest hydrogens are shifted by the relative position to the benzene rings of the host. A fairly good agreement between the observed and calculated values assuming the host structures in the crystal was obtained for the CP44 complexes. But for the CP55, the observed spectra could be explained only by assuming



the quite different conformation for the host molecule. We have constructed the model of the host structure in solution by taking into account of physical and chemical restraints with our conformer generation program CONFOM.

04.5-8 THE VAN DER WAALS RADIUS OF THE SULFUR ATOM. By D. Brodalla and D. Mootz, Institute for Inorganic and Structural Chemistry, University of Düsseldorf, D-4000 Düsseldorf, Germany.

As part of our studies on phase relations and crystal structures at low temperatures we investigated the variety of intermediate solid phases formed in quasi-binary systems with hydrogen sulfide (D. Brodalla, Dissertation, Universität Düsseldorf 1983). Crystal structure determinations, also of the respective other components, yielded new aspects for the assessment of molecular interactions.

Comparative studies of the crystal structures of carbon disulfide, carbon sulfide selenide and carbon diselenide, together with an examination of the hydrogen atom position in thiophenol and metathioiboric acid, show intermolecular S...S interactions of the charge transfer or electron donor acceptor (EDA) type which with characteristic directional properties of their own compete with and can dominate over S-H...S hydrogen bonding of SH groups. Consideration of such intermolecular forces leads to a new and probably more accurate value of the van der Waals radius of the sulfur atom of 195 pm, instead of the previous value of 185 pm. (At 202 pm the radius of selenium was largely confirmed.)

The intermolecular S...S separations of EDA or charge transfer interactions are smaller than 370 pm (e.g. 365 pm in the case of thiophenol at 173 K). The strongest intermolecular S-H...S hydrogen bonds which are known up to the present have S...S separations of 375 pm to 384 pm (B. Krebs, Angew. Chem. (1983) 95, 113). In contrast, intermolecular separations between sulfur atoms are in the range 386 - 396 pm, when no special type of bonding forces occur and steric factors can be largely neglected. In structures previously used to determine van der Waals radii such interactions or steric influences could not always be excluded.

04.5-9 LOCATION OF TAILOR-MADE ADDITIVES IN THE CRYSTAL AND THEIR EFFECT ON CRYSTAL HABIT; A STUDY ON THE HOST / ADDITIVE SYSTEM L ASPARAGINE  $\text{H}_2\text{O}$  / L ASPARTIC ACID. J.L. Wang, Z. Berkovitch-Yellin, L. Leiserowitz, Structural Chemistry Dept., Weizmann Inst. of Science, Rehovot, 76 100, Israel.

The crystals of L asparagine  $\text{H}_2\text{O}$  (ASN) undergo a dramatic change in morphology when crystallized in the presence of the additive L aspartic acid (ASP). The change was explained in terms of a two stage mechanism of adsorption of ASP on {010} faces of ASN and retardation of growth of these faces due to a replacement, at the site of the additive, of an NH...O bond by an O...O repulsion (L. Addadi, Z. Berkovitch-Yellin, N. Domb, E. Gati, M. Lahav and L. Leiserowitz, Nature (1982) 296, 21-26). Up to 15% ASP may be occluded in the crystal of ASN. To explain the change in morphology it was necessary to locate the occluded ASP. The ambiguity in position of the hydrogen atom arises from the possibility that the carboxyl group may adopt either a syn- or anti-planar O=C-OH conformation.

We undertook a low temperature ( $-170^\circ\text{C}$ ) X-ray structure analyses of pure ASN and of the solid solution 85:15 ASN/ASP. The results of these analyses indicated a syn planar conformation of occluded ASP which is compatible with the proposed mechanism.