04.5-6 The Structural Study on Polymeric Inclusion Compound, Monosubstituted β-Cyclo-dextrin. By Y. Hirotsu, K. Kato and K. Odashima, Faculty of Pharmaceutical Sciences, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan.

In order to clear the molecular interaction (host-guest interaction) of monosubstituted β-cyclo-dextrin 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)-(1), 6-deoxy-6-(n-octylthio)-(1'), 6-deoxy-6-(phenylthio)-β-cyclo-dextrin (III). (I): orthorhombic, space group P2_12_12 (I); orthorhombic, P2_12_12 (II); tetragonal, P4_2_2 (III). Intensity data was collected at -100°C for (I), at room temperature for (II) and (III) respectively. Analysis of these data suggest that the structures of complexes and free-paracyclophanes are different. The chemical shift of the guest hydrogens are shifted by the relative position of the guest molecules are included in the cavity of the host molecules adopting the 'face conformation'. In some cases, the structures suggested by NMR spectra and X-ray data are in poor agreement, we consider these as the result of the crystallographic determination, also of the respective other components, yielded new aspects for the assessment of molecular interactions.

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, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan.

The water-soluble paracyclophanes with different ring sizes (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 in 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 X-ray data do not agree with those obtained by NMR. 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 chemical shifts suggests that the inclusion structure in solution is similar to the crystal structure of one of the complexes.

04.5-8 The Van der Waals Radius of the Sulfur Atom. By D. Brodda and D. Hofft, 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. Brodda, 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 disulfide selenide and carbon diselenide, together with an examination of the hydrogen atom position in thiophenol and methathioboric acid, show intermolecular S-S interactions of the charge transfer or electron donor acceptor (EDA) type which with characteristic direction 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 190 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 internal S···H hydrogen bonds which are known up to the present have S-S separations of 375 pm to 384 pm (B. Kooze, Angew. Chem. 1982, 95, 113). In contrast, intermolecular separations between sulfur atoms 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 H2O / L-Aspartic Acid. By J. L. Wang, Z. Berkovitch-Yellin, L. Leiserowitz, Structural Chemistry Dept., Weizmann Inst. of Science, Rehovot, 76100, Israel.

The crystals of L asparagine H2O (ASN) undergo a dramatic change in morphology when crystallized in the presence of the additive L-aspartic acid (ASP). This was explained in terms of a two stage mechanism of sorption 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. Dorn, E. Gat, M. Labav and L. Leiserowitz, Nature 1983, 306, 21-26). Up to 15% ASP may be occluded in the crystal of ASP. 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-0H conformation. We undertook a low temperature (-170°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.