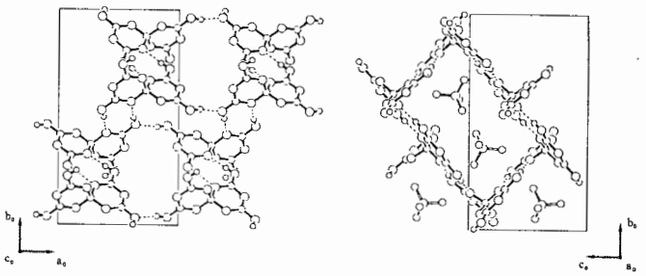

a) b)

Figure 1 : Parts of the structure of $NMe_4[B_5O_6(OH)_4]0.25\ H_2O$ (SG $P2_1/c$; a_0=9.268, b_0=16.759, c_0=9.194, β=95.94), Z=2.
a) view ∥ [001] without guest species **b**) view ∥ [100] without water molecules C-hydrogen atoms are omitted for clearness.

On the other hand, the three-dimensional networks of the inclusion compounds
$NHEt_3[B_5O_6(OH)_4][B(OH)_3]$ and
$NR_4[B_5O_6(OH)_4][B(OH)_3]_2$
with the guest cations $N(n\text{-}Pr)_4^+$ and $N(n\text{-}Bu)_4^+$ are built up of pentaborate ions and boric acid molecules. In the latter two compounds with isotypic host frameworks the pentaborate ions by themselves form a distorted diamond structure.
Indeed, the spirocyclic pentaborate ion with its four terminal OH groups being arranged at the corners of an elongated tetrahedron constituts a kind of "tetrahedral building unit", and thus resembles tetrafunctionalized molecules such as adamantane-1,3,5,7-tetra-carboxylic acid and some derivaties (1) or some rigid pyridones (2) which crystallize with hydrogen-bonded "diamandoid" network structures capable to guest inclusion and/or self-inclusion i.e. interpenetration.
For comparison each phase of the dimorphic anhydrous borate $K[B_5O_8]$ (3) occurs with two interpenetrating diamond-like networks of "condensed" i. e. covalently bonded $[B_5O_8]^-$ units that possess the same spirocyclic constitution as revealed in the hydrous pentaborate ions of the above given compounds.
More experimental details are given in (4).

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(3) J. KROGH-MOE, Acta Crystallogr. **B28**, 168 (1972)
(4) M.WIEBCKE, C.C.CLEMENS, J.FELSCHE, G.ENGELHARDT, Z.Naturforsch.B (1993) submitted

PS-06.03.10 THE NOVEL HYDRATION PROPERTIES OF U-54,494E($C_{18}H_{23}N_2OCl_2$ * Cl· * 1.5(H_2O)). F.Han.The Upjohn Company, Kalamazoo, MI 49001, USA.

The single crystal structure of U-54,494E (cis-3, 4-dichloro-N-methyl-N-[2(1-pyrrolidinyl)cyclohexyl]benzamide, monohydrochloride), the monohydrochloride salt of an anticonvulsant/antiseizure agent discovered in CNS Diseases Research, has been solved crystallographically in both hydrated and de-hydrated forms. The hydrated form contains two molecules in the asymmetric unit, space group $P2_1/c$, with the following cell parameters: *a=6.74Å, b=38.64Å, c=15.62Å and* β*=90.0°*. Three solvent water molecules were found in the asymmetric unit, displaying strong hydrogen bonds to each other and between cells to form infinite water chains. The drug molecules form channels for these water chains, however no hydrogen bonds exist between the drug molecules and the water molecules. The chloride ions appear to be acceptors for a single hydrogen bond. After heating the crystal, to obtain the dehydrated crystal form, a second X-ray data set was collected. It contains cell constants of *a=6.73Å, b=36.26Å, c=15.84Å* and β*=89.55°*. It is similar to the hydrated form except the *b*-axis has decreased by about *2.38Å*.

Although the cell parameters of the two structures are similar, the change in molecule packing is dramatic : the relative position between molecules in the *a* and *b* direction are almost the same. The largest shift occurs between molecular layers along the *c* direction. If one considering the unit cell being divided into a left part ($0.0 \le y < 0.5$) and a right part ($0.5 \le y < 1.0$), the movement during hydration procedure seems to occur as : the left part shifts 1/4 (≈ 3.9Å) along the *c* axis in one direction and the right part shifting also 1/4 along *c* axis in the opposite direction. The total relative position change is about 7.8Å. These shifts collapse the water channel in the center of the cell and allow the *b* axis to decrease. All of this movement occurs in the solid state of the compound. These results help explain the behavior of the solvent channels. We suggest that the weak interaction between molecular layers is the key to these unusual solid-state hydration characteristics of U-54,494E.

PS-06.03.11
DISORDER IN THIOUREA/SELENOUREA INCLUSION COMPOUNDS.

By B. C. Taverner* & D. C. Levendis, Department of Chemistry, University of the Witwatersrand, South Africa.

Using chiral and racemic camphor and dione as guest molecules and thiourea and selenourea as hosts, a set of isostructural crystals were prepared. All were trigonal with unit cell parameters close to those of the adamantane complex (a,b=16.187(7)Å & c=12.578(7)Å for thiourea), and all had the apparent symmetry of space group $R\bar{3}c$. The guest molecules are included in channels composed of six parallel hydrogen bonded chains of host molecules. They are orientationally disordered and therefor, despite low molecular symmetry, lie on a three fold axis. The length of the a and b axes as well as the volume of the unit cell is directly dependant on the steric size of the host. The c axis, however, varies little. A small reduction in crystallographic symmetry has been observed and appears to be due to interaction between the chiral guests and host chains reducing the level of disorder.

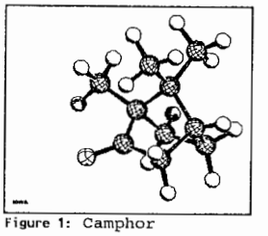

Figure 1: Camphor

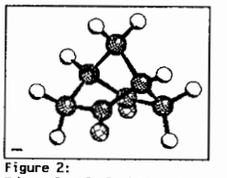

Figure 2:
Bicyclo[2.2.1]hepta-2,5-dione

PS-06.03.12 STRUCTURES OF 1,6,7,8-TETRAPHENYL(3,4-BENZO)BICYCLO[4.2.0]OCT-7-ENE AND ITS MOLECULAR COMPLEX WITH *cis,cis*-1,2,3,4-TETRAPHENYLBUTADIENE. By Yao Xin-kan*, Wang Ruji, Wang Honggen, Huan Zhenwei and Liu Weiguo, Central Laboratory and Department of Chemistry, Nankai University, Tianjin, 300071, China

1,6,7,8-Tetraphenyl(3,4-benzo)bicyclo[4,2,0]oct-7-ene (A), $C_{36}H_{28}$, Mr=460.62, triclinic, P-1, a=10.228(3), b=11.715(3), c=13.218(3) Å, α=65.99(2), ß=76.22(2), r=62.54(2)°, Z=2, D_c=1.194 g/cm³, room temperature, R=0.034, Rw=Q.034 (unit weights for all observed reflections) for 2131 independent observed reflections (I>3σ(I)). *cis,cis*-1,2,3,4-Tetraphenylbutadiene(B)(see I.L. Karle and K.S.Dragonette, *Acta Cryst.*, 19, 500-503,(1965)). The molecular compound A_2B $C_{100}H_{78}$, *Mr*=1279.74,

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monoclinic, $P2_1/a$, a=17.282(3), b=10.669(4), c=19.927 (3) Å, ß=102.99(1)°, Z=2, D_c=1.187 g/cm³, room temperature, R=0.084, R_w=0.086 (unit weights for all observed reflecions) for 1255 independent observed reflections ($I>3\sigma(I)$).

A cyclohexane solution of the mixture of A and B in molar ratio 1:1 was prepared. The single crystal A_2B were obtained by slowly evaporating the solution at room temperatutre in two weeks. The structure was solved by direct methods. All of hydrogens were found in subsequent differential Fourier maps.

Molecular complex crystals which have been known for a long time, are composed of two or more distinct species that are arranged, not in statistical disorder, but in mutually identical positions in all cells in the crystal. In general, the formation of a molecular complex is due to the fact that the packing of a biomolecular crystal comes out to have a better density than the packing of its components, or most frequently, the molecules are capable of producing hydrogen bonds (A.I. Kitaigorodsky, "*Molecular Crystals and Molecules*", volume 29 of "*PHYSICAL CHEMISTRY*", ACADEMIC PRESS New York and London,121-130, (1973)). But this is not the case with the A_2B crystal. There is no the possibility of producing hydrogen bonds in A_2B crystal. The calculated densities of A_2B, A and B crystals are 1.187, 1.194 and 1.191 g/cm³, respectively. That is to say, The crystal A_2B, at least, has no better density. The packing energies (kcal/mol), however, by calculating with "OPEC" program are -68.251 (B), -72.902 (A), and -198.454 (A_2B corrected value). The value of A_2B is the lowest when compared with ones of the pure A crystals and the pure B crystals. Maybe, that is why only A_2B was formed from the mixture solution of A and B with the molar ratio 1:1.

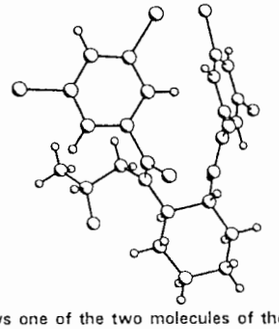
The bond lengths, angles and conformation of A in A_2B crystal are similar to those of A in pure A crystal, and the bond lengths and angles of B in A_2B crystal are similar to those of B in pure B crystal, it is noteworthy that the conformations of B in A_2B and pure B crystals are different. The phenyl rings in the terminals of butadiene chain and the C=C double bond plane are almost located in the same plane (dihedral angle 1.8°), the phenyl rings in the butadiene chain are nearly perpendicular to the C=C double bond plane (dihedral angle 85.7°). The corresponding dihedral angles in the pure B crystal are 33.1° and 74.1°, respectively. Another salient feature of A_2B crystal is the "extra long" C-C single bond length (1.63(1)Å) between the bridge-head carbon atoms of the molecule A component, which is comparable to those of Dewar benzene (1.63Å) (M. J. Cardillo and S. H. Bauer, *J. Am. Chem. Soc.*, **92**, 2399 (1970) and derivatives of bis-norcaradiene (1.622 -1.85Å) M. Pierrot and J. Estienne, "Structure and Properties of Molecular Crystals", edited by M. Pierrot, Elsevier Science Publishers B. V., pp. 51-55, (1990)). We thank Professor Xu Xiaojie (Department of Chemistry, Beijing University) for his help in calculating with "OPEC" program.

PS-06.03.13 X-RAY CRYSTAL STRUCTURE OF A SYNTHETIC CHIRAL "SELECTOR" DERIVED FROM 1R,2R-DIAMINOCYCLOEXANE by °*Cirilli M., §Cirilli R., §Gasparrini F., °Gavuzzo E., §Villani C. from §Dipartimento Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Università La Sapienza, P.le A. Moro 5,Roma and °Istituto di Strutturistica Chimica-CNR, Via Salaria Km. 29.400, Roma.

Only recently the right sort of emphasis has been placed on consequences of stereochemistry in biological processes and therefore on the problem of separating enantiomers. The direct chromatographic separation of enantiomers represent an additional tool for solving stereochemical problems. This technique is based on the preferential interaction of one enantiomer of a raceme compound with a chiral discriminating agent (*selector*) immobilized on an inert support. Proteins, polysaccharides, cyclodextrins, synthetic polymers as well as small, synthetic molecules are generally used as *selector*, frequently bonded to silica micro particles. We have recently developed a family of new chiral stationary phases (CSPs) for HPLC applications, based on different derivatives of (R,R)-1,2-diaminocyclohexane (DACH). One of these CSPs containing the N,N'-(3,5-dichlorobenzoyl) derivative of (R,R)-1,2-DACH, is particularly effective in the separation of the enantiomers of a large number of 1,2-aminoalcohols (pharmacologically active as β-blockers) in the form of oxazolidin-2-ones. It has been shown that the knowledge of the recognition mechanism underlying such separations can lead to the design of improved CSPs. In this respect we are now investigating the origin of the stereo selective interactions between a soluble model of CSP and the enantiomers of a Propranolol by a combination of physicochemical techniques (1D and 2D NMR, FT-IR, UV and CD spectroscopy, X-ray crystallography) with computational methods.

Aims of these investigations are: 1) structural determinations on the isolated species (in solution, in the solid state and "in vacuo" by MM calculations); 2) structural determinations on the interacting species (in solution, in the solid state, "in vacuo" by MM calculations through automatic docking procedures). Here we show some preliminary results on the solid state structure of the *selector*.

The *selector* was crystallized from chloroform. The space group is $P2_12_12_1$,the cell axis are a=20.71Å, b=21.05Å, c=11.40Å and V=4970.68Å³ with Z=8. The data were collected at room temperature by a rotating anode Rigaku AFC5R equipped with a four circle diffractometer from Molecular Structure Corporation. The structure was solved by direct methods with the program SIR92 and anisotropically refined to a final R of 4.8% for 2637 reflections with $I>3\sigma(I)$.



The figure shows one of the two molecules of the *selector* contained in the asymmetric unit held togheter by two intermolecular hydrogen bonds.

PS-06.03.14 RENTGENOGRAPHIC AND SPECTROSCOPIC STUDIES OF THE DIFFERENT CRYSTALLINE FORMS OF BIS(1,2:3,4-DIISOPROPYLIDENO-GALACTOPYRANOZO-6-O,6-O'-TIOPHOSPHORYL) DISULFIDE $C_{48}H_{78}O_{24}P_2S_4$. By M.W. Wieczorek[*1], J. Błaszczyk[1], M.J. Potrzebowski[1], P. Knopik[2], [1]Technical University of Łódź, Institute of Technical Biochemistry, Stefanowskiego 4/10, 90-924 Łódź, Poland; [2]Polish Academy of Sciences, Centre of Molecular & Macromolecular Studies, Sienkiewicza 112, 90-363 Łódź, Poland.

The crystal and molecular structures of three different crystalline forms of bis(1,2:3,4-diisopropylidenogalactopyranozo-6-O,6-O'-tiophosphoryl) disulfide (1a, 1b, & 1c) have been determined - Figure 1.

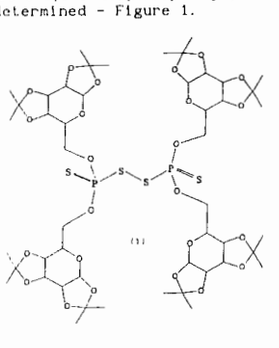


Fig 1 Bis(1,2:3,4-diisopropylidenogalactopyranozo-6-O,6-O'-tiophosphoryl) disulfide (1)
1a (1) · $2C_6H_6$
1b (1) · C_6H_6 · C_6H_{14}
1c (1) · $2CHCl_3$

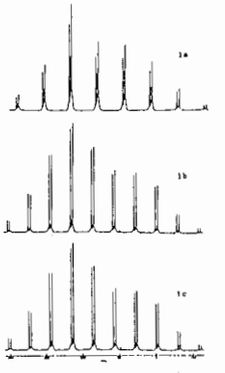


Fig 2 The ^{31}P CPMAS spectra of disulfides 1a,1b,1c