

## 06-Crystallography of Organic Compounds

The observation of only one diastereoisomer of **6** is noteworthy and indicates highly stereospecific character of the oxidation step. This observation may be of great significance and we plan to utilize compound **6** as a chiral precursor in the synthesis of natural products.

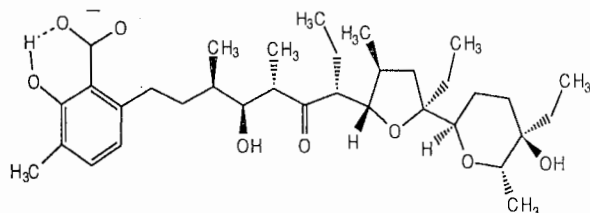
## References.

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 Czarnocki, Z. (1992) *J. Chem. Research (S)*, 334-335.  
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**PS-06.03.07** COMPLEXATION OF GUANIDINIUM AND AMIDIUM CATIONS WITH THE POLYETHER ANTIBIOTIC LASALOCID. Xiuqi Shui\*, Drake S. Eggleston, Nelson Troupe and John W. Westley, SmithKline Beecham Pharmaceuticals, Box 1539, King of Prussia, PA 19406, USA

Studies directed toward the complexation of guanidinium and amidinium groups by organizable recognition sites are expected to be of value for a number of reasons. Among these is the potential for crystallization of otherwise recalcitrant natural products and peptides. As one approach to that goal, complex formation with the highly crystalline naturally occurring ionophore lasalocid A, which has previously been shown to be of value in the complexation and resolution of asymmetric amines (Westley, Evans & Blount, 1977, *J. Am. Chem. Soc.* **99**, 6057-6061), has been investigated for a variety of target molecules. Circular dichroism studies in various polar and nonpolar solvents have confirmed complex formation and several complexes of general formula I have been crystallized. Details of these studies where R = various molecules incorporating guanidinium and amidinium groups and comparisons of the recognition motifs will be presented.

R<sup>+</sup>



**PS-06.03.08** CRYSTAL STRUCTURES OF CIS- $\alpha$ -NITROSTILBENE AND THE ADDUCT: TRANS-STILBENE. (CIS- $\alpha$ -NITROSTILBENE)<sub>2</sub>

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Crystal structure of *cis*- $\alpha$ -nitrostilbene (I) and that of *trans*-stilbene. (*cis*- $\alpha$ -nitrostilbene)<sub>2</sub> (II) have been determined by X-ray diffraction at room temperature.

## Crystal data:

I. formula: C<sub>14</sub>H<sub>11</sub>NO<sub>2</sub>  
 monoclinic, space group: P2<sub>1</sub>/n  
 a=5.839(2) b=16.034(4) c=24.851(5) Å  
 $\beta$ = 90.95(2)<sup>o</sup>  
 V=2326.3(9) Å<sup>3</sup> Z = 8 D<sub>x</sub> = 1.286 Mg/m<sup>3</sup>  
 R = 0.034 wR = 0.043

II. formula: C<sub>14</sub>H<sub>12</sub>·(C<sub>14</sub>H<sub>11</sub>NO<sub>2</sub>)<sub>2</sub>  
 monoclinic, space group: P2<sub>1</sub>/n  
 a=15.755(4) b=5.771(1) c=18.809(3) Å  
 $\beta$ = 101.84(2)<sup>o</sup>  
 V=1763.7(6) Å<sup>3</sup> Z = 2 D<sub>x</sub> = 1.251 Mg/m<sup>3</sup>  
 R = 0.045 wR = 0.050

The unit cell of I contains two independent molecules. The two molecules have similar bond lengths, bond angles and geometry. The nitro group is close to coplanar with the central C=C bond with the two phenyl rings twisted at about 70<sup>o</sup> and 30<sup>o</sup> from this plane. The central C=C bond length is 1.329(4) Å.

The unit cell of II contains one molecule of *cis*- $\alpha$ -nitrostilbene and half a molecule of *trans*-stilbene per asymmetric unit. The geometry, bond lengths and angles of the *cis*- $\alpha$ -nitrostilbene are close to those found in I. The central C=C bond length is 1.323(4) Å. The nitro group is close to coplanar with the C=C bond with the two phenyl rings twisted at 70<sup>o</sup> and 30<sup>o</sup>. The *trans*-stilbene molecule is planar with a central C=C bond length of 1.330(4) Å. The crystal is packed with the *trans*-stilbene molecules wedged between layers of molecules of *cis*- $\alpha$ -nitrostilbene. The efficient packing accounts for the stability of II.

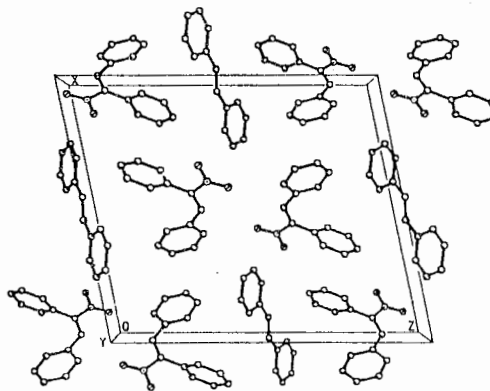


Fig. 1. Crystal packing of II.

**PS-06.03.09**

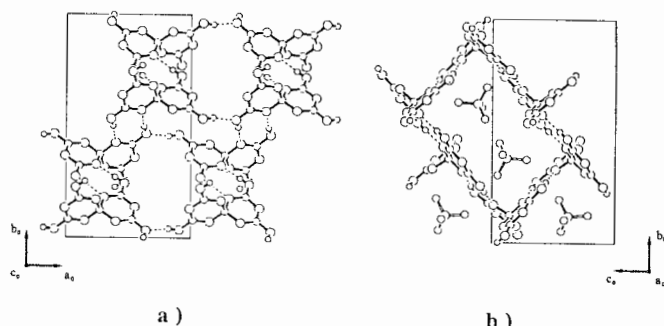
GUEST/HOST-COMPOUNDS WITH <sup>3</sup> NETWORKS OF HYDROGEN BONDED OLIGOMERIC BORATE ANIONS AND BORIC ACID MOLECULES

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The crystalline pentaborates NMe<sub>4</sub>[B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>]·0.25 H<sub>2</sub>O, NEt<sub>4</sub>[B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>], NPhMe<sub>3</sub>[B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>] and pipH[B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>] form a series of unique, closely related inclusion compounds with <sup>3</sup> host structures assembled by hydrogen-bonded pentaborate [B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>]<sup>-</sup> ions (Figure 1 a). The organic cations and water molecules occupy as guest species large straight channels of rectangular cross-section (Figure 1 b).

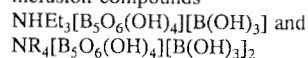
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**Figure 1:** Parts of the structure of  $\text{NMe}_4[\text{B}_5\text{O}_6(\text{OH})_4] \cdot 0.25 \text{H}_2\text{O}$  (SG  $P2_1/c$ ;  $a_0=9.268$ ,  $b_0=16.759$ ,  $c_0=9.194$ ,  $\beta=95.94$ ),  $Z=2$ .  
 a) view  $\parallel [001]$  without guest species b) view  $\parallel [100]$  without water molecules  
 C-hydrogen atoms are omitted for clearness.

On the other hand, the three-dimensional networks of the inclusion compounds



with the guest cations  $\text{N}(\text{n-Pr})_4^+$  and  $\text{N}(\text{n-Bu})_4^+$  are built up of pentaborate ions and boric acid molecules. In the latter two compounds with isotopic 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 constitutes a kind of "tetrahedral building unit", and thus resembles tetrafunctionalized molecules such as adamantane-1,3,5,7-tetracarboxylic acid and some derivatives (1) or some rigid pyridones (2) which crystallize with hydrogen-bonded "diamondoid" network structures capable to guest inclusion and/or self-inclusion i.e. interpenetration.

For comparison each phase of the dimorphic anhydrous borate  $\text{K}[\text{B}_5\text{O}_8]$  (3) occurs with two interpenetrating diamond-like networks of "condensed" i. e. covalently bonded  $[\text{B}_5\text{O}_8]$  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).

- (1) O. ERMER and L. LINDENBERG, *Helv. Chem. Acta* **74**, 825 (1991)
- (2) M. SIMARD, D. SU and J. D. WUEST, *J. Am. Chem. Soc.* **113**, 4696 (1991)
- (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** ( $\text{C}_{18}\text{H}_{23}\text{N}_2\text{OCl}_2 \cdot \text{Cl} \cdot 1.5(\text{H}_2\text{O})$ ). 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-pyrrolidiny)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:  $a=6.74\text{\AA}$ ,  $b=38.64\text{\AA}$ ,  $c=15.62\text{\AA}$  and  $\beta=90.0^\circ$ . 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  $a=6.73\text{\AA}$ ,  $b=36.26\text{\AA}$ ,  $c=15.84\text{\AA}$  and  $\beta=89.55^\circ$ . It is similar to the hydrated form except the  $b$ -axis has decreased by about  $2.38\text{\AA}$ .

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 ( $0.0 \leq y < 0.5$ ) and a right part ( $0.5 \leq y < 1.0$ ), the movement during hydration procedure seems to occur as: the left part shifts  $1/4$  ( $= 3.9\text{\AA}$ ) 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  $7.8\text{\AA}$ . 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 ( $a, b=16.187(7)\text{\AA}$  &  $c=12.578(7)\text{\AA}$  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 therefore, 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.

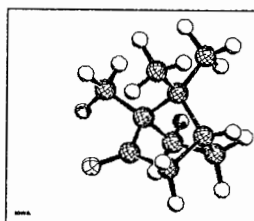


Figure 1: Camphor

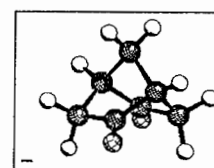


Figure 2: Bicyclo[2.2.1]hepta-2,5-dione

**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 Xinkan\*, 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),  $\text{C}_{36}\text{H}_{28}$ ,  $M_r=460.62$ , triclinic,  $P-1$ ,  $a=10.228(3)$ ,  $b=11.715(3)$ ,  $c=13.218(3)\text{\AA}$ ,  $\alpha=65.99(2)$ ,  $\beta=76.22(2)$ ,  $\gamma=62.54(2)^\circ$ ,  $Z=2$ ,  $D_c=1.194\text{ g/cm}^3$ , room temperature,  $R=0.034$ ,  $R_w=0.034$  (unit weights for all observed reflections) for 2131 independent observed reflections ( $I>3\sigma(I)$ ). *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  $\text{A}_2\text{B}$   $\text{C}_{100}\text{H}_{78}$ ,  $M_r=1279.74$ ,