

PS06.05.07 MOLECULAR TECTONICS. THREE-DIMENSIONAL ORGANIC NETWORKS WITH INORGANIC PROPERTIES, AN UPDATE. Michel Simard and James D. Wuest, Département de chimie, Université de Montréal, C.P. 6128, Succ. centre-ville, Montréal, Québec, H3C 3J7

Noncovalent interactions that are selective, directional, and strongly attractive can induce the self-assembly of predictable supramolecular aggregates. Tectons (from Greek, tekton, builder) of selected local symmetry, length and flexibility are used as simple assembly blocs of Lego type for construction of specialized networks.

Several diamantoid networks were crystallized and studied by X-ray diffraction technique in order to verify the self-assembly properties of those novel tectons. These structures have in common the formation of large chambers whose size and shape follow directly from that of the tecton subunits. The network's large cavities so obtained use self-filling by mutual concatenation of similar networks to minimized the empty space in these structures. Besides the large chambers, large channels remain occupied by solvent molecules.

Novel types of networks, derived from the diamantoid type, were also characterized. Several new two- and three-dimensional networks were crystallized by using tectonic subunits of locally different primary symmetry. By modification of the flexibility and/or the terminal group of the arms, new network types were promoted.

This communication will present an overview of the subject as well as our most recent works in this area.

- 1) M. Simard, D. Su & J.D. Wuest, J.A.C.S. **113**, 4696 (1991).
- 2) X. Wang, M. Simard & J.D. Wuest, J.A.C.S. **116**, 12119 (1994).
- 3) S. Borman, C&EN **73**, 21 (1995).
- 4) J.S Moore, Nature **374**, 495 (1995).

PS06.05.08 MOLECULAR CONFORMATION AND SUPRAMOLECULAR STRUCTURE OF CARBOSILANE, PRECURSOR OF LIQUID CRYSTALLINE PHASE. K. Yu. Suponitskii, T.V. Timofeeva, K.A. Lyssenko, N.N. Makarova Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Vavilov St., 28, 117813, Russia

Several years ago a series of dihydroxitetraalkyldisiloxanes has been studied by physical methods in order to find the structure-property relations for these compounds, which form thermotropic liquid crystalline phases. It was found that liquid crystalline properties are due to the formation of one-dimensional columnar hydrogen bonded associates in crystal and mesophase. These associates have pseudohexagonal packing in crystal and form mesophase with hexagonal type of columnar packing.

In order to find other compounds inclined to form mesophases of the same type we performed conformational calculations and molecular modeling of molecular associates of dihydroxycarbosilanes and dihydroxydisiloxanes. It was shown that conformational properties and associate formation for dihydroxycarbosilanes and dihydroxydisiloxanes is very close, but they are not the same for dihydroxydisiloxanes.

To support the close supramolecular structure of siloxane and carbosilane derivatives crystallization and X-ray analysis of dihydroxitetra-methylcarbosilane was performed. The one-dimensional columnar associate in this crystal was found to be nearly the same as for disiloxane. DSC and multitemperature powder X-ray data are discussed together with the data on single crystal structure.

PS06.05.10 X-RAY AND NEUTRON DIFFRACTION STUDY OF A CROWN ETHER - A CAUTIONARY TALE. R.H. Fenn, University of Portsmouth, S.A. Mason, ILL Grenoble, R.A. Palmer and B. Potter, Birkbeck College, London, O.S. Mills, P.M. Robinson and C.I.F. Watt, University of Manchester, UK

Beware all Ye who regard a diffractometer as a black box and do not appreciate the beauty of crystallography.

The compound $C_{24}H_{30}O_6 \cdot H_2O$ is a water-bound adduct of the tetragol crown ether 9,10-dihydro-, -10,10-dimethyl-, -9-hydroxyanthracene, which binds strongly with neutral molecules and can react to form covalent adducts bonded to the 9-carbon.

Diffractometry offered cell geometry which conformed extremely closely with an orthorhombic one-face-centred lattice. However the Laue symmetry was $2/m$ and spacegroup $P2_1$ with $Z = 4$ and two molecules, i.e. 126 atoms, per asymmetric unit. The primitive cell was related to the centred cell by choice of a diagonal along the ac face.

Meanwhile neutron diffraction data were being collected, at 15K, on D19 at ILL, Grenoble. Initially, difficulties were encountered in reconciling the calculated neutron structure factors, based on the atomic parameters from the X-ray monoclinic data, with the observed neutron structure amplitudes. However, there are two possible choices of diagonal which lead to very similar unit cell parameters as the original centred cell has essentially equal diagonals. Once the appropriate transformation of the reflexion indices from the neutron data to the X-ray cell had been applied, difference Fourier syntheses and isotropic least-squares refinement of the 504 parameters led to a R-factor of 5% for the neutron structure.

The structure of the crown adduct shows that the bound water molecule is held not only by a strong hydrogen bond to the 9-hydroxyl but also by two weaker bonds between the water hydroxyls and two oxygens of the crown which cause the water to point into the crown cavity.