

PS06.06.16 HIGHLY ORGANIZED MULTILAMELLAR STRUCTURES FORMED BY POLYELECTROLYTE NETWORK - SURFACTANT COMPLEXES. Yu. Khandurina, V. Rogacheva, A. Zezin, Polymer Chemistry Department, Moscow State University, Russia

The structure of polymer-surfactant complexes based on cross-linked polyelectrolytes and oppositely charged surfactants of various nature was studied by wide and small-angle X-ray and small-angle neutron scattering. Such complexes are formed as a result of interaction between slightly cross-linked highly swollen polyelectrolyte gel and surfactant in aqueous media. The transfer of surfactant ions into the network proceeds as a frontal heterogeneous cooperative reaction followed by the localized collapse of the initial gel and the formation of "core-shell" type systems, in which weakly swollen polymer-surfactant complex "shell" coexists with highly swollen surfactant free gel interior. The complexes contain equimolar amounts of surfactant ions and ionized polyelectrolyte units and are stabilized by both electrostatic and hydrophobic interactions.

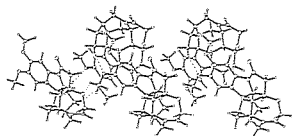
The X-ray diffraction data allow to represent the polyelectrolyte surfactant complex structure as a system of surfactant lamellas inserted into the oppositely charged network. The formation of these constructions occurs by the intergrowth of surfactant lamellas into the gel interior and is accompanied by a macroscopic orientation of multilamellar structure. Thus, the processes under investigation are closely related to selfassembly phenomena in complex macromolecular systems. The parameters of lamellas and internal lamellar structure of polycomplexes depend on the nature of polymer network and surfactant (aliphatic chain length and ionic group nature) and on the external conditions (temperature, pH, water content, etc.). Aliphatic surfactant radicals of the sufficient length produce a crystalline hexagonal packing inside lamellar aggregates.

Exotic Molecules-Organic

MS06.08.01 THE CRYSTAL CHEMISTRY OF ALKALOIDS, NATURE'S EXOTIC MOLECULES, Robert O. Gould, Chemistry Department, The University of Edinburgh, EDINBURGH EH9 3JJ. U.K

Alkaloids are natural products which have evolved in plants, normally for a defensive purpose. They are usually highly asymmetrical, and rather bizarre in appearance. In addition to at least one basic nitrogen centre, they contain a specific collection of functional groups spaced out to recognise and interact with particular receptors, often the proteins of the taste buds of would-be predators. Their high degree of selectivity extends to their tendency to co-crystallise with a range of other materials, usually the anions of acids. This property has been used for over 100 years in the resolution of enantiomeric substances. Many of the classical resolution crystals have yet to have crystal structures reported, and only a few attempts have been made to interpret structural differences between a pair of diastereomeric structures.

The talk will mainly concentrate on attempts to correlate the types of structure found in cocrystals of brucine, an alkaloid closely related to strychnine, and like it extracted from the seeds of plants of the *Strychnos* genus. This molecule is sufficiently large, that many of its crystals involve a significant amount of "selfrecognition", leading to the formation of layers with a relatively few surface topologies. The generally hydrophobic nature of the much of the molecule enables it to form a core, the surface of which is available for hydrophilic interactions. A ribbon structure, characteristic of several crystals containing brucine is shown in the figure.



MS06.08.02 UNUSUAL PRODUCTS IN THE PHOTOCHEMICAL REACTIONS OF DIBENZOBARRELENES. James Trotter & John R. Scheffer. Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada V6T 1Z1.

Photochemical reactions frequently give products with unusual molecular structures. Photolyses of derivatives of dibenzobarrelene (9,10-dihydro-9,10-ethenoanthracene) give two types of photoproduct: (i) dibenzosemi-bullvalenes, produced via the triplet excited state by the well-established di-pi-methane mechanism; (ii) dibenzocyclooctatetraenes (COTs), via the singlet excited state and a (2+2) intramolecular cycloaddition mechanism. Photolysis of a 9,10-dimethyl-11,12-dicarboxylate derivative in solution in acetone (a triplet sensitizer) gives the expected dibenzosemi-bullvalene photoproduct. In benzene solution a COT is formed, but this photoproduct has an abnormal substitution pattern which is not explicable in terms of a (2+2)-cycloaddition mechanism. In solid-state photolysis the major product is a new type, with a pentalene structure, which provides an important clue in deriving a mechanism for its formation, involving a pentalene-like biradical intermediate; this mechanism also accounts for the formation of the unexpected COT. Further studies indicate that derivatives with 3 or 4 substituents give abnormal COTs, while those with 2 substituents give (2+2)-cycloaddition COTs, so that the differences in behaviour probably result from differences in steric crowding. Derivatives with only one substituent give no COTs, but new hydrogen-abstraction products.

MS06.08.03 CUBANES: INTRA- AND SUPRA- MOLECULAR TRENDS. Richard Gilardi, Philip E. Eaton* and Raymond J. Butcher+. Naval Research Laboratory, Washington, DC 20375-5341; *Univ. of Chicago, Chicago, IL; and +Howard Univ., Washington, DC; all USA.

Large bond angle deformations in cubane make it a powerhouse of stored energy. Thus cubane might provide more powerful fuels, propellants, and explosives if its chemistry were mastered. The mere possibility of cubane itself was debated until it was made in 1964 and found to be a stable compound, with a shelf life of years. For ca. 20 years, few derivatives of cubane were known, but substitution methodology for cubanes has now been developed^{1,2}, and X-ray studies of many (>20) substituted cubanes have been reported & recently reviewed³. In 1994 and 1995, pentanitro-cubane, hexanitrocubane, and several octa-substituted cubanes were first made (at the Univ. of Chicago) and studied at NRL².

Surprisingly, the cubane framework is not rigid. Systematic deformations occur. Though saturated CC cube-edge bonds are usually longer (ave. 1.559Å) than those in unstrained compounds, they are shortened, for no apparent reason, when eclipsed with a nitro group or when fused to an imidazolidone ring. Bond angles are also distorted; the interior angles at a cube corner are all larger than 90° at a nitro group site, while at other corners in the same cube they are smaller. Similar effects are seen in alkynylcubanes⁴.

A pseudo-HCP packing was reported for cubane. Polycubanes and alkynyl-cubanes⁴ show a tendency to assemble in simple, perhaps predict-able, patterns (like 'stacked logs') that are hexagonal in one projection.

1. P.E. Eaton, et al, *J. Am. Chem. Soc.* 115, 10195-10202(1993).
2. R. Gilardi et al, *Angewandte Chemie*, (accepted, 1996).
3. R.J. Butcher, et al, *J. Chem. Crystall.* 25, 661-670(1995).
4. P.E. Eaton, et al, *J. Am. Chem. Soc.* 116, 7588-7596(1994).