

07-Crystallography of Organometallic and Coordination Compounds

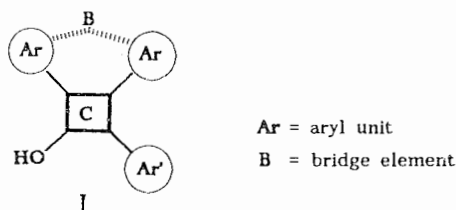
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07.01 -- Molecular Recognition and Inclusion Compounds

MS-07.01.01 NEW SUPRAMOLECULAR ARCHITECTURES: INCLUSION STRUCTURES, BINDING MODES, AND MOLECULAR RECOGNITION. By *Ingeborg Csöreg*,^{*} Department of Structural Chemistry, Arrhenius Laboratory, Stockholm University, Sweden, and *Edwin Weber*, Institut für Organische Chemie der Technischen Universität Bergakademie Freiberg/Sachs., Germany.

Engineering of supramolecular crystalline complexes is an important problem connected with the development of new technologies, including chemical sensor devices and non-linear optical materials. This involves specific interaction and orientation of molecules in particular aggregate patterns. Moreover, the possibility of studying the structural basis of molecular recognition and selectivity by using synthetic hosts as models for biological systems has provided an impetus for much of this research. X-ray diffraction studies may provide a clearer insight into the structural principles of non-covalent interactions being essential here.

In order to learn the rules which govern the interactions between groups of different molecules in different geometric environments, we have developed a new family of host molecules, represented by the general formula I.



This particular design involves a basic triaryl-methanol frame where two of the aryl residues are bridged, thus giving rise to a distinct molecular shape. The structural modifications include variation and substitution of the aryl groups and/or modification of the bridging unit, yielding the structures shown in Figure 1.

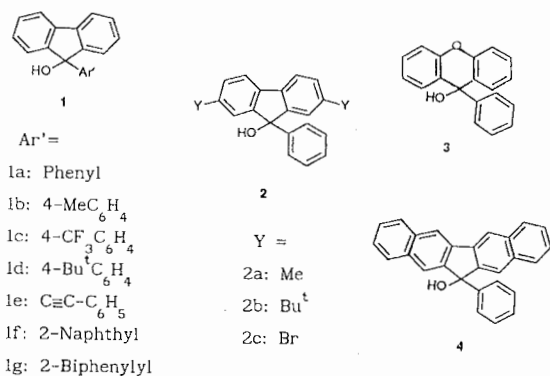


Figure 1.

These hosts form crystalline inclusions with a variety of uncharged organic molecules depending on their structural parameters. Crystal structures of selected inclusion compounds of hosts 1-4, in particular with alcohols and heterocycles, such as dioxane, thioxane, morpholine and piperidine as guests, and also of unsolvated hosts, will

be presented. Versatility in binding modes and packing relations, as well as general features in complexation and molecular recognition, will be discussed.

MS-07.01.02 INCLUSION PROPERTIES OF CALIXARENES, By G.D. Andreetti, Institute of Structural Chemistry, University of Parma, Viale delle Scienze, 43100 Parma, Italy

Calixarenes have received wide attention in recent years in the fields of inclusion chemistry and of molecular recognition (J. Vicens and V. Böhmer, *Calixarenes*, a versatile class of macrocyclic compounds, Kluwer Academic Pub., 1991). They offer good examples of intramolecular cavity complexes formed by neutral molecules and by ions. There are no reports of complex formation by n.m.r. studies and for such compounds the crystal structure analysis is the unique tool to show the topology and the nature of intermolecular and intramolecular interactions which drive their formation. An attempt has been made to correlate the molecular parameters concerning the cavity topology, size and substituent distribution with conformational preferences and complexing properties. Most of the results concern the description of the static structure of complexes and only recently some details have been collected with respect to the dynamic structure of solid state complexes obtained by neutron scattering (F. Uguzzoli, Neutron scattering studies on calixarenes, European meeting on substituted calixarenes, Belfast, 1991) The conformational preference in functionalized calixarenes will be discussed in connection with the requirements of the *cone* conformation in connection with the inclusion process. The calixarene based cation carriers and receptors will receive attention in relation to the applications of these compounds in sensors technology and in the discussion of Cram's complexation principles. Theoretical models for the host-guest interactions will be discussed and related to thermochemical measurements and to phase transitions studies.

MS-07.01.03 RELEVANCE OF X-RAY CRYSTALLOGRAPHIC RECOGNITION OF CLASSICAL AND NON-CLASSICAL HYDRIDES IN TRANSITION METAL COMPLEXES. By F.J. Lahoz, Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., 50009 Zaragoza, Spain.

Within the general field of organometallic and coordination chemistry the study of the structure and chemical reactivity of molecular transition metal hydrides (with *classical* M-H bonds) is an area of current great interest due to the capacity of these compounds to act as catalyst precursors or active intermediates in homogeneous catalytic processes. A significant discovery in this domain was made in 1984 when G.J. Kubas demonstrated the existence of coordinated molecular hydrogen in certain metal complexes. These η^2 -H₂ complexes, commonly referred as *non-classical hydrides*, opened up the possibility of obtaining a more detailed following of the oxidative addition of hydrogen to the metal, decisive step in many catalytic cycles and provided an opportunity of studying a new type of chemical bonding to metals (σ -bond complexes).

Current work in this area is leading to the preparation of a considerable number of complexes containing η^2 -H₂ ligands or where both type of ligands -*classical and non-classical hydrides*- are simultaneously present in the molecules. Although several spectroscopic techniques have been used to evidence the presence of both type of ligands, this information quite commonly results partial in the elucidation of the molecular structure of these compounds, making this assignment non-definitive.

Furthermore, the spatial localization of these hydrogen atoms results of crucial interest to understand or predict their interaction with reacting substrates or with the ancillary ligands of the complex and, eventually to suggest reasonable proposals for the catalytic mechanisms. This structural information is also important to get a