60-Crystallography of Organic Compounds

We found that the chiral cyanocetyl group bonded to the cobaltate atom in a cobaltate complex crystal was racemized by X-ray exposure without degradation of the crystallinity (Ohashi & Sasada, Nature Lond., 1977, 267, 142-144). The mode of the racemization and the reaction rate explained quantitatively by the reaction cavity, which was defined as a void space around the reactive group (Ohashi, Acc. Chem. Res., 1988, 21, 268-274). If the chiral group was replaced with the bulkier methoxybenzyl group, the racemization occurred in two stages, the conformational and configurational changes (Kurilshii, Ichida, Ohashi, Sasada & Ohgo, J. Am. Chem. Soc., 1964, 106, 5718-5724). Recently the bulkier dimethoxybenzyl group was used as a chiral group. The structural change was so fast that the three-dimensional intensity data was obtained by the new type of diffractometer using the imaging plate. The analyzed structures at several intermediate stages revealed complicated disordered structures. Subtracting the original or final structures from the disordered ones, the unstable intermediate state can be observed (Sakai, Ohashi, Araki & Ohgo, Acta Cryst. B, 1992, 48, 149-152). This indicates that if the reactive crystals were analyzed by X-rays more quickly, the dynamical process of reactions should be made clear on the basis of the structure change.


Although it is well known that DMT play an important part in the molecular conductor field, nonlinear optical properties of second harmonic generation (SHG) with DMT derivatives has not be observed until we synthesized α-BNPP-DTT, β-BNPP-DTT and BNPP-DTO recently. The synthesis and the products' structural parameters are as follows:

MS-06.01.10 STRUCTURE AND PROPERTIES OF AN ALKENYL LIQUID CRYSTAL COMPOUND. By S. Gupta, A. Nuth, S. Paul, Department of Physics, University of Calcutta, Kolkata 700009, India. H. Srinivas, Crystallography Laboratory, University of Amsterdam, 1018 WV Amsterdam, The Netherlands.

We have undertaken the structural study of the (3'-pentyl) 4'-cyanobiphenyl (1,1-bicyclicene). Compounds with alkenyl and chains belong to different structural classes. Their common features are low viscosities as well as low optical anisotropies in the liquid crystalline state. The alkanyl compounds differ from each other in many of their properties with respect to the structural changes made in the core of the alkanyl double bond. The molecular arrangement in the crystalline state is one of the factors which sometimes predetermines the properties in the liquid crystalline state. The compound studied here has the following structure:

MS-06.01.08 SUPRAMOLECULAR ARCHITECTURES OF METALLOPORPHYRINS IN CRYSTALLINE SOLIDS. I. Goldberg, H. Krupitsky and C.E. Strouse, Department of Chemistry, Tel-Aviv University, 69978 Tel-Aviv, Israel, and University of California, Los Angeles, California 90024, U.S.A.

Research efforts directed at the construction of mesoporous solids based on functionalized metalloporphyrins as building blocks uncovered a series of new materials with attractive structural features. This approach involves substitution of the rigid porphyrin core with polarized aryl groups, the polar functions being used to induce coordination between the molecular fragments, and thus form crystalline polymers with an extremely high degree of two- and three-dimensional cross-linking. Such structure-entire supramolecular assemblies are then capable of incorporating smaller molecular entities into the lattice. Controlled variation of the microstructure in the resulting solids, consequently of their structure-dependent properties, is effected by changing the type (and shape) of the sensor groups and their disposition in the porphyrin moiety.

Crystallographic investigations have confirmed that the intermolecular interactions of the porphyrin materials is dominated by directional hydrogen bonds and other (e.g., C1–Cl, and metal–nucleophile) interactions, as well as by the molecular shape, yielding continuous networks of strongly coordinated entities which resemble to a large extent the structural rigidity of a zeolite. Guest components can be absorbed in these solids in distinctly defined sites of the porous lattice. The polycrystalline molecular organization, along with the rich chemistry associated with the porphyrin core, make these materials useful in a wide range of applications, including matrix isolation, molecular recognition and chemical separation, and mediation of ligand transport and controlled release. Several examples will be displayed to illustrate the potential for the design of crystalline lattices with different degrees of cross-linking, rigidity and polarity, and for the formation of polar tubular structures capable of aligning organic dipolar guest molecules in the crystal bulk.

06-Crystallography of Organic Compounds

**06.02 – Molecular Correlation with Theory, Spectra and Properties**

**PS-06.02.01 CONFORMATIONAL STUDIES OF TWO CEMBRANIC DITERPENOIDS.** By Jan-Eric Berg¹, Elisabeth Olsson² and Inge Wahlberg², Department of Structural Chemistry, Ångström Laboratory, Stockholm University, S-106 91 Stockholm, Sweden.

The solution conformations of two cembranic diterpenoids (1,2) have been studied by using NMR methods in conjunction with molecular mechanics calculations (MM3). Initially, the acetoxy groups in the energy-minimized solid state structure of the diacete of 1 were replaced by hydroxy groups to give a three-dimensional structure of 1 (X). A three-dimensional structure of 2 (Y) was obtained by reversal of the configuration at C-4 in structure X. The structures X and Y were then subjected to the Ringmaker and MM3 programs for a systematic conformation search and subsequent energy minimization. The vicinal coupling constants calculated for low-energy conformations were compared with those observed for 1 and 2 in solution. The results from NOE experiments were also used in the evaluation.

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**MS-06.01.11 MOLECULAR PACKING OF SOME 4-SUBSTITUTED PHENYL-3-CYANO-1,1-DIPHENYL-1-METHANONES**

By G. Angelioglu¹, J. Maicke², and V. Druyanets⁻¹

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²Chem. Dep., Sofia Univ. Baucher 1, Sofia (Bulgaria).

Crystal structures of eleven functionalized 3-enaminoindenes were determined and their molecular packing investigated. The molecules are held together by van der Waals forces only and obey the close-packed principle (Felthamity, Organic Crystallochemistry, Academic Press, 1953). They crystallize in the face-centered packing space groups P4₁2₁2, P2₁/c, C2/c.

Understanding of the molecular packing is simplified by placing the structure into dense layers parallel to one of the unit cell faces in P4 and to the b-axis in monoclinic space groups. They are related by a system of translation and combinations of (1, 1), (1, 2), and (2, 1). Such symmetry operations produce dense packing. Further every layer is considered as composed of symmetry related chains of molecules. Two types of layers are found: the one containing 4-related single molecules, denoted (1), and the other containing 4-related orthosymmetrical dimer, denoted (2). The table summarizes the newly proposed formulae, where in brackets is given the molecular symmetry, in braces are the layer forming symmetry operations, and finally the layer multiplying symmetry operations along the specified cell axis are written. The number of layers not related by symmetry is given in subscript. Coordination numbers are calculated according to Zaburin and Sokol (Vestn. Moskov. Univ., Ser. Khim., 1983, 13, 954-3).

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<th>Substituent</th>
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<th>Coord. No</th>
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</tr>
<tr>
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<td>P4</td>
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<td>1</td>
</tr>
<tr>
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<td>P4</td>
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<td>P4</td>
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<td>1</td>
</tr>
<tr>
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<td>1</td>
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