

06-Crystallography of Organic Compounds

165

In continuation of our recently started research program (Kopf, J., Köll, P., Morf, M., Zimmer, B. and Jarchow, O., 1990, Abstract PS-05.04.25, IUCr XV, Bordeaux, France) we have determined the crystal and molecular structures of previously not treated pentitols, hexitols, heptitols and several higher alditols up to decitols including peracetylated derivatives in most cases. Contrary to the above mentioned assumptions, our investigations show that the avoidance of 1,3-parallel interactions between the heavy atoms O and C is not a dominating factor in determining the conformations of higher alditols in the solid state. Acetylated alditols in particular are able to adopt "unexpected" conformations. Examples of the structure determinations and further discussions will be given. First results of our respective work have been published already (Kopf, J., Bischoff, M. and Köll, P., Carbohydr. Res., 1991, 217, 1; Kopf, J., Morf, M., Zimmer, B., Bischoff, M. and Köll, P., Carbohydr. Res., 1992, 229, 17 and Köll, P., Morf, M., Zimmer, B., Kopf, J., Berger, A., Dax, K. and Stütz, A. E., Carbohydr. Res., 1993, in press).

MS-06.01.05 The Use of Composite Crystal-Field Environments Derived from Crystal Packing in Molecular Recognition and the 'De-NOVO' Design of Protein Ligands

Gerhard Klebe, Main-Laboratory of BASF-AG, Carl-Bosch Strasse, D-6700 Ludwigshafen, FRG

Information about intermolecular interactions and the mutual recognition of organic molecules can be obtained from their packing in the crystalline state. Structural data has been retrieved from the Cambridge Crystallographic Database [1] to compile composite crystal-field environments about different functional groups, which also occur in proteins and nucleotides. The spatial distribution obtained for these next-neighbor contacts can be used to map-out putative interaction or recognition sites, e.g. about amino acid residues oriented towards the binding site of a given protein. Although influenced by packing forces, these composite environments show systematic patterns which reflect preferred interaction geometries of the functional groups under consideration with their neighboring groups, e.g. hydrogen bonding partners. A detailed analysis reveals differences and similarities in the structural properties of these functional groups which allows guide-lines to be devised for the consequences of mutual functional group replacements. Similar, but substantially less detailed, distributions can be obtained from crystallographically determined ligand/protein complexes (Brookhaven File [2]) for the spatial orientation of ligand functional groups about amino acid residues. These demonstrate that the properties observed in low-molecular weight structures are also representative for the sought-after spatial orientation of interactions between ligands and their receptor proteins [3]. The crystallographically determined binding geometries of three inhibitor/enzyme complexes are compared with the distributions of putative interaction sites predicted from corresponding composite field environments. In some cases, the observed positions of ligand atoms interacting with the proteins coincide with a region which is also frequently occupied by similar bonding partners in organic crystal structures, however, interaction geometries are also found which fall close to the limits of the ranges observed in the small molecule reference data. The information contained in the different composite crystal-field environments can be translated into rules which serve as guide-lines for an automatic docking of small molecule fragments into the active site of proteins [4].

[1] Allen F.H., Kennard O., Taylor R., Acc. Chem. Res. (1983) 16 146

[2] Bernstein F.C., Koetzle T.F., Williams G.J.B., Meyer E.F. Jr., Brice M.D., Rodgers J.R., Kennard O., Shimanouchi T., Tasumi T., J. Mol. Biol. (1977) 112 535

[3] Klebe G., Mietzner T., (1993) in "Organic Crystal Chemistry" ed. Jones D.W., Oxford Univ. Press

[4] Böhm H.J., J. Comp.-Aided Mol. Des., (1992) 6 61-78 and 593-606

MS-06.01.06 KEY ROLE OF SPECIFIC INTERMOLECULAR INTERACTIONS IN FORMATION OF ORGANIC CRYSTAL STRUCTURES

A. E. Masunov* & P. M. Zorky, Chemical Department, Moscow State University, Moscow 119899 Russia.

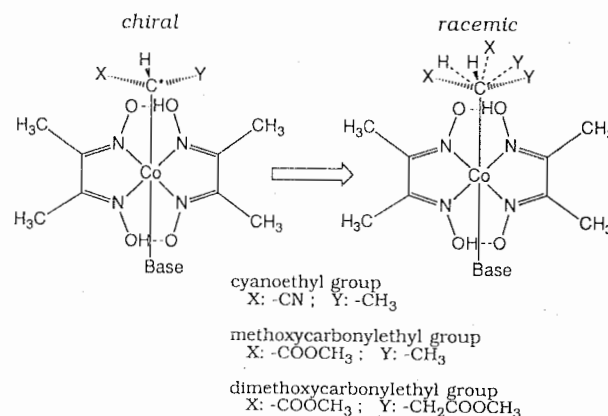
Some contacts of atoms (for ex., CN...Cl, O...C=O, I...I, CH...O) display properties, which could not be described by conventional additive models (such as van der Waals radii, transferable atom-atom potentials, superposition models of electron density, etc.). We call them specific intermolecular contacts (SIC). The rise of SIC is one of the important factors determining the structure of a molecular crystal. Different ways to take into account the influence of SIC on the packing of molecules were considered:

- 1) the addition of SIC energy for the refinement of depths of minima after the energy minimization by atom-atom potential method,
 - 2) the use of the special potentials and/or virtual atoms,
 - 3) the energy minimization under the condition of fixed SIC geometry,
 - 4) a priori construction of packings which contain setted SIC to use the packing as a starting point in energy minimization.
- An application of the last way for uracil and its derivatives gave us initial models which were very close to real structures. The use of donor-acceptor approach based on localized orbitals interaction in the second order of perturbation theory allowed us to reproduce the surface of potential energy for Cl...Cl SIC (contrary to the electrostatic approach).

MS-06.01.07 STRUCTURES OF UNSTABLE INTERMEDIATES IN THE CRYSTALLINE STATE REACTIONS

By Y. Ohashi, A. Sekine, H. Uekusa, Y. Takenaka and Y. Sakai, Department of Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

If the structural change in the process of reaction could be "observed" directly by X-ray analysis, the mechanism would be easily made clear. Such a reaction should proceed in a crystal with retention of crystallinity, which is called as crystalline state reaction.

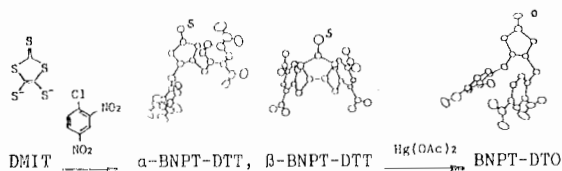


06-Crystallography of Organic Compounds

We found that the chiral cyanoethyl group bonded to the cobalt atom in a cobaloxime complex crystal was racemized by X-ray exposure without degradation of the crystallinity (Ohashi & Sasada, *Nature(London)*, 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 methoxycarbonylethyl group, the racemization occurred in two stages, the conformational and configurational changes (Kurihara, Uchida, Ohashi, Sasada & Ohgo, *J. Am. Chem. Soc.*, 1984, **106**, 5718-5724). Recently the bulkiest dimethoxycarbonylethyl 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 structure can be observed (Sakai, Ohashi, Arai & Ohgo, *Mol. Cryst. Liq. Cryst.*, 1992, **219**, 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.

MS-06.01.08 CONFIGURATION AND NONLINEAR OPTICAL PROPERTIES OF DMIT DERIVATIVES. Q. Fang*, Institute of Crystal Materials, Shandong Univ. 250100, China; Q. Zheng, Chem. Dept., Jiangxi Medical college, 330006, China.

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



system	triclinic	orthorhombic	orthorhombic
group	P1	P212121	P212121
a(Å), a(°)	12.18, 96.5	10.13	10.08
b(Å), b(°)	14.25, 96.9	20.49	19.35
c(Å), c(°)	7.79, 72.3	9.66	9.93
V, Z, Dc	1274, 2, 1.38	2005, 4, 1.76	1936, 4, 1.77
final R	0.069	0.038	0.027

By using a YAG:Nd laser at 1064nm, only BNPT-DTO has SHG at 532nm, which is as strong as that produced by KDP. α -BNPT-DTT belongs to P1, and of course has no SHG effect. β -BNPT-DTT and BNPT-DTO belong to same space group and possess nearly the same cell parameters. What make the differences? The charge distribution does not change much by substituting O=C for S=C for all, respective bond lengths (except O=C, S=C) and the respective NMR shifts of protons in the phenyl do not change. BNPT-DTO is in a stretching configuration whose dipole moment is considerably higher than that of β -BNPT-DTT. So it is the configurations that make the differences.

MS-06.01.09 SUPRAMOLECULAR ARCHITECTURES OF METALLOPORPHYRINS IN CRYSTALLINE SOLIDS.

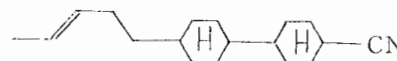
I. Goldberg*, H. Krupitsky and C. E. Strouse, Departments of Chemistry, Tel-Aviv University, 69978 Tel-Aviv, Israel, and University of California, Los Angeles, California 90024, U.S.A.

Research efforts directed at the construction of microporous 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-enforced supramolecular assemblies are then capable of incorporating smaller molecular entities into the lattice. Controlled variation of the microstructure in the resulting solids, and 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.

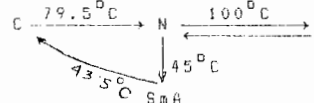
Crystallographic investigations have confirmed that the intermolecular arrangement of the porphyrin materials is dominated by directional hydrogen bonds and other (e.g., Cl...Cl, and metal-nucleophile) interactions, as well as by the molecular shape, yielding continuous networks of strongly coordinated 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 polymeric 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 discussed 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.

MS-06.01.10 STRUCTURE AND PROPERTIES OF AN ALKENYL LIQUID CRYSTALLINE COMPOUND. By S. Gupta, A. Nath, S. Paul, Department of Physics, North Bengal University, Siliguri - 734430, India and H. Schenk, Crystallography Laboratory, University Of Amsterdam, 1018WV Amsterdam, The Netherlands.

We have undertaken the structural study of 4-(3'-pentenyl)-4''-(cyano)-1,1'-bicyclohexane. Compounds with alkenyl end chains belong to different structural classes. Their common features are low viscosities as well as low optical anisotropies in the liquid crystalline state. The alkenyl compounds differ from each other in many of their properties with respect to systematic changes made in the position of the alkenyl 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:



The transition temperatures of different phases as determined by X-ray diffraction and texture studies are given below:



We report here the crystal structure of the compound and try to explain the mesomorphic organization in relation to its solid state packing and molecular interactions. Intensity data were collected in a CAD-4 diffractometer. The compound crystallised in the monoclinic space group $P2_1/n$ with unit cell parameters