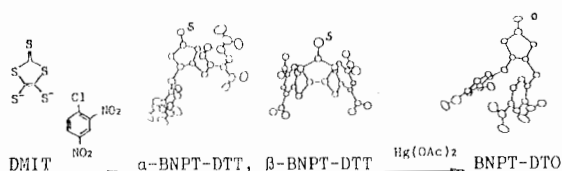


We found that the chiral cyanoethyl group bonded to the cobalt atom in a cobaloxime complex crystal was racemized by X-ray exposure without degradation of the crystallinity (Ohashi & Sasada, *Nature(London)*, 1977, **267**, 142-144). The mode of the racemization and the reaction rate explained quantitatively 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.

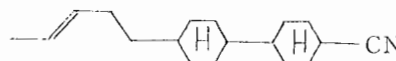
I. Goldberg*, H. Krupitsky and C. E. Strouse, Departments of Chemistry, Tel-Aviv University, 69978 Tel-Aviv, Israel, and University of California, Los Angeles, California 90024, U.S.A.

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.

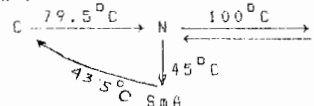
Crystallographic investigations have confirmed that the intermolecular arrangement of the porphyrin materials is dominated by directional hydrogen bonds and other (e.g., Cl...Cl, and metal-nucleophile) interactions, as well as by the molecular shape, yielding continuous networks of strongly coordinated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

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$a = 5.6090(5)\text{\AA}$, $b = 31.3900(22)\text{\AA}$, $c = 9.5626(5)\text{\AA}$, $\beta = 98.8928(61)^\circ$. 3381 reflections were measured of which 2326 were treated as observed with $I > 2.5\sigma(I)$. The crystal structure has been determined by direct method program SIMPEL and has been refined to a R value 6.5%. The bond lengths and bond angles are normal and compare well with other results. The cyclohexyl rings are in chair conformation. The length of the molecule in the crystalline state is 16\AA whereas the theoretical length is at a maximum 16.2\AA indicating that the molecule is in its most extended conformation. Pairs of molecules related through the centre of symmetry are bound together by weak interaction between alkenyl chains and cyano groups. They form a dimer structure. X-ray diffraction study in the nematic phase shows the presence of this dimerisation which is generally observed in the cyano compounds. The molecules are arranged in layers parallel to bc plane and layers are stacked along a -axis. Molecules in the neighbouring layers are arranged in herringbone like pattern. At C-N transition temperature these molecules gain sufficient energy to move within the layers and undergo rotations about axes other than the long molecular axis. The C-N transition is thus of reconstitutive type. X-ray diffraction photographs shows that Smectic A phase consists of both partial bilayers and monolayers, an incommensurate structure. The existence of this incommensurate structure can not be deduced from crystal structure analysis only. Intermolecular interactions in the mesomorphic phase play a role which will be discussed.

MS-06.01.11

MOLECULAR PACKING OF SOME 4-(SUBSTITUTED PHENYL)-3-CYANO-1,1-DIPHENYL-2-AZABUTADIENES

By O. Angelova¹, J. Macicek^{1*} and V. Dryanska²¹Inst. Appl. Mineral., BAS, Rakovski 92, Sofia (Bulgaria);²Chem. Depart., Sofia Univ., Baucher 1, Sofia (Bulgaria)

Crystal structures of eleven functionalized 2-azabutadienes were determined and their molecular packing investigated. The molecules are held together by van der Waals forces only and obey the close-packing principle (Kitaigorodsky, Organic Crystallochemistry, Academic Press, 1955). They crystallize in the close-packing space groups $P1$, $P2_1/c$, $C2/c$.

Understanding of the molecular packing is simplified by slicing the structure into denser layers parallel to one of the unit cell faces in $P1$ and to the b -axis in monoclinic space groups. They are related by a system of I in triclinic SG and combinations of $(2_1, I)$, $(2_1, 2)$, and $(2, I)$ symmetry operations in monoclinic SG . Further every layer is considered as composed of symmetry related chains of molecules. Two types of such chains were found - the one consisting of 2_1 related single molecules, denoted as $2_1\{I\}$, and the other containing I related centrosymmetric dimers, denoted as $(I)\{I\}$ (t = axis translation) (Kitaigorodsky, 1955). 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 Zefirov and Zorkii (Vestn. Moscow Univ., Ser. Khim., 1978, 19, 554-9).

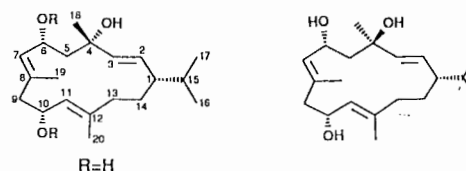
Substituent	SG	Z	Coord. No	Formula
4-methoxy	$P1$	2	12+1	$a(I)\{bc\{I\}\}$
2,4-dimethoxy	$P1$	2	13	$b(I)\{ac\{I\}\}$
4-dimethylamino	$P1$	2	13+1	$a(I)\{bc\{I\}\}$
E-2-bromo	$P1$	4	12+1	$c(I)\{ab\{I\}\}_2$
2-methoxy	$P2_1/c$	4	12+1	$a(2_1, I)\{(I)_c2_1\{I\}\}$
2-Fluoro	$P2_1/c$	4	14	$a(2_1, I)\{(I)_c2_1\{I\}\}$
4-cyano	$P2_1/c$	4	13	$a(2_1, I)\{(I)_c2_1\{I\}\}$
3-methoxy	$P2_1/c$	4	13	$a(2_1, I)\{2_1(I)_c\{I\}\}$
Z-2-bromo	$P2_1/c$	4	11+1	$a(2_1, I)\{2_1(I)_c\{I\}\}$
4-Fluoro	$C2/c$	8	12	$a(2, I)\{(I)_c2_1\{I\}\}$
2,4-dichloro	$C2/c$	8	12	$c(2, I)_2\{a(I)_n\{I\}\}_2$

06.02 - Molecular Correlation with Theory, Spectra and Properties

PS-06.02.01 CONFORMATIONAL STUDIES OF TWO CEMBRANIC DITERPENOIDS.

By Jan-Eric Berg*, Elisabeth Olsson^a and Inger Wahlberg^a. *Department of Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden, ^aReserca AB, S-118 84 Stockholm, Sweden

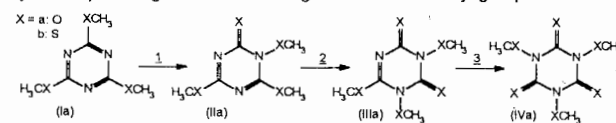
The solution conformations of two cembranic diterpenoids (1,2) have been studied by using NMR methods in conjunction with molecular mechanics calculations (MM3). Initially, the acetoxy groups in the energy-minimized solid state structure of the diacetate of 1 were replaced by hydroxy groups to give a 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 submitted 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.



PS-06.02.02 METHYL REARRANGEMENT IN THE SOLID STATE

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The studies of chemical reactivity, relying on the principle that chemical reactions require mobility of molecules, have focused mostly on reactions that take place in the gaseous, liquid state or in solution. The lack of mobility of molecules in the solid state suggests that no reactions are anticipated in this state of matter. The exceptions are valuable for the study of reaction mechanisms. We are presently interested in the migration of methyl groups in cyanurates that takes place in the solid. 2,4,6-trimethoxy-1,3,5-triazine (methyl cyanurate) and 2,4,6-trimethylthio-1,3,5-triazine (thio cyanurate) undergo thermal rearrangement of the methyl groups.



Studies by MS and NMR (Tosato 1982, 1984), have shown that the migration in the melt is intermolecular. Also, it was found that reaction 1 occurs in the melt while reactions 2 and 3 take place in the solid by an unknown mechanism. We have studied the thermal behavior of the methyl cyanurate by HTXRD (High Temperature X-ray Diffraction), by DSC (Differential Scanning Calorimetry) and by crystal structure determination. Although the crystal structure of (Ia) shows that the molecular arrangement is ideal for methyl migration, the reaction occurs in the melt and not in the solid. We found that the compound undergoes phase transition and, presumably, the structure of the new phase does not have the proper relative geometries that make the methyl migration possible (the crystal structure of this phase is yet unknown). The crystal structure of (IIa) show that methyl migration can take place through two routes: "homo chain mechanism" will lead to compound (IIIa) and "hetero ribon mechanism" will produce (IVa). So far, we cannot rule out one of the two mechanisms although it seems that reaction 3 occurs in the melt and therefore it is possible that (IIa) undergoes a cooperative methyl transfer that leads directly to the end product (IVa).

TOSATO, M. L. (1982). *J. Chem. Soc. Perkin Trans. II*, 1321.TOSATO, M. L. (1984). *J. Chem. Soc. Perkin Trans. II*, 1593.