

## 06-Crystallography of Organic Compounds

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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  $16\text{\AA}$  whereas the theoretical length is at a maximum  $16.2\text{\AA}$  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. Angelova<sup>1</sup>, J. Macicek<sup>1\*</sup> and V. Dryanska<sup>2</sup><sup>1</sup>Inst. Appl. Mineral., BAS, Rakovski 92, Sofia (Bulgaria);<sup>2</sup>Chem. 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).

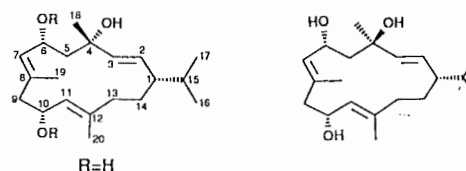
| Substituent     | SG       | Z | Coord. No | Formula                     |
|-----------------|----------|---|-----------|-----------------------------|
| 4-methoxy       | $P1$     | 2 | 12+1      | $a(I)\{bc\{I\}\}$           |
| 2,4-dimethoxy   | $P1$     | 2 | 13        | $b(I)\{ac\{I\}\}$           |
| 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      | $a(2_1, I)\{(I)c_2\{I\}\}$  |
| 2-Fluoro        | $P2_1/c$ | 4 | 14        | $a(2_1, I)\{(I)c_2\{I\}\}$  |
| 4-cyano         | $P2_1/c$ | 4 | 13        | $a(2_1, I)\{(I)c_2\{I\}\}$  |
| 3-methoxy       | $P2_1/c$ | 4 | 13        | $a(2_1, I)\{2_1(I)b\{I\}\}$ |
| Z-2-bromo       | $P2_1/c$ | 4 | 11+1      | $a(2_1, I)\{2_1(I)b\{I\}\}$ |
| 4-Fluoro        | $C2/c$   | 8 | 12        | $a(2, I)\{(I)c_2\{I\}\}$    |
| 2,4-dichloro    | $C2/c$   | 8 | 12        | $c(2, 2)\{a(I)\{I\}\}_2$    |

## 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<sup>a</sup> and Inger Wahlberg<sup>a</sup>, \*Department of Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden, <sup>a</sup>Reserca AB, S-118 84 Stockholm, Sweden

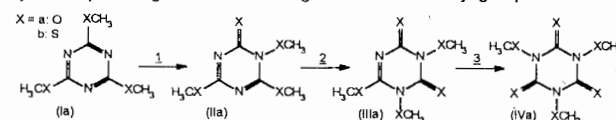
The solution conformations of two cembranic diterpenoids (1,2) have been studied by using NMR methods in conjugation with molecular mechanics calculations (MM3). Initially, the acetoxy groups in the energy-minimized solid state structure of the diacetate of 1 were replaced by hydroxy groups to give a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

M. Kafory\* and E. Handelsman-Benory, Department of Chemistry, Technion Israel Institute of Technology, 32000 Haifa, Israel

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.