06. Crystallography of Organic Compounds


In the course of stereochemical investigation of chiral silicon derivatives crystals of optically active enantiomers of the title compounds were obtained.

The crystal structures of 1 and 2 were determined by a single crystal X-ray diffraction technique. Crystal data are:

<table>
<thead>
<tr>
<th></th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>Space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.467</td>
<td>13.210</td>
<td>14.413</td>
<td>P2_12_2_2 (Z=4)</td>
</tr>
<tr>
<td>2</td>
<td>7.519</td>
<td>11.853</td>
<td>22.428</td>
<td>P2_12_2_2 (Z=4)</td>
</tr>
</tbody>
</table>

The absolute configurations of silicon atoms were obtained by anomalous X-ray scattering. Conformational analysis using molecular mechanics methods and crystallographic data will be also presented.

06.04 - Crystal and Molecular Packing, Hydrogen Bonding

PS-06.04.01 MOLECULAR AND CRYSTAL STRUCTURE OF A NEW X-RAY CONTRAST AGENT, CsH4H9N2O_5. By L. Ehrensbø and B. Fjerntoft Pedersen, Institute of Pharmacy, University of Oslo, Norway.

The title compound, lodoxamol, is a water soluble non-ionic dimeric contrast agent for use in diagnostic imaging. The structure of a non-ionic monomer has previously been reported (Ganzerelli, F. (1985), Acta Cryst. C39, 1570-1572).

The intensity data from a single crystal were collected on a Nicolet P3 diffractometer at liquid nitrogen temperature. 12.132 reflections were measured, out of which 4779 were considered observed (I>2.5σ(I)). Lodoxamol crystallizes in the triclinic space group P1, a=16.86(3)Å, b=18.64(3)Å, c=19.36(4)Å, α=95.68(2)°, β=102.43(2)°, γ=145.36(3)°, V=5147(2)Å³, Z=4. λ(MoKα)=0.7107Å. The structure was solved by direct methods (Gilmore, C.J. (1983), MITHROID, Version 1.0, University of Glasgow, Glasgow, Scotland), refined by full-matrix least-squares minimization of F², where w=1 [(Mullininson, P.R. and Muir, K.W. (1985), J. Appl. Cryst. 18, 51-55). The structure was corrected for absorption, and anisotropic vibration was included for the iodine atoms. The high flexibility of the side chains makes their determination difficult. The structure has an R-factor of 7.5%, and an e.s.d. in the bond distances of 0.04 Å is about 0.15 Å for the outermost atoms. There are two different conformations of the molecule in the asymmetric unit. One of them has a paramolecular hydrogen bond, which gives it a folded conformation.

PS-06.04.02 CRYSTAL AND MOLECULAR STRUCTURE OF A MESOGENE COMPOUND. By P. Mandal and P. Paul, Department of Physics, North Bengal University, Siliguri-734 430, India and K. Gobinath and H. Schep, Crystallography Laboratory, University of Amsterdam, 1018 KV Amsterdam, The Netherlands.

The molecular arrangement in the crystalline state is one of the factors which predetermine the occurrence of thermal mesomorphism in organic compounds. As a part of a series of structural investigations of mesogenic compounds we have determined the crystal structure of Bis(o-butoxybenzylidene) -p - toluidene (BBT). Under crossed polarizing microscope pretransitional effect was observed both before Cr-I-N-I transitions. An unspecified variation of mosaic texture in mesomorphic regions and marked texture in nematic regions were observed. Supercrystallization was noticed as indicated below. X-ray diffraction photographs were taken in mesomorphic range with and without magnetic fields. These indicate the smectic phase as SmC-III. Observed transition temperatures (°C) were:

| 155 | 154 |
| 145 | 142 |

Plate shaped single crystals were grown by slow evaporation from benzene solution. Intensity data were measured in a CAD-4 diffractometer. Cell dimensions are a=3.162(29), b=7.947(25), c=21.424(8) Å, β=92.31(2), γ=94.32(2), Z=22 and space group P1, P2_12_2_1. 3108 reflections were measured of which 2129 were treated as observed with I > 2.5σ(I). The structure was solved by the symbolic phase extension program SIMPHEL and was refined to a R-value of 0.12 and Rw of 0.18. At this stage a-P-BBT showed no mesotic higher than 0.41 eV. M-Sm-A. Bond lengths and angles were normal. However, temperature factors of a few atoms of butoxy chains were very high. Higher R-value may be due to structural disorder of butoxy chains. The symmetrical fractions of the molecule C1-C12 and C19-C36 are planar (Fig. 1), but the angle between them is about 60°. It is observed that molecules are arranged in layers inclined to a-b plane and the layers are stacked along the c-axis (Fig. 1). This tilted layer-like structure is precursor to the tilted smectic phase. Twisted molecular geometry and van der Waals interactions result in very efficient packing of the centro-symmetrically related molecules. Few intermolecular short contacts observed in overlapping region supports this conclusion. The high melting part of the compound may be due to this packing. At the Cr-I transition temperature the molecules gain sufficient energy to move within the layers and to undergo rotations about the long molecular axis. The Cr-Sm transition is likely to be displacive type, details will be discussed.

FIG 1. PERSPECTIVE VIEW OF BBT MOLECULE

FIG 2. CRYSTAL STRUCTURE OF BBT VICINITY ALONG X-AXIS