06-Crystallography of Organic Compounds

A series of quaternary alkyl halide salts of 1,4-diazabicyclo[2.2.2]octane (DBABCO) exhibited first-order phase transition in the temperature range of 62-100°C and showed halide anion conductivity in the high temperature phase (Shinizu, J. et al., 1986 Bull. Chem. Soc. Jpn., 59, 1443-1448). The phase transition temperature (Tc) and heats of transition showed a so-called even-odd number effect of carbon number which was also observed for a series of long chain alkanes and alcohols.

In this study, we investigated the crystal structures of N,N'-didecyldimethyl-1,4-diazabicyclo[2.2.2]octane dibromide (I) and a diphenylcyclohexyl derivative (II). In each crystal, one dimension of the unit cell was very long and crystals showed instabilities against the X-ray irradiation, so that the intensity data from single crystals were collected on the 4P-D-WAS (Weissenberg type diffractometer with Imaging Plate, N. Kanaya et al., 1990 Acta Crystal. A46 Suppl., C10). The molecular structures of (I) and (II) have similar features. Two alkyl chains have trans-gating conformation, and dihedral angles between the planes of alkyl carbons are 128° and 157° for (I) and (II), respectively. Two bromine anions reside near the DBABCO ring. Alkyl chains form sheet-like structures in crystals. In spite of the difference of chain length, the number of van der Waals contacts between alkyl chains in (I) is slightly larger than that in (II). This fact may explain the even-odd number effect that the heat of transition of (I) was greater than that of (II). In the powder X-ray diffraction patterns for (I) and (II) which were measured at the temperature near Tc, sharp diffraction peaks for the high temperature phase appeared at lower 2θ angles. At the temperature beyond the Tc, diffraction peaks assigned for short axes directions disappeared, although the sharp peaks for long axes direction still remained. This disorder along short axes just as the liquid-crystalline from the phase transition.

The molecular structures of 1a and 1r are very similar, intramolecular NH-O hydrogen bond is formed between amino and hydroxyl groups. On the other hand, the molecules of 1o and 1r are rotational isomers. In 1r NH group is hydrogen-bonded to nitro and methoxy groups nitrogenated while in 1o the hydrogen

---

06-Crystallography of Organic Compounds

In order to study the dynamic behavior of the conversion from the orange to red forms, powder diffraction patterns of red crystals were obtained from the solution of Ia in the same solvent that had recrystallized from solution. Temperature dependence of the diffraction patterns showed the drastic conversion from the orange form to the red form just below the melting point. The orange form undergoes a thermal rearrangement into the red form.

PS-06.04.10 THE INFLUENCE OF THE SYMMETRY OF MOLECULES ON THEIR ARRANGEMENT IN CRYSTAL. By K.A.Potekhin* & P.M.Zorky, Chemical Department, Moscow State University, Moscow, 119899, Russia.

Though the native symmetry of a molecule (i.e. symmetry of an isolated molecule) is usually lost in the space group of a crystal except the inversion center, it is, as a rule, partially or completely retained in the pseudo-symmetry groups of some molecular agglomerates (chains, layers, plane substructures) or even of the whole structure. Thus, this symmetry influences substantially the packing of molecules. This influence was studied for a few crystal structures and the variety of pseudosymmetrical molecular exons is noted. The formation of the latter can be successfully interpreted using the method of potential functions symmetry (MPS). Sometimes it is useful to divide the crystal into so-called molecular cells for revealing the pseudosymmetrical sub-systems. As a very interesting example two polymorphs of 2,3,7,8-tetramethyl-1,4,6,9-tetraoxafluorene (5) and 2,2'-dienone investigated by X-ray method recently (Potekhin K.A. et al., to be published) are discussed. The polymorph which exists at room temperature is pseudotetragonal but the exact symmetry is C2/c. At 849°C it transforms into a triclinic form. This transformation consists of a small shift of molecules and the crystal structure retains the pseudotetragonal and pseudomonoclinic symmetry.

PS-06.04.11 THE TWINNED CRYSTAL STRUCTURE OF TETRAIODODAMAMANTANE, C_{18}H_{34}I_8 by Ganatan R. Desiraju, D. Sekhar Reddy, School of Chemistry, University of Hyderabad, Hyderabad 500 134, India, A. David Rae* and Donald C. Craig, School of Chemistry, University of New South Wales, PO Box 1, Kensington N.S.W. 2033, Australia.

The structure crystallised in spacegroup Ia/a, a=b=7.7198(7), c=28.52(2) Å, Z=4, 295 K, with individual molecules of implicit 42/m symmetry on sites of 42/m symmetry in the crystal and was refined using a twin/disorder model to R=0.03 which may be compared to a previous untwinned model of Bremer, Gregory & von Raguse Schleyer, J. Org. Chem. (1989) 54 3796-3799 which refined to R=0.20. The structure may also be compared to the Olympic rings structure of adamantane-1,3,5,7-tetracarboxylic acid, Ermer, J.A.C.S. (1988) 110 3747-3754.

The shortest 1...1 contact of 4.63(1) Å is between centrosymmetrically related molecules at 0/1/4/a and 1/1/4, a–b, a vector of a + 1/2b – 1/4c. The 42/m site symmetry creates a related vector –1/2a + b + 1/4c, the sum of the two being 1/2a + 1/2a + 3/2b. The cell a'=a + 3b, b'=3a + b, c'=c can be used to describe a network of molecules connected by the 4.063 Å contacts. The distribution of molecules in this network is a distorted diamond structure with 8 molecules per F centered cell. This cell has a volume 10 times that of the Z=4 structure in a, b, c. This gives 5 interpenetrating structures, the Olympic rings.