06-Crystallography of Organic Compounds

06.01.01 Molecular Interactions in Organic Crystals

MS-06.01.01 GRAPH SET ANALYSIS OF HYDROGEN-BOND PATTERNS IN ORGANIC CRYSTALS. RECENT DEVELOPMENTS AND APPLICATIONS. By J. Bernasconi* and L. Shimon, Department of Chemistry, Ben-Gurion University of the Negev, Beer Sheva 84120, Israel and R.E. Davis, and N. L. Chang, Department of Chemistry, University of Texas, Austin, TX 78712, U.S.A.


In the course of a number of these works and in our own efforts to expand and apply these methods to different systems, a number of problems, misunderstandings and ambiguities have arisen in the earlier publications we provided for determining the graph set. In this presentation we will review the general rules for applying graph set analysis to hydrogen-bonded systems, point out a number of pitfalls to be avoided, and describe a number of the applications to systems which have not been previously analyzed by this method.

MS-06.01.02 INTRAMOLECULAR N-H---O=C HYDROGEN BOND FORMATION IN CONJUGATED SYSTEMS. By Valerio Bertolasi, Dipartimento di Chimica e Centro di Strutturistica Diffrattometrica, Universita' di Ferrara, Via Borsari 46, 1-44100 Ferrara, Italy.

N-H---O=C hydrogen bonds (hb) play an important role in determining the conformation of the proteins and polynucleotides, and in establishing intra- and inter-molecular interactions in molecular recognition systems. There is a large variety of arrangements having N-H---O=C hb which display different geometries and topologies (Taylor et al. 1984, Acta Crystallogr. B40, 260). According to this, it is clear that the hb strength inevitably depends on various factors such as crystal field environments, cooperative effects, presence of charges on the acceptor and donor atoms. (Jeffrey & Saenger, 1991, Hydrogen Bonding in Biological Structures, Berlin: Springer). Moreover, it has been recently reported that the most relevant effects on hb are produced in non-charged systems, by the presence of z-electron delocalization within the conjugated fragments containing the atoms involved in hb. The role of resonance on the hb strengthening has been so far described mainly for z-diketone enol systems (Giulli et al. 1989, J. Am. Chem. Soc. 111, 1423; Bertolasi et al. 1993, J. Am. Chem. Soc. 113, 491; Giulli et al. 1993, Acta Crystallogr. B49, in the press). Owing to the synergistic coupling between the strength of hydrogen bond and the ability of the conjugation on the O=C=O-C=O fragment this phenomenon has been called Resonance Assisted Hydrogen Bonding (RAHB). In analogy with z-diketone enol systems we have undertaken a study of the intramolecular RAHB effect on similar fragments such as enaminoamides O=C=O-C=O and ketone dioxetones O=C=O=O-C=O. The results show that in these systems the RAHB is reproduced with the following characteristics: the K-O distances decrease up to 2.51 Å, d(90) nmr shift up may become as large as 15 ppm, and the infrared (v90) stretching vibrations may drop from 3300 up to 2600 cm⁻¹. All experimental data, both spectroscopic and structural, are interconnected in agreement with the RAHB model.

MS-06.01.03 A COMMON PACKING PRINCIPLE OF ACYCLIC SUGAR DERIVATIVES. By C. Andre & P. Lugger, Institut f. Kristallographie, Freie Universitat Berlin, Germany.

From the crystal structure of L-mannonic acid hydrizide a general phenomenological packing principle common to many acyclic sugar derivatives of different chirality could be derived for the first time. Amongst those compounds are talo-, gluco-, galacto-, mann- and arabino-configured derivatives. Their crystal structures share a quadrilateral, homodromic hydrogen bond cycle of general connectivity O(x)---O(x+1)---O(x+2)---O(x+3)---O(x+4)---O(x). Both directions in the cycle are realized. There is a relationship between the occurrence of this cycle and the conformational behaviour and the cell dimensions of the sugar derivative. The magnitude of one lattice axis depends on the length of the molecule, whereas the two others are both approximately 5 Å long; the lattices are nearly rectangular. The molecules involved in the cycle are related solely by lattice translations along these 5A axes, no matter in which space group the sugar crystallizes. The spatial orientation of the hydroxygroups forming the cycle is identical in all compounds.

MS-06.01.04 1,3-PARALLEL INTRACHAIN INTERACTIONS IN ALDITOLS ("SUGAR ALCOHOLS"). NEW INSIGHTS. By J. Kreil* and P. Kihl, *Institut für Anorganische und Angewandte Chemie der Universität Hamburg, Martin-Luther-King-Pl. 6, D-20146 Hamburg, FRG; **Fachbereich Chemie der Universität Oldenburg, D-26111 Oldenburg, FRG.

Most of the crystal structures of the pentitols and hexitols have been determined (Jeffrey, G.A. and Kim, H.Y., Chem. Phys., 1970, 14, 207) at the end of the sixties, but some were left. From those previous structure determinations it was derived, that the conformation in the crystal is controlled by the so-called Hamel-Otto effect (Jeffrey, G.A., Acta Crystallogr. 1990, B46, 89).

Generally, a planar sugar conformation is the carbon chain is expected, but in the case when the C(0)-O and C(0)+2-O bonds are arranged parallel in the straight-chain conformation, one or more of the C-C-C-C torsion angles adopt the gauche conformation to avoid this unfavorable 1,3-parallel interaction of atoms (designated as O/O). This claimed general avoidance of O/O interactions (which resembles 3,3-diradial interactions in the cyclic case) is correctly assigned to Hassel and Otto who, indeed, were very cautious in speculations about the steric influence of such a geometry (Hassel, O. and Otto, B., Acta Chem. Scand., 1947, 1, 921).