

06.01 - 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. Bernstein* and L. Shimoni, 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.

A number of recent papers have advocated the use of graph sets for the analysis of hydrogen-bonding patterns in organic crystals (Etter, M.C. *acc. Chem. Res.* **1990**, *23*, 120; Etter, M.C.; MacDonald, J.C.; Bernstein, J. *Acta Crystallogr.* **1990**, *B46*, 256), and these have already been applied to a variety of problems (for instance, Stainton, N.M., Harris, K.D.M.; Howie, R.A. *J. Chem. Soc. Chem. Comm.* **1991**, 1781; Aakeroy, C.B.; Hitchcock, P.B.; Seddon J. *Chem. Soc. Chem. Comm.* **1992**, 553; Stowell, J.G.; Toma, P.H.; Byrn, S.R. *Bioorg. Med. Chem. Lett.* **1992**, *2*, 185; Lynch, D.E., Smith, G.; Byriel, K.A.; Kennard, C.H.L. *J. Chem. Soc. Chem. Comm.* **1992**, 300).

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 prescriptions we provided for determining the graph sets. 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.

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N-H---O=C hydrogen bonds (hb) play an important role in determining the conformation of the proteins and nucleic acids, 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 Cryst.* **B40**, 280). Accordingly, 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, etc. (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 π electron delocalization within the conjugated fragments containing the atoms involved in hb. The role of resonance on the hb strenghtening has been so far described mainly for β -diketone enol systems (Gilli et al. (1989). *J. Am. Chem. Soc.*, *111*, 1023; Bertolasi et al. (1991). *J. Am. Chem. Soc.* *113*, 4917; Gilli et al. (1993). *Acta Cryst.*, **B49**, in the press). Owing to the synergistic coupling between the strength of hydrogen bond and the entity of the conjugation on the O=C-C=O fragment this phenomenon has been called Resonance Assisted Hydrogen Bonding (RAHB).

In analogy with β -diketone enol systems we have undertaken a study of the intramolecular RAHB effect on similar fragments such as enamines O=C-C=C-NH and keto-hydrazones O=C-C=N-NH. The results show that in these systems the RAHB is reproduced with the following characteristics: the N---O distances decrease up to 2.51 Å, δ (H) nmr shifts may become as larger as 16 ppm, and the infrared ν (NH) stretching vibrations may drop from 3300 up to 2600 cm^{-1} . All experimental data, both spectroscopic and structural, are intercorrelated in agreement with the RAHB model.

This research is directed to the study of the mechanisms of formation of strong hydrogen bonds which are assisted by resonance particularly in connection with their presence in important biological systems, such as in the coupling of nucleic bases; moreover it is devoted to understand the more general phenomenon of the tautomerism which is present in many conjugated chemical systems and seems to be strongly dependent by the hb formation.

MS-06.01.03

A COMMON PACKING PRINCIPLE OF ACYCLIC SUGAR DERIVATIVES. By C. André & P. Luger, Institut f. Kristallographie, Freie Universität Berlin, Germany.

From the crystal structure of L-mannonic acid hydrazide a general phenomenological packing principle common to many acyclic sugar derivatives of different chirality could be derived for the first time. Amongst these compounds are *talo*-, *gluco*-, *galacto*-, *mannon*- and *arabino*-configured derivatives. Their crystal structures share a quadrilateral, homodromic hydrogen bond cycle of general connectivity O(x)...O(x+2)...O(x+3)...O(x+1)...O(x). Both directions within 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 5Å axes, no matter in which space group the sugar crystallizes. The spatial orientation of the hydroxylgroups forming the cycle is identical in all compounds.

MS-06.01.04 1,3-PARALLEL INTERACTIONS IN ALDITOLS ("SUGAR ALCOHOLS"): NEW INSIGHTS. By J. Kopf¹ and P. Köll²; ¹Institut für Anorganische und Angewandte Chemie der Universität Hamburg, Martin-Luther-King-Pl. 6, D-20146 Hamburg, FRG; ²Fachbereich 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. S., *Carbohydr. Res.*, **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" Hassel-Ottar effect (Jeffrey, G. A., *Acta Cryst.*, **1990**, *B46*, 89): Generally, a planar zigzag conformation in the carbon chain is expected, but in the case when the C(n)-OH and C(n+2)-OH 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 O atoms (designated as O//O). This claimed general avoidance of O//O interactions (which resembles 1,3-diaxial interactions in the cyclic case) was incorrectly assigned to Hassel and Ottar who, indeed, were very cautious in speculations about the steric influence of such a geometry (Hassel, O. and Ottar, B., *Acta Chem. Scand.*, **1947**, *1*, 929).