04. ATOMIC SCALE MECHANISM AND CHEMICAL PROPERTIES

04.1 - Nombonded Interatomic Potential Energy Functions and Prediction of Crystal Structures. By Donald E. Williams, Chemistry Department, University of Louisville, Louisville, Kentucky 40292, U.S.A.

The energy of interaction between atoms in different molecules with similar modelled nonbonded interatomic potential energy functions. A number of different factors affect the choice of these functions. The mathematical form can be taken from theory: an exponential short range repulsion, a dispersion attraction which varies with the inverse power of the distance, and a coulombic interaction between site charges. Assumption of the geometric-mean combining law for hetero interactions greatly decreases the required number of adjustable parameters. Thermal vibrations normally do not produce large structural effects (for instance, thermal expansion is small). A desired threshold accuracy requirement is established and the simplest model is sought which will meet, or nearly meet, this requirement. The coefficients of the potential functions may be derived from experimental data, especially observed crystal structures. Self-consistent field molecular orbital calculations of the electric potential around the molecule are useful in establishing site electric charges (potential-derived charges). In some cases lone pair electron sites must be introduced in order to achieve threshold accuracy. The potential functions may be tested by using them to predict observed crystal structures. Using these methods hydrogen, carbon, nitrogen, oxygen, and chlorine nonbonded potentials have been proposed and a fluorine potential is under development. The important extension to hydrogen bonding is also under development. An O-H...O hydrogen bond potential function is proposed which is compatible with the nonbonded potentials and is transferable between water dimer, ice, carboxylic acid crystals, and carboxylic acid hydrate crystals.

04.1-2 THE STRUCTURE OF TWO REISSERT COMPOUNDS, 2-BENZOYL-1-CYANO-1,2-DIHYDROISOQUINOLINES, \( \text{H}_1\text{C}_7\text{N}_2\text{O}_3 \) (III) and 1-CYANO-2-METHYCARBONYL-1,2-DIHYDROISOQUINOLINES, \( \text{H}_1\text{C}_7\text{N}_2\text{O}_3 \) (IV). By E. Tyreska, M. Jaszkalski and Z. Kosturtkievs, Department of Crystallography, A. Mickiewicz University, Poznań, Poland.

As a part of our investigations of the confirmation of partially hydrogenated rings we have determined the structure of the title compounds (III) and (IV). The structure has been solved by direct methods and refined to R values of 0.040 and 0.045, respectively. The present dihydroisoquinoline derivatives will be compared with their 1,2,3,4-tetrahydroanalogues (1)(M. Przeworski, E. Tyreska, M. Jaszkalski and Z. Kosturtkievs, Acta Cryst. (1984) in press) and (II)(A. Gesls, M. Jaszkalski, U. Ryohlewska and Z. Kosturtkievs, Acta Cryst. (1984), submitted). The heterocyclic rings have the following conformations: (I) - sofa, (II) - half-chair, (III) and (IV) - planar. The conformation of the heterocyclic ring is influenced by the degree of its hydrogenation and by the shape of the substituents. The O-H group is placed anti to the O(3)-N(2) bond.

04.1-3 INTERMOLECULAR (INTERFACIAL) CONTRIVERSIES. By J.A.R.P. Sarma and Gautam R. Desiraju, School of Chemistry, University of Hyderabad, P.O. Central University, Hyderabad 500134, India.

The 'engineering' of an organic crystal structure has been usually concerned with the effects of various 'steering' groups. For instance, dichlorosubstitution of an aromatic compound is well recognised as an effective device towards realising a 4\(^\circ\)A short axis (8-structure, Schmidt, Pure Appl. Chem. 1979). We have noticed that it is the ability of molecules to form sheets (planar or corrugated) that governs the adoption of the 8-structure rather than the presence of any particular substituent group. These molecular sheets are stabilised for chlorine and oxygenated aromatics through intrasheet Cl...Cl or C-H...O non-bonded interactions.

We have found that the concept of a 'steering' group is rather ambiguous in the case of simple oxygenated aromatics since seemingly related compounds containing the same substituent may adopt different crystal structures. In both 4-acetoxyanilinic acid and 7-acetoxycoumarin, the conformation of the acetoxy group in a single molecule in the crystal is identical yet while the coumarin adopts a 8-structure, the acid does not.

C-H...O interactions (Taylor and Kennard, JACS, 104, 3063, 1982) are of some importance in directing crystal structures and their role in sheet-stabilisation is discussed for the acetoxy compounds above and for other recent examples both from our laboratory and elsewhere. Sheet-stabilisation can, in some cases, lead to a 8-structure since the sheets may be stacked so as to optimise intersheet C-C interactions. In other words, sheet formation is a necessary though not a sufficient prelude to a 4\(^\circ\)A short axis crystal structure.

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