04.X–1 Nonbonded 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 may be modelled with semiempirical 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 potentials 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.

04.1–1 STEERING GROUPS AND INTERMOLECULAR INTERACTIONS IN CRYSTAL ENGINEERING. 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 Å short axis (β-structure, Schmidt, Pure Appl. Chem., 27, 647, 1971). We have observed that it is the ability of molecules to form sheets (planar or corrugated) that governs the adoption of the β-structure rather than the presence of any particular substituent group. These molecular sheets are stabilised for chloro and oxygenated aromatics through intrasheet Cl...Cl or C-H...O non-bonded interactions.

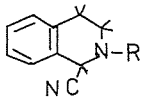
We have found that the concept of a 'steering' group is rather ambiguous in the case of simple oxygenated aromatics since seemingly related compounds containing the same substituent may adopt different crystal structures. In both 4-acetoxycinnamic acid and 7-acetoxycoumarin, the conformation of the acetoxy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

C-H...O interactions (Taylor and Kennard, JACS, 104, 5063, 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 β-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 Å short axis crystal structure.

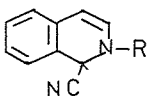
04.1–2 THE STRUCTURE OF TWO REISSERT COMPOUNDS, 2-BENZOYL-1-CYANO-1,2-DIHYDROISOQUINOLINE, $C_{17}H_{12}N_2O$ (III) AND 1-CYANO-2-ETHOXYCARBONYL-1,2-DIHYDROISOQUINOLINE, $C_{13}H_{12}N_2O_2$ (IV). E. Tykarska, M. Jaskólski and Z. Kosturkiewicz, Department of Crystallography, A. Mickiewicz University, Poznań, Poland.

As a part of our investigations of the conformation of partially hydrogenated rings we have determined the structure of the title compounds (III) and (IV). The structure have 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 (I) (M. Przywaczyk, E. Tykarska, M. Jaskólski and Z. Kosturkiewicz, Acta Cryst. (1984) in press) and (II) (A. Gzella, M. Jaskólski, U. Rychlewska and Z. Kosturkiewicz, Acta Cryst. (1984), submitted). The heterocyclic rings have the folloving conformations: (I) - sofa, (II) - half-chair, (III) and (IV) - diplanar. The conformation of the heterocyclic ring is influenced by the degree of its hydrogenation and by the shape of the substituents. The C=O group is placed anti to the C(3)-N(2) bond.



(I), (II)



(III), (IV)

R = COC_6H_5 in (I,III) and $COOC_2H_5$ in (II,IV).

04.1–3 STRUCTURAL, CONFORMATIONAL AND PACKING FEATURES IN DIPEPTIDES INVOLVING PROLYL RESIDUES. By K.K. Chacko and P. Narasimhan, Dept. of Crystallography & Biophysics, University of Madras, Guindy Campus, Madras-600 025, India.

Crystal structure investigation of peptides involving prolyl residues is of particular interest to understand the conformational features of the pyrrolidine ring system and the restrictions that this ring system imposes on the peptide conformation. In this context is is interesting to report certain structural conformational and packing features with regard to the following four dipeptides, namely, (i) L-prolyl L-valine.H_2O (Narasimhan, Chacko & Swaminathan (1982) Cryst. Struct. Comm. 11, 695). (ii) L-prolylglycine.H_2O (Narasimhan & Chacko (1982) Cryst. Struct. Comm. 11, 2051, (iii) L-prolyl L-methionine.H_2O (Padmanabhan & Yadawa (1983) Curr. Sci. 52, 904) and (iv) L-prolyl-L-alanine.H_2O (Yadawa & Padmanabhan (1979) Acta. Cryst. A34, 572). The above structures exhibit marked similarities with regard to the conformational aspects of the peptide linkage, the hydrogen bonding and packing features. Conformational disorder of the pyrrolidine ring exists in structures (i), (ii) & (iii) with the C atom occuring at two alternate sites leading to two possible envelope conformation of the ring system. The C atom of structure (iv) has unusually large thermal parameters, compared to the rest of the atoms of the pyrrolidine ring and similar conformational disorder is likely to exist in (iv). A comparative study will be made between the four peptide structures.

Thanks are due to Dr. V.S. Yadawa for making available the unpublished coordinates of (iv).