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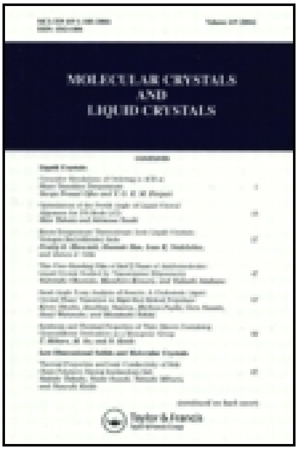

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New Developments

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CRYSTAL STRUCTURE VERSUS MOLECULAR STRUCTURE: NEW DEVELOPMENTS

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In earlier work (1-3) we tried to establish correlations between molecular size or shape and crystal structure descriptors for organic crystals containing C,H,N and O atoms, without fully developed hydrogen bonds. Samples of 391 hydrocarbon, 590 oxohydrocarbon, and 458 azahydrocarbon crystal structures, retrieved from the Cambridge Structural Database (4), were used. Of course size and shape alone are important for crystals which are built under the action of purely isotropic, or at least scarcely directional, intermolecular forces; ideally, for non polar substances like hydrocarbons. In fact, in crystals containing O or N atoms, a rather large number of C-H...X (X=O or N) attractive interactions were detected through a search of the spurious repulsions that result from their treatment as pure van der Waals contacts. These interactions are now recognized as weak hydrogen bonds, and also display some angular selectivity: Figure 1 shows that C=O...H angles for carbonyl compounds cluster in the 110-140° range for R(O...H) < 3Å.

Surveys of geometrical crystal properties, like the ones briefly described above, have provided considerable insight for the recognition of intermolecular forces in organic crystals. However, for the actual calculation of crystal properties like the lattice energy, the lattice vibration frequencies, the elastic moduli, and the barriers to molecular displacements and reorientations, appropriate empirical formulations for the intermolecular potentials must be available. In addition, the prediction of crystal structure from molecular structure is possible if the potentials are sophisticated enough.

In a first attempt to provide suitable potentials for the interactions between C,H and O atoms in crystals, the following scheme was devised. Besides the usual 6-exponential functional form, a supplementary Morse-type functional form was assumed:

$$E_{ij} = A_{ij}(1-\exp(-B_{ij}(R-R_{0ij})))^2-A_{ij}$$

Each atom in C-O-C or C=O groups, and all hydrogens, were assigned a coefficient, D, for the calculation of the A parameter, as follows:

$$A_{ij} = D_i D_j$$

The B, R_0 and D parameters were adjusted to reproduce the sublimation energy of some selected crystals with a relevant contribution from C-H...O and even C...O short attractive interactions. A substantial improvement over the results obtained with standard literature interaction potentials was achieved; the new potential also describes fairly well the energy changes upon variation of cell parameters or with molecular libration in the crystal.

There is no doubt however that a general and transferable set of empirical potential parameters is necessary for the systematic analysis of organic crystal structure; these potentials could also be fruitfully applied in the field of molecular recognition. To this aim, we have recently undertaken an extensive analysis of the existing potential functions for organic crystals contaning C,H,N,O,S and Cl atoms, without hydrogen bonds, and restricting ourselves to the simple 6-exponential functional dependence of the interaction energy from the interatomic distance. The functions were then modified and simultaneously optimized against a selection of about 100 experimental sublimation heats, and against the observed distribution of X...Y intermolecular contacts in about 1500 selected crystal structures; the potentials were required to reproduce the cell parameters of about 70 selected crystals. Thus far, complete results have been obtained for C,H,N,O-containing crystals only. Table 1 collects the optimized functions. Tables 2 and 3 give an overview of the agreement that can be obtained between calculated lattice energies

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Table 1. Optimized atom-atom potential function parameters in the form: $E = A^{*}\exp(-BR_{ij}) - CR_{ij}^{-6}$ (kcal/mole and Å units); hydrocarbon functions from ref.6.

	A	B	C
O,N...N,O	102248.	3.63	719.
C...N,O	10396.	3.19	590.
H...N,O	3217.	3.24	199.
C...C	83630.	3.60	568.
C...H	8766.	3.67	125.
H...H	2654.	3.74	27.3

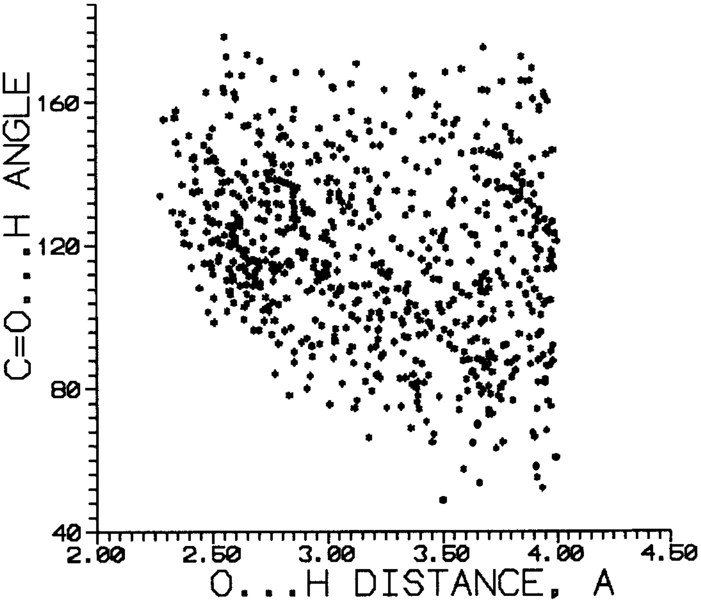

Figure 1. Scattergram of C=O...H angles *versus* O...H distances for a sample of 46 crystal structures of carbonyl compounds.

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Table 2. Heats of sublimation and calculated packing energies (kcal/mol) for azahydrocarbons.

	ΔH_{sub} exptl.	Present	Potentials from Ref.8
Acridine	21.9	24.5	23.9
trans-Azobenzene	22.9	24.5	23.2
4-Pyridinecarbonitrile	17.5	15.0	14.6
Hexamethylentetramine	18.8	20.1	17.8
2,4,6-Trimethylbenzonitrile	18.6	17.2	16.9
Phenazine	21.6	25.0	23.7
Pyrimidine	11.7	12.6	12.1
Pyrazine	13.5	12.7	12.1
Tetracyanomethane	14.6	13.7	13.6
7,7,8,8-Tetracyanoquinodimethane	25.3	25.6	24.4
1,4-Benzenedicarbonitrile	21.2	18.1	17.6

Table 3. Heats of sublimation and calculated packing energies (kcal/mol) for oxohydrocarbons.

	ΔH_{sub} exptl.	Morse (Ref.2)	Present	Potentials from Ref.7
1,3,5-Trioxane	13.4	14.5	15.1	10.5
Maleic anhydride	16.8	15.2	13.9	9.3
Phthalic anhydride	21.1	22.5	20.3	15.2
p-Benzoquinone	16.4	13.6	14.2	10.1
9,10-Anthracenedione	27.1	27.6	28.8	24.0
Cyclohexane-1,4-dione	20.1	19.5	16.3	13.0
Benzil	23.5	24.2	25.3	20.5
Dimethyl oxalate	11.4	16.6	17.8	12.2
Phenyl benzoate	23.7	23.9	25.4	21.6

and experimental heats of sublimation. As can be seen, a considerable, general improvement has been obtained over the existing potential parameter sets for oxohydrocarbons; for azahydrocarbons, the agreement ia about the same, but the new potential functions largely improve the agreement between observed and predicted lattice parameters, and produce reasonable lattice vibrational frequencies.

Only radial potential functions have been considered so far. In fact, the same optimization technique used here for non hydrogen bonded crystals could be applied to crystals with X-H...Y (X,Y=O or N) hydrogen bonds, but, presumably, the simple dependence of the potential from interatomic distance only would no longer be applicable; the results in Figure 1 for weak hydrogen bonds clearly point to this direction. Work along these lines is planned in the near future, in order to provide a complete, coherently derived set of potential parameters for all organic crystal structures. Crystal structure generation, and eventually prediction (5) will then fall within the scope of the organic crystal chemist.

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