

s8b.m4.p3 **PC Crystal Chemistry Analysis of Organic Crystal Structures.** P.N. Oleynikov, P.M. Zorky. *Laboratory of Crystal chemistry, Chemistry Department, Moscow State University, Moscow, Russia.*

Keywords: methods crystallography, data mining, data bases.

Computer software has been developed for *crystal chemistry analysis* of arrangement of molecules in organic crystals on the basis of concepts worked out in the studies conducted by P.M.Zorky et al. Initial information is input in the form accepted in Cambridge Structural Database. Partially ordered crystal structures are excluded from consideration.

In calculations and in descriptions of crystal structures rational designations of molecules of the form $N-HKL$ are used, where N is the index of a subsystem of translationally equivalent molecules, H , K , L are crystallographic coordinates of the molecules of the subsystem; it is conventional to use Roman numerals for N . The reference molecule is designated as I-000. Besides, in effect, symbol $N-HKL$ corresponds to a pair of molecules I-000 – $N-HKL$. Only pairs of adjacent molecules are usually considered; they are called *molecule–molecule contacts* (or simply *contacts*, for short) $N-HKL$. In the case of polysystem crystals, where molecules occupy more than one orbit, symbols $N^{(n)}-HKL$ are used, where n is the index of the orbit.

The standard crystal chemistry analysis includes:

1. Revealing the environment of the reference molecule I-000 (in the case of polysystem crystals molecules $I^{(n)}$ -000 are considered to be reference molecules). The list is made of those pairs of molecules for which there is at least one distance r_{ij} (atoms i and j belonging to different molecules) that is less than a specified limit R_0 .
2. Revealing and calculating the shortest atom-atom contacts r_{ij} ($N-HKL$) and their comparison with the values of $R_i + R_j$ (and $2\sqrt{(R_i R_j)}$ as well), where R_i and R_j are van der Waals radii. These data make it possible to determine the molecular coordination number.
3. Calculating the energy of contacts $N-HKL$ in atom-atom approximation using 6-exp or 6-12 or some other potentials with or without regard to effective charges on atoms, which are calculated with the help of quantum chemistry methods; the calculation of the total potential energy of the crystal structure (U_Σ) and of the energy of molecular agglomerates (U_{agg}), i.e. ensembles of the most tightly bonded molecules. Such agglomerates can be islands (dimers, trimers etc), chains, layers, three-dimensional frameworks. The value of U_{agg}/U_Σ characterizes the efficiency of agglomerates. The determination of the type of the agglomerates that are present in the crystal makes it possible to assign the substance being studied to a particular *structural subclass*.
4. Constructing various graphic representations of the crystal structure and of its fragments, which clearly demonstrate arrangement of molecules, in particular, constructing representations of the most close molecule-molecule contacts.

s8b.m4.p4 **Packing Patterns of Oximes.** W.D.S. Motherwell, L.C.Kerr, P.R. Raithby *Cambridge Crystallographic DataCentre, 12 Union Rd, Cambridge CB2 1EZ and Dept. of Chemistry, Lensfield Rd, Cambridge CB2 1EW UK.*

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Hydrogen bonding patterns of oximes, $R-N=OH$, have been characterised in early surveys of the Cambridge Crystallographic Database, CSD¹, with some later energetic calculations². We report here a study of the H-bond motifs which occur when molecules are restricted to mono-oximes, with no other strong H-bond acceptor or donor group. Visualisation was achieved using the automatic graph set assignment feature of the RPluto program³, which includes also empirical non-bonded energy calculation of molecular coordination spheres. The preferred geometry of H-bonding requires the OH donor to be in same plane as the acceptor oxime group, which allows a variety of patterns, from catemers to dimers, trimers and tetramers. Dimers are the most common (ca 85%) and catemers rare (ca 8%). Catemer formation seems to require small planar R groups, and a similar observation applies to mono-carboxylic acids. This steric factor was explored using a crystal structure prediction program, Rancel, with empirical atom-pair energy potentials, leading to the correct structure in many cases. Calculated structures have also been generated using functions based on the observed distribution of CSD intermolecular distances. Examination of these sets of low-energy close packed structures has shown that the non-bonded interactions other than the H-bonds seem often to be a crystal structure determining factor.

[1] Bertolasi V., Gilli G., Veronese A.C., *Acta Cryst.* (1982), B38,502-511.

[2] Maurin J.K., *Acta Cryst.* (1998), B54, 866-871.

[3] Motherwell W.D.S., Shields G.P., Allen F.H., *Acta Cryst.* (1999), B55, 1044-1056.