

MS22.01.05 A DATABASE STUDY OF THE BONDING AND CONFORMATION OF BIS-SULFONYLAMIDES AND IMIDES. By Alajos Kálmán* and Petra Bombicz, Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1525 Budapest 114, P.O.Box 17., Hungary.

The bonding and conformational characteristics of bis-sulfonylamides and analogous imides are compared. Structures (44 altogether) of type R-SO₂-NQ-SO₂-R' (R, R' = Me, Et, or Aryl) were retrieved from the Cambridge Structural Database (March 1994 release, 120481 entries). They are either neutral (Q = H, alkyl and aryl group or hetero atom like O and S) or charged (Q = e⁻ or metal, like In, Hg, etc.).

Analysis of the S-N bonds varying in the range 1.57-1.76 Å and their observed influence upon the other S-X and X-S-Y parameters enabled us:

- i. to characterize the S-N bonds against the differences in the nitrogen environment (charged N, N-metal and N-covalent bonds),
- ii. to prove the applicability of the *bond order conservation principle* (Johnston, 1961) and the *VSEPR* rules (Gillespie, 1963) on the S(VI)[O,O',N,C] tetrahedra,
- iii. to describe the intra- and intermolecular conditions of the folded conformation vs the energetically favourable open form of the C-SO₂-NQ-SO₂-C moieties,
- iv. and to substantiate the inequalities of the O-S-N angles which is attributable to the *synclinal* position of one of the S-O bonds with N-lone pair (Kálmán *et al.*, 1981).

The marked difference between the archetypes of the S-N bonds indicates that the interdependence of the S-X bonds in the NSO₂C tetrahedra are principally governed by the environment of the nitrogen atoms. (Sponsor: Hungarian Res. Fund, Grant No. OTKA T014539).

GILLESPIE, R.J. (1963). *J.Chem. Educ.*, 40, 295-301.

JOHNSTON, H.S. (1961). *Adv. Chem. Phys.* 3, 131-170.

KÁLMÁN, A., CZUGLER, M. & ARGAY, GY. (1981). *Acta Cryst.*, B37, 868-877.

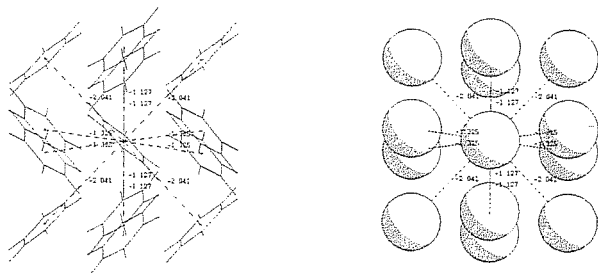
MS22.01.06 AUTOMATIC DETERMINATION OF STRUCTURAL SUBCLASSES. Shishan Guo, Suzanne Fortier, Janice I. Glasgow, Chemistry Department and Computing and Information Science, Queen's University, Kingston, Ontario, Canada K7L 3N6

With the rapid growth of crystallographic databases, fully automatic methods for mining knowledge from these databases are needed. Several classification algorithms are already incorporated into the databases. While these have greatly facilitated the analysis and classification of datasets, considerable user intervention is still required. For example, extensive examination of the dataset may be needed for the selection of clustering algorithm, data parameters, similarity measure, similarity threshold, stopping point, etc. Furthermore, different choices of algorithms and metrics often yield different results. It is thus important to evaluate the robustness of the results and assess their possible dependence on artifacts of the approach used. Thus, a fully automated classification approach requires methods for both pre-classification data preview and post-classification result assessment. This contribution presents a method for the automatic determination of structural subclasses in datasets retrieved from the CSD. Subclasses/clusters are obtained by undergoing a comprehensive automated data preview which is followed by applying clustering algorithms and then by undergoing post-clustering evaluation of the results. The automatic preview component is based on a comprehensive analysis of histograms and scattergrams generated for potential classification parameters. This process helps identify informative

parameters and gives a preliminary clustering of the dataset. For postclassification evaluation, plots of a clustering similarity index are used to assess how the results are affected by different algorithms and by the introduction of random noise into the dataset. These plots help understand the nature of the datasets being analysed by revealing characteristic features associated with the degree of overlap among the subclasses and by identifying where maximum similarity occurs. Application of the automatic classification approach to four representative datasets - valine, hexopyronose sugars, steroid side-chains and six-membered rings - will be presented.

PS22.01.07 PLUTO: CRYSTAL PACKING ENERGIES IN THE CAMBRIDGE STRUCTURAL DATABASE. Sam Motherwell, Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge, CB2 1EZ. U.K.

The Pluto program has been enhanced to allow visual exploration of the packing energy environment of organic molecules. Facilities allow selection of the N strongest interactions. This allows comparison of structures on the basis of the packing energy enclosure shell about a molecule. The energy is calculated by the empirical atom-pair method, using the tables collected by Gavezzotti and others. This allows one to easily compare energy shells for molecules in polymorphs, and in general examine packing patterns on an energy basis. Selective display is allowed at a given energy threshold revealing the most important interactions in the packing. It is also possible to pick any pair of molecules in the packing diagram for energy display. Molecules may be simplified to molecular centre points, or spheres, or enclosure surfaces as ellipsoids or contact probed by a hydrogen atom. Coordinate information may be presented in a simple free format, or the standard Cambridge Structural Database FDAT. or SHELX.



Example. Benzene interactions < -1 Kcal/mole

PS22.01.08 PREQUEST: A DATA INPUT PROGRAM FOR THE CAMBRIDGE STRUCTURAL DATABASE. Paul Edgington, Clare Macrae, Sam Motherwell, Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge, CB2 1EZ. UK

The Prequest program enables users to create new entries for the Cambridge Structural Database (CSD) from common input formats such as CIF and SHELX. Important checks are made for validity and self-consistency of data fields, enabling users to add entries to a local (private) CSD database fully searchable with Quest. This gives the user a method for quickly comparing molecular geometry parameters of current experimental results with the main CSD.

The program also prepares the way for trouble-free depositing of data with the Cambridge Crystallographic Data Centre (CCDC), as private communications to be added to the widely distributed main CSD file.

The use of the CIF input format is now well established.

Prequest gives a friendly interface with which to check out the content of a CIF file, giving interactive graphic display of the 3D molecular structure. Messages are given if items normally expected in CSD entries are missing from the CIF.

Prequest also accepts other common formats such as SHELX. Cartesian coordinates from modelling or theoretical calculations may be input in MOL2 format. Fragments of proteins may be inserted from PDB format with automatic generation of connections and bond types.

Generation of 2D chemical diagrams with bond-type from the 3D coordinates is provided, either automatically or by direct 2D drawing. Checks are made for matching of 2D/3D connectivity before storage.

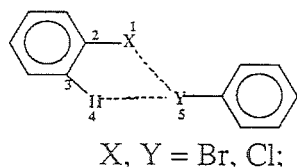
For further details see <http://www.ccdc.cam.ac.uk>

PS22.01.09 STRUCTURAL LIBRARY OF COMMONLY DISORDERED COUNTER IONS AND INCLUDED MOLECULES. ESTABLISHMENT OF SELECTION CRITERIA AND METHODOLOGY. Richard J. Staples, University of Idaho and Joseph H. Reibenspies, Texas A&M University.

Disordered counter ions and/or included molecules often pose a difficult task to model in crystal structure elucidation. The disordered molecules are often modeled by restraining their molecular dimensions to known or estimated parameters or by least squares fitting to structural models taken from the literature or molecular modeling programs. Unfortunately, there appears to be no universally accepted molecular parameters for these common molecules. The first purpose of this work is to establish an ordered set of selection criteria that can be utilized in database searches for the recovery of these molecules. The second purpose is to develop a useful format for rapid incorporation of these results in crystallographic programs. Presentation of these criteria and examples of their use will be presented.

PS22.01.10 INTERMOLECULAR INTERACTIONS A FIVE MEMBERED RING PATTERN CONTAINING HALOGEN...HALOGEN AND HALOGEN...HYDROGEN INTERACTIONS. Oshrit Navon and Joel Bernstein, Department of Chemistry, Ben-Gurion University of the Negev, Beer Sheva 84105 Israel

In the course of a structural study on halogen-substituted benzyldeneanilines we noted the presence of a five-membered ring pattern of the benzyldeneanilines family[1]. Of the six structures studied four are isostructural structures that contain this ring and exhibit an unusual planar molecular conformation, while the remaining two are not planar and do not contain this pattern. The pattern may be defined as an intermolecular ring containing five atoms with hal...hal, C-H...hal interactions:



Using the Cambridge Structural Database (CSD) we have identified and characterized this intermolecular pattern in many other structures.

We will present detailed results for the case where X, Y = Cl, Br on aromatic systems. In addition there is evidence that this pattern may persist over a much wider range of chemical functionality, and preliminary results on such patterns will also be presented.

1. Navon, O., Bernstein, J., Zamir, S., 60th Annual Meeting of the Israel Chemical Society, Weizmann Institute, Rehovot, Israel (1995).

PS22.01.11 TURN AND HELIX MIMETICS FOR PEPTIDE DESIGN. Anke Mueller-Fahrnow & Ursula Egner, Research Laboratories of Schering AG, D-13342 Berlin, F.R.G.

Peptides play an important role in the regulation of a wide variety of biological functions, acting as hormones, neurotransmitters or inhibitors. The therapeutic use of peptides is often hampered by their lack of metabolic stability and their inadequate transport properties. To overcome these problems, the substitution of e.g. helices and turns with appropriate peptidomimetics has been tested.

To build up a database of peptidomimetics, we have performed a thorough search in the recent literature, classified the available beta-turn and helix mimetics according to different criteria and analyzed the results with respect to activity and structure elucidation via X-ray crystallography, NMR spectroscopy or modeling studies. We are currently in the process of incorporating these mimetics as easy to use building blocks in the library of our modeling software.

Although the interest in peptidomimetics is growing permanently and their usefulness in modeling projects is not questioned, only a few beta-turn and helix mimetics have been published and even less characterized with respect to the three-dimensional structure, the potency and the binding mode. Moreover, the application of some of these compounds is restricted due to a time consuming or difficult synthesis.

The opinions expressed above are solely those of the author and are not necessarily those of the Schering AG

Databases II-Inorganic Materials, Powder Diffraction and Polymers

MS22.02.01 COMPUTATIONAL MATERIALS DESIGN: SYNERGY OF FIRST-PRINCIPLES CALCULATIONS AND EXPERIMENTAL DATABASES. E. Wimmer, Molecular Simulations, Inc., Orsay, France

Progress in computational methods combined with the development of novel experimental techniques have created exciting opportunities for materials design. Both computations and experiments are generating data at an increasing rate. Thus, it is of utmost importance to define and implement comprehensive data models to accommodate these results and to create software systems which can operate on this wealth of information. The first part of this contribution provides an overview of current theoretical and computational methods for the prediction of materials properties [1,2]. A particular emphasis is on first-principles density functional methods, which have become truly remarkable tools for structural predictions for a wide variety of systems including organic molecules, organometallic compounds, semiconductors, metals, and ionic compounds. In addition to giving structural information with an accuracy of a few hundredths of one Ångstrom, quantum mechanical methods generate detailed information on the electronic structure and related properties, which is usually complementary to the results of experimental methods such as x-ray diffraction methods, x-ray photoemission spectroscopy, scanning tunneling microscopy, and vibrational spectroscopies. This complementarity can be exploited for analytical purposes, for example in solving crystal structures. In the second part, the capability of present computational methods are illustrated in the context of semiconductors, inorganic pigments, and materials for energy storage. The third part provides an outline of a data model to capture both experimental and computational information. A perspective on emerging computational methods, computer technologies, and communications will conclude this contribution.

1. E. Wimmer, J. Comp.-Aided Mat. Design 1, 215 (1993).
2. E. Wimmer, Science 269, 1397 (1995).