

**PS02.09.03 EXPERIENCES IN THE DETERMINATION AND REFINEMENT OF STRUCTURES INVOLVING TWINNING.** Frederick W. B. Einstein, R. J. Batchelor, Department of Chemistry, Simon Fraser University, Burnaby, B.C., Canada, V5A 1S6

Our Laboratory has been involved in the structure solution and refinement of a number of data sets collected from crystals showing twin lattice symmetry (TLS), this experience has led to procedures which have some general applicability in the structure solution stage where there are a limited number of heavy atoms. The structure solution is sought as if the apparent diffraction symmetry represents untwinned data. The resulting model is then tested against the various alternative space groups by varying only the site occupancies based on the original higher symmetry model. Other experiences with regard to the refinement of twinned data will also be presented. These involve cases where very substantial improvement in the model was achieved by the addition of one variable (twin ratio) to the model.

**PS02.09.04 COMPUTER PREDICTION OF ORGANIC CRYSTAL STRUCTURES USING PARTIAL X-RAY DIFFRACTION DATA.** G. Filippini and A. Gavezzotti, Dipartimento di Chimica Strutturale e Stereochimica Inorganica and CSRSRC CNR, Università di Milano, Milano, Italy.

We have recently developed a computer procedure by which many polymorphic crystal structures are obtained from a rigid molecular structure. A few applications, when only partial crystallographic information (cell and space group) is available, are described. First, five already determined structures selected as validation tests were reproduced, especially when obvious H-bonding patterns could be assigned. As expected, the lattice energies of computational polymorphs are quite similar, even if a preference for the observed structures appears. Next, literature cases were collected where the crystal structure of one polymorph was completely characterized, and mention was made of another polymorph for which only cell and space group were given. The calculations successfully predicted the unknown crystal structure within very short CPU times (a few hours to a few minutes).

Our procedure applies to molecules containing C,H,N,O,S,Cl atoms, in the most frequent space groups for organics. The procedure may provide an alternative to direct methods, when they fail, for the solution of the phase problem. When cell parameters and space group only are available, it can give the full crystal structure with no X-ray diffraction intensity measurements, and if powder data are available, it will conceivably produce a good starting point for Rietveld refinement, reducing the need for well grown single crystals.

We believe that ab initio crystal structure prediction is still a faraway goal. In fact, in none of the above cases could the observed crystal structures have been predicted without the support of X-ray diffraction data.

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**PS02.09.05 A SIMPLIFIED PERTURBATION TREATMENT FOR SAS PHASING.** D. Y. Guo, Robert H. Blessing and David A. Langs, Hauptman Woodward Medical Research Institute, 73 High St. Buffalo, NY 14203, USA.

Via a simple perturbation approximation based on the probabilistic theory for Friedel-pair SAS two-phase structure invariants, it is shown that the SAS three-phase structure invariants tend to predictable positive values, and an SAS perturbed tangent formula is derived. The theoretical probabilistic results are verified by

empirical statistical analyses of model-calculated phases and experimentally measured magnitudes of structure factors for a small-molecule and a protein structure.

The SAS perturbed tangent formula is

$$\tan \phi_H = \frac{\sum_K W_{HK} \sin(\langle \Delta_0 \rangle_H - \phi_K - \phi_{-H-K})}{\sum_K W_{HK} \cos(\langle \Delta_0 \rangle_H - \phi_K - \phi_{-H-K})}$$

Where  $\langle \Delta_0 \rangle = -\langle \xi_H + \xi_K + \xi_{-H-K} \rangle / 2$ ,

$$W_{HK} = E_K E_{-H-K}$$

and  $\xi_H$  is the probabilistic estimate of the two-phase structure invariant  $\phi_H + \phi_{-H}$  (Hauptman, *Acta Cryst.* A38 (1982), 623-641).

The test case for the tangent formula was the single-site  $K_2Pt(NO_2)_4$  derivative of macromycin [P2<sub>1</sub>, Z=2C<sub>46</sub>H<sub>735</sub>N<sub>127</sub>O<sub>160</sub>S<sub>4</sub> • 99.5H<sub>2</sub>O (located) • 3C<sub>6</sub>H<sub>14</sub>O<sub>2</sub>. Ca<sub>0.6</sub>. 3347 Friedel pairs measured to 2.5 Å resolution by Cu Kα x-rays (Van Roey & Beerman, *Proc. Natl. Acad. Sci. USA.* 86(1989), 6587-6591)]. Ambiguous phases for 3028 Friedel-pairs were determined by Harker constructions based on the known Pt position. The tangent formula was used to resolve the two-fold ambiguities. After one or two cycles of tangent refinement starting from random choices of the ambiguous Harker phases, the phase errors were minimized. The average phase error for all 3028 phases, including very small |E|s, is about 48°. For a selected set of 1428 Friedel-pairs with larger |E| values, the phase error is about 37°.

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**PS02.09.06 AN ORIENTATION ON SOLVING SUPRAMOLECULAR COMPOUNDS BY VECTOR SEARCH.** Randy Israel, Lourdes Infantes, Gezina Beurskens, Paul T. Beurskens, Crystallography Laboratory, University of Nijmegen, The Netherlands

One of the main principles of the DIRDIF program system is the application of direct methods to difference structure factors. This procedure makes optimal use of the phase information available when part of the structure is known. This known part may either consist of one or more heavy atoms or of a molecular fragment found by Patterson vector search techniques. Regarding this last method a suitable fragment can be obtained from the structural databases, molecular modelling or from own experience. Then the orientation of the fragment can be determined fully automatic by the program ORIENT [2]. Especially for supramolecular compounds, which not always are easily solved by ab-initio direct methods, and which usually lack heavy atoms, the vector search method proves to be very efficient. However, known fragments of these structures, are either relatively small or show to a larger extent flexibility, which at the end may lead to failure in solving the crystal structure. Therefore some essential parameters of ORIENT were reinvestaged and tested, resulting in a better way of scanning Patterson space in search of optimal overlap with the interatomic vectors of the search fragment and sorting Patterson vectors used.

[1] Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Gelder, R. de, Israel, R. & Smits, J. M. M. (1994) The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, the Netherlands.

[2] Beurskens, P. T., Beurskens, G., Strumpel, M & Norman, C. E. (1987) In Patterson and Pattersons, Eds. J. P. Glusker, B. K. Patterson, and M. Rossi, Clarendon Press, Oxford, 356-367.