

17.4-1 A PRACTICAL ASPECT OF LEAST-SQUARES REFINEMENT OF RIGID GROUPS, AND A SHELX-COMPATIBLE, INTERACTIVE VERSION OF THE ORTEP PROGRAM. By P.R. Mallinson and K.W. Muir, Chemistry Department, University of Glasgow, Glasgow G12 8QQ, U.K.

Rigid group constraints have been available in computer programs for crystal structure refinement for about 20 years, having first been described by C. Scheringer (Acta Cryst. 16, 546 (1963)). The method requires a suitable choice of group axes, since ill-conditioning can occur for certain orientations (R.J. Doedens, 'Crystallographic Computing', Ed. F.R. Ahmed, Munksgaard, 1970, p.198). This problem can be avoided by making a simple assumption in the usual computational method.

Let each group have its own local coordinate system with respect to which the position in orthogonal Angstrom space of an individual atom in the group is represented by a vector $x' = (x', y', z')$. Let x^0 be the fractional coordinates of the origin of this local system (usually the group centroid) with respect to the unit cell axes. There is a global orthogonal system fixed to the crystal axes, which can be made parallel to a group's local axes by successive rotations θ_1 , θ_2 and θ_3 about the global axes. Then $x' = RX$, where X are the coordinates of a group atom with respect to the global axes and local origin, and the rotation matrix R is the product of the matrices for the rotations θ_1 , θ_2 and θ_3 . If U is the orthogonalisation matrix for transformation from the fractional coordinates x of a group atom to its coordinates in the global system, it follows that $x = U^{-1}X + x^0$

$$\text{i.e. } x = x^0 + U^{-1}R^T x' \dots (1)$$

($R^T = R^{-1}$ since R is an orthogonal matrix.)

The variable positional parameters for a group are the local origin coordinates x^0 and the orientation angles θ_1 , θ_2 and θ_3 . The group atom contributions to the derivatives of the structure factors with respect to the group origin are $\partial F / \partial x^0 = \partial F / \partial x \cdot \partial x / \partial x^0 = \partial F / \partial x$, since from (1) $\partial x / \partial x^0 = 1$. The group atom contributions to the derivatives with respect to the orientation angles are $\partial F / \partial \theta_1 = \partial F / \partial x \cdot \partial x / \partial \theta_1 + \partial F / \partial y \cdot \partial y / \partial \theta_1 + \partial F / \partial z \cdot \partial z / \partial \theta_1$. From (1): $\partial x / \partial \theta_1 = U^{-1} [\partial R^T / \partial \theta_1] x'$, similarly for θ_2 and θ_3 .

Equation (1) is used to obtain the group atom fractional coordinates from the new orientation matrix after each least-squares cycle. The local axes are fixed relative to the group atoms and rotate relative to the global axes. Note that the group local axes can always be made (by the program) initially parallel to the global orthogonal axes so that $\theta_1 = \theta_2 = \theta_3 = 0$. Provided that the group is approximately correctly oriented at the start of refinement, changes in the angles will be of no more than a few degrees in magnitude, and the situation leading to matrix singularity ($\theta_2 = 90^\circ$) will not arise.

The method described above has been incorporated into the full-matrix refinement program of the GX crystallographic package (C.J. Gilmore, P.R. Mallinson, K.W. Muir and D.N.J. White, Acta Cryst. A37, C-340 (1981)), and has been found in practice to remove completely the ill-conditioning arising from high correlations between θ_1 and θ_3 . The package also incorporates a highly-developed version of the ORTEP program (C.K. Johnson, Oak Ridge National Laboratory report ORNL-3794 (1970)), designed for interactive use with or without a graphics display terminal. All the GX package programs are compatible with SHELX atom coordinate files (G.M. Sheldrick, 'Program for Crystal Structure Determination' (1976)), and are available by arrangement with the authors.

17.4-2 EASY REFINEMENT OF ABSOLUTE CONFIGURATION AND POLARITY, AND EASY AVOIDANCE OF BIASED POSITIONAL PARAMETERS. By G. Bernardinelli and H.D. Flack, Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24, quai Ernest Ansermet, CH-1211 Genève 4, Switzerland.

The practical use of the enantiomorph-polarity parameter α , defined by $F^2(hkl, \alpha) = (1-\alpha)F^2(hk\bar{l}) + \alpha F^2(\bar{h}k\bar{l})$, in the least-squares refinement of non-centrosymmetric structures is described. Real single-crystal X-Ray-diffraction data from more than 12 samples of organic, organo-metallic, mineral and inorganic compounds containing a wide variety of elements have been analysed. It is found that in most cases the value of α converges in 2 or 3 cycles and is entirely compatible with chemical or physical indications of absolute chirality or polarity where available. By the nature of the defining relationship for α , inversion-tinned crystals are treated naturally as part of this analysis. The value of the estimated standard deviation of α obtained for each structure is compared with more conventional estimates of fit, such as partial (weighted) R factors, partial goodness of fit and Δ/σ distributions, for Friedel or Bijvoet differences. Use of the α parameter is very simple and much less prone to operational errors than is Hamilton's R-factor ratio test or comparison of Bijvoet ratios. Its use immediately avoids an (axial) polar dispersion error and enables an absolute configuration determination with error estimate to be undertaken.

The theory of the α parameter has been given by Flack, H.D., Acta Cryst. (1983) A39, 879-881 and a full account of the current work will be submitted to Acta Crystallographica A.

17.4-3 CONTROLLED REFINEMENT OF A STRUCTURE CONTAINING POORLY DEFINED GROUPS OF ATOMS. By Kenneth J. Haller, Chemistry Department, University of Wisconsin, Madison, WI 53706 USA; and A. David Rae, School of Chemistry, University of New South Wales, Kensington, Australia, 2033.

It is possible to rapidly and successfully refine crystal structures containing disordered and/or largely librating solvent molecules or ligands but constraints must be imposed to maintain structural integrity. Details will be given on how to use and monitor the program RAELS which is based on the use of parameters described relative to various refineable local orthonormal axial systems (Rae, A.D. (1975) Acta Cryst. A31, 560-570). The refinement of the ditoluene solvate of $(C_5H_5)(CO)FeFe[-CO-C(C_6H_5)=C(C_6H_5)-C(=CH_2)](CO)(C_5H_5)$ to $R_1(F) = 0.047$ was rapidly achieved despite one toluene molecule being disordered upon itself about a twofold axis and reasonably large libration of one cyclopentadienyl ring and the other independent toluene. Each phenyl group was given a TL model with the center of libration on the attached carbon atom. A TLX model with a single reorientable relocatable libration axis was used to describe each cyclopentadienyl ring and each toluene. Each group had refineable local atomic coordinates constrained to be planar relative to its refineable local axial system (initially determined by the program). These atomic coordinates were constrained to obey symmetry requirements imposed by the use of equal change, equal but opposite change, and equal percentage change instructions. The disordered toluene was constrained to be identical to the ordered toluene by use of the same refineable local coordinates. Slack constraints controlling geometrical features including constraints causing differences in geometry to approach zero are also very useful but were unnecessary for this structure. The ability to use slack constraints is not restricted by model option.