17. COMPUTATIONAL METHODS AND ERROR ANALYSIS

17.4-1 A PRACTICAL ASPECT OF LEAST-SQUARES REFINEMENT OF RIGID GROUPS, AND A SHELL-COMPATIBLE, INTERACTIVE VERSION OF THE GX PACKAGE. By P.R. Muir, K.W. McElvain and G.M. Sheldrick, Chemistry Department, University of Wisconsin, Madison, Wisconsin 53706 USA; and A. David Rae, School of Chemistry, University of New South Wales, Kensington, Australia, 1983.

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 refinable local ortho-normal axial systems (Rees, A.D. (1983) Acta Cryst. A29, 553-557). The refinement of the ditoluene solvate of (C₆H₅)₂COFe(C₆H₅)₄(C₆H₃-CH=CH₂)(C₆H₅-C(=CH₃))CO(C₆H₅)₄ to R(²) = 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.

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 \( \omega \), defined by \( F_2(\omega)^2 = 1 - \omega F_2(\omega) + \omega F_2(\omega^*) \), 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 \( \omega \) 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 \( \omega \), inversion-twinned crystals are treated naturally as part of this analysis. The value of the estimated standard deviation of \( \omega \) obtained for each structure is compared with more conventional estimates of fit, such as partial (weighted) \( R \) factors, partial goodness of fit and \( \chi^2 \) distribution, for Friedel or Bijvoet differences. Use of the \( \omega \) 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 (excessively) polarisation error and enables an absolute configuration determination with error estimate to be undertaken.

The theory of the \( \omega \) 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.