17.6—7   MOLECULAR MECHANICS CALCULATIONS ON HYDROGEN BONDED COMPLEXES OF 18-CROWN-6 WITH NEUTRAL GUESTS. By J.W.H.M. Uiterwijk, S. Harkema and D. Feil, Chemical Physics Laboratory, Twente University of Technology, Enschede, The Netherlands

Crown ethers can adopt different conformations when complexed with various guest molecules, especially when organic guest molecules are involved. We have previously described a simple method to calculate the number of different conformations of "ideal" crown ethers and to compare their conformational energies (Uiterwijk, Harkema, van de Waal, Göbel & Nibbeling, J. Chem. Soc., Perkin Trans. II, 1983, 1843). More precise conformational energies, obtained with molecular mechanics calculations (MM2: QCPE program no. 395), are presented and discussed. A reasonable agreement (mean difference between observed and calculated endocyclic torsion angles ~5°) is found for various experimental conformations of 18-crown-6. Calculations were done neglecting the influence of the guest molecules. A better agreement was achieved when the interactions between host and guest molecules were included. Initial calculations on a complex of 18-crown-6 with urea (Harkema, van Hummel, Daasvatn and Reinhoudt, J. Chem. Soc., Chem. Commun., 1981, 368) proved the necessity of a H-bond potential in the MM2 force field (taking into account only the electrostatic and van der Waals interactions between host and guest made the agreement worse). We therefore used a modified version of the MM2 program, incorporating a Morse potential for $O-H\cdots O$ hydrogen bonds (MM2HB: Kroon-Batenburg and Kanters, J. Mol. Struct. (Theochem), (1983) 105, 417). For other types of hydrogen bonds ($N-H\cdots O$ and $C-H\cdots O$) we fitted the parameters in the Morse potential to *ab initio* dimer calculations. A significant improvement for the 18-crown-6:urea complex resulted. Calculations for complexes of 18-crown-6 with other organic neutral molecules are in progress and will be presented.

reflection in the same range may be estimated from the average amount by which Δ^2 exceeds σ_c^2 in that range. To calculate σ_s^2, a surface is fit to a plot of $<\Delta^2 - \sigma_c^2>$ versus S and R. σ_s^2 is then expressed as:

$$\sigma_s^2 = A_{00} + A_{10}S + A_{20}S^2 + A_{01}R + A_{02}R^2 + A_{11}RS$$

where $S = ((\sin\theta/\lambda)/(\sin\theta/\lambda)_{max})$ and $R = (|Fo|/|Fo|_{max})$

In contrast to previous methods of estimating σ^2 from $<\Delta^2>$ (Cruickshank et al. in Computing Methods and the Phase Problem in Xray Analysis, Oxford: Pergamon Press (1961)), which replace σ_c^2 by a new σ^2 calculated from $<\Delta^2>$, this method modifies σ_c^2 by adding σ_s^2. The method serves to remove bias from the weighting scheme and a plot of $w\Delta^2$ should be near unity for each range of $|Fo|$ or $\frac{\sin\theta}{\lambda}$.

The method has been tested on the refinement of several structures and has been found to reduce the estimated standard deviations of the crystallographic parameters determined by least squares by approximately 1/3 from those resulting from weights based on σ_c^2 alone. Comparisons have also been made with refinements in which an "ad hoc" attempt is made to modify σ_c^2 by adding a term proportional to $|Fo^2|$ in order to remove bias from the distribution of $w\Delta^2$. Again, decreases of approximately 1/4 were obtained in the estimated standard deviation of the structural parameters determined from least squares. In all cases the values of those least-squared parameters were different by an average amount substantially greater than their e.s.d.'s as obtained from the refinement using the full σ^2.

It is intended that this procedure be incorporated into the crystallographic computing package XTAL.

17.7—1   BIAS IN LEAST-SQUARES WEIGHTS AND ITS EFFECT ON THE ACCURACY OF CRYSTALLOGRAPHIC PARAMETERS. By Wang Hong and B.E. Robertson, Faculty of Science, University of Regina, Regina, Saskatchewan, Canada S4S 0A2.

The function most commonly minimized in the determination of the optimum crystal structure consistent with the observed data is $\sum_h w(h)\Delta^2(h)$ where $w(h)$ is the weight assigned to the reflection h and $\Delta(h)$ is $|Fo(h)|-|Fc(h)|$. The correct value of $w(h)$ is the reciprocal of the variance of $\Delta(h)$, $\sigma^2(\Delta(h))$, where $\sigma(\Delta(h))$ is the standard deviation of $\Delta(h)$. (Rollet, in Computational Crystallography, Oxford Press, edited by Sayre, (1981), 338). We will divide $\sigma^2(\Delta(h))$ into that part which can be calculated from counting statistics, σ_c^2, and that which is systematic and cannot be observed directly, σ_s^2. σ_c is associated entirely with the measurement of $|Fo|$, and $\sigma_c = \sqrt{I + \sigma_c(I)} - \sqrt{I}$, where $I = F^2$.

The variance in I, $\sigma_c^2(I)$, arises out of counting statistics and may be divided further into that based on the measurement of the individual intensity I, $\sigma_i^2(I)$, and the variance manifested by the extent to which the scatter of the counts associated with the measurement of the standard reflections exceeds that predicted from their own counting statistics, $\sigma_e^2(I)$, (Xray 76, Tech. Rep. TR-446, U. of Maryland, USA (1976) edited by Stewart). The variance associated with systematic effects, σ_s^2, has two contributions, σ_{so}^2 and σ_{sc}^2. The former arises mainly from errors in $|Fo|$ which are dependent on crystal orientation. The latter contribution is associated with errors in the model represented by $|Fc|$.

We assume that $<\sigma^2> = <\Delta^2>$ for similar ranges of any variables on which Δ^2 might be dependent, specifically $|Fo|$ and $\sin\theta/\lambda$. Then if $\sigma^2 = \sigma_c^2 + \sigma_s^2$, σ_s^2 for a

17.7—2   THE INFLUENCE OF INDIVIDUAL REFLECTIONS ON THE PRECISION OF PARAMETER ESTIMATES IN LEAST SQUARES REFINEMENT. By E. Prince, National Bureau of Standards, Washington, DC 20234, U. S. A., and W. L. Nicholson, Pacific Northwest Laboratory, P. O. Box 999, Richland, WA 99352, U. S. A.

If **A** is the matrix with elements $A_{ij} = (\partial F_{ci}/\partial x_j)/\sigma_i$, and **y** is the vector with elements $y_i = (|F_{oi}|-|F_{ci}|)/\sigma_i$, where F_c and its partial derivatives are evaluated at the point **x'**, close to the point at which the sum of squares is minimized, then the least squares solution is $\hat{x} - x' = (A^TA)^{-1}A^Ty$, and the variance-covariance matrix for $\hat{x}$ is $V = (A^TA)^{-1}$. The matrix $P = A(A^TA)^{-1}A^T$ is the "projection matrix", so called because it can be viewed as projecting a vector in $\underline{n}$ dimensional observation space into $\underline{p}$ dimensional parameter space. It is readily verified that $P^2 = P$, from which it follows that the eigenvalues of P are either 0 or 1, and that the diagonal elements of P lie in the range $0 \le P_{ii} \le 1$. P has dimensions $\underline{n} \times \underline{n}$ and rank $\underline{p}$, so there are exactly $\underline{p}$ 1 eigenvalues, with the rest 0. The trace of P is $\underline{p}$, so the average value of a diagonal element is therefore $\underline{p}/\underline{n}$. If the value of a diagonal element is 1, that reflection must fit exactly, placing a constraint on some linear combination of parameters. If the value is 0, the reflection will have no influence whatsoever on the refinement. If reflection $\underline{i}$ is remeasured with the same precision as before and included in the fit, the determinant of **V**, and thus the square of the volume of the confidence region, is reduced to $|V'| = |V|[1 - P_{ii}/(1 + P_{ii})]$. Moreover, if we designate by a_i the $\underline{i}$th row of **A**, the updated variance-covariance matrix is $V' = V - Va_i^Ta_iV/(1 + P_{ii})$. It is thus possible, by a relatively simple computation, to determine the effect a remeasurement of a subset of the reflections would have on the variance of each of the estimated parameters.