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 $y_i = (|F_{oi}|^i - |F_{ci}|)/\sigma_i$, where F_{ci} 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 $\hat{x} - x' = (A^T A)^{-1} A^T y$, and the variance-covariance matrix for $\hat{x}$ is $V = (A^T A)^{-1}$. The matrix $P = A(A^T A)^{-1} A^T$ is the "projection matrix", so called because it can be viewed as projecting a vector in n dimensional observation space into 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 $0 \leq P_{ii} \leq 1$. P has dimensions $n \times n$ and rank p, so there are exactly p 1 eigenvalues, with the rest 0. The trace of P is p, so the average value of a diagonal element is therefore p/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 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 ith row of A, the updated variance-covariance matrix is $V' = V - Va_i^T a_i V/(1 + P_{ii})$. 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.

If a reflection has a small value of P_{ii}, but its F
value is discrepant, it becomes an "outlier." This may
result from an inadequate model as well as from sys-
tematic error. Least squares will try to fit this
reflection, with a resulting introduction of bias. In
these circumstances a robust/resistant variant of least
squares [Nicholson, Prince, Buchanan & Tucker,
Crystallographic Statistics, Ramaseshan, Richardson &
Wilson, eds. Indian Acad. Sci. Bangalore, pp 229-263
(1982)] is useful because it helps to identify the out-
liers and reduces the sensitivity of the model to them.
In their multiple refinements of the structure of D(+)-
tartaric acid, using data from the Single-Crystal
Intensity Measurement Project of the IUCr, Hamilton &
Abrahams [Acta Cryst. A26, 18-24 (1970)] used σ_i =
$0.1|F_o|$ to determine the weights. The assumption was
that there was a sufficiently small number of very weak
reflections that any effect of overweighting would be
minor. Analysis of the projection matrix, however, shows
that there is a small number of very weak reflections
with P_{ii} > 0.95, whereas more than 20% of all reflec-
tions, mostly relatively strong, have P_{ii} < 0.1.
Furthermore, a small number of weak reflections provides
the dominant influences on all parameters except scale
and extinction. In a few cases a parameter is determined
overwhelmingly by a single reflection, and in many cases
the parameter is determined by a small subset of the
data. Nearly half of the reflections do not appear among
the five most influential ones for any parameter! The
structure is therefore determined by a subset of the
data, far smaller than the full set, consisting mainly
of weak reflections. The rather large scatter among dif-
ferent data sets of parameter estimates, relative to the
computed standard deviations, that was found by Hamilton
& Abrahams is therefore probably ascribable to the im-
balance of weights between weak and strong reflections.

17.7−3   MODEL-STRUCTURES ILLUSTRATING THE PRESENCE
OF FALSE LEAST-SQUARES R1-MINIMA AND THEIR RESOLUTION
WITH R2-REFINEMENT, A.L.Spek, Vakgroep Algemene Chemie,
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The crystallographic literature contains a few well
documented cases where the refinement converged to a
minimum that was later shown to be false but very close
to the true one. In such cases the derived geometry
shows features that may be chemically intriguing and
statistically significant but that actually are refine-
ment artefacts. A good example is the low-temperature
structure of adamantane (Nordman&Schmitkons, Acta Cryst.
(1965),18,764) for which it was shown (Donohue&Goodman,
Acta Cryst.(1967),22,352) that the reported unusual
variation in related bond-distances and angles was due
to refinement to a false R1-minimum. The true R1-mini-
mum was reached by rigid group refinement on a regular-
ized molecule followed by the release of the constraints

We recently used this example to test the hypothesis
that this false minimum is in fact an artefact of the
R1-refinement. The SHELX-76 package was modified for
this purpose to include R2-refinement facilities. It
was indeed found that the true minimum could be reached
easily with an R2-refinement starting from the false

Minimizing R1 as opposed to R2 is a commonly used pro-
cedure for structure refinement and seems to be mainly
dictated by the wide availability of program packages
that consolidate a practice from the past that was main-
ly introduced for computational reasons that no longer
apply. R2-refinement is usually advocated as a facility
to include 'negative' observed intensities in the refi-
nement. However, the above example shows that there can
be other benefits as well, since, although R1 and R2
(when properly weighted) give essentially the same pa-
rameter values for the true minimum, their behavior
outside this minimum is quite different.

A two parameter model was constructed that exhibits
the same refinement behavior as the adamantane struc-
ture but in a parameter space that is more accessible
for exhaustive investigation, the results of which will
be presented.