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17. COMPUTATIONAL METHODS AND ERROR ANALYSIS

17. 6-7 MOLECULAR MECHANICS CALCULATIONS ON HYDROGEN BONDED COMPLEXES OF 18-CROWN-6 WITH NEUTRAL GUESTS. By J.J.M.H. Utterwijk, S. Hermkes and D. Flei, 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 (Utterwijk, Hermkes, van de Wael, Gobell & Homburg, 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 Hoom, Basavant and Hildbrand, 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 (QCPE program no. 395), incorporating a Morse potential for O-H...-O hydrogen bonds (Sayre, 1961; Kroon-Batenburg and Kanters, J. Mol. Struct. (Theochem), 1983, 105, 417). For other types of hydrogen bonds (N-H...-O and C-H...-O) we fitted the parameters in the Morse potential to ab initio dimer calculations. A significant improvement for the 18-crown-6-units complex resulted. Calculations for complexes of 18-crown-6 with other organic neutral molecules are in progress and will be presented.

17.7-1 BIAS IN LEAST-SQUARES WEIGHTS AND ITS EFFECT ON THE ACCURACY OF CRYSTALLOGRAPHIC PARAMETERS. By K.H. More, R.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 2w(h)2(s(h)) where w(h) is the weight assigned to the reflection h and s(h) is the standard deviation associated with that reflection. The correct value for w(h) is the reciprocal of the variance of the observation s(h)2. The standard deviation of s(h) is the standard deviation of w(h) to the measurement of the individual intensity I, w2(h) = (F2(h) - I2(h))/I2(h), where F(h) 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 x = x0 + (A*A)-1A*y, and the variance-covariance matrix for x is V = (A*A)-1. The matrix P = (A*A)-1 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 P2 = P, for 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 ≤ Pii ≤ 1. P has dimensions n × n and rank p, so there are exactly p eigenvalues, with the rest 0. The trace of P is p, so the average value of a diagonal element is therefore 1/p. If the value of a diagonal element is 1, that reflection must be exact, placing a constraint on some linear combination of parameters. If the value of 0, the reflection will have no influence whatever on the refinement. If reflection j 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 |V1| = |V1|/(1 + Pj). Moreover, if we designate by a, the ith row of R, the updated variance-covariance matrix is V1 = |V1|/|V1|/(1 + Pj). 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 any of the estimated parameters.