

## SHORT COMMUNICATIONS

*Acta Cryst.* (1996). **A52**, 326

### Multiplicity of crystal planes belonging to the point group $\bar{4}m2$ . Erratum

IL-HWAN SUH at Department of Physics, Chungnam National University, Taejon 305-764, Korea.  
E-mail: ihsuh@nspphys.chungnam.ac.kr

(Received 1 October 1995; accepted 9 November 1995)

#### Abstract

There is an error in Table 10.2.2 of *International Tables for Crystallography*, Vol. A (Hahn, 1992, 1995). The multiplicity of  $(00l)$  and  $(00\bar{l})$  belonging to the point group  $\bar{4}m2$  is 2 not 1. The equivalent reflections in the point group  $\bar{4}m2$  (Ibers, 1967; Ibers & Hamilton, 1973) are

$$hkl = \bar{h}kl = h\bar{k}l = \bar{h}\bar{k}l = kh\bar{l} = k\bar{h}\bar{l} = k\bar{h}l = \bar{k}\bar{h}l.$$

Substitution of  $h = k = 0$  into the above relation results in  $00l = 00\bar{l}$ . Therefore, the multiplicity of  $00l$  or  $00\bar{l}$  in the point group  $\bar{4}m2$  is 2.

*Acta Cryst.* (1996). **A52**, 326–328

### *Ab initio* molecular packing analysis

DONALD E. WILLIAMS at Department of Chemistry, University of Louisville, Louisville, KY 40292, USA.  
E-mail: dew01@xray5.chem.louisville.edu

(Received 30 October 1995; accepted 11 December 1995)

#### Abstract

A method is presented which, given a molecular structure and an intermolecular force field, can predict observed polymorphic crystal structures and molecular clusters without any prior assumption of space symmetry.

#### 1. Introduction

In molecular-packing calculations, symmetry constraints are often used to simplify the problem. For example, in early benzene molecular-cluster calculations, Williams (1980) assumed inversion symmetry and limited consideration to clusters containing an odd number of molecules. More recently, symmetry constraints were removed and four different energy-minimum structures for the benzene tetramer cluster have been predicted (Williams, 1992). In the earlier work, 13- and 15-molecule clusters showed some resemblance to the structure of crystalline orthorhombic benzene. Of course, the structure of a sufficiently large cluster should become identical to the crystal. However, the molecular-cluster approach to crystal structure prediction can quickly become intractable because each additional molecule contributes six degrees of freedom to the calculation. When one is attempting to predict a crystal

#### References

- Hahn, T. (1992). *International Tables for Crystallography*, Vol. A, p. 761, Table 10.2.2. Dordrecht: Kluwer.  
Hahn, T. (1995). *International Tables for Crystallography*, Vol. A, p. 761, Table 10.2.2. Dordrecht: Kluwer.  
Ibers, J. A. (1967). *Acta Cryst.* **22**, 604–605.  
Ibers, J. A. & Hamilton, W. C. (1973). *International Tables for Crystallography*, Vol. IV, p. 151. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

structure, it is computationally expedient to assume lattice symmetry, *i.e.* repetition of unit cells in three-dimensional space.

In the traditional approach to prediction of crystal structure from a known molecular structure, the observed crystal space group is utilized. An early example is the prediction of the dibenzoylmethane (IUPAC name: 3-hydroxy-1,3-diphenyl-2-propen-1-one) crystal structure in *Pbca* (Williams, 1966); in this case, a very approximate force field was used along with the observed cell constants. Very often, development of force-field parameters has utilized molecular-packing calculations where the aim was to minimize the difference between the calculated energy-minimum structure (relaxed structure) and the observed structure. The accuracy of today's available intermolecular force fields reflects heavy dependence on such crystal structure calculations.

In the preceding case, only small deviations are considered from observed crystal structures and the space group is known. But what if only the molecular structure is known and the crystal structure must be predicted from first principles? Gavezzotti (1994) has recently reviewed possible approaches to this question. The overwhelming success of experimental diffraction methods has no doubt removed much of the urgency to develop *ab initio* crystal structure prediction, but successful

crystal structure prediction is fundamental to our understanding of the crystallization process.

Recent efforts to predict crystal structure generally make a prior assumption of space-group symmetry (Gdanitz, 1992; Holden, Du & Ammon, 1993; Karfunkel & Gdanitz, 1992; van Eijck, Mooij & Kroon, 1995). In principle, one needs to obtain intermolecular energy minima for up to 230 space groups to include all possibilities in this approach. A survey of observed crystal structures (Baur & Kassner, 1992) shows that some space groups are much more commonly encountered than others. In fact, 93% of organic molecules were found to crystallize in only 18 space groups. But how is one to know if a particular molecule crystallizes in a populous space group? Obviously, there is risk involved and one cannot be certain with this approach that the correct space group was considered. One of the examples below illustrates predicted crystallization in  $P4_2/m$ ; this space group has a frequency of less than 0.39% and is not included among the 32 most populous groups.

## 2. Computer program *mpa*

If one does not assume space symmetry at the outset, attention is focused on the number of molecules in the cell ( $Z$ ) and their interrelationships. One asymmetric molecule per cell is suitable only for  $P1$ ; even  $P1$  requires  $Z = 2$ . Usually, the number of

molecules per cell is equal to the number of space-group operations in the penultimate space group, unless the molecule has symmetry operations that become coincident with space-group operators. Occasionally, there may be several molecules in the asymmetric unit, often with different molecular conformations. To successfully predict the space group, separate energy minimizations must be done for each  $Z$  value and the resulting global energy-minimum structure analyzed for the presence of space symmetry.

Computer program *mpa* (Williams, 1996) is capable of finding intermolecular energy minima for given  $Z$  without any assumption of space-group symmetry; *i.e.* the program can predict space-group-symmetry operations. In the examples below,  $Z$  values of 2 and 4 are considered but there is no restriction on using other values of  $Z$ . The starting point for intermolecular energy minimization is a large cubic cell but with variation of all six cell constants. If  $Z = 2$ , molecules are initially placed in a body-centered cell; if  $Z = 4$ , a face-centered cell is used for the initial point. Then each molecule is randomly rotated to establish the initial model. Care must be taken that rotational space is uniformly sampled (Williams, 1973). Since the translational position of one molecule must be fixed to set the cell origin, the degrees of freedom are 15 and 27 for  $Z = 2$  and 4.

Since this is a Monte Carlo process, most trials led to local minima but the lowest energy minimum found always

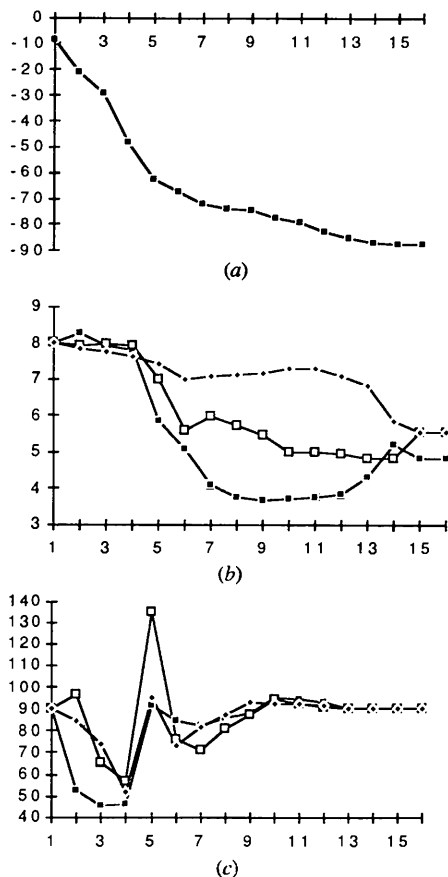


Fig. 1. (a) Urea intermolecular energy (kJ mol<sup>-1</sup>) versus contact table number. (b) Urea cell edges (Å). (c) Urea cell angles (°).

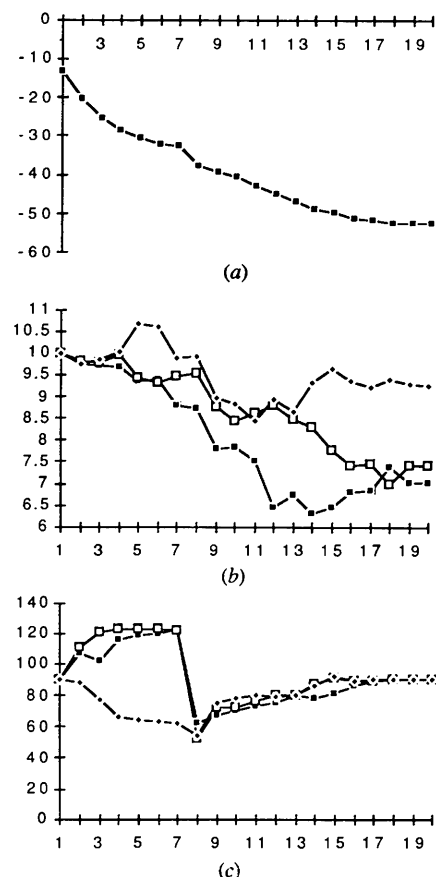


Fig. 2. (a) Benzene intermolecular energy (kJ mol<sup>-1</sup>). (b) Benzene cell edges (Å). (c) Benzene cell angles (°).

corresponded to the observed structure. When a minimum is found, there may be space symmetry relating the molecules. For example, with two molecules in the cell, energy minimization might show a structure in which the molecules are related by a  $2_1$  screw axis. This fact must necessarily be accompanied by the prediction of a monoclinic cell with two right angles, even though these angles are allowed to vary. With four molecules in the cell, additional orthogonal screw axes may lead to an orthorhombic cell with three right angles.

To evaluate lattice sums rapidly, *mpa* saves a contact table of intermolecular atom-atom contacts for repetitive use. The number of entries into the table is reduced by subdivision of the cell into electrically neutral regions. Accelerated convergence (Williams, 1971) is used to obtain maximum accuracy in the lattice sum with a relatively short cut-off distance of 10 Å. Both first (gradient vector) and second (hessian matrix) derivatives of the lattice energy are evaluated analytically, rather than numerically, to obtain maximum speed (Williams, 1972).

The method used for energy minimization depends on the local nature of the energy surface. It is extremely unlikely that the hessian of a random trial structure will be positive definite. More likely, a random point is near one of the many saddle points of the energy surface and the fastest way to go to lower energy is to move in the direction of eigenvectors corresponding to negative eigenvalues; this is the OREM method previously found useful in obtaining global energy minima of benzene molecular clusters (Williams, 1992). OREM shifts usually yield a large energy decrement; if this is not the case, *mpa* can automatically switch to steepest-descent (SD) minimization. SD, while usually slow to converge near a minimum, can be very effective when the calculation is far from a minimum. OREM shifts always lead to positive-definite regions where the Newton-Raphson (NR) method can be used. It should be noted that, since the energy surface is not quadratic, NR shifts are only approximate and they sometimes lead back to a non-positive-definite region where *mpa* reverts to OREM to relocate a NR region.

The following section briefly presents some results obtained with the *mpa* program; a more detailed report is planned for later publication.

### 3. Results

Since hydrogen bonding is an extremely important factor influencing molecular crystal structure, separate trials were made of structures with and without hydrogen bonding present. Urea (observed space group  $P4_2/m$ ) was selected as the hydrogen-bonded structure, using the Biosym force field (Biosym, 1989); benzene (observed space group  $Pbca$ ) was selected as the non-hydrogen-bonded structure, using the WH86 force field (Williams & Houpt, 1986). Net atomic charges were obtained by the electrostatic potential derived method (Williams, 1993). Up to six eigenvectors for OREM and up to three cycles of NR were allowed for each contact table.

#### 3.1. Urea, $Z = 2$

Fig. 1(a) shows the intermolecular energy at each contact table makeup, for a successful Monte Carlo trial. The final energy agrees with the energy of the relaxed observed structure. Fig. 1(b) shows the variation of the cell edges during the calculation. Notice that the values quickly shift from cubic symmetry; the refinement for contact table 14 clearly shows

something like a phase transition to the correct tetragonal lattice constants. Fig. 1(c) shows the variation of the cell angles. Wide fluctuations occur in the intermediate triclinic structures; new reduced cells were defined at contact tables 4, 5, 9 and 14. Beginning at about contact table 10 (or earlier), there is a trend towards an orthogonal cell, but exact space-group symmetry (within numerical error) was not achieved until the final cycle. The final predicted structure and symmetry are identical to the relaxed observed structure.

#### 3.2. Benzene, $Z = 4$

Fig. 2 shows the variation of the intermolecular energy, cell edges and cell angles.

The intermolecular energy drops smoothly to the observed value. As with urea, the trial cubic cell quickly becomes triclinic and remains triclinic until the final stages. The cell angles vary widely from  $90^\circ$ ; new reduced cells were defined at contact tables 7, 8, 11, 15 and 18. Beginning at about contact table 16 (or earlier), there is a trend towards an orthogonal cell. Examination of the final structure shows that it is identical to the relaxed observed structure, with  $Pbca$  symmetry.

If  $Z = 2$ , a  $P2_1/c$  monoclinic structure for benzene is predicted; this structure is nearly identical (with slightly longer cell edges) to the observed high-pressure polymorph but has a higher energy per molecule than the orthorhombic  $Z = 4$  structure. Hall, Starr, Williams & Wood (1980) discuss the stability of the high-pressure form of benzene.

### 4. Conclusions

Program *mpa* is successful for *ab initio* prediction of the structures of molecular clusters and crystal polymorphs. *Ab initio* in this context means that only the molecular structure and force field are necessary as inputs. The program does not require specification of space-group symmetry and can in fact predict space symmetry.

### References

- Baur, W. H. & Kassner, D. (1992). *Acta Cryst.* **B48**, 356–369.
- Biosym (1989). Program *Discover*. Biosym Technologies, San Diego, CA, USA.
- Eijk, B. P. van, Mooij, W. T. M. & Kroon, J. (1995). *Acta Cryst.* **B51**, 99–103.
- Gavezzotti, A. (1994). *Acc. Chem. Res.* **27**, 309–314.
- Gdanitz, R. J. (1992). *Chem. Phys. Lett.* **190**, 391–396.
- Hall, D., Starr, T. H., Williams, D. E. & Wood, M. K. (1980). *Acta Cryst.* **A36**, 494.
- Holden, J. R., Du, Z. & Ammon, H. L. (1993). *J. Comput. Chem.* **14**, 422–437.
- Karfunkel, H. R. & Gdanitz, R. J. (1992). *J. Comput. Chem.* **13**, 1171–1183.
- Williams, D. E. (1966). *Acta Cryst.* **21**, 340–349.
- Williams, D. E. (1971). *Acta Cryst.* **A27**, 452–455.
- Williams, D. E. (1972). *Acta Cryst.* **A28**, 629–635.
- Williams, D. E. (1973). *Acta Cryst.* **A29**, 408–414.
- Williams, D. E. (1980). *Acta Cryst.* **A36**, 715–723.
- Williams, D. E. (1992). *Chem. Phys. Lett.* **192**, 538–543.
- Williams, D. E. (1993). Program *pdm93, Potential-Derived Net Atomic Charges and Multipoles*. Department of Chemistry, University of Louisville, Louisville, KY 40292, USA.
- Williams, D. E. (1996). Program *mpa/mpg, Molecular Packing Analysis/Molecular Packing Graphics*. Department of Chemistry, University of Louisville, Louisville, KY 40292, USA.
- Williams, D. E. & Houpt, D. J. (1986). *Acta Cryst.* **B42**, 286–295.