KITAMURA, M. & MORIMOTO, N. (1977). *Phys. Chem. Miner.* **1**, 199–212.

KOREKAWA, M. (1980). Personal communication.

KOREKAWA, M., HORST, W. & TAGAI, T. (1979). *Z. Kristallogr.* **149**, 128–130.

KOREKAWA, M. & JAGODZINSKI, H. (1967). *Schweiz. Mineral. Petrogr. Mitt.* **47**, 269–278.

MEGAW, H. D. (1960). *Proc. R. Soc. London Ser. A*, **259**, 59–78, 159–183, 184–202.

NISSEN, H. U., EGGMANN, H. & LAVES, F. (1967). *Schweiz. Mineral. Petrogr. Mitt.* **47**, 289–302.

SMITH, J. V. & RIBBE, P. H. (1969). *Contrib. Mineral. Petrol.* **21**, 157–202.

TOMAN, K. & FRUEH, A. J. (1976). *Acta Cryst.* **B32**, 521–525, 526–538.

SHORT COMMUNICATIONS

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.

Significance of calculated cluster conformations of benzene: comment on a publication by D. E. Williams.

By B. W. VAN DE WAAL, *Twente University of Technology, Chemical Physics Laboratory, PO Box 217, 7500 AE Enschede, The Netherlands*

Abstract

Results of potential-energy minimization, applied to clusters of benzene molecules, have been reported recently by Williams [*Acta Cryst.* (1980), A**36**, 715–723]. Two stable tridecamer clusters were found and compared with a 13-molecule fragment from crystalline orthorhombic benzene. In this comment the significance of such a comparison is discussed and related to the size of the clusters.

Introduction

The potential energy of a limited number (N) of molecules is a complicated function of the $6N$ molecular coordinates, even if the molecular interaction is represented by a simple model. In general, there will be more than one minimum and the result of a minimization procedure will therefore be dependent on the starting point in configuration space, the initial configuration. Since each minimum that can be localized corresponds to a definite conformation of N molecules in a cluster, the problem arises of establishing the significance of different cluster conformations, relative to one another, particularly in connection with molecular complexation and crystallization. This significance cannot be derived from a direct comparison with experimental material, since no detailed information concerning the structure of small molecular clusters is available.

The procedure adopted by Williams (1980) to find optimum conformations for clusters of benzene molecules, ranging in size from $N = 2$ to $N = 15$, consists of finding the optimum conformation of an N cluster by adding two molecules to an optimized ($N - 2$) cluster, starting with $N =$

3. One molecule is kept fixed at the origin; pairs of additional molecules are related by a centre of symmetry at the origin. In two instances ($N = 7$ and $N = 13$) the results are not unique. In this comment we will fix our attention on the 13-molecule clusters, since they may be considered as a central molecule with a completed coordination shell. Two criteria are applied by Williams to distinguish between clusters of equal size: (*a*) the energy E_r of the central molecule and (*b*) the behaviour of E_r in the sequence $N = 3$, 5, ...,13. It is assumed by Williams that the cluster with the lowest value of E_r and with the most regular decrease of $E_r(N)$ in the 'history' of the cluster, could lead to crystallite formation, whereas other clusters could be broken up by thermal agitation. The cluster that is supposed to play a role in crystallite formation is subsequently compared with the observed crystal structure of orthorhombic benzene.

Although the criteria applied by Williams may be justifiable, they do not appear to be decisive, in view of the small differences in energy and the small number of molecules under consideration. It is the purpose of this comment to investigate whether a comparison with the observed crystal structure is feasible and if it can support Williams's assumption concerning crystallite formation.

Although a cluster conformation can be compared with a fragment of the observed crystal structure, there is little reason to expect the structure of a cluster to be very similar to that of such a fragment, when the number of molecules is small. In the case of benzene, all 13 molecules in a crystal fragment, consisting of a central molecule and its first coordination shell, are equivalent and have the same environment. This environment is not present in a 13-molecule cluster; nearly all molecules are 'surface molecules', and the conformation may therefore be dominated by surface effects.

If the crystal fragment were to be taken out *physically* from the crystal, it could change its conformation drastically, in response to the elimination of forces not originating in the fragment itself. Referring to the conformation of the crystal fragment, before and after removal from the crystal, as the 'unrelaxed' and the 'relaxed' fragment, respectively, it is preferable to compare cluster conformations that result from a minimization procedure, not only with an unrelaxed fragment, but also with a relaxed fragment.

The tridecamer benzene clusters

Two different 13-molecule benzene clusters, with energies $-305{\cdot}0$ and $-325{\cdot}3$ kJ mol^{-1} and labelled normal- and iso-tridecamer, respectively, have been found by Williams (1980) by potential-energy minimization, with exp$-6-1$ non-bonded atom–atom potential functions. Both clusters consist of a central molecule and a completed first coordination shell. Figs. 1 and 2 give stereoviews of both conformations (for easy reference a stereoview of the unrelaxed crystal fragment is represented in the upper half of all figures). The conformations of both clusters are compared (i) with an unrelaxed crystal fragment and (ii) with a relaxed crystal fragment.

(i) Comparison with an unrelaxed fragment

Williams states that the iso-tridecamer (Fig. 2) has a conformation quite different from the crystal fragment, whereas the conformation of the normal-tridecamer (Fig. 1) can be brought into rough correspondence with that of the fragment by a process of plane slippage. Plane slippage is visualized as taking place when more molecules are added to the cluster. In Fig. 3 we have rotated the normal-cluster conformation 60° in a clockwise direction about the sixfold axis of the central molecule. No plane slippage is required to obtain a rough correspondence with the crystal fragment. However, in the absence of a quantitative measure for the similarity of two conformations, any judgement on which cluster is closer to the crystalline fragment is rather arbitrary.

(ii) Comparison with a relaxed fragment

In order to obtain the (predicted) configuration of the relaxed crystal fragment, we have minimized the potential energy of the 13-molecule crystal fragment, allowing all 78 molecular coordinates to vary simultaneously, including those of the central molecule. Initial rotational and translational coordinates were derived from the observed crystal structure of orthorhombic benzene (Bacon, Curry & Wilson, 1964). Non-bonded potential parameters, atomic charges and molecular atomic coordinates were the same as those used by Williams. To minimize the energy a steepest-descent method with Newton–Raphson step-size estimation, employing numerically evaluated second derivatives, was used. To ensure that the result is independent of the computational method, we have introduced small changes in the initial configuration. The result was not affected by these changes, even if they were comparatively large (90° rotations about molecular two-fold axes, cluster expansion by factors $1{\cdot}1-1{\cdot}5$). The conformation of the relaxed crystal fragment was found to be identical with that of the iso-tridecamer. No
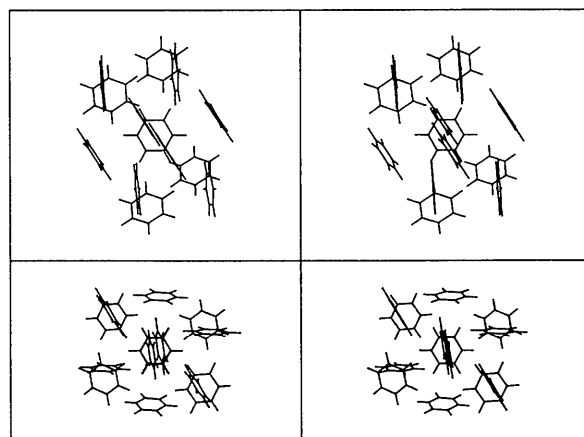

Fig. 1. Tridecamer crystal fragment (upper half). Normal tridecamer cluster (lower half).
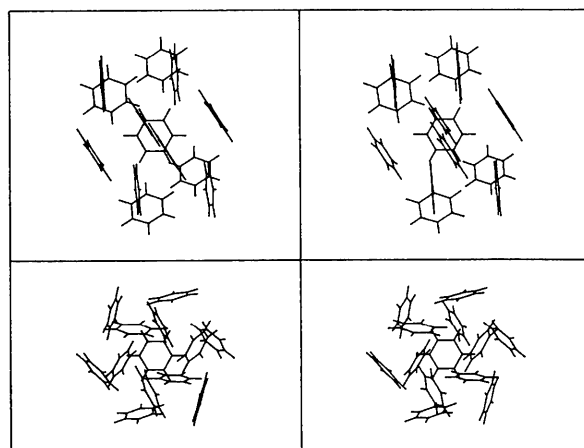

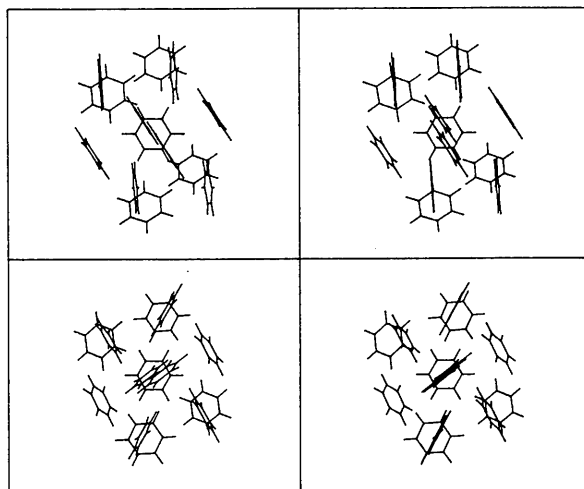Fig. 2. Tridecamer crystal fragment (upper half). Iso-tridecamer cluster (lower half).

Fig. 3. Tridecamer crystal fragment (upper half). Normal tridecamer cluster, after 60° rotation (lower half).

relationship between the normal-tridecamer and the relaxed fragment could be found.

The marked difference between the conformations of the relaxed and the unrelaxed crystal fragments are probably entirely due to the small size of the fragments. Although it cannot easily be verified by calculation (in view of the large number of molecules involved), we anticipate that these differences will decrease, and eventually vanish, when more shells are added (a crystal may be considered as a central molecule with a large number of shells). These differences should be sufficiently small to render the comparison (i) feasible. Even so, the comparison (ii), although leading to the same result, has the advantage that the comparison of cluster conformations can be replaced by a comparison of energies, since a cluster that is *similar* to the unrelaxed fragment is *identical* to the relaxed fragment, with the same energy.

concerning its significance in connection with crystallite formation. Williams's assumption that the normal cluster could lead to crystallite formation, whereas the iso-cluster could be broken up by thermal agitation, is based on the observation that the central molecule has a lower energy in the normal-tridecamer than in the iso-tridecamer. The difference is very small (*ca* 1%) and could easily change sign when more molecules are added. No conclusions can be drawn from the view that the energy of the central molecule should increase in a uniform manner, when molecules are added to the cluster: the figure $-2 \cdot 0$ (Williams, 1980, Table 2) does not fit significantly better in the pattern of energy increments than would the figure $-1 \cdot 7$.

We conclude that it is necessary to add more molecules to the clusters in order to be able to relate their conformations to the observed crystal structure and to establish their significance in relation to crystallization.

Conclusion

The considerable change in conformation of the 13-molecule crystal fragment upon relaxation supports the view that a 13-molecule cluster is too small to justify assumptions

References

BACON, G. E., CURRY, N. A. & WILSON, S. A. (1964). *Proc. R. Soc. London Ser. A*, **279**, 98–110.

WILLIAMS, D. E. (1980). *Acta Cryst.* A**36**, 715–723.

Estimates of the standard deviations of ring-puckering coordinates. By R. NORRESTAM, *Structural Chemistry Group, Chemistry Department B, The Technical University of Denmark, DK-2800 Lyngby, Denmark*

Abstract

Expressions are derived for estimating the standard deviations of Cremer–Pople ring-puckering coordinates, with the assumption that the e.s.d.'s of the atomic positions are approximately isotropic.

The puckering of an N-membered monocyclic ring may be described by the amplitude and phase coordinates introduced by Cremer & Pople (1975). Expressions for calculating the e.s.d.'s of puckering coordinates, assuming independent atomic positions with nonisotropic e.s.d.'s, become rather complicated (Taylor, 1980). As shown in the present paper, considerably simpler expressions for calculating these e.s.d.'s are obtained if isotropic e.s.d.'s of independent positions can be assumed, *viz* $\sigma'_j \sim [(\sigma^2_{xj} + \sigma^2_{yj} + \sigma^2_{zj})/3]^{1/2}$ Å for $j = 1, 2, \ldots, N$. Such an assumption is frequently a good approximation, when deriving the structural parameters from three-dimensional single-crystal diffraction data.

Cremer & Pople define the ring-puckering coordinates $q_m \geq 0$ and $\leq \varphi_m < 2\pi$ by

$$c_m \equiv q_m \cos \varphi_m = (2/N)^{1/2} \sum Z_j \cos [2\pi m(j-1)/N]$$

$$s_m \equiv q_m \sin \varphi_m = -(2/N)^{1/2} \sum Z_j \sin [2\pi m(j-1)/N] \tag{1}$$

for $m = 2, 3, \ldots, (N-1)/2$, and an additional coordinate

$$q_{N/2} = N^{-1/2} \sum (-1)^{j-1} Z_j \tag{2}$$

if N is even. The sums are all over $j = 1, 2, \ldots, N$. The Z_j values occurring in (1) and (2) denote the perpendicular displacement of the jth atom from a uniquely defined mean plane (*cf.* Cremer & Pople, 1975) passing through the geometrical center of the ring. Since this center has an e.s.d. $\sigma_0 = (1/N)(\sum \sigma^2_j)^{1/2}$ and as the coordinate transformation involved to obtain the Z_j values is unitary, the e.s.d.'s of the Z_j values can be approximated by $\sigma_j \simeq [(\sigma'_j)^2 + \sigma^2_0]^{1/2}$. By deriving the e.s.d.'s of c_m and s_m as $\sigma^2(c_m) = \sum (\sigma_j \times \partial c_m/\partial Z_j)^2$ and $\sigma^2(s_m) = \sum (\sigma_j \times \partial s_m/\partial Z_j)^2$, we obtain from (1)

$$\sigma^2(c_m) = (2/N) \sum \{\sigma_j \cos [2\pi m(j-1)/N]\}^2$$

$$\sigma^2(s_m) = (2/N) \sum \{\sigma_j \sin [2\pi m(j-1)/N]\}^2 \tag{3}$$

$$= [(2/N) \sum \sigma^2_j] - \sigma^2(c_m).$$

From $q^2_m = c^2_m + s^2_m$ and $\tan \varphi_m = s_m/c_m$ we obtain in a similar way

$$\sigma^2(q_m) = \sigma^2(c_m) \cos^2 \varphi_m + \sigma^2(s_m) \sin^2 \varphi_m$$

$$\sigma^2(\varphi_m) = [\sigma^2(c_m) \sin^2 \varphi_m + \sigma^2(s_m) \cos^2 \varphi_m]/q^2_m. \tag{4}$$

For the additional coordinate $q_{N/2}$ (N even), we obtain

$$\sigma^2(q_{N/2}) = (1/N) \sum \sigma^2_j. \tag{5}$$