COMPUTED STRUCTURE OF SMALL BENZENE CLUSTERS

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The structures of small benzene clusters $(C_6H_6)_n$, $n = 2-7$, have been calculated employing potential-energy minimization with respect to molecular translational and rotational coordinates, using exp-6-1 non-bonded atom-atom potential functions. The influence of the adopted point-charge model is discussed for the dimer structure.

1. Introduction

In the past few years structures and energetics of van der Waals clusters of molecules, generated by free jet expansion, have been studied extensively by optical spectroscopy, TOF mass spectrometry and electron diffraction [1,2]. These studies are of considerable interest for the understanding of the molecular interactions since they relate to a state of matter, intermediate between and isolated (gas-phase) molecule and the bulk condensed phase. The most direct information about cluster structure is obtained from electron-diffraction patterns. These may be compared with diffraction patterns obtained from the bulk liquid or with powder patterns from the same species. For very small ($n \approx 10$) solid clusters, however, intensity functions must be calculated on the basis of structural models, consisting of a few molecules (as has been done, e.g., for benzene [2]). These molecules are then arranged as in the crystal, although the crystalline arrangement is probably inappropriate in this size domain.

Consequently other models are required, incorporating equilibrium geometries rather than crystal lattice arrangements. In principle, these geometries can be obtained, for a given interaction model, by minimizing the potential energy with respect to the $6n - 6$ independent (i.e. not related by symmetry) molecular translational and rotational coordinates. However, the choice of an initial configuration presents a severe problem, since the results of a minimization procedure are strongly dependent on this choice, as a conse-

quence of the presence of a (conceivably) large number of local minima in the potential energy surface. In a previous study [3] it was found that the minimum energy configurations of 13-molecule clusters of benzene are closely related to the pentagonal growth structures of rare-gas atom assemblies. We speculate that this similarity is retained in smaller clusters and hence that these clusters may be modeled after the postulated rare-gas-type atom configurations [4].

2. Method

The potential energy of a benzene cluster was calculated assuming pairwise additivity and using exp-6-1 potential functions for all non-bonded interactions, with a charge of $\pm 0.153e$ on carbon and hydrogen atoms [5]. Minimization was effected as described previously [3]. The molecules were assumed to have D_{6h} symmetry, with CC and CH bond lengths of 1.397 and 1.027 Å, respectively. Starting configurations were derived from the icosahedral 13-molecule cluster (cf. fig. 7 of ref. [3]) by removal of appropriate molecules, or by removal of molecules from relaxed clusters so obtained.

As stated above, it was assumed that the growth sequence of benzene clusters is similar to that of rare-gas-type clusters, i.e. a sequence based on tetrahedral coordination polyhedra. In this sequence it is possible to select unambiguously the atom (or symmetry equivalent atoms) in a given cluster that must have been

added last and, consequently, the atom that must be removed to arrive at the next smaller cluster in the sequence. Positions that are symmetry-equivalent in an atomic cluster may be different in a molecular cluster, however, owing to different molecular orientations. In such cases the removals of all quasi-equivalent molecules were considered in turn. It was assumed that the cluster with the highest binding energy so obtained offered the best starting point for further calculations. Since this strategy was thought to be unreliable and unpractical for the larger clusters, $n = 8-12$, (with, for example, 30 different 11-clusters to be dealt with) it was decided to start with the 7-cluster.

3. Results

The icosahedral 13-cluster, from which the present clusters are derived, has been described in detail in ref. [3] *. Apart from the central molecule there are two types of molecular positions in this cluster: (i) the apices of the two equilateral triangles, 4.58 Å before and behind the central molecule and parallel to it, and (ii) the remaining six apices which are alternatingly 1.06 Å before and behind the central molecular plane.

3.1. 7-clusters

Starting with the icosahedral 13-cluster, a pentagonal bipyramidal 7-cluster (i.e. a compact structure, consisting of 5 fused coordination tetrahedra) can be formed by removing all molecules, except the central molecule and a surface molecule with its 5 nearest neighbours. In this way 6 different starting configurations can be formed. They relax to either of two slightly different structures, with binding energies of 131.3 and 134.1 kJ/mol, respectively, according to whether the chosen surface molecule was a type (i) or a type (ii) molecule in the 13-cluster (cf. fig. 9 of ref. [3]). The average center-to-center distance in the pentagonal ring is 5.2(1) Å (rms deviations in parentheses). The distances involving one of the apex molecules range from 5.0 to 5.8 Å. The longest nearest-neighbour distance is between the two apex molecules: 6.3 Å. These molecules are nearly at right angles, the dihedral angle be-

tween the molecular planes being 88° . To a lesser extent this applies to neighbouring molecules in the ring, with dihedral angles of $78(7)^\circ$. The 7-cluster is thus seen to be composed of fused tetrahedral 4-clusters with two pairs of molecules in each 4-cluster, with approximately the same dihedral angle between their planes. This feature is found to be more pronounced in the isolated 4-clusters (see below).

3.2. 6-clusters

Five 6-clusters are constructed from the 7-cluster by removal of one of the molecules in the pentagonal ring. (Removal of an apex molecule would be inconsistent with the supposed tetrahedral growth sequence). Subsequent relaxation results in either of two structures with binding energies of 102.3 and 106.1 kJ/mol, respectively. The configuration of the first is essentially the same as that of the unrelaxed cluster, i.e. the molecules are arranged at the vertices of a pentagonal bipyramid, with one molecule in the pentagonal ring missing (tritetrahedron). The second structure is a flattened octahedron or square bipyramid (not shown). The center-to-center intermolecular distances in the central square are 5.8(1) Å, i.e. 0.6 Å longer than in the pentagonal ring of the 7-cluster. The distances involving an apex molecule are much shorter: 5.1(1) Å. Again, the distance between the apex molecules is 6.3 Å and the dihedral angle is 88° . The dihedral angle between molecules in the ring is $77(2)^\circ$. The relationship between the apex molecules and the ring molecules is the same for both apex molecules, with a rotation of 90° .

3.3. 5-clusters

5-clusters can be obtained in different ways: (i) by removing an apex molecule from the square bipyramidal 6-cluster, (ii) by removing a ring molecule from the same cluster, and (iii) by removing two neighbouring ring molecules from the pentagonal 7-cluster. The latter method should be applied as well, since the octahedron does not fit in the tetrahedral growth sequence and thus tetrahedral structures might be overlooked if only the 6-cluster were to be considered. Surprisingly, the starting configuration (i) relaxes into a cluster consisting of two fused tetrahedra sharing a face (fig. 1; all figures are stereo-pairs), with binding energy 79.1 kJ/mol. A different structure, with a slight-

* The molecular coordinates of the clusters, discussed in this Letter, are available from the author.

Fig. 1. Ditetrahedral 5-cluster.

ly smaller binding energy of 78.7 kJ/mol (not shown) is obtained by applying method (ii), it may be viewed as an incomplete square bipyramid, with one ring molecule missing. Both structures are found with method (iii), depending on what molecules are removed from the ring. Intermolecular distances in the tetrahedral cluster range from 5.0 to 5.7 Å, dihedral angles from 32° to 95°.

3.4 4-clusters

10 different starting configurations can be obtained directly from the icosahedral 13-cluster, by removing all molecules, except a triangular arrangement of neighbouring surface molecules and the central molecule. Relaxation results in either of two structures, with binding energies of 52.2 and 55.6 kJ/mol. The latter structure (fig. 2) is also found when one or the other apex molecule is removed from the 5-cluster of fig. 1. It may be viewed as a tetrahedral arrangement, consisting of two pairs of molecules, the intermolecular distance and the dihedral angle in each pair being 5.76 Å and 55.3°, respectively; all distances and angles, relating to molecules of different pairs, are equal, viz. 5.04 Å and 77.5°, respectively. The arrangement of the molecules in the other structure is essentially the same as that found for type (i) molecules with the central molecule in the 13-molecule icosahedral cluster.

Fig. 2. Tetrahedral 4-cluster.

Fig. 3. Trimer.

3.5. 3-clusters

Since all faces in the tetrahedral cluster of fig. 2 are equivalent, only one 3-cluster can be derived. After relaxation all distances and angles become equal: 4.98 Å and 61.1° (fig. 3). Since the molecular planes are not exactly at right angles to the plane of the coordination triangle, the potential-energy minimum must be part of a double minimum well, symmetrical about the perpendicular arrangement with dihedral angles exactly 60°. Similar features, although less evident, may be connected with the larger clusters. This configuration of 3 molecules is essentially the same as that found in the icosahedral structure for type (i) molecules. The binding energy is 32.1 kJ/mol.

3.6. 2-clusters

If one molecule is removed from the trimer of fig. 3 the remaining two molecules rotate towards each other so as to decrease the dihedral angle from 61.1° to 26.3°. At the same time the intermolecular center-to-center distance is reduced to 4.69 Å (fig. 4). This may be compared with the smallest intermolecular distance in the crystal: 5.02 Å. A comparable dihedral angle (29°) is found between molecules at a distance 5.81 Å apart. The binding energy is 11.0 kJ/mol. This dimer structure is at variance with the T-shape, which is usually assumed for the ground electronic state,

Fig. 4. Dimer.

since this configuration dominates the crystal structure. It is clear however from the above discussion that features, energetically favourable for the dimer, may be lost, in going to the trimer, the tetramer, and so on, since they cannot be realized any longer when more molecules are added. The differences in dihedral angle in the trimer and in the dimer is illustrative in this respect. However, the T-arrangement is pronounced in the tetramer. The crystalline T-arrangement of dimers turns out to be unstable under relaxation and results in the configuration of fig. 4. It is suggested by optical absorption spectra [6], however, that the dimer may have a parallel stacked and displaced configuration of C_{2h} symmetry, inconsistent with the calculated dihedral angle. Since it was suspected that the calculated dihedral angle in the dimer (more than in the larger clusters) might be very sensitive to the applied point-charge distribution, the point charges were varied. It was found that point charges smaller than $0.13e$ resulted in essentially parallel displaced configurations. If the charges were made larger ($\approx 0.17e$), a T-shaped configuration (as has also been proposed to account for the observed dipole moment of the benzene dimer [7]) could be found as well, corresponding with a second, slightly less favourable, minimum.

Recently it has been suggested that the Coulombic interaction in the dimer should be described by a quadrupole-quadrupole term [8]; in that case only the parallel displaced configuration is obtained. It is important to realize that charge redistribution, accompanying the dimer formation, may also affect the dimer geometry.

4. Conclusion

Equilibrium structures of benzene clusters, consisting of 2–7 molecules, have been calculated assuming an intermolecular interaction model based on summed atom-atom interactions, including electrostatic. Although these structures seem plausible by their appearance, it cannot be ruled out that they correspond to local rather than global minima of the potential energy surface (alternative structures have been proposed previously [9], e.g., a linear arrangement for the trimer and a planar configuration for the pentamer; these structures are energetically less favourable than the present ones, however, and must correspond to local

minima). Moreover, the structures may be very sensitive to the molecular interaction model applied (as observed for the dimer), conceivably much more than the results of crystal-packing calculations are.

Conversely, much information concerning this interaction should be present in cluster diffraction experiments [2] and a comparison of observed diffraction intensities with diffraction intensities derived from calculated structures, will be of considerable interest.

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