Buckminsterfullerane: The Inside Story

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The stereoisomers of fully reduced buckminsterfullerene $C_{60}H_{60}$ have been investigated with the molecular mechanics program MM3. Although it might be expected that chemical reduction would deliver all of the hydrogens to the outside, the symmetric structure produced in this way is predicted to be highly strained. Moving just one hydrogen to the inside is predicted to decrease the energy by 53 kilocalories (kcal) per mole. Putting additional hydrogens on the inside further lowers the predicted energy (depending on the steric relations between them). The minimum energy isomer is predicted to have ten hydrogens inside with C_1 symmetry and to have an energy 400 kcal/mol less than that of the all-outside isomer. These results suggest that a process which could achieve isomerization would produce a mixture of isomers, most of which with ten hydrogens on the inside.

There has been much recent interest in buckminsterfullerene (C_{60}) (*1*). Its availability in quantity (*2*) has permitted the observation of many of its physical properties (*3*). In addition, this substance has the potential of being converted to many derivatives that have unusual features. One of these is the corresponding fully reduced hydrocarbon $C_{60}H_{60}$, which might be called buckminsterfullerane. Why is this structure of interest? One would expect that the hydrogens introduced by the chemical reduction of C_{60} would have to be delivered from the outside. This all-outside isomer (Fig. 1) would be very highly strained due to the 90 unfavorable eclipsing CCCC dihedral angles and the 120 120° CCC bond angles. (Preferred dihedral angles in a saturated hydrocarbon are staggered—either 60° or 180°—rather than the 0° in this structure, and the ideal CCC bond angle is ~110°.) This strain results from its 20 planar cyclohexane rings.

Optimization by MM3 (*4*) maintains the high symmetry of C_{60} and predicts a steric energy (S.E.) of 836.1 kcal/mol and a heat of formation of +559 kcal/mol. However, putting just one hydrogen on the inside of the molecule (Fig. 2) rather than on the outside lowers the predicted energy by 53 kcal/mol! In addition, the loss of symmetry favors this isomer by a factor of 60. This mono-inside isomer (S.E. = 783.0 kcal/mol) has three fewer eclipsing interactions but also many CCC bond angles are decreased. If one inside hydrogen provides such a large amount of stabilization, what about two? The more general question is how many hydrogens should be inside to get the lowest S.E. and how should they be arranged. In this report, a search for the lowest energy stereoisomer of this structure is described.

The stochastic search method (*5*) might be considered as a procedure for seeking the lowest energy arrangements. In principle, if a kick size were used that was large enough to invert the tetrahedral sense of carbons, this technique would find all of the isomers with different numbers of inside hydrogens, with enough time. However, the number of isomers is enormous (2^{60} divided by the average number of identical copies of each one), and a stochastic search for them would never finish with the use of current computers. In flexible systems with fewer atoms, stochastic search is effective in finding all of the conformers (*6*). However, the isomers of buckminsterfullerane are very rigid. Once a particular set of hydrogens is put inside, optimization occurs fairly rapidly to a particular minimum for each one. A fast method of generating sets of inside hydrogens likely to yield low-energy structures is required.

One might first ask how many different di-inside isomers there are. This could be answered by inspection; however, it is easier to write a computer program to get the answer. If one calculates the 1770 distances between all pairs of atoms in the symmetrical all-outside structure and then sorts them, one finds that these distances fall into 21 groups. Therefore, there are just 21 distinct isomers with two hydrogens inside. Those with the inside hydrogens fairly well separated are reduced in MM3 strain energy by about twice as much as mono-inside isomer. The lowest energy one has S.E. = 729.7 kcal/mol and has the two inside carbons in the 15th distance category apart. (The carbons closest together are in the first distance category and those furthest apart are in the 21st.) The isomers in the ninth distance category have an S.E. that is only 6 kcal/mol greater than that of the best arrangement.

On finding the distinct ways of putting *N* hydrogens inside, one could optimize all of the structures and find the one with the

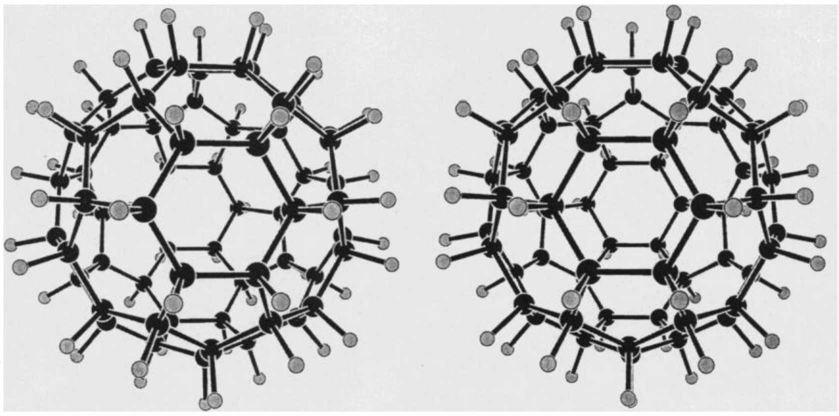

Fig. 1. All-outside buckminsterfullerane (S.E. = 836.1 kcal/mol).

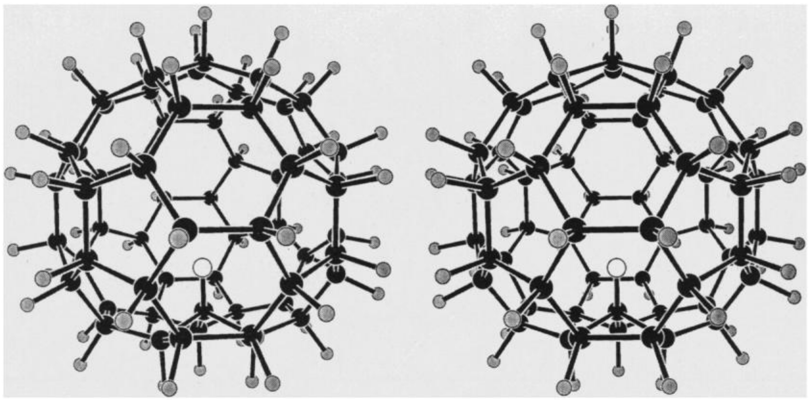

Fig. 2. Buckminsterfullerane with one inside hydrogen (open circle) (S.E. = 783.0 kcal/mol).

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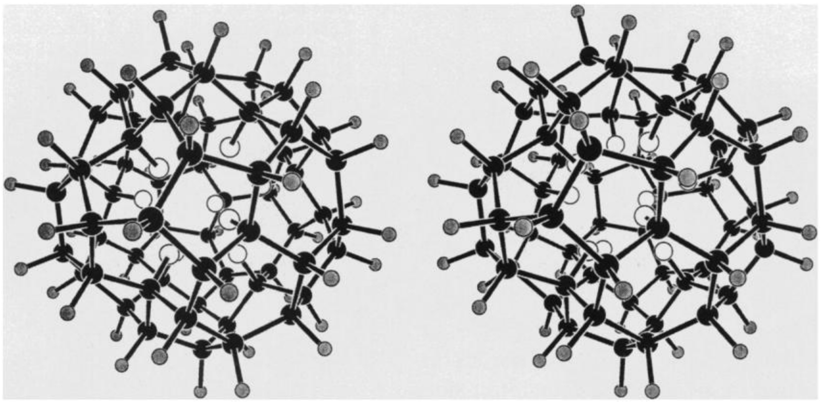

Fig. 3. The best isomer found for buckminsterfullerane (S.E. = 434.2 kcal/mol) with ten hydrogens (open circles) inside.

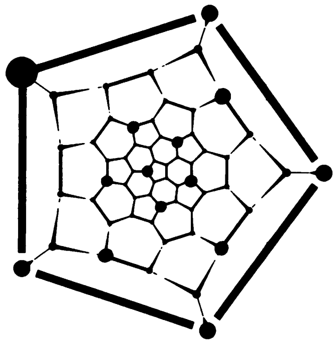

Fig. 4. "Exploded view" of the structure in Fig. 3. Enlarged dots show where there are inside hydrogens.

lowest energy. This was done for the 290 different isomers with three inside hydrogens. They were found by randomly choosing three hydrogens to be inside at a time and then getting the (three) distance categories between the corresponding carbons in the parent all-outside isomer by looking in an array of such distances. The three distance classes constitute a descriptor of the isomer. These were stored by the program, and the table of these distances was consulted for each new group of three to discover whether it already had been found. The lowest energy conformer turned out to have S.E. = 676.1 kcal/mol and have distances of 14 14 14. There are many other isomers that are close to it in energy. (For example, 12 16 19 has S.E. = 677.7 kcal/mol.) Examination shows that when distances of closer than 9 are present, the energy increases significantly. (For example, 8 14 17 has an S.E. = 682.9 kcal/mol.)

An exhaustive search with four inside hydrogens yielded 4002 unique isomers. It was considered unnecessary to optimize them all, since those with one or more relatively small distances were certain to be higher in energy than the others. Optimizing those with no close distances yielded the isomer with distances 13 14 14 15 15 18 and S.E. = 622.4 kcal/mol as the lowest. Similar studies of isomers with 5 through 11 inside hydrogens yielded 576.0 (for 5), 524.7(6), 493.4(7), 462.8(8), 444.2(9), 434.2(10), and 462.0(11) kcal/mol, respectively, as having the lowest S.E. value. At first, the decrease in energy is linear in the number of inside hydrogens, but as more are put inside, some of the inside hydrogens must be too close together for comfort. The incremental decrease in energy becomes smaller and finally, with 11 inside hydrogens, the energy of the best arrangement is greater than that for 10 inside. It should be noted that the searches for isomers with many inside hydrogens may not have been carried out for long enough to be absolutely certain of finding the very lowest one (200 million 11-inside isomers and around 1 billion 10-inside isomers were examined), but it is not likely that ones much lower in energy will be discovered.

The lowest energy structure found (ten inside hydrogens) is shown in Fig. 3. The closest pairs of inside hydrogens (distance of 1.87 Å) are those attached to pairs of carbons which are near one another. Those belonging to carbons on opposite sides of the molecule are more than 3 Å apart. Examination of the structure shows that each of the 20 six-membered rings contains just one of the inside hydrogens. (Every carbon is in two six-membered rings and one five-membered ring.) Since there are 12 five-membered rings, 2 of them contain no inverted carbon. An "exploded view" of the structure where the heavy dots correspond to inside hydrogens (Fig. 4) illustrates these observations. Nine other different arrangements have been found that share these properties. Only the tenth isomer, 19 kcal/mol higher in energy than the best one, has symmetry (an S_{10} axis).

A process able to isomerize hydrogens from the outside to the inside should ultimately yield this 10-inside isomer and liberate ~400 kcal/mol, starting from the all-outside isomer. One possible means of doing this is simply heating the hydrocarbon, which might break a C–C bond to give a diradical intermediate in which a hydrogen on one radical might be able to pass its neighbor and go to the inside before the bond recloses. Another possibility would be to use a superacid to protonate a carbon. Although tetracoordinated carbon requires a great deal of energy to invert, pentacoordinated carbon (analogous to CH_5^+) is known through calculations to distort with little change of energy. Caution should be advised, however, since an efficient catalyst for this isomerization might produce an explosion.

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