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FSGO Investigation of Several Conformers of Cyclohexane

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Abstract: Four conformations of cyclohexane have been theoretically calculated by the ab initio floating spherical Gaussian orbital model (FSGO). The order of energies is as expected but the energy differences are exaggerated as has previously been found in other ring systems and rotational barriers.

In this paper, we wish to report the results of an investigation of the geometry of four conformations of cyclohexane, chair (D_{3d}), boat (C_{2v}), half-chair (C_2), and planar (D_{6h}), by means of the FSGO (floating spherical Gaussian orbital) model. The FSGO model makes use of an absolute minimum basis set, where each orbital is doubly occupied. As currently applied, the model predicts the electronic and geometric structure of singlet ground states of molecules with local orbitals without the use of any arbitrary or semiempirical parameters. The local orbitals are constructed by using single normalized spherical Gaussian functions

$$\Phi(\mathbf{r} - \mathbf{R}_i) = (2/\pi\rho_i^2)^{3/4} \exp\,[-(\mathbf{r} - \mathbf{R}_i)^2/\rho_i^2]$$

with orbital radius ρ_i and position $\mathbf{R}_i$. A single Slater determinant represents the total electronic wave function. The total energy can be minimized by a direct search procedure with respect to all parameters: orbital radii, ρ_i, orbital positions, $\mathbf{R}_i$, and nuclear positions. The advantage of the FSGO model as described above is that no SCF iterations are required. This model has been used previously for small ring systems and other small hydrocarbon molecules with some success,[1] particularly in the area of geometry optimization.

Unless otherwise indicated, the geometrical parameters for the chair, boat, and planar conformations were those of their ideal representations. All C-C and C-H bond lengths were assumed equal at 1.54 and 1.10 Å, respectively, for all calculations. The bond angles and the dihedral angles for the half-chair conformation were taken from the empirical conformational study of Hendrickson.[2] For the half-chair and planar conformations, all H-C-H angles were set equal to 107.5°. The results are shown in Table I.

It has been known for quite some time that the equilibrium ground-state conformation of cyclohexane is a slightly flattened version of the chair conformation rather than an ideal chair with C-C-C bond angles of 109.47°. The bond angle has been experimentally determined to be 111.05-111.55°.[9,10] It is calculated to be 111.13° by the FSGO model. This angle and other geometrical quantities are determined by fitting to a parabola the three calculated points closest to the energy minimum of the particular surface under examination.

There are four coplanar carbon atoms in the half-chair conformation. This gives rise to considerable eclipsing of the hydrogens of neighboring methylene groups. The FSGO model calculations indicate that a slight "rocking" of these

Table I. Energy Results for Cyclohexane

Conformation	Negative total energy, au[a]	Relative energies, kcal/mol FSGO	Hoyland[b]	Allinger et al.[c]	Exptl
Chair	198.040024	0.00	0.00	0.00	0.00
Boat	198.016753	14.61	7.19	6.59	4.8–5.9[d]
Half-chair (ideal)	198.014148	16.24	11.22	11.04	10.8[e]
Planar	197.975922	40.23			
Chair (flattened, 111.13°)	198.041865	−1.15			
Half-chair (rocked)	198.014521	16.01			

[a] 1 au = 627.503 kcal/mol. [b] Reference 3. [c] Reference 4. [d] References 5, 6, and 7. [e] Reference 8.

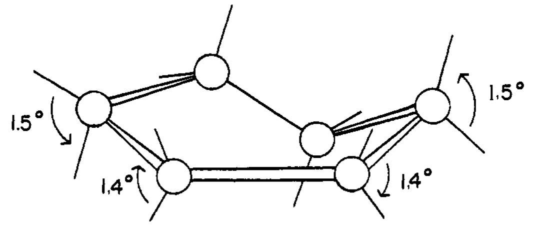

Figure 1. Half-chair conformation with minimum energy. Arrows indicate rock angles of methylene groups.

methylene groups relieves some of the eclipsing interactions. This is indicated in Figure 1. These results are in accord with those observed for cyclopentane[1] and cyclobutane.[11]

As can be seen from Table I, the relative energies of the various conformations give the correct ordering. However, the energy differences between the chair and the other conformations are larger than those obtained in previous calculations[12] and experimental studies. There is considerable eclipsing of methylene groups in all conformations other than the chair. The FSGO model is known to overestimate by approximately a factor of 2 such eclipsing interactions as in cyclopentane,[1] cyclobutane, and ethane.[11] Thus, the overestimation of the calculated energy differences between the various conformations and the chair conformation is not unexpected.

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Effect of Dielectric Constant on the Conformational Behavior of Tryptamine and Serotonin

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Abstract: Using an empirical method, the conformational behavior of tryptamine and serotonin has been investigated as a function of dielectric constant. The properties such as conformational energy, percent population, dipole moment, optical anisotropy, and depolarization ratio are considered. The shape of the contour maps changes considerably when the dielectric constant increases even though the position of the global minimum remains unaltered. The potential barrier between the trans and gauche forms also decreases. When the dielectric constant is low, the gauche forms dominate, and while it is high, the trans forms predominate due to conformational transition. The dipole moments slightly increase as the dielectric constant increases. The optical anisotropies and depolarization ratios increase sharply when the dielectric constant increases from 1.0 to 8.0, and then decrease steadily as the dielectric constant further increases. The range of 20 to 30 for the dielectric constant has been proposed for the conformational study of drug molecules. The difference between tryptamine and serotonin has been further explored in terms of intramolecular forces.

The methods that are available for the calculation of the conformational energies of any molecule can be classified into two categories: (i) the molecular orbital methods (MO), and (ii) the empirical method. The MO methods, such as EHT (Extended Hückel Theory), INDO (Intermediate Neglect of Differential Overlap), and PCILO (Pertur-