ROTATIONAL BARRIERS FROM SEMIEMPIRICAL MOLECULAR ORBITAL CALCULATIONS

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A possible approach to structure and reactivity problems in organic chemistry is the employment of all-electron molecular wave functions and their associated energies to compare relative stabilities of conformations, intermediates, and transition states. Within the Roothaan formulism, ab initio calculations which include all electrons are possible, even for large molecular species, but such calculations are very expensive in terms of computer time. However, several semi-empirical LCAO-MO methods have been suggested which include all valence electrons (1-5). The popularities of two of these methods, the extended Hückel technique (EHT) of Hoffmann (1) and the SCFMO method (CNDO/2) of Pople and Segal (3), are in part due to the ready availability of computer programs to carry out the calculations (6).

Energy barriers to rotations around carbon-carbon single bonds for several simple hydrocarbon molecules have been calculated by these semiempirical methods and reasonable values have been obtained (1,2). Barriers and most stable geometries for several hetero-atom molecules have also been calculated (2,3, 7-11). It has been stressed that the geometry is the most predictable property of a molecule (1,12). The EHT method has even been extended to estimations of the most stable conformations for ions and radicals (13-17). One relies, in these studies, on the expectation that the several errors which are made in the calculation of energy by a semi-empirical method will cancel in the energy difference between two conformations of the same molecule.

The purpose of this letter is to demonstrate that such expectations are not always realizable. Even qualitative agreement between calculated and experimental potential energy barriers is not always obtainable under the EHT and CNDO/2 methods. The qualitative disagreement may extend to both the numbers of energy extrema and their relative heights. To exemplify these points one can carry out calculations on some simple molecules. CNDO/2 results for propene, 1-butene, acetaldehyde, propionaldehyde, formic acid, and acetic acid are presented below. We also discuss the differences between EHT and CNDO/2 results where EHT results are available.

The EHT and CNDO/2 methods are described in detail in the original publications (1-3). Both methods are attempts to approximate a many electron Hartree-Fock solution. EHT includes overlap integrals, but completely neglects electron repulsion integrals. CNDO/2 is an SCF method which employs zero differential overlap, thereby limiting the calculation of repulsion integrals to one and two-center terms. Both methods require atomic coordinates as input to the respective computer programs. We obtained these from a standard compilation of molecular data (18). A separate calculation was made for each chosen dihedral angle and an attempt was made to define the entire energy

variation for rotation around each single bond.

CNDO/2 and EHT results for propene and acetaldehyde are quite reasonable. Both microwave experiments (19,20) and thermodynamic arguments (21) for propene give a conformation in which one of the methyl hydrogen atoms is eclipsed with respect to the double bond. The barrier to rotation of the methyl group is 1.98 kcal/mole. CNDO/2 calculations give the correct geometry with a barrier of 0.98 kcal/mole. The geometry with the EHT method is also correct, and the barrier is calculated to be 1.2 kcal/mole. For acetaldehyde, the experimental (22-24) and calculated conformations are again eclipsed. The barriers to rotation are 0.71 kcal/mole (CNDO/2), 0.8 kcal/mole (EHT) (8), and 1.16 kcal/mole (microwave experiments) (23). In our acetaldehyde CNDO/2 calculations we also varied the HCH angle from $106.3°$ to $110.3°$ in $1°$ steps and calculated the barrier to rotation of the methyl group for each angle. The minimum energy configuration is at $108.3°$ which is exactly that found by microwave spectroscopy (23). The barrier to rotation was not very sensitive to the size of the HCH angle. It increases about 4% for each degree increase in the size of the angle.

Refer to figure 1 for the calculated results for propionaldehyde and 1-butene. Propionaldehyde has been the subject of microwave (25) and nuclear magnetic resonance studies (26). Two stable conformers exist, differing in energy by 0.9 kcal/mole. The most stable conformer has the methyl group eclipsed with the carbonyl group ($\theta = 180°$ in figure 1). The other stable conformer is at $\theta = 49°$. The barrier to internal rotation is 2.28 kcal/mole. CNDO/2 calculations are in complete disagreement with these experimental facts since only one energy minimum is found at $\theta = 90°$. EHT calculations seem more reliable in this case (8). The lowest energy minimum is located correctly ($\theta = 180°$). The calculated barrier, 2.2 kcal/mole, is quite close to the experimental barrier. However, the

Fig. 1

CNDO/2 Calculations ●,   EHT Calculations ○ .
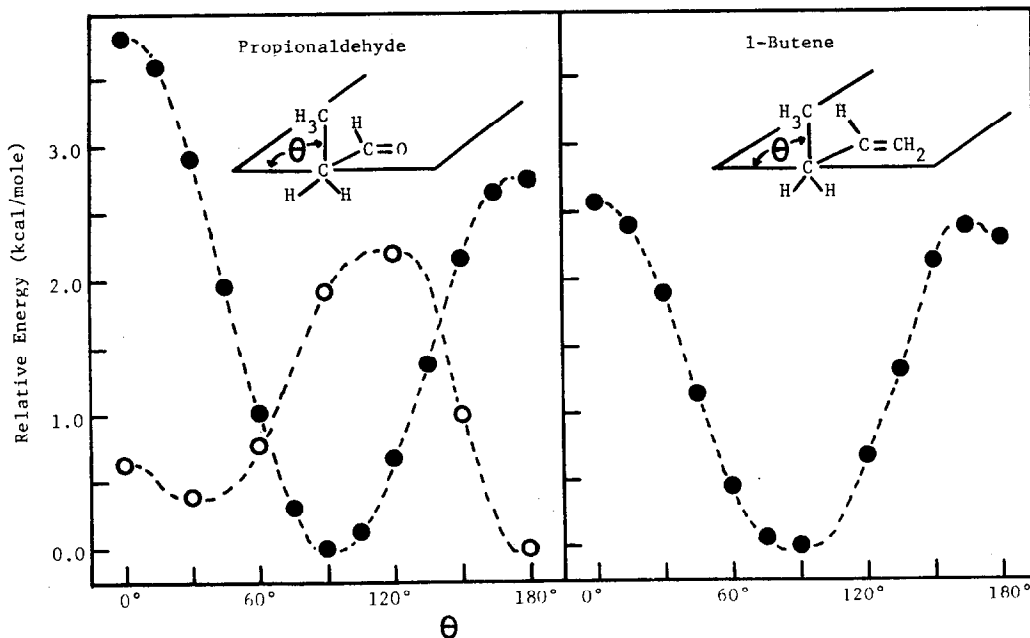
position of the second calculated minimum is incorrect, which leads us to believe that the foregoing correspondence of theoretical and experimental results is fortuitous. For 1-butene, the most stable calculated configuration is at $\theta = 90°$, analogous to propionaldehyde. A shallow minimum is found at $\theta = 180°$ where the methyl group eclipses the double bond. These results are in conflict with the conclusions of Dauben and Pitzer (21), but may be in agreement with the infra-red studies of Harrah and Mayo (27).

In acetic acid, CNDO/2 calculations yield the correct probable configuration of the hydroxyl group, that is, planar with hydrogen atom _cis_ to carbonyl oxygen atom (28,29). EHT gives an incorrect minimum with the hydroxyl group oriented _trans_ to the carbonyl group (8). If one orients the hydroxyl group correctly, both semi-empirical methods give a conformation for the methyl group which is probably correct, with a hydrogen atom eclipsing the carbonyl group. The barriers to rotation of the methyl group are 0.20 kcal/mole (CNDO/2), 0.40 kcal/mole (EHT), and 0.48 kcal/mole (microwave spectroscopy) (29).

We found that the size of the methyl rotation barrier in acetic acid was very sensitive to the chosen length of the carbon-carbon bond, and again relatively insensitive to small variations in HCH bond angle. For a carbon-carbon bond distance of 1.54 A instead of the reported value of 1.50 A, the calculated rotational barrier was 0.06 kcal/mole. This result reemphasizes that correspondence of calculated and experimental barriers to rotation may be fortuitous, especially when bond lengths and angles are assumed to have some standard value, as is true for many of the papers we cited in the earlier part of this letter.

Formic acid geometry was calculated correctly by CNDO/2, planar with hydroxyl _cis_ to carbonyl. EHT again gives incorrect results in this respect, planar, hydroxyl _trans_ to carbonyl group. The barrier to rotation around the carbon-oxygen single bond is 34.9 kcal/mole (CNDO/2), 2.3 kcal/mole (EHT) (8), and 17.0 kcal/mole (microwave spectrosocpy) (28).

A consideration of the results reported here leads us to the conclusion that semiempirical MO methods, in their present form, are not generally suitable for the calculation of energy barriers or the most stable configurations of molecules, ions or radicals, especially if the molecular species are relatively large or contain hetero-atoms. Careful comparisons of calculated results with experimental facts should be made wherever possible.

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