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Response of Semi-empirical and *Ab Initio* Methods to Angle Strain and Conjugation Effects in (*Z,Z,Z*)-Cycloocta-1,3,5-triene

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ABSTRACT

The results of MNDO, AM1 and PM3 semi-empirical calculations and HF/6-31G*, MP2/6-31G*, MP2/6-311+G**, B3LYP/6-311G** and QCISD/6-31G* *ab initio* methods for angle strain and conjugation effects in twist-boat, boat, and half-chair geometries of (*Z,Z,Z*)-cycloocta-1,3,5-triene indicate that all methods, except PM3, predict wrong ordering of the conformations.

Keywords: Medium rings; Stereochemistry; Molecular modeling; Conformational analysis; *Ab initio* calculations

INTRODUCTION

The molecular structure of (*Z,Z,Z*)-cycloocta-1,3,5-triene (**1**) is of interest to determine how this molecule relives its strain [1-3]. This point is important since two of the most potent driving forces in organic chemistry, angle strain and conjugative stabilization, are forced here into direct confrontation. The conformational properties of **1** have been extensively studied by dynamic NMR spectroscopy [1-3]. Compound **1** can undergo a process that interconverts the ground state conformation **1-TB** which is unsymmetrical and chiral, with its mirror image, presumably *via* C_S symmetric (achiral) boat form (**1-TB**). The free-energy barrier for this process has been found to be 18.0 kJ mol^{-1} by dynamic ^{13}C NMR spectroscopy. The free-energy barrier for ring inversion in **1**, a process that has a transition state with C_2 symmetry, has been found to be 26.0 ± 2.1 [2] and 28.0 ± 0.8 [3] kJ mol^{-1}. The results of iterative force-field calculations[1] of **1** using Boyd's program [4], are in excellent agreement with the NMR data (see Table 1 and Figures 1 and 2).

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RESULTS AND DISCUSSION

Semi-empirical methods, especially MNDO [5], AM1 [6] and PM3 [7], along with *ab initio* quantum-mechanical calculations [8] are currently used to study various structural aspects of organic molecules [9-11]. These methods have been successful at reproducing molecular energies, replicating molecular structures and interpreting chemical reactions [12]. The kind of approximations used in these calculations differ in significant ways, making it difficult to evaluate the performance of extant methods. A good test of quantum-mechanical methods is to find how well they reproduce experimental data for rather unusual systems such as **1**. We wish to report the results of MNDO, AM1, PM3, HF/6-31G*, MP2/6-31G*, MP2/6-311+G**, B3LYP/6-311G** and QCISD/6-31G* calculations for **1-TB**, **1-Boat,** and **1-HC** geometries of **1**. Heats of formation (ΔH_f°), total energies and representative structural parameters for the three geometries of **1**, as calculated by semi-empirical and *ab initio* methods, are shown in Table 1 and Figure 2. The unsymmetrical **TB** conformation is calculated by all methods to be the most stable geometry, in agreement with the experimental results [1-3]. The results of empirical force-field calculations are in excellent agreement with the experimental values (see Table 1 and Figure 2). The results of PM3 method are in agreement with the experimentally determined order of stabilities of **TB**, **Boat,** and **HC**; however, the other methods fail to predict the correct order of stabilities of **boat** and **HC** geometries. As shown in Table 1 and Figure 2, the calculated energies for **1-Boat** by these methods are higher than those for **1-HC**. In a simplistic way, one would expect the ordering given by the advanced techniques and not that given by the simpler methods. The C_2 structure has a conjugated set of double bonds that are nearly planar and the two CH_2 groups that are somewhat staggered to each other, while the C_s structure has little conjugation and eclipsing CH bonds. Table 1 may indicate that things are not as they are supposed. The competing effect is the ring strain, which is not described properly by the *ab initio* methods.

In conclusion, semi-empirical and *ab initio* methods in general are useful when one mechanism dominates the effect examined, but when there are two opposing contributions, such as π bonding *vs.* angle strain, modeling the small resultant of two large contributions is much more difficult. However, each method has its limitation, and the failures, when they occur, may be rather spectacular. Our conclusion is that earlier methods prove better in modeling the effects of angle strain and later approximations are not necessarily going to be better in all applications. Therefore, caution is always necessary in the interpretation of the results obtained for compounds such as **1**.

Table 1. Calculated heats of formation (kJ mol^{-1}), total and zero-point vibrational energies (*Hartree*; zero-point vibrational energy is scaled by a factor of 0.9135 to eliminate known systematic errors in calculations), relative energy (including zero-point energy, kJ mol^{-1}) of (*Z,Z,Z*)-cycloocta-1,3,5-triene (**1**)

Feature	**TB,** C_1	**Boat,** C_s	**HC,** C_2
Experimental	0.0	18.0	28.0
Force-Field Calculations (E_{rel})	0.0	20.1	27.6
MNDO	143.21	149.92	147.59
E_{rel}	0.0	6.7	4.4
AM1	156.27	169.38	164.61
E_{rel}	0.0	13.1	8.4
PM3	178.47	189.24	194.94
E_{rel}	0.0	10.8	16.5
HF/6-31G*//HF/6-31G*	-308.7069	-308.6955	-308.6981
E_{rel}	0.0	28.0	23.6
ZPE	0.1689	0.1681	0.1691
MP2/6-31G*//HF/6-31G*	-309.7225	-309.7116	-309.7161
E_{rel}	0.0	26.8	17.3
MP2/6-311+G**//MP2/6-31G*	-309.9115	-309.9006	-309.9052
E_{rel}	0.0	26.6	16.9
B3LYP/6-311G**//HF/6-31G*	-310.8940	-310.8824	-310.8898
E_{rel}	0.0	28.6	11.6
QCISD/6-31G*//MP2/6-31G*	-309.7224	-309.7115	-309.7159
E_{rel}	0.0	26.8	17.4

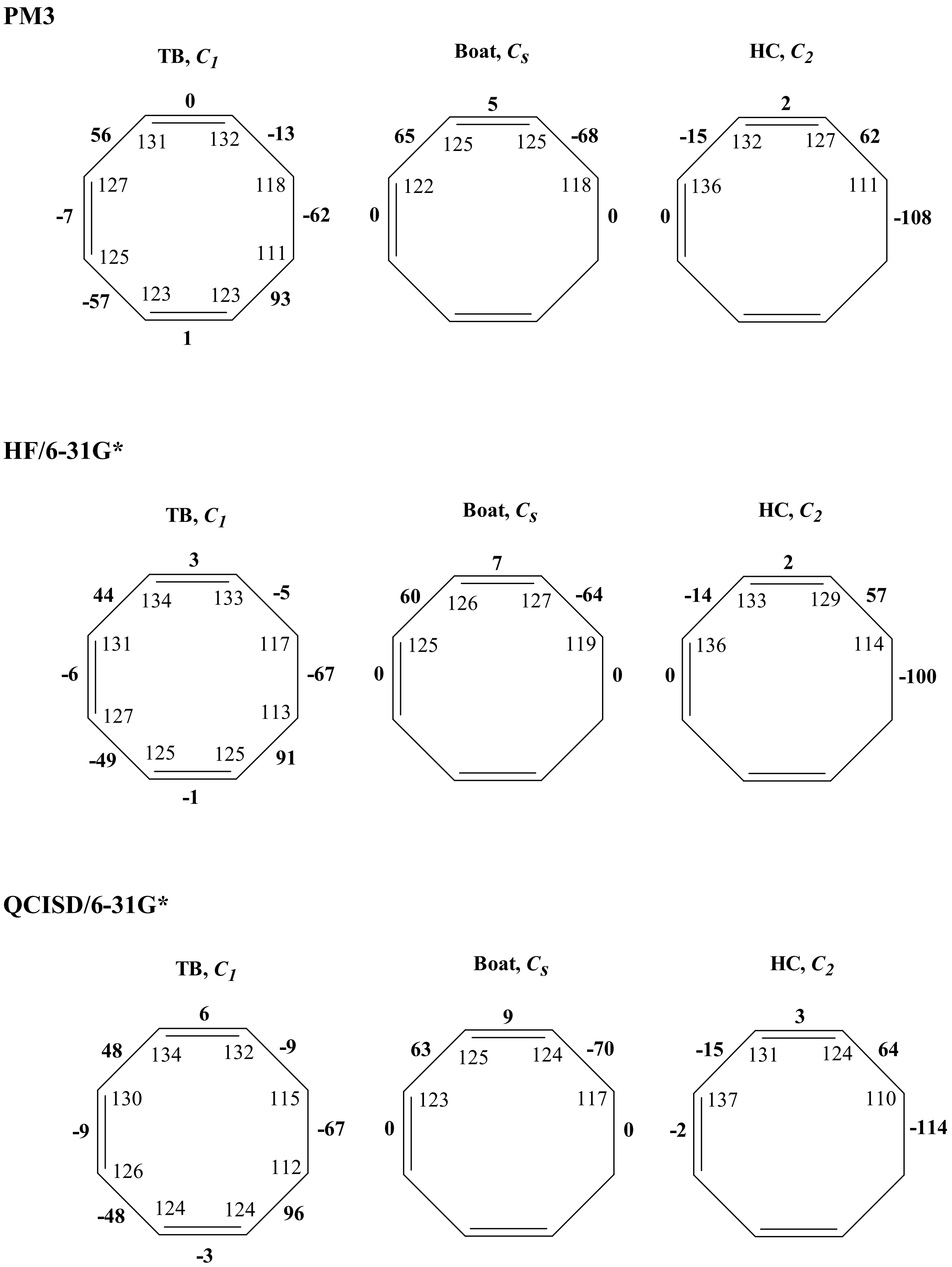

Figure 1. Calculated bond angles and dihedral angles (in °) in twist-boat, boat, and half-chair geometries of (*Z,Z,Z*)-cycloocta-1,3,5-triene (**1**) calculated by PM3, HF/6-31G*, and QCISD/6-31G*

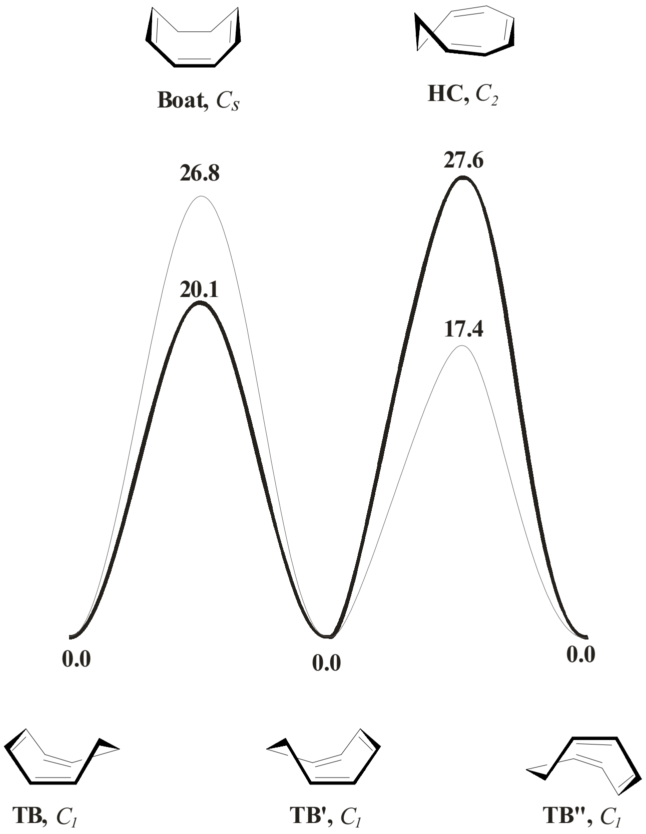

Figure 2. Calculated strain energy (kJ mol^{-1}) profile for conformational interconversional of various geometries of (Z,Z,Z) –cycloocta-1, 3, 5-triene using Boyd's iterative program (bold line, Ref. 1) and QCISD/6-31G*//MP2/6-31G* (this work).

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