An *Ab Initio* SCF-MO Study of Conformational Properties of (Z)-Cyclooctene

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ABSTRACT

Ab initio calculations at HF/6-31G* level of theory for geometry optimization and MP2/6-31G*//HF/6-31G* for total energy calculation are reported for Z-cyclooctene (1). The most favorable conformation of 1 is the unsymmetric boat-chair (1-BC) geometry. Potential energy profiles for two different boat-chair/boat-chair interconversion processes were calculated. The process via a chair transition state of C_s symmetry has calculated barrier of 39.7 kJ mol^{-1} and is suggested to interpret a ^{1}H-NMR coalescence of 1 observed with $\Delta G^{\neq}$ = 22.2 kJ mol^{-1}. The calculated energy barrier for boat (C_s) process is 47.1 kJ mol^{-1}. Thus, the boat process explains a second observed ^{1}H NMR coalescence with $\Delta G^{\neq}$ = 34.3 kJ mol^{-1}.

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

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INTRODUCTION

The conformational properties of (Z)-cyclooctene (**1**) has been the subject of several experimental [1-3] and theoretical [4, 5] investigations. Compound **1** has been known for a considerable time [6-8], and its conformational properties have been studied [1-8]. Thermal and photochemical transformations of **1** have been the subject of several investigations [3-5].
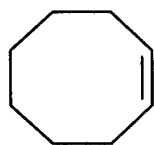
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This study was undertaken to investigate the structural optimization and conformational interconversion pathways of (Z)-cyclooctene (**1**) by comparing the geometries (HF/6-31G*) and conformational energies (MP2/6-31G*//HF/6-31G*). The results from MP2/6-31G*//HF/6-31G* calculations are used in the conformational energies discussions below.

RESULTS AND DISCUSSION

The preferred conformation of (Z)-cyclooctene is a slightly twisted boat-chair form [1-4]. There is good experimental evidence as to the type of conformation of (Z)-cyclooctene (**1**) [5-7], though its detailed structure and conformational interconversion pathways has not yet been determined. The boat-chair conformation of **1** can be derived from the boat-chair geometry of cyclooctane by placing the double bond at the position of the smallest torsion angle. Pauncz and Ginsburg [4], considering only the three regular conformations of **1**. These authors favored the chair form over the boat by 1.3 kJ mol^{-1} and over the twist by 52.6 kJ mol^{-1}. An examination of Dreiding molecular models of **1** show these regular forms to suffer from ethane type H/H torsional interactions as well as other nonbonded H...H interactions. Favini, et al. [8], considered another conformation of **1**, described as an intermediate in a chair-to-boat interconversion, and calculated it to be 33.1 kJ mol^{-1} less strained than either the chair or boat and 47.7 kJ mol^{-1} less strained than the twist.

The results of ab initio calculations for structure optimization and conformational interconversion pathways of (Z)-cyclooctene (**1**) are shown in Figures 1 and 2, and Tables 1 and 2. Five potential energy minima and six transition states were found important for a description of the conformational features of **1**. The unsymmetrical boat-chair (**1-BC**) structure is calculated to be the most stable conformation of **1**, in agreement with the dynamic NMR studies [1-4] and previous calculations [5-7]. This conformation was also observed in the crystals of enantholactam hydrochloide [7]. The unsymmetrical twist-boat (**1-TB**) form corresponds to a true energy minimum with a calculated potential energy higher than 10.0 kJ mol^{-1}. The energy increase is due to the unfavorable torsion angles of **1-TB** as compared with **1-BC** around both types of carbon-carbon single bonds (see Table 1). The calculated potential energies of the unsymmetrical twist-boat-chair (**1-TBC**), the C_1-symmetric twist-chair (**1-TC**), and the axial-symmetrical twist (**1-Twist**) conformations are 18.0, 29.2, and 29.6 kJ mol^{-1}, respectively.

As shown in Figures 1 and 2, the boat-chair conformation can undergo two different processes, namely, chair and boat, which both lead to time-averaged C_s symmetry. Anet [1] has shown that two successive sets of changes occur in the dynamic NMR spectrum of **1** as the temperature is lowered and these correspond to conformation processes with barriers of 22.2 kJ mol^{-1} and 34.3 kJ mol^{-1} which were called pseudrotation and inversion, respectively. Our results (Figures 1 and 2, and Tables 1 and 2) suggest that the lower-energy process is caused by the chair process (with calculated energy barrier of 39.7 kJ mol^{-1}). The high-energy process can be attributed to the boat process (with calculated energy barrier of 47.1 kJ mol^{-1}).

Representative structural parameters for various geometries of **1** are given in Tables 1 and 2. The five energy minimum conformations have strongly expanded internal angles. The comparison of bond lengths showed fairly small differences.

In conclusion, the most favorable conformation of **1** is the boat-chair (**1-BC**) geometry, which lakes symmetry. Potential energy profiles for the two different boat-chair interconversion processes were calculated. The process via a chair transition state of C_s symmetry has calculated barrier of 39.7 kJ mol^{-1}. The calculated energy barrier for boat (C_s) process is 47.1 kJ mol^{-1}. It would be valuable, of course, to have direct structural data on 1 for comparison with the results of the ab initio calculations.

Computational details

Semiempirical calculations were carried out using the AM1 method [9] with the MOPAC 6.0 program package [10].

The AM1 results were used as input for the *ab initio* molecular orbital calculations, which were carried out using the GAUSSIAN 98 [12] program.

Geometries for all structures were fully optimized by means of analytical energy gradients by Berny optimizer with no geometrical constraints [13].

The restricted The geometries of the transition states for conformational interconversion of the equilibrium structures were obtained using the optimized geometries of the equilibrium Energy minimum geometries were located by minimizing energy, with respect to all geometrical coordinates, and without imposing any symmetry constraints.

structures according to procedure of Dewar *et al.* [11] (Keyword SADDLE).

Hartree-Fock calculations with the split-valence 6-31G* basis set which include a set of d-type polarization functions on all non-hydrogen atoms were used in these calculations [14]. Single point energy calculations at MP2/6-31G*//HF/6-31G* level were used to evaluate the electron correlation effect in the energies and order of stability of conformers.

Vibrational frequencies were calculated at the 6-31G* level for all minimum energies and transition states, which were confirmed to have zero and one imaginary frequency, respectively. The frequencies were scaled by a factor of 0.91 [15] and used to compute the zero-point vibrational energies.

Table 1. Calculated total and zero-point vibrational (zero-point vibrational energy is scaled by a factor of 0.9135 to eliminate known systematic errors in calculations) energies (hartree), relative energy (including zero-point energy, kJ.mol^{-1}) and structural parameters for various conformations of (Z)-cyclooctene (1)

Structure	1-BC, C_I	TS1	1-Twist, C_2	TS2	1-TC, C_I	1-Chair, C_S
HF/6-31G*//HF/6-31G*	-311.07469	-311.06257	-311.06547	-311.06258	-311.06413	-311.06032
MP2/6-31G*//HF/6-31G*	-312.11398	-312.09990	-312.10212	-312.10120	-312.10258	-312.09842
B3LYP/6-31G*//HF/6-31G*	-313.26448	-313.25315	-313.25586	-313.25351	-313.25467	-313.25131
ZPE	0.21925	0.21928	0.21862	0.21917	0.21897	0.21880
E_{rel}[a]	0.0	31.90	22.68	31.58	27.04	36.64
E_{rel}[b]	0.0	37.03	29.62	33.61	29.24	39.72
E_{rel}[c]	0.0	29.80	21.05	28.86	25.08	33.48
r_{12}/ A°	1.321	1.321	1.322	1.321	1.322	1.320
r_{23}/ A°	1.506	1.516	1.513	1.505	1.512	1.510
r_{34}/ A°	1.539	1.555	1.542	1.542	1.549	1.551
r_{45}/ A°	1.536	1.546	1.534	1.530	1.537	1.537
r_{56}/ A°	1.544	1.540	1.529	1.545	1.536	1.557
r_{67}/ A°	1.539	1.529	1.534	1.542	1.542	1.537
r_{78}/ A°	1.539	1.542	1.542	1.565	1.546	1.551
r_{81}/ A°	1.513	1.506	1.513	1.517	1.516	1.510
θ_{123}/ °	124.5	127.8	131.9	123.1	127.5	125.0
θ_{234}/ °	113.0	120.6	118.8	110.0	112.5	114.4
θ_{345}/ °	115.7	119.7	116.2	112.8	115.3	115.6
θ_{456}/ °	116.4	116.6	117.3	114.9	117.7	120.4
θ_{567}/ °	116.8	116.1	117.3	118.6	117.8	120.4
θ_{678}/ °	117.2	113.4	116.2	121.8	115.8	115.6
θ_{781}/ °	115.1	110.0	118.8	119.9	117.9	114.4
θ_{812}/ °	125.7	125.7	131.9	124.6	128.6	125.0
ϕ_{1234}/ °	-90.2	-45.5	-36.9	-91.6	-74.9	-73.0
ϕ_{2345}/ °	50.7	-24.7	96.6	96.9	107.2	106.7
ϕ_{3456}/ °	51.7	97.0	-84.3	-66.0	-41.1	-72.1
ϕ_{4567}/ °	-99.3	-79.4	58.8	85.6	-48.5	0.0
ϕ_{5678}/ °	71.1	59.3	-84.3	-77.8	99.4	72.1
ϕ_{6781}/ °	-72.0	-95.0	96.6	-9.1	-85.8	-106.7
ϕ_{7812}/ °	79.0	91.4	-36.9	· 69.3	57.7	73.0
ϕ_{8123}/ °	-1.9	4.9	-2.4	-7.5	-3.1	0.0

[a]Relative energy with respect to the most stable conformation from HF/6-31G*// HF/6-31G* calculations.
[b]Relative energy with respect to the most stable conformation from MP2/6-31G*// HF/6-31G* calculations.

[c]Relative energy with respect to the most stable conformation from B3LYP/6-31G*// HF/6-31G* calculations.

Table 2. Calculated total and zero-point vibrational (zero-point vibrational energy is scaled by a factor of 0.9135 to eliminate known systematic errors in calculations) energies (hartree), relative energy (including zero-point energy, kJ.mol^{-1}) and structural parameters for various conformations of (Z)-cyclooctene (1)

| Structure	1-BC, C_I	TS1	1-TBC, C_I	1-BB, C_I	1-TB, C_I	1-Boat, C_S
HF/6-31G*//HF/6-31G*	-311.07469	-311.06562	-311.06955	-311.05646	-311.07143	-311.05553
MP2/6-31G*//HF/6-31G*	-312.11398	-312.10212	-312.10711	-312.09536	-312.11033	-312.09562
B3LYP/6-31G*//HF/6-31G*	-313.26448	-313.25600	-313.25953	-313.24720	-313.26145	-313.25018
ZPE	0.21925	0.21887	0.21924	0.21918	0.21945	0.21878
E_{rel}[a]	0.0	22.89	13.46	47.68	9.04	49.17
E_{rel}[b]	0.0	30.23	17.99	48.68	10.04	47.08
E_{rel}[c]	0.0	21.34	12.94	45.17	8.40	36.40
r_{12}/ A°	1.321	1.327	1.322	1.321	1.324	1.323
r_{23}/ A°	1.506	1.509	1.514	1.516	1.513	1.515
r_{34}/ A°	1.539	1.540	1.542	1.545	1.534	1.545
r_{45}/ A°	1.536	1.526	1.532	1.540	1.540	1.535
r_{56}/ A°	1.544	1.532	1.534	1.552	1.534	1.558
r_{67}/ A°	1.539	1.528	1.546	1.557	1.531	1.535
r_{78}/ A°	1.539	1.528	1.532	1.542	1.541	1.545
r_{81}/ A°	1.513	1.506	1.509	1.506	1.514	1.515
θ_{123}/ °	124.5	139.6	130.5	126.9	131.7	131.5
θ_{234}/ °	113.0	127.9	114.3	116.9	119.5	119.2
θ_{345}/ °	115.7	120.5	115.8	113.5	116.1	116.0
θ_{456}/ °	116.4	114.1	117.4	118.8	117.9	117.4
θ_{567}/ °	116.8	114.7	115.4	122.0	117.1	117.4
θ_{678}/ °	117.2	113.5	115.1	120.9	116.1	116.0
θ_{781}/ °	115.1	116.5	119.1	116.0	114.5	119.2
θ_{812}/ °	125.7	134.9	131.5	124.9	128.9	131.5
ϕ_{1234}/ °	-90.2	22.8	-81.6	-40.5	-2.3	47.7
ϕ_{2345}/ °	50.7	25.6	89.8	-40.1	75.3	28.8
ϕ_{3456}/ °	51.7	-78.8	-57.1	101.3	-44.3	-83.8
ϕ_{4567}/ °	-99.3	100.9	73.8	-26.3	-64.6	0.0
ϕ_{5678}/ °	71.1	-94.5	-110.3	-18.0	57.0	-83.8
ϕ_{6781}/ °	-72.0	80.4	56.3	-45.2	48.4	-28.8
ϕ_{7812}/ °	79.0	-52.0	17.3	92.9	-73.0	-47.7
ϕ_{8123}/ °	-1.9	-3.8	0.0	-2.0	-0.7	0.0

[a]Relative energy with respect to the most stable conformation from HF/6-31G*// HF/6-31G* calculations.
[b]Relative energy with respect to the most stable conformation from MP2/6-31G*// HF/6-31G* calculations.
[c]Relative energy with respect to the most stable conformation from B3LYP/6-31G*// HF/6-31G* calculations.
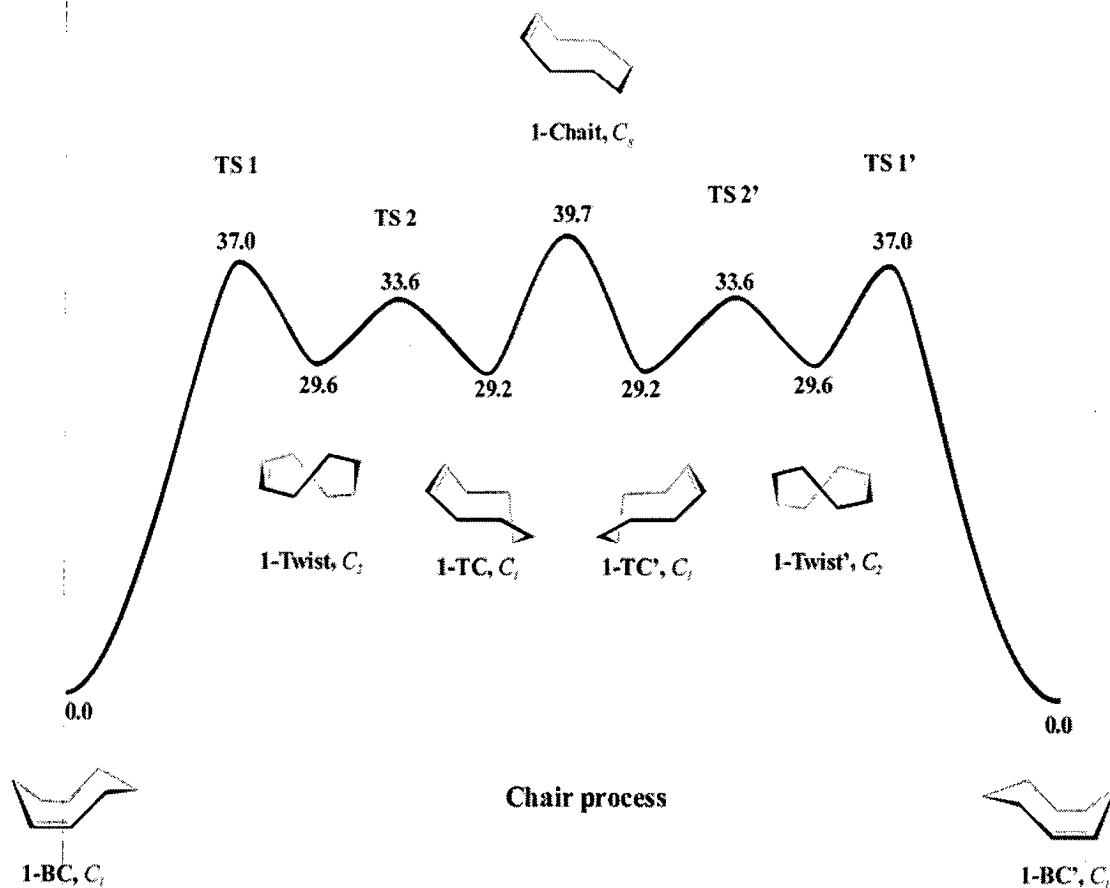
Figure 1. Calculated MP2/6-31G*//HF/6-31-G* strain energy (kJ mol-1) profile for conformational interconversion of various geometries (chair process) of (Z)-cyclooctene (**1**).
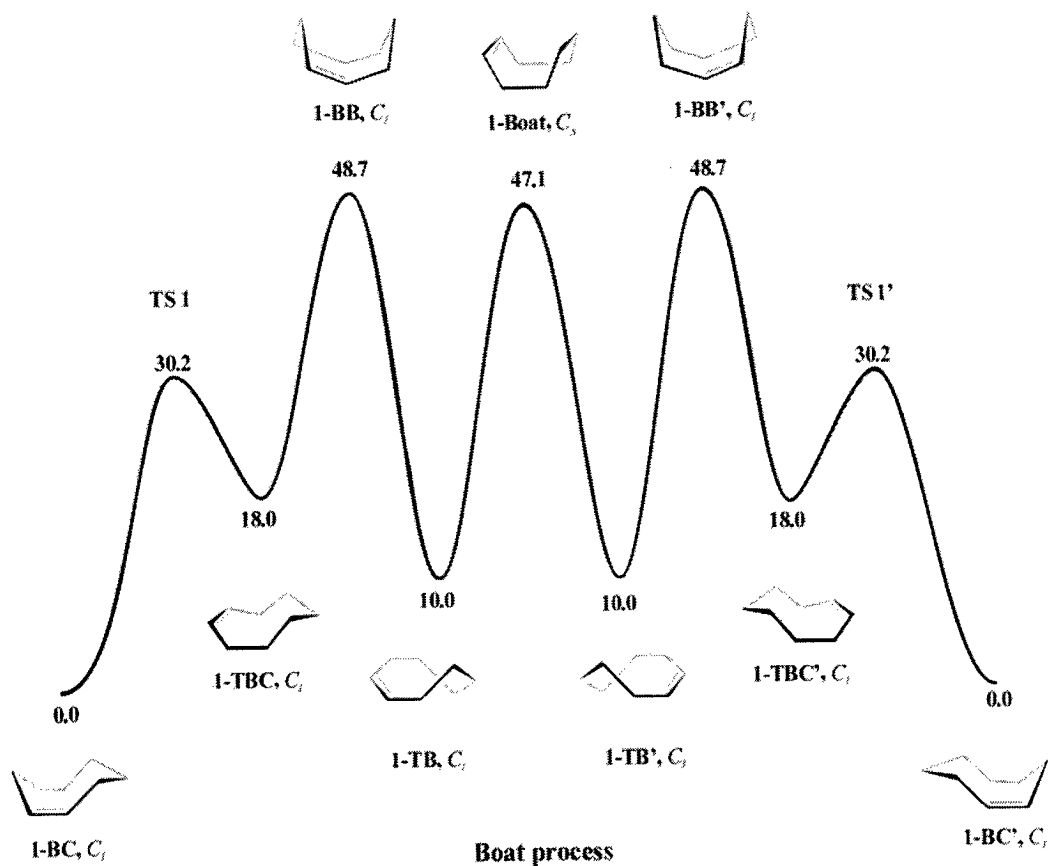
Figure 2. Calculated MP2/6-31G*//HF/6-31-G* strain energy (kJ mol-1) profile for conformational interconversion of various geometries (boat process) of (Z)-cyclooctene (**1**).

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