

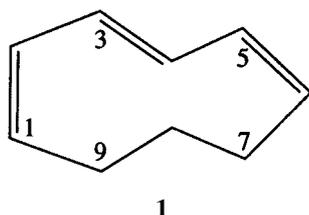
## SHORT PAPER

**Ab initio study of conformational properties of  
(Z,E,Z)-cyclonona-1,3,5-triene**Issa Yavari<sup>a,\*</sup>, Behrooz Adib<sup>b</sup>, and K. Zare<sup>b</sup><sup>a</sup>Department of Chemistry, University of Tarbiat Modarres, PO Box 14155-4838, Tehran, Iran<sup>b</sup>Department of Chemistry, Science and Research Campus, Islamic Azad University, Ponak, Tehran, Iran

*Ab initio* HF/6-31G\* and MP2/6-31G\*//HF/6-31G\* methods were used to calculate the relative energies of the important energy-minimum conformations and transition-state geometries of (Z,E,Z)-cyclonona-1,3,5-triene; the calculated energy barrier for ring inversion of the twist-chair (C<sub>1</sub>) conformation is 29.35 kJ/mol, while the barrier for swivelling of the *trans* double bond through the polymethylene bridge is 59.76 kJ/mol.

**Keywords:** strained molecules, *Ab initio* molecular orbital, cyclic trienes, conformational energy

(Z,E,Z)-Cyclonona-1,3,5-triene (**1**) have been prepared in low yield by irradiation of a pentane solution of *trans*-bicyclo[4.3.0]nona-2,4-diene at 254 nm.<sup>1</sup> While much work has been dedicated to the study of conformational properties of unsaturated eight-membered rings,<sup>2–6</sup> much less effort have been devoted to unsaturated nine-membered ring systems.<sup>7–10</sup> This study was undertaken to investigate the structural optimisation and conformational interconversion pathways of the highly strained nine-membered-ring triene **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.



Theoretical calculations provide energy differences and structural parameters for isolated molecules at 0 K. Therefore, theoretical calculations are not expected, in principle, to reproduce the experimental values quantitatively.<sup>11</sup> Nevertheless, it is possible to carry out *ab initio* calculations at the Hartree–Fock level, from which many properties and structures can be obtained with an accuracy that is competitive with experiment.<sup>12–15</sup> Since the theoretical results are free from intermolecular interferences, they are a valuable tool for a systematic study of conformational effects in simple organic molecules.

Six geometries were found important for a description of the conformational features of (Z,E,Z)-cyclonona-1,3,5-triene (**1**). Three of these geometries correspond to energy minima and three are one-dimensional energy maxima (saddle points or transition states) as shown in Fig. 1 and Table 1. The unsymmetrical twist-chair (TC,C<sub>1</sub>) conformation of **1** is predicted to be the most stable geometry (see Fig. 1 and Table 1). The energy surface for the conformational interconversion of TC with itself was investigated in detail by changing different torsional angles. The results are shown in Figure 1 and Table 1. There are three distinct, different transition states (not counting mirror images) which are required to describe the

degenerate conformational dynamics in (Z,E,Z)-cyclonona-1,3,5-triene. The internal and torsional angles of these transition states are given in Table 1.

Two simple conformational processes for degenerate interconversion of twist-chair (TC,C<sub>1</sub>) conformation with itself, via the axial-symmetrical geometries, such as TB and boat forms, as intermediates are shown in Fig. 1. These processes are calculated to have similar energy barriers. Any of these processes when fast, introduces a time-averaged axis of symmetry.

The third conformational process, and the one with the highest barrier, is the interconversion of the TC conformer with its mirror image via swivelling of the *trans* double bond through the polymethylene chain. The swivelling process was simulated by rotation of the double bond about an axis containing the two adjacent double bonds. This high-energy process leads to conformational racemisation of the chiral twist-chair geometry of **1**. The calculated swivelling barrier (59.76 kJ/mol) for compound **1** is about 20 kJ/mol lower than the racemisation barrier for (*E*)-cyclononene.<sup>7</sup> Since the two conformational enantiomers of (*E*)-cyclononene are rapidly interconverted at ambient temperature, compound **1** is expected to lack chiral stability at room temperature as a result of its relatively low conformational racemisation energy.

In summary, HF/6-31G\* calculations provide a fairly clear picture of the conformational properties of (Z,E,Z)-cyclonona-1,3,5-triene **1** from both structural and dynamic points of view. According to these calculations, the energy barrier for ring inversion of the unsymmetrical twist-chair conformation via the axial-symmetrical twist-boat or boat forms is about 30 kJ/mol. The calculated barrier for swivelling of the *trans* double bond through the polymethylene chain in TC conformation is 59.76 kJ/mol. Thus, conformational racemization of **1** is expected to be fast at ambient temperature. It would be valuable, of course, to have direct structural data on **1** for comparison with the results of the *ab initio* calculations.

**Calculations**

The *ab initio* molecular orbital calculations, were carried out using the GAUSSIAN 98 program.<sup>16</sup> Geometries for all structures were fully optimised by means of analytical energy gradients by Bery optimiser with no geometrical constraints.<sup>17</sup> The restricted Hartree–Fock calculations with the split-valence 6-31G\* basis set which include a set of *d*-type polarisation functions on all non-hydrogen atoms were used in these calculations.<sup>18</sup> Single point energy calculations at MP2/6-31G\*//HF/6-31G\* level were used to evaluate the

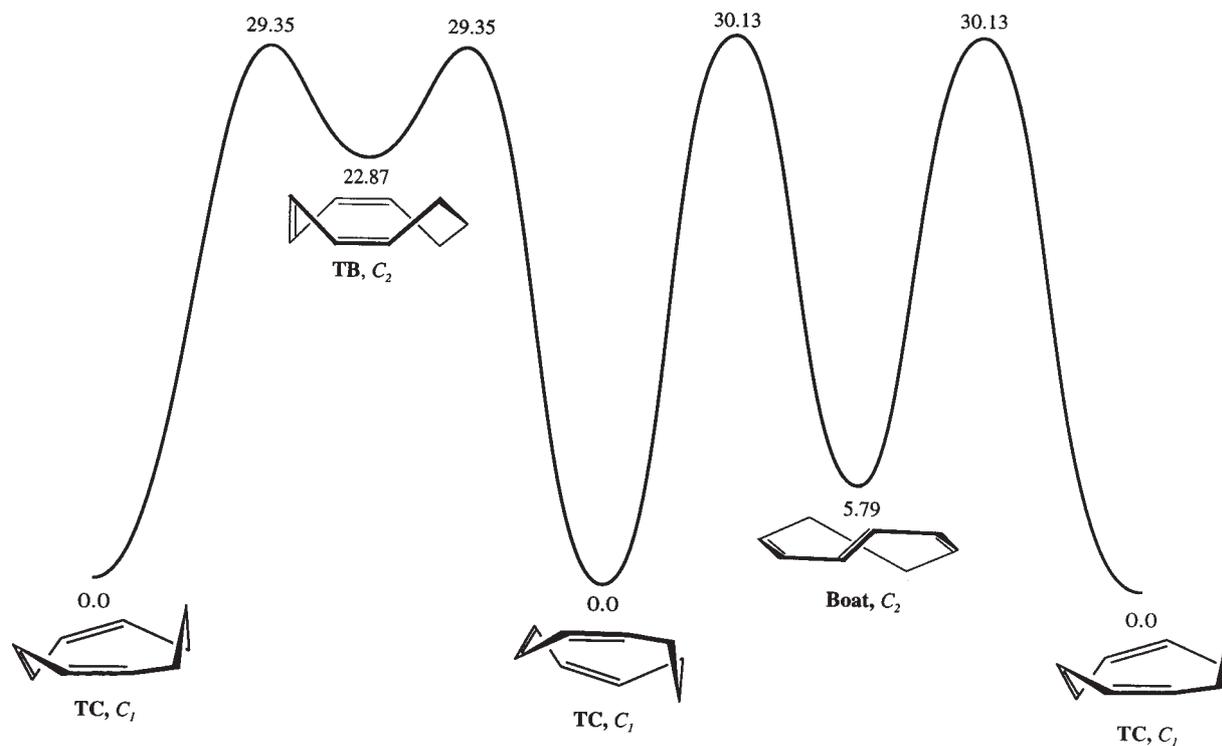
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† This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

**Table 1** Calculated total and zero-point vibrational<sup>a</sup> energies (hartree), relative energy (including zero-point energy, kJ mol<sup>-1</sup>) and structural parameters for important geometries of (*Z,E,Z*)-cyclonona-1,3,5-triene

Feature	TC, C <sub>1</sub>	Boat, C <sub>2</sub>	TB, C <sub>2</sub>	(TC=TB) <sup>#</sup> , C <sub>1</sub>	(TC=Boat) <sup>#</sup> , C <sub>1</sub>	Swivelling
HF/6-31G*//HF/6-31G*	-347.527383	-347.522397	-347.516967	-347.512932	-347.514845	-347.499459
[MP2/6-31G*//HF/6-31G*]	[-348.858192]	[-348.855989]	[-348.849486]	[-348.847018]	[-348.846721]	[-348.835443]
ZPE	0.198914	0.199665	0.198558	0.198687	0.198960	0.200253
Erel	0.00	13.10	27.36	37.96	32.93	73.35
[Erel]	[0.00]	[5.79]	[22.87]	[29.35]	[30.13]	[59.76]
<i>r</i> <sub>12</sub>	1.324	1.329	1.327	1.326	1.326	1.340
<i>r</i> <sub>23</sub>	1.480	1.475	1.448	1.495	1.477	1.485
<i>r</i> <sub>34</sub>	1.320	1.323	1.319	1.320	1.322	1.324
<i>r</i> <sub>45</sub>	1.477	1.475	1.448	1.489	1.467	1.448
<i>r</i> <sub>56</sub>	1.327	1.329	1.327	1.328	1.327	1.336
<i>r</i> <sub>67</sub>	1.527	1.529	1.526	1.527	1.525	1.539
<i>r</i> <sub>78</sub>	1.561	1.551	1.548	1.549	1.579	1.571
<i>r</i> <sub>89</sub>	1.549	1.551	1.548	1.547	1.557	1.580
<i>r</i> <sub>91</sub>	1.524	1.529	1.526	1.524	1.529	1.540
$\theta$ <sub>123</sub>	118.8	118.7	115.3	114.5	116.5	127.5
$\theta$ <sub>234</sub>	120.8	122.3	120.8	120.0	119.8	113.3
$\theta$ <sub>345</sub>	124.2	122.3	120.8	120.8	123.6	147.7
$\theta$ <sub>456</sub>	120.0	118.7	115.3	115.5	120.8	113.7
$\theta$ <sub>567</sub>	130.7	127.6	124.0	124.3	131.7	128.9
$\theta$ <sub>678</sub>	122.9	120.3	120.1	119.5	127.8	124.5
$\theta$ <sub>789</sub>	118.3	123.2	121.0	119.3	125.7	118.2
$\theta$ <sub>891</sub>	116.9	120.3	120.1	117.8	115.7	120.8
$\theta$ <sub>912</sub>	126.5	127.6	124.0	122.4	125.4	131.7
$\phi$ <sub>1234</sub>	-54.5	-52.1	-87.1	-89.5	-59.3	10.3
$\phi$ <sub>2345</sub>	149.1	138.6	134.8	133.7	144.7	173.9
$\phi$ <sub>3456</sub>	-79.3	-52.1	-87.1	-86.1	-50.2	-177.3
$\phi$ <sub>4567</sub>	-0.2	7.6	-7.2	-6.8	8.6	-3.8
$\phi$ <sub>5678</sub>	28.4	-69.9	93.8	93.8	-40.3	30.1
$\phi$ <sub>6789</sub>	-82.9	60.3	-60.6	-59.1	-0.4	-83.8
$\phi$ <sub>7891</sub>	126.6	60.3	-60.6	-65.4	100.4	117.2
$\phi$ <sub>8912</sub>	-48.7	-69.9	93.8	97.8	-59.5	-69.6
$\phi$ <sub>9123</sub>	0.6	7.6	-7.2	-5.9	-1.5	8.1

<sup>a</sup>Zero-point vibrational energy is scaled by a factor of 0.9135 to eliminate known systematic errors in calculations.

**Fig.1** Calculated MP2/6-31G\*//HF/6-31G\* strain energy (kJ/mol) profile for ring inversion of (*Z,E,Z*)-cyclonona-1,3,5-triene.

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 and used to compute the zero-point vibrational energies.<sup>19</sup>

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