

Ab initio study of conformational properties of (Z,Z,Z)-cyclonona-1,3,6-triene

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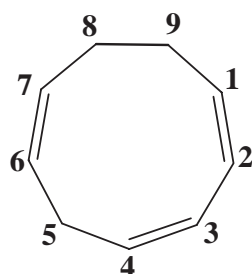
Ab initio molecular orbital and density functional theory (DFT) calculations, applied to (Z,Z,Z)-cyclonona-1,3,6-triene (**1**) have revealed that the calculated energy barrier for ring inversion of the twist-boat (C_1 symmetry) conformation of **1** as a most stable form is 8.41 kcal mol⁻¹, as calculated by the MP2/6-31G*//HF/6-31G* method

Keywords: medium rings, stereochemistry, molecular modeling, ab initio calculation, cyclic trienes

Contrary to the unsaturated eight-membered rings, much less effort has been devoted to unsaturated nine-membered ring systems.¹⁻⁵ Recently, Yavari *et al.* reported the structural optimisation and conformational interconversion pathways of (Z,Z,Z)-cyclonona-1,3,5-triene and (Z,E,Z)-cyclonona-1,3,5-triene by HF/6-31G* and MP2/6-31G*//HF/6-31G* methods.^{6,7} It is interesting to know that (Z,Z,Z)-cyclonona-1,3,6-triene (**1**) does not exist except for some methyl-derivatives for which NMR measurements are available.⁸ Methyl-derivatives of (**1**), have been prepared by protonation and methylation of cyclononatetraenyl dianion solutions generated in liquid ammonia.⁹⁻¹³ NMR measurements in the range 130 to -70°C on 8,8-dimethyl- and 9,9-dimethyl-cyclonona-1,3,6-triene have shown that the geminal dimethyl groups become equivalent near 0°C. The determined ΔG^\ddagger values from the Eyring equation are 12.91 and 11.96 kcal mol⁻¹ for 9,9-dimethyl- and 8,8-dimethyl-(Z,Z,Z)-cyclonona-1,3,6-triene respectively.⁸

Buemi *et al.*¹⁴⁻¹⁷ have theoretically investigated the stability of the probable conformers of (**1**) by a partially modified semi-empirical Hendrickson's treatment. Their results showed that the energy barrier of the conformational interconversion of **1** is about 25.11 kcal mol⁻¹, which is an overestimation in comparison to the reported dynamic NMR data.⁶

Since the reported theoretical data for the interconversion pathways of compound **1** are not consistent with the previously reported NMR data,¹⁶ it can be concluded that the proposed interconversion pathways are not proper or possibly the implement method is poor.



In this work, the clarification of the interconversion pathways of **1** are investigated using *ab initio* and DFT methods.

Calculations

Ab initio calculations were carried out using HF/6-31G*//HF/6-31G*, MP2/6-31G*//HF/6-31G* and B3LYP/6-31G*//HF/6-31G* levels of theory with the GAUSSIAN 98 package of programs¹⁸ implemented on a Pentium-PC computer with a 550 MHz processor. Initial structure geometries of compound **1** were obtained by a molecular mechanic program PCMODEL (88.0)¹⁹ and for future reoptimisation of geometries, PM3 method of the MOPAC 6.0 computer program was used.^{20,21}

The GAUSSIAN 98 package of programs (serial number: PC42919962W-0772N) was finally used to perform *ab initio* calculations at the HF/6-31G* level in order to obtain the energy minimum structures and MP2/6-31G*//HF/6-31G* and B3LYP/6-31G*//HF/6-31G* methods for single point energy calculations.

The nature of the stationary points for compound **1** has been determined by means of the number of imaginary frequencies. For minimum state structures, only real frequencies values and in the transition state, only single imaginary frequency values are accepted.²²

The structure of the transition state geometries were located using the optimised geometries of the equilibrium structure according to the procedure of Dewar *et al.* (keyword SADDLE).²³ These structures were then reoptimised by QST2 option at the HF/6-31G* level. The vibrational frequency of ground state and transition states was calculated by keyword FREQ.

Results and discussion

Corrected zero point (ZPE^c) and total electronic (E_{el}) energies ($E_0 = \text{ZPE}^c + E_{el}$) for the four conformation of (Z,Z,Z)-cyclonona-1,3,6-triene (**1**), as calculated by HF/6-31G* level of theory, are listed in Table 1. Two of these geometries correspond to energy minima (ground state) and two are energy maxima (transition state), as shown in Fig. 1. For single-point energy calculation both *ab initio* MP2/6-31G*//HF/6-31G* and DFT method (B3LYP/6-31G*//HF/6-31G*) were used. All three methods predicted the unsymmetrical twist-boat (TB, C_1 point group) to be the most stable geometry of **1** (see Fig. 1 and Table 1)

The energy surface for the conformational interconversion of TB with itself was investigated in detail by changing different torsional angles. There are two distinct different transition states, which are required to describe the nondegenerate conformational dynamics in (Z,Z,Z)-cyclonona-1,3,6-triene

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

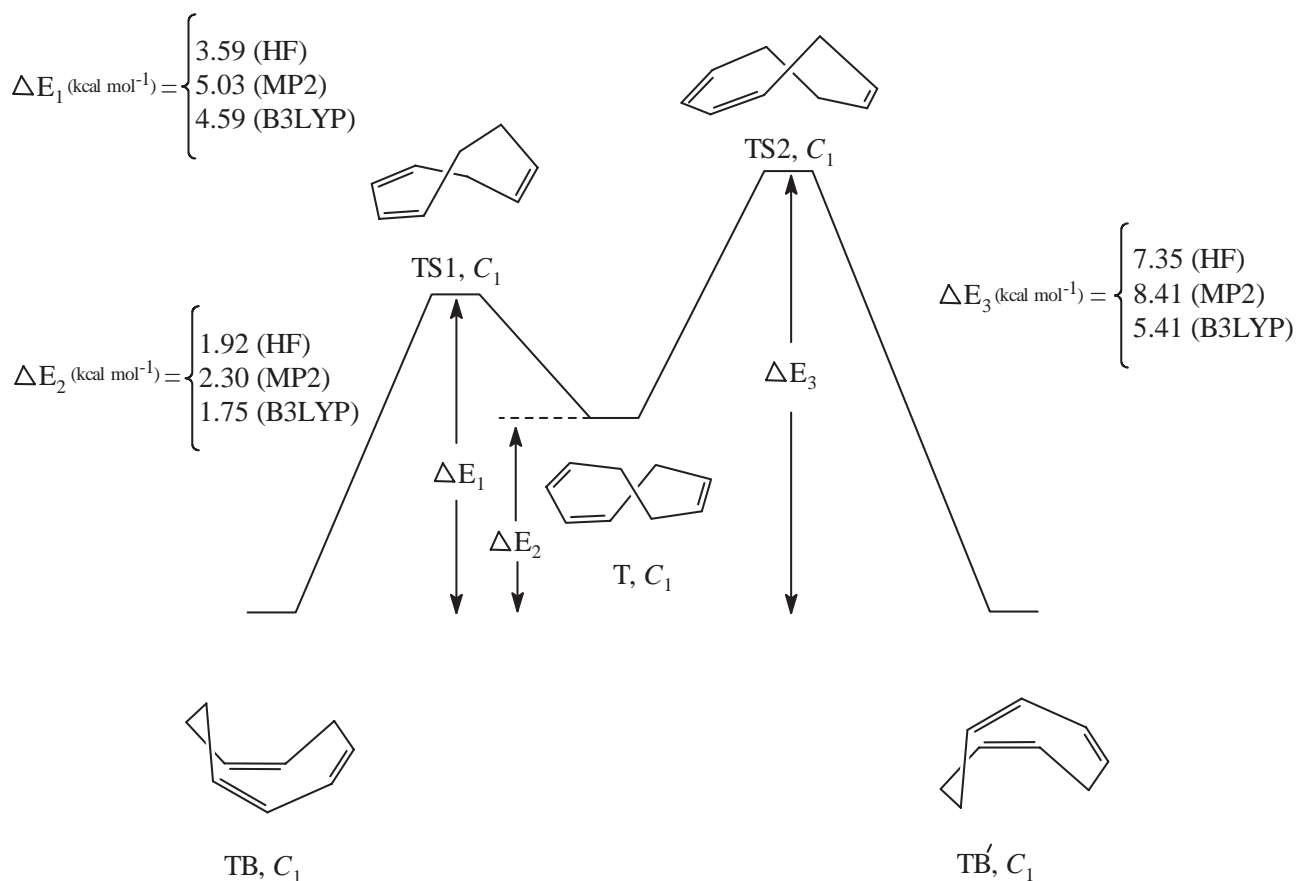


Fig. 1 Calculated HF/6-31G**//HF/6-31G*, MP2/6-31G**//HF/6-31G* and B3LYP/6-31G**//HF/6-31G* profile for ring inversion of (Z,Z,Z)-cyclonona-1,3,6-triene (**1**).

Table 1 Calculated energies (in Hartree) for the important geometries of (Z,Z,Z)-cyclonona-1,3,6-triene (**1**)

Geometry	HF/6-31G*				MP2/6-31G**//HF/6-31G*		B3LYP/6-31G**//HF/6-31G*	
	ZPE ^c	E_{el}	E_0	ΔE^a_0	E_{el}	ΔE^a	E_{el}	ΔE^a
TB, (C ₁)	0.182420	-347.730493	-347.540073	0.000000 (0.000000)	-348.876191	0.000000 (0.000000)	-350.111578	0.000000 (0.000000)
T, (C ₁)	0.182230	-347.727249	-347.545019	0.003054 (1.917637)	-348.872521	0.0036695 (2.304116)	-350.108789	0.002789 (1.750989)
(TB → T) [#] , (C ₁)	0.181638	-347.723992	-347.542354	0.007190 (3.591017)	-348.868174	0.0080172 (5.034080)	-350.104261	0.007317 (4.594605)
(T → TB') [#] , (C ₁)	0.182700	-347.719071	-347.536371	0.011702 (7.347803)	-348.862794	0.0133964 (8.411734)	-350.102963	0.008615 (5.409381)

^aRelative to the most stable geometry.

^bNumbers in parenthesis are the corresponding values in kcal mol⁻¹.

^cCorrected by multiplying by a scaling factor (0.9135).

(**1**). The internal and torsional angles of these transition states are given in Table 1.

The obtained results show that the energy barrier for the ring inversion of **1** is 7.35, 54.1 and 8.41 kcal mol⁻¹, as calculated by HF/6-31G**//HF/6-31G*, MP2/6-31G**//HF/6-31G* and B3LYP/6-31G**//HF/6-31G* methods, respectively. In comparison to the reported experimentally data for the ring inversion of methyl-derivatives of **1** (about 12 kcal mol⁻¹), the obtained barrier height by MP2/6-31G**//HF/6-31G* is closer to the reported experimentally data. In comparison to the reported theoretical data obtained by Buemi *et al.*¹⁷, it can be concluded that the proposed interconversion pathways are not proper or the implemented method is poor.

Conclusion

In conclusion, HF, MP2 and B3LYP calculations provide a fairly clear picture of the conformational properties of (Z,Z,Z)-cyclonona-1,3,6-triene (**1**) from the structural and dynamic points of view. According to the obtained results by MP2/6-31G**//HF/6-31G* level of theory, the energy barrier for ring inversion of the asymmetrical twist-boat (TB) conformation of **1** via the unsymmetrical *pseudo*-crown (T) conformation is about 8.5 kcal mol⁻¹, which is in agreement with the dynamic NMR data for 8- and 9- methyl derivatives of **1**.

We would like to acknowledge Dr. D. Tahmassebi for providing us Gaussian 98 computer program (serial number: PC42919962W-0772N) and helpful discussion.

Table 2 HF/6-31G* calculated structural parameters for important geometries of (Z,Z,Z)-cyclonona-1,3,6-triene (1)

Feature	TB, C ₁	T, C ₁	(TB→T) [#] , C ₁	(T→TB) [#] , C ₁
Bond lengths (Å)				
r ₁₋₂	1.324	1.326	1.322	1.332
r ₂₋₃	1.479	1.478	1.486	1.480
r ₃₋₄	1.328	1.323	1.323	1.325
r ₄₋₅	1.518	1.506	1.516	1.506
r ₅₋₆	1.510	1.518	1.515	1.515
r ₆₋₇	1.320	1.322	1.320	1.321
r ₇₋₈	1.515	1.516	1.503	1.510
r ₈₋₉	1.517	1.550	1.541	1.540
r ₉₋₁	1.502	1.514	1.513	1.518
Bond angles (°)				
θ ₁₋₂₋₃	129.1	130.5	129.9	136.7
θ ₂₋₃₋₄	132.2	127.5	131.6	133.1
θ ₃₋₄₋₅	131.6	126.6	132.6	127.8
θ ₄₋₅₋₆	117.1	111.9	122.5	111.0
θ ₅₋₆₋₇	127.0	126.0	129.6	129.4
θ ₆₋₇₋₈	127.3	128.1	127.6	132.8
θ ₇₋₈₋₉	114.9	116.4	111.6	120.9
θ ₈₋₉₋₁	112.6	119.8	116.1	117.1
θ ₉₋₁₋₂	126.7	132.8	129.7	135.5
Torsion angles (°)				
φ ₁₋₂₋₃₋₄	-42.6	-50.1	-76.1	11.6
φ ₂₋₃₋₄₋₅	0.2	2.0	-0.8	-0.6
φ ₃₋₄₋₅₋₆	-38.1	105.1	30.2	-87.0
φ ₄₋₅₋₆₋₇	97.9	-58.6	37.5	90.9
φ ₅₋₆₋₇₋₈	-4.6	-1.3	-5.9	3.4
φ ₆₋₇₋₈₋₉	-47.1	-55.1	-103.8	-0.6
φ ₇₋₈₋₉₋₁	-47.1	105.2	51.9	-82.9
φ ₈₋₉₋₁₋₂	102.3	-21.7	39.1	71.8
φ ₉₋₁₋₂₋₃	3.0	-2.2	4.2	-2.7

Received 23 March 2003; accepted 9 June 2003

Paper 03/1841

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