SHORT PAPER

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AM1 study of conformational properties of (*E*)-cyclononene[†]

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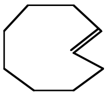
The unsymmetrical chair–chair (CC) conformation of (*E*)-cyclononene is calculated to be 5.7 kJ/mol more stable than the axial-symmetrical twist-chair-chair (TCC) form; the calculated energy barrier for ring inversion of the CC conformation is 45.6 kJ/mol, while the barrier for swivelling of the double bond through the polyethylene bridge is 119.5 kJ/mol.

When the saturated segment of a *trans*-cycloalkene is sufficiently short, it is forced out of the plane of the olefinic moiety, which is normally a symmetry plane of the molecule.[1] The *trans*-cycloalkene then become chiral, its chirality being of the planar type.[2,3] *Trans*-cycloalkenes have long attracted the interest of chemists as a measure of the amount of strain that can be placed across a double bond.[4] That (*E*)-cyclononene (**1**) is, in principle, chiral was recognized by Blomquist[5] at 1952; however the two enantiomers of this *trans*-cycloalkene are rapidly interconverted. Swivelling of the double bond through the polymethylene bridge is rapid at ambient temperature and the racemization barrier is measured at low temperature.[6]

While the conformational properties of (*Z*)-cyclononene have been extensively studied by theoretical and experimental methods,[7] the extent of our present understanding regarding the conformations of (*E*)-cyclononene (**1**) is meagre. We report the results of AM1[8] (Austin Model 1) SCF MO calculations for structure optimization and conformational interconversion pathways for different geometries of compound **1.**



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Altogether, seven geometries were found to be important for a description of the conformational features of compound **1**. Four correspond to energy minima and three to one-dimensional energy maxima (saddle points or transition states) as shown in Fig. 1. The heats of formation of various molecular geometries of compound **1** as calculated by the AM1 method are given in Table 1.

Table 1 Calculated heats of formation (kJ/mol) and structural parameteres (bond lengths *r* and bond angles *θ* and dihedral angles *ϕ* in degrees) for (*E*)–cyclononene.

Swivelling	**TCC**	**CB = TCC**	**CB**	**TCB = CB**	**T CB**	**CC = TCB**	**CC**	
	C_2	C_1	C_1	C_1	C_2	C_1	C_1	Feature
42.5	–71.3	–30.8	–64.4	–43.0	–60.8	–31.4	–77.0	ΔH^o_f
119.5	5.7	46.2	12.6	34.0	16.2	45.6	0.0	$\Delta\Delta H^o_f{}^a$
1.33	1.34	1.34	1.34	1.34	1.34	1.34	1.34	r_{12}
1.47	1.48	1.48	1.48	1.48	1.48	1.48	1.48	r_{23}
1.54	1.53	1.53	1.53	1.53	1.53	1.52	1.52	r_{34}
1.53	1.52	1.52	1.52	1.52	1.52	1.52	1.52	r_{45}
1.54	1.52	1.52	1.52	1.52	1.52	1.52	1.52	r_{56}
1.54	1.52	1.52	1.52	1.52	1.52	1.52	1.52	r_{67}
1.53	1.52	1.52	1.52	1.53	1.52	1.53	1.52	r_{78}
1.54	1.52	1.53	1.52	1.53	1.53	1.53	1.53	r_{89}
1.51	1.48	1.48	1.48	1.48	1.48	1.48	1.48	r_{91}
148	121	121	123	122	121	120	123	θ_{123}
107	107	111	110	109	107	108	110	θ_{234}
116	113	124	115	114	113	113	114	θ_{345}
117	115	124	113	114	115	113	114	θ_{456}
116	117	114	115	122	118	120	114	θ_{567}
117	115	119	118	122	115	127	113	θ_{678}
120	113	120	116	113	113	124	113	θ_{789}
118	107	113	110	107	107	112	109	θ_{891}
115	121	123	121	120	121	124	122	θ_{912}
–170	–87	–101	–82	–65	–65	–50	–65	ϕ_{1234}
–38	60	36	–11	–30	–46	–38	–39	ϕ_{2345}
82	–112	2	82	109	121	112	90	ϕ_{3456}
–109	68	–87	–140	–105	–61	–126	–115	ϕ_{4567}
112	69	140	60	0.0	–61	51	130	ϕ_{5678}
–102	–112	–50	57	92	121	33	–85	ϕ_{6789}
65	60	5	–62	–57	–46	–34	47	ϕ_{7891}
–24	–87	–63	–50	–64	–66	–81	122	ϕ_{8912}
–175	149	160	154	154	148	159	161	ϕ_{9123}

[a]The standard strain energy in each geometry of a molecule is defined as the difference between the standard heats of formation $(\Delta H^O)_f$ for that geometry and the most stable conformation of the molecule.[14]

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

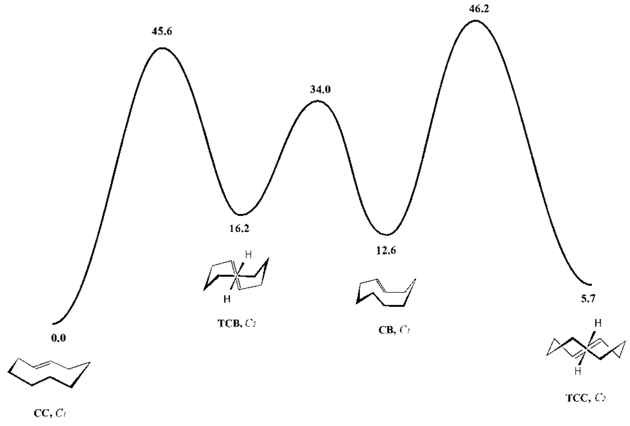

Fig. 1 Calculated strain energy (kJmol) profile for conformational interconversion of various geometries of (E)-cyclonene.

Ring internal and torsional angles for seven geometries of **1** are given in Table 1. The energy surface for interconversion of various conformations of compound **1** was investigated in detail by changing different dihedral angles and the results are shown in Fig. 1. There are three distinct and different transition states (not counting mirror images) and four energy-minimum geometries which are required to describe the conformational dynamics in **1**.

The simplest conformational process, and the one with the highest barrier is the degenerate interconversion of chair–chair (CC) conformation with itself *via* the axial-symmetrical geometries, such as TCB and TCC, as well as the unsymmetrical CB conformation, as intermediates. This process, when fast, introduces a time-averaged axis of symmetry. The calculated strain-energy barrier for this process is 46.2 kJ/mol and it is expected to be observed by dynamic NMR experiments.

We carried out AM1 calculations in an attempt to predict the barrier for swivelling of the double bond through the polymethylene chain in (*E*)-cyclononene (**1**). The lowest energy conformer of **1** was used as the starting structure for determining rotation barrier. The structural parameters for the transition-state geometry of the swivelling process are given in Table 1. The swivelling process was simulated by rotation of the double bond about an axis containing the two allylic methylene groups. The agreement between the calculated swivelling barrier (119.5 kJ/mol) and the experimental[6] value (83.7 kJ/mol) is rather weak. Most likely this error results from exaggerated values for the van der Waals repulsion terms at close interatomic distance in the AM1 method.

In conclusion, AM1 calculations provide a fairly clear picture of the conformational properties of (*E*)-cyclononene **1** from both structural and energetic points of view . According to these calculations, the energy barrier for ring inversion of the unsymmetrical chair-chair conformation *via* the axial-symmetrical twist–chair–boat and twist-chair-chair forms is about 46.2 kJ/mol. It would be valuable, of course, to have direct structural data on **1** for comparison with the results of the AM1 semi-empirical SCF MO calculations.

Calculations

Initial estimates of the geometry of structures **1** were obtained by a molecular-mechanics program PCMODEL (88.0)[9] followed by full minimization using the semiempirical AM1 method[8] in the MOPAC 6.0 computer program,[10,11] implemented on a VAX 4000-300 computer .

Optimum geometries are located by minimizing energy, with respect to all geometrical coordinates, and without imposing any symmetry constraints. The structures of the transition state geometries were obtained using the optimized geometeris of the equilibrium structures according to the procedure of Dewar *et al.*[12] (keyword SADDLE). All geometries were characterized as stationary points, and true local energy minima and transition states on the potential energy surface were found using the keyword FORCE. All energy minima and transition state geometries obtained in this work are calculated to have $3N$–6 and $3N$–7 real vibrational frequencies, respectively.[13]

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