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AM1 Study of the Conformational Properties of (*Z,Z*)-Cyclonona-1,3-diene†

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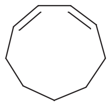
The unsymmetrical boat–chair **BC** conformation of (*Z,Z*)-cyclonona-1,3-diene is calculated to be 5 kJ mol^{-1} more stable than the axial-symmetrical twist-boat–chair **TBC** form; while the calculated energy barrier for limited pseudorotation of **BC** and **TBC** is only 10.2 kJ mol^{-1}, ring inversion of **BC** *via* plane-symmetrical boat geometry requires 24.4 kJ mol^{-1}.

While the conformational properties of (*Z,Z*)-cycloocta-1,3-diene have been extensively studied by theoretical and experimental methods,[1] the extent of our present understanding regarding the conformations of (*Z,Z*)-cyclonona-1,3-diene **1** is meager. We report the results of AM1 (Austin Model 1) SCF MO calculations for structure optimization and conformational interconversion pathways for different geometries of compound **1**.



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Altogether eight geometries were found important for a description of the conformational features of compound **1**. Four correspond to energy minima, and four to one-dimensional energy maxima (saddle points or transition states) as shown in Fig. 1.

The heats of formation for various molecular geometries of compound **1** calculated by the AM1 method are given in Table 1. Two families of conformations, *viz.* the boat–chair (BC) and the twist-boat (TB), are found for (*Z,Z*)-cyclonona-1,3-diene. Ring internal and torsional angles for eight 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 torsional angles and the results are shown in Fig. 1. There are four 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 lowest barrier, is the degenerate interconversion of the boat–chair conformation with itself *via* the twist-boat–chair (TBC) intermediate. Since the TBC has C_2 symmetry, this process, when fast, introduces a time-averaged axis of symmetry. The calculated strain-energy barrier for this process is 10.2 kJ mol^{-1} and it is not expected to be observed by dynamic NMR experiments even at −180 °C. A second, and higher energy, process undergone by the boat–chair family of conformations is also degenerate, and involves the boat (B) transition state, which has C_s symmetry. In this case a time averaged plane of symmetry results when the interconversion is fast. If both degenerate processes just considered are fast the time-averaged symmetry of the boat–chair conformation becomes C_{2v}, which is the maximum symmetry allowed by the chemical structure of **1**. The chair, unlike the boat, does not take part in any easy degenerate conformational process, but it interconverts with the TBC *via* a transition state, which is substantially (11 kJ mol^{-1}) higher than the (boat) barrier separating the two TBC conformations.

In conclusion, AM1 calculations provide a fairly clear picture of the conformational properties of (*Z,Z*)-cyclonona-1,3-diene **1** from both structural and energetic points of view. According to these calculations, the energy barrier for limited pseudorotation of the unsymmetrical boat–chair conformation *via* the axial-symmetrical twist-boat–chair form is about 10 kJ mol^{-1}; ring inversion of the boat–chair *via* the plane-symmetrical boat geometry requires 24.4 kJ mol^{-1}. It would be valuable, of course, to have direct structural data on **1** for comparison with the results of the AM1 semiempirical SCF MO calculations.

Calculations

Initial estimates of the geometry of structures **1** was obtained by a molecular-mechanics program PCMODEL (88.0)[2] followed by full minimization using the semiempirical AM1 method[3] in the MOPAC 6.0 computer program,[4,5] implemented on a VAX 4000-300 computer. Optimum geometries were located by minimizing energy, with respect to all geometrical coordinates, and without

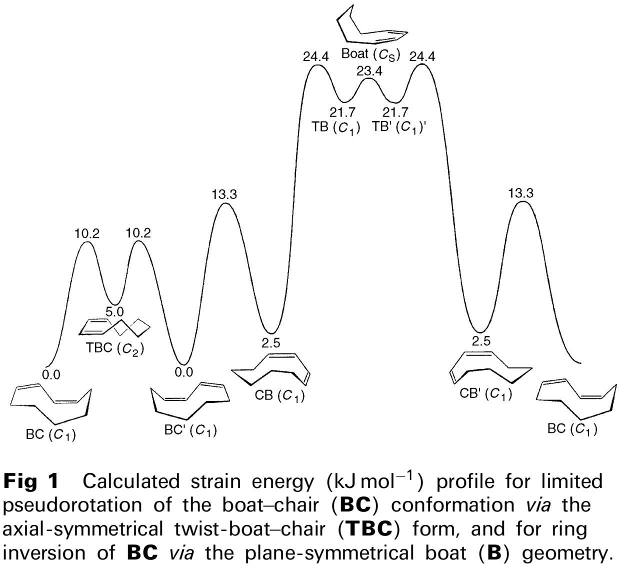

Fig 1 Calculated strain energy (kJ mol^{-1}) profile for limited pseudorotation of the boat–chair (**BC**) conformation *via* the axial-symmetrical twist-boat–chair (**TBC**) form, and for ring inversion of **BC** *via* the plane-symmetrical boat (**B**) geometry.

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Table 1 Calculated heats of formation (kJ mol^{-1}) and selected structural parameters[a] (bond angles θ and dihedral angles ϕ in degrees) for (*Z,Z*)-cyclonona-1,3-diene

Feature	BC C_1	(BC = TBC)$^{\#}$ C_1	TBC C_2	CB C_1	(BC = CB)$^{\#}$ C_1	(CB = TB)$^{\#}$ C_1	TB C_1	Boat C_s
ΔH_f°	17.9	28.1	22.9	20.4	31.2	42.3	39.6	41.3
$\Delta\Delta H_f^{\circ\ b}$	0.0	10.2	5.0	2.5	13.3	24.4	21.7	23.4
θ_{123}	125	126	127	128	125	131	134	136
θ_{234}	126	125	127	125	124	129	132	136
θ_{345}	126	124	126	125	124	126	127	132
θ_{456}	113	112	111	113	113	114	113	114
θ_{567}	114	113	115	113	114	119	115	115
θ_{678}	114	118	117	113	114	120	115	115
θ_{789}	114	118	115	113	117	117	116	115
θ_{891}	113	113	111	116	117	114	117	114
θ_{912}	124	126	126	129	125	130	133	132
ϕ_{1234}	−74	−60	−57	−83	−85	43	32	−1
ϕ_{2345}	−2	−1	1	2	−1	0	−2	4
ϕ_{3456}	86	103	104	97	92	−107	−91	−80
ϕ_{4567}	−102	−125	−123	−78	−83	44	39	56
ϕ_{5678}	111	72	43	76	96	32	83	72
ϕ_{6789}	−60	0	43	−128	−104	32	−47	−72
ϕ_{7891}	−52	−97	−123	59	4	−119	−73	−56
ϕ_{8912}	111	116	104	39	80	40	63	80
ϕ_{9123}	0	−3	1	1	−3	0	−5	−4

[a] Bond lengths: C=C, 1.34; C sp^2–C sp^2, 1.44–1.45; C–C sp^2, 1.47–1.48; C–C ,1.51–1.52 Å. [b] The standard strain energy in each geometry of a molecule is defined as the difference between the standard heats of formation (ΔH_f°) for that geometry and the most stable conformation of the molecule.[8]

imposing any symmetry constraints. The structures of the transition-state geometries were obtained using the optimized geometries of the equilibrium structures according to the procedure of Dewar *et al.*[6] (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.[7]

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