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Ab initio Study of Structural and Conformational Properties of Five- to Nine-Membered Cyclic 1,2,3-Trienes

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Summary. The structures and relative energies of fundamental conformations of cyclopenta-1,2,3-triene, cyclohexa-1,2,3-triene, cylohepta-1,2,3-triene, cycloocta-1,2,3-triene, and cyclonona-1,2,3-triene were calculated by the HF/6-31G* and MP2/6-31G*//HF/6-31G* methods. Only a C_{2v} symmetric planar conformation is available to cyclopenta-1,2,3-triene and cyclohexa-1,2,3-triene. The calculated energy barrier for ring inversion of the C_S symmetric puckerd conformation of cyclohepta-1,2,3-triene *via* the planar geometry is 62.2 kJ · mol^{-1}. The C_2 symmetric twist conformation of cycloocta-1,2,3-triene was calculated to be the most stable one. Conformational racemization of the twist form takes place *via* the C_S symmetric half-chair geometry, which is by 60.8 kJ · mol^{-1} less stable than the twist conformer. The C_S symmetric chair and unsymmetrical twist-boat conformations of cyclonona-1,2,3-triene were calculated to have similar energies; their interconversion takes place *via* an unsymmetrical low-energy (18.4 kJ · mol^{-1}) transition state. The twist (C_2) and boat (C_S) geometries of cyclonona-1,2,3-triene are higher in energy by 13.2 and 33.9 kJ · mol^{-1}, respectively. Ring inversion in chair and twist-boat conformations takes place *via* a twist form as intermediate and requires 33.6 kJ · mol^{-1}.

Keywords. Cyclic cumulenes; Strained molecules; Conformational analysis; Molecular modelling.

Introduction

Cyclic structures containing (*Z*) double bonds are stable in any ring size [1]. For cyclic allenes [2], small rings engender considerable deformation from a linear geometry in which π orthogonality is maintained. Thus, the smallest kinetically

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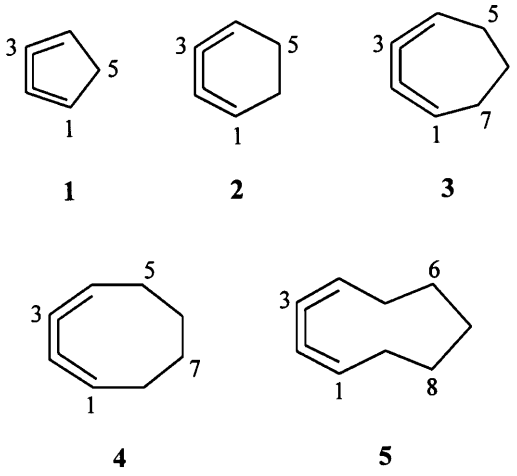


Scheme 1

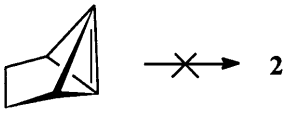
stable cyclic allene is cyclonona-1,2-diene [3]. In contrast to cyclic allenes, little is known about the structure of cyclic buta-1,2,3-trienes (Scheme 1). The smallest isolable cyclic butatriene reported to date is cyclonona-1,2,3-triene [4]. Elegant experiments have been described for generation and trapping of the smaller cyclic butatrienes [5–7]. One of the most fascinating aspects of these compounds is their smooth transition from shelf-stable compounds to reactive intermediates as ring size diminishes. This study was undertaken to investigate the structural optimization and conformational interconversion pathways of the strained cyclic butatrienes **1**–**5** 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 discussions below.

Cyclic butatrienes **1**–**5** comprise a fascinating and fundamental collection of molecules, for which very little data are presently available. The only quantitative estimates of strain energies and geometries in compounds **1**–**5** originates from a series of semiempirical (MNDO) calculations [4].

Results and Discussion

Cyclopenta-1,2,3-triene (**1**) *and cyclohexa-1,2,3-triene* (**2**)

Not surprisingly, there appear to be no reported examples of **1** and **2**; the synthesis of **2** from the pyramidalized olefin **6** has been attempted without success [8].



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Representative structural parameters for the five- and six-membered cyclic trienes **1** and **2** as calculated by AM1 and HF/6-31G* methods are shown in Table 1. Only a single C_{2v} symmetric planar conformation is available to **1** and **2**. The bond

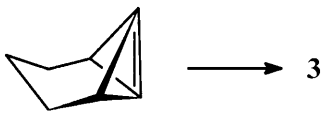
Table 1. Calculated heats of formation, total and zero-point vibrational energies (*Hartree*; zero-point vibrational energy is scaled by a factor of 0.9135 to eliminate known systematic errors in calculations), relative energy (including zero-point energy), and structural parameters for cyclopenta-1,2,3-triene (**1**) and cyclohexa-1,2,3-triene (**2**)

	1-Planar, C_{2v}		**2**-Planar, C_{2v}	
	AM1	*ab initio*	AM1	*ab initio*
$\Delta H_f^o/kJ \cdot mol^{-1}$	812.95		555.51	
HF/6-31G*//HF/6-31G*		− 191.409589		− 230.507186
MP2/6-31G*//HF/6-31G*		− 192.066578		− 231.279548
ZPE		0.071345		0.103789
$(H_{298}^o - H_0^o)/kJ \cdot mol^{-1}$		12.63		14.94
$(G_{298}^o - G_0^o)/kJ \cdot mol^{-1}$		− 67.48		− 71.87
$S_{298}^o/J \cdot mol^{-1} \cdot K^{-1}$		268.43		287.14
r_{12}/Å	1.336	1.326	1.312	1.302
r_{23}/Å	1.321	1.277	1.292	1.272
r_{34}/Å	1.336	1.326	1.312	1.302
r_{45}/Å	1.567	1.550	1.531	1.556
r_{51}/Å	1.567	1.550		
r_{56}/Å			1.543	1.573
r_{61}/Å			1.531	1.556
$\theta_{123}/°$	115.6	115.4	131.4	131.7
$\theta_{234}/°$	115.6	115.4	131.4	131.7
$\theta_{345}/°$	102.2	103.4	109.5	111.0
$\theta_{451}/°$	104.4	102.4		
$\theta_{512}/°$	102.2	103.4		
$\theta_{456}/°$			119.0	117.4
$\theta_{561}/°$			119.0	117.4
$\theta_{612}/°$			109.5	111.0

length of the $C_{sp^2} - C_{sp^3}$ carbons are somewhat larger than the normal value of about 1.51 Å [9]. The C=C=C and C–C=C arrangements are fairly bent in **1**, but less so in **2**. The θ_{456} and θ_{561} bond angles in **2** are 117.4°, which is higher than the normal value of 111° found in cyclohexane [10].

Cyclohepta-1,2,3-triene (**3**)

In 1981, *Sziemies* and co-workers have reported an elegant synthesis of **3** as a transient intermediate in the rearrangement of a bridged bicyclo[1.1.0]butene [5]. The cyclic butatriene **3** has been trapped with numerous cyclic and acyclic dienes as well as with dipolar species [6].



The results of semiempirical and *ab initio* calculations for the seven-membered cyclic triene **3** are shown in Table 2 and Fig. 1. Conceptually, **3** may be regarded to

Table 2. Calculated heats of formation, total and zero-point vibrational energies (*Hartree*; zero-point vibrational energy is scaled by a factor of 0.9135 to eliminate known systematic errors in calculations), relative energy (including zero-point energy), and structural parameters for various geometries of cyclohpta-1,2,3-triene (**3**)

	3-HC, C_S		**3**-Planar, C_{2v}	
	AM1	*ab initio*	AM1	*ab initio*
$\Delta H_f^o/kJ \cdot mol^{-1}$	416.39		459.15	
$\Delta\Delta H_f^o/kJ \cdot mol^{-1}$	0.0		42.76	
HF/6-31G*//HF/6-31G*		− 269.581945		− 269.561307
MP2/6-31G*//HF/6-31G*		− 270.478844		− 270.454772
ZPE		0.136043		0.135640
$E_{rel}^a/kJ \cdot mol^{-1}$		0.0		53.22
$E_{rel}^b/kJ \cdot mol^{-1}$		0.0		62.23
$(H_{298}^o - H_0^o)/kJ \cdot mol^{-1}$		17.96		17.60
		(0.0)		(− 0.36)
$G_{298}^o - G_0^o)/kJ \cdot mol^{-1}$		− 77.17		− 76.89
		(0.0)		(0.28)
$S_{298}^o/J \cdot mol^{-1} \cdot K^{-1}$		320.45		318.32
		(0.0)		(− 2.13)
r_{12}/Å	1.311	1.305	1.304	1.301
r_{23}/Å	1.275	1.264	1.271	1.260
r_{34}/Å	1.311	1.305	1.304	1.301
r_{45}/Å	1.512	1.528	1.502	1.518
r_{56}/Å	1.531	1.557	1.543	1.591
r_{67}/Å	1.531	1.557	1.543	1.591
r_{71}/Å	1.512	1.528	1.502	1.518
$\theta_{123}/°$	144.4	144.8	145.6	145.8
$\theta_{234}/°$	144.4	144.8	145.6	145.8
$\theta_{345}/°$	111.2	112.5	113.2	114.7
$\theta_{456}/°$	115.1	115.7	124.3	123.3
$\theta_{567}/°$	120.4	122.1	133.8	132.4
$\theta_{671}/°$	115.1	115.7	124.3	123.3
$\theta_{712}/°$	111.2	112.5	113.2	114.7
$\phi_{1234}/°$	0.0	0.0	0.0	0.0
$\phi_{2345}/°$	0.2	2.7	0.0	0.0
$\phi_{3456}/°$	29.5	25.9	0.0	0.0
$\phi_{4567}/°$	− 74.5	− 68.5	0.0	0.0
$\phi_{5671}/°$	74.5	68.5	0.0	0.0
$\phi_{6712}/°$	− 29.5	− 25.9	0.0	0.0
$\phi_{7123}/°$	− 0.2	− 2.7	0.0	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

be constructed by inserting two sp-hybridized carbon atoms in the carbon–carbon double bond of (*Z*)-cyclopentene. Therefore, **3** can be either planar or puckered. The planar ring has maximal torsional strain because of its four pairs of eclipsing

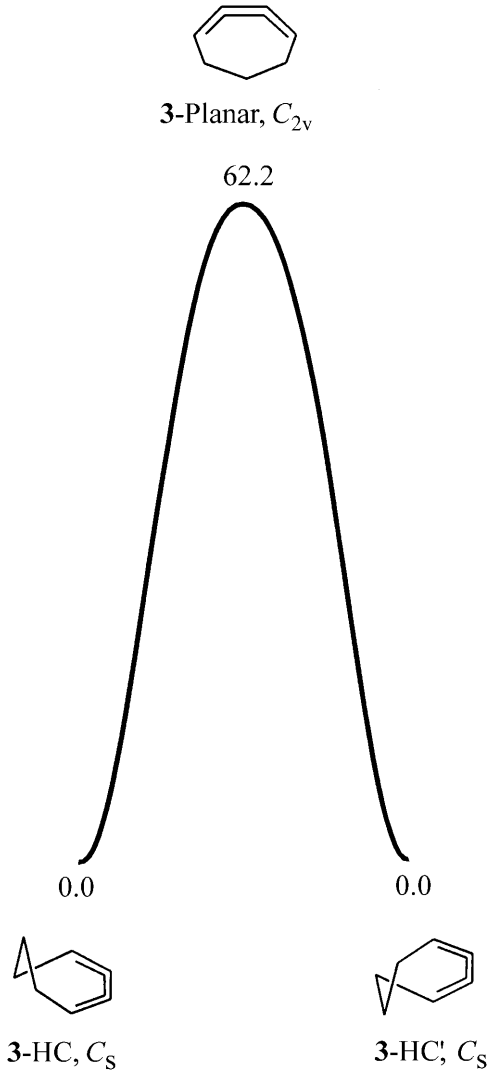


Fig. 1. Calculated MP2/6-31G*//HF/6-31G* strain energy profile ($kJ \cdot mol^{-1}$) for ring inversion of the half-chair conformation of cyclohepta-1,2,3-triene (**3**)

hydrogen atoms. The torsional strain can be reduced by puckering, and this is exactly what happens in **3**, which is therefore a wing-shaped molecule with a barrier to ring inversion of $62.2\,kJ \cdot mol^{-1}$ (see Fig. 1). This barrier is much larger than that reported for cyclopentene ($2.9\,kJ \cdot mol^{-1}$, [11]).

Selected geometrical data for puckered and planar structures of **3** are given in Table 2. The comparison of bond lengths shows fairly small differences. However, bond angle opening, particularly at the moving part of the inverting ring, *i.e.* θ_{456}, θ_{567}, and θ_{671}, is likely to be the least energy-expensive way of approaching a planar transition state.

Cyloocta-1,2,3-triene (**4**)

Although the lower and the higher homologues of **4** have been reported as transient intermediates and isolable species, nothing has been published on the synthesis of

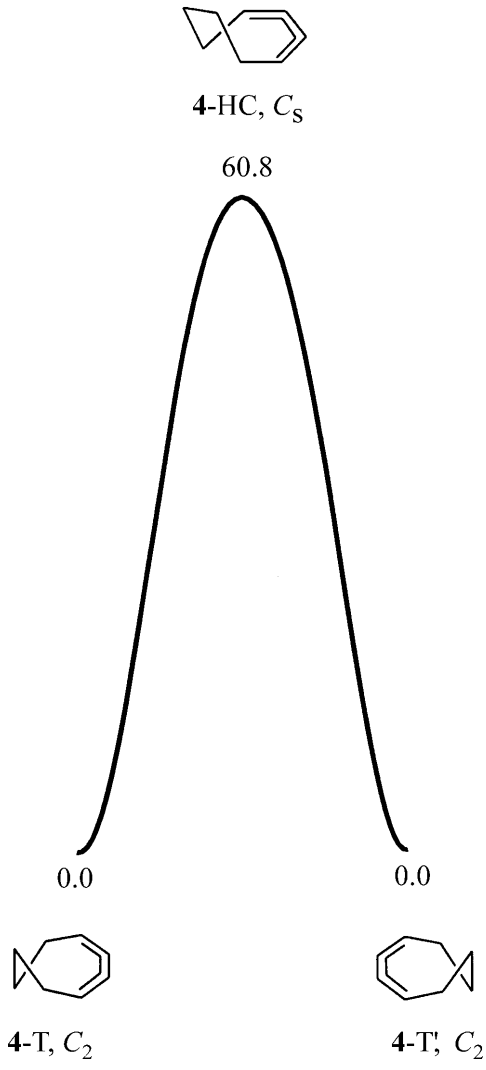


Fig. 2. Calculated MP2/6-31G*//HF/6-31G* strain energy profile ($kJ \cdot mol^{-1}$) for ring inversion of the twist conformation of cycloocta-1,2,3-triene (**4**)

Table 3. Calculated heats of formation, total and zero-point vibrational energies (*Hartree*; zero-point vibrational energy is scaled by a factor of 0.9135 to eliminate known systematic errors in calculations), relative energy (including zero-point energy), and structural parameters for various geometries of cycloocta-1,2,3-triene (**4**)

	4-T, C_2		**4**-HC, C_S	
	AM1	*ab initio*	AM1	*ab initio*
$\Delta H_f^o/kJ \cdot mol^{-1}$	306.10		366.60	
$\Delta\Delta H_f^o/kJ \cdot mol^{-1}$	0.0		60.50	
HF/6-31G*//HF/6-31G*		− 308.642379		− 308.618435
MP2/6-31G*//HF/6-31G*		− 309.666435		− 309.642868

(*continued*)

Table 3 (*continued*)

	4-T, C_2		**4**-HC, C_S	
	AM1	*ab initio*	AM1	*ab initio*
ZPE		0.167439		0.166973
E_{rel}^{a}		0.0		61.75
E_{rel}^{b}		0.0		60.76
$(H_{298}^{o} - H_{0}^{o})/kJ \cdot mol^{-1}$		20.38		19.55
		(0.0)		(−0.83)
$(G_{298}^{o} - G_{0}^{o})/kJ \cdot mol^{-1}$		−78.80		−80.26
		(0.0)		(−1.46)
$S_{298}^{o}/J \cdot mol^{-1} \cdot K^{-1}$		330.78		334.41
		(0.0)		(3.63)
r_{12}/Å	1.309	1.303	1.309	1.302
r_{23}/Å	1.266	1.262	1.269	1.262
r_{34}/Å	1.309	1.303	1.309	1.302
r_{45}/Å	1.501	1.522	1.508	1.529
r_{56}/Å	1.527	1.545	1.521	1.548
r_{67}/Å	1.524	1.558	1.530	1.581
r_{78}/Å	1.527	1.545	1.521	1.548
r_{81}/Å	1.501	1.522	1.508	1.529
θ_{123}/°	156.5	156.5	151.4	152.8
θ_{234}/°	156.5	156.5	151.4	152.8
θ_{345}/°	115.0	116.3	112.5	114.3
θ_{456}/°	113.8	114.8	113.9	115.7
θ_{567}/°	115.5	117.6	124.4	126.5
θ_{678}/°	115.5	117.6	124.4	126.5
θ_{781}/°	113.8	114.8	113.9	115.7
θ_{812}/°	115.0	116.3	112.5	114.3
ϕ_{1234}/°	2.2	4.9	0.0	0.0
ϕ_{2345}/°	−0.6	−1.0	−3.2	2.8
ϕ_{3456}/°	20.0	17.8	56.5	49.2
ϕ_{4567}/°	−76.0	−72.0	−80.6	−73.4
ϕ_{5678}/°	124.2	118.4	0.0	0.0
ϕ_{6781}/°	−76.0	−72.0	80.6	73.4
ϕ_{7812}/°	20.0	17.8	−56.5	−49.2
ϕ_{8123}/°	−0.6	−1.0	3.2	−2.8

[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

4. Compound **4** can be formally obtained by inserting two sp-hybridized carbon atoms in the carbon–carbon double bond of (*Z*)-cyclohexene. Therefore, a chiral C_2 symmetric energy minimum conformation, such as twist the form **4**-T, and a C_S-symmetric transition state (**4**-HC) can be envisaged for this cyclic triene (Fig. 2, Table 3). The energy barrier for the conformational enantiomerization of **4**-T is $60.8\,kJ \cdot mol^{-1}$, which is substantially higher than that reported for cyclohexene

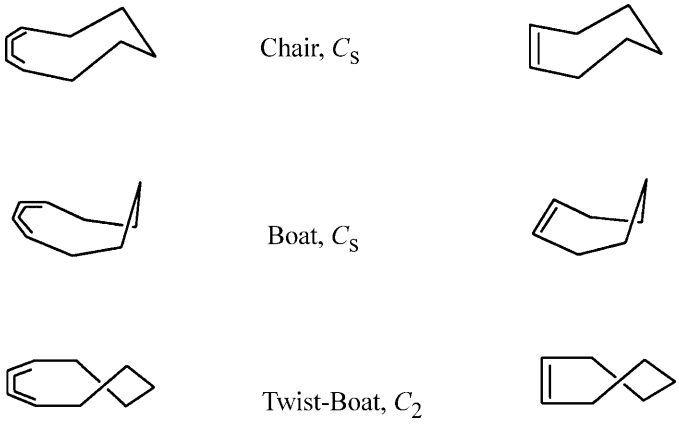


Fig. 3. Important conformations of cyclonona-1,2,3-triene (**5**) and (*Z*)-cycloheptene

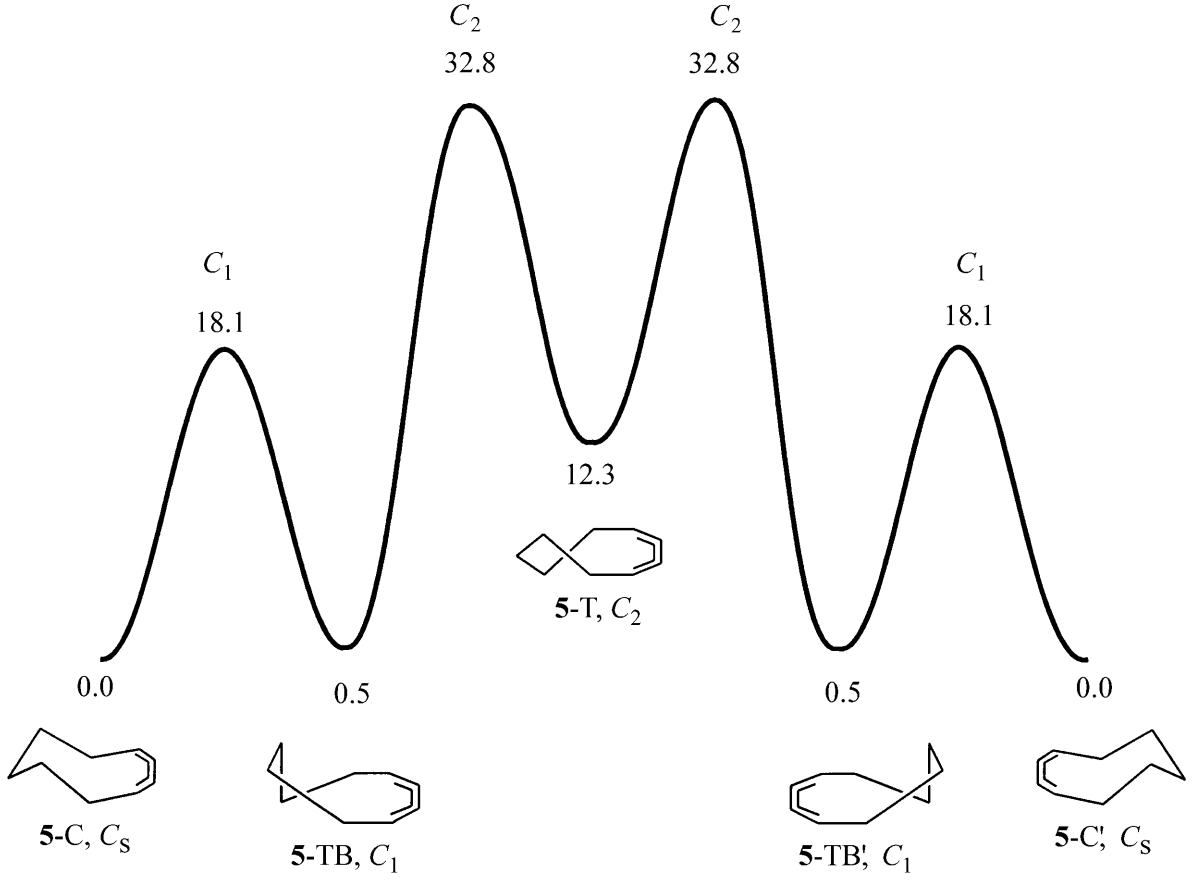


Fig. 4. Calculated MP2/6-31G*//HF/6-31G* strain energy profile ($kJ \cdot mol^{-1}$) for ring inversion of cyclonona-1,2,3-triene (**5**)

Table 4. Calculated heats of formation, total and zero-point vibrational energies (*Hartree*; zero-point vibrational energy is scaled by a factor of 0.9135 to eliminate known systematic errors in calculations), relative energy (including zero-point energy), and structural parameters of cyclonona-1,2,3-triene (**5**)

	5-Chair, C_S		**5**-TB, C_1		**5**-Twist, C_2		**5**-Boat, C_S		**5**-(Chair $\rightleftharpoons$ TB), C_1		**5**-(TB $\rightleftharpoons$ Twist), C_1	
	AM1	*ab initio*	AM1	*ab initio*	AM1	*ab initio*	AM1	*ab initio*	AM1	*ab initio*	AM1	*ab initio*
ΔH_f°/kJ · mol^{-1}	238.49		254.09		258.91		295.76		257.90		273.80	
$\Delta\Delta H_f^\circ$/kJ · mol^{-1}	0.00		15.60		20.42		57.27		19.41		35.31	
HF/6-31G*//HF/6-31G*		− 347.685773		− 347.683518		− 347.680051		− 347.668823		− 347.678533		− 347.672370
MP2/6-31G*//HF/6-31G*		− 348.839023		− 348.839041		− 348.834032		− 348.826152		− 348.832043		− 348.826245
ZPE		0.198600		0.198810		0.198240		0.198572		0.198482		0.198277
E_{rel}^a/kJ · mol^{-1}		0.00		6.42		14.16		44.43		18.73		34.42
E_{rel}^b/kJ · mol^{-1}		0.00		0.47		12.26		33.74		18.05		32.78
$(H_{298}^\circ - H_0^\circ)$/kJ · mol^{-1}		23.36		22.94		23.64		23.35		21.52		21.85
		(0.0)		(− 0.42)		(0.28)		(− 0.01)		(− 1.84)		(− 1.51)
$(G_{298}^\circ - G_0^\circ)$/kJ · mol^{-1}		− 84.95		− 83.80		− 83.59		− 84.55		− 82.73		− 83.19
		(0.0)		(1.15)		(1.36)		(0.40)		(2.22)		(1.76)
S_{298}°/J · mol^{-1} · K^{-1}		363.27		358.00		359.65		361.91		349.64		352.29
		(0.0)		(− 5.27)		(− 3.62)		(− 1.36)		(− 13.63)		(− 10.98)
r_{12}/Å	1.305	1.304	1.308	1.305	1.309	1.302	1.309	1.305	1.305	1.302	1.309	1.303
r_{23}/Å	1.263	1.263	1.265	1.263	1.265	1.262	1.266	1.263	1.263	1.262	1.264	1.262
r_{34}/Å	1.305	1.304	1.309	1.305	1.309	1.302	1.309	1.305	1.309	1.304	1.308	1.303
r_{45}/Å	1.493	1.518	1.497	1.521	1.499	1.522	1.496	1.526	1.496	1.520	1.496	1.523
r_{56}/Å	1.521	1.538	1.524	1.539	1.525	1.549	1.524	1.549	1.523	1.536	1.527	1.546
r_{67}/Å	1.523	1.556	1.518	1.547	1.517	1.542	1.519	1.547	1.520	1.548	1.517	1.569
r_{78}/Å	1.523	1.556	1.517	1.542	1.517	1.542	1.519	1.547	1.518	1.545	1.526	1.554
r_{89}/Å	1.521	1.538	1.521	1.548	1.525	1.549	1.524	1.549	1.525	1.568	1.520	1.542
r_{91}/Å	1.493	1.518	1.494	1.525	1.499	1.522	1.496	1.526	1.487	1.519	1.497	1.517
θ_{123}/°	166.3	165.7	164.6	163.8	161.4	162.2	158.6	156.7	167.7	168.9	163.6	162.9
θ_{234}/°	166.3	165.7	161.4	161.3	161.4	162.2	158.6	156.7	162.2	160.6	161.7	162.1
θ_{345}/°	118.9	120.5	117.3	119.0	161.5	118.3	115.8	115.0	117.3	118.5	116.9	118.6
θ_{456}/°	114.3	115.2	113.8	114.4	113.4	114.9	117.1	115.1	113.2	113.6	114.0	115.6
θ_{567}/°	114.8	117.1	113.3	114.3	116.3	119.0	121.2	121.2	113.9	115.7	115.0	116.5

(*continued*)

Table 4 (*continued*)

	5-Chair, C_S		**5**-TB, C_1		**5**-Twist, C_2		**5**-Boat, C_S		**5**-(Chair ⇌ TB), C_1		**5**-(TB ⇌ Twist), C_1	
	AM1	*ab initio*	AM1	*ab initio*	AM1	*ab initio*	AM1	*ab initio*	AM1	*ab initio*	AM1	*ab initio*
$\theta_{678}/^\circ$	113.5	114.5	115.6	117.1	117.7	122.6	118.2	121.9	114.0	114.8	122.0	123.4
$\theta_{789}/^\circ$	114.8	117.1	119.4	119.5	116.3	119.0	121.2	121.2	122.0	122.0	122.3	122.7
$\theta_{891}/^\circ$	114.3	115.2	117.6	117.3	113.4	114.9	117.1	115.1	121.9	121.8	113.5	113.8
$\theta_{912}/^\circ$	118.9	120.5	118.3	118.6	116.5	118.3	115.8	115.0	121.4	123.8	117.2	117.9
$\phi_{1234}/^\circ$	0.0	− 0.1	1.8	5.2	− 5.3	− 13.3	0.0	0.0	− 4.3	− 9.4	− 2.6	− 9.4
$\phi_{2345}/^\circ$	− 5.9	− 20.5	− 9.2	− 13.8	1.5	2.8	21.5	14.5	− 8.8	− 10.7	− 0.8	3.0
$\phi_{3456}/^\circ$	− 26.0	− 18.0	− 3.6	− 0.4	− 33.4	− 28.3	− 63.0	− 71.9	− 10.2	− 7.3	− 13.1	− 6.0
$\phi_{4567}/^\circ$	71.4	66.2	69.2	66.4	106.5	97.5	31.7	47.1	71.7	71.0	91.5	80.0
$\phi_{5678}/^\circ$	− 130.3	− 126.7	− 149.7	− 145.0	− 70.2	− 67.2	91.9	75.5	− 150.3	− 147.7	− 112.2	− 111.8
$\phi_{6789}/^\circ$	130.3	126.7	59.0	54.9	− 70.2	− 67.2	− 91.9	− 75.5	85.1	85.6	− 15.9	− 9.1
$\phi_{7891}/^\circ$	− 71.4	− 66.2	43.3	47.4	106.5	97.5	− 31.7	− 47.1	5.0	− 2.6	87.8	84.3
$\phi_{8912}/^\circ$	26.0	18.0	− 54.3	− 56.6	− 33.4	− 28.3	63.0	71.9	− 28.6	− 21.4	− 48.3	− 46.7
$\phi_{9123}/^\circ$	5.9	20.5	14.1	13.8	1.5	2.8	− 21.5	− 14.5	18.6	20.1	0.9	− 1.1

[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

($22.3\,kJ \cdot mol^{-1}$, [12]). Representative geometrical data for the energy-minimum and transition-state geometries of **4** are shown in Table 3. The internal angles are fairly expanded in **4**-HC.

Cyclonona-1,2,3-triene (**5**)

Compound **5**, with a butatrienic chromophore, is generally considered as the smallest stable cyclic butatriene [5]. Conceptually, **5** may be regarded to be constructed by inserting two sp-hybridized carbon atoms in the carbon–carbon double bond of (*Z*)-cycloheptene [13]; therefore, it can potentially exist in chair- or boat-family conformations (Fig. 3). **5** is a fascinating molecule, for which little data are presently available.

The results of semiempirical and *ab initio* calculations for structure optimization and conformational interconversion pathways of **5** are shown in Fig. 4 and Table 4. Six geometries (four energy minima and two transition states) were found to be important for the description of the conformational properties of **5**. The most stable conformation of **5** is the C_S-symmetric chair (**5**-Chair) form. The calculated energy for the second energy-minimum conformation, the unsymmetrical twist-boat (**5**-TB), is only $0.5\,kJ \cdot mol^{-1}$ above that of **5**-Chair. These conformations are important because they are expected to be equally populated at ambient temperature. Interconversion of **5**-Chair and **5**-TB conformations is possible by limited pseudorotation [14] and requires $18.1\,kJ \cdot mol^{-1}$. As the C_2 symmetric twist form is by $12.3\,kJ \cdot mol^{-1}$ higher than the **5**-Chair conformation, it is not expected to be significantly populated at room temperature. The calculated energy for the C_S symmetric boat form (**5**-B) is by $33.7\,kJ \cdot mol^{-1}$ higher than that of the **5**-Chair conformation.

The simplest conformational process for ring inversion between **5**-Chair and the structure with the lowest barrier ($32.8\,kJ \cdot mol^{-1}$) takes place *via* the C_2 symmetric **5**-T as intermediate (Fig. 4). If this process is fast, the time-averaged symmetry of **5**-Chair becomes C_{2v}, which is the maximum symmetry allowed by the constitution of **5**.

Selected data for various geometries of **5** are given in Table 4. A comparison of bond lengths showed fairly small differences; however, the bond angles are expanded in transition-state geometries. The calculated thermodynamic parameters (H^o, S^o, G^o) [15, 16] for various geometries of compounds **1**–**5** at 0 and 298 K are shown in Tables 1–4. The entropy differences for transition state geometries of **5** are considered to be substantial.

Conclusions

The present calculations indicate that only a rigid C_{2v} symmetric planar geometry is available to **1** and **2**. The energy barrier for ring inversion of the puckered conformation of **3** *via* the planar geometry is $62.2\,kJ \cdot mol^{-1}$. Conformational racemization of the chiral twist form of **4** requires $60.8\,kJ \cdot mol^{-1}$. Compound **5** can exist as a mixture of chair (C_S) and twist-boat (C_1) conformations. Ring inversion in chair and twist-boat conformations takes place *via* a C_2-symmetric

intermediate. It would be valuable, of course, to have direct structural data on **1**–**5** for comparison with the results of the *ab initio* calculations.

Methods

Semiempirical calculations were carried out using the AM1 method [17, 18] with the MOPAC 6.0 program package [19, 20]. Energy minimum geometries were located by minimizing the energy with respect to all geometrical coordinates and without imposing any symmetry constraints. The geometries of the transition states for conformational interconversion of the equilibrium structures were obtained using the optimized geometries of the equilibrium structures according to procedure of *Dewar et al.* [21] (Keyword SADDLE).

The AM1 results were used as input for the *ab initio* molecular orbital calculations which were carried out using the GAUSSIAN 98 [22] program. Geometries for all structures were fully optimized by means of analytical energy gradients by the *Berny* optimizer with no geometrical constraints [23]. Restricted *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 procedures [24]. Single point energy calculations at the MP2/6-31G*//HF/6-31G* level were used to evaluate the electron correlation effect in the energies and the 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 [25] and used to compute the zero-point vibrational energies.

Theoretical calculations are not expected, in principle, to reproduce the experimental values quantitatively [26]. Nevertheless, it is possible to carry out *ab initio* calculations at the *Hartree-Fock* level from which many properties and structural features can be obtained with an accuracy that is competitive with experiment [27, 28]. 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.

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