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Ab Initio Study of Conformational Properties of (*Z*,*Z*)-, (*E*,*Z*)-, and (*E*,*E*)-Cyclonona-1,5-dienes

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Summary. *Ab initio* calculations at the HF/6-31G* level of theory for geometry optimization and MP2/6-31G*//HF/6-31G* for a single point total energy calculation are reported for the important energy-minimum conformations and transition-state geometries of (*Z*,*Z*)-, (*E*,*Z*)-, and (*E*,*E*)-cyclonona-1,5-dienes. The C_2 symmetric chair conformation of (*Z*,*Z*)-cyclonona-1,5-diene is calculated to be the most stable form; the calculated energy barrier for ring inversion of the chair conformation *via* the C_s symmetric boat-chair geometry is 58.3 kJ mol^{-1}. Interconversion between chair and twist-boat-chair (C_1) conformations takes place *via* the twist (C_1) as intermediate. The unsymmetrical twist conformation of (*E*,*Z*)-cyclonona-1,5-diene is the most stable form. Ring inversion of this conformation takes place *via* the unsymmetrical chair and boat-chair geometries. The calculated strain energy for this process is 63.5 kJ mol^{-1}. The interconversion between twist and the boat-chair conformations can take place by swiveling of the *trans* double bond with respect to the *cis* double bond and requires 115.6 kJ mol^{-1}. The most stable conformation of (*E*,*E*)-cyclonona-1,5-diene is the C_2 symmetric twist-boat conformation of the crossed family, which is 5.3 kJ mol^{-1} more stable than the C_s symmetric chair–chair geometry of the parallel family. Interconversion of the crossed and parallel families can take place by swiveling of one of the double bonds and requires 142.0 kJ mol^{-1}.

Keywords. Medium rings; Stereochemistry; Conformational analysis; *Ab initio* calculations; Molecular modeling.

Introduction

The medium rings (C_8–C_{11}) are particularly disfavored because of the adverse entropic term, the *Bayer* strain, and the *Pitzer* strain, as well as transannular interactions. Therefore, angle deformation will occur and the conformational pictures of such rings with normal bond angles suggested by mechanical molecular models are

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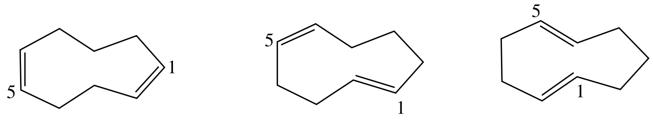


1 **2** **3**

Scheme 1

incorrect [1]. Cyclonona-1,5-diene as a medium-ring diene has three structural isomers, namely, (*Z*,*Z*)-, (*Z*,*E*)-, and (*E*,*E*)-cyclonona-1,5-diene (**1**–**3**) (Scheme 1).

We here report the results of *ab initio* calculations for structural optimization and conformational interconversion pathways of the strained nine-membered ring dienes **1**–**3** 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 discussion below.

Results and Discussion

*(Z,Z)-Cyclonona-1,5-diene (**1**)*

(*Z*,*Z*)-Cyclonona-1,5-diene (**1**) is the most stable member of the isomeric cyclononadienes and is readily available [2–9]. Several uses of this compound in organic and organometallic synthesis have been reported [10]. The conformational properties of **1** have been studied by low-temperature NMR measurements [11] and molecular mechanics calculations [11–13]. Dynamic NMR spectroscopy has indicated that the compound exists in solution as a mixture of chair and boat-chair conformations. The free-energy barrier for interconversion of chair with itself has been determined to be 43.1 kJ mol^{-1}.

The results of *ab initio* calculations for structure optimization and conformational interconversion pathways of **1** are shown in Fig. 1 and Table 1. Six geome-

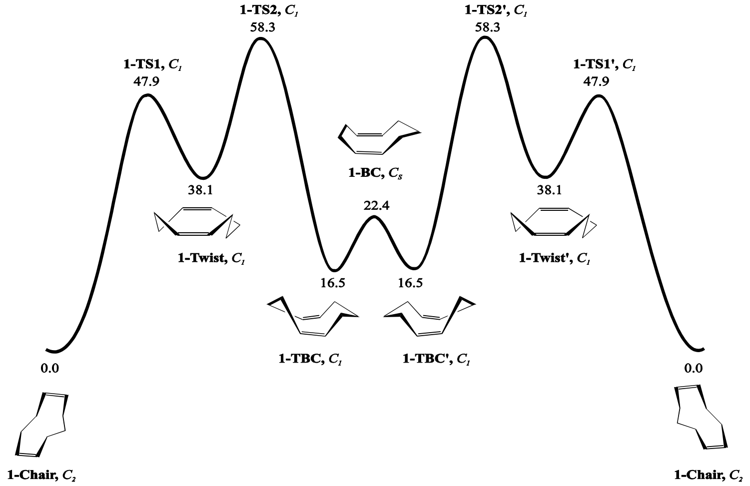


Fig. 1. Calculated MP2/6-31G*//HF/6-31G* strain energy (kJ mol^{-1}) profile for conformational interconversion of various geometries of (*Z*,*Z*)-cyclonona-1,5-diene (**1**)

Table 1. Calculated 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) and relative energy (including zero-point energy, kJ mol^{-1}) for various conformations of (*Z*,*Z*)-cyclonona-1,5-diene (**1**)

Structure	**1-Chair**, C_2	**1-TS1**, C_1	**1-Twist**, C_1	**1-TS2**, C_1	**1-TBC**, C_1	**1-BC**, C_S	**1-Twist**, C_2	**1-B**, C_1	**1-BB**, C_S
HF/6-31G*//HF/6-31G*	−348.922474	−348.904025	−348.908193	−348.900839	−348.916721	−348.913335	−348.912772	−348.907257	−348.904245
MP2/6-31G*//HF/6-31G*	−350.080233	−350.061563	−350.065664	−350.057538	−350.073752	−350.071224	−350.070283	−350.064758	−350.062099
ZPE	0.224978	0.224513	0.224929	0.224458	0.224775	0.224468	0.225114	0.224933	0.224412
$E_{rel}{}^{a}$/kJ mol^{-1}	0.0	47.32	37.37	55.55	14.61	22.76	25.80	39.84	46.49
$E_{rel}{}^{b}$/kJ mol^{-1}	0.0	47.90	38.13	58.34	16.53	22.43	26.45	40.52	46.20
$H^\circ_{298} - H^\circ_0$/kJ mol^{-1}	23.10	22.24	23.65	22.15	23.43	21.54	23.22	23.66	24.45
	0.0	−0.86	0.55	−0.95	0.33	−1.56	0.12	0.56	1.35
$G^\circ_{298} - G^\circ_0$/kJ mol^{-1}	−82.55	−84.29	−85.37	−83.90	−84.85	−82.71	−82.68	−85.18	−90.78
	0.0	−1.74	−2.82	−1.35	−2.30	−0.16	−0.13	−2.63	−8.22
S°_{298}/J mol^{-1} K^{-1}	354.34	357.31	365.64	355.68	363.17	349.66	355.22	365.05	386.48
	0.0	2.97	11.30	1.34	8.83	−4.68	0.88	10.71	32.14
$H^\circ_{213} - H^\circ_0$/kJ mol^{-1}	12.96	12.64	13.39	12.51	13.22	12.02	13.03	13.40	14.12
	0.0	−0.32	0.43	−0.45	0.26	−0.94	0.07	0.44	1.16
$G^\circ_{213} - G^\circ_0$/kJ mol^{-1}	−54.12	−55.52	−55.99	−55.27	−55.68	−54.57	−52.13	−55.80	−59.58
	0.0	−1.40	−1.87	−1.15	−1.56	−0.45	1.99	−1.68	−5.47
S°_{213}/J mol^{-1} K^{-1}	341.68	319.69	325.52	317.98	323.21	312.24	315.31	324.88	346.02
	0.0	−5.01	−10.84	−3.30	−8.23	−2.26	−0.63	−10.20	31.34

[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

tries (three energy minima and three transition states) were found to be important in a description of the conformational properties of **1**. The most stable conformation of **1** is the C_2 symmetric **1-C** form (see Fig. 1 and Tables 1 and 2), in agree-

Table 2. Structural parameters and experimental values (in parentheses) for various conformations of (*Z*,*Z*)-cyclonona-1,5-diene (**1**)

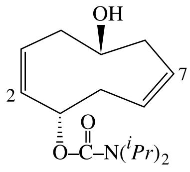
Structure	**1-Chair**, C_2	**1-TS1**, C_1	**1-Twist**, C_1	**1-TS2**, C_1
r_{12}/Å	1.323 (1.313)	1.321	1.325	1.321
r_{23}/Å	1.514 (1.488)	1.505	1.513	1.506
r_{34}/Å	1.555 (1.540)	1.557	1.562	1.554
r_{45}/Å	1.514 (1.550)	1.516	1.517	1.515
r_{56}/Å	1.323 (1.280)	1.322	1.322	1.324
r_{67}/Å	1.510 (1.474)	1.512	1.508	1.508
r_{78}/Å	1.540 (1.431)	1.554	1.551	1.551
r_{89}/Å	1.540 (1.522)	1.564	1.533	1.556
r_{91}/Å	1.510 (1.446)	1.510	1.519	1.516
θ_{123}/°	128.2 (130.7)	127.7	131.2	124.2
θ_{234}/°	113.9 (113.6)	113.1	114.4	112.8
θ_{345}/°	113.9 (113.8)	115.2	114.8	114.7
θ_{456}/°	128.2 (129.6)	128.2	126.1	126.3
θ_{567}/°	127.4 (125.4)	128.0	124.8	132.4
θ_{678}/°	112.5 (113.2)	112.7	113.3	120.1
θ_{789}/°	114.0 (115.3)	117.9	113.5	116.4
θ_{891}/°	112.5 (111.3)	118.7	118.5	116.1
θ_{912}/°	127.4 (131.0)	127.8	132.4	125.5
ϕ_{1234}/°	83.1 (71.4)	106.2	97.0	91.0
ϕ_{2345}/°	−95.1 (−88.6)	−104.3	−113.2	−131.9
ϕ_{3456}/°	83.1 (89.3)	58.6	63.5	52.3
ϕ_{4567}/°	−1.5 (−3.4)	−0.65	−0.9	−0.12
ϕ_{5678}/°	−102.2 (−101.8)	92.0	−86.9	32.8
ϕ_{6789}/°	60.3 (53.6)	114.9	136.9	−109.8
ϕ_{7891}/°	60.3 (66.1)	−9.7	−55.0	113.0
ϕ_{8912}/°	−102.2 (−102.6)	−62.2	−22.4	−63.7
ϕ_{9123}/°	−1.5 (−2.4)	1.8	1.5	91.0

1-TBC, C_1	**1-BC**, C_S	**1-Twist**, C_2	**1-B**, C_1	**1-BB**, C_S
1.321 (1.352)	1.321	1.323	1.321	1.321
1.516 (1.437)	1.508	1.515	1.515	1.510
1.546 (1.669)	1.569	1.540	1.543	1.568
1.504 (1.539)	1.508	1.515	1.508	1.510
1.321 (1.457)	1.321	1.320	1.323	1.321
1.513 (1.565)	1.508	1.510	1.513	1.515
1.540 (1.449)	1.541	1.537	1.536	1.537
1.544 (1.630)	1.541	1.537	1.560	1.537
1.510 (1.550)	1.508	1.510	1.511	1.515
129.8 (126.1)	126.5	132.8	127.6	128.1
117.0 (122.2)	116.1	121.6	115.7	116.7
112.9 (102.7)	116.1	121.6	113.1	116.7
126.2 (124.1)	126.5	132.8	129.3	128.1
127.0 (129.5)	127.3	129.6	133.1	129.9
116.0 (112.3)	114.9	112.4	121.8	119.6

(*continued*)

Table 2 (*continued*)

1-TBC, C_1	**1-BC**, C_S	**1-Twist**, C_2	**1-B**, C_1	**1-BB**, C_S
115.6 (113.8)	115.2	113.0	118.6	116.3
115.1 (111.2)	114.9	112.4	116.6	119.6
129.7 (135.4)	127.3	129.6	126.8	129.9
43.4 (32.0)	81.8	−24.1	45.5	79.8
45.8 (51.0)	0.0	84.4	54.5	0.0
−106.9 (−108.0)	−81.8	−24.1	−89.4	−79.8
−3.3 (−1.0)	−0.68	−1.9	0.94	−1.0
86.1 (87.0)	99.3	−83.2	−90.3	36.0
−70.6 (−74.0)	−75.9	63.8	2.5	66.5
87.0 (91.0)	75.9	63.8	73.1	66.5
−104.6 (−112.0)	−99.3	−83.2	−13.8	36.0
2.9 (12.0)	0.68	−1.9	1.7	−1.0



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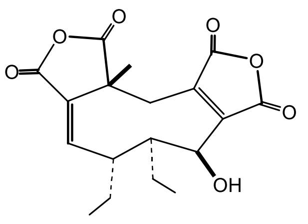
Scheme 2

ment with previous studies [11–13]. This conformation is similar to that observed in the crystals of carbamic acid bis(*i*-propyl)-(1*R*,2*Z*,5*R*,7*Z*)-5-hydroxy-2,7-cyclononadien-1-yl ester (**4**) [9] (see Scheme 2 and Table 1). It can be seen from Table 2 that the differences between dihedral angles of **4** and **1-C** are a result of steric hindrance of the bulky substituent present in **4**.

The second energy-minimum conformation of **1** is the unsymmetrical twist-boat-chair (**1-TBC**), which is 16.5 kJ mol^{-1} above **1-C**. This conformation is similar to those observed in the X-ray structures of glauconic acid **5** [14] and byssochlamic acid derivative **6** [15] (Scheme 3), which are in good agreement with **1-TBC** conformation, despite different substitution patterns (see Scheme 3 and Table 2).

The chair conformation is 38.1 kJ mol^{-1} more stable than the **1-twist** form and the transition state linking **1-C** and **1-twist** is calculated to be higher in energy by 47.9 kJ mol^{-1}. The degenerate interconversion of **1-C** with itself takes place *via* the C_s symmetric boat-chair (**1-BC**) as transition state, as well as the unsymmetrical geometries, such as twist-boat-chair (**1-TBC**) and twist (**1-twist**) as intermediates. The calculated strain energy barrier for this process is 58.3 kJ mol^{-1}, which is in poor agreement with the experimentally determined barrier of 43.1 kJ mol^{-1} [11]. When this interconversion is fast, the time averaged symmetry of **1** will become C_{2V}, the highest symmetry allowed by the chemical structure of **1**.

In addition to the conformations discussed above, we have also found three additional energy minimum geometries (Scheme 4), which are 26–46 kJ mol^{-1} less



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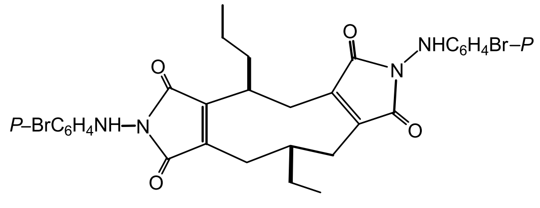

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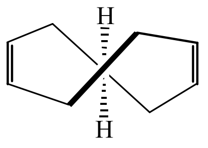
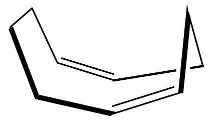
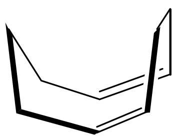
Scheme 3



1-Twist, C_2



1-B, C_1



1-BB, C_s

Scheme 4

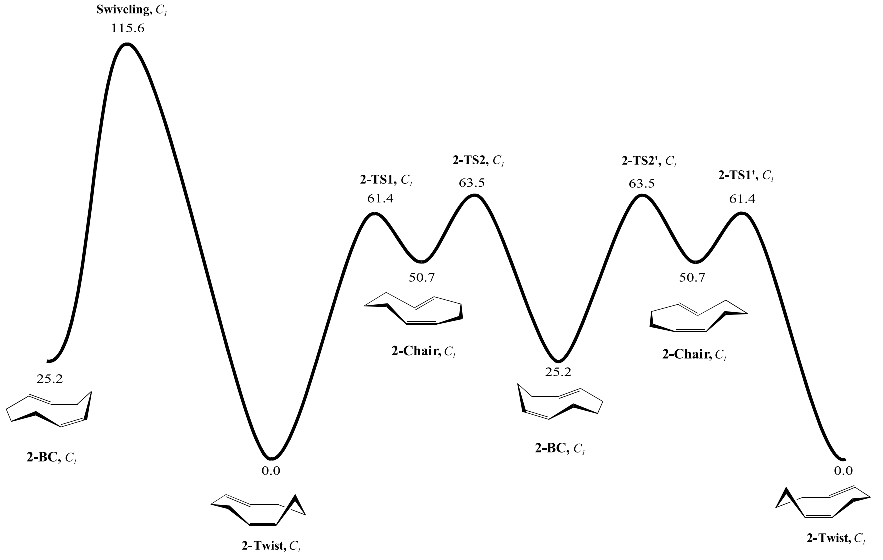


Fig. 2. Calculated MP2/6-31G*//HF/6-31G* strain energy (kJ mol^{-1}) profile for conformational interconversion of various geometries of (*Z*,*E*)-cyclonona-1,5-diene (**2**)

Table 3. Calculated 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, kJ mol^{-1}), experimental values (in parentheses), and structural parameters for various conformations of (Z,*E*)-cyclonona-1,5-diene (**2**)

Structure	**2-Twist**, C_1	**2-TS1**, C_1	**2-Chair**, C_1
HF/6-31G*//HF/6-31G*	−348.913503	−348.890872	−348.894569
MP2/6-31G*//HF/6-31G*	−350.074819	−350.051172	−350.055582
ZPE	0.224582	0.224303	0.224672
$E_{rel}{}^{a}$/kJ mol^{-1}	0.0	58.75	49.93
$E_{rel}{}^{b}$/kJ mol^{-1}	0.0	61.42	50.72
$H^\circ_{298} - H^\circ_0$/kJ mol^{-1}	22.98	22.09	23.45
	0.0	−0.88	0.47
$G^\circ_{298} - G^\circ_0$/kJ mol^{-1}	−83.89	−83.91	−84.87
	0.0	−0.02	−0.98
S°_{298}/J mol^{-1} K^{-1}	358.44	355.55	363.29
	0.0	−2.89	4.85
r_{12}/Å	1.319 (1.329)	1.318	1.318
r_{23}/Å	1.498 (1.505)	1.560	1.523
r_{34}/Å	1.556 (1.546)	1.525	1.533
r_{45}/Å	1.512 (1.493)	1.503	1.505
r_{56}/Å	1.326 (1.346)	1.329	1.330
r_{67}/Å	1.514 (1.521)	1.480	1.520
r_{78}/Å	1.549 (1.535)	1.549	1.553
r_{89}/Å	1.550 (1.531)	1.550	1.553
r_{91}/Å	1.498 (1.476)	1.498	1.496
θ_{123}/°	123.8 (121.7)	125.2	124.6
θ_{234}/°	106.9 (107.5)	115.5	113.6
θ_{345}/°	113.0 (111.7)	125.3	122.1
θ_{456}/°	129.6 (127.4)	139.9	138.5
θ_{567}/°	130.8 (129.4)	136.3	136.4
θ_{678}/°	113.7 (112.3)	113.7	114.9
θ_{789}/°	114.7 (113.7)	113.9	114.2
θ_{891}/°	109.0 (110.3)	108.7	106.8
θ_{912}/°	122.8 (121.5)	121.4	122.1
ϕ_{1234}/°	−88.5 (−87.3)	−52.0	−22.3
ϕ_{2345}/°	69.2 (72.2)	−7.3	−49.6
ϕ_{3456}/°	−82.8 (−77.7)	−18.5	18.2
ϕ_{4567}/°	−2.2 (−9.1)	−0.6	−4.6
ϕ_{5678}/°	112.9 (123.2)	99.7	90.7
ϕ_{6789}/°	−87.3 (−98.5)	−91.4	−93.6
ϕ_{7891}/°	46.0 (59.8)	41.8	41.9
ϕ_{8912}/°	−95.5 (−102.4)	−89.4	−92.5
ϕ_{9123}/°	150.1 (146.9)	156.0	148.8

(*continued*)

Table 3 (*continued*)

Structure	**2-TS2**, C_1	**2-BC**, C_1	**2-Swiveling**, C_1
HF/6-31G*//HF/6-31G*	−348.888615	−348.903973	−348.867321
MP2/6-31G*//HF/6-31G*	−350.050263	−350.064893	−350.031043
ZPE	0.224187	0.224206	0.224871
$E_{rel}{}^{a}$/kJ mol^{-1}	64.40	24.12	121.94
$E_{rel}{}^{b}$/kJ mol^{-1}	63.52	25.16	115.63
$H^\circ_{298} - H^\circ_0$/kJ mol^{-1}	21.77	23.93	21.70
	−1.20	0.95	−1.28
$G^\circ_{298} - G^\circ_0$/kJ mol^{-1}	−83.08	−85.92	−83.03
	0.81	−2.03	0.86
S°_{298}/J mol^{-1} K^{-1}	351.70	368.44	351.29
	−6.69	9.99	−7.19
r_{12}/Å	1.316	1.319	1.314
r_{23}/Å	1.505	1.509	1.533
r_{34}/Å	1.559	1.553	1.570
r_{45}/Å	1.510	1.507	1.530
r_{56}/Å	1.326	1.329	1.331
r_{67}/Å	1.530	1.519	1.534
r_{78}/Å	1.566	1.557	1.565
r_{89}/Å	1.546	1.553	1.557
r_{91}/Å	1.499	1.508	1.500
θ_{123}/°	121.5	122.8	114.2
θ_{234}/°	105.2	107.9	114.6
θ_{345}/°	111.1	112.9	119.6
θ_{456}/°	130.4	128.5	131.2
θ_{567}/°	134.0	130.6	131.6
θ_{678}/°	126.2	113.7	116.7
θ_{789}/°	121.0	115.5	115.0
θ_{891}/°	106.1	110.8	105.0
θ_{912}/°	123.8	123.8	146.9
ϕ_{1234}/°	−69.5	−66.9	22.0
ϕ_{2345}/°	−48.2	−50.7	−72.8
ϕ_{3456}/°	−95.9	88.1	95.1
ϕ_{4567}/°	11.1	2.1	−2.4
ϕ_{5678}/°	−64.5	−103.2	−94.8
ϕ_{6789}/°	−20.9	101.4	88.1
ϕ_{7891}/°	74.2	−34.4	−39.9
ϕ_{8912}/°	−101.2	−61.1	−173.6
ϕ_{9123}/°	141.1	151.9	174.2

[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

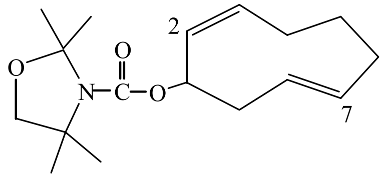
stable than the **1-C** conformation. Since these forms have high energies, thay are not expected to be significantly populated at ambient temperatures. The structural parameters and energies of these forms are given in Tables 1 and 2.

The calculated thermodynamic parameters (H°, S°, and G°) [16, 17] for various geometries of (*Z*,*Z*)-**1** at different temperatures are shown in Table 1. The free-energy barrier for the degenerate interconversion of **1-C** conformation with itself ($\Delta G^{\#} = 43.1\,\mathrm{kJ\,mol^{-1}}$) is lower than that ($\Delta G^{\#} = 58.3\,\mathrm{kJ\,mol^{-1}}$) calculated at 213 K (see Table 1).

Representative structural parameters for various geometries of **1** are given in Table 2. The agreement between the geometry of the **1-C** conformation with the observed X-ray data of **4** is generally good. The **1-C** and **1-TBC** geometries proposed from theoretical calculations and X-ray diffraction were tested by regression analysis. The correlation coefficient between the calculated values of dihedral angels of **1-C** and those experimentally determined for **4** was 0.9970. A correlation coefficent of 0.9971 was found between the calculated dihedral angles of **1-TBC** and those experimentally determined for **6**.

(E,Z)-Cyclonona-1,5-diene (2)

(*E*,*Z*)-Cyclonona-1,5-diene (**2**) has been prepared by several methods [18–24]. The results of *ab initio* calculations for **2** are shown in Fig. 2 and Table 3. Six geometries are found to be important for a description of the conformational features of **2**.



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Scheme 5

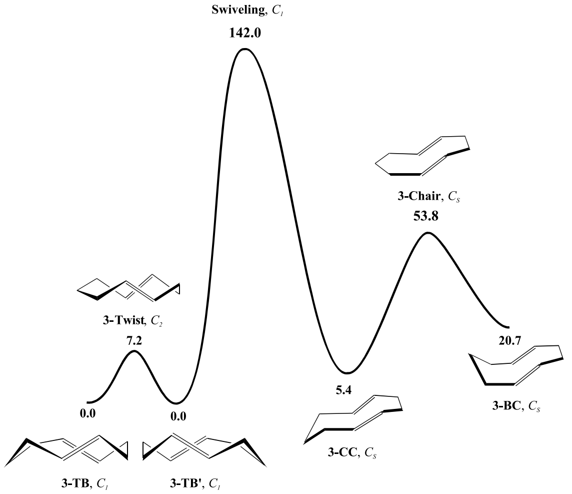

Fig. 3. Calculated MP2/6-31G*//HF/6-31G* strain energy ($\mathrm{kJ\,mol^{-1}}$) profile for conformational interconversion of various geometries of (*E*,*E*)-cyclonona-1,5-diene (**3**)

Table 4. Calculated 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, kJ mol^{-1}), and structural parameters for various conformations of (*E*,*E*)-cyclonona-1,5-diene (**3**)

Structure	**3-TB**, C_1	**3-Twist**, C_2	**3-CC**, C_S
HF/6-31G*//HF/6-31G*	−348.895115	−348.892173	−348.894077
MP2/6-31G*//HF/6-31G*	−350.060266	−350.057396	−350.058111
ZPE	0.22370	0.223545	0.223573
$E_{rel}{}^{a}$/kJ mol^{-1}	0.0	7.34	2.41
$E_{rel}{}^{b}$/kJ mol^{-1}	0.0	7.17	5.35
$H^\circ_{298} - H^\circ_0$/kJ mol^{-1}	23.69	21.95	24.00
	0.0	−1.74	0.31
$G^\circ_{298} - G^\circ_0$/kJ mol^{-1}	−85.02	−81.40	−86.05
	0.0	3.62	−1.03
S°_{298}/J mol^{-1} K^{-1}	364.67	346.64	369.11
	0.0	−18.03	4.44
r_{12}/Å	1.319	1.321	1.319
r_{23}/Å	1.507	1.504	1.506
r_{34}/Å	1.574	1.568	1.602
r_{45}/Å	1.504	1.504	1.506
r_{56}/Å	1.317	1.321	1.319
r_{67}/Å	1.510	1.504	1.507
r_{78}/Å	1.554	1.558	1.553
r_{89}/Å	1.562	1.558	1.553
r_{91}/Å	1.508	1.504	1.507
θ_{123}/°	120.7	122.6	123.5
θ_{234}/°	110.9	100.5	110.7
θ_{345}/°	108.5	100.5	110.7
θ_{456}/°	121.4	122.6	123.5
θ_{567}/°	126.8	124.6	124.6
θ_{678}/°	108.9	113.7	111.1
θ_{789}/°	118.8	120.8	117.9
θ_{891}/°	113.4	113.7	111.1
θ_{912}/°	128.1	124.6	124.6
ϕ_{1234}/°	81.6	85.6	82.3
ϕ_{2345}/°	−48.6	−53.5	0.0
ϕ_{3456}/°	88.7	85.6	−82.3
ϕ_{4567}/°	−145.7	−149.9	146.3
ϕ_{5678}/°	111.9	112.2	−107.5
ϕ_{6789}/°	−68.8	−25.9	61.6
ϕ_{7891}/°	31.4	−25.9	−61.6
ϕ_{8912}/°	80.1	112.2	107.5
ϕ_{9123}/°	−154.4	−149.9	−146.3

(*continued*)

Table 4 (*continued*)

Structure	**3-Chair**, C_S	**3-BC**, C_S	**3-Swiveling**, C_1
HF/6-31G*//HF/6-31G*	−348.875222	−348.886660	−348.839043
MP2/6-31G*//HF/6-31G*	−350.039406	−350.052012	−350.006464
ZPE	0.223299	0.223318	0.224049
$E_{rel}{}^{a}$/kJ mol^{-1}	51.18	21.27	148.04
$E_{rel}{}^{b}$/kJ mol^{-1}	53.80	20.70	142.00
$H^\circ_{298} - H^\circ_0$/kJ mol^{-1}	20.97	24.86	22.11
	−2.72	1.17	−1.58
$G^\circ_{298} - G^\circ_0$/kJ mol^{-1}	−82.75	−90.83	−83.30
	2.27	−5.81	1.72
S°_{298}/J mol^{-1} K^{-1}	347.89	388.02	353.55
	−16.78	23.35	−11.12
r_{12}/Å	1.319	1.320	1.318
r_{23}/Å	1.506	1.509	1.543
r_{34}/Å	1.602	1.658	1.548
r_{45}/Å	1.506	1.509	1.524
r_{56}/Å	1.319	1.320	1.327
r_{67}/Å	1.504	1.518	1.521
r_{78}/Å	1.582	1.546	1.585
r_{89}/Å	1.582	1.546	1.568
r_{91}/Å	1.504	1.518	1.506
θ_{123}/°	122.4	122.5	117.0
θ_{234}/°	112.0	111.8	120.8
θ_{345}/°	112.0	111.8	114.0
θ_{456}/°	122.4	122.5	123.0
θ_{567}/°	125.1	124.9	124.2
θ_{678}/°	116.8	112.4	111.9
θ_{789}/°	124.6	118.6	120.1
θ_{891}/°	116.8	112.4	106.7
θ_{912}/°	125.1	124.9	150.5
ϕ_{1234}/°	76.0	77.9	−19.0
ϕ_{2345}/°	0.0	0.0	47.8
ϕ_{3456}/°	−76.0	−77.9	−102.3
ϕ_{4567}/°	154.7	150.4	135.1
ϕ_{5678}/°	−88.5	−61.1	−101.0
ϕ_{6789}/°	−2.6	−53.8	69.7
ϕ_{7891}/°	2.6	53.8	−45.3
ϕ_{8912}/°	88.5	61.1	−169.0
ϕ_{9123}/°	−154.7	−150.4	−170.0

[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

Three of them correspond to energy minima and three to one-dimensional energy maxima. The lowest energy conformation of **2** is the unsymmetrical twist form (**2-twist**). This conformation is similar to that observed in the crystals of **7** [21, 25] (see Scheme 5 and Table 3).

The **2-twist** conformation is more stable than the unsymmetrical boat-chair (**2-BC**) form by 25.2 kJ mol^{-1}. The simplest conformational process is the degenerate interconversion of the **2-twist** conformation with itself *via* the unsymmetrical chair (**2-C**) and boat-chair (**2-BC**) geometries. The calculated strain-energy barrier for this process is 63.5 kJ mol^{-1}. A second (high-energy) process involves degenerate interconversion of the **2-twist** conformation with its mirror-image geometry, which involves swiveling of the *trans* double bond with respect to the *cis* double bond, and requires 115.6 kJ mol^{-1}.

(E,E)-Cyclonona-1,5-diene (3)

(*E,E*)-Cyclonona-1,5-diene (**3**) has been obtained only as a transient species [19]. It might be expected to exist as two families of conformational diastereoisomers with a relatively high-energy barrier between them. These two families are the parallel and crossed structures, which are consistent with our calculations. The results of *ab initio* calculations for structural optimization and conformational interconversion pathways for different geometries of **3** are given in Fig. 3 and Table 4. The C_2 symmetric twist-boat (**3-TB**), the plane symmetrical chair–chair (**3-CC**), and the boat-chair (**3-BC**) forms of **3** are found to be energy-minimum conformations. The **3-TB** conformer is the most stable form of the crossed family, which is calculated to be 5.4 kJ mol^{-1} more stable than the **3-CC** conformation of the parallel family.

The simplest conformational process, and the one with the lowest barrier, is the degenerate interconversion of the **3-BC** conformation with itself *via* the C_2 symmetric twist (**3-twist**) transition state. The calculated strain energy barrier for this process is calculated to be 7.2 kJ mol^{-1} and it is not expected to be observed by dynamic NMR experiments even at −180°C. This process, when fast, introduces a time averaged axis of symmetry. The second process is the interconversion of the parallel and crossed families of **3**, which can take place by swiveling of one of the double bonds with respect to the other double bond and requires 142.0 kJ mol^{-1}. If the processes just considered are fast, the time averaged symmetry of the **3-TB** conformation becomes C_{2V}, which is the maximum symmetry allowed by the structure of **3**.

Conclusions

The aim of this work was to calculate the structures and relative conformational energies for cyclonona-1,5-diene isomers **1**–**3**. According to these calculations, **1** is conformationally homogeneous. Ring inversion of the **1-C** conformation takes place *via* a C_S symmetric boat-chair (**1-BC**) geometry and requires 58.3 kJ mol^{-1}. The unsymmetrical twist conformation of **2** can undergo ring inversion *via* the unsymmetrical chair (**2-C**) and boat-chair (**2-BC**) intermediates. Compound **3** is predicted to exist as a mixture of parallel and crossed families. The minimum energy conformation of **1** is 13.3–46.6 kJ mol^{-1} more stable than the lowest energy forms of **2** and **3**.

Methods

Ab initio molecular orbital calculations were carried out using the GAUSSIAN 98 [26] program. Geometries for all structures were fully optimized by means of analytical energy gradients by *Berny* optimizer with no geometrical constraints [27, 28]. The restricted *Hartree-Fock* calculations with the split-valence 6-31G* basis set which includes a set of d-type polarization functions on all non-hydrogen atoms were used in these calculations [29]. Single point energy calculations at MP2/6-31G*//HF/6-31G* level were used to evaluate the 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. The frequencies were scaled by a factor of 0.9135 [30] and used to compute the zero-point vibrational energies.

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