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An *Ab Initio* Study of Conformational Properties of (*Z,Z*)-, (*E,Z*)- and (*E,E*)-Cycloocta-1,5-diene

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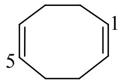
Ab initio calculations at HF/6-31G* level of theory for geometry optimization and MP2/6-31G*//HF/6-31G* for a single point total energy calculation are reported for the three geometrical isomers of cycloocta-l,5-diene **1-3**.

Keywords: Medium rings, Stereochemistry, Conformational analysis, Ab *initio* calculations

INTRODUCTION

Cycloocta-1,5-dienes **1-3** belong to a family of cyclic dienes, with diametric olefinic bonds connected by even polymethylene chains. Isomerization experiments indicate that the (*Z,Z*)-isomer **1** is certainly the predominant configuration of cycloocta-1,5-diene [1]. Although the conformational properties of (*Z,Z*)-cycloocta-1,5-diene **(1)** has been the subject of several experimental [2,3] and theoretical [4,5] investigations, the extent of our knowledge concerning the conformations of (*E,Z*)- and (*E,E*)-isomers **2** and **3** is meager. Recent *ab initio* molecular orbital studies on cycloocta-1,5-dienes **1-3** were limited to calculations of the energy-minimum conformations [6]. An electron diffraction study of **1** in the gas phase has shown the presence of a C$_2$ symmetric twist-boat form **(1-TB)** with possible minor amounts of the chair **(1-Chair, C$_{2h}$)** [2]. The detection of one spectral process in the ^{13}C NMR spectrum of **1**, and two processes in the ^{1}H NMR spectrum, is consistent with the twist-boat as the ground state conformation of the (*Z,Z*)-isomer [3]. The flexibility of the boat (C_{2v}), twist-boat (C_2), and twist (D_2) forms of **1**, in contrast to the rigidity of the chair form, has been discussed from a restricted geometric point of view [7].



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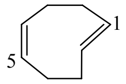

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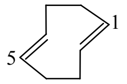

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This study was undertaken to investigate the structural optimization and conformational interconversion pathways of cycloocta-1,5-dienes **1-3** by comparing the geometries (HF/6-31G*) and conformational energies (MP2/6-31G*//HF/6-31G*). The results from MP2/6-31G*//HF/6-31G* calculations are used in the conformational energy discussions below.

CALCULATIONS

The *ab initio* molecular orbital calculations, were carried out using the GAUSSIAN 98 program [8]. Geometries for all structures were fully optimized by means of analytical energy gradients by Berny optimizer with no geometrical constraints [9,10]. 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 [11]. Single point energy calculations at MP2/6-31G*//HF/6-31G* level were used to evaluate the

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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, respectively. The frequencies were scaled by a factor of 0.9135 [12] and used to compute the zero-point vibrational energies.

RESULTS AND DISCUSSION

(Z,Z)-Cycloocta-1,5-diene (1)

The results of *ab initio* calculations for structure optimization and conformational interconversion pathways of (*Z,Z*)-cycloocta-1,5-diene **(1)** are shown in Fig. 1 and Tables 1 and 2. Three potential energy minima and four transition states were found important for a description of the conformational features of **1**. The C_2 symmetric twist-boat **(1-TB)** structure is calculated to be the most stable conformation of **1**, in agreement with the dynamic NMR studies [3] and calculations [4-6]. This conformation was also observed in the crystals of *syn*-3,7-dibromo-(*Z,Z*)-cycloocta-1,5-diene **(4)** [13]. The experimentally observed ring geometry of **4** is also given in Table 1. The C_{2h} symmetric chair form **(1-Chair)** corresponds to a true minimum with a calculated potential energy higher than **1-TB** by 8.1 kJ mol^{-1}. The energy increase is due to the unfavorable torsion angles of **1-Chair** as compared with **1-TB** around both types of carbon-carbon single bonds (see Table 1). The C_S symmetric half-chair **(1-HC)** conformation has slightly more calculated potential energy as the chair, and forms an intermediate in twist-boat/chair interconversion path.

As shown in Fig. 1, the twist-boat conformation can undergo three energetically different processes, namely, twist, boat, and chair, which lead to time-averaged symmetries of D_2, C_{2v} and C_{2h}, respectively. The **1-TB** structure contains four symmetry independent methylene protons. The twist or boat process, when fast, each lead to time-averaged structures with two groups of four CH_2 protons. A complete averaging of all CH_2 protons is effected by the chair process, or by a combination of the twist and boat processes.

Anet and Kozerski have observed two absorption coalescences in the dynamic ^{1}H NMR spectra of **1** kJmol^{-1} [3]. They interpreted these as originating from twist-

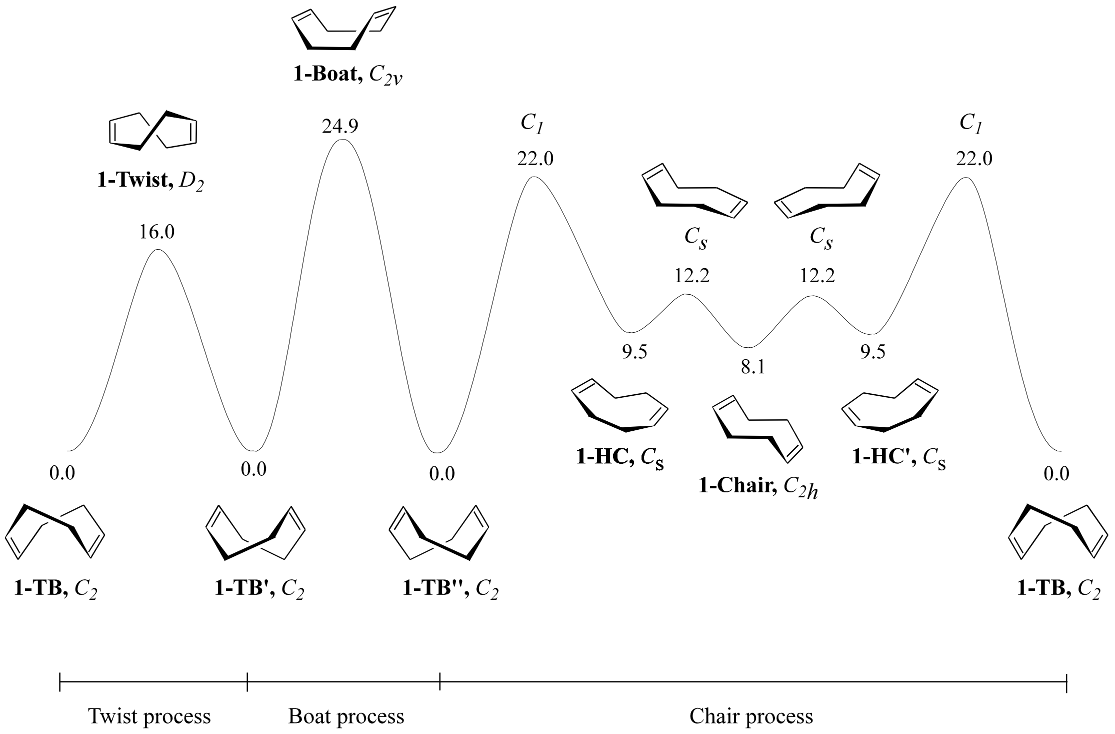

Fig. 1. Calculated MP2/6-31G*//HF/6-31G* strain energy (kJ mol^{-1}) profile for conformational interconversion of various geometries of **1**.

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), Relative Energy (Including Zero-Point Energy, kJ mol^{-1}) and Experimental Values (in Brackets) for Different Geometries of (*Z,Z*)-Cycloocta-1,5-diene **(1)**

Structure	**mm-TB,** C_2	**1-HC,** C_s	**1-Chair,** C_{2h}	**1-Twist,** D_2	**1-Boat,** C_{2v}	**(1-TB $\rightleftharpoons$ 1-HC),** C_1	**(1-HC $\rightleftharpoons$ 1-Chair),** C_s
HF/6-31G*//HF/6-31G*	-309.884338	-309.880796	-309.879770	-309.877861	-309.870853	-309.874363	-309.879133
MP2/6-31G*//HF/6-31G*	-310.907604	-310.903845	-310.904037	-310.900859	-310.897254	-310.898781	-310.548250
ZPE (kJ mol^{-1})	0.194054	0.193914	0.193544	0.193354	0.193117	0.193584	0.193548
E_{rel}^{a} (kJ mol^{-1})	0.0	8.96	10.77	15.33	33.16	25.06	12.45
E_{rel}^{b} (kJ mol^{-1})	0.0	9.53	8.14	16.03	24.93	22.04	13.86
$H^{\circ}_{298}-H^{\circ}_{0}$ (kJ mol^{-1})	20.71	20.80	21.30	19.39	19.62	19.13	19.16
	(0.0)	(0.09)	(0.59)	(-1.32)	(-1.09)	(-1.58)	(-1.55)
$G^{\circ}_{298}-G^{\circ}_{0}$ (kJ mol^{-1})	-80.04	-81.98	-81.04	-76.74	-79.52	-80.04	-79.98
	(0.0)	(-1.94)	(-1.00)	(3.30)	(0.52)	(0.0)	(0.06)
S°_{298} (J mol^{-1} K^{-1})	337.92	344.75	343.24	333.64	332.53	332.62	332.51
	(0.0)	(6.83)	(5.32)	(-4.28)	(-5.39)	(-5.30)	(-5.41)
$H^{\circ}_{96}-H^{\circ}_{0}$ (kJ mol^{-1})	3.80	3.84	3.95	3.57	3.80	3.58	3.54
	(0.0)	(0.04)	(0.15)	(-0.23)	(0.0)	(-0.22)	(-0.26)
$G^{\circ}_{96}-G^{\circ}_{0}$ (kJ mol^{-1})	-20.23	-20.80	-20.33	-19.52	-20.24	-20.64	-20.64
	(0.0)	(-0.57)	(-0.10)	(0.71)	(-0.01)	(-0.41)	(-0.41)
S°_{96} (J mol^{-1} K^{-1})	250.27	256.69	252.91	240.54	250.42	252.28	251.79
	(0.0)	(6.42)	(2.64)	(-9.73)	(0.15)	(2.01)	(1.52)
$H^{\circ}_{105}-H^{\circ}_{0}$ (kJ mol^{-1})	4.27	4.32	4.46	4.00	4.26	4.01	3.96
	(0.0)	(0.05)	(0.19)	(-0.27)	(-0.01)	(-0.26)	(-0.31)
$G^{\circ}_{105}-G^{\circ}_{0}$ (kJ mol^{-1})	-22.50	-23.14	-22.62	-21.71	-22.51	-22.93	-22.92
	(0.0)	(-0.64)	(-0.12)	(0.79)	(-0.01)	(-0.43)	(-0.42)
S°_{105} (J mol^{-1} K^{-1})	254.95	261.46	257.90	254.93	254.93	256.55	256.05
	(0.0)	(6.51)	(2.95)	(-0.02)	(-0.02)	(1.60)	(1.10)

[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.

boat/twist-boat interconversion processes and concluded that the coalescence at lower temperature is due to either the twist or the boat process, the one at higher temperature either to the combined twist and boat processes or to the chair process. Our results (Fig. 1 and Table 1) suggest that the low-temperature coalescence is caused by the twist process (calculated energy barrier 16.0 kJ mol^{-1}), while for the-high-temprature coalescence the chair process (calculated energy barrier 22.0 kJ mol^{-1}) has to be taken into consideration. The boat process, with a relatively high calculated energy barrier of 24.9 kJ mol^{-1}, is not expected to play a significant role in twist-boat/twist-boat interconversion unless there are serious errors in calculations.

The calculated thermodynamic parameters (H°, S°, and G°) [14,15] for various geometries of (*Z,Z*)-cycloocta-1,5-diene at different temperatures are shown in Table l. The calculated $\Delta G^{\neq}$ values of 16.8 and 21.6 kJ mol^{-1} for the twist and chair processes are in better agreement with the experimentally determined values of 18.4 and 20.5 kJ mol^{-1}, respectively. The calculated $\Delta G^{\neq}$ value of 24.9 kJ mol^{-1} for the boat process is higher than the experimental values.

Representative structural parameters for various geometries of **1** are given in Table 1. The three energy-minimum conformations exhibit important geometrical differences. The twist-boat and half-chair have strongly expanded internal angles whereas the angles in chair form are more or less normal. The transition state linking **1-TB** and **1-HC** has a fairly reduced C-CH_2-C angle, but two expanded olefinic angles.

(*E,Z*)-Cycloocta-1,5-diene (2)

The labile cyclooctadiene prepared by Willstatter and Veraguth [16] from *N,N*-dimethylcyclooct-4-enylamine was shown by ozonolysis to be a 1,5-diene [17]. In later work this diene, prepared by Hofmann degradation of *N,N*-dimethyl-(*Z*)-cyclooct-4-enylamine [1] was found to be the (*E,Z*)-cycloocta-1,5-diene **(2)**. Compound **2** can be prepared in 60% yield from the monoepoxide of (*Z,Z*)-cycloocta-1,5-diene by treatment with lithium diphenylphosphide followed by methyl iodide [18]. Because of the rigidity of **2**, the *trans* double bond is unable to rotate with respect to the rest of the ring (swiveling) at ambient temperature and the molecule can exist as two optically active enantiomers. This has been confirmed by stereoselective synthesis of the diene from optically active (+ or −) *N,N*-dimethyl-(*E*)-cyclooct-4-enylamine [19] and by resolution of (*E,Z*)-cycloocta-1,5-diene *via* a platinum complex containing an optically active amine [20].

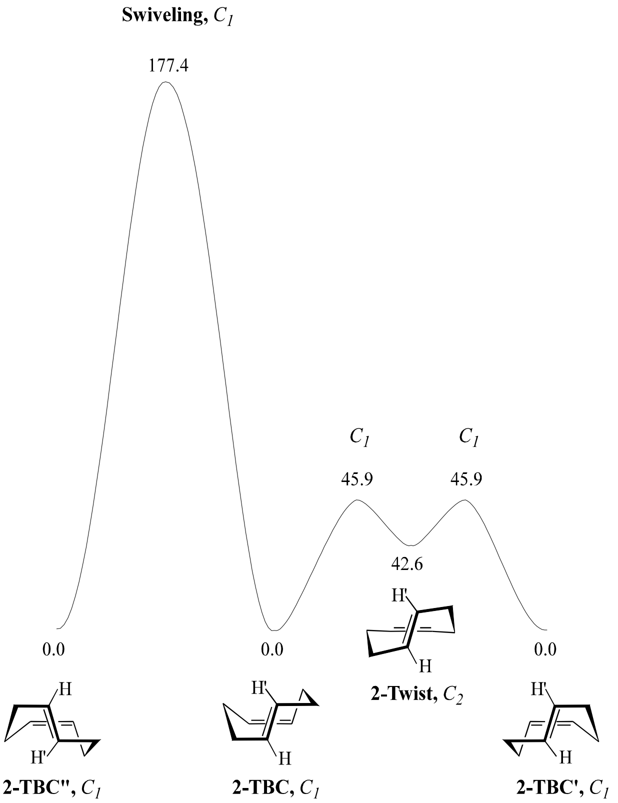

Fig. 2. Calculated MP2/6-31G*//HF/6-31G* strain energy (kj mol^{-1}) profile for conformational interconversion of twist-boat-chair and twist geometries of **2**.

Altogether four geometries were found important for a description of the conformational features of **2**. Two of these geometries correspond to energy minima and two to one-dimensional energy maxima (saddle points or transition states) as shown in Fig. 2 and Table 3. The most stable conformation of **2** is twist-boat-chair **(2-TBC)**, which lacks symmetry. The C_2 symmetric twist conformation is calculated to be 42.6 kJ mol^{-1}, less stable than **2-TBC** (see Fig. 2). The olefinic protons of both the *cis* and *trans* double bonds in **2-TBC** conformation are geometrically nonequivalent. However, compound **2** can average the magnetic environments of the protons on each type of double bond by a flipping process *via* **2-Twist** intermediate. The calculated energy barrier for this process is 45.9 kJ mol^{-1}.

As shown in Table 2, the stable conformation of **2** has

Table 2. Structural Parameters for Different Geometries of (*Z*,*Z*)-Cycloocta-1,5-diene **(1)**

Structure	**1-TB,** C_2	**1-HC,** C_s	**1-Chair,** C_{2h}	**1-Twist,** D_2	**1-Boat,** C_{2v}	**(1-TB $\rightleftharpoons$ 1-HC),** C_1	**(1-HC $\rightleftharpoons$ 1-Chair),**
d_{15} (Å)	3.19	3.25	3.47	3.52	2.92	3.06	3.42
d_{24} (Å)	3.19	3.25	3.47	3.52	2.92	3.09	3.42
r_{12} (Å)	1.322(1.37)	1.318	1.321	1.321	1.320	1.318	1.319
r_{23} (Å)	1.513(1.49)	1.505	1.513	1.513	1.511	1.510	1.508
r_{34} (Å)	1.535(1.51)	1.531	1.551	1.543	1.570	1.562	1.543
r_{45} (Å)	1.509(1.47)	1.514	1.513	1.513	1.511	1.521	1.518
r_{56} (Å)	1.322(1.37)	1.326	1.321	1.321	1.320	1.324	1.325
r_{67} (Å)	1.513(1.49)	1.514	1.513	1.513	1.511	1.510	1.518
r_{78} (Å)	1.535(1.51)	1.531	1.551	1.543	1.570	1.532	1.543
r_{81} (Å)	1.509(1.47)	1.505	1.513	1.513	1.511	1.505	1.508
θ_{123} (°)	131.0(128)	124.0	127.5	129.6	124.9	123.4	125.6
θ_{234} (°)	118.1(119)	113.4	114.1	116.9	116.6	117.9	113.4
θ_{345} (°)	113.9(113)	121.1	114.1	116.9	116.6	122.2	117.5
θ_{456} (°)	129.4(130)	137.7	127.5	129.6	124.9	134.3	133.0
θ_{567} (°)	131.0(128)	137.7	127.5	129.6	124.9	133.5	133.0
θ_{678} (°)	118.1(119)	121.1	114.1	116.9	116.6	117.6	117.5
θ_{781} (°)	113.9(113)	113.4	114.1	116.9	116.6	111.4	113.4
θ_{812} (°)	129.4(130)	124.0	127.5	129.6	124.9	123.3	125.6
ϕ_{1234} (°)	81.7(82)	-87.1	-69.9	-42.5	69.6	-70.0	-80.2
ϕ_{2345} (°)	-62.2(-65)	65.2	96.3	94.1	0.0	9.0	87.8
ϕ_{3456} (°)	-12.9(-11)	-11.4	-69.9	-42.5	-69.6	49.7	-49.8
ϕ_{4567} (°)	0.0(1)	0.0	0.0	-3.1	0.0	-4.2	0.0
ϕ_{5678} (°)	81.7(82)	11.4	69.9	-42.5	69.6	-18.0	49.8
ϕ_{6781} (°)	-62.2(-65)	-65.2	-96.3	94.1	0.0	-55.5	-87.8
ϕ_{7812} (°)	-12.9(-11)	87.1	69.9	-42.5	-69.6	93.7	80.2
ϕ_{8123} (°)	0.0(1)	0.0	0.0	-3.1	0.0	4.7	0.0

a nearly planar *cis* double bond with the $\phi_{4.567}$ angle -1.0° and a strongly twisted *trans* double bond with the corresponding to $\Delta G^{\neq}$ values of 18.4 ± 0.4 and 20.5 ± 0.4 $\phi_{812.3}$ angle -131.2°. The corresponding angles for the less stable conformation are 9.6° and -137.8°. A high-energy process involving degenerate interconversion of the twist-boat-chair conformation with its mirror image geometry is shown in Fig. 2. This process involves swiveling [21] of the *trans* double bond through the unsaturated bridge, which requires 177.4 kJ mol^{-1}.

(*E*,*Z*)-Cycloocta-1,5-diene (3)

Two families of conformations, *viz*., parallel and crossed are possible for **3**. The D_2 symmetric twist conformation of the crossed family is calculated to be 34.8 kJ mol^{-1} more stable than the C_{2h} symmetric chair

Table 3. Calculated Total and Zero-point Vibrational (Zero-point Vibrational Energy is Scaled by a Factor of 0.9135 to Eliminate Known Systematic Errors in Calculations) Energies (Hartree), Relative Energy (Including Zero-point Energy, kJ mol^{-1}) and Structural Parameters for Various Conformations of (*E*,*Z*)-Cycloocta-1,5-diene **(2)**

Structure	**2-TBC, C_1**	**2-Twist, C_2**	**(2-TBC ⇄ 2-Twist),**	**Swiveling**
HF/6-31G*//HF/6-31G*	-309.856332	-309.841983	-309.841183	-309.786460
MP2/6-31G*//HF/6-31G*	-310.888837	-310.872133	-310.870784	-310.821565
ZPE (kJ mol^{-1})	0.193470	0.192944	0.192863	0.193934
E_{rel}^{a} (kJ mol^{-1})	0.0	36.41	38.32	184.56
E_{rel}^{b} (kJ mol^{-1})	0.0	42.60	45.94	177.37
H^o_{298}-H^o_0 (kJ mol^{-1})	20.21	21.91	19.80	19.25
	(0.0)	(1.70)	(-0.41)	(-0.96)
G^o_{298}-G^o_0 (kJ mol^{-1})	-80.25	-82.98	-81.20	-80.07
	(0.0)	(-2.73)	(-0.95)	(0.18)
S^o_{298} (J mol^{-1} K^{-1})	336.93	361.84	338.75	333.11
	(0.0)	(24.91)	(1.82)	(-3.82)
d_{15} (Å)	2.97	2.90	2.89	3.37
d_{24} (Å)	2.75	2.90	2.89	2.76
r_{12} (Å)	1.318	1.317	1.316	1.315
r_{23} (Å)	1.507	1.502	1.504	1.499
r_{34} (Å)	1.560	1.549	1.547	1.575
r_{45} (Å)	1.524	1.533	1.531	1.554
r_{56} (Å)	1.329	1.336	1.335	1.343
r_{67} (Å)	1.524	1.533	1.533	1.561
r_{78} (Å)	1.561	1.549	1.560	1.581
r_{81} (Å)	1.498	1.502	1.494	1.541
θ_{123} (°)	120.9	120.8	120.3	159.9
θ_{234} (°)	104.5	107.0	106.9	101.0
θ_{345} (°)	113.6	120.2	117.8	116.8
θ_{456} (°)	129.8	139.1	137.9	133.3
θ_{567} (°)	130.8	139.1	142.1	133.4
θ_{678} (°)	115.0	120.2	123.8	123.4
θ_{781} (°)	103.9	107.0	107.9	114.3
θ_{812} (°)	120.7	120.8	121.5	110.1
ϕ_{1234} (°)	61.2	48.3	45.4	170.9
ϕ_{2345} (°)	42.1	37.0	42.7	41.6
ϕ_{3456} (°)	-82.5	-40.0	-53.6	-58.0
ϕ_{4567} (°)	-1.0	9.6	6.8	-3.4
ϕ_{5678} (°)	74.0	-40.0	-10.5	76.4
ϕ_{6781} (°)	-63.3	37.0	10.8	-61.2

Table 4. Calculated Total and Zero-point Vibrational (Zero-point Vibrational Energy is Scaled by a Factor of 0.9135 to Eliminate Known Systematic Errors in Calculations) Energies (Hartree), Relative Energy (Including Zero-point Energy, kJ mol^{-1}) and Structural Parameters for Various Conformations of (E,E)-Cyclooct-1,5-diene **(3)**

Structure	**3-Twist,** D_2	**3-Chair,** C_{2h}	Swiveling
HF/6-31G* //HF/6-31G*	-309.837177	-309.825203	-309.742600
MP2/6-31G* //HF/ 6-31G*	-310.875796	-310.862231	-310.786983
ZPE (kJ mol^{-1})	0.192775	0.192448	0.192790
E_{rel}^{a} (kJ mol^{-}	0.0	30.66	248.35
$^{-}E_{rel}^{b}$ (kJ mol^{-1})	0.0	34.83	233.21
H°_{298}-H°_{0} (kJ mol^{-1})	20.25	21.32	19.38
	(0.0)	(1.07)	(-0.87)
G°_{298}-G°_{0} (kJ mol^{-1})	-76.67	-80.78	-79.77
	(0.0)	(-4.11)	(-3.10)
S°_{298} (J mol^{-1})	336.60	348.15	332.57
	(0.0)	(11.55)	(-4.03)
d_{15} (Å)	2.70	2.59	2.67
d_{24} (Å)	2.70	2.59	3.17
r_{12} (Å)	1.322	1.321	1.321
r_{23} (Å)	1.510	1.511	1.558
r_{34} (Å)	1.584	1.607	1.611
r_{45} (Å)	1.510	1.511	1.534
r_{56} (Å)	1.322	1.321	1.337
r_{67} (Å)	1.510	1.511	1.524
r_{78} (Å)	1.584	1.607	1.637
r_{81} (Å)	1.510	1.511	1.508
θ_{123} (°)	122.4	122.5	113.0
θ_{234} (°)	106.7	109.0	119.3
θ_{345} (°)	106.7	109.0	113.5
θ_{456} (°)	122.4	122.5	124.0
θ_{567} (°)	122.4	122.5	119.8
θ_{678} (°)	106.7	109.0	109.0
θ_{781} (°)	106.7	109.0	105.8

Table 4. Continued

θ_{812} (°)	122.4	122.5	166.1
ϕ_{1234} (°)	-84.9	77.4	-18.2
ϕ_{2345} (°)	45.7	0.0	44.9
ϕ_{3456} (°)	-84.9	-77.4	-96.7
ϕ_{4567} (°)	132.8	134.7	121.9
ϕ_{5678} (°)	-84.9	-77.4	-76.3
ϕ_{6781} (°)	45.7	0.0	32.0
ϕ_{7812} (°)	-84.9	77.4	173.6
ϕ_{8123} (°)	132.8	-134.7	178.4

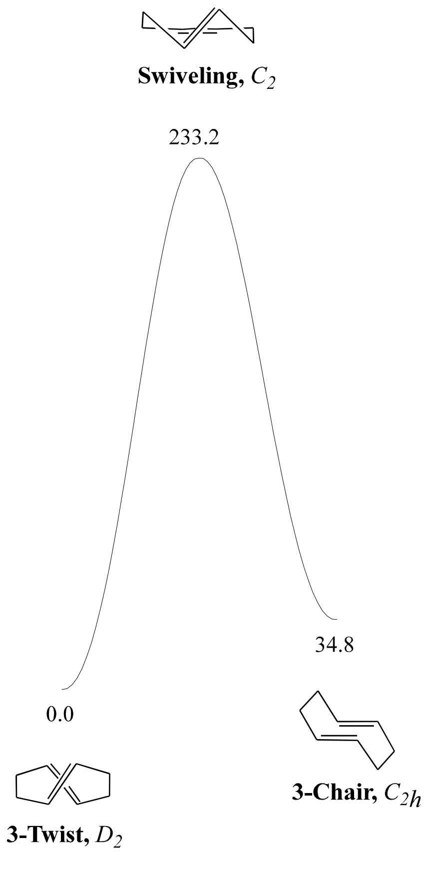

Fig. 3. Calculated MP2/6-31G*//HF/6-31G* strain energy (kJ mol^{-1}) profile for conformational interconversion of twist and chair geometries of **3**.

geometry (see Fig. 3 and Table 4). Interconversion of the crossed and parallel conformations of 3 can take place by swiveling of one of the double bonds through the unsaturated bridge [21]. However, the energy required for this process (233.2 kJ mol^{-1}) is higher than the π bond dissociation energy.

The thermodynamic parameters for important geometries of the parallel and crossed families of (*E,E*)-cycloocta-l,5-diene at 0 K and 298 K are shown in Table 4. The twist conformation of the crossed family is calculated to be the most favourable geometry at these temperatures.

CONCLUSIONS

HF/6-31G* calculations provide a picture of the conformations of isomeric cycloocta-1,5-dienes **1-3** from both structural and energetic points of view. The agreement between the HF/6-31G* results obtained for **1** and the dynamic NMR spectroscopic results [3] is excellent. Compounds **2** and **3** are expected to be conformationally homogeneous. The most stable conformation of **2** lacks symmetry. The highly symmetrical twist (D_2) conformation of **3** with crossed double bonds, is calculated to be 34.8 kJ mol^{-1} more stable than the chair (C_{2h}) form.

REFERENCES

[1] A.C. Cope, C.F. Howell, J. Bowers, R.C. Lord, G.M. Whitesides, J. Am. Chem. Soc. 89 (1967) 4024.

[2] L. Hedberg, K. Hedberg, Perspect. Struct. Chem. 4 (1971) 60.

[3] F.A.L. Anet, L. Kozerski, J. Am. Chem. Soc. 95 (1973) 3407.

[4] G. Favini, F. Zuccarello, G. Buemi, J. Mol. Struct. 3 (1969) 385; N.L. Allinger, J.T. Sprague, Tetrahedron 31 (1975) 21.

[5] O. Ermer, J. Am. Chem. Soc. 98 (1976) 3964.

[6] T. Shimizu, K. Iwata, N. Kamigata, S. Ikuta, J. Chem. Res. (S) (1994) 436.

[7] J.D. Dunitz, J. Waser, J. Am. Chem. Soc. 94 (1972) 5645.

[8] Gaussian 98, Revision A. 6, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Startmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rubuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Oritz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Comperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian. Inc. Pittsburgh PA 1998.

[9] F. Jensen, Introduction to Computational Chemistry, Wiley, New York, 1999.

[10] W. J. Hehre, L. Radom, P.v.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, Wiley, New York, 1986.

[11] P.C. Hariharan, J.A. Pople, Theor. Chim. Acta 28 (1973) 213.

[12] S. Moon, C.R. Ganz, J. Org. Chem. 34 (1969) 465; 35 (1970) 1241.

[13] R.K. Mackenzie, D.O. MacNicol, H.H. Mills, R.A. Raphael, F. B. Wilson, J.A. Zabkiewicz, J. Chem. Soc. Perkin Trans. 2 (1972) 1632.

[14] K.B. Wiberg, J.D. Hammer, H. Castejon, W. F. Bailey, E.L. Deleon, R.M. Jerret, J. Org. Chem. 64 (1999) 2085

[15] K.B. Wiberg, H. Castejon, W.F. Bailey, J. Ochterski, J. Org. Chem. 65 (2000) 1181.

[16] R. Willstatter, H. Veraguth, Ber. 38 (1905) 1975; 40 (1907) 957.

[17] K. Ziegler, H. Wilms, Ann. 567 (1950) 1.

[18] E. Vedejs, K.A.J. Snoble, P.L. Fuchs, J. Org. Chem. 38 (1973) 1178.

[19] A.C. Cope, C.F. Howell, A. Knowles, J. Am. Chem. Soc. 84 (1962) 3190.

[20] A.C. Cope, J.K. Hecht, H.W. Johnson, Jr., H. Keller, H.J.S. Winkler, J. Am. Chem. Soc. 88 (1966) 761.

[21] E.L. Eliel, S.H. Wilen, Stereochemistry of Organic Compounds, Wiley-Interscience, New York, 1994 .