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Ab Initio Study of Conformational and Configurational Properties of 1, 3-Diazacyclohepta-1, 2-diene and 1, 3-Diazacycloocta-1, 2-diene

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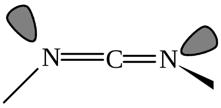
ABSTRACT

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 important energy-minimum conformations and transition-state geometries of 1, 3-diazacyclohepta-1, 2-diene (**2**) and 1, 3-diazacycloocta-1, 2-diene (**3**). The C_2 symmetric twist-chair (**2**-**TC**) conformation of **2** is calculated to be 7.4 kJ mol^{-1} more stable than the twist-boat (**2-TB,** C_2) conformer. Interconversion of **2**-**TC** and **2**-**TB** conformations takes place by a relatively high-energy (58.2 kJ mol^{-1}) transition state. The unsymmetrical chair (**3**-**C**) conformation of **3** is calculated to be 6.6 kJ mol^{-1} more stable than the C_2 symmetric twist-boat (**3**-**TB**) form. The transition state linking **3**-**C** and **3**-**TB** conformations is 40 kJ mol^{-1} above **3**-**C**. Racemization of **2**-**TC** and **3**-**C** conformations occures by *cis*-rotation and requires 77.9 and 83.5 kJ mol^{-1}, respectively.

***Keywords*:** Cyclic carbodiimides; Conformational analysis; *Ab initio* calculations; Chiral stability; Stereochemistry.

INTRODUCTION

Heterocumulenes are substances in which one or more carbon atoms of the cumulene system are replaced by a heteroatom. A variety of heterocumulenes are known, but only a few have been incorporated in strained rings. Cyclic carbodiimides are the best known among strained cyclic heterocumulenes. Carbodiimides (1) are an important class of unsaturated compounds with two carbon-nitrogen double bonds in an orthogonal geometry, a relatively uncommon feature in organic chemistry. They have attracted considerable attention because of their importance as versatile reagents in organic and biochemical syntheses [1-4]. That these compounds have dissymmetric allene-like structures (1) is well established. Optical isomerism is possible but resolution has not been achieved because of the low energy barrier to racemization [5-11].



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In recent years, with the development of computer hardware and software, computational chemistry has become a popular tool for chemists studying molecular structures, properties, and chemical reactions [12].

While the structural properties and dynamics of cyclic allenes [4, 13] have been studied both experimentally [14, 15] and theoretically [16-18], there is only a few reports on the synthesis and conformational studies of cyclic carbodiimides [8, 19, 20]. The configurational flexibility of 1,3-diazacyclonona-1,2-diene has been studied by dynamic ^{1}H NMR measurements [8] and the free energy of activation for racemization was found to be 28.0 kJ mol^{-1}. Recently, we reported [20] AM1 study of equilibrium geometries and racemization mechanisms in open-chain carbodiimides and medium rings containing two adjacent carbodiimide units. This study was undertaken to investigate the structural optimization, conformational and configurational interconversion pathways of the highly strained seven- and eight-membered ring cyclic carbodiimides **(2)** and **(3)** by computing 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 discussions below.

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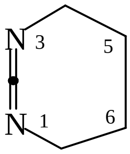

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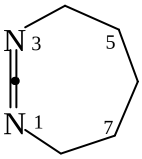

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RESULTS AND DISCUSSION

1, 3-Diazacyclohepta-1, 2-diene (*2*)

Not surprisingly, there appear to be no reported example of **2**. However, the parent hydrocarbon, cyclohepta-1, 2-diene, has been reported as a transient intermediate in the rearrangement of bicyclo [4.1.0] hepta-7-ylidene generated from 7-bromo-7-lithiobicyclo [4.1.0] heptane [21].

Representative structural parameters for the cycloaliphatic carbodiimide **2** as calculated by AM1 and HF/6-31G* methods are shown in Figure 1 and Table 1. Two C_2 symmetric conformations are available to **2**. The twist-chair (**2-TC**) conformation is 7.35 kJ mol^{-1} more stable than the twist-boat (**2-TB**) form. Twist-chair and twist-boat conformations are important because they are expected to be significantly populated at room temperature.

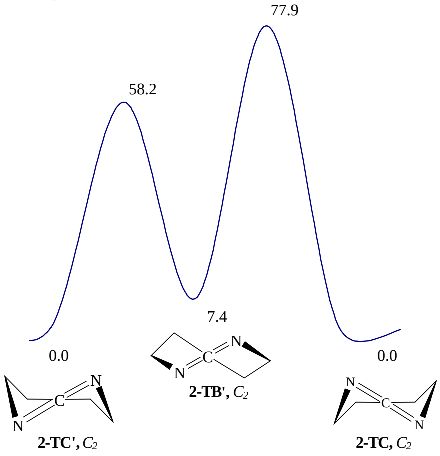

Fig.1. Calculated strain energy (kJ mol^{-1}) profile for conformational interconversion of 1, 3-diazacyclohepta-1, 2-diene (**2**).

The conformational process linking twist-chair and twist-boat forms is shown in Figure 1. The unsymmetrical transition state for this interconversion is 58.18 kJ mol^{-1} above twist-chair conformation. The second conformational process, and the one with the higher barrier, is interconversion of the twist-chair conformer with its mirror image via *cis*-rotation around the N=C=N moiety. The energy barrier for this process is 77.90 kJ mol^{-1}. Thus, compound **2** is expected to lack chiral stability at room temperature as a result of its relatively low racemization energy. Selected geometrical data for various geometries of **2** are shown in Table 1. The comparison of bond lengths shows fairly small differences. However, some of the internal angles are compressed from the unstrained values in energy-minimum conformations, but are expanded in transition state geometries. The calculated N=C=N bond angles in different geometries of **2** are about 167°. The C=C=C bond angle in cyclohepta-1, 2-diene is about 20° more compressed [22].

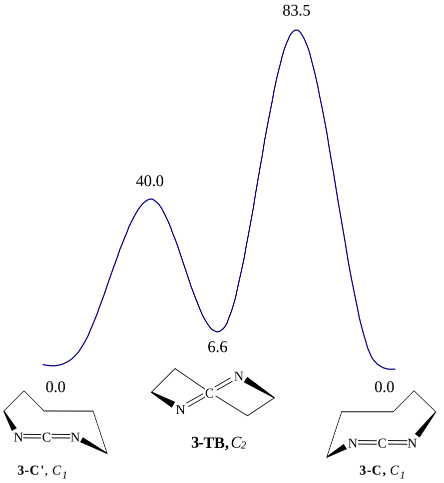

Fig.2. Calculated strain energy (kJ mol-1) profile for conformational interconversion of 1, 3-diazacycloocta-1, 2-diene (3).

1, 3-Diazacycloocta-1, 2-diene (3)

1, 3-Diazacycloocta-1, 2-diene (3), with a carbodiimide chromophore, is generally considered as the smallest fairly stable cyclic carbodiimide. Compound 3 has been prepared by stirring a dichloromethane solution of pentamethylene thiourea with excess yellow mercury (II) oxide and anhydrous magnesium sulfate at ambient temperature [23].

Four geometries (two energy minima and two transition states) were found to be necessary in a description of the conformational properties of 3. The most stable conformation of 3 is the chair (3-C), which lacks symmetry (see Figure 2). The axial symmetrical twist-boat (3-TB, C2) conformation is calculated to be 6.62 kJ mol-1 less stable than 3-C. Conformations chair and twist-boat are important because they are expected to be significantly populated at room temperature. The calculated strain energy for the transition state separating chair and twist-boat conformations is 40.0 kJ mol-1. Enantiomerization of the chiral chair conformation can takes place by cis-rotation around the carbodiimide moiety and requires 83.47 kJ mol-1 (see Figure 2).

The higher racemization energy for 3, as compared to that of 2, is attributed to the stability of the ground-state conformations in the eight-membered cycloaliphatic carbodiimide. Selected geometrical data for various geometries of 3 are shown in Table 2. The comparison of bond lengths and bond angles shows fairly small differences. The Csp3-Csp3 bonds are almost staggered in twist-boat conformation, but less so in chair form and transition-state geometries. The internal angles are expanded in transition-state geometries. The N=C=N bond angles in energy-minimum conformations of 3 are about 175°, which is slightly compressed from the strain-free value of 180°. Having found the conformational transition states and intermediates of 2 and 3 (see Figures 1 and 2), still we need to determine whether the potential energy surface is the lowest path. Since potential energy surface is highly multidimentional, it is not possible to explore all possibilities, but we have carried out sufficient calculations to feel confident that the lowest path, or something close to it, has been obtained for each compound. In conclusion, HF/6-31G* calculations provide a fairly clear picture of the conformations of 2 and 3 from both structural and energetics points of view. Both compounds are expected to exist as a mixture of two conformers. Compounds 2 and 3 are expected to lack chiral stability at ambient temperature. It would be valuable, of course, to have direct structural data on 2 and 3 for comparison with the results of ab initio calculations.

Table 1. Calculated heats of formation (kJ mol^{-1}), total and zero-point vibrational (zero-point vibrational energy is scaled by a 0.9135 to eliminate known systematic errors in calculations) energies (hartree), relative energy (including zero-point energy, kJ mol^{-1}) and structural parameters for 1,3-diazacyclohepta-1,2-diene (**2**)

Structure	**2-TB**, *C*2		**2-TC**, *C*2		(**2-TB↔2-TC**)$^{\neq}$, *C*1		(**2-TB ↔ 2-TC′**)$^{\neq}$, *C*2	
	AM1	*ab nitio*	AM1	*ab initio*	AM1	*ab initio*	AM1	*ab initio*
ΔH_f°	256.02		269.53		297.94		317.65	
$\Delta\Delta H_f^{\circ}$	0.0		13.51		41.92		61.63	
HF/6-31G*//HF/6-31G*		-302.7065		-302.7091		-302.6889		-302.6824
MP2/6-31G*//HF/6-31G*		-303.7922		-303.7950		-303.7729		-303.7654
ZPE		0.1261		0.1262		0.1261		0.1253
*E*rel[a]		6.74		0.0		52.92		70.17
*E*rel[b]		7.35		0.0		58.18		77.90
*r*12	1.267	1.210	1.267	1.210	1.266	1.210	1.264	1.205
*r*23	1.267	1.210	1.267	1.210	1.265	1.210	1.264	1.205
*r*34	1.465	1.486	1.470	1.487	1.459	1.476	1.473	1.480
*r*45	1.544	1.549	1.544	1.541	1.535	1.535	1.535	1.540
*r*56	1.526	1.549	1.522	1.552	1.543	1.546	1.521	1.553
*r*67	1.544	1.549	1.544	1.541	1.543	1.547	1.537	1.540
*r*71	1.465	1.486	1.470	1.487	1.460	1.485	1.460	1.480
θ123	163.1	168.6	163.3	167.8	162.8	167.2	175.2	173.6
θ234	110.5	110.3	109.2	107.9	109.8	109.7	110.5	113.2
θ345	114.4	113.0	111.3	110.4	116.1	116.4	115.4	113.6
θ456	115.8	114.4	117.8	117.4	127.7	126.1	117.1	115.6
θ567	115.8	114.4	117.8	117.4	127.6	126.0	117.1	115.6
θ671	114.4	113.0	111.3	110.4	115.6	114.3	115.3	113.6
θ712	110.5	110.3	109.2	107.9	109.2	108.2	110.6	113.2
ϕ2345	24.2	20.4	53.6	55.0	45.4	46.3	-17.3	-16.7
ϕ3456	35.4	38.7	-66.6	-65.0	-18.5	16.4	55.2	55.9
ϕ4567	-83.5	-85.7	68.2	65.3	-4.3	-3.4	-80.7	-83.1
ϕ5671	35.4	38.7	-66.6	-65.0	-22.2	-21.3	55.3	55.8
ϕ6712	24.2	20.2	53.6	55.0	47.8	49.2	-17.2	-16.7
ϕCNNC	-53.6	-51.4	-50.0	-53.4	-59.7	-62.6	1.0	-0.7

[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.

Table 2. Calculated heats of formation (kJ mol^{-1}), total and zero-point vibrational (zero-point vibrational energy is scaled by a 0.9135 to eliminate known systematic errors in calculations) energies (hartree), relative energy (including zero-point energy, kJ mol^{-1}) and structural parameters for1, 3-diazacycloocta-1, 2-diene (**3**)

Structure	**3-C**, *C*1		**3-TB**, *C*2		(**3-TB**↔**3-C**)$^{\#}$, *C*1		(**3-TB**↔**3-C′**)$^{\#}$, *C*1	
	AM1	*ab initio*	AM1	*ab initio*	AM1	*ab initio*	AM1	*ab initio*
ΔH°_{f}	173.97		191.08		209.45		254.30	
$\Delta\Delta H^{\circ}_{f}$	0.0		17.11		35.48		80.33	
HF/6-31G*//HF/6-31G*		-341.7293		-341.7261		-341.7139		-341.6973
MP2/6-31G*//HF/6-31G*		-342.9751		-342.9726		-342.9598		-342.9433
ZPE		0.1546		0.1547		0.1545		0.1500
*E*rel^{a}		0.0		8.35		40.43		83.79
*E*rel^{b}		0.0		6.62		40.00		83.47
*r*12	1.26	1.209	1.26	1.209	1.256	1.211	1.262	1.221
*r*23	1.26	1.209	1.26	1.209	1.256	1.202	1.243	1.201
*r*34	1.45	1.472	1.46	1.476	1.442	1.462	1.431	1.457
*r*45	1.54	1.533	1.53	1.534	1.535	1.558	1.538	1.554
*r*56	1.52	1.550	1.52	1.550	1.535	1.558	1.521	1.553
*r*67	1.52	1.550	1.52	1.550	1.517	1.548	1.518	1.547
*r*78	1.54	1.536	1.53	1.534	1.536	1.540	1.544	1.545
*r*81	1.45	1.472	1.46	1.476	1.457	1.476	1.450	1.464
θ123	175.4	175.2	170.6	173.2	172.2	174.9	174.4	178.2
θ234	115.9	114.7	113.9	114.9	117.2	122.1	122.5	123.3
θ345	113.3	110.9	115.5	114.1	119.5	119.2	117.7	118.4
θ456	115.7	117.1	117.7	117.6	126.4	123.1	122.5	123.0
θ567	115.5	117.7	121.8	121.2	125.4	120.2	120.8	118.2
θ678	114.5	115.9	117.7	117.6	114.0	112.3	113.4	114.0
θ781	115.1	114.8	115.5	114.1	114.4	112.3	114.3	115.4
θ812	114.5	116.0	113.9	114.8	112.9	113.2	113.3	114.3
ϕ2345	-59.2	-69.2	-13.2	-12.4	-27.5	-35.5	33.3	30.3
ϕ3456	57.8	62.1	-63.7	-63.7	-19.1	-16.5	-25.9	-21.8
ϕ4567	-86.9	-78.1	53.9	53.4	-8.0	-9.5	-45.1	-43.7
ϕ5678	112.5	104.6	53.9	53.4	90.5	96.9	112.1	108.7
ϕ6781	-47.6	-56.0	-63.7	-63.7	-60.4	-54.1	-67.2	-61.8
ϕ7812	-19.8	-12.3	-13.2	-12.4	-17.6	-19.3	9.1	8.4
ϕCNNC	67.5	69.4	66.0	66.6	69.7	67.8	-0.9	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.

CALCULATIONS

Semiempirical calculations were carried out using AM1 method [24, 25] with the MOPAC 6.0 program package [26, 27]. Energy-minimum geometries were located by minimizing 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 [28] (Keyword SADDLE).

The AM1 results were used as input for the ab initio molecular orbital calculations, which were carried out using the GAUSSIAN 98 [29] program. Geometries for all structures were fully optimized by means of analytical energy gradients by Berny optimizer with no geometrical constraints [30, 31]. The restricted Hartree-Fock calculations with the split-valance 6-31G* basis set which include a set of d-type polarization functions on all non-hydrogen atoms were used in these calculations [32]. 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, respectively. The frequencies were scaled by a factor of 0.9135 [33] and used to compute the zero-point vibrational energies.

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