Short communication

Ab initio study of the conformational properties
of (Z,Z)-cyclodeca-1,6-diene and its heterocyclic
analogue containing oxygen

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Abstract

Ab initio molecular orbital and density functional theory methods were used to investigate the structure and conformational interconversion of (Z,Z)-cyclodeca-1,6-diene (1) and (Z,Z)-1,6-dioxa-cyclodeca-3,8-diene (2). Consistent with the previously reported AM1 semi-empirical data, a chair conformation with $C_{2v}$ symmetry is found to be the most stable geometry for compounds 1 and 2. However, further investigations reveal the presence of both two ground states, i.e. 1-Twist–Chair–Boat–Chair ($C_1$ symmetry) and 1-Twist–Boat–Boat–Chair ($C_i$ symmetry) and two transition state structures ([1-Chair→1-Twist–Chair–Boat–Chair]$^*$ and [1-Twist–Chair–Boat–Chair→1-Twist–Boat–Boat–Chair]$^*$), which were not previously reported by the AM1 investigation [I. Yavari, M.R. Hosseini-Tabatabaei, D. Nori-Shargh, A. Jabbari, J. Mol. Struct. (Theochem) 574 (2001) 9], and therefore, the correct ring inversion process for compound 1 is now presented. In addition, the conformational properties of heterocyclic analogue of compound 1 (containing oxygen atom), i.e. (Z,Z)-1,6-dioxa-cyclodeca-3,8-diene (2), is also reported in this work.

Keywords: Molecular modeling; Ab initio; Stereochemistry; Conformational analysis; (Z,Z)-cyclodeca-1,6-diene

1. Introduction

Molecular models of (Z,Z)-cyclodeca-1,6-diene (1), in which the diametric olefinic bonds of the same geometry connected by odd polymethylene chains, have been predicted to be capable of existing in fairly strain-free conformations [1–3]. An electron diffraction structure of the (Z,Z)-isomer, which is certainly the predominant conformation of cyclodeca-1,6-diene, reveals a chair conformation with $C_{2b}$ symmetry [4,5]. Also, the variable temperature $^1$H NMR spectra of (Z,Z)-isomer of 1 have been analyzed in term of a $C_{2b}$ structure [6], in which the two double bonds are widely separated and, owing to their $cis$ nature, should impart a residual strain. Molecular mechanics, which is limited to calculation on the energy minimum conformations [7–9] and semi-empirical reported data [10] showed a preference for a chair conformation ($C_{2h}$ symmetry), although boat form ($C_{2v}$ symmetry) is calculated to be not much higher in energy. Len and Feigenbann, in a study of heterocycle (Z,Z)-1,6-dioxa-cyclodeca-3,8-diene (2), have suggested that the values of the bond angles at positions 4 and 9 can influence the ring inversion of compound 2 [11].

In this work, we investigated the structural and conformational properties of (Z,Z)-cyclodeca-1,6-diene (1) and (Z,Z)-1,6-dioxa-cyclodeca-3,8-diene (2) by ab initio molecular orbital (MO) [12] and density functional theory (DFT) methods (B3LYP) [13,14] and observed that the previously reported AM1 semi empirical results [10] are incorrect. The results of this investigation permitted to find...
a correct pathway for ring flipping of compound 1 and also to see the influence of the presence of the oxygen heteroatom in the ring flipping potential energy surface of compound 2.

2. Computational details

Ab initio calculation were carried out using HF/6-31G**// HF/6-31G* and B3LYP/6-31G*/HF/6-31G* levels of theory with the GAUSSIAN 98 package programs [12] implemented on a Pentium-PC computer with 550 MHz processor. Initial structure geometries of compounds 1 and 2 were obtained by a molecular mechanic program PCMODEL (88.0) [15] and for reoptimization of geometries, AM1 method of MOPAC 6.0 computer program [16–18] was used. The GAUSSIAN 98 package programs was finally utilized to perform ab initio calculation at HF/6-31G* level in order to obtain the energy minimum and energy maximum structures and B3LYP/ HF/6-31G*/HF/6-31G* method for single point calculations. Energy minimum molecular geometries were located by minimizing energy with respect to all geometrical coordinates without imposing any symmetrical constraints. The nature of the stationary points for reactant compounds has been fixed by means of the number of imaginary frequencies. For minimum state structures, only real frequency values and in the transition state only single imaginary frequency value were accepted [19,20]. The structure of the molecular transition state geometries was located by using the optimized geometry of the equilibrium molecular structures according to the procedure of Dewar et al. (SADDLE keyword) [21]. These geometry structures were further reoptimized by QST3 option at the HF/3-21G level. The vibrational frequencies of ground state and transition states were calculated by FREQ subroutine.

3. Results and discussion

Corrected zero point (ZPE*) and total electronic ($E_{el}$) energies ($E_0=ZPE + E_{el}$) for compounds 1 and 2, as calculated at the ab initio HF/6-31G* level of theory are given in Table 1. For single-point energy calculations, DFT

<table>
<thead>
<tr>
<th>System</th>
<th>ZPE*</th>
<th>HF-6-31G**//HF-6-31G*</th>
<th>B3LYP-6-31G**//HF-6-31G*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$E_0$</td>
<td>$E_0$</td>
</tr>
<tr>
<td>I-C, C_{3h}</td>
<td>0.233746</td>
<td>$-387.962395$</td>
<td>$-387.726849$</td>
</tr>
<tr>
<td>I-TC, C_{1}</td>
<td>0.233283</td>
<td>$-387.4527$</td>
<td>$-387.711244$</td>
</tr>
<tr>
<td>I-TBCC, C_{1}</td>
<td>0.233710</td>
<td>$-387.933786$</td>
<td>$-387.700076$</td>
</tr>
<tr>
<td>I-BBC, C_{1}</td>
<td>0.188904</td>
<td>$-459.569715$</td>
<td>$-459.381811$</td>
</tr>
<tr>
<td>I-BBC, C_{1}</td>
<td>0.187683</td>
<td>$-459.566037$</td>
<td>$-459.378534$</td>
</tr>
<tr>
<td>I-TC→TBCC, C_{1}</td>
<td>0.187453</td>
<td>$-459.544115$</td>
<td>$-459.356662$</td>
</tr>
</tbody>
</table>

* Corrected by multiplying by a scaling factor (0.9135).
* Relative to the most stable conformation.
* Numbers in parenthesis are the corresponding $\Delta E$ values in kJ mol$^{-1}$. 
ties of compound 1 were found to be the most important in the description of the conformational properties of \((Z,Z)\)-cyclodeca-1,6-diene (1). The most stable conformation of 1 is 1-Chair form (\(C_{2h}\) symmetry). The energy of the second minimum conformation, i.e. 1-Boat (\(C_{2v}\) symmetry), is 17.09 and 14.44 kJ mol\(^{-1}\) above that of chair conformation, as calculated by HF/6-31G*//HF/6-31G* and B3LYP/6-31G*//HF/6-31G* methods, respectively. Contrary to the previously reported AM1 semiempirical results [10], only the chair conformation is expected to be significantly populated at room temperature. The plane symmetrical 1-Boat–Boat–Chair form (\(C_{i}\) symmetry), in which one prow of the boat is tipped back over the ring, is an intermediate in the conformational interconversion of chair and boat conformations. HF/6-31G*/HF/6-31G* and B3LYP/6-31G*/HF/6-31G* calculations show that the energy of 1-Boat–Chair–Boat (\(C_{i}\) symmetry) is 45.70 and 40.67 kJ mol\(^{-1}\), respectively, above that of the chair form. These new HF and B3LYP calculated energy values are higher than those calculated by AM1 method [10]. It is interesting to note that, the results reveal also two new intermediate forms between 1-Chair (\(C_{2v}\) symmetry) and 1-Boat–Boat–Chair conformations (\(C_{i}\) symmetry), namely 1-Twist–Boat–Boat–Chair (\(C_{i}\) symmetry) and 1-Twist–Chair–Boat–Chair (\(C_{i}\) symmetry) conformations. HF/6-31G*/HF/6-31G* results show that 1-Twist–Boat–Chair and 1-Twist–Chair–Boat–Chair conformations are about 52.78 and 33.00 kJ mol\(^{-1}\) less stable than 1-Chair (\(C_{2h}\) symmetry), respectively, while B3LYP/6-31G*/HF/6-31G* results show the values of 46.93 and 30.17 kJ mol\(^{-1}\) for these energy differences, respectively. Since, the calculated HF/6-31G*/HF/6-31G* and B3LYP/6-31G*/HF/6-31G* energies for the 1-Boat–Boat–Chair, 1-Twist–Boat–Boat–Chair and 1-Twist–Chair–Boat–Chair conformations are about 30–40 kJ mol\(^{-1}\) higher than that of the 1-Chair form, these conformations are not expected to be populated at room temperature.

The calculated energy profile for ring flipping of compound 1 shows that the required energy for this process is 80.10 and 72.14 kJ mol\(^{-1}\), as calculated by HF/6-31G*/HF/6-31G* and B3LYP/6-31G*/HF/6-31G* levels of theory, respectively (see Fig. 1). Consequently, the ring flipping of compound 1 could not occur easily at room temperature.

The 1-Twist–Chair–Boat–Chair (\(C_{i}\) symmetry) and 1-Twist–Boat–Boat–Chair (\(C_{i}\) symmetry) as ground states and \([1-C\rightarrow 1-TCBC]\)# and \([1-TCBC\rightarrow 1-TBCC]\)# as transition state structures were not signaled in the previously AM1 semi-empirical results [10].

Conformational properties of compound 2 are similar to compound 1. The most stable conformation of 2 is the 2-Chair form with \(C_{2h}\) symmetry. The 2-boat conformation (\(C_{2v}\) symmetry) of compound 2 is 12.31 and 11.17 kJ mol\(^{-1}\) less stable than 2-Chair, as calculated by HF/6-31G*/HF/6-31G* and B3LYP/6-31G*/HF/6-31G*, respectively. Therefore, based on similar arguments used for compound 1, this conformation is not expected to be populated at room temperature.

Representative structural parameters for various geometries of compound 1 are given in Table 2. For compound 1, the \(C_{sp}–C_{sp}\) bonds are almost staggered in 1-Chair, 1-Boat and 1-Boat–Boat–Chair, but less so in 1-Twist–Boat–Boat–Chair form and transition state geometries. For chair conformation of compound 1, the \(C_{sp}–C_{sp}–O–C_{sp}\) bond angle is 114.7°, while for the chair conformation of compound 2, the \(C_{sp}–O–C_{sp}\) bond angle is 116.6°. The energy profiles of ring flipping of compounds 1 and 2, as calculated by HF/6-31G*/HF/6-31G* and
B3LYP/6-31G*/HF/6-31G*, show that the 2-Chair, 2-Twist–Chair–Boat–Chair and 2-Twist–Boat–Boat–Chair conformations are important and are expected to be populated at room temperature, while in compound 1, only 1-Chair conformation can be populated at this temperature. This fact could be related to the larger transannular non-bonded repulsions between the axial hydrogens of C4 and C8. It is clear that the Van der Waals repulsions between C–H bonds are larger than the non-bonded axial lone pairs of oxygen atoms and C–H bonds. Also, the bond length of Csp3–O bond is greater than Csp3–C bond, and in addition, the Van der Waals repulsions between the axial hydrogens of C4 and C8. Since the Van der Waals repulsions between C–H bonds are larger than non-bonded axial lone pairs of oxygen atom and other C–H bonds, consequently, the energy difference between 1-Chair (C3v symmetry) and 1-Boat–Chair (C3 symmetry) is greater than the energy difference between 2-Chair and 2-Boat–Boat–Chair forms. Contrary to the previously reported semi-empirical AM1 results, the B3LYP/6-31G*/HF/6-31G* and HF/6-31G*/HF/6-31G* data revealed that only 1-Chair is expected to be populated at room temperature.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>I-C, C2v</th>
<th>I-TC, C1v</th>
<th>I-TBBC, C1v</th>
<th>I-BBC, C1v</th>
<th>I-B, C2v</th>
<th>I-TC → TC1v, C1v</th>
<th>I-TBBC → BBC1v, C1v</th>
<th>I-BBC → B1v, C1v</th>
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<tr>
<td>Bond lengths (Å)</td>
<td>1.324</td>
<td>1.325</td>
<td>1.325</td>
<td>1.321</td>
<td>1.321</td>
<td>1.324</td>
<td>1.322</td>
<td>1.326</td>
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<td>r1–2</td>
<td>1.507</td>
<td>1.509</td>
<td>1.509</td>
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<td>1.515</td>
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<td>r3–4</td>
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<td>1.539</td>
<td>1.545</td>
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<td>1.552</td>
<td>1.547</td>
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<td>1.519</td>
<td>1.519</td>
<td>1.522</td>
</tr>
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</table>

Bond lengths are in angstrom (Å) unit and angles in degrees (°).

Table 2

HF/6-31G* calculated structural parameters for the energy minima and transition states structures of compound 1

4. Conclusion

The ab initio and B3LYP density functional theory calculations, reported in this work, provided a picture from both structural and dynamic point of view for compounds 1 and 2. The results calculated by HF/6-31G*/HF/6-31G* and B3LYP/6-31G*/HF/6-31G* methods show that the energy barrier for ring flipping in compound 1 is higher than in compound 2. This fact was attributed to the larger transannular non-bonded repulsions between the axial hydrogens of C4 and C8. Since the Van der Waals repulsions between C–H bonds are larger than non-bonded axial lone-pairs of oxygen atom and other C–H bonds, consequently, the energy difference between 1-Chair (C3v symmetry) and 1-Boat–Chair (C3 symmetry) is greater than the energy difference between 2-Chair and 2-Boat–Boat–Chair forms. Contrary to the previously reported semi-empirical AM1 results, the B3LYP/6-31G*/HF/6-31G* and HF/6-31G*/HF/6-31G* data revealed that only 1-Chair is expected to be populated at room temperature.
temperature. Similarly, in compound 2, the B3LYP/6-31G*//HF/6-31G* and HF/6-31G*//HF/6-31G* results show also that only 2-Chair structure ($C_{2h}$ symmetry) is expected to be populated at room temperature.

B3LYP and HF results revealed also the presence of two new ground states (i.e. 1-Twist–Chair–Boat–Chair with $C_1$ symmetry, and 1-Twist–Boat–Boat–Chair with $C_1$ symmetry) and also two transition state structures (i.e. [1-Chair→1-Twist–Chair–Boat–Chair] and [1-Twist–Chair–Boat–Chair→1-Twist–Boat–Boat–Chair]), which were not reported by the previous AM1 investigation [10]. Since (Z,Z)-cyclodec-1,6-diene (1), is a relatively important medium-sized ring compound, it is necessary to know its correct conformational behavior. Therefore, as the previously reported AM1 ring inversion process for compound 1 was incorrect, the corrected path is now presented in this work.

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References

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[17] J.J.P. Stewart, QCPE 581. Department of Chemistry, Indiana University, Bloomington, IN, USA.