Inversion of the C₈ non-planar ring

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Abstract

Inversion of the recently reported non-planar cyclic minimum-energy structure of C₈ (D₂d symmetry) is studied by means of the second-order Møller-Plesset perturbation treatment with the 6-31G* basis set. Two new planar cyclic saddle points have been found, possessing D₄h and C₂h symmetry and exhibiting two and one imaginary frequencies, respectively. The former and the latter saddle point are located 71 and 54 kJ/mol, respectively, above the D₂d minimum. Calculated harmonic vibrational frequencies for the activated complex C₂h are presented.

1. Introduction

Carbon aggregates have recently been subject of considerable research interest [1], from both computational [2-17] and experimental [18-31] point of view. The interest has particularly been enhanced by the large carbon spheroidal, fullerene-like aggregates [32]. Nevertheless, small clusters Cₙ still offer various open problems. The computational studies [1] mostly reported linear arrangements for odd-numbered small carbon aggregates while with the even-numbered ones two isomers were suggested, planar cyclic and linear (triplet electronic state). Recent observations [28,29] suggested that most carbon clusters Cₙ (at least [28] for n from 3 to 60) have more than one stable form. Computed cyclic minimum-energy structures have very recently been reported for C₇ [16] and C₁₁ [13], indeed.

Our recent correlated ab initio study of C₈ at the MP2/6-31G* level [17] revealed a non-planar minimum-energy structure of D₂d symmetry. This marks a considerable difference from the Hartree–Fock level where the cyclic minimum is predicted to be planar [3] (C₄h symmetry). In our correlated treatment the planar C₄h structure was located 55.5 kJ/mol above the D₂d minimum. Moreover, the C₄h species exhibits two imaginary vibrational frequencies. Although this indicates that the inversion barrier for the D₂d isomer will be relatively low, the value of the barrier and the form of the related activated complex can only be clarified after additional computations. In the present Letter, we would like to report the additional results obtained within the same level of approximation [17].

2. Computations

The present computations were performed with the GAUSSIAN 92 program package [33]. The standard
6-31G* basis set was used and the electron correlation was included through all-electron second-order Möller–Plesset (MP2) perturbation treatment (unrestricted open shell approach for triplet states). Within this MP2/6-31G* approach geometry optimization and harmonic vibrational analysis were carried out. The optimization employed internal coordinates in order to work within the smallest possible set of optimized variables. The energy gradient was constructed analytically. For the resulting optimized structures a harmonic vibrational analysis was carried out with the force-constant matrix again evaluated analytically. The force-constant matrix was constructed in the full Cartesian coordinate set.

3. Results and discussion

The location of the non-planar minimum and the planar saddle point with two imaginary frequencies [17] represent a clear impetus for a further search on the MP2/6-31G* potential hypersurface for a planar activated complex, i.e. a saddle point with just one imaginary frequency. The activated complex will then determine the inversion barrier (so far only an upper bound of the barrier is available, given by the C₄₅ structure, i.e. 55.5 kJ/mol).

There may be a natural candidate, the planar D₄h structure. As shown in Fig. 1, the structure is composed of two different squares rotated exactly by 45° so that only two geometrical degrees of freedom are present. Its harmonic vibrational modes possess the following symmetry structure:

\[
\Gamma_{D_{4h}} = 2A_{1g} + A_{2g} + A_{2u} + 2B_{1g} + B_{1u} + 2B_{2g} + B_{2u} + E_g + 3E_u.
\]  

(1)

Although degenerate representations are present, the structure cannot simply be excluded on the basis of the Murrell–Laidler theorem [34] as it is not obvious why a mode with imaginary frequency should belong to the degenerate representation. Further vibrational analysis concluded that there are in fact two modes with imaginary frequencies, 167i and 318i cm⁻¹, belonging to B₂g and B₁u representations, respectively. Hence, the D₄h structure is not the searched activated complex. This fact is also indicated by the energy separation of 71.2 kJ/mol from the D₂d minimum (Table 1).

Although the D₄h structure is not our target, it deserves a comment. There are two high frequencies in its vibrational spectrum, 2026 and 4452 cm⁻¹. While the former value is still reasonable for a carbon cluster, the latter is clearly a computational artifact. As the force-constant matrix was constructed analytically, and not numerically, we cannot explain the artifact by reaching another electronic state in a deformed structure. Although the constrained geometry optimization was only done, during the following Cartesian-coordinate vibrational analysis the first derivatives with respect to the Cartesian coordinates are calculated, too. Hence, a check that the localized structure is a stationary point in the full coordinate space was indeed done. Moreover, there are six practically zero frequencies, representing the translations and rotations of the system as a whole. With the exception of the one very high frequency there is no apparent irregularity in the spectrum. We believe that the high frequency can be considered as a kind of a failure of the MP2/6-31G* treatment. Anyhow, as the D₄h species does not represent our required activated complex we do not analyze its nature further.

After elimination of the D₄h structure, and an analysis of the eigenvectors with the imaginary frequencies for both the D₄h and C₄h [17] structures, we selected another candidate for the activated complex, viz. a C₂h structure (Fig. 2). The new species is composed of two mutually rotated rhomboids and exhibits seven geometrical degrees of freedom. Hence, the geometry optimization was a more demanding matter. It should be noticed that an otherwise effec-
Table 1
Structures and energies of two planar cyclic saddle points on the MP2/6-31G* hypersurface of C₈

<table>
<thead>
<tr>
<th>Structure</th>
<th>Structural parameters *</th>
<th>( t ) b</th>
<th>( E_{\text{total}} ) (au)</th>
<th>( \Delta E_{\text{rel}} ) c (kJ/mol)</th>
</tr>
</thead>
</table>
| \( \text{D}_{4h} \) | CC=1.325 \( ^d \)  \\
|           | \( \angle C_1C_2C_3 = 99.55 \) \( ^d \)  \\
|           | \( C_1C_8 = 1.259 \) *  \\
|           | \( C_2C_7 = 1.401 \) *  \\
|           | \( C_3C_6 = 1.271 \) *  \\
|           | \( C_4C_5 = 1.375 \) *  \\
|           | \( \angle C_1C_2C_3 = 90.24 \) *  \\
|           | \( \angle C_2C_3C_4 = 167.24 \) *  \\
|           | \( \angle C_3C_4C_5 = 113.81 \) *  | 2 | -303.49134 | 71.15 |
| \( \text{C}_{2h} \) | 1 | -303.49800 | 53.66 |

*a Bond lengths in Å, bond angles in deg.

*b The number of imaginary vibrational frequencies.

*c Related to the minimum-energy structure of \( \text{D}_{4h} \) symmetry [17].

*d See Fig. 1.  * See Fig. 2.

Fig. 2. Planar \( \text{C}_{2h} \) structure of \( \text{C}_8 \). It is composed of two mutually rotated rhomboids (for the MP2/6-31G* optimal structural parameters, see Table 1).

Table 2 presents the critical test of the \( \text{C}_{2h} \) structure – its harmonic vibrational analysis. The symmetry structure of the modes reads in this case:

\[
\Gamma_{\text{C}_{2h}} = 7A_g + 3A_u + 2B_g + 6B_u. \quad (2)
\]

There is just one imaginary vibrational frequency, 116i cm⁻¹, in the spectrum (which indeed belongs to the studied interconversion motion) so that we deal with the activated complex. It should be noted that, in contrast to the \( \text{D}_{4h} \) structure, there is no apparent irregularity in the frequency values. According to the symmetry selection rules, only the \( A_u \) and \( B_u \) modes can be IR active and their calculated intensities are included in Table 2 (an activated complex could, in principle, be stabilized by an interaction with a solid matrix, though it would perturb the frequency values).

The \( \text{D}_{2d} \) local energy minimum reported in Ref. [17] exhibits equal (relatively short) CC bonds. Thus, it can be described as a nonplanar cycle of cumulated double bonds. Before this structure can be considered as the \( \text{C}_8 \) ground state, triplet electronic states should also be checked. Table 3 completes the \( \text{C}_8 \) picture with the information. We were able to localize two stationary points with triplet electronic states, both possessing the planar \( \text{D}_{4h} \) form (Fig. 1). The lower of the states is located about 68 kJ/mol above the supposed ground state of the \( \text{D}_{2d} \) symmetry. Hence, computations predict a low-lying \( \text{C}_8 \) triplet state. We were unable to find a triplet stationary state for other point groups of symmetry relevant for the singlet states. We also checked the triplet–singlet separations at the Hartree–Fock level (HF/6-31G*)
Table 2
MP2/6-31G* harmonic vibrational frequencies * for the C_{2h} activated complex

<table>
<thead>
<tr>
<th>Mode symmetry</th>
<th>ω_{n} (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A_{g}</td>
<td>132</td>
</tr>
<tr>
<td></td>
<td>1243</td>
</tr>
<tr>
<td>A_{u}</td>
<td>116 (0.4)</td>
</tr>
<tr>
<td></td>
<td>452 (0.4)</td>
</tr>
<tr>
<td></td>
<td>529 (58)</td>
</tr>
<tr>
<td>B_{g}</td>
<td>374</td>
</tr>
<tr>
<td></td>
<td>483</td>
</tr>
<tr>
<td>B_{u}</td>
<td>273 (104)</td>
</tr>
<tr>
<td></td>
<td>594 (99)</td>
</tr>
<tr>
<td></td>
<td>1006 (92)</td>
</tr>
<tr>
<td></td>
<td>1174 (80)</td>
</tr>
<tr>
<td></td>
<td>2017 (748)</td>
</tr>
<tr>
<td></td>
<td>2154 (1706)</td>
</tr>
</tbody>
</table>

* IR intensities (km/mol) are given in parentheses (if non-zero). The imaginary frequency is expressed by means of i = √−1.

Table 3
MP2/6-31G* structure and energy of two C_{8} stationary points in triplet electronic state

<table>
<thead>
<tr>
<th>Structure symmetry</th>
<th>Structural parameters *</th>
<th>Electronic state</th>
<th>E_{total} (au)</th>
<th>ΔE_{mol} (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D_{2h}</td>
<td>CC = 1.319 \text{ Å} \quad \angle C_{1}C_{2}C_{3} = 105.98 ° \text{ deg}</td>
<td>$^{3}A_{2g}$</td>
<td>-303.49259</td>
<td>67.86</td>
</tr>
<tr>
<td>D_{2h}</td>
<td>CC = 1.346 \text{ Å} \quad \angle C_{1}C_{2}C_{3} = 99.96 ° \text{ deg}</td>
<td>$^{3}B_{1u}$</td>
<td>-303.45203</td>
<td>174.4</td>
</tr>
</tbody>
</table>

* Bond lengths in Å, bond angles in deg.
* Related to the singlet minimum-energy structure of D_{2d} symmetry [17].
* See Fig. 1.

in the MP2/6-31G* optimized geometries. The triplet states were found 248 and 125 kJ/mol above the single states in the D_{2d} and C_{2h} stationary points, respectively. Finally, for the former structure we tried to examine stability of the Hartree–Fock wavefunction using the stability-testing option [33], however, the treatment could not be finished owing to convergence difficulties.

The C_{2h} structure enables evaluation of the C_{8} inversion barrier as 53.4 kJ/mol at the MP2/6-31G* level. Hence, it turns out that there is not a substantial gain with respect to the previous, already significantly small, upper bound [17]. Incidentally, this similarity of the two potential barriers can serve as an indication of a pseudo-rotation motion in the ring, recalling to the original cyclopentane case [35]. Although the inversion barrier could be computed at a still more sophisticated level, we do not expect that it should change the conclusion on its relatively low value. Such low inversion barrier should cause splitting into symmetric and anti-symmetric levels as it is well known from the ammonia case. Hence, it would be useful to study the inversion motion in a double-well potential. Our search on the MP2/6-31G* potential hypersurfaces reveals interesting structural and energy relationships in the C_{8} system. However, the findings should still be checked at a higher methodical level when computationally possible.

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