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Computational Study of the Stone−Wales Transformation in C_{36}

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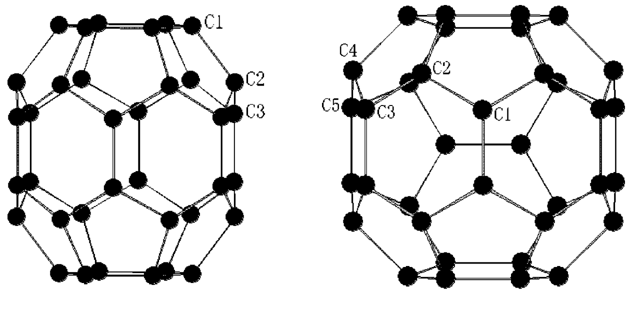
The transition of the D_{6h} neutral and charged isomers to D_{2d} isomers of C_{36} via Stone−Wales transformation has been studied by means of the hybrid density functional method (B3LYP). The results show that the transition state (TS) and reaction pathway could be identified for the rearrangement from C_{36}-D_{6h} to C_{36}-D_{2d} on the potential energy surface. We found that the neutral and charged transition states all have C_2 molecular point group symmetry with the two migrating carbon atoms remaining close to the fullerene surface. The other kind of possible TS with a carbene-like structure along the stepwise reaction path does not exist as a stationary point with the density functionals utilized here. The classical barriers are 6.23 eV through the neutral TS, 6.37 eV through the anionic TS, and 6.29 eV through the cationic TS at the B3LYP/6-31G level of theory.

1. Introduction

Since the discovery[1] and macroscopic scale synthesis[2] of C_{60}, the fullerenes have attracted extensive scientific interest because of their novel and unusual physical and chemical properties. Most researchers have focused mainly on C_{60}, C_{70}, and some larger fullerenes. The bulk synthesis of C_{36} suggests that this situation may be about to change. Piskoti et al.[3] synthesized C_{36} crystal by the arc-discharge method, which is the first time that a fullerene smaller than C_{60} has been produced on a large scale. The C_{36} molecule is far more chemically reactive than C_{60}. This fullerene and its derivatives are believed to make a class of promising materials with new structural and electronic properties, such as covalent bonding, high reactivity, significant steric strain, low gap, high strength, and superconductivity.[4−6] So, scientific interest in the C_{36} fullerene has been growing very rapidly.

Piskoti et al.[3] reported a solid-state nuclear magnetic resonance (NMR) measurement on a C_{36} solid and suggested that the C_{36} molecule has D_{6h} symmetry. However, on the theoretical side, Grossman et al.[7] investigated six likely isomers of the C_{36} molecule using density functional theory (DFT) with both local density and generalized gradient approximations (LDA and GGA, respectively). They predicted the D_{6h} and D_{2d} isomers to be the most favorable structures in energy and to be essentially isoenergetic. Varganov et al.[8] concluded that according to the PM3, HF, and B3LYP methods, the D_{2d} isomer is always more stable than the D_{6h} isomer in the singlet state. In contrast, however, the relative energies calculated with MRMP2 indicated that the D_{6h} singlet is 183 kJ/mol lower in energy than the D_{2d} singlet. Yuan et al.[9] presented an explanation of the experimental fact that the C_{36} molecule with D_{6h} symmetry is found in the soot of the welding process. In the arc-discharge process, the carbon atoms and ions first form C_{36} anions and then the anions are aggregated to form the solid by losing extra electrons. The C_{36}-D_{6h} anion is about 0.2 eV in energy lower than the C_{36}-D_{2d} anion using the DFT method.

In our work, during the optimization of the two isomers of C_{36}, D_{6h} and D_{2d} (shown in Figure 1), we found that the two isomers' structures can be transformed via the Stone−Wales transformation. The discovery of this transformation dates back to 1986, when Stone and Wales pointed out that there are many stable C_{60} isomers which do not follow the well-known isolated pentagon rule and which are related to the I_h form, buckminsterfullerene, involving transformations by the rotation of two carbon atoms around the center of the bond connecting them.[10] The rotation of a C_2 unit by 90° is known in fullerene literature as the Stone−Wales transformation,[11] which enables a pair of hexagons and pair of pentagons to switch places (Figure 2). Holger et al.,[12] applying PBE and B3LYP to study the Stone−Wales transformation of C_{60}-I_h symmetry, found it to yield a C_{60} isomer of C_{2v} symmetry. They found two different transition states and reaction pathways, with the classical barriers of both mechanisms being essentially identical, 6.9 eV using PBE and 7.3 eV with B3LYP. That result led us to pose the following questions: Since the C_{36} molecule in the solid is of D_{6h} symmetry, why can the neutral and charged D_{6h} isomers not be transformed to the D_{2d} structure through a Stone−Wales transformation while in an ambient condition? And how high are the barriers preventing this transformation?



(a) (b)

Figure 1. Geometries of C_{36}: (a) the D_{6h} isomer; (b) the D_{2d} isomer.

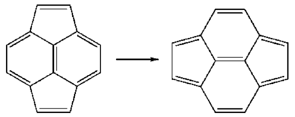


Figure 2. Stone−Wales transformation in fullerene interchange pentagons and hexagons.

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TABLE 1: Energy Differences (eV) for the C_{36} Neutral and Charged Isomers As Computed at Various Levels of Theory Relative to the Neutral D_{6h} Isomer[a]

	energy difference (in eV)					
	neutral		anionic		cationic	
theory	D_{6h}	D_{2d}	D_{6h}	D_{2d}	D_{6h}	D_{2d}
B3LYP/3-21G	0.00	−0.23 (−0.21)	−3.15 (−3.24)	−2.88 (−2.99)	7.05 (7.02)	6.73 (6.74)
B3LYP/6-31G	0.00	−0.24 (−0.23)	−3.00 (−3.09)	−2.79 (−2.89)	6.85 (6.81)	6.49 (6.49)
B3LYP/6-311G*//B3LYP/6-31G	0.00	−0.11 (−0.10)	−3.16 (−3.25)	−2.88 (−2.98)	6.95 (6.91)	6.65 (6.65)

[a] Zero-point vibrational energies (ZPVE) were obtained with the 6-31G basis set, and the ZPVE corrected data are given in parentheses.

In this paper, we perform a comprehensive study of both the neutral and charged C_{36} molecules with the two most likely geometries, D_{6h} and D_{2d} (shown in Figure 1), and the neutral and charged transition states connecting the two isomers in the hope of clarifying the above questions.

2. Computational Details

We employed the semiempirical AM1[13] level of theory, as well as Becke's[14] three-parameter hybrid functional as implemented in the Gaussian[15] program in conjunction with the correlation functional of Lee, Yang, and Parr (B3LYP).[16] Except for the minimal basis set AM1, the basis sets employed were the standard 3-21G,[17] 6-31G,[18] and 6-311G*[19] basis sets. First, full geometry optimization was carried out at the semiempirical AM1 level of theory without any symmetry restriction. Then the AM1 optimized geometry was used as an initial guess for a B3LYP/3-21G and 6-31G geometry optimization in the corresponding symmetry group. The harmonic vibrational frequencies were calculated to ensure true stationary points had been found. Intrinsic reaction coordinates (IRCs) were computed at B3LYP/3-21G for transition structures to establish the connectivity of minima and saddle point. Energies were refined by single point computations at the B3LYP/6-311G* level of theory employing the B3LYP/6-31G geometries (B3LYP/6-311G*//B3LYP/6-31G). Corrections for zero-point vibrational energies (ZPVE) were computed with the 6-31G basis set, and corrected energy differences are given in parentheses in Tables 1 and 2.

3. Results and Discussion

A. Energies, Geometries, and Vibrational Frequencies of Two Molecular Isomers. Many calculations on the C_{36} fullerene have been published since its first observation in 1998.[6] The bond lengths and the infrared-active vibrational frequencies of the neutral D_{6h} and D_{2d} isomers were investigated in our work. Our B3LYP data are in agreement with previous investigations using this hybrid functional.[9,10,20,21]As can be seen from Table 1, the neutral D_{6h} isomer is 0.10−0.24 eV higher in energy than the neutral D_{2d} one, and the cationic D_{6h} isomer is 0.26−0.36 eV higher in energy than the cationic D_{2d} one as well. Whereas the anionic D_{6h} isomer is more stable than the anionic D_{2d} one, the energy difference between them is as large as 0.28 eV. These energy differences are similar to results obtained previously with the hybrid functional.[9,22]

B. Concerted Reaction from C_{36}-D_{6h} to C_{36}-D_{2d}. The search for the transition state (TS) of the concerted Stone−Wales transformation resulted in the C_2 symmetric structure. The neutral TS is depicted in Figure 4. Bond lengths were obtained at the B3LYP/3-21G and the B3LYP/6-31G levels of theory, respectively. The distance between the migrating carbon atoms is reduced from 1.445 Å in C_{36}-D_{6h} (1.443 Å in C_{36}-D_{2d}) to 1.292 Å in the neutral TS. This bond length is close to the one found in alkynes (e.g., the C−C distance is 1.205 Å in acetylene at B3LYP/6-31G*), and hence the bond can be characterized as a stretched triple bond. Considering the Lewis structure given in Figure 3, we found that the neutral TS for the concerted Stone−Wales transformation formally is a diradical.

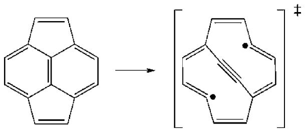

Figure 3. The neutral TS for concerted rotation of a C_2 unit is formally a diradical.

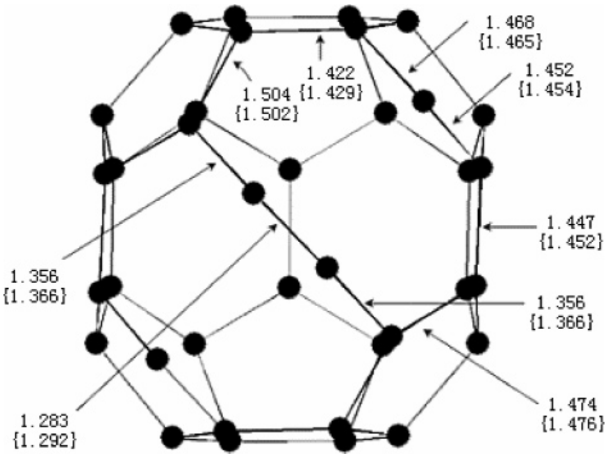

Figure 4. Structure of the C_2 symmetry neutral TS for concerted Stone−Wales transformation in C_{36} fullerene. Bond lengths were obtained at the B3LYP/3-21G and B3LYP/6-31G (in curly brackets) levels of theory and are given in Å.

TABLE 2: Barriers (in eV) for the Stone−Wales Transformation from Neutral and Charged D_{6h} Isomers to Neutral and Charged D_{2d} Isomers, Respectively, through Transition States (the Neutral TS is shown in Figure 4) As Obtained at Various Levels of Theory[a]

method	neutral TS	anionic TS	cationic TS
B3LYP/3-21G	6.32 (6.10)	6.54 (6.38)	6.39 (6.21)
B3LYP/6-31G	6.23 (6.00)	6.37 (6.21)	6.29 (6.11)
B3LYP/6-311G*//B3LYP/6-31G	6.15 (5.93)	6.26 (6.10)	6.46 (6.26)

[a] ZPVE were obtained with the 6-31G basis set, and the ZPVE corrected data are given in parentheses.

The TS structure in Figure 4 is a first-order stationary point, that is, a true TS, at the UB3LYP/6-31G level of theory with an imaginary harmonic vibrational frequency of 823i cm^{-1} (transforming according to the A irreducible representation). The barrier for the concerted rearrangement through the neutral TS is very high with the B3LYP density functional and the largest basis set (Table 2), where a value of 6.15 eV (141.8 kcal mol^{-1}) is obtained. At the same time the barriers through anionic and cationic transition states have been investigated, and they are 6.26 and 6.46 eV, respectively, at the B3LYP/6-311G*//B3LYP/6-31G level. We note that the computed barriers do not significantly depend on the size of the basis set employed since

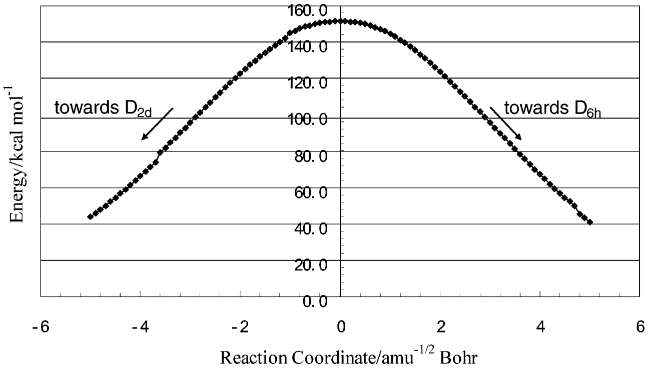

Figure 5. Plot of the intrinsic reaction coordinate (in amu$^{-1/2}$ bohr) versus energy (in kcal mol^{-1}, relative to C_{36}-D_{2d}) starting from the neutral TS as computed at the B3LYP/3-21G level of theory.

the values differ by at most 0.2 eV between 3-21G, 6-31G, and 6-311G*. Finally, correcting our barriers for ZPVE effects results in 5.93, 6.10, and 6.26 eV through neutral, anionic, and cationic transition states, respectively (B3LYP/6-311G*//B3LYP/6-31G). The IRC mapped out in both directions for 50 steps (with a step size of 0.1 amu$^{-1/2}$ bohr) away from the neutral TS shows that the TS indeed connects C_{36}-D_{6h} and C_{36}-D_{2d} without the involvement of any intermediates (Figure 5).

As can be seen from Figure 5, the forward and backward paths both descend steeply toward C_{36}-D_{6h} and C_{36}-D_{2d} fullerenes, respectively. In addition, the trends of descending are almost the same. This can be explained by the computational fact that neutral C_{36}-D_{6h} and C_{36}-D_{2d} are essentially isoenergetic, and they are both the most stable isomers of the C_{36} fullerene.

There are two different transition states connecting C_{60}-I_h and C_{60}-C_{2V} directly.[12] One has C_2 molecular point group symmetry with the two migrating carbon atoms remaining close to the fullerene surface. The other one has a high-energy carbene-like structure. In our research, all of our attempts to locate a TS with a carbene-like structure along the stepwise pathway for the Stone−Wales transformation turned out to be unsuccessful with the hybrid density functionals employed in this study. This is probably because the tension of the C_{36} cage is much larger than that of the C_{60}.

4. Summary and Conclusions

We have found the Stone−Wales transformation in neutral and charged C_{36}-D_{6h} molecules to yield neutral and charged C_{36}-D_{2d} symmetry isomers and have found a channel for the reaction as well. The channel is the concerted 90° rotation of a C_2 unit with a C_2 symmetry TS in which the two rotating carbon atoms are located close to the fullerene surface. The carbine-like TS which exists in the Stone−Wales transformation from C_{60}-I_h to C_{60}-C_{2v} could not be found with the hybrid density functionals employed here. Our investigations of the pathway using intrinsic reaction coordinate computations indicate that there are no intermediate steps along the Stone−Wales transformation pathway. The channel is found to have nearly identical energy requirements, 6.23 eV through the neutral TS, 6.37 eV through the anionic TS, and 6.29 eV through the cationic TS at the B3LYP/6-31G level of theory.

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