

Computational studies on C_{36} and its dimer

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Abstract

The energetics of three competing low-energy isomers of C_{36} (D_{6h} , D_{2d} and C_{2v} forms) in their singlet and triplet states were computed at the AM1, HF/3-21G, HF/6-31G* and B3LYP/6-31G* levels. The most stable structure is predicted to be the D_{6h} isomer with a triplet ground state of $^3A_{2u}$ symmetry. This electronic structure can account for the 'covalent' interactions noted in solid C_{36} . The dimeric structure with D_{2h} symmetry was optimized using the AM1 and HF/3-21G methods. Dimerization is calculated to be energetically favorable. Important changes expected due to dimerization in the vibrational and electronic spectra are pointed out. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The chemistry of fullerenes has been dominated by studies on C_{60} and to some extent on C_{70} . While a few larger fullerenes have also been characterized, systems with less than 60 carbon atoms have received little attention. In principle, fullerenes are conceivable with 12 pentagons and less than 20 hexagons [1]. Such structures inevitably have at least a pair of pentagons fused to each other. Violation of the isolated pentagon rule [2] has been implicated, besides increased pyramidalization at the sp^2 -hybridized carbon centers, as one of the principal reasons for the instability of the smaller fullerenes. Surprisingly, preparation and spectral characterization of C_{36} has been reported recently [3]. The preferred molecular structure has been the subject of some debate.

A systematic enumeration reveals 598 isomers with exclusively 5- and 6-membered rings and numerous additional quasi-fullerene structures with at least one 4-membered ring. A few forms have been repeatedly considered. On the basis of a qualitative examination, a highly symmetric D_{6h} structure was proposed for C_{36} . Feyereisen et al. [4] carried out geometry optimization at the ab initio SCF level using a structure with D_3 symmetry as the initial guess and found that it converged to the D_{6h} form. A more recent density functional calculation using the LDA and GGA methods by Grossman et al. [5] revealed that the D_{6h} isomer is isoenergetic with another fullerene structure with D_{2d} symmetry. A similar result, but with a small energy difference in favor of the D_{6h} isomer, was obtained by a semi-empirical covalent potential study [6]. On the other hand, a comprehensive examination using the semi-empirical SAM1 procedure by Slalina et al. [7] led to the conclusion that the D_{2d} form and a C_{2v} isomer as

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well as a quasi-fullerene structure with C_s symmetry were the most stable isomers. The D_{6h} structure was placed nearly 30 kcal mol⁻¹ higher in energy.

The electronic structure of C_{36} is also an open question. Feyereisen et al. [4] pointed out that the ground state of the D_{6h} structure is a triplet with $^3A_{2g}$ symmetry. However, no further details were provided. Grossman et al. [5] listed relatively low HOMO–LUMO gaps in the singlet states for the D_{6h} and D_{2d} isomers, but did not consider the triplet electronic states. The other computational studies were also restricted to the singlet states, although Slalina et al. [7] have pointed out the Jahn–Teller distortion in the D_{6h} form due to degenerate frontier orbitals. Recently, Fowler et al. have analyzed the Hückel molecular orbitals of C_{36} and also have pointed out the possibility of oligomerization using density functional tight binding calculations [8].

In this Letter, we examine the possibility of open-shell structures for the more stable isomers of C_{36} in detail. The large amount of strain in the carbon skeleton and the high degree of unsaturation may indeed lead to biradicaloid character for most smaller fullerenes, and in particular, also for C_{36} . We report computational evidence using semi-empirical, ab initio and DFT methods in favor of a triplet ground state for C_{36} . We also examine the structure, energies and spectral properties of a dimer of C_{36} .

2. Computational details

Geometry optimizations were carried out on the singlet and triplet states of C_{36} using the semi-empirical AM1 [9] hamiltonian and also ab initio

Hartree–Fock procedure with the split-valence 3-21G basis set [10]. Three structures with D_{6h} , D_{2d} and C_{2v} symmetry (Fig. 1) were considered. Additional computations were performed at the HF/6-31G* level and using the B3LYP procedure [11] in conjunction with the 6-31G* basis set. The spin-unrestricted procedure was used for describing the triplet state. The geometry of the dimeric form with D_{2h} symmetry was optimized using both the AM1 and HF/3-21G methods.

Harmonic vibrational frequencies were computed at the AM1 level. Electronic transition wavelengths and oscillator strengths were computed using the AM1 procedure including configuration interaction [12,13]. All single and pair excitations spanning 18 frontier MOs (PECI = 18) were taken into account.

3. Results and discussion

The computed isomer energies for the singlet states at the AM1 level parallel previous semi-empirical studies. The D_{2d} and C_{2v} forms are substantially lower in energy than the D_{6h} isomer (Table 1). Interestingly, the same trend is found at the HF level too, with both 3-21G and 6-31G* basis sets. However, the D_{6h} isomer is computed to be the most stable isomer at the B3LYP/6-31G* level, which includes electron correlation to a significant extent. As suggested by an earlier DFT study, the D_{2d} isomer is nearly isoenergetic with the D_{6h} form. The C_{2v} structure is indicated to be a higher-energy isomer.

The various isomers have several closely spaced MOs as well as relatively low frontier orbital separations. We therefore considered triplet states derived

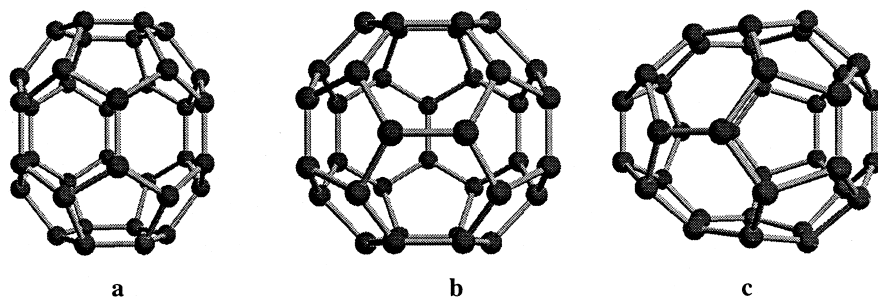


Fig. 1. The structures of C_{36} with: (a) D_{6h} ; (b) D_{2d} ; and (c) C_{2v} symmetry.

Table 1

Calculated AM1 heats of formation (kcal mol^{-1}) and ab initio total energies ($-\text{hartree}$) of the lowest-energy singlet and triplet states of isomers of C_{36}

Method	D_{6h}		D_{2d}		C_{2v}	
	singlet	triplet	singlet	triplet	singlet	triplet
AM1	996.4 (87.3)	949.2 (40.1)	957.7 (48.6)	926.8 (17.7)	966.4 (57.3)	909.1 (0.0)
HF/3-21G	1354.86519 (58.3)	1354.95807 (0.0)	1354.91352 (28.0)	1354.90764 (31.7)	1354.91124 (29.4)	1354.92080 (23.4)
HF/6-31G*	1362.52795 (54.1)	1362.61408 (0.0)	1362.56887 (28.4)	1362.50375 (69.2)	1362.56686 (29.6)	1362.58006 (21.3)
B3LYP/6-31G*	1371.24760 (4.8)	1371.25524 (0.0)	1371.24644 (5.5)	1371.21655 (24.3)	1371.23524 (12.5)	1371.22856 (16.7)

Relative energies in kcal mol^{-1} at each level of theory are given in parentheses.

from HOMO–LUMO excitation. For the D_{6h} form, this involves singly occupied b_{2u} and b_{1g} MOs leading to a ${}^3A_{2u}$ state. While the HOMO of the D_{2d} form is non-degenerate with b_1 symmetry, the LUMO has e symmetry. This implies Jahn–Teller distortion in the corresponding triplet state. The molecule has another MO with a_1 symmetry very close to the e orbital (< 0.01 hartree higher in energy). The triplet state obtained by promoting an electron from the a_1 to the b_1 orbital is expected to retain the D_{2d} structure and hence was examined. For the C_{2v} structure, the HOMO (a_2) to LUMO (b_2) excitation is likely to lead to the lowest-energy triplet (3B_1) state.

The triplet states are calculated to be substantially lower in energy for all the three isomers at the AM1 level. The C_{2v} form is calculated to be the most stable isomer, followed by the D_{2d} form. The triplet D_{6h} isomer is indicated to be the least favored energetically. However, these trends are altered at the ab initio level of calculations. The triplet state of the D_{6h} isomer is found to be preferentially stabilized.

While the computed energy differences are subject to errors because of excessive spin contamination noted in the triplet state wavefunctions, the B3LYP results are likely to be reliable. The most favored structure of C_{36} is predicted to be the triplet state of the D_{6h} isomer. The D_{2d} and C_{2v} isomers are indicated to prefer singlet states, but are higher in energy than the most stable D_{6h} form.

In the above calculations, we have considered open-shell triplets and closed-shell singlet states. What is the likelihood of the D_{6h} isomer preferring to have an open-shell diradicaloid singlet ground state? An analysis of the singly occupied MOs of the triplet state of the D_{6h} isomer is instructive [8]. The MOs (Fig. 2) correspond to in-phase (b_{2u}) and out-of-phase (b_{1g}) combinations of two non-bonding orbitals localized on alternate carbon atoms of the 12-atom cycles in the two halves of the molecule. The splitting between these orbitals arises from long-range through-space and through-bond interactions and is necessarily small. More importantly,

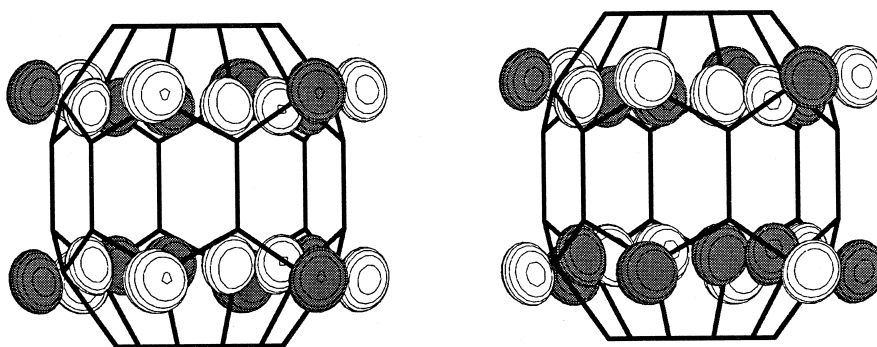


Fig. 2. The frontier orbitals of the D_{6h} isomer of C_{36} .

since the atomic orbital coefficients are concentrated on the same set of atoms, the exchange integral involving these two MOs would have a large magnitude. These two factors must lead to an open-shell triplet ground state, in preference to a closed-shell singlet or an open-shell singlet.

The nonbonding nature of the b_{2u} and b_{1g} orbitals has another interesting consequence. The optimized geometries of the singlet and triplet states of the D_{6h} isomer are remarkably similar. The two equivalent hexagons in the polar region have symmetrical ‘aromatic’ bond lengths of 1.39 Å (HF/3-21G). The six hexagons at the center, forming the hexacene belt, also do not show much bond alternancy, with bond lengths in the range 1.42–1.44 Å. The central hexagons are connected by essentially single bonds, with lengths of 1.50 Å, to the polar hexagons. All these distances are virtually identical in the singlet and triplet states. Redistributing the electrons in the two nonbonding orbitals evidently has no effect on the molecular geometry.

Interestingly, it has been pointed out that C_{36} behaves as a covalent solid [6], unlike fullerenes which are primarily held by van der Waals’ interactions. Interactions involving adjacent spins may be responsible for the unusual nature of solid C_{36} . In order to quantify the magnitude of interaction possible between neighboring C_{36} units, the geometry of the dimer derived from two D_{6h} units was optimized at the AM1 and HF/3-21G levels. In view of the nature of the frontier orbitals of C_{36} , face to face interaction between two hexagon rings of the central hexacene belts is expected to be favorable, leading to the formation of two new C–C bonds. The resulting structure with D_{2h} symmetry (Fig. 3) is indeed calcu-

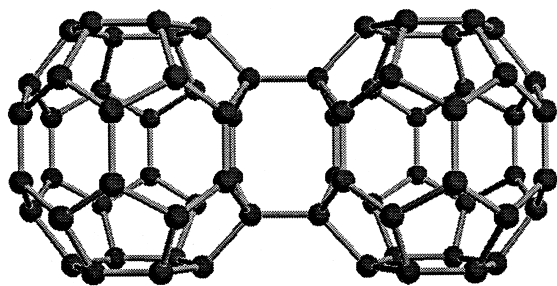


Fig. 3. The structure of $(C_{36})_2$ with D_{2h} symmetry.

Table 2

Calculated AM1 harmonic vibrational frequencies (cm^{-1} , scaled by 0.9) of the IR^a and Raman^b active modes

IR frequencies			Raman frequencies				
1575	1180	871	1580	1303	1057	733	454
1501	1137	814	1539	1295	1030	700	415
1456	1070	800	1522	1265	928	603	342
1305	1059	789	1456	1240	796	567	158
1258	987	759	1402	1178	766	534	
1218	966	702	1358	1148	739	501	

^aData given only for those modes calculated to have intensity greater than 10 km mol^{-1} .

^bData given only for the a_g modes.

lated to be quite stable at both theoretical levels. The dimerization energy is 43 kcal mol^{-1} using the ab initio method and is presumably larger since the triplet state of the monomer is computed using the more flexible UHF procedure. The large stabilization implies that C_{36} is unlikely to be monomeric in the condensed phase.

The newly formed C–C bonds are fairly long at the ab initio level (1.59 Å), indicating the strain involved in the system. Dimerization also results in partial localization and enhanced bond-alternation in the 12-carbon cycles of the hexacene units. These bond lengths vary from 1.34 to 1.46 Å. The dimer is also characterized by an enhanced frontier orbital separation ($> 5.2 \text{ eV}$ at all levels studied), compared to that in the monomer ($< 3 \text{ eV}$).

Based on the computed molecular and electronic structures, the spectral characteristics are expected to differ widely for the monomer and dimer of C_{36} . The singlet state of the monomer, with its low frontier orbital separation, irrespective of the molecular geometry, must have electronic absorption bands at very long wavelengths. We quantified this by a fairly extensive singles and pair excitation configuration interaction calculation spanning 18 frontier orbitals at the AM1 level [12,13] on the D_{6h} isomer. While the longest wavelength absorption at 1056 nm is calculated to be symmetry forbidden, allowed transitions are computed at 827, 627, 409, 296, 282 and 254 nm. On the other hand, if the singlet state is not thermally accessible, the observed electronic spectrum of the monomer must entirely result from triplet–triplet absorption. Since the frontier orbital

separation is substantially greater for the dimer, the electronic absorption bands are computed to have shorter wavelengths. While a band at 594 nm is forbidden, allowed transitions with relatively high oscillator strengths are computed at 505, 457, 392, 319, 290, 272 and 266 nm.

The bond localization associated with dimerization should also lead to increased stretching frequencies in the IR and Raman spectra. Harmonic frequencies of all the infrared active modes, with a calculated intensity of $> 10 \text{ km mol}^{-1}$, and the a_g modes, which are expected to be the prominent bands in the Raman spectra, are provided in Table 2.

4. Conclusions

Semi-empirical, ab initio and DFT calculations yield differing energy differences for the isomers of C_{36} . However, at all levels of theory, the D_{6h} isomer is indicated to prefer a triplet ground state with ${}^3A_{2u}$ symmetry. This form is predicted to be the lowest-energy structure for C_{36} using the more reliable procedures. The diradicaloid nature of C_{36} is conducive to covalent bond formation. The dimeric form with D_{2h} symmetry is calculated to be highly stabilized, with a fair degree of bond localization and enhanced frontier orbital separation.

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