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Structure and Stability of C_{48} Fullerenes

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The structure and stability of 27 C_{48} fullerene isomers have been computed at B3LYP. The most stable isomer (**1**) with the least number of shared pentagonal C−C bonds has a [5,6] type structure in C_2 symmetry, but isomers **2**−**4** are very close in energy (within 5 kcal/mol). The vertical ionization potential and the nucleus-independent chemical shift (NICS) at the cage center are computed for the first four most stable isomers to aid experimental study.

Introduction

After the discovery of C_{60},[1] the structure and stability of fullerenes with less than 60 carbons have attracted considerable attention both experimentally and theoretically.[2,3] For example, the experimental generations of C_{36}[4] and C_{20}[5] have been reported, and a set of small fullerenes has been detected with the mass spectroscopic method.[2a] Since the stability of C_{60} is governed by the isolated pentagon rule, i.e., the twelve pentagons have their maximal separation, small fullerenes should obey the same rule.

Among small fullerenes studied, C_{48} has gained special attention as a result of its possible structure flexibility. Using tight binding molecular dynamics, Zhang[6] found that the ground state of C_{48} has a C_2 symmetrical [5,6] structure, in which there are two sets of three fused pentagons sharing two C−C bonds and three sets of two fused pentagons sharing one C−C bond and no isolated pentagons. As a general trend, fullerenes prefer geometries positioning the pentagonal rings as far apart as possible.[6] On the basis of MNDO calculations, Gao and Herndon[7] found a [4,5,6] C_{48} structure with two squares, eight pentagons, and sixteen hexagons in D_{4d} symmetry to be close in energy with a C_1 symmetrical [5,6] isomer, despite the strained squares. Using matching polynomials, Balasubramanian[8] reported a [5,6] C_{48} structure in D_3 symmetry to be the most likely structure. Using local density functional calculation, Dunlap and Taylor[9] calculated a [4,6,8] structure with twelve squares, eight hexagons, and six octagons in O_h symmetry, which is found to be higher in energy than a [5,6] isomer by more than 180 kcal/mol with MNDO.[10] On the basis of a genetic algorithm, Hobday[11] found that the ground state of C_{48} should have a C_2 symmetrical [5,6] structure to be the most stable isomer, in which there are three sets of three fused pentagons sharing two C−C bonds, one set of two fused pentagons sharing one C−C bond, and one isolated pentagon. Recently, the structure and stability of C_{48} cages with deltas and hexagons have been reported by Ceulemans.[12] Theoretically, there are 199 possible fullerene isomers for a C_{48} cage following the isolated pentagon rule,[13] but what is the most stable C_{48} isomer?

In this letter, we present our study on the structure and stability of C_{48} fullerenes on the basis of a selection rule, compared with all literature isomers. It is still not possible at the present time to have all possible isomers of fullerene cages in an easy way due to the fact that the number of isomers increases considerable with the increased cage size. For example, the isomers of C_{34} are 6, while those of C_{68} are 6331.[13] Structures were optimized at B3LYP/6-31G*.[14] Single-point energies at B3LYP/6-311G* are used for discussion, while those at MP2/6-31G* for comparison (MP2/6-311G* gives the same qualitative results as MP2/6-31G* in small fullerene calculations[15]). All calculations were done with the Gaussian 98 program.[16] It is found that the most stable C_{48} structure has the smallest number of shared pentagonal bond (N_{55}) and no squares and deltas, and all the reported literature structures are higher in energy. The optimized structures are shown in Figure 1, and energetic data are listed in Table 1. To aid further experimental study, we computed the vertical ionization potentials of the first four most stable isomers, and the energy as well as the nucleus independent chemical shift (NICS) of their dianions to model the endohedral chemical shifts.[17]

Results and Discussion

Structures. On the basis of the maximal separation of the strained rings, we have constructed 27 isomers for the C_{48} cage and these are shown in Figure 1, although there are 199 possible isomers.[13] Structures **1**−**20** are [5,6] isomers with twelve pentagons and fourteen hexagons. They differ from the separations of the pentagons and the number of fused pentagons. To get the location of the pentagons in an easy way, we introduce a ($n \times F_m$) nomenclature, in which F is the number of the fused pentagons, m is the shared C−C bonds among the fused pentagons, and n is the number of the F_m combination. The sum of $n \times F_m$ is equal to the number of the shared pentagonal C−C bonds. For example, structure **1** has two sets of three fused pentagons sharing two C−C bonds ($2 \times 3_2$), two sets of two fused pentagons sharing one C−C bond ($2 \times 2_1$), and two isolated pentagons without shared C−C bonds ($2 \times 1_0$). The nomenclature for **1** is $(2 \times 3_2) + (2 \times 2_1) + (2 \times 1_0)$, and the number of the C−C bonds sharing fused pentagons is six ($N_{55} = 6$), which is the smallest among isomers **1**−**20**. The nomenclature for other structures is given in Table 1. Isomer **2** is the structure by Zhang having $N_{55} = 7$ and isolated pentagons $(2 \times 3_2) + (3 \times 2_1)$.[6]

Structure **5** has the same nomenclature as **1**; they are different in symmetry and N_{55}. Structures **6**, **7**, **8**, and **9** have the same

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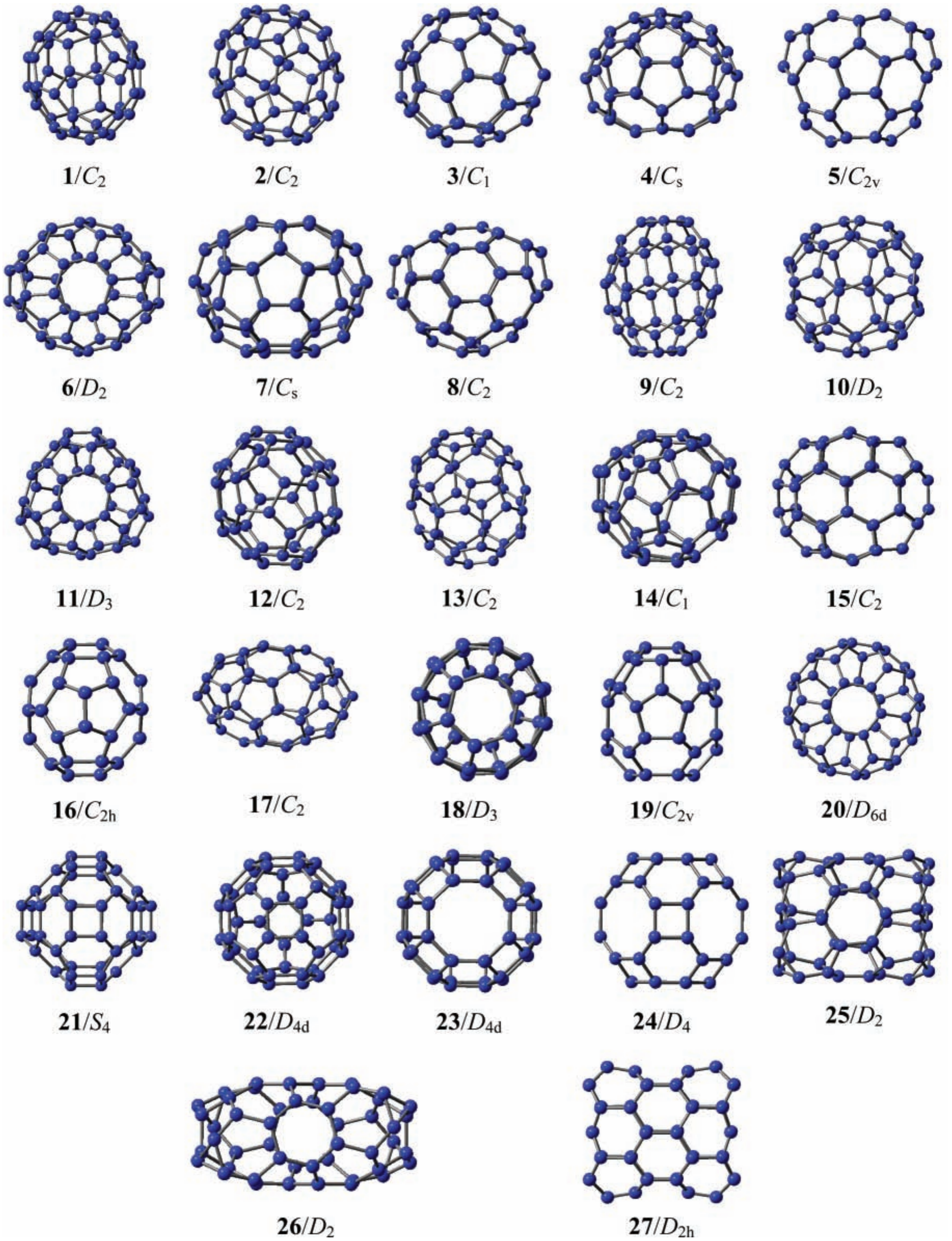

1/C_2 **2**/C_2 **3**/C_1 **4**/C_s **5**/C_{2v}
6/D_2 **7**/C_s **8**/C_2 **9**/C_2 **10**/D_2
11/D_3 **12**/C_2 **13**/C_2 **14**/C_1 **15**/C_2
16/C_{2h} **17**/C_2 **18**/D_3 **19**/C_{2v} **20**/D_{6d}
21/S_4 **22**/D_{4d} **23**/D_{4d} **24**/D_4 **25**/D_2
26/D_2 **27**/D_{2h}

Figure 1. B3LYP/6-31G* C_{48} isomers (**1**−**27**).

nomenclature, and differ with respect to the position of the pentagons. Structure **5** has a nomenclature of $(2 \times 3_3) + (2 \times 2_1) + (2 \times 1_0)$. Structure **11** is the isomer by Balasubramanian.[8]

Structure **21** is S_4 symmetrical with six squares and twenty hexagons [4,6], and all six squares are separated perfectly ($6 \times 1_0$, for six isolated squares). Structure **22** in D_{4d} symmetry with two squares, eight pentagons, and sixteen hexagons is the isomer $(2 \times 1_0) + (8 \times 1_0)$, for two isolated squares and eight isolated pentagons) by Gao and Herdon.[7] Structure **23** is [4,6,8] type in D_{4d} symmetry with eight squares, sixteen hexagons, and two octagons ($8 \times 1_0$, for eight isolated squares). Structure **24** is another [4,6,8] type in D_4 symmetry with twelve square, eight hexagons, and six octagons ($12 \times 1_0$, for twelve isolated squares), but the O_h symmetrical structure has imaginary frequency (379i cm^{-1} at B3LYP/6-31G*), which is eliminated in D_4 symmetry. At B3LYP/6-31G* and MP2/6-31G*, the D_4 isomer is 0.3 and 0.9 kcal/mol more stable that the O_h isomer, but becomes 1.2 kcal/mol less stable at B3LYP/6-311G*. These small energy differences reveal the rather flat potential energy surface. Structures **25**−**27** are [3,6] type with four delta and twenty-two hexagons ($4 \times 1_0$, for four isolated deltas) locating in different positions.

TABLE 1: The Structure Character of C_{48} Cluster Isomers

#	symmetry	sum ($n \times F_m$)	N_{55}	E_{rel}[a,b]
1	C_2-[5,6]	$(2 \times 3_2) + (2 \times 2_1) + (2 \times 1_0)$	6	0.0 (0.0)
2[c]	C_2-[5,6]	$(2 \times 3_2) + (3 \times 2_1)$	7	2.1 (−1.8)
3	C_1-[5,6]	$(3 \times 3_2) + (1 \times 2_1) + (1 \times 1_0)$	7	3.1 (−)
4	C_s-[5,6]	$(3 \times 3_2) + (1 \times 2_1) + (1 \times 1_0)$	7	5.0 (19.0)
5	C_{2v}-[5,6]	$(2 \times 3_3) + (2 \times 2_1) + (2 \times 1_0)$	8	9.9 (16.5)
6	D_2-[5,6]	$(2 \times 4_3) + (2 \times 2_1) + (0 \times 1_0)$	8	17.8 (30.1)
7	C_s-[5,6]	$(2 \times 4_3) + (1 \times 3_2) + (1 \times 1_0)$	8	20.0 (32.4)
8	C_2-[5,6]	$(2 \times 4_3) + (2 \times 2_1) + (0 \times 1_0)$	8	22.0 (17.1)
9	C_2-[5,6]	$(2 \times 4_3) + (2 \times 2_1) + (0 \times 1_0)$	8	26.6 (28.7)
10	D_2-[5,6]	$4 \times 3_2$	8	29.8 (41.7)
11[d]	D_3-[5,6]	$3 \times 4_3$	9	35.0 (49.6)
12	C_2-[5,6]	$(1 \times 6_5) + (2 \times 3_2)$	9	43.6 (45.7)
13	C_2-[5,6]	$(2 \times 5_4) + (1 \times 2_1)$	9	45.7 (45.7)
14	C_1-[5,6]	$(1 \times 5_4) + (1 \times 4_3) + (1 \times 3_2)$	9	54.0 (−)
15	C_2-[5,6]	$(1 \times 6_5) + (2 \times 3_2)$	9	70.6 (75.3)
16	C_{2h}-[5,6]	$(2 \times 4_5) + (4 \times 1_0)$	10	72.4 (88.0)
17	C_2-[5,6]	$(2 \times 4_5) + (1 \times 2_1) + (2 \times 1_0)$	11	81.4 (100.2)
18	D_3-[5,6]	$2 \times 6_6$	12	111.7 (70.0)
19	C_{2v}-[5,6]	$(2 \times 4_5) + (2 \times 2_1)$	12	122.9 (147.5)
20	D_{6d}-[5,6]	$1 \times 12_{12}$	12	204.4 (225.8)
21	S_4-[4,6]	$6 \times 1_0$	0	242.8 (269.7)
22[e]	D_{4d}-[4,5,6]	$(2 \times 1_0) + (8 \times 1_0)$	0	13.4 (35.6)
23	D_{4d}-[4,6,8]	$8 \times 1_0$	0	220.6 (268.0)
24[f]	D_4-[4,6,8]	$12 \times 1_0$	0	346.0 (430.3)
25[g]	D_2-[3,6]	$4 \times 1_0$	0	460.1 (465.1)
26[g]	D_2-[3,6]	$4 \times 1_0$	0	483.7 (473.8)
27[g]	D_{2h}-[3,6]	$4 \times 1_0$	0	470.0 (473.8)

[a] At B3LYP/6-311G*. [b] At MP2/6-31G* in parentheses. [c] Ref 6. [d] Ref 8. [e] Ref 7. [f] Relaxed from the O_h structure in ref 9. [g] Ref 11.

TABLE 2: HOMO−LUMO Gap (eV), Relative Energies (kcal/mol), Vertical Ionization potential (VIP, eV), and NICS Values (ppm) for 1−4

	1	**2**	**3**	**4**
gap[a]	1.56	1.16	1.30	1.64
E(triplet)[a,b]	0.0 (^{3}B)	−5.7 (^{3}B)	−2.4 (^{3}A)	7.9 (^{3}A′)
E(T−S)[c]	8.1	0.4	2.6	11.0
VIP[a]	7.92	7.27	7.78	7.08
NICS[d]	−37.4	−24.4	−27.6	−17.3
	1^{2-}	**2**$^{2-}$	**3**$^{2-}$	**4**$^{2-}$
E_{rel}[a]	0.0	−13.6	−0.3	10.3
NICS[d]	−27.1	−40.4	−36.8	−32.0

[a] B3LYP/6-311G*//B3LYP/6-31G*. [b] The symmetry state of the triplet states in parentheses. [c] Energy difference between singlet and triplet. [d] HF-GIAO/6-31+G*//B3LYP/6-31G*.

Stability. The relative energies and the number (N_{55}) of the shared C−C bonds in fused pentagons are summarized in Table 1. For the [5,6] structures, **1** with $N_{55} = 6$ is the most stable isomer at B3LYP. However, it should also be noted that the first four isomers are very close in energy (within 5 kcal/mol) despite their difference in the shared pentagon C−C bonds ($N_{55} = 6$ or 7). In contrast, **2** is the most stable isomer at MP2/6-31G*, and which is 1.8 kcal/mol more stable than isomer **1**.

Due to such very small energy differences and small HOMO−LUMO gaps, we have computed the related triplet states for isomers **1**−**4**. As given in Table 2, the relative stability of the triplet states (**2** > **3** > **1** > **4**) differs from those of the singlet states (**1** > **2** > **3** > **4**). Both triplets of **1** and **4** are higher in energy than the singlets by 8.1 and 11.0 kcal/mol, while the triplets and singlets of **2** and **3** are very close in energy (0.4 and 2.6 kcal/mol). However, the most stable singlet **1** is more stable than the most stable triplet **2** by 2.5 kcal/mol; therefore, the potential energy surface might be dominated by the singlet states.

With increased number of N_{55}, the relative energies increase considerably (Table 1). For example, structures **5**−**10** with eight N_{55} bonds ($N_{55} = 8$) are higher in energy than isomer **1**. The same is also true for isomers **11**−**15** with $N_{55} = 9$. It is interesting to note that the most stable isomer (**11**) from matching polynomials[8] is higher in energy than **1** by 35 kcal/mol. The least stable [5,6] type isomer is structure **20** with $N_{55} = 12$, and higher in energy than **1** by 204 kcal/mol at B3LYP or 225 kcal/mol at MP2.

On the basis of the enhanced strain in four- and three-membered rings, it is to be expected that structures **22**−**24** and **25**−**27** should be higher in energy, and this is indicated by our calculations (Table 1). However, it is interesting to note that the [4,5,6] structure (**22**) by Gao and Herdon[7] is much more stable than the other [4,6] and [4,6,8] structures and only 13.4 kcal/mol higher in energy than **1**. This energy difference is close to that (9.0 kcal/mol) from MNDO calculation. As shown in Table 1, the [3,6] isomers are more than 460 kcal/mol higher in energy than **1** at both B3LYP and MP2.

To aid experimental study, we have computed the vertical ionization energies (VIP) for the first four most stable singlet states (**1**−**4**). As shown in Table 2, the most stable singlet state **1** has the largest VIP (7.92 eV), while structure **4** has the smallest VIP (7.08 eV). The difference between **1** and **2** is 0.65 eV, which is large enough for quantitative analysis.

In addition to the neutral isomers, we have computed the dianion structures of **1**−**4**. As shown in Table 2, the most stable dianion is structure **2**$^{2-}$ (−13.6 kcal/mol), and the other isomers (**3**$^{2-}$, −0.3; **1**$^{2-}$, 0.0; and **4**$^{2-}$, 10.3 kcal/mol) are higher in energy.

Aromaticity. Recently, Hirsch[18] has proposed the $2(N + 1)^2$ rule to represent the spherical analogy to the $4N + 2$ rule for annulene systems and demonstrated that the aromaticity and cluster distortions of the fullerenes depend on the number of delocalized π electrons in the valence shell. Since the C_{48}^{2-} cage has 50 valence electrons, which fulfills the spherical counting rule ($N = 4$). It is therefore interesting to get the insight of the electron delocalization or the aromaticity of both neutral and dianion species of **1**−**4**. Experimentally, the ^{3}He NMR chemical shift is an effective aromaticity probe for fullerenes,[19] and theoretically the calculated nucleus independent chemical shift (NICS)[17] has proved to be a simple and sufficient criterion of aromaticity. Since the endohedral ^{3}He NMR chemical shifts agree well with the calculated NICS values at the cage centers, the easily computed NICS values instead of δ^3He have been used to characterize fullerenes, which enables the so-called NICS characterization.[20]

As shown in Table 2, the most stable singlet **1** has the largest NICS value (−37.4 ppm) in magnitude, indicating the enhanced aromaticity, while the less stable neutral isomers **2**−**4** have relatively smaller NICS values. In the case of the dianions, the most stable **2**$^{2-}$ has also the most negative NICS value (−40.4 ppm) and those of the less stable isomers are smaller (Table 2). It is interesting to note that the NICS value from **1** to **1**$^{2-}$ has a downfield shift of 10.3 ppm, while that from **2** to **2**$^{2-}$ has an upfield shift of 16.0 ppm. This behavior might be used to identify the possible structure of the most stable [5,6] C_{48} fullerene.

Conclusion

In summary, the structure and stability of twenty-seven C_{48} fullerenes have been investigated theoretically. In comparison with the available isomers from literature, our C_{48} isomer (**1**) with the least number of shared pentagonal C−C bonds ($N_{55} =$

6) is the most stable structure and has the largest vertical ionization potential. However, the low-lying isomers **2**−**4** are very close in energy, and the most stable triplet state is structure **2**. In addition, we have also computed the dianion species of **1**−**4**, and the most stable dianion is $\mathbf{2}^{2-}$. Both the stable neutral isomer (**1**) and dianion ($\mathbf{2}^{2-}$) have the largest NICS values. By reduction into dianion, it is found that isomer **1** has a downfield shift of NICS, while isomer **2** has an upfield shift of NICS.

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Supporting Information Available: Total electronic energies and zero-point energies (ZPE) as well HOMO−LUMO gap. This material is available free of charge via the Internet at http://pubs.acs.org.

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