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# Electronic Structure and Stability of C<sub>86</sub> Fullerene Isolated-Pentagon-Rule Isomers

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*Received 1 December 2009; accepted 21 January 2010*

*Published online 19 May 2010 in Wiley Online Library (wileyonlinelibrary.com).*

*DOI 10.1002/qua.22603*

**ABSTRACT:** All 19 Isolated-Pentagon-Rule isomers of fullerene C<sub>86</sub> were investigated by Density Functional Theory (DFT) methods with B3LYP functional at 6-31G, 6-31G\*, and 6-31+G\* levels. Preliminary distribution of single, double, and delocalized pi-bonds in molecules of these isomers of fullerene C<sub>86</sub> is fulfilled. Obtained results are perfectly supported by DFT quantum-chemical calculations of electronic and geometrical structures of these isomers. The main reason of instability of isomers 1, 3–15, 18, and 19 are phenalenyl-radical substructures. Thus, there is a possibility to obtain them only as endohedral metallofullerenes or exohedral derivatives. Isomer 2 (C<sub>2</sub>) is unstable due to higher local molecular strain. It is shown that empty C<sub>86</sub> may be produced and extracted only as isomers 16 (C<sub>s</sub>) and 17 (C<sub>2</sub>). ©2010 Wiley Periodicals, Inc. *Int J Quantum Chem* 111: 2966–2971, 2011

**Key words:** IPR fullerene C<sub>86</sub>; stability; structure; bonds distribution

## Introduction

A search of the criteria of stability of fullerene molecules is an important task in view of their prospective practical applications. Experimental studies of higher fullerenes are substantially limited by difficulties of their production. There is a significant volume of structural infor-

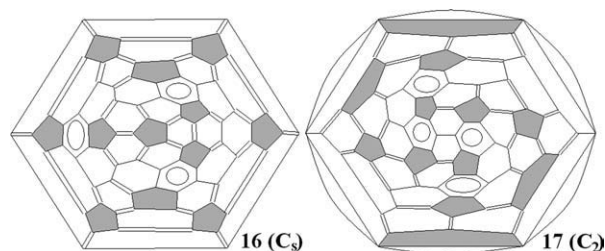
mation for the most accessible fullerenes C<sub>60</sub> and C<sub>70</sub> as well as for some higher fullerenes such as C<sub>84</sub>. Very few publications are devoted to structural investigations of fullerene C<sub>86</sub> due to a lack of produced and isolated species of C<sub>86</sub>.

Fullerene C<sub>86</sub> is well known to have 19 isomers, according to the isolated pentagon rule (IPR) [1]. According to the literature, only two isomers with symmetries C<sub>s</sub> and C<sub>2</sub> are extracted and tentatively characterized by <sup>13</sup>C NMR [2]. Based on quantum-chemical calculations, these isomers were assigned as isomers 16 and 17, respectively [3–6] (see Fig. 1). Two isomers were

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Contract grant sponsor: President of Russian Federation.

Contract grant number: MK-3166.2008.3.



**FIGURE 1.** Schlegel diagrams of stable (experimentally produced) IPR isomers 16 (C<sub>s</sub>) and 17 (C<sub>2</sub>) of fullerene C<sub>86</sub> (hereinafter, all pentagons are marked gray; single and double bonds are marked with single and double lines, respectively; delocalized pi-bonds in hexagons are marked by circle).

produced as endohedral metallofullerenes Sc<sub>2</sub>@C<sub>86</sub>, but they have not been identified [7]. Based on the results of the calculations of C<sub>86</sub><sup>6-</sup> [8], isomer 19 (D<sub>3</sub>) was suggested as the most probable cage structure for endohedral metallofullerene Tb<sub>3</sub>N@C<sub>86</sub>, Tm<sub>3</sub>N@C<sub>86</sub>, and Dy<sub>3</sub>N@C<sub>86</sub> which agrees with X-ray crystallographic studies of Tb<sub>3</sub>N@C<sub>86</sub> [9]. Recently, isomer 19 (D<sub>3</sub>) also was assigned for Y<sub>3</sub>N@C<sub>86</sub> [10].

It has not yet been explained why other isomers cannot be obtained as “empty” molecules. Generally, an instability of fullerenes can be caused by the presence of uncoupled electrons in a molecule (an open shell) and/or by the strain of a molecule caused by cage distortions [11]. In fact, an apparent discrepancy between higher stability and a strain (per one carbon atom) in molecules C<sub>60</sub> and C<sub>70</sub> greater than the strain in other higher fullerene molecules shows a strong influence of the fullerene envelope topology. More uniform distribution of the pentagons (C<sub>60</sub>, C<sub>70</sub>, isomers 23 and 22 of fullerene C<sub>84</sub>) defines their high stability [12]. “Missing” fullerenes C<sub>74</sub> and C<sub>72</sub> are characteristic examples of these two types of instability [13]. In the present work, we attempt to establish how instability of fullerene C<sub>86</sub> isomers is connected with their electronic and geometrical structure and to predict the possibility of their production. For this purpose, an analysis of energy and geometrical parameters of molecules of 19 C<sub>86</sub> fullerene IPR isomers were carried out on the basis of earlier developed criteria [14] followed by DFT calculations.

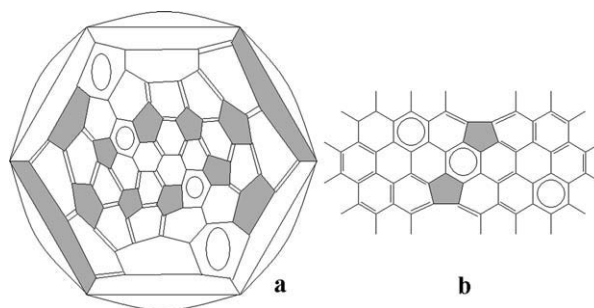
We have developed an approach based on topological analysis of the molecular structure of fullerenes [11–16]. It allows for predicting the distribution of single, double, and delocalized  $\pi$ -bonds

before carrying out quantum–chemical calculations. Application of this approach allows to identify a number of typical substructures related to their aromatic analogs, such as naphthalene, indacene, pyrene, perylene, corannulene, coronene, etc. In general, these substructures retain their identity in terms of electronic properties irrespective of the fullerene molecule they belong to. Results of bond distributions are presented in the form of Schlegel diagrams with distribution of single, double, and delocalized pi-bonds within the molecules of these isomers (Figs. 1, 2, 3, and 4).

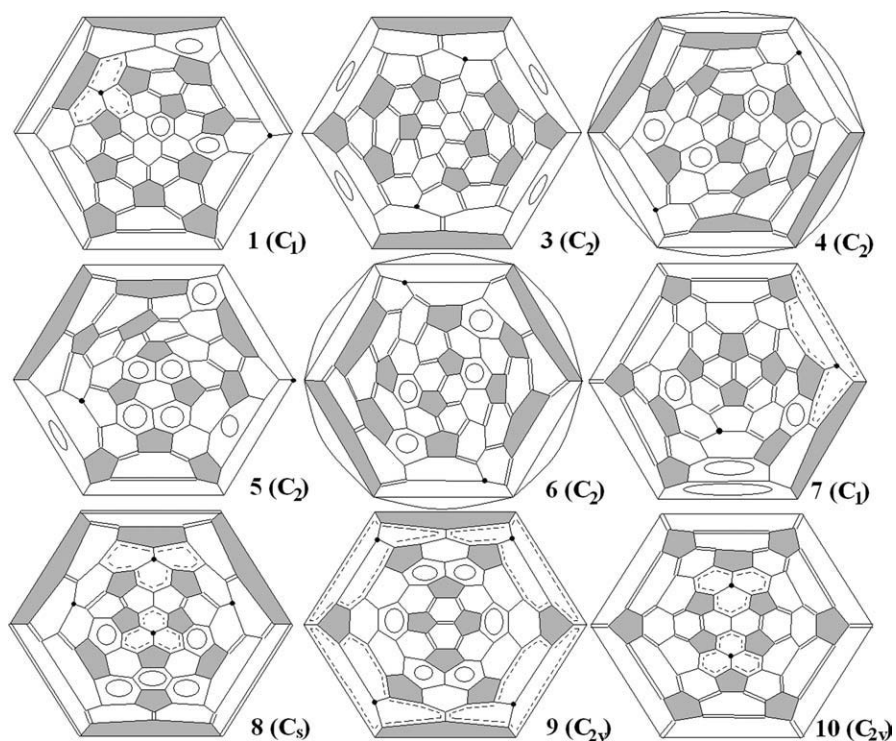
The molecular structures of all IPR isomers were fully optimized using DFT B3LYP functional with 6-31G basis. In the first step, geometry optimization was performed without symmetry constraints. The calculations showed that in all cases the equilibrium geometry was very close to topologic symmetry of each isomer. Therefore, the subsequent optimization was carried out with the corresponding symmetry constraint. To improve energies, geometry optimization was followed by single-point calculation with 6-31G\* and 6-31+G\* basis. Some isomers were suggested as radicals and the quantum–chemical calculations were carried out both in singlet and in triplet configurations using unrestricted Kohn-Sham methodology. Additionally, to provide an asymmetrical initial guess for calculations on singlet biradicals the keyword guess = mix was used. All calculations were carried out using the GAUSSIAN 98 program [17].

## Results and Discussion

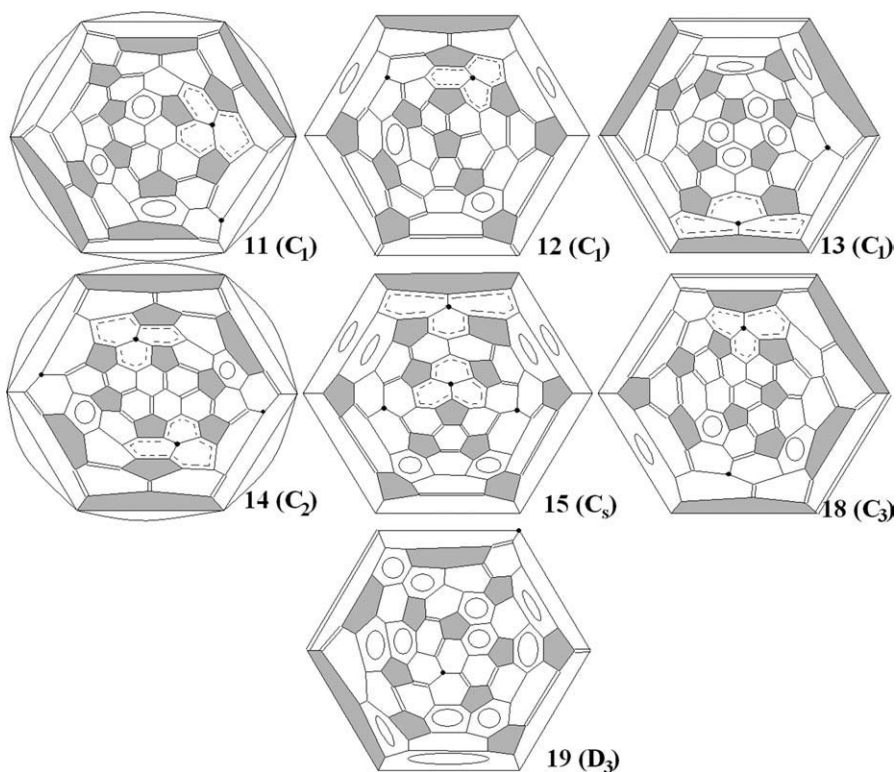
Characteristics of topological and electronic structures of the most stable and isolable isomers



**FIGURE 2.** Schlegel diagrams of unstable IPR isomer 2 (C<sub>2</sub>) of fullerene C<sub>86</sub>.



**FIGURE 3.** Schlegel diagrams of unstable open-shell IPR isomers 1 ( $C_1$ ), 3 ( $C_2$ ), 4 ( $C_2$ ), 5 ( $C_2$ ), 6 ( $C_2$ ), 7 ( $C_1$ ), 8 ( $C_s$ ), 9 ( $C_{2v}$ ), and 10 ( $C_{2v}$ ) of fullerene  $C_{86}$  (hereinafter, phenalenyl-radical substructures are marked with dotted lines).



**FIGURE 4.** Schlegel diagrams of unstable open-shell IPR isomers 11 ( $C_1$ ), 12 ( $C_1$ ), 13 ( $C_1$ ), 14 ( $C_2$ ), 15 ( $C_s$ ), 18 ( $C_3$ ), and 19 ( $D_3$ ) of fullerene  $C_{86}$ .

**TABLE I**  
**Relative energies E (kcal/mol) and HOMO-LUMO gaps (eV) of 19 IPR isomers of fullerene C<sub>86</sub>.**

Fullerene C <sub>86</sub> isomers		E			HOMO-LUMO		6-31+G*
		6-31G	6-31G*	6-31+G*	6-31G	6-31G*	
1 (C <sub>1</sub> )	Singlet	28.52	24.29	26.90	1.10	1.12	1.11
	Triplet	32.47	29.90	31.75	0.75	0.75	0.72
	Singlet biradical	28.52	24.73	27.05	1.10	1.15	1.14
2 (C <sub>2</sub> )	Singlet	29.23	26.26	26.58	2.10	2.10	2.09
	Triplet	57.65	56.21	56.21	0.28	0.25	0.27
3 (C <sub>2</sub> )	Singlet	20.85	17.01	17.49	1.12	1.14	1.13
	Triplet	26.83	23.47	24.42	0.60	0.58	0.57
	Singlet biradical	20.85	12.12	16.95	1.12	1.15	1.14
4 (C <sub>2</sub> )	Singlet	22.01	20.51	20.54	0.90	0.87	0.88
	Triplet	22.05	18.23	20.14	0.89	0.91	0.89
5 (C <sub>1</sub> )	Singlet	21.38	15.82	33.81	1.02	1.00	1.00
	Triplet	25.06	21.24	24.55	0.67	0.68	0.67
6 (C <sub>2</sub> )	Singlet	15.87	19.42	14.76	0.99	0.97	0.96
	Triplet	18.91	18.50	17.31	0.72	0.79	0.74
	Singlet biradical	15.81	12.99	14.76	1.03	1.02	1.01
7 (C <sub>1</sub> )	Singlet	24.94	22.20	24.19	0.88	0.87	0.86
	Triplet	23.79	14.67	22.80	0.95	0.97	0.95
8 (C <sub>s</sub> )	Singlet	36.67	33.33	38.21	0.82	0.82	0.82
	Triplet	36.92	31.12	39.78	0.84	0.82	0.77
9 (C <sub>2v</sub> )	Singlet	43.17	36.61	40.49	0.78	0.79	0.78
	Triplet	42.91	44.39	40.78	0.87	0.81	0.83
	Singlet biradical	42.67	38.74	40.29	0.87	0.81	0.81
10 (C <sub>2v</sub> )	Singlet	18.82	21.36	17.22	1.06	1.06	1.06
	Triplet	21.77	20.35	20.49	0.82	0.82	0.83
	Singlet biradical	18.75	17.18	17.28	1.10	1.10	1.09
11 (C <sub>1</sub> )	Singlet	10.81	16.76	11.23	1.17	1.15	1.14
	Triplet	16.53	7.13	15.64	0.65	0.67	0.67
	Singlet biradical	10.81	5.95	9.37	1.17	1.13	1.12
12 (C <sub>1</sub> )	Singlet	10.79	7.95	11.27	1.20	1.18	1.17
	Triplet	16.77	7.79	15.99	0.68	0.69	0.69
	Singlet biradical	10.79	7.93	11.46	1.20	1.20	1.19
13 (C <sub>1</sub> )	Singlet	14.88	14.90	16.30	1.22	1.19	1.19
	Triplet	20.98	21.43	22.02	0.67	0.69	0.69
	Singlet biradical	14.88	17.88	16.31	1.22	1.21	1.19
14 (C <sub>2</sub> )	Singlet	22.29	21.03	20.89	0.97	0.97	0.95
	Triplet	25.83	11.91	27.75	0.69	0.69	0.68
	Singlet biradical	22.29	21.19	20.17	0.97	1.00	1.00
15 (C <sub>s</sub> )	Singlet	22.67	23.02	21.25	1.07	1.05	1.04
	Triplet	31.11	28.02	29.32	0.55	0.57	0.56
	Singlet biradical	22.67	20.03	21.28	1.07	1.03	1.02
16 (C <sub>s</sub> )	Singlet	6.52	3.26	7.49	1.91	1.88	1.85
	Triplet	28.92	12.94	29.38	0.02	0.01	0.03
17 (C <sub>2</sub> )	Singlet	0.00	0.00	0.00	1.56	1.53	1.50
	Triplet	16.11	15.98	15.28	0.19	0.23	0.28
18 (C <sub>3</sub> )	Singlet	11.87	6.71	12.06	1.14	1.13	1.13
	Triplet	19.41	18.89	19.61	0.48	0.54	0.49
	Singlet biradical	11.87	9.29	12.16	1.14	1.13	1.12
19 (D <sub>3</sub> )	Singlet	24.25	23.22	23.16	1.02	0.99	0.99
	Triplet	29.28	22.83	27.55	0.59	0.62	0.61
	Singlet biradical	24.29	21.51	22.37	1.09	1.06	1.08



17 ( $C_2$ ) and 16 ( $C_s$ ) of fullerene  $C_{86}$  (see Fig. 1) are close to the structure of fullerene  $C_{60}$  and  $C_{70}$ : both have a closed shell, pentagons are rather uniformly distributed by the cage, and both contain corannulene substructures and indacene substructures with delocalized pi-bonds. At the same time, one coronene substructure occurs in isomer 16 ( $C_s$ ) what confirms our previous thesis that their presence becomes less critical for larger fullerenes, which can remain stable [11, 15]. The obtained results of bonds distribution are perfectly supported by DFT calculations.

The quantum-chemical calculations found isomers 17 ( $C_2$ ) and 16 ( $C_s$ ) to be the most energetically favorable (Table I). This agrees with the results of other theoretical studies [3–6]. The third and the last isomer that has closed electronic shell is isomer 2 ( $C_2$ ) [Fig. 2(a)]. However, a pair of adjacent coronene substructures (each one represents a rosette of seven symmetrically condensed hexagons) [Fig. 2(b)] makes its molecule substantially strained leading to thermodynamical instability of this isomer (see Table I). Thus, in Ref. 18 it was shown that the presence of a pair of coronene substructures is the reason of instability of  $C_{72}$  IPR fullerene. These fragments induce essential local strain because these substructures tend to be planar, whereas a fullerene cage must be spherical [12].

Molecules of all other 16 isomers of  $C_{86}$  have either phenalenyl-radical substructures [11] or substructures that suspected to be radical (Figs. 3, 4), i.e., containing two or more unpaired electrons (depicted by dots on Figs. 3, 4), as well as in a case of fullerene  $C_{74}$  [13] or other similar open-shell fullerenes [19–22]. Accordingly they should be kinetically unstable. The possibility of isolation of a fullerene in an individual form is governed by its stability (both thermodynamic and kinetic). We relate those fullerenes that can be synthesized (the thermodynamic stability) and that possess reactivities allowing them to remain unchanged for a long period of time under normal conditions, i.e., on air at room temperature (the kinetic stability) to stable fullerenes [11]. Undoubtedly, the more number of uncoupled electrons on fullerene shell the less stable will be this structure. Thus, there is a possibility to obtain them only as endohedral metallofullerenes or exohedral derivatives.

In fact, quantum-chemical calculations show that the lowest energy wave functions of these unstable open-shell isomers are triplet configura-

tions or singlet biradical (keyword guess = mix). This is in agreement with our estimates (Table I). Additional confirmation of a higher stability of triplet states of these isomers has been revealed by checking the wave function stability, showing that in case of a singlet state of these isomers RHF-to-UHF instability is observed. It means that triplet is a lower-lying state than a singlet. The wave functions of triplet states are stable under the perturbations considered. However, it was found that in some cases singlet configurations are more energetically favorable, which require more careful calculations at higher level of approach.

## Summary

Distribution of single, double, and delocalized pi-bonds in molecules of 19 isomers of fullerene  $C_{86}$  is shown. The main reason of instability of isomers 1, 3–15, 18, and 19 are phenalenyl-radical substructures. Thus, there is a possibility to obtain them only as endohedral metallofullerenes or exohedral derivatives. Isomer 2 ( $C_2$ ) is unstable due to higher local molecular strain. It is shown that empty  $C_{86}$  can be produced and extracted only as isomers 16 ( $C_s$ ) and 17 ( $C_2$ ).

## ACKNOWLEDGMENTS

Calculations were performed in the Supercomputer Center of Kazan Scientific Centre of the Russian Academy of Science.

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