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Stability of small fullerenes C_n (n=36,40 and 60): A topological and molecular orbital approach

Kuniko Nasu[1], Tetsuya Taketsugu[2], Takashi Nakano[2], Umpei Nagashima[3], Haruo Hosoya[3]

[1] Department of Chemistry, Faculty of Science, Ochanomizu University, 2-1-1 Otsuka, Bunkyo-ku, Tokyo 112, Japan

[2] Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

[3] Department of Information Sciences, Faculty of Science, Ochanomizu University, 2-1-1 Otsuka, Bunkyo-ku, Tokyo 112, Japan

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Summary. By semi-empirical molecular orbital calculations stability of fullerenes was analyzed in terms of topological parameters, such as the number of special fragments and the number of three types of abutting bonds between two 5-membered rings. Relative stability was compared by AM1 method for all spectrally distinct closed-shell isomers of C_{36} and C_{40} fullerenes, and for some closed-shell isomers of C_{60} fullerene. Molecular geometries of these fullerenes were also optimized. Their relative stabilities were well explained by the instability of abutting bonds.

Key words: Stability of fullerenes – AM1 method – Topological parameters – Fused 5-membered rings – Abutting bond

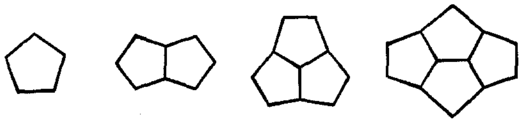
1. Introduction

The proposal of a soccerball structure of C_{60} in 1985 by Kroto et al. [1] has aroused considerable interest in studying experimentally and theoretically the carbon clusters, the so-called fullerenes [2, 3]. Here a fullerene skeleton is to be meant by the "penta-hexahedron", which is composed of only pentagons and hexagons.

According to Euler's rule, a penta-hexahedron has just 12 pentagons. For the discussion of the stability of a fullerene, it is important to examine how 12 pentagons fuse with each other. Fused 5-membered rings bring about larger curvature than isolated pentagons. For a fullerene with small and uniform curvature, the σ-skeleton can nearly achieve the ideal sp^2 geometry with large overlap of adjacent π orbitals. Thus, fused 5-membered rings are regarded to destabilize a fullerene, as suggested by the "isolated pentagon rule" [4]. Actually, no fullerene with fused 5-membered rings has ever been synthesized or extracted.

The degree of local σ strain of pentagons is expected to increase in the order (a) → (d) given in Fig. 1 [5]. A naive discussion is that an eight-membered cycle around the periphery of a pair of 5-membered rings with an abutting bond

Correspondence to: H. Hosoya



(a) (b) (c) (d)

p q r

Fig. 1. Four types of possible fused pentagon configurations (possibly overlapping) in the surface of a fullerene. These configurations seem to exhibit varying degrees of strain-related instability. It is expected that the local strain increases in the order (**a**) → (**d**) [5]. It is indicated that these fragments contribute to the instability of the antiaromatic eight-membered cycle, respectively by 0, $\frac{1}{2}$, 1 and $\frac{5}{4}$ [7]

destabilizes the π electronic energy [6]. Manolopoulos et al. [7] pointed out that the numbers of antiaromatic eight-membered cycles per pentagon for isolated pentagon clusters or isolates of the types (a)–(d) are, respectively, 0, $\frac{1}{2}$, 1 and $\frac{5}{4}$, thus leading to destabilization in this order. Thus, from both σ and π bonding viewpoints, the instability of a fullerene is expected to increase as the 12 pentagons fuse with each other.

In order to examine the effect of fused pentagons upon stability of fullerenes, the molecular fragment method is effective. Schmalz et al. [6, 8] introduced the topological parameters p and q, which are the number of fragments in Fig. 1b and c, respectively. Namely, p and q are, respectively, the numbers of bonds common to two 5-membered rings and of atoms common to three 5-membered rings. The numbers of p and q for various isomers of C_n ($n = 28$–80) have been tabulated [8]. Rough correlation between the π-electronic resonance energy and p has been observed for many fullerenes [6]. However, very few discussions have been given on the analysis of these topological factors, especially on the effect of the third parameter r, which is the number of quadruples of 5-membered rings (Fig. 1d). As another approach based on the molecular fragment method, Balasubramanian et al. expressed nth order moments ($n = 0$–14) of characteristic polynomials in terms of the number of special fragments for fullerenes having no fused-5-membered rings, and proposed the method to predict the stability of fullerene using the relation of moments and Hückel rule [9, 10].

The structure of fullerene can simply be regarded as a spherical skeleton of sp^2 hybridized carbons covered with conjugated π electron clouds. Thus, many previous studies have discussed the stability of fullerenes in the framework of π electron theory [6, 11–19]. Recently, however, Bakowies and Thiel [20] carried out MNDO calculation for 30 fullerenes, and concluded that only 35–40% of the total destabilization is accounted for by the π-electronic part, while the rest must come from σ strain in their model.

The purpose of the present paper is to clarify the topological dependency of the stability of smaller fullerenes, such as C_{36} and C_{40}, with particular reference to the role and meaning of three topological parameters, p, q and r, and also to the effect of σ strain upon the stability of fullerenes. For this purpose we have employed the HMO and AM1 methods.

2. Calculation

It is reported that the number of all spectrally distinct isomers of C_{36}, C_{40} and C_{60} fullerenes are 15, 40 and 1812, respectively [7]. For C_{36} and C_{40} fullerenes, HMO

Table 1. The value of topological parameters $\{p, q, r\}$, ring spiral representations and energies by HMO (in β) and AM1 methods (in eV) for the calculated (a) 13 isomers of C_{36} fullerenes, (b) 37 isomers of C_{40} fullerenes and (c) 14 isomers of C_{60} fullerenes

No.	p	q	r	Ring spiral	HMO	AM1
Calculated 13 isomers of C_{36} fullerenes						
1	12	0	0	6 5 5 6 5 5 6 5 6 5 5 5 6 5 6 5 6 6 5 5	54.787	– 4574.612
2	13	2	0	6 6 5 5 5 6 5 5 5 5 6 6 5 5 6 5 6 5 5 6	54.668	– 4573.148
3	13	2	0	6 6 5 5 5 5 5 5 5 6 5 6 6 6 6 5 6 5 5 5	54.602	– 4573.551
4	13	2	1	6 6 5 5 5 5 5 5 5 5 6 6 6 6 6 6 5 5 5 5	54.664	– 4574.234
5	14	2	0	6 6 6 5 6 5 5 5 5 5 5 5 5 5 6 5 6 6 6	54.566	– 4571.721
6	14	3	1	6 6 5 6 5 5 5 5 6 5 5 5 6 6 5 5 6 5 6	54.604	– 4572.760
7	14	4	1	6 6 5 5 5 6 5 5 5 6 5 6 5 5 6 5 5 6 5 6	54.605	– 4572.938
8	14	4	2	6 6 5 5 5 6 5 5 5 6 6 5 5 5 6 5 5 5 6 6	54.634	– 4573.416
9	15	5	2	6 6 5 5 5 5 6 5 5 6 5 6 5 6 5 5 5 6 5 6	54.411	– 4571.551
10	16	4	2	6 6 6 5 5 5 6 5 5 5 5 5 5 6 5 5 5 6 6 6	54.699	– 4569.799
11	16	6	3	6 6 5 5 5 5 6 5 5 6 5 6 5 5 6 5 5 6 6 5	54.394	– 4570.217
12	16	6	4	6 6 5 5 5 5 6 5 5 6 6 5 5 6 5 5 5 5 6 6	54.299	– 4570.969
13	18	8	6	5 6 5 5 5 5 6 6 6 5 6 6 5 5 5 5 6 6 5 5	54.519	– 4568.506
Calculated 37 isomers of C_{40} fullerenes						
1	10	0	0	6 6 5 6 5 5 5 6 5 5 6 5 5 6 6 5 5 6 5 6 5 6	61.021	– 5087.300
2	10	0	0	6 6 5 6 5 5 5 5 5 6 6 5 5 6 6 6 5 5 5 6 5 6	61.127	– 5086.878
3	11	0	0	6 6 6 6 5 5 5 5 5 5 5 5 5 5 6 6 6 6 6 6 5 5	60.992	– 5085.702
4	11	0	0	6 6 6 5 6 5 5 5 5 5 5 6 5 5 6 6 6 5 6 6 5	60.809	– 5084.674
5	11	0	0	6 6 6 5 6 5 5 5 5 5 5 5 6 5 5 6 6 6 6 5 6 5	60.781	– 5085.136
6	11	1	0	6 6 6 5 5 5 5 6 5 5 5 6 6 5 6 5 5 6 5 5 6 6	60.889	– 5085.056
7	11	1	0	6 6 6 5 5 5 5 6 5 5 5 6 5 6 6 5 5 6 5 6 5 6	60.911	– 5085.320
8	11	2	0	6 6 5 6 5 5 5 6 5 6 5 5 6 5 6 5 5 5 6 5 6 6	60.891	– 5085.554
9	11	2	0	6 6 5 6 5 5 5 6 5 5 6 5 6 5 6 5 5 6 5 5 6 6	60.927	– 5086.202
10	12	1	0	6 6 6 6 5 5 5 5 5 5 5 5 5 6 5 6 6 6 6 5 6 5	60.907	– 5084.014
11	12	1	0	6 5 5 6 6 5 5 5 6 6 5 5 5 6 6 5 6 5 6 5 6 5	60.679	– 5083.048
12	12	2	0	6 6 6 5 5 5 6 5 5 5 5 6 5 6 5 6 5 6 5 6 5 6	60.954	– 5083.972
13	12	2	0	6 6 5 5 5 5 6 5 6 5 6 5 6 6 5 5 5 6 6 5 6 5	60.857	– 5084.266
14	12	2	0	6 6 5 5 5 5 5 6 5 6 6 5 6 6 5 5 6 5 6 6 5 5	60.957	– 5083.663
15	12	2	0	6 6 5 6 5 5 5 5 5 6 5 5 6 6 6 5 6 6 5 5 6 5	60.826	– 5084.614
16	12	2	0	6 6 6 5 5 5 5 5 5 6 5 6 5 6 6 6 5 5 5 6 5 6	60.988	– 5084.364
17	12	2	1	6 6 5 6 5 5 6 5 5 6 5 5 5 6 5 6 5 5 6 6 5 6	60.778	– 5083.695
18	12	3	1	6 6 5 5 5 5 6 5 5 6 6 5 6 6 5 5 6 5 6 5 6 5	60.762	– 5084.194
19	13	2	0	6 6 6 6 5 6 5 5 5 5 5 5 5 5 5 5 6 5 6 6 6 6	61.038	– 5082.470
20	13	3	1	6 6 5 5 5 5 6 5 6 5 6 5 6 5 6 5 5 6 6 6 5 5	60.935	– 5082.967
21	13	3	1	6 5 6 6 5 5 5 5 5 6 5 5 6 6 6 6 5 6 5 5 6 5	60.956	– 5083.118
22	13	3	1	6 6 6 5 5 5 6 5 5 5 5 6 6 5 5 6 5 6 5 5 6 6	60.918	– 5083.633
23	13	4	1	6 5 6 5 5 5 6 5 5 6 6 6 5 6 5 6 5 5 5 6 6 5	60.714	– 5083.337
24	13	4	1	6 6 5 6 5 5 6 5 5 5 6 5 6 5 5 6 5 6 5 5 6 6	60.849	– 5083.441
25	13	4	2	6 6 5 6 5 5 6 5 5 6 5 5 6 5 5 6 5 5 6 5 6 6	60.788	– 5083.301
26	13	4	2	6 5 6 5 6 5 5 5 5 6 5 6 5 6 6 6 5 6 5 5 6 5	60.809	– 5084.027
27	14	4	0	6 6 5 5 5 5 6 6 5 6 5 6 5 6 5 5 5 5 6 6 5 6	60.767	– 5081.805
28	14	4	0	6 6 5 5 5 5 6 5 6 6 5 6 5 6 5 5 5 5 6 6 6 5	60.666	– 5081.529
29	14	4	1	6 6 6 5 5 5 5 5 5 6 5 6 5 6 6 5 6 5 5 6 6 5	60.970	– 5081.981
30	14	4	2	6 6 5 5 5 5 5 6 6 5 6 5 6 6 5 5 5 6 6 6 5 5	60.851	– 5082.391
31	14	5	3	6 5 6 5 6 5 5 5 5 5 6 6 5 6 6 6 6 5 5 5 6 5	60.834	– 5082.614
32	15	4	2	6 6 6 6 5 5 6 5 5 5 5 5 5 5 6 5 5 6 6 6 6	60.894	– 5080.183
33	15	5	2	6 5 6 5 5 5 5 5 6 6 6 5 6 6 6 5 5 5 6 6 5 5	60.850	– 5080.736

Table 1. (Continued)

No.	*p*	*q*	*r*	Ring spiral	HMO	AM1
34	15	5	3	6 5 6 6 5 5 5 5 5 5 6 5 6 6 6 6 6 5 5 5 6 5	60.918	− 5080.629
35	15	6	4	5 6 5 5 5 6 5 6 6 6 5 6 5 6 5 5 6 6 6 5 5 5	60.748	− 5081.191
36	16	6	4	6 5 5 6 6 5 5 5 5 6 5 6 5 6 6 6 6 5 5 5 6 5	60.800	− 5080.346
37	18	8	6	5 5 6 5 5 5 5 6 6 6 6 6 6 6 5 5 6 6 5 5 5 5	60.663	− 5079.323
Calculated 14 isomers of C_{60} fullerenes						
1	0	0	0	5 6 6 6 6 6 5 6 5 6 5 6 5 6 5 6 6 5 6 5 6 5 6 5 6 5 6 6 6 6 6 5	93.162	− 7651.361
2	2	0	0	6 5 6 6 6 5 6 6 6 5 5 6 5 5 6 6 5 6 5 6 6 6 6 6 5 6 5 6 5 6 5 6	92.939	− 7649.288
3	3	0	0	5 6 6 6 6 6 6 5 5 6 5 5 6 6 5 6 5 6 6 6 6 6 5 6 5 6 6 5 6 5 6 5	92.866	− 7648.174
4	3	0	0	6 6 6 5 6 6 5 6 5 5 6 5 6 5 6 5 6 5 6 6 6 6 6 5 6 6 6 5 6 5 6 5	92.607	− 7647.614
5	9	0	0	6 6 6 6 6 6 6 6 5 5 5 6 5 5 5 5 5 5 6 5 6 6 6 6 6 6 6 6 5 5 6 6	92.427	− 7638.340
6	9	0	0	6 6 6 6 6 5 5 6 5 5 6 6 6 6 5 6 6 5 5 6 6 5 5 5 5 5 6 6 6 6 6 6	92.543	− 7639.780
7	9	1	0	6 5 6 6 6 5 6 6 5 6 6 6 6 5 6 6 5 5 6 6 5 5 5 5 5 6 6 5 6 6 6 6	92.448	− 7639.060
8	9	1	0	5 6 6 6 6 6 5 5 6 6 6 6 6 5 6 6 5 6 5 6 5 5 5 5 5 6 6 5 6 6 6 6	92.504	− 7639.590
9	9	1	0	6 5 6 6 5 6 6 6 5 6 6 6 6 5 6 6 5 6 5 6 6 5 5 5 6 6 5 5 6 6 6 5	91.877	− 7640.790
10	9	2	0	5 6 6 6 6 6 6 6 5 5 6 6 6 5 5 6 6 5 5 6 6 5 5 5 6 5 6 6 5 6 6 6	92.350	− 7641.009
11	9	2	0	6 6 6 5 5 6 6 5 5 6 6 6 5 6 5 6 6 6 6 5 5 5 6 6 6 5 5 6 6 6 6 5	92.379	− 7640.563
12	11	2	0	6 6 5 6 6 6 6 5 6 5 5 6 6 6 6 5 6 5 5 6 6 6 5 5 5 5 5 6 6 6 6 6	92.311	− 7635.910
13	11	3	1	6 6 6 6 6 5 6 5 5 6 5 6 6 5 6 6 5 5 6 6 5 5 6 6 5 5 6 6 6 6 6 5	91.873	− 7638.540
14	11	4	1	6 6 5 6 5 6 6 6 6 5 5 6 6 6 6 6 5 5 6 6 6 5 6 5 5 6 6 5 5 6 6 5	92.241	− 7641.390

calculations were performed for all the isomers with closed-shell electronic structure, i.e., 13 and 37 isomers, respectively. In order to compare the topological dependency of smaller and larger fullerenes, HMO calculations were also performed for 14 closed-shell isomers of C_{60} with less σ strain. The *p*, *q* and *r* values and ring spiral representations [21] for all isomers calculated here are given in Table 1. To examine the effect of σ strain, we also performed AM1 calculations for these fullerenes with MOPAC Ver. 6.01 [22]. All geometrical parameters were fully optimized without symmetrical restriction.

3. Results and discussion

3.1 Topological parameters p, q and r

The calculated energies by HMO and AM1 methods for all the isomers are given in Table 1. Table 2 shows correlations of the topological parameter *p* with HMO energy, and with AM1 energy for C_{36}, C_{40} and C_{60} closed-shell fullerenes. Although correlation was not so good in HMO calculation, good results were obtained by AM1 calculations. These results support the necessity for including the effect of σ electron for the MO calculation of fullerenes. Figure 2a–c shows the plots of the AM1 energies versus *p* for C_{36}, C_{40} and C_{60} fullerenes. As shown in these figures, fullerenes get thermodynamically more unstable with the increase of *p*. Thus, fused 5-membered rings are shown to play a dominant role to destabilize fullerenes.

Next, let us consider the correlation between the geometrical structure and the stability of fullerenes. As a structural parameter, the deviation from a sphere is

Table 2. Correlation coefficients between p and HMO energy, and between p and AM1 energy for C_n closed-shell fullerenes (n = 36, 40, and 60). Fitting parameters[a] are also given

n	HMO			AM1		
	Correlation coeff.	Fitting parameter		Correlation coeff.	Fitting parameter	
		A_p	B_p		A_p	B_p
36	0.618	− 0.0505	55.30	0.962	1.061	− 4588
40	0.448	− 0.0278	61.22	0.958	1.042	− 5097
60	0.847	− 0.0823	93.08	0.958	1.231	− 7651

[a] The energy E is fitted to the function, $E = A_p p + B_p$

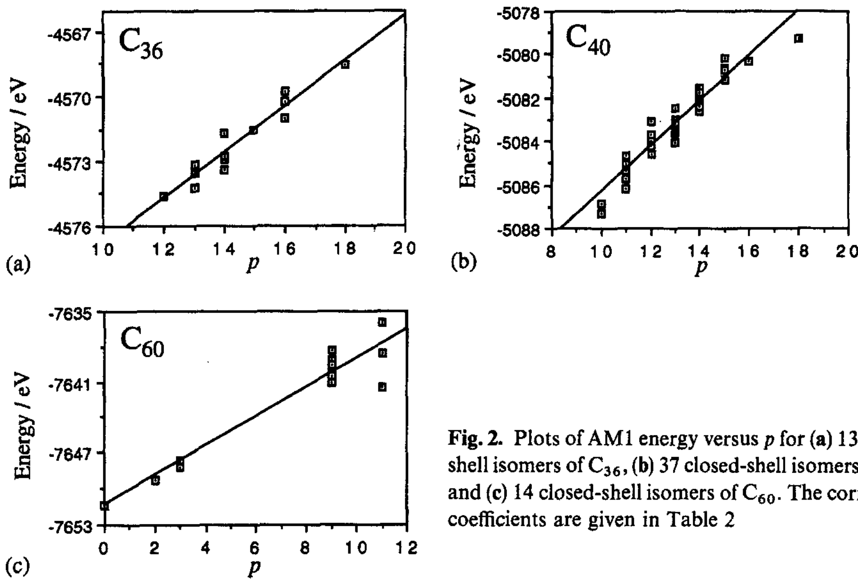


Fig. 2. Plots of AM1 energy versus p for (**a**) 13 closed-shell isomers of C_{36}, (**b**) 37 closed-shell isomers of C_{40}, and (**c**) 14 closed-shell isomers of C_{60}. The correlation coefficients are given in Table 2

considered. Namely, for each isomer, we calculated the standard deviation (s in Å) of the distance from its center of gravity to each atom and divided that value s by the average distance (r_{ave} in Å) from its center of gravity to each atom. Figure 3a shows the plots of p versus s/r_{ave} for the optimized structures of 37 C_{40}-fullerene isomers. It is shown that the steric strain is in some sense reflected to the parameter p in small fullerenes. Figure 3b shows the plots of the AM1 energy versus the deviation from the sphere for C_{40} isomers. It is shown that the closer to a sphere these fullerenes are the more stable they become.

When we discuss the stability of fullerenes in terms of only p, i.e. the number of abutting bonds, instability is equally counted for all the abutting bonds in the fragments, (b), (c) and (d), in Fig. 1. For example, p values are given as 1, 3 and 5 for (b), (c) and (d), respectively. Namely, the relative instability of these fragments is estimated to be 1:3:5 in this order. However, it seems that the instability per abutting bond becomes larger as more pentagons fuse together. Thus, in order to see the effect of abutting bonds in detail, we should take the environment of these

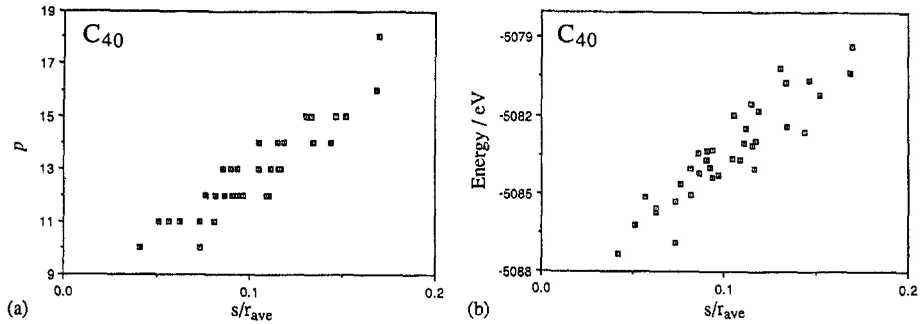


Fig. 3. (**a**) Plots of p versus the deviation of fullerene structure from sphere (s/r_{ave}), and (**b**) plots of AM1 energies versus the deviation (s/r_{ave}) for 37 closed-shell isomers of C_{40} fullerene. The deviation is calculated by dividing standard deviation (s in Å) in the distance from its center of gravity to each atom by the average distance (r_{ave} in Å) from its center of gravity to each atom

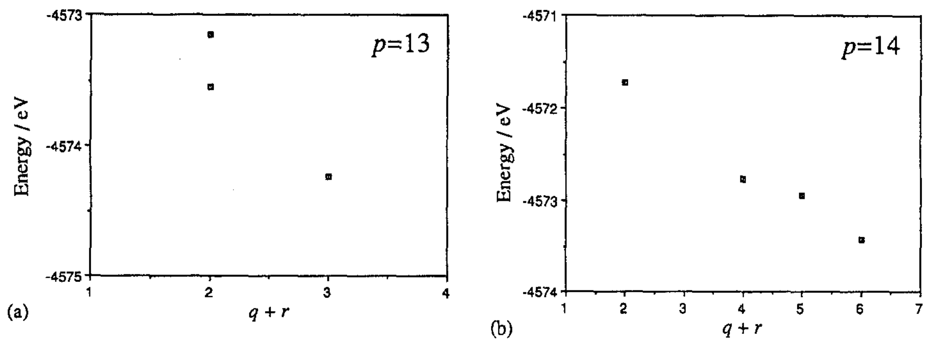


Fig. 4. Plots of AM1 energy versus $q + r$ of C_{36} for (**a**) 3 isomers ($p = 13$) and (**b**) 4 isomers ($p = 14$)

bonds into consideration. For this purpose, the topological parameters, q and r, were employed to see the degree of fusion of 5-membered rings. Fullerenes with large q and/or r value are considered to be more unstable in energy. In Fig. 4, the plots of the AM1 energy versus $q + r$ for isomers of C_{36} fullerenes with (a) $p = 13$ and (b) $p = 14$ are depicted. It suggests, however, that fullerenes with larger q or r value are more stable among the isomers with the same p value (though the number of the data is small). Thus, *q and r seem to work as the stabilizing factors.*

Figure 5 shows the (a) Schlegel diagrams and (b) optimized structures by AM1 calculation for C_{36}-fullerene isomers I and II, which have the same p but different q and r values, namely (14, 4, 2) and (14, 2, 0), respectively. As to total energies, I and II have -4573.42 and -4571.72 eV, respectively. As to deviations from a sphere, s/r_{ave}, I and II have 0.101 and 0.086, respectively. Though the structure of II is closer to a sphere, it is less stable in energy. This result is in contrast to the general tendency observed for the C_{40} isomers shown in Fig. 3b. However, it can be explained from the viewpoint of the degree of fusion of pentagons. As shown in Schlegel diagrams, where thick lines encircle the 5-membered rings, the pentagons in I are more localized than II. This is reflected in the values of q and r. Since q and r work as the stabilizing factors, I is more stable than II.

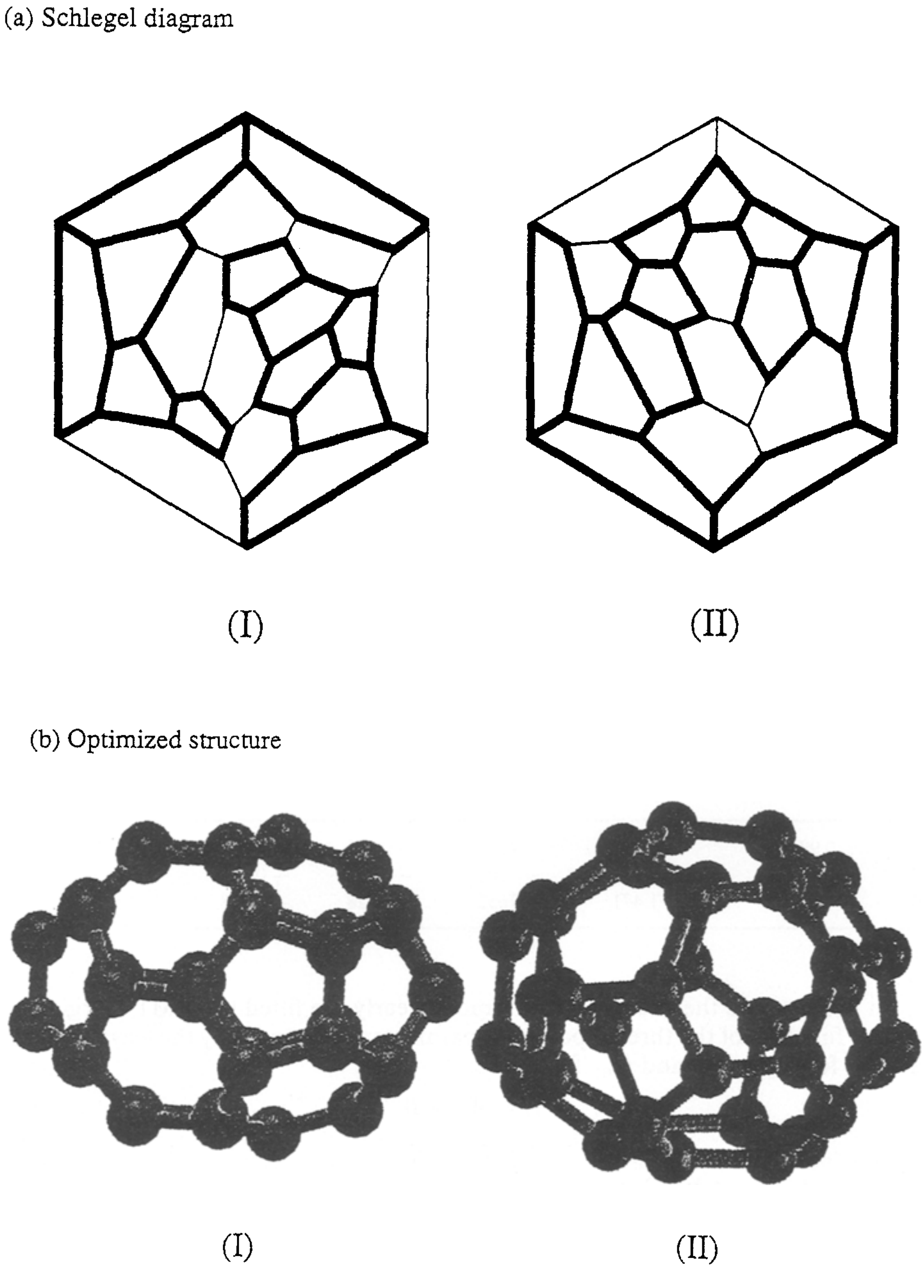
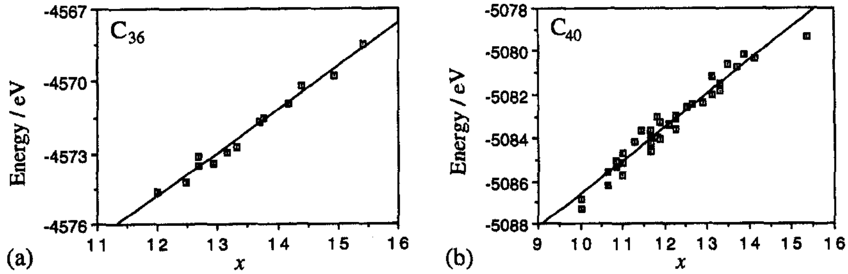


Fig. 5. (**a**) Schlegel diagrams and (**b**) optimized structures by AM1 calculation for two isomers of C_{36} fullerene. Thick lines in (**a**) encircle 5-membered rings. For isomer (I), $p = 14$, $q = 4$ and $r = 2$. For isomer (II), $p = 14$, $q = 2$ and $r = 0$. The deviations from sphere are 0.10128 and 0.08583, and the total energies for isomers (I) and (II) are -4573.42 and -4571.72 eV, respectively



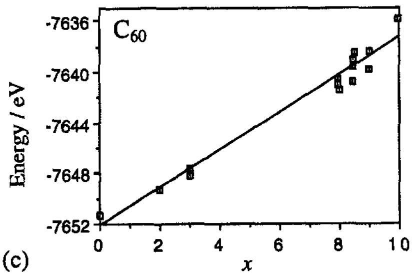


Fig. 6. Plots of AM1 energy versus $x\,(=p+Cq+Dr)$ for (**a**) 13 closed-shell isomers of C_{36}, (**b**) 37 closed-shell isomers of C_{40}, and (**c**) 14 closed-shell isomers of C_{60}. Fitting parameters were obtained based on least-squares method. The correlation coefficients are given in Table 3

Table 3. The correlation coefficients between AM1 energy and linearly fitted function of p, q, and r for C_n closed-shell fullerenes ($n = 36$, 40, and 60). Fitting parameters in Eqs. (1) and (2) were also given

n	Correlation coeff.	Fitting parameter			
		A	B	C	D
36	0.992	1.805	− 4596	− 0.157	− 0.221
40	0.976	1.549	− 5102	− 0.172	− 0.211
60	0.985	1.471	− 7652	− 0.528	− 0.908

In order to see the effect of q and r more clearly, we fitted the AM1 energies to a linear function of the three topological parameters, p, q and r, by the least-squares method for C_{36}, C_{40} and C_{60} fullerenes:

$$E = Ax + B\,, \tag{1}$$

$$x = p + Cq + Dr\,, \tag{2}$$

where A, B, C and D are fitting parameters and E the total energy of fullerene. Figure 6a–c shows the energy profile for each case. The results of fitting are given in Table 3. The correlation coefficient becomes better by adding q and r as independent variables for a fitting function (see Tables 2 and 3). If q and r work as destabilizing factors, C and D in Eq. (2) should have plus sign. However, the signs of C and D were found to be minus; fullerenes with larger q or r value are more stable in total energy as long as they have the same p value. This suggests that the instability due to abutting bonds decreases in the region where more pentagons fuse with each other. If we classify three types of abutting bonds and estimate the instability of each abutting bond as 1, a and b as shown in Fig. 7, the values of a and b are expected to be smaller than 1.

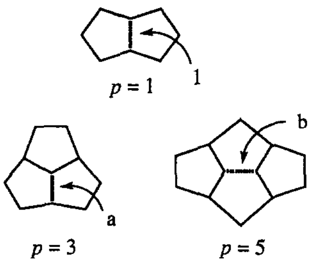


Fig. 7. The instability of three types of abutting bonds in fused pentagon fragments. The degree of instability for abutting bond is denoted by a and b

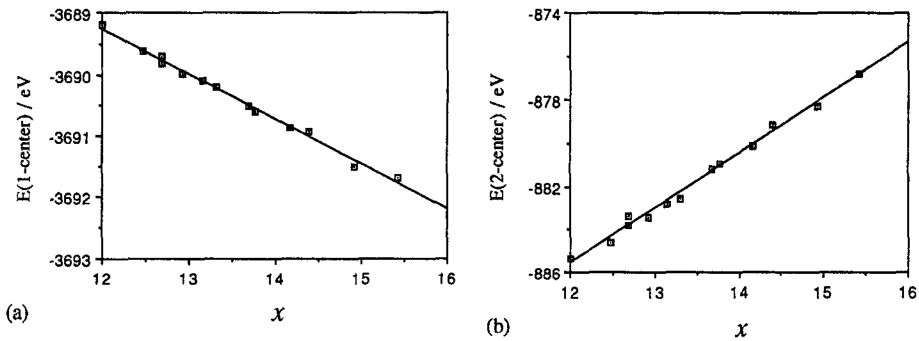


Fig. 8. Plots of (**a**) one-center energy and (**b**) two-center energy, for 13 closed-shell isomers of C_{36} fullerene versus x ($= p + Cq + Dr$): C and D are the values obtained in the fitting of the "total" energy (i.e. C and D in Table 3). The correlation coefficients are 0.997 and 0.995 for one-center and two-center energy, respectively

It should also be noted that the parameters, p, q and r, can be defined differently as follows: p is equal to the number of edges common to two 5-membered rings, q is equal to the number of vertices common to three 5-membered rings, and r is equal to the number of edges surrounded by four 5-membered rings. Namely, p and r count the number of specific bonds, while q the number of specific atoms. Thus, the chosen set of topological parameters, p, q and r, seems to be inconsistent if we analyze the physical meaning of these topological factors. To examine this problem in detail, the energy decomposition was performed in the next section.

3.2 Topological parameters α, β and γ

In the semi-empirical NDDO (neglect of diatomic differential overlap) approximation, three- and four-center two electron repulsion energies are ignored. Therefore, the total energy E_{total} can be represented as the sum of one- and two-center energies;

$$E_{\text{total}} = \sum_{\text{A}} E_{\text{A}} + \sum_{\text{A}} \sum_{\text{B}>\text{A}} E_{\text{AB}}. \tag{3}$$

The two-center energy E_{AB} can be considered approximately as the binding energy for the pair of atoms A and B.

Figure 8 gives the plots of the one- and two-center energies against x in Eq. (2) (i.e. $p + Cq + Dr$, where C and D are the values obtained by fitting of the total

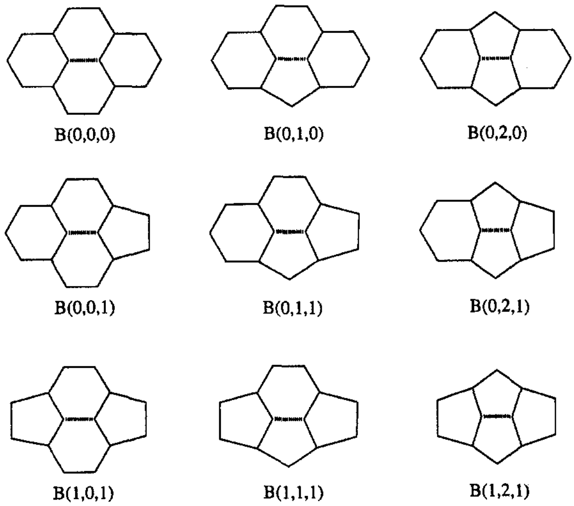


Fig. 9. The nine types of C–C bonds in the network of penta-hexahedra. Each bond, depicted by thick dotted line, is named $B(i, j, k)$ $(0 \leqslant i \leqslant k \leqslant 1, 0 \leqslant j \leqslant 2)$. The abutting bonds correspond to $B(i,2,k)$

energy), for C_{36} fullerenes. Good correlations are obtained for both the cases, meaning that the ratio of the coefficients for p, q and r is almost the same for one- and two-center energies. The one- and two-center energies, respectively, decrease and increase with x. As shown in Fig. 8, the slope of the fitted line for the two-center energy is four times as large as that of the one-center energy. It suggests that the relative stability of fullerene isomers is mainly governed by the two-center energy; in other words, instability of a fullerene is brought about by the instability of bonds.

In order to estimate the degree of instability of bonds in fullerenes, we classified the C–C bonds into nine topological types, $B(i, j, k)$ $(0 \leqslant i \leqslant k \leqslant 1, 0 \leqslant j \leqslant 2)$, as shown in Fig. 9. Then i is the number of 5-membered rings on the left side of the C–C bond, k the number of 5-membered rings on the right side of the C–C bond, and j the number of 5-membered rings containing the C–C bond. This classification is effective as long as we are concerned with penta-hexahedra. The most stable C_{60} fullerene, i.e. the soccer ball, consists of 60 $B(0,1,0)$'s and 30 $B(1,0,1)$'s.

In this scheme, the abutting bonds are represented by $B(i, 2, k)$. Let the number of abutting bonds, $B(0,2,0)$, $B(0,2,1)$ and $B(1,2,1)$, be denoted by α, β and γ, respectively. In contrast to the set of p, q and r, the set of α, β and γ have clear physical meaning.

From topological reasoning we could find a novel relation between the two sets of parameters (p, q, r) and (α, β, γ). Namely, they are related to each other through the linear transformation as

$$\begin{pmatrix} p \\ q \\ r \end{pmatrix} = \begin{pmatrix} 1 & 1 & 1 \\ 0 & 1/3 & 2/3 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}, \tag{4}$$

and these are mathematically equivalent. Substituting Eq. (4) into Eq. (2), we obtain the following equation:

$$x = \alpha + (1 + C/3)\beta + (1 + 2C/3 + D)\gamma. \tag{5}$$

Thus, the AM1 energy can be expressed in terms of the set of α, β and γ. By using the C and D values in Table 4, x can be expressed as

$$C_{36}: \quad x = \alpha + 0.948\beta + 0.674\gamma, \tag{6}$$

$$C_{40}: \quad x = \alpha + 0.943\beta + 0.674\gamma, \tag{7}$$

$$C_{60}: \quad x = \alpha + 0.824\beta - 0.260\gamma. \tag{8}$$

In the previous section, we represented the instability of abutting bonds, $B(0,2,0)$, $B(0,2,1)$ and $B(1,2,1)$, as 1, a and b (see Fig. 7), and predicted that a and b should be smaller than 1 because of the negative coefficients of q and r in the fitted function. In the scheme based on $\{\alpha, \beta, \gamma\}$, a and b correspond to coefficients of β and γ in Eq. (5), respectively, and we can estimate the value of a and b quantitatively. For C_{36} fullerenes, $a = 0.948$ and $b = 0.674$. For C_{40} fullerenes, $a = 0.943$ and $b = 0.674$. For C_{60} fullerenes, $a = 0.824$ and $b = -0.260$. Since $1 > a > b$, the instability of abutting bond decreases in the order of $B(0,2,0)$, $B(0,2,1)$ and $B(1,2,1)$.

The value of b for C_{60} fullerenes is much smaller than those for C_{36} and C_{40} fullerenes. However, as mentioned in the previous section, we calculated only a small fraction of C_{60} isomers. Besides, most of the calculated 14 isomers have the same r (i.e. γ) value "0", as shown in Table 1. Therefore, the values for C_{60} fullerenes, especially the value b, are not expected to be reliable due to insufficiency of the number of data and imbalance of data. The possible errors, though large, in the data are not likely to change the order $1 > a > b$. Namely, contrary to chemical intuition we can conclude that for these fullerenes studied instability of an abutting bond is weakened as pentagons are fused more and more.

4. Conclusion

In this paper, we discussed the effect of fused 5-membered rings on the stability of fullerenes (closed-shell isomers of C_{36}, C_{40} and C_{60}) in terms of topological parameters: $\{p, q, r\}$ and $\{\alpha, \beta, \gamma\}$, which can easily be counted.

By examining the correlation of the number of fused 5-membered rings, p, with HMO and AM1 energies for each C_n ($n = 36, 40$, or 60), we found that p has a good correlation with AM1 energies but no correlation with HMO energies in each case. This result suggests that, even for the qualitative discussion of the stability of fullerenes, the effect of σ electron cannot be removed. From the result of the relation between p and AM1 energies, fused 5-membered rings proved to work as a destabilizing factor for fullerenes.

To see the effect of fusion of pentagons on the stability of fullerenes in detail, we also carried out a linear fitting for AM1 energies with p, q (the number of triples of pentagon), and r (the number of quadruples of pentagon). The correlation coefficients become better. From the result of fitting the parameters q and r proved to behave as stabilizing factors among the fullerenes having the same p value. It suggests that instability of fused 5-membered rings decreases with the increase of degree of fusion of pentagons.

In order to see the above results from the viewpoint of abutting bonds, we introduced topological parameters α, β and γ as the number of abutting bonds, $B(0,2,0)$, $B(0,2,1)$ and $B(1,2,1)$, respectively. The set $\{\alpha, \beta, \gamma\}$ can be related to the set $\{p, q, r\}$ by the linear transformation. From the fitted function in terms of $\{\alpha, \beta, \gamma\}$, the instability of abutting bond was found to decrease in the order of

$B(0,2,0)$, $B(0,2,1)$ and $B(1,2,1)$. Namely, the instability gets weaker in the region where more pentagons fuse mutually. This order of instability of the abutting bonds is contrary to chemical intuition.

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