

**CORRELATION BETWEEN STRAIN ENERGIES OF PROPER  
FULLERENES AND THEIR TOPOLOGICAL INVARIANTS.  
PART II. I FULLERENES WITH ISOLATED PENTAGONS**

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**Abstract.** By selecting 5 or 6 parameters from the 14 possible topological parameters referring to the disposition of the 5- and 6-membered rings around each edge in a proper fullerene with isolated pentagons, it is possible to obtain good correlations with calculated (MM+) energies of fullerenes. The correlations were tested on all isomers of IPR fullerenes with 94 to 100 carbon atoms, and standard deviations around 2.5 kcal/mol were obtained.

**Introduction**

Proper fullerenes  $C_N$  are defined as consisting only of carbon atoms arranged in pentagons and hexagons. All experimentally obtained fullerenes have isolated pentagons. The isolated pentagon rule (IPR) was instrumental in explaining why  $C_{60}$  and  $C_{70}$  were the species with highest intensity in the mass spectra that led to the discovery of fullerenes:<sup>2,3</sup> among all proper fullerenes with less than 72 carbon atoms, these two species are the only ones with isolated pentagons. Unlike fullerenes with abutting pentagons which

have 8-membered antiaromatic rings, IPR-fullerenes have no electronic destabilizing features. Thus, among all their isomers, they are the most stable thermodynamically; when adequate annealing conditions are provided, the only survivors of isomerization will be "preferable fullerenes" with isolated pentagons, and non-IPR isomers will be totally absent.

### Descriptors for proper IPR fullerenes

The topological invariants that were used in the preceding part <sup>1</sup> for fullerenes with abutting pentagons were based on the sizes of four polygons incident to each edge, corresponding to fractional hybridizations. Nine types of edges (denoted by letters a through i) were possible, as seen in the second row of Fig. 1. For proper fullerenes with isolated pentagons, the first five types are excluded, and the remaining four types are insufficient for topological characterization. Therefore one has to consider also the sizes of the four polygons once remote (bordering the polygons in the immediate vicinity of each edge). In this case, 14 edge types are possible, as seen in the last rows of Fig. 1, and the numbers of each of these types for any IPR fullerene constitute the invariants we shall use. The following relationships hold among the 14 parameters; we denote by N the number of carbon atoms. Since the number of edges in a cubic graph (trivalent graph in mathematical terminology) is  $3N/2$ , this will be the sum of all 14 parameters.

$$\sum_{i=1}^3 f_i + \sum_{i=1}^3 g_i + \sum_{i=1}^7 h_i = 3N/2 \quad (1)$$

By counting the vertices and edges of the 12 pentagons we obtain two more equations:

$$2g_1 + h_1 + h_2 + h_3 = 60 \quad (2)$$

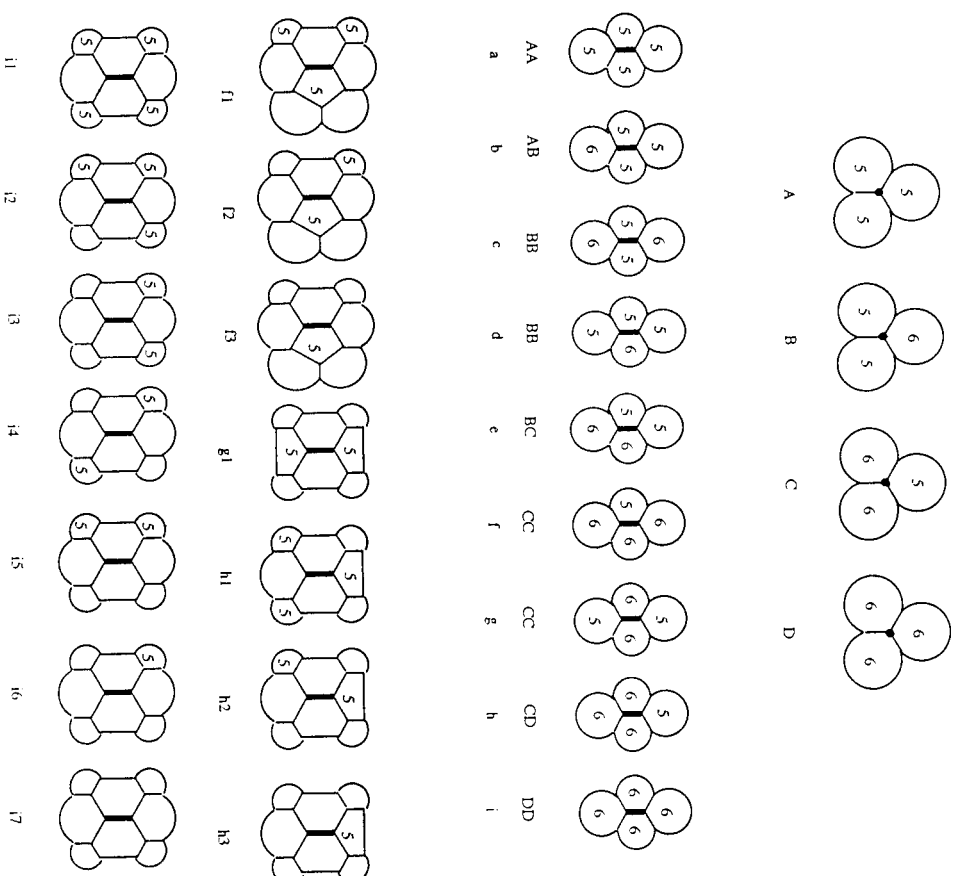


FIG. 1. First row : the four types of vertices in proper fullerenes; second row : the nine types of edges (only immediate adjacencies of 5- or 6-membered rings are considered in this and the preceding case); last two rows : the 14 types of edges considering also the four next faces, to simplify the picture, ring sizes of 6-membered rings have been omitted in this last case.

$$f_1 + f_2 + f_3 = 60 \quad (3)$$

Taking into account that in a proper fullerene  $C_N$  there are  $N/2 - 10$  hexagons, and counting the edges of these hexagons, we may obtain two more equations :

$$g_1 + h_1 + h_2 + h_3 + i_1 + i_2 + \dots + i_7 = (3N - 120) / 2 \quad (4)$$

$$i_1 + i_2 + \dots + i_7 - g_1 = 3(N - 80) / 2 \quad (5)$$

Actually only three independent equations exist in the set (1) through (5) because (4) = (1) - (3), and (5) = (1) - (2) - (3).

In addition to equations (1) through (3) there are *four* other independent relationships between the 14 descriptors, which may be chosen among the following ones.

$$f_2 = 4g_1 - 2f_1 = 4i_1 + 2i_2 + 2i_5 \quad (6,7)$$

$$f_3 = 60 - 4g_1 + f_1 \quad (8)$$

$$h_2 = 4i_1 + 2i_2 + 2i_3 \quad (9)$$

$$h_3 = i_2 + 2i_4 + 2i_5 + i_6 \quad (10)$$

$$2i_1 = 2g_1 - f_1 - 2h_3 + 2i_4 + i_5 + i_6 \quad (11)$$

$$i_2 = 2h_3 - 2i_4 - 2i_5 - 2i_6 \quad (12)$$

$$2i_3 = h_2 - 4g_1 + 2f_1 + 2i_5 \quad (13)$$

A possible condition for "super-stability" was expressed by Schmalz, Klein et al.,<sup>4,5</sup> and by Taylor,<sup>6</sup> in terms of maximizing the number of hexagons sharing a double bond; when among the Kekulé structures of proper IPR fullerenes there is one in which no double bond is in a pentagon, then such a "Clar structure" confers enhanced stability. A particular consequence is that in such "Clar-structure IPR fullerenes" there is no hexagon with two pentagons on opposing edges.<sup>7</sup> Fowler used for such systems the name "leapfrog" fullerenes,<sup>8-10</sup> perhaps "Fries-sextet fullerenes" would also be appropriate. As seen in Table 1, such "Clar-structure IPR fullerenes" exist only for  $N \geq 60$  values that are multiples of 6.

TABLE 1. Counts for IPR fullerenes and for Clar-sextet (CS) fullerenes

N	60	70	72	74	76	78	80	82	84	86	88	90	92	94	96	98	100
IPR	1	1	1	1	2	5	7	9	24	19	35	46	86	134	187	259	450
CS	1	0	1	0	0	1	0	0	2	0	0	3	0	0	6	0	0

It should be noted that many IPR fullerenes have open-shell electronic structures, e. g. the isomer 1 of  $C_{80}$  (symmetry  $I_h$ ) in the *Atlas of Fullerenes*.<sup>8</sup>

#### Other factors influencing the stability of fullerenes

In addition to the IPR which restricts severely the number of isomeric "preferable fullerenes", other electronic factors are bound to influence the stability of fullerenes. Liu, Klein and Schmalz argued that "topologically aromatic" fullerenes are those that possess Clar sextets, and have enumerated them. Their results are reproduced in Table 1, wherefrom it may be seen that for such Clar-sextet cages one must have  $N = 6k$ , where  $k = 10$  or any integer larger than 11. However, for smaller IPR cages with up to  $N = 100$  the steric factors outweigh any electronic advantage that the presence of Clar sextets may offer, as seen from the fact that no such smaller Clar-sextet cage was obtained experimentally. Fowler argued that for  $N \geq 60$  steric and electronic effects on stability act in opposite directions, with steric effects prevailing.

The leapfrog and carbon cylinder rules explain the stability of  $C_{60}$  and  $C_{70}$  respectively, both of these having electronic closed-shell structures and being the major observed and isolated fullerenes. When, in addition to the isolated pentagon rule, one considers Raghavachari's hexagon-neighbor

rule,<sup>11</sup> it becomes possible to explain also the experimental data on the yields of isolating (from fullerene soot) the observed isomers of  $C_{76}$ ,  $C_{78}$ ,  $C_{82}$ , and  $C_{84}$ ,<sup>12-19</sup>

### Examples of IPR fullerenes with $60 \leq N \leq 100$

Fowler and Manopoulos's *Atlas of Fullerenes*<sup>8</sup> contains pictures of all possible fullerenes with  $20 \leq N \leq 50$  and of all possible IPR fullerenes with  $20 \leq N \leq 100$ , as well as information on their symmetry point groups, the number of signals in their  $^{13}\text{C}$ -NMR spectra, their ring spiral codes, as well as other data.

In Table 2 one can see, for a few selected IPR proper fullerenes with high symmetry and  $60 \leq N \leq 100$ , all their 14 parameters and the calculated strain energies. Numbers after N relate to the numbers in the *Atlas of Fullerenes*.<sup>8</sup> High symmetry is not necessarily associated with higher stability. The data in this table are useful for checking the 14 parameters used in this study with the best known fullerene structures.

Equilibrium geometries and molecular mechanics energies were computed using MM+ force field (HyperChem)<sup>20</sup> and initial geometries (HyperChem).<sup>20</sup> No local minima were observed, as in the previous part.<sup>1</sup>

The most symmetrical proper fullerenes, which have only one type of vertex, are  $C_{20}$  and buckminsterfullerene, i.e.  $C_{60}$  ( $I_h$ ). The former is vertex- and edge-transitive, the latter only vertex-transitive. Next come  $C_{24}$  ( $D_{6d}$ ), which has two types of vertices and three types of edges, and  $C_{28}$  ( $T_d$ ), which has three types of vertices and edges. Several other fullerenes have three vertex types, but more than three edge types, such as  $C_{26}$  ( $D_{3h}$ ),  $C_{30}$  ( $D_{5h}$ ),  $C_{36}$  ( $D_{6h}$ ),  $C_{40-39}$  ( $D_{5d}$ ),  $C_{40-40}$  ( $T_d$ ),  $C_{48-186}$  ( $D_{6d}$ ). Among IPR proper fullerenes the most symmetrical are  $C_{60}$  ( $I_h$ ) mentioned above and  $C_{80}$

TABLE 2. Descriptors and calculated energies (kcal/mole) of selected IPR fullerenes

N	Sym.	$f_1$	$f_2$	$f_3$	$g_1$	$h_1$	$h_2$	$h_3$	$i_1$	$i_2$	$i_3$	$i_4$	$i_5$	$i_6$	$i_7$	Energy
60	$I_h$	60	0	0	30	0	0	0	0	0	0	0	0	0	0	267.63
70	$D_{5h}$	30	20	10	20	0	20	0	5	0	0	0	0	0	0	275.75
72	$D_{6d}$	36	24	0	24	0	0	12	0	0	0	0	12	0	0	300.81
74	$D_{3h}$	18	24	18	15	6	24	0	6	0	0	0	0	0	0	274.45
76	$T_d$	12	24	24	12	12	24	0	6	0	0	0	0	0	0	273.09
78:4	$D_{3h}$	12	28	20	13	6	24	4	4	4	0	0	2	0	0	278.94
78:5	$D_{3h}$	6	24	30	9	18	24	0	6	0	0	0	0	0	0	270.67
80:1	$D_{5d}$	30	20	10	20	0	0	20	0	0	0	10	10	0	0	295.05
80:6	$D_{5h}$	0	20	40	5	30	20	0	5	0	0	0	0	0	0	266.56
80:7	$I_h$	0	0	60	0	0	0	0	0	0	0	0	0	0	0	259.86
84:20	$T_d$	12	24	24	12	0	32	4	4	4	4	0	0	4	2	309.53
84:24	$D_{6h}$	0	48	12	12	0	24	12	6	0	0	0	12	0	0	289.28
88:34	T	12	24	24	12	0	24	12	0	12	0	0	0	12	0	293.61
90:1	$D_{5h}$	30	20	10	20	0	0	20	0	0	0	0	10	20	5	326.45
92:86	T	0	36	24	9	0	24	18	3	6	0	6	6	6	0	290.28
96:184	$D_{6h}$	0	24	36	6	0	48	0	6	8	12	0	0	0	12	286.13
96:185	$D_{6d}$	0	48	12	12	0	0	36	0	0	0	12	24	0	0	299.78
96:187	$D_{6d}$	0	0	60	0	36	24	0	0	0	12	0	0	0	12	297.59
100:1	$D_{5d}$	30	20	10	20	0	0	20	0	0	0	0	10	20	20	336.68
100:321	T	12	24	24	12	0	0	36	0	0	0	18	12	12	0	293.73
100:450	$D_5$	0	0	60	0	30	20	10	0	0	10	5	0	10	5	280.42

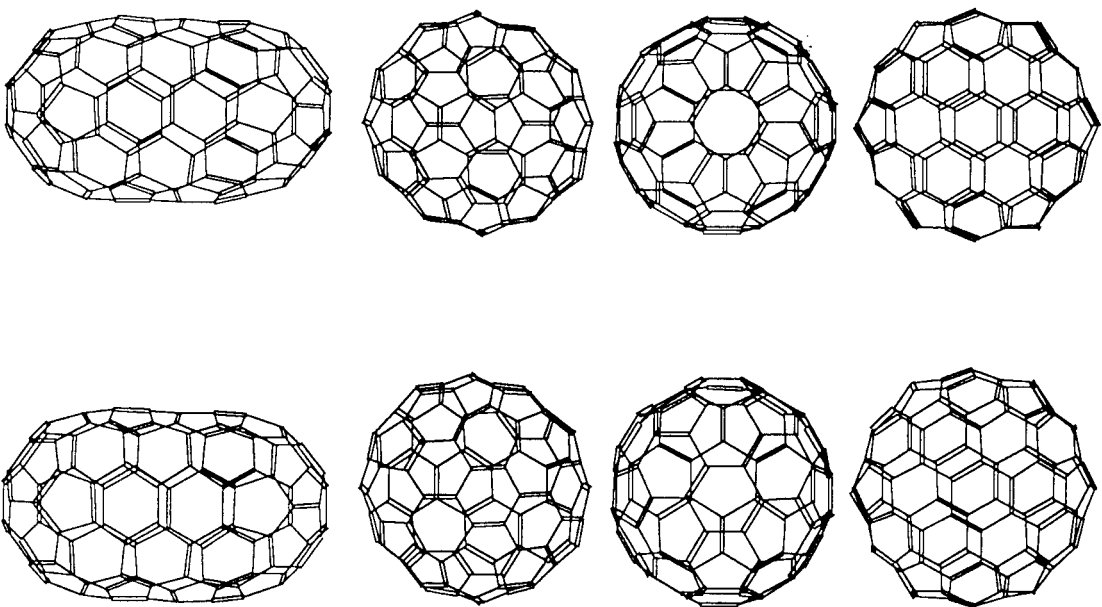


FIG. 2. Stereo-views of three isomers of  $C_{96}$  (# 184, 185, 187) and of  $C_{100}$  (#1).

( $I_h$ ), which have two types of edges; the latter has also two types of vertices. Next comes  $C_{180}$  ( $I_h$ ) which has three types of vertices.

In this paper we shall deal with IPR proper fullerenes with  $N = 94$  (134 isomers), 96 (187 isomers), 98 (259 isomers) and 100 (450 isomers).

As in the preceding paper, only constitutional isomerism is taken into consideration, ignoring stereoisomerism (of course, enantiomers of fullerenes have exactly the same energies). Therefore a total of 1030 structures are considered, differing in energies by about 70 kcal/mol.

One can see in Figure 2 stereoviews of the three  $C_{96}$  isomers, as well as of one isomer of  $C_{100}$ .

### Correlations

For the molecular mechanics energies of the 450 isomers of  $C_{100}$  IPR fullerenes, Table 3 presents the partial correlation coefficients for the 14 parameters.

In Table 4 we present the intercorrelation coefficients of these 14 parameters. One may see from the latter table that parameters  $f_3$ ,  $g_1$ ,  $h_2$ ,  $h_3$  and  $i_5$  have three or more intercorrelation coefficients equal to, or higher than, 0.8 with other parameters. From the former table one can see that the energies are mainly depending, in decreasing order, on parameters :  $g_1$ ,  $f_3$ ,  $i_7$ ,  $f_1$ ,  $h_2$ ,  $i_6$  and  $i_5$ . Parameters  $i_1$ ,  $h_1$ ,  $h_3$ ,  $i_2$  and  $f_2$  (in this order) have the smallest coefficients.

On testing progressively smaller numbers of parameters from those that are not highly intercorrelated and influence energies significantly, we arrived at the results shown in Table 5. We preferred to keep at least one descriptor from each of the classes  $f$ ,  $g$ ,  $h$ , and  $i$ .

Some comments on the data presented in Table 5 are necessary. For each separate set of fullerene isomers with  $N = 94$  through 100 carbon atoms,



Table 5. Coefficients of selected invariants and statistical data for correlations with energies

N	f1	g1	h2	i3	i5	i6	i7	Param. N	Free term	No. of param.	r	s
94	-0.1003	0.8273	-0.0009	-0.8372	0.9182	1.0097	3.5785	-	269.77	7	0.985895	1.574
	-0.9375	2.5017	-0.4195	-	0.0809	1.0097	3.5785	-	269.77	6	0.985895	1.568
	-0.9892	2.6065	-0.4514	-	-	0.9809	3.6044	-	270.39	5	0.985879	1.563
96	-0.1211	0.9367	0.0227	-1.2523	0.7309	0.6191	3.4971	-	273.42	7	0.978541	2.403
	-1.3733	3.4412	-0.6034	-	-0.5214	0.6191	3.4971	-	273.42	6	0.978541	2.397
	-1.0179	2.6859	-0.4128	-	-	0.7561	3.3649	-	270.32	5	0.977925	2.424
98	-0.1232	0.8619	0.0965	-0.9379	0.8609	0.8531	3.3695	-	267.25	7	0.980601	1.835
	-1.0611	2.7377	-0.3724	-	-0.0769	0.8531	3.3695	-	267.25	6	0.980601	1.831
	-1.0133	2.6227	-0.3506	-	-	0.8826	3.3576	-	266.81	5	0.980585	1.828
100	0.2466	0.7424	0.0549	-0.7906	0.9134	0.8703	2.9949	-	267.79	7	0.964658	2.555
	-1.0372	2.3236	-0.3404	-	0.1229	0.8703	2.9949	-	267.79	6	0.964658	2.552
	-1.1049	2.4869	-0.3801	-	-	0.8254	3.0039	-	268.84	5	0.955835	2.549
All of above	-0.9548	2.4299	-0.3415	-	0.1044	0.8634	3.1519	-0.8881	355.03	7	0.971314	2.371
	-1.0173	2.5764	-0.3756	-	-	0.8267	3.1659	-0.8518	352.21	6	0.971283	2.371

In addition to the results presented in Table 5, other correlations were also tested for the 1030 IPR fullerenes, without trying to have at least one representative descriptor from each of the four classes plus the number N of carbon atoms. The best results are presented below, each time for a set with N and a set without N. Equations with 7 descriptors are not unique, but those with 6 or 5 descriptors are unique.

*7-Descriptor set :*

$$E = -0.0820 N - 0.5617 h_1 - 3.0427 i_1 - 1.4577 i_2 - 2.2733 i_3 - 1.1402 i_4 + 2.7079 i_7 + 322.713$$

$$r = 0.97415; s = 2.25; F = 2715.0$$

$$E = -1.4206 f_1 + 5.2526 g_1 + 0.6145 h_1 - 1.2455 i_1 - 0.3222 i_5 + 0.5354 i_6 + 2.6648 i_7 + 245.681$$

$$r = 0.97415; s = 2.25; F = 2714.9$$

*6-Descriptor set :*

$$E = -1.7937 N + 1.0080 i_2 + 0.5363 i_4 + 1.6622 i_5 + 1.4217 i_6 + 3.8089 i_7 + 426.897$$

$$r = 0.97396; s = 2.26; F = 3146.9$$

$$E = 0.0409 f_1 - 0.5452 h_1 - 0.7250 h_2 - 0.8184 i_3 - 1.1776 i_4 + 2.6156 i_7 + 314.822$$

$$r = 0.97411; s = 2.25; F = 3165.3$$

*5-Descriptor set :*

$$E = -1.4929 N + 0.6930 i_2 + 1.6629 i_5 + 1.3342 i_6 + 3.3056 i_7 + 404.334$$

$$r = 0.97056; s = 2.40; F = 3325.0$$

$$E = -0.5609 h_1 - 0.7465 h_2 - 0.7897 i_3 - 1.1876 i_4 + 2.6368 i_7 + 315.347$$

$$r = 0.97404; s = 2.25; F = 3792.0$$

As one can see by comparison with the last two rows of Table 5, these results are slightly better.

The only serious outlier (with MM+ energy of about 30 kcal/mol higher than calculated values from the correlations and from quantum-chemical approach) is one of the C<sub>100</sub> isomers with many adjacent hexagons, namely the last one in Fig. 2 which is an IPR buckyube (such buckytubes with larger numbers of hexagons, i. e. longer hexagonal "belts", were tested and also led to large deviations from our correlations). Only two or three other isomers have energy differences around 10-14 kcal/mol, and all other IPR fullerenes have energy differences lower than 10 kcal/mol.

### Conclusions

As in the preceding Part I, descriptors based on the topology of edges in proper fullerenes are able to lead to multilinear correlations which describe satisfactorily the strain energy of IPR fullerenes. Only one exception was found among IPR fullerenes with up to 100 carbon atoms, indicating that for even better correlations one should also add another type of descriptor.

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