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Standard Enthalpies of Formation of Fullerenes and Their Dependence on Structural Motifs

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Abstract: Accurate standard enthalpies of formation of 115 isolated pentagon rule (IPR) fullerenes with 60−180 carbon atoms have been derived from energies of isodesmic interconversion reactions computed at the B3LYP/6-31G* level of theory. The calculated values of ΔH_f°, which may serve as benchmarks for both calorimetric measurements and less sophisticated theoretical studies, are reproduced within 3 kcal/mol by a simple scheme based upon counts of 30 distinct structural motifs composed of hexagons together with their first and second neighborhoods. The extremely low computational cost of such a scheme makes it ideally suited for a rapid prescreening for thermodynamically viable IPR fullerenes with cages composed of hundreds of carbon atoms. With the inclusion of a global curvature term, this scheme is expected to be equally successful for small and large carbon clusters.

Introduction

The recent progress in chemistry of spheroidal carbon clusters (fullerenes) vividly illustrates the benefits of employing electronic structure calculations in tandem with experiments. By identifying thermodynamically favorable isomers and allowing assignment of individual structures to NMR spectra, theoretical predictions have provided invaluable assistance in fullerene research, which in turn has verified their validity on numerous occasions.[1] Thus, for example, only the D_2 isomer of C_{76} has been extracted from the fullerene soot[2] and later resolved into enantiomers,[3,4] in agreement with the presence of a vanishing HOMO−LUMO gap in the other isolated pentagon rule[5] (IPR) structure of T_d symmetry.[6] Synergies between theory and experiment played a crucial role in the investigations[7−12] that culminated in the recent isolation of two major[13] and five minor[14] isomers of C_{84}.

The C_{60}, C_{70}, C_{76}, and C_{84} species are not the only currently known fullerenes. Three isomers of C_{78} have been isolated and characterized,[15−17] and the other two IPR isomers appear to be also present in the fullerene soot.[11] The isolation of a chiral C_{80} species with D_2 symmetry has been reported recently.[18] NMR spectra have provided evidence for several isomers of C_{82}.[16]

The C_{86-102}, C_{90}, C_{94}, and C_{96} fractions[19−21] have been separated by HPLC. A method designed to enhance the yield of these fractions has been described.[22] Species with as many as 300 carbon atoms have been extracted from the fullerene soot with quinoline and 1,2,3,5-tetramethylbenzene.[23,24] However, experimental data on properties of individual isomers of fullerenes beyond C_{84} have been lacking so far.

Because of their diminishing solubility in common solvents and the plethora of potential structures, isolation and characterization of the higher fullerenes is certain to present considerable experimental challenges. These challenges will undoubtedly

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Table 1. IPR Fullerene Isomer Counts for Various Numbers of Carbon Atoms

N^a	no. of IPR isomers[b]		N^a	no. of IPR isomers[b]	
60	1	1	86	19	19
70	1	1	88	35	34
72	1	1	90	46	46
74	1	1	92	86	86
76	2	1	94	134	131
78	5	5	96	187	186
80	7	5	98	259	259
82	9	8	100	450	446
84	24	24	102	616	616

[a] The number of carbon atoms. [b] The total isomer counts followed by the counts of isomers with nonvanishing HOMO−LUMO gaps.

further underline the need for reliable theoretical estimates of their thermodynamic stabilities. Unfortunately, with a few notable exceptions,[25−29] most of such estimates have been so far computed with semiempirical methods. Extrapolating from the experience with smaller fullerenes,[1,30] one expects many of these data to be invalidated by both higher-level predictions and experimental results.

The number of possible fullerene cages grows very rapidly with the number of carbon atoms, increasing from 1812 for C_{60}[31] to 1 207 119 for C_{116}.[32] For larger fullerenes, the structures are too numerous (Table 1)[31] to be individually examined with ab initio electronic structure methods, even after a very efficient prescreening for thermodynamically relevant species offered by the isolated pentagon rule.[5] Although sets as large as that of the 6063 IPR C_{116} isomers have been subject to searches for the lowest-energy structure with semiempirical approaches,[32] it is clear that further progress in this area hinges upon the availability of more sophisticated prescreening tools. Ideally, such tools would allow a very rapid estimation of standard enthalpies of formation ΔH_f° within a few kilocalories per mole, drastically reducing the number of species to be evaluated quantum mechanically.

Involving iterative construction of approximate Hamiltonians and matrix diagonalizations, semiempirical methods are too expensive as prescreening tools for fullerenes with hundreds of thousands of IPR structures. On the other hand, simple topological approaches, such as the hexagon neighbor rule,[7] lack sufficient accuracy.[32] This is so because the relative stabilities of IPR fullerenes reflect intimate interplays between strain and conjugation in individual carbon cages.[1] A successful estimator of ΔH_f° must faithfully account for both of these effects.

Prompted by the above considerations, we have recently developed an accurate method for the estimation of standard enthalpies of formation of IPR fullerenes. This method has been parametrized with a set of 73 carbon cages and tested on an additional 42 fullerene structures. Overall, values of ΔH_f° for 115 IPR fullerenes with 60−180 carbon atoms have been computed at the B3LYP/6-31G* level of theory and then reproduced within 3 kcal/mol with the new estimator. These theoretical developments are reported here.

Details of Calculations

The geometries of the 115 IPR fullerene cages listed in Table 2 were fully optimized at the B3LYP/6-31G* level of theory. The use of a DFT method in conjunction with a basis set of moderate size allows for a cost-effective inclusion of electron correlation effects. All calculations were carried out with the GAUSSIAN 98 suite of programs.[33] The numbering of fullerene isomers follows that used in ref 34, except for the C_{102} carbon cages that are numbered according to their order of appearance in the output produced by the fullerene generation program described in ref 31.

The standard enthalpies of formation were computed from the enthalpies ΔH_r° of the respective fullerene interconversion reactions,[1,12]

$$(N/60)C_{60} \rightarrow C_N \tag{1}$$

in order to further reduce errors due to residual electron correlation effects and deficiencies in the basis set. Such an approach also makes it possible to employ energies at $T = 0$ K rather than standard enthalpies, eliminating the need for the prohibitively expensive computations of zero-point energies and thermal corrections. The experimental standard enthalpy of formation $\Delta H_f^\circ(C_{60},g) = 618.1 \pm 3.4$ kcal/mol, obtained by combining an average of two recently reported values of $\Delta H_f^\circ(C_{60},s)$[35,36] with the corresponding ΔH_{subl}°,[35] was used in conjunction with this approach.

Standard Enthalpies of Formation of 115 Ipr Fullerenes

It is instructive to compare the present estimates of ΔH_r° for the reactions (1) with the previously published data. In the case of C_{70}, a direct comparison with the experimental value of −73 kcal/mol,[12] derived from rather inaccurate calorimetric measurements,[37,38] is possible. The present approach yields −63.4 kcal/mol, whereas the theoretical predictions available in the literature range from −75 to −11 kcal/mol.[1] The B3LYP/6-31G* estimate is close to its HF/6-31G//MNDO counterpart of −62.4 kcal/mol.[39] It is worth noting that although the HF/STO-3G level of theory also yields $\Delta H_r^\circ = -62.4$ kcal/mol,[30] the agreement is fortuitous since upgrading the basis set to 3-21G results in $\Delta H_r^\circ = -50.8$ kcal/mol.[40] The estimates produced by the methods of molecular mechanics are too low, as illustrated by $\Delta H_r^\circ = -29.0$ kcal/mol obtained with the MM3 approach.[30] For the D_2 isomer of C_{76}, the present calculation yields $\Delta H_r^\circ = -83.8$ kcal/mol, while the previously published HF/STO-3G

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Table 2. B3LYP/6-31G* Standard Enthalpies of Formation of 115 IPR Fullerenes and Their Estimates[a]

fullerene	isomer[b] (symmetry)	ΔH°_f (kcal/mol)		
		calcd	est[c]	error
C_{60}	*1 (I_h)*	*618.1*	*616.8*	*−1.3*
C_{70}	*1 (D_{5h})*	*657.7*	*662.3*	*4.6*
C_{72}	*1 (D_{6d})*	*704.8*	*703.9*	*−0.9*
C_{74}	*1 (D_{3h})*	*694.6*	*686.4*	*−8.2*
C_{76}	*1 (D_2)*	*699.1*	*700.5*	*1.4*
C_{78}	1 (D_3)	712.5	715.9	3.4
C_{78}	*2 (C_{2v})*	*709.2*	*711.1*	*1.9*
C_{78}	*3 (C_{2v})*	*702.6*	*704.5*	*1.8*
C_{78}	4 (D_{3h})	727.2	733.0	5.8
C_{78}	*5 (D_{3h})*	*707.1*	*713.1*	*6.0*
C_{80}	*1 (D_{5d})*	*727.2*	*728.4*	*1.2*
C_{80}	*2 (D_2)*	*724.6*	*724.8*	*0.2*
C_{80}	3 (C_{2v})	731.3	724.1	−7.2
C_{80}	*4 (D_3)*	*733.6*	*731.2*	*−2.3*
C_{80}	5 (C_{2v})	732.9	727.0	−6.0
C_{82}	1 (C_2)	727.8	728.6	0.8
C_{82}	2 (C_s)	726.8	727.6	0.8
C_{82}	3 (C_2)	720.1	719.1	−1.0
C_{82}	4 (C_s)	724.0	725.9	1.9
C_{82}	5 (C_2)	728.4	729.8	1.4
C_{82}	6 (C_s)	732.3	730.2	−2.1
C_{82}	8 (C_{3v})	750.8	741.7	−9.1
C_{82}	9 (C_{2v})	738.4	728.8	−9.7
C_{84}	*1 (D_2)*	*768.1*	*765.2*	*−2.8*
C_{84}	*2 (C_2)*	*749.6*	*751.2*	*1.6*
C_{84}	3 (C_s)	748.6	740.7	−7.9
C_{84}	4 (D_{2d})	731.3	734.0	2.7
C_{84}	*5 (D_2)*	*732.4*	*737.2*	*4.8*
C_{84}	6 (C_{2v})	733.7	732.9	−0.8
C_{84}	7 (C_{2v})	741.1	741.6	0.5
C_{84}	8 (C_2)	738.5	735.9	−2.6
C_{84}	9 (C_2)	742.8	739.8	−3.0
C_{84}	10 (C_s)	745.1	739.3	−5.8
C_{84}	11 (C_2)	724.7	725.4	−0.6
C_{84}	12 (C_1)	728.7	729.7	1.0
C_{84}	13 (C_2)	741.2	743.6	2.4
C_{84}	14 (C_s)	731.5	734.4	2.9
C_{84}	15 (C_s)	727.7	727.8	0.0
C_{84}	16 (C_s)	724.4	723.9	−0.6
C_{84}	17 (C_{2v})	738.1	742.6	4.5
C_{84}	18 (C_{2v})	732.1	734.8	2.7
C_{84}	19 (D_{3d})	726.7	727.3	0.6
C_{84}	20 (T_d)	747.1	756.8	9.6
C_{84}	21 (D_2)	732.7	732.1	−0.6
C_{84}	22 (D_2)	716.7	712.9	−3.8
C_{84}	23 (D_{2d})	716.4	712.9	−3.4
C_{84}	24 (D_{6h})	723.6	720.5	−3.1
C_{86}	*1 (C_1)*	*761.6*	*764.2*	*2.6*
C_{86}	*2 (C_2)*	*762.6*	*770.4*	*7.8*
C_{86}	*3 (C_2)*	*753.9*	*756.6*	*2.7*
C_{86}	*4 (C_2)*	*756.7*	*751.4*	*−5.3*
C_{86}	*5 (C_1)*	*755.7*	*760.2*	*4.6*
C_{86}	*6 (C_2)*	*750.7*	*746.5*	*−4.2*
C_{86}	*7 (C_1)*	*759.8*	*756.1*	*−3.7*
C_{86}	*8 (C_s)*	*770.1*	*765.8*	*−4.3*
C_{86}	*9 (C_{2v})*	*776.2*	*776.4*	*0.2*
C_{86}	10 (C_{2v})	753.5	752.1	−1.3
C_{86}	11 (C_1)	745.8	749.1	3.3
C_{86}	12 (C_1)	745.7	749.6	3.9
C_{86}	13 (C_1)	749.7	753.4	3.7
C_{86}	14 (C_2)	756.8	762.3	5.5
C_{86}	15 (C_s)	757.4	765.7	8.3
C_{86}	16 (C_s)	741.6	745.4	3.8
C_{86}	17 (C_2)	735.4	733.9	−1.4
C_{86}	18 (C_3)	746.7	754.9	8.2
C_{86}	19 (D_3)	759.0	770.0	11.0
C_{88}	*1 (D_2)*	*804.6*	*798.7*	*−5.9*
C_{88}	*2 (C_1)*	*765.1*	*765.2*	*0.1*
C_{88}	*4 (C_s)*	*776.8*	*778.1*	*1.3*
C_{88}	5 (C_{2v})	763.3	760.7	−2.7
C_{88}	*7 (C_2)*	*745.2*	*747.7*	*2.5*
C_{88}	10 (C_{2v})	765.3	760.7	−4.6
C_{88}	*31 (C_s)*	*771.1*	*769.1*	*−2.1*
C_{90}	*1 (D_{5h})*	*763.7*	*764.8*	*1.2*
C_{90}	*2 (C_{2v})*	*784.0*	*782.9*	*−1.1*
C_{90}	*3 (C_1)*	*775.3*	*772.5*	*−2.8*
C_{90}	*4 (C_2)*	*766.7*	*769.3*	*2.6*
C_{90}	*5 (C_s)*	*777.5*	*776.5*	*−1.1*
C_{90}	*8 (C_2)*	*765.7*	*767.7*	*2.1*
C_{92}	*5 (C_s)*	*776.3*	*779.8*	*3.5*
C_{92}	*6 (C_s)*	*797.2*	*790.8*	*−6.4*
C_{92}	*21 (C_s)*	*799.8*	*796.7*	*−3.0*
C_{92}	*22 (C_{2v})*	*826.7*	*827.0*	*0.3*
C_{92}	*25 (C_2)*	*801.7*	*801.3*	*−0.4*
C_{92}	*29 (D_{2h})*	*810.5*	*811.1*	*0.6*
C_{92}	*35 (C_{2v})*	*803.5*	*802.9*	*−0. 6*
C_{92}	*45 (C_s)*	*778.7*	*776.6*	*−2.0*
C_{92}	81 (D_2)	761.1	754.8	−6.3
C_{92}	82 (D_2)	757.5	754.8	−2.7
C_{94}	*46 (C_s)*	*839.3*	*837.9*	*−1.5*
C_{94}	*52 (C_{2v})*	*813.0*	*811.7*	*−1.3*
C_{96}	*33 (D_{3h})*	*878.3*	*872.2*	*−6.1*
C_{96}	*110 (C_{2v})*	*848.1*	*848.1*	*0.0*
C_{96}	*148 (D_{2h})*	*846.3*	*850.2*	*3.8*
C_{96}	*149 (C_{2v})*	*820.1*	*821.9*	*1.8*
C_{96}	*184 (D_{6h})*	*794.8*	*793.7*	*−1.1*
C_{98}	*18 (C_s)*	*822.0*	*815.9*	*−6.0*
C_{98}	*23 (C_s)*	*836.7*	*843.7*	*7.1*
C_{100}	431 (D_2)	794.8	798.4	3.5
C_{100}	432 (D_2)	793.9	798.4	4.5
C_{102}	32 (C_1)	810.6	808.4	−2.2
C_{102}	34 (C_1)	809.0	808.4	−0.6
C_{102}	*369 (C_1)*	*838.3*	*842.4*	*4.2*
C_{102}	*371 (C_1)*	*817.0*	*815.9*	*−1.1*
C_{102}	*409 (C_1)*	*811.6*	*808.4*	*−3.3*
C_{102}	*451 (C_1)*	*839.3*	*840.7*	*1.4*
C_{102}	*452 (C_1)*	*820.5*	*822.5*	*2.0*
C_{102}	*453 (C_1)*	*823.8*	*821.7*	*−2.1*
C_{102}	*562 (C_{2v})*	*815.4*	*815.8*	*0.5*
C_{102}	*570 (C_{2v})*	*852.2*	*855.3*	*3.1*
C_{102}	*598 (C_s)*	*827.5*	*828.9*	*1.4*
C_{102}	*606 (C_s)*	*827.0*	*825.8*	*−1.2*
C_{102}	*611 (C_s)*	*833.4*	*838.4*	*5.0*
C_{102}	*616 (D_3)*	*806.1*	*799.3*	*−6.8*
C_{180}	*1 (I_h)*	*944.9*	*944.9*	*0.0*

[a] The members of the minimal training set are italicized. [b] See the text for the explanation of the fullerene numbering system. [c] Equation 3.

and MM3 predictions amount to −89.1 and −42.7 kcal/mol, respectively.[30]

Standard enthalpies of formation were calculated for all five IPR isomers of the C_{78} fullerene (Table 2). The lowest-energy C_{2v} structure 3 lies 4.5 kcal/mol below the D_{3h} isomer 5 and 6.6 kcal/mol below another C_{2v} structure 2. The D_3 isomer 1 is placed 9.9 kcal/mol above the lowest-energy structure, whereas the other D_{3h} isomer 4 lies a distant 24.6 kcal/mol above it. The predicted energetic preference for the isomer 3 is in agreement with the previously published results of various electronic structure calculations.[9,41] The same is true about the energy difference between the isomers 4 and 3, for which the estimates of 19.4, 21.1, and 20.2 kcal/mol have been obtained at the HF/DZ//MNDO, BP86/3-21G,[9] and HF/6-31G*//HF/3-21G[41] levels of theory, respectively. However, those methods find either the isomer 2 (BP86/3-21G) or both the isomers 1 and 2 (HF/DZ//MNDO and HF/6-31G*//HF/3-21G) more stable than the lower-energy D_{3h} species. Although the isomers 1, 2,

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(41) Raghavachari, K.; Rohlfing, C. M. *Chem. Phys. Lett.* **1993**, *208*, 436.

and 3 are formed predominantly during vaporization of graphite, their abundances depend very strongly upon the pressure of the inert carrier gas, suggesting kinetic rather than thermodynamic control of the formation process.[42] Therefore, the resolution of the discrepancies among theoretical predictions has to await future calorimetric measurements for individual isomers of the C_{78} fullerene.

Among the five IPR isomers of the C_{80} fullerene with nonvanishing HOMO−LUMO gaps, the D_2 structure 2 is predicted to possess the lowest ΔH_f° and the D_3 structure 4 the highest (Table 2). Although this finding is in disagreement with the previously published results of HF/4-31G//SAM1 calculations that afford the D_{5d} isomer 1 as the lowest-energy structure,[27] it matches the experimental observation of the exclusive formation of the D_3 species.[18]

Standard enthalpies of formation were also calculated for all the 24 IPR C_{84} fullerenes. The isomers 22 (D_2) and 23 (D_{2d}) are predicted to be almost isoenergetic, the latter being favored by a mere 0.3 kcal/mol (Table 2). This difference in the values of ΔH_f° is in agreement with the previously published HF/DZ//MNDO,[9] MNDO, AM1, and PM3,[8] and BP86/3-21G[9] energy differences that amount to 0.3, 0.4, 0.4, 0.4, and 1.4 kcal/mol, respectively. The present prediction is also in accordance with the experimentally observed abundances.[43] Lying 51.7 kcal/mol above the isomer 23, the D_2 isomer 1 is found to be the least stable structure.

There are 19 IPR structures for the C_{86} carbon cage, all of which are included in the set compiled in Table 2. The lowest-energy species turns out to be the C_2 isomer 17, which lies 6.2 kcal/mol below the next most stable structure 16 with C_s symmetry. This order of stabilities agrees with the results of HF/3-21G//SAM1[26] and HF/4-31G//SAM1 calculations,[27] which predict the relative energies of 6.2 and 7.9 kcal/mol, respectively. The least stable species is the C_{2v} isomer 9, again in agreement with the aforementioned lower-level calculations. Overall, the energies of IPR C_{86} fullerenes span the ranges of 40.8, 78.8, and 69.9 kcal/mol at the B3LYP/6-31G*, HF/3-21G//SAM1, and HF/4-31G//SAM1 levels of theory.[27]

For higher fullerenes, only the members of the minimal training set and some cases of isomotif structures (see below) were considered. Among the 7 isomers of the C_{88} fullerenes listed in Table 2, the C_2 structure 7 is the most stable and the D_2 species 1 is the least stable. The computed difference in their ΔH_f° values equals 59.4 kcal/mol, which is close to the HF/3-21G//SAM1 relative energy of 63.7 kcal/mol.[27] A similar agreement is observed in the case of the C_{90} fullerenes, where the spread of 20.3 kcal/mol between the standard enthalpies of formation of the isomers 1 (D_{5h}) and 2 (C_{2v}) matches reasonably well the respective energy difference of 28.4 kcal/mol computed at the HF/4-31G//SAM1 level of theory.[25]

A Scheme for Rapid Estimation of Standard Enthalpies of Formation of IPR Fullerenes

Since all of the presently known chemical processes that lead to the formation of fullerenes take place at high temperatures, predictions of the ΔH_f° values within a few kilocalories per mole suffice for the purpose of preliminary screening for thermodynamically feasible carbon cages. Still, attaining this level of accuracy calls for a faithful description of strain and conjugation, both of which strongly affect fullerene stabilities.[1,41] The strain associated with a given carbon cage depends on both global factors (such as the cage size and shape) and local structural details (such as the presence of large assemblies of hexagons devoid of pentagonal intrusions). Similarly, the contribution of conjugation to the overall stability of a given fullerene is determined both by the global cage properties (such as the number of Kekule structures) and by the local arrangements of pentagons and hexagons.

A systematic approach to modeling properties of any class of molecules involves identification of relevant structural motifs. In the case of IPR fullerenes, such motifs can be either the C−C bonds together with the four incident rings[44] or the six-member rings together with their first and second neighbors. As the latter choice leads to a greater variety of structural motifs, it is adopted here.

Due to the absence of abutting pentagons, hexagons in IPR fullerenes possess only five distinct first neighborhoods: one with no pentagons, one with a single pentagon, two with two pentagons, and one with three pentagons (Figure 1). These arrangements of rings give rise to 30 possible structural motifs that are denoted according to the rings present in the second neighborhoods (except for those originating from the neighborhoods with two pentagons, for which the prefixes 13- and 14- are added for the sake of full characterization). The counts $\{N_\mathrm{I}\}$ of these motifs in any given fullerene are not entirely independent, as the following relationships hold:

$$2N_{666665} + 2N_{666655} + 4N_{666565} + 4N_{665665} + 2N_{666555} + 4N_{665655} + 6N_{656565} + 2N_{665555} + 4N_{656555} + 4N_{655655} + 2N_{655555} - 2N_{6666} - N_{6665} + N_{6565} + N_{5655} = 0 \quad (2a)$$

$$N_{666655} + 2N_{666555} + N_{665655} + 3N_{665555} + 2N_{656555} + 2N_{655655} + N_{655555} + 6N_{555555} + N_{6556} + N_{6555} + N_{5555} - N_{13/66} = 0 \quad (2b)$$

$$N_{6655} + N_{6555} + N_{5655} + 2N_{5555} - \mathrm{N}_{13/56} = 0 \quad (2c)$$

$$N_{6665} + N_{6565} + 2N_{5665} + N_{5655} + 2N_{13/55} + 2N_{13/56} - N_{14/66} - 2N_{14/56} = 0 \quad (2d)$$

and

$$N_{6666} + N_{6665} + N_{6656} + N_{6655} + N_{6565} + N_{6556} + N_{5665} + N_{6555} + N_{5655} + N_{5555} + 2N_{13/66} + 2N_{13/56} + 2N_{13/55} + 2N_{14/66} + 2N_{14/56} + 2N_{14/55} + 3N_{135} = 60 \quad (2e)$$

Thus, the motif counts provide *25* linearly independent structural descriptors.

IPR fullerenes with identical motif counts (isomotif fullerenes) possess very similar stabilities. One prominent example of such fullerenes are the isomers 22 and 23 of C_{84} (see above). The values of ΔH_f° for the isomotif isomers 5 and 10 of C_{88} fall within 2.0 kcal/mol (Table 2). Narrow spreads in ΔH_f° (3.6, 0.9, and 2.6 kcal/mol, respectively) are also predicted for the isomotif pairs 81/82 of C_{92} and 431/432 of C_{100}, and the isomotif triplet 32/34/409 of C_{102}.

The aforedescribed structural motifs occur in fullerenes of various sizes, some appearing only in cages with at least 102 carbons. Let Q_I denote the set of the smallest IPR fullerenes with nonvanishing HOMO−LUMO gaps that contain the motif I. The set $\{Q_I\}$ of such sets consists of 73 members (Table 3).

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(42) Wakabayashi, T.; Kikuchi, K.; Suzuki, S.; Shiromaru, H.; Achiba, Y. *J. Phys. Chem.* **1994**, *98*, 3090.

(43) Manolopoulos, D. E.; Fowler, P. W.; Taylor, R.; Kroto, H. W.; Walton, D. R. M. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 3117.

(44) Ivanciuc, O.; Babić, D.; Balaban, A. T. *Fullerene Sci. Technol.* **1999,** *7*, 1. Balaban, A. T.; Ivanciuc, O.; Babić, D. *Fullerene Sci. Technol.* **1997**, *5*, 1479.

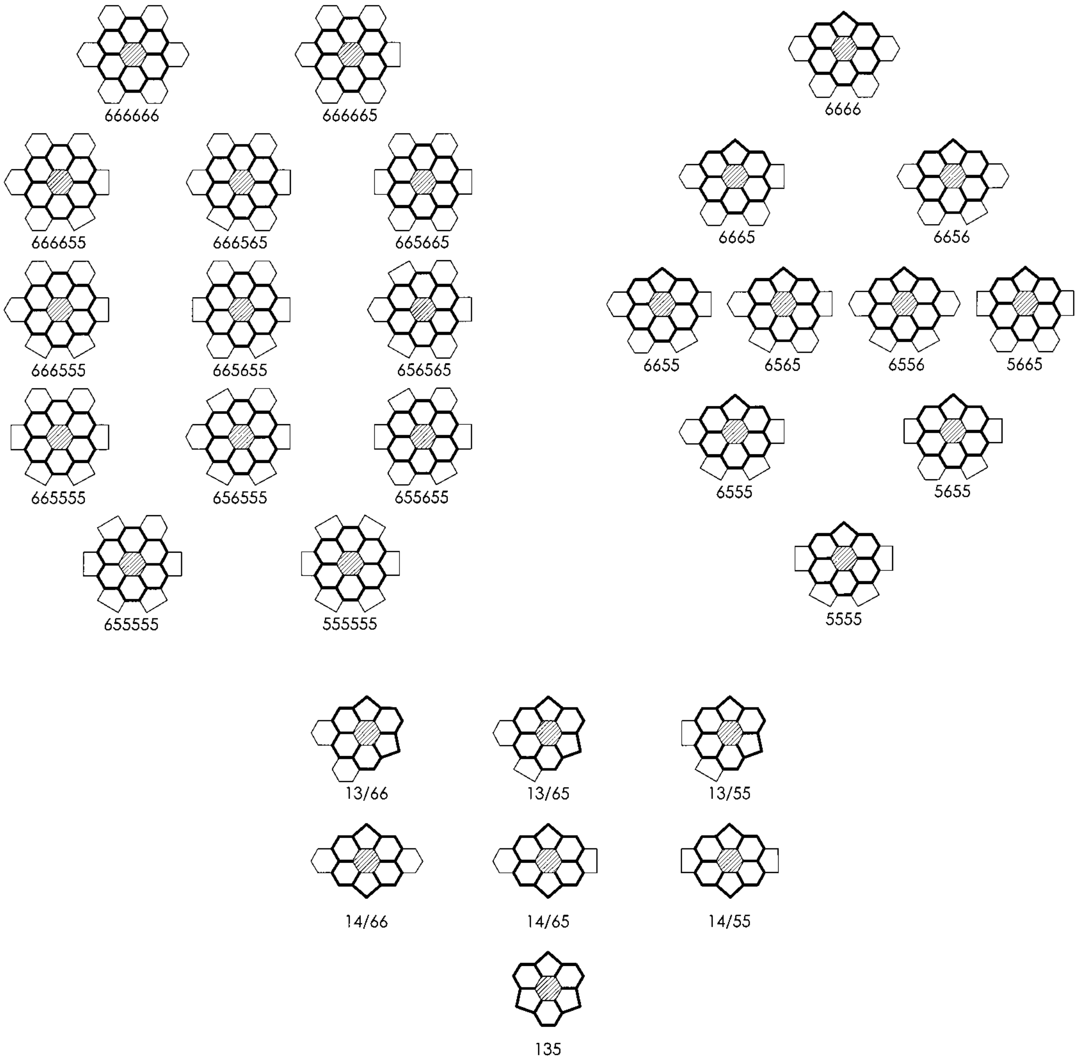

Figure 1. Structural motifs of IPR fullerenes. The first neighborhoods of the shaded hexagons are delineated by bold lines.

These 73 IPR fullerenes (which are listed in italics in Table 2) constitute the minimal training set that was employed in the testing of various estimation schemes for ΔH_f°.

When used in combination with the numbers of carbon atoms N, the total π-electron energies E_π correlate very poorly with ΔH_f° (Table 4). The errors in the predicted standard enthalpies of formation are substantially larger for the entire set of 115 IPR fullerenes than for the minimal training set employed in the fitting of the linear regression coefficients. Such a trend indicates the presence of size-dependent effects that are not accounted for by the Hückel method. Indeed, the addition of a term proportional to $(N - A)^{-1}$, where A is a constant, brings about both significant improvement and equalization in the error statistics for the two sets (Table 4). Still, as expected from the previously published studies,[32] estimation schemes for ΔH_f° based solely upon E_π and N lack sufficient predictive power to be of much practical relevance.

Although, as mentioned above, the counts of structural motifs provide 25 rather than 30 linearly independent structural descriptors, each motif can be assigned a unique contribution to ΔH_f° with the help of the singular value decomposition formalism[45] by fitting the predicted standard enthalpies of formation to their computed counterparts for the members of the minimal training set. The resulting estimation scheme for ΔH_f° exhibits disappointingly poor errors statistics for the entire set of 115 IPR fullerenes (the error increasing steadily with N), which is barely improved upon the addition of a term proportional to E_π (Table 4). On the other hand, the approximate formula

$$\Delta H_f^\circ \approx \sum_I \epsilon_I N_I - 8050.751(N - 30.050)^{-1}\ \text{kcal/mol} \quad (3)$$

with the contributions $\{\epsilon_I\}$ listed in Table 5 and the global curvature term proportional to $(N - A)^{-1}$ is remarkably accurate.

The success of the aforedescribed estimator can be equally attributed to the use of relatively large motifs that allows for a flexible description of local structural characteristics and the inclusion of a global curvature term. It is worth noting that this term contributes negatively to ΔH_f°, suggesting a substantial overestimation of strain by the motif contributions. This overestimation results in values of ΔH_f° that are too positive and thus have to be revised downward to match their experimental counterparts. The average error of ca. 3 kcal/mol in the estimates provided by eq 1 is low enough to make the present scheme a viable alternative to semiempirical approaches such as QCFF/PI or the methods of the MNDO family. The observation that this error is not substantially lowered upon the inclusion of an additional term proportional to E_π (Table 4)

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[45] Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes*; Cambridge University Press: New York, 1992; Chapter 2.

Table 3. The Members of the Minimal Training Set

		smallest IPR fullerenes with nonvanishing HOMO−LUMO gaps			
motif[a]	formula	isomer[b] (symmetry)			
666666	C_{96}	33 (D_{3h})	110 (C_{2v})	148 (D_{2h})	149 (C_{2v})
		184 (D_{6h})	187 (D_{6h})		
666665	C_{94}	46 (C_s)	52 (C_{2v})		
666655	C_{92}	21 (C_s)	22 (C_{2v})	35 (C_{2v})	45 (C_s)
666565	C_{98}	18 (C_s)	23 (C_s)		
665665	C_{92}	28 (D_{2h})			
666555	C_{88}	1 (D_2)	4 (C_s)		
665655	C_{92}	25 (C_2)			
656565	C_{102}	369 (C_1)	371 (C_1)	451 (C_1)	452 (C_1)
		453 (C_1)	562 (C_{2v})	570 (C_{3v})	598 (C_s)
		606 (C_s)	611 (C_s)	616 (D_3)	
665555	C_{86}	1 (C_1)	2 (C_2)		
656555	C_{92}	5 (C_s)	6 (C_s)		
655655	C_{90}	1 (D_{5h})	2 (C_{2v})	3 (C_1)	4 (C_2)
		5 (C_s)	8 (C_2)		
655555	C_{84}	1 (D_2)	2 (C_2)		
555555	C_{72}	1 (D_{6h})			
6666	C_{84}	1 (D_2)	2 (C_2)		
6665	C_{84}	2 (C_2)	5 (D_2)		
6656	C_{86}	1 (C_1)	3 (C_2)	4 (C_2)	5 (C_1)
		6 (C_2)	7 (C_1)	8 (C_s)	
6655	C_{80}	4 (D_3)			
6565	C_{88}	2 (C_1)	7 (C_2)	8 (C_s)	
6556	C_{80}	1 (D_{5d})	2 (D_2)		
5665	C_{86}	9 (C_{2v})			
6555	C_{76}	1 (D_2)			
5655	C_{84}	2 (C_2)	5 (D_2)		
5555	C_{78}	2 (C_{2v})	3 (C_{2v})		
13/66	C_{72}	1 (D_{6d})			
13/56	C_{76}	1 (D_2)			
13/55	C_{70}	1 (D_{5h})			
14/66	C_{70}	1 (D_{5h})			
14/56	C_{74}	1 (D_{3h})			
14/55	C_{78}	3 (C_{2v})	5 (D_{3h})		
135	C_{60}	1 (I_h)			

[a] See the text and Figure 1 for the explanation of the motif notation.
[b] See the text for the explanation of the fullerene numbering system.

demonstrates the accuracy of the description of conjugation by the present structural motif approach.

Conclusions

Accurate standard enthalpies of formation of 115 IPR fullerenes with 60−180 carbon atoms have been derived from energies of isodesmic interconversion reactions computed at the B3LYP/6-31G* level of theory.[46] The calculated values of ΔH_f°, which may serve as benchmarks for both calorimetric measurements and less sophisticated theoretical studies, are reproduced within 3 kcal/mol by a simple scheme based upon counts of 30 distinct structural motifs composed of hexagons together with their first and second neighborhoods. The extremely low computational cost of such a scheme makes it ideally suited for a rapid prescreening for thermodynamically viable IPR fullerenes with cages composed of hundreds of carbon atoms. With the inclusion of a global curvature term, this scheme is expected to be equally successful for small and large carbon clusters.

Table 4. Error Statistics of Various Estimation Schemes for ΔH_f°

	error (kcal/mol)[a]		
scheme	average	RMS	maximum
E_π and N[b]	14.01/17.24	18.20/34.32	61.90/311.05
E_π, N, and curvature[c]	13.95/15.41	17.50/18.72	59.51/59.51
motifs[d]	3.51/6.94	4.64/11.24	10.73/75.50
motifs and E_π	3.46/6.57	4.58/10.29	11.05/60.18
motifs and curvature[e]	**2.77/3.13**	**3.47/3.99**	**8.18/11.00**
motifs, curvature, and E_π	2.08/2.82	2.72/3.65	7.65/11.53

[a] Errors for the minimal training set followed by those for the entire set. [b] $\Delta H_f^\circ \approx 330.90245 + 13.27073E_\pi - 15.65634N$ kcal/mol. [c] $\Delta H_f^\circ \approx 5724.13010 + 20.32682E_\pi - 40.92109N - 1218684.187(N + 206.950)^{-1}$ kcal/mol. [d] Equation 3 without the global curvature term. [e] Equation 3.

Table 5. Motif Contributions to ΔH_f° [a]

I	ϵ_I (kcal/mol)	I	ϵ_I (kcal/mol)	I	ϵ_I (kcal/mol)
666666	30.336	655655	−6.576	6555	8.007
666665	18.636	655555	−0.133	5655	11.087
666655	13.560	555555	−0.313	5555	1.245
666565	6.351	6666	18.498	13/66	30.422
665665	−0.145	6665	16.476	13/56	34.103
666555	4.162	6656	14.792	13/55	26.377
665655	−2.468	6655	12.519	14/66	31.455
656565	−5.563	6565	14.779	14/56	32.167
665555	1.559	6556	14.255	14/55	29.980
656555	−0.807	5665	13.427	135	44.281

[a] Equation 3; see the text and Figure 1 for the explanation of the motif notation.

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[46] The B3LYP/6-31G* optimized geometries of these fullerenes and their total energies are available from the corresponding author upon request. A FORTRAN program for extracting motif counts from Cartesian coordinates of carbon atoms or from adjacency matrixes is also available.