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Structural Predictions for the C_{116} Molecule

Y. Achiba,[†] P. W. Fowler,*[,‡] D. Mitchell,[‡] and F. Zerbetto*[,§]

Department of Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo 192-03, Japan, Department of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD, U.K., and Dipartimento di Chimica, "G. Ciamician", Universitá di Bologna, via F. Selmi 2, 40126 Bologna, Italy

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A combination of topological and quantum mechanical techniques is used to predict the energetically favored isomer set for the experimentally detected but as yet uncharacterized C_{116} fullerene. A systematic search and calculation at the QCFF/PI (quantum-consistent force field/π) semiempirical level of the energies of the 6063 isomers of C_{116} that satisfy the isolated-pentagon rule (IPR) find that the isomers in the most stable group have low degrees of eccentricity and are predicted by the highly discriminating hexagon-neighbor rule (HNR), for which a more generally applicable formulation is proposed.

Introduction

The aim of this paper is to identify the thermodynamically most stable fullerene or fullerenes of formula C_{116}. A material of this formula has been separated by Achiba and co-workers[1] from Krätschmer−Huffman soot and is thought to consist of at most a few isomers. There are indications from scanning tunneling microscopy[2] that the individual molecules are spherical or ellipsoidal with moderate eccentricity, but there is as yet no definitive structural characterization. Systematic search and calculation of energies for likely candidate structures can help to narrow the range of possibilities for consideration by experimentalists and may highlight the different predictions of kinetic and thermodynamic modeling of fullerene formation.

The third allotropic form of carbon to become available in macroscopic quantities is based on the discrete cages now known as fullerenes. These molecular phases are less stable than graphite by about 40 kJ mol^{-1}, and yet it seems clear that, at least for low nuclearities, the most stable isomers at a given size are preferentially selected by the self-assembly process that produces the fullerenes present in the Krätschmer−Huffman soot. A paradigm of this behavior is C_{60} itself: out of the 1812 possible different ways of assembling 12 pentagons and 20 hexagons,[3] nature selects only one. Evidence that icosahedral C_{60} is also the energetically best of all the 1812 isomers is given by systematic search and calculation at the semiempirical level of the internal energies of all the isomers.[4] For the next fullerene separated in macroscopic quantities, C_{70}, a similarly exhaustive proof has not yet been reported, but physical and chemical intuition require its 12 pentagons to be isolated from one another (isolated-pentagon rule, IPR[5,6]). The unique IPR structure coincides with the observed molecular shape of C_{70}. For higher nuclearities where more than one isomer can have isolated pentagons, explicit calculations of the total energies are necessary. Whenever all the IPR isomers have been screened computationally and the molecular structure of the carbon cages determined by independent methods, it has been found that the major experimental isomers are also those of lowest energy. So far structures for C_{76}, C_{78}, and C_{84}[7−9] have been determined with certainty. Cages therefore correspond to a thermodynamically unstable allotropic form of carbon, but the assembly process appears to privilege the most stable of them, though not to the total exclusion of nonoptimal isomers.[1,8] At some high nuclearity, however, other factors must become important, as it is possible to synthesize tubes though these forms remain less stable than their spherical counterparts. It becomes crucial to identify the predictions of purely energetic arguments in a larger size range for eventual comparison with experimental evidence and the kinetic and equilibrium models. C_{116} offers a tractable model system for this purpose.

A fully unconstrained search of all classical C_{116} fullerenes, i.e., of all cages made up of 116 carbon atoms arranged in 12 pentagonal and 48 hexagonal faces, would require energy calculations for each of 1 207 119 structural isomers,[3] most, if not all, of which are expected to correspond to local minima on the potential energy surface. As this search is clearly not feasible, some filtering principle or rule of thumb must be applied to reduce the problem to a manageable number of cases.

The best available filter of this kind is the IPR:[5,6] the most stable isomer of any fullerene C_n ($n = 60$ or $n \geq 70$) is expected to have its 12 pentagons isolated from one another by intervening hexagons. The IPR is consistent with all experimentally determined higher-fullerene structures and is part of a more general correlation in which minimization of N_p, the number of pentagon adjacencies, is associated with high relative stability.[11,12]

In the case of C_{116}, imposition of the IPR reduces the set of candidates to 6063 structural isomers.[3,11] It is not claimed that these will coincide exactly with the 6063 most stable isomers, since some overlap in energy between the worst IPR and the best low-N_p cages is to be expected, but at least all those structures within 70−150 kJ mol^{-1} of the global minimum should fall within the IPR set since this is the estimated energetic cost of a single pentagon adjacency.[12−15] All energetically accessible isomers should therefore be covered by a search of the IPR set. The strategy adopted here was to make a complete calculation of optimal geometries and energies of all 6063 isolated-pentagon isomers within a well-defined semiempirical model[16] which has been used extensively before for similar purposes.[4,12,17] This gives a direct prediction of the most stable

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[†] Tokyo Metropolitan University.

[‡] University of Exeter.

[§] Universitá di Bologna.

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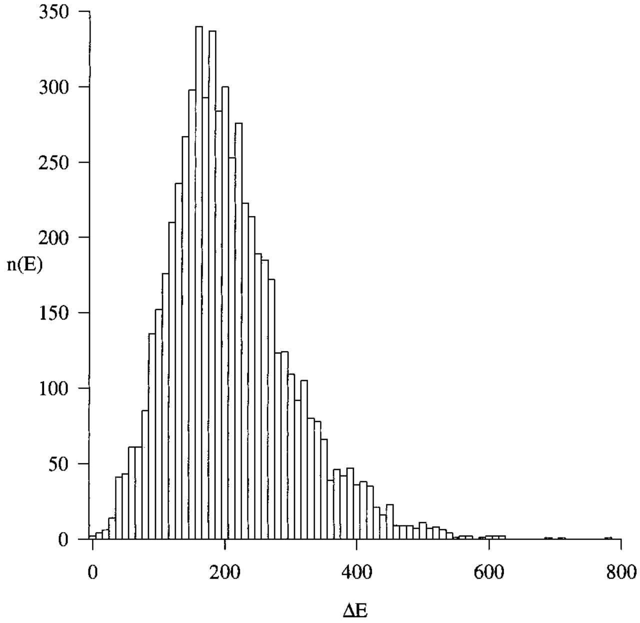

Figure 1. Distribution of energies of IPR isomers of C_{116}. $n(E)$ is the number of isomers with energies $\Delta E \pm 5$ kJ mol^{-1}. All energies are calculated within the QCFF/PI approximation and are quoted relative to that of the optimal isomer (116:6047) in the same model.

isomer (in fact, of a group of stable isomers), but it also gives a large and varied set of structures on which hypotheses about the relationship between structure and stability may be tested. Consideration of the computed distribution of isomers across the energy range can be used to place qualitative error bounds on the predictions.

Initial Calculations

Spiral codes[11,18] for the complete set of isomeric C_{116} fullerene structures with isolated pentagons were generated and used to construct the 6063 distinct adjacency matrices. Relative stabilities of all structures were estimated by carrying out a full geometry optimization on each cage using the QCFF/PI semiempirical method to incorporate σ and π contributions to the total energy. Starting geometries were produced by molecular mechanics refinement of "topological coordinates" [19] derived by diagonalization of the adjacency matrix. Every structure investigated was found to correspond to a local minimum.

The IPR isomers were found to span a range of 776 kJ mol^{-1} from best to worst, with a distribution illustrated by the histogram in Figure 1. The shape of this curve illustrates the main difficulty with predictions that attempt to distinguish between species that are basically similar; nine isomers have energies within the first 20 kJ mol^{-1} relative to the cage of lowest energy, and a total of 86 are found within the first 50 kJ mol^{-1}. Predictions of ordering are therefore likely to be strongly sensitive to the level of theory employed. In the QCFF/PI model, the isomer of lowest total energy turns out to be 116: 6047, which has D_2 symmetry. This is clearly not a definitive prediction, since even with an optimistic estimate of 10 kJ mol^{-1} for the basic energy resolution of the method, 6047, 6046, 5112, and 5939 would be indistinguishable (see Table 1) and could be reordered on inclusion of zero-point vibrational effects. The distribution has a mean energy of 208.2 kJ mol^{-1} relative to isomer 6047, with 3440 isomers lying below the mean and 2063 above. The standard deviation is 91 kJ mol^{-1}, the skewness 0.90, and kurtosis 1.38.

The spirals, relative QCFF/PI energies, and some topological characteristics of the 20 isomers of lowest energy are listed in Table 1. Their structures are illustrated in Figure 2a. Although the prediction of the single best isomer is not absolutely clear-cut, some general features of low-energy isomers can be established from the QCFF/PI data.

Structure−Energy Relationships

The first relationship is connected with the role of steric strain. In the QCFF/PI model, the energy contributions related to

TABLE 1: Twenty Low-Energy Isomers of C_{116}[a]

N_E	N_S	spiral	G	Δ	Δ_Q	H	ΔE	ΔE_ϕ
1	6047	1, 7, 12, 20, 27, 30, 35, 38, 45, 53, 58, 60	D_2	0.113	4.430	22.7500	0.0	0.0
2	6046	1, 7, 12, 20, 27, 30, 35, 38, 45, 53, 57, 59	D_2	0.219	4.601	22.7500	4.2	−0.8
3	5112	1, 7, 10, 14, 23, 30, 32, 40, 46, 49, 58, 60	C_2	0.116	4.167	22.7500	6.3	18.4
4	5939	1, 7, 10, 24, 27, 31, 33, 36, 42, 51, 57, 60	C_2	0.070	3.898	22.7500	7.9	25.1
5	4761	1, 7, 10, 13, 30, 32, 35, 38, 40, 52, 56, 60	C_1	0.139	4.331	22.8333	12.6	33.1
6	5462	1, 7, 10, 18, 24, 26, 36, 41, 44, 46, 57, 59	C_2	0.218	4.565	22.8333	14.6	31.8
7	5916	1, 7, 10, 24, 26, 32, 35, 41, 43, 45, 49, 59	C_2	0.177	4.418	22.8333	17.2	27.2
8	2795	1, 7, 9, 22, 24, 26, 40, 43, 45, 47, 58, 60	C_1	0.240	4.733	23.0000	18.0	96.2
9	5748	1, 7, 10, 23, 25, 30, 33, 41, 44, 48, 52, 58	C_2	0.160	4.537	22.8333	19.7	39.3
10	5927	1, 7, 10, 24, 27, 30, 33, 36, 51, 53, 56, 58	C_1	0.041	4.009	22.7500	20.5	25.1
11	5372	1, 7, 10, 18, 23, 26, 33, 40, 48, 52, 55, 58	C_2	0.136	4.490	22.9167	21.3	75.3
12	5373	1, 7, 10, 18, 23, 26, 33, 40, 49, 52, 55, 57	C_s	0.207	4.663	22.9167	22.6	74.1
13	4991	1, 7, 10, 14, 19, 35, 39, 41, 46, 49, 55, 60	C_1	0.246	4.746	22.9583	25.1	101.3
14	5857	1, 7, 10, 24, 26, 28, 31, 34, 48, 53, 56, 59	C_2	0.211	4.553	22.8333	25.9	42.7
15	1339	1, 7, 9, 12, 25, 32, 39, 42, 46, 49, 55, 59	C_2	0.321	4.895	23.0833	28.5	134.3
16	5880	1, 7, 10, 24, 26, 29, 33, 36, 44, 52, 56, 59	C_1	0.111	4.150	22.8333	29.3	43.5
17	1389	1, 7, 9, 12, 25, 34, 39, 42, 44, 49, 55, 59	C_1	0.096	4.199	22.9583	31.0	106.3
18	5769	1, 7, 10, 23, 25, 32, 35, 41, 43, 45, 52, 58	C_2	0.190	4.430	22.8333	31.4	47.3
19	5128	1, 7, 10, 14, 23, 30, 34, 40, 44, 49, 58, 60	C_2	0.095	4.072	22.8333	31.8	53.6
20	5855	1, 7, 10, 24, 26, 28, 31, 34, 47, 49, 54, 59	C_1	0.238	4.692	22.9167	31.8	50.2

[a] N_E is a label denoting the position of the isomer in the order of QCFF/PI energies. N_S is the position in the lexicographically ordered sequence[11] of 6063 spiral codes for all the isolated-pentagon fullerenes at this nuclearity. For each structure the spiral code is given as the set of 12 pentagon positions in the string of 60 faces. G is the maximal symmetry group of the cage, Δ is its HOMO−LUMO gap (in units of $|\beta|$) in the Hückel model, Δ_Q is the gap (in eV) as computed in the QCFF/PI approximation, and H is the second moment of the hexagon-neighbor signature. ΔE and ΔE_ϕ are respectively the total energy and its torsional component (in kJ mol^{-1}) calculated within the QCFF/PI approach and expressed relative to the isomer of lowest energy in that model, 116:6047.

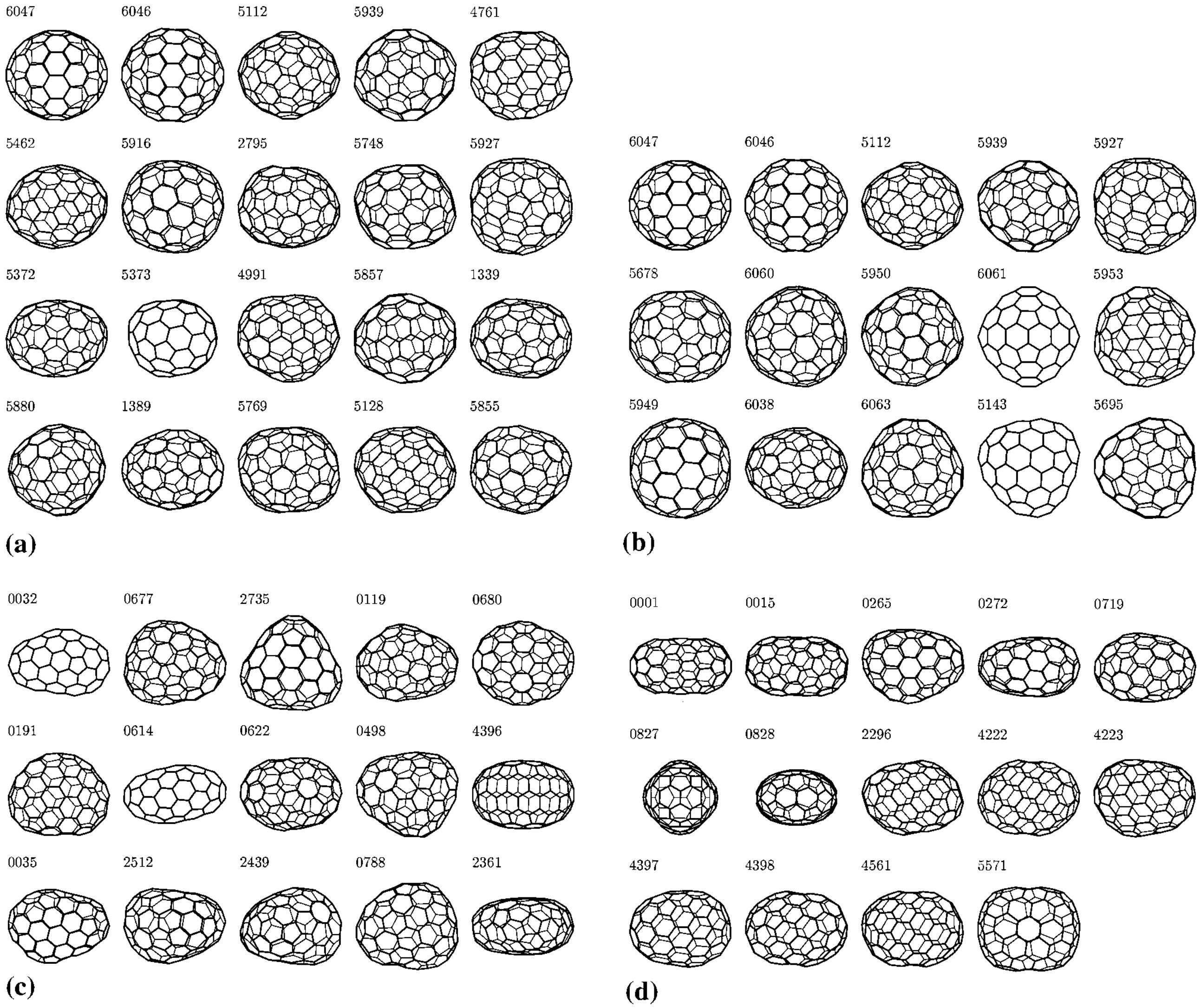

Figure 2. Optimized structures of C_{116} fullerene isomers calculated with the QCFF/PI model, arranged in order of increasing energy ((a) and (b)), spiral code (d), or band gap (c). Each isomer is labeled by its spiral number; other information on the isomers is listed in the tables. (a) The 20 isomers of lowest energy according to model; (b) the 15 HNR isomers; (c) the 15 isomers of largest Hückel HOMO−LUMO gap; (d) the sample set of 14 tubular isomers.

torsion and pyramidalization are collected together in the term E_ϕ. As Figure 3 shows, this term runs parallel to the total energy for the whole set of IPR isomers, establishing an important role for steric strain in isomer preference. A similar parallelism has been found in calculations on non-IPR isomers of C_{60}, C_{40}, and C_{76}.[4,12,17]

The isolated-pentagon rule itself is consistent with this trend, since isolation of pentagons is favored on both π-electronic and steric grounds. A further rule of thumb for the steric strain is the hexagon-neighbor rule (HNR), which first emerged from calculations on small IPR fullerenes (C_{84}) performed by Raghavachari.[20] The idea behind the HNR is that in a stable fullerene the hexagons should have environments that are as similar as possible in order that the steric strain be spread evenly. This idea is given quantitative form through the hexagon-neighbor signature, $\{h_k\}$, in which h_k is the number of hexagons with exactly k hexagonal neighbors. The HNR is then a requirement for minimal spread in $\{h_k\}$. This requirement can be made more precise as follows.[11]

Any IPR fullerene has $h_0 = h_1 = h_2 = 0$, and counting hexagons gives

$$h_3 + h_4 + h_5 + h_6 = n/2 - 10 \tag{1}$$

while counting pentagon−hexagon contacts gives

$$3h_3 + 2h_4 + h_5 = 60 \tag{2}$$

The ideal signatures $\{h_3, h_4, h_5, h_6\}$ are therefore readily shown to be

$$\begin{aligned} &\{80 - n,\quad 3n/2 - 90, 0, 0\}\ 60 \le n \le 80 \\ &\{0, 70 - n/2,\quad n - 80, 0\}\ 80 \le n \le 140 \\ &\{0, 0, 60,\quad n/2 - 70\}\ 140 \le n \end{aligned} \tag{3}$$

and thus for C_{116} the HNR selects the subset of the 6063 IPR isomers with signatures $h_3 = 0$, $h_4 = 12$, $h_5 = 36$, $h_6 = 0$. Direct search identifies 3128 isomers with $h_3 = 0$ but only 15 that also have $h_6 = 0$; all of the latter have the ideal HNR signature. The HNR is thus highly selective at this nuclearity and in fact becomes even more so for $n = 118$ and beyond.[11]

The hexagon-neighbor signature has also been used in work on lower fullerenes to define a single parameter to represent

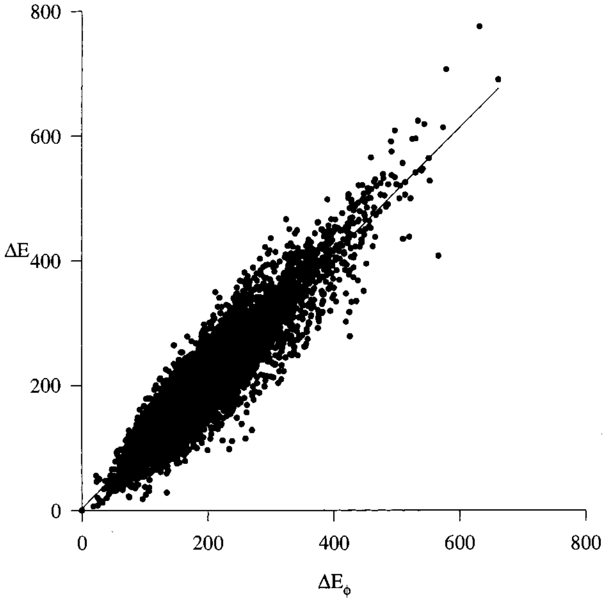

Figure 3. Correlation of total energy (ΔE) and its torsional component (ΔE_ϕ) and its torsional component (ΔE_ϕ) for the 6063 IPR isomers of C_{116}. Energies are calculated in kJ mol^{-1} and taken relative to those of isomer 116:6047. The straight line shows the least-squares fit: (ΔE/kJ mol^{-1}) = 1.018(ΔE_ϕ/kJ mol^{-1}) + 3.53 (standard deviation $\sigma = 35.0$).

steric strain. H is the normalized second moment of the signature

$$H = \sum_{k=0}^{6} k^2 h_k \Big/ \sum_{k=0}^{6} h_k \tag{4}$$

(i.e., a mean square coordination number of the hexagons). It has been found to correlate in roughly linear fashion with relative stability within the set of 1812 C_{60} isomers[4] where those isomers with higher values of H were in general found to be less stable than isomers with low values. One rationalization of this observation is that although graphitic patches may be intrinsically stabilizing, their presence in a finite fullerene implies crowding of pentagonal defects elsewhere on the surface so they cannot grow too large.

Minimization of H within the set of 6063 IPR isomers of C_{116} gives exactly the 15 HNR structures illustrated in Figure 2b and listed in Table 2, where their rankings in the order opf QCFF/PI energy and other topological and energetic properties are also given. It can be seen from a simple argument that the ideal HNR isomers will always minimize H for $n \le 140$. The proof is as follows. IPR fullerenes have four potentially nonzero h_k linked by the two relations (1) and (2). If we take h_5 and h_6 to be the two independent parameters in h_k, then h_3 and h_4 are

$$h_3 = 2h_6 + h_5 + 80 - n \ge 0 \tag{5}$$

$$h_4 = -3h_6 - 2h_5 - 90 + 3n/2 \ge 0 \tag{6}$$

For a fullerene with n atoms, the steric parameter H is a function of h_5 and h_6:

$$\begin{aligned}(n/2 - 10)H &= 9h_3 + 16h_4 + 25h_5 + 36h_6 \\ &= 6h_6 + 2h_5 - 720 + 15n \end{aligned} \tag{7}$$

from which it follows that $h_5 = h_6 = 0$, if realizable, will minimize H. Ideal HNR signatures (3) as described by the equation will therefore minimize H in the range $60 \le n \le 80$. When h_6 is zero but h_5 is not, (5) gives a lower bound of $n - 80$ for h_5 and therefore the ideal HNR signature (3) also minimizes H in the range $80 \le n \le 140$. Since fixing h_5 and h_6 determines the values of h_3 and h_4 through (5) and (6), the signatures that minimize H in the whole range $60 \le n \le 140$ are exactly those optimal under the HNR, and the correspondence works both ways, QED.

Although the ideal HNR signatures are not always realizable (e.g., for n = 72, 126, 128, and 132−138) and the minimal $(n/2 - 10)H = 15n - 720$ is therefore unattainable in some cases,[11] *some* structure or structures of lowest H must always exist. Minimization of H could therefore be used as a way of *defining* a hexagon-neighbor rule that would apply uniformly to isolated-pentagon fullerenes throughout the range $60 \le n \le 140$. For C_{116}, the 6063 IPR fullerenes span the relatively compressed range in H of 1140/48 = 23.75 to 1092/48 = 22.75.

Application of the minimal-H criterion to C_{116} gives encouraging results. A scatter plot of energy against H for the IPR set does indeed show a general trend to higher stability with lower values of H, though with considerable overlap in the energy ranges for successive values of the H parameter (Figure 4). Most importantly, the 4 isomers of lowest energy on the QCFF/PI model lie within the minimal-H set. A search of this set of 15 isomers alone would therefore have been enough to identify all the best candidates for the most stable C_{116} fullerene.

A further qualitative indication of the importance of the steric factor is the fact that the optimized structures (Figure 2) appear to show a general tendency to "roundness" in the more stable structures. This rough generalization can be given numerical form by computing a "sphericity" $S = \sum_i (r_i - \bar{r})^2/\bar{r}^2$, i.e., the

TABLE 2: The 15 IPR Fullerene Isomers of C_{116} That Obey the Hexagon-Neighbor Rule[a]

N_E	N_S	spiral	G	Δ	Δ_Q	H	ΔE	ΔE_ϕ
1	6047	1, 7, 12, 20, 27, 30, 35, 38, 45, 53, 58, 60	D_2	0.113	4.430	22.7500	0.0	0.0
2	6046	1, 7, 12, 20, 27, 30, 35, 38, 45, 53, 57, 59	D_2	0.219	4.601	22.7500	4.2	−0.8
3	5112	1, 7, 10, 14, 23, 30, 32, 40, 46, 49, 58, 60	C_2	0.116	4.167	22.7500	6.3	18.4
4	5939	1, 7, 10, 24, 27, 31, 33, 36, 42, 51, 57, 60	C_2	0.070	3.898	22.7500	7.9	25.1
10	5927	1, 7, 10, 24, 27, 30, 33, 36, 51, 53, 56, 58	C_1	0.041	4.009	22.7500	20.5	25.1
47	5678	1, 7, 10, 23, 25, 27, 32, 42, 44, 47, 51, 57	C_2	0.019	3.764	22.7500	39.7	41.8
70	6060	1, 7, 20, 22, 25, 28, 32, 38, 41, 44, 48, 60	D_3	0.262	3.923	22.7500	46.4	23.4
90	5950	1, 7, 10, 24, 27, 32, 36, 40, 43, 47, 50, 55	C_2	0.197	3.892	22.7500	50.6	27.6
118	6061	1, 7, 20, 23, 25, 28, 32, 35, 41, 44, 50, 60	T_h	0.331	3.986	22.7500	56.1	23.0
176	5953	1, 7, 10, 24, 27, 32, 36, 43, 47, 51, 54, 57	C_3	0.231	3.920	22.7500	66.1	47.7
256	5949	1, 7, 10, 24, 27, 32, 36, 40, 43, 45, 48, 59	C_2	0.049	3.688	22.7500	78.7	53.1
751	6038	1, 7, 12, 14, 20, 30, 35, 40, 45, 49, 53, 60	C_2	0.133	3.677	22.7500	113.4	74.9
872	6063	1, 8, 10, 23, 25, 28, 30, 45, 47, 50, 53, 60	T	0.253	3.807	22.7500	120.1	94.1
992	5143	1, 7, 10, 14, 23, 31, 40, 42, 46, 48, 50, 54	C_{3h}	0.010	3.764	22.7500	125.1	104.2
1083	5695	1, 7, 10, 23, 25, 28, 32, 43, 47, 49, 52, 55	D_3	0.036	3.742	22.7500	129.7	107.1

[a] The notation is as in Table 1, and the isomers are ordered by increasing QCFF/PI energy.

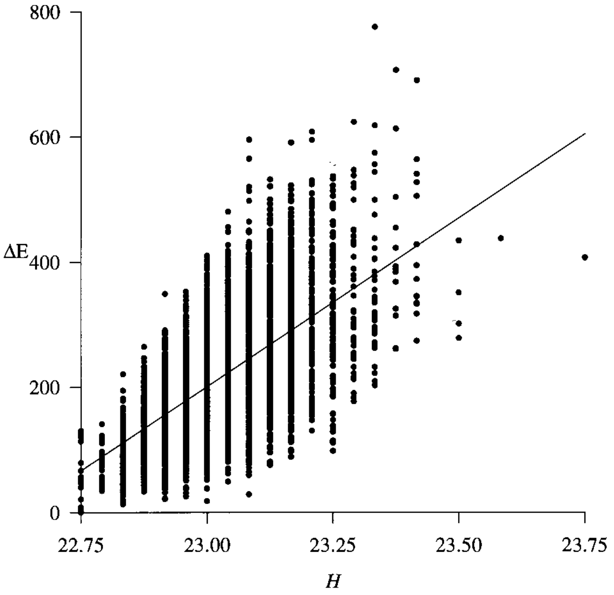

Figure 4. Correlation of total energy (ΔE) and second moment of the hexagon-neighbor signature (H) for the 6063 IPR isomers of C_{116}. Energies are calculated in kJ mol^{-1} and taken relative to that of isomer 116:6047. H is dimensionless. The straight line shows the least-squares fit: (ΔE/kJ mol^1) = 539.9H − 12217.7 (standard deviation $\sigma = 71.3$).

sum over all atoms of their normalized square deviation from the average distance from the centre of gravity of the cluster. A survey based on topological coordinates of all 6063 IPR isomers shows that the HNR criterion produces nearly spherical cages: six of the eight most spherical of all IPR cages are HNR, and 116:6047 is in the first three on the *S* criterion. When the optimized coordinates are used instead, the computed *S* values rise, but HNR isomers still figure as the four most spherical. Unfortunately, the detailed energy ordering of the whole set is not predicted well by the *S* parameter with either topological or computed coordinates, so that its usefulness remains only qualitative.

Electronic versus Steric Control of Total Energy

Though steric effects appear to dominate, overall stability of a fullerene is of course a compromise between competing steric and π-electronic effects. To assess this competition a further set of IPR isomers was selected for inspection. The 15 isomers of largest HOMO−LUMO gap according to simple Hückel theory are listed in Table 3 and illustrated in Figure 2c. Only one of these has a formal properly closed shell with a bonding HOMO and antibonding LUMO, and this is the "sporadic"[11] isomer 116:2361; its gap of 0.3626|β| is only the 15th largest in the IPR set, exceeded by those of 14 pseudoclosed shells with formally bonding LUMO energies, none of which obey the hexagon-neighbor rule. The HNR isomers would fare badly on the HOMO−LUMO gap criterion: the structure with the largest gap in the minimal-*H* set is 116:6061 which comes only 48th in gap in the full IPR set, and the next, 116:6060, is ranked 254th. Equally, all the large-gap isomers have poor values of *H*. No isomer satisfies both requirements.

As the QCFF/PI energies for this set show (Table 3), possession of a large gap in the Hückel approximation is neither sufficient nor necessary for overall stability. The isomers in this set are all at least 170 kJ mol^{-1} above the most stable structure. Figure 5 shows the correlations between Hückel and QCFF/PI parameters for the full set of IPR isomers. Neither delocalization energy nor HOMO−LUMO gap (Hückel or QCFF/PI) correlates with the computed total energy, and the Hückel and QCFF/PI gaps themselves are poorly correlated. On the whole, therefore, π-electronic structure at the molecular orbital level does not seem to be a useful predictor of the overall stability within the IPR set.

Tubular Fullerenes

It has been suggested[1] that isolable fullerenes in the size range of 100 or more atoms will be cylindrical and characterized by a limited number of caps (hemispherical patches containing six pentagons). This criterion is unrelated to electronic and steric arguments but is inspired by fact of the synthesis of nanotubes at high molecular weight. Although isolability is not the same as thermodynamic stability, the implications of cylindrical shape for stability can be explored using the dataset of 6063 QCFF/PI isomer energies.

Isomer topologies of a cylindrical type were constructed by idenfying all possible tubular extensions of C_{76}. First, all possible spiral codes for the D_2 IPR isomer of C_{76} were listed, and for each it was attempted to insert (116 − 76)/2 = 20 new hexagons after the sixth pentagon in the sequence. If the resulting sequence can be wound up as a fullerene, it will be one with two hemi-C_{76} caps on a hexagonal barrel. The eight distinct IPR isomers produced in this way are listed in Table 4.The same technique was used to produce tubular extensions of the two most stable C_{84} fullerenes (the D_2 84:22 and D_{2d} 84:23)[4] and the five extra isomers derived in this way are 9−13 in the table. Finally, a cylindrical structure of D_2 symmetry

TABLE 3: The 15 IPR Fullerene Isomers of C_{116} with the Largest HOMO−LUMO Gaps in Simple Hückel Theory, Ordered by Decreasing gap Δ[a]

N_E	N_S	spiral	G	Δ	Δ_Q	H	ΔE	ΔE_ϕ
1563	32	1, 7, 9, 11, 13, 37, 40, 43, 46, 56, 58, 60	C_s	0.404	4.968	23.2500	147.7	246.0
2448	677	1, 7, 9, 12, 20, 26, 37, 42, 47, 51, 55, 59	C_1	0.394	4.908	23.2083	175.7	229.7
760	2735	1, 7, 9, 20, 23, 26, 37, 41, 44, 48, 53, 60	C_1	0.390	4.897	23.2500	113.8	180.7
1551	119	1, 7, 9, 11, 22, 25, 38, 41, 44, 56, 58, 60	C_1	0.386	4.882	23.2083	147.3	224.3
5564	680	1, 7, 9, 12, 20, 26, 37, 44, 51, 55, 58, 60	C_1	0.383	4.786	23.2500	344.3	341.8
5978	191	1, 7, 9, 11, 22, 38, 41, 46, 50, 52, 55, 57	C_1	0.381	4.759	23.3750	454.8	456.5
5165	614	1, 7, 9, 12, 18, 25, 31, 46, 50, 54, 56, 59	C_{2h}	0.377	4.805	23.2500	300.8	360.2
2426	622	1, 7, 9, 12, 20, 24, 39, 42, 49, 55, 57, 60	C_1	0.377	4.826	23.2083	175.3	211.3
1184	498	1, 7, 9, 11, 25, 36, 40, 43, 46, 48, 53, 60	C_1	0.374	4.884	23.2500	133.5	214.6
496	4396	1, 7, 10, 13, 19, 30, 39, 45, 48, 50, 56, 59	D_2	0.369	5.051	23.0833	97.5	170.3
3791	35	1, 7, 9, 11, 13, 37, 41, 44, 50, 55, 57, 60	C_1	0.367	4.816	23.3333	222.2	320.5
1866	2512	1, 7, 9, 13, 30, 32, 35, 39, 48, 50, 52, 55	C_1	0.366	4.815	23.2500	157.7	237.7
3617	2439	1, 7, 9, 13, 23, 32, 39, 46, 50, 52, 54, 56	C_1	0.363	4.898	23.2917	215.9	261.9
4520	788	1, 7, 9, 12, 20, 37, 40, 45, 48, 51, 53, 57	C_1	0.363	4.806	23.2500	256.5	270.3
6058	2361	1, 7, 9, 13, 23, 29, 42, 44, 48, 50, 57, 60	C_1	0.363	4.766	23.3750	613.8	573.6

[a] The notation is as in Table 1.

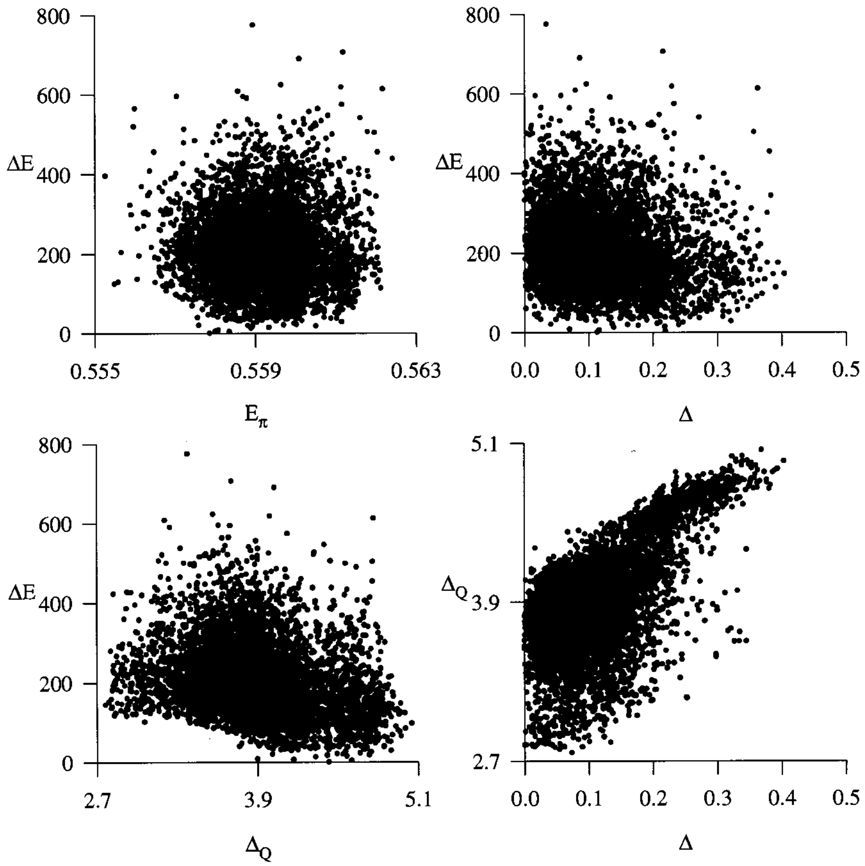

Figure 5. Correlation of Hückel quantities with those from the more explicit QCFF/PI model of electronic structure. ΔE is the energy (kJ mol^{-1}) relative to that of isomer 116:6047. E_π is the delocalization energy per electron, and Δ is the Hückel HOMO−LUMO gap, both calculated in units of a single β parameter common to all bonds. Δ_Q is the HOMO−LUMO gap (eV) calculated in the QCFF/PI model.

TABLE 4: A Sample of Cylindrical IPR Fullerene Isomers of C_{116}, Ordered by Increasing Spiral Number, N_S[a]

N_E	N_S	spiral	G	Δ	Δ_Q	H	ΔE	ΔE_ϕ
5856	1	1, 7, 9, 11, 13, 18, 46, 51, 53, 55, 57, 59	D_2	0.123	4.161	23.7500	407.9	566.5
5176	15	1, 7, 9, 11, 13, 30, 43, 46, 49, 54, 56, 58	C_2	0.271	4.356	23.5000	302.1	419.7
4281	265	1, 7, 9, 11, 23, 32, 39, 43, 48, 50, 53, 58	C_1	0.021	4.019	23.2083	243.9	281.6
5677	272	1, 7, 9, 11, 23, 34, 37, 41, 43, 51, 57, 60	C_1	0.134	4.052	23.2083	366.1	387.4
2971	719	1, 7, 9, 12, 20, 34, 38, 40, 43, 49, 56, 59	C_1	0.216	4.350	23.1250	192.5	217.1
5478	827	1, 7, 9, 12, 21, 34, 38, 43, 49, 51, 53, 60	D_{2d}	0.000	3.570	23.4167	333.5	428.4
6041	828	1, 7, 9, 12, 21, 34, 40, 49, 51, 53, 55, 57	D_2	0.198	4.324	23.4167	528.0	552.7
2763	2296	1, 7, 9, 13, 22, 33, 38, 42, 49, 52, 54, 56	C_2	0.020	4.064	23.1667	185.4	236.4
3591	4222	1, 7, 10, 13, 18, 22, 37, 49, 52, 54, 56, 59	C_2	0.071	3.389	23.0833	214.6	225.9
3024	4223	1, 7, 10, 13, 18, 22, 37, 50, 52, 54, 56, 58	C_1	0.035	3.105	23.0417	194.1	184.1
2030	4397	1, 7, 10, 13, 19, 33, 37, 41, 47, 50, 54, 59	C_1	0.200	3.893	23.0000	162.3	166.5
802	4398	1, 7, 10, 13, 19, 33, 38, 41, 47, 49, 54, 59	C_2	0.297	4.679	23.0000	116.3	151.9
2389	4561	1, 7, 10, 13, 26, 28, 43, 45, 47, 50, 54, 58	C_2	0.105	3.112	23.0000	174.1	158.2
300	5571	1, 7, 10, 18, 26, 33, 36, 38, 41, 45, 57, 59	D_2	0.286	4.762	23.0833	83.3	151.5

[a] The first 13 are constructed by expansion of stable C_{76} and C_{84} structures, as described in the text, and the final isomer is a structure consistent with a hypothetical ring-stacking growth mechanism.[1] The notation is as in Table 1.

consistent with ring-stacking[1] extension of one of the isomers of C_{92} (92:84 in the spiral listing)[11] was also considered; this is entry 14 in the table. All the considered tubular isomers perform poorly in total energy terms; the best of them lies over 80 kJ mol^{-1} above isomer 6047 and is 300th in the energy order. The structures are shown in Figure 2d.

Conclusions

To summarize this survey of over 6000 geometry optimizations: the QCFF/PI method does not choose a clear winner from the list of candidates but points to a small set of structures of similar energy, all worthy of further investigation. In this respect, C_{116} appears to parallel C_{84}, where two isomers (84:22 and 84:23)[11] are found to be almost isoenergetic.[9] Nonetheless, several clear distinctions between structural hypotheses are made. The hexagon-neighbor rule is successful in picking out the best few isomers. Large band gap is not a necessary concomitant of stability, nor is high symmetry. Cages with T and T_h symmetry, for example, figure in the HNR list of 15 isomers but are well down the energy order. Cylindrical extension of smaller stable fullerenes is also not conducive to high stability, whether or not it may be kinetically favored in the growth mechanism. All these features are reminiscent of C_{84}.

A safe conclusion seems to be that the most stable isomer of C_{116} is one that obeys the hexagon-neighbor rule. Its precise identification may require considerable further work, both theoretical and experimental.

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