J. Am. Chem. Soc. 1995, 117, 10113−10118 10113

Can Large Fullerenes Be Spherical?

Dirk Bakowies, Michael Bühl, and Walter Thiel*

Contribution from the Organisch-Chemisches Institut, Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

Received June 1, 1995⊗

Abstract: MNDO geometry optimizations predict a single energy minimum for each of the Goldberg type (I_h) fullerenes C_{180}, C_{240}, C_{540}, and C_{960} which corresponds to an icosahedrally shaped structure with strong curvature at the 12 pentagons and nearly planar segments composed of hexagons. Constrained geometry optimizations preserving a spherical shape lead to considerably larger energies and show that an evenly distributed curvature is strongly disfavored. The results are confirmed quantitatively by ab initio SCF calculations for C_{180} and C_{240} employing a split valence basis set, but contrast the conclusions from a previous density functional study. The observed trends are discussed on the basis of curvature-corrected Hückel calculations and simple force field estimates.

1. Introduction

There is a striking similarity in the architecture of the geodesic domes constructed by R. Buckminster Fuller[1] and the carbon cage molecules discovered by Kroto et al.[2] Both the macroscopic and the microscopic objects are three-valent convex polyhedra composed of an arbitrary number of hexagons which are connected by exactly 12 pentagons to yield a closed surface. This correspondence prompted Kroto to call the new class of carbon molecules fullerenes, and the prototypical C_{60} buckminsterfullerene, in honor of the famous architect.[3] To what extent does the similarity hold? Fuller's domes are geodesic, they exhibit a completely spherical shape, as can be seen on photographs of the best-known example, the U.S. pavillon at the 1967 Expo in Montréal.[1] Can large fullerenes adopt the same shape, can they be spherical, or do they generally prefer polyhedrally facetted shapes?[4,5]

There is no doubt that the most probable candidates to be spherical are fullerenes with icosahedral symmetry. This forces all 60 atoms participating in the 12 five-membered rings to be equivalent and hence to lie on the same sphere. Hence, symmetry requires I_h-C_{60} to be spherical, whereas larger fullerenes with icosahedral symmetry may either be spherical or facetted depending on whether the curvature is spread uniformly over the cage or concentrated at the five-membered rings.

Though little is known experimentally about icosahedral fullerenes other than C_{60},[6] they are generally assumed to be among the most stable isomers of carbon cages with a given number of atoms.[7−9] This may be rationalized with their maximum possible separation of five-membered rings.[10] Ab initio SCF calculations employing minimal basis sets showed a marked thermodynamic preference for I_h-C_{180} and I_h-C_{240} over tube-shaped isomers.[9] Some of the "bucky onions" which have been observed by electron microscopy may also be composed of icosahedral carbon cages. Their micrographs are consistent with those simulated for an assembly of concentric shells of fullerenes with I_h symmetry.[11]

In the first known theoretical work on giant fullerenes, Jones assumed a spherical shape to estimate the stability against inversion of one-half of the molecule at its equator.[12,13] Molecular mechanical[5] and semiempirical quantum-chemical[4] calculations, however, indicated a marked tendency of fullerenes with I_h symmetry to form icosahedrally shaped cages. Further evidence stemmed from simple geometrical arguments.[14,15] This contrasts recent density functional calculations for I_h-C_{240} employing the novel divide and conquer technique[16] which resulted in two distinct energy minima, the energetically more favorable of which refers to a nearly spherical structure.[17,18]

In the light of these controversial results we decided to reinvestigate the problem both by semiempirical and by ab initio SCF techniques. The results are compared to simple force field estimates and to curvature-corrected Hückel calculations which have been useful in previous studies[4,19,20] to interpret calculated relative stabilities of homologous and isomeric fullerenes.

2. Fullerenes To Be Studied

Fullerenes with icosahedral (I or I_h) symmetry belong to the class of Goldberg polyhedra[21,22] which have $n = 20(b^2 + bc + c^2)$ vertices where b and c are non-negative integers. Of these only fullerenes with a multiple of 60 atoms (($b - c$) mod 3 = 0) are expected to have closed-shell electronic ground states.[21] Full icosahedral symmetry (I_h) further requires b to be equal to either 0 or c. This yields two different series of closed-shell

---

⊗ Abstract published in *Advance ACS Abstracts*, September 15, 1995.

[1] Staber, M. *Graphis (Zürich)* **1967**, *23*, 378.

[2] Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.

[3] Kroto, H. W. *Nature* **1987**, *329*, 529.

[4] Bakowies, D.; Thiel, W. *J. Am. Chem. Soc.* **1991**, *113*, 3704.

[5] Yoshida, M.; Osawa, E. *Fullerene Sci. Technol.* **1993**, *1*, 55.

[6] Kroto, H. W.; Allaf, A. W.; Balm, S. P. *Chem. Rev.* **1991**, *91*, 1213.

[7] Adams, G. B.; Sankey, O. F.; Page, J. B.; O'Keeffe, M.; Drabold, D. A. *Science* **1992**, *256*, 1792.

[8] Schmalz, T. G.; Seitz, W. A.; Klein, D. J.; Hite, G. E. *J. Am. Chem. Soc.* **1988**, *110*, 1113.

[9] Scuseria, G. E. In *Buckminsterfullerenes*; Billups, W. E., Ciufolini, M. A., Eds.; VCH: New York, 1992; pp 103−124.

[10] Raghavachari, K. *Chem. Phys. Lett.* **1992**, *190*, 397.

[11] McKay, K. G.; Kroto, H. W.; Wales, D. J. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2815.

[12] Jones, D. E. H. *New Scient.* **1966**, *32*, 345.

[13] Jones, D. E. H. *The Inventions of Daedalus*; W. H. Freeman & Co., Ltd.: Oxford, 1982; pp 118−119.

[14] Kroto, H. W. *Chem. Br.* **1990**, *26*, 40.

[15] Tarnai, T. *Phil. Trans. R. Soc. London, A* **1993**, *343*, 145.

[16] Yang, W. *Phys. Rev. Lett.* **1991**, *66*, 1438.

[17] Lu, J. P.; Yang, W. *Phys. Rev. B* **1994**, *49*, 11421.

[18] York, D.; Lu, J. P.; Yang, W. *Phys. Rev. B* **1994**, *49*, 8526.

[19] Bakowies, D.; Gelessus, A.; Thiel, W. *Chem. Phys. Lett.* **1992**, *197*, 324.

[20] Bakowies, D.; Kolb, M.; Thiel, W.; Richard, S.; Ahlrichs, R.; Kappes, M. M. *Chem. Phys. Lett.* **1992**, *200*, 411.

[21] Fowler, P. W. *Chem. Phys. Lett.* **1986**, *131*, 444.

[22] Goldberg, M. *Tohoku Math. J.* **1937**, *43*, 104.

0002-7863/95/1517-10113$09.00/0

fullerenes with I_h symmetry, C_{60}, C_{240}, C_{540}, C_{960}, ... ($b = c$), and C_{180}, C_{720}, C_{1620}, C_{2880}, ... ($b = 0$). In the present paper, we study consecutive members of the first series (C_{240},C_{540},C_{960}) but also include C_{180}, the smallest of the icosahedral fullerenes for which both spherical and facetted structures are conceivable.

3. Computational Details

Semiempirical closed-shell SCF calculations were carried out using the standard MNDO parameters[23] and the current MNDO95 program.[24] The molecular geometries of C_{180}, C_{240}, C_{540}, and C_{960} were completely optimized within I_h symmetry. Since no stationary points corresponding to approximately spherically shaped fullerenes could be located, we performed a second series of geometry optimizations subject to the additional constraint that all atoms lie on the same sphere. This requirement reduces the number of degrees of freedom from 6 (C_{180}), 7 (C_{240}), 15 (C_{540}), and 26 (C_{960}) to 4, 5, 10, and 17, respectively. Suitable input geometries were generated automatically by a computer program specifically designed for such purposes.[25]

Ab initio SCF calculations were carried out using the TURBOMOLE program[26] and a split-valence basis set denoted as sv7s4p.[27] This (7s4p)/[3s2p] basis set with a 511/31 contraction has been energy-optimized for the carbon atom and is known to provide reasonable molecular structures for fullerenes at the SCF level, with errors of typically 0.01 Å, but no larger than 0.02 Å, in bond lengths.[28] The present ab initio study comprises single point calculations at MNDO geometries for C_{180} and C_{240} as well as complete geometry optimizations for C_{180} (with and without the constraint of sphericity).

To our knowledge, the semiempirical calculations for C_{960} (3840 basis functions) are among the largest geometry optimizations which have ever been carried out using MNDO or related methods. The ab initio geometry optimizations for C_{180} (1620 basis functions) likewise belong to the largest which have ever been performed employing ab initio Hartree Fock methods. Using the optimized MNDO geometry as the starting point for the constrained optimization and the resulting geometry as the starting point for the unconstrained optimization, these ab initio calculations converged in 30–40 cycles with an energy criterion of 10^{-5} hartree, each cycle requiring typically 5 h of CPU time on an IBM RS/6000–580 workstation.

4. Results

Despite considerable effort only one energy minimum could be located with MNDO for each of the fullerenes under study. The resulting geometries correspond to icosahedrally facetted shapes showing the twelve pentagons connected by nearly planar sheets of hexagons as depicted in the left column of Figure 1. Constrained optimizations forcing all atoms to have the same distance R to the center of gravity resulted in the spherical structures shown in the right column of Figure 1. In contrast to the former[29] none of these spherically shaped geometries corresponds to a minimum of the potential energy surface, nor even to a stationary point. The structures are, however, minimal in energy with respect to distortions which preserve sphericity, as has been checked for C_{180} and C_{240}. Hence we may conclude that the lowest-energy geometries of both the facetted and the spherical forms exhibit icosahedral symmetry.

Further evidence that there is only one energy minimum for each of the fullerenes comes from the observation that any full MNDO geometry optimization starting from a spherical structure resulted in the same icosahedrally facetted geometry which was also obtained starting from other trial structures. For computational reasons this was only checked for the smaller fullerenes C_{180}, C_{240}, and C_{540}, but there is no reason to doubt that it holds true for C_{960} either. The ab initio geometry optimization of C_{180} confirmed these results. Again, the spherical structure obtained from a constrained optimization relaxed to an icosahedrally facetted geometry after removal of the constraint.

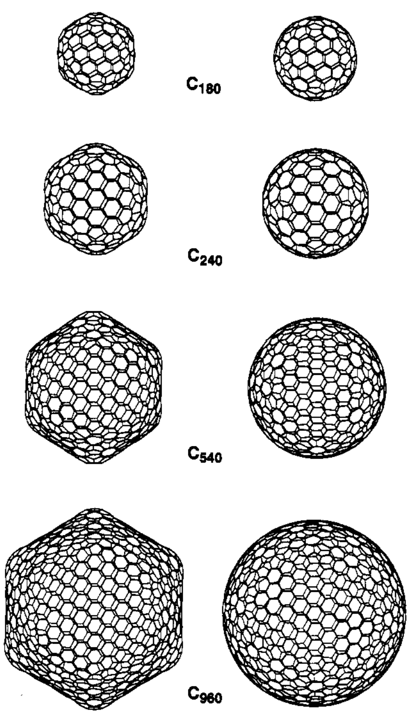

Figure 1. Facetted (left) and spherical (right) geometries of the fullerenes I_h-C_{180}, I_h-C_{240}, I_h-C_{540}, and I_h-C_{960}.

Table 1. Structural Data (Distances) for Goldberg-Type Fullerenes: Ab Initio and MNDO Results[a,b]

molecule	shape	R_{av}	R_{min}	R_{max}	r_{av}	r_{min}	r_{max}
C_{180}	icosahedral	6,197	6,078	6.365	1.443	1.396	1.463
		6.131	*6,022*	*6.289*	*1.427*	*1.376*	*1.450*
C_{240}	icosahedral	7.146	7.012	7.416	1.442	1.394	1.465
C_{540}	isocahedral	10.663	10.329	11.472	1.440	1.395	1.458
C_{960}	icosahedral	14.181	13.677	15.552	1.439	1.396	1.455
C_{180}	spherical	6.211	6.211	6.211	1.444	1,385	1.470
		6.147	*6.147*	*6.147*	*1.428*	*1.365*	*1.464*
C_{240}	spherical	7.167	7.167	7.167	1.443	1.378	1.476
C_{540}	spherical	10.750	10.750	10.750	1.443	1.356	1.497
C_{960}	spherical	14.332	14.332	14.332	1.442	1.341	1.493

[a] MNDO values are reported in normal type, ab initio SCF values are reported in italics. [b] Average, minimum, and maximum distances to the center of gravity (R, in Å) and bond lengths (r, in Å).

(a) Geometries. All relevant geometrical data are collected in Tables 1 and 2. The overall agreement between the MNDO and the ab initio results for C_{180} is satisfactory. Bond distances are calculated slightly shorter in the ab initio case, the differences being somewhat larger for the minimum bond lengths (0.02 Å) than for the maximum bond lengths (0.01 Å). Quantitatively similar trends have been observed for C_{60},[4,28,30] C_{70},[4,28] and C_{84}.[20] The cage diameters $2R$ are smaller (by about 0.13 Å) in the ab initio case, consistent with the results for bond lengths. Good agreement is also found for all types of angles reported in Table 2, the largest deviation being 1.6°. Even more important than the satisfactory absolute agreement between the MNDO and the ab initio data is the nearly quantitative agreement for relative values when comparing the facetted and the spherically shaped

---

(23) Dewar, M. J. S.; Thiel, W. J. Am. Chem. Soc. **1977**, *99*, 4899.

(24) Thiel, W. Program MNDO95, Universität Zürich, 1995.

(25) Bakowies, D.; Thiel, W. To be submitted for publication.

(26) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165.

(27) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

(28) Richard, S. Diplomarbeit, Universität Karlsruhe, 1992.

(29) The fully optimized geometries of I_h-C_{180} and I_h-C_{240} have, by force constant analysis, been confirmed to be true energy minima.[4]

(30) Schneider, U.; Richard, S.; Kappes, M. M.; Ahlrichs, R. *Chem. Phys. Lett.* **1993**, *210*, 165.

Table 2. Structural Data (Angles) for Goldberg-Type Fullerenes: Ab Initio and MNDO Results[a,b]

molecule	shape	α_{av}	α_{max}	$\Sigma(\Delta\alpha_i)^2$	Θ_{av}	Θ_{min}	Θ_{max}	$\Sigma\Theta_i^2$
C_{180}	icosahedral	118.48	122.52	3.332	6.83	5.01	9.71	2.791
		118.50	*121.93*	*3.139*	*6.81*	*5.29*	*9.58*	*2.754*
C_{240}	icosahedral	118.79	123.01	3.426	5.95	4.22	9.67	2.947
C_{540}	icosahedral	119.34	121.55	3.167	4.00	2.24	10.31	3.625
C_{960}	icosahedral	119.58	121.28	3.096	3.01	1.61	10.38	4.060
C_{180}	spherical	118.65	126.54	5.881	6.68	6.56	6.79	2.444
		118.67	*124.87*	*4.836*	*6.67*	*6.51*	*6.83*	*2.441*
C_{240}	spherical	118.99	129.47	7.400	5.78	5.67	5.83	2.442
C_{540}	spherical	119.55	133.13	16.069	3.85	3,71	3.91	2.438
C_{960}	spherical	119.75	134.90	28.293	2.89	2.75	2.93	2.437

[a] MNDO values are reported in normal type, ab initio SCF values are reported in italics. [b] Average, minimum, and maximum in-plane (α) and POAV (Θ) angles in deg, sum over squared angles in rad^2, $\Delta\alpha_i = \alpha_i - 2\pi/3$. α_{min} is equal to 108.0° in any case.

Table 3. Energies of Spherical Fullerene Structures Relative to Their Facetted Counterparts[a]

molecule	MNDO	ab initio[b]	force field[c]
C_{180}	0.77	0.88 (0.81)	0.69
C_{240}	0.85	0.92	0.82
C_{540}	1.96		1.47
C_{960}	2.63		1.79

[a] Energies per atom in kcal/mol. [b] Ab initio values at optimized MNDO geometries (in parentheses: at optimized ab initio geometries). The corresponding total energies are, in au, as follows: −6 809.346 30, −6 809.114 73 (C_{180}, ab initio geometry); −6 809.263 85, −6 809.012 07 (C_{180}, MNDO geometry); −9 079.438 79, −9 079.085 82 (C_{240}, MNDO geometry). [c] Force field estimates composed of stretching, in-plane, and out-of-plane bending contributions at the optimized MNDO geometries. See text.

Table 4. MNDO Heats of Formation and Related Data for Goldberg-Type Fullerenes[a,b]

molecule	shape	ΔH_f	ΔH_f^C	ΔE_π^C	ΔE_{str}^C	ΔE_{inp}^C	ΔE_{oop}^C	ΔH_f^C(est)
C_{180}	icosahedral	1392.4	7.74	1.83	0.37	1.12	3.11	7.60
C_{240}	icosahedral	1595.5	6.65	1.52	0.32	0.86	2.46	6.65
C_{540}	icosahedral	2580.2	4.78	1.07	0.18	0.35	1.34	4.88
C_{960}	icosahedral	3756.8	3.91	0.76	0.13	0.19	0.85	4.17
C_{180}	spherical	1530.4	8.50	1.51	0.60	1.96	2.74	8.30
C_{240}	spherical	1800.7	7.50	1.22	0.56	1.85	2.05	7.46
C_{540}	spherical	3636.6	6.73	0.76	0.67	1.76	0.91	6.34
C_{960}	spherical	6281.1	6.54	0.60	0.71	1.74	0.51	5.96

[a] Heat of formation: total (ΔH_f) and per atom (ΔH_f^C); force field estimate (ΔH_f^C(est)) based on the extrapolated MNDO value ΔH_f^C = 3.0 kcal/mol for a planar graphite sheet[4] and the sum of stretching (ΔE_{str}^C), in-plane (ΔE_{inp}^C), and out-of-plane bending (ΔE_{oop}^C) contributions; diminished π interaction energy (ΔE_π^C) relative to a planar graphite sheet estimated from curvature corrected Hückel calculations. ΔE_π^C is identical to D_{CREPE} as defined in ref 4. [b] All values in kcal/mol.

forms of C_{180}. This confirms earlier experience that MNDO predicts trends in the geometries of isomeric fullerenes reliably.[20]

Assuming a constant number of atoms per unit surface area one should expect the cage diameters to increase in ratios of $\sqrt{3}$ (C_{180}), 2 (C_{240}), 3 (C_{540}), and 4 (C_{960}). This prediction is nicely confirmed by the calculated data for the facetted species ($\sqrt{3}$:1.997:2.980:3,964, approximating the surface area as $4\pi R_{av}^2$), but for obvious reasons the agreement is even better in the case of the spherical species ($\sqrt{3}$:1.999:2.998:3.997). The accuracy of this simple geometrical estimate reflects the rapid convergence of average bond lengths, approaching the limiting value of 1.437 Å which has been extrapolated for an infinite graphite sheet.[4] The degree of bond length alternation is considerably larger for the spherical species, and in contrast to the facetted geometries, it even increases with the fullerene size. For spherical C_{960}, the minimum bond length approaches a value (1,341 Å) which is characteristic of double bonds, and the maximum bond length (1.493 Å) is only slightly smaller than a typical single bond, indicating a very unusual and extreme situation for fullerenes. In each case, r_{min} belongs to the bonds exocyclic to the five-membered rings. The considerable decrease of this bond length parallels the increase of the adjacent bond angle (α_{max}) which can vary substantially for the spherical geometries.

The curvature at a given atom i may be measured with the help of the π orbital axis vector (POAV)[31] which is geometrically defined such that it has equal angles β_i with the three bonds of that atom. The corresponding POAV angle is then defined as $\Theta_i = \beta_i - \pi/2$, and approaches a value of 0 in the planar case. The average POAV angles decrease regularly with increasing fullerene size, and they are always slightly smaller (by 0.1 to 0.2°) for the spherical forms. The range spanned by the minimum and maximum POAV angles is very narrow (ca. 0,2°) for the spherical structures, reflecting their even distribution of curvature. For the facetted molecules this range is much larger, and it extends considerably with increasing fullerene size. This indicates a concentration of curvature at the atoms of five-membered rings which are always associated with the maximum POAV angles.

Under certain simplifying assumptions it has been shown that the sum of the squared POAV angles should be a constant for fullerenes of arbitrary size:[8]

$$\sum_i \Theta_i^2 \approx 4\pi/(3\sqrt{3}) \approx 2.418 \qquad (1)$$

Since the derivation of this formula requires a Taylor series expansion of Θ_i terminated after the quadratic term, one should expect that it is more accurate for spherically shaped fullerenes which avoid large POAV angles. Indeed, the approximation is accurate to within 1% for the spherical structures, whereas errors of 15% to 68% occur for the facetted structures. One even notices the convergence of $\sum\Theta_i^2$ against the expected limiting value for the spherical species.

(b) Energies. The energies necessary to convert the icosahedrally facetted fullerenes to spherical geometries are collected in Table 3. There is a very good agreement between the MNDO and the ab initio results for C_{180} and C_{240}, in line with similar previous experience for fullerene isomers.[20] Relative energies differ by only 0.11 and 0.07 kcal/mol per carbon atom if single point ab initio calculations for MNDO geometries are considered, and an even closer agreement is achieved for C_{180} if results for optimized geometries are compared. The energetic preference for the facetted structures becomes significantly more pronounced with increasing size, mirroring the increasing amount of geometrical distortion apparent in the spherical structures (see Tables 1 and 2, and preceding section). For C_{960}, this energy difference is predicted to be nearly three times as large as the destabilization of the facetted geometry with respect to an infinite graphite sheet (2.63 vs 0.91 kcal/mol per carbon atom, see Table 4).

5. Discussion

Both the semiempirical and the ab initio calculations yield only one energy minimum for each of the fullerenes, corresponding to an icosahedrally facetted geometry. Spherically shaped structures are considerably higher in energy, by 138.0 (C_{180}), 205.2 (C_{240}), 1056.3 (C_{540}), and 2524.3 kcal/mol (C_{960}) (MNDO values, see Table 4). These results are clearly

---

(31) Haddon, R. C.; Scott, L. T. *Pure Appl. Chem.* **1986**, *58*, 137.

incompatible with a recent density functional study based on the divide and conquer strategy[16] which predicts a nearly spherical structure of C_{240} to be about 400 kcal/mol more stable than a facetted geometry.[18] Our results are, however, in line with previous force field calculations[5] and simple estimates from geometrical considerations.[14,15] The very close agreement of the semiempirical and ab initio SCF data provides further support for our results. In an attempt to gain insight into the factors that govern the energetic preference for facetted geometries we consider several models which have been successfully applied in an earlier study on fullerenes.[4]

The Hückel model has frequently been used to discuss relative stabilities of isomeric fullerenes on the basis of π resonance arguments,[8,32–37] completely disregarding effects of σ-strain. While the simple Hückel model has been found useful in some cases, it could not reproduce the energetic order of C_{78}[19] and C_{84}[20] isomers predicted by more sophisticated quantum-chemical methods. This failure has been overcome by introducing a curvature correction for the resonance integral, $\beta_C = (S_C/S_G)\beta_G$,[4,19,20] where S_C is the average MNDO $\pi\pi$ overlap integral for the fullerene, S_G is the reference overlap integral for a graphite sheet, and β_G is the MNDO resonance integral for graphite. This correction accounts for the reduced $\pi\pi$ interactions due to the curvature of the fullerene, in the spirit of the POAV/3D HMO model.[38] Fullerene structures which are characterized by identical bond connectivity patterns and only differ by their shape can obviously only be distinguished upon introduction of this curvature correction. The corrected Hückel model, however, favors the spherical geometries, as can be seen from the data in Table 4. The overall reduction of $\pi\pi$ interactions is obviously smaller if the curvature is spread uniformly over the cage. This result might have been anticipated from the fact that the spherical geometries exhibit much smaller values of $\sum\Theta_i^2$ (see Table 2), since the curvature-corrected Hückel resonance energy is roughly proportional to $n - \sum\Theta_i^2$ (where n denotes the number of carbon atoms).[39] On a per atom basis, both the geometrical and the energetical measures of diminished $\pi\pi$ interaction showed a good correlation with the heats of formation of fullerenes in their *equilibrium geometry*.[4] It was concluded that curvature-induced σ- and π-strain cover the major part (ca. 65%) of the total destabilization energy with respect to a planar graphite sheet.[4] The additional strain of spherically shaped *non-equilibrium geometries*, however, is apparently governed by other factors.

In an attempt to identify the most important of these factors we characterized the spherical and the facetted geometries using a simple force field approach. This included out-of-plane (τ) and in-plane (α) bending as well as bond stretching (r) terms. The force constants have been taken from a force field[40–42] which has been designed to describe the vibrations in aromatic molecules and which predicts reasonable vibrational frequencies for buckminsterfullerene.[43]

$$\Delta E_{\mathrm{oop}} = (k_\tau/2)\sum_i \tau_i^2 \tag{2}$$

$$\Delta E_{\mathrm{inp}} = (k_\alpha/2)\sum_i (\alpha_i - 2\pi/3)^2 \tag{3}$$

$$\Delta E_{\mathrm{str}} = (k_r/2)\sum_i (r_i - r_0)^2 \tag{4}$$

Table 5. Geometrical Data for the Corannulene Subunits of C_{960}[a]

	spherical	icosahedral
a	1.392	1.450
b	1.341	1.396
c	1.430	1.455
d	1.433	1.428
α	108.0	108.0
β	125.7	121.2
γ	112.2	117.8
δ	134.9	121.3
ϵ	122.2	120.2

[a] For optimized MNDO geometries, in Å and deg, respectively. See Figure 2 for a definition of the bond lengths and angles.

In eq 2 τ_i is defined as 3 sin Θ_i.[4] All relevant results are included in Tables 3 and 4. The heats of formation estimated from the force field terms are in excellent agreement with the calculated MNDO values for the facetted geometries, and a reasonable agreement is found for the spherical geometries. It seems even more important that the force field model successfully reproduces the relative energies of facetted and spherical structures (Table 3). From the data in Table 4 we conclude that the out-of-plane bending terms are the only terms which favor spherical geometries. Note that they cover the effects of diminished $\pi\pi$ interactions and that their contribution to the relative energy is only moderate (0.3–0.4 kcal/mol per C atom). They are clearly outweighed by in-plane bending (0.8–1.6 kcal/mol) and stretching (0.2–0.6 kcal/mol) contributions, both favoring icosahedrally facetted geometries. Both increase considerably with increasing fullerene size, mirroring similar trends for the maximum bond angles and maximum bond lengths (see Tables 1 and 2).

A major part of the difference in in-plane bending strain is due to bond angles centered at atoms next to five-membered rings. Although there are only 180 such bond angles (compared to a total of 540 (C_{180}), 720 (C_{240}), 1620 (C_{540}), and 2880 (C_{960})) their contribution amounts to 56% for C_{180}, 67% for C_{240}, 38% for C_{540}, and 24% for C_{960}. These pronounced energetic effects are caused by extreme angle bending deformations in the corannulene subunits of the spherical geometries. Table 5 compares the relevant data for spherical and facetted C_{960} to illustrate this situation (see Figure 2 for the definition of bond lengths and angles). While all the angles in six-membered rings are close to the ideal value of 120° for the facetted species, a substantial variation is observed for the spherical species (112.2° to 134.9°). It is most noteworthy that the large value of δ and

---

(32) Fowler, P. W. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 2073.

(33) Manolopoulos, D. E.; May, J. C.; Down, S. E. *Chem. Phys. Lett.* **1991**, *181*, 105.

(34) Liu, X.; Klein, D. J.; Seitz, W. A.; Schmalz, T. G. *J. Comp. Chem.* **1991**, *12*, 1265.

(35) Fowler, P. W. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1945.

(36) Manolopoulos, D. E. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2861.

(37) Fowler, P. W.; Batten, R. C.; Manolopoulos, D. E. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3103.

(38) Haddon, R. C. *J. Am. Chem. Soc.* **1987**, *109*, 1676.

(39) Assuming zero dihedral angles between any pair of neighboring POAVs and neglecting the distance dependence of the resonance integral β_C, the original formula for β_C[4] may be simplified to yield $\beta_C = (\beta_G/S_G)\cdot\langle\cos\Theta_i \cos\Theta_j\rangle S_{\pi\pi}$, where $S_{\pi\pi}$ is the standard overlap integral for an average CC distance. Developing Θ as a Taylor series and dropping any term higher than second order, one obtains $\beta_C = (\beta_G/S_G)(1 - \sum_i\Theta_i^2/n)S_{\pi\pi}$. The correspondence between Hückel resonance energies ($\propto n\beta_C$) and the sum of squared POAV angles becomes obvious from this relation.

(40) Cyvin, B. N.; Neerland, G.; Brunvoll, J.; Cyvin, S. J. *Z. Naturforsch.* **1980**, *35A*, 731.

(41) Bakke, A.; Cyvin, B. N.; Whitmer, J. C.; Cyvin, S. J.; Gustavsen, J. E.; Klaeboe, P. *Z. Naturforsch.* **1979**, *34A*, 579.

(42) The force constant $k_\tau = (21.59\ \mathrm{kcal\ mol^{-1}\ rad^{-2}})(r_{av}/\text{Å})^2$ has been taken from ref 40, $k_\alpha = (57.57\ \mathrm{kcal\ mol^{-1}\ rad^{-2}})(r_1r_2/\text{Å}^2)$ and $k_r = 676.48$ kcal mol^{-1} Å^{-2} are from ref 41. The two bonds with lengths r_1 and r_2 refer to the angle α. r_0 equals the MNDO value extrapolated for an infinite graphite sheet (1.437 Å).[4]

(43) Cyvin, S. J.; Brendsdal, E.; Cyvin, B. N.; Brunvoll, J. *Chem. Phys. Lett.* **1988**, *143*, 377.

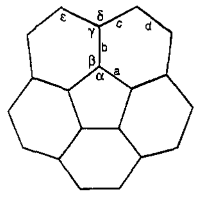

Figure 2. Corannulene subunit in I_h-C_{960}.

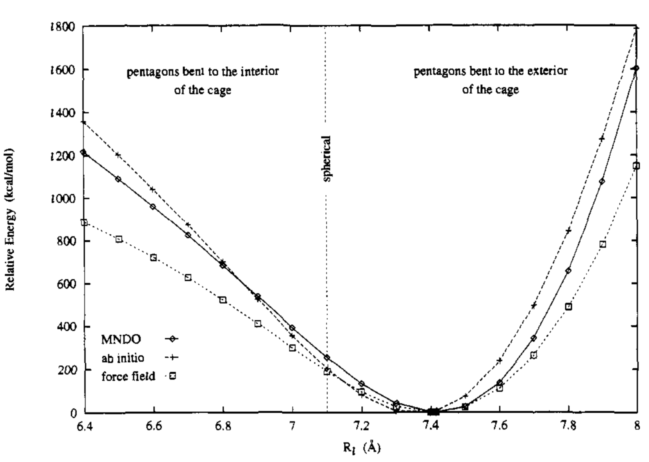

Figure 3. Energy of I_h-C_{240} as a function of the distance R_1 of atoms in five-membered rings from the center of gravity.

the small value of γ (see Figure 2) inevitably follow from the requirement of sphericity. Assuming planar corannulene subunits (which is a good approximation for large *spherical* fullerene geometries) one may obtain a useful expression for δ by simple trigonometry;

$$\delta = 2 \arcsin \frac{a - d + 2b\cos(3\pi/10)}{2c} + 2\pi/5 \qquad (5)$$

In the case of equal bond lengths we have $\delta = 144°$ and, consequently, $\gamma = 108°$. Assuming the bond lengths of the facetted geometry as equilibrium reference data for the spherical structure, slightly more favorable values of $\delta = 141.7°$ and $\gamma = 109.1°$ are obtained. According to eq 5, a significant reduction of δ and hence a larger value of γ can only be achieved through considerable contraction of bonds a and b. The spherical fullerene geometries adopt a compromise, balancing both types of strain (see data in Table 5).[44] These considerations on the relationship between geometry and energy do not invoke any quantum-chemical arguments and thus are equally valid for macroscopic models.[15] Note that even the geodesic domes of R. Buckminster Fuller show markedly compressed struts and deformed angles in the vicinity of the pentagons.[1,45]

To illustrate our main conclusions we performed a reaction coordinate calculation monitoring the energy of I_h-C_{240} as a function of the distance R_1 between an atom in a five-membered ring and the center of gravity. The geometries were completely optimized at the MNDO level, keeping R_1 fixed, without invoking the constraint of sphericity. Additional single point energies have been calculated at the ab initio level and with the force field model. The results are depicted in Figure 3. The vertical line dividing the diagram into two halfs corresponds to an approximately spherical structure.[46] The region right of the vertical line includes the equilibrium geometry and generally refers to geometries which show the pentagons bent to the exterior of the cage (R_1 being the maximum of all distances to the center of gravity) while the region left of the vertical line covers those geometries where the pentagons are bent to the interior of the cage (R_1 being the minimum distance). Again we note an excellent agreement between the MNDO and the ab initio data. The force field model approximates the quantum-chemical data reasonably well although it tends to underestimate the energies of extremely distorted geometries. The corresponding energy curve shows a minimum ($R_1 \approx 7.4$ Å) very close to the optimized MNDO equilibrium geometry, resulting from considerably different minima for the bond stretching ($R_1 \approx 7.4$ Å), in-plane ($R_1 \approx 7.6$ Å), and out-of-plane bending ($R_1 \approx 7.0$ Å) contributions. Bond stretching and in-plane bending energy terms thus prefer icosahedrally facetted geometries, the latter favoring even more strongly curved geometries than the equilibrium geometry. The out-of-plane bending terms favor approximately spherical geometries with the pentagons slightly bent to the interior of the cage. We have also performed single point calculations applying the curvature-corrected Hückel model. As expected, the corresponding energy curve displays a qualitative pattern similar to that of the out-of-plane bending contribution, with a minimum also occurring for $R_1 \approx 7.0$ Å. The MNDO geometry for this point roughly corresponds to the nearly spherical structure which has been proposed to be the most stable one on the basis of density functional calculations.[47] Our reaction coordinate, however, provides no evidence for an energy minimum in the vicinity of this point. MNDO predicts this geometry 393.2 kcal/mol less favorable than the facetted equilibrium structure, in accord with both the ab initio result (350.0 kcal/mol) and the force field estimate (298.3 kcal/mol) which results from the superposition of all three sources of strain.

The implications of recent HREM (high resolution electron microscopy) studies[48-51] on the shape of fullerenes deserve a final comment. Upon strong electron bombardment, Ugarte observed the conversion of carbon soot to onion-like particles composed of concentric shells of fullerenes which appeared spherical in HREM images.[49-51] This has been taken as experimental evidence supporting the density functional result.[18] We note, however, that icosahedrally facetted fullerenes may also appear spherical, depending on the line of vision. While the facetted shape is quite obvious when looking along a 3-fold symmetry axis, it is much less evident on views along a 5-fold symmetry axis (see Figure 4, left and middle picture). The micrographs simulated from concentric shells of icosahedrally facetted fullerenes indeed nicely agree with Ugarte's HREM images.[52,53] Hence, there is no obvious discrepancy between our results and the experimental observations.

---

(44) Note that the actual value of δ differs by only 2° from the prediction of eq 5 (136.9°), indicating the validity of our model assumption that the corannulene subunits of large spherical fullerene geometries may be treated as planar.

(45) Kroto, H. *Science* **1988**, *242*, 1139.

(46) Strictly speaking, the reaction coordinate does not include the spherical geometry since at any point 6 degrees of freedom are optimized (instead of 5). The geometry indicated in Figure 3 is, however, reasonably close to the spherical structure depicted in Figure 1, with $R_1 = 7.10$ Å, $R_2 = 7.12$ Å, $R_3 = 7.11$ Å, $\Delta H_f^0 = 1850.0$ kcal/mol.

(47) According to the MNDO results, the three inequivalent carbon atoms are $R_1 = 7.000$, $R_2 = 7.117$, and $R_3 = 7.143$ Å off the center of gravity in this structure, and the bond lengths (see Figure 2) are $a = 1.423$ Å, $b = 1.366$ Å, $c = 1.465$ Å, $d = 1.440$ Å. The corresponding density functional results are reported as[18] 7.009, 7.128, 7.143, 1.428, 1.434, 1.446, and 1.421 Å.

(48) Iijima, S. *J. Phys. Chem.* **1987**, *91*, 3466.

(49) Ugarte, D. *Nature* **1992**, *359*, 707.

(50) Ugarte, D. *Europhys. Lett.* **1993**, *22*, 45.

(51) Ugarte, D. *Chem. Phys. Lett.* **1993**, *207*, 473.

(52) Kroto, H. W. *Nature* **1992**, *359*, 670.

(53) Maiti, A.; Brabec, C. J.; Bernholc, J. *Phys. Rev. Lett.* **1993**, *70*, 3023.

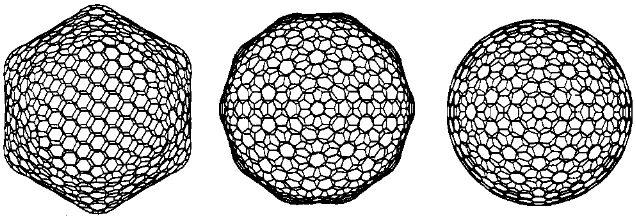

Figure 4. Facetted (left, middle) and spherical (right) geometries of I_h-C_{960}. The pictures refer to the views of a distant spectator looking along a 3-fold (left) or 5-fold (middle, right) symmetry axis.

6. Conclusions

According to MNDO and ab initio SCF calculations, large fullerenes with I_h symmetry adopt icosahedral shapes with facets built from nearly planar hexagonal sheets and vertices located at the pentagons. Spherical shapes are substantially higher in energy, and they do not correspond to minima of the potential energy surface. The requirement of sphericity favors π resonance stabilization, but inevitably leads to strong bond length and bond angle deformations which induce considerable strain and govern the loss of stability.

Acknowledgment. Financial support from the Alfried-Krupp-Stiftung and the Fonds der Chemischen Industrie is gratefully acknowledged. Generous amounts of computer time have been provided by the Centro Svizzero di Calcolo Scientifico at Manno TI, the Competence Center for Computational Chemistry at ETH Zürich, and the Cray Research Center at Eagan, MN. We thank Dr. Brad Elkin, Cray Research, for technical assistance with some of the calculations.

JA951782C