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Energetics of C_{20} and C_{22} Fullerene and Near-Fullerene Carbon Cages

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Model semiempirical studies using quantum consistent force field/π (QCFF/PI) and density functional tight binding (DFTB) methods show the C_{20} dodecahedral fullerene to have the lowest energy of all 7595 mathematically possible 20-vertex trivalent polyhedral cages by a substantial margin (estimated at 521 (QCFF/PI) or 125 (DFTB) kJ mol^{-1}). A topological invariant based on the distribution of face sizes is used to correlate the energies and predict the best polyhedral structure for C_{22}, which must be a nonfullerene cage. With 1 square, 10 pentagonal, and 2 hexagonal faces, this structure is verified to be more stable (by 259 (QCFF/PI), 60 (DFTB) kJ mol^{-1}) than its nearest trivalent polyhedral rival.

1. Introduction

From a combination of experimental and theoretical work, the outlines have emerged of a general picture of the thermodynamically favored structures for clusters consisting of a few to a few hundred carbon atoms (for reviews, see for example refs 1, 2 and references therein). Open chains for very small C_n molecules give way to cyclic and then more highly connected structures to be replaced, in turn, by polyhedra, which for atom counts of 60, 70, 76, 78, and 84 among others have been characterized as the now-famous fullerenes, generalizing the icosahedral C_{60} cage.[3] A fullerene C_n is a trivalent polyhedral cage made up of exactly 12 pentagonal and (n/2−10) hexagonal faces; at least one such cage can be constructed in principle for all even values $n \geq 20$ apart[4] from $n = 22$. The precise limits of the different size regimes are not yet established, but the general tendency to increase in connectivity from chain to ring to cage is clear.

The present study is concerned with the relative stabilities of different types of cage structure, rather than the competition between open and closed topologies. For a test case, it deals with the relative stabilities of fullerenes and other carbon polyhedra at fixed nuclearity in a more comprehensive way than attempted hitherto, and suggests a simple topological criterion that can be used to assess stability of nonfullerene structures and to predict candidate cages where fullerenes are not mathematically possible.

Various theoretical studies have suggested that trivalent cages containing some rings of other sizes (nonclassical fullerenes) may be competitive with and even occasionally superior in stability to fullerenes. For example, it is predicted that all C_{40} cage isomers made up of exactly 1 heptagonal, 13 pentagonal, and 8 hexagonal faces would be of lower energy than at least some C_{40} classical fullerene[5] and that a specific one-heptagon isomer of C_{62} would be of lower energy than *any* classical fullerene with 62 atoms.[6]

While it is a chemically reasonable expectation that fullerenes should be more stable than structures with very small or very large rings, the number and variety of trivalent structures is immense, and fullerenes form a small, and in the limit vanishingly small, fraction of the possibilities. At 20 vertices there are 7595 trivalents of which only one is a fullerene. The number of trivalents climbs steeply (49 566 for $n = 22$, 339 722 for $n = 24$, 2 406 841 for $n = 26$, and so on[7]) and by 60 vertices has reached an estimated 5×10^{21} of which only 1812 are fullerenes[8] (all counts refer to structural isomers). It is therefore at least conceivable that some class of trivalent polyhedra will improve in energy on the fullerenes. To test this idea we need a rule of thumb for estimating the stability of an arbitrary trivalent carbon cage. A first step to obtaining this would be a systematic survey of all possible trivalent polyhedra at some n. With even the most economical semiempirical methods a complete study would be computationally feasible only for C_{20}, and so that is the case chosen for examination here.

The plan of the paper is as follows. Energies are to be evaluated by a semiempirical method for all 7595 trivalent polyhedral C_{20} cages in their respective equilibrium geometries (§2) and tested for correlation with topological/structural invariants (§3). It is fully expected that the sole possible fullerene structure, based on the regular Platonic dodecahedron, will emerge as the most stable of the polyhedra, though this expectation has not so far been tested by direct calculation, but we do not claim that this closed cage will necessarily be the globally optimal structure for 20 carbon atoms. The main interest of the explicit calculations reported here will lie in their ranking of the nonfullerene polyhedra and the light that they shed on the case of C_{22} (§4), for which there are almost 6 times as many possible polyhedra but no classical fullerene candidate.

2. Trivalent Structural Isomers of C_{20}

In this comparison of cage energetics, we consider only those isomers that are closed trivalent polyhedra. A trivalent, pseudospherical polyhedron with v vertices, e edges, and f faces obeys Euler's theorem

$$v + f = e + 2 \tag{1}$$

and its trivalence forces the conditions

$$e = 3n/2 \tag{2}$$

$$f = v/2 + 2 = \sum_r f_r \tag{3}$$

where f_r is the number of faces of size r, i.e., of r-sided polygons.

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The signature $\{f_r\}$ of face sizes is therefore subject to the restriction

$$\sum_r (6-r) f_r = 3f_3 + 2f_4 + f_5 - f_7 - 2f_8 \ldots = 12 \qquad (4)$$

which implies that any trivalent polyhedron must have some subhexagonal faces and that any superhexagonal faces will be balanced by extra faces of size 5 or smaller. Not every set $\{f_r\}$ obeying (4) is geometrically realizable, but those sets that can be realized as polyhedra will often correspond to multiple isomeric structures. The minimal face size is 3, and the maximal face size can be seen in general to be $v/2 + 1$ from the following argument: any trivalent has an even number of vertices, and for $v > 4$ it is, therefore, possible to construct a prism isomer with two rings of $v/2$ vertices separated by squares ($f_4 = v/2$, $f_{v/2} = 2$), but for $v > 6$ this structure can be squashed on one side to give a wedge-shaped isomer where two larger rings, each of size $v/2 + 1$, share an edge ($f_3 = 2$, $f_4 = v/2 - 2$, $f_{v/2+1} = 2$); further increase in face size is not possible for a 3-connected structure, i.e., one for which no pair of faces share more than one edge.

The range of face sizes for C_{20} is thus $3 \leq r \leq 11$. Complete enumeration by the highly efficient algorithm of McKay and Brinkmann[7] gives a total of 7595 structural isomers of polyhedral C_{20} spanning 445 of the 480 distinct signatures that would be compatible with (3) and (4).

From the adjacency list for each isomer given by the enumeration program, approximate topological Cartesian coordinates were calculated by diagonalization of the adjacency matrix, adjusted where necessary by human intervention and smoothed by passage through a proprietary molecular mechanics optimizer. All 7595 isomeric structures were then optimized using the QCFF/PI (quantum consistent force field/π) semiempirical method.[9] This model incorporates a molecular mechanics treatment of the σ framework and an explicit molecular orbital treatment of the π electrons in a carbon cage. It has been used successfully for calculation of structural, energetic, and vibrational data on both classical and nonclassical fullerenes.[5,6,10−12] Comparisons with other methods that use quite different approximation schemes suggest that reliance may be placed on the general trends predicted by QCFF/PI, though it probably exaggerates the energetic cost of departure from the fullerene recipe. Similar methodological comparisons will also be made in the present work.

The calculated energies of trivalent C_{20} cages span a range of 6533 kJ mol^{-1} and, as expected, the dodecahedral fullerene isomer has the lowest total energy in the set. As the perfect I_h cage would have an open π shell (two electrons in four orbitals[13]), the closed-shell QCFF/PI calculation produces a small stabilizing Jahn−Teller distortion to a less symmetrical structure.

Figure 1 shows the optimized structures for the 10 isomers of lowest energy within the QCFF/PI model, and the details of energies, symmetries, and rankings in the two models are given in Table 1. All are roughly spherical in shape, and the lowest five include only square, pentagonal, and hexagonal faces. In contrast, isomers with many triangular faces or with the very large nonagonal, decagonal, or undecagonal rings have angular shapes and appear at the top of the energy range. Figure 2 illustrates this general tendency of the energy to rise with the number of three-membered rings and suggests that a correlation based on composition of the face signature could give an appropriate way to systematize the energy data.

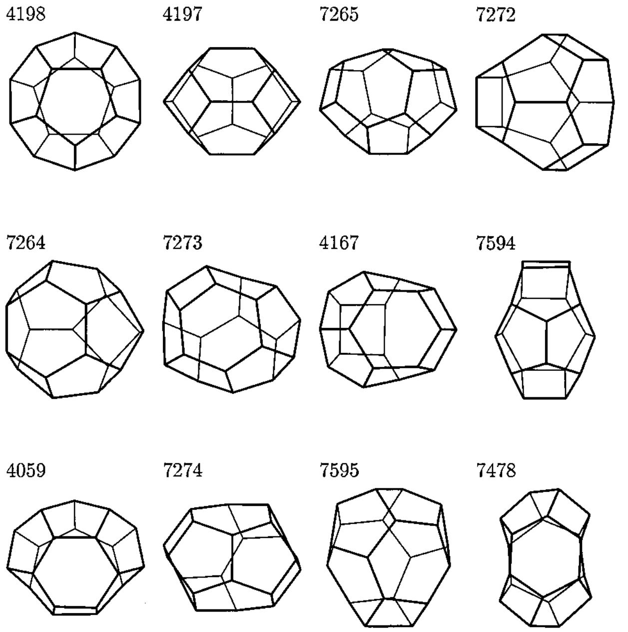

Figure 1. Optimized geometries for the polyhedral C_{20} isomers of lowest energy in two semiempirical models. The 12 isomers shown span the 10 of lowest energy in each of the QCFF/PI and DFTB models. Each isomer is labeled by its position in the sequence of structures generated by the Brinkmann/McKay program.[7] Details of energies, symmetries and rankings in the two models are given in Table 1.

TABLE 1: Relative Energies of the 10 Most Stable Polyhedral Isomers of C_{20} in Two Semiempirical Models[a]

			rank		energy	
N	G	F	QCFF	DFTB	ΔE_Q	ΔE_D
4198	I_h	12	1	1	0.0	0.0
4197	C_{2v}	16	2	2	521.3	125.3
7265	C_2	16	3	5	622.6	255.0
7272	C_s	18	4	3	707.9	148.7
7264	C_s	18	5	4	754.0	194.9
7273	C_1	18	6	7	815.5	298.0
4167	C_s	20	7	13	925.5	356.3
7594	C_s	18	8	15	945.2	376.8
4059	C_s	20	9	9	949.3	336.0
7274	C_2	20	10	6	983.7	277.5
7295	C_2	20	12	10	1047.3	342.5
7478	D_2	20	16	8	1179.9	335.3

[a] N is the position of the isomer in the complete list of trivalent polyhedra produced by the Brinkmann/McKay algorithm,[7] G is the maximal symmetry group, F is the parameter $\sum_r (6-r)^2 f_r$ giving the distance of the face recipe from the classical fullerene, ΔE_Q and ΔE_D are the energies (in kJ mol^{-1}) relative to the best polyhedral isomer in QCFF/PI and DFTB models, respectively, and the "rank" column lists the position of the isomer in the overall energy order for both models. Optimized (QCFF/PI) structures for all isomers are illustrated in Figure 1.

Given that all the signatures $\{f_r\}$ obey constraints on zeroth and first moments ((3) and (4)), functions based on the second moment may usefully discriminate between them. Figure 3 illustrates the correlation of calculated energy with the parameter

$$F = \sum_r (6-r)^2 f_r \geq 12$$

F measures the departure in a least-squares sense of a trivalent polyhedron from the fullerene recipe (for $n \geq 20$, $F = 12 \Leftrightarrow \{f_r\} = \{0, 0, 12, n/2 - 10, 0, \ldots\}$) and does indeed pick out the low-energy structures, with the distribution in Figure 3 pointing sharply down to the fullerene limit. As a first filter, F could be used to effect a drastic reduction in the size of the isomer set for explicit energy calculations and will be used in this way for C_{22} (see below).

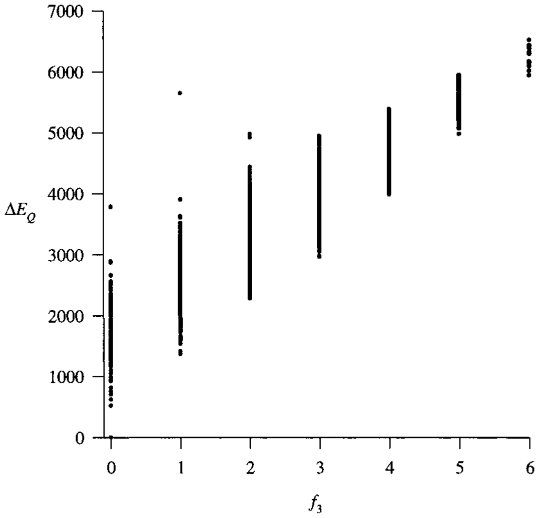

Figure 2. Correlation of relative energy ΔE_Q (QCFF/PI method, in kJ mol^{-1}) of all 7595 trivalent polyhedral structural isomers of C_{20} with f_3, the number of triangular faces in the cage.

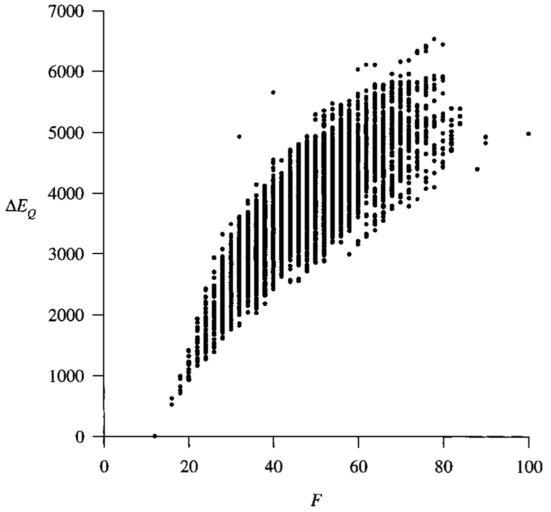

Figure 3. Correlation of relative energy ΔE_Q (QCFF/PI method, in kJ mol^{-1}) of all 7595 trivalent polyhedral structural isomers of C_{20} with F, the second-moment parameter describing departures from the fullerene ideal. The point $F = 12$ represents a fullerene.

F has the advantage over more detailed measures of curvature/strain that it depends on the graph connectivity alone and so avoids the need for an explicit knowledge of the geometrical embedding of the graph in three-dimensional space. Hückel parameters such as highest occupied molecular orbital−lowest unoccupied molecular orbital (HOMO−LUMO) gap and delocalization energy are also defined entirely by the graph but, as Figure 4 shows, give no help at all in the selection of stable structures. The reasons for their failure are understandable in that the crude single-α, single-β, π-only Hückel model takes no account of the wide range of local environments and strong variation in steric strain for polyhedra with different ring sizes and thereby ignores the energetic role of three-quarters of the valence electrons.

With any semiempirical model it is wise to check calculated trends for excessive dependence on the parametrization. Here this was done by repeating a large sample of the optimizations with the density functional tight binding (DFTB) method. DFTB is parametrized to reproduce full density-functional results for small molecules[14] and has been used in a number of studies on classical and nonclassical fullerenes. General qualitative agreement between DFTB and QCFF/PI on trends in energy and geometry has been found in these studies,[5,6,11,12] reinforcing confidence in both models. All 478 C_{20} isomers with QCFF/PI energies below a cutoff of 2500 kJ mol^{-1} relative to the fullerene isomer were reoptimized with DFTB and, in the absence of any special precautions to preserve connectivity or encourage convergence, 410 of these gave distinct local minima. The fullerene isomer again emerged as the most stable in the set, and the methods agreed on the composition of the set of the best 5 isomers, though with changes in the detailed ordering and a compression of the energy scale by a factor of 2 or more. As the scatter plots of Figure 5 show, there is general agreement on the low-energy set of isomers and the shape of the overall correlation of energy and *F* between the QCFF/PI and DFTB methods.

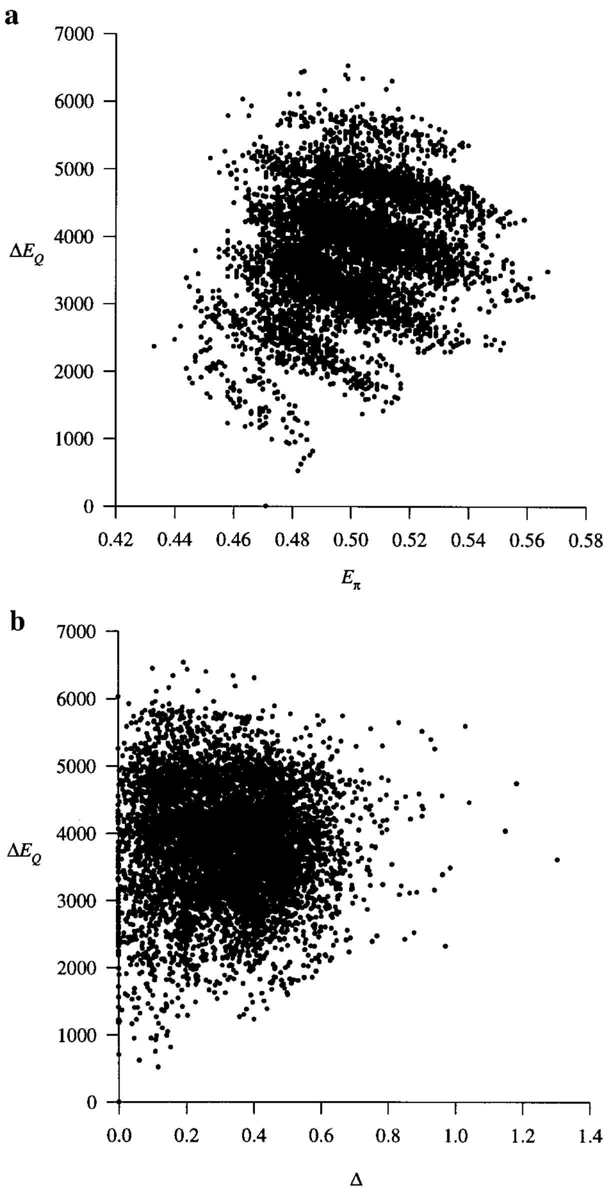

Figure 4. Correlations of Hückel quantities with relative energy ΔE_Q (QCFF/PI method, in kJ mol^{-1}) for all 7595 trivalent polyhedral structural isomers of C_{20}. (a) E_π is the delocalization energy per atom, and (b) Δ is the HOMO−LUMO gap, both given in units of $|\beta|$, the bond parameter assumed to be common to all edges of all polyhedral cages.

The polyhedral cage next lowest in energy after the fullerene is agreed by both methods to be the two-square, eight-pentagon C_{2v} structure that would be produced by a generalized Stone−Wales rotation[15,16] of an edge of the dodecahedron, with an

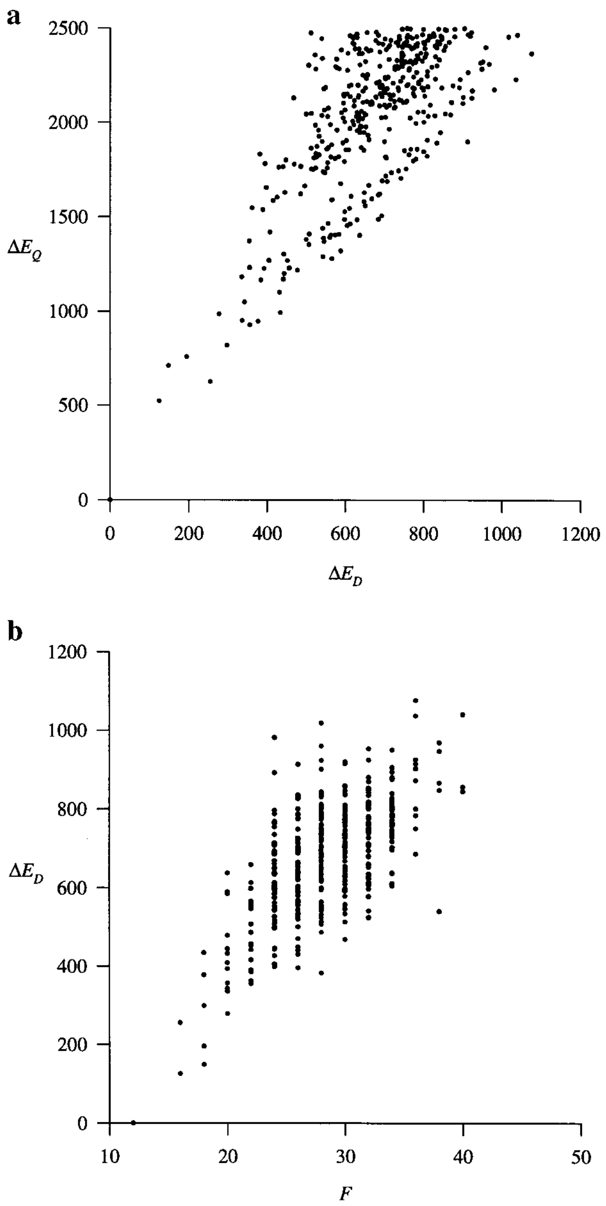

Figure 5. (a) Correlation between the relative energies (in kJ mol^{-1}) calculated in QCFF/PI (ΔE_Q) and DFTB (ΔE_D) models for 410 trivalent polyhedral isomers of C_{20} with $\Delta E_Q \leq 2500$ kJ mol^{-1}. (b) Correlation of DFTB energies for this isomer set with the second-moment parameter, *F*.

energy of 521 (QCFF/PI), 125 (DFTB) kJ mol^{-1} relative to the original fullerene.

For the present purpose, it is sufficient to note that all 7595 trivalent polyhedra lie in local minima on the potential energy surface for 20 carbon atoms, the fullerene in the lowest of these. There is much discussion in the literature about the global optimum,[1,2,17–24] with close competition between cage, ring, and bowl structures, converging to the conclusion that thermodynamic and experimental structures (not necessarily identical) are open isomers.

3. A Cage Structure for C_{22}

A fullerene polyhedron is mathematically possible for $n = 20 + 2k$ for integer values of $k \geq 0$ with the sole exception of $k = 1$, the nonexistent 12-pentagon, 22-atom cage.[4] Since C_{22} cannot be a fullerene, which is the most stable of its cage isomers? (We reserve judgment on the question of whether such a cage will itself be more stable than a cyclic or bowl-like structure).

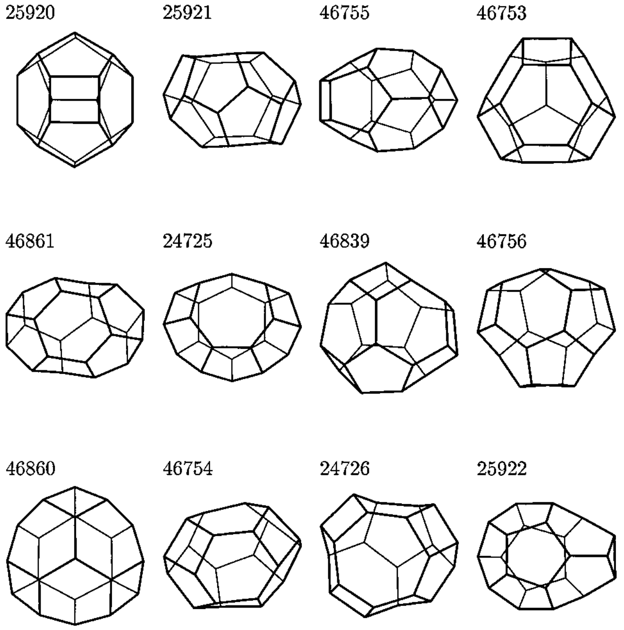

Figure 6. Optimized geometries for C_{22} polyhedral cages. Notation and isomer labeling are as in Figure 1; details of symmetry and energy data are listed in Table 2.

TABLE 2: Relative Energies of the 10 Most Stable Polyhedral Isomers of C_{22} in Two Semiempirical Models[a]

			rank		energy	
N	*G*	*F*	QCFF	DFTB	ΔE_Q	ΔE_D
25 920	C_{2v}	14	1	1	0.0	0.0
25 921	C_2	16	2	2	259.4	59.8
46 755	C_s	16	3	6	297.9	98.9
46 753	C_{3v}	18	4	3	378.7	61.1
46 861	C_2	16	5	13	401.7	189.9
24 725	C_s	18	6	10	431.4	167.3
46 839	C_1	18	7	5	461.5	72.7
46 756	C_2	18	8	7	479.9	134.7
46 860	C_{3v}	18	9	11	499.6	187.5
46 754	C_1	18	10	9	533.9	161.2
24 726	C_1	20	12	8	585.8	147.9
25 922	C_{3v}	18	24	4	738.1	66.0

[a] Notation as in Table 1.

There are 49 566 trivalent polyhedra with 22 vertices, with face sizes ranging from 3 to 12. The values of *F* for these cages range from 14 to 126. Minimization of *F* as a criterion of energy gives a unique best candidate: the C_{2v} structure with 1 square, 2 hexagons, and 10 pentagons that would be obtained by bevelling one edge of a dodecahedron ($f_4 = 1$, $f_5 = 10$, $f_6 = 2$, $F = 14$).

To check this qualitative prediction we took all 745 trivalent C_{22} cages with $14 \leq F \leq 28$ and optimized them in QCFF/PI and DFTB models. Both models agreed in placing the minimal-*F* isomer lower in energy than any of its fellows, 259 (QCFF/PI) or 60 (DFTB) kJ mol^{-1} below a C_2 cage with $F = 16$. Figure 6 shows optimized geometries for the lowest-energy polyhedral isomers of C_{22}, and the details of symmetry and energy data are listed in Table 2. Again the DFTB energy scale is strongly compressed with respect to QCFF/PI: the 745 selected isomers span a range of 3259 kJ mol^{-1} in QCFF/PI, and the 704 of them that converged easily in DFTB span only 1323 kJ mol^{-1}. Qualitative correlation between the two models for this set is good, and *F* is once again shown to be a useful indicator of relative stability (Figure 7).

While we cannot claim that the cage discussed here is the most stable of all possible forms for C_{22}, it is the best poly-

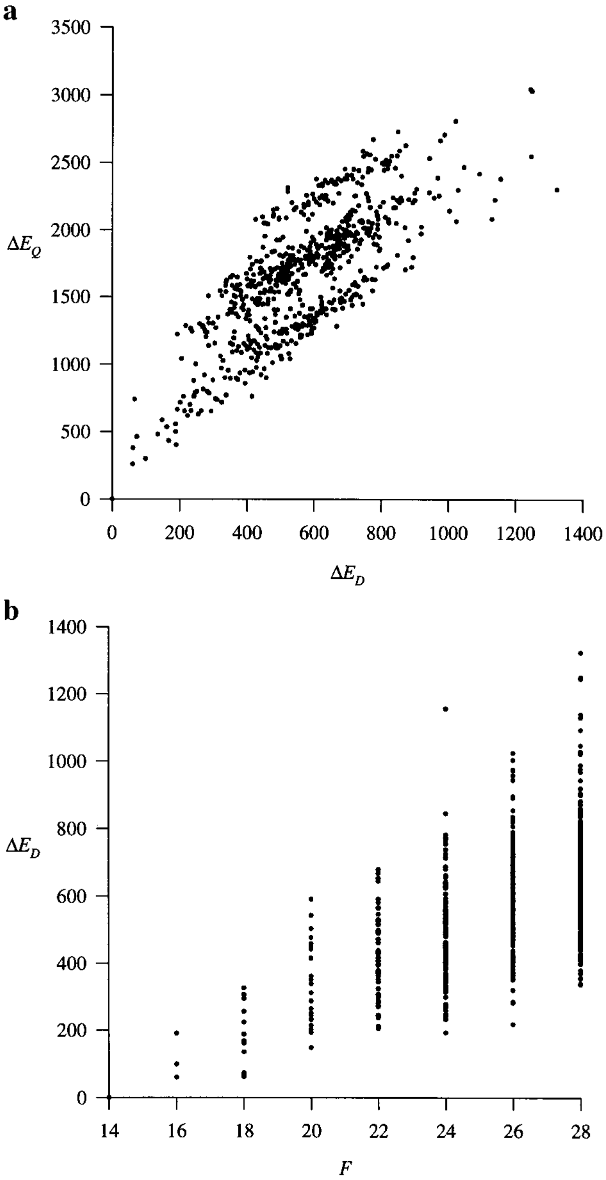

Figure 7. (a) Correlation between the relative energies (in kJ mol^{-1}) calculated in QCFF/PI (ΔE_Q) and DFTB (ΔE_D) models for 704 trivalent polyhedral isomers of C_{22} with second-moment parameter $14 \leq F \leq 28$. (b) Correlation of DFTB energies for this isomer set with the F parameter.

hedron, coming closest in a well-defined way to the unattainable fullerene ideal, and it should certainly be considered in future searches. The DFTB model suggests that monocyclic C_{22} will lie 41 kJ mol^{-1} below, and linear C_{22} 62 kJ mol^{-1} above, the cage form, again indicating a close competition between differently connected structures.

4. Conclusion

Comprehensive model calculations on C_{20} and C_{22} have shown that classical fullerene polyhedra, where available, will generally be of lower total energy than other trivalent cage structures. A topological invariant based on the distribution of face sizes has been found to be a useful guide to relative energies of the various nonclassical structures. F may be expected to be useful as a filter at high nuclearity too. Even for the one case (C_{62}) where a nonclassical structure is reliably predicted to be of lower energy than a fullerene,[6] F takes its next-to-minimal value of 14. In the regime below $n = 20$, where there are too few atoms to form a fullerene, the structures that minimize F may again be expected to be the lowest in energy of the conceivable carbon polyhedra, though less stable than the more open structures at these nuclearities; the n-vertex trivalent polyhedra of minimal and next-to-minimal F are illustrated for $4 \leq n \leq 18$ in Figure 8.

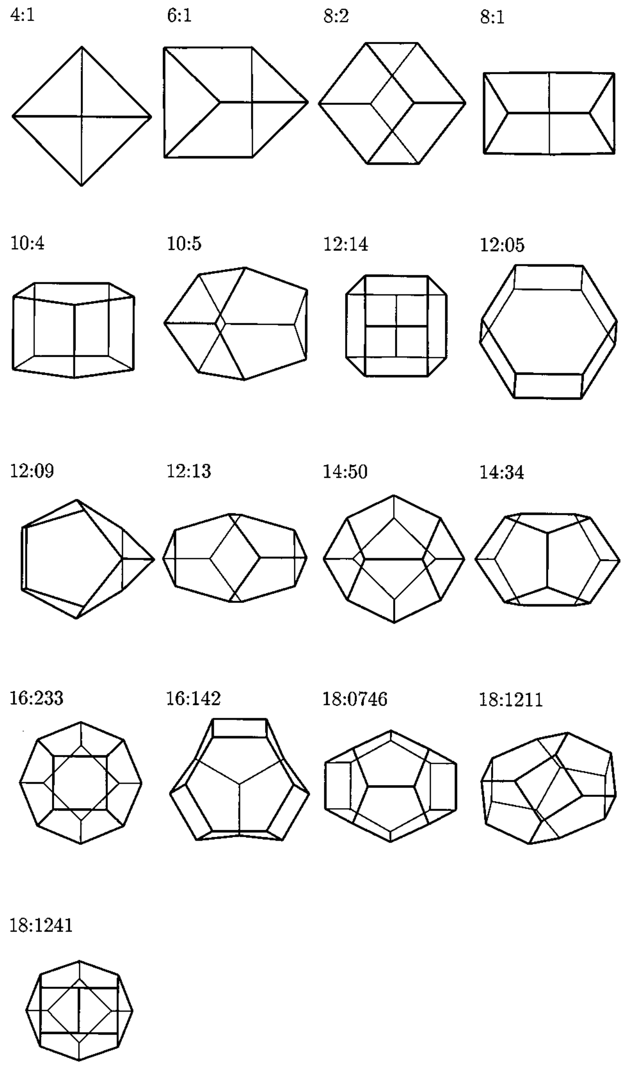

Figure 8. Trivalent n-vertex polyhedra with minimal and next lowest values of the F parameter ($4 \leq n \leq 18$). A unique solution is found for minimal F at each value of n in the range. Vertex counts, isomer labels in the Brinkmann/McKay convention, point groups, and F values for the illustrated structures (n, N, G, F) are 4, 1, T_d, 36; 6, 1, D_{3h}, 30; 8, 2, O_h, 24; 8, 1, C_{2v}, 28; 10, 4, D_{5h}, 22; 10, 5, C_{3v}, 24; 12, 14, D_{2d}, 20; 12, 5, D_{6h}, 24; 12, 9, C_s, 24; 12, 13, C_{2h}, 24; 14, 50, D_{3h}, 18; 14, 34, C_{2v}, 20; 16, 233, D_{4d}, 16; 16, 142, C_{3v}, 18; 18, 746, C_{2v}, 16; 18, 1211, C_2, 18; 18, 1241, C_{2v}, 18.

It is gratifying to note that the latest large-scale systematic full density-functional calculations with and without gradient corrections confirm this set of mimimal-F polyhedra of special stability. In the calculations by Jones and Seifert,[24] the minimal-F structures for C_{14} (14:50), C_{16} (16:233), C_{18} (18:746), C_{20}, and C_{22} are all found to be the cage isomers of lowest energy at their respective nuclearities. For 14−18 atoms there are more open, noncage structures of lower total energy at both local-density and gradient-corrected levels, whereas for C_{20} and C_{22} the open structures are found to be globally optimal only when the calculation includes gradient corrections. There is also an excellent correlation between the full density functional and model DFTB predictions for the best few isomers in each structural class, confirming the general aptness of the DFTB and related models for the present wider survey of polyhedral isomer space.

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References and Notes

(1) Weltner, W., Jr.; Van Zee, R. J. *Chem. Rev.* **1989**, *89*, 1713.

(2) von Helden, G.; Hsu, M. T.; Gotts, N. G.; Kemper, P. R.; Bowers, M. T. *Chem. Phys. Lett.* **1993**, *204*, 15.

(3) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.

(4) Grünbaum, B. *Convex Polytopes*; Wiley-Interscience: New York, 1967.

(5) Fowler, P. W.; Heine, T.; Mitchell, D.; Orlandi, G.; Schmidt, R.; Seifert, G.; Zerbetto, F. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2203.

(6) Ayuela, A.; Fowler, P. W.; Mitchell, D.; Schmidt, R.; Seifert, G.; Zerbetto, F. *J. Phys. Chem.* **1996**, *100*, 15634.

(7) Brinkmann, G.; McKay, B. Version 1.0 of the programme plantri.c and its documentation are obtainable at http://cs.anu.edu.au/people/bdm.

(8) Fowler, P. W.; Mitchell, D. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4145.

(9) Warshel, A.; Karplus, M. *J. Am. Chem. Soc.* **1972**, *94*, 5612.

(10) Negri, F.; Orlandi, G.; Zerbetto, F. *Chem. Phys. Lett.* **1988**, *144*, 31.

(11) Fowler, P. W.; Manolopoulos, D. E.; Orlandi, G.; Zerbetto, F. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1421.

(12) Fowler, P. W.; Heine, T.; Manolopoulos, D. E.; Mitchell, D.; Orlandi, G.; Schmidt, R.; Seifert, G.; Zerbetto, F. *J. Phys. Chem.* **1996**, *100*, 6984.

(13) Fowler, P. W.; Woolrich, J. *Chem. Phys. Lett.* **1986**, *127*, 78.

(14) Seifert, G.; Porezag, D.; Frauenheim, Th. *Int. J. Quantum Chem.* **1996**, *58*, 185.

(15) Stone, A. J.; Wales, D. J. *Chem. Phys. Lett* **1986**, *128*, 501.

(16) Mitchell, D.; Fowler, P. W.; Zerbetto, F. *J. Phys. B* **1996**, *29*, 4895.

(17) Parasuk, V.; Almlöf, J. *J. Chem. Phys.* **1989**, *91*, 1137.

(18) Brabec, C. J.; Anderson, E.; Davidson, B. N.; Kajihara, S. A.; Zhang, Q. M.; Bernholc, J.; Tomanek, D. *Phys. Rev.* B **1992**, *46*, 7326.

(19) Raghavachari, K.; Strout, D. L.; Odom, G. K.; Scuseria, G. E.; Pople, J. A.; Johnson, B. G.; Gill, P. M. W. *Chem. Phys. Lett.* **1993**, *214*, 357.

(20) Slanina, Z.; Adamowicz, L. *Thermochim. Acta* **1992**, *205*, 299.

(21) Varga, F.; Nemes, L.; Csonka, G. I. *J. Mol. Struct.* **1996**, *376*, 513.

(22) Taylor, P. R.; Bylaska, E.; Weare, J. H.; Kawai, R. *Chem. Phys. Lett.* **1995**, *235*, 558.

(23) Raghavachari, K. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; Electrochemical Society: New Jersey, 1996; Vol. 3, p 894.

(24) Jones, R. O.; Seifert, G. *Phys. Rev. Lett.*, in press.