Relative stabilities of fullerene, cumulene, and polyacetylene structures for C_n: $n=18$–60

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The relative stabilities of closed fullerene, cumulene, and polyacetylene carbon structures, as well as the cohesive energies for clusters of size $n = 18$, 20, 22, 24, 26, 28, 30, 32, 34, 36, 50, and 60 have been examined using *ab initio* self-consistent-field and second-order Møller–Plesset perturbation theory and analytical derivative geometry optimization methods. These geometries and relative stabilities constitute the primary findings of this work. All calculations were carried out using the DISCO program with atomic basis sets derived from van Duijneveldt's carbon ($6s,3p$) primitive orbital basis set, contracted to [$3s2p$]. For $n \geqslant 32$, the fullerenes are predicted to be the most stable, and their cohesive energies are predicted to increase monotonically as n varies from 24 to 60. The optimized geometries obtained here are very near those obtained earlier by others for the few species where such data exist. Based on earlier work employing larger atomic orbital bases, the relative energies of the fullerene structures are expected to be lowered even further as larger basis sets are employed. Hence, it is likely that the smallest cluster for which the fullerene structure is the most stable has $n < 32$. Comparing our computed electron binding energy for C_{24}^- to the experimental vertical detachment energy of this species supports the claim that $n = 24$ may be the smallest energetically favored fullerene.

I. INTRODUCTION

The experimental and theoretical study of carbon clusters is a subject with a long history.[1-5] Much of this history as well as the exciting more recent developments surrounding the C_{60} species and other fullerenes are covered in several recent reviews.[6-23] Although carbon clusters have long been the subject of much experimental and theoretical study, the experimental work of several groups commencing in 1984 on C_{60} sparked a resurgence and expansion of interest in the stability, structures, and properties of carbon clusters. In 1989, Weltner and Van Zee[6] provided an extensive review of the experimental gas-phase, matrix-isolation, and theoretical state of the art for many C_n clusters as well as their positive and negative ions. In that review, much attention was devoted to clusters in the $n = 4$–10 range, as well as the extensive body of work on C_{60}. However, clusters in the intermediate range $n = 20$–50 have been discussed in considerably less detail, and have not been subjected to comparable levels of spectroscopic and theoretical examination. This is due to their comparatively low relative stability, as evidenced by the bimodal distribution of their abundances in mass-spectral measurements.[7]

For many of the C_n clusters, the energies of two or more geometrical isomers are similar enough to make the prediction of the true lowest-energy structure very difficult. Pitzer and Clementi concluded from early molecular-orbital (MO) calculations that the smaller clusters should be linear, with the odd-numbered species having an additional preference for linearity.[3] More recent work on even-numbered clusters for $n \leqslant 10$[24-32] shows that the relative energies of linear and monocyclic structures cannot be reliably predicted unless large atomic-orbital basis sets are used and electron correlation at a reasonably high level is included for essentially all valence electrons. These studies indicate that once $n = 10$ is reached, the monocyclic isomer is more stable, with the cumulene, distorted cumulene, and acetylenic isomers being essentially isoenergetic.

The above theoretical results are in reasonable agreement with the ultraviolet photoelectron (UPS) detachment data on the negative ions of C_n^- species.[33,34] The experimental data indicate that for $2 \leqslant n \leqslant 9$, linear chains seem to be more stable, and for $10 \leqslant n \leqslant 29$, monocyclic rings are the most stable.[34] Near C_{30}^- there is a qualitative shift in the observed UPS peak patterns. This is taken to indicate a change in the energetically favored geometries from two- to three-dimensional structures.[33,34] Below C_{40}^-, the intensities of the peaks in the mass spectrum are low,[8] which indicates that the lower C_n^- clusters are not unusually stable. Above C_{40}^- intense peaks occur for even numbered clusters;[8] for such species, closed fullerene structures (i.e., closed networks of five and six membered rings) were postulated to be present.[7,8]

Previous theoretical studies of fullerenes emphasized the C_{60} molecule. Early semiempirical calculations found a per-atom resonance stabilization energy for buckminsterfullerene only slightly smaller than in graphite, and predicted the now well-known fullerene structure to be stable.[35-37]

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More recent self-consistent-field (SCF) calculations confirmed the thermodynamic stability of the buckyball structure and predicted a 0.08 Å difference between the two distinct bond lengths in this structure.[38,39] However, when electron correlation is introduced at the second-order Møller–Plesset (MP2) level and extended atomic-orbital basis sets are used, the bond-length difference reduces to 0.04 Å,[40] in excellent agreement with recent experimental information.[41-43] Coupled Hartree–Fock calculations[44,45] indicate that this molecule has a polarizability and magnetizability characteristic of aromatic π-orbital systems. The vertical electron affinity of C_{60}, deduced from the ultraviolet detachment spectrum of C_{60}^-, is 2.6–2.8 eV,[33] whereas the SCF value is only 0.88 eV.[38]

Earlier calculations on fullerenes other than C_{60} were carried out by Newton and Stanton at the modified neglect of differential overlap (MNDO) level,[46] and they found the "crossover" in energy per carbon atom for planar or polyhedral carbon clusters to occur near $n = 40$. Very recent MP2 results of Parasuk and Almlöf[31] indicate that C_{20} may be the smallest carbon cluster for which the fullerene structure is energetically most stable. However, these authors also point out that the MP2 method is known to overestimate correlation energies and may do so in a manner that favors the fullerene structure.

In the present work, we focus on the relative stabilities of closed fullerene, cumulene, and polyacetylene structures as well as the cohesive energy for clusters of size $n = 18$, 20, 22, 24, 26, 28, 30, 32, 34, 36, 50, and 60. *Ab initio* self-consistent-field and second-order Møller–Plesset perturbation theory methods, combined with analytical derivative geometry optimization methods have been used to address these questions. Details concerning our approach and our findings are presented in subsequent sections.

In view of the limited accuracy of *ab initio* predictions of thermodynamic stabilities as discussed above, we decided to further test the MP2 method and our atomic-orbital basis sets by computing the electron binding energies of a few C_n^- anions so that comparison with experimental binding energies[33,34] could be made. The results reported here were concentrated on calibration of the MP2 method within the particular atomic-orbital bases that were practical to use on the larger clusters that are the species of primary interest here.

II. ATOMIC-ORBITAL BASIS SETS, OPEN-SHELL SCF, AND TREATMENT OF ELECTRON CORRELATION

All SCF and MP2 calculations were carried out using the direct SCF and MP2 program DISCO.[47] The basis set used was derived from van Duijneveldt's carbon $(6s,3p)$ primitive orbital basis set,[48] contracted to $[3s,2p]$ using a general contraction to atomic-orbitals scheme.[49] In the calculations of electron affinities, a more extended basis $[4s,3p]$ was employed. This basis was constructed by adding one diffuse s and one diffuse p function (with exponents 0.072 74 and 0.079 91, respectively) to the original $(6s,3p)$ primitive orbital set and then contracting the set to $[4s,3p]$ size.

For all open-shell calculations, the state with the highest possible spin multiplicity was studied, in accordance with Hund's rules. A symmetry-restricted formalism [i.e., restricted open-shell Hartree–Fock (ROHF) and restricted open-shell MP2 (OS-MP2)] was employed.[50] Therefore, spin and spatial symmetries were preserved in all calculations. The OS-MP2 formalism used here is based on a single set of orbitals obtained from the ROHF calculation, whereas different sets of orbital energies are defined for the α and β orbitals as expectation values of different Fock operators. While not formally rigorous, the approach has been found to remedy many of the anomalies seen in unrestricted Møller–Plesset (UMP) schemes due to severe spin contamination. In general, the approach gives results which fall between the usual UMP method and the restricted open-shell MP2 (ROMP2) scheme recently proposed by Handy and coworkers,[51] while being less computationally expensive than any of these other methods since only one set of orbitals is used.

In situations for which the direct product of the spatial symmetries of the occupied open-shell orbitals contains more than one irreducible representation, the ROHF results do not describe a single state; they correspond to an average of all the states whose irreducible symmetry is contained in the orbital direct product. Moreover, in such cases, the OS-MP2 calculation cannot be carried out because this formalism requires that the orbital direct product specifies a unique symmetry. For the latter reason, the MP2 energies of C_{20} and C_{28} fullerene structures are absent in Fig. 3.

In the course of this study we encountered many clusters with more than one open shell. Application of the ROHF procedure requires knowledge of the shell coupling coefficients which appear in the expression for the expectation value of the energy.[52] In the Appendix we present compact formulas for these coupling coefficients. Our derivation of them is a natural extension of the approach given by Golebiewski.[53]

III. SUMMARY OF RESULTS

A. Geometry optimization

All cluster geometries were optimized at the SCF level using a combination of analytic SCF gradients and single-point energy calculations.

1. Cumulene and polyacetylene structures

For the cumulene and polyacetylene ring systems having n atoms, the geometries were constrained to D_{nh} and $D_{(n/2)h}$ symmetry, respectively, and the C–C distances were optimized for the clusters from $n = 18$ to $n = 26$ in single-point energy calculations. Typical cumulene and polyacetylene structures are illustrated in Figs. 1(a) and 1(b) for $n = 18$; the cumulene structures are characterized by one unique bond distance, while the polyacetylene structures possess two unique distances. Once $n = 26$ was reached, the optimized bond lengths remained fixed at 1.28 Å for cumulenes and 1.20 and 1.36 Å for polyacetylenes. The lowest electronic states found for all the polyacetylene structures are closed-shell $^1A_{1g}$ states. For the cumulene structures, the lowest electronic state alternates between $^1A_{1g}$ for the "doubly aromatic"[54] species with $n = 4N + 2$ (N integer) and $^5A_{1g}$ for the "doubly antiaromatic" ones ($n = 4N$). This al-

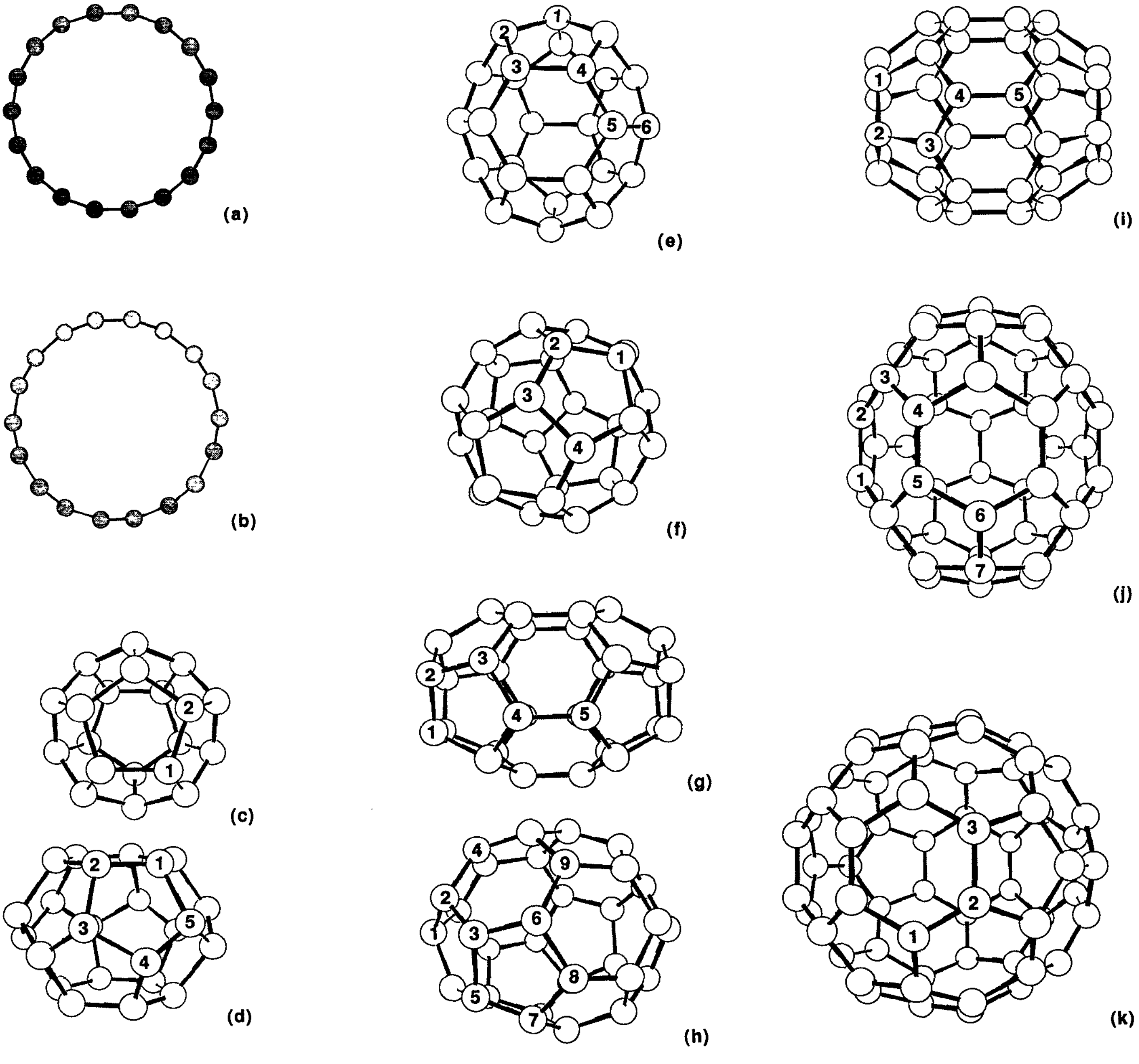

FIG. 1. (a),(b) Cumulene and polyacetylene structures for C_{18}. (c)–(k) Fullerene structures for all C_n species studied.

ternation, and the resulting variation in relative stability seen in Figs. 2 and 3, is consistent with the discussion of in-plane aromaticity by McEwen and Schleyer.[55]

2. Fullerene structures

The optimization of the fullerene structures was somewhat more complicated. The Euler network closure requirement

$$\sum_i (6-i)m_i = 12$$

constrains the number m_k of k-sided polygons that can be formed into a closed structure. This constraint, when applied to rings having only five or six members,

$$12 = m_5 + 0m_6,$$

can be used to define the family of fullerene structures. It specifies that any such closed structure must have 12 five-sided elements, but any number (0,1,2,...) of hexagons are possible. As a result, a fullerene having the chemical formula C_n must have 12 pentagonal faces and $(n-20)/2$ hexagons. In the study presented here, the number of hexagons varies from zero for C_{20} to 20 for C_{60}.

Given the number of pentagons and hexagons as specified by n, we generated closed structures belonging to the point groups indicated in Table I. It was not computationally feasible to optimize the structures for several electronic

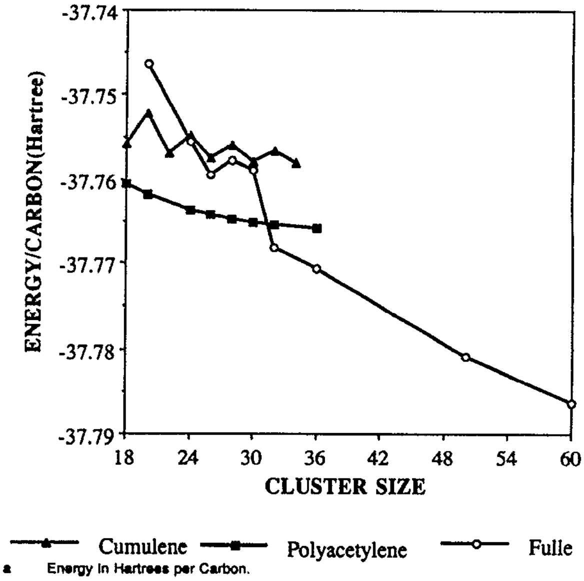

FIG. 2. Relative SCF energies of carbon clusters studied.

states for each fullerene. Rather, we focused on the lowest electronic states. These lowest states for the fullerenes were determined first with all bond lengths fixed at 1.4 Å, after which geometry optimization was undertaken. The fact that the subsequently optimized C–C distances remained near 1.4 Å (see Table II) supports this approach to beginning our geometry optimization calculations.

For each of the fullerene clusters with $n \geqslant 20$, the structures were optimized using the lowest reasonable point group for the "initial guess" of the structure. For several of the structures, the geometries converged to a higher symmetry than was initially used. In all such cases, the spatial symmetry of the resulting ground state belonged to a single nondegenerate representation. The symmetry character of these species are thus well determined and not subsequent to first-order Jahn–Teller distortion.

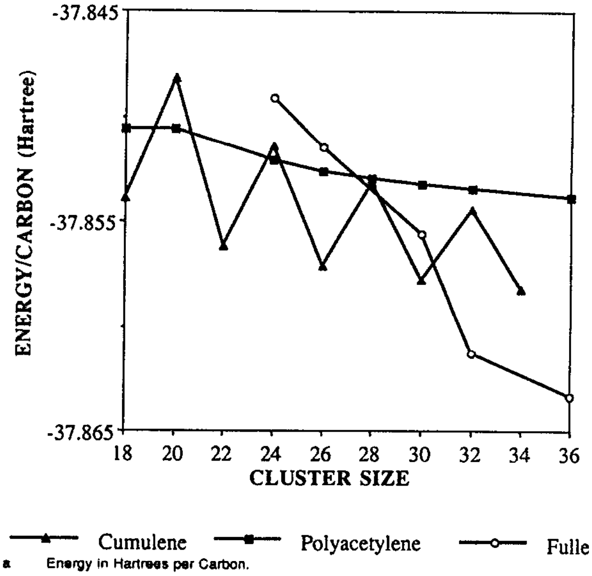

FIG. 3. Relative MP2 energies of carbon clusters studied.

TABLE I. Symmetries of fullerene clusters.

Cluster size	Geometry Initial	Geometry Converged	Electronic state
20	I_h	I_h	${}^3T_{1g}, {}^3T_{2g}$
24	D_3	D_6	${}^1A_1$
26	D_3	D_{3h}	${}^5A_1'$
28	T_d	T_d	${}^5T_1, {}^5T_2, {}^5E, {}^5A_1$
30	D_5	D_{5h}	${}^3A_2'$
32	D_3	D_3	${}^1A_1$
36	D_3	D_{6h}	${}^3A_{2g}$
50	D_{5h}	D_{5h}	${}^1A_1'$
60	I_h	I_h	${}^1A_g$

For C_{20} and C_{28}, the lowest-energy states are spatially degenerate within the point group used in the calculation. They are thus subject to first-order Jahn–Teller distortion. We did not examine the distortions that occur in these cases; we retained the constraints to I_h and T_d symmetry, respectively. However, Parasuk and Almlöf[31] have studied C_{20} and found the distortion away from I_h symmetry to be small.

The spatial symmetries for which the fullerene geometries were optimized along with the symmetries of the optimized structures and the symmetries of the ground electronic states are given in Table I. The optimized geometries of the fullerene clusters are shown in Figs. 1(c)–1(k). Table II contains the unique bond lengths for all of these optimized structures. For C_{60}, the optimized bond lengths (1.454 and 1.370 Å) agree well with previous results of Lüthi and Almlöf (1.453 and 1.369 Å).[38] A complete set of Cartesian coordinates for all species considered is available from the authors upon request.

B. Relative stabilities

For $20 \leqslant n \leqslant 30$, we predict the fullerenes, cyclic polyacetylenes, and cyclic cumulenes to be nearly equal in stability (see Figs. 2 and 3). At the SCF level, the polyacetylenes seem to be more stable for $n \leqslant 30$. However, when correlation is accounted for (at the MP2 level), the cumulene structures that do not obey the $4m + 2$ rule (e.g., C_{20}, C_{24}, C_{28}, and C_{32}) are found to be essentially isoenergetic with the polyacetylenes (see Fig. 3). The polyacetylenes display a cohesive energy that monotonically increases with n, whereas the cumulene structures show the alternation expected from Hückel's $4m + 2$ rule.

For $n \geqslant 32$, we find the fullerenes to be the most stable, and we find the cohesive energy to increase monotonically as n varies from 24 to 60. Based on the earlier work of Parasuk and Almlöf, who examined the relative stabilities of fullerene, cumulene, and polyacetylene structures for C_{20} using MP2 correlation but with a larger atomic-orbital basis than ours, we expect the *relative* energies of the fullerene structures to be lowered even further as larger bases are employed. In Ref. 31, the C_{20} optimized geometries are very near those that we obtain (at the SCF level), but the relative

TABLE II. Bond lengths (Å) of optimized carbon clusters.

Size	Cumulene	Polyacetylene	Fullerene
18	$r = 1.27$	$r_1 = 1.20, r_2 = 1.36$	
20	$r = 1.27$	$r_1 = 1.20, r_2 = 1.36$	$r_{12} = 1.45$
22	$r = 1.27$		
24	$r = 1.28$	$r_1 = 1.20, r_2 = 1.37$	$r_{12} = 1.41, r_{23} = 1.55,$ $r_{34} = 1.48, r_{45} = 1.34,$ $r_{15} = 1.55$
26	$r = 1.28$	$r_1 = 1.20, r_2 = 1.36$	$r_{12} = 1.43, r_{23} = 1.50,$ $r_{34} = 1.43, r_{45} = 1.40,$ $r_{56} = 1.56$
28	$r = 1.28$	$r_1 = 1.20, r_2 = 1.36$	$r_{12} = 1.44, r_{23} = 1.43,$ $r_{34} = 1.50$
30	$r = 1.28$	$r_1 = 1.20, r_2 = 1.36$	$r_{12} = 1.43, r_{23} = 1.46,$ $r_{34} = 1.44, r_{45} = 1.42$
32	$r = 1.28$	$r_1 = 1.20, r_2 = 1.36$	$r_{12} = 1.43, r_{23} = 1.39,$ $r_{24} = 1.45, r_{35} = 1.54,$ $r_{36} = 1.42, r_{57} = 1.35,$ $r_{68} = 1.47, r_{69} = 1.42,$ $r_{78} = 1.51$
34	$r = 1.28$		
36		$r_1 = 1.20, r_2 = 1.36$	$r_{12} = 1.40, r_{23} = 1.50,$ $r_{34} = 1.42, r_{45} = 1.44$
50			$r_{12} = 1.46, r_{23} = 1.37,$ $r_{34} = 1.48, r_{45} = 1.40,$ $r_{56} = 1.40, r_{67} = 1.47$
60			$r_{12} = 1.37, r_{23} = 1.45$

energies from Ref. 31 place the fullerene structure below the others by 3 kcal/mol per C atom.

Accordingly, the smallest C_n cluster for which the fullerene structure is lowest in energy may well have n less than 32, which is the value obtained in the present work. In this case, the geometries predicted for these structures, depicted in Figs. 1(c)–1(k) and listed in Table II, will be of significant interest to experimental groups studying these species.

C. Electron affinities

It is well established that accurate computations of electron affinities usually require large atomic basis sets and state-of-the-art treatment of electron correlation.[56] The MP2 calculations, even if performed with extended atomic-orbital basis sets, do not treat the electron correlation energy accurately enough to determine precisely the relative thermodynamic stability of different conformers, especially in the "crossover" regions.[24] To better calibrate the accuracy of the MP2 method using the basis sets employed throughout most of this work, we have undertaken calculations of vertical detachment energies for selected isomers of a few C_n^- cluster anions. Our goals were to compare our computed values with earlier theoretical results on certain of these species (to demonstrate the limitations of the method and the basis sets we used) and to compare our computed binding energies to the experimental electron binding energies[33,34] for larger clusters to gain further evidence for or against preference for fullerene structures in the $n \leqslant 30$ region. Examination of the *ab initio* calculated vertical electron detachment energies for a larger number of anionic clusters, including several fullerene structures, will be the subject of our future study.

Our SCF and MP2 electron affinities of linear C_3, C_5 clusters and the fullerene C_{24} are presented in Table III, where they are compared with experimental estimates of corresponding vertical electron detachment energies.[34] In our calculations, the MP2 optimized geometries of C_3 and C_5 were used.[57] The results clearly show that an extension of the original [3*s*,2*p*] basis set and incorporation of electron correlation effects are essential to obtaining reasonably accurate electron affinities (EAs). The EAs obtained with the [4*s*,3*p*] basis set are significantly larger for the clusters C_3 and C_5 than those obtained with the [3*s*,2*p*] basis. However, for C_{24} the basis-set dependence of the EA is not so dramatic. The OS-MP2 [4*s*,3*p*] EAs are systematically higher than the ROHF results and closer to, but below, the experimental results. It is interesting to note that, in this respect, the behavior of the restricted HF and MP2 methods are qualitatively different from their unrestricted counterparts.[57]

TABLE III. Electron affinities (eV) of linear C_3, C_5, and fullerene C_{24} compared with vertical photodetachment energies.

	C_3	C_5	C_{24}
SCF [3*s*,2*p*]	0.63	1.61	1.23
MP2 [3*s*,2*p*]	0.56	1.45	2.11
SCF [4*s*,3*p*]	1.25	2.07	1.44
MP2 [4*s*,3*p*]	1.46	2.14	2.65
expt. (Ref. 34)	1.95	2.80	2.90

The data of Table III clearly illustrate that the $[3s,2p]$ basis employed to study the geometries and relative stabilities of structures of C_n with $18 \leqslant n \leqslant 60$ is not able to treat the diffuse charge densities and electron correlations present in the corresponding anions. Even the larger $[4s,3p]$ basis, which contains additional diffuse s and p orbitals, does not accurately reproduce the EAs. This does not, of course, imply that the relative energies and geometries of the neutral species examined here and discussed earlier are unreliable. In fact, evidence was presented earlier in this paper that supports our geometry findings. These observations about basis sets do mean that the larger $[4s,3p]$ basis must be used if, in our future work on the C_n^- cluster anions, we wish to compare computed EAs to experimental UPS electron binding energies[33,34] to support or negate claims that fullerene structures are thermodynamically favored for certain cluster sizes. Along these lines, the computed EA for the fullerene structure of C_{24}, obtained with the larger basis set, is in reasonable agreement with the UPS detachment energy for this species. This would support the claim that the fullerene structures are energetically favored for n at least as small as $n = 24$.

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APPENDIX

The expectation value of the ROHF energy[52] for a molecular system with two open shells is

$$E = 2\sum_{i}^{c} h_{ii} + \sum_{i}^{c}\sum_{j}^{c}(2J_{ij} - K_{ij}) + 2f_1\sum_{m}^{o_1} h_{mm} + 2f_1\sum_{i}^{c}\sum_{m}^{o_1}(2J_{im} - K_{im}) + f_1^2\sum_{m}^{o_1}\sum_{n}^{o_1}(2a_1J_{mn} - b_1K_{mn})$$
$$+ 2f_2\sum_{k}^{o_2} h_{kk} + 2f_2\sum_{i}^{c}\sum_{k}^{o_2}(2J_{ik} - K_{ik}) + f_2^2\sum_{k}^{o_2}\sum_{l}^{o_2}(2a_2J_{kl} - b_2K_{kl}) + f_1f_2\sum_{m}^{o_1}\sum_{k}^{o_2}(2\alpha J_{mk} - \beta K_{mk}), \qquad (A1)$$

where the symbols J and K stand for the Coulomb and exchange integrals, respectively. The indices i, j label the closed-shell orbitals (c), the indices m, n label orbitals from the first open shell (o_1), and k, l label orbitals from the second open shell (o_2). Equation (A1) can be generalized in a natural way to the case of more than two open shells.

The orbital degeneracy of the open shell o_i $(i = 1,2)$ is

$$g_i = d_i + s_i + e_i,$$

where d_i, s_i, and e_i are the number of doubly occupied, singly occupied, and empty orbitals, respectively. The total number of electrons in the ith open shell is

$$n_i = n_{d_i} + n_{s_i},$$

where $n_{d_i} = 2d_i$ and $n_{s_i} = s_i$. The fractional occupation of the ith open shell is

$$f_i = n_i/2g_i.$$

General expressions for the coefficients a_i and b_i of Eq. (A1) have been derived by Golebiewski[53]

$$a_i = \frac{g_i}{g_i - 1}\left(1 - \frac{n_i + n_{d_i}}{n_i^{\,2}}\right), \qquad (A2)$$

$$b_i = \frac{g_i}{g_i - 1}\,\frac{n_{d_i}^{\,2} + 2n_i(n_{s_i} - 1)}{n_i^{\,2}}. \qquad (A3)$$

Below, we show how the expressions for the open-shell coupling coefficients α and β of Eq. (A1) are derived. From here on, we assume that unpaired electrons from open shells o_1 and o_2 have all parallel spins, in accordance with Hund's rule.

The number of equivalent distributions of n_i electrons among g_i orbitals of the shell o_i, with s_i orbitals singly occupied, is

$$L_i = \binom{g_i}{d_i}\binom{g_i - d_i}{s_i}$$

and the total number L of equivalent electron distributions in open shells o_1 and o_2 is L_1L_2.

Let us consider two orbitals: $m \in o_1$, and $k \in o_2$. The number of distributions with m and k being both doubly occupied is

$$\binom{g_1 - 1}{d_1 - 1}\binom{g_1 - d_1}{s_1}\binom{g_2 - 1}{d_2 - 1}\binom{g_2 - d_2}{s_2} = \frac{L_1d_1}{g_1}\,\frac{L_2d_2}{g_2}$$

and every distribution contributes $4J_{mk} - 2K_{mk}$ to the energy. Next, the number of distributions with m doubly occupied and k singly occupied is

$$\binom{g_1 - 1}{d_1 - 1}\binom{g_1 - d_1}{s_1}\binom{g_2 - 1}{s_2 - 1}\binom{g_2 - s_2}{d_2}$$
$$= \frac{L_1d_1}{g_1}\,\frac{L_2s_2}{g_2}$$

and every distribution contributes $2J_{mk} - K_{mk}$ to the energy. Similarly, the number of distributions with m singly occupied and k doubly occupied is $(L_1s_1/g_1)(L_2d_2/g_2)$ and the related energy contribution is again $2J_{mk} - K_{mk}$. Finally, the number of distributions with both m and k singly occupied is

$$\binom{g_1 - 1}{s_1 - 1}\binom{g_1 - s_1}{d_1}\binom{g_2 - 1}{s_2 - 1}\binom{g_2 - s_2}{d_2} = \frac{L_1s_1}{g_1}\,\frac{L_2s_2}{g_2}$$

and every distribution contributes $J_{mk} - K_{mk}$ to the energy.

Multiplying the above energy contributions by the derived statistical factors and dividing the sum by the total number of distributions L we obtain the average electron–electron interaction energy for the orbital pair m,k,

$$\frac{d_1}{g_1}\frac{d_2}{g_2}(4J_{mk} - 2K_{mk}) + \left(\frac{d_1}{g_1}\frac{s_2}{g_2} + \frac{s_1}{g_1}\frac{d_2}{g_2}\right)(2J_{mk} - K_{mk}) + \frac{s_1}{g_1}\frac{s_2}{g_2}(J_{mk} - K_{mk}).$$

On the other hand, according to Eq. (A1), the electron–electron repulsion energy for the orbital pair m,k is $f_1 f_2 (2\alpha J_{mk} - \beta K_{mk})$. Comparison of these two expressions leads to

$$\alpha = 2, \tag{A4}$$

$$\beta = 2\left(1 + \frac{n_{s_1} n_{s_2}}{n_1 n_2}\right). \tag{A5}$$

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