

Fullerenes with Four-Membered Rings

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Received November 30, 1992

Fullerenes^{1,2} can be generally defined as spherical, polyhedral structures comprised of even numbers of trivalent (sp^2) carbon atoms. The numbers of possible C_n fullerenes with $(n/2 - 10)$ six-membered rings (R6) and 12 five-membered rings (R5) have been enumerated.^{3–5} Criteria suggested for selecting the more stable C_n structural isomers from among the large number of alternatives for each value of n include: carbon skeleton features that minimize strain, e.g., no small rings (three- and four-membered rings); high symmetry and disjoint pentagons (the isolated pentagon rule); and favorable Huckel molecular orbital (HMO) characteristics, e.g., closed-shell π electronic configurations, high delocalization energies, and an absence of antiaromatic substructures.^{6–10}

Experimental evidence for the existence of fullerenes with less than 60 carbon atoms is summarized (with leading references) in the review articles by Kroto et al.¹ and Smalley.² We developed an interest in structural requirements for these smaller fullerenes, induced by the realization that no such structure could obey the isolated pentagon rule and encouraged by the facile construction of the highly symmetric D_{4d} C_{48} (R6 = 16, R5 = 8, R4 = 2) shown in Figure 1, containing two four-membered rings with all 10 small rings disjoint. We were also intrigued by previously suggested structures and calculations for small fullerenes.^{6–8,11–20} Postulated structures included systems with zero five-membered rings and six (required) four-membered rings,^{13–16} but the possible coexistence of R5 and R4 substructures in fullerenes has not been delineated in any previous study.

Several calculated results are listed in Table I for C_n (R6 = $n/2 - 10$, R5 = 12, R4 = 0) and C_n (R6 = $n/2 - 8$, R5 = 8, R4 = 2) structures, where n is 60, 56, 48, 40, and 32. The theoretical methods consisted of the HMO approach, π -SCF calculations,

molecular mechanics, and semiempirical MNDO procedures.²¹ All π -SCF and MNDO calculations were carried out at both restricted and unrestricted Hartree–Fock levels (RHF and UHF).

The R6/R5 systems in Table I were chosen from inventories of all possible C_n ($n/2 - 10, 12, 0$) fullerenes,²² applying the previously accepted stability criteria as far as possible. The structures of the R6/R5/R4 compounds were obtained by trial and error and by means of systematic structural rearrangements analogous to pyracylene transformations previously used in rationalizing fullerene structural relationships.²³ A three-dimensional rendition for each structure is given in Figure 1, and every structure is also specified by the spiral code introduced by Manolopoulos and co-workers.^{5,24}

The following observations generally disregard the HMO results, since the HMO delocalization energies and HOMO–LUMO gaps are not adequate to correlate the more consistent trends produced by the other calculational procedures. Note, however, the slightly larger HMO π delocalization energy, the much larger HOMO–LUMO gap, and the normal closed-shell electronic structure for the C_{48} (R5 = 8, R4 = 2) compound contrasted to the same HMO parameters for C_{48} (R5 = 12).

Replacement of four R5s by two R4s and two R6s in the I_h C_{60} (20, 12, 0) framework produces the expected increase in strain energy (77.8 kcal, MMX) and decrease in π delocalization energy (18.6 kcal, π -SCF). In the smaller C_n pairs, the destabilizing difference in strain energies is ameliorated, but it is still 25.8 kcal at C_{32} . However, the π -SCF resonance energy terms generally favor the R6/R5/R4 compounds, except at C_{40} ; where the π energies are essentially equivalent. The UHF MNDO ΔH_f° increment favoring R5 = 12 compounds is 94 kcal/mol in the case of Buckminsterfullerene (C_{60}) compared with the R4 = 2, C_{20} structure. This difference decreases to 48 kcal/mol for C_{56} systems; calculated relative energies are comparable for C_{48} structures; and R4 = 2 systems are preferred in the cases of C_{40} and C_{32} .

The general trend in calculated ΔH_f° s clearly favors the R4 = 2 structures as the size of the polyhedral system becomes smaller. The relative π -SCF HOMO–LUMO energy gaps do not show a consistent trend, but the UHF MNDO HOMO–LUMO separations are also largely in favor of the R4 = 2 structures, even for the C_{60} compounds. There is no evidence that would infer that four-membered rings induce any aspect of “antiaromaticity” into the molecular structure. Therefore, presence of a putative “antiaromatic” substructure should not be used as a criterion for excluding potentially existent fullerene structures.

The results presented above indicate that a definition of fullerenes which limits consideration to cages consisting solely of R6 and R5 rings may be inadequate to describe the full range of possible fullerene structures and chemistry. We have provided evidence that polyhedral carbon structures with fewer than 60 carbon atoms may actually be stabilized by incorporation of two four-membered rings in the fullerene molecular framework. We find that strain energies are always higher in the R4 = 2 fullerenes and that the stabilizing R4 effects are generally due to stabilization of the π systems, even at HMO levels of calculation.

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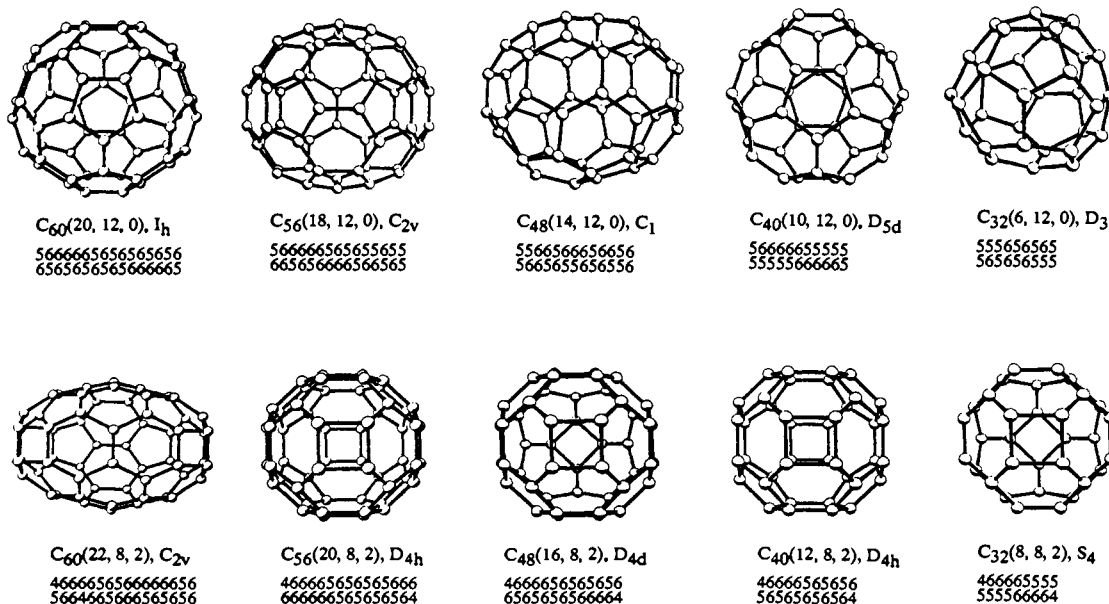
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Table I. Calculated Properties of C_n ($R6 = n/2 - 10$, $R5 = 12$) and C_n ($R6 = n/2 - 8$, $R5 = 8$, $R4 = 2$) Fullerenes

HMO π energy (β)	HMO LUMO type	HMO HOMO-LUMO gap (β)	MMX ΔH_f° (kcal)	MMX strain energy (kcal)	SCF-UHF π energy (kcal)	SCF-UHF HOMO-LUMO gap (eV)	MNDO-UHF ΔH_f° (kcal)	MNDO-UHF HOMO-LUMO gap (eV)
93.162	normal	0.7566	782.563	$C_{60}(20, 12, 0)$, I_h 738.854	-3539.133	7.0515	812.08	5.0101
92.994	normal	0.5811	874.032	$C_{60}(22, 8, 2)$, C_{2v} 816.717	-3520.460	6.6679	906.449	7.6942
86.947	bonding	0.0717	830.401	$C_{56}(18, 12, 0)$, C_{2v} 725.505	-3233.662	5.4292	846.611	7.6451
86.761	nonbonding	0.5293	856.491	$C_{56}(20, 8, 2)$, D_{4h} 787.078	-3263.900	6.1939	894.212	7.9962
74.252	bonding	0.3843	795.476	$C_{48}(14, 12, 0)$, C_1 696.256	-2757.396	6.0759	833.002	8.0003
74.203	normal	0.7066	788.055	$C_{48}(16, 8, 2)$, D_{4d} 722.215	-2794.347	6.9211	841.971	7.8753
61.581	bonding	0.3731	740.921	$C_{40}(10, 12, 0)$, D_{5d} 643.434	-2288.399	6.8676	805.970	8.1375
61.755	bonding	0.1031	764.983	$C_{40}(12, 8, 2)$, D_{4h} 668.738	-2286.691	5.8608	785.281	8.3418
49.150	bonding	0.3639	705.259	$C_{32}(6, 12, 0)$, D_3 580.976	-1772.203	5.4867	756.466	8.4608
48.868	nonbonding	0.6458	702.890	$C_{32}(8, 8, 2)$, S_4 606.780	-1804.615	7.4859	745.603	8.4180

**Figure 1.** Structure, Schlegel diagram, and unique spiral code for $C_{48}(16, 8, 2)$ with eight R5 and two R4.

There is no evidence for "antiaromaticity" due to topological or electronic effects of four-membered ring substructures.

We anticipate that fullerene structures with a single R4 ring will also exhibit interesting calculated properties. Studies on R4 = 1 fullerenes and additional R4 = 2 structures ($n = 24-84$) are in progress.

Acknowledgment. The financial support of the Welch Foundation of Houston, Texas, and of the University of Texas at El Paso Materials Research Center of Excellence (sponsored by the National Science Foundation) is gratefully acknowledged. We also thank Prof. Douglas J. Klein for many instructive and helpful comments.