

Communications to the Editor

C₃₆: The Best Fullerene for Covalent Bonding

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Lower fullerenes (those pentagon–hexagon carbon cages C_n with n < 60) are certain to include pentagon–pentagon fusions and pyramidal unsaturated carbon atoms.¹ In consequence, they are predicted to have high reactivity, significant steric strain and low HOMO–LUMO gap, and have generally been assumed to be unlikely candidates for isolation. A recent report by Piskoti et al.² of a C₃₆ fullerene solid prepared by a modified Krätschmer–Huffman procedure³ calls for some revision of this view. Although the precise attribution in ref 2 to a particular cylindrical isomer of C₃₆ (36:15 in the lexicographic spiral order¹) is yet to be confirmed, the question arises whether this isomer is in some sense “special”, or is just one example of a new class of fullerenes equally qualified to form solids of a type different from the C₆₀ and C₇₀ molecular crystals.^{4,5} The interplay of two factors has a major bearing on this question: these are (i) the overall relative stability of the individual isomeric fullerene molecule and (ii) its reactivity as determined by its electronic structure.

The first has been explored extensively in previous systematic calculations^{6–13} within the QCFF/PI model,¹⁴ where the π electrons are treated via a parameterized self-consistent-field (SCF) approach and the σ framework is replaced by a set of anharmonic springs. Numerical penalty functions for different structural motifs,¹⁰ proposals for stability of nonclassical isomers,⁸ and rules of thumb such as the minimum-pentagon-adjacency principle⁷ emerged naturally from this work and were found to

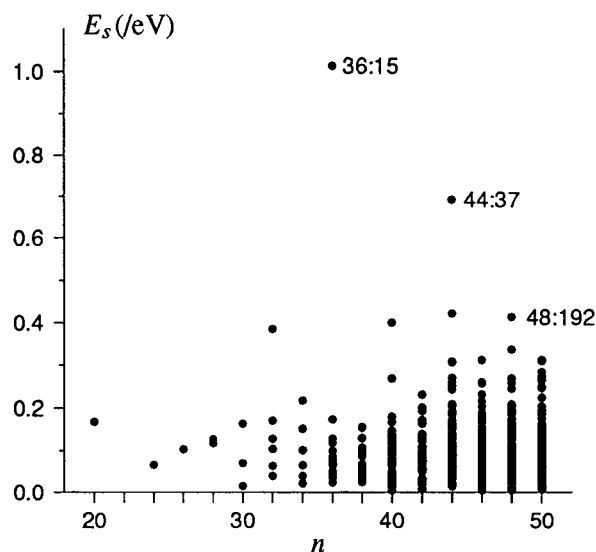


Figure 1. Correlation stabilization energy E_s (eV) as calculated in the CI version of the QCFF/PI model for the lower fullerenes C_n (20 ≤ n ≤ 50). Three significant peak isomers are labeled as a guide to the eye.

be in qualitative agreement with the results of other semi-empirical and more sophisticated methods (see refs 8, 15–17).

The present paper builds on that experience and extends the previous SCF approach using a configuration-interaction (CI) version of the QCFF/PI model that includes single and double excitations in the space of the four frontier orbitals (HOMO-1, HOMO, LUMO, LUMO+1). This study is motivated by the observation of unusual sensitivity of the energy of 36:15 to the level of theory used^{18–20} which suggests a strong electron correlation effect. The aim is to check whether specific features of the electronic structure set this isomer apart from the generality of lower fullerenes.

Doubly excited configurations can contribute strongly to the electronic structure of a molecular ground state that corresponds to a diradical. Such structures are notoriously poorly described at the SCF level which, for instance, predicts ionic rather than homolytic dissociation of the simplest polyelectronic molecule, namely H₂. CI has the effect of lowering the energy from the SCF value, usually as a result of the mixing into the ground state of the doubly excited configuration (HOMO)⁰(LUMO)².

Typical stabilization energies obtained within the QCFF/PI model for polyenes, organic systems in which this effect is particularly large, are between ~0.2 and ~0.3 eV.^{21,22} Stabilization energies for all 812 lower fullerenes in the nuclearity range were calculated as follows: initial structures were created from the topological coordinates¹ based on the spiral code and then optimized, without enforcing symmetry, as closed shells within

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the QCFF/PI model; correlation energies were then calculated at these fixed geometries. Bearing in mind the polyene example, a threshold for appreciable diradical character could be set at, for example, ~ 0.4 eV.²³ Stabilizations calculated for closed-shell configurations of lower fullerenes at their QCFF/PI optimal geometries generally fall well below this value (Figure 1). With a 0.4 eV threshold, only five of the 812 classical fullerenes C_n ($20 \leq n \leq 50$) meet the criterion for radical character; these are 36:15 (stabilization 1.01 eV), 44:37 (0.69 eV), 44:38 (0.42 eV), 48:192 (0.41 eV), and 40:21 (0.40 eV). Seven more fullerenes have a stabilization energy higher than 0.3 eV. They are: 32:6, 44:16, 44:39, 46:46, 48:90, 50:208, 50:263. From this data and from the Figure 1, it is clear that isomer 36:15 stands out as exceptional.

Significantly, the implied highly diradicaloid nature of the exceptional isomer of C_{36} is compatible with predictions of its readiness to form six or more σ bonds to addends or to other C_{36} molecules in a tightly bound solid,^{18,19,24} a tendency which rationalizes much of the experimental evidence reported by Piskoti et al.² An isolated C_{36} molecule would have a small HOMO–LUMO gap and would be distorted from its ideal symmetry of D_{6h} (one of the 28 possible maximal symmetry groups of fullerene graphs¹) down to C_{6v} geometry.¹⁸ In a hexagonal close-packed solid, it could attain local D_{3h} symmetry as part of a macromolecular σ -bonded array, with an intermolecular separation of ~ 1.7 Å.¹⁸

Energetic considerations, i.e., stability with respect to other cages with the same number of carbons, also serve to distinguish 36:15 further from the rest of the lower fullerenes. It is known that in the higher-fullerene regime the process of fullerene self assembly consistently yields the most stable isomer(s) at a given nuclearity. The uniquely stable isomers of C_{60} and C_{70} , the chiral D_2 isomer of C_{76} ,²⁵ and the isoenergetic D_2 and D_{2d} isomers of C_{84} ,²⁶ all with isolated pentagons, exemplify this tendency. Diener and Alford²⁷ have suggested that higher fullerenes fall into two classes: those with large band gaps isolable as molecular solids and those with small gaps but good stability that can be solubilized by electrochemical reduction but would otherwise form polymeric solids in the neutral state. A distinction between higher and lower fullerenes could be made along the same lines. In lower fullerenes, pentagons cannot all be isolated one from another, but minimization of the number of pentagon fusions can maximize relative

stability within an isomer set. For every lower fullerene in a given range, the isomer of lowest energy is predicted to be one with the minimum count of pentagon adjacencies, N_p , that is achievable at that nuclearity.^{1,7} Let this minimum value for each n be $N_p^*(n)$. Of all the highly diradicaloid structures corresponding to peaks in Figure 1, only 36:15 achieves the minimum number $N_p^*(n)$ of pentagon fusions ($N_p^*(36) = 12$, $N_p^*(38) = 11$, $N_p^*(40) = 10$, $N_p^*(42) = 9$, $N_p^*(44) = N_p^*(46) = 8$, $N_p^*(48) = 7$, and $N_p^*(50) = 6$)¹ and is consequently closer in energy to the best C_{36} (which is, by a narrow margin, 36:14, also with the minimal 12 adjacencies). The energy difference 36:15 – 36:14 is 70 kJ mol⁻¹ (QCFF/PI/CI), falling to 10 (DFTB) or 20 kJ mol⁻¹ (DFT) in density-functional-based calculations, but is much higher in SCF-based approaches, e.g., 160 (QCFF/PI without CI), 110 kJ mol⁻¹ (AM1).^{18–20} The other peak diradicaloid species are less stable with respect to the best isomer at a given value of n , with $\Delta E = E(n:m) - E(\text{best}) = 150$ (40:21), 380 (44:37), 450 (44:38), and 110 kJ mol⁻¹ (48:192). Of these, the last achieves a near-minimal count of pentagon adjacencies (8 instead of 7) and seems the next best candidate after 36:15 for solid formation; isolated 48:192 is of C_2 symmetry, and has a moderate HOMO–LUMO gap in Hückel theory.¹

Thus, it appears that isomer 15 of C_{36} has a second special feature that could aid its accumulation in the Krätschmer–Huffman process. Its energy is very close to the minimum attainable for 36 carbon atoms, which implies low steric strain during its self assembly. Reaction with itself to form a polymeric solid could then remove C_{36} from the process, leading to a cul-de-sac on the “fullerene road”.^{28,29}

In this sense, C_{36} could well be a uniquely suitable candidate for formation of a covalently bound fullerene solid, in opposition to its larger homologues C_{60} and C_{70} which form molecular crystals.^{4,5}

Isomer 36:15 has been implicated as the monomer unit in the newly synthesised fullerene solid;² the present survey has pointed to a unique property of this one isomer that distinguishes it from all other lower fullerenes.

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