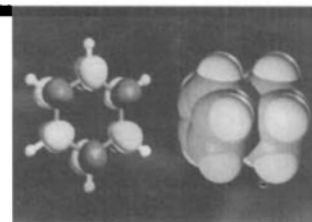# COMPUTATIONAL CHEMISTRY COLUMN

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Recent Theoretical Fullerene Research

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Experimental and theoretical work in fullerene chemistry continues to grow at a rapid pace [1]. This article offers a selective survey of topics from the recent literature which is motivated by the proceedings of the *Sanibel Symposium* organized by the University of Florida in February 1994 and of the Fullerene Workshop at the Technical University of Berlin in March 1994.

Fullerenes C_n are carbon cages with 12 pentagons and $(n/2-10)$ hexagons. They consist of pyramidalized sp^2 C-atoms. Introducing a π-orbital axis vector [2] with equal angles $\theta_{\sigma\pi} > 90°$ to the three σ bonds at a given C-atom (POAV1 convention) the pyramidalization angle may be defined as $\theta_p = \theta_{\sigma\pi} - 90°$. These angles are usually quite large (*e.g.* $\theta_p = 11.6°$ in C_{60}) and imply a large strain energy. It has been estimated [3] that the strain per C-atom in C_{60} is 8 kcal/mol, and that fullerenes such as C_{60} are, therefore, the most strained organic molecules ever isolated. The strain energy may be analyzed in terms of isotropic curvature, anisotropic curvature, and curvature mismatch in a given fullerene structure [4] but, for practical purposes, it is often sufficient to assess the global strain by the average of the squared pyramidalization angles, $\bar{\theta}^2 = \Sigma\theta_p^2/n$. Systematic quantum-chemical calculations for fullerenes from C_{20} to C_{540} have indeed shown a good correlation between $\bar{\theta}^2$ and thermodynamic stability [5]. This is not too surprising, because the proportion of hexagons must grow with increasing fullerene size which is normally accompanied by a decrease in $\bar{\theta}^2$ and an increased stability. In fact, the optimized structures of large icosahedral fullerenes (C_{540}, C_{960}) may be viewed as

almost planar graphite segments with 12 pentagonal defects, where curvature and strain are localized [5]. The correlation between structure ($\bar{\theta}^2$) and stability is also useful in rationalizing the structural preferences in giant fullerenes which may occur in spheroidal and cylindrical shapes ('buckyspheres' *vs.* 'buckytubes'). Since the buckytubes have a higher curvature and hence higher strain, they are expected to be less stable thermodynamically. This is confirmed both by quantum-chemical calculations [6] and by experimental observations [7] that buckytubes in the originally formed fullerene soot are converted to buckyspheres upon high-energy electron bombardment.

Many isomers exist for a given fullerene size, *e.g.* 1812 for C_{60} [4]. Their relative stability is governed by strain and π-conjugation. The most important stability criterion is the isolated pentagon rule (IPR) which states that fused pentagons are energetically unfavorable. In this case, strain and π-conjugation work in the same direction, because a pentalene substructure in a fullerene causes a higher local curvature and contains an antiaromatic 8π subsystem. The combined effect amounts to a destabilization of *ca.* 20 kcal/mol per pair of fused pentagons [8]. Generally, the observed fullerenes have isolated pentagons (*e.g.* C_{60}, C_{70}). For the higher fullerenes (C_n, $n \geq 76$), there are several IPR isomers [9], and usually there is a competition between strain and π-conjugation in determining the relative stabilities. Sometimes (*e.g.* in C_{78} [10]) high-level *ab initio* calculations are required for a reliable assessment of these competing factors, but in most cases more approximate (*e.g.* semiempirical) treatments are sufficient to identify the most stable IPR isomers. It appears that minimization of strain is usually more important in the higher fullerenes than maximization of π-conjugation. For example, in C_{84} [11], the isomer with the highest *Hückel* resonance energy (and a fairly 'edgy' shape) is

the least stable of the 24 IPR isomers, and the two lowest, almost isoenergetic isomers of D_{2d} and D_2 symmetry (according to semiempirical and *ab initio* SCF calculations) are those with the lowest overall curvature ($\bar{\theta}^2$). The experimental ^{13}C-NMR spectrum of C_{84} [9] is consistent with a 1:2 mixture of a D_{2d} and a D_2 isomer. The range of observed ^{13}C-NMR shifts agrees well with that from an *ab initio* calculation for the two lowest-energy isomers [12]. Other D_2 isomers with a less spherical shape can be excluded, because they are computed to have a much larger range of ^{13}C-NMR shifts [12] due to the larger variation in pyramidalization angles.

Curvature influences not only the thermodynamic stabilities of fullerenes through differences in global strain (see above), but also the ease of reactions and the regiochemistry through the relief of local strain. It is well established both experimentally and theoretically that additions to fullerenes occur most easily at a 6–6 bond (shared by two hexagons). In C_{70} and higher fullerenes, there are several types of 6–6 bonds, and one may expect that the most strained 6–6 bond will react most easily, because the addition will lead to the largest possible decrease in strain energy. This is indeed found in the η_2 complexation of C_{70} with transition metals [3] and in the osmylation of C_{70} [13] and C_{76} [14]. In the latter case, OsO_4 selectively adds to 2 of the 15 types of 6–6 bonds in C_{76}, *i.e.*, most likely to those where both C-atoms show pyramidalization angles of $\theta_p \geq 12.0°$ in the theoretical structure [14]. In view of these findings, recent theoretical work on the 46 IPR isomers of C_{90} and the 187 IPR isomers of C_{96} [15] has marked the atoms with the highest pyramidalization angles in the low-energy species, in order to predict the probable regiochemistry simply from the calculated geometries.

Having focused on the structure and stability of fullerenes up to this point, we now turn to the formation and decay of fullerenes. Possible formation mechanisms and the associated experimental evidence have been recently reviewed [16]. One of the major advances in this area comes from gas-phase ion chromatography which allows to separate charged carbon clusters of specific mass into families of isomers based on their mobilities through He-filled drift tubes [17–19]. These families (*e.g.* monocyclic rings, bi- and tricyclic compounds, fullerenes) are identified by comparing the observed mobilities with those calculated from optimized semiempirical equilibri-

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um geometries [18]. Such studies lead to product distributions of the cations C_n^+ as a function of n [16–19] and allow the tentative formulation of a detailed mechanism for fullerene synthesis [19]. Other recent experimental work [20] indicates selective fullerene formation in ion/molecule reactions involving large monocyclic rings (e.g. C_{18}, C_{24}, C_{30}). Computational studies on such mechanisms are apparently still missing, but would be desirable.

By contrast, the mechanisms for fullerene annealing and fragmentation have recently been investigated theoretically in much detail [21–23] using semiempirical geometry optimizations with higher-level single-point energy calculations [21][23] as well as tight-binding molecular-dynamics simulations [22]. Annealing denotes rearrangements which move the pentagons and hexagons on a fullerene surface by changing the interconnections between the C-atoms. The simplest annealing process is the *Stone-Wales* [24] pyracylene rearrangement with an 'in-plane' rotation of a 6–6 bond by 90° which may yield an IPR-violating isomer, as e.g. in C_{60} where two pairs of fused pentagons are generated in this manner. The *Stone-Wales* rearrangement is formally forbidden [24] and requires much activation. An alternative 'out-of-plane' pathway for this rearrangement has been found computationally [21] [23] which involves two successive 1,2 C-shifts *via* an intermediate with one sp^3 C-atom and which needs almost 2 eV less activation than the traditional 'in-plane' pathway. Under the conditions of the usual fullerene synthesis ($T > 1000$ K), such a relatively easy annealing mechanism will allow the sampling of many different fullerene isomers and thus increase the chances to find the most stable one. Considering the current experimental work on fullerene formation [16–20] which involves cations (see above), it may be relevant that the barriers for the 'out-of-plane' pathway are even lower for positively charged fullerenes [23].

Experimentally, fragmentation of fullerenes normally occurs by loss of C_2 units, down to C_{32} [25]. The originally proposed mechanism assumes the elimination of C_2 from a 5–5 bond (shared by two pentagons), i.e., from an IPR-violating isomer which may have to be generated by annealing [25]. Computational studies show [21–23] that, for IPR isomers, there is an energetically competitive mechanism where the leaving C_2 unit comes from a 5–6 bond and which proceeds through the sp^3 intermediate of the 'out-of-planet' annealing pathway. However, when comparing C_2 loss from an IPR and an IPR-violating fullerene, the calculated barrier is appreciably lower in the latter case [23]. Hence, under the usual experimental conditions, fullerenes with isolated pentagons such as C_{60} and C_{70} should be kinetically more stable against C_2 loss than their neighbors (C_{58}/C_{62} and C_{68}/C_{72}, respectively) which do have fused pairs of pentagons. Likewise, C_{60} and C_{70} are thermo-

dynamically more stable than their neighbors, as expected from the isolated pentagon rule and confirmed by theoretical calculations [23]. Taken together, these computational results further rationalize the prominence of C_{60} and C_{70} in fullerene production.

As our last topic we address endohedral fullerene-He complexes which have originally been prepared by high-energy collisions between He and C_n^+ in a mass spectrometer [26]. The barrier for a direct mechanism, i.e., for the passage of He through a hexagon, has been calculated to be around or above 200 kcal/mol [26][27]. More recently, He (and other noble gases) have been incorporated into C_{60} (and other fullerenes) by heating to high temperature [28], preferably under high pressure [29]. The observed *Arrhenius* activation energy of ca. 80 kcal/mol [28] for He release is incompatible with a direct mechanism and has been associated with an alternative pathway where a C–C bond breaks and opens a 'window' on the fullerene surface. Quantum-chemical calculations [30] using semiempirical geometry optimizations with higher-level single-point energy evaluations support this window mechanism, at least in the triplet state. It would seem likely that a similar pathway also exists in the singlet state although it has not yet been found computationally [30].

^{3}He-NMR shifts have been measured [29] for He@C_{60} (–6.3 ppm) and for He@C_{70} (–28.8 ppm). *Ab initio* GIAO-SCF calculations reproduce these values reasonably well [31][32] and predict an even higher shift of –58.3 ppm for He@ C_{60}^{6-} [32]. The overall variation of the ^{3}He-NMR shifts for these three hosts has been predicted qualitatively on the basis of simple *Hückel-London* calculations [33] and attributed to ring current effects, e.g. with diamagnetic currents in the hexagons and paramagnetic currents in the pentagons of C_{60} [33]. The *ab initio* results are consistent with the ring current concept in the sense that the computed shifts of neutral endohedral guests do not depend on the nature of the guest, but are remarkably sensitive to the degree of bond alternation in the host [32][34]. Hence, the chemical shift of endohedral He (from experiment or theory) may serve as an aromaticity criterion for fullerenes [3] to the extent that ring currents are accepted as a signature of aromaticity. In any event, these shifts are sensitive probes of the electronic structure of the host and will, therefore, be useful in studying higher fullerenes as well as fullerene derivatives [34][35].

In summary, this article has intended to provide some illustration of how theoretical work has contributed to recent progress in fullerene chemistry, without any attempt for a comprehensive coverage. The theoretical studies in this field have offered not only valuable numerical answers to specific questions, but also new qualitative insights, e.g. with regard to the correlation between curvature and stability, the relative importance of

strain and π-conjugation, the connection between structure and reactivity, the mechanism for fullerene annealing and fragmentation, and the significance of the observed NMR chemical shifts.

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