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## C<sub>240</sub> — The most chemically inert fullerene?

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### Abstract

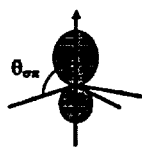
The reactivity of the fullerenes is primarily a function of their strain, as measured by the pyramidalization angle or curvature of the conjugated carbon atoms. The development of faceting in the structure of large icosahedral fullerenes leads to a minimum in the value of the maximum fullerene pyramidalization angle that lies in the vicinity of C<sub>240</sub>. On this basis it is argued that C<sub>240</sub> will be the most chemically inert fullerene. This observation explains the production of [10,10] single-walled nanotubes because a C<sub>240</sub> hemisphere is required for the nucleation of such tubes. © 1997 Elsevier Science B.V.

It is generally assumed that the properties of the fullerenes (C<sub>n</sub>) extrapolate smoothly to those of graphite at large values of *n*. However, it is already clear that some fullerene properties do not monotonically approach those of graphite. A good example is provided by the magnetic properties, which are strongly dependent on the details of fullerene topology [1]. Another case is provided by the molecular shapes, for it is now clear that the large icosahedral fullerenes show a faceted, rather than a spherical shape [2-6]. However, there is a further aspect of fullerene shape that has apparently been overlooked and which has important implications for the chemical reactivity and formation of these species and that may have ramifications for the mechanism of formation of the recently discovered monodisperse single-wall nanotubes [7].

The development of faceted surfaces in the shapes of the icosahedral fullerenes leads to a concentration of the curvature (or carbon atom pyramidalization) [8] at the five-membered rings (5-MRs), which start

to assume the role of vertices in the polyhedral fullerene shape [2-6]. This observation has implications for the chemical reactivity of these fullerenes because it is now recognized that the chemistry [9,10] of these aromatic species arises primarily from the large strain inherent in the spheroidal structure [11]. Addition reactions to the carbon atoms serves to release some of the strain by converting the atoms at the point of attachment into tetrahedral carbon atoms [11].

The pyramidalization angle [ $\theta_p = (\theta_{\sigma\pi} - 90)^\circ$ , Scheme 1], obtained from the  $\pi$ -orbital axis vector (POAV) analysis has been shown to provide a useful index of the degree of nonplanarity and the strain energy at the individual carbon atoms in fullerenes [11]. Thus in the case of C<sub>70</sub> and C<sub>76</sub> where the carbon atoms are no longer all equivalent, it is found that the carbon atoms showing the largest values of  $\theta_p$  also exhibit the greatest reactivity [12,13] toward certain reagents [11-21]. Thus it is of interest to ask which fullerene exhibits the smallest maximum pyra-



Scheme 1. The POAV pyramidalization angle is given by  $\theta_p = (\theta_{\sigma\sigma} - 90)^\circ$ .

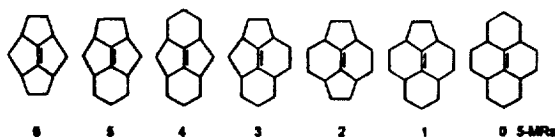
pyramidalization angle ( $\theta_p^{\max}$ ), for this should be the most chemically inert fullerene. It is important to distinguish this approach from the usual considera-

tions based on thermodynamic stability, for in this latter case the available evidence suggests that the thermodynamic stabilities of the isolable fullerenes are monotonically dependent on molecular size, at least to a fairly good approximation [5,6,22,23]. In Table 1, we collect  $\theta_p^{\max}$  values for a variety of different fullerenes, some of which are taken from the work of Raghavachari [24,25], Bakowies et al. [4,26], and Scuseria [5]. The carbon atoms of maximum pyramidalization angle are invariably located in 5-MRs, and it is thus the exocyclic [5] radialene-

Table 1  
Calculated maximum pyramidalization angles [ $\theta_p = (\theta_{\sigma\sigma} - 90)^\circ$ ] across a partial double bond in fullerenes

Fullerene	Ring junctions at carbon atoms	Double bond category	$\theta_p^{\max}$ ( $^\circ$ )	
			ab initio HF	MNDO
C <sub>20</sub> (I <sub>h</sub> , determined by symmetry)	[5-5-5]	(6)	20.91	20.91
	[5-5-5]		20.91	20.91
C <sub>60</sub> isomer (C <sub>2v</sub> )	[5-5-6]	(4)	15.0	15.0
	[5-5-6]		15.0	15.0
C <sub>60</sub> (I <sub>h</sub> , determined by symmetry)	[5-6-6]	(2)	11.64	11.64
	[5-6-6]		11.64	11.64
C <sub>70</sub> (D <sub>5h</sub> )	[5-6-6]	(2)	11.96	11.97
	[5-6-6]		11.96	11.92
C <sub>76</sub> (D <sub>2</sub> )	[5-6-6]	(2)		12.25
	[5-6-6]			12.22
C <sub>78</sub> (C <sub>2v</sub> )	[5-6-6]	(2)		12.27
	[5-6-6]			12.14
C <sub>78</sub> (D <sub>3d</sub> )	[5-6-6]	(2)		12.02
	[5-6-6]			11.97
C <sub>78</sub> (C <sub>2v</sub> )	[5-6-6]	(2)		12.24
	[5-6-6]			12.24
C <sub>84</sub> (D <sub>2</sub> )	[5-6-6]	(2)		11.18
	[5-6-6]			10.98
C <sub>84</sub> (D <sub>2h</sub> )	[5-6-6]	(2)		11.15
	[5-6-6]			11.15
ZC <sub>180</sub> (I <sub>h</sub> )	[5-6-6]	(1)	9.52	9.70
	[6-6-6]		5.59	5.78
C <sub>240</sub> (I <sub>h</sub> )	[5-6-6]	(1)	9.36	9.67
	[6-6-6]		5.74	5.67
C <sub>540</sub> (I <sub>h</sub> )	[5-6-6]	(1)	10.08	10.31
	[6-6-6]		5.6	5.69
C <sub>960</sub> (I <sub>h</sub> )	[5-6-6]	(1)		10.38
	[6-6-6]			5.81

type partial double bonds (henceforth referred to as double bonds) that are reactive toward most reagents [11–13]. Also included in Table 1 are the  $\theta_p$  values for carbon atoms at the other end of these double bonds, as the total strain energy in the bond is expected to be the most important factor in determining its reactivity.

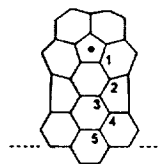


The fullerene double bonds may be classified according to the number of terminations that the ends of the double bond make in 5-MRs. This gives rise to seven possibilities, not all of which are expected to be important experimentally. In order of decreasing strain we obtain: double bonds in which one end terminates in three 5-MRs (5 and 6), double bonds in which one end terminate in two 5-MRs (4 and 3), double bonds in which each end of the double bond terminates in one 5-MR (2), double bonds in which only one end of the double bond terminates in a 5-MR (1), and double bonds that only terminate in 6-MRs (0). It is convenient to now categorize fullerenes in terms of their most strained double bond classification. Category (6)–(3) fullerenes do not obey the isolated pentagon rule [27,28] and are presumably too strained and chemically reactive to be isolated. So far the fullerenes that have been isolated contain double bonds that fall into the latter three categories [referred to as category (2) fullerenes], but it is clear from the table that the most chemically inert fullerenes should be those possessing only double bonds in category (1), in which only one of the atoms in the most strained double bond is in a 5-MR. Such fullerenes have yet to be isolated, but it is clear that they will have a different chemistry than the existing fullerenes, characterized by reduced reactivity. Based on the cases examined (Table 1), the fullerenes may be approximately classified in terms of their maximum pyramidalization angles. Too strained to exist in condensed form:  $\theta_p^{\max} > 13^\circ$  [categories (6)–(3)] and isolable fullerenes:  $13^\circ > \theta_p^{\max} > 9^\circ$  [categories (2) and (1)];

this classification is in accord with other strained organic molecules that have been isolated and characterized. Thus  $\theta_p \approx 13^\circ$  appears to be the maximum double bond pyramidalization angle for isolable organic molecules [29]. Note that the fullerenes that can be made available for study exist in a narrow range of maximum pyramidalization angles and it is only when the second carbon atom at the other end of the partial double bond is considered that there is strong discrimination.

We cite the known chemistry of  $C_{70}$  as evidence of the importance of the distinction between category (2) and (1) double bonds. The double bonds that are considered in the reactions of this molecule, together with their HF/3-21G pyramidalization angles are as follows: 1–2 11.96–11.96°; 3–3 11.46–11.46°; 4–5 10.06–8.78°; 5–5 8.78–8.78°. The functionalization of this fullerene has been studied by a number of authors and the products of thermal reactions are usually confined to additions across the 1–2 and 2–3 bonds, with the former predominating [12–21]. As may be seen from the  $C_{70}$  fragment (Scheme 2), these are both category (2) double bonds, whereas the category (1) double bonds are inert to most of these reagents. The only reported exception at this point is the study by Diederich and coworkers utilizing ortho-quinodimethanes, in which a small amount of the addition product resulting from Diels–Alder reaction at the 4–5 bond was isolated [18].

The development of faceting [2–6] in the icosahedral fullerene structure leads to a further fullerene selection. As they increase in size the spheroidal shape gives way to the development of the 20 faces of the icosahedron which are composed of 6-MRs and thus the curvature of these structures becomes concentrated at the 5-MRs (which become vertices) and the ridges joining the 5-MRs (which become the



Scheme 2. Schlegel diagram of a  $C_{70}$  fragment showing the location of the five-fold axis (solid circle) and the plane that bisects the molecule (dashed lines).

edges). It may be seen that the  $\theta_p^{\max}$  values reach a distinct minimum in the vicinity of  $C_{240}$  and thus there is not expected to be a monotonic dependence of fullerene chemical reactivity on molecular size. This behavior is shown more clearly in Fig. 1 for the icosahedral fullerenes, where the calculated values of the maximum double bond fullerene strain energy [30] are plotted against  $n$  ( $C_n$ ), for the ab initio geometries [5]. From this standpoint  $C_{60}$  is found to be the most reactive of the (isolable) icosahedral fullerenes. However, some of the icosahedral fullerenes such as  $C_{80}$  are expected to be open shell species [23], and this factor will also lead to an enhanced chemical reactivity.

How will these variations in pyramidalization angle affect the production of isolable fullerenes and nanotubes? It is known that the different techniques for the production of fullerenes lead to a large variation in the distribution of the fullerenes that are detected by mass spectroscopy. However, the isolated products invariably consist of particular fullerenes that obey the isolated pentagon rule. While most reaction mechanisms for fullerene formation focus on the construction of the cage, it is appropriate to ask if fullerene destruction does not play a role in determining the distribution of isolated fullerenes. In such a model (which neglects pre-fullerene structures) [31–35], the production of fullerenes is considered to be essentially statistical but the nature of the isolated fullerenes is decided by a Darwinian

process of fullerene selection based on the degree of chemical inertness.

In fact rather similar models for the formation of the isolable fullerenes have been proposed by Heath [32] and by Jarrold and coworkers [34]. Mass spectrometric experiments show that fullerene structures ( $C_n$ ), begin to be important for  $n$  greater than about 30 [33,34]. Why then do  $C_{60}$  and  $C_{70}$  predominate? While fullerenes in the range  $C_{30}$ – $C_{58}$  and  $C_{62}$ – $C_{68}$  do exist in the gas phase, they are sufficiently reactive to be either destroyed or to add  $C_2$  units until they reach the inert  $C_{60}$  and  $C_{70}$  cluster sizes (or occasionally progress to the higher fullerenes). Certainly such high category ( $> 2$ ) fullerenes will not survive isolation in the solid state and on condensation may lead to some of the insoluble soot that is typically produced. This is in accord with the isolated pentagon rule and the results in Table 1.

Are there conditions under which these principles lead to fullerene selection rules that differentiate between the fullerene categories (2) and (1) (above)? The recently discovered monodisperse single-wall nanotubes [7] may provide such a case. In these experiments it was shown that under a particular set of experimental conditions, virtually the whole of the reaction product consisted of single-walled [10,10] nanotubes. If it is assumed that these nanotubes grow from a hemispherical cap, then the high-symmetry form of this cap which is needed to nucleate a [10,10] nanotube is just half of  $C_{240}$ . Thus it may be that the reaction conditions are too severe for other sized caps to survive, and the production of the [10,10] nanotube results from the fact that its nucleation site is a fragment of the least chemically reactive fullerene —  $C_{240}$ . Although  $C_{180}$  appears competitive to  $C_{240}$  with regard to strain, the electronic structure of the growing edges of the nanotubes are apparently sufficient to differentiate between these precursors [7].

Thus we argue that it is possible to account for virtually the whole of fullerene chemistry including the formation of the fullerenes and [10,10] nanotubes from simple considerations based on reactivity (or chemical inertness). The index of reactivity is the amount of strain at the individual carbon atoms as obtained from their degree of pyramidalization (or curvature) [8]. We further suggest that category (1) fullerenes will show reduced chemical reactivity in

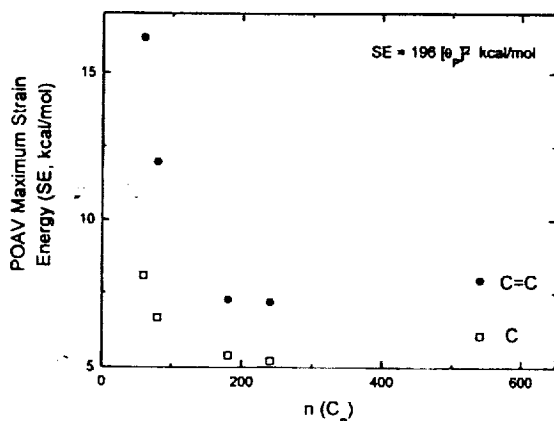


Fig. 1. POAV maximum strain energy [30] for icosahedral fullerenes, calculated from ab initio geometries [5], on a per carbon (C) and per double bond (C=C) basis.

comparison to the previously isolated category (2) fullerenes, but that C<sub>240</sub> will prove to be the most chemically inert fullerene.

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