

Fullerene growth and the role of nonclassical isomers

E. Hernández,^{1,*} P. Ordejón,¹ and H. Terrones²

¹*Institut de Ciència de Materials de Barcelona—CSIC, Campus de la Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain*

²*Instituto de Física, UNAM, Laboratorio Juriquilla, Apartado Postal 1-1010, 76000 Querétaro, Mexico*

(Received 22 January 2001; published 12 April 2001)

We report results of a survey of the energetics and stability of classical and 1-heptagon nonclassical fullerene clusters in the range of sizes C_{30} to C_{70} , using both total-energy tight-binding and first-principles density functional theory methods. We conclude from this survey that 1-heptagon isomers of high stability exist at every nuclearity, and that these nonclassical isomers play an important part in the growth mechanism of fullerenes.

DOI: 10.1103/PhysRevB.63.193403

PACS number(s): 61.48.+c

The discovery^{1,2} of C_{60} has fueled an intense debate in the scientific community over the question of how fullerenes form and grow.³ Fullerenes only become topologically possible from C_{20} onward (excluding C_{22}), so one question is how fullerenes are formed (from other clusters) and at what size range this occurs, and another is how (once formed) they continue to grow to larger sized fullerenes. Two proposals exist for the formation mechanism, known as the *pentagon road*⁴ and the *ring road*.^{5,6} The pentagon road has been largely dismissed, because the precursors and intermediates envisaged in this mechanism have never been found experimentally. The ring road, on the other hand, has been strongly backed by experiments^{5,6} and is now the accepted mechanism of formation. As for the question of growth, our main concern in this Brief Report, we know of only one proposed mechanism, known as the *fullerene road*.⁷ The fullerene road assumes that these grow by the incorporation of dimers and perhaps other small clusters into already existing fullerene cages. Recently, this mechanism has received strong experimental support,⁸ and it is now widely considered as the best explanation for fullerene growth currently available. In spite of this, its mechanistic details remain rather obscure. In this Brief Report we present theoretical arguments that strongly indicate that nonclassical⁹ fullerene structures (containing heptagons) play an important role in understanding fullerene growth and help to explain the great abundance of certain cluster sizes, such as C_{60} . We base this conclusion on the following observations: (i) nonclassical one-heptagon isomers are competitive in energy with classical isomers; (ii) simple mechanisms exist for incorporating a carbon dimer into the heptagonal ring of a one-heptagon isomer; (iii) in certain circumstances, one of these mechanisms can lead directly [i.e., without requiring any subsequent Stone-Wales¹⁰ (SW) relaxation] from low energy one-heptagon isomers of size C_n to the most stable classical isomers of size C_{n+2} ; and (iv) the mechanisms referred to in (ii) have activation energy barriers similar to or lower than those for the incorporation of carbon dimers into classical fullerene structures. Let us now discuss these observations.

The comparative stability of one-heptagon isomers. We have performed a systematic study of classical and one-heptagon nonclassical isomers of fullerenes in the range C_{30} to C_{70} . Isomer structures were generated using the SPIRAL

algorithm¹¹ in an implementation by Brinkmann *et al.*¹² Our aim was to study the relative stability of the different isomers in the range of sizes indicated above. Using a tight-binding (TB) model¹³ due to Porezag and co-workers,¹⁴ we relaxed the structures of classical and nonclassical one-heptagon isomers from C_{30} to C_{70} using the conjugate gradients technique,¹⁵ obtaining the energy ordering of each isomer at each fullerene size considered. We systematically considered all the classical isomers in the range C_{30} to C_{70} . The same was done with the one-heptagon isomers, but only in the range C_{30} to C_{58} . Above this size the number of possible isomers containing one heptagon is so large as to make an exhaustive study of all structures prohibitive. We therefore used the generalized isolated pentagon rule (GIPR) of Fowler *et al.*¹⁶ to select several hundreds of the most promising isomers according to how well they fulfilled the GIPR, and relaxed only these. The GIPR states that the most stable fullerene cages are those that, having a minimum number of pentagon-pentagon adjacencies, maximize the number of pentagon-heptagon adjacencies. We have not considered isomers containing more than one heptagon, or other types of ring such as squares.¹⁷ Each of the classical and one-heptagon isomers considered was found to lead to a distinct minimum in the potential energy surface. In order to corroborate the accuracy of the results obtained with the TB model, the four classical and one-heptagon isomers at each cluster size that were predicted by TB to be the most stable were also analyzed using density functional theory (DFT) combined with the pseudopotential method and the local density approximation (LDA), calculations that were carried out with the SIESTA code.¹⁸ We found that, up to the number of isomers considered for each cluster size, the energy ordering predicted by both methods was generally the same, and when it was not, the total energies of the two clusters that the methods predicted to be in reverse energy ordering were very small (less than 0.04 eV). A full account of these calculations will be reported elsewhere.¹⁹

In Fig. 1 we illustrate the results obtained. It is obvious from these results that as the cluster size is increased the difference of total energies per atom between the most stable isomer of each kind is reduced. In particular, in the ranges from C_{52} to C_{58} and C_{62} to C_{68} , energy differences are very small, and in one particular case, C_{62} , a one-heptagon struc-

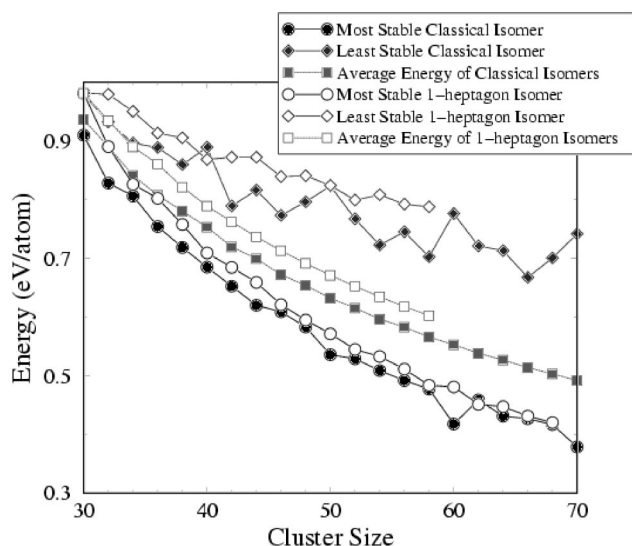


FIG. 1. Energies of the most stable isomer (circles), least stable isomer (diamonds), and average (squares) for classical and one-heptagon isomers in the range C_{30} to C_{70} . Filled symbols correspond to classical isomers, and empty ones to nonclassical ones. The energy is given with respect to that of an infinite graphene sheet.

ture exists that is predicted to be more stable than any of its classical counterparts, in agreement with the results of Ayuela *et al.*²⁰ But perhaps the most noteworthy observation to be extracted from Fig. 1 is the fact that C_{48} , C_{58} , and C_{68} are all cases in which the most stable one-heptagon isomer is particularly close in energy to the overall most stable (classical) isomer. This will be relevant when we consider growth by dimer addition along the fullerene road mechanism below.

In Fig. 2 we show the energy distribution of C_{58} isomers. As seen in the inset, although the most stable isomer is a

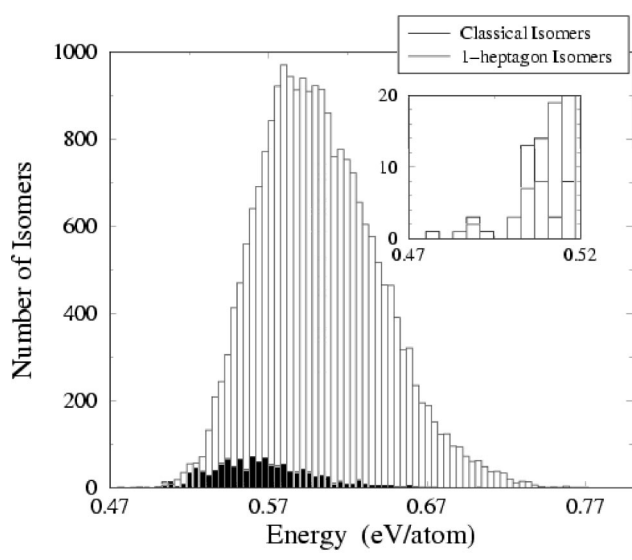


FIG. 2. Histogram of C_{58} isomers (classical and one-heptagon) vs energy. The inset shows the lower left corner of the distribution. Energies are given with respect to a flat infinite graphene sheet.

classical one, the second most stable isomer is not, this being only 0.35 eV (0.21 according to the DFT calculations) above the most stable structure. The number of one-heptagon isomers in this range of sizes is much larger than that of the classical ones,²¹ yet our results show that the range of energies spanned by the classical and one-heptagon isomers is not very different (see Figs. 1 and 2). This means that at intermediate sizes (above C_{50} , say) there will be many one-heptagon isomers having energies close to that of any classical isomer; in particular, this is true for the low lying classical isomers. This observation alone would lead one to consider the possibility of one-heptagon isomers playing an important role in the growth process of fullerenes, but there are further considerations that strengthen this view.

Let us remark at this point that the results described thus far agree with earlier work in this field. In particular, the C_{62} structure found to be most stable in our search coincides with that reported by Ayuela *et al.*²⁰ Our conclusions regarding the relative stability of classical and one-heptagon fullerene clusters extend the results of Fowler *et al.*¹⁶ and Albertazzi *et al.*²² for the particular case of C_{40} . The possible involvement of heptagon-containing structures in the process of fullerene fragmentation and annealing has been reported by Murry *et al.*²³ and by Xu and Scuseria.²⁴

The reaction of carbon dimers with fullerene cages. As noted above, the available experimental data^{5,6,8} accumulated in recent years seem to favor the fullerene road over the pentagon road. This being the case, it is important to consider how carbon dimers can be incorporated into already closed fullerene structures. To our knowledge, only two possible mechanisms have been so far proposed,²⁵ and they are illustrated in Figs. 3(a) and 3(b). In view of the relatively high stability of many one-heptagon cages, we deem it necessary to consider other mechanisms for dimer incorporation involving heptagonal rings. These mechanisms are illustrated in Figs. 3(c), 3(d), and 3(e). The reaction illustrated in Fig. 3(c) converts a one-heptagon structure into a classical fullerene by addition of a dimer and is a straightforward generalization of Fig. 3(a). However, in spite of the similarities there is an important and far-reaching difference: while reactions of type 3(a) lead necessarily to isomers with a pentagon adjacency [and thus relatively less stable, according to the GIPR (Ref. 16)], this need not be the case for reactions of type 3(c). Indeed, we have found that a dimer-incorporation reaction of type 3(c) exists that, starting from the most stable one-heptagon isomer of C_{58} leads directly to the $I_h C_{60}$ isomer of C_{60} [see Figs. 4(e)–4(f)]. This is not possible from any of the classical isomers of C_{58} via reactions of type 3(a) or 3(b) without invoking a certain amount of SW relaxation.²⁶ That this is so for reactions of type 3(a) is immediately apparent since the $I_h C_{60}$ has no pentagon adjacencies. The corroboration of this statement for reactions of type 3(b) is less obvious but straightforward, employing arguments based on the adjacency matrices²⁷ of the clusters involved. This path to $I_h C_{60}$ could partly explain why this cluster is observed in such high abundance in the mass spectra of carbon clusters. Reactions 3(d) and (e) illustrate how a one-heptagon cluster can result from a dimer addition onto a one-heptagon or classical cluster, respectively.

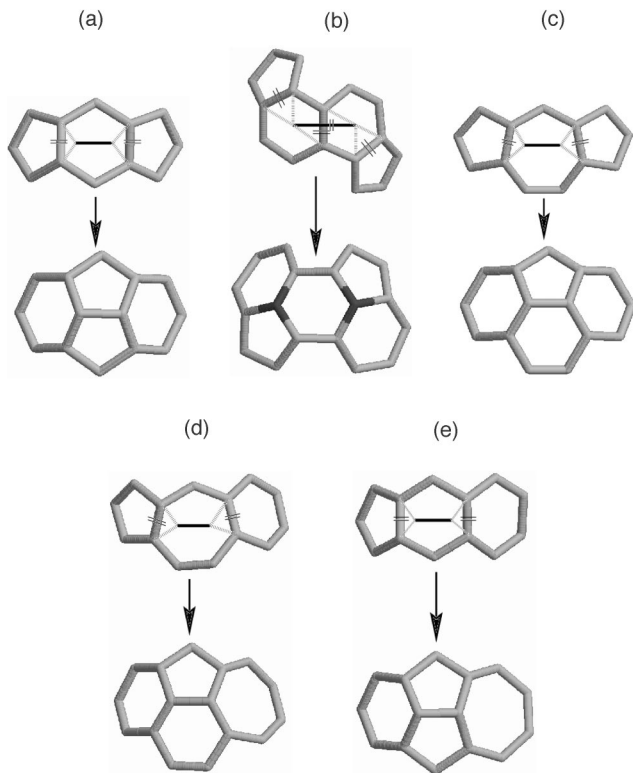


FIG. 3. Possible mechanisms for the incorporation of carbon dimers into closed fullerene cages. The broad dark lines represent the approaching dimer; the discontinuous lines represent the newly formed bonds after the reaction, and the parallel narrow lines mark the bonds broken in the process. (a) and (b) show two paths for structures involving pentagons and hexagons only; in (b) the shaded atoms are the ones originally forming the dimer. (c) shows a possible path involving the heptagonal ring of a nonclassical one-heptagon cage which leads to a classical isomer; (d) shows a dimer addition onto a one-heptagon isomer resulting in another one-heptagon structure; and (e) shows how a one-heptagon cluster can result from the addition of a dimer to a classical fullerene structure.

We should stress that, except for reaction 3(b), which should have a higher activation energy barrier due to the fact that four bonds need to be broken before the reaction can take place, all other reactions should have similar activation energies (only two bonds are broken in each case), and should therefore occur with roughly equal probability.

Taking into account these different possibilities for dimer incorporation into closed cages, it is immediately apparent that a large number of possible growth paths exist, and it is not possible to invoke a single path as responsible for fullerene growth. Indeed, we have identified many such paths involving low energy isomers, both classical and one-heptagon. Given that reactions 3(a), 3(c), 3(d), and 3(e) should all have similar activation energy barriers, it is most probable that at some stage during the growth a cluster adopts nonclassical structures, at least temporarily. For most closed cages there is a large number of sites suitable for reactions of type 3(e) which result in one-heptagon structures. In fact, our survey reveals that typically there are twice as many of these sites as of either 3(a) or 3(b) in any one

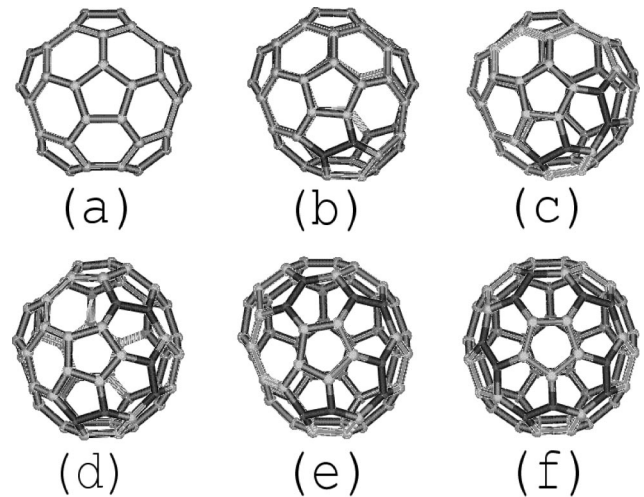


FIG. 4. One-heptagon route from $C_{50} (D_{5h})$ (a) to $C_{60} (I_h)$ (f). The mechanism involves the generation of a one-heptagon nonclassical isomer of C_{52} by the addition of a carbon dimer via reaction 3(e). Further addition of carbon dimers at the heptagonal ring [via reaction 3(d)] causes the heptagonal ring to rotate around the five-fold axis of the initial $C_{50} (D_{5h})$ structure, as shown in (c) for C_{54} , (d) for C_{56} , and (e) for C_{58} . When a fifth carbon dimer is added, this last structure produces $C_{60} (I_h)$.

cluster. We have found that all mechanisms illustrated in Fig. 3 involving low energy isomers of C_n tend to lead to low energy isomers of C_{n+2} . On the other hand, high energy isomers of C_n will not generally lead to low energy isomers of C_{n+2} , and therefore these reactions should not be significant sources of relaxation. However, it is likely that sufficient time elapses between two consecutive dimer incorporation reactions to allow the system to relax via the SW mechanism.^{10,26} In favorable cases, a dimer incorporation reaction may release enough energy to activate the SW relaxation process and thus gain further stability.

As an example of fullerene growth involving one-heptagon isomers, we illustrate in Fig. 4 one of the possible paths that exist from $C_{50} (D_{5h})$ to $C_{60} (I_h)$, both being the most stable clusters of their size. All the intermediate one-heptagon clusters shown in Figs. 4(b), 4(c), 4(d), and 4(e) are highly stable, having energies of only 0.033 (0.016), 0.024 (0.018), 0.020 (0.021), and 0.006 (0.004) eV/atom higher than the most stable cluster of each size, according to our TB (DFT-LDA) calculations. Note that this path requires no SW relaxation¹⁰ in order to reach $C_{60} (I_h)$. We stress that this is by no means the only possible path linking $C_{50} (D_{5h})$ and $C_{60} (I_h)$; however, the C_{58} one-heptagon isomer shown in Fig. 4(e) is the only one leading [via reaction 3(c)] to $C_{60} (I_h)$ directly. All other possible paths that do not involve this isomer will require some degree of SW relaxation. Applying the same procedure as illustrated in Fig. 4 to $C_{60} I_h$ leads to $C_{70} D_{5h}$.

Considering all the above, a picture of fullerene growth emerges that does not conform to a unique mechanism, but rather consists of a multitude of possible growth paths, which can involve both classical and nonclassical fullerene isomers. The different growth paths may link at each nucle-

arity by means of SW isomerizations, thus further increasing the number of possibilities. It seems to us unlikely that mobility experiments could discriminate between one-heptagon and classical fullerenes, due to their structural similarity; however, vibrational spectroscopy may offer a better chance of experimentally testing the involvement of one-heptagon isomers during fullerene growth. We return to this important issue in a forthcoming publication.¹⁹ We have shown how the presence of certain high stability one-heptagon clusters can facilitate the formation of magic number clusters by pro-

viding a direct link to them. Such is the case of the C₅₈ one-heptagon isomer illustrated in Fig. 4(e), which provides a direct link to C₆₀ I_h.

E.H. and P.O. thank the European Commission (Directorate-General XIII) for supporting this work through Contract No. IST-1999-10593 (SATURN). H.T. thanks CONACYT and DGAPA-UNAM of Mexico for support. We thank C4 (Center de Computació i Comunicacions de Catalunya) for the use of their computational facilities.

*Author to whom correspondence should be addressed. Email address: ehe@icmab.es

¹H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, and R.E. Smalley, *Nature* (London) **318**, 162 (1985).

²W. Krätschmer, L.D. Lamb, K. Fostiropoulos, and D.R. Huffman, *Nature* (London) **347**, 354 (1990).

³R.F. Curl, *Philos. Trans. R. Soc. London, Ser. A* **343**, 19 (1993).

⁴J.R. Heath, S.C. O'Brien, R.F. Curl, W.H. Kroto, and R.E. Smalley, *Comments Condens. Matter Phys.* **13**, 119 (1987).

⁵G. von Helden, N.G. Gotts, and M.T. Bowers, *Nature* (London) **363**, 60 (1993).

⁶J. Hunter, J. Fye, and M.F. Jarrold, *Science* **260**, 784 (1993).

⁷J.R. Heath, in *Fullerenes: Synthesis, Properties and Chemistry of Large Carbon Clusters*, edited by G.S. Hammond and V.J. Kuck, ACS Symposium Series No. 481 (American Chemical Society, Washington, DC, 1991), p. 1.

⁸A.A. Shvartsburg, R.R. Hudgins, P. Dugourd, R. Gutierrez, T. Frauenheim, and M.F. Jarrold, *Phys. Rev. Lett.* **84**, 2421 (2000).

⁹In this Brief Report we mean by *classical* fullerene isomers closed structures consisting only of pentagons and hexagons. Structures containing any other kind of ring (such as a heptagon) will be labeled as *nonclassical*.

¹⁰A.J. Stone and D.J. Wales, *Chem. Phys. Lett.* **128**, 501 (1986).

¹¹D.E. Manolopoulos, J.C. May, and S.E. Down, *Chem. Phys. Lett.* **181**, 105 (1991).

¹²G. Brinkmann, O.D. Frederichs, A. Dress, and T. Harmuth, *Match Commun. Math. Comput. Chem.* **36**, 233 (1997).

¹³C.M. Goringe, D.R. Bowler, and E. Hernández, *Rep. Prog. Phys.* **60**, 1447 (1997).

¹⁴D. Porezag, T. Frauenheim, T. Köhler, G. Seifert, and R. Kaschner, *Phys. Rev. B* **51**, 12 947 (1995).

¹⁵W.H. Press, S.A. Teukolsky, W.T. Vetterling, and B.P. Flannery, *Numerical Recipes, The Art of Scientific Computing*, 2nd ed. (Cambridge University Press, Cambridge, 1992).

¹⁶P.W. Fowler, T. Heine, D. Mitchell, G. Orlandi, R. Schmidt, G. Seifert, and F. Zerbetto, *J. Chem. Soc., Faraday Trans.* **92**, 2203 (1996).

¹⁷P.W. Fowler, T. Heine, D.E. Manolopoulos, D. Mitchell, G. Orlandi, R. Schmidt, G. Seifert, and F. Zerbetto, *J. Phys. Chem.* **100**, 6984 (1996).

¹⁸D. Sanchez-Portal, P. Ordejón, E. Artacho, and J.M. Soler, *Int. J. Quantum Chem.* **107**, 453 (1997).

¹⁹E. Hernández, P. Ordejón, and H. Terrones (unpublished).

²⁰A. Ayuela, P.W. Fowler, D. Mitchell, R. Schmidt, G. Seifert, and F. Zerbetto, *J. Phys. Chem.* **100**, 15 634 (1996).

²¹For C₅₀ there are 271 classical isomers, compared to 2784 one-heptagon isomers (counting enantiomeric pairs as only one isomer). For C₇₀ the count is 8149 classical isomers, and 28 9921 one-heptagon ones.

²²E. Albertazzi, C. Domene, P.W. Fowler, T. Heine, G. Seifert, C. Van Alsenoy, and F. Zerbetto, *Phys. Chem. Chem. Phys.* **1**, 2913 (1999).

²³R.L. Murry, D.L. Strout, G.K. Odom, and G.E. Scuseria, *Nature* (London) **366**, 665 (1993).

²⁴C. Xu and G.E. Scuseria, *Phys. Rev. Lett.* **72**, 669 (1994).

²⁵M.S. Dresselhaus, G. Dresselhaus, and P.C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, New York, 1996).

²⁶T.R. Walsh and D.J. Wales, *J. Chem. Phys.* **109**, 6691 (1998).

²⁷P.W. Fowler and D.E. Manolopoulos, *An Atlas of Fullerenes*, Vol. 30 of *International Series of Monographs in Chemistry* (Oxford University Press, Oxford, 1995).