Modelling of C$_2$ addition route to the formation of C$_{60}$

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Abstract

To understand the phenomenon of fullerene growth during its synthesis, an attempt is made to model a minimum energy growth route using a semi-empirical quantum mechanics code. C$_2$ addition leading to C$_{60}$ was modelled and three main routes, i.e. cyclic ring growth, pentagon and fullerene road, were studied. The growth starts with linear chains and, at $n=10$, ring structures begin to dominate. The rings continue to grow and, at some point $n>30$, they transform into close-cage fullerenes and the growth is shown to progress by the fullerene road until C$_{60}$ is formed. The computer simulations predict a transition from a C$_{38}$ ring to fullerene. Other growth mechanisms could also occur in the energetic environment commonly encountered in fullerene synthesis, but our purpose was to identify a minimal energy route which is the most probable structure. Our results also indicate that, at $n=20$, the corannulene structure is energetically more stable than the corresponding fullerene and graphene sheet, however a ring structure has lower energy among all the structures up to $n\leq 40$. Additionally, we have also proved that the fullerene road is energetically more favoured than the pentagon road. The overall growth leading to cage closure for $n=60$ may not occur by a single route but by a combination of more than one route.

(Some figures in this article are in colour only in the electronic version)

$^1$ Supplementary data files are available from stacks.iop.org/Nano/17/4654

1. Introduction

Fullerene and nanotube growth has been the subject of intense discussion ever since the discovery of C$_{60}$ by Kroto et al [1]. Researchers have used a number of computational and theoretical tools to explain the experimental observations and develop a picture of the dynamics for fullerene growth, yet no universally agreed model exists for the fullerene growth. During the 1990s it was established that linear chains are favourable for $n<10$ [2], rings for $n>10$ [2] and fullerenes for $n>30$ [3]. Similarly, Tomanek, using tight-binding calculations [4], established that graphene sheets are more stable than rings at $n>26$ and open-caged caps are more favourable than graphene sheets for $n>38$. Four basic mechanisms of fullerene growth have been established [5], namely graphene-to-fullerene transformation, the pentagon road or Limacon model, ring-stacking and the fullerene road. In graphene-to-fullerene transformation, sputtered or vapourized graphene sheet transforms into a closed-cage fullerene by ejecting a number of smaller carbon clusters. In ring stacking, which got its idea from Diedrich’s synthesis of C$_{60}$ from C$_{30}$ rings [6], carbon rings fuse together to form closed-cage fullerenes. In the pentagon road, an open-cage structure like corannulene grows by the addition of carbon atoms or molecules at its edges, and eventually the cage is closed [7, 8]. In the fullerene road, a smaller closed-cage fullerene grows into a larger one by C$_1$, C$_2$ or C$_3$ insertion into the cage. Recent work supports the fullerene road as being more favourable than other mechanisms [9].

As most of the fullerene formation mechanisms occur at high temperatures, molecular dynamics seems to be the best way to simulate fullerene growth. Oh et al [10], Melker et al [5] and Zhao et al [11] used molecular dynamics to establish some picture for carbon cluster growth from carbon
atoms, but the results are quite complicated, and in none of the work has C$_{60}$ been observed, which is experimentally the most dominant carbon cluster. The main problem area with molecular dynamics is that the formation mechanism progresses on its own without much manipulation and, like any other probabilistic process, the code takes a large number of random pathways. Taking leads from our previous work related to nano-elasticity [12, 13], in which we used nano-elastic arguments to predict fullerene and nanotube formation by the pentagon road, we attempted to establish a picture of C$_{60}$ growth using semi-empirical quantum mechanical simulations. Instead of establishing a dynamic model, we took snapshots of carbon clusters at various formation steps and calculated the heat of formation associated with the geometry-optimized structure at 298 K. In our previous work [13] we focused on the pentagon road; in this communication we attempt to see if the pentagon road is favoured energetically or not when all other possible synthesis routes are available.

2. Molecular modelling methods

A semi-empirical quantum mechanical method was selected for this computational effort based on its efficiency to model nano-clusters in less time and with considerable accuracy. The three most commonly used semi-empirical methods are MNDO [14], AM1 [15] and PM3 [16]. These are parameterized methods in which the optimized parameters are either taken from experimental observations or theoretical arguments. They belong to the family of NDDO (neglect of diatomic differential overlap) methods, in which all terms arising from the overlap of two atomic orbitals which are on different centres or atoms are set to zero [17].

Fullerene electronic structures differ from conventional carbon structures in hydrocarbons, on which most of these parameterization methods are based; in the former case, the carbon–carbon network forms a curved structure. The parameterization methods may not be entirely accurate for fullerenes. We employed a brute-force approach and compared the results of geometry optimization with those of the experimentally reported results. Table 1 presents the output of geometry optimization calculations carried out using the three parameterization methods, i.e. MNDO, AM1 and PM3, and, when compared with the experimental results [18], indicates that the MNDO method is more accurate for the case of fullerenes, i.e. it has the lowest norm of 1.05. Additionally, MNDO has been a favourite method for fullerene modelling by various researchers [19–21].

3. Justification for C$_2$ insertion based growth

C$_{60}$ growth can be modelled by the sequential addition of C$_1$, C$_2$, C$_3$ or larger carbon molecules, but experimental observations from emission spectra of regenerative sooting discharge indicate C$_2$ to be an important constituent of carbonaceous plasma, which may lead to the formation of fullerenes [22]. Additionally, Scheier et al [23] also provide experimental evidence for the critical role of C$_2$ in fullerene fragmentation. We attempted to isolate the role of C$_2$ by modelling a hypothetical plasma with C$_2$ as the predominant species. A hypothetical model for the ingestion of two carbon atoms in a fullerene-to-fullerene conversion was first described by Endo and Kroto [24]. The parent fullerene C$_n$ should have, somewhere on its surface, a patch consisting of two pentagons linked to opposite edges of a central hexagon; the ingestion process is illustrated in figures 1(a) and (b). If the appropriate set of three rings is present, an isomer C$_{n+2}$ should gain two atoms in this way, but the process yields what is presumably a high-energy form of C$_{n+2}$ with fused pentagons. A further rearrangement is needed to give a final product that has isolated pentagons; Stone–Wales transformation is one such mechanism [19, 25], as illustrated in figures 1(c) and (d).

4. Criterion for stability

The heat of formation ($\Delta H_f$) is the energy released when isolated atoms combine to form a stable molecule. From thermodynamic arguments, it could be proved that this excess energy released is actually the binding energy of the molecule. In the case of C$_2$ molecule formation:

$$C + C \rightarrow C_2 + E, \quad E = -\Delta H_f = \text{binding energy},$$

$$\frac{\Delta H_f}{n} = \text{binding energy per atom.}$$
For fullerenes in which all atoms are similar, ΔH_f per carbon atom is approximately equal to the negative value of binding energy per atom (energy required to remove an atom from the molecule). The more tightly an atom is bound in a molecule, the more stable the molecule, thus one can treat ΔH_f per atom as a criterion for judging the molecular stability. The lower the value of ΔH_f per atom, the more stable the molecule.

5. Results of molecular modelling

C_2 addition routes, as modelled by MNDO using the ArgusLab 3.1 code [26] for the pentagon and fullerene roads, is presented in figure 2, where the heat of formation per carbon atom is given for both routes by the filled pentagons and filled squares, respectively. Three-dimensional (3D) rotatable images are also available at stacks.iop.org/Nano/17/4654 in MDL MOL file format as multimedia 1 and multimedia 2, respectively. Heats of formation per carbon atom for the most stable fullerene isomers, as given by the Atlas of Fullerenes [19], are also presented in figure 2 plotted by unfilled square. The corresponding 3D rotatable images are available at stacks.iop.org/Nano/17/4654 as multimedia 3. The growth routes of C_20 fullerene and C_20 graphene by C_2 additions are plotted in figure 2 by filled diamonds and unfilled hexagons, respectively, and their 3D rotatable images are given as multimedia 4 and multimedia 5, respectively at stacks.iop.org/Nano/17/4654. For detailed analysis, the growth of C_n from n = 4 to 20, resulting in a corannulene, fullerene, graphene, linear chain and ring routes, is presented in figure 3. The geometry-optimized structures are plotted next to each data point. The growth by the pentagon and fullerene roads, along with stable fullerene isomers and rings for n = 20 up to n = 60, is given in figure 4. The geometry-optimized structures are plotted next to each data point, with the exception of ring structures, which in all cases are circular.

6. Growth of clusters up to C_20

In figure 3 the sequence of growth of four possible C_20 isomers is presented. As individual carbon dimers fuse together to form larger carbon clusters, they initially show a tendency to form linear chains, which is quite evident in figure 3 from data points L2 to L4. This is in agreement with similar studies in the literature, i.e. Hutter et al [2] proposed linear chains to be more stable than other isomers for n < 10. As these linear chains grow, further ring structures become energetically more favourable, as indicated in figure 3 by data points R5 to R10. This is because the energy gain in killing the dangling
bonds at the two ends over-compensates for the strain energy incurred by folding up the chain [8]. The ring structure consists of alternating single and triple bonds [6]; the carbon atom appears to be in distorted sp2 hybridization. As these rings grow, this distortion energy is reduced and they become more stable, which is quite evident from figure 2 (unfilled circles) and figure 3 (unfilled circles). As fullerene synthesis is usually carried out at high temperature, the possibility of the formation of energetically less favoured isomers may exist for finite times. In that case, coronulene and linear chains have higher chances compared with that of the corresponding fullerene and graphene. It is quite evident from figure 3, data point G10, that, for such a small number of carbon atoms, the formation of graphene is energetically least favoured. It is also worth mentioning that transition from the two-dimensional sp2 hybridized structure to the three-dimensional sp3 structure (2 ≤ x ≤ 3) occurs much earlier in the case of the route leading to C20 fullerene, i.e. at n = 12, than that for the coronulene route, where it occurs at n = 18. Hence, n = 20 coronulene is seen to be more stable than its corresponding fullerene, which is in line with the results shown in the literature, i.e. detailed theoretical studies on C20 fullerene using quantum Monte Carlo simulation have indicated that C20 fullerene is at the cross-over of stability [27].

7. Growth beyond C20 and cage closure

Figure 4 presents the energetics of cluster growth beyond C20 by the sequential addition of C2s. The energy gain with the increasing diameter of rings reduces significantly after n = 20 and becomes very small after n = 30, as is evident from almost a straight line in figure 2 (unfilled circles). The ring structure being the lowest energy isomer up to n = 38 is quite evident, which is in line with von Helden et al [3], however the transition point is shifted from n = 30 to 38. The rings become less stable for n > 44 compared with the structures growing via the fullerene or pentagon routes. The rings seem to dominate other competing structures in the ingestion of C2s up to n ≤ 40. From the energetics point of view, growth by the fullerene route is more favoured than that by the pentagon route, which is evident from figure 4. For the sake of a more thorough comparison, the ΔHf of the most stable isomers, as identified by Fowler [19], were also calculated. Geometry-optimized structures of these closed-cage systems are illustrated in figure 4; the corresponding ΔHf per atom are plotted against the pentagon and fullerene road. The growth sequence by this route needs to be further investigated in the future with the transformation of less symmetric and less energetically favoured isomers into more energetically favoured isomers, possibly by SW transformation. In the case of the fullerene road, the cage’s average diameter increases with the increasing number of carbon atoms; as a result, the steric strain is significantly reduced, leading to more stable structures. The fullerene stability increases significantly with an increase in the number of carbon atoms, while the stability of the ring structure remains almost constant at n > 30. As a result, the cross-over occurs at n = 38 and the fullerene road becomes energetically favoured. One reason for this may be that the edge atoms in open-cage fragments (the pentagon road) are highly strained. The C–C bond length at the arm-chair edge is 1.25 Å (the C–C triple bond length is 1.2 Å in C2H2), indicating a triple bond [10]. Assuming carbon to be sp hybridized, the bond angle is much smaller than 180° (the equilibrium sp hybridized bond angle) and hence there is severe sp distortion in the edge atoms. The atoms other than the edge atoms appear to be in a distorted sp2 hybridization state, which Fowler [19] termed sp3 (2 ≤ x ≤ 3). On the contrary, all atoms in closed-cage fullerenes are in sp3 hybridization and there is no distorted sp hybridization. This may be a possible explanation for the lower stability of the pentagon road than that of the fullerene road.

The ring structure appears to be the predominant isomer compared to the structures based on both pentagon and fullerene roads [28] but, in actual conditions, temperatures up to 2000 K [5] may lead to the formation of other structures. On the basis of symmetry, it may be possible for a ring structure to transform into symmetry-wise more stable fullerene structures much earlier than n = 38. Hua et al [8] have demonstrated computationally a method of C60 fullerene formation from the stacking of C20 rings, which is also an experimental observation [6].

8. Conclusion

Based on the ΔHf per atom calculated computationally by using the MNDO method, it appears to be that the end product of C60 may be the result of competing structures that include rings, coronulene and fullerenes from C2-rich plasma by C2 addition. The growth initially starts with linear carbon chains and, at n = 10, linear chains transform into rings, which further grow by C2 ingestion [28]. At around n = 38, the rings appear to transform into fullerenes, and from there onwards the growth of C60 is achieved by the fullerene road. Based on symmetry arguments, the ring-to-fullerene transition may be reached much earlier than n = 38 in a collision-dominated environment during fullerene synthesis. At n > 38, the fullerene road is more favourable than the pentagon road hence, if insufficient energy is available, fullerene formation is more favoured than the cap formation, which may lead to the nanotube growth. A clear message from this work is that the pentagon road is not the energetically favoured route for fullerene formation, while the single-walled nanotube growth based on the pentagon road needs to be re-investigated.

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References

[1] Kroto H W, Heath J R, O’Brien S C, Curl R F and Smalley R E 1985 Nature 318 162
