

## MINDO/3 STUDY OF INTERACTION OF SMALL CARBON CLUSTERS

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### 1. Introduction

After the discovery of fullerenes many efforts were made to investigate the process of carbon vapor condensation. The experiments [1,2] have shown that, at first, linear chains with size  $n \leq 9 \div 10$  atoms are formed, the larger clusters are purely monocyclic rings for  $n \leq 20$ , bicyclic isomer appears at  $n > 20$ , tricyclic at  $n > 30$  and so on. This indicates that coagulation of rings is an important stage of carbon condensation process. Besides, it was discovered, that polycyclic rings are the fullerenes precursors [3,4], so their formation evidently plays a key role in fullerenes synthesis. The coalescence of rings leading to fullerenes appearance was also observed in [5].

The polycyclic structures were studied in [1,2] using PM3 method, but the mechanism of their formation has not been considered. We applied the MINDO/3 method in standard parametrization [6] to consider the reactions of coagulation for clusters with  $n \leq 20$ . The evolution of resulted isomers was considered too.

The typical energetic barriers for coagulation and further isomerization reactions were estimated. The barrier height has different significance for coagulation and isomerization reactions. The characteristic frequency of clusters collisions  $\nu$  is much lower than the frequency of bond oscillations  $\omega$ , and thus the barrier  $U$  for isomerization reaction may be regarded as small if  $U/kT < \ln(\omega/\nu) = 10 \div 15$ . But for the coagulation reactions barriers of few  $kT$  are significant. It can be assumed that at initial stage of condensation, when a lot of new bonds are formed, the temperature is high enough, maybe  $kT = 0.2 \div 0.3$  eV. It was noticed, that the efficient synthesis of fullerenes requires temperatures higher than 0.1 eV [7].

### 2. Energetics of rings

The small carbon clusters are now investigated very well (see [8,9] and refs. in [1,2]). It is well-known, that the odd chains are more stable than the even ones, but for the rings the situation is opposite. The atoms at the chains edges have low valency (about 2.5), making the chains highly reactive. In MINDO/3 the even rings have all atoms equivalent and with valency of

3.9, the bonds are acetylenic-type alternated. But the odd ring has one atom with low valency (increasing with size from 2.7 for  $n = 11$  to 3.4 for  $n = 45$ ). Thus the odd rings have properties of radicals, while the even ones can be treated as molecules. We found that the reactions involving odd rings have lower barriers and higher energetic effects than with the even ones. It is interesting, that the odd ring has an isomer with the low-valency atom sticking out, making an even ring with a triangular cycle added. In MINDO/3 such isomer is almost isoenergetic with the monocyclic odd ring. The atomization energies for rings with  $n \geq 10$  are fitted very well by the expressions:

$$E_n = 6.705n - 59.98/n, \text{ even } n;$$

$$E_n = 6.705n - 59.98/n - 1.887 + 123.8/n^2, \text{ odd } n.$$

The rings become more stable than chains when  $n \geq 10$ . The isomerization barrier of chain-to-ring closure never exceeds 2.6 eV and decreases with chain length.

### 3. Reactions with linear clusters

We have found, that coagulation of two chains leads to formation of chain (or a ring if it is favorable). Various possible intermediate structures (for example, Y-, X-, or H-shaped) quickly transform to more stable linear configuration through isomerization barriers less than 1.5 eV. The coagulation barrier never exceeds 0.5 eV, and the liberated energy is over 5 eV. As the interaction of chains occurs at the early stage of condensation, when the temperature of vapor is high ( $T \approx 0.3$  eV), these barriers can be considered as low.

A chain would rather bind with a ring by its edge atom, with the barrier lower than 0.3 eV. Any other case is energetically unfavorable and meets barriers higher than 1 eV. The energy gain depends upon the clusters parity and vary from 3 to 6 eV, slightly decreasing with ring size. Further isomerization proceeds by drawing the attached chain into the cyclic fragment, which is energetically favorable and liberates 1  $\div$  3 eV more. Isomerization barriers on this pathway are mostly less than 1 eV and never exceed 2 eV. The final structure is always a monocyclic ring.

The detailed consideration of the described above reactions is to be published in [10].

Coagulation of rings leads to a bicyclic cluster which is relatively stable. Its structure depends upon the parity of rings. When both rings are odd, the most stable structure has one bond between rings, and the energy of binding is about 5 eV. Since odd rings have radical properties, the barriers for coagulation are less than 0.3 eV. Dissociation of such structure requires at least 5 eV barrier. Its transition to monocyclic ring needs an isomerization pathway with at least 3.7 eV barrier, increasing with rings size. We can conclude that such structures may serve as precursors for tricyclic and more complex clusters.

For two even rings connection by two bonds is more favorable. Since both reactants are not radicals, the barrier of coagulation is 0.7 eV and higher now, increasing with ring size. The binding energy here is lower than  $1.6 \div 2.5$  eV and decreases with size. It may be not sufficient to keep them from dissociation at high temperature. But these connected rings can transform through  $1 \div 1.5$  eV barrier to a 8-shaped structure with one bond belonging to both cycles, which is  $1.5 \div 2$  eV more stable and seems to be the best final configuration for the case of even rings coagulation. Its transition to a monocyclic ring requires now barrier of 3.8 eV and higher, increasing with ring fragments size.

When even and odd rings are binding, the observed barrier heights were lower than 0.5 eV. The most stable final configuration is reached when the ring fragments lay in perpendicular planes. The central atom in this structure belongs to both cycles and has coordination of 4. Here the final energy effect from coagulation is  $3 \div 4$  eV.

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