FULLERENES
AND ATOMIC CLUSTERS

Possible Scheme of Synthesis–Assembling of Fullerenes

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Abstract—A new scheme of fullerene formation is proposed on the basis of the similarity between the experimentally detected carbon structures. According to experimental data, the microclusters of C_2 and C_{10} are synthesized first and then either an intermediate nucleus cluster or an obtainable lower fullerene is assembled from them. A high-symmetry fullerene can be assembled with a high probability from a nucleus cluster with a "good" symmetry. The atomic and electronic structures of molecules such as C_{36}, C_{60}, C_{70}, and C_{76} are analyzed. For C_{36}, the NMR spectra are calculated and compared with the experimental data. © 2001 MAIK "Nauka/Interperiodica".

INTRODUCTION

The very fact of the existence of fullerenes with a definite symmetry is astonishing, although the reasons behind the formation of precisely such fullerenes among the variety of carbon structures are unknown. For example, only one isomer for C_{60} (Fig. 1) and for C_{70} with the highest symmetry [1, 2] and, hence, with a minimal entropy has been detected in a macroscopic amount, although a much larger number of isomers can exist theoretically for each molecule. It is not completely clear why only some fullerenes with a definite symmetry are formed under identical conditions. In all probability, a comparison of the peculiarities in the structure of the existing molecules with the theoretically constructed fullerenes would clarify the mechanism of formation of carbon-based nanostructures.

1. A REVIEW OF SOME MODELS

The first assumption explaining the formation of fullerenes was that fragments of monolayers ejected from the surface of evaporating graphite are coiled into a spherical molecule [1, 3]. However, subsequent experiments with carbon isotopes proved that the growth of fullerenes begins from monatomic vapor. According to the experimental data [4, 5], the condensation of carbon atoms follows the following scheme: after the complete mixing of atoms in a plasma, clusters grow in the form of linear chains. After the chain length becomes ten or more atoms, the chains are closed to form stable ring-shaped structures.

At present, several models of the synthesis of fullerene molecules exist [6–11]. These models are mainly constructed using the methods of molecular-dynamic simulation. We will consider models of two types: the droplet model [7–9] and the model of polycyclic structures [10].

In the droplet model, the following mechanism of fullerene formation from the supersaturated carbon vapor is proposed. At the initial stage of the process (condensation), nanosize nuclei are formed. With decreasing temperature, the nuclei are grouped into clusters whose size increases and the structure becomes more and more complex, leading to the formation of fullerenes. Thus, according to the droplet model, the formation of carbon molecules passes through the following three stages: the formation of a nuclei in the form of small linear clusters and their branching; the formation of cycles and of a two-dimensional surface; and the growth of the surface and its closure into fullerene structures.

The droplet model explains the growth of "droplets" (fullerenes) as the result of collisions. The structural rearrangement occurs during the annealing between collisions. However, this model has a number of obvious drawbacks. In particular, it fails to explain the formation of high-symmetry molecules and the absence of structural isomers. For example, apart from the I_h symmetry (Fig. 1), C_{60} can theoretically exist in the form of a molecule with symmetry D_{2d}, C_2, C_{2v}, D_5, etc. Along with the experimentally obtained molecules, the theory erroneously predicts the highly probable formation of undetected fullerenes such as C_{58}.

In the model of polycyclic structures [10], for $N > 20$ (N is the number of carbon atoms), clusters are formed whose structure is interpreted as two coupled rings in the form of a propeller. For $N > 30$, clusters appear in the form of three coupled rings resembling a
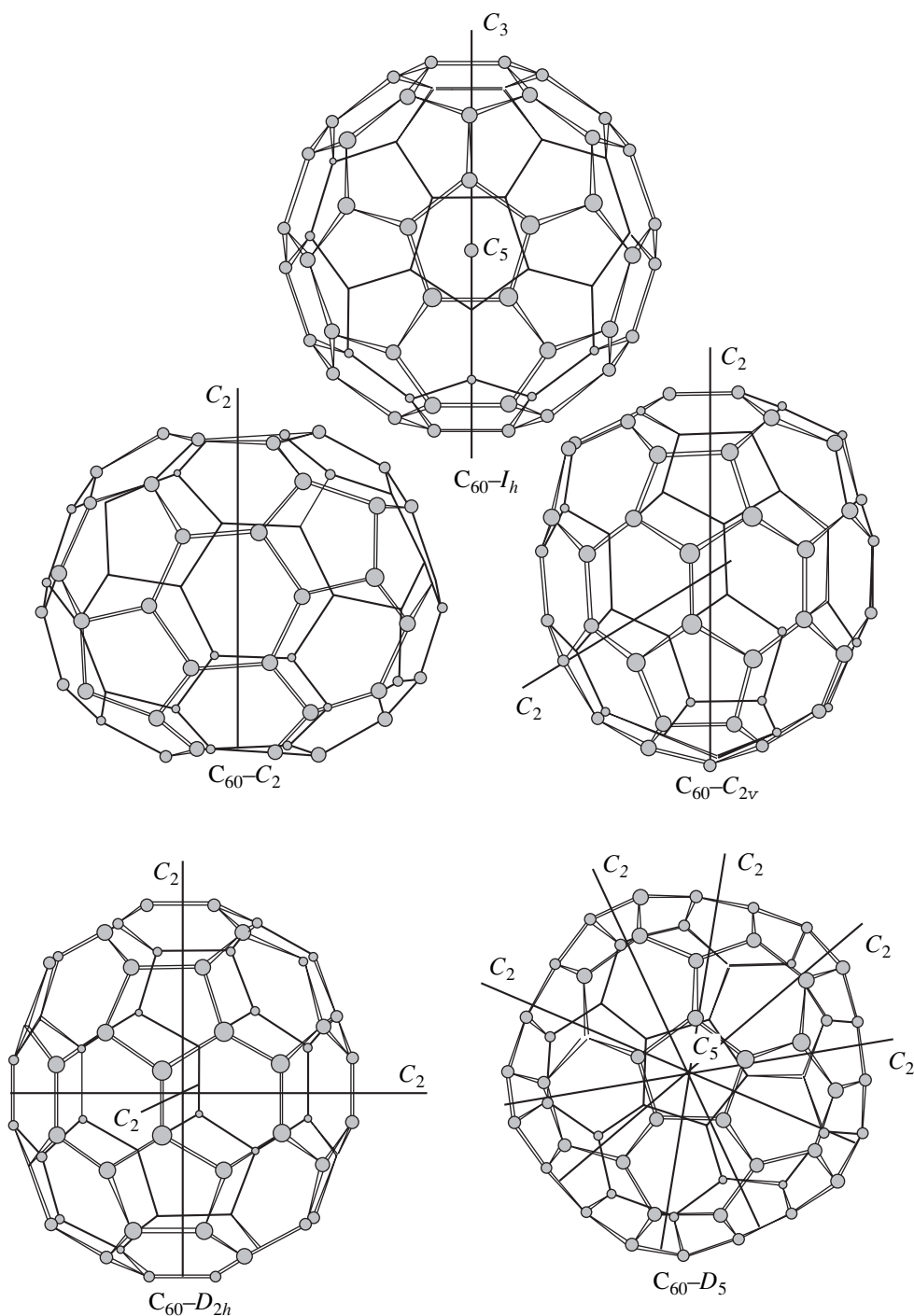
Fig. 1. Some isomers of fullerene C_{60}.

flower bud, and so on. The relative concentration of such polycyclic structures increases with the cluster size, significantly exceeding the concentration of simple rings for $N > 30$. It is assumed that the growth of coarse clusters occurs predominantly through the coagulation of ring structures. Aleksandrov *et al.* [10] analyzed the coiling into a fullerene of the structures con-

sisting of three rings connected to form a bud or a three-blade propeller. The formation occurs through the connection of the nearest atoms at the base of the structure and resembles the closing of a bud. The fullerene formed in this way has an ellipsoidal shape and contains adjacent pentagons (it can also have heptagonal cycles). Subsequently, the pentagons grow apart over a

Table 1. Heat of formation for isomers of fullerene C_{78} calculated using the Hartree–Fock semiempirical method PM3

Fullerene	Heat of formation, K/mol	Experimentally detected fullerenes [13]
$C_{78}–C_{2v}$	6100	+
$C_{78}–C'_{2v}$	6075	+
$C_{78}–D_3$	6115	+
$C_{78}–D_{3h}$	6110	–
$C_{78}–D'_{3h}$	6185	–

sphere (as in the droplet model), which leads to a decrease in the angular stress in the structure (Stone–Wales isomerization [12]).

The model of polycyclic structures cannot explain the absence of intermediate fullerenes such as C_{62}, C_{64}, C_{66}, etc., as well as the isomers of C_{60} and C_{70}. In view of its reversibility, the Stone–Wales isomerization generally presumes the existence of several structural isomers for a fullerene, e.g., for C_{60}. However, it can be seen, for example, for higher fullerenes (Table 1) that not all isomers are formed in spite of all the premises including the small difference in energy. The model also predicts a high probability for the existence of

Table 2. Maximum and minimum atomic spacings in fullerene molecules*

	Fullerene	Bond length, Å			Fullerene	Bond length, Å	
		min	max			min	max
1	$C_{20}–I_h$	1.45	1.52	25	$C_{54}–C_{2v}$	1.38	1.49
2	$C_{24}–D_{6h}$	1.38	1.52	26	$C_{56}–D_2$	1.36	1.49
3	$C_{26}–D_{3h}$	1.38	1.50	27	$C_{58}–C_s$	1.35	1.49
4	$C_{28}–T_d$	1.39	1.54	28	$C_{60}–I_h$	1.38	1.46**
5	$C_{30}–C_{2v}$	1.36	1.53	29	$C_{60}–C_2$	1.37	1.48
6	$C_{30}–D_{5h}$	1.39	1.50	30	$C_{60}–C_{2v}$	1.45	1.49
7	$C_{32}–D_2$	1.39	1.52	31	$C_{60}–D_{2h}$	1.35	1.50
8	$C_{32}–D_3$	1.39	1.51	32	$C_{60}–D_{5d}$	1.38	1.49
9	$C_{34}–C_1$	1.39	1.52	33	$C_{62}–C_2$	1.37	1.48
10	$C_{36}–D_{2d}$	1.38	1.50	34	$C_{64}–D_2$	1.39	1.48
11	$C_{36}–D_{3h}$	1.37	1.49	35	$C_{66}–C_2$	1.38	1.48
12	$C_{36}–D_{6h}$	1.41	1.50	36	$C_{68}–C_2$	1.39	1.48
13	$C_{38}–C_2$	1.36	1.53	37	$C_{70}–D_{5d}$	1.38	1.46***
14	$C_{40}–D_2$	1.37	1.51	38	$C_{76}–D_2$	1.37	1.47
15	$C_{40}–D_{2h}$	1.35	1.53	39	$C_{76}–T_d$	1.37	1.48
16	$C_{40}–D_{5d}$	1.40	1.51	40	$C_{78}–C_{2v}$	1.36	1.47
17	$C_{40}–T_d$	1.39	1.49	41	$C_{78}–C'_{2v}$	1.36	1.48
18	$C_{42}–D_3$	1.37	1.50	42	$C_{78}–D_3$	1.37	1.47
19	$C_{44}–D_2$	1.37	1.50	43	$C_{78}–D_{3h}$	1.35	1.48
20	$C_{46}–C_2$	1.37	1.50	44	$C_{78}–D'_{3h}$	1.36	1.46
21	$C_{48}–C_2$	1.38	1.50	45	$C_{80}–I_h$	1.39	1.47
22	$C_{50}–C_2$	1.40	1.49	46	$C_{84}–D_2$	1.36	1.47
23	$C_{50}–D_{5h}$	1.38	1.48	47	$C_{84}–D_2$ (helical)	1.36	1.46
24	$C_{52}–C_2$	1.37	1.49	48	$C_{84}–D_{2d}$	1.36	1.47
				49	$C_{84}–T_d$	1.36	1.46

 * The average of the minimum values is 1.38 Å; the average of the maximum values is 1.49 Å.

 ** Experiment: min 1.37 ± 0.01; max $1.47 \pm \binom{0.01}{0.03}$ [2].

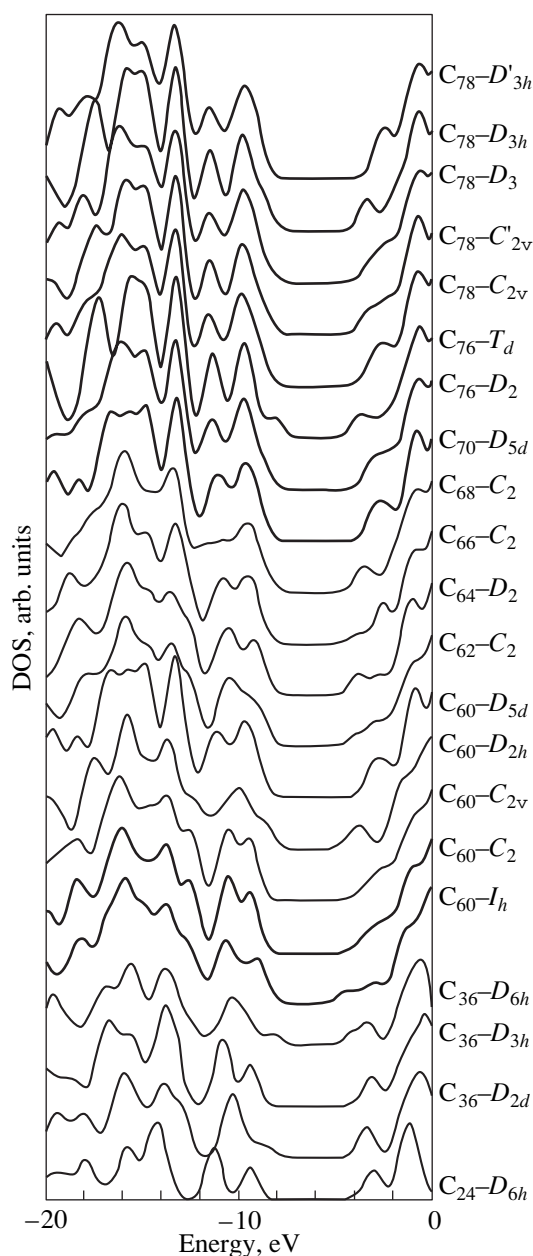 *** Experiment: min 1.39 ± 0.01; max 1.44 ± 0.01 [2].

Fig. 2. Total electron densities of states for some fullerene molecules (bold curves correspond to experimentally detected structures).

molecules which have not been detected experimentally.

The electronic structure has been disregarded in the current models of fullerene formation. Simulations of the synthesis conditions have been carried out using the methods of molecular dynamics on the basis of model potentials which do not reflect the complex electronic structure at plasma temperatures (3000 to 5000 K).

The present work is devoted to an analysis of the electronic structure and the energy parameters of the possible fullerenes in the ground state in order to deter-

mine the potential difference between the experimentally detected and undetected molecules. The problem was solved using the quantum-chemical approach.

2. QUANTUM-CHEMICAL ANALYSIS

In order to calculate the equilibrium atomic and electronic structures, we applied the Hartree–Fock semiempirical quantum-chemical method PM3 using the program GAMESS [14]. The choice of the quantum-chemical approach was dictated by the fact that the application of semiempirical quantum-chemical methods reduces the computer time as compared to the *ab initio* methods. At the same time, the results obtained by using *ab initio* and semiempirical quantum-chemical methods are in good agreement. Semiempirical methods correctly describe the electronic structure, as well as the equilibrium geometry of the C_{60} and C_{70} molecules (Table 2 also presents, for comparison, the experimental results obtained in [2]). It was proved in [15] that the semiempirical MNDO and PM3 methods reproduce the results obtained by *ab initio* calculations (3–21G) and provide a satisfactory description for the experimental photoelectronic-microscopy data [16]. The semiempirical methods successfully describe carbon-based systems such as fullerenes. Thus, the choice of the semiempirical methods for such systems is quite justified.

In order to determine the behavior of carbon clusters in the atomic and electronic structures, we consider here the maximum number of theoretically possible and experimentally obtained carbon clusters and their isomers. In all, 49 fullerenes were constructed, from C_{20} to C_{84} [13, 17–21]. First of all, we considered the experimentally observed fullerenes C_{60}–I_h, C_{70}–D_{5d}, C_{78}–C_{2v}, C_{78}–C'_{2v}, and C_{78}–D_3 [1, 2, 13] and their isomers, as well as intermediate fullerenes such as C_{40}, C_{42}, …, C_{62}, C_{64}, …. The choice of the isomers was determined by the computer time and by their reasonable number (for example, about five hundred different isomers with trigonal, tetragonal, pentagonal, hexagonal, and heptagonal cycles can be constructed for C_{36} [20]).

Table 2 gives the bond lengths in fullerene molecules. In view of a considerable spread in the values of bond lengths, only the minimum and maximum nuclear spacings were taken for the analysis. It follows from Table 2 that the minimum lengths of the bonds for all the molecules presented here lie in the same interval with an average minimum bond length of 1.38 Å. The same is true of the maximum bond lengths for which the average value is 1.49 Å. Proceeding from the fact that the nuclear spacings for various types of bonds lie in definite intervals, we can assume that the atomic structures of these fullerenes are identical.

The total densities of states were constructed as the energy spectrum of a cluster in which the energy of each molecular orbital was presented as a line, and the
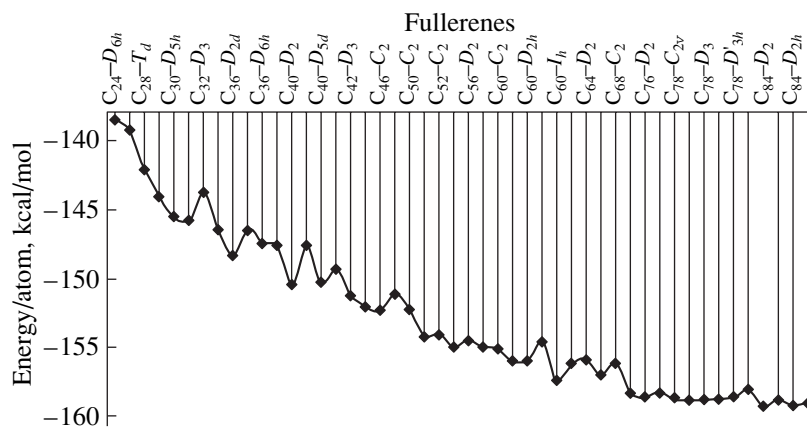
Fig. 3. Dependence of the total energy per atom on the molecular weight of fullerenes.

intensities of all lines were assumed to be equal to unity. Further, each line was replaced by the Gaussian distribution with a half-width of 0.4 eV, and the intensities of all the distributions for each energy value were summed. The electron density distribution in Fig. 2 shows the absence of any basic difference in the structures of the top of the valence bands, primarily in the gap width and the shape of peaks both for known fullerenes and for undetected molecules.

An analysis of the dependence of the total energy per atom on the molecular weight of fullerenes (Fig. 3) indicates a general tendency towards an increase in the fullerene stability upon an increase in their molecular weight. It can be seen from this dependence that the choice according to the total energy per atom in the process of the formation of molecules does not play any significant role. For example, the energies of formation of the experimentally detected fullerenes C_{60} and C_{36} differ approximately by a factor of two, but no intermediate fullerenes (C_{38}, C_{40}, C_{42}, C_{44}, etc.) were detected in macroscopic amounts in spite of the fact that their energies of formation lie in the interval between those for C_{60} and C_{36}.

The right-hand side of the graph in Fig. 3 shows that the difference in the total energy for higher fullerenes is small. This can apparently be explained by the fact that the isomeric effect does not play any significant role here as, for example, in the case of lower fullerenes since pentagons in different isomers are in isolated states. Thus, judging from the energy criterion, all isomers of higher fullerenes must exist since the energy difference between them is small (see Table 1).

A comparison of the electron densities, the bond lengths, and the binding energies of the theoretically predicted molecules shows that, from the viewpoint of the electronic and atomic structures, all fullerenes can rightfully exist. The entropy does not noticeably affect the formation of fullerenes either since isomers with the highest symmetry (I_h for C_{60}) are predominantly formed. Consequently, it can be concluded that the pos-

sibility of the formation of a certain isomer of a fullerene cannot be determined proceeding from the atomic and electronic structures and energy stability.

Thus, while constructing the model of the fullerene synthesis on the basis of the analysis of the atomic and electronic structures of calculated carbon clusters, we must exclude such factors as the energy advantage of a certain fullerene or an isomer, the peculiarities of the electronic structure, and the binding energy for the obtained fullerene. Proceeding from the above-mentioned factors, it is impossible to construct a model correctly describing the obtaining of only certain fullerenes and, hence, it is impossible to select the existing molecules by comparing their energies. Consequently, we must determine other conditions affecting the process of fullerene formation.

3. MODEL OF SYNTHESIS–ASSEMBLING OF FULLERENES

After the quantum-chemical analysis was completed, we endeavored to find some other differences morphologically between the obtained and undetected molecules on the basis of the above conclusions. For this purpose, we considered the mutual arrangement of pentagons and hexagons, as well as the fullerene synthesis conditions.

The experiments show (see above, as well as [4, 5]) that first the C_2 ("twos") and similar structures, as well as the ring structures with a size starting from ten atoms, are synthesized in the plasma from a monatomic vapor, the presence of C_{10} ("tens") being regarded as preferable [10]. On the basis of these experimental data, molecules were disassembled into their components with the subsequent recognition of similar fragments among detected molecules and with revealing the differences between the experimentally observed and the possible fullerenes.

While disassembling the experimentally detected fullerene molecules (C_{60} with I_h, C_{70} with D_{5h}, C_{78} with
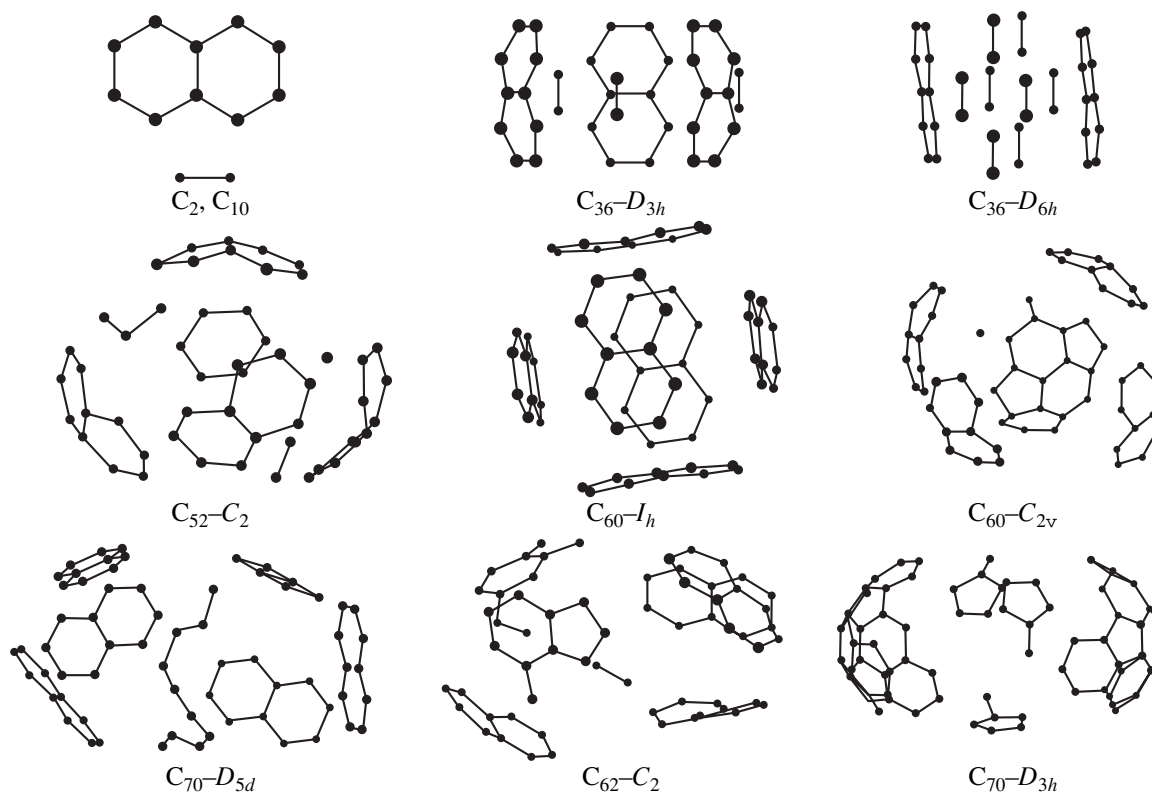
Fig. 4. Various fullerene molecules disassembled visually into components, in which the common fragments C_2 and C_{10} are singled out.

C_{2v}, C_{78} with C'_{2v}, C_{78} with D_3, etc.) into components, we paid attention to the fact that all the existing fullerenes have similar fragments C_2 and C_{10} or only the fragment C_{10} (in the form of a doubled hexagon), as in the case of C_{60} (Fig. 4). The remaining (undetected) fullerenes contain additional fragments in the form of hexagons, solitary carbon atoms, etc., which are not encountered in the experimental data. Consequently, while analyzing the model of fullerene synthesis, we must presume that at a certain stage, fullerenes are probably synthesized via the C_{10} and C_2 structures, which are combined into the "initial" carbon cluster, viz., a nucleus cluster.

Let us now consider a possible process of formation of molecules such as C_{60} and C_{70}. At the first stage, carbon structures are synthesized in the form of linear chains from a monatomic plasma flow [4, 5]. At the second state, the linear structures are closed when the chain length comprises ten or more atoms. Judging from the experimental data, the formation of twos and tens is preferential [10]. Then these structures successively collide and coalesce to form carbon nucleus clusters. At this stage, the C_2 microclusters are also absorbed in the case of C_{70}.

Figure 5 shows a possible course of the formation of carbon clusters. The end product of the synthesis is determined by the symmetry of the nucleus cluster. The figure illustrates a possible course of the synthesis for C_{60} and C_{70} molecules (in the case of C_{70}, five more C_2 fragments are added). For fullerene molecules with the number of atoms greater than 70, the number of fragments in nucleus clusters can exceed three and the dimension of the fragments themselves may be larger.

As the number of nucleus clusters increases, they start colliding, which leads to assembling large clusters followed by crystallization into fullerene molecules. At this stage, we must pay attention to the symmetry of the nucleus clusters obtained, which determines the number of effective collisions leading to the growth of the carbon skeleton. In the case of C_{60}, the nucleus cluster has the principal symmetry axis C_3 (see Fig. 5 (*4*)). In the given case, this is apparently the optimal symmetry since three ways of bonding with a similar cluster are possible (each time, through an angle of $2\pi/3$) (see Fig. 5 (*5*)). It is perhaps for this reason that the probability of the formation of a fullerene on the basis of a nucleus cluster with a low symmetry (C_1) is low, because the cluster structure contains surface regions inaccessible for effective collisions which may lead to the formation of a closed system such as a fullerene.

It should be emphasized that the scheme of assembling presented here is not the only possible scheme;

the formation of the initial clusters with another symmetry and, hence, with a different probability of assembling into a fullerene is also possible.

Piskoti *et al.* [21] recently synthesized the lower fullerene C_{36} in a macroscopic amount. At the same time, they investigated the obtained fullerene by using ^{13}C NMR spectroscopy and compared the results with the theoretical NMR spectra for various hypothetical isomers of C_{36}. We used the synthesis–assembling model constructed by us to analyze the lower fullerene C_{36} and to find its isomer which can be formed in accordance with the results of the NMR experiments. It follows from spatial considerations (see Fig. 4) that in all probability the formation of C_{36} with D_{3h} is easier and preferred.

Piskoti *et al.* [21] stated that the NMR spectrum corresponds to the D_{6h} symmetry. However, the experimental spectrum obtained with such a resolution can be interpreted in a different way. To this end, we theoretically calculated the ^{13}C NMR spectra for three isomers of C_{36}: with D_{6h}, D_{2d}, and D_{3h} (the first two correspond to the fullerenes reported in [21]) by using the GIAO method with the 6–31(d) basis. The experimental spectrum was compared with our theoretical NMR spectra. It can be seen from Fig. 6 that the theoretically calculated spectrum of the molecule with symmetry D_{6h} may correspond to the experimental spectrum. It should be noted that the peak in the experimental spectrum with a chemical shift ~137.5 ppm has a relatively larger half-width than the peak with ~149 ppm, although the areas under these peaks are approximately equal (see Fig. 6b). For this reason, two lines in the peak with the larger amplitude (with a chemical shift of 149 ppm) are closely spaced and give an amplitude twice as large as that in the peak with 137.5 ppm. Similarly, the latter peak may also contain two lines, but their separation is larger than in the peak with 149 ppm; consequently, the 137.5 ppm peak has a larger half-width but a smaller amplitude. The broadening of the peak with the 137.5 ppm shift cannot be explained by the existence of only one isomer with D_{6h} (see Figs. 6c, 6d) as in [21]. The situation is possible when the system contains other isomers, e.g., with D_{3h} (see Fig. 6e), which can explain the experimentally observed broadening of the 137.5 ppm peak. In our opinion, the isomer with the D_{3h} symmetry is advantageous from the spatial considerations (see Fig. 4), although it is less advantageous from the energy point of view (see Fig. 3).

Thus, the synthesis–assembling model of carbon structures presented above can explain the existence of structures C_{36}, C_{60}, C_{70}, … and the absence of many lower fullerenes; the intermediate structures between C_{60} and C_{70} (such as C_{62}, C_{64}, C_{66}, …); and the structural isomers of the C_{60} and C_{70} molecules, as well as the absence of a large number of isomers for the molecules of higher fullerenes since they cannot be assem-
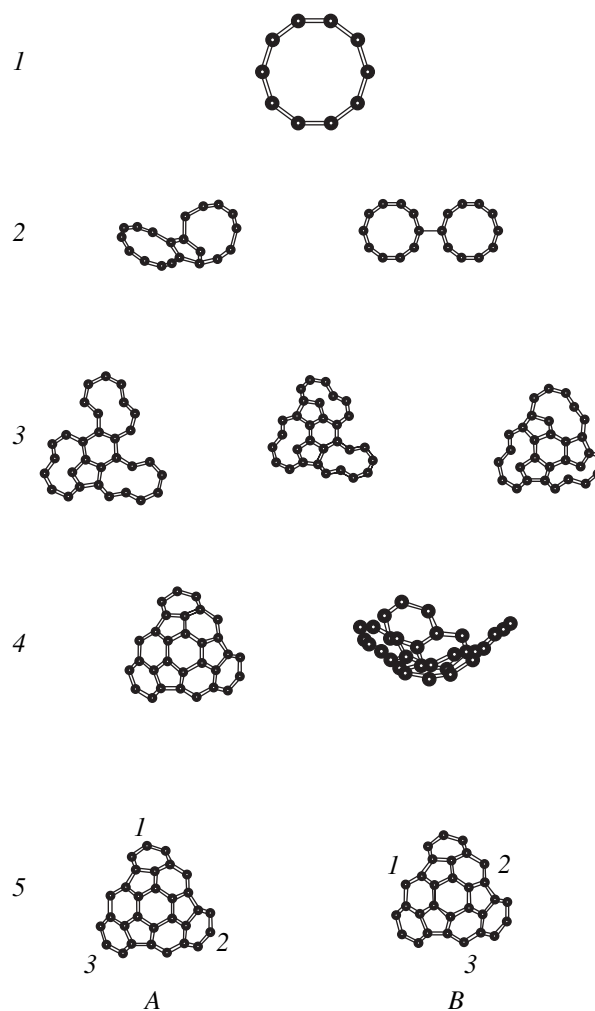

Fig. 5. Hypothetical scheme of synthesis–assembling of fullerene molecules: (*1*) formation of carbon chains from a monatomic vapor; (*2*, *3*) the result of collision of ring structures leading to the formation of one of the possible nucleus clusters; (*4*, *5*) three possible ways of collision between nucleus clusters *A* and *B* (1A–1B, 2A–2B, 3A–3B), (1A–2B, 2A–3B, 3A–1B), (1A–3B, 2A–1B, 3A–2B).

bled from the intermediate clusters C_{10} and C_2. Consequently, the assembling of fullerenes is determined by the symmetry of the nucleus cluster obtained and by the symmetry-dependent probability of the effective collision between the fragments of clusters in the plasma. These factors determine the molecular weight of fullerenes, as well as the number of molecules with a definite symmetry being synthesized.

4. CONCLUSIONS

Our results can be summarized as follows.

(1) In order to develop the model of the formation of carbon clusters, we theoretically constructed 49 fullerenes. First of all, the experimentally detected
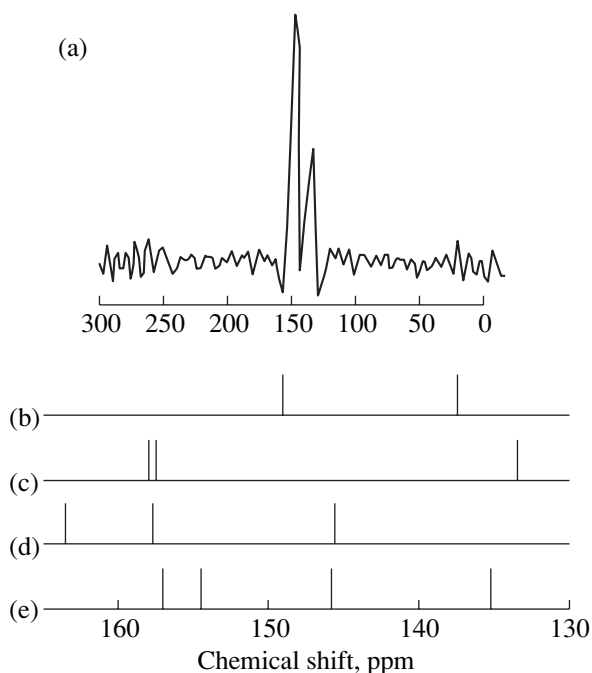
Fig. 6. The ^{13}C NMR spectrum for the lower fullerene C_{36}: (a) experimental spectrum from [21]; (b) experimental spectrum; (c) calculated spectrum for C_{36} with D_{6h} from [21], (d) our calculation of the spectrum for C_{36} with D_{6h}, and (e) our calculation of the spectrum for C_{36} with D_{3h}.

molecules C_{60}–I_h, C_{70}–D_{5d}, C_{78}–C_{2v}, C_{78}–C'_{2v}, and C_{78}–D_3 and their isomers were constructed. Since the symmetry of C_{36} is unknown as yet, we constructed three isomers with D_{6h}, D_{2d}, and D_{3h}. We also considered intermediate fullerenes such as C_{40}, C_{42}, ..., C_{62}, C_{64}, ...

(2) The existence of any fullerene with five- and six-atom cycles in the structure is not forbidden from the viewpoint of the atomic and the electronic structure.

(3) The synthesis–assembling model was verified for the recently discovered lower fullerene C_{36}. On the basis of our model and from a comparison with the experimental NMR spectra, it can be predicted that the formation of fullerene C_{36} with D_{3h} is most probable.

(4) We proposed a possible scheme of the formation of fullerene molecules on the basis of "twos" and "tens," which was developed from the similarity of the experimentally detected molecules (their components) and, accordingly, from the difference between the experimentally obtained fullerenes and hypothetical carbon clusters. In this model, the effect of the electronic structure and the energy parameters as factors in the process of high-temperature synthesis can be regarded as insignificant. The Stone–Wales isomerization should apparently also be disregarded.

The impossibility of a correct quantum-chemical simulation under the conditions of the high-tempera-ture synthesis of fullerenes necessitates the construction of formal phenomenological models based on the experimental data concerning the behavior of carbon atoms in the plasma and on the indirect evidence based on the morphological similarity between the experimentally detected carbon clusters.

The probability of effective collisions resulting in the formation of a fullerene with a high symmetry is higher for nucleus clusters with a high symmetry. Consequently, the form of the nucleus cluster determines the symmetry of the future fullerene, its molecular weight, and the number of molecules being synthesized.

REFERENCES

1. H. W. Kroto, J. K. Heath, S. C. O'Brien, *et al.*, Nature **318**, 162 (1985).
2. A. V. Eletskiĭ and B. M. Smirnov, Usp. Fiz. Nauk **165**, 977 (1995) [Phys. Usp. **38**, 935 (1995)].
3. D. H. Robertson, D. W. Brenner, and C. T. White, J. Phys. Chem. **96**, 6133 (1992).
4. G. Meijer and D. S. Bethune, J. Chem. Phys. **93**, 7800 (1990).
5. J. M. Hawkins, A. Meyer, S. Loren, and R. Nunlist, J. Am. Chem. Soc. **113**, 9394 (1991).
6. Yu. E. Lozovik and A. M. Popov, Usp. Fiz. Nauk **167**, 751 (1997) [Phys. Usp. **40**, 717 (1997)].
7. S. Maruyama and Y. Yamaguchi, Chem. Phys. Lett. **286**, 336 (1998).
8. S. Maruyama and Y. Yamaguchi, Therm. Sci. Eng. **3**, 105 (1995).
9. T. Yu. Astakhov, G. A. Vinogradov, and Sh. A. Shaginyan, Zh. Fiz. Khim. **2**, 310 (1997).
10. A. L. Aleksandrov, V. M. Bedanov, Yu. N. Morokov, and V. A. Shveĭgert, Zh. Strukt. Khim. **37**, 664 (1996).
11. V. I. Berezkin, Fiz. Tverd. Tela (St. Petersburg) **42**, 567 (2000) [Phys. Solid State **42**, 580 (2000)].
12. A. J. Stone and D. J. Wales, Chem. Phys. Lett. **128**, 501 (1986).
13. X.-Q. Wang, C. Z. Wang, B. L. Zhang, and K. M. Ho, Chem. Phys. Lett. **200**, 35 (1992).
14. M. W. Shmidt, K. K. Baldridge, J. A. Boatz, *et al.*, J. Comput. Chem. **14**, 1347 (1993).

15. S. A. Varganov, P. V. Avramov, and S. G. Ovchinnikov, Fiz. Tverd. Tela (St. Petersburg) **42**, 378 (2000) [Phys. Solid State **42**, 388 (2000)].

16. A. L. Shakhmin, S. V. Murashov, N. V. Baranov, and M. A. Khodorovskiĭ, Fiz. Tverd. Tela (St. Petersburg) **40**, 168 (1998) [Phys. Solid State **40**, 150 (1998)].

17. G. B. Adams, M. O'Keeffe, and R. S. Ruoff, J. Phys. Chem. **98**, 9465 (1994).

18. B. L. Zhang, C. Z. Wang, and K. M. Ho, Phys. Rev. B **47**, 1643 (1993).

19. B. L. Zhang, C. Z. Wang, K. M. Ho, *et al.*, J. Chem. Phys. **97**, 5007 (1992).

20. Z. Slanina, X. Zhao, and E. Osawa, Chem. Phys. **219**, 193 (1997).

21. C. Piskoti, J. Yargen, and A. Zettl, Nature **393**, 771 (1998).

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