Quantum Chemistry Simulation of 60-Fullerene Interaction under External Pressure

Alexey V. Khavryutchenko and Vladimir D. Khavryutchenko [a]

Chemical Department of Kiev National Taras Shevchenko University, Vladimirskaya Street 64,
Kiev 01033, Ukraine
[a] Institute for Sorption and Problems of Endoecology of the National Academy of Sciences of
Ukraine, Gen. Naumova Street 17, Kiev 03680, Ukraine

Reprint requests to Dr. A. V. K.; E-mail: alexk@univ.kiev.ua or alexk@compchem.kiev.ua

Z. Naturforsch. **60a,** 41 – 46 (2005); received October 25, 2004

The results of the interaction of two 60-fullerene molecules interaction under external pressure, studied by a semi-empirical PM3 quantum chemical method, are reported. A set of 15 space structures of 60-fullerene dimers from the simplest one up to partially graphitized material has been simulated. Calculated pressures referring to the dimers' formation reproduce the experimental order of magnitude rather well. The dependences of the heat of formation and the force ballancing the applied pressure versus compression have been determined. A mechanism of the dimerization is proposed.

Key words: Quantum Chemistry; Semi-empirical Method; 60-Fullerene Dimers; High Pressure; High Temperature; PM3.

1. Introduction

The isolation in 1991 of 60-fullerene by Kretchmer and co-workers has stimulated intense investigations of pure carbon compounds [1]. One of the most attractive branches of fullerene science is the examination of its behavior at high-pressure and high-temperature (*hp*-*ht*). Resulting 60-fullerene dimers and polymers might possess precursor properties and new features. For instance, ultrahard composites are formed under high pressures in the vicinity of 12 GPa [2]. Several forms of the poly-fullerenes exhibit the ability of magnetic self-organization [3]. The orthorhombic, tetrahedral and rhombohedral poly-fullerene phases have been isolated and analyzed [3]. The polymerization of AC_{60} (A is an alkali-metal) was studied in [4].

However, there are still many problems with the interpretation of the experimental results [1 – 3]. The majority of the phases synthesized under *hp*-*ht* conditions is X-ray amorphous and therefore can not be studied with direct crystallographic methods. Comparing results of X-ray powder diffraction (XRPD) and Raman examination of the isolated forms one could derive hypothetic structures or at least motives for unknown phases. However, these hypothetic structures are not proven [2, 5 – 7]. The mechanism of thermally activated pressure-induced processes could make the situation clear, but this mechanism is still controversial.

Models proposed for pressure-induced processes either do not reveal the chemical nature of the process [8] or are directed on one of the hypotheses [8] without checking of other probable pathways. Another problem concerns the multiciply state of pressure-induced polymerization. Now it is assumed that this type of process may pass in the singlet state (^1S). This point should be studied more precisely, since many facts indicate the triplet-state (^3T) pathway. The [2+2] cycloaddition, which is supposed to be the main mechanism of inter-fullerene chemical interaction in the case of symmetrical double bonds, as in the 60-fullerene, should pass through the ^3T transition state [9]. The process of AC_{60} polymerization passes via states of higher multiplicity [10]. The 60-fullerene molecule in the ^1S state is highly symmetrical as to geometry and electronic structure, while electronic excitation distorts them both and therefore should facilitate polymerization.

The aim of the present study is the creation of a quantum chemical (QC) model, which introduces directly an external pressure, and to simulate the process of the C_{60}–C_{60} interaction. In this article the dimerization of two fullerene molecules is calculated by the PM3 semi-empirical method using 'QuChem' software [11, 12].

0932–0784 / 05 / 0100–0041 $ 06.00

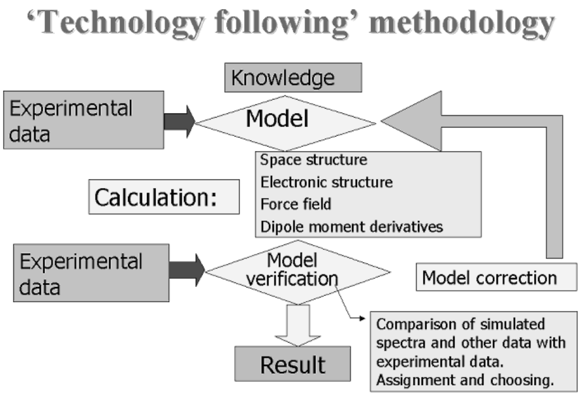

Fig. 1. Block scheme of investigation using simulations.

2. Methodology

2.1. Methods and Values

A block-scheme of investigations using QC simulations is shown in Figure 1. The simulation model is constructed starting from general data about the structure and experimental properties of the object. The space as well as the electronic structure, the force field, the dipole moments derivatives and other data (for instance, the hyperpolarizability and the mechanical strain) are determined. These data usually contain two types of errors, namely ones of the computational method and others of the model inaccuracies or simplifications. In order to check the summary error, one must compare the simulated data with the experimental ones. The verification for crystalline substances is performed using X-ray crystallography by direct comparison of the refined structure with the simulated one. Sometimes other experimental methods are used.

Statistical methods, such as vibration spectroscopy and radial distribution functions (RDF), which express the properties of structural assemblies, are the main ones in the case of amorphous materials. If there are divergences between the simulated and experimental properties, then a correction of the model is performed. Further, the simulation cycle is iterated until the deviation becomes negligible. Such a model is called "an adequate to the investigations objective" and is used to determine the physical (the heat of formation, ionization potential, dipole moment, etc.) and chemical (bonding energy, reactions pathways, etc.) properties.

Using the methodology for amorphous object simulations, approved in [13, 14], the 60-fullerene dimerization has been studied based on the QC methodology and different methods of verification in order to choose the best theoretical models. The main idea of this method is to reproduce the unknown structure of a product by reproducing in the best possible way the technology process conditions applied to the known precursors, i. e. the 60-fullerene. This should give us several speculative models based on which one could simulate the products vibration (IR, Raman, INS) spectra and interpret the chemical behavior.

The semi-empirical QC method PM3 [12] (QuChem complex [11, 15, 16]) has been chosen to perform calculations, since mechanochemical simulations deal with great amounts of atoms, while standard potentials of molecular mechanics and dynamics in strained systems are inapplicable.

Every quantum chemically examined cluster has been characterized by the following parameters: a) the optimized space structure; b) the calculated heat of formation $\Delta_f H$ (in kcal/mol); c) the force applied to the system (in kcal/mol·Å).

2.2. Model Building

Firstly, two fullerene spheres were freely optimized resulting in pentagon-pentagon mutual orientation. Then the distance between opposite pentagons has been fixed as a reaction coordinate and step-by-step has been shortened by 0.2 Å with full optimisation of all non-fixed coordinates at each step. The dependencies of $\Delta_f H$ and the force on this shift have been plotted.

Since the forces needed to keep the system under defined mechanical stress (along the axis of interaction) were calculated on each step, we could derive the external pressure, dividing this force by the area of pressure

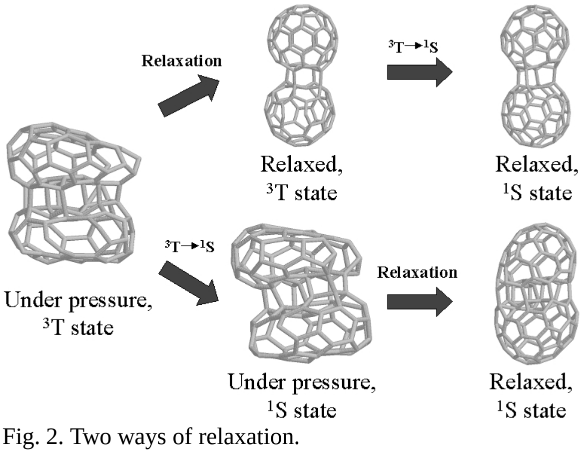

Fig. 2. Two ways of relaxation.

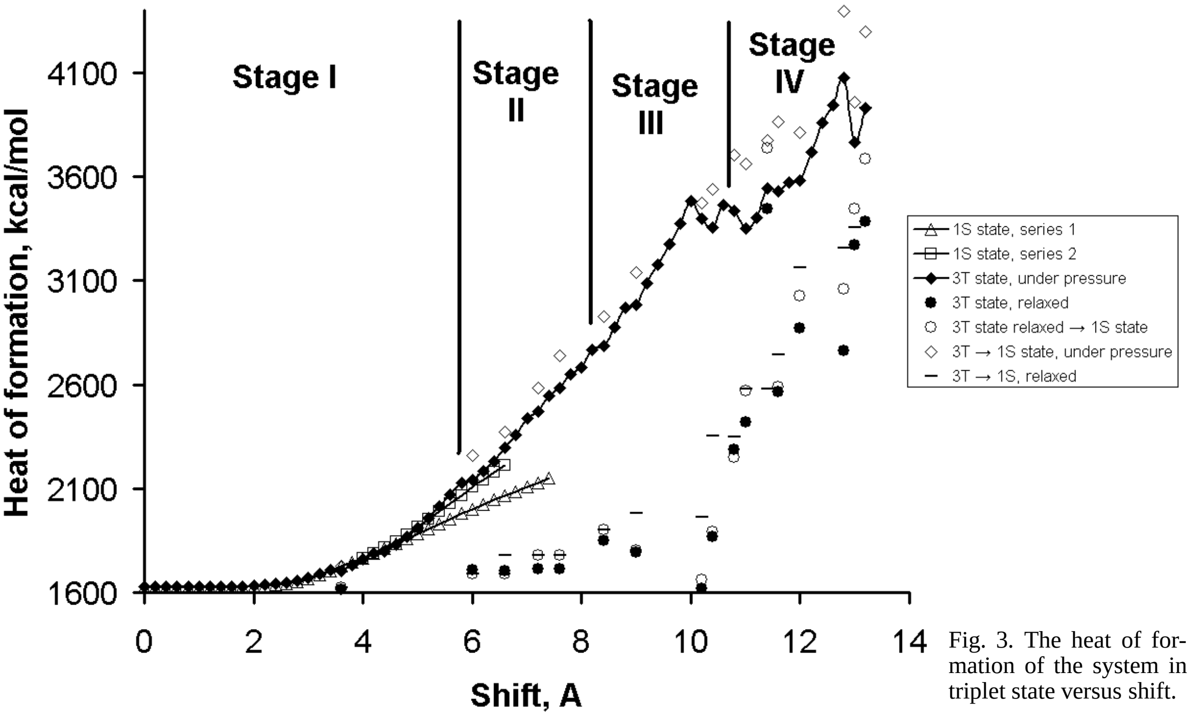

Fig. 3. The heat of formation of the system in triplet state versus shift.

application. Since the direction of force application is not clear, we have calculated the pressure with respect to the minimal and maximal surfaces. The (1 1 1) plane with the surface 86.1 Å^2 per 1 fullerene molecule has been taken as the smallest, and the (2 1 1) plane with the surface 487.0 Å^2 per fullerene molecule has been taken as the largest one. So, calculated pressures are given in these borders. As will be shown below, several forms of C_{60}-dimers were obtained through simulations of reactions in the ^3T state. Each structure was relaxed in two ways: all parameters were optimized in the ^3T state and then the state was changed to ^1S; or the state was changed to ^1S under pressure and then relaxed. These two ways are illustrated on Figure 2.

Since there is no direct way to introduce the temperature into quantum chemistry calculations, we have used a temperature free approach. However, we assume that the temperature is high enough, allowing fullerene molecules to rotate freely before the pressure application.

3. Results

In order to be sure that no chemical interaction could take place in the ^1S state, it has been simulated. The dependences of $\Delta_f H$ (Fig. 3) and force (Fig. 4) on the shift show that no chemical processes take place. Basing on the performed simulations, the pressure-induced interaction of two 60-fullerene spheres in the ^3T state can be discriminated into four stages (Fig. 3 and Fig. 4) as follows: (i) the approachment and partial shift deformation of 60-fullerene spheres; (ii) the dimerization and formation of interfacial carbon polyhedra (Fig. 5, Forms I – VI); (iii) the reversible collapse (Fig. 5, Forms VII – IX); (iv) the irreversible collapse and graphitization (Fig. 5, Forms X – XV). 15 forms were isolated on the stages II – IV. Their snapshot is shown in Figure 5. In most cases the chemical reaction passes between 5 – 6 edges of 60-fullerene, involving not symmetrical faces. For example, the interfacial polyhedron of Form III originates from the hexagon with two adjacent pentagons on one side and the pentagon-hexagon group on the other side.

The structure of 60-fullerene spheres has changed, slightly flattening under applied pressure, at the first stage. At the second stage covalent bonds form between 60-fullerenes, carbon atoms hybridization changes there from sp^2 to sp^3, the dimers formed possess rather high symmetry. The third stage is characterized by rupture of some C,C bonds. Different relaxation ways of the dimers simulated at the third stage (see section 2) lead to different forms both in

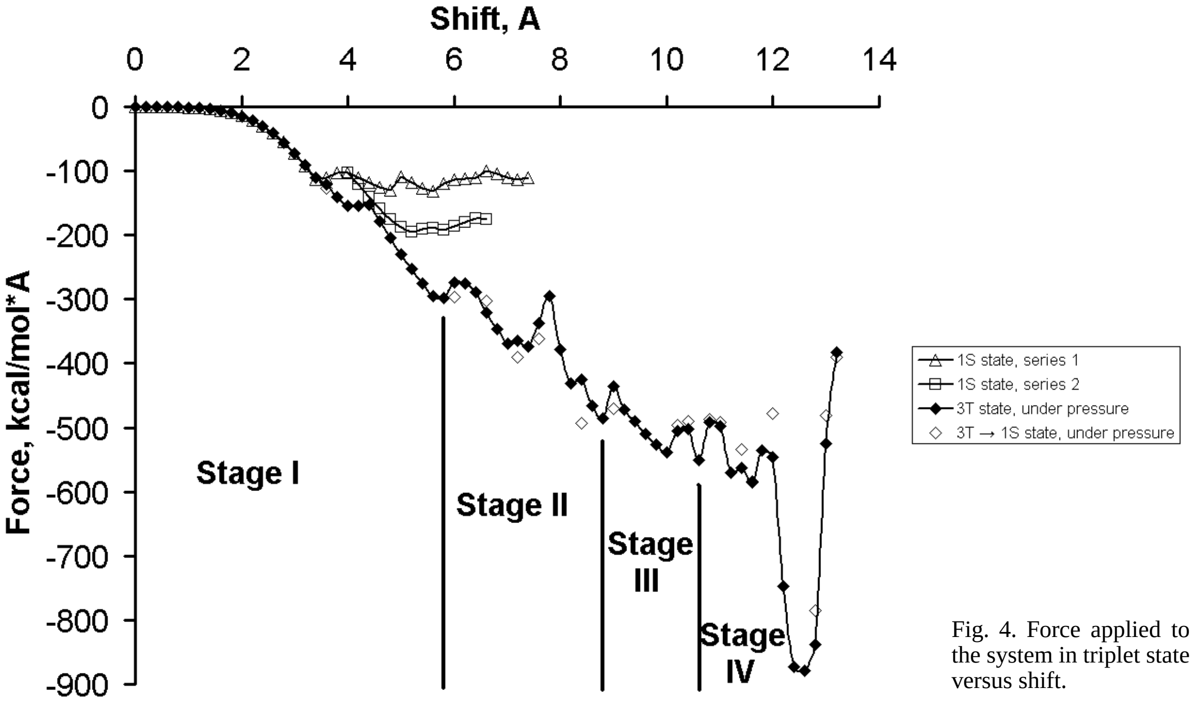

Fig. 4. Force applied to the system in triplet state versus shift.

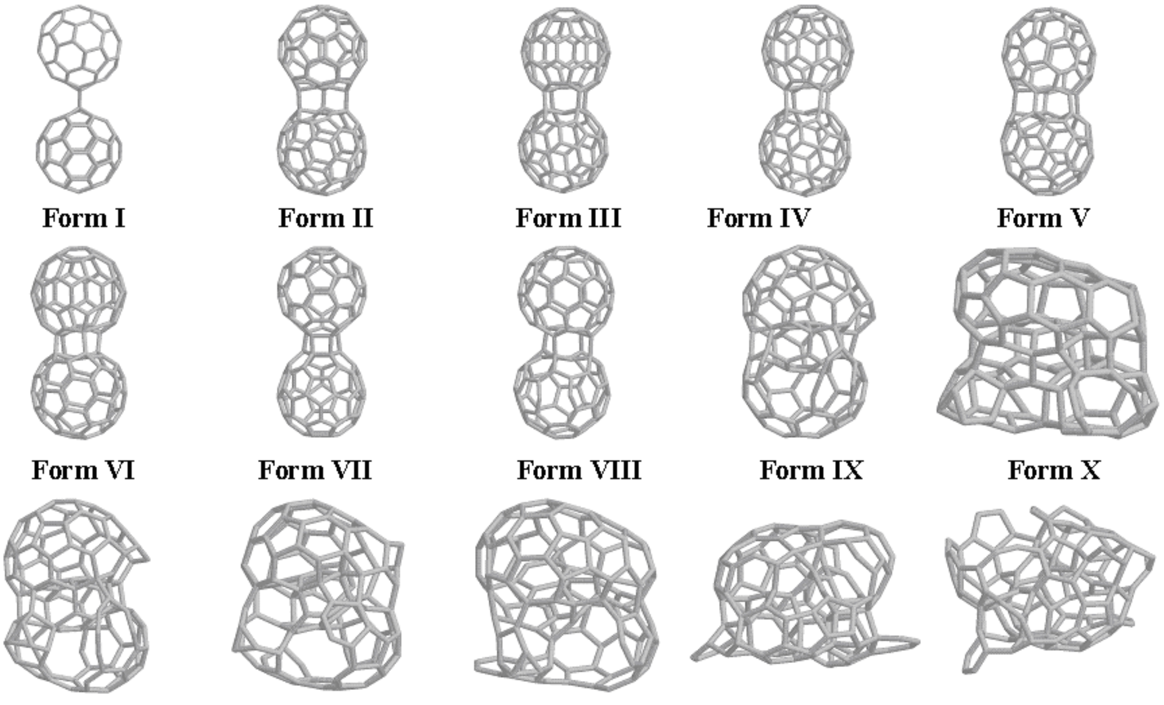
Form I Form II Form III Form IV Form V
Form VI Form VII Form VIII Form IX Form X
Form XI Form XII Form XIII Form XIV Form XV

Fig. 5. Snapshot of 60-fullerene dimer models isolated (relaxed, ^3T state).

terms of geometry and energy (see Figure 3). Relaxing in the ^3T state, these forms return to the usual 60-fullerene constitution, i. e. order of bonding. Relaxation in the ^1S state often results in formation of three-fold carbon cycles, thus having much higher $\Delta_f H$ values. At the fourth stage the 60-fullerene constitution is completely disrupted; interfacial polyhedra, formed at the second stage are very dense and have almost parallel sides. The process of carbon structures self-organization is observed on the interface between destructing 60-fullerene spheres under applied pressure.

One can see that polyhedra formed at the stages II and III often possess high symmetry. Sides of these polyhedra actually are fully substituted molecules of hexane or heptane in the boat conformation, resembling adamantane. It is important to note that interfacial polyhedra are rather flexible. Two carbon atoms, once having formed a bond, can break it, permitting the formation of a more preferable bond at an other place.

It is known that the dimerization of 60-fullerene occurs in the ^3T or higher state of multiplicity. The $^3T \rightarrow {}^1S$ transition may happen before or after relaxation, so both cases have been simulated. At the second stage of dimerization one can see that an odd or even quantity of interfacial bonds is formed in the ^3T and ^1S states, correspondingly.

The ^1S state is energetically less preferable, since it has higher $\Delta_f H$ both under applied pressure and after relaxation (see Fig. 3, unfilled diamonds).

Starting from Form VII found in the third stage, the transition to the ^1S state stabilizes strained three-fold carbon cycle and relaxation in the ^3T states becomes more preferable. Further, at the fourth stage the relaxation in the ^1S state leads to misshapen distortions.

4. Discussion

As was mentioned above, the pressure required to produce a given deformation is calculated with respect to the maximum and minimum possible surfaces of force application (section 2). Corresponding values of pressure for each form of fullerene dimers are listed in Table 1.

Table 1. QC evaluated mechanical parameters for 60-fullerene dimers.

Name of form	Force [kcal/mol·Å][a]	Applied pressure [GPa] (2 1 1) plane	Applied pressure [GPa] (1 1 1) plane
I	−120.3789	1.72	9.71
II	−273.282592	3.90	22.06
III	−364.972789	5.21	29.46
IV	−337.059154	4.81	27.21
V	−424.542680	6.06	34.27
VI	−435.607748	6.22	35.16
VII	−505.300429	7.21	40.78
VIII	−502.693643	7.17	40.58
IX	−497.754331	7.10	40.17
X	−562.149988	8.02	45.37
XI	−586.015493	8.36	47.30
XII	−545.703296	7.78	44.04
XIII	−838.709010	11.97	67.69
XIV	−525.455496	7.50	42.41
XV	−383.219838	5.47	30.93

[a] The force can be recalculated in Newtons (F_n) by the formula: $F_n = F \cdot 4.184 \cdot 10^{13} / N_A$, where N_A is Avogadro's constant.

From the applied pressure values one can conclude that they are probably overstated but reproduce the experimental data quite well. One can compare these results with experimental data: Pressures of 1 – 8 GPa correspond to the formation of the orthorhombic phase, ~ 2 GPa to the tetragonal phase, ~ 6 GPa to the rhombohedral phase, > 12 GPa to the superhard phase and > 25 GPa to 'graphitized' forms [3]. One can see that two sudden increases of the pressure correspond to lowering of the resulting dimers symmetry (Figure 5). They are observed one at Form V (the resulting dimer becomes less sphere-like) and the other at Form X (the dimer hardly resembles fullerene). These transitions refer to the formation of X-ray amorphous and 'graphitized' phases, correspondingly.

The results of the simulations are reliable since they show the immediate effect of the external pressure on the material under investigation, so they explain on the atomic level the mechanism of 60-fullerene dimerization from the chemical point of view.

As regards to pressure-induced polymerization we can formulate the process as follows: Two fullerene spheres under pressure are by either way excited to the ^3T state. After rapprochement they interact, giving a stable covalent bond.

Under greater pressure interfacial high-symmetrical and obviously mechanically stable polyhedra arise. Material relaxed at this stage may possess high mechanical stability, due to the lability of carbon-carbon bonds in such polyhedra and their ability to damp electronic excitations. It can explain the phenomena of ultra-hard poly-fullerenes [2]. Subsequent application of external pressure leads to rupture of the fullerene backbone and formation of active centers that can combine with neighboring species. Finally, at the highest pressures the core of interfacial polyhedra remains the most organized part of the resulting carbon material, while the rest of the 60-fullerene body forms microcrystalline graphite-like zones of amorphous carbon (with linear dimensions up to 5 Å).

5. Summary

Semi-empirical quantum chemistry PM3 simulation of 60-fullerene dimerization under external pressure has been performed. Structures of 15 phases from a simple dimer up to partially graphitized material have been isolated. These could be used in future work to simulate vibration spectra and to study physical properties and chemical reactions. Corresponding pressures of formation are calculated, reproducing the magnitude of experimental values rather well. A mechanism of dimerization is proposed.

Acknowledgements

We thank Dr. T. Makarova (Institutionen för fysik, Umeå University, Sweden) and Dr. V. V. Lisnyak (Chemistry Department of Kiev National Taras Shevchenko University, Kiev) for the stimulating discussions.

[1] B. Sundqvist, Adv. Phys. **48**, 1 (1999).

[2] V. D. Blank, S. G. Buga, G. A. Dubitsky, N. R. Serebryanaya, M. Yu. Popov, and B. Sundqvist, Carbon **36**, 319 (1998).

[3] T. L. Makarova, Semiconductors **35**, 243 (2001).

[4] K. Kamaras, S. Pekker, L. Forro, and D. B. Tanner, Chem. Phys. Lett. **295**, 279 (1998).

[5] T. Hara, J. Onoe, and K. Takeuchi, J. Appl. Phys. **92**, 7302 (2002).

[6] J. Onoe, T. Nakayama, M. Aono, and T. Hara, Appl. Phys. Lett. **82**, 595 (2003).

[7] B. L. Zhang, C. Z. Wang, K. M. Ho, and C. T. Chan, Europhys. Lett. **28**, 219 (1994).

[8] C. D. Latham, M. I. Heggie, R. Jones, and P. R. Briddon, Recent Advances in the Chemistry and Physics of Fullerenes (Eds. R. S. Ruoff and K. M. Kadish), Electrochemical Soc., Pennington, NJ 1995, vol. 2, p. 1552.

[9] Comprehensive Organic Chemistry: The Synthesis and Reactions of Organic Compounds (Eds. Sir D. Barton and W. D. Ollis), Pergamon Press, Oxford - New York 1979, vol. 1.

[10] K. Komatsu, K. Fujiwara, T. Tanaka, and Y. Murata, Carbon **38**, 1529 (2000).

[11] A. T. Pilipenko, V. A. Zayetz, V. D. Khavryutchenko, and E. R. Falendysh, J. Struct. Chem. **28**, 155 (1987).

[12] J. J. P. Stewart, J. Comp. Chem. **10**, 221 (1989).

[13] E. Sheka, V. D. Khavryutchenko, and I. Markichev, Russ. Chem. Rev. **64**, 389 (1995).

[14] E. F. Sheka and V. D. Khavryutchenko, NanoStructured Materials **6**, 803 (1995).

[15] V. D. Khavryutchenko, E. A. Nikitina, T. A. Golubina, A. I. Malkin, V. S. Yushchenko, and E. F. Sheka, Int. J. Quant. Chem. **29**, 161 (1995).

[16] V. D. Khavryutchenko, E. F. Sheka, and V. A. Zayetz, Int. J. Quant. Chem. **57**, 741 (1996).