

COMPUTATIONAL STUDIES OF SWCNTs CAPPED BY HEMISPHERES OF C₆₀ FULLERENE, BASED ON SEMI-EMPIRICAL METHODS

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Abstract. The computations were performed using a dual CPU (2x2.0 GHz) personal computer (PC) motherboard, with the AM1, PM3, MNDO, and MINDO/3 semi-empirical quantum-chemical methods. Optimized bond distances, effective charge values, total energies, heats of formation and core-core interactions were calculated for zigzag and armchair type capped SWCNTs with maximum stoichiometry C₁₆₈ and C₁₆₀, respectively. For C₆₀ and C₇₀ fullerenes, Gaussian STO-3G *ab-initio* and B3-LYP/3-21G* DFT calculations were additionally performed, allowing us to compare the computed results with the experimental ones. We have shown that currently available relatively low-cost high-power personal computers can be successfully used in semi-empirical quantum-chemical computations even for large-sized carbon nano-structures, for which optimized structures provide data being in good agreement with the experimental results.

1. INTRODUCTION

Advanced quantum-mechanical calculations concerning large molecules, for instance carbon nanotubes [1-3], containing from several dozen to several hundred atoms usually require specialized computation centers with high-power super-computers [4,5], whose cost is estimated at hundreds of thousands or even millions of US dollars. Current progress in the technology for PC-type high-power computers on a broad scale is so advanced (coupled with relatively low production costs) that those interested in quantum-chemical computations, especially of the semi-empirical kind, can successfully use these type of computers. Investing approx. \$2,000 allows for the purchase, in a typical shop, of a dual CPU motherboard Pentium IV with 2.0 – 2.4 GHz processors, plus 1 GB RAM and 100 GB HDD as well as other components necessary to set up ready-to-use PC. This kind of

computers could be combined into clusters with a power comparable to that of workstations, thus comprising serious competition for super-computers, especially in terms of cost. Another important factor is that PC-type computers can be easily modified, without any necessity to replace the whole set, by replacing only the processors to a newer type and possible extending the RAM up to 2 GB and HDD to more than 100 GB.

One problem that always arises is the choice of appropriate software for calculations, and also the level of advancement and accuracy of those calculations.

In this paper we have shown systematic studies of the changes of the geometric structures (bond lengths, angles between carbon atoms) and thermodynamic data of the fullerene family depending on the number of the carbon atoms in SWCNTs, their arrangement (here zigzag or armchair type

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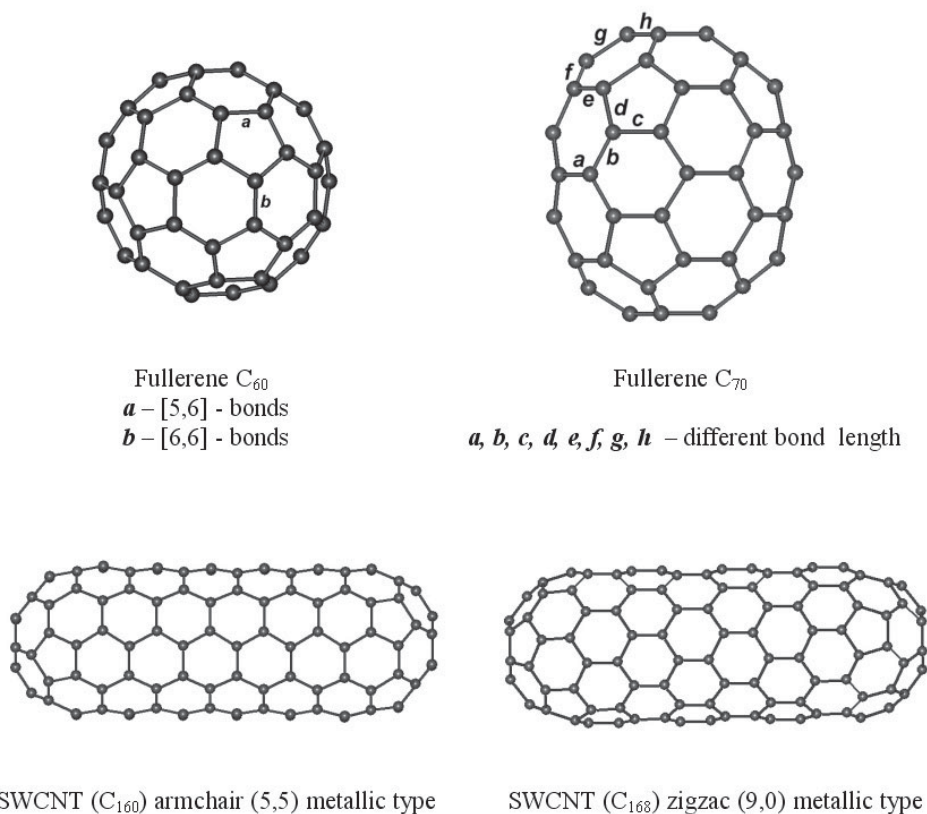


Fig. 1. The geometry structure of the fullerenes and SWCNTs.

only), diameter and length using quantum-chemistry semi-empirical methods. In our model of the 3D carbon nano-structures we have assumed that their aromaticity is not the same as in a graphene sheet and it can be well described by the global and local aromaticity [6-10]. The introduction of pentagonal rings within the carbon nanotube cap, necessary to curve the graphene structure as well as the curving the plane of the hexagon rings caused by their being rolled into a cylinder, introduces stresses in molecule nano-structures and induces disturbances in the distribution of the pi-electron densities [1-3, 6-10].

2. COMPUTATIONAL DETAILS

In this work we present the results of quantum-mechanical computations based on semi-empirical methods: AM1, PM3, MNDO and MINDO/3 [11]. The optimizations concern large carbon structures, e.g. capped, single-wall, zigzac and armchair carbon nanotubes (SWCNTs) systematically derived, one by one, from the structures of C_{60} and C_{70} fullerenes. A PC Pentium IV with the above-listed parameters was used in the computations, based

on the HyperChem7 (Hypercube, Inc.) package under MS Win 2000. Additional *ab initio* and DFT computations were performed only for C_{60} and C_{70} , with the use of the Gaussian 98 package [11]. The results of the computations are presented in the enclosed tables. For the initial structures, i.e. C_{60} and C_{70} , all the computation results were compared with experimental data available in the literature. The compatibility of the computed results, first of all for the *ab initio* methods and also for the semi-empirical methods, with the experimental data has been assumed in this paper as the criterion of correctness for computations of the carbon nano-structure models, not only for C_{60} and C_{70} fullerenes, but also for all other carbon nanotubes for which no experimental data are available in the literature.

All the optimizations for the carbon nano-structures were performed at RMS (kcal/Å·mol) and a convergence limit of SCF control with accuracy of 10^{-5} . All the computations presented here took approx. 2 months of continual work of the above-described PC Pentium IV.

Table 1. The bonds length (Å) between pentagon-hexagon ([5,6]-bonds) and hexagon-hexagon ([6,6]-bonds) rings in the fullerene C₆₀ [2,6] (see Fig. 1: Fullerene C₆₀).

Experimental results			Calculated results		
Method	[5,6]-bonds	[6,6]-bonds	Method	[5,6]-bonds	[6,6]-bonds
NMR	1.448	1.370	HF(STO-3G)	1.465	1.376
Neutron diffr.	1.444	1.391	HF (7s3p/4s2p)	1.453	1.369
Electron diffr.	1.458	1.401	LDF (11s6p)	1.430	1.390
X-Ray	1,467	1.355	HF	1.448	1.370
			MP2	1.446	1.406

3. THE CONSTRUCTION OF THE FAMILY OF ZIGZAC AND ARMCHAIR TYPE CARBON NANOTUBES, ON THE BASIS OF THE C₆₀ AND C₇₀ FULLERENES

The construction of new carbon structures on the basis of C₆₀ and C₇₀ fullerenes (see Fig. 1: Fullerenes C₆₀ and C₇₀) requires the determination of the means of cutting those structures and the principle by which rings composed of hexagons are inserted [10]. We have focused on single-walled armchair and zigzag type capped carbon nanotubes only. To construct capped armchair nanotubes (5,5), with the pentagon located at the top of the cap, we applied the formula: C_{60+10n} (where n=1, 2, 3....) for n_{max}=10 (e.g. C₁₆₀) (see Fig. 1: SWCNT (C₁₆₀)). For zigzag capped nanotubes (9,0), with the hexagon located at the top of the cap, we used the formula: C_{60+18n} (where n=1, 2, 3....) for n_{max}=6 (e.g. C₁₆₈) (see Fig. 1: SWCNT (C₁₆₈)).

Table 2. Our calculated results.

Calculation Method	[5,6]-bonds	[6,6]-bonds
AM1	1.46392	1.38472
PM3	1.45751	1.38394
MNDO	1.47377	1.39998
MINDO/3	1.49646	1.41934
Gaussian	1.46436	1.37687
STO-3G		
Gaussian	1.45992	1.39067
B3LYP/3-21G*		

4. RESULTS AND DISCUSSIONS

Table 1 and 2 present bond lengths in the C₆₀ molecule (see Fig. 1: Fullerene C₆₀) available in the literature and also the results of our calculations by means of the above-mentioned semi-empirical, *ab initio* and DFT methods. First of all the AM1 and PM3 methods provide data being in good agreement with experimental results as well as with those calculated by the *ab initio* and DFT methods. We can state that the parameterization in the AM1 and PM3 methods and also the accuracy of the applied calculations are good enough for the geometry optimization of the C₆₀ molecule. Small deviations from experimental results can be seen for the MNDO and MINDO/3 methods. This could be related to the different parameterization model that is included in assumptions of these methods.

Table 3 presents the bond lengths in the C₇₀ molecule (see Fig. 1: Fullerene C₇₀). The semi-empirical AM1 and PM3 calculation methods provide results that are also in agreement with experimental ones as well as those calculated by the *ab initio* and DFT methods.

Figs. 2 and 3 show bond lengths and their distribution in the molecules: C₆₀, C₁₃₂, C₁₆₈ (SWCNT zigzag type (9,0)) and C₇₀, C₁₀₀ and C₁₆₈ (SWCNT armchair type (5,5)). We can notice that with the increasing number of carbon atoms in the SWCNT, its middle structure becomes more uniform. In short SWCNT (such as C₁₃₂), bond lengths range between 1.37 and 1.45 Å, but in longer ones (such as C₁₆₈), only between 1.41 and 1.43 Å. We can conclude that strains distribution in a longer SWCNT is smaller, what means that the molecule becomes more thermodynamically stable.

Other thermodynamical data, like total energies, binding energies, core-core interactions and enthalpies formation for optimized carbon nano-structures

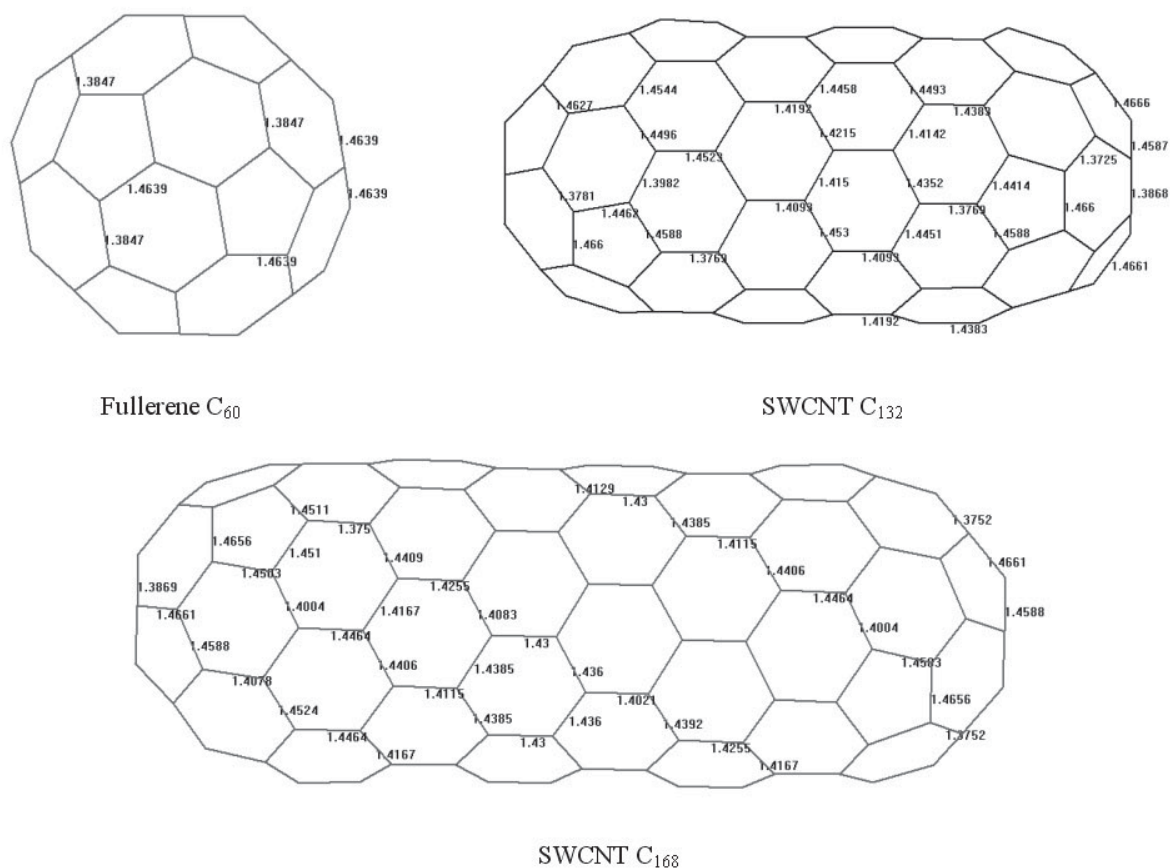


Fig. 2. The bond distances in SWCNTs zigzag type (9,0).

Table 3. Bond lengths – experimental and calculated results for C₇₀ [2,6] (see Fig. 1: Fullerene C₇₀). A – crystal structure of the complex: (η^2 -C₇₀) Ir (CO)Cl (PPh₃)₂ B – crystal structure C₇₀6(S₈).

Bond type	Experiment		Theory	Our ab initio and DFT calculated results		Our semi-empirical calculated results			
	A	B	(dzp/SCF)	HF/STO-3G	B3LYP/3-21G* AM1	PM3	MNDO	MINDO/3	
a	1.462	1.462	1.475	1.487	1.476	1.465	1.463	1.484	1.510
b	1.423	1.414	1.407	1.415	1.420	1.414	1.412	1.430	1.451
c	1.441	1.426	1.415	1.419	1.436	1.434	1.426	1.442	1.459
d	1.432	1.447	1.457	1.472	1.456	1.467	1.463	1.478	1.504
e	1.372	1.378	1.361	1.365	1.383	1.375	1.374	1.389	1.408
f	1.453	1.445	1.446	1.457	1.455	1.461	1.453	1.469	1.492
g	1.381	1.387	1.375	1.379	1.392	1.387	1.386	1.402	1.422
h	1.463	1.453	1.451	1.463	1.459	1.464	1.457	1.473	1.495

Table 4. Thermodynamic data for SWCNTs zigzag type (9,0).

AM1 method	C60	C78	C96	C114	C132	C150	C168
Total Energy (kcal/mol)	-176449.169	-229494.790	-282898.471	-335664.508	-388749.435	-441979.805	-495270.210
Binding Energy (kcal/mol)	-9280.902	-217318.746	-15429.244	-18044.802	-20979.249	-24059.139	-27199.064
Core-Core Interaction (kcal/mol)	2166311.889	3304771.558	4604100.675	6043245.260	7599409.846	9259492.385	11011758.102
Heat of Formation (kcal/mol)	972.498	1153.376	976.196	1436.658	1578.231	1574.361	1510.456
PM3 method	C60	C78	C96	C114	C132	C150	C168
Total Energy (kcal/mol)	-163347.185	-212446.365	-261895.845	-310707.799	-359839.086	-409115.849	-458245.229
Binding Energy (kcal/mol)	-9442.683	-12370.513	-15648.642	-18289.246	-21249.179	-24354.595	-27312.624
Core-Core Interaction (kcal/mol)	2146995.823	3278620.826	4571141.581	6003622.527	7553293.835	9206954.131	10953105.229
Heat of Formation (kcal/mol)	810.716	958.907	756.798	1192.214	1308.298	1278.905	1396.895
MNDO method	C60	C78	C96	C114	C132	C150	C168
Total Energy (kcal/mol)	-176117.102	-229066.545	-282363.380	-335020.935	-387998.364	-440982.919	-494096.918
Binding Energy (kcal/mol)	-9384.688	-12314.407	-15591.518	-18229.350	-21187.054	-24151.885	-27246.160
Core-Core Interaction (kcal/mol)	2151430.612	3279261.039	4565752.025	5990457.430	7531121.857	9174258.866	10908396.943
Heat of Formation (kcal/mol)	868.712	1015.012	813.922	1252.110	1370.426	1481.615	1463.360
MINDO/3 method	C60	C78	C96	C114	C132	C150	C168
Total Energy (kcal/mol)	-174549.446	-226996.031	-279461.858	-331935.244	-384406.282	-436884.438	-489537.804
Binding Energy (kcal/mol)	-9243.586	-12098.413	-14972.481	-17854.109	-20733.389	-23619.788	-26681.396
Core-Core Interaction (kcal/mol)	2089448.107	3189305.539	4445235.407	5836292.180	7341520.892	8947281.781	10642692.717
Heat of Formation (kcal/mol)	1009.814	1231.007	1432.958	1627.350	1824.091	2013.712	2028.124

Table 5. Thermodynamic data for SWCNTs zigzag type (5,5).

AM1 method	C70	C80	C90	C100	C110	C120	C130	C140	C150	C160
Total Energy (kcal/mol)	-205930.954	-235386.689	-264913.188	-294392.951	-323862.937	-353373.974	-382858.457	-412333.462	-441836.268	-471322.329
Binding Energy (kcal/mol)	-10901.309	-12495.666	-14160.788	-15779.173	-17387.782	-19037.441	-20660.546	-22274.173	-23915.602	-25540.285
Core-Core Interaction (kcal/mol)	2777152.336	3441417.191	4156036.172	4913417.037	5709396.327	6542836.720	7409046.177	8305986.802	9234244.318	10188494.553
Heat of Formation (kcal/mol)	1060.991	1175.533	1219.312	1309.827	1410.118	1469.359	1555.154	1650.426	1717.898	1802.115
PM3 method	C70	C80	C90	C100	C110	C120	C130	C140	C150	C160
Total Energy (kcal/mol)	-190634.591	-217896.192	-245224.946	-272508.918	-299783.255	-327097.119	-354385.687	-381664.968	-408970.752	-436260.893
Binding Energy (kcal/mol)	-11079.339	-12690.189	-14368.193	-16001.415	-17625.002	-19288.115	-20925.933	-22554.464	-24209.498	-25848.888
Core-Core Interaction (kcal/mol)	2754112.728	3414457.701	4125348.881	4878924.118	5671054.818	6501024.921	7363575.959	8256680.235	9181788.983	10132408.116
Heat of Formation (kcal/mol)	882.961	981.010	1011.907	1087.585	1172.898	1218.685	1289.767	1370.136	1424.002	1493.512
MINDO method	C70	C80	C90	C100	C110	C120	C130	C140	C150	C160
Total Energy (kcal/mol)	-205544.914	-234944.583	-264407.036	-293826.890	-323238.841	-352688.027	-382112.507	-411529.074	-440970.841	-470396.658
Binding Energy (kcal/mol)	-11023.765	-12634.698	-14308.416	-15939.534	-17562.749	-19223.200	-20858.944	-22486.776	-24139.807	-25776.889
Core-Core Interaction (kcal/mol)	2756828.661	3414417.207	4121768.238	4871624.917	5659665.937	6484653.581	7342194.286	8229810.094	9148564.692	10093020.754
Heat of Formation (kcal/mol)	938.535	1036.502	1071.684	1149.466	1235.151	1283.600	1356.756	1437.824	1493.693	1565.511
MINDO/3 method	C70	C80	C90	C100	C110	C120	C130	C140	C150	C160
Total Energy (kcal/mol)	-203696.859	-232817.715	-261996.666	-291136.692	-320268.363	-349434.078	-378578.669	-407715.059	-436873.455	-466019.380
Total Energy (a.u.)	-324.605	-371.011	-417.510	-463.947	-510.370	-556.847	-603.291	-649.722	-696.188	-742.634
Binding Energy (kcal/mol)	-10840.023	-12409.902	-14037.876	-15626.925	-17207.618	-18822.358	-20415.971	-22001.385	-23608.805	-25203.753
Core-Core Interaction (kcal/mol)	2679702.248	3321094.747	4011381.676	4743481.772	5512930.879	6318925.415	7168825.248	8024175.132	8922589.982	9845907.382
Heat of Formation (kcal/mol)	1122.277	1261.298	1342.224	1462.075	1590.281	1684.442	1799.728	1923.215	2024.695	2138.647

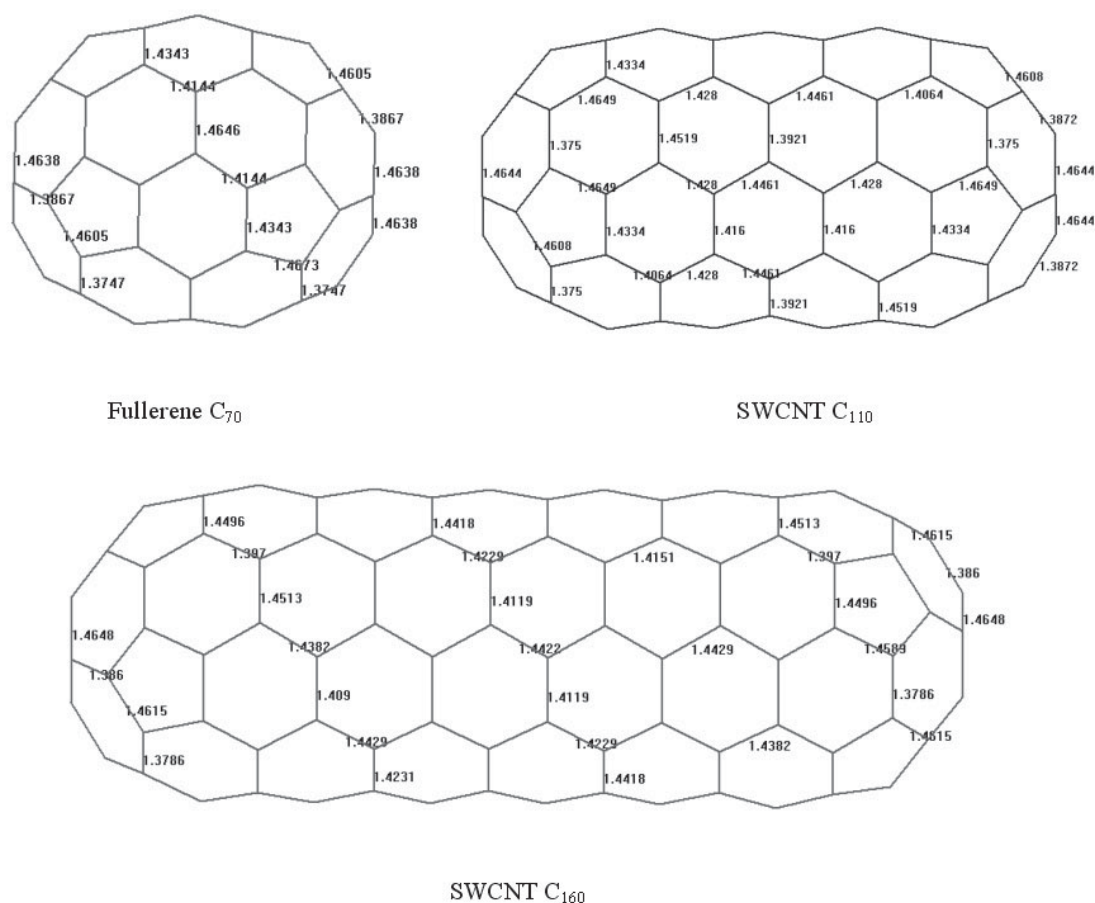


Fig. 3. The bond distances in SWCNTs armchair type (5,5).

can also be determined for these molecules by the semi-empirical methods. Tables 4 and 5 present these data for SWCNTs derived on the basis of C_{60} and C_{70} . For C_{60} and C_{70} we can compare calculated formation heats with the available experimental ones. For C_{60} (gas) this is equal to 2506 kJ/mol (~ 607 kcal/mol) [12] and for C_{70} (gas) - 2652 kJ/mol (~ 642 kcal/mol) [13]. We can notice (see Tables 4 and 5) that the calculated values of the formation heats for C_{60} are within the range 810-1010 kcal/mol and for C_{70} : 883-1122 kcal/mol. The values calculated by the PM3 method are overstated in the smallest degree, compared to the others, against the experimental ones (about 33% for C_{60} and 37% for C_{70}). For other data shown in Tables 4 and 5 we can expect at the first approximation that they also could be a little bit overstated.

5. ACKNOWLEDGMENTS

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REFERENCES

- [1] R. Saito, G. Dresselhaus and M.S. Dresselhaus, *Physical Properties of Carbon Nanotubes*, (Imperial College Press, London 1998).
- [2] M. Terrones, W.K. Hsu, H.W. Kroto and D.R.M. Walton, In: *Fullerenes and Related Structure*, ed. by A. Hirsch (Springer-Verlag, Berlin 1999) p. 189.
- [3] P.M. Ajayan, In: *Carbon Nanotubes, Preparation and Properties*, ed. by T.W. Ebbesen (CRS-Press, 1997) p. 111.
- [4] Z. Slanina, L. Stobinski, P. Tomasik, H.-M. Lin and L. Adamowicz // *J. Nanosci. Nanotech.* **3** (2003) 1.
- [5] Z. Slanina, F. Uhlik, L. Stobinski, H.-M. Lin and L. Adamowicz // *Inter. J. Nanosci.* **1** (2002) 303.
- [6] M. Buhl and A. Hirsch // *Chem. Rev.* **101** (2001) 1153.

- [7] P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N.J.R. van E. Hommes // *J. Am. Chem. Soc.* **118** (1996) 6317.
- [8] J. Aihara // *Phys. Chem. Chem. Phys.* **2** (2000) 3121.
- [9] G. Van Lier, F. De Proft and P. Geerlings // *Chem. Phys. Lett.* **366** (2002) 311.
- [10] G. Van Lier, P.W. Fowler, F. De Proft and P. Geerlings // *J. Phys. Chem. A* **106** (2002) 5128.
- [11] J. B. Foresman and A. Frisch, In: *Exploring Chemistry with Electronic Structure Methods* (Gaussian, Inc. Pittsburg, PA, 1996) p. 111.
- [12] C.K. Mathews, M.S. Baba and T.S.L. Narasimhan, In: *Fullerens, Recent Advances in the Chemistry and Physics of Fullerens and Related Materials*, ed. by K.M. Kadish and R.S. Ruoff (1994) p. 468.
- [13] S.M. Pimenova, S.V. Melkhanova and V.P. Kolesov // *J. Chem. Thermodynamics* **35** (2003) 189.