Materials Science-Poland, Vol. 25, No. 3, 2007

Simulated geometry of open-end single-wall carbon nanotubes with adsorbed long-chain normal alkanes and resulting implications

L. STOBIŃSKI[1*], J. MAZURKIEWICZ[2], P. TOMASIK[3, 4], J. PESZKE[5], H.M. LIN[6**]

[1]Institute of Physical Chemistry, Polish Academy of Sciences,
ul. Kasprzaka 44/52, 01-224 Warsaw, Poland

[2] Department of Physics, University of Agriculture, al. Mickiewicza 21, 31-120 Cracow, Poland

[3]Department of Chemistry, Agricultural University, ul. Balicka 122, 30-149 Cracow, Poland

[4]School of Biotechnology, Agricultural University, al. 29 Listopada, 54, 31-452 Cracow, Poland

[5]Institute of Chemistry, Jan Długosz Academy, ul. Armii Krajowej 13/15, 42-201, Częstochowa, Poland

[6]Department of Materials Engineering, Tatung University, Taipei 104, Taiwan, ROC

Successful designing and computation of optimized, large (up to 10 000 atoms), complex structures of isomeric zigzag, armchair, and chiral open-end single-wall carbon nanotubes (SWCNTs) with normal-chain C_8, C_{16}, C_{40}, C_{80}, and C_{96} hydrocarbons was performed by means of HyperChem 7.0 (Molecular Dynamics and Molecular Mechanics MM+) and Gaussian 03 (Molecular Mechanics UFF) programs. The diameter of the nanotubes was around 0.4, 0.7, 0.9, 1.1, 1.3, and 1.7 nm. Octane and hexadecane positioned themselves on the nanotube surfaces in the manner influenced by the pattern of the carbon atoms in the tubes, i.e., in the manner dependent on the isomerism of the nanotubes. Longer-chain hydrocarbons usually coiled around the nanotubes, unless they were 0.4 nm in diameter. In such cases a kind of clip-shape arrangement of the hydrocarbons on the nanotube surface was noted instead of coiling. The numbers of carbon atoms in one full turn of the hydrocarbon chain coiling around the SWCNT increased with the diameter of the nanotubes, corresponding to 35, 46, 52, and 64 carbon atoms for 0.7, 1.1, 1.3 and 1.7 nm diameter nanotubes, respectively. However, the comparison of the energy of complexation calculated per one carbon atom of the alkane chain adsorbed on the nanotube surface suggests that in some cases, complexation of long-chain normal hydrocarbons to the carbon nanotube could result in the separation of those nanotubes according to their diameter.

Key words: *carbon nanotube; normal hydrocarbon; computer simulations*

---

[*] Corresponding author, e-mail: lstob@ichf.edu.pl
[**] Corresponding author, e-mail: hmlin@ttu.edu.tw

1. Introduction

There are three isomeric forms of single-wall nanotubes (SWCNTs): zigzag, armchair, and chiral nanotubes. As far as we know, none of the developed methods of synthesis of such nanotubes provides pure, isomerically uniform products. Thus far, the proposed methods available for separation of isomers [1] were based on their selective chemical functionalization. In our preliminary opinion, the separation of isomeric nanotubes could be possible by the formation of complexes with long-chain normal hydrocarbons. This view is based on results available in the literature [2–17].

Hydrocarbons have been shown to adsorb on single and bundled carbon nanotubes. Preliminary modelling studies [2, 3] suggested that methane did not adsorb on the surface of bundled SWCNTs and further investigations [4, 5] led to the conclusion that methane diffused inside the nanotubes. Based on the changes of the SWCNTs electrical resistivity caused by the adsorption of methane, a corresponding gas sensor was proposed [6]. Computational simulations suggested that a mixture of C_1–C_8 *n*-and *i*-alkanes could be separated on the carbon nanotubes. The results depended on the length of the SWCNTs. The adsorption improved with the increasing hydrocarbon chain length and it was obscured, to a certain extent, by chain branching. The diameter of a carbon nanotube is another crucial factor [7–12]. Also cycloalkanes and cycloalkenes adsorb on the surface of the SWCNTs although their adsorption is worse than that of *n*-alkanes of the same number of carbon atoms in the chain [13, 14]. As the chain of alkanes became longer, their surface adsorption on the SWCNTs was faster and predominated over the inclusion inside channels. This was found in the case of *n*-decane [15]. Such a tendency was also observed for the sorption of alkanes on multiwalled carbon nanotubes (MWCNTs) [16]. In general, sorption of alkanes on the surface of MWCNTs has a priority over their condensation inside the channels. Again, the nanotube diameter was a factor [17].

A formal curvature of graphene plane into a single-walled carbon nanotube changed the properties of the molecular orbitals on both sides of the wall of the system to an extent depending on the degree of the curvature, that is, the diameter of the resulting nanotubes [18]. Originally, sp^2 hybridized carbon atoms of graphene structure changed their hybridization slightly towards sp^3. Hence, the electrical, emissive, and other properties of the nanotubes were modified. Obviously, the possibilities of interaction of the resulting outer molecular orbital with a sorbate were also perturbed. Additionally, three types of localizations of the carbon atoms of the nanotube walls in a manner providing isomerism might have subtly influenced the mode and energy of surface–sorbate interactions.

Thus, in this paper, the energy and structure of surface complexes of single-wall zigzag, armchair, and chiral carbon nanotubes of varying length and diameter with *n*-octane (C_8) and selected higher *n*-alkanes, C_{16}, C_{40}, C_{80}, and C_{96}, were simulated to either prove or disprove this concept.

2. Computations

First, the HyperChem 7.0 program using PC IV with double CPU optimized the complex geometries. Energy minima were found by molecular dynamics (MD) calculations at 300 K (run time was 100 ps at step size of 0.001) and then by molecular mechanics (MM+) with RMS gradient of 0.001. Original parameters of the program were applied.

The Gaussian 03 computations, using molecular mechanics (UFF) with four default convergence criteria set in the program, were additionally performed with the SGI 2800 grizzly computer in the Academic Computer Centre Cyfronet in Cracow, Poland.

In every case, computations were started using the HyperChem program (MD) with an initially optimized individual structure of SWCNT and linear alkane. This procedure was initiated by situating straight hydrocarbon chains close to the nanotube surface but perpendicularly or at an angle to their long CNT axes. MD was applied for the first optimization run. During optimization, straight alkane could coil tightly around (and/or adhere along) CNT and the CNT–alkane complex was transferred through many local energetic minima, finally approaching the global minimum energy. Then the molecular mechanics MM+ method was used and a stationary point on the potential surface was found. Afterwards, the Gaussian 03 program (molecular mechanics UFF) was used to enhance the precision of the complex optimization process. This kind of computations was performed for zigzag, armchair, and chiral open-end single wall carbon nanotubes of the structure and the atomic composition specified in Table 1.

After a proper optimization of the CNT/alkane system geometry, the whole alkane chain should tightly adhere to the CNT surface independently of the alkane location on the CNT surface (coil and/or clip shape). Also, no part of the alkane chain could protrude from the CNT structure (as well as along the CNT axis and also perpendicular or at an angle to the CNT axis). In an optimized complex structure, the alkane chain could not self-cross. If one of those coincidences took place, optimization of the complex structure was repeated to avoid cases where the CNT surface was not fully covered by the whole alkane chain and the calculated complex formation energy would be significantly lowered (sometimes by over 20–30%).

It was shown that the relation between the length of the CNT and the alkane chain was not important. The alkane could be much longer than the CNT and could tightly coil around the CNT several times or adhere to the CNT surface along the CNT axis, creating a kind of clip as shown below.

3. Results and discussion

Computations were performed for six sets of open-end SWCNTs varying in their diameters, that is 0.4, 0.7, 0.9, 1.1, 1.3, and 1.7 nm. Each set contained three SWCNTs isomeric models, namely armchair (A), zigzag (Z), and chiral (C) nanotubes. Their structure and atomic composition is presented in the first column of Table 1.

Table 1. Energies of the complex formation of *n*-alkanes with the isomeric open end, single wall carbon nanotubes calculated with HyperChem 7.0 and Gaussian 03[1]

Nanotube			Alkane				
			C_8	C_{16}	C_{40}	C_{80}	C_{96}
0.4	A	3,3 330C + 12H	7083.77 –42.22, –5.28	7040.85 –41.47, –2.59	7141.62 –56.33, –1.41	7248.09 –44.68,–0.56	7223.93, –43.19,–0.45
	Z	5,0 276C + 12H	4578.74, 14.08, 1.76	4561.96 32.02, 2.00	4557.94 64.02, 1.60	4534.41, 121.42, 1.51	4546.86 133.30, 1.39
	C	4,2 227C + 13H	4499.49, 17.09, 2.14	4498.32 26.73, 1.67	4499.13 62.79, 1.57	4446.67 118.22, 1.48	4461.53 148.04, 1.54
0.7	A	5,5 330C + 20H	3501.07, 13.48, 1.68	3499.25 25.43, 1.59	3485.57 68.46, 1.71	3471.69 136.07, 1.70	3456.85 164.73, 1.72
	Z	9,0, 432C + 18H	4406.58, 16.00, 2.00	4399.75, 30.03, 1.88	4396.49 65.46, 1.64	4392.46 132.43, 1.66	4383.12 159.86,1.67
	C	8,2 396C + 20H	3945.92 14.91, 1.86	3943.48 25.44, 1.59	3923.83 72.87, 1.82	3461.38 133.09, 1.66	3852.54 173.15, 1.80
0.9	A	7,7 476C + 28H	3655.74 19.57, 2.44	3659.42 29.74, 1.86	3632.16 81.22, 2.03	3608.14 157.00, 1.96	3604.01 172.36, 1.80
	Z	12,0 576C + 24H	4449.45 14.60, 1.83	4440.37 29.97, 1.87	4412.08 82.32, 2.06	4400.44 151.53, 1.89	4395.64 175.46, 1.83
	C	8,5 436C + 26H	3512.55, 16.23, 2.03	3506.95 32.47, 2.03	3496.09 75.89, 1.90	3461.37, 146.42, 1.83	3430.57 171.29, 1.74
1.1	A	8,8 480C + 32H	3325.35, 19.22, 2.40	3325.81, 30.61, 1.91	3296.31 82.35, 2.06	3253.96, 160.29, 2.00	3222.40 187.45, 1.95
	Z	14,0 672C + 28H	4809.44, 17.78, 2.22	4803.82 34.45, 2.15	4771.09, 85.02, 2.13	4748.70, 163.47, 2.04	4615.65 190.54, 1.98
	C	12,3 610C + 30H	4216.38, 19.73, 2.47	4205.72 37.10, 2.32	4186.78 79.49, 1.99	4148.49, 152.24, 1.90	4158.92 186.84, 1.95
1.3	A	10,10 460C + 40H	2772.46, 19.51, 2.44	2770.66 33.29, 2.08	2770.52 76.59, 1.91	2710.80, 162.15, 2.03	2710.47 184.35, 1.92
	Z	16,0 448C + 32H	2843.44, 15.30, 1.91	2868.28 29.28, 1.83	2944.89 73.44, 1.84	3052.39, 156.39, 1.95	3126.49 95.12, 0.99
	C	15,2 468C + 34H	2959.15, 12.51, 1.56	2966.08 34.36, 2.15	3038.62, 79.20, 1.98	3161.39, 165.23, 2.07	3258.00 186.18, 1.94
1.7	A	13,13 910C + 52H	5243.77, 20.13, 2.52	5126.39 30.98, 1.94	5326.56, 89.34, 2.23	5306.44, 169.32, 2.11	5367.71 194.79, 2.03
	Z	22,0 1056C + 44H	5516.16, 17.97,2.25	5555.23 32.31, 2.02	5591.21, 88.50, 2.21	5748.43, 163.21, 2.04	5781.10 202.65, 2.11
	C	18,6 826C + 48H	4366.10, 19.11, 2.39	4390.06 34.03, 2.13	4450.39, 87.59, 2.19	4576.79, 159.21, 1.99	4663.41 188.49, 1.96

[1] In the "Nanotube" column of the table the nanotube diameter [nm], type of isomer (A – armchair, Z – zigzac, C – chiral), structure of nanotube (*m*,*n*), and number of the carbon and hydrogen atoms are given. In the "Alkane" columns, subsequent values report energy [kcal/mole] of the SWCNT complex with a given alkane, difference between energy of the complex and the sum of energies of the non-complexed partners, and the complex energy calculated for one alkane carbon atom, respectively.

Although these SWCNTs had almost the same diameters and similar lengths, they differed from one another in the number of carbon and edge hydrogen atoms. In order to evaluate the effect of the SWCNTs length, computations were additionally performed for selected longer nanotubes. Subsequently, computations were performed for complexes of those SWCNTs with a series of *n*-alkanes of 8 (octane), 16 (hexadecane), 40, 80, and 96 carbon atoms in their chains. In every further column the first value is the energy of the complex, the second value is the complexation energy, presented as the difference of the energy of the complex from which the sum of energy of individual SWCNTs and the particular hydrocarbon was subtracted. The third value is the energy of the complex calculated per one hydrocarbon carbon atom. All energies are expressed in kcal/mole.

Simulations showed that octane and hexadecane positioned themselves on the SWCNT surface in a manner influenced by the pattern of the carbon atoms in the SWCNTs, that is in a manner dependent on the isomerism of the nanotubes (Fig. 1).

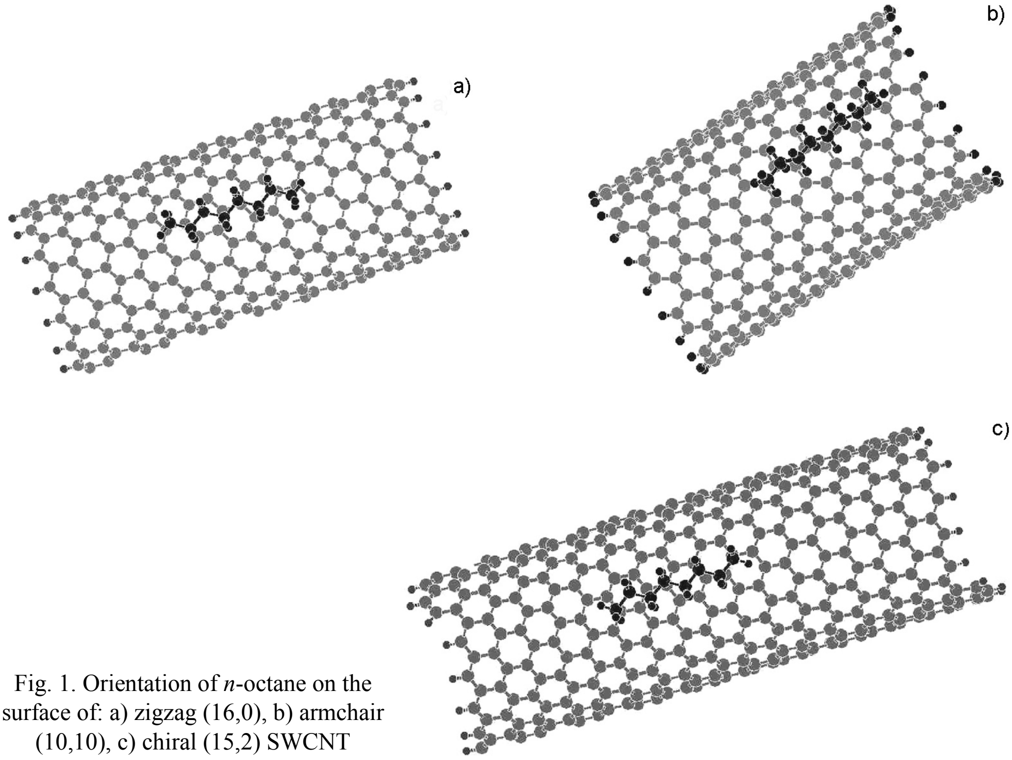

Fig. 1. Orientation of *n*-octane on the surface of: a) zigzag (16,0), b) armchair (10,10), c) chiral (15,2) SWCNT

In similar simulations for longer-chain hydrocarbons one could observe that in the case of 0.4 nm diameter SWCNTs, the hydrocarbon chains did not coil around the nanotubes but, instead, formed a kind of a clip shape along the long axis of the nanotubes (Fig. 2).

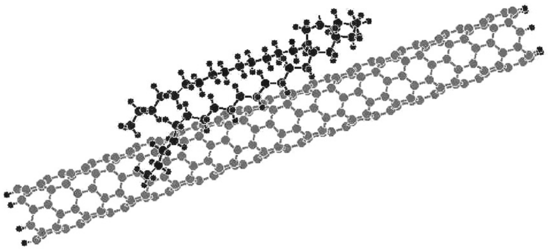

Fig. 2. Orientation of a C_{40} hydrocarbon molecule along the 0.4 nm zigzag (5,0) SWCNT

Table 1 shows that the complex energy for one of the narrowest SWCNT (3,3) was almost twice as large as that for the other narrowest SWCNTs: (5,0) and (4,2). Also, the energy benefit due to complexation was negative. This means the structure of the narrowest SWCNT (3,3) was very unstable and the formation of its complex with alkane was impossible. Our conclusion about the high instability of the narrowest CNT was in good agreement with results published previously [19, 20].

The sp^3 hybridization of the carbon atoms in the chain, and the resulting bond angles did not provide a diameter of the turn within the hydrocarbon coils offering the energy of the complex lower than that when the hydrocarbon chain formed a clip-shape on the SWCNTs' surface. As found by computations for the SWCNTs –hydrocarbon complexes, the atoms of the SWCNT surface and the atoms of the hydrocarbon chain were normally situated at the distance of about 0.3 nm from one another. Because of the C–C bond distances and C–C–C bond angles in the hydrocarbon chain, the distance between the alkane helical turn and the SWCNT surface exceeded 0.3 nm when the diameter of the SWCNT was 0.4 nm. Under such circumstances the "clip-like" arrangement of the hydrocarbon chain on the SWCNT surface was energy -beneficial. As the diameter of the nanotubes expanded, e.g. the curvature of the CNT structure decreased, the long-chain hydrocarbons preferably coiled around them (Fig. 3).

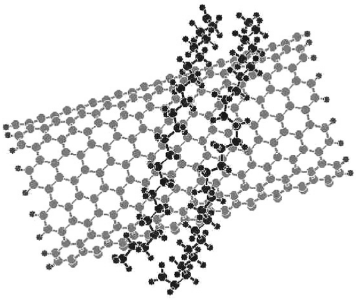

Fig. 3. Coiling of the C_{40} hydrocarbon around 1.3 nm (10,10) armchair SWCNT

The number of carbon atoms in one full turn of the hydrocarbon chain coiling around the SWCNT increased with the diameter of the SWCNTs, and amounted to 35, 40, 46, 52, and 64 carbon atoms for 0.7, 0.9, 1.1, 1.3 and 1.7 nm diameter SWCNTs, respectively.

Examination of Table 1 reveals that the energy of the complexes and the energy benefit due to complexation was usually independent of the SWCNTs diameter and the hydrocarbon chain length. This pointed to the intervention of the effect of individual fitting of hydrocarbons to a given isomeric SWCNT. The comparison of the complexation energy calculated per one carbon atom in the nanotubes (Table 1) suggests that in some cases, complexation of long-chain normal hydrocarbons to SWCNTs could provide a separation of those nanotubes according to their diameter.

Computations for longer SWCNTs pointed to a negligible effect of the SWCNTs length on the complex energy. Thus, the complexation of SWCNTs with normal hydrocarbons as a means of separating them according to isomer type appeared fairly unlikely. The differences in the complexation energy, in particular for SWCNTs complexes of a given diameter, only randomly exceeded 10 kcal/mole, and they were within the portion of energy available from the thermal motions of hydrocarbons.

4. Summary and conclusions

Simulation of an optimized (even up to 10000 atoms) complex structure with CNT and hydrocarbons can be successfully performed by combining two programs: HyperChem and Gaussian. Using the HyperChem (Molecular Dynamics) program we can create an optimized complex structure starting from free CNT molecules and hydrocarbons. Then, by applying the Gaussian 03 program we can enhance the precision of the complex optimization. Independently on the standard convergence criteria set up in the HyperChem and Gaussian programs, additionally three criteria should be fulfilled to cover completely the CNT surface by the alkane chain: *i)* the long hydrocarbon chain should tightly adhere to the CNT surface regardless of the way the hydrocarbon adsorbs on the CNT surface (coil and/or clip shape), *ii)* after optimization no part of the hydrocarbon chain can protrude from the CNT structure (as well as along the CNT axis and also perpendicular or at an angle to the CNT surface), *iii)* the hydrocarbon chain cannot be self-crossed in the optimized complex structure.

The complexation of SWCNTs with normal hydrocarbons can be useful as a means of separating SWCNTs according to their diameter but is unlikely to work as way to separate them according to their isomeric type.

Acknowledgements

The authors are very much indebted for the MniI/SGI2800/AR/057/2003 grant received for calculations of the SWCNTs-hydrocarbon conformations in Academic Computer Center Cyfronet in Cracow, Poland. The author (HML) would like to thank the National Science Council of the Republic of China for a partial financial support for this research.

References

[1] BANERJEE S., HEMRAJ-BENNY T., WONG S.S., J. Nanosci. Nanotechnol., 5 (2005), 841.
[2] MAO Z., SINNOTT S.B., J. Phys. Chem., 194 (2000), 4618.
[3] TALAPATRA S., ZAMBANO A.Z., WEBER S.E., MIGONE A.D., Phys. Rev. Lett., 85 (2000), 138.

[4] MURIS M., DUFAU N., BIENFAIT M., DUPONT-PAVLOVSKY N., GRILLET Y., PALMARI J., Langmuir, 16 (2000), 7019.
[5] BIENFAIT M., ASMUSSEN B., JOHNSON M., ZEPPENFELD P., Surf. Sci., 460 (2000), 243.
[6] VALENTINI L., ARMENTANO I., LOZZI L., SANTUCCI S., KENNY J.M., Mater. Sci. Eng., C 24 (2004), 527.
[7] MAO Z., SINNOTT S.B., J. Phys. Chem. B, 105 (2001), 6916.
[8] JIANG J., SANDLER S.I., SCHENK M., SMIT B., Phys Rev., 72 (2005), 045447.
[9] JIANG J., SANDLER S.I., SMIT B., Nano Lett., 4 (2004), 241.
[10] JIANG J., SANDLER S.I., J. Chem. Phys., 124 (2006), 024717.
[11] BHIDE S.Y., YASHONATH S., J. Am. Chem. Soc., 125 (2003), 7425.
[12] JIANG J., SANDLER S.T., Fluid Phase Equil., 228 (2005), 189.
[13] BITTNER E.W., SMITH M.R., BOCKRATH B.C., Carbon, 40 (2003), 1231.
[14] AGNIKOTRI S., ROOD M.J., ROSTAN-ABADI M., Carbon, 43 (2005), 2379.
[15] SUPPLE S., QUIRKE N., J. Chem. Phys., 121 (2005), 8571.
[16] LI Q.L., YUAN D.X., LIN Q.M., J. Chromatogr. A, 1026 (2004), 283.
[17] HILDING J., GRULKE E.A., SINNOTT S.B., QIAN D., ANDREWS R.R., JOGTOYEN M., Langmuir, 17 (2001), 7540.
[18] KOSTOV M.K., CHENG H., COOPER A.C., PEZ G.P., Phys. Rev. Lett., 89 (2002), 146105.
[19] TANG Z.K., ZHANG L., WANG N., ZHANG X.X., WEN G.H., LI G.D., WANG J.N., CHAN C.T., SHENG P., Science, 292 (2001), 2462.
[20] SUN H.D., TANG Z.K., CHEN J., LI G., Appl. Phys. A, 69 (1999), 381.

Received 4 November 2006
Revised 18 December 2006