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The Interaction between Dopamine and Carbon Nanotube: A DFT and NBO Approach

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ABSTRACT

The Density Functional Theory (DFT) and the Natural Bond Orbital (NBO) calculations based method B3LYP/6-31G were carried out to study the interaction of Dopamine with carbon nanotube. The nanotube used in this study, includes 60 C atoms (6, 6) type. Relative and formation energies of compounds, Muliken charges, occupancy, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the HOMO-LUMO band gap and the electronic chemical potential (μ) were calculated. The NBO analysis showed there is a hyperconjugative interaction between Oxygen and Nitrogen lone – pair electrons of dopamine and σ^* or π^* orbitals of carbon atom of nanotube. Results indicated that the composite between nanotubes and the N-centered dopamine is more stable than O_1 - centered dopamine and both of them are stable than the single agent.

Keywords: Nanotube; Dopamine; NBO; DFT; HOMO- LUMO gap

INTRODUCTION

Dopamine (4-(2-aminoethyl) benzene-1, 2-diol and its abbreviation is DA) is available as an intravenous medication acting on the sympathetic nervous system, producing effects such as increased heart rate and blood pressure. However, because dopamine cannot cross the blood-brain barrier, it given as a drug does not directly affect the central nervous system. To increase the amount of dopamine in the brains of patients with diseases such as Parkinson's disease and dopa-responsive dystonia, L-DOPA (the precursor of dopamine), is often given because it crosses the blood-brain barrier relatively easily [1-4].

Carbon nanotubes exhibit many unique intrinsic physical and chemical properties and have been intensively explored for biological and biomedical applications. Drug molecules carried into the reticuloendothelial system are released from carbon nanotubes (CNTs) and excreted via biliary pathway without causing obvious toxic effects to normal organs. Thus, nanotube drug delivery is promising for high treatment efficacy and minimum side effects with low drug doses [5-9]. Because functionalized CNT display low toxicity and are not immunogenic such systems hold great potential in the field of nanobiotechnology and nanomedicine [10-12].

In this paper, Based on the Density Functional Theory (DFT) methods and Natural Bond Orbital (NBO) analysis, electron transport mechanism of carbon nanotube with dopamine have investigated. Finally the lowering HOMO-LUMO energy gaps have also been discussed.

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COMPUTATIONAL METHOD

All of the calculations were carried out by a pc computer which has Intel(R) Pentium(R) Dual CPU with 2 GB RAM. At first a nanotube including 60 C atoms (6, 6) is formed by Nanotube Modeler Package [13]. Then this nanotube is optimized by Gauss View [14] and Gaussian 03 software [15] by DFT/B3LYP method and 6-31G basis set (fig.1). Dopamine is made by GaussView and optimized by Gaussian 03 using B3LYP functional with the basis set 6-31G [16] (fig. 2).Then the composites between nanotube and Dopamine are formed and optimized by B3LYP/6-31G method (Fig. 3-4). Because the two Oxygen atoms have almost the same positions, one of them was studied. After optimization of composites, the single point energies obtained by B3LYP/6-311++G** method. Delocalization of electron density between the filled (bond or lone pair) Lewis type NBOs and empty antibonding non-Lewis NBOs calculated by NBO (Natural Bond Orbital) analyzing by B3LYP/6-31G level [17].

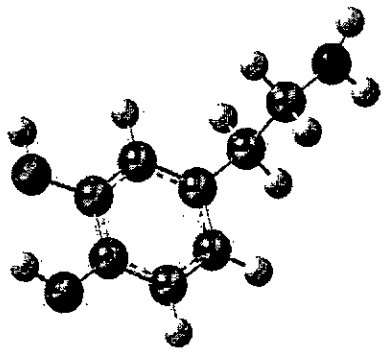

Fig. 2. Dopamine.

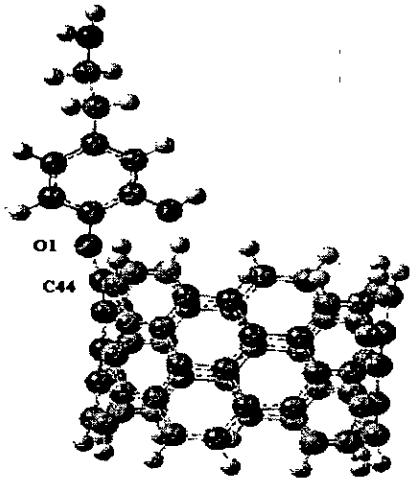

Fig. 3. Composite 1: Nanotube – (O_1 - centered dopamine).

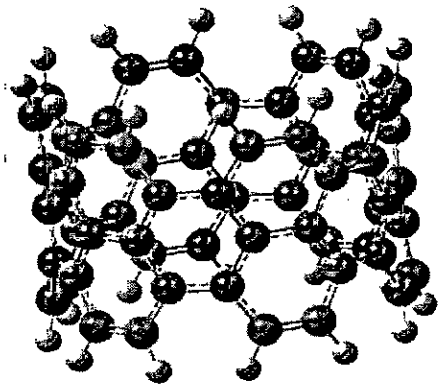

Fig. 1. Nanotube (6, 6).

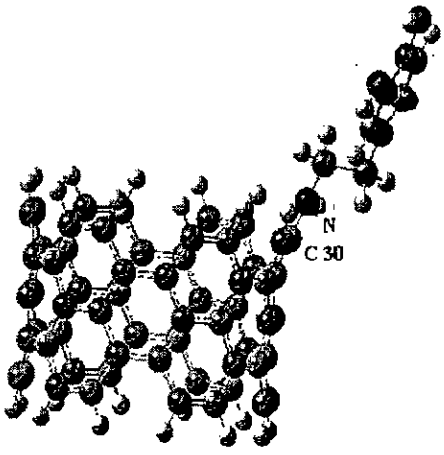

Fig. 4. Composite 2: Nanotube – (N- centered dopamine).

Table 1. NBO calculated based on the B3LYP/6-31G level

Agent	C Hybrid	C Mulliken Charge	O Mulliken Charge	N Mulliken Charge	C-O bond length/A°	C-N bond length/A°
composite 1	$SP^{3.15}$	0.0806	-0.5650	-	1.361	-
composite 2	$SP^{2.49}$	0.1983	-	-0.7144	-	1.389

RESULTS AND DISCUSSION

The results indicate that the Mulliken charges for the Carbon atoms are positive and centered atoms (Oxygen and Nitrogen) are negative. The negative charge on the O in O_1 - centered dopamine is smaller than N-centered dopamine. Therefore, the interaction in the composite 2 stronger than composite 1 that causes large negative charge on it.

The formation and relative energy values, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the HOMO-LUMO band gap and the electronic chemical potential (μ) as half of the energy of the HOMO and LUMO have been found as a measure of the structural stability properties. These descriptors for the complexes and each component listed in tables 2, 3. As can be observed the composites between drugs and nanotube are more stable than the single agents. Also the composite 2 is more stable than the composite 1. The lower HOMO-LUMO gaps confirm this stability.

Table 2. Obtained relative energies and single point energies by B3LYP/6-31G and B3LYP/6-311++G** level, respectively

Agent	Energy/kcalmol^{-1}	Single point energy/kcalmol^{-1}
Nanotube	323156.5279	323033.2589
Dopamine	1442741.7299	1442586.3490
composite 1	11.813126	-720.1916
composite 2	0	-732.0047

Table 3. Obtained some descriptors by B3LYP/6-31G level

Descriptors/ kcalmol^{-1}	composite 1	composite 2
ΔE_f	-1765886.4448	-1765898.2579
HOMO	-0.1508	-0.1549
LUMO	-0.0833	-0.0897
HOMO-LUMO GAP	0.0675	0.0652
Electronic potential energy (μ)	0.1171	0.1223

Table 4. Calculated natural hybrids, occupancies and the second-order perturbation energy E_2 at B3LYP 6-31G level

Agent	Lews-type NBOs			Non-Lews NBOs		E_2/ kcalmol^{-1}	$\sum E_2$/ kcalmol^{-1}
	Type	Hybrid	Occupancy	Type	Occupancy		
composite 1	$LP(1)_O$	$SP^{3.24}$	1.93875	π*C36-C44	0.23639	0.8	21.83
				σ*C36-C44	0.02754	6.72	
				σ*C37-C44	0.03796	1.80	
	$LP(2)_O$	$SP^{4.74}$	1.89691	π*C36-C44	0.23639	7.50	
				σ*C36-C44	0.02754	0.54	
				σ*C37-C44	0.03796	4.42	
composite 2	LP_N	$SP^{59.92}$	1.75710	□ π *C30-C24	0.31257	30.58	31.49
				σ *C30-C44	0.02343	0.91	

Delocalization of electron density between the filled Lewis type (bond or lone-pair) NBOs and empty antibonding non-Lewis NBOs lead to loss of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbitals. For each donor NBO and acceptor NBO the stabilization energy (E_2) is presented as the second-order perturbation interaction energy (E_2) [18-20]. The E_2 energy values confirmed the stability of composite 2, too. These results show the hyperconjugation between the nitrogen lone pair electrons as donors and some σ^* or π^* orbitals as acceptors can occure. The most important transfer in composite 2 is $LP_N \rightarrow$ π^*_{C30-2} and in composite 1 is $LP(2)_O \rightarrow$ π^*_{C36-4} composite 2 have the highest energy and can make the structure more stable than the other composite.

The NBO analysis also described that by increase of the LP (donor) $\rightarrow$ $\pi^*_{C=C}$ (acceptor) resonance energy and the p orbital share of the lone pair electrons of Nitrogen or Oxygen, the occupancies decrease.

CONCLUSION

In this work, the stability of Dopamine with carbon nanotube has investigated. The data and discussion in the previous sections, lead us to the following major conclusions:

-The nanotube with dopamine is more stable than the single agent.

- The nanotube- (N- centered dopamine) compound is more stable than the nanotube - (O_1 - centered dopamine).

- The Mulliken charges confirm the stability of nanotube- (N- centered dopamine).

- The stabilization of the N-center Dopamine is mainly due to LP (N) $\rightarrow$ π^*_{C30-34} charge delocalization.

- NBO analysis indicated that the higher second-order perturbation interaction (E_2) and the electronic chemical potential energy (μ) and the lower HOMO-LUMO gap in nanotube - (N- centered dopamine). Therefore, this composite is more stable than the other drug.

- The occupancy decreases with increasing p orbital share of the lone pair electrons of Nitrogen or Oxygen atoms.

REFERENCES

[1] D. Merims and N. Giladi, Parkinsonism Relat. Disord, 14 (2008) 273.

[2] L. Yavich, M. Forsberg, M. Karayiorgou, JA. Gogos and PT. Mannisto, Journal of Neuroscience, 27 (2007) 196.

[3] RD. Heijtz, B. Kolb and H. Forssberg, Physiol Behav, 92 (2007) 155.

[4] PB. Wood, Expert Rev Neurother, 8 (2008) 781.

[5] JM. Bailey, BJ. Swanson, T. Hamada, JP. Eggers, PK. Singh and T. Caffery, Clin Cancer Res, 14 (2008) 5995.

[6] Zhuang Liu, Kai Chen, Corrine Davis, Sarah Sherlock, Qizhen Cao, Xiaoyuan Chen and Hongjie Dai, Cancer Res, 68 (2008) 6652.

[7] Shanta Dhar, Zhuang Liu, Jurgen Thomale, Hongjie Dai and Stephen J. Lippard, J. Am. Chem. Soc, 130 (2008) 11467.

[8] J. Liang Zang, Q. Yuan, F. Chao Wang and Y. Pu Zhao, Computational Materials Science 46 (2009) 621.

[9] A.Favila, M. Gallo and D. Glossman, J. Mol. Mod, 13 (2007) 505.

[10] K. Kostarelos Nature, 2 (2007)108.

[11] A. Maiti, Microelectonics Jornal. Article in press, 2006.

[12] K. I. Tserpesa and P. Papanikos, Part B 36 (2005) 468.

[13] www.jcrystal.com/ products/ wincnt/ Nanotube.

[14] A. Frisch, A.B. Nielsen and A. J. Holder, Gaussview Users Manual, Gaussian Inc (2000).

[15] M. J. Frisch Gaussian03, Revision D. 01, Gaussian Inc. Walling ford CT (2004).

[16] A. D. Becke, J.chem. phys, 8 (1993) 785.

[17] L. Padmaja 1, M. Amalanathan, C. Ravikumar and I. Hubert Joe, Spectrochimica Acta A 74 (2009) 349.

[18] E. Zahedi, M. Aghaie and K. Zare, J. Mol. struct. Theochem, 905 (2009)101.

[19] H. Roohi, A. Ebrahimi, S. M. Habibi and E. Jarahi, J.Mol. Struct. Theochem, 772 (2006) 65.

[20] D.Nori-shargh, F.Roohi, F.Deyhimi, R.Naeem-Abyaneh, J. Mol.struct. Theochem, 763 (2006) 21.