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Study on Effect of Addition of Nicotine on Nanofullerene Structure C_{60} as a Medicine Nano Carrier

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ABSTRACT

In recent years, many studies have been done on structure of fullerene as medicine nano-carriers compounds. On this basis, some studies were done on this field and effect of nicotine compound on structure of nanofullerene C_{60} was studied. Mechanical quantum calculations in theory level of B3LYP/6-31G and HF/6-31G were performed on structure of nicotine and nanofullerene-nicotine with different halogen substitutions and some different properties such as energetic levels and stability, HOMO and LUMO levels, chemical hardness, chemical potential and electrophilicity value were studied. The obtained results showed that energy levels decreased considerably by linking structure of nicotine to structure of nanofullerene C_{60} and study of dipole moment values shows that linking between nicotine to nanofullerene C_{60} reduces its solubility. In study of some other characters such as chemical potential, chemical hardness, electrophilicity in these two structures showed that change in substitution (X=F, Cl, Br and H) changed values of these parameters. These changes show dependency of the results on power of electro negativity and atomic radius of substitution X.

Key words: DFT; Electrophilicity; Chemical hardness; Chemical potential; Nano Fullerene.

INTRODUCTION

Nicotine was obtained from tobacco for the first time in 1828 by a Germany chemist[1,2]. Melsen obtained its chemical formula experimentally in 1843[3] and nicotine was processed for the first time in the laboratory in 1893[4]. Nicotine is a nitrogen organic compound which is mostly found in plants such as tobacco and rarely found in tomato, potato, eggplant and green pepper. The 0.3% to 5% of the tobacco dried plant is made by nicotine and is effective on neural system which is used in many insecticides. Nicotine is a biological stimulus in smaller sizes and causes addiction and many mental characteristics f tobacco smoke[5,6]. This chemical material has molecular formula of $C_{10}H_{14}N_2$ and its chemical name is 3-[(2*S*)-1-methylpyrrolidin-2-yl]pyridine. This compound had different chemical and medical effects such as increased sobriety, memory, and activity but it results in heartbeat, blood pressure and decreased appetite in larger sizes. Nicotine is a stimulating and depressing and its effect is made evident on the basis of consumption method. Studies show that as small sizes have stimulating effect, larger sizes cause depression[7-20]. Fullerene is one of the

other artificial forms of carbon element which is made by heating graphite. Due to its similarity to ball, it is called buckyball. Fullerene has different types and can be as spherical, elliptical and cylindrical. Kroto and Curl are known as discoverers of fullerene. In 1990, Wolfgang Kratschmer and Donald Huffman et al described the first practical method C_{60}[21]. this material was prepared for the first time with formula C_{60} in 1985 by Richard Smalley, Robert Curl, James Heath, Sean O'Brien, and Harold Kroto at Rice University of Texas State[22]. Low solubility of the fullerenes in fluids limits application of these materials as medicinal effective material. But hydrophobic size, three-dimensionality and electron properties cause its use as medicine. For example, their spherical form causes ability and position of fullerene molecules in enzymes or cells hydrophobic solutions. This action causes interesting medicinal properties which increase rate of such characters by adding nano properties of this structure[23-25]. The electrophilicity concept was expressed for the first time in 1999 by Parr et al [26]. The electrophilicity index, which measures the stabilization in energy when the system acquires an additional electronic charge, ΔN, from the environment is given by equation 8 and is presented in terms of the electronic chemical potential, μ (the negative of electronegativity, χ) and the chemical hardness, η. Both quantities may be approximated in terms of the energies of frontier molecular orbitals (ε_{HOMO} and ε_{LUMO}) as $\eta = (\varepsilon_H + \varepsilon_L)/2$ and $\eta = \varepsilon_L - \varepsilon_H$ (Eqs. 9 and 10). Electrophilicity can also be approximated in terms of the ionization potential (I) and electron affinity (A) (Eqs. 8-10)[26]. High values of μ and low values of η, characterize a good electrophone species. The maximum amount of electronic charge, ΔN_{max}, that the electrophone system may accept is given by equation 11 as[26]. Thus, while the quantity of ù describes the propensity of the system to acquire additional electronic charge from the environment, the quantity of ΔN_{max} describes the charge capacity of the molecule[26].

$$\omega = \mu^2/2\eta = \chi^2/2\eta \quad ...(8)$$

$$\chi = -\mu = -(\delta_E/\delta_N)_{V(r)} = (I+A)/2 = -1/2(\varepsilon_{HOMO} + \varepsilon_{LUMO}) \quad ...(9)$$

$$\eta = (\delta_{2E}/\delta_{N2})_{V(r)} = (I-A) = (\varepsilon_{LUMO} - \varepsilon_{HOMO}) \quad ...(10)$$

$$\Delta N_{max} = -\mu/\eta \quad ...(11)$$

Computational Methods

All structures relating to structure of nicotine and nano fullerene nicotine (NFN) were

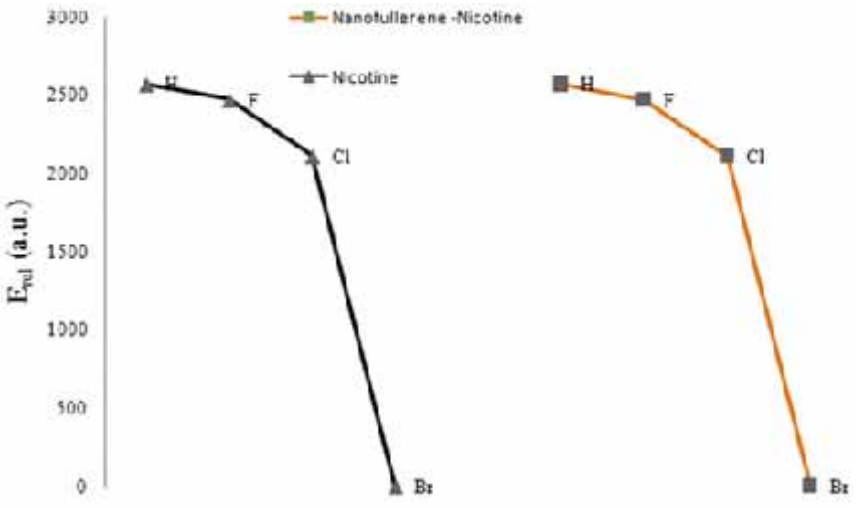

Fig 1. Comparison of relative energies for Nicotine and Nano Fullerene-Nicotine attach obtained by HF/6-31G level of theory.

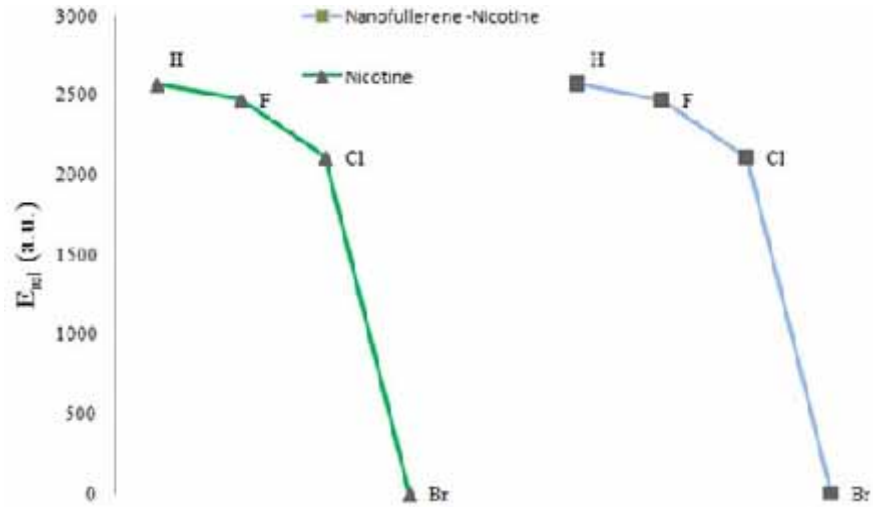

Fig 2. Comparison of relative energies for Nicotine and Nano Fullerene-Nicotine attach obtained by B3LYP/6-31G level of theory.

designed primarily with use of *Chemoffice 2005* and nanotube modeler version 1.3.0.3 softwares, primary optimizations of structures were done with use of AM1 method. In order to do final optimization, *GAUSSIAN W98* program of package, B3LYP and HF method were used. However, for this purpose, 6-31G basis set was used. Total computations were done with use of Pentium IV computer with processor Intel® core i7 with memory of 4 gigabytes and inside the operating system of windows XP®. All computations were performed under gas phase, 1 atmosphere pressure and 298 Kelvin temperature.

RESULTS AND DISCUSSION

At first, all results were extracted and we discussed and concluded finally. On the basis of these results, some separate issues such as energetic characters, electrophilicity, chemical potential, chemical hardness and dipole moment values were discussed of which results in this section (Fig 3).

Energetic indices

Energy property and stability

In order to compare energetic levels, extracted electron energy of nicotine and nano fullerene nicotine attach structure with different halogen substitutions(Table 1). Energetic levels have direct relationship with stability and our compounds so that the more negative the rate, the more stable our structure thermodynamic. In order to compare two different states when structure of nicotine is used individually and when nicotine was sued in combination with nano fullerene structure, calculated relative energy values. On this basis, considered the lowest energy level zero and tested other compound. In both states, our energetic levels changed by changing substitution type so that the more the atomic radius of substitution, the lower the energetic levels. Comparison of two different states when studied nicotine individually with the time when nicotine was used on nano fullerene structure shows that use of nano fullerenes causes to increase stability and decrease energy level (Fig 1 and 2).

Dipole moment

The reason for moment is an effective factor which has direct relationship with solubility and the more this parameter, the more the solubility inside the polar solvent. Structure of nicotine changes considerably by changing type of substitution due to small structure so that the more electronegative our substitution, the more dipole the moment. But in nano fullerene-nicotine attach compounds, this trend follows change of atomic radius and effect of electronegativity of substitutions decreases to great extent. The more the atomic radius of substitution, the lower the dipole moment will be (Table 1).

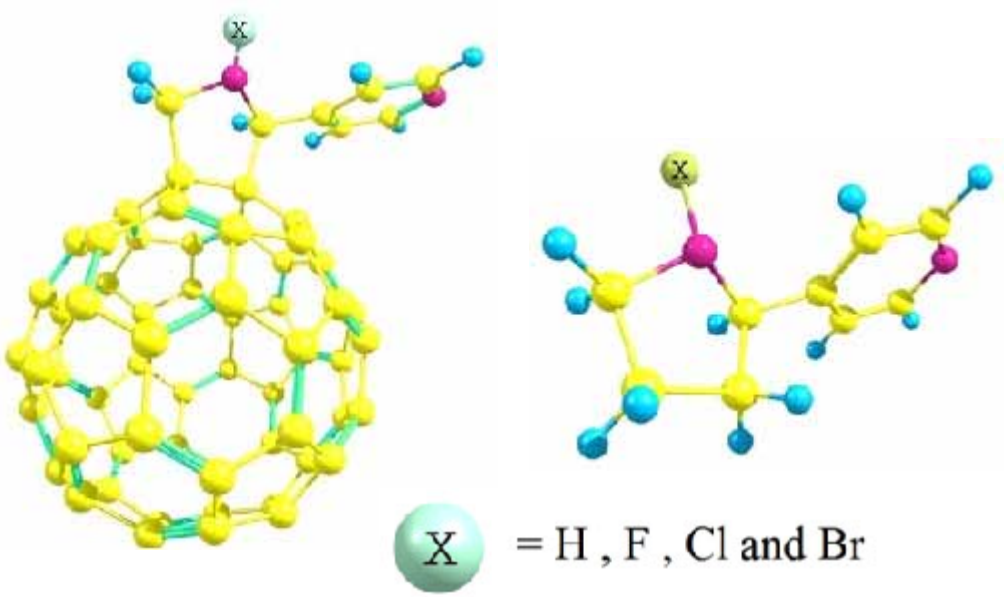

Fig 3. Various show of Nicotine and Nanofullerene-Nicotine attach conformation.

Table.1: Calculated Electronic energy (a.u.), Relative energy (a.u.), Dipole moment (Debye) for the Nicotine and Nano Fullerene-Nicotine by B3LYP/6-31G and HF/6-31G levels of theory.

Method			**HF/6-31G**		
Structure	**X**	**Entry**	**E_{ele} (a.u.)**	**E_{rel} (a.u.)**	**Dipole moment (Debye)**
Nicotine	H	1a	- 456.4968	2569.1472	4.1479
	F	2a	-555.2564	2470.3876	5.2288
	Cl	3a	-915.3347	2110.3093	5.0058
	Br	4a	-3025.6441	0.0000	4.6826
Nanofullerene -Nicotine	H	1b	-2649.4494	2569.1450	4.0017
	F	2b	-2748.2051	2470.3893	3.2674
	Cl	3b	-3108.2835	2110.3110	3.0246
	Br	4b	-5218.5945	0.0000	2.9683
Method			**B3LYP/6-31G**		
Nicotine	H	1c	-459.5448	2570.9460	4.0200
	F	2c	-558.7011	2471.7896	4.8593
	Cl	3c	-919.0881	2111.4026	4.8085
	Br	4c	-3030.4908	0.0000	4.4813
Nanofullerene-Nicotine	H	1d	-2666.5344	2570.9436	3.8140
	F	2d	-2765.6872	2471.7908	3.0442
	Cl	3d	-3126.0740	2111.4041	2.9344
	Br	4d	-5237.4781	0.0000	2.7760

Table. 2: Calculated ε_{HOMO} and ε_{LUMO} (eV), Chemical hardness h, chemical potential η, electrophilicity values ω and maximum amount of electronic charge transfer ΔNmax in atomic units, for the Nicotine and Nano Fullerene-Nicotine by B3LYP/6-31G and HF/6-31G levels of theory.

Method			HF/6-31G					
Structure	**X**	**Entry**	**HOMO**	**LUMO**	**μ**	**η**	**ω**	**ΔN_{max}**
	H	1a	-0.34270	0.13082	-0.10594	0.47352	0.01185	0.22372
	F	2a	-0.34778	0.10923	-0.11927	0.45701	0.01556	0.26099
Nicotine	**Cl**	3a	-0.34980	0.11818	-0.11581	0.46798	0.01432	0.24746
	Br	4a	-0.34778	0.10923	-0.11927	0.45701	0.01556	0.26099
	H	1b	-0.28043	-0.01552	-0.14797	0.26491	0.04132	0.55858
Nanofullerene -Nicotine	**F**	2b	-0.28821	-0.02245	-0.15533	0.26576	0.04539	0.58447
	Cl	3b	-0.28677	-0.02125	-0.15401	0.26552	0.04466	0.58003
	Br	4b	-0.28528	-0.01994	-0.15261	0.26534	0.04388	0.57514
Method			**B3LYP/6-31G**					
	H	1c	-0.20912	-0.01655	-0.11283	0.19257	0.03305	0.58594
	F	2c	-0.24194	-0.02472	-0.13333	0.21722	0.04091	0.61380
Nicotine	**Cl**	3c	-0.24236	-0.06307	-0.15271	0.17929	0.06503	0.85177
	Br	4c	-0.23931	-0.06456	-0.15193	0.17475	0.06604	0.86944
	H	1d	-0.21768	-0.12051	-0.16909	0.09717	0.14712	1.74019
Nanofullerene -Nicotine	**F**	2d	-0.22486	-0.12725	-0.17605	0.09761	0.15877	1.80365
	Cl	3d	-0.22433	-0.12689	-0.17561	0.09744	0.15824	1.80223
	Br	4d	-0.22287	-0.12553	-0.17420	0.09734	0.15587	1.78960

Table 3: Relative chemical hardness h, relative chemical potential η, relative electrophilicity ω, and relative maximum amount of electronic charge transfer ΔN_{max}, for the Nicotine and Nano Fullerene-Nicotine by B3LYP/6-31G and HF/6-31G levels of theory.

Method			HF/6-31G			
Structure	X	Entry	μ_{rel}	η_{rel}	ω_{rel}	$\Delta N_{max(rel)}$
	H	1a	0.04939	0.20861	0.00000	0.00000
Nicotine	F	2a	0.03606	0.19210	0.00371	0.03727
	Cl	3a	0.03952	0.20307	0.00247	0.02374
	Br	4a	0.03606	0.19210	0.00371	0.03727
	H	1b	0.00736	0.00000	0.02947	0.33486
Nanofullerene -Nicotine	F	2b	0.00000	0.00085	0.03354	0.36075
	Cl	3b	0.00132	0.00061	0.03281	0.35631
	Br	4b	0.00272	0.00043	0.03203	0.35142
Method			**B3LYP/6-31G**			
	H	1c	0.06322	0.09540	0.00000	0.00000
Nicotine	F	2c	0.04272	0.12005	0.00786	0.02786
	Cl	3c	0.02334	0.08212	0.03198	0.26583
	Br	4c	0.02412	0.07758	0.03299	0.28350
Nanofullerene -Nicotine	H	1d	0.00696	0.00000	0.11407	1.15425
	F	2d	0.00000	0.00044	0.12572	1.21771
	Cl	3d	0.00044	0.00027	0.12519	1.21629
	Br	4d	0.00185	0.00017	0.12282	1.20366

HOMO and LUMO indices

Chemical potential

In order to compare the obtained results, consider the lowest value zero and measured other values. On the basis of the obtained results, when structure of nicotine is linked to nano fullerene, it decreases chemical potential of the structure but change of substitution will be effective on chemical potential. Increase of electronegativity property enhances substitution of the structure chemical potential. This trend was obtained for nanofullerene-nicotine attach structure. The obtained trend for nicotine is only based on chemical potential as H>Cl>Br=F in HF method and as H>F>Br>Cl with use of B3LYP method (Table 2).

Chemical hardness

This factor is effective on solubility and it decreases considerably by linking nicotine to structure of nanofullerene. In nanofullerene-nicotine attach, chemical hardness changes by changing substitution X. On this basis, the more electronegative the substitution, the more the parameter value will be. But we will have another trend in nicotine structure so that have H>CL>Br=F in HF method and H>F>Br>Cl with use of B3LYP method (Table 2).

Electrophilicity index

Electrophilicity value in nanofullerene-nicotine attach structure follows a regular trend so that the more electronegative the substitution X, the more the parameter value will be. But it doesn't follows regular trend so that have F=Br> H>Cl>H in HF method and Cl>Br>F>H with use of B3LYP method (See Table 2). Linkage between nicotine and nanofullerene structure will not change electrophilicity results.

Maximum amount of electronic charge transfer

As mentioned above, most electron charge which a system accepts can be calculated by parameter ΔN_{max}. The obtained results for this parameter were obtained like the previous parameters. For nanofullerene-nicotine attach, changes trend is based on increase of ΔN_{max} so that the more electronegative the substitution X, the more the parameter value will be. But have F=Br>H>Cl>H

in HF method and Br>Cl>F>H with use of B3LYP method (Table 2). The results show that decrease of atomic radius reduces this parameter.

CONCLUSION

Quantum mechanic calculation in theoretical level of HF and B3LYP on two structures of nicotine and nanofullerene-nicotine attach shows that link between nicotine structure and nanofullerene structure C_{60} decreases energetic levels of this structure and the structure will be more stable. Increase of atomic radius of substitution X decreases energy level but changes cause to decrease dipole moment. Link between nicotine and nanofullerene C_{60} changes energetic HOMO and LUMO levels and chemical potential, chemical hardness, and electrophilicity change so that these changes have direct relationship with atomic radius of substitution X and electronegativity of substitution X.

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