Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 7 (4) 279-284: Winter 2011
(J. Phys. Theor. Chem. IAU Iran)
ISSN: 1735-2126

Computational Investigation on Alcohol Nano Sensors in Combination with Carbon Nanotube; A Monte Carlo and Ab Initio Simulation

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Received January 2011; Accepted February 2011

ABSTRACT

Single walled nanotubes (SWNT) are common interested nanovehicle to make biosensors more sensitive. Carbon nanotubes (CNTs) have many distinct properties make them to be exploited to develop the next generation of such nano sensors .The Keto-Enol tautomerization is one of the most common investigated subjects of isomerism in this regards, sensors are devices that are able to detect and change the physical properties of such reactions to measurable electrical signal. Some chemicals with the properties to do Keto-Enol tautomerization are substituted to CNTs and the physico chemical properties are simulated. Hyperchem is used as main software to design the CNT Sensor and the main physical properties are calculated after monte carlo simulation. The systems have been optimized at first by UFF method. In all situation the energy minimization have been done by MM^+ and the fully optimized systems have transferred to Guassian98, after final optimization with 6-31G , HF method. The stability, electrical changes and physico chemical properties were calculated and compared to find in which situation Caffeic Acid and SWNT have the most stability state.

Keywords: Caffeic Acid; Chloro-genic acid; Hydrazine; keto and enol tautomerism; Single-walled carbon nanotube

INTRODUCTION

Sensors continue to make a significant impact on everyday life. It has been a strong demand for producing highly selective, sensitive, responsive, and cost-effective sensors [1]. Carbon nanotubes (CNTs) have many distinct properties that may be exploited to develop the next generation of sensors. Utilization of these properties has led to applications of individual nanotubes or ensembles of nanotubes as scanning probes [2,3] electron field emission sources [4] ,actuators [5] ,and nano-electronic devices [6]. Here we report the realization of individual semiconducting single walled carbon nanotube (S-SWNT)-based chemical sensors capable of detecting small concentrations of alcohol gas molecules through quantum mechanical calculations of thermochemical and other electronic structural parameters. The nanotube sensors show a fast response and a substantially higher sensitivity than that of existing solid-state sensors at room temperature. Sensor reversibility is succeeded by slow recovery under ambient conditions or by heating to high temperatures [7]. The interactions between molecular species and SWNTs and the mechanisms of molecular sensing with nanotube molecular wires have been of great interest to the authors.

Catechol compounds including quinizarine, caffeic acid (Fig.1), catechine hydrate ,chlorogenic acid(Fig.2), pyrocatechol, hematoxylin,rutin, coumestan, 3,4-dihydroxybenzaldehyde and other derivatives, have been used as electron transfer mediators in electrochemical processes due to their high electron transfer efficiency, excellent redox reversibility and low cost. The catechol derivative mediators were immobilized on the electrodes surfaces by methods such as adsorption [8], mixing

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into carbon paste, direct electropolymerization and sol-gel techniques [9]. They also have some disadvantages, such as significant leaching of electron transfer mediator, poor long term stability, complex preparation procedure and time consuming for fabrication as well as renewing. Carbon nanotubes (CNTs) are new kinds of carbon nanostructure materials possessing properties such as high electrical conductivity, high surface area, chemical stability and significant mechanical strength [10]. They can be used to encourage electron transfer reactions when applied as electrode materials in electrochemical devices [11]. The keto↔enol tautomerism is one of the most common investigated subjects of isomerism that occurs for carbonyl compounds. Sensors are devices that detect or measure physical and chemical quantities such as temperature, pressure, sound and concentration. The main requirements of a good sensor are high sensitivity, fast response, low cost, high volume production and high reliability. In this work, alcohol sensors based on SWNT have been considered. Generally, the keto form is more stable than the enol form for neutral systems.

The results for oxidation of hydrazine were observed.

caffeic acid (reduced form) → caffeic acid (oxidation form) $+2e^- +2H^+$ (1)

2caffeic acid (oxidation form) + N_2H_4→ N_2+2caffeic acid (reduction form)[9]. (2)

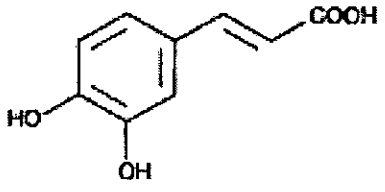

Fig. 1. 3,4-dihydroxy cinamic acid(Caffeic Acid).

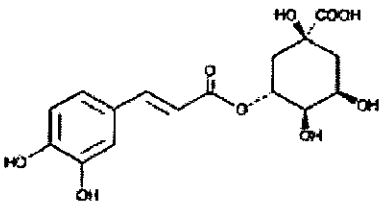

Fig. 2. 3,4-dihydroxycinamate(chloro-genic acid)(CGA).

THEORETICAL METHODS

There are three steps in carrying out any quantum mechanical calculation in HyperChem 7.0 program package [12]. First, prepare a molecule with an appropriate starting geometry. Second, choose a calculation method and its associated (Setup menu) options. Third, choose the type of calculation (single point, geometry optimization, molecular dynamics, Langevin dynamics, Monte Carlo (MC), and vibrational analysis with the relevant (Compute menu) options. These geometry optimization calculations can use either molecular mechanics or quantum mechanics to further refine the molecular geometry beyond that given by the Model Builder. HyperChem uses the Metropolis method [13], which chooses random configurations with this probability, to concentrate sampling of configurations in regions of space that make important contributions to the calculation of thermodynamic averages.

Monte Carlo simulation

In order to compute the average properties from a microscopic description of a real system, one should evaluate integrals over phase space. This may be calculated for an N-particle system in an ensemble with distribution function $P(r^N)$, the experimental value of a property $A(r^N)$ from:

$$\langle A(r^N)\rangle = \int A(r^N)P(r^N)dr^N \quad (3)$$

For MC calculation the energies are essentially the only quantities available from a single point calculation. An analysis of the components of this molecular mechanics energy is placed in the log file for further detail. In the case of MM^+, a much more complete description of the individual contributions to the energy, including individual stretch energies, bending energies, etc., is placed in the log file along with the system dipole moment, if bond dipoles are available.

The accuracy of the semi-empirical quantum mechanics method depends on the database used to parameterize the method. We can use the information obtained from semi-empirical calculations to investigate many thermodynamic and kinetic aspects of chemical processes. Energies and geometries of molecules have clear relationships to chemical phenomena.

Ab Initio NMR parameters

In this work we investigate some NMR parameters which were calculated by formula below:

If $|\sigma_{11}-\sigma_{iso}| \geq |\sigma_{33}-\sigma_{iso}|$, $\Delta\sigma$, Chemical Shift Anisotropy, η, Asymmetry Parameter, Ω, Shielding Tensor Anisotropy for molecule and κ, slop are shown as below:

$$\Delta\sigma = \sigma_{11} - \frac{\sigma_{22}+\sigma_{33}}{2} \quad (4)$$

$$\eta = \sigma_{11} - \frac{\sigma_{22}+\sigma_{33}}{\sigma} \quad (5)$$

$$\sigma = \sigma_{11} - \sigma_{iso} \quad (6)$$

If $|\sigma_{11}-\sigma_{iso}| \leq |\sigma_{33}-\sigma_{iso}|$:

$$\Delta\sigma = \sigma_{33} - \frac{\sigma_{22}+\sigma_{11}}{2} \quad (7)$$

$$\eta = \frac{\sigma_{22}-\sigma_{11}}{\sigma} \quad (8)$$

$$\sigma = \sigma_{33} - \sigma_{iso} \quad (9)$$

$$\Omega = \sigma_{33} - \sigma_{11} \quad (10)$$

$$k = \frac{3(\sigma_{iso}-\sigma_{22})}{\Omega} \quad (11)$$

and

$$\sigma_{iso} = \frac{(trace\hat{\sigma})}{3} = \frac{\sigma_{11}+\sigma_{22}+\sigma_{33}}{3} \quad (12)$$

There are some method for Ab initio NMR parameter such as Gauge-Including atomic orbitals (GIAO), Individual gauge for localized orbitals (IGLO), Localized orbitals local origin (LORG) and Continuous set of gauge transformations (CSGT).

RESULT AND DISCUSSION

CNTs (7,4) have been used as sensing materials in pressure, flow, thermal, gas, optical, mass, position, stress, strain, chemical and biological sensors .The sensor was based on the principle that the electronic properties of CNTs change when subjected to strains. The isotropic nature of CNT films helps in measuring strains in multiple locations and in different directions. First we linked Caffeic Acid and SWNT by HyperChem 7.0 then we use single point to study transitional energy and rotational energy which shown in Table 1. We have shown in Fig. 4. that Caffeic Acid and SWNT in which distance have the most stability condition. So we have selected atom C_{70} from SWNT(7,4) and atom H_{161} of Caffeic Acid in all situation.We have seen minimum energy is in 2.7 angstrom. Table 2 is showing potential energy values in some temperatures to compare in various solvent that comes in Fig. 5. for the linking of Caffeic Acid and SWNT , and Figure 6 for the linkage of CGA and SWNT. In this work solvents are vacuum, water, methanol and ethanol. Also, we calculated NMR chemical shielding tensors data that shown in Table 3. Corresponding to isotropic shielding tensor, 4^{th} and 7^{th} atoms in Caffeic Acid have more electronic density than other atoms. The 4^{th} and 7^{th} atoms are characterized in Fig 3.

Table 1. The Thermodynamic properties of reaction between Caffeic Acid with SWNT (7,4) by B3LYP/6-21G method

Compounds	Angles	Rotational Energy(kcal/mol)	Distances (Å)	Transitional Energy(kcal/mol)
SWNT (7,4)	0.0,0.0,0.0	-1389360.346	3.1	-1389316.508
	0.0,0.0,20.0	-1389360.297	3.0	-1389316.531
	0.0,0.0,60.0	-1389360.257	2.9	-1389316.555
	0.0,0.0,100.0	-1389358.843	2.8	-1389316.569
	0.0,0.0,160.0	-1389349.067	2.7	-1389316.570
	0.0,0.0,180.0	-1389349.473	2.6	-1389316.577
	0.0,0.0,200.0	-1389349.902	2.5	-1389316.552
Caffeic Acid	0.0,0.0,0.0	-1389360.346	2.4	-1389316.461
	0.0,0.0,335.0	-1389360.138	2.3	-1389316.287
	0.0,0.0,350.0	-1389360.386	2.2	-1389315.987
	0.0,270.0,3.0	-1389360.096	2.1	-1389315.515
	2.0,340.0,0.0	-1389360.332	2.0	-1389314.792
	4.0,300.0,0.0	-1389360.329	1.9	-1389313.667
	7.0,280.0,0.0	-1389360.340	1.8	-1389311.985
	10.0,285.0,0.0	-1389360.345	1.7	-1389309.586
	15.0,315.0,0.0	-1389360.344	1.6	-1389306.177

Table 2. MC investigation in four solvent for the linking of Caffeic Acid – SWNT and CGA – SWNT in various temperature.

Comp.	Solvent	Temperature (K) 260	280	300	320	340	360	380	400
Caffeic Acid	Gas	833.84	725.73	839.952	743.305	753.157	781.872	782.11	794.75
	Water	972.285	1016.41	1039.18	1026.74	1041.94	1103.95	1106.65	1149.83
	Methanol	1515.04	2057.12	1624.87	1655.12	1847.56	1918.75	2067.8	2060.79
	Ethanol	3576.61	3544.84	3323.58	3589.99	3929.88	3492.58	3644.08	3654.08
CGA	Gas	830.651	711.383	693.412	712.862	745.714	776.318	775.096	771.555
	Water	710.495	733.531	727.157	770.008	794.07	783.744	775.271	820.384
	Methanol	812.704	877.307	887.733	865.396	921.972	923.768	980.351	927.741
	Ethanol	849.184	863.483	861.479	939.981	951.521	948.491	1008.41	982.868

Table 3. NMR isotropic and anisotropic values of Caffeic Acid at HF/6-31G

Compound	NMR Values					
	Number Of Atom	σ Isotropic	σ Anisotropic	η	δ	$\Delta\sigma$
Caffeic Acid	C1	61.6194	138.8688	0.7632	92.5792	138.8688
	C2	80.3350	147.3987	0.7698	98.2658	147.3987
	C3	62.5476	133.9517	0.7884	89.3011	133.9517
	O4	271.5244	64.7982	0.9608	-44.0623	-66.0934
	C5	77.1763	182.5536	0.4987	121.7024	182.5536
	C6	90.9817	145.0146	0.8993	96.6764	145.0146
	O7	269.4238	40.5730	0.5126	-35.7641	-53.6462
	C8	85.8916	174.0110	0.7212	116.0073	174.011
	C9	54.4626	176.8880	0.9053	-123.7887	-185.683
	C10	94.0275	112.1071	0.5167	-98.9474	-148.4211
	C11	29.2104	127.1824	0.3419	-126.3643	-143.3502
	O12	-111.1612	639.0308	0.2553	426.0206	292.3273
	O13	181.5456	173.2452	0.5713	-147.0081	-220.5122
	H14	26.1194	12.5034	0.3196	8.3356	5.5857
	H15	28.0359	31.1053	0.2577	20.7369	13.4378
	H16	27.2446	11.4052	0.3955	7.6035	11.3996
	H17	31.6396	11.5636	0.3658	-11.2879	16.9318
	H18	25.9523	9.2480	0.9055	6.1653	9.248
	H19	25.1353	13.2387	0.0781	8.8259	13.2388
	H20	27.0721	10.2729	0.5052	6.8486	10.273
	H21	28.4265	14.6335	0.1808	9.7557	14.7235

Table 4. Thermodynamic functions of Caffeic Acid at HF/6-31G

Thermodynamic Function	ΔS	ΔH	ΔG
0°	8.491	-1.9262506	-2.898277
30°	7.717	-3.005201	-3.844839
60°	6.982	-3.592495	-4.340824
90°	7.678	-2.434646	-3.268985
120°	-0.443	-1.813032	-1.631427
160°	2.088	-1.844091	-1.980601
270°	2.028	-1.772099	-1.901078

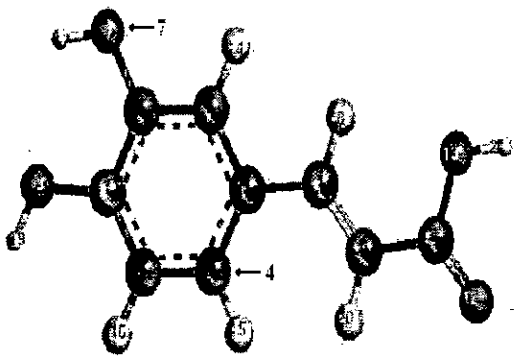

Fig.3. 4th and 7th atoms in Caffeic Acid.

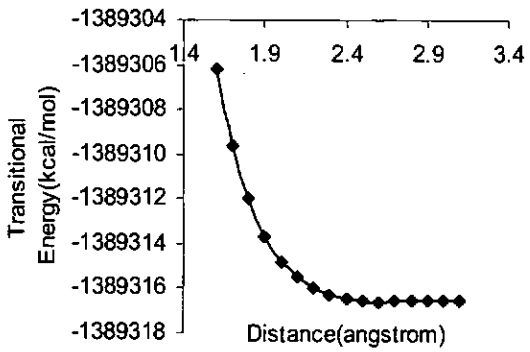

Fig. 4. Transitional Energy versus distance between Caffeic Acid and SWNT.

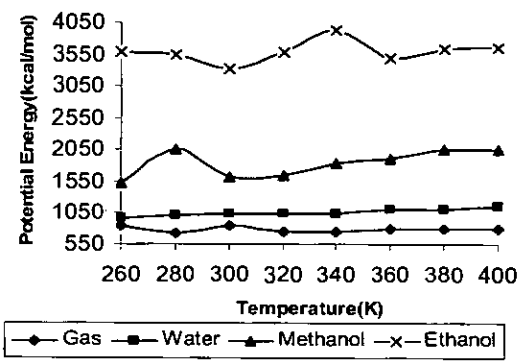

Fig. 5. Potential energy vs. temperature for Caffeic Acid and SWNT.

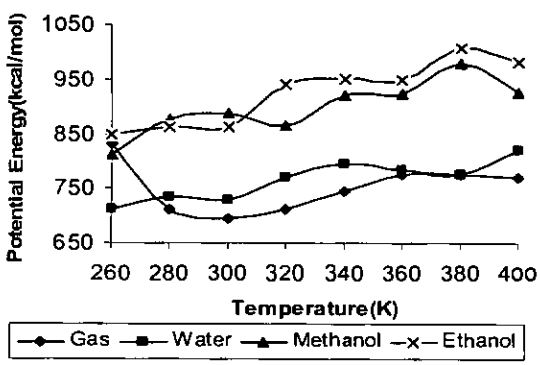

Fig. 6. Potential energy vs. temperature for CGA and SWNT.

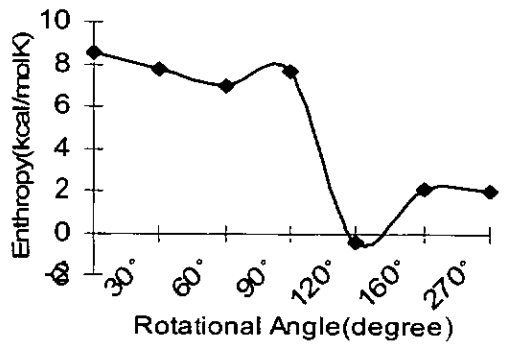

Fig.7. The lower Enthropy difined in 120 degree.

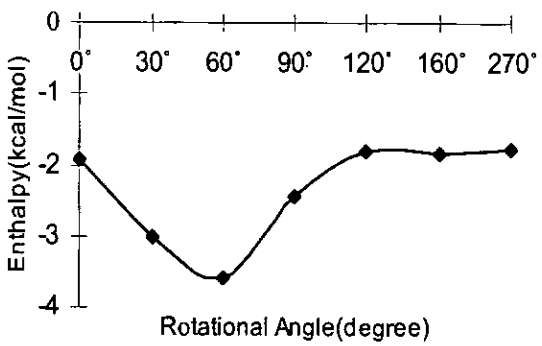

Fig.8. The most stahility condition of Caffeic Acid in rotational angle equal to 60 degree.

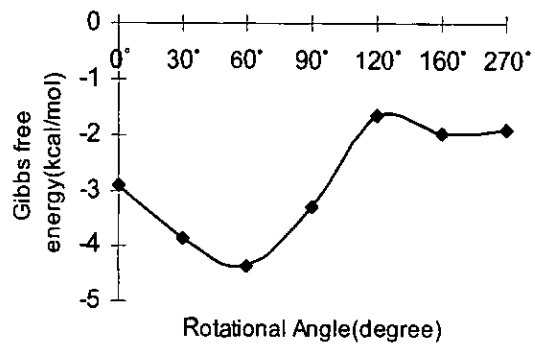

Fig.9. The most stability condition of Caffeic Acid in rotational angle equal to 60 degree.

Also, we worked on a single bond in Caffeic Acid which stand between aromatic and aliphatic groups .Then study on rotation of Caffeic Acid (by Guassian98) around the single bond afford some thermodynamic functions that shown in Table 4. In figures 7 - 9 that is shown calculated thermodynamic functions for rotation around the single bond we can find most stability condition of Caffeic Acid in rotational angle equal to 60 degree.

CONCLUSION

The current research sets a goal to investigate the interactions between the molecules of caffeic acid or CGA and carbon nanotubes. These calculations will carry find the most preferable tautomer in keto↔enol tautomerism which fulfills the structural stability. The sensors developed with alcohols were found to have good selectivity and sensitivity and were unaffected by various environmental conditions. MC investigation shows CGA linkage has the lower energy than Caffeic Acid linkage. Also these two linkages have the most stability situation in 260 K and Methanol solvent.

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