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ORIGINAL PAPER

Computational investigation on alcohol nanosensors in combination with carbon nanotube: a Monte Carlo and ab initio simulation

M. Monajjemi · M. Falahati · F. Mollaamin

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Abstract Single-walled nanocarbons (SWNT) are common nanovehicles of interest for making biosensors more sensitive. Carbon nanotubes (CNTs) have many distinct properties, causing them to be exploited in the development of the next generation of such nanosensors. The keto–enol tautomerization is one of the most common investigated subjects of isomerism in this regard; sensors are devices that are able to detect and change the physical properties of such reactions. Some chemicals with the properties to do keto–enol tautomerization are substituted to CNTs, and the physicochemical properties are simulated. HyperChem is used as the main software to design the CNT sensor, and the main physical properties are calculated after Monte Carlo simulation. In all situations, the energy minimization has been done by MM^{+}, and the fully optimized systems have transferred to Guassian98. After final optimization with 3–21 G, Hartree–Fock (HF) method, SWNT have been linked up to caffeic acid and chlorogenic acid. Then, frequency and intensity were investigated using AM1 and PM3 codes. Also, we determined some nuclear magnetic resonance parameters in the HF method and several basis sets.

M. Monajjemi (✉)
Department of Chemistry, Science and Research Branch,
Islamic Azad University,
Tehran, Iran
e-mail: m_monajjemi@yahoo.com

M. Falahati
Science and Research Branch, Islamic Azad University,
Tehran, Iran

F. Mollaamin
Department of Chemistry, Qom Branch, Islamic Azad University,
Qom, Iran

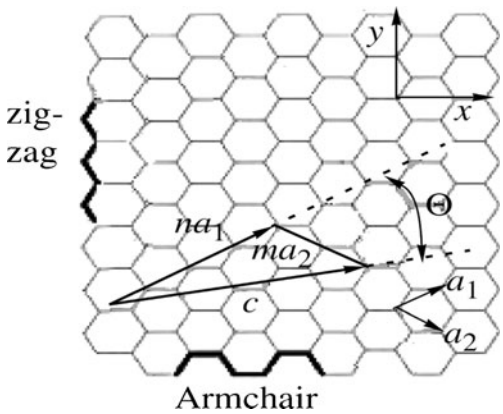
Keywords Caffeic acid · Chlorogenic acid · Single-walled carbon nanotube

Introduction

The carbon nametape (carbon nanotubes, CNT) is a representative nanomaterial. CNT is a cylindrically shaped carbon material with a nanometer-level diameter. Its structure, which is in the form of a hexagonal mesh, resembles a graphite sheet, and it carries a carbon atom located on the vertex of each mesh. The sheet is rolled, and its two edges are connected continuously. Although it is a common place material that is used in pencil leads, its unique structure causes it to present characteristics that are not found in any other materials. CNT can be classified into single-walled CNT, double-walled CNT, and multi-walled CNT on the basis of the number of layers of the rolled graphite. The type attracting the most attention is the single-walled CNT, which has a diameter deserving the name of "nanotube" of 0.4–2 nm. The length is usually in the order of microns, but the single-walled CNT with a length in the order of centimeters has recently been released. Since the discovery of single-walled nanotubes (SWCNTs) by Iijima and Bethune in 1993 [1], many applications as molecular components for nanotechnology including conductivity and high-strength composites; energy storage and energy conversion devices; sensors; field emission displays and radiation sources; hydrogen storage media; and nanometer-sized semiconductor devices, probes, and interconnects are known [2]. The best-known example for a sudden change in the nanotube properties with their particular structure is their electronic dispersion. Depending on the direction, the confinement direction with respect to graphite nanotubes is metallic or semiconducting. The band structure can even be further

manipulated, by introducing defects into a tube. So, the discovery of CNTs which are nanosized materials with excellent mechanical and electrical properties has been proposed to be used in a variety of application fields [3]. CNTs are a new allotrope of carbon originated from the fullerene family, which will revolutionize the future nanotechnological devices [4]. There are two types of CNTs: single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs) [5]; they have three conformations: armchair, zigzag, and chiral, and these conformations have individual properties. In this paper, we look at single-walled nanotubes since their properties are more reliable for nanoelectronic device purposes. Also, depending upon their chirality, diameter, and electronic structure, carbon nanotubes can be metallic or semiconducting. Multi-walled carbon nanotubes have a layer of carbon shells with differing physics that can all potentially interact. It is shown that only the outer shell of MWCNTs contributes to electrical transport, and so, only small-diameter MWCNTs could be used to make transistor devices. SWCNTs can be chiral or nonchiral, again depending on the way of the rolling up vector (Scheme 1).

As described earlier, the properties of nanotubes are determined by their diameter and chiral angle, both of which depend on n and m. Typically, SWCNT is presented by a pair of integers (n, m). Its geometrical structure as shown in Fig. 1 can be represented in terms of a chiral vector **C** on a two-dimensional sp^2_carbon sheet where $\mathbf{C}=n\mathbf{a}_1+m\mathbf{a}_2=(n,\ m)$ with integer n and m. Here, $\mathbf{a}_1$ and $\mathbf{a}_2$ represent the unit vectors of the hexagonal graphene lattice. This sheet is then rolled up to a cylinder so that **C** becomes the circumference of the tube. The direction of the nanotube axis is naturally perpendicular to **C**. The diameter, d, is simply the length of the chiral vector divided by 1/4, and $d = \left(\frac{3}{\pi}\right)^{\frac{1}{2}} a_{c-c}(n^2 + m^2 + nm^2)^{\frac{1}{2}}$, where a_{C-C} is the distance between neighboring carbon atoms in the flat sheet. In turn, the chiral angle (θ) is given by $\tan^{-1}(3n/(2m+n))^{\frac{1}{2}}$. The translational period, a, is the shortest possible lattice vector along the z direction. SWCNTs are classified into three types, namely armchair (n, n) nanotubes, zigzag (n, 0) nanotubes, and chiral (n, m) nanotubes with $n \neq m$ [6].



Scheme 1 Generating the chirality vector for the nanotube from the graphene sheet. **a** 3,4-Dihydroxy cinamic acid. **b** [1,3,4,5-Tetrahydroxycyclohexane carboxylic acid 3- (3,4-dihydroxycinamate)]

Sensors continue to make an important impact on everyday life. They have been in strong demand for producing highly selective, sensitive, responsive, and cost-effective sensors [7]. CNTs have many distinct properties that may be exploited to develop the next generation of sensors. 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 [8]. They can be used to encourage electron transfer reactions when applied as electrode materials in electrochemical devices. The keto↔enol tautomerism is one of the most common investigated subjects of isomerism that occurs for carbonyl compounds [9]. 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, catechol compound sensors based on SWNT have been considered. Generally, the enol form is more stable than the keto form for neutral systems.

Catechol compounds including quinizarine, caffeic acid, chlorogenic acid, catechine hydrate, pyrocatechol, hematoxylin, rutin, coumestan, 3,4-dihydroxybenzaldehyde, and other derivatives are used as electron transfer mediators in electrochemical processes due to their high electron transfer efficiency, excellent redox reversibility, and low cost [10].

The catechol derivatives which we chose as shown in Scheme 2 are caffeic acid and chlorogenic acid. Then, they have bonded to SWNT (7,4) separately. In this paper, at first, these two compounds (SWNT–caffeic acid (CFA) and SWNT–chlorogenic acid (CGA)) were optimized by Gaussian 98 package in the HF method and 3–21 G basis set. The next step is the simulation of some periodic box such as H_2O, CH_3OH, and C_2H_5OH performed by HyperChem 8.0 and Chemoffice 2004 packages on SWNT–CFA and SWNT–CGA for investigating the dielectric effects. Finally, we used three ways to find the best situation, temperature, and solution for the mentioned compounds. In the first method, the interaction between these phenolic acids(CFA, CGA) and CNT (7,4) has been studied by quantum mechanics calculations, and the structural stability of the considered nanotube based on chemical sensors in different solvent media and temperatures have been compared and analyzed. So, we chose the Monte Carlo simulation in MM+, AMBER, and OPLS force field to calculate potential energy. Then, we investigated vibrational analysis in the semi-empirical method. These two mentioned

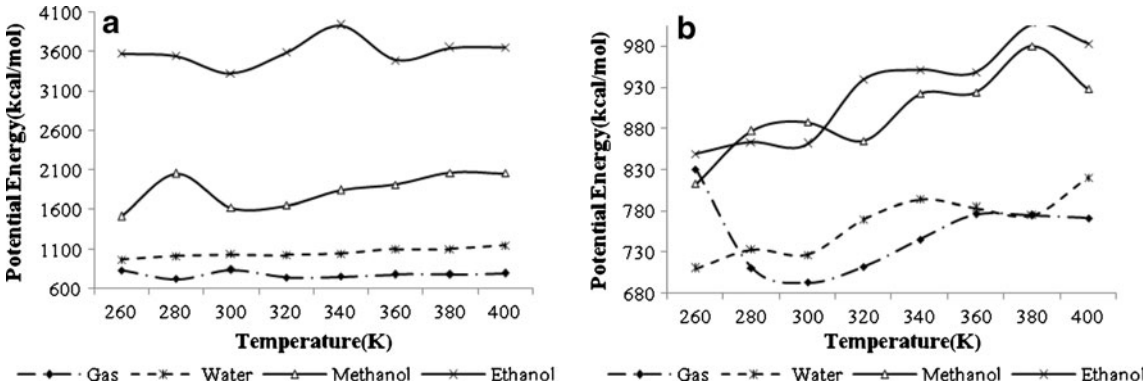


Fig. 1 Potential energy of **a** SWNT–CFA, **b** SWNT–CGA vs. temperature by the molecular mechanic method (MM+)

methods have been done by HyperChem 8.0 software. The last one is to determine the NMR parameters.

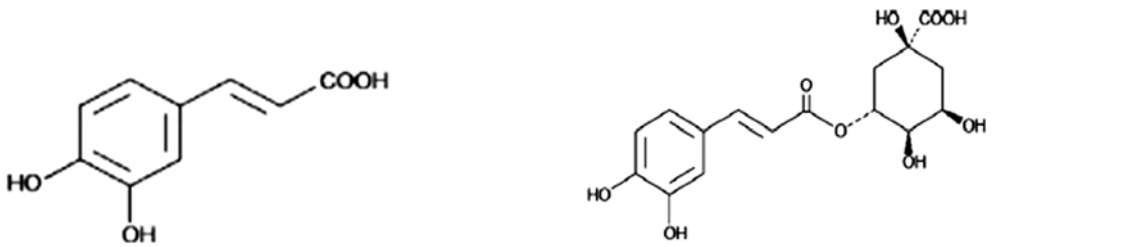
Computational method and background

Monte Carlo simulation

The term "ab initio" is given to computations which are derived directly from theoretical principles, with no inclusion of experimental information. The most common type of ab initio calculation is called a Hartree–Fock calculation (abbreviated HF), in which the primary approximation is called the central field approximation. A method, which avoids making the HF mistakes in the first place, is known as Quantum Monte Carlo (QMC). Also, in contrast to the MD method which is entirely deterministic, the MC simulation method is based on the use of probabilistic concepts. In this method, a system composed of *N* interacting atoms is given a group of initial coordinates. The evolution of this initial configuration is then generated by these successive random displacements of the atoms. There are some flavors of QMC, namely variational, diffusion, and Green's functions. These methods work with a clearly correlated wave function and evaluate integrals numerically using a Monte Carlo integration. These calculations can be very time consuming, but they are apparently the most accurate methods known today. Ab initio calculations give very good qualitative results and can give increasingly accurate quantitative results as the molecules in question become smaller, generally [11]. There are three steps in carrying out any quantum mechanical calculation in the HyperChem 8.0 program package. First, set up a molecule with an appropriate starting geometry. Second, choose a calculation method and its associated choices. Third, choose the type of calculation with the relevant options. The Monte Carlo simulations always detect the so-called "important phase space" regions which are of low energy [12]. Because of defects of the force field, this lowest energy basin usually does not correspond to the native state in most cases, so the rank of the native structure in those decoys produced by the force field itself is poor. In this study, the difference in force field is illustrated by comparing the energy calculated by using force fields, MM+, Amber, and Opls. Also, we investigated polar solvent and the temperature effects (between 260 and 400 K) on the stability of SWCNT bonded to CFA (or CGA) in various solvents. The quantum mechanics (QM) calculations were carried out with the HyperChem 8.0 program.

Vibration analysis

Two major classes of electronic structure methods have been devised and are frequently used in the literature: semi-empirical and ab initio methods. In this study, the ab initio method has been used for optimizing molecules, illustrating NMR parameters, and the semi-empirical method is used for



(a) 3,4- dihydroxy cinamic acid **(b)** [1,3,4,5-tetrahydroxycyclohexane carboxylic acid 3- (3,4-dihydroxycinamate)]

Scheme 2 The structure and IUPAC name of **a** caffeic acid (CFA) and **b** chlorogenic acid (CGA)

Table 1 Potential energy of CFA and CGA bonding to SWNT (7,4) in some solvent vs. temperature by the molecular mechanic method (MM+)

Comp.	Medium	Dielectric constant	Temperature (K)							
		E (kcal/mol)	260	280	300	320	340	360	380	400
CFA–SWNT	Gas	1	833.84	725.73	839.952	743.305	753.157	781.872	782.11	794.75
	Water	78.39	972.285	1,016.41	1,039.18	1,026.74	1,041.94	1,103.95	1,106.65	1,149.83
	Methanol	32.63	1,515.04	2,057.12	1,624.87	1,655.12	1,847.56	1,918.75	2,067.8	2,060.79
	Ethanol	24.55	3,576.61	3,544.84	3,323.58	3,589.99	3,929.88	3,492.58	3,644.08	3,654.08
CGA–SWNT	Gas	1	830.651	711.383	693.412	712.862	745.714	776.318	775.096	771.555
	Water	78.39	710.495	733.531	727.157	770.008	794.07	783.744	775.271	820.384
	Methanol	32.63	812.704	877.307	887.733	865.396	921.972	923.768	980.351	927.741
	Ethanol	24.55	849.184	863.483	861.479	939.981	951.521	948.491	1,008.41	982.868

vibrational analysis. The development of semi-empirical methods gained popularity in the 1970s–1980s. These methods use derived parameters from experimental data to fit into the computations. Many studies have shown that carbon nanotubes possess remarkable mechanical and physical properties leading to many potential applications such as fluid transport, fluid storage at nanoscale, and nanodevices for drug delivery. Since controlled experiments at the nanometer scale are difficult, the simulation techniques have been widely and successfully used to investigate the mechanical property, wave propagation, and resonant frequency [13]. The vibration of molecules is best described using a quantum mechanical approach. A harmonic oscillator does not exactly describe molecular vibrations. Bond stretching is better described by a Morse potential, and conformational changes have sine-wave-type behavior. However, the harmonic oscillator description is useful as an approximate treatment for low vibrational quantum numbers [14]. A harmonic oscillator approximation is most widely used for computing molecular vibrational frequencies because more accurate methods require very large amounts of CPU time. In this paper, we used the semi-empirical method, Austin Model-1 (Am1) and Parameterized Model number 3 (PM3) codes, to investigate the resonant frequency.

Table 2 Potential energy values using MM+, AMBER, and OPLS force fields in different media

	Medium	Dielectric constant	MM+ *E* (kcal/mol)	AMBER	OPLS
SWNT–CFA	Gas phase	1	426.691	980.695	241.645
	Water	78.39	442.324	1,075.01	366.526
	Methanol	32.63	530.367	1,036.76	323.833
	Ethanol	24.55	585.972	978.125	280.096
SWNT–CGA	Gas phase	1	429.633	943.563	221.198
	Water	78.39	426.44	1,078.72	335.714
	Methanol	32.63	509.795	1,002.7	298.957
	Ethanol	24.55	589.664	954.047	261.648

NMR studies

In the Gaussian program, a simple approximation is used in which the volume of the solute is used to compute the radius of a cavity which forms the hypothetical surface of the molecule [15, 16]. Then, we have compared the gas phase and different solvent media such as water, methanol, and ethanol. So, we investigated polar solvent effects on SWCNT–CFA (and SWCNT–CGA) within the Onsager self-consistent reaction field (SCRF) model using a Hartree–Fock method in various solvents. It is now possible to describe the molecular properties of relative small molecules with nearly chemical accuracy using theoretical methods due to recent advances in computational methods and common access to large-scale powerful computers and software. The fundamental assumption of the Hartree–Fock theory that each electron sees all of the others as an average field allows for tremendous progress to be made in carrying out practical molecular orbital calculations. In this paper, calculating NMR data using quantum mechanical computational methods relies directly on the accurate calculation of the energy. This is because the computed NMR shift is a mathematical second derivative of the energy function. To

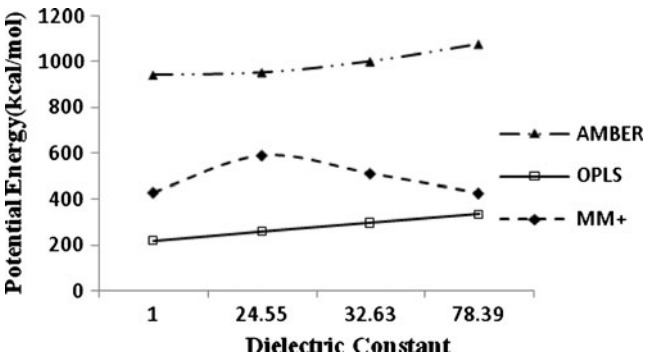


Fig. 2 Potential energy values using different force fields for SWNT–CFA and SWNT–CGA

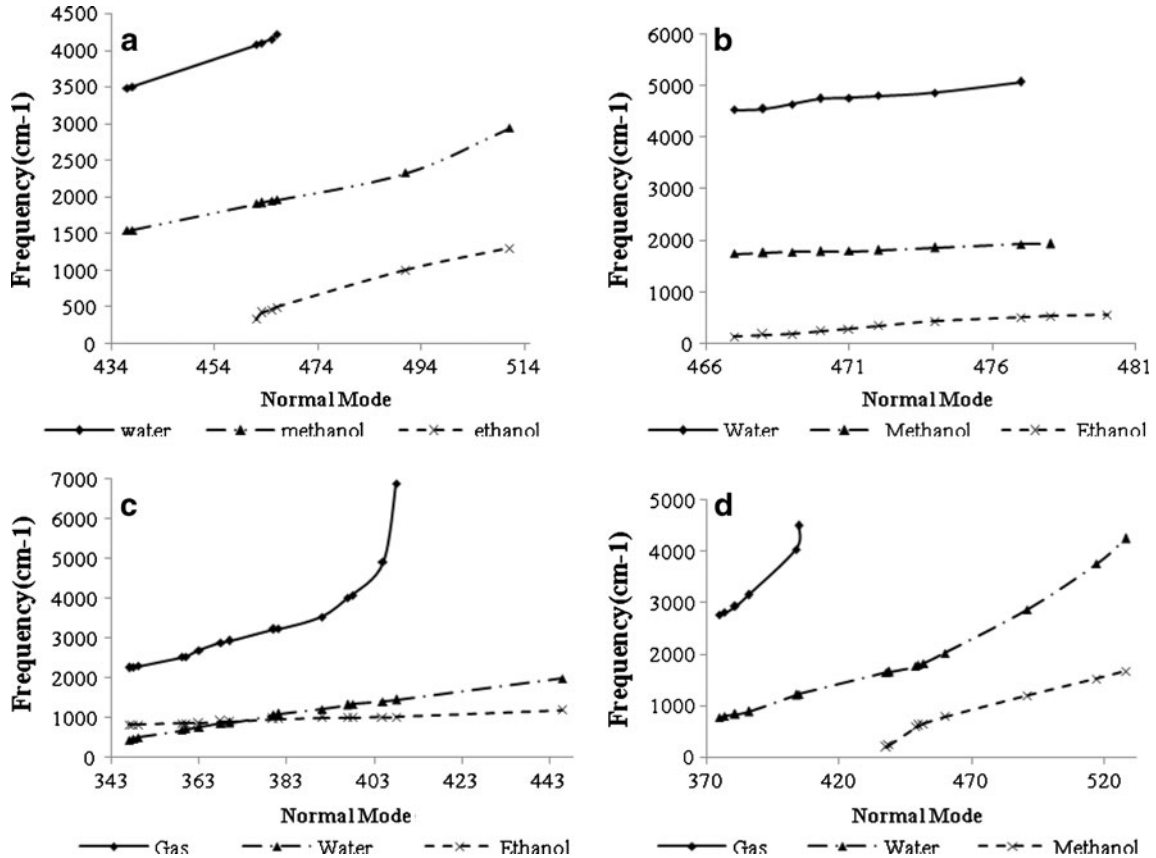


Fig. 3 Changes of frequency vs. normal mode on **a** caffeic acid in AM1, **b** caffeic acid in PM3, **c** CGA in AM1, and **d** CGA in PM3

Scheme 3 The structure of **a** SWNT–CFA and **b** SWNT–CGA

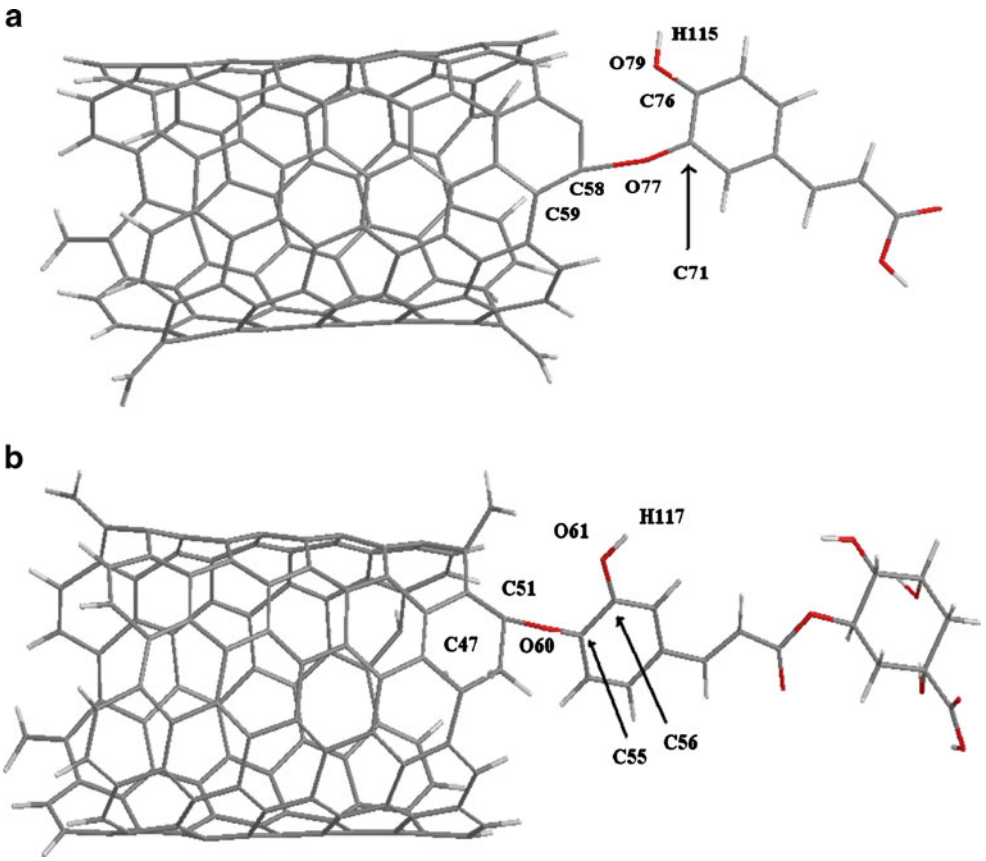


Table 3 NMR properties of caffeic acid bonding to SWNT (7,4) in the HF method

Basis set	Atomic no.	Water					Methanol					Ethanol				
		σ_{iso}	σ_{aniso}	δ	$\Delta\sigma$	η	σ_{iso}	σ_{aniso}	δ	$\Delta\sigma$	η	σ_{iso}	σ_{aniso}	δ	$\Delta\sigma$	η
STO–3 G	58	102.1558	86.3006	57.5338	86.30065	0.721758	102.1563	86.3001	57.5334	86.3001	0.721824	102.1578	86.299	57.5327	86.299	0.721836
	59	122.5186	137.8027	91.8685	137.8028	0.157848	122.5183	137.8029	91.8687	137.803	0.157861	122.5178	137.8043	91.8695	137.8043	0.157878
	71	109.9947	90.072	60.048	90.07205	0.19363	109.995	90.072	60.048	90.072	0.193605	109.9949	90.0677	60.0452	90.06775	0.193592
	76	107.9494	105.497	70.3313	105.497	0.139486	107.9496	105.497	70.3313	105.497	0.139478	107.9511	105.4913	70.3275	105.4913	0.139566
	77	237.9098	99.068	−99.3499	−149.025	0.32955	237.9147	99.0599	−99.3483	−149.022	0.329462	237.9213	99.0381	−99.3498	−149.025	0.32915
	79	249.7329	74.1995	−59.414	−89.121	0.66514	249.7292	74.1909	−59.4128	−89.1192	0.664983	249.7268	74.1736	−59.4095	−89.1142	0.664685
	115	29.3798	10.8693	−7.2716	−10.9074	0.993014	29.3799	10.8692	−7.2718	−10.9077	0.992945	29.38	10.8686	−7.2725	−10.9088	0.99263
3–21 G	58	59.247	90.1615	−66.4697	−99.7046	0.808573	59.248	90.1602	−66.4708	−99.7063	0.808516	59.2499	90.1578	−66.4723	−99.7085	0.808427
	59	89.2611	142.7447	95.1632	142.7447	0.227109	89.261	142.7442	95.1628	142.7442	0.227133	89.2591	142.7446	95.1631	142.7447	0.227144
	71	69.1988	89.8889	59.926	89.88895	0.634354	69.1992	89.889	59.926	89.88895	0.634284	69.1995	89.8853	59.9235	89.8852	0.634205
	76	67.0575	110.1217	72.9997	109.707	0.402932	67.0581	110.1203	73.4136	110.1203	0.400615	67.06	110.1137	73.4091	110.1137	0.400615
	77	192.5692	66.3097	−58.8297	−88.2446	0.502862	192.5732	66.3048	−58.8299	−88.2449	0.502746	192.5781	66.2918	−58.8267	−88.2402	0.502532
	79	210.5883	51.5698	−46.2555	−69.3833	0.486519	210.5867	51.5584	−46.2549	−69.3823	0.486214	210.5855	51.541	−46.2491	−69.3736	0.485897
	115	29.4098	13.2314	8.821	13.23145	0.673246	29.4099	13.2313	8.8209	13.2313	0.673265	29.4101	13.231	8.8206	13.231	0.673469
6–21 G	58	60.668	89.8587	−65.8716	−98.8074	0.818866	60.669	89.8574	−65.8728	−98.8092	0.818807	60.6709	89.855	−65.8743	−98.8114	0.818717
	59	90.7234	141.6062	94.4041	141.6062	0.232128	90.7232	141.6058	94.4039	141.6059	0.23215	90.7213	141.6062	94.4041	141.6061	0.232164
	71	70.59	89.2308	59.4872	89.2308	0.627476	70.5904	89.2308	59.4873	89.23085	0.627406	70.5906	89.227	59.4847	89.22705	0.627326
	76	68.3653	109.6256	73.0837	109.6255	0.393573	68.366	109.6241	73.0827	109.6241	0.393535	68.3677	109.6175	73.0784	109.6176	0.393535
	77	191.1258	65.0886	−58.2361	−87.3542	0.490223	191.1298	65.0838	−58.2362	−87.3543	0.490111	191.1347	65.0708	−58.2329	−87.3494	0.489895
	79	210.1597	49.7901	−46.8803	−70.3205	0.416089	210.158	49.7787	−46.8796	−70.3194	0.415789	210.1567	49.761	−46.8737	−70.3106	0.415463
	115	29.4641	12.9262	8.6175	12.92625	0.6881	29.4643	12.9261	8.6174	12.9261	0.688119	29.4644	12.9258	8.6172	12.9258	0.688321
4–31 G	58	36.6488	102.7654	−75.9642	−113.946	0.803751	36.65	102.7639	−75.9653	−113.948	0.803699	36.6526	102.7611	−75.9663	−113.949	0.803627
	59	69.1526	160.4804	106.9869	160.4804	0.221522	69.1524	160.4798	106.9866	160.4799	0.221546	69.1505	160.4808	106.9872	160.4808	0.221554
	71	47.0437	104.005	69.3366	104.005	0.625146	47.0442	104.005	69.3367	104.0051	0.625079	47.0448	104.0012	69.3341	104.0012	0.625006
	76	46.2364	120.9843	80.6562	120.9843	0.469504	46.2371	120.9824	80.6549	120.9823	0.469472	46.2394	120.9752	80.6502	120.9753	0.469462
	77	161.492	66.158	−56.2357	−84.3537	0.568587	161.4961	66.1538	−56.2374	−84.3561	0.56844	161.4997	66.1397	−56.2396	−84.3594	0.568046
	79	192.2504	40.2592	−44.9276	−67.3915	0.194787	192.2489	40.2467	−44.9272	−67.3908	0.194426	192.2485	40.2278	−44.9196	−67.3794	0.194069
	115	29.3097	12.9535	8.6356	12.9535	0.726967	29.3098	12.9534	8.6356	12.9534	0.726991	29.31	12.9531	8.6354	12.9531	0.72717
6–31 G	58	39.1311	101.9739	−74.8932	−112.34	0.815455	39.1323	101.9725	−74.8944	−112.342	0.815401	39.1348	101.9695	−74.8949	−112.342	0.815333
	59	71.6841	158.9868	105.9911	158.9867	0.211108	71.6839	158.9861	105.9907	158.9861	0.211134	71.6822	158.9875	105.9917	158.9875	0.211137
	71	49.9862	103.0983	68.7322	103.0983	0.606723	49.9868	103.0983	68.7322	103.0983	0.606656	49.9876	103.0948	68.7298	103.0948	0.606585
	76	49.4901	119.351	79.5673	119.351	0.466942	49.4908	119.3491	79.5661	119.3491	0.466909	49.4931	119.342	−58.354	−87.531	−1.72685
	77	162.0502	65.9492	−96.101	−124.093	0.332455	162.0542	65.9452	−55.9846	−83.977	0.570555	162.0577	65.9299	−55.9867	−83.9801	0.57013
	79	193.8344	38.1393	−42.9547	−64.4321	0.183861	193.833	38.1265	25.4176	38.12645	2.379867	193.8325	38.1067	−42.946	−64.419	0.183093
	115	29.177	12.6985	8.4657	12.69855	0.773911	29.1772	12.6984	8.4655	12.6983	0.773941	29.1773	12.6981	8.4654	12.6981	0.774139

Table 4 NMR properties of CGA bonding to SWNT (7,4) in the HF method

Basis set	Atomic no.	Water					Methanol					Ethanol				
		σ_{iso}	σ_{aniso}	δ	$\Delta\sigma$	η	σ_{iso}	σ_{aniso}	δ	$\Delta\sigma$	η	σ_{iso}	σ_{aniso}	δ	$\Delta\sigma$	η
STO–3 G	47	124.3312	107.555	71.7033	107.555	0.622868	124.3329	107.5542	71.7028	107.5542	0.622847	124.3309	107.5492	71.6994	107.5492	0.622856
	51	103.0096	78.8967	52.5978	78.8967	0.972044	103.0091	78.8961	52.5974	78.8961	0.972018	103.0109	78.8942	52.5961	78.8942	0.971905
	55	111.3344	90.716	60.4773	90.71605	0.178316	111.3354	90.7155	60.4771	90.71555	0.178231	111.3378	90.7211	60.4807	90.7211	0.178311
	56	106.1422	108.147	72.098	108.147	0.121363	106.1421	108.1488	72.0992	108.1489	0.121268	106.1358	108.1584	72.1056	108.1585	0.121163
	60	248.8338	73.9394	−58.0072	−87.0107	0.699548	248.8244	73.9256	−58.0083	−87.0124	0.699196	248.8142	73.9376	−58.0147	−87.0221	0.699283
	61	242.7558	118.8356	−110.364	−165.545	0.435687	242.7627	118.8337	−110.367	−165.551	0.435618	242.771	118.8464	−110.347	−165.52	0.436034
	117	28.9255	11.1245	−7.4942	−11.2413	0.979237	28.9254	11.1228	−7.4935	−11.2403	0.979102	28.9246	11.1235	−7.4921	−11.2382	0.979592
3–21 G	47	86.7238	109.198	72.7987	109.1981	0.781177	86.7258	109.198	72.7987	109.198	0.781146	86.7243	109.194	72.7965	109.1947	0.781116
	51	60.6222	76.9432	−66.3376	−99.5064	0.546499	60.6215	76.9417	−66.3359	−99.5039	0.546508	60.622	76.9446	−66.3258	−99.4887	0.546802
	55	69.9933	88.5392	59.0262	88.53925	0.815609	69.995	88.5377	59.0252	88.53775	0.815535	69.9985	88.5385	59.0257	88.53845	0.815945
	56	65.517	113.7959	75.8639	113.7959	0.509584	65.5174	113.796	75.8639	113.796	0.509477	65.5079	113.807	75.8713	113.807	0.509635
	60	212.2958	41.7819	−45.1593	−67.739	0.233613	212.2894	41.7587	−45.1618	−67.7427	0.232863	212.2874	41.7579	−45.1791	−67.7687	0.232364
	61	202.623	86.54	−67.0494	−100.574	0.720921	202.6321	86.5521	−67.0618	−100.593	0.720841	202.6403	86.5927	−67.0597	−100.59	0.721703
	117	29.0972	13.0886	8.7257	13.08865	0.739689	29.0973	13.0866	8.7244	13.0866	0.739787	29.0974	13.0866	8.7244	13.08665	0.739524
6–21 G	47	88.2939	108.2354	72.157	108.2355	0.788835	88.2959	108.2354	72.1569	108.2354	0.788805	88.2944	108.2321	72.1547	108.2321	0.788773
	51	61.9378	76.7911	−65.9905	−98.9858	0.55156	61.9371	76.7896	−65.9888	−98.9832	0.551566	61.9374	76.7926	−65.9787	−98.9681	0.551866
	55	71.5604	87.8903	58.5935	87.8903	0.812493	71.5621	87.8888	58.5925	87.88875	0.81242	71.5659	87.8896	58.5931	87.88965	0.812838
	56	66.907	113.432	75.6213	113.432	0.503129	66.9074	113.432	75.6214	113.4321	0.50302	66.8981	113.4432	75.6288	113.4433	0.503177
	60	211.8266	40.0852	−44.7235	40.0852	2.417954	211.82	40.0612	−45.6721	−68.5081	0.16953	211.8179	40.0603	−45.689	−68.5335	0.169074
	61	201.6305	86.1165	−66.6263	−99.9395	0.723375	201.6397	86.1295	−66.6389	−99.9583	0.723307	201.6479	86.1725	−66.6364	−99.9547	0.724233
	117	29.1424	12.7387	8.4925	12.73875	0.762473	29.1425	12.7367	8.4911	12.73665	0.762598	29.1426	12.7366	8.4911	12.73665	0.762339
4–31 G	47	66.7992	125.2713	83.5142	125.2713	0.760795	66.801	125.2709	83.514	125.271	0.760765	66.7996	125.2672	83.5115	125.2672	0.76074
	51	38.2137	88.6767	−74.6418	−111.963	0.584039	38.213	88.6749	−74.6399	−111.96	0.584047	38.2143	88.6771	−74.6294	−111.944	0.58431
	55	48.0363	104.0754	69.3836	104.0754	0.78635	48.0383	104.0745	69.383	104.0745	0.78627	48.0425	104.0763	69.3842	104.0763	0.786614
	56	44.8382	126.0105	84.007	126.0105	0.564097	44.8388	126.0103	84.0068	126.0102	0.564004	44.8288	126.0254	84.0169	126.0253	0.564165
	60	193.9777	41.1253	−46.3604	−69.5407	0.18277	193.9704	41.1526	−46.3604	−69.5407	0.183555	193.9691	41.1881	−46.3818	−69.5726	0.184033
	61	168.9047	85.8723	−67.2789	−100.918	0.701817	168.9129	85.8802	−67.2921	−100.938	0.701643	168.9205	85.913	−67.2882	−100.932	0.702389
	117	28.9258	12.7767	8.5178	12.7767	0.834347	28.9259	12.7749	8.5166	12.77495	0.834453	28.9259	12.775	8.5167	12.775	0.834196
6–31 G	47	69.2769	124.1203	82.7469	124.1203	0.749792	69.2786	124.1196	82.7463	124.1196	0.749765	69.2774	124.1157	82.7438	124.1157	0.749741
	51	40.9721	87.7588	−73.1297	−109.695	0.600057	40.9715	87.757	−73.1277	−109.692	0.600068	40.9732	87.7593	−73.1173	−109.676	0.600339
	55	51.0135	103.6222	69.0814	103.6222	0.765029	51.0156	103.6216	69.0811	103.6217	0.764946	51.0199	103.6238	69.0825	103.6238	0.765284
	56	47.9779	124.6664	83.111	124.6665	0.561169	47.9785	124.6663	83.1108	124.6663	0.561071	47.9688	124.682	83.1213	124.682	0.561234
	60	195.5623	40.6239	−44.7827	−67.174	0.209514	195.5548	40.6503	−44.7816	−67.1724	0.210327	195.5535	40.6862	−44.803	−67.2045	0.210818
	61	168.5237	84.9379	−67.3725	−101.059	0.680962	168.5318	84.9446	−67.3852	−101.078	0.680777	168.5388	84.9747	−67.3817	−101.073	0.681458
	117	28.7834	12.5297	8.3531	12.5297	0.892746	28.7835	12.5279	8.3519	12.5279	0.892851	28.7835	12.5281	8.3521	20.43155	−0.99998

calculate the energy with reasonable accuracy, the ab initio theory was used, meaning "from first principles." Simulation techniques of NMR parameters underwent important development in the last three decades. For example, the origin dependence of calculated chemical shifts [17, 18] was overcome in many ways. Formalism based on the gauge invariant atomic orbitals (also called London- or magnetic field-dependent AOs) has been established as a good standard [19, 20]. Appreciable popularity was gained in the past years by the Onsager–SCRF, elaborated by Wong [21] for the Gaussian program. The Onsager model is the simplest version of the MPE approach. The appealing feature of Onsager–SCRF was that it permitted one to directly exploit almost all of the computational facilities of the Gaussian packages. For its very limited computational cost, it is still in use by people not requiring an accurate description of solvation effects but just a guess or a qualitative correction to the values obtained for the isolated molecule. The dielectric continuum models such as the self-consistent reaction field method are efficient in taking account of long-range solute–solvent electrostatic interaction and the effect of solvent polarization. An alternative which can overcome the weak points of the dielectric continuum model is the QM/MM method. Since full quantum chemical treatment of molecules is computationally too demanding, the electronic structure of the solute molecule is only treated quantum mechanically whilst the MM is introduced to describe the solvent molecule.

Result and discussion

In the first step of the calculations, we optimized the geometry and defined the potential energy of the SWNT–CFA and SWNT–CGA structures by performing molecular mechanics calculation using the MM+ force field. If too large a time step is used in Monte Carlo simulation, it is possible to have a basic instability in the equations that results in a molecule blowing apart, so we need small time steps to preserve integration accuracy. However, in the Monte Carlo time step, 50 fs (0.05 ps) was appropriate. According to this method, the potential energy of solute and solvent, which depends on the dielectric constant ε, has been listed in Table 1 and Fig. 1. In this work, we studied the structural properties of water, methanol, and ethanol surrounding

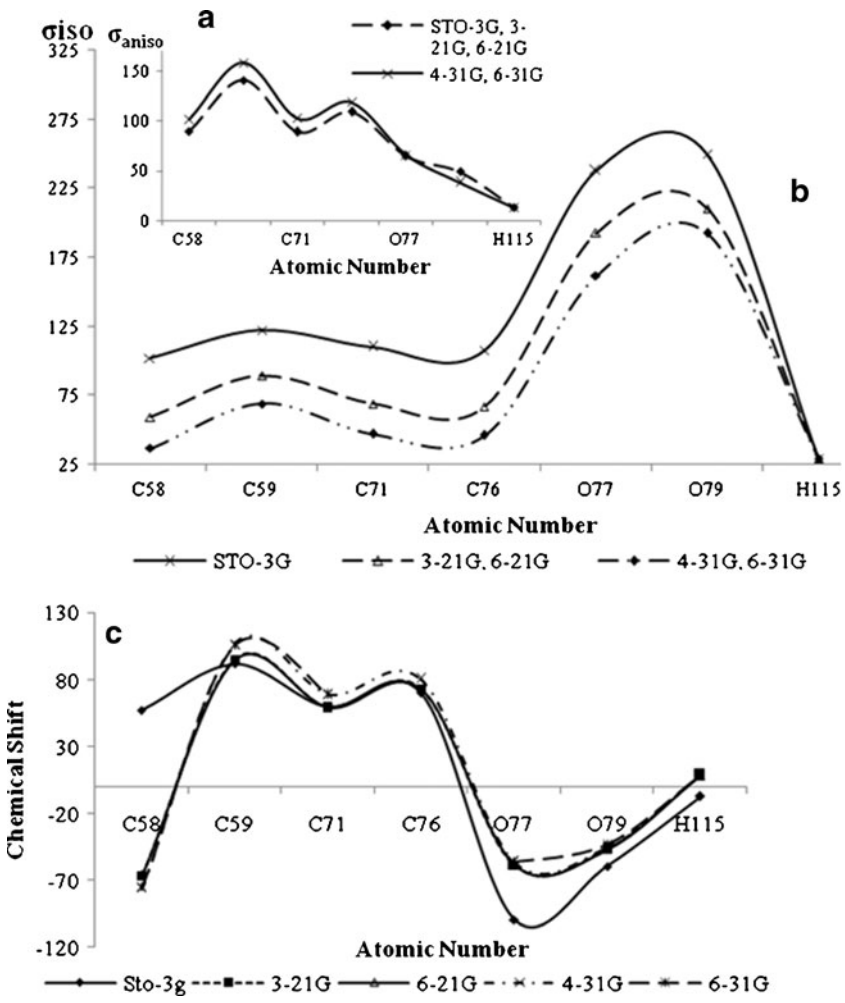


Fig. 4 Calculated NMR values of **a** σanisotropic, **b** σisotropic, and **c** chemical shift (δ) for SWNT–CFA

SWCNT and CFA/CGA using molecular mechanic simulations. We used different force fields for the determination of energy on the particular SWCNT. Because of the differences among force fields, the energy of a molecule calculated using three different force fields will not be the same. So, it is not reasonable to compare the energy of one molecule calculated with a particular force field with the energy of another molecule calculated using a different force field. In this study, the difference in force field is illustrated by comparing the energy calculated by using force fields, MM+, AMBER, and OPLS. Theoretical energy values using different force fields which are the combination of attraction of van der Waals forces due to dipole–dipole interactions and empirical repulsive forces due to Pauli repulsion have been demonstrated in Table 2 and Fig. 2. The results of calculating energy in different force fields for SWNT–CFA and SWNT–CGA are the same. Dielectrics from $\varepsilon=1$ to $\varepsilon=78.39$ are randomly selected and have been used as H_2O, CH_3OH, C_2H_5OH molecular for solvent phase. Their results are (H_2O) [$\varepsilon=78.39$], (CH_3OH) [$\varepsilon=32.63$], and (C_2H_5OH) [$\varepsilon=24.55$].

In the next step, we calculated the vibrational modes of SWNT–CFA and SWNT–CGA by applying the semi-empirical molecular orbital method AM1 and PM3 to the HyperChem 8.0 package. All calculations presented here were performed with the semi-empirical method (AM1 [22], PM3 [23]). In 1989, Stewart improved the techniques of parameterization and published PM3, which gave lower average errors than AM1 and are sufficient to study carbon systems mainly for the enthalpies of formation [23]. The resulting method was denoted PM3 and is essentially AM1 with all the parameters fully optimized. In a sense, it is the best set of parameters (or at least a good local minimum) for the given set of experimental data. The optimization process, however, still requires some human intervention in selecting the experimental data and assigning appropriate weight factors to each set of data. At the first glance in

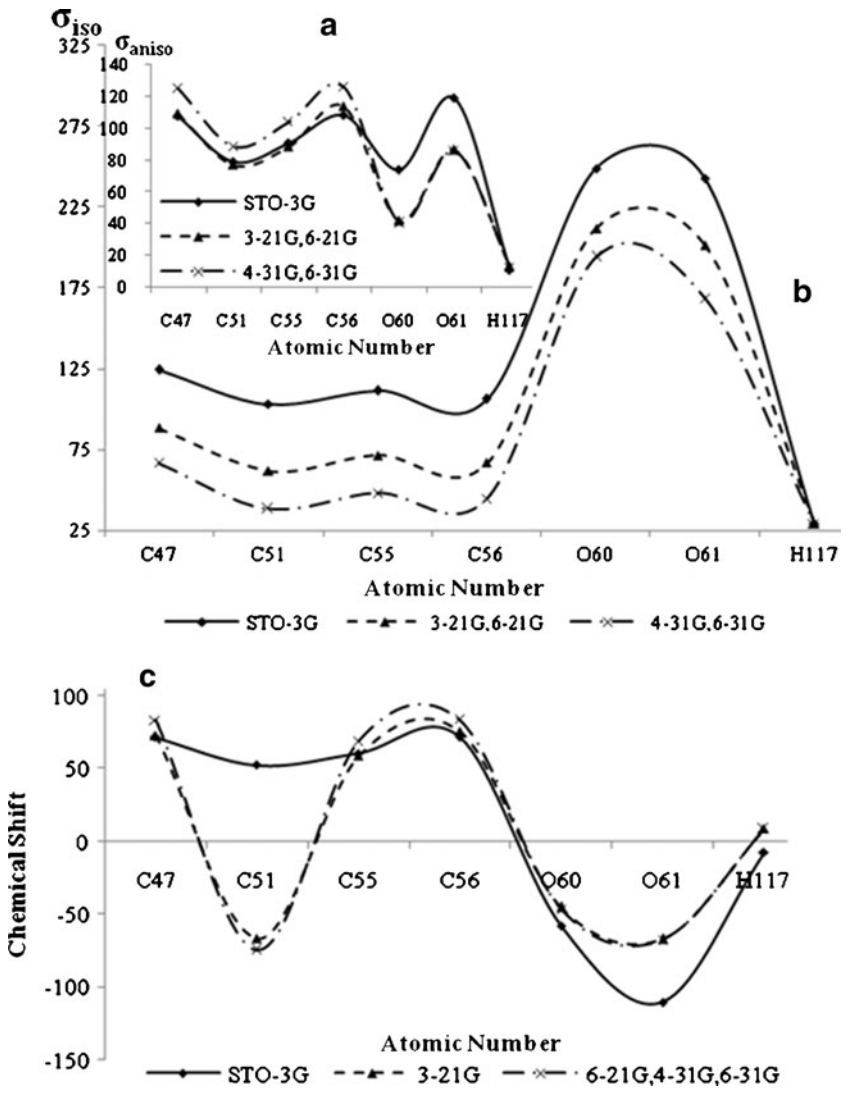


Fig. 5 Calculated NMR values of **a** σanisotropic, **b** σisotropic, and **c** chemical shift (δ) for SWNT–CGA

Fig. 3, it can be observed by increasing dielectrics that normal modes will move to lower normal modes ratio, and vibrational frequencies resulting from semi-empirical calculations tend to be qualitative. Therefore, by increasing dielectric, the higher frequency will be gained in which both methods, AM1and PM3, will have the same operating procedure.

Since the influence between a molecule in solution and its medium can describe most simply by using the Onsager model, in this model, we have assumed that the solute is placed in a spherical cavity inside the solvent. The latter is described as a homogeneous, polarizable medium of dielectric constant. We started our studies with HF/3–21 G gas phase geometry and water, methanol, and ethanol surrounding SWCNT–CFA and SWNT–CGA. The results obtained from the Onsager model calculations are illustrated using the energy difference between these conformers which are quite sensitive to the polarity of the surrounding solvent. The solvent effect has been calculated using the SCRF model.

After using the SCRF model, we investigated NMR parameters. These two compounds are too large; because of that, we selected few atoms from each of them to determine the NMR parameters. As shown in Scheme 3, we chose the seventh atom from each compound. Some NMR parameters were determined by the HF method and several basis sets in different solution such as: H_2O, CH_3OH, and C_2H_5OH as shown in Table 3 for SWNT–CFA and in Table 4 for SWNT–CGA. The minimum charge transfer in SWNT–CFA is O77, and for SWNT–CGA, it is O60, so here is a maximum excited charge. It means the system is more stable in these linkages. Figures 4 and 5 are showing the relation between the $\sigma_{isotropic}$, $\sigma_{anisotropic}$, and chemical shift for the mentioned compounds. In Fig. 4, the $\sigma_{isotropic}$ for O77 is in maximum value, but $\sigma_{anisotropic}$ and chemical shift have a negative value. Also, in Fig. 5, $\sigma_{isotropic}$ for O60 is in maximum value, but $\sigma_{anisotropic}$ and chemical shift have a negative value. Comparing the NMR parameters for other specified atoms will show the same result.

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