Solvent effects on tamoxifen molecule interacting with a single-walled carbon nanotube: a theoretical NMR study

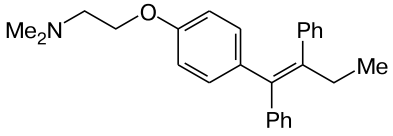
F. Mollaamin,[a] K. Shahani pour,[a] K. Shahani pour,[b] A. R. Ilkhani,[c] Z. Sheckari,[d] and M.Monajjemi[e]*

[a]*Department of Chemistry, Qom Branch, Islamic Azad University, Qom, Iran*
[b]*Department of Biochemistry, Falavarjan Branch, Islamic Azad University, Falavarjan, Iran*
[c]*Department of Chemistry, Yazd Branch, Islamic Azad University, Yazd, Iran*
[d]*Department of Chemistry, Gachsaran Branch, Islamic Azad University, Gashsaran, Iran*
[e]*Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran.*
E-mail: smollaamin@gmail.com

Quantum chemical calculations of the electronic structure of tamoxifen molecule interacting with an open end of a single-walled carbon nanotube (SWCNT) were carried out and the effects of solvents (water, methanol, DMSO, acetone) on the ^{1}H, ^{13}C, ^{15}N, and ^{17}O NMR parameters were studied by the GIAO-HF/STO-3G, GIAO-HF/3-21G, and GIAO/B1LYP/3-21G methods using the GAUSSIAN-98 program. The largest σ_{iso} value was obtained for acetone, whereas the smallest one for water. The opposite trend was obtained for the shielding asymmetry η. According to calculations, atoms at interaction site bear negative charges. The O(43) and N(38) atoms produce negative charge because they have high electron affinities. The dipole moment of tamoxifen molecule in different solvents increases with increasing the dielectric constant of the solvent. The largest dipole moment value was obtained for water by the B1LYP/3-21G method.

Key words: single-walled carbon nanotubes, tamoxifen, drug delivery, solvent effect, NMR spectra, Hartree—Fock method, density functional theory, SCRF model.

Tamoxifen **1**, a member of the selective estrogen receptor modulator (SERM) family, is widely used in the treatment of estrogen receptor (ER)-expressing breast cancer.[1—3] Because the antitumor effects of **1** were predominantly observed in patients with ER-positive tumors, it is generally accepted that the primary action of hydroxytamoxifen (active metabolite of **1**) is mediated through inhibition of the ER pathway. However, some ER-negative cancers also respond to **1**,[4,5] which means that the molecule can be active because of an ER-independent antitumor mechanism that has not yet been clearly identified.[6]



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Studies on carbon nanotubes (CNTs) represent a topical area in medical research on efficient drug delivery systems and in biosensing methods for disease treatment and health monitoring. The interaction of drugs with single-walled carbon nanotubes (SWCNTs) is widely investigated because of many advantages compared to other drug delivery systems.

Systems being used currently for drug delivery include dendrimers, polymers, and liposomes. Carbon nanotubes present the opportunity to work with effective structures that have high drug loading capacities and good cell penetration qualities. Larger inner volume of CNTs can be used as the drug container, large aspect ratios are suitable for numerous functionalization attachments. Also, CNTs show the ability to be readily taken up by the cell.[7]

Carbon nanotube technology has shown to have the potential to alter drug delivery and biosensing methods for the better, and thus, CNTs have recently garnered interest in the field of medicine. The use of SWCNTs in drug delivery and biosensing technology has the potential to revolutionalize medicine. Functionalization of SWCNTs enhances their solubility and allows for efficient tumor

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targeting/drug delivery. It prevents SWCNTs from being cytotoxic and altering the function of immune cells.

Single-walled CNTs have unique chemical, size, optical, electrical, and structural properties that make them attractive as drug delivery and biosensing platforms for the treatment of various diseases and the noninvasive monitoring of blood levels and other chemical properties of the human body.[8,9] Single-walled CNTs are considered to be ideal candidates for biomedical applications due to their remarkable structure-dependent properties including high tensile strength and large surface area, high electric and thermal conductivity, as well as high stability in suspension when properly functionalized.

Carbon nanotubes are quasi-one-dimensional objects and may be derived from graphite sheets.[10] There are three types of CNTs described by two integers (m, n), namely, armchair-type CNTs ($m = n$), zigzag-type CNTs ($m = 0$ or $n = 0$), and chiral CNTs (m and n can take any values except those specified above).[11,12] Each type of CNTs exhibits its own properties.[13] Nanotubes show high chemical, electrical, and mechanical stability.[14]

In this study, only open-end SWCNTs are considered. They are composed of hexagons and are therefore expected to be highly aromatic structures.[15] Single-walled CNTs are obtained by rolling single graphite sheets, their diameters range from 0.4 to 2 nm,[16,17] and they can bind to polymers and biomolecules, such as DNA, carbohydrates, and drugs.[18] Recently, covalent and noncovalent bonding of **1** to SWCNTs was reported,[19–21] but details of these interactions are still to be clarified.

In this paper, we studied the interaction of **1** with the open end of a SWCNT and the effects of water and some solvents (MeOH, DMSO, acetone) on this interaction.

Nuclear magnetic resonance (NMR) spectroscopy is a valuable technique for obtaining chemical information and a powerful tool for studying the structure dynamics and interaction of biological molecules, *e.g.*, proteins and nucleic acids in solutions.[22–25] NMR spectra are very sensitive to changes in the molecular structure, which makes them a difficult case for molecular modeling.[26–28]

In this study, we carried out quantum chemical calculations aimed at increasing the practical application field of the **1**—SWCNT system. We believe that our results can be used in nanotechnology as well as drug design.

Calculation Procedure

Molecule **1** and its interaction with selected atoms of a SWCNT was modeled using published results[29] and the Hyperchem 7.0 program.[30]

The density functional theory (DFT) methods implemented in the GAUSSIAN-98 program[31] for vacuum and for inclusion of solvent effects provide logical accuracy and are particularly suitable for the study of defects in a wide range of materials.[32] DFT is based on two Hohenberg—Kohn theorems, one of which states that all ground-state properties are functions of the total electron density $\rho(\mathbf{r})$.[33,34]

In the Hartree—Fock theory, the expression for energy has the form

$$E_{HF} = V + <h_p> 1/2<P_{j\rho}> - 1/2<P_{k\rho}>, \quad (1)$$

where V is the nuclear repulsion energy, ρ is the density matrix, $<h_p>$ is the one-electron energy (the sum of the kinetic and potential energies); $1/2<P_{j\rho}>$ is the classical Coulomb repulsion of electrons, and $-1/2<P_{k\rho}>$ is the exchange energy resulting from the quantum (fermion) nature of electrons.

In DFT, the exact Hartree—Fock exchange for a single determinant is replaced by a more general expression for the exchange correlation functional, which can include terms accounting for both exchange energy and the electron correlation, which is ignored by the Hartree—Fock theory:

$$E_{KS} = V + <h_p> 1/2<P_{j\rho}>E_{\chi\rho}E_{c\rho}, \quad (2)$$

where $E_{\chi\rho}$ is the exchange function and $E_{c\rho}$ is the correlation functional. The correlation function[35] includes both local and nonlocal terms.

After full optimization of tamoxifen interaction with the open end of a SWCNT, we calculated NMR parameters by the GIAO-HF method. The results are presented in Table 1.

To account for the solvent effects, the self-consistent reaction field (SCRF) method is most commonly used.[36] Hence, SCRF based on the Onsager model was used to include the solvent effects on tamoxifen interaction with the open end of a SWCNT. The Onsager model considers a solute molecule whose charge distribution is represented by a simple dipole; the solute is embedded in a spherical cavity and interacts with the solvent. The energy of solute—solvent interaction (E_{int}) is equal to the energy difference between the solvated (E_{solv}) and isolated (E_{isol}) solute molecules[37]:

$$E_{int} = E_{solv} - E_{isol}. \quad (3)$$

Therefore, the electronic Schrödinger equation for electroneutral dipolar solute molecules can be solved using the self-consistent field method as follows:

$$(H_0 + \hat{V})\psi = E_{solv}\psi, \quad (4)$$

where H_0 is the total electronic Hamiltonian for the isolated molecule, ψ is the electron wave function, and $\hat{V}$ is the reaction field potential[37] given by:

$$\hat{V} = \frac{2(\varepsilon - 1)}{(2\varepsilon + 1)a_0^3}\left\langle \varphi\middle|\hat{\mu}\middle|\varphi\right\rangle\hat{\mu} \quad (5)$$

where $\hat{\mu}$ denotes the dipole moment operator, $\left\langle \varphi\middle|\hat{\mu}\middle|\varphi\right\rangle$ indicates the expectation value of the total dipole moment of the solute molecule,[38] ε is the solvent static dielectric constant, and a_0 is the cavity radius.[39] In this work, a_0 = 6.79 Å (determined from HF/STO-3G calculations).

In this paper, we calculated the total dipole moment values, atomic charges, and ^{1}H, ^{13}C, ^{15}N, ^{17}O NMR spectral parameters for the interaction of **1** with the open end of a SWCNT in water, DMSO, methanol, and acetone by the HF/STO-3G method. For the interaction in water, these parameters were also obtained by the B1LYP/3-21G and HF/3-21G methods.

NMR is based on the quantum properties of atomic nuclei. The chemical shielding refers to the phenomenon which is associated with the secondary magnetic field created by the moving electrons surrounding atomic nuclei in an external magnetic field.

The chemical shielding tensor describes how the shielding varies with the molecular orientation. The three principal components of this tensor are often given by:

$$\sigma_{11} \le \sigma_{22} \le \sigma_{33}.$$

The values of the shielding tensor are frequently expressed as the isotropic and anisotropic parts (σ_{iso} and σ_{aniso}, respectively), shielding anisotropy ($\Delta\sigma$), and the shielding asymmetry (η).[40,41]

Results and Discussion

The results of our theoretical study of solvent effects on the ^{1}H, ^{13}C, ^{15}N, and ^{17}O NMR shielding parameters in the case of interaction between **1** and the open end of a SWCNT (Fig. 1) in a wide range of solvent polarity values and hydrogen-bonding properties are presented in Table 1.

As was expected, the NMR shielding tensors of ^{1}H, ^{13}C, ^{15}N, and ^{17}O nuclei are drastically affected by the atom to which they are bonded and by the type of the bond to the neighboring atom. The results obtained give strong evidence that intermolecular interactions play a very important role in determining the ^{1}H, ^{13}C, ^{15}N, and ^{17}O NMR chemical shielding tensors. Some systematic trends appeared from the analysis of the calculated values.

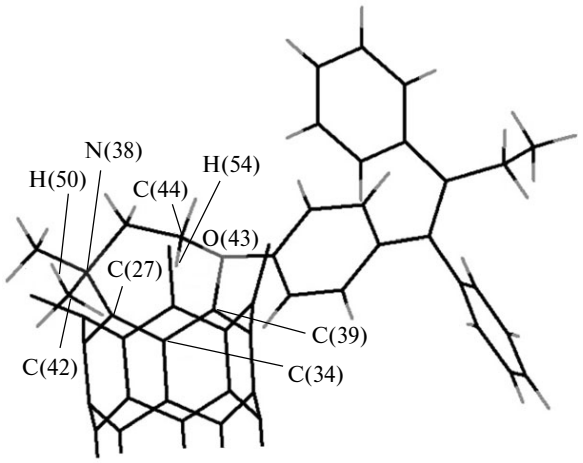

Fig. 1. Interaction between tamoxifen molecule and the open end of a SWCNT.

A comparison of the σ_{iso}, σ_{aniso}, and δ values for the O(43) and N(38) atoms with other shielding values in Table 1 revealed that the largest and smallest σ_{iso} values were obtained by the HF/3-21G method for acetone and water, respectively. Interestingly, the shielding asymmetry (η) values demonstrate the opposite trend.

An important piece of information can be obtained by analyzing correlations between the NMR parameters and dielectric constants (ε) of different solvents (see Table 1).

Table 1. Components of the magnetic shielding tensor (σ, ppm), magnetic shielding anisotropy ($\Delta\sigma$, ppm), shielding asymmetry (η), and the chemical shift tensor (δ) calculated for C, H, N, and O nuclei in the active site of tamoxifen **1** and for carbon atoms of the open end of a SWCNT

Method	Parameter	C(27)	C(34)	C(39)	C(42)	N(38)	O(43)	C(44)	H(50)	H(54)
					Gas phase (ε = 1)					
HF/ 3-21G	σ_{iso}	95.1866	62.5618	35.8729	166.1880	229.4833	315.9576	143.2694	30.1460	27.6460
	σ_{aniso}	112.7857	175.1518	216.2723	67.2957	22.3461	79.0340	71.8656	12.0984	6.6939
	σ_{11}	−1.5782	−13.3636	−164.8032	134.0664	215.0095	258.4308	110.3494	25.7756	21.9210
	σ_{22}	116.7610	21.7193	92.3675	153.4459	229.0596	320.7951	128.2790	26.4507	28.9084
	σ_{33}	170.3771	179.3297	180.0545	211.0518	244.3807	368.6470	191.1797	38.2116	32.1086
	$\Delta\sigma$	−145.14729	175.15185	−301.0142	67.29565	22.34615	−86.29025	71.8655	12.09845	−8.5875
	η	0.55409	0.30045	0.43696	0.43196	0.94312	0.83182	0.37423	0.08370	0.55899
	δ	−96.7648	116.7679	−200.6761	44.8638	14.8974	−57.5268	47.9103	8.0656	−5.725
					Water (ε = 78.39)					
HF/ 3-21G	σ_{iso}	93.1051	28.2099	214.0322	173.2326	236.9963	304.9508	146.5885	30.1777	27.9090
	σ_{aniso}	254.2409	197.8119	194.4644	53.5668	22.6763	64.2407	67.4331	12.4295	8.7129
	σ_{11}	−129.4336	−54.3366	101.1151	153.3175	220.7284	248.4664	114.4351	24.9586	18.3244
	σ_{22}	146.1499	−21.1181	197.3065	157.4365	238.1466	318.6081	133.7864	27.1105	31.6850
	σ_{33}	262.5991	160.0846	343.6752	208.9438	252.1138	347.7779	191.5439	38.4641	33.7176
	$\Delta\sigma$	−333.8081	197.81195	194.4644	53.5668	−24.4018	−84.7266	67.43315	12.42955	−14.3769
	η	0.52328	0.25189	0.85857	0.74197	0.11534	0.51642	0.43046	0.25969	0.21207
	δ	−222.5387	131.8747	129.643	35.7112	−16.2679	−56.4844	44.9554	8.2864	−9.5846

(*to be continued*)

Table 1 (*continued*)

Method	Parameter	C(27)	C(34)	C(39)	C(42)	N(38)	O(43)	C(44)	H(50)	H(54)
					Water (ε = 78.39)					
HF/	σ_{iso}	167.7629	81.4765	55.2370	192.3122	276.1111	373.2649	180.1912	30.7114	29.1089
STO-3G	σ_{aniso}	65.2363	185.2129	134.6094	67.6476	7.5775	78.0386	70.0900	12.5187	5.7506
	σ_{11}	119.1187	−14.9200	−92.5785	164.9908	268.4221	314.3569	148.5173	25.9569	23.9130
	σ_{22}	172.9163	54.3976	113.3130	174.5352	278.7483	380.1472	165.1384	27.1201	30.4712
	σ_{33}	211.2537	204.9517	144.9766	237.4106	281.1627	425.2907	226.9179	39.0572	32.9427
	Δσ	−72.9663	185.2129	−221.7233	67.6476	−11.5334	−88.38205	70.09005	12.5187	−7.79395
	η	0.788119	0.56139	0.21421	0.21164	0.31401	0.76634	0.35571	0.13938	0.47566
	δ	−48.6442	123.4752	−147.8155	45.0984	−7.689	−58.908	46.7267	8.3458	−5.1959
					DMSO (ε = 46.7)					
HF/	σ_{iso}	167.7711	81.484	54.7353	192.3179	276.1156	373.2744	180.2127	30.7114	29.1103
STO-3G	σ_{aniso}	65.2207	185.1801	135.0902	67.6363	7.5717	77.9612	70.0553	12.5192	5.7495
	σ_{11}	119.1672	−14.9936	−93.8854	164.9997	268.4292	314.3863	148.555	25.9579	23.9135
	σ_{22}	172.8947	54.5081	113.2958	174.5453	278.7542	380.1883	165.1698	27.1187	30.4741
	σ_{33}	211.2516	204.9374	144.7954	237.4088	281.1634	425.2486	226.9162	39.0575	32.9433
	Δσ	−72.90595	185.18015	−222.931	67.6363	−11.5296	−88.33215	70.0553	12.5192	−7.7952
	η	0.78917	0.56298	0.21195	0.21170	0.31344	0.76519	0.35569	0.13908	0.47514
	δ	−48.6039	123.4534	−148.6207	45.0909	−7.6864	−58.8881	46.7035	8.3461	−5.1968
					Methanol (ε = 32.63)					
HF/	σ_{iso}	167.78	81.494	54.229	192.32	276.12	373.28	180.23	30.711	29.112
STO-3G	σ_{aniso}	65.203	185.14	135.58	67.625	7.5646	77.894	70.02	12.519	5.7481
	σ_{11}	119.22	−15.06	−95.2	165.01	268.44	314.41	148.59	25.959	23.914
	σ_{22}	172.88	54.622	113.27	174.55	278.76	380.23	165.2	27.117	30.478
	σ_{33}	211.25	204.92	144.61	237.41	281.16	425.21	226.91	39.058	32.944
	Δσ	−72.84	185.14	−224.1	67.625	−11.53	−88.31	70.02	12.519	−7.797
	η	0.7902	0.5646	0.2097	0.2117	0.3127	0.7641	0.3557	0.1388	0.4745
	δ	−48.56	123.43	−149.4	45.083	−7.684	−58.87	46.68	8.3462	−5.198
					Acetone (ε = 20.7)					
HF/	σ_{iso}	167.81	81.514	53.296	192.33	276.13	373.3	180.27	30.711	29.114
STO-3G	σ_{aniso}	65.175	185.07	135.49	67.604	7.5521	77.769	69.956	12.519	5.7456
	σ_{11}	119.32	−15.18	−97.62	165.03	268.45	314.46	148.66	25.961	23.915
	σ_{22}	172.85	54.833	113.22	174.57	278.77	380.3	165.25	27.115	30.484
	σ_{33}	211.26	204.9	144.29	237.4	281.16	425.15	226.91	39.058	32.945
	Δσ	−72.73	185.07	−226.4	67.604	−11.52	−88.26	69.956	12.519	−7.8
	η	0.7922	0.5675	0.2059	0.2118	0.3112	0.7622	0.3557	0.1383	0.4733
	δ	−48.49	123.38	−150.9	45.069	−7.679	−58.84	46.637	8.3463	−5.2

The results reported here point to a significant cooperative effect that can strongly affect these parameters.

Figure 1 illustrates the interaction of nitrogen, oxygen, carbon and hydrogen atoms of molecule **1** with carbon atoms of the open end of a SWCNT. Circumferential character of this interaction causes the formation of a dense region in the interaction site. We have investigated the structural and electrical reasons for this fact. Table 2 presents the total atomic charges (in a. u.) of the dense region calculated by the B1LYP and HF methods with the STO-3G and 3-21G basis sets for water and by the HF/STO-3G method for other solvents. Calculations revealed a negative charge at the interaction site. The O(43) and N(38) atoms at the interaction site produce a negative charge because they have high electron affinities.

Negative charge distribution is produced by the interacting atoms that induce the total dipole moment. Thus, the type of tamoxifen interaction with the open end of the SWCNT influences the dipole moment and structural stability of the **1**—SWCNT system and, consequently, its electrical properties. Table 3 lists the dipole moment values of the **1**—SWCNT system calculated by the B1LYP and HF methods with the STO-3G and 3-21G basis sets for water and with HF/STO-3G method for other solvents. According to calculations, the dipole moment values in different solvents increase with increasing dielectric

Table 2. Total atomic charges (in a.u.) in molecule **1** obtained from B1LYP and HF calculations

Method	C(27)	C(34)	C(39)	C(42)	N(38)	O(43)	C(44)	H(50)	H(54)
Gas phase (ε = 1)									
HF/3-21G	0.27763	−0.117003	0.07677	−0.418358	−0.796053	−0.719861	−0.087331	0.213379	0.289586
Water (ε = 78.39)									
HF/STO-3G	−0.07729	−0.024502	−0.067664	−0.080354	−0.149347	−0.16934	0.02725	0.085398	0.112185
HF/3-21G	0.269297	−0.021372	0.028278	−0.423862	−0.865043	−0.749585	−0.101837	0.236075	0.290487
B1LYP/3-21G	−0.2752	−0.2570	0.1218	−0.4140	−0.6094	−0.5931	−0.1925	0.2747	0.3495
DMSO (ε = 46.7)									
HF/STO-3G	−0.07727	−0.024708	0.067432	−0.080371	−0.149357	−0.169475	−0.027209	0.085408	0.112132
MeOH (ε = 32.63)									
HF/STO-3G	−0.077254	−0.024912	−0.0672	−0.080388	−0.149366	−0.169611	0.027167	0.085417	0.112079
Acetone (ε = 20.7)									
HF/STO-3G	−0.077232	−0.025284	0.066765	−0.080419	−0.149381	−0.16986	0.027092	0.085434	0.11198

constant. The largest dipole moment was obtained for water by the B1LYP/3-21G method.

In conclusion, the interaction between tamoxifen molecule **1** and the open end of a SWCNT was studied to extend the practical application field of the **1**—SWCNT system. Calculations predict the largest σ_{iso} value for acetone and the smallest one to water. Contrary to this, the shielding asymmetry (η) demonstrates the opposite trend. In addition, the orientation of water molecules on the surface of the **1**—SWCNT—water system can influence the orientation of the dipole moment vector. The reason is that a dipole in the molecule will induce a dipole in the medium, and the electric field applied by the solvent dipole will in turn interact with the molecular dipole leading to net stabilization. Thus, we can say that an increase in the dipole moment of the molecule will make the interaction between the solute and solvent molecules stronger.

Also, atoms of molecule **1** involved in the interaction with the SWCNT exhibit a particular charge distribution in the solvents considered. The nitrogen and oxygen atoms (O(43) and N(38)) in the **1**—SWCNT system bear different charges.

According to the results of our calculations, solvent effects seem to play a significant role in biological or physicochemical behavior. Therefore, unique features of this type of interaction may appear to be useful for practical applications of the **1**—SWCNT system in, *e.g.*, drug design.

Numerical values determined in this work remain constant in the solvents considered due to the formation of the dense region in the **1**—SWCNT system. Water, methanol, and ethanol can form hydrogen bonds with the system in question. In these solvents, the dense region is protected from changes.

Table 3. Theoretical values of the total dipole moment (μ) induced by the interaction of molecule **1** with the open end of a SWCNT

Solvent	Method	μ/D
Water	HF/STO-3G	23.301
	HF/3-21G	24.8144
	B1LYP/3-21G	26.9051
DMSO	HF/STO-3G	23.2666
MeOH	HF/STO-3G	23.2319
Acetone	HF/STO-3G	23.1682

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