Research Article

Fukui Function Analysis and Optical, Electronic, and Vibrational Properties of Tetrahydrofuran and Its Derivatives: A Complete Quantum Chemical Study

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The spectroscopic, optical, and electronic properties of tetrahydrofuran and its derivatives were investigated by FTIR techniques. We have done a comparative study of tetrahydrofuran and its derivatives with B3LYP with 6-311 G (d, p) as the basis set. Here we have done a relative study of their structures, vibrational assignments, and thermal, electronic, and optical properties of tetrahydrofuran and its derivatives. We have plotted frontier orbital HOMO-LUMO surfaces and molecular electrostatic potential surfaces to explain the reactive nature of tetrahydrofuran and its derivatives.

1. Introduction

Tetrahydrofuran (THF) is an organic compound with the formula $(\text{CH}_2)_4\text{O}$. The compound is classified as heterocyclic compound, specifically a cyclic ether. It is a colorless, water-miscible organic liquid with low viscosity. THF has an odor similar to acetone. Being polar and having a wide liquid range, THF is a versatile solvent. THF is often used in polymer science. For example, it can be used to dissolve polymers prior to determining their molecular mass using gel permeation chromatography. THF is also a starting material for the preparation of tetrahydrothiophene. In the presence of a solid acid catalyst, it reacts with hydrogen sulfide. THF is frequently utilized as a solvent in many pharmaceutical synthetic procedures because of its good solvency for polar and nonpolar compounds. THF is particularly capable of dissolving many ionic species and organometallics which are commonly used in specialty syntheses. In many cases, THF makes higher yields and faster reaction rates possible. In addition, THF's high volatility and very high purity facilitate solvent removal and recovery without leaving residues in the desired product [1, 2]. Tetrahydrofuran (THF) is a synthesized organic compound that is not found in the natural environment. THF is highly flammable and upon thermal decomposition may

form carbon monoxide and carbon dioxide. Under certain conditions, such as prolonged storage in contact with air, THF can decompose into explosive peroxides [3]. THF can also be synthesized by catalytic hydrogenation of furan [4, 5]. THF has been explored as a water-based cosolvent to aid in the deconstruction and delignification of plant lignocellulosic biomass, which are relevant to the production of renewable platform chemicals and sugars. THF is used as a component in mobile phases for reversed-phase liquid chromatography. It has a greater elution strength than methanol or acetonitrile but is less commonly used than these solvents [6].

As a part of our ongoing research work [7–9], we report the comparative study of tetrahydrofuran (THF) and its derivatives by DFT study. To the best of our knowledge no comparative quantum chemical calculations of these molecules have been reported so far in the literature.

2. Experimental and Computational Methods

2.1. Structure and Spectra. The molecular structures of the tetrahydrofuran (THF) and its derivatives are made by molecular modeling. The model molecular structures of tetrahydrofuran (THF) and its derivatives are given in Figure 1.

FIGURE 1: Model molecular structures of tetrahydrofuran and its derivatives.

We have taken the infrared spectrum of tetrahydrofuran (THF) from literature which was recorded with FTIR Perkin Elmer spectrometer in KBr dispersion in the range of 500 to 4000 cm^{-1} for the title molecule as shown in Figure 3 [10].

2.2. Computational Methods. All the calculations were performed by the B3LYP [11, 12] method using the 6-311 G (d, p) basis set of density functional theory [13]. All computations were carried out with the GAUSSIAN 09 package [14]. By combining the results of the GAUSSVIEW'S program [15] with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy. Vibrational frequencies for these molecules were calculated with these methods and then scaled by 0.9613 [16].

3. Results and Discussion

3.1. Geometry Optimization. Alternate dispositions of amino groups have been studied, but finally we get these five optimized structures of THF derivatives. Optimized parameters of tetrahydrofuran (THF) and its derivatives (amino tetrahydrofuran, 1,2-diamino tetrahydrofuran, 1,2,3-triamino tetrahydrofuran, and 1,2,3,4-tetra-amino tetrahydrofuran) calculated by B3LYP method with 6-311 G (d, p) basis set are listed in Table 1 in accordance with the atom numbering scheme as shown in Figure 1. Local minimum energies are -232.5134 a.u., -287.8832 a.u., -343.2555 a.u., -398.6109 a.u.,

and -453.9997 a.u., for tetrahydrofuran (THF), amino tetrahydrofuran, 1,2-diamino tetrahydrofuran, 1,2,3-triamino tetrahydrofuran, and 1,2,3,4-tetra-amino tetrahydrofuran, respectively. Tetrahydrofuran (THF) and all its derivatives have C_1 point group symmetry. The amino groups attached to all derivatives do not lie in the plane of ring and alternatively they are in the opposite direction to each other.

For tetrahydrofuran (THF) and its derivatives, C–C bond distances are found to be in the range of 1.542–1.553 Å, 1.529–1.543 Å, 1.529–1.552 Å, 1.540–1.542 Å, and 1.532–1.549 Å while, for C–N (except THF), these values are 1.443 Å, 1.438–1.467 Å, 1.435–1.461 Å, and 1.428–1.462 Å, respectively, for amino tetrahydrofuran, 1,2-diamino tetrahydrofuran, 1,2,3-triamino tetrahydrofuran, and 1,2,3,4-tetra-amino tetrahydrofuran. For C–O, these values are 1.423 Å, 1.434 Å, 1.429 Å, 1.431 Å, and 1.435–1.462 Å, respectively, for THF, amino tetrahydrofuran, 1,2-diamino tetrahydrofuran, 1,2,3-triamino tetrahydrofuran, and 1,2,3,4-tetra-amino tetrahydrofuran. In case of C–H bond distances, they lie in the range of 1.091–1.101, 1.093, 1.092–1.094, 1.097–1.102, and 1.096–1.101, respectively. In the literature, bond lengths for THF-water complex [17] have a little bit lower values of 1.527–1.537 Å (for (C–C)) and a little bit higher values of 1.443–1.446 Å (for (C–O)). This may be due to shifting of charge in interaction of THF with water molecule. Optimized structures of tetrahydrofuran and its derivatives by B3LYP/6-311 G (d, p) method are shown in Figure 1.

TABLE 1: Optimized geometrical parameters of tetrahydrofuran and its derivatives by B3LYP/6-311 G (d, p) method.

THF		Amino THF		1,2-Diamino THF		1,2,3-Triamino THF		1,2,3,4-Tetra-amino THF	
Parameters	6-311 G (d, p)	Parameters	6-311 G (d, p)	Parameters	6-311 G (d, p)	Parameters	6-311 G (d, p)	Parameters	6-311 G (d, p)
R(1, 2)	1.5432	R(1, 2)	1.5418	R(1, 2)	1.5292	R(1, 2)	1.5423	R(1, 2)	1.5325
R(1, 5)	1.1011	R(1, 5)	1.0999	R(1, 5)	1.0924	R(1, 5)	1.097	R(1, 5)	1.0961
R(1, 6)	1.0906	R(1, 12)	1.4347	R(1, 6)	1.0965	R(1, 10)	1.431	R(1, 9)	1.4353
R(1, 13)	1.4235	R(1, 13)	1.4439	R(1, 11)	1.4291	R(1, 11)	1.4351	R(1, 19)	1.437
R(2, 3)	1.5535	R(2, 3)	1.5295	R(2, 3)	1.5337	R(2, 3)	1.538	R(2, 3)	1.5383
R(2, 7)	1.0915	R(2, 6)	1.0962	R(2, 7)	1.093	R(2, 6)	1.1027	R(2, 8)	1.1019
R(2, 11)	1.0918	R(2, 10)	1.0923	R(2, 10)	1.0939	R(2, 14)	1.46	R(2, 16)	1.4594
R(3, 4)	1.5422	R(3, 4)	1.5356	R(3, 4)	1.5521	R(3, 4)	1.54	R(3, 4)	1.5497
R(3, 8)	1.0918	R(3, 7)	1.0942	R(3, 8)	1.0989	R(3, 9)	1.1016	R(3, 6)	1.0984
R(3, 12)	1.0915	R(3, 11)	1.092	R(3, 15)	1.4672	R(3, 17)	1.4619	R(3, 13)	1.462
R(4, 9)	1.1012	R(4, 8)	1.0935	R(4, 9)	1.0945	R(4, 7)	1.094	R(4, 7)	1.0951
R(4, 10)	1.0906	R(4, 9)	1.0978	R(4, 11)	1.4492	R(4, 8)	1.097	R(4, 9)	1.4623
R(4, 13)	1.4233	R(4, 12)	1.4316	R(4, 12)	1.4383	R(4, 10)	1.4345	R(4, 10)	1.4288
A(2, 1, 5)	110.59	R(13, 14)	1.0139	R(12, 13)	1.0140	R(11, 12)	1.0099	R(10, 11)	1.0139
A(2, 1, 6)	114.00	R(13, 15)	1.0156	R(12, 14)	1.0161	R(11, 13)	1.013	R(10, 12)	1.0164
A(2, 1, 13)	105.68	A(2, 1, 5)	109.82	R(15, 16)	1.0146	R(14, 15)	1.0148	R(13, 14)	1.0168
A(5, 1, 6)	108.53	A(2, 1, 12)	104.71	R(15, 17)	1.0158	R(14, 16)	1.016	R(13, 15)	1.0126
A(5, 1, 13)	110.07	A(2, 1, 13)	118.27	A(2, 1, 5)	113.45	R(17, 18)	1.0134	R(16, 17)	1.0166
A(6, 1, 13)	107.85	A(5, 1, 12)	108.94	A(2, 1, 6)	110.73	R(17, 19)	1.0163	R(16, 18)	1.0149
A(1, 2, 3)	103.35	A(5, 1, 13)	106.64	A(2, 1, 11)	104.92	A(2, 1, 5)	108.92	R(19, 20)	1.0145
A(1, 2, 7)	110.79	A(12, 1, 13)	108.17	A(5, 1, 6)	108.92	A(2, 1, 10)	103.40	R(19, 21)	1.017
A(1, 2, 11)	111.71	A(1, 2, 3)	102.64	A(5, 1, 11)	108.20	A(2, 1, 11)	117.42	A(2, 1, 5)	109.37
A(3, 2, 7)	110.69	A(1, 2, 6)	109.05	A(6, 1, 11)	110.49	A(5, 1, 10)	110.09	A(2, 1, 9)	104.13
A(3, 2, 11)	112.63	A(1, 2, 10)	112.24	A(1, 2, 3)	102.05	A(5, 1, 11)	107.87	A(2, 1, 19)	112.24
A(7, 2, 11)	107.66	A(3, 2, 6)	110.68	A(1, 2, 7)	113.41	A(10, 1, 11)	108.98	A(5, 1, 9)	109.70
A(2, 3, 4)	103.31	A(3, 2, 10)	114.04	A(1, 2, 10)	110.29	A(1, 2, 3)	101.55	A(5, 1, 19)	107.76
A(2, 3, 8)	112.69	A(6, 2, 10)	108.04	A(3, 2, 7)	112.77	A(1, 2, 6)	106.59	A(9, 1, 19)	113.54
A(2, 3, 12)	110.65	A(2, 3, 4)	101.29	A(3, 2, 10)	109.88	A(1, 2, 14)	112.73	A(1, 2, 3)	101.74
A(4, 3, 8)	111.81	A(2, 3, 7)	110.39	A(7, 2, 10)	108.30	A(3, 2, 6)	107.83	A(1, 2, 8)	106.95
A(4, 3, 12)	110.69	A(2, 3, 11)	113.81	A(2, 3, 4)	102.30	A(3, 2, 14)	114.08	A(1, 2, 16)	111.71
A(8, 3, 12)	107.68	A(4, 3, 7)	110.55	A(2, 3, 8)	111.46	A(6, 2, 14)	113.14	A(3, 2, 8)	107.89
A(3, 4, 9)	110.60	A(4, 3, 11)	112.78	A(2, 3, 15)	110.20	A(2, 3, 4)	100.24	A(3, 2, 16)	114.45
A(3, 4, 10)	114.02	A(7, 3, 11)	107.93	A(4, 3, 8)	109.35	A(2, 3, 9)	111.23	A(8, 2, 16)	113.21
A(3, 4, 13)	105.58	A(3, 4, 8)	112.97	A(4, 3, 15)	109.78	A(2, 3, 17)	109.07	A(2, 3, 4)	101.38
A(9, 4, 10)	108.54	A(3, 4, 9)	111.11	A(8, 3, 15)	113.16	A(4, 3, 9)	110.64	A(2, 3, 6)	111.63
A(9, 4, 13)	110.10	A(3, 4, 12)	106.54	A(3, 4, 9)	110.01	A(4, 3, 17)	110.92	A(2, 3, 13)	109.53
A(10, 4, 13)	107.87	A(8, 4, 9)	108.09	A(3, 4, 11)	106.27	A(9, 3, 17)	113.88	A(4, 3, 6)	109.58
A(1, 13, 4)	105.45	A(8, 4, 12)	108.85	A(3, 4, 12)	112.46	A(3, 4, 7)	110.82	A(4, 3, 13)	110.85
—	—	A(9, 4, 12)	109.18	A(9, 4, 11)	106.73	A(3, 4, 8)	111.61	A(6, 3, 13)	113.23
—	—	A(1, 12, 4)	110.98	A(9, 4, 12)	107.64	A(3, 4, 10)	107.36	A(3, 4, 7)	110.69
—	—	A(1, 13, 14)	110.92	A(11, 4, 12)	113.55	A(7, 4, 8)	108.85	A(3, 4, 9)	105.55
—	—	A(1, 13, 15)	110.93	A(1, 11, 4)	110.13	A(7, 4, 10)	109.52	A(3, 4, 10)	111.81
—	—	—	—	A(4, 12, 13)	110.02	A(8, 4, 10)	108.62	A(7, 4, 9)	106.37
—	—	—	—	A(4, 12, 14)	109.06	A(1, 10, 4)	109.9819	A(7, 4, 10)	108.40
—	—	—	—	A(13, 12, 14)	107.59	A(1, 11, 12)	113.46	A(9, 4, 10)	113.85

TABLE 1: Continued.

THF		Amino THF		1,2-Diamino THF		1,2,3-Triamino THF		1,2,3,4-Tetra-amino THF	
Parameters	6-311 G (d, p)	Parameters	6-311 G (d, p)	Parameters	6-311 G (d, p)	Parameters	6-311 G (d, p)	Parameters	6-311 G (d, p)
—	—	—	—	A(3, 15, 16)	109.93	A(1, 11, 12)	113.46	A(1, 9, 4)	110.34
—	—	—	—	A(3, 15, 17)	109.19	A(1, 11, 13)	113.56	A(4, 10, 11)	110.56
—	—	—	—	A(16, 15, 17)	107.21	A(12, 11, 13)	111.02	A(4, 10, 12)	108.57
—	—	—	—	—	—	A(2, 14, 15)	110.84	A(11, 10, 12)	108.78
—	—	—	—	—	—	A(2, 14, 16)	109.77	A(3, 13, 14)	108.28
—	—	—	—	—	—	A(15, 14, 16)	106.59	A(3, 13, 15)	110.98
—	—	—	—	—	—	A(3, 17, 18)	111.18	A(14, 13, 15)	109.23
—	—	—	—	—	—	A(3, 17, 19)	108.87	A(2, 16, 17)	108.48
—	—	—	—	—	—	A(18, 17, 19)	108.95	A(2, 16, 18)	110.81
—	—	—	—	—	—	—	—	A(17, 16, 18)	106.92
—	—	—	—	—	—	—	—	A(1, 19, 20)	110.63
—	—	—	—	—	—	—	—	A(1, 19, 21)	109.69
—	—	—	—	—	—	—	—	A(20, 19, 21)	107.19

TABLE 2: Vibrational assignments of tetrahydrofuran (modes having high IR intensity only) with B3LYP/6-311 G (d, p).

B3LYP (calculated) unscaled	B3LYP (calculated) scaled (in lit.)	IR (int.)	Exp. IR	Exp. Raman	Vibrational assignments
281	271 (267)	8.1672	—	276	Out of plane bend in CH ₂ -O-CH ₂
644	620 (635)	4.7345	625	—	τ (C-O-C-C)
799	769	5.8498	765	—	Twist CH ₂
866	834	4.358	825	—	Twist CH ₂ in whole
901	868 (883)	5.7608	865	—	τ (C-C-C-O)
941	906	22.7829	915	913	Twist CH ₂ in whole
959	924 (934)	17.9192	930	—	Ring breathing
1046	1007	4.7743	995	—	β (C-C-H) + β (C-O-C)
1097	1056 (1068)	83.1142	1045	1071	Ring deformation
1214	1169	6.4279	1175	1174	β (C-C-H)
1261	1214 (1214)	5.8725	1205	—	Twist CH ₂
1268	1221	5.1994	1220	1234	Twist CH ₂
1395	1343	4.7295	1335	1335	β (C-C-H)
1506	1450 (1454)	5.5918	1445	1452	S(CH ₂)
2958	2848	43.4017	2840	—	ν (C-H)
2964	2854	118.3793	2855	—	ν (C-H)
3052	2939 (2936)	24.963	2930	2938	ν (C-H)
3062	2949	40.015	2950	—	ν (C-H)
3082	2968 (2968)	19.4174	2965	2975	ν (C-H)
3098	2983 (2989)	34.7534	2980	—	ν (C-H)
3110	2995	77.426	2990	—	ν (C-H)

3.2. *Assignment of Fundamentals.* Tetrahydrofuran has 13 atoms with 33 normal modes of vibration while amino tetrahydrofuran has 15 atoms with 39 normal modes of vibration. 1,2-Diamino tetrahydrofuran, 1,2,3-triamino tetrahydrofuran, and 1,2,3,4-tetra-amino tetrahydrofuran have 17, 19, and 21 atoms with 45, 51, and 57 normal modes of vibration, respectively. From our calculated data and experimental FTIR spectra, we observe similarities and differences between the experimental and the calculated frequencies

by DFT/B3LYP method. Assignments are done using the animated view of normal mode description. A good agreement is found between the theoretical and experimental data. Here we are discussing only important modes. Vibrational frequencies, calculated for tetrahydrofuran and experimental frequencies (FTIR), have been compared in Table 2. We are also discussing the assignments for tetrahydrofuran derivatives which are useful for the experimentalists in absence of its experimental data.

TABLE 3: Vibrational assignments of amino tetrahydrofuran (modes having high IR intensity only) with B3LYP/6-311 G (d, p).

B3LYP (calculated) unscaled	B3LYP (calculated) scaled	IR (int.)	Vibrational assignments
197	190	48.1062	Rock NH ₂
378	364	16.1235	Group NH ₂ bend from joint
778	749	174.8209	Rock NH ₂
877	845	23.6231	$\beta(\text{C}-\text{C}-\text{H}) + \beta(\text{C}-\text{C}-\text{C})$
957	922	65.1906	$\beta(\text{C}-\text{C}-\text{H})$
1067	1028	52.4498	Ring deformation
1133	1091	73.4975	$\beta(\text{C}-\text{C}-\text{C})$
1443	1390	25.3256	$\beta(\text{C}-\text{C}-\text{H})$
1647	1586	38.9601	S(NH ₂)
2971	2861	74.2781	$\nu(\text{C}-\text{H})$
2993	2882	62.1676	$\nu(\text{C}-\text{H})$
3023	2911	28.6539	$\nu(\text{C}-\text{H})$
3058	2945	64.6532	$\nu(\text{C}-\text{H})$
3095	2980	55.4994	$\nu(\text{C}-\text{H})$
3595	3462	0.4042	$\nu(\text{N}-\text{H})$

3.3. Vibrational Modes Description

3.3.1. C-H Vibrations. We have seen in the literature that the C-H stretching vibrations are usually observed in 2800–3200 cm⁻¹ region. In the study of tetrahydrofuran, the (C-H) functional group is present at 2848, 2854, 2939, 2949, 2968, 2983, and 2995 cm⁻¹ in calculated spectra which is in good agreement with the experimental data as given in Table 2. In vibrational assignments, the C-H stretching vibrations are in the same range for all derivatives of tetrahydrofuran listed in Tables 3, 4, 5, and 6.

3.3.2. N-H Vibrations. There is no NH₂ group added to tetrahydrofuran but they are presented in all derivatives of tetrahydrofuran. The N-H stretching vibrations are normally viewed in the region 3300–3600 cm⁻¹. For amino tetrahydrofuran, the N-H stretching vibration is calculated at 3462 cm⁻¹ while it is 3446 cm⁻¹ for 1,2-diamino tetrahydrofuran. A strong scissoring vibration of H-N-H is found at 1586 and 1584 cm⁻¹ for amino tetrahydrofuran and 1,2-diamino tetrahydrofuran, respectively. In case of 1,2,3-triamino tetrahydrofuran and 1,2,3,4-tetra-amino tetrahydrofuran, the N-H vibration is at 3447 and 3354 cm⁻¹ in calculated spectra. There are also strong scissoring vibrations at 1587 and 1588 cm⁻¹ for 1,2,3-triamino tetrahydrofuran and 1,2,3,4-tetra-amino tetrahydrofuran. Some strong rocking and twisting vibrations of NH₂ are also seen in the assignment of all derivatives of tetrahydrofuran. We see that scissoring modes in THF are lower than all the derivatives of THF. This is due to the addition of amino group (charge transfer) to THF molecule. The interpretation of vibrational spectra of THF is in good agreement with the literature [18] as given in Table 2.

TABLE 4: Vibrational assignments of 1,2-diamino tetrahydrofuran (modes having high IR intensity only) with B3LYP/6-311 G (d, p).

B3LYP (calculated) unscaled	B3LYP (calculated) scaled	IR (int.)	Vibrational assignments
257	247	77.5282	Rock NH ₂
424	408	30.1483	Twist NH ₂
753	725	46.0965	$\tau(\text{C}-\text{C}-\text{C}-\text{C})$
859	827	83.126	Rock NH ₂
905	872	171.3772	Rock NH ₂
921	887	45.5585	Rock NH ₂
954	919	112.828	Rock NH ₂
1029	991	33.4007	Twist CH ₂
1068	1028	80.3998	Ring deformation
1164	1121	20.3894	$\beta(\text{C}-\text{C}-\text{H})$ in whole molecule
1446	1392	14.2825	$\beta(\text{C}-\text{C}-\text{H})$
1645	1584	63.057	S(NH ₂)
1669	1607	31.4909	S(NH ₂)
2974	2864	55.4405	$\nu(\text{C}-\text{H})$
3010	2899	61.7424	$\nu(\text{C}-\text{H})$
3038	2926	34.5478	$\nu(\text{C}-\text{H})$
3044	2931	53.5102	$\nu(\text{C}-\text{H})$
3074	2960	46.2551	$\nu(\text{C}-\text{H})$
3090	2976	46.8808	$\nu(\text{C}-\text{H})$
3578	3446	3.4588	$\nu(\text{N}-\text{H})$

3.3.3. Other Modes of Vibration. In tetrahydrofuran, a ring deformation mode is calculated at 1056 cm⁻¹ which is in good agreement with experimental data, that is, 1055 cm⁻¹, while in all derivatives of tetrahydrofuran (except the last one) ring deformation mode is at 1028, 1028, and 1036 cm⁻¹ having appropriate IR intensity. As expected, torsion modes along with wagging modes appear in the lower frequency range. For tetrahydrofuran, strong torsion mode of C-O-C-C is at 628 cm⁻¹ in calculated spectrum which matches well with the experimental one, that is, 625 cm⁻¹, while strong torsion modes of C-C-C-C are at 725 and 474 cm⁻¹ in calculated spectrum for 1,2-di-ATHF and 1,2,3-tri-ATHE, respectively. A very strong stretching vibration of C-O is found at 981 cm⁻¹ while there is also a strong torsion mode of C-C-C-O at 731 cm⁻¹ in calculated spectra for 1,2,3,4-tetra-ATHE. There are some frequencies in lower region having appreciable IR intensity. Furthermore, the study of low frequency vibrations is of great significance, because it gives information on weak intermolecular interactions, which take place in enzyme reactions [19]. Knowledge of low frequency mode is also essential for the interpretation of the effect of electromagnetic radiation on biological systems [20]. The aim of vibrational analysis is to acquire direct information on lower and higher frequency vibrations of such THF and its derivatives. No experimental FTIR spectrum is available for comparison of derivatives of THF so it will provide a suitable path for experimental researchers.

TABLE 5: Vibrational assignments of 1,2,3-triamino tetrahydrofuran (modes having high IR intensity only) with B3LYP/6-311 G (d, p).

B3LYP (calculated) unscaled	B3LYP (calculated) scaled	IR (int.)	Vibrational assignments
187	180	38.0082	Twist NH ₂
274	264	29.2943	Twist NH ₂
324	312	23.6603	Twist NH ₂
376	362	23.1528	Twist NH ₂
492	474	18.1122	$\tau(\text{C}-\text{C}-\text{C})$
635	612	213.3144	Rock NH ₂
832	801	68.3448	Rock NH ₂
859	827	130.0253	Rock NH ₂
936	901	46.5701	Ring deformation
994	957	65.805	$\beta(\text{C}-\text{C}-\text{C})$
1026	988	47.4846	$\beta(\text{C}-\text{C}-\text{H})$
1076	1036	78.3665	Ring deformation
1132	1090	33.1727	$\beta(\text{C}-\text{C}-\text{H})$
1153	1110	30.0604	$\beta(\text{C}-\text{C}-\text{H})$
1167	1124	48.7819	$\beta(\text{C}-\text{C}-\text{H})$
1442	1389	21.4953	$\beta(\text{C}-\text{C}-\text{H})$
1648	1587	47.0934	S(NH ₂)
1660	1599	29.1316	S(NH ₂)
2934	2825	37.6667	$\nu(\text{C}-\text{H})$
2950	2841	86.3504	$\nu(\text{C}-\text{H})$
3006	2895	115.4219	$\nu(\text{C}-\text{H})$
3057	2944	47.6972	$\nu(\text{C}-\text{H})$
3579	3447	5.6057	$\nu(\text{N}-\text{H})$

3.4. *Electrical, Optical, Dipole Moment and Thermodynamical Properties.* Frontier orbital energy gap, that is, the gap between HOMO and LUMO, shows the interaction of that molecule with other species. Frontier orbital energy gap helps to differentiate the chemical reactivity of the molecules. In case of tetrahydrofuran and its derivatives, frontier orbital energy gap is 7.9402, 6.9066, 6.8312, 6.4991, and 6.8870 eV, respectively, and is given in Table 7. So it can be concluded that 1,2,3-triamino tetrahydrofuran is the most reactive compound among all. The pictures of HOMO, LUMO, and electrostatic potential (MESP) for tetrahydrofuran and its derivatives are shown in Figure 2.

Dipole moment (μ), polarizability (α), and total first static hyperpolarizability β [21, 22] can be expressed in terms of x , y , z components and are given by the following equations:

$$\begin{aligned}
 \mu &= (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}, \\
 \langle \alpha \rangle &= \frac{1}{3} [\alpha_{xx} + \alpha_{yy} + \alpha_{zz}], \\
 \beta_{\text{Total}} &= (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \\
 &= [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 \\
 &\quad + (\beta_{yyy} + \beta_{yxx} + \beta_{yzz})^2 \\
 &\quad + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2}.
 \end{aligned} \tag{1}$$

TABLE 6: Vibrational assignments of 1,2,3,4-tetra-amino tetrahydrofuran (modes having high IR intensity only) with B3LYP/6-311 G (d, p).

B3LYP (calculated) unscaled	B3LYP (calculated) scaled	IR (int.)	Vibrational assignments
260	250	43.2432	Twist NH ₂
301	290	22.3762	Twist NH ₂
347	334	25.9587	Rock NH ₂
366	352	21.3354	Rock NH ₂
426	410	18.1696	Twist NH ₂
513	494	54.7952	Torsion in whole molecule
593	571	38.3343	$\tau(\text{C}-\text{C}-\text{O}-\text{C})$
663	638	28.8211	$\tau(\text{C}-\text{C}-\text{C}-\text{C})$
759	731	56.9814	$\tau(\text{C}-\text{C}-\text{C}-\text{O})$
802	772	106.1627	Rock NH ₂
850	819	60.9417	Rock NH ₂
865	833	73.3106	Twist NH ₂ in whole places
881	848	335.8006	Twist NH ₂
902	869	149.2133	Rock NH ₂
944	909	85.627	Rock NH ₂
972	936	31.7804	$\beta(\text{C}-\text{C}-\text{C}) + \text{Twist NH}_2$
1019	981	132.2283	$\nu(\text{C}-\text{O})$
1097	1056	16.8407	Twist NH ₂
1167	1124	27.6511	Bending in whole molecule
1183	1139	25.494	$\beta(\text{C}-\text{C}-\text{H})$
1441	1388	19.585	$\beta(\text{C}-\text{C}-\text{H})$
1635	1575	55.77	S(NH ₂)
1649	1588	56.9828	S(NH ₂)
2946	2837	39.5477	$\nu(\text{C}-\text{H})$
2984	2874	58.3297	$\nu(\text{C}-\text{H})$
3033	2921	82.6875	$\nu(\text{C}-\text{H})$
3483	3354	19.1928	$\nu(\text{N}-\text{H})$
3585	3452	11.9623	$\nu(\text{N}-\text{H})$

The β components of Gaussian output are reported in atomic units.

Where 1 a.u. = 8.3693×10^{-33} e.s.u., the calculated dipole moments for tetrahydrofuran and its derivatives are 1.585, 2.855, 1.667, 4.022, and 1.743 Debye, respectively. So, 1,2,3-triamino tetrahydrofuran is a better solvent among them all. A greater contribution of α_{yy} is seen in THF, amino THF, and 1,2,3-triamino THF while α_{zz} is seen in 1,2-diamino THF and α_{xx} in 1,2,3,4-tetra-amino THF. For THF and 1,2,3-triamino THF, molecules are elongated more towards Y direction and more contracted in the X direction while amino THF molecule is elongated more towards Y direction and more contracted in the X direction. For 1,2-diamino THF, molecule is elongated more towards Z direction and more contracted in the X direction while 1,2,3,4-tetra-amino THF molecule is elongated more towards X direction and more contracted in the Y direction. It is seen that the components β_{xxz} , β_{xxy} , β_{yyy} , β_{yyx} , and β_{xxx} contribute larger part of hyperpolarizability from THF to 1,2,3,4-tetra-amino THF. This shows that

TABLE 7: Lowest energy, HOMO-LUMO gap (frontier orbital energy gap), and dipole moment of tetrahydrofuran and its derivatives by B3LYP/6-311 G (d, p) method.

Parameters	THF	Amino THF	1,2-Diamino THF	1,2,3-Triamino THF	1,2,3,4-Tetra-amino THF
Energy (in au)	-232.5134	-287.8832	-343.2555	-398.6109	-453.9997
Dipole moment (in Debye)	1.585	2.855	1.667	4.022	1.743
HOMO	-0.25509	-0.23322	-0.22235	-0.21917	-0.22375
LUMO	0.03683	0.02070	0.02880	0.01977	0.02945
Frontier orbital energy gap (eV)	7.9402	6.9066	6.8312	6.4991	6.8870

FIGURE 2: Pictures of HOMO-LUMO and molecular electrostatic potential of tetrahydrofuran and its derivatives.

FIGURE 3: Experimental IR spectra of tetrahydrofuran.

XZ and XY planes and Y- and X-axes are more optically active in these directions. The values of hyperpolarizability indicate a possible use of these compounds in electrooptical applications.

Internal thermal energy (E), constant volume heat capacity C_v , and entropy S , calculated at B3LYP/6-311 G (d, p) level, are listed in Table 9. We know that conduction band is almost empty at the room temperature, so electronic contribution in total energy is negligible. All the thermodynamic data

supplies helpful information for the further study on the THF and its derivatives. They can be used to compute the other thermodynamic energies according to relationships of thermodynamic functions and estimate directions of chemical reactions according to the second law of thermodynamics in the thermochemical field. So thermodynamic properties show that vibrational motion plays an important role.

3.5. Reactivity Descriptors

3.5.1. Global Reactivity Descriptors. Global reactivity descriptors are described as

$$\text{Energy band gap} = (\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}),$$

$$\text{Electronegativity } (\chi) = -\frac{1}{2} (\epsilon_{\text{LUMO}} + \epsilon_{\text{HOMO}}),$$

$$\text{Chemical potential } \mu = -\chi,$$

$$\text{Global hardness } \eta = \frac{1}{2} (\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}),$$

TABLE 8: Polarizability and hyperpolarizability of tetrahydrofuran and its derivatives by B3LYP/6-311 G (d, p) methods.

Polarizability	THF	Amino THF	1,2-Diamino THF	1,2,3-Triamino THF	1,2,3,4-Tetra-amino THF
α_{xx}	-29.2994	-35.5422	-41.5883	-43.8040	-55.7761
α_{xy}	-0.0137	4.5742	-2.1265	6.8303	0.1740
α_{yy}	-34.8626	-40.9807	-41.9550	-50.3155	-50.3145
α_{yz}	-0.7807	-0.8029	-0.1374	0.0764	2.3250
α_{zz}	-31.4458	-35.4849	-43.4920	-49.1301	-53.4053
α_{zx}	0.0077	0.5506	-0.9605	-0.3221	-2.4170
α	31.8692	37.3359	42.3451	47.7498	53.1653
Hyperpolarizability					
β_{xxx}	-0.0052	5.6681	-0.2912	-6.3842	-6.7955
β_{xxy}	-4.0970	6.2139	-8.0690	13.6734	-4.4365
β_{xyy}	0.0298	-1.6268	6.3043	-3.2086	-1.8247
β_{yyy}	-0.6535	-0.2718	14.9291	14.4296	-0.2671
β_{zzz}	-1.1489	1.5867	0.4088	2.4337	-0.1471
β_{xxz}	-1.9217	1.5767	-6.1872	-0.5541	-3.9772
β_{xzz}	-0.0222	3.9764	2.7638	6.3393	-2.8358
β_{yzz}	-0.4033	-1.2208	-3.7949	2.7311	-4.7413
β_{yyz}	0.9213	-0.3137	-0.8388	6.3633	1.4539
β_{xyz}	0.0193	-1.1644	-0.5408	-3.0478	-4.4281
β total	5.5840	9.7200	11.4027	32.0675	15.0620

TABLE 9: Calculated thermodynamic properties of tetrahydrofuran and its derivatives by B3LYP/6-311 G (d, p) methods.

	THF	Amino THF	1,2-Diamino THF	1,2,3-Triamino THF	1,2,3,4-Tetra-amino THF
E (thermal) (kcalmol ⁻¹)					
Total	75.553	87.449	99.560	110.546	122.799
Translational	0.889	0.889	0.889	0.889	0.889
Rotational	0.889	0.889	0.889	0.889	0.889
Vibrational	73.776	85.672	97.783	108.769	121.022
C_V (cal K ⁻¹ mol ⁻¹)					
Total	14.943	22.356	26.632	32.701	36.652
Translational	2.981	2.981	2.981	2.981	2.981
Rotational	2.981	2.981	2.981	2.981	2.981
Vibrational	8.982	16.394	20.671	26.739	30.690
S (cal K ⁻¹ mol ⁻¹)					
Total	67.259	78.055	81.513	88.746	91.737
Translational	38.741	39.305	39.779	40.188	40.548
Rotational	24.911	26.233	27.149	28.115	28.869
Vibrational	3.607	12.517	14.584	20.443	22.320

$$\text{Global softness} \left(S = \frac{1}{2\eta} \right),$$

$$\text{Global electrophilicity index } \omega = \frac{\mu^2}{2\eta} \quad (2)$$

(see [23–27]). All these parameters for tetrahydrofuran and its derivatives have been listed in Table 6.

According to these parameters, the chemical reactivity varies with the structural configuration of molecules. Chemical hardness (softness) value of 1,2,3-amino THF is lesser (greater) among all the three molecules. Thus, 1,2,3-amino

THF is found to be most reactive among all, whereas THF configuration is less reactive. THF configuration possesses higher electronegativity while 1,2,3-amino THF possesses lower electrophilicity index among them all as given in Table 10. Correlations have been found between electrophilicity of various chemical compounds and reaction rates in biochemical systems.

3.6. Local Reactivity Descriptors. Fukui function (FF) provides information on the local site reactivity within the molecule and as such it provides a system for understanding of chemical reactions. These values correspond to the

TABLE 10: Calculated ϵ_{HOMO} , ϵ_{LUMO} , energy band gap ($\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$), chemical potential (μ), electronegativity (χ), global hardness (η), global softness (S), and global electrophilicity index (ω) for tetrahydrofuran and its derivatives at B3LYP/6-311 G (d, p) level.

Compounds	ϵ_H	ϵ_L	$\epsilon_L - \epsilon_H$	χ	μ	η	S	ω
THF	-0.25509	0.03683	0.29192	0.10913	-0.10913	0.14596	3.425596054	0.0408
1,2 THF	-0.23322	0.02070	0.25391	0.1011	-0.1011	0.13398	3.7319	0.03814
1,2,3-Amino THF	-0.22235	0.02880	0.25114	0.10323	-0.10323	0.12631	3.95867	0.04218
1,2,3,4 THF	-0.21917	0.01977	0.23893	0.09814	-0.09814	0.13043	3.83347	0.03692
Amino THF	-0.22375	0.02945	0.25319	0.10014	-0.10014	0.1349	3.70645	0.03717

TABLE 11: Fukui functions (f_k^+ , f_k^-), local softness (s_k^+ , s_k^-), and local electrophilicity indices (ω_k^+ , ω_k^-) for selected atomic sites of CPPC, using Mulliken population analysis at B3LYP/6-311 G (d, p) level.

THF	M	M-	M+	f_k^+	f_k^-	s_k^+	s_k^-	ω_k^+	ω_k^-
C1	0.09218	-0.13948	0.308091	0.231663	0.215911	0.793585	0.739625	0.009452	0.008809
C2	0.006981	-0.24299	0.12914	0.249968	0.122159	0.85629	0.418468	0.010199	0.004984
C3	0.00709	-0.24193	0.129566	0.249016	0.122476	0.853029	0.419554	0.01016	0.004997
C4	0.092228	-0.13921	0.307449	0.231433	0.215221	0.792797	0.737261	0.009442	0.008781
O13	-0.198474	-0.23646	0.125765	0.037987	0.324239	0.130128	1.110713	0.00155	0.013229
Amino THF	M	M-	M+	f_k^+	f_k^-	s_k^+	s_k^-	ω_k^+	ω_k^-
C1	0.122663	0.009106	0.241709	0.113557	0.119046	0.420893	0.441238	0.004221	0.004425
C2	-0.008726	-0.24682	0.114327	0.238093	0.123053	0.88248	0.45609	0.00885	0.004574
C3	0.010672	-0.19419	0.113287	0.204865	0.102615	0.759322	0.380337	0.007615	0.003814
C4	0.089502	-0.09679	0.248705	0.186288	0.159203	0.690467	0.590078	0.006924	0.005918
O12	-0.203353	-0.23584	-0.04207	0.032482	0.161283	0.120393	0.597787	0.001207	0.005995
N13	-0.010961	-0.2358	0.323848	0.224837	0.334809	0.833347	1.240953	0.008357	0.012445
1,2-Amino THF	M	M-	M+	f_k^+	f_k^-	s_k^+	s_k^-	ω_k^+	ω_k^-
C1	0.080415	-0.0421	0.22964	0.12251	0.149225	0.457195	0.556893	0.004673	0.005691
C2	0.004480	-0.17372	0.087954	0.178204	0.083474	0.66504	0.311517	0.006797	0.003184
C3	0.035609	-0.10002	0.115193	0.135632	0.079584	0.506165	0.297	0.005173	0.003035
C4	0.119975	0.005564	0.199748	0.114411	0.079773	0.42697	0.297705	0.004364	0.003043
O11	-0.21865	-0.24652	-0.06071	0.02786	0.157941	0.103971	0.58942	0.001063	0.006024
N12	-0.00822	-0.16639	0.232471	0.158162	0.240694	0.590245	0.898246	0.006032	0.00918
N15	-0.01388	-0.27714	0.195416	0.263249	0.209305	0.982419	0.781105	0.01004	0.007983
1,2,3-Amino THF	M	M-	M+	f_k^+	f_k^-	s_k^+	s_k^-	ω_k^+	ω_k^-
C1	0.115624	0.073205	0.190554	0.042419	0.07493	0.167923	0.296623	0.001789	0.003161
C2	0.022828	-0.08061	0.076666	0.103439	0.053838	0.409481	0.213127	0.004363	0.002271
C3	0.025129	-0.0762	0.118366	0.101328	0.093237	0.401124	0.369095	0.004274	0.003933
C4	0.078038	-0.01158	0.206247	0.089616	0.128209	0.35476	0.507537	0.00378	0.005408
O10	-0.20327	-0.22649	-0.09324	0.023211	0.110038	0.091885	0.435604	0.000979	0.004641
N11	-0.00094	-0.20016	0.211528	0.19922	0.212469	0.788646	0.841095	0.008403	0.008962
N14	-0.00158	-0.3101	0.089629	0.308517	0.091209	1.221317	0.361066	0.013013	0.003847
N17	-0.03592	-0.16821	0.20016	0.132288	0.236083	0.523685	0.934575	0.00558	0.009958
1,2,3,4-Amino THF	M	M-	M+	f_k^+	f_k^-	s_k^+	s_k^-	ω_k^+	ω_k^-
C1	0.108686	0.070775	0.163507	0.037911	0.054821	0.145331	0.210155	0.0014	0.002024
C2	0.030688	-0.08776	0.063705	0.118443	0.033017	0.454048	0.12657	0.004373	0.001219
C3	0.028906	-0.0894	0.100662	0.118308	0.071756	0.45353	0.275074	0.004368	0.002649
C4	0.110441	0.02905	0.179846	0.081391	0.069405	0.31201	0.266062	0.003005	0.002562
O9	-0.233907	-0.2548	-0.12637	0.020888	0.107535	0.080074	0.412232	0.000771	0.00397
N10	-0.024483	-0.11068	0.209354	0.086201	0.233837	0.330449	0.896407	0.003183	0.008633
N13	-0.023684	-0.16618	0.165895	0.142499	0.189579	0.546266	0.726745	0.005261	0.006999
N16	0.004591	-0.24299	0.065478	0.24758	0.060887	0.949091	0.233408	0.009141	0.002248
N19	-0.001198	-0.14799	0.177963	0.146794	0.179161	0.56273	0.686808	0.00542	0.006615

qualitative descriptors of reactivity of different atoms in the molecule. A study by Ayers and Parr [27] has shown that FF is larger when attacked by soft reagents and in places where the FF is smaller when attacked by hard reagents. Fukui functions for electrophilic and nucleophilic attacks have been made with the basis of B3LYP/6-311 G (d, p) level of theory. With the help of Mulliken atomic charges of cationic and anionic states, local Fukui functions (f_k^+ , f_k^-), local softness values (s_k^+ , s_k^-), and local electrophilicity indices (ω_k^+ , ω_k^-) have been calculated using the following equation:

$$\begin{aligned} f_k^+ &= [q(N+1) - q(N)] \quad \text{for nucleophilic attack} \\ f_k^- &= [q(N) - q(N-1)] \quad \text{for electrophilic attack} \\ f_k^0 &= \frac{1}{2} [q(N+1) + q(N-1)] \quad \text{for radical attack.} \end{aligned} \quad (3)$$

Local softness values and electrophilicity indices are calculated using

$$\begin{aligned} s_k^+ &= S f_k^+, & s_k^- &= S f_k^- \\ \omega_k^+ &= \omega f_k^+, & \omega_k^- &= \omega f_k^-, \end{aligned} \quad (4)$$

where + and - signs show nucleophilic and electrophilic attack, respectively.

Fukui functions, local softness values, and local electrophilicity indices for selected atomic sites in tetrahydrofuran and its derivatives have been listed in Tables 7 and 8. For amino hydrofuran, the maximum value for local nucleophilic reactivity descriptors (f_k^- , s_k^- , ω_k^-) at N13 indicates that this site is more prone to electrophilic attack. But in comparison with N16 of 1,2,3,4-tetra-amino hydrofuran it is found that the N16 of 1,2,3,4-tetra-amino hydrofuran has lower affinity towards electrophile as given in Table 11. This situation changes because of change of position of the nitrogen of 1,2,3,4-tetra-amino hydrofuran, and hence the charge density around N16 decreased.

4. Conclusions

All calculated wave numbers are real in nature for all the molecules and thus all the compounds are stable. We have done density functional calculations on tetrahydrofuran and its derivatives. The calculated parameters (bond lengths and bond angles) and wave numbers show a good agreement with the corresponding experimental data showing the strength of density functional calculations. Normal modes are discussed in detail with the help of Gauss view program. The chemical reactivity of molecules shows the supremacy of 1,2,3-triamino tetrahydrofuran over the remaining molecules. A possible use of these compounds in electrooptical applications is discussed with the help of hyperpolarizability. In addition, to assess the utility of global reactivity descriptors, the relationships between the reactivity and electrophilicity have been discussed. THF configuration possesses higher electronegativity while 1,2,3-amino THF possesses lower electrophilicity index among them all. Correlations have been found between electrophilicity of various chemical compounds and reaction rates in biochemical systems.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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