

Research Article



Theoretical Spectroscopic Study (IR, Raman, UV, and NMR) for Furan and Two of its Derivatives

Safaa Jumma Tumaa, Shatha Fadil AL-Saidi*

College of Sciences, Al-Nahrain University, Baghdad, Iraq.

*Corresponding author's E-mail: shathaalsaidi1954@gmail.com

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ABSTRACT

Furan and its derivatives are important compounds in industrial applications, biological activity, bio-fuels food and nutrition. The ground-state molecular geometry, and harmonic vibrational frequencies with infrared intensities and Raman activities, of furan (F) and its derivatives [2- methylfuran (MF) and 2, 5- dimethylfuran (DMF)] were computed, by using the Density Functional Theory (DFT/B3LYP) method plus the basis set cc-pVTZ. The time-dependent (TD-DFT) was performed to obtain the electronic absorption spectra. Furthermore the chemical shifts of the nuclear magnetic resonance were calculated by the Gauge-Invariant Atomic Orbital (GIAO) method. The result showed that the Furan ring bond angle C2O1C5 was lower than the 2-methylfuran and 2, 5- dimethylfuran, due to the attachment of methyl group at C2 position in 2-methylfuran, and C2, C5 positions in 2,5-dimethylfuran molecules. The vibrational spectra demonstrated that the ring C-C symmetric and asymmetric stretching vibrations, ranged between 1414- 1033 cm^{-1} . These vibrations decreased in the following order (F > MF > DMF), while the C=C stretching vibrations decreased in the opposite order (DMF > MF > F). The UV spectra of furan and its studied derivatives in gas phase and solvent (ethanol) showed one peak. Therefore the type of transition is $\pi \rightarrow \pi^*$. The NMR for the protons (C=CH-) of furan ring illustrated more shielding in MF than F molecule. Also in DMF molecule the protons demonstrated a high shielding, which influence by the presence of CH₃ donating group.

Keywords: Furan, 2- methylfuran, 2, 5- dimethylfuran, DFT, Vibrational spectra, UV spectra, and NMR spectra.

INTRODUCTION

The DFT-B3LYP method is widely used in many investigations. This method gives reasonable energies, molecular structures, vibrational frequencies, UV-Vis, and nuclear magnetic resonance, in addition, it needs less computation resource¹.

Furan (F) and its derivatives are significant molecules, due to its high energy density, it is also considered in the exchange of fuel, plus its importance in the of biology and industries fields². Furan is a heterocyclic organic compound colorless liquid, highly volatile, flammable, has low solubility in water, and low boiling point^{3,4}. 2- Methyl furan (MF), and 2,5- dimethyl furan (DMF) have attracted the attention, since they have a greater volumetric energy density, lower water solubility, high boiling point, and higher octane number⁽²⁾. These properties make to convert abundant renewable biomass resources into liquid fuels, which may minimize the dependence on petroleum^{3,5}.

The target of the present theoretical work was to calculate the molecular optimized geometry. From the computed optimized geometrical parameters. Then the vibrational spectra results were employed to characterize the harmonic vibrational wave numbers in the ground state, and the NMR spectra. Also the electronic properties such as: the molecular electrostatic potential (MEP), HOMO, and LUMO energies, plus the electronic absorption spectra for the optimized molecule were computed. All the theoretical calculations were done by

using the density functional theory DFT /B3LYP method with the cc-pVTZ (2d,2p) basis set level, for furan (F), 2- methylfuran (MF), and 2,5- dimethylfuran (DMF) molecules.

Computational Details

The DFT is a significance quantum chemical method (1) due to its high accuracy (2) consuming short time^{6,7}. The time-dependent density functional theory (TD-DFT) gives a satisfactory theoretical result when compared with experiment work, for electronic absorption spectra⁸. The B3LYP with the GIAO method is one of the most common approaches for calculating the nuclear magnetic shielding tensors⁹. The present calculations were performed using the Gaussian 09 program on a windows-XP operating PC^{10,11}.

The molecular structure in ground state for the studied compounds was examined by the DFT with the B3LYP/ cc-pVTZ (2d, 2p) basis set, utilizing the vibrational frequencies, UV-Vis, NMR spectra. Electronic absorption spectra, vertical excitation energies, maximum absorption wavelengths (λ max), and oscillator strengths were computed by the (TD-DFT) methods. The GIAO method was employed to evaluate the nuclear magnetic shielding tensors.



RESULTS AND DISCUSSION

Molecular geometry

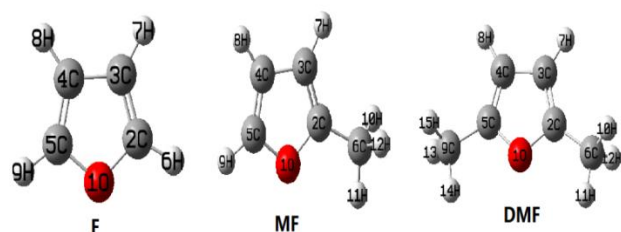


Figure 1: The calculated molecular structure scheme, for the studied compound along with their atom numbering.

The calculated molecular structure results for F, MF, and DMF molecules were presented in figure 1, and Table 1. The calculations outcome revealed that the structural parameter data were coincidence with the available theoretical and experimental results for Furan molecule, Table 1^{12, 13}.

The furan ring bond angle $C_2O_1C_5$ demonstrated small decreasing in the following order F, MF, DMF. This due to the substitution of one methyl group in C_2 position, or two groups in C_2 and C_5 positions.

Table 1: The optimized geometry data of F (compared with other works), MF, and DMF molecules.

Structural parameter	Other Work				This work DFT cc-pVTZ (2d, 2p)		
	Exp.		Theoretical				
	(13)	(12)	(13)	(12)	F	MF	DMF
Bond length in (Å^o)							
O ₁ -C ₂	1.362	1.362	1.361	1.354	1.361	1.367	1.369
O ₁ -C ₅						1.367	
C ₂ =C ₃	1.361	1.361	1.354	1.349	1.355	1.359	1.357
C ₄ =C ₅						1.353	
C ₃ -C ₄	1.431	1.431	1.438	1.433	1.431	1.432	1.431
C ₂ -C ₆						1.489	1.489
C ₂ -H ₆	1.075	1.075	1.075	1.069	1.075		
C ₃ -H ₇	1.077	1.077	1.076	1.070	1.076	1.076	1.077
C ₄ -H ₈					1.076	1.076	1.077
C ₅ -H ₉					1.075	1.075	
C ₆ -H ₁₀						1.090	1.092
C ₆ -H ₁₁						1.088	1.089
Bond angle in degree							
C ₂ O ₁ C ₅	106.5	106.7	106.8	106.6	106.8	107.6	108.1
O ₁ C ₂ C ₃	110.7	110.7	110.4	110.8	110.4	109.2	109.1
O ₁ C ₅ C ₄					110.4	110.1	109.1
C ₂ C ₃ C ₄	106.0		106.2		106.1	106.9	106.8
C ₃ C ₄ C ₅		106.0		105.9	106.1	106.2	106.8
C ₃ C ₂ C ₆						134.1	134.2
O ₁ C ₂ C ₆						116.7	116.6
O ₁ C ₂ H ₆	115.9	115.9	115.9	115.8	116.0		
C ₃ C ₂ H ₆	133.4		133.6		133.6		
C ₂ C ₃ H ₇	126.1	126.1	126.5	126.3	126.4	127.1	126.1
C ₄ C ₃ H ₇	127.9		127.3		127.4	125.2	127.1
C ₃ C ₄ H ₈					127.4	127.3	127.1
C ₅ C ₄ H ₈					126.4	126.4	126.1
O ₁ C ₅ H ₉					116.0	116.1	
C ₄ C ₅ H ₉					133.5	133.8	
C ₂ C ₆ H ₁₀						111.4	111.7
C ₂ C ₆ H ₁₁						109.9	109.8
H ₁₀ C ₆ H ₁₁						108.1	107.9
H ₁₀ C ₆ H ₁₂						107.6	107.6
C ₅ C ₉ H ₁₃							111.7
C ₅ C ₉ H ₁₄							109.8

Vibrational band assignments

Since Furan molecule has C_{2v} symmetry point group, so it possesses 21 fundamental vibrations divided as $8A_1 + 3A_2 + 3B_1 + 7B_2$. While the MF molecule has 30 fundamental vibrations, with point group C_s . The DMF molecule has 39 fundamental vibrations, belong to the C_{2v} equilibrium configuration. All vibrations for the studied molecules appeared in infrared and Raman spectra, except the A_2 species which presented in Raman only. The computed vibrational frequencies results with the complete analyzing for furan and its derivatives were presented in Tables 2-4.

CH vibrations

The calculated vibrational frequency results for F molecule and its derivatives indicated that the spectra of F molecule had two CH symmetric stretching located at 3241, and 3217 cm^{-1} , plus two CH asymmetric stretching vibrations presented at 3233, and 3207 cm^{-1} . The MF molecule showed three stretching vibrations, one of them C-H symmetric, and the others CH asymmetric stretching

vibrations occurred at 3276, and 3249, 3239 cm^{-1} respectively. The spectra of the DMF molecule illustrated only two C-H symmetric and asymmetric vibrations (ν_1, ν_2) at 3247, 3115 cm^{-1} , Table 4. It's well known that the CH vibrations of aromatic and hetero-aromatic structure usually appear within the region of 3000-3100 cm^{-1} (14).

The F molecule spectra had two pure CH in-plane modes presented at 1008, 1298 cm^{-1} , with four pure CH out-of-plane vibrations located at 908, 711, 869, and 752 cm^{-1} , Table 1. The spectra of the MF molecule showed three modes $\nu_{24}-\nu_{26}$ assigned as pure CH out-of-plane motion indicated at 887, 816, and 736 cm^{-1} , Table 3. The DMF demonstrated only two pure CH out-of-plane modes at 851, and 800 cm^{-1} , Table 4.

Methyl group vibrations

The 2-Methylfuran molecule gave one C-H₂ asymmetric vibrations at 3083 cm^{-1} . But the 2,5-Dimethylfuran spectra produced two degenerate C-H₂ asymmetric vibrations ν_{14}, ν_{21} appeared at 3073 cm^{-1} (15).

Table 2: The calculated fundamental vibrations of F compared with other theoretical and observation data.

NO.	Sym.	This work			Other work ¹³		Assignment
		Freq. (cm^{-1})	IR intensity ($km\ mol^{-1}$)	Raman activity ($A^\circ\ ^4\ amu^{-1}$)	Theoretical Freq. (cm^{-1})	Exp. Freq. (cm^{-1})	
ν_1	A_1	3241	000.29	00.29	3278	3169	$\nu_s CH + ring\ breath$
ν_2		3217	000.84	03.99	3251	3140	$\nu_s CH$
ν_3		1493	014.69	36.43	1509	1491	$\nu_s C=C + \beta CH$
ν_4		1414	008.16	23.20	1410	1385	$\nu_s C-C + \beta CH$
ν_5		1148	000.33	25.42	1164	1140	$\nu_s C-C + \beta CH$
ν_6		1070	008.44	05.52	1089	1067	$\nu_s C-C + \beta CH$
ν_7		1008	044.43	02.21	1013	0995	βCH
ν_8		0891	015.27	00.91	0884	0870	$\nu_s COC + \beta CH$
ν_9	A_2	0908	000.00	00.48	0871	0864	γCH
ν_{10}		0711	000.00	00.09	0730	0722	γCH
ν_{11}		0617	000.00	00.03	0614	0600	$\gamma CH + ring\ puck$
ν_{12}	B_1	0869	000.57	00.51	0845	0838	γCH
ν_{13}		0752	106.54	00.92	0758	0745	γCH
ν_{14}		0627	016.60	01.67	0622	0603	$\gamma CH (wing)$
ν_{15}	B_2	3233	000.84	03.90	3271	3161	$\nu_{as} CH$
ν_{16}		3207	003.27	94.22	3240	3130	$\nu_{as} CH$
ν_{17}		1575	000.13	00.24	1584	1558	$\nu_{as} C=C + \beta CH$
ν_{18}		1298	003.27	00.84	1290	1267	βCH
ν_{19}		1160	011.68	02.01	1203	1181	$\nu_{as} COC + \beta CH$
ν_{20}		1063	000.13	04.01	1060	1043	$\nu_{as} COC + \beta CH$
ν_{21}		0889	000.77	02.54	0890	0873	$\nu_s CCC + \beta CH$

The calculated vibrational spectra of the MF molecule had two CH₃ asymmetric and symmetric stretching vibrations ν_4, ν_5 at (3119, and 3036 cm^{-1}).



Table 3: The calculated fundamental vibrations of MF with the complete assignment for the fundamental vibrations of MF molecule.

NO	Sym.	Freq. (cm ⁻¹)	IR intensity (km mol ⁻¹)	Raman activity (A ⁻⁴ amu ⁻¹)	Assignment
ν_1	A'	3276	00.3600	249.05	ν_s CH
ν_2		3249	01.2100	143.02	ν_{as} CH
ν_3		3239	07.3800	165.05	ν_{as} CH
ν_4		3119	13.6800	132.97	ν_{as} CH ₃
ν_5		3036	33.3400	482.20	ν_s CH ₃
ν_6		1625	18.9500	033.54	ring def. (ν_{as} C = C)
ν_7		1529	39.0400	211.07	CH ₃ bend + ring def. (ν_s C= C)
ν_8		1485	13.3300	006.82	CH ₃ bend
ν_9		1417	03.4200	029.42	β CH + CH ₃ umbrella
ν_{10}		1406	07.1900	014.58	ring def. (ν_s C-C) + β CH + CH ₃ bend
ν_{11}		1262	16.5900	006.68	clock and anticlock wise
ν_{12}		1234	21.1200	012.69	ring def. (ν C-C + ν CO) + CH ₃ bend
ν_{13}		1162	16.5900	011.59	ring def.
ν_{14}		1098	12.5700	029.34	ν CO
ν_{15}		1033	29.7100	003.24	ν C-C + β CH
ν_{16}		0992	05.6800	002.19	CH ₃ bend + β CH
ν_{17}		0930	40.6600	009.75	ring def. + β CH+ CH ₃ bend
ν_{18}		0902	04.4500	007.47	ring def. + β CH
ν_{18}		0902	04.4500	007.47	ring def. + β CH
ν_{19}		0657	00.4300	012.72	β C=C-O + ν C-C(H ₃)
ν_{20}		0349	04.3800	001.47	CH ₃ bend + clock wise (ring + CH)
ν_{21}	A''	3083	17.2200	175.60	ν_{as} CH ₂
ν_{22}		1470	10.3400	016.06	CH ₃ bend
ν_{23}		1058	02.2600	000.73	CH ₃ bend
ν_{24}		0887	00.1300	002.11	γ CH
ν_{25}		0860	31.4800	002.70	γ CH
ν_{26}		0763	83.2800	001.81	γ CH
ν_{27}		0643	02.6500	003.31	Ring def.+ γ CH+ CH ₃ bend
ν_{28}		0618	12.6300	000.89	γ CH + ring def.
ν_{29}		0247	09.1500	003.58	γ ring + CH ₃ bend
ν_{30}		-0140	00.0002	000.63	CH ₃ Fan

But the spectra of the DMF molecule presented three fundamental vibrations of CH₃ symmetric and asymmetric stretching motions ν_3 , and ν_2 , ν_{29} respectively.

Ring vibrations

The ring of furan in the three studied molecules had several C-C symmetric and asymmetric stretching vibrations, ranged between 1414- 1033 cm⁻¹. These vibrations decreased in the following order F, MF, DMF, while the C=C stretching vibrations showing opposite order decreasing (DMF, MF, F), Tables 2-4.

Electronic absorption spectra

Table 5, presented the results of the UV-Visible spectra, containing the molecular orbital energies difference $\Delta E = E_f - E_i$ (corresponds to the vertical excitation according to the Frank-Condon principle¹⁶). Also the maximum absorption wavelength (λ_{max}), and oscillator strength (f) based on the optimized geometry in ethanol, and gas phase with their major contributions. The calculations revealed that λ_{max} for the three compounds belonged to transition H \rightarrow L (with a major contribution of 70%), increased in following sequence F, MF, DMF. A *bathochromic* shift with *hyperchromism* for the UV band were noticed during the transferring from the gas to solution (in polar solvent ethanol) phase⁽¹⁷⁾.



Table 4: The calculated fundamental vibrations of DMF.

NO.	Sym.	Freq. (cm ⁻¹)	IR intensity (km mol ⁻¹)	Raman activity (A ⁻⁴ amu ⁻¹)	Assignment
ν_1	A ₁	3247	02.00	123.29	ν_s CH
ν_2		3115	13.69	122.02	ν_{as} CH ₃
ν_3		3030	04.77	532.84	ν_s CH ₃
ν_4		1580	27.07	156.00	ring def. (ν_s C=C)
ν_5		1501	12.58	012.72	CH ₃ bend
ν_6		1422	00.24	019.90	CH ₃ bend
ν_7		1388	04.36	010.39	CH ₃ bend + ring def. (ν_s C-C) + β CH
ν_8		1239	07.91	007.95	CH ₃ bend + ring def. (ν_s C-C)
ν_9		1048	19.30	008.01	β CH
ν_{10}		1007	00.08	006.21	Ring breath + β CH
ν_{11}		0952	21.33	006.12	COC bend + CH ₃ bend
ν_{12}		0616	00.89	010.22	COC bend + CH ₃ bend
ν_{13}		0265	01.72	001.53	CH ₃ bend
ν_{14}	A ₂	3073	08.00	201.92	ν_{as} CH ₂
ν_{15}		1481	00.00	008.27	CH ₃ bend
ν_{16}		1052	00.00	000.24	CH ₃ bend
ν_{17}		0851	00.00	002.17	γ CH
ν_{18}		0630	00.00	000.92	Ring puck + CH ₃ bend
ν_{19}		0277	00.00	001.69	CH ₃ bend + γ ring + γ CH
ν_{20}		-0145	00.00	000.15	CH ₃ Fan
ν_{21}	B ₁	3073	29.84	000.30	ν_{as} CH ₂
ν_{22}		1483	12.44	000.51	CH ₃ bend
ν_{23}		1065	02.50	000.12	CH ₃ bend
ν_{24}		0800	46.31	000.04	γ CH
ν_{25}		0657	00.22	002.00	Ring puck + CH ₃ bend
ν_{26}		0196	08.55	000.39	γ ring
ν_{27}		0143	00.02	000.58	CH ₃ bend
ν_{28}	B ₂	3233	08.91	072.27	ν_{as} CH
ν_{29}		3115	02.93	003.27	ν_{as} CH ₃
ν_{30}		3030	63.23	008.37	ν_{as} CH ₃
ν_{31}		1647	09.31	003.79	ring def. (ν_{as} C=C) + β CH
ν_{32}		1493	00.36	003.49	CH ₃ bend
ν_{33}		1416	00.11	008.01	CH ₃ umbrella
ν_{34}		1265	34.14	000.00	ring def. (ν_{as} CO C) + β CH + CH ₃ bend
ν_{35}		1232	00.26	002.73	β CH
ν_{36}		1003	00.74	000.08	β CH + CH ₃ bend
ν_{37}		0984	02.93	000.00	ring def. + CH ₃ bend
ν_{38}		0700	00.05	000.75	ring def. + β CH + CH ₃ bend
ν_{39}		0414	02.62	000.95	clock wise + CH ₃ bend

Molecular Orbital

The frontier molecular orbital's ($\Delta E = E_{LUMO} - E_{HOMO}$) specifies the molecule chemical stability, reactivity, optical polarizability, and chemical softness-hardness. The lower the value of ΔE indicates that these molecule is more

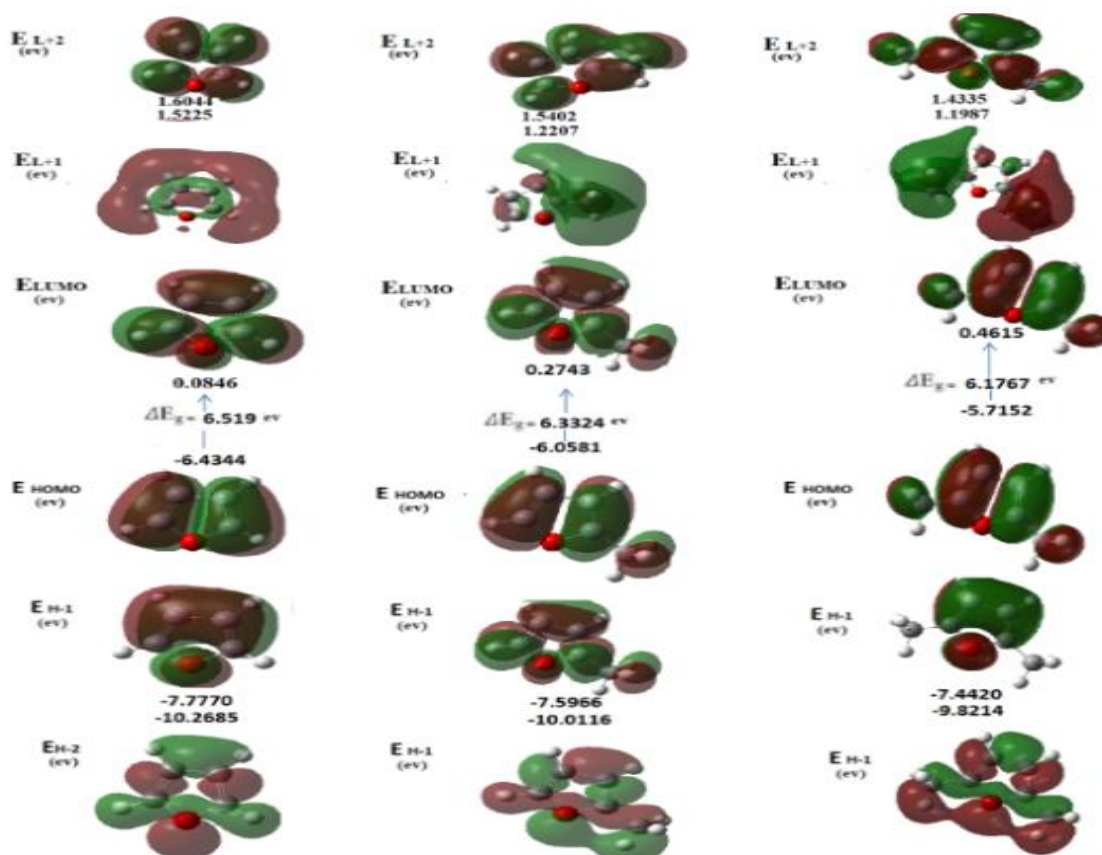
reactive and less stable^(18, 19). The energies results with shapes of these orbitals were demonstrated in figure 2. The calculated ΔE for all molecules in gas phase were increased in the following order DMF, MF, F, and inversely proportional with λ_{max} (as expected).



Table 5: The absorption wavelength, energies, and oscillator strengths of the F, MF and DMF compounds using the TD-DFT/ B3LYP/ CC-PVTZ (2d, 2p) method.

Compound	Gas				Ethanol			
	λ (nm)	E(eV)	f	Major contribution	λ (nm)	E(eV)	f	Major contribution
F	196.64	6.3052	0.1524	H \rightarrow L (70%)	199.53	6.2139	0.1835	H \rightarrow L (70%)
	182.25	6.8030	0.0000	H-1 \rightarrow L (52%) H \rightarrow L+2 (48%)	181.87	6.8172	0.0000	H-1 \rightarrow L (52%) H \rightarrow L+2 (48%)
	179.26	6.9164	0.0000	H \rightarrow L+1(70%)	173.55	7.1440	0.0000	H \rightarrow L+1(70%)
MF	203.76	6.0850	0.2255	H \rightarrow L (70%)	206.61	6.0008	0.2643	H \rightarrow L (70%)
	194.53	6.3737	0.0009	H \rightarrow L+1(70%)	188.80	6.5671	0.0010	H \rightarrow L+1(70%)
	187.35	6.6179	0.0063	H-1 \rightarrow L (45%) H \rightarrow L+2 (55%)	186.67	6.6419	0.0107	H-1 \rightarrow L (44%) H \rightarrow L+2 (56%)
DMF	210.06	5.9024	0.2976	H \rightarrow L (70%)	212.60	5.8318	0.3443	H \rightarrow L (70%)
	205.52	6.0326	0.0000	H \rightarrow L+1(70%)	200.39	6.1870	0.0000	H \rightarrow L+1(70%)
	196.84	6.2986	0.0006	H \rightarrow L+2 (70%)	192.95	6.4258	0.0302	H-1 \rightarrow L (35%) H \rightarrow L+2 (65%)

Hint: H= HOMO, L=LUMO, H-1= bonding MO, one level lower than HOMO, H-2 = represent two levels lower than HOMO, L+1=anti Bonding MO (one level higher than LUMO), L+2 = antibonding MO (two levels higher than LUMO).

**Figure 2:** The energies and the compositions for some molecular orbital's of F, MF, and DMF compounds, in gas phase.

Molecular electrostatic potential (MEP)

The MEP usually illustrates the density of the charge for molecule, which affords useful information in predicting the sites for the attacks of electrophilic and nucleophilic reactions. The red, blue, green, and orange colors appear on molecular surface related to the electrostatic potential energy differences. Where the red indicates the high and

the blue indicates less attractiveness²⁰. Figure 3, showed the MEP maps for furan and its derivatives. The red was concentrated around the O atoms; this means that the region is higher negative. The blue color around the H atoms indicating that the region is more positive. Therefore O atom shows higher repulsion, and H higher attraction²¹.

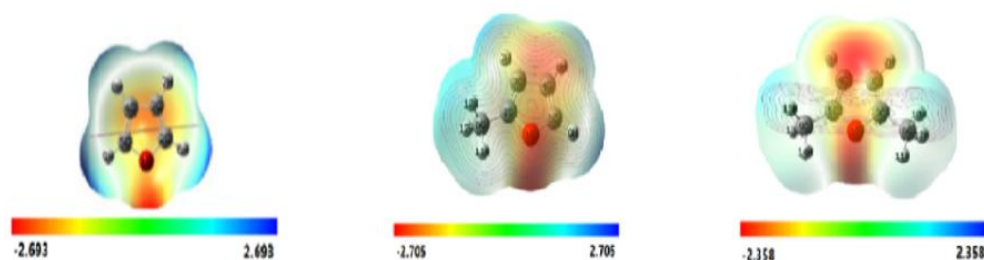


Figure 3: The MEP map for F, MF, and DMF molecules in gas phase.

NMR spectroscopy

The NMR analysis is usually used to identify the structure of molecules. The position of the NMR signals aid to realize the proton nature (aliphatic or aromatic) adjacent to attracting or releasing electron group, or the electronic environment. The calculated NMR results for furan and its derivatives, in gas phase, and solvent (dimethyl sulfoxide DMSO) were employed to express the chemical shifts δ (ppm) [where the tetramethylsilane (TMS) compound was used as a reference], Table 6. From the computed results it can be noticed that the chemical shifts for $O > C > H$ nucleus. This difference is due to the high electronic cloud density surrounding the nucleus (because O has higher electronic negativity)²².

The effect of substitution CH_3 (electron donating group) at C_2 position in MF, and the two CH_3 groups at C_2 and C_5 positions in DMF molecules revealed:

1- The δ value of oxygen nucleus decreased in following manner F, MF, DMF.

2- In furan, the δ of C_2 and C_5 nucleus were equal 107.1 ppm due to the symmetry, and lower for C_2 in MF (99.9 ppm). A further decreasing was noticed at C_2 , and C_5 nucleus for DMF molecules (98.5 ppm).

3- The proton of furan ring H_7 illustrated more shielding in MF than F molecule. Also the two protons H_7 , and H_8 indicated the high shielding in DMF molecule. This related to the greater electron density around these protons.

Table 6: The calculated NMR chemical shifts in ppm for F, MF and DMF molecule in (gas phase and DMSO solvent).

F			MF			DMF		
Atom	Chemical shift (ppm)		Atom	Chemical shift (ppm)		Atom	Chemical shift (ppm)	
	Gas phase	DMSO		Gas phase	DMSO		Gas phase	DMSO
O(1)	330.05	327.34	O(1)	276.51	276.51	O(1)	231.71	229.07
C(2)	107.10	108.07	C(2)	107.72	107.72	C(2)	098.49	099.25
C(3)	136.78	138.14	C(3)	125.49	125.49	C(3)	120.85	120.85
C(4)	136.78	138.14	C(4)	133.29	133.29	C(4)	120.85	120.85
C(5)	107.10	108.07	C(5)	099.93	099.93	C(5)	098.49	099.25
H(6)	002.75	002.74	C(6)	032.82	032.82	C(6)	032.92	033.18
H(7)	001.98	001.95	H(7)	003.60	003.60	H(7)	003.37	003.29
H(8)	001.98	001.95	H(8)	001.71	001.71	H(8)	003.37	003.29
H(9)	002.75	002.74	H(9)	002.62	002.63	C(9)	032.92	033.18
			H(10)	008.84	008.84	(10)H	008.95	009.02
			(11)H	007.51	007.51	H(11)	007.12	007.21
			H(12)	008.84	008.84	H(12)	008.95	009.02
						H(13)	008.95	009.02
						H(14)	007.12	007.21
						H(15)	008.95	009.02

CONCLUSIONS

Furan ring bond angle $\text{C}_2\text{O}_1\text{C}_5$ showed small decreasing according to the following sequence F, MF, DMF, due to the presence of CH_3 groups in C_2 , and C_2 , C_5 positions for MF, and DMF molecules respectively. The vibrational spectra demonstrated that the ring of furan in the three molecules had several C-C symmetric and asymmetric

stretching vibrations. These vibrations decreased in the following manner F, MF, DMF, while the C=C stretching vibrations decreased in the opposite order DMF, MF, F.

The UV-Vis results revealed that the maximum absorption wavelength (λ_{max}) for the F and its derivatives belong to the H \rightarrow L transition, increased in this sequence F, MF, DMF. During the transferring from the gas to solution

(polar solvent ethanol) phase, a bathochromic shift with hyperchromic showed a unique UV band for the three molecules, which means that the transition is $\pi \rightarrow \pi^*$ type. The energy difference between the frontier molecular orbitals $\Delta^{\text{TM}}E$ for all molecules in gas phase increased according to this order DMF, MF, F. The ΔE values were inversely proportional with the λ_{max} . The NMR data for the proton of furan ring H₇ illustrated more shielding in MF than F molecule. Also the two protons H₇, and H₈ demonstrated a high shielding in DMF molecule. This related to the biggest electron density surrounding these protons (the presence of CH₃ donating group).

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