

Research Article

Open Access

Spectroscopic Aspects, Structural Elucidation, Vibrational and Electronic Investigations of 2-Methoxy-1,3-Dioxolane: An Interpretation Based on DFT and QTAIM Approach

Prabaharan A and Xavier JR*

PG and Research, Department of Physics, Periyar EVR College (Autonomous), Tiruchirappalli, Tamil Nadu, India

Abstract

Extensive vibrational spectroscopic investigations along with theoretical quantum chemical studies on 2-methoxy-1,3-dioxolane (MDOL) have been consummated. The experimentally observed spectral data (FT-IR and FT-Raman) of the title compound were compared with the spectral data obtained by DFT/B3LYP method. The ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were simulated by using the gauge independent atomic orbital (GIAO) method and the absolute chemical shifts related to TMS were compared with experimental spectra. The theoretical UV-Visible spectrum of the title compound was measured in different solvent and the electronic properties, such as excitation energies, oscillator strength and wavelengths were performed by time-dependent density functional theory (TD-DFT) approach. The kinetic stability of the molecule has been determined from the frontier molecular orbital (FMO) energy gap. Total density of state (TDOS) and partial density of state (PDOS) of the MDOL in terms of Mulliken population analysis were calculated and analyzed. Reduced density gradient (RDG) of the MDOL was given to investigate interactions of the molecule. Topological parameters at bond critical point have been analyzed in MDOL by Bader's 'Atoms in molecules' (AIM) theory in detail. In addition, the temperature dependence thermodynamic properties and magnetic susceptibility of MDOL were calculated with the help of DFT/B3LYP method using 6-311++G(d,p) basis set.

Keywords: 2-methoxy-1,3-dioxolane; FMO; DOS; RDG; AIM

Introduction

Dioxolane and its derivatives are widely used in natural product syntheses as protecting groups for aldehydes, ketones and 1,2-diols. 1,3-Dioxolane derivatives, which have been used in commercial purposes and industrial including important intermediates, pharmaceutical manufacturing, fragnance and polymer industries have been studied extensively [1-3]. Aryl, alkyl, imidazole, triazole, pyrazole, benzimidazole, benzotriazole, oxypurine, pyrimidinyl and naphtyl groups are linked to 1,3-dioxolane ring at different positions like 2, 4 or 5. Depending on the position of the substituents, these compounds exhibit a broad spectrum of biological activities such as antifungal [4], antibacterial [5,6], antineoplastic [7], antiviral [8,9], anesthetic [10,11] and anticonvulstant ones [12]. According to the literature survey, several 1,3-dioxolanes are used co-monomer for manufacture of polyacetals and other polymers, solvent for chemical reactions (including inorganic salts), stabilizer for halogenated organic solvents and as a starting material or reagent for organic synthesis [13]. Among the major biological activities, 1,3-dioxolane is a powerful aprotic solvent for use in formulations, in production processes and good toxicity profile. In recent years, among the computational methods calculating the electronic structure of molecular systems, DFT has been favourite one due to its great accuracy in reproducing the experimental values in molecular geometry, vibrational frequencies, atomic charges, dipole moment, thermodynamic properties, etc. [14-16]. Literature survey reveals that to the best of our knowledge, no experimental and computational spectroscopic study on 2-methoxy-1,3-dioxolane (MDOL) has been published in the literature yet. This inadequacy is observed in the literature encouraged us to make this theoretical and experimental vibrational spectroscopic study to give a correct assignment of the fundamental bands in the experimental FT-IR and FT-Raman spectra. The isotropic chemical shifts and electronic transitions were analyzed by NMR and UV spectroscopic techniques. The work also encompasses calculation of thermodynamic and magnetic properties, frontier molecular orbital, density of states (DOS), reduced density gradient (RDG), natural bond orbital (NBO) analysis and topological parameters. Related to this phenomenon, with the hope the results of present study may be helpful in the prediction of its mechanism of biological activity.

Experimental Methods

The compound 2-methoxy-1,3-dioxolane (MDOL) in liquid state is purchased from Sigma Aldrich Chemical Suppliers with the stated purity of 98%. Then the compound is used as such for spectral measurements without further purification. In the present study, the Fourier transform infrared spectrum (FT-IR) of the title compound is recorded in the wavenumber region 4000-400 cm⁻¹ on a NEXUS 670 spectrophotometer equipped with an MCT detector in a KBr pellet technique. The FT-Raman spectrum is recorded in the wavenumber region 3500-100 cm⁻¹ on a NEXUS 670 spectrophotometer equipped with Raman module accessory operating at 1.5 W power with Nd:YAG laser of wavelength 1064 nm is used as an excitation source. The ¹H (400 MHz; CDCl₃) and ¹³C (100 MHz; CDCl₃) nuclear magnetic resonance (NMR) spectra were recorded on a BRUKER HC400 instrument using CDCl₃ solvent. Chemical shifts for protons are reported in parts per million (ppm) scales (δ scale) downfield from tetramethylsilane.

*Corresponding author: John Xavier R, PG and Research, Department of Physics, Periyar EVR College (Autonomous), Tiruchirappalli-620 023, Tamil Nadu, India, Tel: +914312780286; Fax: +919443073908; E-mail: rj_xavier@yahoo.com

Received November 14, 2015; Accepted November 26, 2015; Published November 29, 2015

Citation: Prabaharan A, Xavier JR (2015) Spectroscopic Aspects, Structural Elucidation, Vibrational and Electronic Investigations of 2-Methoxy-1,3-Dioxolane: An Interpretation Based on DFT and QTAIM Approach. J Theor Comput Sci 2: 138. doi:10.4172/2376-130X.1000138

Copyright: © 2015 Prabaharan A, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Quantum Chemical Calculations

The combination of vibrational spectroscopy along with quantum chemical calculations is effective for understanding the fundamental mode of vibrations of the title compound. The quantum chemical calculations have been performed with GAUSSIAN-09W [17] program, invoking gradient geometry optimization [18]. The density functional theory (DFT) [19] with the three parameter hybrid functional (B3) [20,21] for the exchange part and the Lee-Yang-Parr (LYP) correlation functional [15] have been utilised for the computation of molecular structure optimization, vibrational frequencies, thermodynamic properties and energies of the optimized structure. All the computations have been done by adding'd' polarization functions on heavy atoms and 'p' polarization functions on hydrogen atoms as well as diffuse functions for both hydrogen and heavy atoms [22-25]. The absolute Raman and IR absorption intensities were calculated in the harmonic approximation at the same level of theory as used for the optimized geometries associated with each normal mode, respectively. The normal coordinate analysis was performed and the potential energy distribution (PED) was calculated along the internal coordinates using localized symmetry.

The vibrational modes were assigned by means of visual inspection using Gauss View 5.0 program [26]. The vibrational mode analysis of MDOL is presented in some detail inorder to better describe the basis for the assignments, from the basic theory of Raman scattering. A comparison is made between the theoretically calculated frequencies and the experimentally measured frequencies. In this investigation it was observed that the calculated frequencies were slightly greater than the fundamental frequencies. To improve the agreement between the predicted and observed frequencies, the computed harmonic frequencies are usually scaled for comparison. In this work, the force field was scaled according to the SQM procedure [27] and the Cartesian representation of the force constants were transferred to a nonredundant set of local symmetry coordinates, chosen in accordance to the recommendations of Pulay et al. [28]. Calculation of the potential energy distribution (PED) and the prediction of IR intensities and Raman activities were done on a PC with the MOLVIB Program (Version V7.0-G77) written by Sundius [29,30].

The prediction of Raman intensities were carried out by the following procedure outlined below. The Raman activities (S_i) calculated by GAUSSIAN-09W and adjusted during scaling procedure with MOLVIB were converted to relative Raman intensity (I_i) using the following relation from the basic theory of Raman scattering [31,32].

$$I_{i} = \frac{f(v_{0} - v_{i})^{4} S_{i}}{v_{i} \left[1 - exp(-hcv_{i} / kT)\right]}$$

Where v_0 is the laser exciting wavenumber in cm⁻¹ (in this work, we have used the excitation wavenumber v_0 =9398.5 cm⁻¹, which corresponds to the wavelength of 1064 nm of a Nd:YAG laser), v_i is the vibrational wavenumber of the ith normal mode (in cm⁻¹) and S_i is the Raman scattering activity of the normal mode v_i , f (is a constant equal to 10⁻¹²) is a suitably chosen common normalization factor for all the peak intensities. h, k, c and T are Planck constant, Boltzmann constant, speed of light and temperature in Kelvin, respectively.

Results and Discussion

Molecular geometry

The geometry of a molecule can be characterised by analysing the bond length and bond angle. Bond length and bond angle are the two important parameters which determine the shape and size of a molecule. Bond length is the distance between the nuclei of two bonded atoms whereas bond angle is the angle formed between two adjacent atoms in a molecule. They always range from 100 to 180 degrees. A dihedral angle or torsion angle is the angle between two planes. It defines the conformations around rotatable bonds. The dihedral angle changes only with the distance between the first and fourth atoms; the other inter atomic distances are controlled by the chemical bond lengths and bond angles. Its value ranges from -180° to +180°. The torsion angle is considered to be positive if a clockwise rotation is performed with the molecule and it will be negative when an anticlockwise rotation is performed with the molecule in its plane. The molecular structure and the numbering of the atoms of MDOL are shown in Figure 1. The values of important geometrical parameters like bond lengths, bond angles and dihedral angles of the optimized MDOL molecule are determined by B3LYP level with 6-311++G(d,p)as basis set and found in close agreement with experimental parameters obtained from the X-Ray diffraction studies [33] as shown in Table 1. The observed C2-O1, C2-O3, C4-O3 and C5-O1 bond length values were found to be 1.358, 1.358, 1.428 and 1.428 Å and the calculated

Page 2 of 14



Figure 1: Molecular structure of 2-methoxy-1,3-dioxolane along with numbering of atoms.

Tag	Symbol	NA	NB	NC	Bond ler	ngth (Å)	Bond ar	Dihedral angle (°)	
					Theory ^a	Expt. ^b	Theory ^a	Expt. ^b	Theory ^a
1	0								
2	С	1			1.386	1.358			
3	0	2	1		1.413	1.358	107.188	111.67	
4	С	3	2	1	1.438	1.428	107.889	108.71	22.430
5	С	1	2	3	1.435	1.428	105.716		-35.481
6	Н	2	1	5	1.095		110.071		-153.414
7	0	2	1	5	1.402		108.494		85.191
8	С	7	2	1	1.424		113.835		175.654
9	Н	8	7	2	1.094		111.338		64.260
10	Н	8	7	2	1.089		106.540		-176.137
11	Н	8	7	2	1.098		111.004		-57.558
12	Н	4	3	2	1.093		108.102		-121.099
13	Н	4	3	2	1.092		109.928		119.540
14	Н	5	1	2	1.089		107.788		153.743
15	н	5	1	2	1.093		110.061		-86.440

For numbering of atom refer Figure 1.

^aTheoretical values are calculated by DFT/B3LYP/6-311++G(d,p) method. ^bExperimental values are taken from Ref. [33].

Table 1: Geometrical parameters such as bond lengths, bond angles and dihedral angles of 2-methoxy-1,3-dioxolane molecule calculated at DFT/B3LYP/6-311++G(d,p) method.

bond length values were 1.386, 1.413, 1.438 and 1.435 Å by B3LYP method using 6-311++G(d,p) basis set. Furthermore, O3-C2-O1 and C4-O3-C2 bond angles in the structure were observed at 111.67 and 108.71°, corresponding angle value were calculated at 107.19 and 107.89° by B3LYP with 6-311++G(d,p) basis set, respectively. For visual depiction of optimized geometrical parameters of MDOL under B3LYP/6-311++G(d,p) level, has been shown in Figures 2-4, respectively. From the theoretical results of the title molecule, one could find that the optimized bond lengths and angles are slightly smaller as well as longer than the experimental value, this is due to the fact that the theoretical calculations belongs to isolated molecule in liquid state. The internal coordinates and local symmetry coordinates of MDOL were shown in Supplementary document, Tables S1 and S2 respectively.

Vibrational assignments

Inorder to obtain the spectroscopic signature of the MDOL, the computational calculations are performed for frequency analysis. The title molecule contains 15 atoms and hence it has 39 normal modes (3N-6) of vibrations. The harmonic vibrational frequencies calculated at B3LYP level with 6-311++G(d,p) basis set and observed FT-IR and FT-Raman frequencies for various modes of vibrations have been presented in Table 2. The vibrational assignments are made on the basis of the spectral regions of the respective modes and with the help of Gauss View 5.0 visualisation program. The calculated vibrational frequencies were in good agreement with the experimental results. The observed and theoretical FT-IR and FT-Raman spectra of the title compound are shown in Figures 5 and 6, respectively.

C-O vibrations: The C-O stretching vibration [34-36] is expected in the region 1300-1000 cm⁻¹ and is very intense in the infrared and only moderately active in Raman. However, in the present study the C-O stretching vibration is observed in the region between 1076 - 920 cm⁻¹ in FT-IR and FT-Raman spectra, for MDOL. The C-O in-plane and the out-of-plane bending vibrations are expected in the regions 725 \pm 70 cm⁻¹ and 540 \pm 80 cm⁻¹, respectively [37,38]. In the title compound, the in-plane bending vibration is identified at 616 cm⁻¹ in FT-IR spectrum.

C-H vibrations: C-H stretching vibrations [39,40] of heterocyclic structure were observed within the region 3100-3000 cm⁻¹. In MDOL, the C-H stretching vibration is found at 2905 cm⁻¹ in FT-IR spectrum. The C-H in-plane and out-of-plane bending vibrations [41] were generally lie in the region 1300 - 1000 cm⁻¹ and 1000 - 675 cm⁻¹, respectively. In accordance with literature, in the present study, the bands observed at 1362 cm⁻¹ in FT-Raman spectrum and 1304 cm⁻¹ in FT-IR spectrum were assigned to C-H in-plane and out-of-plane bending vibrations, respectively.

CH₂ **vibrations:** For the assignments of CH₂ group frequencies, basically six fundamentals can be associated to each CH₂ group namely, CH₂ ss - symmetric stretch; CH₂ ass - asymmetric stretch; CH₂ sciss - scissoring and CH₂ rock - rocking which belong to in-plane vibrations and two out-of-plane vibrations, viz., CH₂ wag - wagging and CH₂ twist - twisting modes, which are expected to be depolarized [42]. The asymmetric CH₂ stretching vibrations are generally observed above 3000 cm⁻¹, while the symmetric stretch [43] will appear in the region 3000 and 2900 cm⁻¹. In this study, the asymmetric and symmetric stretching vibrations are observed at 2960, 2946 and 2841, 2839 cm⁻¹ in FT-Raman and FT-IR spectra, respectively. The CH₂ scissoring vibrations [44] appear normally in the region 1490 - 1435 cm⁻¹. For MDOL, The CH₂ scissoring modes are assigned at 1534 and 1527 cm⁻¹ in

Page 3 of 14

FT-Raman spectrum, respectively. Similarly, the CH_2 rocking, wagging and twisting vibrations are also established within the characteristic region and are attributed in Table 2.

CH₃ vibrations: For the assignment of CH₃ group frequencies, nine fundamental vibrations can be associated with each CH₃ groups. Three stretching, three bending, two rocking modes and single torsional mode describe the motion of the methyl group [45]. The C-H methyl group stretching vibrations [46,47] are generally observed in the range 3000 - 2800 cm⁻¹. Hence in the present investigation, the FT-Raman band observed at 2909 cm⁻¹ has been assigned to CH₂ symmetric stretching vibration. The FT-IR bands found at 3139 and 2813 cm⁻¹ have been assigned to CH₂ in-plane and out-of-plane stretching vibrations for MDOL. The methyl deformation modes mainly coupled with the inplane bending vibrations and are also well established. The in-plane methyl deformation mode of MDOL is found at 1521 cm⁻¹ in FT-IR spectrum. The bands at 1445 and 1204 cm⁻¹ in FT-IR is attributed to CH₃ out-of-plane deformation modes of MDOL. The methyl rocking modes of vibration [48-50] usually appears within the region 1070 -1010 cm⁻¹. With reference to literature data, the observed band at 1139 cm⁻¹ is assigned to in-plane CH₃ rocking vibration for MDOL. The twisting vibrations are not observed in the FT-IR and FT-Raman spectrum because these appear at very low frequency.

NMR spectral studies

NMR spectroscopy is currently used for structure and functional









S No	Observed	d frequency (cm ⁻¹)	Calculated fr	equency (cm ⁻¹)	IP Intoncity	Raman	Assignments along with PED (%)		
3 110	FT-IR	FT-Raman	Unscaled	Scaled	IN Intensity	Intensity			
1	3139	-	3169	3142	20.74	8.74	CH ₃ ips(100)		
2	-	2960	3122	2971	29.92	10.65	CH ₂ ass(100)		
3	2946	-	3087	2972	27.80	8.52	CH ₂ ass(100)		
4	-	2909	3064	2913	31.58	6.59	CH ₃ ss(100)		
5	2905	-	3056	2909	39.60	19.42	CH(99)		
6	-	2841	3047	2847	47.02	12.17	CH ₂ ss(99)		
7	2839	-	3044	2846	56.24	9.46	CH ₂ ss(99)		
8	2813	-	2994	2821	57.90	16.12	CH ₃ ops(96)		
9	-	1534	1588	1542	0.93	2.45	CH ₂ sciss(87)		
10	-	1527	1534	1531	5.71	2.40	CH ₂ sciss(88)		
11	1521	-	1511	1526	6.89	6.35	CH ₃ ipb(84)		
12	1494	1499	1487	1498	6.39	5.86	CH ₃ sb(86)		
13	1445	-	1473	1449	5.03	0.68	CH ₃ opb(88)		
14	1373	-	1398	1378	31.25	1.24	CH ₂ wag(80)		
15	-	1362	1379	1367	14.45	3.45	bCH(77), Rbend2(21)		
16	-	1329	1371	1331	1.09	1.67	CH ₂ wag(81)		
17	1304	-	1321	1309	7.51	3.56	ωCH(69), tR torsion(23)		
18	-	1226	1246	1231	4.23	4.13	CH ₂ twist(79)		
19	-	1211	1222	1216	21.68	1.88	CH ₂ twist(80)		
20	1204	-	1221	1209	3.89	5.42	CH ₃ opr(77)		
21	1139	-	1174	1142	2.85	2.07	CH ₃ ipr(73)		
22	1124	-	1157	1127	36.85	0.23	Rbend1(71), bCC(23)		
23	1076	-	1143	1079	202.97	1.04	CO(74), Rbend1(21)		
24	1037	-	1099	1041	250.33	3.30	CO(76), bCH(19)		
25	1019	-	1041	1022	69.14	0.55	CO(75), CH(23)		
26	987	-	992	993	94.42	4.56	CO(88), Rbend(10)		
27	973	-	981	979	122.71	6.62	CO(77), bCO(21)		
28	-	947	955	951	46.43	8.30	CC(73), bOCH ₃ (19)		
29	-	920	940	927	67.55	7.62	CO(81)		

30	847	-	867	851	6.42	2.13	CH ₂ rock(70)
31	-	800	811	804	5.09	6.06	Rbend1(69), CH(17)
32	663	-	696	667	5.22	2.73	CH ₂ rock(67)
33	616	-	543	621	5.16	3.44	bCO(60), CC(21)
34	561	-	508	566	2.13	7.09	Rbend2(59), Rbend1(27)
35	498	-	302	501	1.71	5.45	bOCH ₃ (69), Rbend2(19)
36	-	-	191	201	6.60	2.14	CH ₃ twist(58)
37	-	-	157	168	6.67	3.42	tR torsion 1(56), ωCH(21)
38	-	-	110	116	4.00	9.70	ωOCH ₃ (57)
39	-	-	46	53	3.88	100	tR torsion 2(57)

For numbering of atom refer Figure 1.

^aTheoretical values are calculated by DFT/B3LYP/6-311++G(d,p) method.

^bExperimental values are taken from Ref. [33].

Table 2: The observed (FTIR and FT-Raman) and calculated (Unscaled and Scaled) frequencies (cm⁻¹) using B3LYP /6-311++G (d, p) along with their probable assignments and potential energy distribution (PED) of 2-methoxy-1,3-dioxolane.

determination of biological macromolecules. Recent advances in experimental and computational techniques have made it possible to exploit NMR chemical shifts to obtain structures of proteins and macromolecules [51]. The optimized molecular structure of the title compound was used to simulate 1H and 13C NMR spectra of the molecule at DFT/B3LYP/6-311++G(d,p) level using the Gauge-Including Atomic Orbital(GIAO) method in which an exponential term containing the vector potential is including with each atomic orbital. The calculated ¹H and ¹³C NMR chemical shifts of the title molecule in gas phase, taking trimethylsilane (TMS) as a reference, is given in Table 3 along with the experimentally observed values. The atom positions are listed according to Figure 1. The recorded ¹H and ¹³C NMR spectra in CDCl, solution are as shown in Figures 7 and 8, respectively. Normally, the range of ¹³C NMR chemical shifts is greater than 100 ppm [52] and the accuracy ensure that the reliable interpretation of spectroscopic parameters. In the case of MDOL, the calculated chemical shift of C2, C4, C5 and C8 are 134.91, 64.73, 63.89 and 51.68 ppm, respectively as shown in Table 3. The shift is less in C8 (expt. 51.45 ppm) than rest of others. This is mainly due to the breaking of paramagnetic shield of proton by the substitutions of oxygen and methyl group. The C2 in the ring has more shifted than other due to the delocalization of σ and π electrons.

Generally, the proton chemical shift of organic molecules varies greatly with the electronic environment of the proton. Hydrogen attached or nearby electron-withdrawing atom or group can decrease the shielding and move the resonance of attached proton towards to a higher frequency, whereas electron-donating atom or group increases the shielding and moves the resonance towards to a lower frequency [53]. There are eight hydrogen atoms (ring and CH₃ group) in the title molecule. The chemical shifts of aromatic protons of organic molecules are usually observed in the region 6.15 - 6.17 ppm [54]. The calculated and observed proton chemical shifts are attributed in Table 3. The chemical shifts of aromatic protons of organic molecules are higher than the other protons. Therefore, the electronic charge density around of these atoms can be affected the influence of rapid proton exchange, hydrogen bond, solvent effect, etc. in the molecular system.

UV-Vis spectral analysis

The analysis of the wave function indicates that the electron absorption corresponds to the transition from the ground to the first excited state and is mainly described by one-electron excitation from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital(LUMO). In order to understand electronic transitions of compound, time dependent DFT(TD-DFT) calculations on electronic absorption spectrum were performed for MDOL by B3LYP/6-311++G(d,p). The calculated absorption wavelengths (λ), oscillator strengths (f) and excitation energies (E) of molecule in gas phase as well as water, ethanol and methanol solvent medium were given in Table 4. The electronic transition predicted by TD-DFT/B3LYP/6-311++G(d,p) method as shown in Figure 9. According to Frank-Condon principle, the maximum absorption peaks (λ_{max}) correspond in a UV-Vis spectrum to vertical excitation. Life spans of first excited state for solvents were calculated applying the definition τ =1.499/f(E²) in which E (in cm⁻¹) is the energy gap between ground state and a given excited state; f is the oscillator strength of excited state [55]. It is seen from Table 4, calculations performed at water, ethanol and methanol were close to each other when compared with gas phase and also the absorption maxima values of gas phase are larger than that of the organic solvents.

Page 5 of 14

Thermodynamic properties

The calculation of thermodynamic properties of MDOL includes total internal energy (*E* or *U*), entropy (*S*) and heat capacity at constant volume (C_v). These thermodynamic attributes has been calculated by DFT/B3LYP/6-311++G(d,p) method. The *E*, *S*, and C_v are contributed from the translational, rotational and vibrational motions along with the partition function of corresponding components [56]. The entropy (*S*) can be calculated from the partition function of any motion [57] by the given relation,

$$S = R \left(\left(Inq_t q_e q_r q_v e \right) + T \left(\frac{\partial Inq}{\partial T} \right)_v \right)$$

The *E* is derived from the given partition function,

$$T = Nk_B T^2 \left(\frac{\partial Inq}{\partial T}\right)$$

But the C_v can be derived from *E* which as follows,

$$C_v = \left(\frac{\partial E}{\partial T}\right)_{t}$$

The participation of *S*, *E*, and C_v with respect to translational, rotational and vibrational molecular motion at different temperatures ranging from 100 K to 1000 K is tabulated and shown in Table 5. The translational partition function (\mathbf{q}_t) is implemented to calculate entropy contributed from translational motion (*S*_t). The mathematical relationship for *S*_t can be given by,

$$S_t = R\left(In(q_t e) + T\left(\frac{3}{2T}\right)\right)$$

The rotational component that will take part in entropy (S_r) through the respective partition function (q_r) can be comprehend from the following equation,

Page 6 of 14



A 4	Isotropic chemical shifts (ppm)						
Atoms	B3LYP	Experimental					
¹³ C							
C2	134.91	115.96					
C4	64.73	64.09					
C5	63.89	64.09					
C8	51.68	51.45					
1H							
H6	5.06	5.74					
H9	3.05	3.32					
H10	2.94	3.32					
H11	2.48	3.32					
H12	2.85	3.96					
H13	3.23	4.08					
H14	3.11	4.08					
H15	3.02	3.96					

Table 3: Theoretical and experimental ¹H and ¹³C NMR Isotropic chemical shifts (with respect to TMS, all values in ppm) of 2-methoxy-1,3-dioxolane.





J Theor Comput Sci, an open access journal ISSN: 2376-130X

Solvent	Excitation	Wave length (nm)	Oscillator strength (f)	Energy (eV)	Life span (т)
	HOMO→LUMO	189.62	0.0104	6.5386	0.05
Gas	HOMO-1→LUMO	181.26	0.0053	6.8401	0.09
	HOMO-1→LUMO	176.82	0.0043	7.0118	0.10
	HOMO→LUMO	178.93	0.0075	6.9294	0.06
Water	HOMO-1→LUMO	172.00	0.0019	7.2085	0.23
	HOMO-1→LUMO	169.05	0.0024	7.3341	0.17
	HOMO→LUMO	179.31	0.0081	6.9145	0.05
Ethanol	HOMO-1→LUMO	172.38	0.0020	7.1923	0.22
	HOMO-1→LUMO	169.31	0.0022	7.3229	0.19
	HOMO→LUMO	179.17	0.0078	6.9201	0.06
Methanol	HOMO-1→LUMO	172.24	0.0019	7.1985	0.23
	HOMO-1→LUMO	169.21	0.0023	7.3271	0.18

Table 4: Calculated electronic absorption spectral data of 2-methoxy-1,3-dioxolane.



$$S_r = R \left(In(q_r) + T \left(\frac{\partial Inq_r}{\partial T} \right)_v \right)$$

$$S_{\nu} = R \sum_{k} \left(\frac{\Theta_{\nu,k} / T}{e^{\Theta_{\nu,k}/T} - 1} - In \left(1 - e^{-\Theta_{\nu,k}/T} \right) \right)$$

The comparative plot of S_r , S_r and S_v against different temperature reports the interesting trend of behavior which is shown in Figure 10. When temperature is about 100 K then the entropy follows $S_r > S_r > S_v$ order. But while the temperature gradually increases from 100 K to 1000 K, $S_v > S_r > S_r$ trend is noticed which indicates significant change or increase in entropy contributed by vibrational motion. These results concluded that though the initial entropy of MDOL is supported by translational and rotational motion but at the higher temperature (above 750 K) the entropy is largely enhanced by vibrational motion.

The *E*, due to translational (E_r) and rotational (E_r) contribution can be described as,

$$\begin{split} E_{t} &= N_{A}k_{B}T^{2} \bigg(\frac{\partial Inq_{t}}{\partial T} \bigg)_{v} \\ E_{r} &= RT^{2} \bigg(\frac{\partial Inq_{r}}{\partial T} \bigg)_{v} \end{split}$$

The E_t and E_r values for various temperature demonstrate to

Page 7 of 14

be gradual equal increase. It is evident the same from Table 5 and illustrated in Figure 11, respectively.

And the internal energy favour by vibration (E_{ν}) motions is high even for 100 K and increases till 1000 K. This denotes that the internal energy of MDOL is largely sustained by vibrational motion. The E_{ν} can be expressed by,

$$E_{v} = R \sum_{K} \Theta_{v,k} \frac{1}{2} + \frac{1}{e^{-\Theta_{v,k}} \frac{K}{T} - 1}$$

Unlike the *S* and *E*, the C_v must be derived from the *E* of respective motion rather than partition functions. The C_v on the ground of translational, rotational and vibrational motion can be presented as,

$$C_{r} = \left(\frac{\partial E_{r}}{\partial T}\right)_{v}$$

$$C_{r} = \left(\frac{\partial E_{r}}{\partial T}\right)_{v}$$

$$C_{v} = R \sum e^{\Theta_{v,k}/T} \left(\frac{\Theta_{v,k}/T}{e^{-\Theta_{v,k}/T}}\right)_{v}$$

From Figure 12 and Table 5 the C_t and C_r values for MDOL is same for 100 - 1000 K of temperature. Since the value is about 2.981 Kcal/







Figure 11: Total internal energy of 2-methoxy-1,3-dioxolane for different motions at various temperatures.

Mol, there is no any significant trend is observed. But as like E and S the C_v is amplified by vibrational motion. Since the C_v is derived from E, the trend of E against various temperature is reflected in the behaviour of C_v as well.

Magnetic susceptibility

Atoms, molecules and free radicals or ions which contain one or more unpaired electron will possess permanent magnetic dipole moment that arises from the residual spin and angular momentum of the unpaired electrons. All substances having permanent magnetic moment display paramagnetic behaviour in nature. When a paramagnetic substance is placed in a magnetic field, they will align themselves in the direction of the field and thus produces positive magnetic susceptibility, which depends on the temperature; since thermal agitation will oppose the alignment of the magnetic dipoles. The



Figure 12: Heat capacity at constant volume of 2-methoxy-1,3-dioxolane for different motions during various temperatures.

effectiveness of the field diminishes with increase in temperature. The magnetic susceptibility (χ_m) of the molecules for various temperatures are predicted with knowledge of unpaired electron [58] and presented in Table 6. The corresponding fitting equation and the correlation graph between magnetic susceptibility (χ_m) and Temperature⁻¹ (1/T) is shown in Figure 13. The effective magnetic moment is found to be a constant, which is 1.7864 × 10⁻⁵ (BM) and the Curie constant is obtained from the magnetic moment (μ_m) and is found to be 3 × 10⁻⁴.

Page 8 of 14

Frontier molecular orbitals

To explain several types of reactions and for predicting the most reactive position in conjugated systems, molecular orbital and their properties such as energy are used [59]. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the most important orbital in a molecule. The eigen values of HOMO and LUMO and their energy gap reflect the biological activity of the molecule. A molecule having a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity and low kinetic stability [60,61]. HOMO, which can be thought of the outer orbital containing electrons, tends to give these electrons as an electron donor and hence the ionization potential is directly related to the energy of the HOMO. On the other hand, LUMO can accept electrons and the LUMO energy is directly related to electron affinity [62]. The energies of HOMO and LUMO and their orbital energy gap are calculated by B3LYP/6-311++G(d,p) method and the pictorial illustration of their HOMO-LUMO distribution and their respective positive and negative region are shown in Figure 14. The positive and negative phase is represented in red and green colour, respectively. For understanding various aspects of pharmacological sciences including drug design and the possible eco-toxicological characteristics of the drug molecules, several new chemical reactivity descriptors have been proposed. Conceptual DFT based descriptors have helped in many ways to understand the structure of molecules and their reactivity by calculating the chemical potential, global hardness and electrophilicity.

Temperature (K)		Inslational mot	otion		Rotational motion			Vibrational motion			
Temperature (K)	S _t	E,	C _t	S _r	E,	C _r	S _v	E,	C _v		
100	34.409	0.298	2.981	23.666	0.298	2.981	3.434	79.799	2.978		
150	36.423	0.447	2.981	25.035	0.447	2.981	8.641	79.237	8.925		
200	37.853	0.596	2.981	25.893	0.596	2.981	11.545	79.744	11.465		
250	38.961	0.745	2.981	25.558	0.745	2.981	14.429	80.393	14.607		
298.15	39.836	0.889	2.981	27.083	0.889	2.981	17.297	81.180	18.129		
300	39.867	0.894	2.981	27.102	0.894	2.981	17.410	81.214	18.271		
350	40.633	1.043	2.981	27.561	1.043	2.981	20.519	82.225	22.181		
400	41.296	1.192	2.981	27.959	1.192	2.981	23.736	83.432	26.077		
450	41.881	1.341	2.981	28.310	1.341	2.981	27.024	84.829	29.791		
500	42.405	1.490	2.981	28.624	1.490	2.981	30.344	86.406	33.239		
550	42.878	1.639	2.981	28.908	1.639	2.981	33.662	88.148	36.397		
600	43.311	1.788	2.981	29.168	1.788	2.981	36.955	90.041	39.272		
650	43.708	1.938	2.981	29.406	1.938	2.981	40.203	92.071	41.888		
700	44.076	2.087	2.981	29.627	2.087	2.981	43.396	94.226	44.272		
750	44.419	2.236	2.981	29.833	2.236	2.981	46.526	96.495	46.449		
800	44.740	2.385	2.981	30.025	2.385	2.981	49.588	98.868	48.442		
850	45.041	2.534	2.981	30.206	2.534	2.981	52.580	101.336	50.272		
900	45.325	2.683	2.981	30.376	2.683	2.981	55.502	103.893	51.956		
950	45.594	2.832	2.981	30.537	2.832	2.981	58.354	106.530	53.508		
1000	45.848	2.981	2.981	30.690	2.981	2.981	61.135	109.242	54.941		

Unit for S, S, S, C, C, and C, is Cal/Mol-Kelvin; Unit for E, E, and E, is KCal/Mol

Table 5: Participation of S, E and C, for the various motions at different temperature.

Using HOMO and LUMO orbital energies, the ionization energy and electron affinity can be expressed as: I=-E_{HOMO}, A=-E_{LUMO}, η =(-E_{HOMO} + E_{LUMO}) / 2 and μ =1/2 (E_{HOMO} + E_{LUMO}) [63]. Parr et al. [64] proposed the global electrophilicity power of a ligand as $\omega = \mu^2/2\eta$. This index measures the stabilization in energy when the system acquires an additional electronic charge from the environment. Electrophilicity encompasses both the ability of an electrophile to acquire additional electronic charge and the resistance of the system to exchange electronic charge with the environment. It contains information about both electron transfer (chemical potential) and stability (hardness) and is a better descriptor of global chemical reactivity. The hardness $\eta = (I-A)/2$ and $\mu = -(I+A)/2$, where I and A are the first ionization potential and electron affinity of the chemical species [65]. For the title compound, $\mathrm{E}_{\mathrm{HOMO=}}\text{-}7.1961$ eV, E_{LUMO}=-1.2588 eV, energy gap=HOMO-LUMO=5.9373 eV, ionization potential I=7.1961 eV, electron affinity A=1.2588 eV, global hardness η =2.9686 eV, chemical potential μ =-4.2274 eV, global electrophilicity ω =3.01 eV. It is seen that the chemical potential of the title compound is negative and it means that the compound is stable. They do not decompose spontaneously into the elements they are made up of. The hardness signifies the resistance towards the deformation of electron cloud of chemical systems under small perturbation encountered during chemical process. The principle of hardness works in Chemistry and Physics but it is not physical observable. Soft systems are large and highly polarizable, while hard systems are relatively small and much less polarizable.

Temperature	1/ Temperature	Magnetic susceptibility				
100	0.010	2.642E-06				
150	0.007	1.761E-06				
200	0.005	1.321E-06				
250	0.004	1.057E-06				
298.5	0.003	8.850E-07				
300	0.003	8.806E-07				
350	0.003	7.548E-07				
400	0.003	6.605E-07				
450	0.002	5.871E-07				
500	0.002	5.284E-07				
550	0.002	4.803E-07				
600	0.002	4.403E-07				
650	0.002	4.064E-07				
700	0.001	3.774E-07				

Table 6: Magnetic susceptibility of 2-methoxy-1,3-dioxolane by B3LYP/6-311+ +G(d,p).





Page 9 of 14

Total, partial, and overlap population density-of-states

In the boundary region, neighbouring orbitals may show quasi degenerate energy levels. In such cases, consideration of only the HOMO and LUMO may not yield a realistic description of the frontier orbitals. For this reason, the total density of states (TDOS), partial density of states (PDOS), and overlap population density of states (OPDOS) or crystal orbital overlap population (COOP) density of states [66-68], in terms of Mulliken population analysis were calculated and created by convoluting the molecular orbital information with Gaussian curves of unit height and full width at half maximum (FWHM) of 0.3 eV by using the GaussSum2.2 program [69]. The TDOS, PDOS and OPDOS of MDOL are plotted in Figures 15-17, respectively. They provide a pictorial representation of molecular orbital (MO) compositions and their contributions to chemical bonding. The most important application of the DOS plots is to demonstrate MO compositions and their contributions to the chemical bonding through the OPDOS plots which are also referred in the literature as COOP diagrams. The bonding, anti-bonding and nonbonding nature's of the interaction of the two orbitals, atoms or groups are shown by OPDOS diagram. A positive value of the OPDOS indicates a bonding interaction (because of the positive overlap population), whereas negative value indicates that there is an anti-bonding interaction (due to negative overlap population) and zero value indicates nonbonding interactions [70]. Additionally, the OPDOS diagrams allow us to determine and compare the donor-acceptor properties of the ligands and ascertain the bonding and non-bonding. The PDOS plot mainly presents the composition of the fragment orbitals contributing to the molecular orbitals which are seen from Figure 16. As seen Figure 16, HOMO orbitals are localized on the ring $(C_3H_5O_2)$ and methoxy (OCH_3) group, their contributions about 59% and 41%, respectively. Similarly, the LUMO orbitals are localized on the ring (C₂H₅O₂) (78%) and methoxy (OCH₂) group (22%) of the compound. However to have information about bonding and anti-bonding properties is very hard according to percentage sharing of atomic orbitals or molecular fragments in the molecule. Therefore OPDOS diagram (some of its orbitals of energy values of interaction between selected groups) is shown on the figure easily, ring ↔ methoxy group (blue line) system is positive and negative (bonding and antibonding interaction). As can be seen from the OPDOS plot, the MDOL have bonding and anti-bonding character both HOMO and LUMO.

Reduced density gradient (RDG)

Johnson et al. [71] published an approach to investigate a weak interactions in real space based on the electron density and its

ISSN: 2376-130X

derivatives called Reduced density gradient (RDG) is dimensionless quantity defined as, following:

$$RDG(r) = \frac{1}{2(3\pi^2)^{\frac{1}{3}}} \frac{|\nabla\rho(r)|}{\rho(r)^{\frac{4}{3}}}$$

The region with low electron density and low RDG value obtained density and its first derivative, indicate weak interactions. To learn about the interaction in more detail, the sign of λ_2 is used to distinguish the bonded (λ_2 <0) from non-bonded (λ_2 >0) interactions. The sign of λ_2 multiplied electron density ρ obtained the plots of RDG versus permit to investigate and visualize of a wide range of interactions types. The RDG calculations are performed by Multiwfn program [72] and plotted by VMD program [73], respectively. The RDG versus sign (λ_2) ρ (electron density value) peaks provide information about the strength of interaction. There is one spike in the low-density, low gradient region as seen Figure 18, indicative of strong repulsion positive values of sign (λ_2) ρ .

Large, positive values of sign $(\lambda_2)\rho$ are indicated that strong repulsion interactions and negative ones indicates stronger attractive interactions. The strength of weak interactions have positive correlations with electron density ρ in corresponding region, Van der Waals (VdW) interaction regions always have very small ρ , while the regions correspond to strong steric effect and hydrogen bond always have relative large ρ . The regions are identified by color as different type seen from Figure 19. The color from blue to red means from stronger







Figure 17: The OPDOS (or COOP) diagrams for 2-methoxy-1,3-dioxolane.



Figure 18: Plots of the RDG versus the electron density ρ multiplied by the sign of λ_a for 2-methoxy-1,3-dioxolane.



Figure 19: The surfaces are colored on a blue-green-red scale according to values of sign λ_2 .

attraction to repulsion, respectively. The center of ring for MDOL molecule shows that strong steric effect, filled by red color. And VdW interactions identified by green or light brown color, between ring and methoxy group for MDOL.

J Theor Comput Sci, an open access journal ISSN: 2376-130X

Natural bond orbital (NBO) analysis

The natural bond orbital analysis (NBO) unlock the secrets about stability, bonding, intramolecular charge transfer (ICT) and donoracceptor relationship which are all collectively contribute to determine the electronic structure property of the title compound MDOL. The question on MDOL molecular stabilization can be answered by second order perturbation theory analysis. The stabilization interaction energy [74] can be mathematically expressed as below.

$$E(2) = -n_{\sigma} \frac{\sigma |F| \sigma^2}{\varepsilon \sigma^* - \varepsilon \sigma} = -n_{\sigma} \frac{F_{ij}^2}{\Delta E}$$

The donor, acceptor stabilisation interaction is often influenced by numerator and denominator terms involved in the given equation. The amplification of stabilisation energy is reciprocally related with ΔE . The ΔE can be expressed as $\Delta E = E(j) - E(i)$ where E(j) and E(i) denotes orbital energies of non-Lewis and Lewis orbitals [75]. The |F_u| represents cooperating element. As the NBO algorithm calculates all possible donor acceptor combinations [76], several significant interactions have been given in Table 7. The pictorial projections of selected thirteen donors, acceptors and their stabilizing interactions have been shown in Figure 20 based on descending interaction stabilization energy. Though several types of electronic interactions available between bonding, non-bonding and anti-bonding orbitals, the prominent stabilization includes lone pair (LP) to π^* and π to π^* transition in MDOL. The highest stabilization about 56.02 kJ mol⁻¹ is observed at the interaction between LP(2) O3 $\Rightarrow \pi^*$ (C2-O7). The $\pi \Rightarrow \pi^*$ type of transition was observed in twelfth and thirteenth interaction. The twelfth interaction holds 12.43 kJ mol⁻¹ of stabilization energy whereas the thirteenth interaction bear 11.55 kJ mol⁻¹. The stabilization energy difference between these two interactions was 0.88 kJ mol-1.

Topological parameters

The charge density distribution of the molecules can be determined from the wave function using Bader's Quantum Theory of Atoms in Molecules (QTAIM) [77], which are very useful to understand the nature of chemical bonds, reactivity and stability of molecular systems. Also, it provides the essential bond topological properties of the electron density $\rho_{\rm bcp}(\mathbf{r}) = 0$. The

Donor (i)	Orbital energy E(i) a.u	Acceptor (j)	Orbital energy E(j) a.u	E(2)ª (kJ mol⁻¹)	E(j)-E(i)⁵ (a.u)	F(i,j)⁰ (a.u)
LP(2) O3	1.90851	π [*] (C2-O7)	0.08655	56.02	0.61	0.081
LP(2) 07	1.89887	π [*] (C2-O7)	0.08655	55.73	0.61	0.081
LP(2) 07	1.90462	π [*] (C2-O3)	0.07773	54.68	0.59	0.079
LP(2) O1	1.89887	π [*] (C5-H15)	0.02459	29.83	0.7	0.064
LP(2) 07	1.90462	π [*] (C8-H9)	0.01916	26.90	0.7	0.061
LP(2) O3	1.90851	π [*] (C4-H13)	0.01960	22.22	0.7	0.055
LP(2) 07	1.90462	π [*] (C2-H6)	0.04614	21.38	0.68	0.053
LP(2) 07	1.90462	π [*] (C8-H11)	0.01963	21.30	0.68	0.054
LP(2) O1	1.89887	π [*] (C2-O3)	0.07773	20.42	0.6	0.048
LP(2) O3	1.90851	π [*] (C4-H12)	0.02186	19.96	0.7	0.052
LP(1) 07	1.95665	π [*] (O1-C2)	0.04828	17.61	0.88	0.054
π (C2-H6)	π (C2-H6) 1.98000 π (C		0.01903	12.43	0.82	0.044
π (C8-H10)	1.99214	π [*] (C2-O7)	0.08655	11.55	0.82	0.043

^aStabilisation (delocalisation) energy.

^bEnergy difference between i (donor) and j (acceptor) NBO orbitals. ^cF(i,j) means the Fock matrix element between i and j orbitals.

Table 7: Second order perturbation theory analysis of Fock matrix in NBO basis for 2-methoxy-1,3-dioxolane by B3LYP/6-311++G(d,p).



Page 11 of 14

critical point of molecule can be classified according to its rank(ω) and signature(σ) [78]. The rank, ω of critical point is equal to the number of non-zero Eigen values of the Hessian matrix of $\rho_{\text{bcp}}(r)$ and the signature, σ is the algebraic sum of the signs of the Eigen values. If the Eigen values are positive, its associated Eigen vector or gradient path originates at, and is directed away from the critical point. For negative Eigen value the gradient path terminates at, and is directed towards the critical point. Among the four type of non-degenerate critical points; (3,-3) nucleus critical point, (3,+3) cage critical point, (3,+1) ring critical point, and (3,-1) bond critical point, only the (3,-1) type of bond critical points (bcp's) were considered in this study. The wave function obtained from the optimization is used to calculate the bond topological properties at the bcp's using the Bader's theory of AIM implemented in AIMPAC software [79]. The topological parameters; electron density, Laplacian of electron density, ellipticity, Eigen values and energy density values for all the (3,-1) critical points have been investigated and presented in Table 8.

The Laplacian of electron density bear the chemical significance. If $\nabla^2 \rho_{bcp}(r) > 0$, the charges are locally concentrated, the interaction is a open-shell type interaction and if $\nabla^2 \rho_{bcp}(r) > 0$ the charges are locally depleted and the atomic interaction is a closed-shell type interaction. It is much more valid when the Laplacian of electron density is correlated with local total energy density H(r) [80], which facilitates for the identification of strong and weak bonds in the molecule. The local total energy density is defined as

H(r)=G(r)+V(r)

where G(r) and V(r) are the local kinetic and potential energy density. V(r) is always negative and G(r) is positive; the sign of H(r) indicates the dominant one in the bonding regions.

From the Laplacian of electron density values it is clear that the O7-C8 bond is depleted in nature, since it Laplacian of electron density gives a lesser negative value (-9.729). Whereas the highly concentrated bonds are found to be C-H bonds. Apart from these bonds, the Laplacian of electron density corresponds to C4-C5 bond in the molecule is found to be -13.696 eÅ^{-5} , revealing that the C4-C5 bond is lesser concentrated compared to the C-H bonds. The total energy density H(r) for the C4-C5 bond is -1.330 HÅ⁻³, this value is found to be

very small on compared with all other bonds in the molecule, indicates, the weakness of C4-C5 bond in MDOL molecule.

Page 12 of 14

The bond ellipticity [81], $\epsilon = [(\lambda_1/\lambda_2) - 1]$ is defined as the measure of anisotropy of electron distribution at BCP, where λ_1 and λ_2 are the negative Eigen values of Hessian matrix. The high ellipticity value indicates the large anisotropy of bonding density $\rho_{bcp}(r)$ and hence a strong deviation from σ -type bond character. The ellipticity of C2-H6 bond is found to be small; it indicates that the bond density is highly isotropic. The large ellipticity value is occurred in C2-O7 bond, it shows that the C2-O7 bond density is highly anisotropic.

Conclusion

The complete molecular structural parameters, fundamental vibrational frequencies and thermodynamic properties of the optimized geometry of MDOL have been reported for the first time using DFT calculations. The computed geometrical parameters are compared with the observed X-Ray diffraction data of similar compound. Theoretical ¹H and ¹³C NMR chemical shift values (with respect to TMS) are reported and compared with experimental data, showing a very good agreement both ¹H and ¹³C NMR. Theoretical UV-Visible spectrum for various solvents is discussed. In the case of solvents, the peaks are somewhat shifted slightly to the lower wavelengths resulting the influence of solvent effect on the title molecule. The frontier molecular orbital have been visualized and the HOMO-LUMO energy gap has been calculated. The lesser value of HOMO-LUMO energy gap has substantial influence on the bioactivity of the molecule. The electronic stabilization of MDOL was understood by NBO analysis by means of Donor and Acceptor orbital interactions producing hierarchy of stabilization energy. The topological analysis based on the AIM theory shows the difference of charge distribution in all bonds. The proceedings on thermodynamic analysis draw the attention by its trend fastidiously the behavior between temperature and entropy (S), internal energy (E)and heat capacity $(C_{..})$ with constant volume. The overall computational spectral analysis, electronic structure calculations, thermodynamic and magnetic properties on MDOL leaves the legacy and open up the way to extend its application in the field of pharmaceutical discipline and molecular drug designing.

Bonds	$\rho_{_{bcp}}(r)^{a}$	$\nabla^2 \rho_{bcp}(r)^{b}$	٤c	λ_1^{d}	$\lambda_2^{\ d}$	λ_3^{d}	d ₁ °	d2e	Df	G(r) ^g	V(r) ^g	H(r) ⁹
O1 - C2	1.956	-17.053	0.033	-15.050	-14.565	12.562	0.496	0.891	1.387	1.505	-4.204	-2.699
C2 - O3	1.841	-15.811	0.041	-13.638	-13.106	10.933	0.896	0.519	1.414	1.273	-3.653	-2.380
O3 - C4	1.657	-10.949	0.015	-10.497	-10.344	9.891	0.924	0.515	1.439	1.317	-3.400	-2.083
O1 - C5	1.672	-10.826	0.021	-10.606	-10.383	10.164	0.925	0.511	1.436	1.368	-3.494	-2.126
C4 - C5	1.666	-13.696	0.042	-11.644	-11.177	9.124	0.770	0.767	1.537	0.371	-1.702	-1.330
C2 - H6	1.971	-25.067	0.003	-19.746	-19.695	14.373	0.718	0.362	1.080	0.197	-2.149	-1.952
C2 - O7	1.876	-16.089	0.124	-14.676	-13.061	11.647	0.894	0.509	1.403	1.357	-3.840	-2.483
O7 - C8	1.679	-9.729	0.011	-10.584	-10.473	11.328	0.499	0.927	1.425	1.498	-3.676	-2.179
C8 - H9	1.897	-23.065	0.040	-18.414	-17.713	13.062	0.375	0.705	1.080	0.251	-2.116	-1.866
C8 - H10	1.912	-23.589	0.040	-18.671	-17.954	13.036	0.374	0.701	1.075	0.246	-2.144	-1.898
C8 - H11	1.868	-22.392	0.041	-17.866	-17.157	12.631	0.703	0.381	1.084	0.260	-2.087	-1.827
C4 - H12	1.913	-23.480	0.036	-18.601	-17.963	13.084	0.703	0.376	1.079	0.247	-2.137	-1.890
C4 - H13	1.910	-23.439	0.033	-18.549	-17.955	13.065	0.375	0.703	1.078	0.247	-2.134	-1.888
C5 - H14	1.921	-23.806	0.031	-18.759	-18.190	13.143	0.702	0.373	1.075	0.241	-2.148	-1.907
C5 - H15	1.915	-23.491	0.033	-18.653	-18.058	13.219	0.374	0.705	1.079	0.245	-2.135	-1.890

^aElectron density (eÅ³); ^bLaplacian of Electron density (eÅ⁵); ^cBond ellipticity; ^dHessian eigen values (eÅ⁵); ^cDistance between the critical point and respective bonded atomic nucleus (Å); ^lTotal bond path length (Å); ^eEnergy density (HÅ³)

 Table 8: Bond topological properties of 2-methoxy-1,3-dioxolane molecule.

Page 13 of 14

References

- 1. Greene TW, Wuts PGM (1991) Protective Group in Organic Synthesis. John Willey and Sons, New York.
- 2. Kociensky PJ (1994) Protecting Groups. Georg Thieme Verlag, New York.
- Gemal AL, Luche JL (1979) Lanthanoids in organic synthesis. 4. Selective ketalization and reduction of carbonyl groups. J Org Chem 44: 4187-4189.
- Baji H, Kimny T (1997) Synthesis, antifungal activity and structure-activity relationships of 2-(alkyl or aryl)-2-(alkyl or polyazol-1-ylmethyl)-4-(polyazol-1ylmethyl)-1, 3-dioxolanes. Eur J Med Chem 32: 637-650.
- Crawley GC, Briggs MT (1995) Chiral dioxolane inhibitors of leukotriene biosynthesis: structure-activity relationships and syntheses using asymmetric dihydroxylation. J Med Chem 38: 3951-3956.
- Genta MT, Villa C, Mariani E, Loupy A, Petit A, et al. (2002) Microwaveassisted preparation of cyclic ketals from a cineole ketone as potential cosmetic ingredients: solvent-free synthesis, odour evaluation, in vitro cytotoxicity and antimicrobial assays. Int J Pharm 231: 11-20.
- Shirai R, Takayama H, Nishikawa A, Koiso Y, Hashimoto Y (1998) Asymmetric synthesis of antimitotic combretadioxolane with potent antitumor activity against multi-drug resistant cells. Bioorg Med Chem Lett 8: 1997-2000.
- Nguyen-Ba N, Lee N, Chan L, Zacharie B (2000) Synthesis and antiviral activities of N-9-oxypurine 1,3-Dioxolane and 1,3-oxathiolane nucleosides. Bioorg Med Chem Lett 10: 2223-2226.
- Beraa S, Malika L, Bhata B, et al. (2003) Synthesis and evaluation of optically pure dioxolanes as inhibitors of hepatitis C virus RNA replication. Bioorg Med Chem Lett 13: 4455-4458.
- Aepkers M, Wünsch B (2005) Structure-affinity relationship studies of noncompetitive NMDA receptor antagonists derived from dexoxadrol and etoxadrol. Bioorg Med Chem Lett 13: 6836-6849.
- Zapata-Sudo G, Pontes LB, Gabriel D, Mendes TC, Ribeiro NM, et al. (2007) Sedative-hypnotic profile of novel isatin ketals. Pharmacol Biochem Behav 86: 678-685.
- Özkanli F, Güney A, Calis U, Uzbay T (2003) Synthesis and anticonvulsant activities of some new dioxolane derivatives. Arzneimittelforschung 53: 758-762.
- 13. Toxicology and Regulatory Affairs (2000) USEPA HPV Challenge Program Submission.
- Peter MW Gill, Johnson BG, Pople JA (1992) The performance of the Becke-Lee-Yang-Parr (B-LYP) density functional theory with various basis sets. Chem Phys Lett 197: 499-505.
- Lee C, Yang W, Parr RG (1998) Development of the Colle-Salvetti correlationenergy formula into a functional of the electron density. Phys Rev B 37: 785-789.
- Karabacak M, Kurt M, Ataç A (2009) Experimental and theoretical FT-IR and FT-Raman spectroscopic analysis of N1-methyl-2-chloroaniline. J Phys Org Chem 22: 321-330.
- 17. Frisch MJ et al. (2009) Gaussian 09, Revision A1 Gaussian. Inc., Wallingford CT.
- Schlegel HB (1982) Optimization of equilibrium geometries and transition structures. J Comput Chem 3: 214-218.
- Hohenberg H, Kohn W (1964) Inhomogeneous Electron Gas. Phys Rev B 136: 864-871.
- Becke AD (1993) Density-functional thermochemistry. III. The role of exact exchange. J Chem Phys 98: 5648-5652.
- 21. Becke AD (1988) Density-functional exchange-energy approximation with correct asymptotic behavior. Phys Rev A 38: 3098-3100.
- 22. Clark T, Chandrasekhar J, Spitznagel GW, Ragué Schleyer PV (1983) Efficient diffuse function-augmented basis sets for anion calculations. III. The 3-21+G basis set for first-row elements, Li-F. J Comput Chem 4: 294-301.
- Michael JF, John AP, Binkley JS (1984) Self-consistent molecular orbital methods 25. Supplementary functions for Gaussian basis sets. J Chem Phys 80: 3265.
- 24. Young DC (2001) Computational Chemistry: A Practical guide for applying Techniques to Real world Problems (Electronic). John Wiley and Sons, New York.
- Karabacak M, Karagöz D, Kurt M (2009) FT-IR, FT-Raman vibrational spectra and molecular structure investigation of 2-chloro-4-methylaniline: A combined experimental and theoretical study. Spectrochim Acta A 72: 1076-1083.

- 26. Frisch MJ, Nielsm AB, Holder AJ (2008) Gaussview User Manual, Gaussian Pitsburgh.
- 27. Baker J, Jarzecki AA, Pulay P (1998) Direct Scaling of Primitive Valence Force Constants: An Alternative Approach to Scaled Quantum Mechanical Force Fields. J Phys Chem A 102: 1412-1424.
- Pulay P, Fogarasi G, Pang F, Boggs JE (1979) Systematic ab initio gradient calculation of molecular geometries, force constants, and dipole moment derivatives. J Am Chem Soc 101: 2550-2560.
- Sundius T (1990) Molvib A flexible program for force field calculations. Mol Struct 218: 321-326.
- 30. Sundius T (2002) Scaling of ab initio force fields by MOLVIB. Vib Spectrosc 29: 89-95.
- Polavarapu PL (1990) Ab initio vibrational Raman and Raman optical activity spectra. J Phys Chem 94: 8106-8112.
- Keresztury G, Holly S, Varga J (1993) Vibrational spectra of monothiocarbamates-II. IR and Raman spectra, vibrational assignment, conformational analysis and ab initio calculations of S-methyl-N,N-dimethylthiocarbamate. Spectrochim Acta A 49: 2007-2017.
- Matias PM, Jeffrey GA, Wingert LM, Ruble JR (1989) Single crystal neutron diffraction analysis (15 K) and ab initio molecular orbital calculations for ethylene carbonate. J Mol Struct Theochem 184: 247-260.
- 34. Roeges NGP (1994) A Guide to the Complete Interpretation of the Infrared Spectra of Organic Structures. Wiley, New York.
- Barthes M, De Nunzio G, Ribet M (1996) Polarons or proton transfer in chains of peptide groups? Synth Met 76: 337-340.
- 36. Gyömöre Á, Kovács Z, Nagyb T, Kudarc V, Szabód A, et.al. (2008) DNMR, DFT and preparative study on the conformation of (Z)-4,5,6,7-tetrahydropyrazolo[1,5-e] benzo[g][1,5]diazonin-8-ones and (Z)-4,5-dihydropyrazolo [1,5-d]benzo[f][1,4] diazocin-7(6H)-ones. Tetrahedron 64: 10837-10848.
- Scheibye S, El-Barbary AA, Lawesson SO (1982) Studies on organophosphorus compounds-XLI: Formation of 3-pyrazoline-5-thione disulfides from 3,5-pyrazolidinediones. C-alkylation of 3,5-pyrazolidinediones. Tetrahedron 38: 3753-3760.
- EI-Shahawy AS, Ahmed SM, Sayed NK (2007) INDO/SCF-CI calculations and structural spectroscopic studies of some complexes of 4-hydroxyacetanilide. Spectrochim Acta A 66: 143-152.
- Xavier RJ, Prabaharan A (2015) Vibrational spectroscopic investigations of 4,4-dimethyl-2-oxazoline: A density functional theory approach. Spectrochim Acta A 136: 1530-1542.
- Jag M (2001) Organic Spectroscopy-Principles and Applications. 2nd edn. Narosa Publishing House, New Delhi.
- Balachandran V, Karunakaran V (2013) Quantum mechanical study of the structure and vibrational spectroscopic (FT-IR and FT-Raman), first-order hyperpolarizability, NBO and HOMO-LUMO studies of 4-bromo-3-nitroanisole. Spectrochim Acta A 106: 284-298.
- 42. Litivinow G (1992) Proceedings of the XII International Conference on Raman Spectroscopy. Wurzburg, Germany.
- 43. Paulraj El, Muthu S (2013) Molecular structure analysis and spectroscopic characterization of 5-ethyl-5-phenyl-1,3-diazinane-4,6-dione with experimental (FT-IR and FT-Raman) techniques and quantum chemical calculations. Spectrochim Acta A 106: 310-320.
- 44. Bellamy LJ (1980) The Infrared Spectra of Complex Molecules. 2nd edn. Chapman and Hall, London.
- 45. Arivazhagan M, Anitha Rexalin D (2013) Vibrational spectra, UV-vis spectral analysis and HOMO-LUMO studies of 2,4-dichloro-5-nitropyrimidine and 4-methyl-2-(methylthio)pyrimidine. Spectrochim Acta A 107: 347-358.
- Dollish FR, Fateley WG, Bentely FF (1997) Characteristic Raman Frequencies on Organic Compounds. John Wiley, New York.
- Silverstein RM, Clayton BG, Morril TC (1991) Spectrometric Identification of Organic Compounds. John Wiley, New York.
- Karthikeyan B (2006) Density functional calculations on the structure, vibrational frequencies and normal modes of 7-Azaindole. Spectrochim Acta A 64: 1083-1087.

Page 14 of 14

- Sundaraganesan N, Ilakiamani S, Dominic JB (2007) Vibrational spectroscopy investigation using ab initio and density functional theory analysis on the structure of 3,4-dimethylbenzaldehyde. Spectrochim Acta A 68: 680-687.
- Endredi H, Billes F, Keresztury G (2004) Revised assignment of the vibrational spectra of methylpyrazines based on scaled DFT force fields. J Mol Struct Theochem 677: 211-225.
- 51. Schlick T (2010) Molecular Modeling and Simulation: An Interdisciplinary Guide. 2nd edn. Vol. 21. Springer, New York.
- Vander Maas JH, Lutz ETH (1974) Structural information from OH stretching frequencies monohydric saturated alcohols. Spectrochim Acta A 30: 2005-2019.
- Subramania N, Sundaraganesan N, Jayabharathi J (2010) Molecular structure, spectroscopic (FT-IR, FT-Raman, NMR, UV) studies and first-order molecular hyperpolarizabilities of 1,2-bis(3-methoxy-4-hydroxybenzylidene)hydrazine by density functional method. Spectrochim Acta A 76: 259-269.
- 54. Pathak SK, Srivastava R, Sachan AK, Prasad O, Sinha L, et al. (2015) Experimental (FT-IR, FT-Raman, UV and NMR) and quantum chemical studies on molecular structure, spectroscopic analysis, NLO, NBO and reactivity descriptors of 3,5-Difluoroaniline. Spectrochim Acta A 135: 283-295.
- 55. Rohatgi-Mukherjee KK (1978) Fundamentals of Photochemistry. Wiley, New York.
- Xian-Wei L, Shibata E, Nakamura T (2003) Thermodynamic Properties of Polybrominated Dibenzo-p-dioxins and Dibenzofurans Calculated by Density Functional Theory. Mater Trans 44: 1004-1013.
- 57. McQuarrie DA, Simon JD (1999) Molecular Thermodynamics. University Science Books, Sausalito, California.
- Gupta MC (2001) Atomic and Molecular Spectroscopy. New Age International (P) Limited Publishers, New Delhi.
- Choudhary N, Bee S, Gupta A, Tandon P (2013) Comparative vibrational spectroscopic studies, HOMO-LUMO and NBO analysis of N-(phenyl)-2,2dichloroacetamide, N-(2-chloro phenyl)-2,2-dichloroacetamide and N-(4-chloro phenyl)-2,2-dichloroacetamide based on density functional theory. Comp Theor Chem 1016: 8-21.
- Sinhaa L, Prasada O, Narayana V, Shuklab SR (2011) Raman, FT-IR spectroscopic analysis and first-order hyperpolarisability of 3-benzoyl-5-chlorouracil by first principles. J Mol Simul 37: 153-163.
- Lewis DFV, Loannides C, Parke DV (1994) Interaction of a series of nitriles with the alcohol-inducible isoform of P450: Computer analysis of structure-activity relationships. Xenobiotica 24: 401-408.
- Kosar B, Albayrak C (2011) Spectroscopic investigations and quantum chemical computational study of (E)-4-methoxy-2-[(p-tolylimino)methyl]phenol. Spectrochim Acta A 78: 160-167.
- 63. Koopmans T (1993) Über die Zuordnung von Wellenfunktionen und Eigenwerten zu den Einzelnen Elektronen Eines Atoms. Physica 1: 104-113.

- 64. Parr RG, Szentpály LV, Liu S (1999) Electrophilicity Index. J Am Chem Soc 121: 1922-1924.
- 65. Parr RG, Pearson RG (1983) Absolute hardness: companion parameter to absolute electronegativity. J Am Chem Soc 105: 7512-7516.
- 66. Hoffmann R (1988) Solids and Surfaces: A Chemist's View of Bonding in Extended Structures. VCH Publishers, New York.
- Hughbanks T, Hoffmann R (1983) Chains of trans-edge-sharing molybdenum octahedra: metal-metal bonding in extended systems. J Am Chem Soc 105: 3528-3537.
- Malecki JC (2010) Synthesis, crystal, molecular and electronic structures of thiocyanate ruthenium complexes with pyridine and its derivatives as ligands. Polyhedron 29: 1973-1979.
- O'boyle NM, Tenderholt AL, Langner KM (2008) cclib: A library for packageindependent computational chemistry algorithms. J Comput Chem 29: 839-845.
- 70. Chen M, Waghmare UV, Friend CM, Kaxiras EA (1998) density functional study of clean and hydrogen-covered α -MoO₃(010): Electronic structure and surface relaxation. J Chem Phys 109: 6854.
- Johnson ER, Keinan S, Mori-Sánchez P, Contreras-García J, Cohen AJ, et al. (2010) Revealing noncovalent interactions. J Am Chem Soc 132: 6498-6506.
- Lu T, Chen F (2012) Multiwfn: a multifunctional wavefunction analyzer. J Comput Chem 33: 580-592.
- Humphrey W, Andrew D, Klaus S (1996) VMD: Visual molecular dynamics. J Mol Graph 14: 33-38.
- Weinhold F, Landis CR (2005) Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective. Cambridge University Press.
- Weinhold F, Landis CR (2001) Natural Bond Orbitals and extensions of localized bonding concepts. Chem Educ Res Pract 2: 91-104.
- 76. Glendening ED, Reed AE, Carpenter JE, Weinhold F; NBO 3.1 Program Manual.
- 77. Bader RFW (1990) Atoms in Molecules: A Quantum Theory. Oxford University Press, Oxford.
- Popelier PLA (1999) Atoms in Molecules-An Introduction. Pearson Edition, Harlow, UK.
- 79. Keith TA (2010) AIMAII.
- Bader RFW, Nguyen-Dang TT (1981) Quantum Theory of Atoms in Molecules-Dalton Revisited. Adv Quantum Chem 14: 63-124.
- Biegler-konig FW, Bader RFW, Tang TH (1982) Calculation of the average properties of atoms in molecules II. J Comput Chem 13: 317-328.