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Vibrational Spectra of 2-Formyl-3-(4-Hydroxy-1-methyl-2-oxo-1,2-dihydro-quinolin-3-yl) 3-oxo-propionic acid (FHMQP): Combined Experimental and Theoretical Studies

***M. A. M. El-Mansy*[1,*], *H. M. Hassanin*[2] *and M .A. Mostafa*[2]**

[1]Physics Department, Faculty of Education, Ain Shams University, Roxy, Cairo, Egypt.
[2]Chemistry Department, Faculty of Education, Ain Shams University, Roxy, Cairo, Egypt.

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Abstract: Our results showed that FHMQP possesses a high dipole moment value of 9.3 Debye. FHMQP spin is doublet state which enhances frontier molecular orbitals to split into alpha (spin ↑) and beta (spin ↓) molecular orbitals with two different energy gaps 4.2 and 2.9 eV, respectively. FHMQP is highly recommended to be a more promising structure for many applications in optoelectronic devices such as solar cells.

Keywords: FHMQP, DFT/B3LYP, FT-IR, Dipole Moment, HOMO-LUMO energy gap, DOS

1 Introduction

As is well-known, hetero-cycles compounds are widespread in natural products and have attracted considerable attention from wide area of science, including physical chemistry, medicinal chemistry, natural product chemistry, synthetic organic chemistry and polymer science [1]. Quinoline-2-one derivatives are well known for their biological and pharmaceutical importance as antitumor, antimalarial, antiplatelet, antidepressant, antiulcer, plant virucides, antioxidant activity and herbicides. Also, they are used in control the manufacture of proteins, functions of cells in living organisms and drug synthesis of anti-bacterial and anti-fungal activity [2,3]. One of the most quinoline-2-one derivatives is 2-Formyl-3-(4-Hydroxy-1-methyl-2-oxo-1,2-dihydro-quinolin-3-yl)3-oxo-propionic acid (FHMQP) which is the interest of our studies. FHMQP is a new synthesized organic compound which has a chemical formula of C14H10NO6. Triplet-state dynamics in Chl-a/Per mixtures in organic solvent and in native H-PCP were studied by means of step-scan FT-IR spectroscopy [4]. A new three-dimensional structured was designed by anodizing of anisotropic KOH etched silicon wafer. The structure is applied for the detection of organic volatile by FT-IR spectroscopy. FT-IR photoacoustic spectroscopic experiments were carried out to investigate kerogen and minerals in oil shale. The dissolved organic matter which extracted from fermentation effluent of swine manure slurry was characterized by FT-IR. Other conformational spectroscopic tools could be helpful for better understanding of molecular structures. Many authors apply molecular modeling as promising conformational tool for confirming their FT-IR experimental work [5,6,7]. The present investigation was undertaken to study the optimized molecular structural parameters, vibrational frequencies, thermo-chemical parameters, total dipole moment, nuclear repulsion energy, spin, number of alpha (spin ↑) and beta (spin ↓) electrons and finally HOMO-LUMO energy gap for FHMQP using DFT/B3LYP utilizing 6-311G(d,p) basis set.

* Corresponding author e-mail: Mohamed_Mansy878@yahoo.com

2 Materials and Methods

2.1 Synthesis of 2-Formyl-3-(4-Hydroxy-1-methyl-2-oxo-1,2-dihydro-quinolin-3-yl)3-oxo-propionic acid (FHMQP)

A mixture of compound (6-methyl-6H-pyrano[3,2-c]quinoline-2,4,5-trione]) (2 gm) and Triethylorthoformate (5 ml) was heated under fusion condition for 10hrs. The deposited solid during heating was filtered, washed with diethyl ether to give 2-Formyl-3-(4-Hydroxy-1-methyl-2-oxo-1,2-dihydro-quinolin-3-yl)3-oxo-propionic acid (FHMQP) as brownish yellow crystals, mp $> 300\ ^{\circ}C$,^{1}H NMR (DMSO-d_6, δ): 2.05(s, 3H, NCH_3), 5.80 (s, 1H, O=CCHC=O), 10.04 (s, 1H, CHO), 7.51 (t, 1H, J = 7.2 Hz, H-6), 7.77 (d, 1H, J = 8.4 Hz, H-8), 7.79 (t, 1H, J = 7.2 Hz, H-7), 8.10 (d, 1H, J = 8.1 Hz, H-5), 13.45 (s, 1H, OH exchangeable with D_2O), 13.7 (s, 1H, OH exchangeable with D_2O).

2.2 FT-IR spectroscopy

1 mg of FHMQP powder was mixed with 50 mg of vacuum dried IR-grad KBr then compressed to a circular disk for performing FT-IR analysis using Thermo Scientific Nicollet 460_{plus} Spectrophotometer at room temperature in the spectral range 500-4000 cm^{-1}.

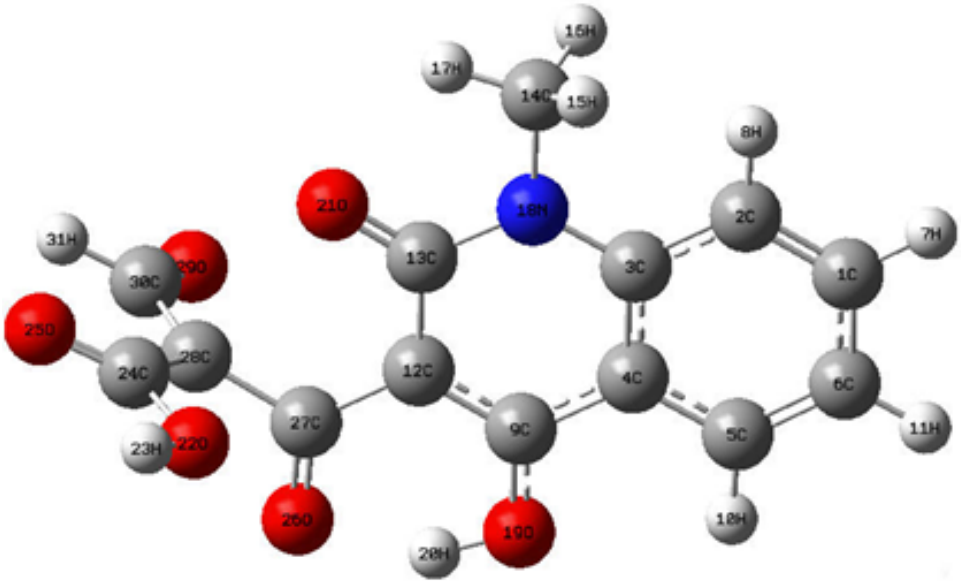

Fig. 1: Optimized molecular structure of FHMQP at B3LYP/6-311G(d,p).

3 Computational details

The molecular structure of FHMQP and corresponding vibrational harmonic frequencies were calculated using BeckeLeeYangParr (B3LYP) with 6-311G(d,p) basis set Gaussian 09W program package [8,9,10] on a PC Core I5/2.8 GHz without any constraint on the geometry. The harmonic vibrational frequencies have been analytically calculated by taking the second order derivative of energy using the same level of theory. The ground state optimized geometry of FHMQP molecule is shown in Fig. (1). We add polarization functions for better treatment of polar bonds such as C=O, C=C, C-N, C-O, C-C and CH groups. All the calculations were performed by using Gauss View 5 molecular visualization program Package [11].

Table 1: Computational Optimized Structural Parameters for FHMQP at B3LYP/6-311G(d,p).

Bond Length (Å)				Bond Angle (0)			
C1-C2	1.4	C24-O25	1.2	C2-C1-C6	121.3	C12-C13-O21	122.5
C1-C6	1.4	C24-C28	1.5	C2-C1-H7	118.9	N18-C13-O21	120.6
C1-H7	1.1	O26-C27	1.2	C6-C1-H7	119.8	H15-C14-H16	109.5
C2-C3	1.4	C27-C28	1.5	C1-C2-C3	120.4	H15-C14-H17	109.5
C2-H8	1.1	C28-C30	1.5	C1-C2-H8	119.2	H15-C14-N18	110.6
C3-C4	1.4	O29-C30	1.2	C3-C2-H8	120.4	H16-C14-H17	109.5
C3-N18	1.4	C30-H31	1.1	C2-C3-C4	118.2	H16-C14-N18	110.5
C4-C5	1.4			C2-C3-N18	121.2	H17-C14-N18	107.3
C4-C9	1.4			C4-C3-N18	120.5	C3-N18-C13	122.7
C5-C6	1.4			C3-C4-C5	120.3	C3-N18-C14	120.1
C5-H10	1.1			C3-C4-C9	118.5	C13-N18-C14	117.2
C6-H11	1.1			C5-C4-C9	121.3	C9-O19-H20	106.5
C9-C12	1.4			C4-C5-C6	120.7	H23-O22-C24	106.7
C9-O19	1.3			C4-C5-H10	118.1	O22-C24-O28	123.1
C12-C13	1.5			C6-C5-H10	121.2	O22-C24-C28	112.3
C12-C27	1.5			C1-C6-C5	119.1	O25-C24-C28	124.6
C13-N18	1.4			C1-C6-H11	120.4	C12-C27-O26	122.1
C13-O21	1.2			C5-C6-H11	120.5	C12-C27-C28	119.7
C14-H15	1.1			C4-C9-C12	120.0	026-C27-C28	118.2
C14-H16	1.1			C4-C9-O19	117.9	C24-C28-C27	121.4
C14-H17	1.1			C12-C9-O19	122.1	C24-C28-C30	119.6
C14-N18	1.5			C9-C12-C13	121.4	C27-C28-C30	118.8
O19-H20	1.0			C9-C12-C127	119.5	C28-C30-O29	122.7
O22-H23	1.0			C13-C12-C27	119.2	C28-C30-H31	115.0
O22-C24	1.4			C12-C13-N18	116.9	O29-C30-H31	122.4

4 Results and Discussion

4.1 Geometry Optimization

The calculated optimized geometrical parameters (bond lengths & bond Angles) for FHMQP at B3LYP/6-311G(d,p) basis set are listed in Table (1). Since the exact crystal structure of FHMQP is not available this time, the optimized structure can be only compared with other similar systems for which the crystal structures have been solved.

4.2 Vibrational Assignments

FHMQP has 31 atoms and 87 normal vibrations are distributed as $59A^{'} + 28A^{''}$ considering Cs symmetry. All calculated modes are gradually numbered from the lowest to the highest frequency within each fundamental wavenumbers. For comparison with experimental results only 23 active modes of vibrations were presented for FHMQP, $17A^{'} + 6A^{''}$. The modes $A^{'}$ are in plane and stretching vibrations while modes $A^{''}$ correspond to the out-of-plane vibrations. The calculated vibrational wavenumbers for FHMQP at B3LYP/6-311G(d,p) basis set has been scaled with scaling factor 0.96 [12] according to the level of theory used in our calculations. Both calculated and experimental FT-IR wavenumbers and the corresponding assignments for FHMQP are collected in Table (2). Both experimental and calculated FT-IR spectra at B3LYP/6-311G(d,p) basis set for FHMQP are shown in Fig. (2). Results showed that calculated vibrational frequencies at B3LYP/6-311G(d,p) gives reasonable deviations from the experimental values. Any discrepancy noted between calculated and experimental vibrational frequencies may be due to the fact that the calculations have been actually performed on a single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions. The assignment could be achieved extensively as in the following:

The O-H stretching vibration is observed in the region 3400-3800 cm^{-1} [13]. The computed vibration (mode 23) is assigned to C=O stretching at 3692 cm^{-1} which is comparable with the experimental result at 3442 cm^{-1}. The computed vibration (mode 14) is assigned to O-H in plane bending vibrations at 1331 cm^{-1} which is comparable with the experimental result at 1329 cm^{-1}. The computed vibration (mode 8) is assigned to O-H out of plane bending vibrations at 864 cm^{-1} which is comparable with the experimental result at 887 cm^{-1}.

Table 2: Experimental and Computational Calculated Vibrational Wavenumbers (Harmonic Frequency (cm^{-1})), IR Intensities, Species and Assignments for FHMQP at B3LYP/6-311G(d,p).

No	MR Wavenumber (cm^{-1})		IR Intensity		Exp.	Species	Vibrational Assignments
	Unscaled	Scaled	Rel.	Abs.			
1	590	578	29	3	555	A”	γ C-C + γ C-O+ γ C-N
2	603	591	56	5	580	A”	
3	654	641	33	3	648	A’	β C-C+ β C-O+ β C-N
4	689	675	25	2	667	A’	
5	737	722	24	2	700	A”	γ C-H
6	809	793	4	0	790	A”	
7	838	821	11	1	814	A”	
8	882	864	0	0	887	A”	γ O-H
9	985	965	33	3	959	A’	υ C-C + υ C-O + υ C-N
10	1096	1074	50	5	1060	A’	β C-H
11	1115	1093	37	4	1127	A’	
12	1196	1172	193	19	1164	A’	
13	1309	1283	117	11	1250	A’	
14	1358	1331	136	13	1329	A’	β O-H
15	1457	1428	75	7	1410	A’	CH3 Deformation
16	1605	1573	173	17	1531	A’	υ C=C
17	1658	1625	311	30	1638	A’	υ C=O
18	1679	1645	1039	100	1679	A’	
19	1756	1721	271	26	1747	A’	
20	2994	2934	53	5	2850	A’	υ_s C-H in CH3
21	3040	2979	37	4	2945	A’	υ_{as} as C-H in CH3
22	3069	3008	414	40	3081	A’	υ C-H (aromatic)
23	3767	3692	98	9	3442	A’	υ O-H

υ (stretching); β (in plane bending); γ (out of plane bending)

Table 3: The Optimized Calculations of Total Energies (a.u), Zero Point Vibrational Energies (kcal mol^{-1}), Rotational Constants (GHz), Entropies (cal k^{-1}), Specific Heat Cv (cal k^{-1}), Total Dipole Moment (Debye), Nuclear Repulsion Energy (eV) and HOMO-LUMO Energy Gap (eV) for FHMQP at B3LYP/6-311G(d,p).

Parameters	B3LYP/6-311G(d,p)	
Total Energy	-1137.065	
Zero Point Energy	134.995	
Rotational Constants	0.593	
	0.189	
	0.170	
Entropy		
Total	145.229	
Translational	43.042	
Rotational	34.089	
Vibrational	66.720	
CV		
Total	69.923	
Translational	2.981	
Rotational	2.981	
Vibrational	63.961	
Dipole Moment	9.3	
Nuclear Repulsion Energy	5.01 x 103	
Spin	Doublet	
	Beta (spin $\downarrow$)	Alpha (spin $\uparrow$)
No. of Electrons	78	79
	Beta MOs	MOs
Energy Gap	2.9	4.2

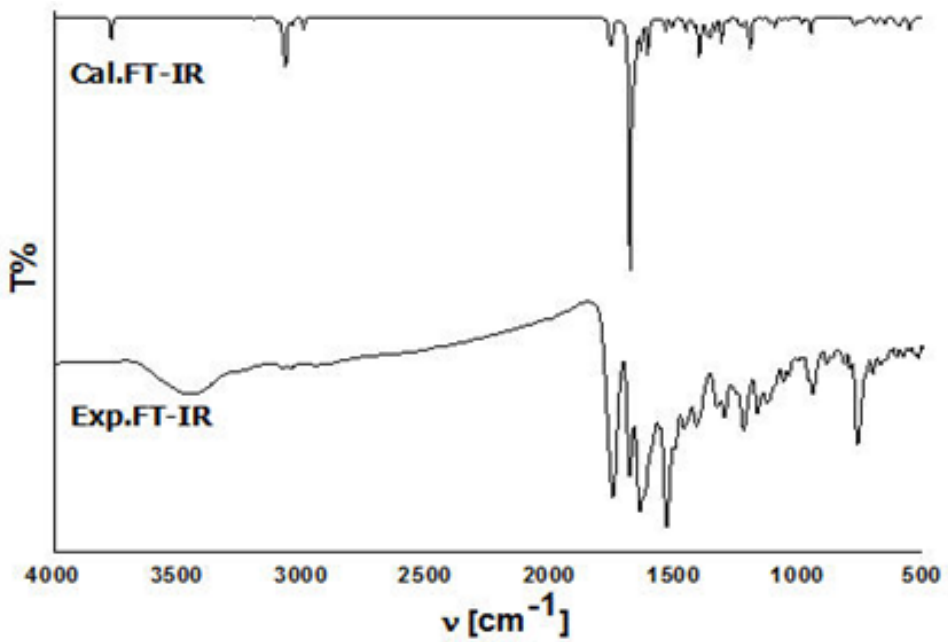

Fig. 2: Experimental and calculated FT-IR spectra for FHMQP at B3LYP/6-311G(d,p).

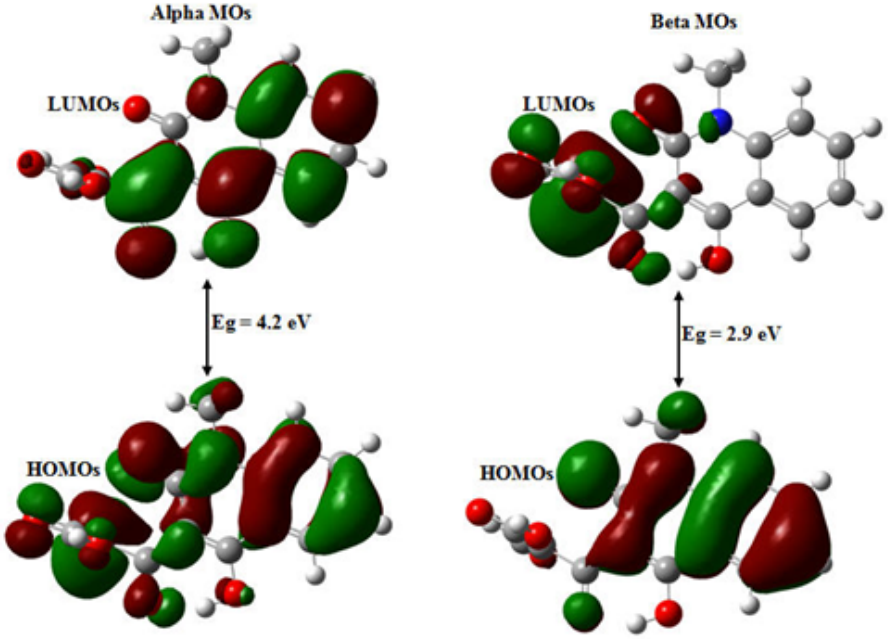

Fig. 3: HOMO-LUMO molecular orbitals for FHMQP at B3LYP/6-311G(d,p).

The aromatic C-H stretching vibrations are observed in the region 3000-3100 cm^{-1} [14]. The computed vibration (mode 22) is assigned to C-H aromatic stretching vibration at 3008 cm^{-1} which is comparable with the experimental result at 3081 cm^{-1}. The C-H in plane bending vibration is observed in the region 1025-1280 cm^{-1} [14] and C-H out of plane bending vibration in the region 690-850 cm^{-1}. The computed vibrations (modes 10, 11, 12, 13) are assigned to C-H in plane bending vibrations at 1074, 1093, 1172, 1283 cm^{-1} which are comparable with the experimental results at 1060,

1127, 1164, 1250 cm^{-1}. The computed vibrations (modes 5, 6, 7) are assigned to C-H out of plane bending vibrations at 722, 793, 821 cm^{-1} which are comparable with the experimental results at 700, 790, 814 cm^{-1}.

The C=O stretching vibration is observed in the region 1800-1600 cm^{-1} [15]. The computed vibrations (mode 17, 18, 19) are assigned to C=O stretching at 1625, 1645, 1721, cm^{-1} which are comparable with the experimental result at 1638, 1679, 1747 cm^{-1}. The C = C vibration is observed in the region 1480-1550 cm^{-1} [16]. The computed vibration (mode 16) is assigned to C=C stretching vibrations at 1573 cm^{-1} which is comparable with the experimental result at 1531 cm^{-1}.

The computed vibration (mode 9) is assigned to C-O, C-N, C-C stretching vibration at 965 cm^{-1} which is comparable with the experimental result at 959 cm^{-1}. The computed vibration (mode 3, 4) is assigned to C-O, C-N, C-C in plane bending vibrations at 641, 675 cm^{-1} which are comparable with the experimental result at 648, 667 cm^{-1}. The computed vibration (mode 1, 2) is assigned to C-O, C-N, C-C out of plane bending vibrations at 578, 591 cm^{-1} which is comparable with the experimental result at 555, 580 cm^{-1}.

The computed vibration (mode 21) is assigned to asymmetric C-H stretching vibration in CH_3 at 2979 cm^{-1} which is comparable with the experimental result at 2945 cm^{-1}. The computed vibration (mode 20) is assigned to symmetric C-H stretching vibration in CH_3 at 2934 cm^{-1} which is comparable with the experimental result at 2850 cm^{-1}. The computed vibration (mode 15) is assigned to CH_3 deformation at 1428 cm^{-1} which is comparable with the experimental result at 1410 cm^{-1}.

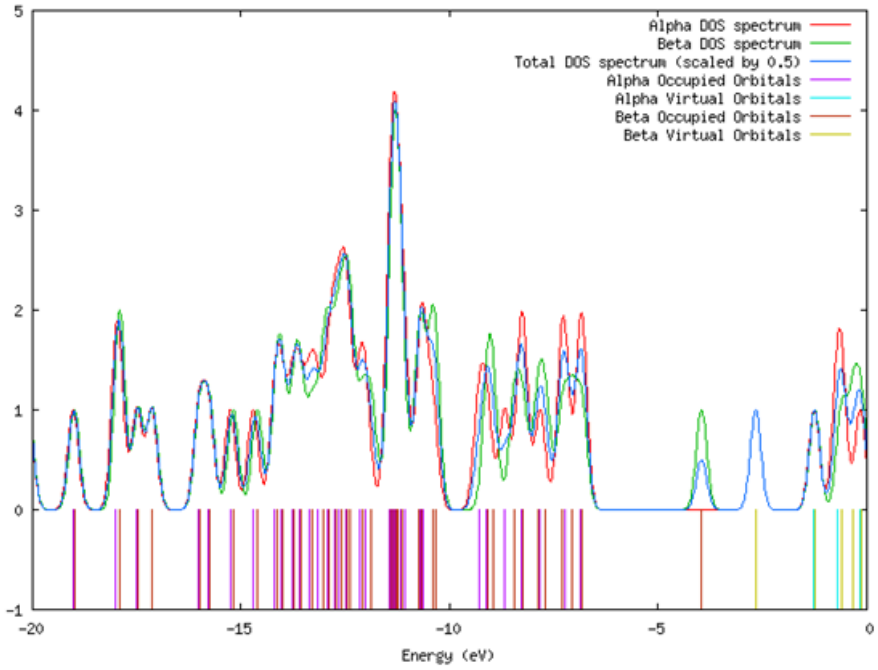

Fig. 4: Density of state (DOS) spectrum for FHMQP at B3LYP/6-311G(d,p).

4.3 Thermo-Chemical Properties

The calculated thermo-chemical parameters are presented in Table (3) such as total energy, zero-point vibrational energy, rotational constants, entropy, specific heat at constant volume (Cv), dipole moment, nuclear repulsion energy, spin, number of alpha (spin ↑) and beta (spin ↓) electrons and finally HOMO-LUMO energy gap for FHMQP at room temperature using B3LYP/6-311G(d,p) basis set.

4.4 HOMO-LUMO energy gap and related molecular properties

Spatial distribution of molecular orbital's, especially those of highest occupied molecular orbitals (HOMOs) and lowest available unoccupied molecular orbitals (LUMOs), are excellent indicators of electron transport in molecular systems.

The conjugated molecules are characterized by a small HOMO-LUMO separation, which is the result of a significant degree of intramolecular change transfer (ICT) from the end-capping electron-donor groups to the efficient electron-acceptor ones through-conjugated path [17,18,19]. FHMQP has a dipole moment of 9.3 Debye which indicates its high reactivity to interact with the surrounding molecules. FHMQP spin is doublet state which enhances frontier molecular orbitals to split into alpha (spin $\uparrow$) and beta (spin $\downarrow$) molecular orbitals with two different energy gaps of 4.2 and 2.9 eV, respectively. Therefore, FHMQP is highly recommended to be a more promising structure for many applications in optoelectronic devices such as solar cells. Fig. (3) shows the calculated HOMO-LUMO molecular orbitals of FHMQP at B3LYP/6-311G(d,p). Fig. (4) shows the calculated density of state (DOS) spectrum for FHMQP at B3LYP/6-311G(d,p). It is clear that the HOMOs of HMQNP are π orbitals while the LUMOs are π^* orbitals.

5 Conclusion

FHMQP possesses a high dipole moment value of 9.3 Debye which indicates its relatively high reactivity to interact with the surrounding molecules. FHMQP spin is doublet state which enhances frontier molecular orbitals to split into alpha (spin $\uparrow$) and beta (spin $\downarrow$) molecular orbitals with two different energy gaps 4.2 and 2.9 eV, respectively. FHMQP is highly recommended to be a more promising structure for many applications in optoelectronic devices such as solar cells.

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