

Theoretical Studies of Molecular Structure and Vibrational Spectra of Acetoxy-4-methyl Phenyl Methyl Acetate

Ujval Gupta, Vivek K. Singh, and Yugal Khajuria*

Abstract: In the present paper we have performed the quantum chemistry calculations by using Gaussian 09 program to compute optimized geometry, atomic charges, and vibrational frequencies along with intensities in infra-red at B3LYP/6-31G (d) and HF/6-31G (d) for Acetoxy-4-methyl Phenyl Methyl Acetate, an acylal class of organic materials, in the ground state. The optimized geometry, bond length and bond angles are in very good agreement with X-rays data. The title compound with 30 atom gives (3N-6) 84 vibrational levels in the spectral range 26-3224 cm^{-1} . The assignments for these 84 vibrational levels have been proposed and show some structure spectra correlation. These methods are proposed as a tool to be applied in the structural characterization of the acylal class of organic material.

Keywords: Acetoxy-4-methyl Phenyl Methyl Acetate, DFT Theory, Gaussian 09.

I. INTRODUCTION

Acetoxy-4-methyl Phenyl Methyl Acetate is an acylal class of organic materials. In organic chemistry acylal are also known as 1, 1 diacetates [1, 2]. The molecular formula of the title compound is $(\text{C}_{12}\text{H}_{14}\text{O}_4)$ consists of 30 atoms and the molecular weight is 222.23. In organic chemistry acylal are a group of chemical compounds having a functional group with the general structure $\text{R-C}(\text{OOCR})_2$. They can be obtained by reaction of aldehydes with acetic anhydride and a suitable catalyst (sulfated zirconia) at low temperatures. High temperature exposure converts the acylal back to the aldehyde. To the best of our knowledge, neither quantum chemical applications, nor the vibrational spectra of the title compound have been reported, as yet. The molecular structure and vibrational spectra of Acetoxy-4-methyl Phenyl Methyl Acetate ($\text{C}_{12}\text{H}_{14}\text{O}_4$) have been investigated by Hartree-Fock and density functional theory (DFT) using standard B3LYP functional and 6-31G (d) basis sets. In the present paper, the quantum chemistry calculations have been performed by using Gaussian 09 program [3] to compute optimized geometry, atomic charges, and vibrational frequencies along with intensities in IR at B3LYP/6-31G (d) and HF/6-31G (d) for acetoxy-4-methyl phenyl methyl acetate in the ground state.

The assignments have also been reported by the potential energy distribution, which is a part of the normal coordinate analyses. Recently, the title compound has been synthesized by Rajnikant *et al.* [4] and investigated the X-ray structure of the compound. We have compared our theoretical data with the experimental X-ray experimental data by Rajnikant *et al.* [4].

II. COMPUTATIONAL DETAILS

The first step in this case was to determine the optimized geometry of the given molecule. The molecular structure of Acetoxy-4-methyl Phenyl Methyl Acetate in the ground state is optimized by Hartree-Fock (HF) and density functional theory (DFT) using standard B3LYP functional and 6-31G (d) basis sets.

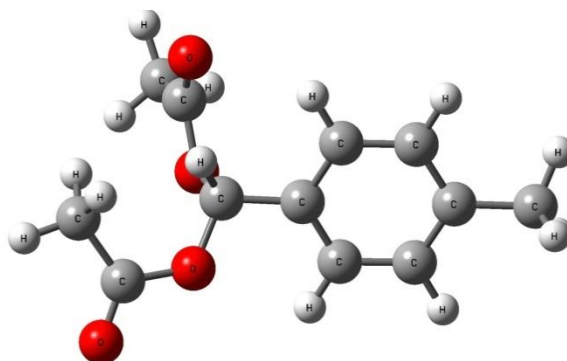


Fig. 1 Optimized structure of Acetoxy-4-methyl Phenyl Methyl Acetate.

Calculations of bond lengths, bond angles, vibrational frequencies, IR intensities and Raman intensities of the title compound (Fig.1) were carried out using Gaussian 09 program package through DFT approaches. The vibrational frequency calculated with these methods and then scaled by the factor 0.96. Molecular geometry is not restricted and all the calculations are performed by using the gauss-view molecular visualization program on a computer. Gauss view program has been considered to get visual animation and for the verification of the normal modes assignment [5]. A few of the discrepancies is observed between the experimental and computed data of vibrational frequencies and their assignments have also been discussed. The assignments of the calculated normal modes have been made by the corresponding PEDs. The PEDs are computed from quantum chemically calculated vibrational frequencies using VEDA program [6].

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III. RESULTS AND DISCUSSIONS

3.1 Molecular geometry

The atom numbering scheme of the title compound is shown in Figure 1 and the optimized geometrical parameters, namely, bond lengths and bond angles at HF/6-31G (d) and B3LYP/6-31G (d) are given in Table 1 and Table 2 respectively. The largest difference between experimental and calculated bond length by B3LYP method is about 0.045 Å. The RHF method leads to geometry parameters which are much closer to experimental data obtained by Rajnikant *et al.* [4]. The C-O bond length increases from HF to B3LYP level. The C-C bond lengths are greater than C-O bond lengths.

Table 1 Selected bond lengths and bond angles for non-hydrogen atoms

Parameters	Experimental	Calculated (6-31G*)	
		B3LYP	HF
Bond lengths	XRD data		
O1-C11	1.358	1.377	1.348
O1-C8	1.452	1.407	1.387
O2-C11	1.203	1.203	1.180
O3-C9	1.369	1.358	1.332
O3-C8	1.422	1.456	1.422
O4-C9	1.197	1.213	1.188
C8-C1	1.500	1.507	1.507
C4-C7	1.510	1.511	1.511
C9-C10	1.494	1.509	1.502
C11-C12	1.497	1.514	1.510

Table 2 Selected bond lengths and bond angles for non-hydrogen atoms

Parameters	Experimental	Calculated (6-31G*)	
		B3LYP	HF
Bond angles	XRD data		
C11-O1-C8	116.2	122.2	123.4
O3-C8-O1	105.2	105.7	105.8
O1-C8-C1	108.9	109.3	108.9
C2-C1-C8	122.1	121.3	120.9
C3-C4-C7	120.7	120.8	120.3
O4-C9-C10	126.2	126.0	125.3
O2-C11-O1	123.4	117.7	118.4
O1-C11-C12	110.9	118.3	118.4
C9-O3-C8	115.2	117.2	118.8
O3-C8-C1	109.9	110.5	111.1
C6-C1-C8	118.3	119.4	119.9
C5-C4-C7	120.8	121.0	121.4
O4-C9-O3	123.0	123.9	123.5
O3-C9-C10	110.8	110.6	111.2
O2-C11-C12	125.7	123.9	123.1

The four C-C bond lengths are found to have a magnitude of about 1.500 Å in bond angle calculation of acetoxy-4-methyl

phenyl methyl acetate, the bond angles of C11-O1-C8, O3-C8-O1, O2-C11-O1, C9-O3-C8, O3-C8-C1, C6-C1-C8, C5-C4-C7, O3-C9-C10 increases from B3LYP level to HF level and the remaining bond angles decreases from B3LYP level to HF level as shown in Tables 1 & 2. The experimental bond lengths and bond angles of the title compound have shown similar agreement with the theoretical ones. Thus, it can be concluded that the theoretical experimental bond lengths and bond angles are in good agreement with each other.

3.2 Atomic charges

Mulliken atomic charges of title compound are calculated at RHF/6-31G* and B3LYP/6-31G* levels are tabulated in Table 3. The magnitudes of hydrogen atoms decrease from RHF to DFT level of calculations and the magnitudes of oxygen atoms increase from RHF to DFT level of calculations. The charges on hydrogen atoms exhibit positive charges. The range of hydrogen atom charges in case of RHF/6-31G* is from 0.176 to 0.238 where as the range of hydrogen atom charges in case of B3LYP /6-31G* is from 0.128 to 0.197. The charge distribution shows that C1, C11, C14, C20 are positively charged where as the remaining carbon atoms are negatively charged.

Table 3 Atomic charges for optimized geometry of title compound

Atom no.	HF/6-31G*	B3LYP/6-31G*
C1	0.050	0.184
C2	-0.227	-0.184
C3	-0.179	-0.157
C4	-0.053	0.110
C5	-0.203	-0.178
C6	-0.238	-0.187
C11	0.479	0.268
C14	0.764	0.609
C15	-0.567	-0.526
C20	0.780	0.602
C22	-0.631	-0.566
C26	-0.510	-0.531
H7	0.203	0.129
H8	0.238	0.160
H9	0.228	0.155
H10	0.202	0.128
H16	0.204	0.185
H17	0.211	0.186
H18	0.212	0.193
H23	0.230	0.197
H24	0.205	0.190
H25	0.204	0.189
H27	0.180	0.161
H28	0.176	0.158
H29	0.183	0.170
H30	0.216	0.173
O12	-0.635	-0.460
O13	-0.644	-0.463
O19	-0.564	-0.469
O21	-0.516	-0.424

Table 4. The B3LYP/6-31G* calculated frequencies scaled by the factor 0.96, IR (I_{IR}) intensities and mode assignments PED (%) of Acetoxy-4-methyl Phenyl Methyl Acetate molecule.

Unscaled frequency	Scaled frequency	I_{IR}	Veda frequency	PED	Interpretation
3224	3095	3.01	3224	S1-95	C-H sym. stretch
3207	3079	6.06	3207	S3-87	C-H sym. stretch
3186	3059	5.33	3185	S2-82	C-H asym. stretch
3184	3057	6.33	3184	S5-90	C-H asym. stretch
3183	3056	16.45	3182	S4-93	C-H sym. stretch
3182	3055	17.17	3180	S9-80	C-H asym. stretch
3140	3014	8.29	3140	S8-96	C-H sym. stretch
3138	3012	4.63	3138	S10-85	C-H asym. stretch
3138	3012	4.36	3135	S6-81	C-H sym. stretch
3127	3002	15.64	3127	S13-93	C-H asym. stretch
3100	2976	19.77	3100	S12-93	C-H asym. stretch
3073	2950	1.14	3073	S7-95	C-H sym. stretch
3070	2947	1.84	3070	S11-89	C-H sym. stretch
3043	2921	29.68	3043	S14-96	C-H sym. stretch
1870	1795	312.27	1870	S16-91	O-C stretch
1820	1747	199.31	1820	S15-86	O-C stretch
1676	1609	11.01	1660	S17-59, S33-20	C-C stretch
1636	1571	0.25	1636	S21-68	C-C stretch
1567	1504	9.26	1553	S34-65, S49-17	Bend (HCC)
1524	1463	12.48	1524	S42-74	Bend (HCH)
1518	1457	5.29	1518	S43-91	Bend (HCC)
1516	1455	10.39	1515	S39-78	Bend (HCH)
1504	1444	9.20	1503	S38-74	Bend (HCH)
1500	1440	18.83	1499	S40-68, S69-16	Bend (HCH)
1499	1439	12.78	1499	S37-82	Bend (HCH)
1469	1409	9.86	1468	S18-27, S31-23	C-C stretch
1443	1385	0.18	1442	S44-92	Bend (HCH)
1427	1370	48.78	1426	S36-83	Bend (HCH)
1422	1365	89.16	1422	S35-79	Bend (HCH)
1416	1359	12.80	1414	S41-43	Bend (HCH)
1372	1317	2.41	1372	S64-68	Bend (HCC)
1355	1300	0.77	1355	S32-53, S19-25	Bend (HCC)
1343	1289	43.69	1343	S19-44, S32-23	C-C stretch
1282	1231	393.03	1282	S23-48	C-C stretch
1245	1195	22.94	1243	S24-55	C-C stretch
1239	1189	27.36	1233	S22-47	C-C stretch
1233	1184	352.55	1220	S33-70, S17-19	Bend (HCC)
1220	1170	35.08	1159	S31-52, S18-29	Bend (HCC)
1159	1113	51.83	1131	S29-52	O-C stretch
1131	1086	160.77	1078	K70-65, S81-16	TORS (HCC0)
1077	1034	7.38	1076	S62-73	TORS (HCC0)
1076	1033	12.35	1068	K68-62, S80-22	OUT (CHCH)
1068	1025	9.28	1044	S49-64	Bend (CCC)
1044	1002	10.26	1038	S63-48	Bend (HCC)
1037	996	123.04	1025	S22-11	C-C stretch
1024	983	121.00	1019	S67-63	Bend (HCC)
1019	978	19.06	979	S59-74	TORS (HCCC)
979	940	2.92	972	S58-74	TORS (HCCC)
971	932	0.57	960	S28-58	C-C stretch

Table 4. Continued

959	921	39.53	941	S25-50	O-C stretch
941	903	169.44	907	S20-50	C-C stretch
887	852	16.15	867	S27-42	C-C stretch
862	828	1.17	862	S61-96	TORS (HCCC)
859	825	5.85	853	S60-46	TORS (HCCC)
830	797	43.70	817	S27-10, S30-16	Bend (CCC)
793	761	8.25	776	S26-70	C-C stretch
732	703	3.43	732	S82-58	OUT (CCCC)
662	636	15.60	662	S48-62	Bend (CCC)
653	627	11.15	652	S46-57	Bend (CCC)
622	597	4.41	620	S45-62	Bend (CCC)
601	577	12.50	601	S81-56	OUT (OCOC)
580	557	3.01	571	S80-61, S68-14	OUT (OCOC)
569	546	19.08	564	S84-36, S53-23	OUT (CCCC)
549	527	6.53	495	S51-10	Bend (CCC)
490	470	0.26	484	S83-10	OUT (OCOC)
472	453	7.30	450	S51-46	Bend (CCC)
417	400	0.58	417	S72-88	TORS (CCCC)
390	374	0.61	390	S52-16, S74-11	Bend (CCC)
366	351	0.91	362	S52-63	Bend (CCC)
337	324	2.55	336	S54-49	Bend (COC)
284	273	1.97	263	S55-60	Bend (CCC)
239	229	2.57	231	S74-42	OUT (CCCC)
230	221	3.75	219	S56-79	Bend (CCC)
214	205	4.92	167	S66-90	TORS (HCCO)
167	160	0.01	132	S73-59	TORS (CCOC)
130	125	0.75	127	S78-42	TORS (CCCC)
94	90	0.97	92	S50-28	Bend (CCC)
82	79	0.56	82	S65-75	TORS (HCCO)
59	57	0.10	56	S73-11, S65-10	TORS (CCOC)
56	54	5.04	54	S75-48	TORS (CCCC)
52	50	3.39	42	S71-54, S79-31	TORS (HCCC)
42	40	0.59	38	S79-51, S71-32	TORS (CCOC)
38	36	1.76	27	S76-79	TORS (CCOC)
26	25	1.11	702.23	K47-57	BEND (CCC)

3.3 Vibrational analysis

The goal of the vibrational analysis is to find vibrational modes connected with specific molecular structures of calculated compound. Vibrational frequencies were calculated by using RHF/6-31G* and B3LYP/6-31G*. Table 4 represents the calculated vibrational frequencies and assignments of Acetoxy-4-methyl Phenyl Methyl Acetate. The title compound with 30 atom gives (3N-6) i.e. 84 vibrational levels in the range 26-3224 cm^{-1} at B3LYP/6-31G* and 29-3399 cm^{-1} at HF/6-31G*. The assignments for these 84 vibrational levels have been proposed and show some structure spectra correlation. Out of these 84 vibrational modes 29 are stretching modes 28 are bending modes and 27 are torsional modes. These methods are proposed as a tool to be applied in the structural characterization of the acylal class of organic material. The frequency from 3224 to 3043 cm^{-1} is assigned as C-H

stretching. The frequency from 1870 to 1820 cm^{-1} is assigned as O-C stretching. The frequency from 1676 to 1636 cm^{-1} is assigned as C-C stretching and the other types of bending and torsional modes are shown in the Table 4. We have also calculated the potential energy distribution (PED) values by using Veda 4 software.

3.4 Frontier molecular orbital analysis

Molecular orbital's (HOMO and LUMO) are very important terms in quantum chemistry and their energy are very useful for physicists and chemists [7]. The HOMO represents an ability to loose an electron where as LUMO represents the ability to gain an electron. The energy of the HOMO is directly proportional to the ionization potential and the energy of the LUMO is directly proportional to the electron affinity [8]. The energy difference between the HOMO and LUMO orbital is called HOMO-LUMO gap

which explains the eventual charge transfer interaction within the molecule. The energy difference between HOMO and LUMO has been used to prove the bioactivity from intramolecular charge transfer [9, 10]. The plots of higher HOMOs and LUMOs are shown in the Figure 2.

HOMO energy (B3LYP) = -0.24489 a.u

LUMO energy (B3LYP) = -0.01799 a.u

HOMO-LUMO energy gap (B3LYP) = 0.2269 a.u

In case of electron volt the HOMO-LUMO energy gap is 6.17 eV.

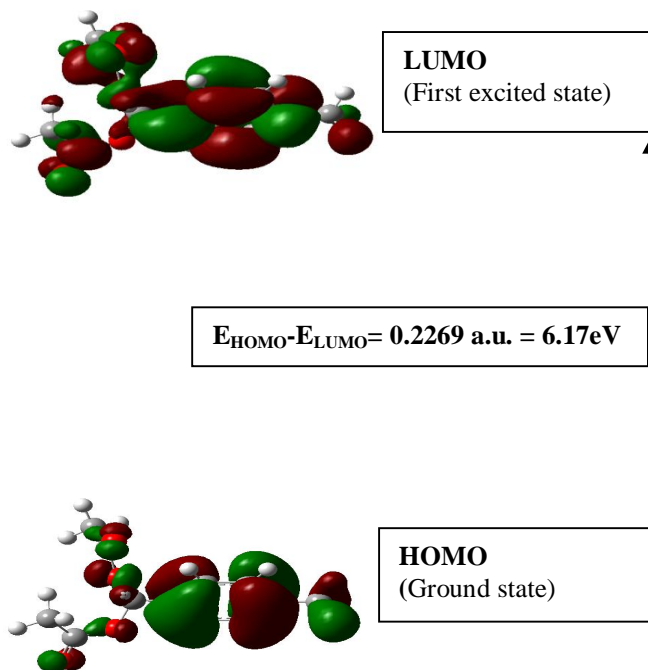


Fig. 2 Frontier molecular orbitals of Acetoxy-4-methyl Phenyl Methyl Acetate molecule

IV. CONCLUSION

The normal mode frequencies and corresponding vibrational assignment of title compound are examined theoretically using the Gaussian 09 package. We have calculated the geometric parameters and vibrational frequencies of title compound by using DFT and HF method with 6-31G (d) basis set. We have to multiply the data by 0.96 in case for DFT and 0.89 for HF. Multiplication factors results gained seemed to be in good agreement. However HF method seems to be more appropriate than DFT method for calculation of geometrical parameters of the title compound.

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