



Molecular Structure, Experimental and Theoretical Spectroscopic Studies and Quantum Chemical Calculation of Phenoxyacetic Acid and its p-chloro Derivative

ANJU SRIVASTAV^{1*}, SUBHA R. SAXENA², SUNIL MISHRA² and Y. SINGH¹

¹Department of Chemistry, Udai Pratap Autonomous College, Varanasi - 221 002, India.

²Department of Physics, A. K. A. P. G. College, Varanasi - 221 002, India.

*Corresponding author E-mail: srivastavanju10@gmail.com

(Received: July 20, 2012; Accepted: August 29, 2012)

ABSTRACT

The Fourier Transform Infrared spectra of crystallized phenoxyacetic acid and p-chloro derivative have been recorded in the region 4000-400 cm⁻¹. The geometry was calculated by Hartree-Fock (HF), Density Functional Theory (B3LYP) and Moller Plesset(MP2) Perturbation theory invoking 6-311++g(d,p) basis set. The harmonic vibrational frequency and, infrared intensities have been investigated with the help of B3LYP methods. The scaled theoretical wavenumbers showed very good agreement with the experimental values. The thermodynamic functions of the title compounds were also performed at B3LYP/6-311++g(d,p) level of theory. A detailed interpretation of the infrared spectra of Phenoxyacetic acid and p-chloro derivative of Phenoxy acetic acid have been reported.

Key words: Vibrational spectra, DFTcalculation, Moller Plesset Perturbation theory.

INTRODUCTION

Aryloxyacetic acid are interesting to study by various chemical and physical methods. Phenoxyacetic acid is one of the best known aryloxyacetic acid, which is useful in the treatment of insulin resistance and hyperglycemia which has been investigated by various researchers ¹⁻². Phenoxyacetic acid and substituted phenoxyacetic acids have potential biological properties. These acids are widely used in herbicides ³ and pesticide⁴ formulations. Recently phenoxyacetic acid invoke much interest among the spectroscopists owing to their novel bioactivity such as anticancer, antitumour; anti-inflammatory ⁵, antimicrobial, plant

growth regulator and inhibition of tillage etc ^{6,7}.

Vibrational spectroscopy is a valuable tool for the elucidation of molecular structure ⁸. It also provides important information about the intermolecular forces acting between the atoms in a molecule. The vibrational and rotational energies of molecules can be studied by IR and Raman spectroscopy ^{9,10}. The advent of fast computer along with sophisticated computational methods make the task of solving various structural chemical problem a simple. Ab initio DFT computations have recently become an efficient tool in the prediction of molecular structures, harmonic force fields, vibrational frequencies and IR spectral properties

of biological compounds^{11,14}. The calculation of vibrational frequency using DFT provides a promising cost effective approach for calculating vibrational spectra of large molecules. In the recent studies, the harmonic vibrational frequencies for a large number of small and well-studied organic molecules were computed with HF and DFT methods¹⁵⁻¹⁸.

Many researches have been done on the vibrational analysis of phenols¹⁹. However, for phenoxyacetic acid and p-chloro derivative of phenoxyacetic acid, such a kind of work are limited. Only IR spectral assignments and normal coordinate analysis has been carried out for some phenoxyacetic acid²⁰⁻²³. The molecular and crystal structure of phenoxyacetic acid and p-chloro phenoxy acetic acid were reported by Colin H.L.Kennard²⁴ and by Vijaykumar and Rao²⁵. Karthikeyan and Saravanan²⁶ reported tentative Raman spectral assignments of phenoxyacetic acid and chlorine substituted phenoxy acetic acid with the aid of ab initio calculation HF/3-21G(d) basis set, however some of its assignments was ambiguous. Ab initio HF and DFT calculation of p-chlorophenoxy acetic acid was done by N.Sunaraganeshan and B.Karthikeyan²⁷ but no MP2 calculation was done. For phenoxy acetic acid neither MP2 nor DFT calculation have been reported. Therefore, the present investigation was undertaken to study the vibrational spectra of phenoxyacetic acid and p-chloro derivative. MP2, ab initio HF and density functional theory calculations have been performed to predict molecular structure of phenoxyacetic acid and p-chloro derivative.

MATERIALS AND METHODS

Phenoxyacetic acid was prepared by using slightly modified method of Koelsch²⁸. The same procedure was followed for substituted phenoxy acetic acid i.e. p-chlorophenoxy acetic acid by using corresponding substituted phenols. Both the compounds i.e. phenoxyacetic acid and p-chloro derivative were recrystallized using water as a solvent.

Computational details

Gaussian 09 package was used for

calculating theoretical vibrational frequencies²⁹. Density functional theory³⁰ with the three-parameter hybrid functional (B3)³¹ for the exchange part and Lee-yang Parr [LYP] correlation function³² was used for the computation of molecular structure, vibrational frequency and energies of optimized structure. The atom numbering and the structure which was used for the input was given in Fig. 1. The bond lengths and bond angles were taken from the X-ray crystal studies³³⁻³⁵. This structure was optimized (Cs) point group using Hartree-Fock, B3LYP and MP2 levels, adopting the standard 6-311++g(d,p) basis set. Raw frequency values computed at B3LYP level contain known systematic error due to the neglect of electron correlation, resulting in overestimation of about 10-12%. Therefore, the obtained frequencies were scaled by an empirical factor 0.98²⁷.

RESULTS AND DISCUSSION

Optimized geometries

The optimized geometry of phenoxyacetic acid and p-chloro derivative are calculated by ab initio HF, DFT and MP2 levels with the 6-311++g(d,p) basis set. The molecular conformation and numbering are illustrated in Fig. 2. and bond lengths and angles for phenoxyacetic acid and p-chloro derivative are given in Table 1-2. Table 1-2. compares the calculated bond lengths and angles for phenoxyacetic acid and p-chloro derivative with those of experimentally available from X-ray data for phenoxy acetic acid (23) and p-chloro (24) derivative.

As there are three rotomers around C3-O12, O12-C13 and around C13-C16, the molecule can exist a variety of conformations. In all the computations the carbon atom skeleton of benzene moiety and oxyacetic acid both were found to be planar. A general observation from comparing the calculated and available X-ray structural parameter is that the most of HF bond lengths are slightly shorter than the experimental data. This may be the result of the neglect of electron correlation by HF theory.

As we can see most of the MP2 and B3LYP bond lengths and angles match with the experimental data, the best agreement between

calculated and experimental values is the MP2/6-311++g(d,p) bond lengths and angles.

The optimized bond length of C-C in phenyl ring fall in the range from 1.383 to 1.385 Å (HF), 1.395 to 1.397 Å (B3LYP) and 1.402 to 1.396 Å for phenoxy acetic acid. The same bond length fall in the range from 1.382 to 1.391 Å (HF), 1.396 to 1.397 Å (B3LYP) and 1.401 to 1.402 Å (MP2) for p-chloro derivative, which are in good agreement with those of experimentally reported values for C-C bond length of phenyl ring of similar molecules³⁶.

Vibrational spectral assignments

In the present study the vibrational assignments are based on the scaled B3LYP/6-311++G(d,p) frequencies, infrared intensities, as well as characteristic "group frequencies" from similar molecules. The 51 normal modes of

phenoxyacetic acid and p-chloro derivative of phenoxyacetic acid are distributed amongst the symmetry species at $\Gamma_{3N-6}=35A'$ (in plane)+ $16A''$ (out of plane) in agreement with Cs symmetry. The detailed vibrational assignment of fundamental modes of phenoxy acetic acid and p-chloro derivative of phenoxyacetic acid along with the experimental and calculated frequencies, IR intensities and normal mode description are reported in Table 3-4. For visual comparison the experimental and calculated FT-IR spectra of phenoxyacetic acid and p-chloro derivative of phenoxyacetic acid are presented in Fig. 1-2 respectively. Comparison of the frequency calculated at B3LYP with experimental value reveals the overestimation of the calculated vibrational modes due to neglect of anharmonicity in real system. It is customary to scale down the

Table 1: Geometrical Parameters for Phenoxyacetic acid

Parameters	HF/6-311++g(d,p)	B3LYP/6-311++g(d,p)	MP2/6-311++g(d,p)	Experimental
Bond length(Å°)				
C1C2	1.383	1.395	1.402	1.391
C2C3	1.384	1.397	1.400	1.389
C3C4	1.383	1.395	1.401	1.393
C4C5	1.385	1.395	1.394	1.381
C5C6	1.385	1.396	1.402	1.385
C6C1	1.385	1.396	1.396	1.377
C3O12	1.369	1.388	1.374	1.378
O12C13	1.386	1.407	1.404	1.421
C13C16	1.515	1.526	1.522	1.499
C16O17	1.178	1.206	1.204	1.266
C16O18	1.328	1.356	1.357	1.260
Bond angle(°)				
C1C2C3	119.6	119.4	119.2	118.9
C2C3C4	120.6	120.7	120.2	120.4
C3C4C5	119.2	119.3	119.9	119.4
C4C5C6	120.5	120.4	120.4	121.0
C5C6C1	119.6	119.7	119.3	119.1
C2C1C6	120.2	120.2	120.8	121.2
C2C3O12	119.6	120.3	124.5	124.4
C4C3O12	119.6	118.8	115.2	115.3
C3O12C13	117.8	116.5	116.4	115.6
O12C13C16	113.2	112.4	112.1	110.9
C13C16O17	126.6	126.5	125.8	121.1
C13C16O18	109.9	109.8	109.6	114.8
O17C16O18	123.3	123.5	124.4	124.1

calculated harmonic frequencies in order to improve the agreement with the experimental.

Vibrational spectral assignments

In the present study the vibrational assignments are based on the scaled B3LYP/6-311++G(d,p) frequencies, infrared intensities, as well as characteristic "group frequencies" from similar molecules. The 51 normal modes of phenoxy acetic acid and p-chloro derivative of phenoxy acetic acid are distributed amongst the symmetry species at $\Gamma_{3N-6}=35A'$ (in plane)+ $16A''$ (out of plane) in agreement with Cs symmetry. The detailed vibrational assignment of fundamental modes of phenoxyacetic acid and p-chloro derivative of phenoxyacetic acid along with the experimental and calculated frequencies, IR intensities and normal

mode description are reported in Table 3-4. For visual comparison the experimental and calculated FT-IR spectra of phenoxyacetic acid and p-chloro derivative of phenoxyacetic acid are presented in Fig. 1-2 respectively. Comparison of the frequency calculated at B3LYP with experimental value reveals the overestimation of the calculated vibrational modes due to neglect of anharmonicity in real system. It is customary to scale down the calculated harmonic frequencies in order to improve the agreement with the experimental.

Carboxylic acid vibrations

Vibrational assignments of -COOH group is significant because the herbicidal activity of the title compound is mainly due to either the presence of this moiety or a group that is easily converted to it

Table 2: Geometrical parameters for p-chloro derivative of phenoxyacetic acid

Parameters	HF/6-311++g(d,p)	B3LYP/6-311++g(d,p)	MP2/6-311++g(d,p)	Experimental
Bond length(A°)				
C1C2	1.382	1.396	1.401	1.39
C2C3	1.392	1.399	1.402	1.40
C3C4	1.376	1.386	1.397	1.39
C4C5	1.387	1.394	1.393	1.40
C5C6	1.373	1.386	1.393	1.39
C1C6	1.391	1.397	1.402	1.36
C2O11	1.350	1.368	1.369	1.34
O11C12	1.386	1.408	1.412	1.42
C12C15	1.512	1.517	1.513	1.46
C15O16	1.183	1.205	1.211	1.23
C15O17	1.314	1.340	1.343	1.33
Bond angles(°)				
C1C2C3	119.7	119.7	119.9	117.3
C2C3C4	120.3	120.3	120.3	119.8
C3C4C5	119.7	119.5	119.5	122.3
C2C1C6	119.7	119.8	119.6	120.8
C1C6C5	120.0	119.8	120.0	120.4
C1C2O11	124.6	125.7	124.8	126.2
C3C2O11	115.5	115.8	115.2	116.1
C4C5Cl19	119.6	119.6	119.6	—
C6C5Cl19	119.9	119.7	119.7	—
C2O11C12	119.7	118.3	116.3	117.3
O11C12C15	111.5	111.8	109.6	109.5
C12C15O16	120.8	121.5	123.1	126.1
C12C15O17	115.3	114.4	112.4	111.7
O16C15O17	123.7	124.0	124.3	122.9

Table 3: Vibrational assignment, calculated wavenumbers in cm⁻¹ with relative intensity of Phenoxyacetic acid at B3LYP/6-311++g (d, p).

Vib no.	Sym.	ν (cal.)	ν (scaled)	Rel. int.	ν (exp.)	Approximate description of vibration
1	A'	3764	3688	75.72	3498	O-H stretching
2	A'	3177	3113	1.90		C-H stretching
3	A'	3173	3109	13.79		C-H stretching
4	A'	3166	3102	20.24	3108	C-H stretching
5	A'	3152	3088	8.63		C-H stretching
6	A'	3144	3081	1.77	3028	C-H stretching
7	A'	3086	3024	7.41	3020	-CH ₂ asymmetric stretching
8	A'	3029	2968	24.07	2960	-CH ₂ symmetric stretching
9	A'	1808	1771	273.48	1752	C=O stretching
10	A'	1624	1591	61.29	1580	C=C stretching
11	A'	1609	1576	27.59	1564	C=C stretching
12	A'	1518	1487	87.10	1478	C=C stretching
13	A'	1485	1455	16.50		CH ₂ scissoring
14	A'	1477	1447	4.25	1442	-CH ₂ scissoring + C-C stretching
15	A''	1414	1385	15.78	1386	-CH ₂ wagging
16	A'	1354	1326	2.64	1334	C-H bending (in plane)
17	A'	1331	1304	27.76	1304	O-H bending (in plane)
18	A'	1311	1284	24.42		O-H bending (in plane) + C-C stretching
19	A'	1286	1260	44.60		O-H scissoring + C-H bending (in plane)
20	A'	1243	1218	135.23		O-H scissoring + C-C bending (in plane)
21	A'	1199	1175	13.22		C-H scissoring
22	A'	1176	1152	3.02		C-H bending (in plane)
23	A'	1140	1117	210.08		C-O stretching + O-H bending
24	A'	1107	1084	146.79	1098	C-H bending (in plane)
25	A'	1100	1078	101.21	1078	C-C stretching
26	A'	1044	1023	6.78	1034	O-C stretching
27	A'	1035	1014	5.06	982	C-C stretching (aromatic)
28	A'	1004	984	1.74		C-C stretching
29	A''	989	969	0.10		C-H bending (out of plane)
30	A''	973	953	0.10	950	C-H bending (out of plane)
31	A''	901	882	6.32	880	C-H twisting
32	A'	860	842	8.64	842	C-C stretching (aliphatic)
33	A'	836	819	0.56	804	C-C bending (in plane) (aromatic) + C-O stretching
34	A'	798	782	21.27	778	C-C bending (in plane) (aromatic)
35	A''	769	753	71.86	748	C-H bending (out of plane)
36	A''	706	691	14.53	682	C-C wagging
37	A''	677	663	24.02		O-H bending (out of plane)

38	A''	658	644	95.08		O-H wagging
39	A'	628	615	2.82		C-C bending (in plane) (aromatic)
40	A''	567	555	10.40	584	O-H bending (out of plane)
41	A''	529	518	22.63	558	O-H bending (out of plane)
42	A''	517	506	20.91		C-C bending (aromatic) + O-H wagging
43	A''	501	490	23.77		C-C bending (out of plane) + O-H wagging
44	A''	430	421	0.08		C-C bending (out of plane) (aromatic)
45	A'	368	360	1.84		C-O rocking
46	A'	308	301	0.52		C-O rocking
47	A'	279	273	2.35		C-O bending (in plane)
48	A''	204	199	0.30		O-CH ₂ bending (out of plane)
49	A''	107	104	1.50		C-O bending (out of plane)
50	A''	76	74	1.23		C-O twisting

Table 3: Vibrational assignment, calculated wavenumbers in cm⁻¹ with relative intensity of Phenoxyacetic acid at B3LYP/6-311++g (d, p).

Vib no.	Sym.	ν (cal.)	ν (scaled) of vibration	Rel. int.	ν (exp.)	Approximate description
1	A'	3739	3664	53.94	3478	O-H stretching
2	A'	3193	3129	6.30	3128	C-H stretching
3	A'	3187	3123	4.03		C-H stretching
4	A'	3175	3111	2.90		C-H stretching
5	A'	3173	3109	6.16		C-H stretching
6	A'	3068	3006	14.16		-CH ₂ asymmetric stretching
7	A'	2995	2935	28.09	2946	-CH ₂ symmetric stretching
8	A'	1790	1754	398.08	1742	C=O stretching
9	A'	1625	1592	23.39	1590	C=C stretching
10	A'	1600	1568	9.63	1572	C=C stretching
11	A'	1525	1494	142.30	1484	C=C stretching
12	A'	1501	1470	87.01	1464	-CH ₂ scissoring
13	A'	1434	1405	7.34		C-C stretching + -CH ₂ scissoring
14	A	1423	1394	33.13		C-C stretching + O-H stretching + CH ₂ wagging
15	A	1382	1354	38.77		C-C stretching + O-H bending + CH ₂ wagging
16	A'	1330	1303	3.70	1298	O-H bending (in plane)
17	A'	1300	1274	85.68		C-C stretching + O-H bending (in plane)
18	A'	1284	1258	21.24		O-H bending (in plane)
19	A'	1262	1236	243.50	1208	C-C stretching
20	A'	1201	1176	88.27	1184	C-H bending (in plane)

21	A'	1196	1172	179.89		C-O stretching
22	A'	1132	1109	14.31	1096	C-H bending (in plane)
23	A'	1116	1093	32.48	1080	C-H bending (in plane)
24	A'	1089	1067	81.22	1056	O-C stretching
25	A''	1048	1027	17.05	1020	-CH ₂ bending (out of plane)
26	A''	1023	1002	11.57	996	C-C bending (out of plane) (aromatic)
27	A''	963	943	0.31	938	C-H bending (out of plane)
28	A''	935	916	0.75		C-H bending (out of plane)
29	A'	899	881	18.76	862	C-C stretching (aliphatic)
30	A''	840	823	33.37		C-H bending (out of plane)
31	A'	828	811	33.70	806	C-C bending (in plane) (aromatic) + C-O stretching
32	A''	812	795	15.72	788	C-H bending (out of plane)
33	A''	723	708	79.74	704	O-H bend (out of plane)
34	A'	708	693	1.30		C-C bending (in plane) (aromatic)
35	A'	682	668	80.82	658	C-Cl stretching
36	A'	646	633	1.35		C-C bending (in plane) (aromatic)
37	A''	610	597	42.55	598	O-H bending (out of plane)
38	A''	563	551	48.72		O-H bending (out of plane)
39	A''	522	511	10.61		C-C bending (out of plane) (aromatic)
40	A''	485	475	8.51		-CH ₂ wagging
41	A'	454	444	8.20		C-C bending (in plane) (aromatic)
42	A''	431	422	0.06		C-C bending (out of plane) (aromatic)
43	A'	361	353	0.25	402	C-Cl bending (in plane)
44	A''	331	324	2.28		C-Cl bending (out of plane)
45	A''	269	263	0.01		C-O wagging
46	A'	210	205	0.55		O-C scissoring
47	A''	154	150	3.54		O-C bending (out of plane)
48	A''	109	101	0.82		C-Cl bending (out of plane)
49	A'	95	91	0.46		C-O scissoring
50	A'	72	68	1.56		O-H stretching
51	A'	52	50	0.21		Lattice vibration

within the plant tissue³⁷⁻³⁸. Vibrational analysis of carboxylic acid is made on the basis of carbonyl group and hydroxyl group both.

The -OH stretching band is characterised by very broad band appearing in the region 3700-3500 cm⁻¹. Accordingly, in the present study, the broad FT-IR bands at 3688cm⁻¹ has been assigned to -OH stretching vibration for phenoxyacetic acid and 3664cm⁻¹ for p-chloro derivative of

phenoxyacetic acid. However the calculated wavenumber shows positive deviation of ~190 cm⁻¹ for phenoxyacetic acid and 158cm⁻¹ for p-chloro derivative of phenoxyacetic acid may be due to presence of strong hydrogen bonding. Carbonyl absorption are sensitive and both the carbon and oxygen atoms of the carbonyl group move during the vibration and they have nearly equal amplitude. Normally carbonyl group vibrations³⁹⁻⁴⁰ occur with strong intensity in the region 1740-1660cm⁻¹.The

strong FT-IR bands at 1752cm^{-1} for phenoxyacetic acid and at 1742cm^{-1} for p-chloro derivative are assigned to C=O stretching vibrations. The theoretically computed values of 1771cm^{-1} for

phenoxyacetic acid and 1751cm^{-1} for p-chloro derivative respectively with strong intensity also coincides with experimental observation. The in-plane and out-of-plane bending vibrations have also

Table 5: Atomic charges in Phenoxyacetic acid and its p-chloro derivative at MP2/6-311++g(d,p) level

No	Atom	Atomic charges	No	Atom	Atomic charges
Phenoxyacetic acid			p-chloro derivative of Phenoxyacetic acid		
1	C	-0.099744	1	C	0.011929
2	C	0.479519	2	C	-0.588066
3	C	-0.316776	3	C	0.045844
4	C	-0.369413	4	C	-0.719014
5	C	-0.101998	5	C	0.463912
6	C	-0.489360	6	C	-0.120701
7	H	0.221575	7	H	0.211443
8	H	0.187684	8	H	0.253854
9	H	0.217280	9	H	0.233175
10	H	0.216691	10	H	0.240550
11	H	0.176201	11	O	-0.119089
12	O	-0.108336	12	C	-0.198560
13	C	-0.488658	13	H	0.204667
14	H	0.263425	14	H	0.212038
15	H	0.212952	15	C	-0.069570
16	C	0.166210	16	O	-0.360332
17	O	-0.291783	17	O	-0.238041
18	O	-0.196286	18	H	0.295696
19	H	0.320816	19	Cl	0.331953

Table 6: Theoretically computed energies (a.u.), zero point vibrational energies (Kcal mol⁻¹), rotational constant (GHz), entropies (cal mol⁻¹K⁻¹) and dipole moment (D) for phenoxyacetic acid and p-chloro derivative of Phenoxyacetic acid

Parameters	B3LYP/6-311++g(d,p)	
	Phenoxyacetic acid	p-chloroderivative of Phenoxyacetic acid
Total energy	-525.49394670	-997.11525128
Zero point energy	86.43366	92.52680
Rotational constants	3.48347	2.47945
	0.28471	0.68576
	0.26646	0.62056
Entropy		
Total	95.379	105.307
Translational	40.967	41.568
Rotational	30.100	31.476
Vibrational	24.312	32.263
Dipole moment	2.1420	1.1901

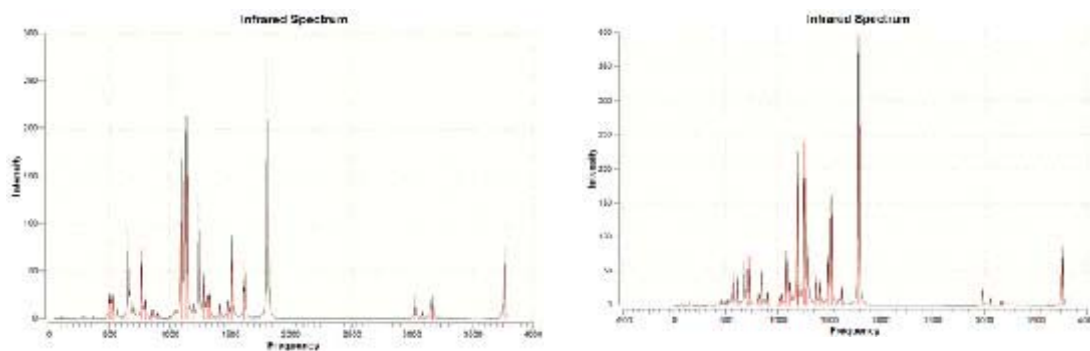


Fig. 1: Theoretical FT-IR spectrum of phenoxyacetic acid and p-chloro derivative



Fig. 2: Optimized structure of Phenoxyacetic acid

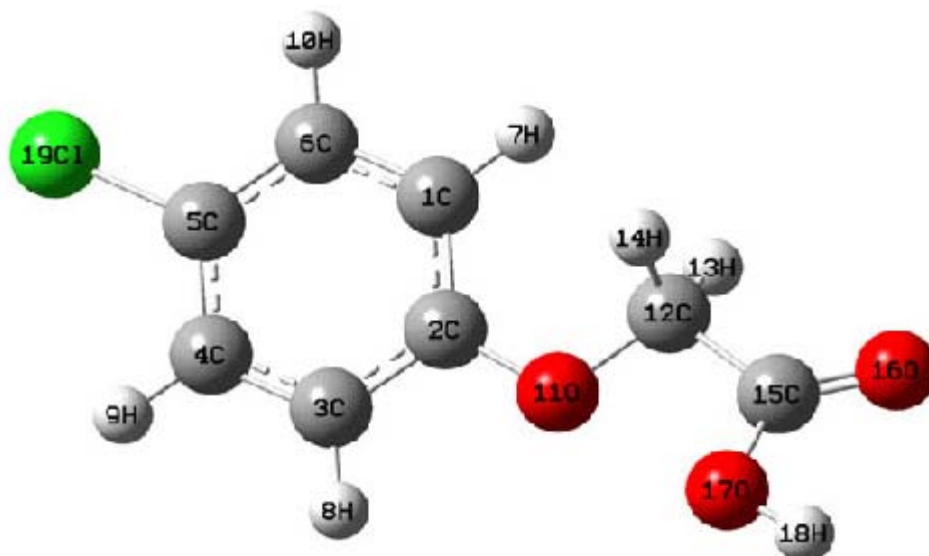


Fig. 3: Optimized structure of p-chloro derivative of Phenoxyacetic acid

been identified and presented in Table 3-4 for the title compound. The calculated IR bands at 1304, 1284, 1260, 1218 cm^{-1} for phenoxyacetic acid and at 1354, 1303, 1274, 1258 cm^{-1} for p-chloro derivative have substantial –OH bending character with enhanced intensities resulting from intermolecular hydrogen bonding interactions. The calculated low frequency bands below 400cm^{-1} are out of range in the measured spectra.

C-C vibrations

The C-C aromatic stretch known as semicircle stretching predicted at 1591, 1576, 1487 cm^{-1} for phenoxyacetic acid and 1592, 1568, 1494 cm^{-1} for p-chloro derivative were in excellent agreement with experimentally observed FT-IR values at 1580, 1564, 1478 cm^{-1} and 1590, 1572, 1484 cm^{-1} for phenoxyacetic acid and p-chloro derivative of phenoxyacetic acid respectively. The

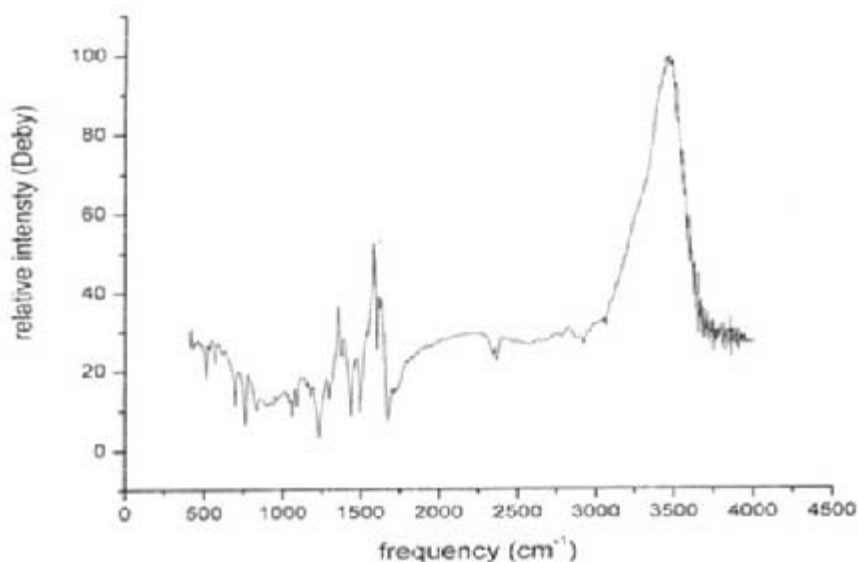


Fig. 4: Experimental FT-IR spectra of Phenoxyacetic acid

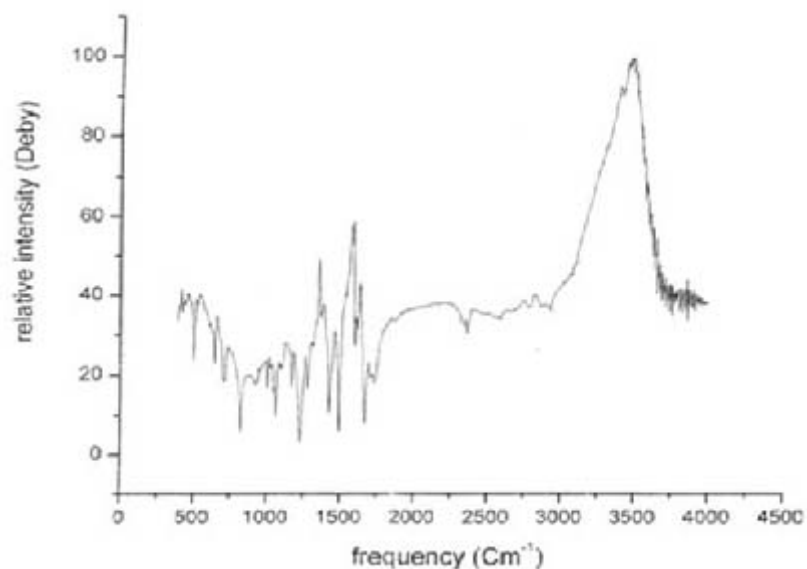


Fig. 5: Experimental FT-IR spectra of p-chloro derivative of Phenoxyacetic acid

C-C-C in plane bending modes are attributed to 782 and 615 cm^{-1} for phenoxyacetic acid and 824 and 633 cm^{-1} for p-chloro derivative respectively. The C-C-C out of plane bending vibrations for phenoxyacetic acid are attributed to 506 and 421 cm^{-1} . The same vibration for p-chloro derivative of phenoxyacetic acid are observed at 511 and 422 cm^{-1} .

C-H vibration

The region 3100-3000 cm^{-1} is the characteristic region for the ready identification of C-H stretching vibrations⁴¹. In this region, the bands are not affected appreciably by the nature of substituents. There is a broad absorption band in the region 2500-3000 cm^{-1} upon which the C-H stretching frequencies are superimposed. Hence the FT-IR bands at 3028 cm^{-1} for phenoxyacetic acid and 3046 cm^{-1} for p-chloro derivative have been designated to C-H stretching vibrations. The C-H in plane bending vibrations assigned at 1023-1084 cm^{-1} even though found to be contaminated by CH₂ deformation vibrations are found in literature 38-39, while the experimental observations are at 1098 cm^{-1} for phenoxyacetic acid and 1096 cm^{-1} for p-chloro derivative. The calculated frequencies at 753-969 cm^{-1} in phenoxyacetic acid and 795-943 cm^{-1} in p-chloro derivative for the C-H out of plane bending mode correlates well with the recorded FT-IR values of 748-950 cm^{-1} in phenoxyacetic acid and 790-934 cm^{-1} in p-chloro derivative.

OCH₂ vibrations

For the assignments of CH₂ group frequencies, basically six fundamentals can be associated to each CH₂ group, namely, CH₂: symmetric stretching; CH₂: asymmetric stretching; CH₂: scissoring and CH₂: rocking which belong to in plane (A') species vibrations. In addition to that CH₂ wagging and CH₂ twisting modes of the CH₂ group would be expected to be depolarized for out of plane (A'') symmetry species.

A major coincidence of theoretical values with that of experimental evaluation is found in the symmetric and asymmetric stretching vibrations of methylene moiety. The antisymmetric CH₂ stretching vibrations are generally observed in the region 3000-2900 cm^{-1} while the symmetric stretching will appear between 2900 and 2850 cm^{-1} ⁴². The CH₂ antisymmetric stretching vibrations was observed

in IR spectra at 3020 cm^{-1} in phenoxy acetic acid and 3010 cm^{-1} in p-chloro derivative respectively. The symmetric stretching vibration was also identified in IR at 2960 cm^{-1} in phenoxy acetic acid and 2946 cm^{-1} in p-chloro derivative respectively. The theoretically computed values of CH₂ asymmetric and symmetric stretching vibration correlates with experimental observations. The deformation vibrations of -CH₂- group (scissoring, rocking, wagging, twisting) contribute to several normal modes in low frequency region. It follows from table 3 and 4 that the FT-IR band observed at 1442 cm^{-1} in phenoxyacetic acid and 1464 cm^{-1} in p-chloro derivative, respectively are assigned to CH₂ scissoring vibration. The scaled CH₂ scissoring vibrations are at 1447 cm^{-1} in phenoxyacetic acid and 1470 cm^{-1} in p-chloro derivative. The wagging and rocking modes are distributed wide range. The assignments of these bands are also shown in Table 3-4. The O-C stretching mode of paraffinic moiety is identified as medium FT-IR band at 1034 cm^{-1} in phenoxyacetic acid. The same vibration in p-chloro derivative of phenoxyacetic acid is at 1056 cm^{-1} in FT-IR. The calculated values are at 1023 and 1067 cm^{-1} shows agreement with experimental observations.

C-Cl vibrations

The vibrations belonging to the bond between the ring and the halogen atoms are worth to discuss here, since mixing of several vibrations are possible due to the lowering of the molecular symmetry and the presence of heavy atoms on the periphery of the molecule⁴³.

The assignment of C-Cl stretching and deformation vibrations have been made by comparison with similar molecules, p-bromophenol⁴² and halogen substituted benzene derivatives⁴³. The C-Cl stretching vibration of substituted phenoxyacetic acids were observed around at 720 cm^{-1} ¹⁹. The FT-IR band at 658 cm^{-1} in p-chloro derivative of phenoxyacetic acid assigned to C-Cl stretching vibration. The theoretical wavenumber of C-Cl stretching vibration at 668 cm^{-1} coincide very well with experimental values. The C-Cl in plane bending and out of plane bending vibration are assigned at 355 cm^{-1} and 324 cm^{-1} . These assignments are in agreement with literature data⁴⁴⁻⁴⁸.

CONCLUSION

We have carried out density and ab initio calculations on the structure and vibrational spectrum of phenoxyacetic acid and p-chloro derivative. Comparison between the calculated and experimental structural parameters indicate that MP2 method is in good agreement with experimental ones. Vibrational frequencies and infrared intensities calculated by B3LYP/6-311++G(d,p) method agree very well with experimental results.

On the basis of agreement between the calculated and observed results, assignments of fundamental vibrational modes of phenoxyacetic acid and p-chloro derivative were examined. The assignments made higher basis set with only reasonable deviations from the experimental values, seems to be correct. This study demonstrate that scaled DFT/ B3LYP calculations are powerful approach for understanding the vibrational spectra of medium sized organic compound.

REFERENCES

- R. Gurumurthy, K. Sathyanarayana, M. Gopalakrishnan, *Bull. Chem. Soc., Jpn.*, **65**: 1096 (1992).
- B. Karthikeyan, R. Gurumurthy, M. Gopalakrishnan, M. Selvaraju, *Asian Chem. Lett.* **2-3**: 97 (1998).
- T. Csrhati, E. Forgacs, J.Chromatogr. B: Biomed, *Sci. Appl.*, **717**(1-2): 157 (1998).
- A. S. Crafts, *Adv. Pest Control Res.*, **1**: 39 (1957).
- S. Sarac, C. Safak, H. Erdogan, U. Abbasoglu, Y. Gunay, *Eczacilik Fak. Derg.* **11**(1): 1 (1991).
- M. Negwar, *Organic Chemical Drugs and their Synonyms*, Academic Verlag, Berlin., 1996.
- H. Marlin, *The Scientific Principles of Crop Protection*, Arnold, London, 1973.
- E.B. Wilson, J.C. Decius, P.C. Cross, *Molecular Vibration*, Mc. Graw Hill, Newyork, 1955.
- G. M .Barrow, *Introduction to Molecular Spectroscopy*, Mc-Graw Hill Book Co., Tokyo (1962).
- C. N .Banwell and E.M. Mc. Cash, *Fundamentals of Molecular Spectroscopy*, Tata Mc Graw. Hill, Publication Co, Ltd. New Delhi, Sixth reprint (1999).
- J. Bina, C. James, I. Hubert, Joe, V. S .Jayakumar, *J. Mol. Struct.* , **32**: 784 (2006).
- C. James, A .Amal Raj, R. Raghunathan, V.S. Jayakumar, I. Hubert Joe, *J. Raman Spectroscopy*, **37**: 1381 (2006).
- C. Y. Panicker, Hema Tera Varghere and Asha Chandran., *Orient. J. Cehm.*, **27**(4): 1771-1774 (2011).
- Sheena Mary Y., S. Suprabhan, H. T. Vargeher and C.Y. Panicker, *Orient. J. Chem.*, **27**(1):215-220 (2011).
- R. F. Liu, R. T. Dennis, A. C. Jeffery, R. M. Paula, *J. Phys. Chem.*, **100**: 3430 (1996).
- X. F. Zhou, R. F. Liu, *Spectrochim Acta.*, **53A**: 259 (1997).
- O. Nwobi, J. Higgins, X. F. Zhou, R. F. Liu, *Chem. Phys. , Lett.*, **272**: 155 (1997).
- Z. Y. Zhou, D. M. Du, A. P. Fu, *Vibr. Spectro.*, **23**: 1951 (2000).
- O. Tichcheno, E. S. Kryachko, M. T. Nguven, *Spectrochim, Acta A.*, **58**: 1951 (2002).
- V. Ashok Babu, G. Ramana Rao, *Ind. J. Pure Applied Phys.*, **25**: 203 (1987).
- V. Ashok Babu, G. Ramana Rao, *Ind. J. Pure Applied Phys.*, **25**: 209 (1987).
- V. Ashok Babu, G. Ramana Rao, *Ind. J. Pure Applied Phys.*, **25**: 216 (1987).
- V. Ashok Babu, G. Ramana Rao, *Ind. J. Pure Applied Phys.*, **28**: 1 (1990).
- Colin H. L. Kennard, Graham Smith, Allan H. White, *Acta Cryst B.*, **38**: 868-875 (1982).
- S. Vijaykumar, L. M. Rao, *Acta Crystallogr B.*, **38**: 2062 (1982).
- B. Karthikeyan, B. Saravanan, *Spectrochim Acta A.*, **63**(3): 619 (2006).
- N .Sundaraganeshan, C. Meghanathan, B.Karthikeyan, *Spectrochim Acta Part A.*, **70**: 430-438 (2008).
- C. F. Koelsch, *J. Am. Chem. Soc.*, **53**: 304 (1931).
- Gaussian 09, Revision A.02, M.J. Frisch, G.W.

- Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian, Inc., Wallingford, CT, (2009).
30. P. Hohenberg, W. Kohn, *Phys. Rev.*, **136**: B 864 (1964).
31. D. Becke, *J. Chem. Phys.*, **98**: 5648 (1993).
32. C. Lee, W. Yang, R. G. Parr, *Phys. Rev.*, **B37**: 785 (1988).
33. K. Chandrasekar, P. Vasantha, *Acta Cryst.*, **B33**: 1257 (1977).
34. C. H. L. Kennard, G. Smith, *Acta Cryst.*, **B37**: 1454 (1981).
35. S. V. Kumar, L. M. Rao, *Acta Cryst.*, **B38**: 2062 (1982).
36. M. Kurt, M. Yurdakul, S. Yurdakul, *J. Mol. Structure (Thiochem)*, **711**: 25 (2004).
37. R. Cremlyn, *Pesticides*, Wiley, New York, (1979).
38. G. S. Gruzdyev, V. A. Zinchenko, V. A. Kalinin, R. I. Slotvsov, *The Chemical Protection of Plants*, Mir. Pub. , Moscow, (1983).
39. R. L. Peesole, L. D. Shields, I. C. Cairns, M. C. Willam, *Modern methods of chemical analysis*, Wiley, New York, (1976).
40. T. Chithambarathanu, V. Umayourbagan, V. Krishnakumar, *Ind. J. Pure Appl. Phys.*, **40**: 72 (2002).
41. G. Varsanyi, *Assignments for Vibrational Spectra of Seven Hundred Benzene derivatives*, vols and *Academic Kiaclo, Budapest*. (1973).
42. V. Krishnakumar, R. John Xavier, T. Chithambarathanu, *Spectrochim Acta.*, **62A**: 931 (2005).
43. M. Bakiler, I. V. Maslov, S. Akyuz, *J. Mol. Structure.*, **475**: 83 (1999).
44. W. Zierkiewicz, D. Michalska, Th Zeegers-Huyskens, *J. Phys. Chem.*, **104A**: 11685 (2000).
45. G. Varsanyi, *Assignments for Vibrational Spectra of Seven Hundred Benzene derivatives*, vols and Adam Hilger, (1974).
46. E. F. Mooney, *Spectrochim Acta*, **20**: 1021 (1964).
47. E. F. Mooney, *Spectrochim Acta*, **19**: 877 (1963).
48. M. Alcolea, Palafox, *Int. J. Quantum Chem.*, **77**: 661 (2000).