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Vibrational Spectroscopic Studies and NBO Calculations of 3-Hydroxy Benzylidyne Trifluoride

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ABSTRACT

The FT-IR and FT-Raman spectra of 3-hydroxy benzylidyne trifluoride(3HBT)have been recorded in the range of 4000–400 cm^{-1} and 3500–50 cm^{-1} respectively. The molecular geometry and vibrational frequencies in the ground state are calculated using the B3LYP method with 6-311+G(d, p) and 6-311++G (d, p) basis sets. The computed values of frequencies are scaled using a suitable scale factor to yield good coherence with the observed values. Most of the modes have wave numbers in the expected range. The calculated HOMO–LUMO energy gap shows that charge transfer occur within the molecule. NBO analysis has been performed in order to elucidate charge transfers or conjugative interaction, the intra-molecule hybridization and delocalization of electron density within the molecule. The total energy distribution (TED) has also been calculated for each mode of the vibration of the molecule.

1. Introduction

The benzylidyne and its derivatives are of great interest in biological activity and widely used as a parent compound to make drugs. The sample 3-Hydroxy benzylidyne Trifluoride (3HBT) is a clear liquid with aromatic odour. Its melting point is –29°C and boiling point is 102°C [1]. It is also known as trifluoromethyl benzene and benzylidyne trifluoride (or benzotrifluoride). It is a raw material for the synthesis of some pharmaceuticals and present invention to simulate insulin and used as a therapeutic agent [2,3]. It is also used as an intermediate in the preparation of chemical products [4]. It is used as an intermediate for dyes, vulcanizing agent and insecticide and other organic compounds in dielectric fluids, such as transformer oils. Similarly, fluorinated compounds are widely used in industries as heat transfer fluids, chemical intermediates and polymers etc. Therefore, the study of fluorinated compounds is of considerable importance. Due to highest electro-negativity of fluorine atom, fluorinated compounds show entirely different physical and chemical properties compared to the other halogenated compounds. As the vibrational modes of molecules are closely related to its geometrical and electronic structures, the vibrational spectra provide considerable information regarding the physical and chemical properties of the molecules [5].

The literature survey reveals that no theoretical calculations or detailed vibrational infrared and Raman analysis have been performed on 3-Hydroxy Benzylidyne Trifluoride (3HBT) molecule so far. So, in the present investigation, the vibrational wave numbers, geometrical parameters, NBO and HOMO–LUMO analysis of within the molecule. Have been performed using density functional theory (DFT) based on the calculated and vibrational spectral analysis.

2. Experimental Details

The pure compound 3-Hydroxy benzylidyne triflouride (3HBT) was purchased from Lancaster chemical company, U.K. and used as such without any further purification. The room temperature Fourier transform infrared (FT-IR) spectrum of 3HBT is recorded in the range of 4000–400 cm^{-1} at a resolution of ± 1 cm^{-1} using a BRUKER IFS 66V FT-IR spectrophotometer equipped with a cooled MCT detector. Boxcar apodization is used for the 250 averaged interferograms collected for both the samples and background. The FT-Raman spectrum is recorded on a computer interfaced BRUKER IFS model interferometer, equipped with FRA 106 FT-Raman accessories in the 3500–50 cm^{-1} Stokes region, using the 1064 nm line of Nd:YAG laser for excitation operating at 200 mW power. The reported wave numbers are believed to be accurate within ± 1 cm^{-1}.

3. QUANTUM CHEMICAL CALCULATIONS

Density functional theory calculations are carried out for 3HBT using GAUSSIAN 09W program package [6]. Geometry is optimized at DFT level employing the B3LYP keyword, which invokes Becke’s three-parameter hybrid method [7] using the correlation function of Lee *et. al.*, [8], implemented with 6-31+G(d) and 6-31++G(d) basis sets for better description of the bonding properties of amino group. All the parameters are allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true minimum, as revealed by the lack of imaginary values in the wave number calculations. The multiple scaling of the force constants are performed according to SQM procedure [9] using selective scaling in the natural internal coordinate representation [10].

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Table 1.Optimized geometrical parameters of 3-hydroxy benzylidyne trifluoride by B3LYP/6-31+G(d,p) and B3LYP/ 6-31++G(d,p) methods.

Bond Length	**Value (Å)**		**Bond Angle**	**Value (°)**		**Diheadral Angle**	**Value (°)**	
	B3LYP/ 6-31+G(d,p)	**B3LYP/ 6-31++G(d,p)**		**B3LYP/ 6-31+G(d,p)**	**B3LYP/ 6-31++G(d,p)**		**B3LYP/ 6-31+G(d,p)**	**B3LYP/ 6-31++G(d,p)**
C1-C2	1.3914	1.3994	C2-C1-C6	121.135	120.8959	C6-C1-C2-C3	0.2108	-0.0711
C1-C6	1.383	1.3964	C2-C1-C7	118.5287	119.0243	C6-C1-C2-H11	179.6631	-179.719
C1-C7	1.4914	1.5062	C6-C1-C7	120.2808	120.0296	C7-C1-C2-C3	177.507	-177.4958
C2-C3	1.3818	1.397	C1-C2-C3	119.0604	119.4121	C7-C1-C2-H11	-3.0407	2.8563
C2-H11	1.0732	1.0871	C1-C2-H11	120.2818	120.1648	C2-C1-C6-C5	-0.2607	0.1196
C3-C4	1.3888	1.4002	C3-C2-H11	120.6556	120.4222	C2-C1-C6-H16	-179.7903	179.7617
C3-O12	1.3742	1.3683	C2-C3-C4	120.6429	120.2556	C7-C1-C6-C5	-177.5099	177.5185
C4-C5	1.3823	1.3929	C2-C3-O12	122.7189	122.5704	C7-C1-C6-H16	2.9606	-2.8393
C4-H14	1.0711	1.0857	C4-C3-O12	116.638	117.1738	C2-C1-C7-F8	38.9868	-154.984
C5-C6	1.3923	1.3985	C3-C4-C5	119.6088	119.5925	C2-C1-C7-F9	-79.9777	85.232
C5-H15	1.0721	1.0864	C3-C4-H14	118.7424	118.9775	C2-C1-C7-F10	160.0443	-34.108
C6-H16	1.0708	1.0844	C5-C4-H14	121.6486	121.4298	C6-C1-C7-F8	-143.6932	27.5685
C7-F8	1.37	1.3546	C4-C5-C6	120.6243	120.9001	C6-C1-C7-F9	97.3424	-92.2156
C7-F9	1.3745	1.3624	C4-C5-H15	119.7112	119.4623	C6-C1-C7-F10	-22.6356	148.4444
C7-F10	1.365	1.3583	C6-C5-H15	119.6645	119.6375	C1-C2-C3-C4	-0.0762	0.0094
O12-H13	0.95	0.9701	C1-C6-C5	118.9281	118.9436	C1-C2-C3-1C2	179.7687	-179.8054
			C1-C6-H16	120.5945	120.4046	H11-C2-C3-C4	-179.5264	179.6563
			C5-C6-H16	120.4757	120.6508	H11-C2-C3-1C2	0.3185	-0.1585
			C1-C7-F8	112.4987	112.4613	C2-C3-C4-C5	-0.0031	0.0018
			C1-C7-F9	112.2322	111.7845	C2-C3-C4-H14	179.877	-179.8398
			C1-C7-F10	112.9267	112.3134	O12-C3-C4-C5	-179.8571	179.8264
			F8-C7-F9	105.6263	106.5277	O12-C3-C4-H14	0.023	-0.0152
			F8-C7-F10	106.8528	107.0785	C2-C3-O12-H13	0.2627	-0.2263
			F9-C7-F10	106.1762	106.2618	C4-C3-O12-H13	-179.8866	179.9536
			C3-O12-H13	115.9452	110.2953	C3-C4-C5-C6	-0.0483	0.0483
						C3-C4-C5-H15	179.8874	-179.8221
						H14-C4-C5-C6	-179.9249	179.8859
						H14-C4-C5-H15	0.0108	0.0155
						C4-C5-C6-C1	0.1782	-0.1081
						C4-C5-C6-H16	179.7083	-179.7493
						H15-C5-C6-C1	-179.7575	179.762
						H15-C5-C6-H16	-0.2274	0.1208

Transformation of force field, the subsequent normal coordinate analysis including the least square refinement of the scale factors and calculation of the total energy distribution (TED) are done on a PC with the MOLVIB program (version V7.0 - G77) written by Sundius [11,12]. The systematic comparison of the results from DFT theory with results of experiments has shown that the method using B3LYP functional is the most promising in providing correct vibrational wave numbers. Normal coordinate analysis was carried out for 3HBT to provide a complete assignment of fundamental frequencies.

4. Results and Discussion

4.1. Molecular Geometry

The optimized molecular structure of 3HBT along with numbering of atoms is shown in Fig. 1. Detailed description of vibrational modes of 3HBT can be given by means of normal coordinate analysis. The optimized structure parameters of 3HBT obtained by DFT-B3LYP/6-31+G(d,p) and DFT-B3LYP/6-31++G(d,p) levels are listed in Table 1. For this purpose, the full set of 55 standard internal coordinates (containing 13 redundancies) is presented in Table 2. From these, a non-redundant set of local symmetry coordinates are constructed by suitable linear combinations of internal coordinates following the recommendations of Fogarasi *et. al.*, [13,10] and they are summarized in Table 3. The detailed vibrational assignment of fundamental modes of 3HBT along with normal mode descriptions (characterized by TED) is reported in Table 4.

From the structural data given in Table .1, it is observed that the various bond lengths are found to be almost same at DFT-B3LYP/6-31+G(d,p) and DFT-B3LYP/6-31++G(d) levels of theory. The global minimum energy obtained by DFT with 6-31+G(d) and 6-31++G(d,p) methods of structure optimization is found to be –644.5406 a.u. and –40.977 a.u. The geometrical optimization study of 3HBT reveals that the molecule belongs to C1 symmetry and it has 42 fundamental modes of vibrations. The observed FT-IR and FT-Raman spectra are shown in Figs.4.2 and 4.3, respectively.

Trifluoride Group

Usually symmetric and antisymmetric CF_3 stretching vibrations are in the ranges 1270–1235 and 1226–1200 cm^{-1} respectively [14,15]. Therefore the bands located at 1221 cm^{-1} in FT-Raman spectrum and 1197 cm^{-1} in FT-IR spectrum are assigned to symmetric and anti symmetric stretching vibrations. They were also supported by the literature [16]. C–F deformation vibrations usually occur in the regions 690–631 cm^{-1}, 640–580 cm^{-1} and 590–490 cm^{-1}, match well with the literature [15].

Accordingly CF_3sb, CF_3ipb and CF3opb are identified at 696, 513 cm^{-1} in FT-IR spectrum and 461 cm^{-1} in FT-Raman spectrum, respectively.

Table 2. Definition of internal co-ordinates of 3-hydroxy benzylidyne trifluoride.

Number	Symbol	Type	Definition
Stretching			
1-7	a_i	C – C	C1-C2, C2-C3, C3-C4, C4-C5, C5-C6, C6-C1, C1-C7
8-11	b_i	C –H	C2-H11, C4-H14, C5-H15, C6-H16
12	c_i	C –O	C3-O12
13	d_i	O –H	O12-H13
14-16	e_i	C – F	C7-F8, C7-F9, C7-F10
In-plane bending			
17-22	β_i	Ring	C1-C2-C3, C2-C3-C4, C3-C4-C5 C4-C5-C6, C5-C6-C1, C6-C1-C2
23-30	δ_i	βCH	C1-C2-H11, C3-C2-H11, C3-C4-H14, C5-C4-H14, C4-C5-H15, C6-C5-H15, C5-C6-H16, C1-C6-H16
31-32	δ_i	βCO	C2-C3-O12, C4-C3-O12
33-34	δ_i	βCC	C2-C1-C7, C6-C1-C7
35-37	ρ_i	βFCC	C1-C7-F8, C1-C7-F9, C1-C7-F10
38-40	Σi	βFCF	F8-C7-F10, F8-C7-F9, F9-C7-F10
41	θ_i	βCOH	C3-O12-H13
Out-of-plane bending			
42-45	Ωi	gCH	H11-C2-C1-C3, H14-C4-C3-C5, H15-C5-C4-C6, H16-C6-C1-C5
46	Ωi	gCO	O12-C3-C2-C4
47	Ωi	gCC	C7-C1-C2-C6
Torsion			
48-53	τ i	t ring	C1-C2-C3-C4, C2-C3-C4-C5, C3-C4-C5-C6, C4-C5-C6-C1, C5-C6-C1-C2, C6-C1-C2-C3
54	τ i	tCF_3	(C2,C6)-C1-C7-(F8,F9,F10)
55	T	tOH	H13-O12-C3-(C2,C4)

[a]For numbering of atoms refer Fig.1.

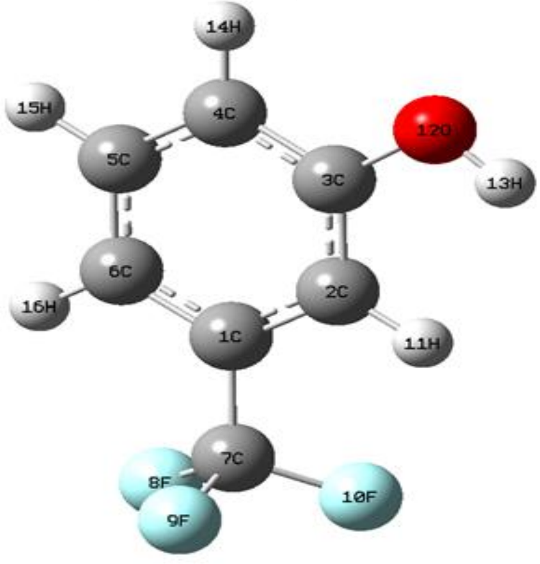

Fig 1. Molecular structure of 3-hydroxy benzylidyne trifluoride.

CF_3 rocking vibrational frequency ranges are 450–350 cm^{-1} and 350–260 cm^{-1} [16,15]. The bands located at 306 and 326 cm^{-1} in FT-Raman spectrum are assigned to rocking modes of the CF_3 group called CF_3 ipr and CF_3 opr, respectively.

C–H Vibrations

The heteroaromatic structure shows the presence of C–H stretching vibration in the region 3100–3000 cm^{-1} [17]. This is the characteristic region for the ready identification of C–H stretching vibration. In this region, the bands are not affected appreciably by the nature of the substitutions. In the present investigation, the C–H vibrations are observed at 3361, 3092 cm^{-1} in the FT-Raman spectrum and at 3076, 3054 cm^{-1} in the FT-IR spectrum for 3HBT. The C–H in-plane and out-of-plane bending vibrations of the 3HBT have been identified and listed in Table 4

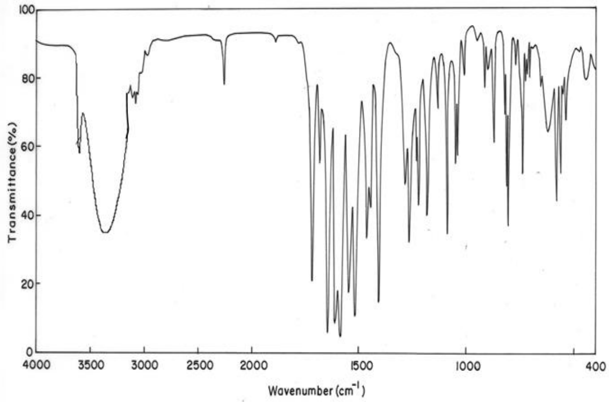

Fig 2. FT-IR spectrum of 3-hydroxy benzylidyne trifluoride.

Table 3. Definition of local symmetry co-ordinates of 3-hydroxy benzylidine trifluoride.

No	Symbol	Definition
1-7	C-C	a1, a2, a3, a4, a5, a6, a7
8-11	C-H	b8, b9, b10, b11
12	C-O	c12
13	O-H	d13
14	CF3 ss	(e14+e15+e16)/ $\sqrt{3}$
15	CF3ips	(-e14-e15+2e16)/ $\sqrt{6}$
16	CF3ops	(e15-e14)/ $\sqrt{2}$
17	Rtrigd	(β17- β 18+ β 19- β 20+ β 21 – β 22)/ $\sqrt{6}$
18	Rsymd	(-β 17- β 18+2 β 19- β 20- β 21+ β 22)/ $\sqrt{12}$
19	Rasymd	(β 17- β 18+ β 20- β21)/2
20-23	bCH	(δ23-δ24)/ $\sqrt{2}$, (δ25-δ26)/ $\sqrt{2}$ (δ27-δ28)/ $\sqrt{2}$, (δ29-δ30)/ $\sqrt{2}$
24	bCO	(δ31-δ32)/ $\sqrt{2}$
25	bCC	(δ33-δ34)/ $\sqrt{2}$
26	CF3 sb	(-ρ35 - ρ36 - ρ37 + σ38 + σ39 + σ40)/ $\sqrt{6}$
27	CF3 ipb	(2Σ38 - Σ39 - Σ40)/ $\sqrt{6}$
28	CF3opb	(-Σ39 + Σ40)/ $\sqrt{2}$
29	CF3 ipr	(-ρ35 - ρ36 - 2ρ37)/ $\sqrt{6}$
30	CF3 opr	(-ρ35 + ρ36)/ $\sqrt{2}$
31	bCOH	θ41
32-35	ωCH	Ω42, Ω43, Ω44, Ω45
36	ωCO	Ω46
37	ωCC	Ω47
38	t ring	(τ48-τ 49+ τ50- τ51+τ 52-τ53)/ $\sqrt{6}$
39	t symd	(τ48- τ50+τ 51- τ53)/2
40	t asymd	(-τ48+2τ 49-τ 50-τ 51+2τ (52- 53)/ $\sqrt{2}$
41	tCF3	τ54
42	tOH	τ55

[a] These symbols are used for description of normal modes by TED in Table 4.

[b] The internal coordinates used here are defined in Table 2.

Table 4. Vibrational assignments of fundamental modes of 3-hydroxy benzylidyne trifluoride along with calculated frequencies and normal mode descriptions (characterized by TED) based on quantum mechanical force field calculations using B3LYP method.

Modes	Symmetry Species	Observed fundamentals (cm^{-1})		Calculated fundamentals (cm^{-1})				Assignments with TED %
				B3LYP/6-31+G(d,p)		B3LYP/6-31++G(d,p)		
		FT-IR	FT-Raman	Unscaled	Scaled	Unscaled	Scaled	
1	A	3680(m)	---	3752	3672	3759	3689	γ OH(100)
2	A	---	3361(s)	3231	3349	3281	3349	γCH(90) tsymd(10)
3	A	---	3092(m)	3219	3103	3269	3081	γCH(92) CF3ips(8)
4	A	3076(vw)	---	3199	3085	3244	3065	γ CH(89) γCO(11)
5	A	3054(vw)	---	3193	3065	3242	3065	γ CH(87) tring (13)
6	A	1651(w)	---	1660	1657	1779	1672	γ C=C(72)β OH(10)
7	A	1620(vs)	---	1656	1629	1772	1629	γ CC(64) B CCC(19) β CH(7)
8	A	---	1611(w)	1550	1621	1680	1623	γ C=C(66) β OH(24)
9	A	1591(w)	---	1494	1578	1608	1599	γ CC(77) β CH (15)
10	A	---	1572(vw)	1376	1558	1517	1561	γ CC(81) γ CO(12) β CH(9)
11	A	1535(w)	---	1359	1243	1463	1523	γ CC(69) γ CO(16)
12	A	1497(vs)	---	1344	1488	1424	1484	γ CC(34) Rasym(13) BCH(8)
13	A	---	1438(w)	1266	1429	1357	1445	γ CO (53) β CH (27) γ CC (18)
14	A	1265(w)	---	1204	1254	1339	1276	β OH(64) β CH(31) CF3SS(3)
15	A	1242(w)	---	1195	1229	1315	1253	β CH (39) β CC (21)
16	A	---	1221(vw)	1166	1208	1277	1235	CF3SS(62) tOH(17) tOH(11)
17	A	---	1208(vw)	1120	1197	1241	1213	CF3 ips (83) Rsym (10)
18	A	1197(w)	---	1111	1185	1219	1205	CF3ass(72)tCH(9) Rasym(5)
19	A	1170(m)	---	1083	1158	1200	1182	β CH (45) CF3 ips (12)
20	A	1128(m)	---	1013	1117	1164	1135	β CH (71) CF3SS(27)
21	A	1098(m)	---	990	1087	1121	1108	β CH(73) β CC(10)
22	A	1055(s)	---	914	1042	1092	1067	trigd (38) γ CC(19)
23	A	1023(vw)	---	910	1011	1068	1032	β CH(23) γ CO(18)
24	A	975(s)	979(vs)	873	966	982	978	R symd(76) γCH (13)
25	A	895(vs)	---	806	889	963	902	t CH(62) tasymd(24)
26	A	874(w)	---	745	863	811	863	Rasymd(69) CF3 SS(17)
27	A	790(vs)	---	699	778	792	791	t CH (73) β CCC (18)
28	A	748(vs)	751(s)	662	734	730	741	t CH(79) t sym (16)
29	A	703(vw)	---	641	691	710	707	t CH (79) tsymd (16)
30	A	691(s)	---	575	678	664	679	CF3sb(53) Rasym(21)
31	A	669(vs)	---	535	659	618	661	tasym (77)
32	A	642(s)	---	519	631	580	631	β CO(32) CF3 ops (25)
33	A	613(m)	---	460	601	567	602	t CCC(67) CF3SS(18) tsym(4)
34	A	513(m)	---	447	502	518	516	CF3 ipb (47) tasym(23)
35	A	461(vw)	---	360	449	485	473	CF3 opb(41) tasym(23) β OH(19)
36	A	438(w)	---	352	425	384	425	ω OH(40) CF3ips(22) tasym(12)
37	A	---	393(vw)	331	384	366	381	trig (64) ωOH(12)
38	A	---	365(vw)	316	356	336	354	ωco (61) tasym(23)
39	A	---	326(vw)	230	317	268	312	CF3 opr(63) β OH(22)
40	A	---	305(m)	175	293	185	293	CF3 ipr(41) t OH(25) t asy(10)
41	A	---	241(m)	127	229	152	229	t sym (72) t CF3(18)
42	A	---	95(w)	18	83	38	82	t CF3 opt(79) tsym (19)

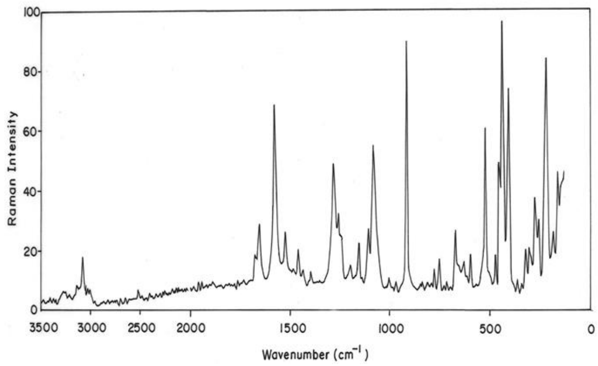

Fig 3. FT-Raman spectrum of 3-hydroxy benzylidyne trifluoride.

C–C Vibrations

The benzene possesses six stretching vibrations of which the four with highest wave numbers occurring near 1650–1400 cm^{-1} are good group vibrations [18]. With heavy substituents, the bonds tend to shift to somewhat lower wavenumbers and greater the number of substituents on the ring, broader the absorption regions. As predicted in the earlier references, the C–C stretching vibrations observed at 1651, 1620, 1591, 1535 and 1497 cm^{-1} in FT-IR spectrum and 1611 and 1572 cm^{-1} in FT-Raman for 3HBT. The C–C in-plane and out-of-plane bending modes of 3HBT are summarized in Table 4

C–O Vibrations

The interaction of the carbonyl group with a hydrogen group does not produce drastic and characteristic changes in the frequency of C=O stretch as does by O–H stretch. A great deal of structural information can be derived from the exact position of the carbonyl stretching absorption peak. Susi and Ard [19] identified the C=O stretching mode at 1645 and 1614 cm^{-1}. On referring to the above findings and on the basis of

Table 5. Second-order perturbation theory analysis of Fock matrix in NBO basis for 3-hydroxy benzylidyne trifluoride.

Donor (i)	Type	ED/e	Acceptor (j)	Type	ED/e	E(2)a (kcal/mol)	E(j)−E(i)b (a.u.)	F(i,j)c (a.u.)
C1-C2	σ	1.97084	C1-C6	σ^*	0.02218	4.31	1.27	0.066
			C3-O12	σ^*	0.02379	3.70	1.04	0.055
C1-C2	π	1.69993	C3-C4	π^*	0.38474	20.08	0.27	0.068
			C5-C6	π^*	0.32265	18.56	0.29	0.065
			C7-F9	σ^*	0.11420	8.01	0.43	0.055
C1-C6	σ	1.97336	C1-C2	σ^*	0.01987	4.23	1.28	0.066
C5-C6	π	1.66659	C1-C2	π^*	0.36520	18.44	0.29	0.065
C3-C4	π	1.65183	C5-C6	π^*	0.32265	20.98	0.29	0.070
F8	n_3	1.93624	C7-F9	σ^*	1.93624	10.52	0.59	0.071
			C7-F10	σ^*	0.09879	12.08	0.60	0.077
F9	n_3	1.93619	C7-F8	σ^*	1.93619	11.37	0.59	0.074
F10	n_3	1.93655	C7-F8	σ^*	0.10492	12.40	0.60	0.078
			C7-F9	π^*	0.11420	10.54	0.59	0.072

E (2) means energy of hyperconjugative interactions.

[b] Energy difference between donor and acceptor i and j NBO orbitals.

[c] F(i,j) is the Fock matrix element between i and j NBO orbitals.

the results of the normal coordinate analysis, in this present investigation, the C–O stretching vibrations have been found at 1438 cm^{-1} in FT-IR spectrum. The C–O in-plane and out-of-plane bending vibrations of 3HBT also have been identified and presented in Table 4

O–H Vibrations

The hydroxyl stretching vibrations are generally [20] observed in the region around 3500 cm^{-1}.

The peak is broader and its intensity is higher than that of a free O–H vibration, which indicates involvement in an intramolecular hydrogen bond. Hence, in the present investigation, the O–H stretching vibrations of 3HBT are observed at 3680 cm^{-1} in FT-IR spectrum. The O–H in-plane deformation vibration usually appears as strong band in the region 1440–1260 cm^{-1}, which gets shifted to higher wave number in the presence of hydrogen bonding. The bands observed at 1265 cm^{-1} in FT-IR correspond to the O–H in-plane bending mode. The O–H out-of-plane bending vibrations give rise to broadband identified in the region 700–500 cm^{-1}. The Raman band observed at 438 cm^{-1} corresponds to out-of-plane bending mode of hydroxyl vibration undergoes a large up shift due to hydrogen bonding.

5. NBO ANALYSIS

The NBO analysis is carried out by examining all possible interactions between 'filled' (donor) Lewis-type NBO's and 'empty' (acceptor) non-Lewis NBOs and estimating their energetic important by second order perturbation theory. Since these interactions lead to loss of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbitals, they are referred to as delocalization corrections to the zeroth-order natural Lewis structure. For each donor NBO (i) and acceptor NBO (j) with delocalization $i \rightarrow j$ is estimated as

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i} \qquad \dots (1)$$

Where q_i is the donor orbital occupancy ε_j and ε_i are diagonal elements orbital energies and F(i,j) is the off diagonal NBO Fock matrix element. The larger E(2) value, the more intensive is the interaction between electron donors and acceptors i.e., the more donation tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system, DFT/B3LYP/6-311+G(d,p) level computation is used to investigate the various second-order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem, which is a measure of the delocalization or hyper-conjugation. NBOs are localized electron pair orbitals for bonding pairs and lone pairs [21]. The hybridization of the atoms and the weight of each atom in each localized electron pair bond are calculated in the idealized Lewis structure. A normal Lewis structure would not leave any antibonding orbitals, so the presence of antibonding orbitals shows deviations from normal Lewis structures.

Anti bonding localized orbitals are called non-Lewis NBOs. If the occupancy is not 2.0, then there are deviations from an ideal Lewis structure. In order to study the small deviations from idealized Lewis structure, the Donor-Acceptor interaction approach is adopted.

The localized orbitals in best Lewis structure can interact strongly. A filled bonding or lone pair orbital can act as a donor and an empty or filled bonding, antibonding or lone pair orbital can act as an acceptor. These interactions can strengthen and weaken bonds. A lone pair donor □□antibonding acceptor orbital interaction will weaken the bond associated with the antibonding orbital. Conversely, an interaction with a bonding pair as the acceptor will strengthen the bond. Strong electron delocalization in best Lewis structure will also show up as donor-acceptor interactions. This calculation is done by examining all possible interactions between 'filled' (donor) Lewis-type NBOs and ‘empty’ (acceptor) non-Lewis NBOs. Since these interactions lead to loss-of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbitals, they are referred to as ‘delocalization’ corrections to the natural Lewis structure. In HTB, π(C3-C4) □ π*(C5-C6) interaction is seen to give a strong stabilization 20.98 KCal/mol. This strong stabilization denotes the larger delocalization. The interesting interactions in HTB compound are LP_3F_{10} and LP_3F_8 with that of antibonding C7-F8 and C7-F10. These two interactions result the stabilization energy of 12.40 and 12.08 KCal/mol respectively. This highest interaction around the ring can induce the large bioactivity in the compound. This shows that the lone pair orbital participates in electron donation in the compound. The calculated values of E(2) are shown in Table 5.

Conclusion

Density functional theory (B3LYP) calculations on the structure and vibrational spectra of 3-Hydroxy benzylidyne Trifluoride (3HBT) have been done. The vibrational frequencies are analysed by B3LYP/6-31+G(d,p) and B3LYP/ 6-31++G(d,p) methods. Therefore, the assignments made at higher level of the theory with higher basis set with reasonable deviations from the experimental values, seems to be correct. NBO study reveals that lone pair orbital participates in electron donation to stabilize the compound.

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