

Analyses of Molecular Structure, Vibrational Spectra, NBO and NMR Studies of 3-Hydroxy Benzylidyne Trifluoride

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Abstract

In this analysis a combined theoretical and experimental studies on molecular structure, vibrational spectra, NBO and NMR properties of 3-Hydroxy Benzylidyne Trifluoride have been reported. The FT-IR and FT-Raman spectra of the title molecule were recorded in the region 4000-400 cm^{-1} and 3000-50 cm^{-1} respectively. The molecular geometry, vibrational frequencies and the bonding features of 3-Hydroxy Benzylidyne Trifluoride are precisely evaluated density functional theory B3LYP/6-311+G(d,p) & 6-31++G(d,p) basis sets. The theoretically calculated vibrational frequencies are compared with the experimental FT-IR and FT-Raman spectra. The stability of the title molecule interpreted by NBO analysis.

Key Words: FTIR; FT-Raman; 3-HYDROXY BENZYLIDYNE TRIFLUORIDE, NBO, NMR

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1. INTRODUCTION

“The benzylidyne and its derivatives are of great interest use for 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 the present invention is to stimulate insulin and use it 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 electronegativity 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 are performed on 3-Hydroxy Benzylidene Trifluoride (3HBT) molecule so far. So, in the present investigation, the vibrational wave numbers, geometrical parameters, mode of vibrations, minimum energy, ^1H and ^{13}C NMR chemical shifts are calculated with GIAO approach by applying B3LYP method”.

2. EXPERIMENTAL DETAILS

“The pure compound 3-Hydroxy benzylidene trifluoride (3HBT) was purchased from Lancaster chemical company, U.K. and used without any further purification. The room temperature Fourier transform infrared (FT-IR) spectrum of 3HBT is recorded in the range of $4000\text{--}400\text{ cm}^{-1}$ at a resolution of $\pm 1\text{ cm}^{-1}$ 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 $3500\text{--}50\text{ cm}^{-1}$ 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” $\pm 1\text{ cm}^{-1}$.

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 are 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]. 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) and DFT-B3LYP/6-31++G(d) levels are listed in Table 1. The detailed vibrational assignment of fundamental modes of 3HBT along with normal mode descriptions (characterized by TED) are reported in Table .2

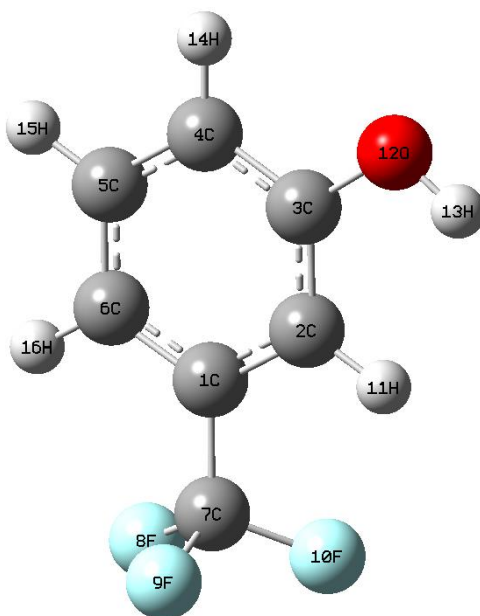


Fig. 1: Molecular structure of 3-hydroxy benzylidene trifluoride

“From the structural data given in Table 1, it is observed that the various bond lengths are found to be almost the same at DFT-B3LYP/6-31+G(d) 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) 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 has 42 fundamental modes of vibrations. The observed FT-IR and FT-Raman spectra are shown in Figs. 2 and 3, respectively”.

Trifluoride Group

“Usually symmetric and antisymmetric CF_3 stretching vibrations are in the ranges $1270\text{--}1235$ and $1226\text{--}1200$ cm^{-1} respectively [13-14]. 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 [15]. C-F deformation vibrations usually occur in the regions $690\text{--}631$ cm^{-1} , $640\text{--}580$ cm^{-1} and $590\text{--}490$ cm^{-1} , match well with the literature [14].

Accordingly CF_3sb , CF_3ipb and CF_3opb are identified at 696 , 513 cm^{-1} in FT-IR spectrum and 461 cm^{-1} in FT-Raman spectrum, respectively. CF_3 rocking vibrational frequency ranges are $450\text{--}350$ cm^{-1} and $350\text{--}260$ cm^{-1} [14-15]. 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} [16]. 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 are identified and listed in Table 2”.

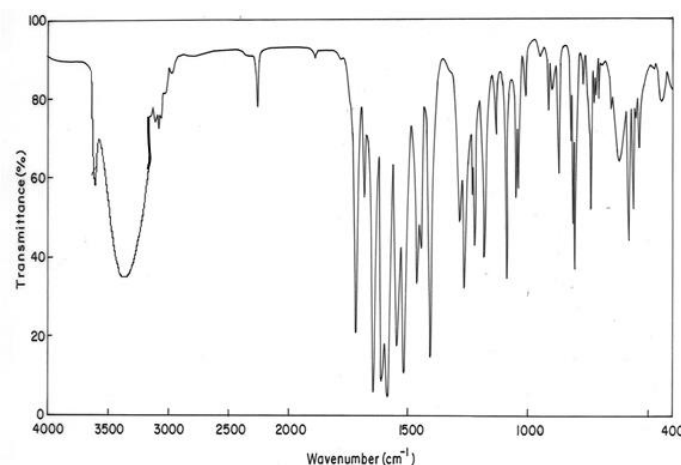


Fig. 2: FT-IR spectrum of 3-hydroxy benzylidene trifluoride

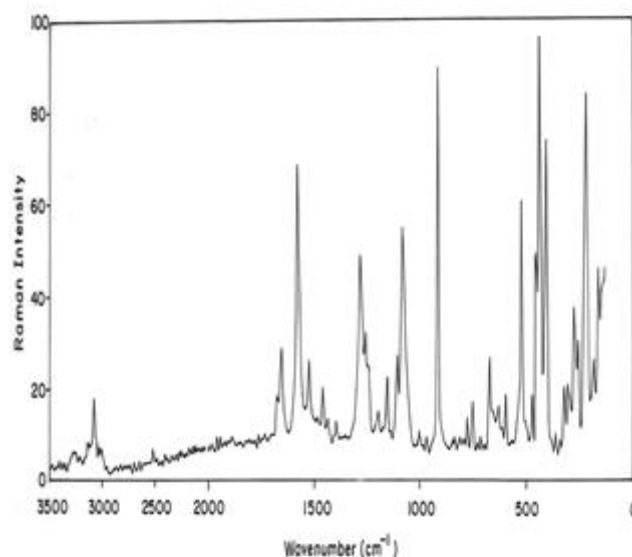


Fig. 3: FT-Raman spectrum of 3-hydroxy benzylidene trifluoride

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 [16]. With heavy substituents, the bonds tend to shift to considerable lower wave numbers and greater, the number of substituents on the ring, broader the absorption regions. As predicted in the earlier references, the C–C stretching vibrations are 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 2

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 it was done with 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 [17] identified the C=O stretching mode at 1645 and 1614 cm^{-1} . On referring to the above findings and on the basis of the results of the normal coordinate analysis, in this present investigation, the C–O stretching vibrations are found at 1438 cm^{-1} in FT-IR spectrum. The C–O in-plane and out-of-plane bending vibrations of 3HBT are also identified and presented in Table 2.

O–H Vibrations

The hydroxyl stretching vibrations are generally [18] 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 $1440\text{--}1260 \text{ cm}^{-1}$, which gets shifted to higher wave number in the presence of hydrogen bonding. The bands observed at 1265 cm^{-1} in FT-IR corresponds to the O–H in-plane bending mode. The O–H out-of-plane bending vibrations give rise to broadband identified in the region $700\text{--}500 \text{ cm}^{-1}$. The Raman band observed at 438 cm^{-1} corresponds to out-of-plane bending mode of hydroxyl vibration that undergoes a large upshift 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 NBO’s and estimating their energetic importance by second order perturbation theory. Since these interactions lead to loss of occupancy from the localized NBO’s 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 NB’O (i) and acceptor NB’O (j) with delocalization $i \rightarrow j$ is estimated as

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\epsilon_j - \epsilon_i} \quad \dots (1)$$

where q_i is the donor orbital occupancy \square_j and \square_i are diagonal elements orbital energies and $F(i,j)$ is the off diagonal NBO Fock matrix element. The larger the $E(2)$ value is 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 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 [19]. 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 the 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 \rightarrow 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 the 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 NBO's and 'empty' (acceptor) non-Lewis NBO's. 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, $\pi(\text{C3-C4}) \rightarrow \pi^*(\text{C5-C6})$ interaction is seen to produce a strong stabilization at 20.98 KCal/mol. This strong stabilization denotes the larger delocalization. The interesting interactions in HTB compound are LP3F10 and LP3F8 with that of antibonding C7-F8 and C7-F10. These two interactions result in 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 within the compound. The calculated values of E(2) are shown in Table 3”.

6. NMR SPECTRAL ANALYSIS

“The isotropic chemical shifts are frequently used as an aid in the identification of reactive organic as well as ionic species. It is recognized that accurate predictions of molecular geometries are essential for reliable calculations of magnetic properties. Therefore, full geometry optimization of 3HBT are performed by using B3LYP/6-311+G(d) method. Then, Gauge-Including Atomic Orbital (GIAO) ¹H and ¹³C chemical shift calculations of the compound are made by the same method. Application of the GIAO [20] approach to molecular systems are significantly improved by an efficient application of the method to the *ab initio* SCF calculations, using the techniques borrowed from analytic derivative methodologies. GIAO procedure is somewhat superior since it exhibits a faster convergence of the calculated properties upon extension of the basis set used. Taking into account, the computational cost and the effectiveness of calculation, the GIAO method seems to be preferable in many aspects at the present state of this subject. On the other hand, the density functional methodologies offer an effective alternative to the conventional correlated methods, due to their significantly lower computational cost. The result in Table 4 shows that the range ¹³C NMR chemical shift of the typical organic molecule usually is > 100 ppm [21-22], the accuracy ensures reliable

interpretation of spectroscopic parameters. It is true from the above literature value, in the present investigation, the 3HBT also falls with the above literature data except with the carbon atoms (C4).

Due to the influence of electropositive oxygen atom, the chemical shift value of C3 is higher, 143.1089 ppm than the other carbon atoms. The other carbons are in the range 121.98–101.05 ppm. The ¹H NMR spectrum of the compound was assigned according to the coupling pattern and the coupling constants. ¹H chemical shifts of 3HBT was obtained by complete analysis of their NMR spectra and interpreted critically in an attempt to quantify the possible different effects acting on the shielding constant of protons. 3HBT possesses one oxygen atom which can act as an acceptor site and on the basis of its basicity, the oxygen O12 is expected to be a good acceptor atom. Thus, the downfield signal at 220.0942 ppm is assigned to the H13 proton of the molecule, strongly indicative of the acceptor nature of O12. The remaining protons of the molecule are also calculated and assigned”.

7. CONCLUSION

“Density functional theory (B3LYP) calculations on the structure and vibrational spectra of 3-Hydroxy benzylidene Trifluoride (3HBT) are done. The vibrational frequencies are analysed by B3LYP/6-31+G(d) and B3LYP/6-31++G(d) methods. Therefore, the assignments made at higher level of the theory with higher basis set at 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. In NMR calculation, due to the presence of electronegative oxygen atom, the chemical shift value of C3 is higher than the other atoms, due to the presence of electron”.

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

Bond Length	Value (Å)		Bond Angle	Value (°)		Dihedral Angle	Value (°)	
	B3LYP / 6-31+G(d)	B3LYP/ 6-31++G(d)		B3LYP / 6-31+G(d)	B3LYP/ 6-31++G(d)		B3LYP / 6-31+G(d)	B3LYP/ 6-31++G(d)
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-C7-C1	119.060	119.4121	C7-C1-C7	-3.0407	2.8563

			C2-C3	4		C2-H11		
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-	120.475	120.6508	H11-C2-	0.3185	-0.1585

			C6-H16	7		C3-1C2		
			C1-C7-F8	112.498 7	112.4613	C2-C3-C4-C5	-0.0031	0.0018
			C1-C7-F9	112.232 2	111.7845	C2-C3-C4-H14	179.877	- 179.8398
			C1-C7-F10	112.926 7	112.3134	O12-C3-C4-C5	- 179.857 1	179.8264
			F8-C7-F9	105.626 3	106.5277	O12-C3-C4-H14	0.023	-0.0152
			F8-C7-F10	106.852 8	107.0785	C2-C3-O12-H13	0.2627	-0.2263
			F9-C7-F10	106.176 2	106.2618	C4-C3-O12-H13	- 179.886 6	179.9536
			C3-O12-H13	115.945 2	110.2953	C3-C4-C5-C6	-0.0483	0.0483
						C3-C4-C5-H15	179.887 4	- 179.8221
						H14-C4-C5-C6	- 179.924 9	179.8859
						H14-C4-C5-H15	0.0108	0.0155
						C4-C5-C6-C1	0.1782	-0.1081
						C4-C5-C6-H16	179.708 3	- 179.7493
						H15-C5-C6-C1	- 179.757 5	179.762
						H15-C5-C6-H16	-0.2274	0.1208

^aFor numbering of atoms refer Fig. 1.

Table 2: Vibrational assignments of fundamental modes of 3-hydroxy benzylidene trifluoride along with calculated frequencies and normal mode descriptions (characterized by TED) based on quantum mechanical force field calculations using B3LYP method.

Mo des	Symmetry Species	Observed fundamentals (cm ⁻¹)		Calculated fundamentals (cm ⁻¹)				Assignments with TED %
				B3LYP/6-31+G(d)		B3LYP/6-31++G(d)		
		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(v w)	1166	120 8	1277	1235	CF3SS(62) tOH(17) tOH(11)
17	A	---	1208(v w)	1120	119 7	1241	1213	CF3 ips (83) Rsym (10)
18	A	1197(w)	---	1111	118 5	1219	1205	CF3ass(72)tCH(9) Rasym(5)
19	A	1170(m)	---	1083	115 8	1200	1182	β CH (45) CF3 ips (12)
20	A	1128(m)	---	1013	111 7	1164	1135	β CH (71) CF3SS(27)
21	A	1098(m)	---	990	108 7	1121	1108	β CH(73) β CC(10)
22	A	1055(s)	---	914	104 2	1092	1067	trigd (38) γ CC(19)
23	A	1023(vw)	---	910	101 1	1068	1032	β CH(23) γ CO(18)
24	A	975(s)	979(vs)	873	966	982	978	R symd(76) γ CH (13)
25	A	895(v s)	---	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(v s)	---	699	778	792	791	t CH (73) β CCC (18)
28	A	748(v s)	751(s)	662	734	730	741	t CH(79) t sym (16)
29	A	703(v w)	---	641	691	710	707	t CH (79) tsymd (16)
30	A	691(s)	---	575	678	664	679	CF3sb(53) Rasym(21)
31	A	669(v s)	---	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(v w)	---	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(v w)	331	384	366	381	trig (64) ωOH(12)
38	A	---	365(v w)	316	356	336	354	ωco (61) tasym(23)
39	A	---	326(v w)	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)

Abbreviations: R - ring; β - bending; d - deformation; asym - asymmetric; sym - symmetric; ω - wagging; t - torsion; trig - trigonal; ss - symmetric stretching; asy - asymmetric stretching; ips - in-plane stretching; ops - out-of-plane stretching; ipr - in-plane rocking; opt - out-of-plane twisting.

Table 3: Second-order perturbation theory analysis of Fock matrix in NBO basis for 3-hydroxy benzyldiyne 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

^a 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.

Table 4: Calculated by B3LYP/6-31++G(d) chemical shifts of 3-hydroxy benzylidene trifluoride.

Atoms	Isotropic shielding (σ_{iso})	Calculated chemical shift (δ_{iso})
H11	24.8643	7.0178
H13	28.1431	3.739
H14	25.6097	6.2724
H15	24.8143	7.0678
H16	24.9668	7.0678
O12	220.0942	99.9058
C1	60.4856	121.98
C2	81.4146	101.051
C3	39.3567	143.1089
C4	80.7084	101.7572
C5	65.9871	116.4785
C6	76.3803	106.0853
C7	60.3554	122.1102

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