

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

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Abstract. Studies of benzylidyne and its derivatives are of great interest due to their biological, pharmaceutical and industrial importance. In the present investigation, the vibrational wave numbers, geometrical parameters, modes of vibrations, minimum energy, NBO and ¹H and ¹³C NMR chemical shifts of 3-Hydroxy benzylidyne Trifluoride (3HBT) are calculated with DFT/ B3LYP level of theory with 6-31+G(d) and 6-31++G(d) basis sets. The FT-IR spectrum of 3HBT is recorded in the range of 4000–400 cm⁻¹ and the FT-Raman spectrum is recorded in the 3500–50 cm⁻¹ Stokes region. 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.

Keywords: 3-Hydroxy benzylidyne Trifluoride, NBO, NMR, FT-IR and FT-Raman.

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 oil. 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].

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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, modes of vibrations, minimum energy, ¹H and ¹³C NMR chemical shifts are calculated with GIAO approach by applying B3LYP method.

2. Experimental Details

The pure compound 3-Hydroxy benzylidyne trifluoride (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. 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.

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. 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 with the MOLVIB program (version V7.0 - G77) written by Sundius [11,12]. 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. 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) is reported in Table 2.

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) and DFT-B3LYP/6-31++G(d) levels of theory. The global minimum energy obtained by above methods are found to be -644.5406 a.u. and -640.977 a.u. The geometrical optimization study of 3HBT reveals that the molecule belongs to C₁ symmetry. The observed FT-IR and FT-Raman spectra are shown in Figs.2 and 3, respectively.

Trifluoride Group

Usually symmetric and antisymmetric CF₃ stretching vibrations are in the ranges 1270–1235 and 1226–1200 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 supported by the literature [15]. C–F deformation vibrations usually occur in the regions $690\text{--}631\text{ cm}^{-1}$, $640\text{--}580\text{ cm}^{-1}$ and $590\text{--}490\text{ cm}^{-1}$, match well with the literature [14].

Accordingly CF_3 symmetric bending, CF_3 in plane bending and CF_3 out of plane bending are identified at $696, 513\text{ cm}^{-1}$ in FT-IR spectrum and 461 cm^{-1} in FT-Raman spectrum, respectively. CF_3 rocking vibrational frequency ranges are $450\text{--}350\text{ cm}^{-1}$ and $350\text{--}260\text{ cm}^{-1}$ [15,14]. 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 in plane rocking and CF_3 out of plane rocking, respectively.

C–H & C–C Vibrations

The heteroaromatic structure shows the presence of C–H stretching vibration in the region $3100\text{--}3000\text{ cm}^{-1}$ [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 $3361, 3092\text{ cm}^{-1}$ in the FT-Raman spectrum and at $3076, 3054\text{ cm}^{-1}$ 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 2.

The benzene possesses six stretching vibrations of which the four with highest wave numbers occurring near $1650\text{--}1400\text{ cm}^{-1}$ are good group vibrations [16]. 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. 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 2.

C–O & O–H 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 [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 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 2.

The hydroxyl stretching vibrations are generally [18] observed in the region around 3500 cm^{-1} . The intensity of the peak is broader than that of a free O–H vibration, which indicates involvement in an intra molecular 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 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 $700\text{--}500\text{ cm}^{-1}$. The Raman band observed at 438 cm^{-1}

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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 importance 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

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\epsilon_j - \epsilon_i} \quad \dots (9.1)$$

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 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 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 unfilled bonding, antibonding 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 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, $\pi(C3-C4) \rightarrow \pi^*(C5-C6)$ 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 3.

6. NMR Spectral Analysis

The isotropic chemical shifts are frequently used as an aid in 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 has been made by the same method. Application of the GIAO [20] approach to molecular systems is significantly improved by an efficient application of the method to the *ab initio* SCF calculations, using 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 from 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 6 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 posses one oxygen atoms which can act as 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 in Table 4.

7. Conclusion

Density functional theory (B3LYP) calculations on the structure and vibrational spectra of 3-Hydroxy benzyldiyne Trifluoride (3HBT) have been done. The vibrational frequencies are analysed by B3LYP/6-31+G(d) and B3LYP/6-31++G(d) methods. 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. 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. 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.

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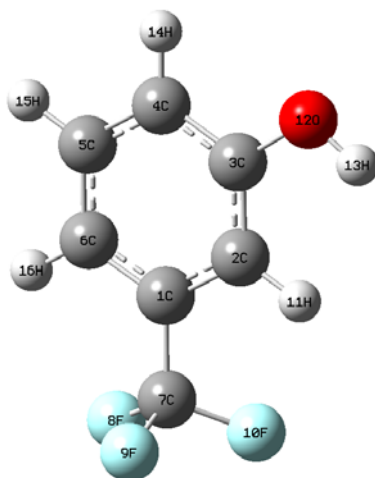


Figure 1: Molecular structure of 3-hydroxy benzylidene trifluoride

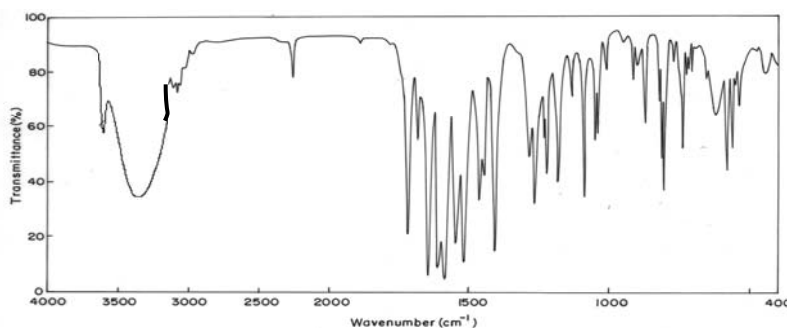


Figure 2: FT-IR spectrum of 3-hydroxy benzylidene trifluoride

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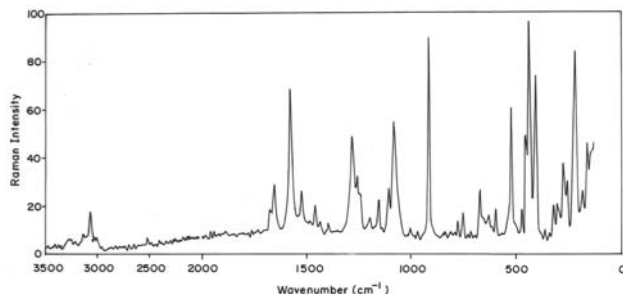


Figure 3: FT-Raman spectrum of 3-hydroxy benzylidene trifluoride

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 (°)	
	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
C1-C6	1.383	1.3964	C2-C1-C7	118.5287	119.0243
C1-C7	1.4914	1.5062	C6-C1-C7	120.2808	120.0296
C2-C3	1.3818	1.397	C1-C2-C3	119.0604	119.4121
C2-H11	1.0732	1.0871	C1-C2-H11	120.2818	120.1648
C3-C4	1.3888	1.4002	C3-C2-H11	120.6556	120.4222
C3-O12	1.3742	1.3683	C2-C3-C4	120.6429	120.2556
C4-C5	1.3823	1.3929	C2-C3-O12	122.7189	122.5704
C4-H14	1.0711	1.0857	C4-C3-O12	116.638	117.1738
C5-C6	1.3923	1.3985	C3-C4-C5	119.6088	119.5925
C5-H15	1.0721	1.0864	C3-C4-H14	118.7424	118.9775
C6-H16	1.0708	1.0844	C5-C4-H14	121.6486	121.4298
C7-F8	1.37	1.3546	C4-C5-C6	120.6243	120.9001
C7-F9	1.3745	1.3624	C4-C5-H15	119.7112	119.4623
C7-F10	1.365	1.3583	C6-C5-H15	119.6645	119.6375
O12-H13	0.95	0.9701	C1-C6-C5	118.9281	118.9436
			C1-C6-H16	120.5945	120.4046
			C5-C6-H16	120.4757	120.6508
			C1-C7-F8	112.4987	112.4613

			C1-C7-F9	112.2322	111.7845
			C1-C7-F10	112.9267	112.3134
			F8-C7-F9	105.6263	106.5277
			F8-C7-F10	106.8528	107.0785
			F9-C7-F10	106.1762	106.2618
			C3-O12-H13	115.9452	110.2953

^aFor numbering of atoms refer Fig. 1.

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

Modes	Observed fundamentals (cm ⁻¹)		Calculated fundamentals (cm ⁻¹)				Assignments with TED %
	FT-IR	FT-Raman	B3LYP/6-31+G(d)		B3LYP/6-31++G(d)		
			Unscaled	Scaled	Unscaled	Scaled	
1	3680(m)	---	3752	3672	3759	3689	γ OH(100)
2	---	3361(s)	3231	3349	3281	3349	γ CH(90) tsymd(10)
3	---	3092(m)	3219	3103	3269	3081	γ CH(92) CF3ips(8)
4	3076(vw)	---	3199	3085	3244	3065	γ CH(89) γ CO(11)
5	3054(vw)	---	3193	3065	3242	3065	γ CH(87) tring (13)
6	1651(w)	---	1660	1657	1779	1672	γ C=C(72) β OH(10)
7	1620(vs)	---	1656	1629	1772	1629	γ CC(64) B CCC(19) β CH(7)
8	---	1611(w)	1550	1621	1680	1623	γ C=C(66) β OH(24)
9	1591(w)	---	1494	1578	1608	1599	γ CC(77) β CH (15)
10	---	1572(vw)	1376	1558	1517	1561	γ CC(81) γ CO(12) β CH(9)
11	1535(w)	---	1359	1243	1463	1523	γ CC(69) γ CO(16)
12	1497(vs)	---	1344	1488	1424	1484	γ CC(34) Rasym(13) BCH(8)

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13	---	1438(w)	1266	1429	1357	144 5	γ CO (53) β CH (27) γ CC (18)
14	1265(w)	---	1204	1254	1339	127 6	β OH(64) β CH(31) CF3SS(3)
15	1242(w)	---	1195	1229	1315	125 3	β CH (39) β CC (21)
16	---	1221(vw)	1166	1208	1277	123 5	CF3SS(62) tOH(17) tOH(11)
17	---	1208(vw)	1120	1197	1241	121 3	CF3 ips (83) Rsym (10)
18	1197(w)	---	1111	1185	1219	120 5	CF3ass(72)tCH(9) Rasym(5)
19	1170(m)	---	1083	1158	1200	118 2	β CH (45) CF3 ips (12)
20	1128(m)	---	1013	1117	1164	113 5	β CH (71) CF3SS(27)
21	1098(m)	---	990	1087	1121	110 8	β CH(73) β CC(10)
22	1055(s)	---	914	1042	1092	106 7	trigd (38) γ CC(19)
23	1023(vw)	---	910	1011	1068	103 2	β CH(23) γ CO(18)
24	975(s)	979(vs)	873	966	982	978	R symd(76) γ CH (13)
25	895(vs)	---	806	889	963	902	t CH(62) tasynd(24)
26	874(w)	---	745	863	811	863	Rasymd(69) CF3 SS(17)
27	790(vs)	---	699	778	792	791	t CH (73) β CCC(18)
28	748(vs)	751(s)	662	734	730	741	t CH(79) t sym (16)
29	703(vw)	---	641	691	710	707	t CH (79) tsymd 16)
30	691(s)	---	575	678	664	679	CF3sb(53) asym(21)
31	669(vs)	---	535	659	618	661	tasynd (77)
32	642(s)	---	519	631	580	631	β CO(32) CF3 ops(25)
33	613(m)	---	460	601	567	602	t CCC(67) CF3SS(18) tsym(4)
34	513(m)	---	447	502	518	516	CF3 ipb (47) tasynd(23)
35	461(vw)	---	360	449	485	473	CF3 opb(41) tasynd(23) β OH(19)
36	438(w)	---	352	425	384	425	ω)22($\sigma\pi$ 13ΦX)04(HO)21($\mu\psi$ σαατ

37	---	393(vw)	331	384	366	381	trig (64) ω OH(12)
38	---	365(vw)	316	356	336	354	ω)32($\mu\nu\sigma\alpha\tau$)16($\sigma\chi$
39	---	326(vw)	230	317	268	312	CF3 opr(63) β OH(22)
40	---	305(m)	175	293	185	293	CF3 ipr(41) t OH(25) t asy(10)
41	---	241(m)	127	229	152	229	t sym (72) t CF3(18)
42	---	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 benzylidene 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^*	0.0222	4.31	1.27	0.066
			C3-O12	σ^*	0.0238	3.7	1.04	0.055
C1-C2	π	1.69993	C3-C4	π^*	0.3847	20.08	0.27	0.068
			C5-C6	π^*	0.3227	18.56	0.29	0.065
			C7-F9	σ^*	0.1142	8.01	0.43	0.055
C1-C6	σ	1.97336	C1-C2	σ^*	0.0199	4.23	1.28	0.066
C5-C6	π	1.66659	C1-C2	π^*	0.3652	18.44	0.29	0.065
C3-C4	π	1.65183	C5-C6	π^*	0.3227	20.98	0.29	0.07
F8	n_3	1.93624	C7-F9	σ^*	1.9362	10.52	0.59	0.071
			C7-F10	σ^*	0.0988	12.08	0.6	0.077
F9	n_3	1.93619	C7-F8	σ^*	1.9362	11.37	0.59	0.074
F10	n_3	1.93655	C7-F8	σ^*	0.1049	12.4	0.6	0.078
			C7-F9	π^*	0.1142	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.

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