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Structural analysis of 4-(Trifluoromethyl) Phenylacetonitrile : FT-IR, FT-Raman and NMR Approaches

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ABSTRACT

In the present work, 4-(Trifluoromethyl)phenylacetonitrile (4TFMNB) has been characterized by FT-IR, FT-Raman and NMR (13C and 1H) analysis. Most of the vibrational assignments of FT-IR and FT-Raman spectra predicted using density functional theory (DFT) approach match well with the experimental findings. The 13C and 1H NMR chemical shifts of the molecules are calculated by the gauge independent atomic orbital (GIAO) method and compared with experimental results.

Keywords: FT-IR, FT-Raman, NMR, DFT

I. INTRODUCTION

Phenylacetonitrile contains molecules with ordered structure and is stabilized by dipole-dipole interactions, whereas alcohols are self-associated through the hydrogen bonding of their hydroxyl groups, creating multimers of different degrees. Alcohols are used as hydraulic fluids, in medications for animals, in manufacturing of perfumes, flavours and dyestuffs, paint removers, as defrosting and as an antiseptic agent. Phenylacetonitrile is used in organic synthesis of dyes, perfumes, pesticides, pharmaceuticals, especially penicillin precursors. Recently, substantial research work has been reported on the excess properties of acetonitrile+alkanols [1], acrylonitrile+alkanols [2,3] and benzonirile+alkanols [4], while that on phenylacetonitrile+alkanol is relatively rare.

Literature survey reveals that no detailed B3LYP with 6-311+G(d,p) basis set of FT-IR, FT-Raman and NMR (^{13}C and ^{1}H) chemical shifts calculation of 4TFMNB have been reported so far. It is, therefore thought worth to make this theoretical and experimental vibrational spectroscopic research based on optimized molecular structure to give the correct assignment of fundamental bands in the experimentally observed FT-IR and FT-Raman spectra. In this study, molecular geometry and vibrational frequencies are calculated using hybrid density functional method. This method predicts relatively accurate molecular structure and vibrational spectra with moderate computational effort.

II. EXPERIMENTAL DETAILS

The fine sample of 4-(Trifluoromethyl)phenylacetonitrile (4TFMNB) is purchased from Sigma-Aldrich chemicals, USA and it was used as such without any further purification. The FT-IR spectrum of the compound has been recorded in Perkin-Elimer 180 spectrometer in the range of 4000–400 cm^{-1}. The spectral resolution is ±2 cm^{-1}. The FT-Raman spectrum of the compound was also recorded in same instrument with FRA 106 Raman module equipped with Nd:YAG laser source operating in the region 3500–100 cm^{-1} at 1064 nm line width with 200 Mw powers. ^{13}C and ^{1}H NMR spectra were taken in $CDCl_3$ solutions and all signals were referenced to TMS on a BRUKER TPX-400 FT-NMR spectrometer.

III. COMPUTATIONAL DETAILS

The molecular structure of the 4TFMNB molecule in the ground state is computed by B3LYP/6-311+G(d,p) method. The optimized structural parameters are used in the vibrational frequency calculations at B3LYP level. The DFT calculations were carried out for 4TFMNB with GAUSSIAN 09W program package [5]. Initial geometry generated from the standard geometrical parameters was minimized without any constraint, which invokes Becke's three parameter hybrid method [6] with Lee-Yang-Parr correlation functional (LYP) [7], implemented with the same basis set for better description of the bonding properties. All the parameters were 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 Cartesian representation of the theoretical force constants have been computed at the fully optimized geometry.

Transformation of force field, the subsequent normal coordinate analysis (NCA) including the least square refinement of the scale factors and calculation of the total energy distribution (TED) were done on a PC with the MOLVIB program (version V7.0-G77) written by Sundius [8, 9]. The calculated frequencies are scaled by 0.9689 scale factor [10, 11]. As a result, the unscaled frequencies, reduced masses, force constants, infrared intensities and Raman activities were obtained. 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.

The Raman activities (S_i) calculated by the Gaussian 09W program was converted to relative Raman intensities (I_i) using the following relationship derived from the intensity theory of Raman scattering [12, 13].

$$I_i = \frac{f(\nu_0 - \nu_i)^4 S_i}{\nu_i[1 - \exp(-hc\nu_i / KT)]} \qquad (1)$$

where ν_0 is the laser exciting wavenumber in cm^{-1} (in this work, we have used the excitation wavenumber ν_0 = 9398.5 cm^{-1}, which corresponds to the wavelength of 1064 nm of a Nd:YAG laser), ν_i is the vibrational wavenumber of the ith normal mode (cm^{-1}), while S_i is the Raman scattering activity of the normal mode ν_i, f (is a constant equal to 10^{-12}) is a suitably chosen common normalization factor for all peak intensities h, k, c and T are Planck and Boltzmann constants, speed of light and temperature in Kelvin, respectively.

In this study, the ^{13}C and ^{1}H NMR chemical shifts and nuclear magnetic shielding tensor values of 4TFMNB in the ground state for B3LYP/6-311+G(d,p) method were calculated with the gauge independent atomic orbital (GIAO) method [14, 15]. All calculations were performed using Gaussian 09W program package [5] employing B3LYP method with 6-311+G(d,p) basis set.

IV. RESULTS AND DISCUSSION

4.1. Vibrational Assignments

The optimized molecular structure of 4TFMNB is shown in Figure 1. From the structural point of view the compound is assumed to have C1 point group symmetry and hence, all the calculated frequency transforming to the same symmetry species (A). The title molecule consists of 16 atoms and expected to have 42 normal modes of vibrations. The detailed vibrational assignments of fundamental modes of

4TFMNB along with the TED are reported in Table 1. The observed FT-IR and FT-Raman spectra of 4TFMNB are shown in Figures 2 and 3, respectively.

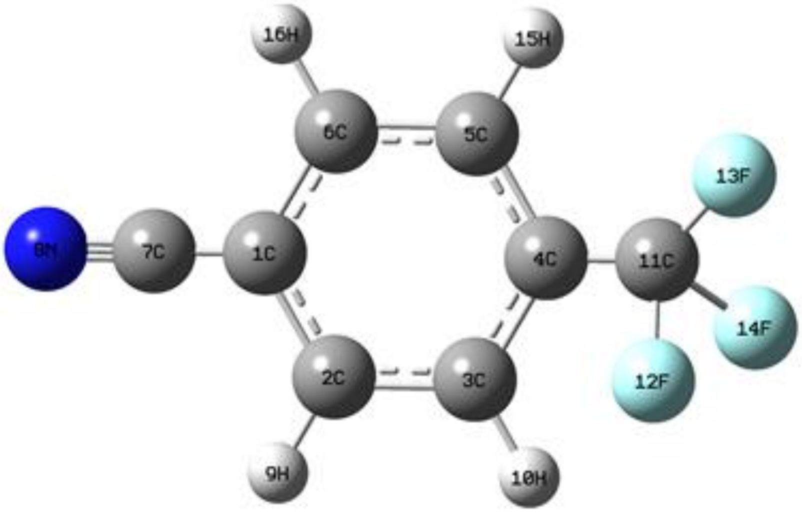

Figure 1. Optimized geometrical structure of 4TFMBN.

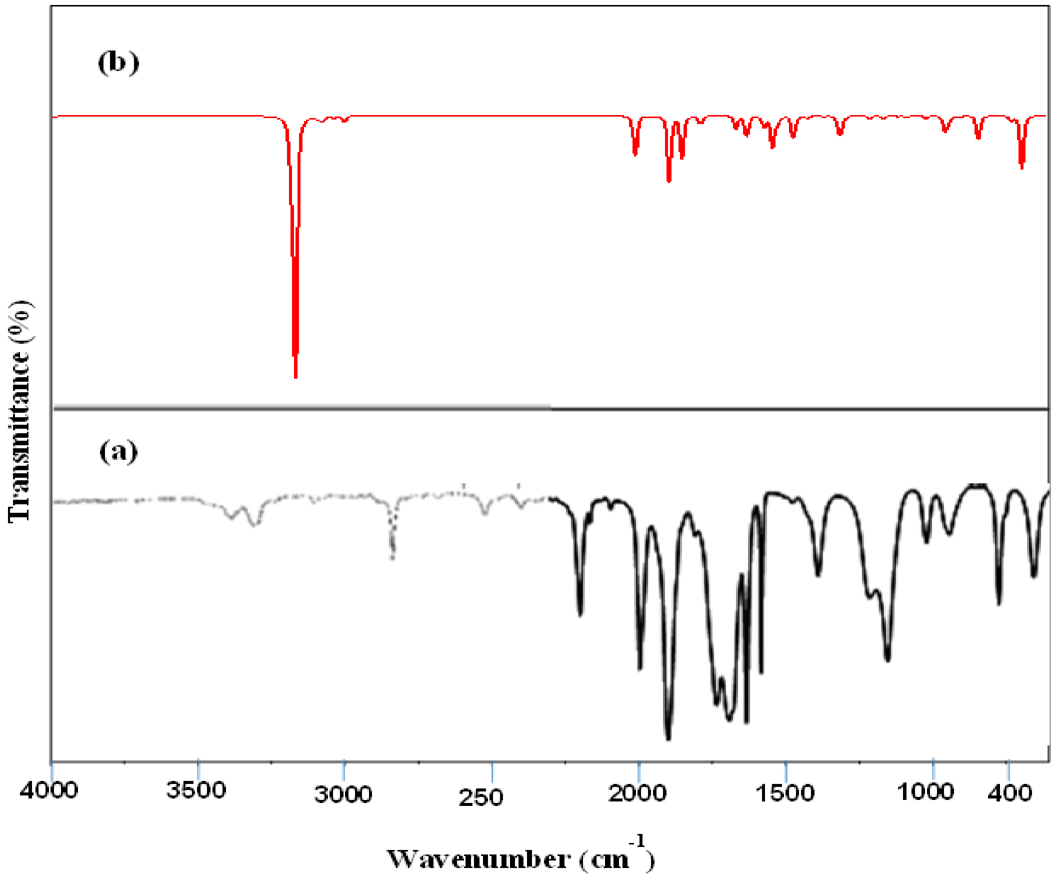

Figure 2

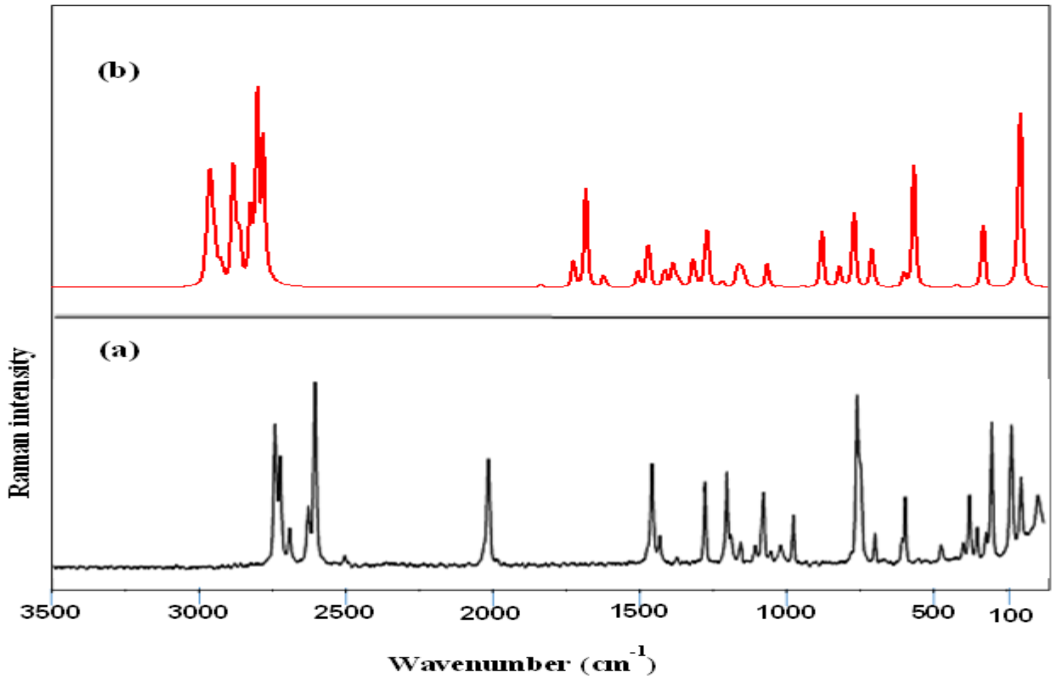

Figure 3

Table 1. Vibrational Assignments of fundamental frequencies are obtained for 4TFMNB using B3LYP/6-311+G(d,p) level of theory.

Sl.No.	Observed frequencies (cm^{-1})		Calculated frequencies (cm^{-1})		Assignments with >10 % of TED
	FT-IR	FT-Raman	B3LYP		
			Unscaled	Scaled	
1	3415(vw)		3400	3378	νC–H (100)
2	3300(vw)		3243	3231	νC–H (99)
3			3125	3178	νC–H (98)
4			3092	3081	νC–H (98)
5			3050	3031	νC–C (95)
6			3037	3018	νC–C (93)
7			3006	2918	νC–C (91)
8			2987	2963	νC–C (91)
9	2780(m)	2750(s)	2932	2908	νC–C (90)
10	2000(s)	2000(s)	1936	1905	νC–C (85)
11	1880(vs)		1816	1793	νC–C (84)
12	1750(vw)		1771	1614	νC–C (82)
13	1700(w)		1706	1607	bC–H (81)
14	1560(vs)		1583	1576	bC–H (83)
15			1545	1523	bC–C (78)
16		1480(s)	1487	1462	bC–C (73)
17			1455	1424	bC–H (71)
18		1425(vw)	1436	1408	bC–H (73)
19	1380(m)		1398	1369	νC–N (76)
20		1310(vw)	1385	1360	bC–C (69)
21		1230(s)	1280	1243	CF3 sym (89)
22	1215(vw)		1219	1207	CF3 asym (83)

23	1180(m)	1200(w)	1202	1193	CF3 asym (84)
24		1115(m)	1115	1085	bC–C (78)
25			1068	1047	bC–C (67)
26		1010(vw)	1015	980	bC–N (61)
27		980(m)	986	963	ωC–H (59)
28	915(m)		917	909	ωC–H (53)
29			855	835	ωC–N (60)
30			851	784	ωC–H (62)
31	820(m)		836	761	ωC–H (65)
32			802	723	ωC–C (57)
33		750(vs)	735	708	ωC–C (55)
34			620	608	bCF3 ipb (58)
35		590(m)	583	571	bCF3 opb (53)
36	450(s)		429	411	bCF3 sb (54)
37			362	345	bCF3 ipr (52)
38		250(s)	334	321	bCF3 opr (50)
39		220(m)	200	168	ωC–C (47)
40			193	172	ωC–C (43)
41		160(s)	185	163	ωC–C (49)
42		100(s)	162	145	tCF3 (44)

Experimental relative intensities are abbreviated as follows: vs-very strong, s-strong, m-medium, w-weak, vw-very weak. Abbreviations; ν-stretching, sym-symmetric stretching, asym-asymmetric stretching, b-in-plane bending, ω-out-of-plane bending, ipb-in-plane bending, opb-out-of-plane bending, sb-symmetric bending, ipr-in-plane rock, opr-out-of-plane rock, t-torsion

4.1.1. C–H vibrations

The C–H stretching vibrations are occurred in the region 3100–3000 cm–1 and these vibrations are not found to be affected due to the nature and position of the substituent [16, 17]. Accordingly, in title compound the C–H stretching vibrations are observed at 3415 and 3300 cm^{-1} in the FT-IR spectrum.

The C–H in-plane bending vibrations usually occurs in the region 1430–990 cm^{-1} [18, 19]. The FT-IR peaks observed at 1700 and 1560 cm^{-1} and FT-Raman peaks observed at 1425 cm^{-1} are assigned to C–H in-plane bending vibrations. C–H out-of-plane bending vibrations are occur in the region 900–667 cm^{-1}. In 4TFMNB peaks obtained at 980, 915 and 820 cm^{-1} in both FT-IR and FT-Raman spectra confirms the C–H out-of-plane bending vibrations which agrees with the calculated values.

4.1.2. C–C vibrations

The bands observed at 1430–1670 cm–1 are assigned to C–C stretching modes. Socrates [20] mentioned that the presence of conjugate substituent such as C–C causes a heavy doublet formation around the region 1625–1575 cm–1. The six ring carbon atoms undergo coupled vibrations called skeletal vibrations and give a maximum of four bands in the region 1660–1420 cm–1 [21]. As predicted in the earlier references, in 4TFMNB compound also there are prominent peaks at 2780, 2000, 1880 AND 1750 cm^{-1} in FT-IR spectrum and peaks observed at 2750 and 2000 cm^{-1} in FT-Raman spectrum are assigned to C–C stretching vibrations. The C–C in-plane AND out-of-plane bending vibrations are appeared at 1480, 1310, 1115 cm^{-1} and 750, 220, 160 cm^{-1} in FT-Raman spectrum are listed in Table 1. These assignments are in good agreement with the literature [22].

4.1.3. C–N Vibrations

The identification of C–N vibrations are a very difficult task, since the mixing of several modes are possible in the region. Silverstein *et. al.*, [23] have assigned C–N stretching vibrations in the region 1382–1266 cm^{-1} for aromatic compounds. In the present study, observed band at 1380 cm^{-1} in FT-IR spectrum is assigned to C–N stretching vibration for 4TFMNB. The in-plane and out-of-plane vibrations of the title compound are occurred within the characteristics region.

4.1.4. CF3 Vibrations

Usually symmetric and antisymmetric CF3 stretching vibrations are in the ranges 1290–1235 and 1226–1200 cm^{-1}, respectively [24, 25]. Therefore the band located at 1230 cm^{-1} in FT-Raman spectrum is assigned to symmetric stretching vibrations. CH3asymmetric frequencies are assigned at 1215, 1180 cm^{-1} and 1200 cm^{-1} in FT-IR and FT-Raman spectra for title compound.CF3 deformations usually occur in regions 690–631 cm^{-1}, 640–580 cm^{-1} and 570–510 cm^{-1} [20]. Accordingly CF3 opb is identified at 590 cm^{-1} in FT-Raman spectrum. CF3 rocking vibrational frequency ranges at 460–350 cm^{-1} [26]. In the present study, the CF3 opr band observed at 250 cm^{-1} in FT-Raman spectrum.

V. NMR SPECTRAL ANALYSIS

The ^{13}C and ^{1}H NMR chemical shifts are calculated within gauge independent atomic orbital (GIAO) method using B3LYP /6-311+G(d,p) method. A comparison of the experimental and theoretical spectra can be very useful in making correct assignments and understanding the basic chemical shift molecular structure relationship. The experimental ^{13}C and ^{1}H NMR spectra of the title compound are given in Fig. 4 ((a) ^{13}C and (b) ^{1}H)). In Table 2, the experimental and the theoretical ^{13}C and ^{1}H isotropic chemical shifts in ppm for the title compound are given. The ^{13}C chemical shift values for all calculations have the range from 121 to 72 ppm at B3LYP/6-311+G(d,p) level of theory in average for 4TFMNB. Downfield and upfield chemical shift values observed at 118 and 68 ppm of carbons C2 and C1 are due to electron donating effect of nitrile group. The carbon atoms C3, C4, C5, C7 and C11 are significantly observed in the upfield with chemical shift values 114, 108, 110, 102 and 112 ppm, respectively, which reveals that the influences of the electronegative nitrile and trifluoromethyl group atoms are negligibly small and their signal are observed in the normal range.

The ^{1}H chemical shift values for all calculations have 7.53 from 4.32 ppm at B3LYP/6-311+G(d,p) method in the average for 4TFMNB molecule. As can be seen from Table 2, theoretical ^{13}C and ^{1}H chemical shift results of the title compound are generally closer to the corresponding experimental chemical shift data except for C6 atom. The small shifts can be explained as a consequence of the change in the molecular environment.

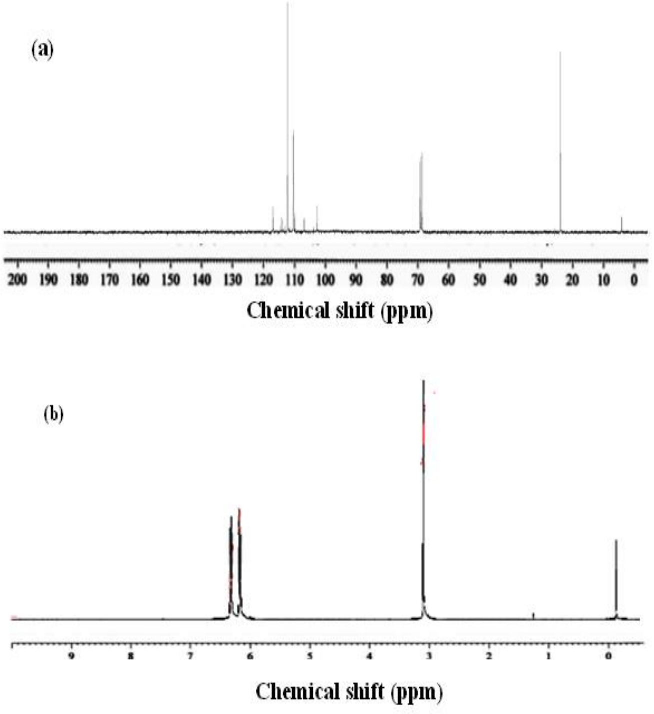

Figure 4. (a) ^{13}C NMR and (b) ^{1}H NMR spectra of 4TFMNB.

Table 2. Experimental and theoretical ^{13}C and ^{1}H chemical shift (ppm) of 4TFMNB.

Atoms	Theoretical Shift (ppm)	Experimental Shift (ppm)
C1	72	68
C2	121	118
C3	115	114
C4	109	108
C5	111	110
C6	93	-
C7	103	102
C11	105	112
H9	7.53	6.8
H10	6.65	6.0
H15	7.23	6.4
H16	4.32	3.4

VI. CONCLUSION

The FT-IR, FT-Raman and NMR (^{13}C and ^{1}H) spectra of the compound 4TFMNB have been recorded and analyzed. The detailed interpretations of the vibrational spectra have been carried out. The observed wavenumbers are found to be in good agreement with the calculated values. The ^{13}C and ^{1}H NMR chemical shifts results seemed to be in a good agreement with experimental data.

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