FT-IR and FT Raman: Experimental and Theoretical Studies and HOMO-LUMO Analysis of 1,2,4,5-Tetracyanobenzene

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Abstract: Experimental and theoretical studies on molecular and vibrational structure of 1,2,4,5-Tetracyanobenzene (TCNB) have been undertaken in the present work. The FT-IR spectrum and FT Raman spectrum of TCNB were recorded respectively in the region 4000–400 cm^{-1} and 2500-400 cm^{-1}. The optimized geometries in the ground state were calculated by DFT (B3LYP) methods with 6-311G basis set. The optimized structural shown the difference in the bond lengths and some angles are very little affected with a small reduction. The computational results indicate that the molecule adopts a plane geometry and belongs to the D_2h point group with the aromatic ring lying in the plane of symmetry. The molecular electrostatic potential shown that the two protons of TCNB as well as the benzene ring are in electron deficient region whereas the CN group are in electron rich region. The carbon atom of CN group and the carbon on the benzene ring are in antibonding interactions in HOMO and in bonding interactions in the LUMO. The harmonic vibrational frequencies, infrared intensities and Raman activities of the TCNB were evaluated. After scaling, the computational wavenumbers are in agreement with the experimental values. A detailed interpretation of the infrared and Raman spectra of TCNB is presented.

Keywords: Tetra-Cyanobenzene, DFT Calculations, Symmetry, IR and Raman

1. Introduction

When van der Waals interactions rule the building of organic molecular materials, their optical and electronic properties are logically related to the energy of the frontier molecular orbital, the highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO, of the molecular units [1]. It is result an occupied binding molecular through the hybridization of the HOMO and LUMO orbital which causes a filled valence band in the solid state and makes the material semiconducting or insulating [2]. When strong intermolecular interactions, like donor–acceptor tandems or hydrogen-bonding, takes place in the solid state, material display generally unique crystalline structure and optoelectronic properties. The interaction between an electron donating precursors with an electron accepting can produce a new molecular material called Charge Transfer Complexes (CTCs). Various molecules organics like 1,2,4,5-tetracyanobenzene (TCNB) can behave as electron acceptor and form molecular complexes with electron-donor molecules. In the molecule of 1,2,4,5-tetracyanobenzene, the two hydrogen atom as well the benzene ring are highly electron deficient due to the strong electron with-drawing effect of the four CN group. TCNB has been widely used to form CTCs in the solid state with different electron donors because of his important role as an electron acceptor [3-7]. Different vibrational studies have been reported on the TCNB molecule. For example, the calculations of the atomic movements of the fundamental vibrations of the TCNB were carried out in terms of the Cartesian displacement coordinates

and the precise vibrational modes were schematically drawn in diagrams [8]. The polarized IR and far-IR spectra of single crystals of TCNB were recorded and the normal coordinate calculated with the modified Urey-Bradley force field and the valence force field for the in-plane and out-of-plane vibrations, respectively [9]. Using electron diffraction and by ab initio calculations at different levels of theory, the molecular structure of TCNB in gas-phase has been determined [10]. Chakraborty and al. have characterized the vibrational levels of TCNB in the electronic ground and first excited states by dispersed fluorescence and laser induced fluorescence spectroscopy [11]. In this present work, the number of vibrational mode of TCNB in solid state was determined according to group theory and symmetry and the complete vibrational analysis was realized via the combination of the experimental and theoretical results obtained by density functional theory (DFT) based on scaled quantum chemical. Density functional theory calculations are reported to provide excellent vibrational frequencies of organic compounds, if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for the anharmonicity effects [12]. The vibrational wavenumbers, complete geometrical parameters, modes of vibrations and other parameters of TCNB molecule were investigated using B3LYP calculations with 6-311G basis sets. Specific scale factors were employed in the predicted frequencies for the accuracy.

2. Material and Methods

2.1. Experimental Details

The compound which is of spectroscopic grade was purchased from commercial sources and hence used directly for recording the spectra without further purification.

FT-IR spectrum were recorded between 4000 and 400cm^{-1} using a PerkinElmer Spectrum 100 FT-IR spectrometer. Raman spectroscopy was conducted employing a Renishaw in Via Raman microscope with a 633 nm laser between 400 and 2500 cm^{-1}. The frequencies of all sharp bands are accurate to ± 2 cm^{-1}.

2.2. Theoretical Details

The molecular structure optimization of the TCNB molecule and corresponding vibrational harmonic frequencies were calculated using the DFT at Beckee-3-Lee-Yag-Parr (B3LYP) with 6-311G basis set using Gaussian 09W program package without any constraint on the geometry of the molecule [13]. The computed vibrational frequencies have been scaled in order to allow direct comparison with the experimental spectra. It is possible to obtain a better agreement between the computed and experimental frequencies by using appropriate scale factors for the different regions of vibrations. Vibrational frequency assignments were made with accurately by combining the results of the GAUSSVIEW 3 program with symmetry considerations [14-15].

3. Results and Discussion

3.1. Molecular Geometry and Parameters

The optimized molecular structures with the numeration of atoms and the choice of axes obtained from Gaussian 09 and GAUSSVIEW programs is as shown in Figure 1. The global minimum energy obtained by DFT structure optimization using 6-311G basis set for the title molecule as -601.157386332 u. a. The optimized structural parameters, such as bond lengths, bond angles, and dihedral angles determined at the same basis set are listed in Table 1.

The carbon–carbon bonds in TCNB are not in the same order of length as in the case of benzene. It appears a little distorted with shorter C_1–C_2, C_2–C_3, C_4–C_5 and C_5–C_6 and larger C_1–C_6, C_3–C_4. The larger bonds are about 1.4173 Å (141.73 pm) in length, whereas the shorter other are about 1.4Å (140 pm) long. The difference in the bond lengths between the larger and shorter bonds is about 0.0173 Å. The difference of 0.02 Å value has been obtained at MP2 level using 6-31++G** basis set [11].

In the C-C ring of the TCNB molecule, all carbons are hybridized sp^2. This implies that the bond angles around the carbon will be exactly 120°. The computed results shown that the bonds angles slightly deviate from the ideal sp^2 hybridized values. Some angles are very little affected with a small reduction but this change give rises to a slight opening of the others angles. However, the computational results indicate that the molecule adopts a plane geometry and belongs to the D$_2$h point group with the aromatic ring lying in the plane of symmetry.
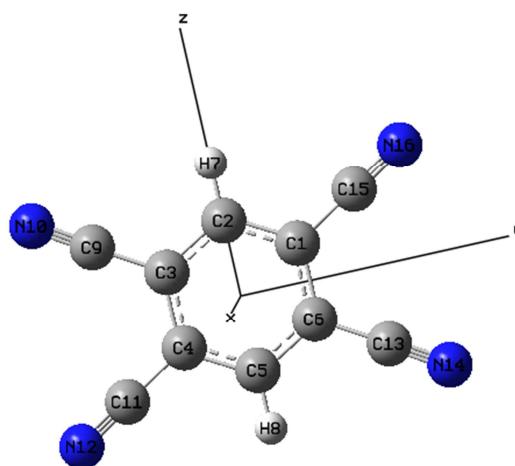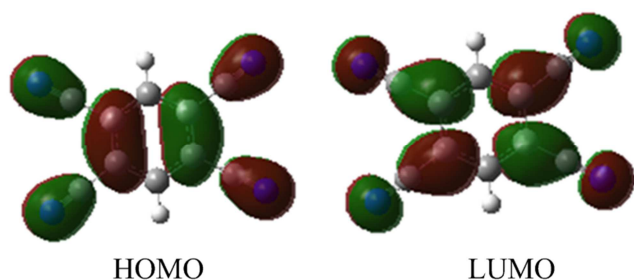

Figure 1. *Molecular structure of TCNB with numbering of atoms.*

3.2. Frontier Molecular Orbital Analysis

The frontier molecular orbital (FMOs) play an important role in the optical and electric properties, as well as in quantum chemistry and UV-visible spectra. The HOMO-LUMO energy gap is an important measure of the stability of the compound. The HOMO has the ability to give an electron, thereby the energy of the molecule is corresponding to the ionization potential whereas the LUMO obtains an electron as an electron acceptor and it corresponds

to the electron affinity. Molecule with large values of frontier orbital gap, are less polarizable, with small chemical reactivity and high kinetic stability and is called a hard molecule and vice versa [16]. In our calculations the energy band gap of TCNB is calculated as 4.7737 eV. The Figure 2 shows the electron density of the HOMO and LUMO using density functional theory (DFT) at B3LYP/6-311G level for the optimized geometry in the ground state.

As seen from the orbital plots in Figure 2, there are antibonding interactions between the carbon atom of CN group and its direct neighbor on the benzene ring in HOMO while they are in bonding interactions in the LUMO.

an indicator of the charge distributions of molecules. The MEP of the TCNB molecule showed in Figure 3 was calculated at the DFT/B3LYP/6–311G level of theory. The different color in the plot indicates the electrostatic potential regions in which the yellow-coloured region is nucleophile and electron rich, the blue colour indicates the electron-poor electrophile region and the white region indicates neutral atoms. As seen from the MEP, the two protons attached to carbons atom number 2 and 5 as well as the benzene ring are in electron deficient region whereas the CN groups are in electron rich region.

Figure 2. *Orbital plots showing the HOMO–LUMO electronic transitions in the TCNB.*

3.3. Molecular Electrostatic Potential

The molecular electrostatic potential (MEP) has been particularly useful in depicting the molecular size and shape as
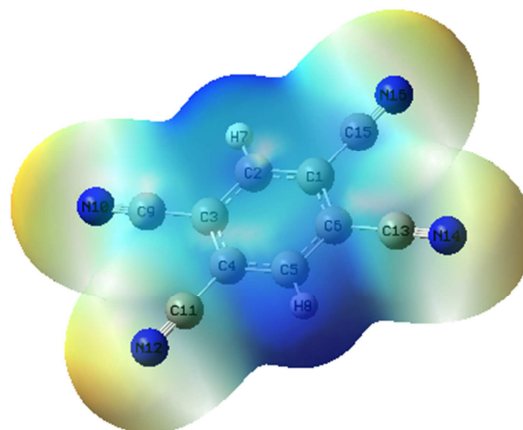
Figure 3. *The molecular electrostatic cpotential surface of the TCNB calculated at the DFT/B3LYP/6-311G.*

Table 1. *Geometrical parameters optimized in 1,2,4,5-tetracyanobenzene, bond length (Å), bond angle (°) and dihedral angle (°).*

ParametersB3LYP/6-311G					
Bond length (Å)					
C1-C2	1.4	C3-C4	1.4173	C6-C13	1.4294
C1-C6	1.4173	C3-C9	1.4294	C9-N10	1.1663
C1-C15	1.4294	C4-C5	1.4	C11-N12	1.1663
C2-C3	1.4	C4-C11	1.4294	C13-N14	1.1663
C2-H7	1.0791	C5-C6	1.4		
C15-N16	1.1663	C5-H8	1.0791		
Bond angle (°)					
C2-C1-C6	119.5182	C2-C3-C4	119.5182	C4-C5-C6	120.9635
C2-C1-C15	119.4869	C2-C3-C9	119.4869	C4-C5-H8	119.5182
C6-C1-C15	120.9949	C4-C3-C9	120.9949	C6-C5-H8	119.5182
C1-C2-C3	120.9635	C3-C4-C5	119.5182	C1-C6-C5	119.5182
C1-C2-H7	119.5182	C3-C4-C11	120.9949	C1-C6-C13	120.9949
C3-C2-H7	119.5182	C5-C4-C11	119.4869	C5-C6-C13	119.4869
Dihedral angle (°)					
C6-C1-C2-C3	0.0	C1-C2-C3-C4	0.0	C3-C4-C5-C6	0.0
C6-C1-C2-H7	180.0	C1-C2-C3-C9	180.0	C3-C4-C5-H8	180.0
C15-C1-C2-C3	180.0	H7-C2-C3-C4	180.0	C11-C4-C5-C6	180.0
C15-C1-C2-H7	0.0	H7-C2-H3-C9	0.0	C11-C4-C5-H8	0.0
C2-C1-C6-C5	0.0	C2-C3-C4-C5	0.0	C4-C5-C6-C1	0.0
C2-C1-C6-C13	180.0	C2-C3-C4-C11	180.0	C4-C5-C6-C13	180.0
C15-C1-C6-C5	180.0	C9-C3-C4-C5	180.0	H8-C5-C6-C1	180.0
C15-C1-C6-C13	0.0	C9-C3-C4-C11	0.0	H8-C5-C6-C13	0.0

3.4. Vibrational Modes

The maximum number of potentially active observable fundamentals modes of vibration from an on-linear molecule

which contains N atoms is equal to (3N-6), apart from three translational and three rotational degrees of freedom. The molecule of TCNB has 16 atoms and belongs to point group D_{2h}. According to the group theory, the three Cartesian

displacements of the 16 atoms provide 48 (3N) internal modes.

The species of fundamentals modes of vibrations are determined by considering the character of a reducible representation of dimension 3N by calculating the character of the matrix representing the effect of each operation of symmetry on the base. Table 2 shows the character tables of point group D_{2h} and table 3 list the character of reducible representation Γ_{3N} for the same point group.

Table 2. *Character table for the D_{2h} point group.*

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma_{(xy)}$	$\sigma_{(xz)}$	$\sigma_{(yz)}$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	Rz	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	Ry	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	Rx	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

Table 3. *Character of reducible representation of point group D_{2h}.*

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma_{(xy)}$	$\sigma_{(xz)}$	$\sigma_{(yz)}$
Nj	16	4	0	0	0	0	4	16
$2\cos\varphi \pm 1$	3	-1	-1	-1	-3	1	1	1
$\Gamma_{3N} = Nj\ (2\cos\varphi \pm 1)$	48	-4	0	0	0	0	4	16

The reducible representation of dimension 3N was reduced using the formula of reduction:

$$a_i = \frac{1}{h}\sum_k \chi\Gamma(R_k) * \chi_i(R_k) * n\ (R_k)$$

h: is total number of operations in the point group;

$\chi\Gamma\ (R_k)$: character of the reducible representation of the operations for the equivalence class;

$\chi_i(R_k)$: character of the irreducible representation of the operations for the equivalence class;

$n\ (R_k)$: number of operations in the kth column of the character table.

For the TCNB molecule, $\Gamma_{3N} = 8A_g + 3B_{1g} + 5B_{2g} + 8B_{3g} + 3A_u + 8B_{1u} + 8B_{2u} + 5B_{3u}$

From the character table $\Gamma_{trans} = B_{1u} + B_{2u} + B_{3u}$ and $\Gamma_{rot} = B_{1g} + B_{2g} + B_{3g}$

Consequently by subtraction of the translation and rotation species, the complete set of vibrational modes is given by:

$$\Gamma_{vib} = 8A_g + 2B_{1g} + 4B_{2g} + 7B_{3g} + 3A_u + 7B_{1u} + 7B_{2u} + 4B_{3u}$$

The TCNB has forty two non-degenerate vibrations. For an N-atomic molecule, 2N-3 of all vibration is in-plane and N-3 is out-of-plane [17]. Thus twenty-nine of all the forty two vibrations are in plane and thirteen are out-of-plane. Since the molecule belongs to D_{2h} group, all vibrations being symmetric through mirror plane of molecule $\sigma_{(yz)} \equiv \sigma_h$ will belong to A_g, B_{3g}, B_{1u} and B_{2u} species and the others being asymmetric through $\sigma_{(yz)} \equiv \sigma_h$ will belong to B_{1g}, B_{2g}, A_u and B_{3u} species.

The character table shows that B_{1u}, B_{2u}, B_{3u} are infrared active while A_g, B_{1g}, B_{2g} and B_{3g} are Raman active. Due to the center of inversion, the modes that are active in the IR are not active in the Raman, and vice versa. This is known as the mutual exclusion rule. Thus, IR and Raman spectra should show respectively 18 bands and 21 bands.

The detailed analysis of fundamental modes of vibration with FT-IR and FT Raman experimental frequencies scaled vibrational frequencies and IR intensity of TCNB using B3LYP method with 6-311G basis set is reported in Table 4. Sometimes, it is necessary to scale down the calculated harmonic frequencies in order to improve the calculated values in agreement with the experimental values. The scaled calculated frequencies minimize the root-mean square difference between calculated and experimental frequencies for bands with definite identifications. Hence, the harmonic calculated frequencies, infrared, and Raman intensities are scaled by 0.965 for the low frequency region and 0.986 for the high frequency region.

The observed experimental spectra; FT-IR recorded between 4000 and 400 cm^{-1} and FT Raman recorded between 2500 and 400 cm^{-1} compare to and theoretical spectra are showed respectivily in Figures 4 and 5.

Table 4. *Comparaison of the observed and calculated vibrational frequencies 1,2,4,5-tetracyanobenzene.*

Mode	Species	Experimental		TheoriticalB3LYP6-311G			Assignments
		FT-IR	Raman	Frequency unscaled	IR Intensity	Scaled	
1	A_u			60.70	0.0000	58.58	γC—CN
2	B_{3u}			96.48	17.7608	93.11	γC—CN
3	A_g			114.91	0.0000	110.89	βC—CN+βC≡N
4	B_{2u}			123.15	2.0166	118.84	βC≡N+βC—CN
5	B_{1u}			130.06	13.0501	125.51	βC—CN + βC≡N

Mode	Species	Experimental		TheoriticalB3LYP6-311G			Assignements
		FT-IR	Raman	Frequency unscaled	IR Intensity	Scaled	
6	B$_{2g}$			158.51	0.0000	152.96	γC≡N, sym
7	B$_{1g}$			219.70	0.0000	212.01	γC—CN
8	B$_{3g}$			233.95	0.0000	225.76	βC≡N
9	A$_u$			356.95	0.0000	344.46	γC-CN
10	B$_{3g}$			366.58	0.0000	353.75	νC—CN
11	B$_{3u}$			387.49	0.2418	373.92	γC—H,
12	A$_g$		405w	416.92	0.0000	402.33	βC—CH—C (ring) νC—CN
13	B$_{2g}$		460vw	481.84	0.0000	464.97	γC-C≡N
14	B$_{1u}$	465w		494.11	0.6543	476.82	βC-C≡N
15	B$_{2u}$			511.63	1.1966	493.72	βC—CN
16	A$_g$		506vw	528.90	0.0000	510.39	βC≡N, βC—CN
17	B$_{3u}$	507vs		553.37	9.9941	534.00	γCN-C-CH-C-CN
18	B$_{1g}$		550m	598.88	0.0000	577.91	γC—CN
19	B$_{1u}$	628vw		642.63	3.4624	620.14	Ring deformation
20	B$_{3g}$		686vw	725.38	0.0000	699.99	βC—CN
21	A$_g$		723m	739.31	0.0000	713.43	βC-CH-C ring νCCN-CCN ring γC-CNring
22	A$_u$			762.42	0.0000	735.74	γC-C ring deformation
23	B$_{2u}$	759w		782.06	6.1802	754.69	νC—CN stretch
24	B$_{2g}$			804.45	0.0000	776.30	γC—H sym, γC-Cring
25	B$_{3u}$	917vs		966.93	41.6692	933.09	γC—H asym
26	B$_{2g}$			968.26	0.0000	934.37	γC—H sym
27	B$_{3g}$		1034vw	1063.38	0.0000	1026.16	νC—CN stretch βC-C ring
28	B$_{1u}$			1208.89	3.7500	1166.58	βC—CH—C βC-C—CH
29	B$_{2u}$	1182vw		1221.42	0.0366	1178.67	βC—H
30	A$_g$			1276.91	0.0000	1232.22	CCN-CH breathing
31	B$_{2u}$	1277s	1261s	1308.26	12.0440	1262.47	νCCN—CCN (ring) νCCN—CH (ring)
32	B$_{3g}$			1321.37	0.0000	1275.13	βC—H
33	B$_{1u}$	1387w		1401.72	3.1162	1352.66	νCCN—CH (ring)
34	B$_{2u}$	1485s		1532.34	36.8901	1478.71	βC—H
35	A$_g$		1540m	1550.99	0.0000	1496.71	νCCN—CCN (ring)
36	B$_{3g}$		1598w	1636.94	0.0000	1579.64	νCCN—CCN (ring)
37	A$_g$		2239vs	2278.26	0.0000	2246.36	νC≡N stretch
38	B$_{3g}$		2249sh	2279.35	0.0000	2247.44	νC≡N stretch
39	B$_{2u}$	2245s		2280.30	2.0959	2248.37	νC≡N stretch
40	B$_{1u}$			2283.98	1.3649	2252.01	νC≡N stretch
41	B$_{1u}$	3048s		3219.60	0.5509	3174.53	νC—H asym
42	A$_g$	3113s		3221.07	0.0000	3175.97	νC-H sym

w-weak, vw-veryweak, s-strong, vs-very strong, m-medium, sh-shoulder, ν-stretching, ν$_{asy}$-asymetric stretching, ν$_{sym}$-symetric stretching, β-in plane bending, γ-out of plane bending, ω-wagging, t-twisting, δ-scissoring, τ-torsion, r-rocking.
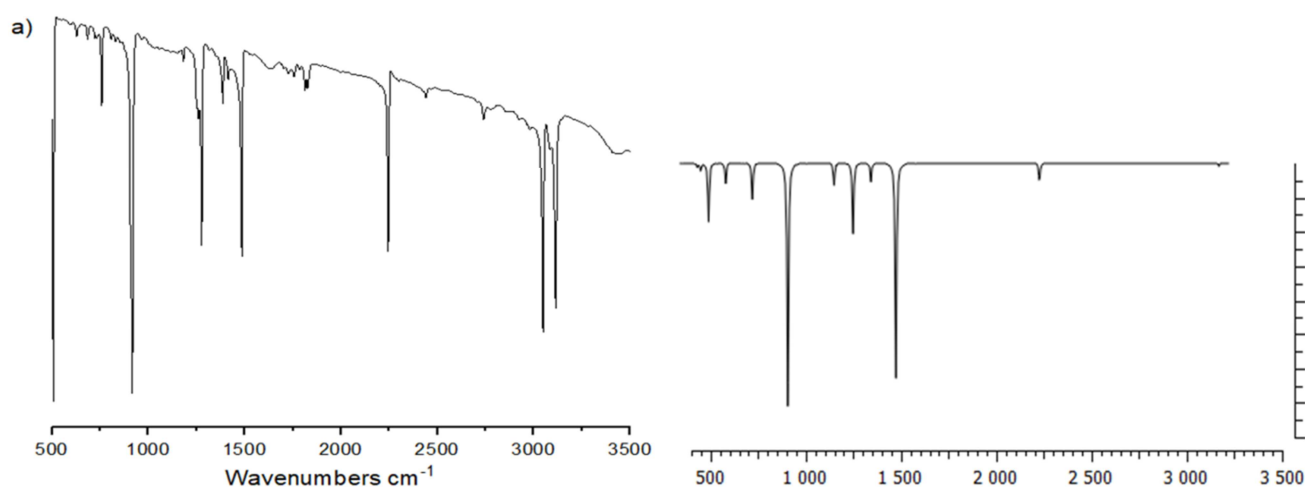

Figure 4. *Comparison of experimental (a) and theoretical FT-IR spectra of TCNB.*
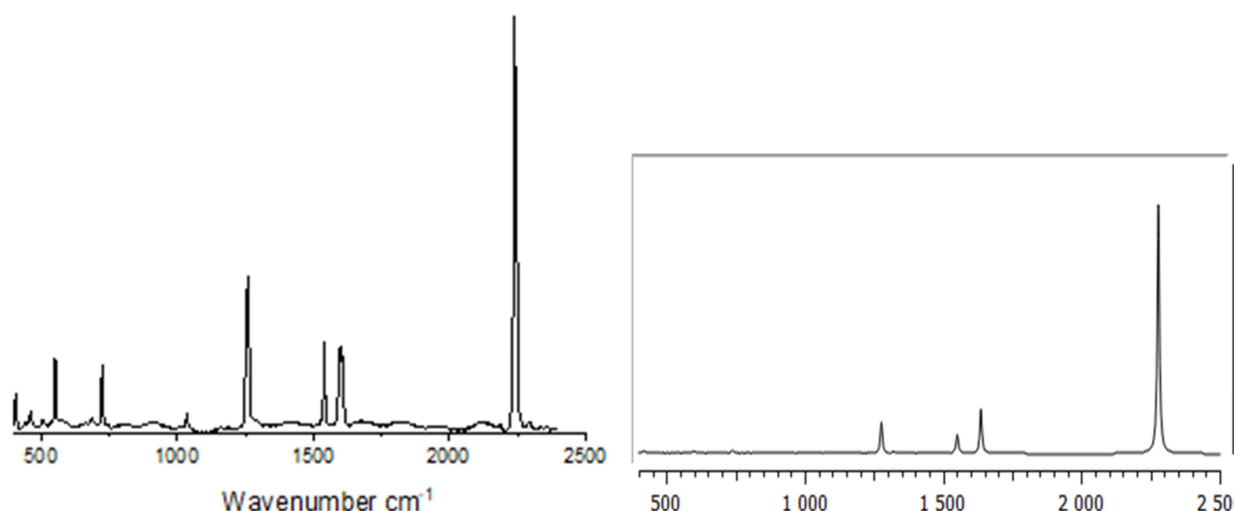
Figure 5. Comparison of experimental and theoretical FT Raman spectra of TCNB.

C-H vibrations

The carbon–hydrogen vibrations in aromatic compounds can be found in the range 3080–3030cm^{-1} (C-H stretching) [18]. The corresponding C–H in plane and out of plane bending vibrations are usually observed between 1000 and 1300 cm^{-1} and between 750 and 1000 cm^{-1} respectively [19-20]. TCNB molecule has two C–H bonds which undergo two stretching vibrations associated with the ring. In the experimental IR spectrum of our title molecule, the asymmetric and symmetric C-H stretching are respectively observed as a fine and intense band at 3048 and 3113 cm^{-1}. The assigned values are in good coherence with the results in the literature [9] and the B3LYP/6-311G basis set. In the experimental IR spectrum of benzene an intense band attributed to C-H stretching is observed at 3064 cm^{-1} and at 3036 cm^{-1} respectively in gas phase [21] and in a condensed phase [22].

In the calculated IR spectrum of our title molecule, the out of plane bending vibration γ (CH) are predicted at 374 cm^{-1}, 776 cm^{-1}, 933 cm^{-1} and 934 cm^{-1}. In the experimental IR spectrum; the very strong band 917 cm^{-1} is attributed to the bending vibration out of plane of the C-H bond. The in plane bending vibrations, β (CH) are predicted in the calculated IR spectrum at 1179 cm^{-1}, 1275 cm^{-1}, 1479 cm^{-1}. In the experimental IR spectrum, the corresponding bands are observed at 1182 cm^{-1}, 1277 cm^{-1} and 1485 cm^{-1} demonstrating a perfect agreement with the theory.

C–C vibrations

The ring carbon–carbon stretching vibrations in benzene derivatives usually occur in the region 1400–1625 cm^{-1} [23]. In general, the bands are of variable intensity are observed at 1256, 1605, 1388, 1278 cm^{-1} from the frequencies given in literature [24]. In this present work, the frequency observed at FT-IR and FT Raman spectra at 1598, 1540, 1387 are assigned to C=C stretching vibrations and the frequencies assigned at 1261 cm^{-1} for C–C stretching vibrations. The theoretically computed frequencies values at 1579 cm^{-1}, 1496 cm^{-1}, 1352 cm^{-1} and 1262 cm^{-1} for C–C stretching vibrations by B3LYP 6-311G method are in excellent agreement with the experimental data.

Cyano group (C≡N) vibrations

For cyano compounds the –C≡N stretching absorption is observed in the narrow region between 2260 and 2200 cm^{-1} [25]. It is frequent to observe the reduction of frequency to 2240–2220 cm^{-1} when the cyano group is engaged in conjugation with aromatic ring. The –C≡N stretching band may be of variable intensity in infrared, and in Raman the band is medium to very strong intensity [26]. The very strong band at 2239 cm^{-1} in Raman and a strong band at 2245 cm^{-1} in IR is assigned to the –C≡N stretching of TCNB. The theoretically computed and assigned by Gaussview program at 2246/2248 cm^{-1} is assigned to –C≡N stretching vibrations.

The in-plane bending of –C≡N bond is obtained in the low frequency region at 507 cm^{-1} in infrared as strong and at 506 cm^{-1} in the Raman as very weak. In the calculated spectrum; this band appears at 510 cm^{-1}. All these assignments coincide well with the literature data and calculated scaled values [25].

4. Conclusion

We have carried out DFT calculations on the structure and vibrational spectra of TCNB. The vibrational frequencies analysis by B3LYP/6-311G method agree overall with experimental results. On the basis of agreement between the calculated and experimental results, assignments of all the fundamental vibrational modes of TCNB were examined and proposed. From the geometrical discussion, it was concluded that the substitutions of H atom by the –CN groups modify the C_1–C_6, C_3–C_4 bonds lengths thus the hexagonal nature of the benzene ring. The frequencies of vibration calculated by B3LYP 6-311G method are in excellent agreement with the experimental data.

Acknowledgements

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