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Comparative vibrational spectroscopic investigation of benzonitrile derivatives using density functional theory

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Abstract

Comparative studies of the vibrational spectra of 4-methyl 3-nitrobenzonitrile and 2-formyl benzonitrile have been made. The spectra are interpreted with the aid of normal mode analysis following full structure optimization based on the density functional theory and different basis set combination. While making complete assignment of vibrational wavenumbers, some interesting facts were noticed for example, how modes of vibrations, bond angles and bond lengths are affected by different groups attached to the benzene ring. The main aim of the present study is to investigate in detail the vibrational spectra and thermo dynamical properties of 4-methyl 3-nitrobenzonitrile and 2-formyl benzonitrile by B3LYP/6-311+G(2df,2p) method and basis set combination, which can presumably help in understanding its behavior i.e. effect on reactivity, stability, nature of state due to the different groups attached to the benzene ring. These effects are also correlated with the chemistry of attached groups.

Keywords: Geometry optimization; Vibrational spectra; DFT

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Introduction

Benzonitrile (BN), is derived mainly from the reaction of benzoic acid with theocyanate, by heating at 191^0C. It, reacts violently with strong acid to produce toxic fumes [1]. Nitrile derivatives have found a wide range of application in industry For example, Phthalonitrile have been used as starting materials for phtalocyanide [2], which is an important component for dyes, pigment, gas sensor, optical limiter, and liquid crystal and is also used in medicine as a singlet oxygen photosensitizer for photodynamic therapy. Nitrile compounds are precursors of tetrazole complexes [3], and benzonitrile is an aprotic polar solvent with a dipole moment of 4.18D, and hence, it is extensively used as a solvent [4].

It can also be mentioned that Benzonitrile has been used as   an enriched precursor for the introduction of isotopes into l-tyrosine and has been used in the electrochemical preparation of polydidodecyle terthiphenes from a mixture of acetonitrile and benzonitrile. Cyanide compound can be degraded   by pseudomonas species and BN biotransformed directly to benzoic acid by

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nitrilase enzyme or by several bacterium or biotransformed to benzohydraxmic acid by rhodochrous bacterium [5-8]. So, after a careful assessment of its importance, it was decided to carry out a comparative study of two well known derivatives of BN viz 2-formyl benzonitrile and 4-methyl 3-nitrobenzonitrile. In the compound $(C_8H_6NO_2)$, the nitro group is rotated 23.2(degree) out of plane of benzene ring. The crystal structure is stabilized by Vander-waals interaction. The molecule 4-methyl 3 nitrobenzonitrile is rotated by 10.2 degree out of plane of benzene ring.

It has been felt that proper knowledge of different normal modes of vibration could be of much help in understanding the dynamical nature of these molecules. Vibrational spectroscopy provides immensely invaluable information about the structure and conformation of organic compounds if used in synergy with quantum chemical calculations. Prediction of vibrational frequency of molecules by quantum chemical computation has become very popular because of its accurate and therefore consistent description of the experimental data. In this article, the performance of density functional theory, employing two types of functional and basis sets have been evaluated.

Materials and methods

The DFT theoretical calculations have been performed at DFT/ B3LYP/6-311+G (2df, 2p) [9-12] level using Gaussian 03W program [13], involving gradient optimized geometry [14]. Combined use of B3LYP and split valence basis set 6-311+G (2df, 2p) shows excellent compromise between accuracy and computational effiency of vibrational spectra of large and medium molecules. It is well known that vibrational frequencies obtained by quantum chemistry calculation are typically larger than that of their experimental counterpart and thus experimental scaling factors are usually employed to have better agreement with the experimental vibrational frequencies [15]. The scaling factor depends on both basis set and method used in the calculation and are determined from the mean deviation between calculated and experimental value of frequencies [16,17]. On the other hand B exchange functional have an advantage of standard frequency very close to unity so B based procedures can be often used with out scaling [18-20].

Results and Discussion

Geometry Optimization
The optimized structure parameters of 4-methyl 3-nitrobenzonitrile calculated are listed in Table 1 in accordance with the atom numbering scheme given in Fig.1. In case of 4-methyl 3-nitrobenzonitrle there is no point group symmetry however in case of 2-formyl benzonitrile have C_S point group symmetry. Moreover, as described by the animated view of the output of 4-methyl 3-nitrobenzonitrile neither two oxygen in nitro group nor three hydrogen in methyl group are found in plane. But in case of 2-formyl benzonitrile nearly all molecule found in one plane. Several bond lengths and bond angles of 4-methyl 3-nitrobenzonitrile are taken from the literature. Since all the carbon atoms in the benzene ring are sp^2 hybridized and having equal bond lengths and bond angles hence, substitution of hydrogen in benzene ring results in a perturbation of the valence electron distribution of the molecule followed by changes in the various chemical and physical properties. The angular changes in benzene ring geometry have proved to be a sensitive indicator of the interaction between the substituent and the benzene ring [21]. The bond length in the ring has also shown characteristic variation but they have been

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small and less well pronounced as compared to the angular changes. All calculated bond lengths and their corresponding experimental data are given in Table 1. In this table, the bond length of aromatic ring carbon atom C5-C8 is 1.3611, and C13-C10 is 1.3547 Å and their corresponding experimental value is 1.381 and 1.379 Å, respectively. As seen in the Table 1 the bond length between C5-C8 and C10- C13 are shorter as compared to the other bond length of aromatic ring carbon. This is due to the valence electron distribution between the nitrile group and p-substituted methyl group, which is a σ-electron donor.
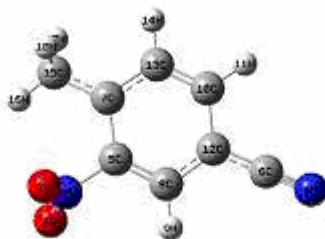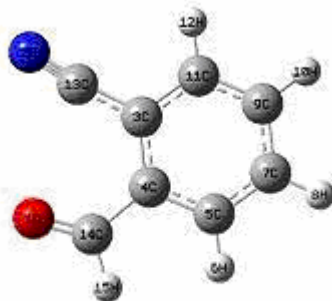

Figure 1. 4-methyl 3-nitrobenzonitrile

Figure 2. 2-formyl benzonitrile

As it is evident in the Table 1, the calculated bond length between O-N is found to be 1.19Å and 1.22Å , whose corresponding value from experimental data is 1.21Å and 1.218Å, these bond lengths are different from each other, which is possibly, due to the vander-waal interaction between the two oxygen atoms of the nitro group and the hydrogen of the methyl group and that's why the resonance between the two oxygen is hindered and the bond lengths of the two N-O bonds is different from each other.

The calculated bond length of the C-CN (sp^2-sp^2) hybridization is 1.39 Å and the corresponding experimental value is 1.450 Å, which is less than the calculated bond length due to the conjugation with the aromatic benzene ring. Moreover, the length of the triple bond of the nitrile group is reduced and therefore the bond length of the C-N is increased. The bond length of the sp^2 C-methyl-C is reduced due to the conjugation with aromatic ring and also due to an electron

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withdrawing nitrile group on para position. Due to the high symmetry of the hexagonal unsubstituted benzene framework and its relative rigidity, the substituted benzene derivatives are well suited for their accurate geometrical studies [22, 23]. Analyses of available experimental data have led to the conclusion that for many of the substituents, the angular distortion of the benzene ring can be interpreted as a superposition of the contribution of the each substituent.

The structural changes on the carbon skeleton concern both the bond distances and bond angles. They are the most pronounced at the place of substitution and depend on the electro negativity as well as on the σ/π donor/acceptor character of the substituent. The bond distances have already been discussed above and now the bond angles needs to be discussed.

Table 1: Optimized bond length of 4-methyl-3-nitrobenzonitrile and 2-formylbenzonitrile at B3LYP/6-311+G(2df,2p) level

S. No	Parameters	X-Ray data of 4-methyl-3-nitrobenzonitrile	Calculated for 4-methyl 3-nitrobenzonitrile	Parameters	Calculated for 2-formylbenzonitrile	X-Ray data of 2-formylbenzonitrile
	Bond lengths					
1	1O-3N	1.210	1.196	1O-14C	1.204	1.214
2	2O-3N	1.218	1.225	2N-13C	1.151	1.149
3	3N-5C	1.478	1.458	3C-4C	1.409	1.411
4	4N-6C	1.144	1.167	3C-11C	1.397	1.390
5	5C-7C	1.400	1.493	3C-13C	1.431	1.450
6	5C-8C	1.381	1.361	4C-5C	1.393	1.387
7	6C-12C	1.450	1.392	4C-14C	1.482	1.480
8	7C-13C	1.400	1.435	5C-6H	1.082	0.950
9	7C-15C	1.513	1.440	5C-7C	1.388	1.387
10	8C-9H	0.930	1.083	7C-8H	1.081	0.950
11	8C-12C	1.390	1.415	7C-9C	1.389	1.383
12	10C-11H	0.930	1.083	9C-10H	1.081	0.950
13	10C-12C	1.392	1.473	9C-11C	1.389	1.390
14	10C-13C	1.379	1.354	11C-12H	1.085	0.950
15	13C-14H	0.930	1.083	14C-15H	1.107	0.950
16	15C-16H	0.930	1.084			
17	15C-17H	0.930	1.107			
18	15C-18H	0.930	1.234			

The calculated substituent impact on the C-C-C bond angles of the benzene ring is summarized in Table 2. The data reflects the well-known trends observed for various substituents: Groups with π-acceptor substituent tend to increase in α_{ipso}, decrease α_{ortho} and it results in a small increase in α_{para} e.g. in the title molecule the bond angle between C7-C5-C8, C5-C7-C13 and C13-C10-C12 are 123.7^0; 116.6^0 and 120.4^0 and their corresponding experimental values are 123.55^0, 115.6^0 and 119.9^0 respectively, which are in good agreement with above discussion. The bond angles between the H17-C15-H16, H17-C15-H18, H16-C15-H18, C7-C15-H16, C7-C15-H17 and C7-C15-H18 are distorted from their tetrahedral angle due to the spatial arrangement of the oxygen of the nitro atom, because of a vander-waal interaction between the oxygen of the

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nitro group and the hydrogen of the methyl group. However, most of the substituents in the present study have a mixed σ/π character and the geometrical parameters of the ring are a result of superposition of overall effects. In the formyl compound the triple bond of the nitrile group is reduced because of the interaction between the nitrile-C and the oxygen of the formyl group, and that's why the carbonyl bond is also reduced. And, due to this reason the bond-angle of the aromatic –C and nitrile group is distorted as compared to the actual bond-angle (Table 2).

Table 2: Optimized bond angles of 4-methyl-3-nitrobenzonitrile and 2-formylbenzonitrile at B3LYP/6-311+G(2df,2p) level

S. No.	Parameters	X-Ray data of 4-methyl-3-nitrobenzonitrile	Calculated for 4-methyl-3-nitrobenzonitrile	Parameters	X-Ray data of 2-formylbenzonitrile	Calculated for 2-formylbenzonitrile
1	1O-3N-2O	122.40	128.76	4C-3C-11C	120.05	119.35
2	1O-3N-5C	118.50	121.61	4C-3C-13H	122.38	123.34
3	2O-3N-5C	119.10	109.62	11C-3C-13C	117.57	117.29
4	3N-5C-7C	121.00	116.74	3C-4C-5C	118.96	119.10
5	3N-5C-8C	115.43	119.77	3C-4C-14C	122.92	123.16
6	7C-5C-8C	123.55	123.60	5C-4C-14C	118.10	117.72
7	5C-7C-13C	115.60	116.69	4C-5C-6H	119.60	118.65
8	5C-7C-15C	125.90	122.75	4C-5C-7C	120.75	121.25
9	13C-7C-15C	118.40	120.53	6H-5C-7C	119.60	120.09
10	5C-8C-9H	120.60	121.87	5C-7C-8H	119.90	120.21
11	5C-8C-12C	118.75	117.16	5C-7C-9C	120.12	119.47
12	9H-8C-12C	120.60	120.96	8H-7C-5C	119.90	119.50
13	11H-10C-12C	120.00	118.16	7C-9C-10H	119.90	120.24
14	11H-10C-13C	120.00	121.43	7C-9C-11C	120.18	120.24
15	12C-10C-13C	119.90	120.39	10H-9C-11C	119.90	119.50
16	6C-12C-8C	120.10	120.35	3C-11C-9C	119.94	120.56
17	6C-12C-10C	120.20	118.30	3C-11C-12H	120.00	119.04
18	8C-12C-10C	119.70	121.34	9C-11C-12H	120.00	120.39
19	7C-13C-10C	122.40	120.71	1O-14C-4C	124.91	125.42
20	7C-13C-14H	118.80	118.71	1O-14C-15H	117.50	120.94
21	10C-13C-14H	118.80	120.54	5C-4C-14C	117.50	113.63
22	7C-5C-16H	109.50	117.40	3C-13C-2N		173.35
23	7C-15C-17H	109.50	109.81			
24	7C-15C-18H	109.50	108.03			
25	16H-15C-17H	109.50	108.92			
26	16H-15C-18H	109.50	108.98			
27	17H-15C-18H	109.50	99.03			

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Since large deviation from experimental X-H, bond length arises from low scattering factor of hydrogen atom in X-ray diffraction experiment hence; we have not discussed the C-H bond length. Several authors have reported that B3LYP method predicts bond length, which is systematically too large, particularly C-H bond length [24-26].

The other calculated bond lengths and bond angles also shown an excellent agreement with experimental values. Based, on the above comparison although, there are some differences between the theoretical values and experimental values, the optimized structural parameters can well reproduce the experimental ones and they are the basis for there after discussion.

Vibrational Analysis

The molecules 4-methyl 3-nitrobenzonitrile, 2-formyl benzonitrile have 18 and 15 atoms respectively with 48 and 39 normal modes of fundamental vibration. Detailed description of vibrational modes can be given by means of normal coordinate analysis and vibrational assignments are achieved by comparing the band positions of calculated and experimental FT-IR and FT-Raman spectra shown in Fig.3 and Fig. 4 of 2-formyl benzonitrile which is taken from the literature [27, 28] with the calculated spectra of 4-methyl 3-nitrobenzonitrile. The vibrational frequencies calculated with these methods contain systematic error [29]. These discrepancies can be correlated either by using scaling equation [30, 31] or directly scaling the calculated wavenumbers with proper factor [32-35]. Vibrational frequencies calculated at B3LYP/6-311+G (2df, 2p) level were scaled by 0.9613 above 800 and 1.0013 below 800 [36]. The calculated normal modes of vibrational frequencies provide thermo dynamical properties by statistical mechanics. All the assignments for frequencies were done by gauss view [37]. Some important modes of vibration have been discussed as follows and are listed in Table 3.
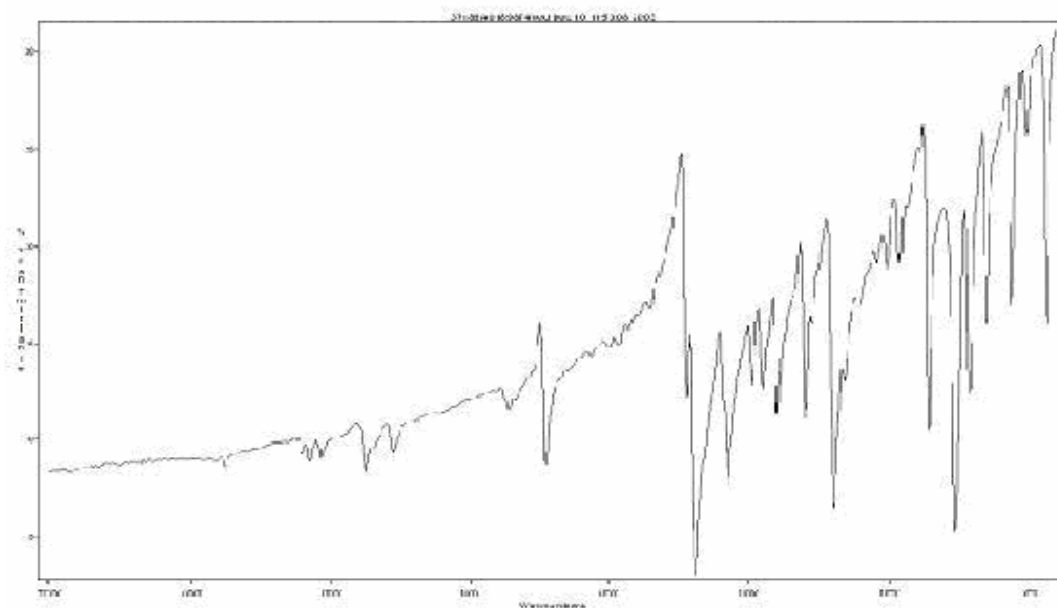
Figure 3. FT-IR spectra of 2-formyl benzonitrile

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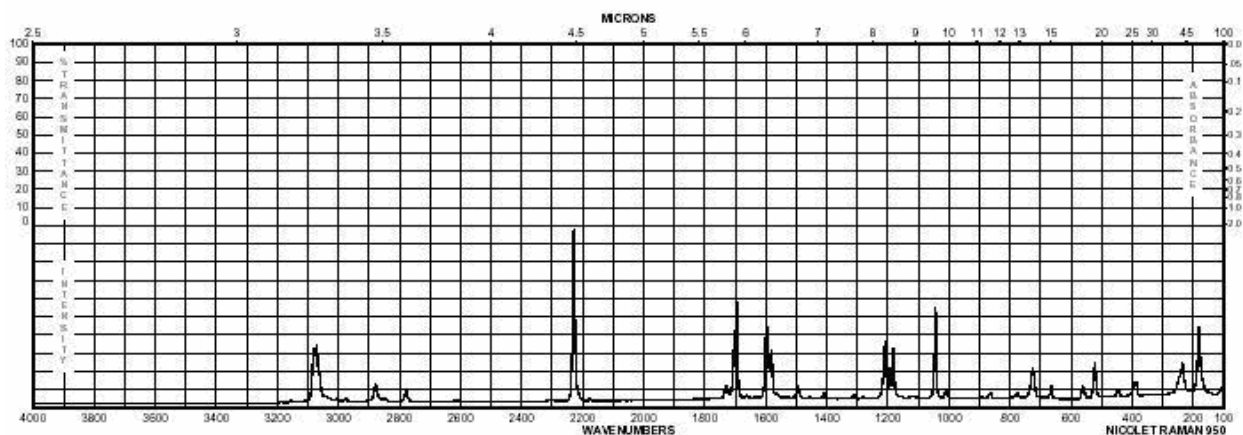Figure 4. FT-Raman spectra of 2-formyl benzonitrile

C-H Stretching

In higher frequency region almost all vibrations belong to C-H stretching. In the present study the C-H stretching vibration of the 4-methyl 3-nitrobenzonitrile are calculated in the range 3075-3066 cm^{-1}, and the corresponding band in 2-formyl benzonitrile are calculated in between 3086-3052 cm^{-1}. In case of 2-formyl benzonitrile one intense IR peak appears due to the C-H stretching in formyl group and theirs corresponding Raman intensity is weak or almost negligible so C-H bond is electrovalent in nature. As it can see that C-H stretching vibrational frequencies of 4-methyl 3-nitrobenzonitrile are at some higher value than 2-formyl benzonitrile. This can be possibly due to the presence of meta directing NO$_2$ which creates deficiency of electron at meta position and hence the ring carbon extracts electron from the hydrogen atom and it reduces the bond strength of C-H. This effect does not occur in case of 2-formyl benzonitrile because of the presence of formyl group at meta-position of the benzene ring. Some in plane bending vibrations of C-H are calculated between 1573-1025 cm^{-1} and out of plane bending between 1003-435 cm^{-1} in 4-methyl 3-nitrobenzonitrile however, in 2-formyl benzonitrile these modes are obtained between 1719-1024 cm^{-1} and 993-777 cm^{-1} respectively and match well.

Methyl Group Vibrations

The CH$_3$ antisymmetric stretching vibrations are generally observed in the region 2940-2980cm^{-1}, while the symmetric stretching vibrations are generally observed between 2850-2890 cm^{-1} [38]. But as seen in Table 1 the CH$_3$ asymmetric stretching vibrations is calculated at 3047 cm^{-1} for B3LYP method, whereas, CH$_3$ symmetric stretching vibrations are also calculated at 2793 cm^{-1}, 2710 cm^{-1} for B3LYP method which is less than the actual value, because cyano group has a vacant antibonding molecular orbital which is nearer to the carbon of nitrile group and therefore, carbon pulls the electron of aromatic ring which directly affects the C-C bond of methyl group and hence, it reduces the bond strength of C-H. So, corresponding frequency is less than the observed value. The bands corresponding to different plane and out of plane bending vibrations of CH$_3$ group are summarized in Table 3.

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Table 3: Vibrational wave numbers and IR intensities of 4- methyl 3-nitrobenzonitrile and 2-formylbenzonitrile at   B3LYP/6-311+(2df,2p)

S.No.	Scaled frequencies Of 4-methyl 3-nitrobenzonitrile 6-311+G(2df,2p)	Approximate mode description of 4-methyl 3-nitrobenzonitrile	Scaled frequencies of 2-formyl-benzonitrile 6-311+G(2df,2p)	Raman data of 2-formyl benzonitrile	IR data of 2-formyl benzonitrile	Approximate mode description of 2-formyl benzonitrile
1	3075.88(43.796)	ν(C-H)	3086(3.70)		3108	ν(C-H)
2	3068.79(78.729)	ν(C-H)	3077(5.99)			ν(C-H)
3	3066.23(8.816)	ν(C-H)R	3065(2.138)		3039s, 3085s	ν(C-H)
4	3053.23(10.925)	ν$_a$CH(in CH$_3$)	3052(2.334)		3072s	ν(C-H)
5	2798.70(338.496)	ν$_s$(CHin CH$_3$)	2787(105.409)		2857	νsym(CH
6	2715.52(381.496)	ν(CHin CH$_3$)	2245(6.568)		2267s, 2228s	ν(C≡N)
7	2149.50(111.7)	ν(C≡N)	1719(212.41)			ν(C=O)+ β (CH) R
8	1573.84(18.932)	ν(C-C)R+β(C-C-C)R+β(C-H)R+S(CH$_3$)	1574(5.119)		1600	ν(CC)R+ β (CH) R
9	1493.25(69.215)	νa(NO$_2$)+ γ(C-C)R+β(C-C- H) +β(C-C-C)R +ν(C-C)R	1545(24.431)))		1579s, 1585s	ν(CC)R+ β (CH) R
10	1474.37(337.64)	β (C-C)+β(C-H)+ νa(NO$_2$) +ν(C-C)R	1461(14.282)		1495m, 1500s	ν(CC)R+β (CH) R
11	1433.45(57.746)	β (C-H)R+S(CH$_3$)	1426(1.943)		1454s, 1408w	β (CH) R+ring bending
12	1399.33(121.1)	β(C-C-C)R + β(C-H)R+S(CH$_3)$ +ν(C-C)R	1374(4.954)		1398s	s(CHO) + β (CH)R
13	1342.30(16.698)	S (NO$_2$)+ β(C-H)R+ γ(CH)+ β(C-C-C)R+ν(C- NO$_2$)R	1284(25.301)			β (CH)R
14	1328.65(8.170)	β (C-C-C)R+ β(C-H)+ γ(NO$_2$)	1248(1.228)		1228vs, 1214s	β (CH) R + ν(CC)R
15	1314.72(11.957)	β (C-H)$_+$ β(C-C-C)R	1170(58.405)		1188w, 1179vs	β (CH) R + ν(CC)R
16	1260.61(21.439)	S(CH$_3$)	1169(2.248)			β (CH)R + β(C-C-C)R + ν (C-CN)

17	1242.62(43.445)	ν (C-CH₃) + β(C-C-C)R+ β (C-H)+ ν (C-CN)	1148(.325)			β (CH) R + ν(CC)R
18	1199.81(16.469)	β(C-C-C)R+ β(C-H)+ S (CH₃)	1090(6..512)		1062w, 1057s	β (CH)R + β(C-C-C)R
19	1177.67(65.733)	S(CH₃)+ ring bending + β(C-H)R+ν (C-CH₃)	1024((.985)			β (CH)R + β(C-C-C)R
20	1169.51(138.564)	β (C-H)+S(CH₃)	992(.503)		993m	γ(CCC)R + γ(C-H inCHO)
21	1113.43(399)	β (C-H)R+ ring twist+ S(CH₃)	988(.356)			γ(CH)R + γ(CCC)R + γ(C-H inCHO)
22	1025.16(32.283)	β(C-C-C)R+ β(CH)R +ν(C- NO₂)R	955(1.341)		979sn	γ (CH) R
23	1003.86(..3251)	γ (C-C-C)R + γ (CH)R	875(.17.3)	864w	874vs	γ (CH) R
24	916.512(70.0951)	ring breathing+ γ (CH)R	843(27.6713)			γ (C-C-N) + ν(C-CHO) + β(C-C-C)R
25	915.873(52.694)	γ(C-H)R	788(53.863)	778s	777vs	γ (CH)R
26	892.675(61.265)	γ (C-C-C)R+ γ (C-CH₃) + γ(CH)R	749(5.083)	728vs	732s	γ(CCC),+ γ(CCN
27	855.901914.470)	β (C-C-C)R+ β(CH)R + S (NO₂)+ ν(C-NO₂)	736(14.809)			ip ring def
28	808.719(11.576)	γ (C-C-C)R + γ (CH)R	677(15.247)	662s		ip ring def
29	785.468(2.4032)	γ(C-H)R+ β(C-C-C)R + γ (C-NO₂)+ β(CH)R	585(4.628)	557s		γ(CC N) + γ(ring bend)
30	735.30(7.4689)	S(NO₂)+ ring breathing	568(.3786)	529s	539m	β(CCC)R + β(CC N))
31	672.642(4.953)	γ (C-C-C)R+ γ(CH)R+ γ(CH₃)+ β(NO₂)	527(1.827)			ip ring def + γ (C-C-N)
32	660.381(.88350	ω(NO₂)+ ring breathing	462(6.057)	444vs	462vs	C-N rocking + oop ring bend
33	622.329(9.854)	γ (C-C-C)R+ γ(C-CN)R + γ(C-NO₂)	397(2.289)			ring wag
34	612.915(5.0480	γ(C-CN)₊ ring bending	393(.194)			γ(CHO)+ γ(CH) + C-N rocking
35	551.221(.439)	γ(C-CN)₊ ring bending	231(2.969)	235		oop ring bend + CN tors + CHO bend
36	454.660(5.240)	γ (C-C-C)R+ γ(CH)R	226(15.108)			ring tors
37	416.0(.6915)	β(C-CH₃)₊ γ(C-CN)	157(.229)			CHO tors + oop.ring bend + ring tors
38	397.743(2.805)	β(C-CH₃)₊ β(C-C-C)R	152(6.4615)			CHO tors + oop.ring bend

39	307.011(.2856)	γ(C-CN) +γ (C-C-C)R	72(1.494)			ring tors + ring bend
40	297.489(13.067)	ring bending				
41	260.627(9.009)	γ (C-C-C)R				
42	203.954(5.038)	ω(NO₂)				
43	155.8098.634)	γ(C-CH₃)				
44	124.580(9.204)	β(C≡N)				
45	97.680(9.5291)	r(CH₃				
46	78.538.0698)	r(CH₃)₊ γ (C-C-C)R				
47	78.9521(6.668)	ring bending				
48	43.8926(.0647)	ring bending + β(NO₂)				

Note :   Abbreviations used here have following meaning
□: stretching; □ₛ, sym: symmetric stretching; □ₐₛ: asymmetric stretching; β,ip:in plane bending; □, tors: torsion; R: Ring;. γ ,oop;out of plane bending ,s,scissoring . w, wag, wagging;def, deformation; w, weak; vs, very strong; s, strong; m, middle; sh, shoulder

C-C Ring Vibrations
The ring C-C stretching vibration in 4-Methyl 3-nitrobenzonitrile are calculated at 1573, 1474 and 1433 cm^{-1} which are in approximately good agreement with the calculated frequencies of 2-formyl benzonitrile at 1573, 1545 and 1461 cm^{-1}. Some deviation can be noticed due to the activating methyl group attached at fourth position of the ring. The theoretically calculated C-C-C bending modes and C-C torsional modes have been found to be consistent with the recorded spectral values.

C-NO₂ and C-CH₃ Vibration
Vibration belonging to bond between ring and other group are important as mixing of vibration is possible due to the presence of heavy atom which shows lower absorption frequencies as compared to C-H, due to the increase reduced mass [39]. C-C stretching in (C-CH3) is calculated at 1242 and 1177 cm^{-1} which is at a higher frequency than the frequency observed in IR-spectra i.e at 1062 cm$^{-1.}$ The frequency in case of (C-CH₃) comes out to be higher in aromatic benzene ring because of the presence of cyano group which increases the bond order between (C-CH₃) group, and hence increases bond strength factor K and consequently there is an increase in the corresponding frequency. In the case of C-CN stretching, calculated at 1245 cm^{-1} in 4-methyl 3-nitrobenzonitrile and 1170 cm^{-1}in 2-formyl benzonitrile, it is observed that it is somewhat shorter in case of 2-formyl benzonitrile because methyl group creates electron excess at ring carbon attached with CN thereby increasing the bond order and hence bond strength.

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C-N Vibrations

The identification of C–N vibrations is a difficult task, since the mixing of vibrations is possible in this region. In this study the C-N stretching vibrations are calculated at 2145 cm^{-1}, which is less than the value calculated at 2245cm^{-1} in case of 2-formyl benzonitrile. This is because cyano group has vacant antibonding molecular orbital and this often reduces the bond order [40, 41], which is more effective than the plane bending created by vander-waal interaction in cyano group and formyl group (oxgen having lone pair electron) in 2-formyl benzonitrile and which is also supported by calculated frequencies of two given molecules.

Some other modes of vibration

At low frequency range almost all the modes of vibrations belong to out of plane bending, rocking and ring torsion. In 4-methyl 3-nitrobenzonitrile, C-CN and C-CH$_3$ plane bending appears in between 612-307 cm^{-1} and 892-155 cm$^{-1,}$ respectively. An out of plane bending is calculated at 297 cm^{-1} in 4-methyl 3-nitrobenzonitrile and a ring wag at 397 cm^{-1} in 2-formyl benzonitrile. At very low frequency, it is very difficult to identify the cause of deviation in the frequency between two derivative compound of benzonitrile because of the anharmonicity [42], incomplete approximation of electron-electron [43] correlation and other interactions which generate perturbation in the frequencies and also the effect of substituent groups attached to the ring.

Other Molecular Properties

Several calculated thermodynamic properties are listed in Table 4. At the room temperature conduction band is almost empty so electronic contribution in total energy is negligible. Thermodynamic parameters clearly indicate that vibration motion plays a crucial role in order to assess the thermo dynamical behavior of title compound. Because all frequencies are real in both the molecules hence, both compounds have stable structure. But 4-Methyl 3-nitrobenzonitrile having less ground state energy (-567.597 a.u) is more stable than 2-formyl benzonitrile (-437.953 a.u). e.g.-As methyl group (σ-Donor) enhances the stability and the nitro group enhance the resonance (canonical) structure of the molecule therefore the molecule is more stable than the previous molecule. This is clearly, indicated by ground state energy of title molecule which is less than 2-formyl benzonitrile. Entropy of 4-methyl 3-nitrobenzonitrile molecule is 107.040 (Cal/Mol-Kelvin) which is greater than entropy of 2-formyl benzonitrile 82.269 (Cal/Mol- Kelvin) and hence more probably 2-formyl benzonitrile has a well ordered structure than 4-methyl 3-nitrobenzonitrile. As seen in Table 4, dipole moment of both molecules are (4-methyl 3-nitrobenzonitrile 6.678D, 2-formyl benzonitrile 7.135D) greater than Benzonitrile (4.18D) so, probably both the molecules can be used as better solvents in chemical industry, biomedical field than BN.

HOMO-LUMO Gap

Presence of methyl group at benzene ring of the 4-methyl 3-nitrobenzonitrile (1.56eV) compound makes it more reactive than 2-formyl benzonitrile (4.79eV). This is also supported by the calculated homo-lumo gap (gap between conduction band and valence band) and the effect on reactivity due to addition of methyl group (electron withdrawing group) on aromatic ring is also seen.

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Table   4: Theoretically computed energies (a.u), zero-point vibrational energies (kcal/mol), entropies (Cal mol^{-1} K^{-1}) and dipole moment (D) for 4-methyl 3-nitrobenzonitrile and 2-formyl benzonitrile

Parameters	4-methyl 3-nitrobenzonitrile	2-formyl benzonitrile
Total energy (thermal)	84.558	72.899
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	82.781	71.122
Total energy	-567.597	-437.953
Entropy		
Total	107.040	89.269
Translational	41.157	40.524
Rotational	30.726	29.326
Vibrational	35.156	19.419
Dipole moment	6.678	7.135

Performance of basis sets

The scaled vibrational signatures using DFT/B3LYP method are presented in this study. It is to be emphasized that the calculated frequencies represent vibrational signatures of the molecules in its gas phase. Hence, the experimentally observed spectra of the solid/liquid samples may differ to some extent from the calculated spectrum. Moreover, the calculated frequencies are usually higher than the corresponding experimental quantities, due to combination of electron correlation effects and basis set deficiencies. This is the reason to use scaling factor for theoretical calculations. As it can be seen in the calculations, scaling factor used in the lower range frequencies is closer to 1 than smaller basis sets. This also shows that calculation done on large basis sets gave more reliable result than the smaller basis set in finger print region. All calculations are done on a single molecule so we ignore inter molecular forces, i.e. van der Waals, molecule-molecule interaction. These interactions produce perturbation in energy levels resulting in the increase or decrease of energy levels. The deviations are found to be (40–4) cm^{-1}. This is quite obvious, since calculated frequencies are harmonic in nature, whereas experimental frequencies may involve anharmonicity. In order to reduce the RMS deviation between the unscaled and the observed fundamental, scaling factors are estimated by using a linear square fitting of calculated experimental wave number.

Conclusion

Considering the fact that the observed frequencies in solid and molten states involve anharmonicity, the comparison is made with the theoretical study in gas phase of the molecules. In the present study, B3LYP hybrid functional, applied to density functional force fields with 6-311+G(2df,2p) basis set most successfully reproduces the vibrational spectra of these disubstituted benzene, though this combination is not quite adequate for the description of the C=O stretching modes, all DFT calculations along with B3LYP functional underestimated the C=O bond lengths, which in turn led to the increase in the force constants and consequently increase in the vibrational wave numbers. A few upshots of the paper are as follows: (i) quantum

chemical calculation helps us to get information about the stability and reactivity of both the molecules; (ii) theoretical mode description makes easy to identify the relatively weak Raman or IR bands more accurately. Furthermore, yet again it is established obviously that the scaled quantum mechanical method in combination of DFT may be used as a reliable tool for the interpretation of vibrational signatures.

As we can see that 2-formyl benzonitrile has low entropy than 4-methyl 3-nitrobenzonitrile so corresponding band of frequency shifts to lower side in case of 2-formyl benzonitrile. ($\upsilon_{gas>}$ υ_{liquid}, $\upsilon_{liquid>}$ υ_{solid}). Shifts in-group of frequencies can also arise in other way depending upon the degree of intermolecular interaction. Some deviations occur due to nature and position of group attached at benzene ring i.e. in the case of given compounds, 2-formyl benzonitrile has a stronger degree of Vander-waal interaction (close proximity between nitrile group and formyl group) than the other compound.

In the case of molecule, 4-methyl 3-nitrobenzonitrile, entropy is more as compared to 2-formyl benzonitrile but, nitro is found in ionic form and formyl is found in liquid form. At the end we, conclude that the state of molecule is affected by other groups and their respective positions in the benzene ring.

Acknowledgements

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