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SCALED QUANTUM CHEMICAL STUDIES OF THE STRUCTURE AND VIBRATIONAL SPECTRA OF 1, 5- DIMETHYLNAPHTHALENEN. Jayamani¹, N. Geetha²¹Dept. of Physics, Vivekanandha College of Arts and Sciences (W), Namakkal, India²Dept of Physics, Bharathiyar Arts and Science College (W), Salem, India

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ABSTRACT

The scaled phase FTIR and FT-Raman spectra of 1,5-dimethylnaphthalene (DMN) has been recorded in the region 4000-400 cm^{-1} and 4000-50 cm^{-1} , respectively. The fundamental vibrational wavenumbers and intensities of vibrational bands are evaluated with the aid of normal coordinate analysis based on density functional theory (DFT) using the standard B3LYP/6-31G** method and basis set combination with scaled quantum mechanical force field. The Infrared and Raman spectra are also predicted from the calculated intensities. Comparison of simulated spectra with the experimental spectra provides important information about the ability of the computational method to describe the vibrational modes.

Keywords: Vibrational spectra, 1,5-dimethylnaphthalene, DFT calculations, Vibrational analysis

INTRODUCTION

The structure of naphthalene is benzene like, having two six membered rings fused together. Naphthalene resembles benzene in many of its reaction altogether, it is mild aromatic but more reactive than benzene. DMN is a relatively new sprout inhibitor for use a maincrop and seed potatoes. No harm is expected to the public, the environment. DMN is used as an intermediate for synthesis of pharmaceuticals, photochemical, plant growth hormones, insecticides dyes and other organic compounds. It is also used as a surfactant; water reducing and dispersant.¹ The department of Health and Human Services [DHS] concluded that naphthalene is reasonably anticipated to be a human carcinogen.²

The vibrational assignments of the compound can be proposed on the basis of wavenumber agreement between the computed harmonics and the observed fundamentals. Quantum chemical computational methods have proven

to be an essential tool for interpretations and prediction of vibrational spectra.^{3,4} A significant advances in this area was made by scaled quantum mechanical (SQM) force field method⁵⁻⁸. In the SQM approach, the systematic errors of the computed harmonic force field are corrected by a few scale factors which were found to be well transferable between chemically related molecules.^{4, 9-11}

In the present study, we extend a probing with the application of the B3LYP/6-31G** (basis set) based on the SQM method¹² to vibrational analysis and deformational stability of DMN. The geometrical parameters of the most optimized geometry obtained were used for the DFT calculations. The Infrared and Raman intensities were also predicted. Based on these calculations, the simulated FTIR and FT-Raman spectra were obtained.

EXPERIMENTAL

The pure crystalline samples of DMN was obtained from Lancaster chemical company, UK, and used without further purification for

the spectral measurements. The room temperature Fourier transform infrared spectra of the title compounds were measured in the region 4000-400 cm^{-1} at a resolution of $\pm 1 \text{ cm}^{-1}$, using BRUKER IFS 66V Fourier transform spectrometer, equipped with MCT detector, a KBr beam splitter and global source. The FT-Raman spectra were recorded on the same instrument with FRA-106 Raman accessories in the region 4000-50 cm^{-1} . The 1064 nm Nd: YAG laser was used as excitation source, and the laser power was set to 200mw.

COMPUTATIONAL DETAILS

The molecular geometry optimization was carried out with the Gaussian 03W program package¹³ at the B3LYP level,^{14,15} supplemented with the standard 6-31G** basis set. The Cartesian representation of the theoretical force constants have been computed at the fully optimized geometry by assuming C_s point group symmetry. Scaling of the force fields were performed by the scaled quantum mechanical procedures with the selective scaling in the local symmetry coordinates representation¹⁶ using transferable scale factors available in the literature.¹² Transformations of the force field and the subsequent normal

$$I_i = \frac{f(\nu_o - \nu_i)^4 S_i}{\nu_i \left[1 - \exp\left(\frac{-hc\nu_i}{kT}\right) \right]} \quad (1)$$

Where ν_o is the exciting wavenumber (in cm^{-1} units), ν_i the vibrational wavenumber of the i^{th} normal mode; h , c and k are fundamental constants; and f is a suitably chosen scale factor for all peak intensities.

RESULT AND DISCUSSION

Molecular geometry: The optimized molecular structure of DMN having C_s

coordinates including the refinement of the scaling factors calculation of potential energy distribution (PED), and the prediction of IR and Raman intensities were done on a PC with the MOLVIB program (version V 7.0-G77) written by Sundius.^{17, 18, 19}

For the plots of simulated IR and Raman spectra, pure Lorentzian band shapes were used with a band width (FWHM) of 10 cm^{-1} . The vibrational modes were assigned by means of visual inspection using the GAUSSVIEW program.²⁰ The symmetry of the molecule was also helpful in making vibrational assignments. The symmetries of the vibrational modes were determined by using standard procedure^{4, 12} of decomposing the traces of the symmetry operations into the irreducible representations. The analysis for the vibrational modes of DMN is presented in some details in order to better describe the basis for the assignments.

Prediction of Raman intensities: The Raman activities (S_i) calculated with the GAUSSIAN-98 program and adjusted during the scaling procedure with MOLVIB were converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering.^{21, 22, 23}

symmetry is shown in fig.1. The global minimum energy obtained by DFT structure optimization for DMN is calculated as 464.5443 Hartrees. The optimized geometrical parameters obtained in this study for DMN is presented in Table 1.

Detailed description of vibrational modes can be given by means of normal coordinate analysis (NCA). For this purpose the full set of 89 standard internal coordinates containing 23

redundancies for DMN was defined in Table 2. From this, a nonredundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates following the recommendations of Fogarasi and Pulay^{7, 16} is summarized in Table 3.

Vibrational spectra

The 66 normal modes of DMN is distributed amongst the symmetry species as

$$\Gamma_{\text{vib}} = 45A' \text{ (in-plane)} + 21A'' \text{ (out-of-plane)}$$

In agreement with C_s symmetry. All vibrations are active in both the Raman scattering and Infrared absorption. In Raman spectrum the A' vibrations give rise to polarized bands while the A'' to depolarized bands.

The detailed vibrational assignments of fundamental modes of DMN along with observed and calculated wavenumbers, IR and Raman intensities and normal mode dichroisms (characterized by PED) is reported in Table 4. For visual comparison, the observed and simulated FTIR and FT-Raman spectra of the title compound is presented in Figs.2-3 which helps to understand the observed spectral features. They are convenient to discuss the vibrational spectra of DMN in terms of characteristic spectral regions as described below.

Methyl Group vibrations: For the assignments of CH_3 group wavenumbers, basically nine fundamentals can be associated to each CH_3 group namely, CH_3 ss – symmetric stretch; CH_3 ips – in-plane stretch (i.e. in-plane hydrogen stretching modes); CH_3 ipb – in-plane bending (i.e. in-plane hydrogen deformation modes); CH_3 sb – symmetric bending; CH_3 ipr – in-plane rocking; CH_3 opr – out-of-plane rocking; $t\text{CH}_3$ – twisting hydrogen bending modes. In addition to that, CH_3 ops – out-of-plane-stretch and CH_3 opb – out-of-plane bending modes of CH_3 group would be

expected to be depolarized for A'' symmetry species. The CH_3 ss wavenumbers are established at 2897 cm^{-1} and 2923 cm^{-1} in IR and CH_3 ips are assigned at 2945 cm^{-1} and 2965 cm^{-1} in IR for DMN. These assignments are also supported by literature²⁴ in addition to PED output.

The four in-plane methyl hydrogen deformation modes are also well established. We have observed the symmetrical methyl deformation modes CH_3 sb at 1447 cm^{-1} and 1438 cm^{-1} in IR and in-plane methyl deformation modes CH_3 ipb at 1471 cm^{-1} and 1453 cm^{-1} in IR. The bands at 2863 cm^{-1} and 2845 cm^{-1} in IR and 1401 cm^{-1} and 1382 cm^{-1} in IR are attributed to CH_3 ops and CH_3 ipb respectively in the A'' species. The methyl deformation modes mainly coupled with in-plane bending vibrations. The bands obtained at 1066 cm^{-1} , 1036 cm^{-1} and 1016 cm^{-1} , 977 cm^{-1} in IR are assigned to CH_3 in-plane and out-of-plane rocking modes. The assignment of the bands at 115 cm^{-1} and 119 cm^{-1} in Raman are attributed to methyl twisting modes

C-H vibrations: Aromatic compounds commonly exhibit multiple weak bands in the region $3100\text{-}3000 \text{ cm}^{-1}$ due to C-H stretching vibrations. The bands due to C-H in-plane bending vibrations interact somewhat with C-C stretching vibrations, are observed as a number of bands in the region $1500\text{-}1100 \text{ cm}^{-1}$. The C-H out-of-plane bending vibrations occur in the region $1000\text{-}700 \text{ cm}^{-1}$ ^{25, 26}. Hence, in the present investigation, the FTIR bands identified at 3081 cm^{-1} , 3069 cm^{-1} , 3066 cm^{-1} , 3035 cm^{-1} , 3026 cm^{-1} , and 3011 cm^{-1} are assigned to C-H stretching vibrations of DMN. The FTIR bands at 1423 cm^{-1} , 1409 cm^{-1} , 1261 cm^{-1} , 1202 cm^{-1} , 1170 cm^{-1} and FT-Raman band at 1262 cm^{-1} are assigned to C-H in-plane bending vibrations of DMN. The C-H out-of-plane bending vibrations of the title compound are well identified in the recorded spectra, within their characteristic region.

Ring vibrations: .In the present study, the bands appeared at 864, 863, 803, 586, 564, 528, 512, 440, 410, 380, 332, 270, 219, 208, 195 and 63 cm^{-1} are assigned to ring in-plane and out-of-plane bending modes, respectively by careful considerations of their quantitative descriptions. Small changes in wave numbers observed for these modes are due to changes in the force constant/reduced mass ratio, resulting mainly due to addition of two methyl groups to DMN and from different extents of mixing between ring and substituent group vibrations.

CONCLUSION

The FTIR and FT-Raman spectra have been recorded and the detailed vibrational assignment is presented for DMN. The equilibrium geometries, harmonic vibrational frequencies, IR and Raman spectra was performed according to the SQM force field method based on DFT calculations at the B3LYP/6-31G** level. The difference between corresponding wavenumbers (observed and calculated) is very small for most of fundamentals. Therefore, the results presented in this work for DMN indicate that the level of theory is reliable for prediction of Infrared and Raman spectra of the title compound (DMN).

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Table 1: Optimized geometrical parameters of 1,5 dimethylnaphthalene(DMN) obtained by B3LYP/6-31G density functional calculations**

Bond length	Value (Å)	Bond angle	Value (°)
	DMN		DMN
C1-C2	1.380	C1-C2-C3	121.458
C2-C3	1.412	C2-C3-C4	120.356
C3-C4	1.374	C3-C4-C5	120.774
C4-C5	1.422	C6-C5-C4	121.712
C5-C6	1.434	C7-C6-C5	119.083
C6-C7	1.380	C8-C7-C6	121.497
C7-C8	1.412	C9-C8-C7	120.345
C8-C9	1.374	C10-C9-C8	120.762
C9-C10	1.421	C10-C1-C11	120.831
C1-C11	1.518	C1-C2-H12	119.280
C2-H12	1.086	C2-C3-H13	119.516
C3-H13	1.086	C3-C4-H14	119.703
C4-H14	1.084	C5-C6-C15	120.844
C6-C15	1.510	C6-C7-H16	119.261
C7-H16	1.086	C7-C8-H17	119.515
C8-H17	1.086	C8-C9-H18	119.710
C9-H18	1.084	C1-C11-H19	111.819
C11-H19	1.096	C1-C11-H20	111.819
C11-H20	1.096	C1-C11-H21	110.655
C11-H21	1.092	C6-C15-H22	111.818
C15-H22	1.096	C6-C15-H23	111.818
C15-H23	1.096	C6-C15-H24	110.657
C15-H24	1.092		

For numbering of atoms refer figure.1

** represents polarization functionals of Basis sets

Table 2 Definition of internal coordinates of 1, 5, dimethylnaphthalene (DMN)

No.(i)	Symbol	Type	Definition
Stretching			
1-6	r_i	C-H	C2-H12, C3-H13, C4-H14, C7-H16, C8-H17, C9-H18.
7-12	r_i	C-H (methyl)	C11-H19, C11-H20, C11-H21, C15-H22, C15-H23, C15-H24.
13-23	R_i	C-C	C1-C2, C2-C3, C3-C4, C4-C5, C5-C10, C10-C1, C9-C10, C5-C6, C6-C7, C7-C8, C8-C9.
24-25	R_i	C-C (methyl)	C1-C11, C6-C15.
Bending			
26-31	\square_i	Ring 1	C1-C2-C3, C2-C3-C4, C3-C4-C5, C4-C5-C10, C5-C10-C1, C10-C1-C2
32-37	β_i	Ring 2	C9-C10-C5, C10-C5-C6, C5-C6-C7, C6-C7-C8, C7-C8-C9, C8-C9-C10.
38-49	\square_i	C-C-H	C1-C2-H12, C3-C2-H12, C2-C3-H13, C4-C3-H13, C3-C4-H14, C5-C4-H14, C6-C7-H16, C8-C7-H16, C7-C8-H17, C9-C8-H17, C8-C9-H18, C10-C9-H18.
50-55	\square_i	C-C-H (methyl)	C1-C11-H19, C1-C11-H20, C1-C11-H21, C6-C15-H22, C6-C15-H23, C6-C15-H24
56-61	δ_i	H-C-H	H19-C11-H20, H19-C11-H21, H20-C11-H21, H22-C15-H23, H23-C15-H24, H22-C15-H24
62-65	\square_i	C-C-C	C10-C1-C11, C2-C1-C11, C5-C6-C15, C7-C6-C15
Out of plane bending			
66-71	\square_i	C-H	C1-C2-C3-H12, C2-C3-C4-H13, C3-C4-C5-H14, C6-C7-C8-H16, C7-C8-C9-H17, C8-C9-C10-H18.
72-73	\square_i	C-C	C10-C1-C2-C11, C5-C6-C7-C15.
Torsion			
74-79	Ψ_i	$\square\square$ Ring 1	C1-C2-C3-C4, C2-C3-C4-C5, C3-C4-C5-C10, C4-C5-C10-C1, C5-C10-C1-C2, C10-C1-C2-C3.
80-85	\square_i	\square Ring 2	C9-C10-C5-C6, C10-C5-C6-C7, C5-C6-C7-C8, C6-C7-C8-C9, C7-C8-C9-C10, C8-C9-C10-C5
86-87	\square_i	\square CH3	(C2,C10)-C1-C11-(H19,H20,H21), (C5,C7)-C6-C15-(H22,H23,H24)
88-89	\square_i	Butterfly	C1-C10-C5-C6, C9-C10-C5-C4

For numbering of atoms refer figure.1

Table 3 Definition of local symmetry coordinates of 1, 5-dimethyl naphthalene

No. (i)	Symbol ^a	Definition ^b
1-6	CH	$r_1, r_2, r_3, r_4, r_5, r_6$
7-8	CH3ss	$(r_7+r_8+r_9)/\sqrt{3}, (r_{10}+r_{11}+r_{12})/\sqrt{3}$
9-10	CH3ips	$(2r_7-r_8-r_9)/\sqrt{6}, (2r_{10}-r_{11}-r_{12})/\sqrt{6},$
11-12	CH3ops	$(r_8-r_9)/\sqrt{2}, (r_{11}-r_{12})/\sqrt{2}$
13-25	CC	$R_{13}, R_{14}, R_{15}, R_{16}, R_{17}, R_{18}, R_{19}, R_{20}, R_{21}, R_{22}, R_{23}, R_{24}, R_{25}$
26	R1trigd	$(\beta_{26}-\beta_{27}+\beta_{28}-\beta_{29}+\beta_{30}-\beta_{31})/\sqrt{6}$
27	R1symd	$(-\beta_{26}-\beta_{27}+2\beta_{28}-\beta_{29}-\beta_{30}+2\beta_{31})/\sqrt{12}$
28	R1asymd	$(\beta_{26}-\beta_{27}+\beta_{29}-\beta_{30})/\sqrt{2}$
29	R2trigd	$(\beta_{32}-\beta_{33}+\beta_{34}-\beta_{35}+\beta_{36}-\beta_{37})/\sqrt{6}$
30	R2symd	$(-\beta_{32}-\beta_{33}+2\beta_{34}-\beta_{35}-\beta_{36}+2\beta_{37})/\sqrt{12}$
31	R2asymd	$(\beta_{32}-\beta_{33}+\beta_{35}-\beta_{36})/\sqrt{2}$
32-37	bCH	$(\alpha_{38}-\alpha_{39})/\sqrt{2}, (\alpha_{40}-\alpha_{41})/\sqrt{2}, (\alpha_{42}-\alpha_{43})/\sqrt{2}, (\alpha_{44}-\alpha_{45})/\sqrt{2},$ $(\alpha_{46}-\alpha_{47})/\sqrt{2}, (\alpha_{48}-\alpha_{49})/\sqrt{2}$
38-39	CH3sb	$(-\alpha_{50}-\alpha_{51}-\alpha_{52}+\delta_{53}+\delta_{54}+\delta_{55})/\sqrt{6}, (-\alpha_{56}-\alpha_{57}-$ $\alpha_{58}+\delta_{59}+\delta_{60}+\delta_{61})/\sqrt{6},$
40-41	CH3ipb	$(-\delta_{53}-\delta_{54}-2\delta_{55})/\sqrt{6}, (-\delta_{59}-\delta_{60}-2\delta_{61})/\sqrt{6},$
42-43	CH3opb	$(\delta_{53}-\delta_{54})/\sqrt{2}, (\delta_{59}-\delta_{60})/\sqrt{2},$
44-45	CH3ipr	$(2\alpha_{50}-\alpha_{51}-\alpha_{52})/\sqrt{6}, (2\alpha_{56}-\alpha_{57}-\alpha_{58})/\sqrt{6},$
46-47	CH3opr	$(\alpha_{51}-\alpha_{52})/\sqrt{2}, (\alpha_{57}-\alpha_{58})/\sqrt{2},$
48-49	bCC	$(\theta_{62}-\theta_{63})/\sqrt{2}, (\theta_{64}-\theta_{65})/\sqrt{2}$
50-55	ω CH	$\omega_{66}, \omega_{67}, \omega_{68}, \omega_{69}, \omega_{70}, \omega_{71}$
56-57	ω CC	$\Psi_{72}, \Psi_{73},$
58	tR1trig	$(\tau_{74}-\tau_{75}+\tau_{76}-\tau_{77}+\tau_{78}-\tau_{79})/\sqrt{6}$
59	tR1sym	$(\tau_{74}-\tau_{76}+\tau_{77}-\tau_{79})/\sqrt{2}$
60	tR1asym	$(-\tau_{74}+2\tau_{75}+\tau_{76}-\tau_{77}+\tau_{78}-\tau_{79})/\sqrt{12}$
61	tR2trig	$(\tau_{80}-\tau_{81}+\tau_{82}-\tau_{83}+\tau_{84}-\tau_{85})/\sqrt{6}$
62	tR2sym	$(\tau_{80}-\tau_{82}+\tau_{83}-\tau_{85})/\sqrt{2}$
63	tR2asym	$(-\tau_{80}+2\tau_{81}-\tau_{82}-\tau_{83}+2\tau_{84}-\tau_{85})/\sqrt{12}$
64-65	tCH3	τ_{86}, τ_{87}
66	Butterfly	$(\tau_{88}-\tau_{89})/\sqrt{2}$

^a These symbols are used for description of the normal modes by PED in Table 4.

^b The internal coordinates used here are defined in Table 2.

Table 4 Detailed assignment of fundamental vibrations of 1, 5 dimethylnaphthalene(DMN) by normal mode analysis based on SQM force field calculations

Sl. No	Symmetry species C _s	Observed wavenumbers cm ⁻¹		Calculated wavenumbers B3LYP/6-31G** force field cm ⁻¹		IR Intensity	Raman Activity	Characterization of normal modes with PED (%)
		FT IR	Raman	unscaled	scaled			
1	A'	3081	-	3214	3068	0.200	0.167	CHs(99)
2	A'	3069	-	3213	3067	0.280	0.353	CHs(99)
3	A'	3066	-	3191	3046	0.003	0.705	CHs(99)
4	A'	3035	-	3191	3046	0.972	1.705	CHs(99)
5	A'	3026	-	3175	3030	0.209	2.410	CHs(99)
6	A'	3011	-	3174	3030	0.375	0.009	CHs(99)
7	A'	2965	-	3127	2947	4.797	0.026	CH ₃ ips(99)
8	A'	2945	-	3127	2947	0.001	5.203	CH ₃ ips(99)
9	A''	2923	-	3089	2911	0.180	3.402	CH ₃ ss(100)
10	A''	2897	-	3089	2911	1.260	5.808	CH ₃ ss(100)
11	A'	2863	-	3036	2861	0.039	1.187	CH ₃ ops(100)
12	A'	2845	-	3036	2861	1.820	0.545	CH ₃ ops(100)
13	A'	-	1628	1672	1627	1.464	5.788	CCs(59), bCH(14), bR1asy(14)
14	A'	1597	-	1656	1597	2.105	8.906	CCs(61), bCH(24)
15	A'	-	1587	1640	1563	1.238	1.165	CCs(67), bCH(14), bR2 sym (10)
16	A'	1509	-	1562	1493	2.299	0.087	CCs(56), bCH (31)
17	A'	-	1471	1522	1463	0.004	31.735	CCs(46), bCH(27), bHCH(18),

18	A'	1453	-	1512	1454	0.010	5.715	CH ₃ ipb (42), bCH(24), CCs(20),
19	A'	1447	-	1507	1541	2.385	1.121	CH ₃ ipb(83), bCH _m (13)
20	A''	1438	-	1498	1436	58.437	0.090	CH ₃ sb(86), bCH _m (14)
21	A''	1423	-	1498	1436	2.027	2.864	CH ₃ sb(86), bCH _m (13)
22	A'	1409	-	1451	1407	0.907	1.342	bCH(39), CCs(32), CC _{ms} (11)
23	A'	-	1401	1446	1386	0.435	0.282	bCH(33), bHCH(28), CCs(23)
24	A'	1382	-	1427	1378	0.041	0.152	CH ₃ opb(48), bHCH(45)
25	A'	-	1378	1426	1378	0.013	3.11	CH ₃ opb(49), bHCH(39)
26	A'	1335	-	1399	1333	0.793	0.748	CCs(84)
27	A'	-	1262	1381	1321	0.304	15.834	CCs(61), bCH(17)
28	A'	1261	-	1288	1261	1.974	0.753	bCH(42), br1tri(19), CCs(14), CC _{ms} (13)
29	A'	1208	-	1263	1224	2.398	1.287	bCH(45), CCs(29), CC _{ms} (18)
30	A'	1202	-	1247	1197	0.217	0.360	CCs(64), bCH(25)
31	A'	1170	-	1202	1170	2.149	0.156	bCH(50), CCs(27)
32	A'	1164	-	1201	1161	5.963	0.329	bCH(66), CCs(25)
33	A'	1126	-	1164	1132	0.049	9.293	CCs(20), bR2tri(19), CC _{ms} (19), bCH(17), bR1tri(13)
34	A'	1068	-	1126	1079	0.068	8.226	CCs(44), bCH(25), bCH _m (24)
35	A'	1066	-	1096	1048	0.604	4.410	CCs(68), bCH(15)
36	A''	1036	-	1065	1032	1.930	3.682	CH ₃ ipr(82)
37	A''	1016	-	1064	1021	2.055	0.155	CH ₃ ipr(79)
38	A'	-	1006	1035	999	0.037	4.700	CH ₃ opr(68), CCs(11)
39	A'	977	-	1006	997	1.163	0.194	ωCH(82)

40	A'	976	-	977	974	0.805	14.883	CH3opr(69), CC(p3),
41	A'	915	-	976	927	0.197	144.379	ω CH(90)
42	A''	903	-	915	886	0.091	35.299	ω CH (83)
43	A''	875	-	903	874	0.703	0.775	ω CH(85)
44	A'	864	-	892	873	0.854	45.041	CC _m s(29), CCs(24), bR1asy(12), bR2sym(11)
45	A'	863	-	864	848	17.638	3.228	bR1trig(25), CC _m s(20), CCs(20), bCHm(12)
46	A''	820	-	820	821	2.727	33.339	tR2tri(59), ω CH (18)
47	A''	803	-	808	791	8.922	10.330	ω CH(83)
48	A'	789	-	798	786	17.425	0.176	bR2tri(39), bR2asy(19), CCs(15), bR1asy(10)
49	A''	751	-	751	736	0.049	4.050	ω CH(88),
50	A''	-	635	645	631	0.090	25.728	CC _m s(48), bR2asy(18), bR1asy(15), CCs(13)
51	A'	586	-	643	601	8.592	3.550	tButterfly(26), ω CC _m (22), ω CH(11) , tR1tri(11)
52	A''	564	-	583	555	0.094	91.761	tR1ti(45), tR2asy(19), ω CH(13),
53	A'	-	528	535	533	13.471	1.154	bR2sym(39), CCs(22), bR1asy(13)
54	A'	512	-	519	503	1.019	7.249	bR1asy(22), bR2sym(19), CCs(15), bR2asy(11), bR1sym(10)
55	A'	480	-	493	470	59.064	0.101	bR2asy(40) ,bCC _m (21), CCs(10), bCH _m (10)
56	A''	-	440	481	448	0.018	338.463	tR1sym(32), tR2sym(27), ω CC _m (25)
57	A''	-	410	467	423	0.642	149.279	bR1sym(74), CCs(10)

58	A'	-	380	466	381	38.443	2.494	tR2asy(22), ω CC _m (21), tR1asy(16), ω CH(15), tR1tri(15)
59	A'	-	332	333	296	24.020	45.070	bCC _m (81)
60	A''	-	270	271	253	12.380	87.425	ω CC _m (35), tR1sym(17), tR2sym(13), tButterfly(11)
61	A'	-	219	262	249	23.209	8.734	bCC _m (70), bR2asy(11)
62	A''	-	208	208	189	1.206	154.041	tR2sym(29), tR2asy(21), ω CC _m (15), ω CH (15)
63	A''	-	195	195	163	7.562	248.034	CC _m ω (22), tR1asy(21), tR1sym(18), CH ω (13)
64	A''	-	189	189	119	35.354	54.678	tCH3(96)
65	A''	-	88	168	115	36.362	3.204	tCH3(84)
66	A''	-	63	97	74	0.416	276.227	tR1asy(54), tR2asy(14)

Abbreviations; R, ring; ss, symmetric stretching; ass, antisymmetric stretching; ips, in-plane stretching; ops-out-of-plane stretching; b, bending; sb, symmetric bending; ipb, in-plane bending; opb, out-of-plane bending; ipr, in-plane rocking; opr, out of plane rocking; d, deformation; sym, symmetric; asy, asymmetric; ω , wagging; t, torsion; trig, trigonal; s, stretching. Only contributions larger than 10% are given.

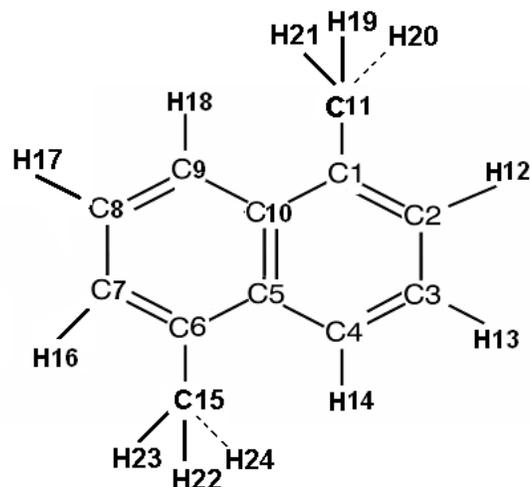


Fig.1. Molecular model of 1, 5-dimethylnaphthalene along with numbering of atoms

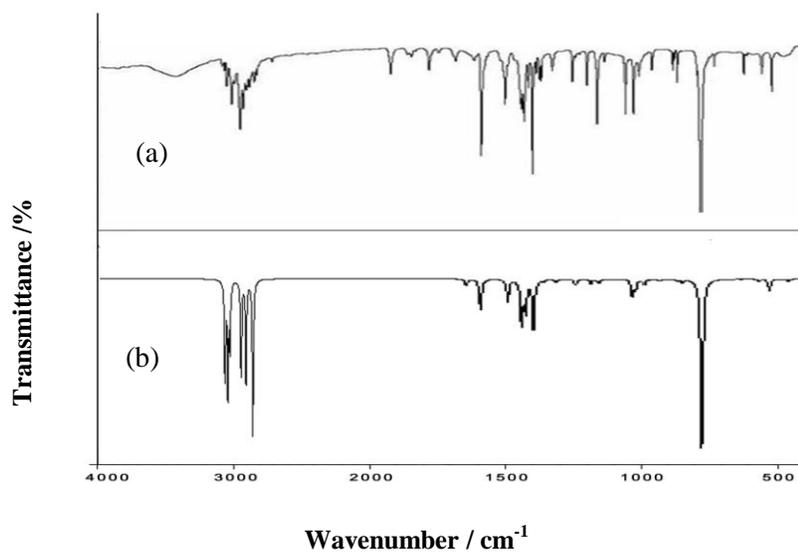


Fig.2. FTIR spectra of 1, 5-dimethylnaphthalene (DMN) (a) Observed and (b) Calculated

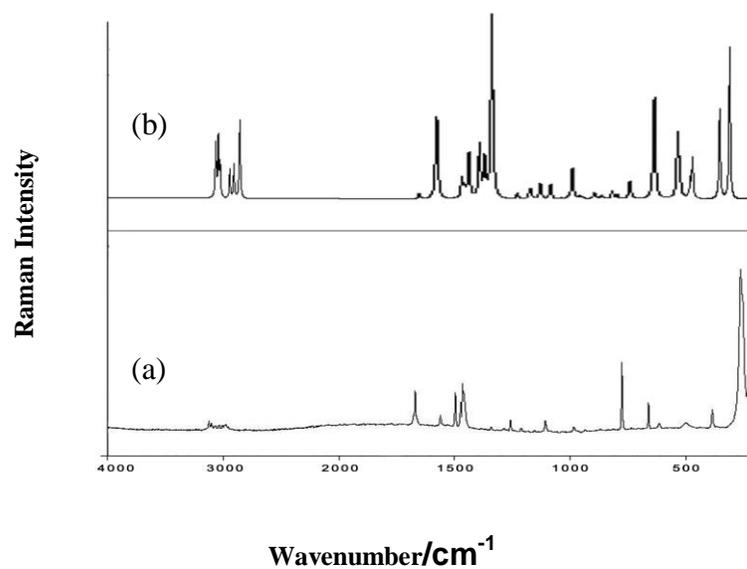


Fig.3. FT-Raman spectra of 1, 5-dimethylnaphthalene (DMN) (a) Observed (b) Calculated

The spectra were interpreted based on density functional theory calculation with B3LYP method and 6-31G** basis set have been carried out to obtain the optimized geometrical parameters, Force fields and prediction of intensities and including scaled quantum mechanical force field.

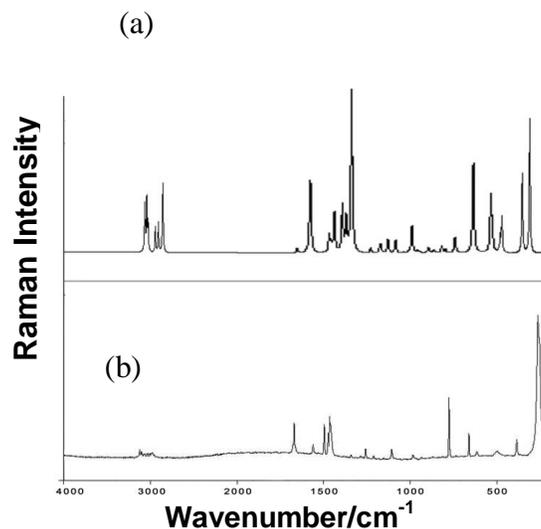


Figure 4: FT-Raman spectra of 1,5-dimethylnaphthalene(DMN)
(a) Observed (b) Calculated with B3LYP/6-31G**.