Vibrational Spectroscopic Studies of Tetralin

R. Ramasamy and V. Prabhakaran

Department of Physics, National College (Autonomous),
Trichy – 620 001, Tamil Nadu, India.
E-mail: ramasamy_ty@yahoo.co.in

Abstract

The molecular vibrations of Tetralin was investigated by FT-IR and FT-Raman spectroscopies. Normal coordinate calculations of Tetralin have been carried out using Wilson's FG matrix mechanism on the basis of General Valence Force Field (GVFF) for both in-plane and out-of-plane vibrations. The potential energy constants obtained in this study are refined using numerical methods.

Key Words: FT-IR, FT-Raman, Tetralin, normal coordinate analysis, Potential energy distribution.

1. Introduction

Tetralin is a hydrocarbon having the chemical formula $C_{10}H_{12}$. This molecule is similar to the napthalene chemical structure except that one ring is saturated. Tetralin is used as a solvent. Normal coordinate analysis of Tetralin compound was carried out to obtain a more complete description of the molecular vibrations involved in the fundamental vibrations of Tetralin.

In the present paper, an effort has been made to record spectra and to assign the observed fundamental modes of vibrations. The evaluation of potential energy constant has been made on the basis of General Valence Force Field (GVFF) by applying Wilson's FG matrix mechanism [1].

2. Experimental Methods

Pure chemical of Tetralin is obtained from Lancaster chemical company, England and used as such without any further purification. The FT-IR spectrum of Tetralin was recorded in the region 4000-400 cm^{-1} using KBr pellet. The Bruker IFS 66V model FT-IR spectrometer was used for the spectral measurements. The globar and mercury are sources, KBr beam splitters are used while recording FT-IR spectrum of the title compound.

The FT-Raman spectrum was recorded on a Bruker IFS 66V model interferometer equipped with an FRA-106 FT-Raman accessory the spectrum was recorded in the stokes region (4000-100cm^{-1}) using the 1064 nm line of a Nd:YAG laser for excitation operating at 200 mW of power.

3. Results and Discussion
3.1. Structure and Symmetry
The molecular structure of Tetralin is shown in Fig. 1. From the structural point of view the molecule is assumed to have C_s point group symmetry. The 60 fundamental modes of vibrations arising for this molecule are distributed into 41 A′ and 19 A″ species. The A′ and A″ species represent the in-plane and out-of-plane vibrations.
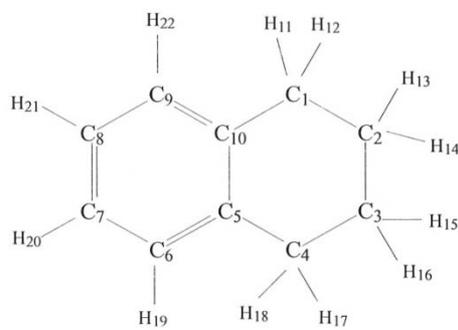

Fig. 1: Molecular structure of Tetralin

3.2. Normal Coordinate Analysis
The evaluation of potential energy constants are made on the basis of GVFF by applying Wilson's FG matrix mechanism. The structural parameters were taken from the Sutton's table [2]. The vibrational secular determinants have been solved using the computer programmes with the SIMPLEX optimization procedure [3]. The initial set of force constants and the vibrational frequencies required for the calculations were taken from the literature [4]. All the force constants have been refined via a non-linear square fit analysis between the calculated and observed frequencies. The refinement converged smoothly in three cycles.

3.3. Symmetry Coordinates
Detailed description of vibrational modes can be given by means of normal coordinate analysis. For this purpose, the full set of 75 standard internal valence coordinates (containing 15 redundancies) were defined as given in Table 1. From these a non-redundant set of local internal coordinates were constructed (Table 2) much like the natural internal coordinates recommended by IUPAC [5,6]. Theoretically calculated force fields were transformed to the latter set of vibrational coordinates and used in all subsequent calculations.

Table 1: Definition of internal coordinates of Tetralin.

No. (i)	Symbol	Type	Definition
Stretching			
1 – 11	r_i	C–C	C1 – C2, C2 – C3, C3 – C4, C4 – C5, C5 – C6, C6 – C7, C7 – C8, C8 – C9, C9 – C10, C10 – C5, C10 – C1
12 – 15	R_i	C–H	C6 – H19, C7 – H20, C8 – H21, C9 – H22
16 – 17	V_i	C–H	C1 – H11, C1 – H12
In-plane bending			
18 – 29	α_i	C–C–H	C1 – C2 – H13, C1 – C2 – H14, C3 – C2 – H13, C3 – C2 – H14, C2 – C3 – H15, C2 – C3 – H16, C4 – C3 – H15, C4 – C3 – H16, C3 – C4 – H17, C3 – C4 – H18, C5 – C4 – H17, C5 – C4 – H18
30 – 37	α_i	C–C–H	C5 – C6 – H19, C7 – C6 – H19, C6 – C7 – H20, C8 – C7 – H20, C7 – C8 – H21, C9 – C8 – H21, C8 – C9 – H22, C10 – C9 – H22
38 – 43	β_i	Ring 1	C1 – C2 – C3, C2 – C3 – C4, C3 – C4 – C5, C4 – C5 – C10, C5 – C10 – C1, C10 – C1 – C2
44 – 49	β_i	Ring 2	C6 – C5 – C10, C5 – C10 – C9, C10 – C9 – C8, C9 – C8 – C7, C8 – C7 – C6, C7 – C6 – C5
Out-of-plane bending			
50 – 61	ω_i	C–H	H19 – C6 – C7 – C5, H20 – C7 – C8 – C6, H21 – C8 – C9 – C7, H22 – C9 – C10 – C8, H18 – C4 – C5 – C3, H17 – C4 – C5 – C3, H16 – C3 – C4 – C2, H15 – C3 – C4 – C2, H14 – C2 – C3 – C1, H13 – C2 – C3 – C1, H12 – C1 – C2 – C10, H11 – C1 – C2 – C10
Torsion			
62 – 67	t_i	τRing 1	C4 – C5 – C10 – C1, C5 – C10 – C1 – C2, C10 – C1 – C2 – C3, C1 – C2 – C3 – C4, C2 – C3 – C4 – C5, C3 – C4 – C5 – C10
68 – 73	t_i	τRing 2	C6 – C7 – C8 – C9, C7 – C8 – C9 – C10, C8 – C9 – C10 – C5, C9 – C10 – C5 – C6, C10 – C5 – C6 – C7, C5 – C6 – C7 – C8
74 – 75	t_i	Butterfly	C4 – C5 – C10 – C9, C6 – C5 – C10 – C1

For numbering of atoms refer Fig. 1.

Table 2: Definition of local symmetry coordinates of Tetralin.

No. (i)	Type	Definition
1 – 11	CC	$r_1, r_2, r_3, r_4, r_5, r_6, r_7, r_8, r_9, r_{10}, r_{11}$
12 – 23	CH	$R_{12}, R_{13}, R_{14}, R_{15}, R_{16}, R_{17}, R_{18}, R_{19}, R_{20}, R_{21}, R_{22}, R_{23}$
24	CH_2 ss	$(\nu_{16} + \nu_{17})/\sqrt{2}$
25	CH_2 ass	$(\nu_{16} - \nu_{17})/\sqrt{2}$
26 – 35	bCH	$(\alpha_{18} - \alpha_{19})/\sqrt{2}$, $(\alpha_{20} - \alpha_{21})/\sqrt{2}$, $(\alpha_{22} - \alpha_{23})/\sqrt{2}$, $(\alpha_{24} - \alpha_{25})/\sqrt{2}$, $(\alpha_{26} - \alpha_{27})/\sqrt{2}$, $(\alpha_{28} - \alpha_{29})/\sqrt{2}$, $(\alpha_{30} - \alpha_{31})/\sqrt{2}$, $(\alpha_{32} - \alpha_{33})/\sqrt{2}$, $(\alpha_{34} - \alpha_{35})/\sqrt{2}$, $(\alpha_{36} - \alpha_{37})/\sqrt{2}$
36	R_1trigd	$(\beta_{38} - \beta_{39} + \beta_{40} - \beta_{41} + \beta_{42} - \beta_{43})/\sqrt{6}$
37	R_1symd	$(-\beta_{38} - \beta_{39} + 2\beta_{40} - \beta_{41} - \beta_{42} + 2\beta_{43})/\sqrt{12}$
38	R_1asyd	$(\beta_{38} - \beta_{39} + \beta_{41} - \beta_{42})/\sqrt{2}$
39	R_2trigd	$(\beta_{44} - \beta_{45} + \beta_{46} - \beta_{47} + \beta_{48} - \beta_{49})/\sqrt{6}$
40	R_2symd	$(-\beta_{44} - \beta_{45} + 2\beta_{46} - \beta_{47} - \beta_{48} + 2\beta_{49})/\sqrt{12}$
41	R_2asyd	$(\beta_{44} - \beta_{45} + \beta_{47} - \beta_{48})/\sqrt{2}$
42 – 53	ωCH	$\omega_{50}, \omega_{51}, \omega_{52}, \omega_{53}, \omega_{54}, \omega_{55}, \omega_{56}, \omega_{57}, \omega_{58}, \omega_{59}, \omega_{60}, \omega_{61}$
54	tR_1trig	$(\tau_{62} - \tau_{63} + \tau_{64} - \tau_{65} + \tau_{66} - \tau_{67})/\sqrt{6}$
55	tR_1sym	$(\tau_{62} - \tau_{64} + \tau_{65} - \tau_{67})/\sqrt{2}$
56	tR_1asy	$(-\tau_{62} + 2\tau_{63} - \tau_{64} - \tau_{65} + 2\tau_{66} - \tau_{67})/\sqrt{12}$
57	tR_2trig	$(\tau_{68} - \tau_{69} + \tau_{70} - \tau_{71} + \tau_{72} - \tau_{73})/\sqrt{6}$
58	tR_2sym	$(\tau_{68} - \tau_{70} + \tau_{71} - \tau_{73})/\sqrt{2}$
59	tR_2asy	$(-\tau_{68} + 2\tau_{69} - \tau_{70} - \tau_{71} + 2\tau_{72} - \tau_{73})/\sqrt{12}$
60	Butterfly	$(\tau_{74} - \tau_{75})/\sqrt{2}$

3.4. Vibrational Band Assignments

The FT-IR and FT-Raman spectra of the title compound are shown in Figs. 2-3.
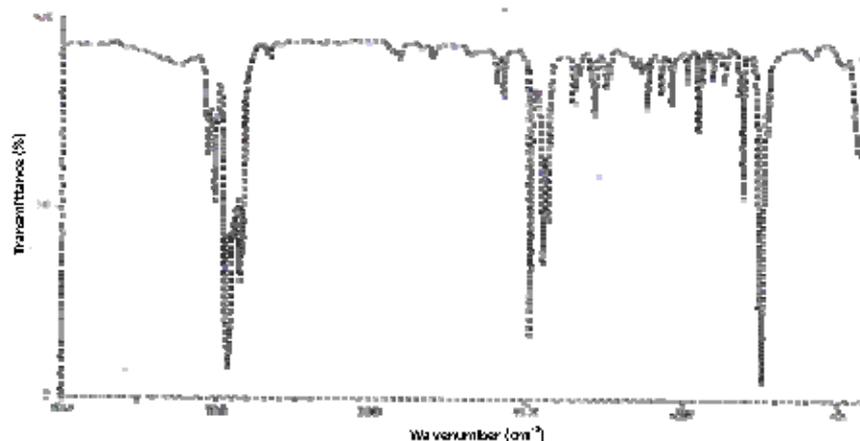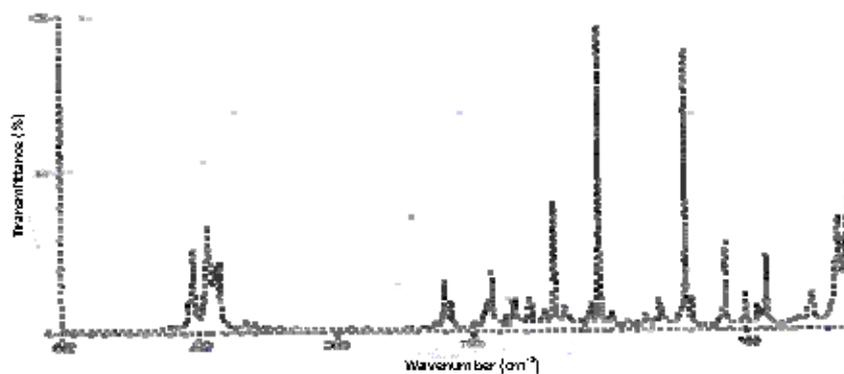
Fig. 2: FT-IR spectrum of Tetralin

Fig. 3: FT-Raman spectrum of Tetralin

The observed frequencies of the title compound together with relative intensities, probable assignment, calculated frequencies and PEDS are presented in Table 3.

Table 3: Vibrational frequencies and assignments of Tetralin.

S. No.	Species	Observed Frequency (cm^{-1})		Calculated Frequency (cm^{-1})	Assignment (% PED)
		FT-IR	FT-Raman		
1	A′	3100	-	3089	C–H stretching (99)
2	A′	-	3080	3070	C–H stretching (98)
3	A′	3073	-	3064	C–H stretching (97)
4	A′	3066	-	3058	C–H stretching (96)
5	A′	-	3059	3051	C–H stretching (98)

6	A′	3049	-	3039	C–H stretching (96)
7	A′	-	3041	3032	C–H stretching (97)
8	A′	-	3025	3014	C–H stretching (99)
9	A′	3016	-	3007	C–H stretching (96)
10	A′	3000	-	2989	C–H stretching (98)
11	A′	-	2939	2949	C–H stretching (97)
12	A′	2928	-	2920	C–H stretching (96)
13	A′	2883	-	2872	CH$_2$ ass (100)
14	A′	-	2849	2839	CH$_2$ ss (99)
15	A′	-	1614	1605	C–C stretching (72)
16	A′	1601	-	1592	C–C stretching (73)
17	A′	1579	-	1569	C–C stretching (70)
18	A′	-	1561	1552	C–C stretching (71)
19	A′	1494	-	1501	C–C stretching (72)
20	A′	1474	-	1484	C–C stretching (70)
21	A′	1463	-	1470	C–C stretching (73)
22	A′	1438	-	1446	C–C stretching (71)
23	A′	-	1430	1420	C–C stretching (73)
24	A′	-	1386	1477	C–C stretching (71)
25	A′	1354	-	1344	C–C stretching (70)
26	A′	1263	-	1254	C–H in-plane bending (70)
27	A′	1249	-	1241	C–H in-plane bending (71)
28	A′	1235	-	1225	C–H in-plane bending (72)
29	A′	-	1203	1195	C–H in-plane bending (71)
30	A′	1176	-	1168	C–H in-plane bending (70)
31	A′	-	1169	1159	C–H in-plane bending (72)
32	A′	1134	-	1141	Ring 1 deformation in-plane bending (59)
33	A′	1112	-	1122	C–H in-plane bending (71)
34	A′	-	1093	1101	C–H in-plane bending (70)
35	A′	1067	-	1074	C–H in-plane bending (72)
36	A′	1034	-	1044	C–H in-plane bending (71)
37	A′	-	1028	1020	Ring 1 deformation in-plane bending (52)
38	A′	986	-	978	Ring 2 deformation in-plane bending (62)
39	A″	-	952	943	C–H out-of-plane bending (64)
40	A″	945	-	935	C–H out-of-plane bending (65)
41	A″	939	-	928	C–H out-of-plane bending (66)
42	A″	899	-	890	C–H out-of-plane bending (59)
43	A″	866	-	858	C–H out-of-plane bending (66)
44	A″	-	859	867	C–H out-of-plane bending (60)
45	A″	817	-	827	C–H out-of-plane bending (65)
46	A″	805	-	813	C–H out-of-plane bending (64)

47	A″	781	-	789	C–H out-of-plane bending (66)
48	A″	-	772	779	C–H out-of-plane bending (60)
49	A′	742	-	750	Ring 1 deformation in-plane bending (53)
50	A″	-	725	733	C–H out-of-plane bending (64)
51	A″	-	702	710	C–H out-of-plane bending (66)
52	A′	-	681	670	Ring 2 deformation in-plane bending (59)
53	A′	-	606	614	Ring 2 deformation in-plane bending (57)
54	A″	-	492	482	Ring 1 deformation out-of-plane bending (51)
55	A″	-	467	476	Ring 1 deformation out-of-plane bending (57)
56	A″	-	424	414	Ring 2 deformation out-of-plane bending (56)
57	A″	-	398	389	Ring 2 deformation out-of-plane bending (57)
58	A″	-	321	330	Ring 1 deformation out-of-plane bending (51)
59	A″	-	266	276	Butterfly (58)
60	A″	-	164	172	Ring 2 deformation out-of-plane bending (51)

3.4.1. C-H Vibrations

The molecular structure shows the presence of C-H stretching vibrations in the region $3000\text{-}3100$ cm^{-1} which is the characteristic region for the ready identification of C-H stretching vibrations [7,8]. In this region the bands are not affected appreciably by the nature of the substituents. Hence, in the present investigation, C-H vibrations have been found at 3100, 3073, 3066, 3049, 3016, 3000, 2928 cm^{-1} in IR and 3080, 3059, 3041, 3025, 2939 cm^{-1} in Raman.

3.4.2. C-C Vibrations

The bands between 1400 and 1650 cm^{-1} in benzene derivatives are due to C-C stretching vibrations [9]. Therefore, the C-C stretching vibrations of the title compound are observed at 1614, 1561, 1430, 1386 cm^{-1} in Raman and 1601, 1579, 1494, 1474, 1463, 1438, 1354 cm^{-1} in IR.

4. Conclusion

Based on the normal coordinate analysis a complete vibrational analysis was performed for Tetralin. A systematic set of symmetry coordinates have been constructed. The closer agreement obtained between the calculated and the observed frequencies and the PED calculations are also supporting the assignments made for various functional groups present in the molecule.

References

[1] E.B. Wilson, Phys. Rev., 45, 706, 1934.

[2] L.E. Sutton, The Inter Atomic Bond Distance and Bond Analysis in Molecules and Ions (Chemical Society, London), 1958.

[3] J.A. Nelder and R. Mead, Comput. J., 7, 308, 1965.

[4] V. Suryanarayan, Pavankumar and G. Ramanarao, Spectrochim. Acta A, 48, 1481, 1992.

[5] IUPAC Commission on Molecular Structure on Spectroscopy, Pure & Apply Chem., 50, 1707, 1978.

[6] P. Pulay and G. Fogarasi, F. Prog and J.E. Boggs, J. Am. Chem. Soc., 101, 2550, 1979.

[7] H.G. Silver and J.L. Wood, Trans Faraday Soc., 60, 5, 1964.

[8] V. Krishnakumar and R. Ramasamy, Indian J. Pure & Appl. Phys., 41, 258-261, 2003.

[9] V. Krishnakumar, K. Parasuraman and A. Nataran, Indian J. Pure & Appl. Phys., 35, 1, 1997.