FT-IR and FT-Raman Spectral Investigation of p-toluidine

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Abstract

Normal coordinate calculations of p-toluidine 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, p-toluidine, Normal coordinate analysis, potential energy distribution.

1. Introduction

There are three isomers of toluidine, which are organic compounds. These isomers are o-toluidine, m-toluidine and p-toluidine. All three are aryl amines whose chemical structures are similar to aniline except that a methyl group is substituted onto the benzene ring. The difference between these three isomers is the position where the methyl group ($-CH_3$) is bonded to the ring relative to the amino functional group ($-NH_2$). Due to the amino group bonded to the aromatic ring, the toluidines are weakly basic. None of the toluidines is very soluble in pure water, but will become soluble if the aqueous solution is acidic due to the formation of ammonium salts, as usual for organic amines. The other name for p-toluidine is 4-amino-1-methyl benzene.

Toluidines are used in the production of dyes. They are a component of accelerators for cyanoacrylate glues. They are toxic and are suspected human carcinogens.

2. Experimental Details

Pure chemical p-toluidine is obtained from Lancaster chemical company, England and used as such without any further purification. The FT-IR spectrum of p-toluidine 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

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globar and mercury arc sources, KBr beam splitters are used while recording FT-IR spectra of the title compound.

The FT-Raman spectrum was recorded on a Bruker IFS 66V model interferrometer equipped with FRA – 106 FT-Raman accessory the spectrum was recorded in the stokes region (4000 – 100 cm^{-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 p-toluidine is shown in Fig. 1. From the structure point of view the molecule is assumed to have C_s point group symmetry. The 45 fundamental modes of vibrations arising for this molecule are distributed into 31 A' and 14 A" species. The A' and A" species represent the in-plane and out-of-plane vibrations.
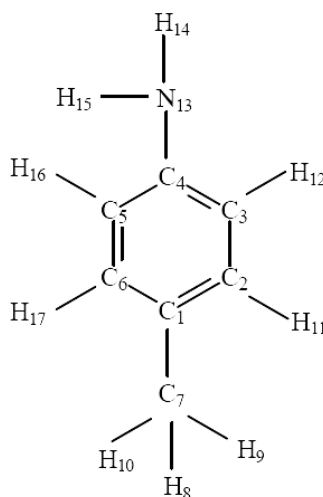

Fig. 1: Molecular Structure of p-toluidine

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 [1]. The vibrational secular determinants have been solved using the computer programmes with the SIMPLEX optimization procedure [2]. The initial set of force constants and the vibrational frequencies required for the calculations were taken from the literature[3]. All the force constants have been

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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 58 standard internal valence coordinates (containing 13 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 recommeded by IUPAC [4,5]. Theoretically calculated force fields were transformed to the latter set of vibrational coordinates and used in all subsequent calculations.

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Table 1: **Definition of internal Coordinates of p-toluidine**

No(i)	Symbol	Type	Definition
Stretching			
1-7	r_i	C–C	C1–C2, C2–C3, C3–C4, C4–C5, C5–C6, C6–C1, C1–C7
8-14	R_i	C–H	C2–H11, C3–H12, C5–H16, C6–H17, C7–H10, C7–H8, C7–H9
15	q_i	C–N	C4–N13
16-17	Q_i	N–H	N13–H14, N13–H15
In-plane bending			
18-25	α_i	C–C–H	C1–C2–H11, C3–C2–H11, C2–C3–H12, C4–C3–H12, C4–C5–H16, C6–C5–H16, C1–C6–H17, C5–C6–H17
26-27	α_i	C–C–N	C3–C4–N13, C5–C4–N13
28-29	α_i	C–C–C	C2–C1–C7, C6–C1–C7
30-31	γ_i	C–N–H	C4–N13–H14, C4–N13–H15
32	γ_i	H–N–H	H14–N13–H15
33-38	β_i	Ring	C1–C2–C3, C2–C3–C4, C3–C4–C5, C4–C5–C6, C5–C6–C1, C6–C1–C2
39-41	θ_i	C-C-H (Methyl)	C1–C7–H8, C1–C7–H9, C1–C7–H10
42-44	σ_i	H–C–H	H8–C7–H9, H8–C7–H10, H10–C7–H9
Out-of-plane bending			
45-48	ω_i	C–H	H11–C2–C1–C3, H12–C3–C2–C4, H16–C5–C4–C6, H17–C6–C5–C1
49	π_i	C–C	C7–C1–C6–C2
50	ψ_i	C–N	N13–C4–C3–C5
Torsion			
51-56	t_i	τ Ring	C1–C6–C5–C4, C6–C5–C4–C3, C5–C4–C3–C2, C4–C3–C2–C1, C3–C2–C1–C6, C2–C1–C6–C5
57	t_i	τC–NH$_2$	C4–N13–H14–H15
58	t_i	τC–CH$_3$	(C2, C6) –C1–C7–(H8, H9, H10)

For numbering of atoms refer Fig.1.

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Table 2: **Definition of local symmetry coordinates of p-toluidine**

No.(i)	Type	Definition
1-7	CC	$r_1, r_2, r_3, r_4, r_5, r_6, r_7$
8-14	CH	$R_8, R_9, R_{10}, R_{11}, R_{12}, R_{13}, R_{14}$
15	CN	q_{15}
16-17	NH	Q_{16}, Q_{17}
18-21	bCH	$(\alpha_{18} - \alpha_{19})/\sqrt{2}, (\alpha_{20} - \alpha_{21})/\sqrt{2}, (\alpha_{22} - \alpha_{23})/\sqrt{2}, (\alpha_{24} - \alpha_{25})/\sqrt{2}$
22	bCN	$(\alpha_{26} - \alpha_{27})/\sqrt{2}$
23	bCC	$(\alpha_{28} - \alpha_{29})/\sqrt{2}$
24	NH$_2$ rock	$(\gamma_{30} - \gamma_{31})/\sqrt{2}$
25	NH$_2$ twist	$(\gamma_{30} + \gamma_{31})/\sqrt{2}$
26	NH$_2$ Sciss	$(2\gamma_{32} - \gamma_{30} - \gamma_{31})/\sqrt{2}$
27	Rtrigd	$(\beta_{33} - \beta_{34} + \beta_{35} - \beta_{36} + \beta_{37} - \beta_{38})/\sqrt{6}$
28	R symd	$(-\beta_{33} - \beta_{34} + \beta_{35} - \beta_{36} - \beta_{37} + 2\beta_{38})/\sqrt{6}$
29	R asymd	$(\beta_{33} - \beta_{34} + \beta_{35} - \beta_{36})/\sqrt{2}$
30	CH$_3$ Sb	$(-\theta_{39} - \theta_{40} - \theta_{41} + \sigma_{42} + \sigma_{43} + \sigma_{44})/\sqrt{6}$
31	CH$_3$ iPb	$(-\sigma_{42} - \sigma_{43} - 2\sigma_{44})/\sqrt{6}$
32	CH$_3$ opb	$(\sigma_{42} - \sigma_{43})/\sqrt{2}$
33	CH$_3$ ipr	$(2\theta_{39} - \theta_{40} - \theta_{41})/\sqrt{6}$
34	CH$_3$ opr	$(\theta_{40} - \theta_{41})/\sqrt{2}$
35-38	ωCH	$\omega_{45}, \omega_{46}, \omega_{47}, \omega_{48}$
39	πCC	π_{49}
40	ψCN	ψ_{50}
41	t Rtrig	$(\tau_{51} - \tau_{52} + \tau_{53} - \tau_{54} + \tau_{55} - \tau_{56})/\sqrt{6}$
42	tRsym	$(\tau_{51} - \tau_{53} + \tau_{54} - \tau_{56})/\sqrt{2}$
43	tRasy	$(-\tau_{51} + 2\tau_{52} - \tau_{53} - \tau_{54} + 2\tau_{55} - \tau_{56})/\sqrt{12}$
44	NH$_2$ wag	τ_{57}
45	t CH$_3$	τ_{58}

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3.4. Vibrational Band Assignments

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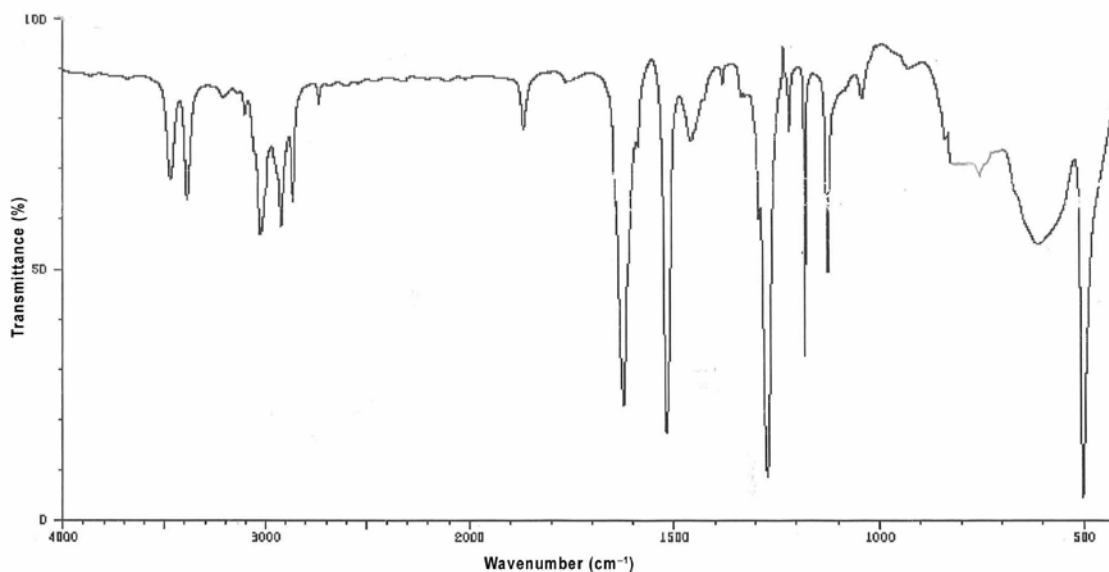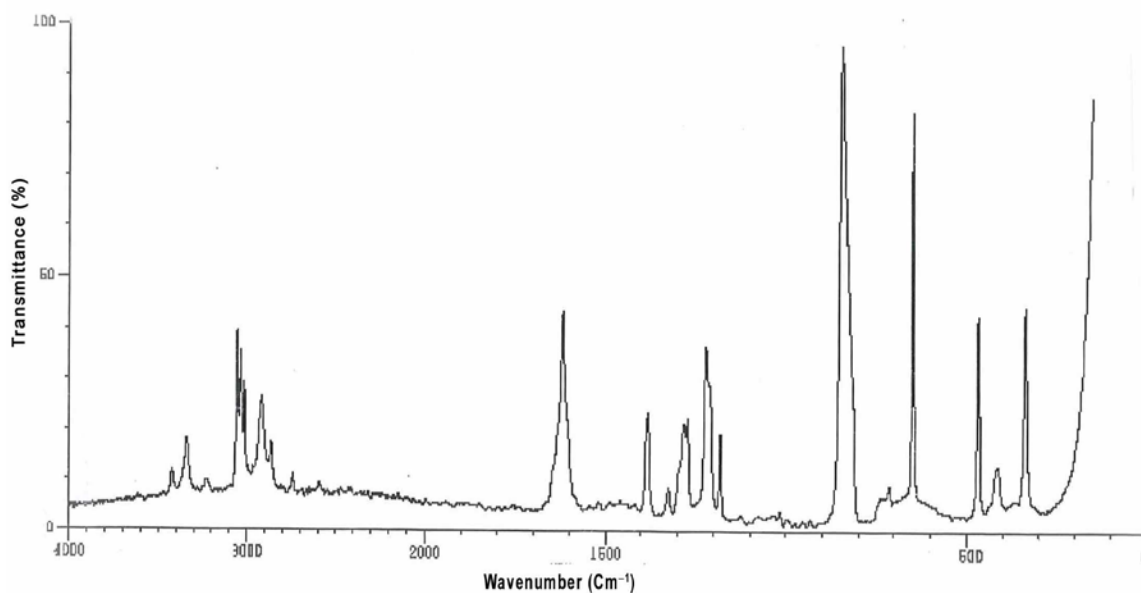

Fig. 2: FT-IR spectrum of p-toluidine

Fig. 3: FT-Raman spectrum of p-toluidine

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

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Table 3: Vibrational frequencies and assignments of p-toluidine

S. No.	Species	Observed frequency (cm^{-1})		Calculated Frequency (cm^{-1})	Assignment (% PED)
		FT-IR	**FT-Raman**		
1	A′	3470	-	3461	N-H Stretching (95)
2	A′	3388	-	3380	N-H Stretching (94)
3	A′	3099	-	3089	C-H Stretching (97)
4	A′	-	3067	3056	C-H Stretching (99)
5	A′	-	3036	3027	C-H Stretching (98)
6	A′	3029	-	3020	C-H Stretching (96)
7	A′	3022	-	3011	C-H Stretching (97)
8	A′	-	3017	3009	C-H Stretching (98)
9	A′	-	3005	2994	C-H Stretching (99)
10	A′	1698	-	1690	NH$_2$ Sciss (84)
11	A′	1624	-	1615	C-C Stretching (71)
12	A′	-	1618	1609	C-C Stretching (70)
13	A′	-	1525	1515	C-C Stretching (72)
14	A′	1518	-	1507	C-C Stretching (71)
15	A′	-	1479	1470	C-C Stretching (70)
16	A′	1465	-	1454	CH$_3$ ipb (84)
17	A′	1457	-	1447	C-C Stretching (72)
18	A′	1421	-	1412	CH$_3$ sb (88)
19	A′	-	1410	1401	C-C Stretching (71)
20	A′	1380	-	1389	C-N Stretching (76)
21	A′	-	1278	1286	C-H in-plane bending (71)
22	A′	1270	-	1280	C-H in-plane bending (72)
23	A′	-	1223	1232	C-H in-plane bending(70)

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24	A′	1216	-	1225	C-H in-plane bending(71)
25	A′	1203	-	1214	C-N in-plane bending(66)
26	A′	-	1197	1188	Ring deformation in-plane bending(53)
27	A′	-	1183	1173	Ring deformation in-plane bending(52)
28	A″	1175	-	1167	CH_3 opb (87)
29	A′	1125	-	1115	NH_2 rock (68)
30	A′	-	1071	1062	Ring deformation in-plane bending(51)
31	A′	1041	-	1030	CH_3 ipr (79)
32	A″	-	961	953	CH_3 opr (77)
33	A″	-	847	855	C-H out-of-plane bending (65)
34	A″	839	-	849	C-H out-of-plane bending (60)
35	A″	831	-	840	C-H out-of-plane bending (64)
36	A″	760	-	769	C-H out-of-plane bending (66)
37	A″	-	720	712	C-N out-of-plane bending (59)
38	A″	651	-	642	NH_2 wag (61)
39	A″	-	644	633	Ring deformation out-of-plane bending(59)
40	A″	611	-	620	Ring deformation out-of-plane bending(57)
41	A′	-	521	529	C-C in-plane bending (65)
42	A″	502	-	511	Ring deformation out-of-plane bending(58)
43	A″	-	467	478	CH_3 torsion (57)
44	A″	-	459	469	C-C out-of-plane bending (54)
45	A″	-	338	347	NH_2 twist (69)

Abbreviations used: Sb – symmetric bending; ipb – in-plane bending; opb – out-of-plane bending; ipr – in-plane rocking; opr – out-of-plane rocking

3.4.1. N–H Vibrations

In all the heterocyclic compounds, the N-H stretching vibrations [6], occur in the region 3500 – 3000 cm^{-1}. Hence the FT-IR band observed at 3470 and 3388 cm^{-1} in p-toluidine have been designated to N-H stretching modes of vibrations.

3.4.2. C–H Vibrations

The molecular structure shows the presence of C-H stretching vibrations in the region 3100 – 3000 cm^{-1} which is the characteristic region for the ready identification of C–H stretching vibrations [7,8]. In the present investigation, the C–H vibrations have been found at 3099, 3029, 3022 cm^{-1} in IR and 3067, 3036, 3017, 3005 cm^{-1} in Raman.

3.4.3. 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 vibrations of the title compound are observed at 1624, 1518, 1457 cm^{-1} in IR and 1618, 1525, 1479, 1410 cm^{-1} in Raman.

3.4.4. C–N Vibrations

The identification of C–N stretching frequency is very difficult task, since the mixing bands are possible in this region. Hence, the FT-IR band observed at 1380 cm^{-1} of the title compound is assigned to C–N stretching modes of vibraion. These assignment is made in accordance with the assignments proposed by Krishnakumar et al. [10].

3.4.5. Amino Group Vibrations

According to Socrates [11] the frequencies of the amino group appear around 1700-1600 cm^{-1} for NH_2 scissoring and 1150 – 900 cm^{-1} for rocking deformations. The band appeared at 1698 cm^{-1} in infrared is assigned unambiguously to the scissoring mode of the NH_2 group. The NH_2 rocking mode has been assigned to 1125 cm^{-1} in IR for the title compound. The IR and Raman bands for wagging and twisting NH_2 modes of p-toluidine are identified at 651 and 338 cm^{-1} respectively.

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3.4.6. Methyl Group Vibrations

The methyl group substituted at the first position of the title compound give raise to asymmetric and symmetric stretching vibrations. We have observed the symmetrical methyl deformation mode CH_3sb at 1421 cm^{-1} in IR and in-plane bending methyl deformation mode CH_3ipb at 1465 cm^{-1} in IR. The band at 1175 cm^{-1} in IR is attributed to CH_3opb in the A" species. The bands obtained at 1041 cm^{-1} in IR and 961 cm^{-1} in Raman are assigned to CH_3 in-plane and out-of-plane rocking modes. These assignments are also supported by the literature [12].

4. Conclusion

Based on the normal coordinate analysis a complete vibrational analysis was performed for p-toluidine. 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.

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