

Vibrational spectroscopic studies and ab initio calculations of 5-methyl-2-(*p*-methylaminophenyl)benzoxazole

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Abstract

FT-IR spectra of 5-methyl-2-(*p*-methylaminophenyl)benzoxazole was recorded and analysed. The vibrational frequencies of the compound have been computed using the Hartree-Fock/6-31G* basis and compared with the experimental values.

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1. Introduction

Benzoxazole derivatives are the structural isoesters of naturally occurring nucleotides such as adenine and guanine, which allows them to interact easily with the biopolymers of living systems and different kinds of biological activity have been obtained [1–5]. Besides, due to their kind of action, it has been reported that they have shown low toxicity in warm-blooded animals [4,6]. Synthesis and microbiological activity of 5-substituted-2-(*p*-substitutedphenyl)benzoxazole derivatives are reported by Yalcin et al. [7–10]. Anto et al. [11] reported the vibrational spectroscopic and ab initio studies of 5-methyl-2-(*p*-fluorophenyl)benzoxazole. Ab initio quantum mechanical method is at present widely used for simulating IR spectrum. Such simulations are indispensable tools to perform normal coordinate analysis so that modern vibrational spectroscopy is unimaginable without involving them. In the present study the FT-IR and theoretical calculations of the wavenumbers of the title compound are reported.

2. Experimental

For the synthesis of the benzoxazole derivative, using aqueous mineral acids as the condensation reagent did not provide successful results, because of the oxazole ring which was easily hydrolysed under these conditions [12]. Reactions which occurred in pyridine or xylene also has low yields. Finally, polyphosphoric acid was chosen as the reagent for cyclodehydration in the synthesis of the title compound as it has good solvent power and contains anhydride group which combine with the water formed in the reaction centre in order to prevent effective acidity. The stability of the oxazole ring increases under these conditions and high temperature could be used [12]. The title compound was prepared by heating 2-hydroxy-5-methylaniline with the appropriate carboxylic acid in polyphosphoric acid [12]. A mixture of 2-hydroxy-5-methylaniline (0.01 mol) and appropriate carboxylic acid (0.02 mol) was heated in polyphosphoric acid (12 g) with stirring for 2.5 h. At the end of the reaction period, the residue was poured into ice-water and neutralized with excess of 10% NaOH solution. After extracted with benzene, the benzene solution was dried over anhydrous sodium sulphate and evaporated under reduced pressure. The residue was boiled with 200 mg charcoal in ethanol and filtered. The filtrate was left to crystallize by addition of water. MP 179.1 °C,

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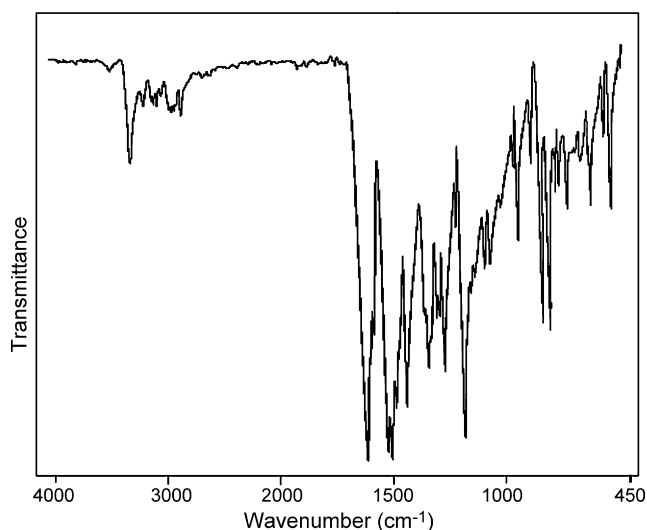


Fig. 1. FT-IR spectrum of 5-methyl-2-(*p*-methylaminophenyl)benzoxazole.

yield 52%, reaction temperature 165–170 °C, UV λ_{max} . 214, 326, 354 (shoulder), $^1\text{H NMR}$ δ ppm 2.68 (s, 3H), 3.49 (s, 3H), 7.59–8.89 (m, 7H).

The FT-IR spectrum (Fig. 1) was recorded using a Perkin-Elmer FT-IR 1760x spectrometer. The spectral resolution was 4 cm^{-1} . Standard KBr technique with 1 mg sample per 300 mg KBr was used.

3. Computational details

Calculations of the title compound were carried out with Gaussian03 program [13] using the HF/6-31G* basis set to predict the molecular structure and vibrational wavenumbers. Molecular geometry was fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wavenumbers were calculated using the analytics second derivatives to confirm the convergence to minima on the potential surface. The wavenumber values computed at the Hartree-Fock level contain known systematic errors due to the negligence of electron correlation [14]. We therefore, have used the scaling factor value of 0.8929 for HF/6-31G* basis set. Parameters corresponding to optimized geometry of the title compound (Fig. 2) are given in Table 1. The absence of imaginary wavenumbers on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy. In total there are 90 vibrations from 3448 to 30 cm^{-1} .

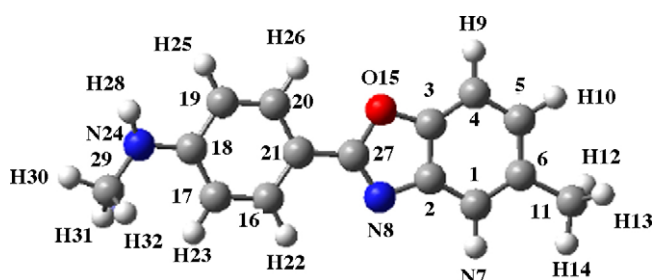


Fig. 2. Optimized geometry of 5-methyl-2-(*p*-methylaminophenyl)benzoxazole.

Table 1

Optimized geometrical parameters of 5-methyl-2-(*p*-methylaminophenyl)benzoxazole, atom labeling is according to Fig. 2

Bond lengths (Å)	Bond angles (°)	Dihedral angles (°)
C ₁ –C ₂	1.3879	A(2,1,6) 118.3 D(6,1,2,3) –0.0
C ₁ –C ₆	1.3860	A(2,1,7) 120.4 D(6,1,2,8) –180.0
C ₁ –H ₇	1.0746	A(6,1,7) 121.3 D(7,1,2,3) –180.0
C ₂ –C ₃	1.3784	A(1,2,3) 120.1 D(7,1,2,8) 0.0
C ₂ –N ₈	1.3892	A(1,2,8) 131.6 D(2,1,6,5) 0.0
C ₃ –C ₄	1.3768	A(3,2,8) 108.3 D(2,1,6,11) –180.0
C ₃ –O ₁₅	1.3590	A(2,3,4) 123.5 D(7,1,6,5) 180.0
C ₄ –C ₅	1.3839	A(2,3,15) 107.2 D(7,1,6,11) 0.0
C ₄ –H ₉	1.0739	A(4,3,15) 129.4 D(1,2,3,4) 0.0
C ₅ –C ₆	1.4034	A(3,4,5) 115.9 D(1,2,3,15) –180.0
C ₅ –H ₁₀	1.0761	A(3,4,9) 122.1 D(8,2,3,4) –180.0
C ₆ –C ₁₁	1.5128	A(5,4,9) 122.0 D(8,2,3,15) –0.0
N ₈ –C ₂₇	1.2753	A(4,5,6) 122.4 D(1,2,8,27) –180.0
C ₁₁ –H ₁₂	1.0860	A(4,5,10) 118.8 D(3,2,8,27) 0.0
C ₁₁ –H ₁₃	1.0836	A(6,5,10) 118.8 D(2,3,4,5) –0.0
C ₁₁ –H ₁₄	1.086	A(1,6,5) 119.9 D(2,3,4,9) 180.0
O ₁₅ –C ₂₇	1.3492	A(1,6,11) 120.7 D(15,3,4,5) 180.0
C ₁₆ –C ₁₇	1.3799	A(5,6,11) 119.4 D(15,3,4,9) –0.0
C ₁₆ –C ₂₁	1.3899	A(2,8,27) 104.6 D(2,3,15,27) –0.0
C ₁₆ –H ₂₂	1.0738	A(6,11,12) 111.2 D(4,3,15,27) 180.0
C ₁₇ –C ₁₈	1.3978	A(6,11,13) 111.2 D(3,4,5,6) 0.0
C ₁₇ –H ₂₃	1.0728	A(6,11,14) 111.2 D(3,4,5,10) 180.0
C ₁₈ –C ₁₉	1.4007	A(12,11,13) 107.8 D(9,4,5,6) –180.0
C ₁₈ –N ₂₄	1.3782	A(12,11,14) 107.5 D(9,4,5,10) 0.0
C ₁₉ –C ₂₀	1.3752	A(13,11,14) 107.8 D(4,5,6,1) –0.0
C ₁₉ –H ₂₅	1.0762	A(3,15,27) 104.8 D(4,5,6,11) 180.0
C ₂₀ –C ₂₁	1.3939	A(17,16,21) 121.2 D(10,5,6,1) –190.0
C ₂₀ –H ₂₆	1.0737	A(17,16,22) 119.8 D(10,5,6,11) –0.0
C ₂₁ –C ₂₇	1.4610	A(21,16,22) 119.0 D(1,6,11,12) –120.1
N ₂₄ –H ₂₈	0.9946	A(16,17,18) 120.4 D(1,6,11,13) –0.1
N ₂₄ –C ₂₉	1.4435	A(16,17,23) 119.2 D(1,6,11,14) 120.1
C ₂₉ –H ₃₀	1.0819	A(18,17,23) 120.5 D(5,6,11,12) 59.8
C ₂₉ –H ₃₁	1.0835	A(17,18,19) 118.3 D(5,6,11,13) 180.0
C ₂₉ –H ₃₂	1.0887	A(17,18,24) 122.3 D(5,6,11,14) –59.9
		A(19,18,24) 119.4 D(2,8,27,15) –0.0
		A(18,19,20) 120.9 D(2,8,27,21) –180.0
		A(18,19,25) 119.4 D(3,15,27,8) 0.0
		A(20,19,25) 119.8 D(3,15,27,21) 180.0
		A(19,20,21) 120.8 D(21,16,17,18) 0.3
		A(19,20,26) 119.4 D(21,16,17,23) –179.9
		A(21,20,26) 119.8 D(22,16,17,18) –179.9
		A(16,21,20) 118.4 D(22,16,17,23) –0.1
		A(16,21,27) 119.9 D(17,16,21,20) –0.1
		A(20,21,27) 121.7 D(17,16,21,27) 179.8
		A(18,24,28) 114.2 D(22,16,21,20) –179.9
		A(18,24,29) 122.4 D(22,16,21,27) 0.0
		A(28,24,29) 114.7 D(16,17,18,19) –0.3
		A(8,27,15) 115.2 D(16,17,18,24) 178.3
		A(8,27,21) 127.5 D(23,17,18,19) 179.9
		A(15,27,21) 117.3 D(23,17,18,24) –1.5
		A(24,29,30) 108.4 D(17,18,19,20) 0.1
		A(24,29,31) 110.7 D(17,18,19,25) 179.7
		A(24,29,32) 113.1 D(24,18,19,20) –178.5
		A(30,29,31) 107.6 D(24,18,19,25) 1.1
		A(30,29,32) 108.5 D(17,18,24,28) 161.6
		A(31,29,32) 108.4 D(17,18,24,29) 15.7
		D(19,18,24,28) –19.8
		D(19,18,24,29) –165.8
		D(18,19,20,21) 0.0
		D(18,19,20,26) –180.0
		D(25,19,20,21) –179.5
		D(25,19,20,26) 0.5
		D(19,20,21,16) –0.0

Table 1 (Continued)

Bond lengths (Å)	Bond angles (°)	Dihedral angles (°)
		D(19,20,21,27) -180.0
		D(26,20,21,16) 180.0
		D(26,20,21,27) 0.1
		D(16,21,27,8) -0.0
		D(16,21,27,15) 180.0
		D(20,21,27,8) 180.0
		D(20,21,27,15) -0.1
		D(18,24,29,30) 175.0
		D(18,24,29,31) -67.2
		D(18,24,29,32) 54.6
		D(28,24,29,30) 29.2
		D(28,24,29,31) 146.9
		D(28,24,29,32) -91.2

The assignments of the calculated wavenumbers are aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes [15,16].

4. Results and discussion

The observed IR bands with their relative intensities and calculated wavenumbers and assignments are given in Table 2.

In aromatic compounds the ν_{NH} appears moderately to strongly in the region $3400 \pm 40 \text{ cm}^{-1}$ [17]. The HF calculations give a value of 3448 cm^{-1} for this ν_{NH} mode and a weak band is observed in the IR spectrum at 3428 cm^{-1} . The anti-symmetric stretching vibrations of the methyl group of NHMe absorb in the regions 2965 ± 25 and $2930 \pm 25 \text{ cm}^{-1}$ [17]. The band intensity varies from weak in *N*-methyl-substituted sulfonamides to moderate in *N*-methyl-substituted amines. The methyl symmetric stretch absorbs, sharply and clearly separated from the antisymmetric counter parts, in the region $2855 \pm 70 \text{ cm}^{-1}$, with a moderate to strong intensity in amines [17]. These low wavenumbers, attributed to a reduced force constant of the CH bond under the influence of the free electron pair of the nitrogen atom, is typical for N–Me compounds [18–23] but also for methyl esters. The asymmetrical stretching modes of the methyl group of NHMe are calculated to be $2948, 2911 \text{ cm}^{-1}$ and the symmetric mode at 2843 cm^{-1} . The weak bands observed at $2940, 2915$ and 2820 cm^{-1} in the IR spectrum are assigned as $\nu_{\text{as}}\text{CH}_3$ and $\nu_{\text{s}}\text{CH}_3$, respectively for NHMe group for the title compound. In *N*-methylamines the δ_{NH} [17] should be expected in the region $1530 \pm 50 \text{ cm}^{-1}$, but the very weak intensity of the band hinders the assignment. Both methyl antisymmetric deformations absorb weakly to moderately and often coincide and is expected in the regions 1470 ± 15 and $1460 \pm 15 \text{ cm}^{-1}$ [17]. The region $1410 \pm 35 \text{ cm}^{-1}$ of the methyl symmetric deformation is typical for *N*-methyl-substituted amines and (thio)amides alike [24]. The intensity of the symmetric deformation slightly exceeds that of the antisymmetric modes. The calculated values for $\delta_{\text{as}}\text{CH}_3$ are at $1479, 1462 \text{ cm}^{-1}$. Experimentally one band is observed at 1479 cm^{-1} . The band at 1431 cm^{-1} in the IR spectrum and at 1442 cm^{-1} (HF) are assigned to $\delta_{\text{s}}\text{CH}_3$. The three weak to moderate absorptions

in the regions $1140 \pm 15, 1055 \pm 25$ and $985 \pm 65 \text{ cm}^{-1}$ are due to two methyl-rocking vibrations and a N–C stretching vibration strongly coupled among themselves [17]. The bands in the above regions are assigned to the N–C stretch as well as methyl rock [25]. The absorption near $1135, 1070 \text{ cm}^{-1}$ in the spectra of *N*-methyl sulfonamide is attributed to ρCH_3 and $\nu_{\text{N–C}}$ stretching vibrations [26,27]. For the title compound ρMe are calculated at $1129, 1114 \text{ cm}^{-1}$ and only one band is observed in the IR spectrum at 1131 cm^{-1} . The band calculated at 1036 cm^{-1} is assigned as $\nu_{\text{C}_{24}\text{–N}_{29}}$ stretching mode. In the spectra of *N*-methyl-substituted benzeneamines the NH wag is observed in the range of $635 \pm 35 \text{ cm}^{-1}$ [17]. The band observed at 642 cm^{-1} in the IR spectrum and the calculated value at 639 cm^{-1} is assigned as wagging NH mode. In *N*-methyl-substituted aliphatic amines and sulfonamides the $\delta_{\text{C–N–C}}$ is found in the region $360 \pm 50 \text{ cm}^{-1}$ [17]. In *N*-methyl benzene amines this vibration is coupled to the substituent sensitive Ph–N deformation. The methyl torsion is often assigned in the region $230 \pm 30 \text{ cm}^{-1}$ and the NHMe torsion may be expected in the neighbourhood of 100 cm^{-1} [28,29].

In aromatic compounds the asymmetric stretching vibrations of CH_3 are expected in the range of $2905\text{–}3000 \text{ cm}^{-1}$ and symmetric CH_3 vibrations in the range of $2860\text{–}2870 \text{ cm}^{-1}$ [17,30]. The first of these results from the antisymmetric stretching $\nu_{\text{as}}\text{CH}_3$ mode in which two C–H bonds of the methyl group are extending while the third one is contracting. The second arises from symmetrical stretching $\nu_{\text{s}}\text{CH}_3$ in which all three of the C–H bonds extend and contract in-phase. The asymmetric stretching modes of the methyl group are calculated to be $2930, 2905 \text{ cm}^{-1}$ and the symmetric mode at 2860 cm^{-1} . The band at 2904 cm^{-1} in the IR spectrum is assigned as $\nu_{\text{as}}\text{CH}_3$. Two bending can occur within a methyl group. The first of these, the symmetrical bending vibration, involves the in-phase bending of the C–H bonds. The second, the antisymmetrical bending vibration, involves out-of-phase bending of the C–H bonds. The asymmetric deformations are expected in the range of $1400\text{–}1485 \text{ cm}^{-1}$ [17]. The calculated values of $\delta_{\text{as}}\text{CH}_3$ modes are at 1470 and 1458 cm^{-1} . Experimentally no bands are observed. In many molecules the symmetric deformation $\delta_{\text{s}}\text{CH}_3$ appears with an intensity varying from medium to strong and expected in the range of $1380 \pm 25 \text{ cm}^{-1}$ [17]. The HF calculation gives $\delta_{\text{s}}\text{CH}_3$ at 1400 cm^{-1} . Aromatic molecules display a methyl rock in the neighbourhood of 1045 cm^{-1} [17]. The second rock in the region $970 \pm 70 \text{ cm}^{-1}$ [17] is more difficult to find among the C–H out-of-plane deformations. For the title compound, these modes ρCH_3 are calculated at 1047 and 988 cm^{-1} . The bands at $1052, 988 \text{ cm}^{-1}$ in the IR spectrum are assigned as ρCH_3 modes.

The C=N stretching skeletal bands are observed in the range of $1672\text{–}1566 \text{ cm}^{-1}$ [12,31–33]. Saxena et al. [31] reported a value 1608 cm^{-1} for polybenzodithiazole and Klots and Collier [34] reported a value of 1517 cm^{-1} for benzoxazole as $\nu_{\text{C=N}}$ stretching mode. Yang et al. [35] reported a band at 1626 cm^{-1} in the IR spectrum as $\nu_{\text{C=N}}$ for the oxazole ring. For the title compound, the HF calculation give the $\nu_{\text{C}_{27}\text{=N}_8}$ mode at 1638 cm^{-1} . The authors have reported a value of 1661 cm^{-1} (Raman), 1671 cm^{-1} (IR) and 1643 cm^{-1} (HF) as $\nu_{\text{C=N}}$ mode [11].

Table 2

Calculated vibrational wavenumbers, measured infrared band positions and assignments for 5-methyl-2-(*p*-methylaminophenyl)benzoxazole

$\nu_{\text{(calculated)}} \text{ (cm}^{-1}\text{)}$	$\nu_{\text{(IR)}} \text{ (cm}^{-1}\text{)}$	IR intensity (KM/mole)	Raman activity (A**4/amu)	Assignments
3448	3428 w	34.6	131.8	ν NH
3043	3066 w	9.3	102.7	ν CH II
3037		7.0	58.1	ν CH II
3034	3031 w	10.3	129.8	ν CH I
3028		11.5	46.7	ν CH II
3023		10.1	68.5	ν CH I
2996		15.9	110.1	ν CH I
2995		26.5	102.9	ν CH II
2948	2940 w	39.7	144.3	ν_{as} Me II
2930		24.7	65.7	ν_{as} Me I
2911	2915 w	52.6	79.6	ν_{as} Me II
2905	2904 w	33.4	116.3	ν_{as} Me I
2860		50.1	190.8	ν_{s} Me I
2843	2820 w	79.8	121.4	ν_{s} Me II
1638		86.5	430.6	ν C=N
1616		362.9	1286.7	ν Ph II
1611	1608 vs	1.5	102.0	ν Ph I
1597		165.4	1038.3	ν Ph II
1577	1571 m	130.8	679.1	ν Ph II
1520	1517 vs	429.6	84.2	ν Ph I
1495	1500 vs	0.9	6.7	ν Ph I
1483	1485 sh	5.6	3.2	δ NH
1479	1479 s	73.4	57.9	δ_{as} Me II
1470		41.5	35.4	δ_{as} Me I
1462		9.3	29.3	δ_{as} Me II
1458		4.2	22.6	δ_{as} Me I
1442	1431 s	11.3	10.1	δ_{s} Me II
1423	1419 sh	31.6	147.4	ν Ph I, II
1402		91.8	70.0	δ CH II
1400		6.1	28.1	δ_{s} Me I
1323	1331 s	68.0	153.6	ν C ₂ -N ₈
1298	1291 s	128.9	116.5	ν Ph II
1273	1279 m	167.7	74.3	ν C ₁₈ -N ₂₄
1273		22.8	1.9	δ CH I, II
1264	1261 s	76.1	405.1	ν_{as} C-O-C
1201	1200 m	1.6	12.6	δ CH I
1196		39.0	14.3	δ CH II
1184		15.5	20.9	δ CH I
1168	1176 vs	191.2	177.9	δ CH II
1129	1131 m	3.0	4.6	ρ Me II
1121	1119 m	31.2	14.3	δ CH I
1114		3.7	11.1	ρ Me II
1097	1100 sh	7.7	13.1	δ CH II
1096		3.1	6.7	δ CH I
1066	1076 m	10.9	48.7	ν_{s} C-O-C
1047	1052 m	3.2	1.3	ρ Me I
1036		23.1	12.0	ν C ₂₄ -N ₂₉
990		0.1	1.9	γ CH II
988	988 w	14.5	2.4	ρ Me I
985		5.6	1.5	γ CH II
976		0.1	5.0	γ CH I
954	942 w	1.9	0.1	γ CH I
923	927 m	3.6	37.9	δ NCO
918		13.5	102.4	δ Ph(X) I
893	864 w	9.4	1.4	γ CH I
838	824 s	57.7	0.3	γ CH II
820		3.1	3.3	γ CH II
815		56.9	1.4	γ CH I
813		25.3	0.3	δ Ph I
782	792 s	4.8	24.9	Ring breathing II
752	752 m	18.5	9.2	γ Ph I, II
744		13.6	5.4	γ Ph I, II
741	738 m	4.1	8.9	Ring breathing I
701	702 m	3.6	0.2	γ Ph II

Table 2 (Continued)

$\nu_{\text{(calculated)}} \text{ (cm}^{-1}\text{)}$	$\nu_{\text{(IR)}} \text{ (cm}^{-1}\text{)}$	IR intensity (KM/mole)	Raman activity ($\text{A}^{**4}/\text{amu}$)	Assignments
639	642 w	4.5	2.8	ωNH
621	619 sh	0.6	7.6	$\delta\text{Ph II}$
594	597 m	3.3	0.1	$\gamma\text{Ph(X) I}$
588		3.0	10.5	$\delta\text{Ph(X) I}$
543	536 w	15.0	0.6	$\delta\text{Ph I, II}$
521		10.9	0.9	$\gamma\text{Ph II}$
493	509 m	37.1	2.3	$\delta\text{Ph I, II}$
453		24.2	7.5	$\delta\text{Ph(X) I, II}$
437		3.8	0.4	$\gamma\text{Ph I}$
411		0.1	0.1	$\gamma\text{Ph II}$
393		41.5	9.1	$\gamma\text{Ph(X) I}$
377		53.7	9.2	$\delta\text{Ph(X) I, } \delta\text{C-N-C II}$
347		97.3	11.9	$\delta\text{Ph I, } \tau\text{Me I}$
316		8.8	4.2	$\gamma\text{Ph I, II}$
280		12.5	1.1	$\gamma\text{Ph(X) I}$
258		1.8	1.8	$\gamma\text{Ph(X) I, } \tau\text{Me II}$
228		0.8	0.7	$\tau\text{Me I}$
214		0.4	2.7	$\tau\text{Me II}$
193		1.1	4.0	$\tau\text{Ph I, II}$
175		1.7	1.2	$\tau\text{Me II}$
127		1.7	1.8	τNHMe
84		1.8	0.5	$\tau\text{Me II}$
71		1.0	0.1	$\tau\text{Ph I, II}$
41		0.2	0.5	$\tau\text{Ph I, II}$
37		1.8	0.5	$\tau\text{Me I, II}$
30		0.3	0.2	$\tau\text{Me I, II}$

ν : stretching; δ : in-plane deformation; γ : out-of-plane deformation; ρ : rocking; τ : torsional; Ph: phenyl; I: Ph attached to methyl; II: Ph attached to NHMe; v: very; s: strong; m: medium; w: weak; sh: shoulder; X: substituent sensitive; Subscripts: as: asymmetric; s: symmetric.

Since the identification of all the normal modes of vibration of large molecules is not trivial, we tried to simplified the problem by considering each molecule as a substituted benzene. Such an idea has already been successfully utilized by several workers for the vibrational assignments of molecules containing multiple homo- and heteroaromatic rings [36–40]. In the following discussion, the phenyl rings attached with the methyl group and NHMe group are designated as rings I and II, respectively. The modes in the two phenyl rings will differ in wavenumber and the magnitude of splitting will depend on the strength of interactions between different parts (internal coordinates) of the two rings. For some modes, this splitting is so small that they may be considered as quasi-degenerate and for the other modes a significant amount of splitting is observed. Such observations have already been reported [36–38,41].

Primary aromatic amines with nitrogen directly on the ring absorb strongly at 1330–1260 cm^{-1} due to stretching of the phenyl carbon–nitrogen bond [30]. For 2-mercaptobenzoxazole this mode [42] is reported at 1340 cm^{-1} (Raman) and 1325 cm^{-1} (ab initio calculations). Sandhyarani et al. [43] reported νCN at $\sim 1318 \text{ cm}^{-1}$ for 2-mercaptobenzothiazole. For benzoxazole $\nu\text{C}_2\text{-N}_8$, the authors have reported [11] a value at 1332 cm^{-1} (IR), 1315 cm^{-1} (Raman) and 1315 cm^{-1} (HF). For the title compound $\nu\text{C}_2\text{-N}_8$ mode is observed at 1331 cm^{-1} in the IR spectrum and the calculated value is 1323 cm^{-1} . The $\nu\text{C}_{18}\text{-N}_{24}$ band is observed at 1279 cm^{-1} in the IR spectrum and at 1273 cm^{-1} theoretically.

As expected the asymmetric C–O–C stretching vibration produce strong band at 1261 cm^{-1} in the IR spectrum [12,32]. The

symmetric C–O–C stretching vibration appears as a weak band in the IR spectrum at 1076 cm^{-1} [12,32]. The ab initio calculation give 1264 and 1066 cm^{-1} as asymmetric and symmetric C–O–C modes, respectively. The C–O–C stretching is reported at 1250 and 1073 cm^{-1} for 2-mercaptobenzoxazole [42] and at 1061 cm^{-1} (Raman), 1055 cm^{-1} (IR), 1060 cm^{-1} (HF) and at 1269 cm^{-1} (Raman), 1263 cm^{-1} (IR) and 1261 cm^{-1} (HF) for 5-methyl-2-(*p*-fluorophenyl)benzoxazole [11]. Fukukawa and Ueda [44] reported the symmetric C–O–C stretch at 1045 cm^{-1} for benzoxazole.

The existence of one or more aromatic rings in a structure is normally readily determined from the C–H and C=C–C ring related vibrations. The C–H stretching occurs above 3000 cm^{-1} and is typically exhibited as a multiplicity of weak to moderate bands, compared with the aliphatic C–H stretch [45]. Klots and Collier [34] reported the bands at 3085, 3074, 3065 and 3045 cm^{-1} as $\nu\text{C-H}$ modes for benzoxazole. In the present case, ab initio calculations give $\nu\text{C-H}$ modes in the range of 3043–2995 cm^{-1} . The bands observed at 3066 and 3031 cm^{-1} in the IR spectrum are assigned as $\nu\text{C-H}$ modes of the benzene ring.

For the *para*-disubstituted benzene, the νPh modes are expected in the range of 1280–1620 cm^{-1} and for the trisubstituted benzene ring these modes are seen in the region 1250–1610 cm^{-1} [17]. For *para*-substituted benzenes the δCH modes are seen in the range of 995–1315 cm^{-1} [17] and for trisubstituted benzenes these modes are in the range of 1050–1280 cm^{-1} [17]. For the title compound, the HF calculation give 1402, 1273, 1201, 1196, 1184, 1168, 1121, 1097,

1096 cm^{-1} as δCH modes. These bands are observed at 1200, 1176, 1119, 1100 cm^{-1} in the IR spectrum.

The C–H out-of-plane deformations are observed between 1000 and 700 cm^{-1} [17]. Generally the C–H out-of-plane deformations with the highest wavenumbers have a weaker intensity than those absorbing at lower wavenumbers. These γCH modes are observed at 942, 864, 824 cm^{-1} in the IR spectrum. The ab initio calculations give these modes at 990, 985, 976, 954, 893, 838, 820, 815 cm^{-1} .

For benzoxazole, Klots and Collier [34] reported the bands at 932, 847 and 746 cm^{-1} as out-of-plane deformations of the benzene ring. According to Collier and Klots [46] the non-planar vibrations are observed at 970, 932, 864, 847, 764, 746, 620, 574, 417, 254, 218 cm^{-1} for benzoxazole and at 973, 939, 856, 824, 757, 729, 584, 489, 419, 207, 192 cm^{-1} for benzothiazole. The planar modes below 1000 cm^{-1} for benzoxazole are reported to be at 920, 870, 778, 622, 538, 413 cm^{-1} and for benzothiazole at 873, 801, 712, 666, 531, 504, 530 cm^{-1} [46]. We have also observed the planar and non-planar modes for the title compound in this region. Two very strong CH out-of-plane deformation bands, occurring at $840 \pm 50 \text{ cm}^{-1}$ is typical for 1,4-disubstituted benzenes [17]. For the title compound, a very strong γCH is observed at 824 cm^{-1} . Again, according to literature [17,30] a lower γCH absorbs in the neighbourhood $820 \pm 45 \text{ cm}^{-1}$, but is much weaker or infrared inactive. The ab initio calculations gives a γCH at 820 cm^{-1} and no band is experimentally observed for this mode. In the case of trisubstituted benzenes, two γCH bands are observed at $890 \pm 50 \text{ cm}^{-1}$ and $815 \pm 45 \text{ cm}^{-1}$ in the IR spectrum. Theoretically the values observed are 954 and 893 cm^{-1} .

The benzoxazole ring stretching vibrations exist in the range of 1608–1419 cm^{-1} in the IR spectrum [31,47]. Bands observed at 1608, 1517, 1500, 1419 cm^{-1} [31] are assigned as the ring stretching vibrations. Klots and Collier [34] reported the bands at 1615, 1604, 1475 and 1451 cm^{-1} as fundamental ring vibrations of the benzoxazole ring.

The ring breathing modes for the *para*-disubstituted benzenes with entirely different substituents [48] have been reported to be strongly IR active with typical bands in the interval 780–840 cm^{-1} . This is confirmed by the strong band in the infrared spectrum at 792 cm^{-1} , which finds support from the computational results. In asymmetric trisubstituted benzenes, when all the three substituents are light, the frequency interval of the breathing mode is between 500 and 600 cm^{-1} . When all the three substituents are heavy, the frequency appears above 1100 cm^{-1} . In the case of mixed substitution the frequency is expected to appear between 600 and 750 cm^{-1} [48]. For the title compound the phenyl ring I ring breathing mode is observed at 738 cm^{-1} in the IR spectrum and at 741 cm^{-1} theoretically as expected.

For the title compound the bond lengths C₃–O₁₅, C₂–N₈ are found to be 1.3590 and 1.3892 Å while for 2-mercaptobenzoxazole [42] these are respectively 1.3436 and 1.3739 Å. The bond length N₈–C₂₇, O₁₅–C₂₇, C₂–C₃ are found to decrease to 1.2753, 1.3492 and 1.3784 Å from the values 1.3001, 1.3804 and 1.3927 Å observed for 2-mercaptobenzoxazole [42]. According to Lifshitz et al. [49]

for benzoxazole, the bond lengths, N₈–C₂₇, C₂₇–O₁₅, O₁₅–C₃, C₃–C₄, C₂–C₁, C₂–C₃ and N₈–C₂ are 1.291, 1.372, 1.374, 1.390, 1.4, 1.403 and 1.401 Å respectively and the corresponding values for the title compound are 1.2753, 1.3492, 1.3590, 1.3768, 1.3879, 1.3784 and 1.3892 Å. These changes in bond lengths for the title compound can be attributed to the conjugation of the phenyl ring. Purkayastha and Chattopadhyay [50] reported N₈–C₂₇, N₈–C₂ bond lengths as 1.3270, 1.400 Å for benzothiazole and 1.3503, 1.407 Å for benzimidazole compounds. For the title compound we have obtained 1.2753 Å as N₈–C₂₇ and 1.3892 Å as N₈–C₂ bond lengths. The carbon–carbon bond lengths in the phenyl ring I lies between 1.3768 and 1.4034 Å while for phenyl ring II, the range is 1.3752–1.4007 Å. The CH bond lengths lies between 1.0739 and 1.0761 Å for Ph I and 1.0728–1.0762 Å for Ph II. Here for the title compound, benzene is a regular hexagon with bond lengths somewhere in between the normal values for a single (1.54 Å) and a double (1.33 Å) bond [51]. The HF calculation gives shortening of angle C₁₉–C₁₈–N₂₄ by 0.6° and increase of angle C₁₇–C₁₈–N₂₄ by 2.3° from 120° at C₁₈ position and this asymmetry of exocyclic angle reveals the repulsion between NHMe group and the phenyl ring.

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