

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

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Abstract

5-Nitro-2-(*p*-fluorophenyl)benzoxazole was prepared by heating 2-hydroxy-5-nitro aniline with *p*-fluorobenzoic acid in polyphosphoric acid. The FT-IR spectrum is recorded and analysed. The vibrational frequencies and corresponding vibrational assignments are examined theoretically using the Gaussian03 set of quantum chemistry codes. Predicted infrared and Raman intensities are reported.
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1. Introduction

The present study is on the analysis of FT-IR spectrum of 5-nitro-2-(*p*-fluorophenyl)benzoxazole, and using the ab initio method theoretically, the wavenumbers are calculated. This work is a part of our investigations on substituted benzoxazole derivatives. 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]. It has been reported that they have shown low toxicity in warm-blooded animals [4,6]. Yalcin et al. [7–10] reported the synthesis and microbiological activity of 5-substituted-2-(*p*-substitutedphenyl)benzoxazole derivatives. Anto et al. [11] reported the vibrational spectroscopic and ab initio calculations of 5-methyl-2-(*p*-fluorophenyl)benzoxazole. Vibrational spectroscopic studies and ab initio calculations of 5-methyl-2-(*p*-methylaminophenyl)benzoxazole is also reported by Ambujakshan et al. [12]. 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.

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 [13]. Reactions, which occurred in pyridine or xylene, also have 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 [13]. The title compound was prepared by heating 2-hydroxy-5-nitro aniline with the *p*-fluorobenzoic acid in polyphosphoric acid [13] and the structure of the title compound were supported by elemental analysis and spectral data. The melting point was measured with a capillary melting point apparatus (Buchi SMP 20 and Electrothermal 9100) and is uncorrected. The FT-IR spectrum (Fig. 1) was recorded on a Jasco FT-IR-420 spectrometer

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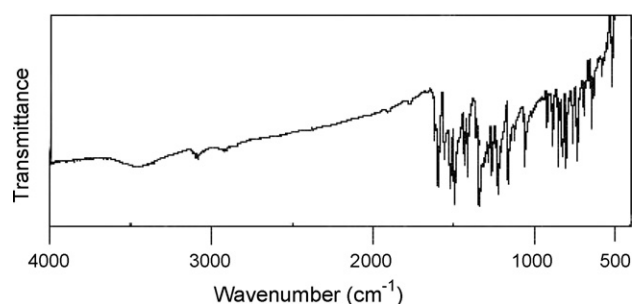


Fig. 1. FT-IR spectrum.

as KBr discs. The ^1H NMR spectrum was recorded employing a VARIAN Mercury 400 MHz FT spectrometer, chemical shifts (δ) are in ppm relative to TMS, and coupling constants (J) are reported in Hertz. Elemental analyses were taken on a Leco 932 CHNS–O analyzer. The result of the elemental analyses (C, H, N) were within $\pm 0.4\%$ of the calculated amounts. ^1H NMR (400 MHz, CDCl_3): δ 7.23–7.27 (m, 2H), 7.67 (d, 1H, J 8.0), 8.26–8.33 (m, 3H), 8.62 (d, 1H, J 2.0).

3. Computational details

Calculations of the title compound are carried out with Gaussian03 program [14] 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 are calculated using the analytic 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 [15]. 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 72 vibrations from 3083 to 35 cm^{-1} . The assignments of the calculated wavenumbers are aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes [16,17].

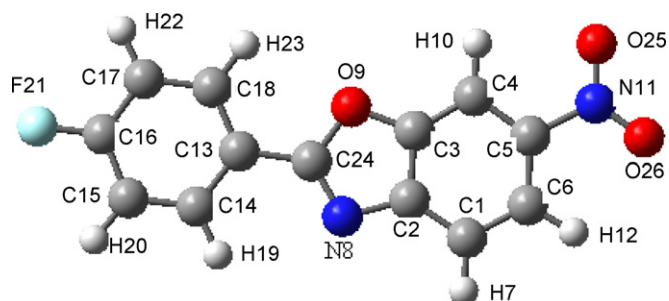
Fig. 2. Optimized geometry of 5-nitro-2-(*p*-fluorophenyl)benzoxazole.

Table 1

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

Bond lengths (Å)	Bond angles (°)	Dihedral angles (°)
C ₁ –C ₂ 1.3872	A(2,1,6) 117.5	D(6,1,2,3) 0.0
C ₁ –C ₆ 1.3812	A(2,1,7) 121.2	D(6,1,2,8) 180.0
C ₁ –H ₇ 1.0729	A(6,1,7) 121.4	D(7,1,2,3) –180.0
C ₂ –C ₃ 1.3854	A(1,2,3) 120.2	D(7,1,2,8) –0.0
C ₂ –N ₈ 1.3827	A(1,2,8) 131.6	D(2,1,6,5) –0.0
C ₃ –C ₄ 1.37	A(3,2,8) 108.3	D(2,1,6,12) –180.0
C ₃ –O ₉ 1.3566	A(2,3,4) 124.2	D(7,1,6,5) –180.0
C ₄ –C ₅ 1.3865	A(2,3,9) 107.0	D(7,1,6,12) –0.0
C ₄ –H ₁₀ 1.0702	A(4,3,9) 128.7	D(1,2,3,4) –0.0
C ₅ –C ₆ 1.3938	A(3,4,5) 114.4	D(1,2,3,9) –180.0
C ₅ –N ₁₁ 1.4556	A(3,4,10) 123.6	D(8,2,3,4) 180.0
C ₆ –H ₁₂ 1.0706	A(5,4,10) 122.0	D(8,2,3,9) 0.0
O ₉ –H ₂₃ 2.4698	A(4,5,6) 123.4	D(2,3,4,5) –0.0
O ₉ –C ₂₄ 1.3456	A(4,5,11) 118.0	D(2,3,4,10) –180.0
C ₂₄ –N ₈ 1.2700	A(6,5,11) 118.6	D(9,3,4,5) 180.0
N ₁₁ –O ₂₅ 1.1948	A(1,6,5) 120.3	D(9,3,4,10) –0.0
N ₁₁ –O ₂₆ 1.1936	A(1,6,12) 120.8	D(2,3,9,23) –179.8
C ₁₃ –C ₁₄ 1.3935	A(5,6,12) 118.9	D(2,3,9,24) –0.0
C ₁₃ –C ₁₈ 1.3911	A(3,9,23) 170.4	D(4,3,9,23) 0.2
C ₁₄ –C ₁₅ 1.3796	A(3,9,24) 104.8	D(4,3,9,24) 180.0
C ₁₄ –H ₁₉ 1.073	A(23,9,24) 84.8	D(3,4,5,6) 0.0
C ₁₅ –C ₁₆ 1.3812	A(5,11,25) 117.6	D(3,4,5,11) 180.0
C ₁₅ –H ₂₀ 1.0733	A(5,11,26) 117.9	D(10,4,5,6) 180.0
C ₁₆ –C ₁₇ 1.3787	A(25,11,26) 124.6	D(10,4,5,11) –0.0
C ₁₆ –F ₂₁ 1.3242	A(14,13,18) 120.0	D(4,5,6,1) –0.0
C ₁₇ –C ₁₈ 1.3825	A(3,14,15) 120.4	D(4,5,6,12) –180.0
C ₁₇ –H ₂₂ 1.0732	A(13,14,19) 119.3	D(11,5,6,1) 180.0
C ₁₈ –H ₂₃ 1.0729	A(15,14,19) 120.3	D(11,5,6,12) –0.0
	A(14,15,16) 118.5	D(4,5,11,25) 0.0
	A(14,15,20) 121.8	D(4,5,11,26) 180.0
	A(16,15,20) 119.7	D(6,5,11,25) –180.0
	A(15,16,17) 122.5	D(6,5,11,26) –0.0
	A(15,16,21) 118.7	D(3,9,23,18) 179.8
	A(17,16,21) 118.8	D(24,9,23,18) 0.0
	A(16,17,18) 118.5	D(18,13,14,15) –0.0
	A(16,17,22) 119.8	D(18,13,14,19) 180.0
	A(18,17,22) 121.7	D(14,13,18,17) –0.0
	A(13,18,17) 120.3	D(14,13,18,23) –180.0
	A(13,18,23) 120.0	D(13,14,15,16) 0.0
	A(17,18,23) 119.6	D(13,14,15,20) –180.0
	A(9,23,18) 96.7	D(19,14,15,16) –180.0
		D(19,14,15,20) 0.0
		D(14,15,16,17) –0.0
		D(14,15,16,21) 180.0
		D(20,15,16,17) –180.0
		D(20,15,16,21) 0.0
		D(15,16,17,18) –0.0
		D(15,16,17,22) 180.0
		D(21,16,17,18) –180.0
		D(21,16,17,22) –0.0
		D(16,17,18,13) 0.0
		D(16,17,18,23) 180.0
		D(22,17,18,13) 180.0
		D(22,17,18,23) –0.0
		D(13,18,23,9) –0.0
		D(17,18,23,9) 180.0

Table 2
 Calculated vibrational wavenumbers, measured infrared band positions and assignments for 5-nitro-2-(*p*-fluorophenyl)benzoxazole

$\nu_{(\text{calculated})}$ (cm ⁻¹)	$\nu_{(\text{IR})}$ (cm ⁻¹)	IR intensity (kM/mol)	Raman activity (A**4/amu)	Assignments
3083	3100 w	7.00	47.37	$\nu(\text{CH})$ II
3074	3087 w	0.97	101.14	$\nu(\text{CH})$ II
3051		2.17	152.48	$\nu(\text{CH})$ I
3050		21.13	40.79	$\nu(\text{CH})$ I
3044		2.14	78.77	$\nu(\text{CH})$ II
3038		0.55	111.09	$\nu(\text{CH})$ I
3036		6.68	49.32	$\nu(\text{CH})$ I
1663	1692 vw	325.51	10.55	$\nu\text{C}=\text{N}$
1637		164.08	217.08	$\nu_{\text{as}}\text{NO}_2$
1620	1622 sh	191.51	643.18	νPh I
1603	1601 s	185.34	490.18	νPh II
1593		7.97	17.10	νPh I
1572	1561 m	127.97	1183.68	νPh II
1508	1521 s	252.23	23.22	νPh I
1475	1497 vs	44.71	55.92	νPh II
1451		757.58	668.16	νPh II
1432	1437 s	26.06	53.70	$\nu_{\text{s}}\text{NO}_2$
1405	1416 s	53.30	57.91	νPh I
1312	1343 vvs	61.40	47.82	$\nu\text{C}_2-\text{N}_8$
1288	1288 w	30.22	107.95	νPh I
1281	1265 s	101.57	326.58	$\nu_{\text{as}}\text{C}-\text{O}-\text{C}$
1249		144.88	9.30	νPh II
1239	1227 s	30.80	69.45	$\nu\text{C}-\text{F}$
1212		73.32	52.97	δCH II
1191		8.24	12.12	δCH II
1160	1162 s	4.73	11.85	δCH I
1144		73.60	45.93	δCH I
1104	1123 w	10.33	13.22	δCH II
1069		13.32	17.73	δCH II
1067	1062 s	40.41	3.20	$\nu_{\text{s}}\text{C}-\text{O}-\text{C}$
1056		9.85	161.08	δCH I
994	1000 w	0.01	0.32	δCH I
994		5.42	0.26	γCH I
987		0.00	2.75	γCH I
975		0.01	4.09	γCH II
931	935 w	0.59	26.30	γCH I
925		9.94	28.53	δNCO
924	923 m	24.77	2.02	γCH II
857	889 m	63.28	0.16	$\nu\text{C}-\text{C}$
853	849 s	25.15	0.87	γCH I
840		12.43	20.88	δNO_2
834	828 s	0.58	2.54	γCH II
820		27.57	1.38	γCH I
795	804 s	63.45	25.81	Ring breathing I
769	762 m	77.01	9.09	ωNO_2
748		6.99	8.81	$\delta\text{Ph}(\text{X})$ I
738	733 s	11.20	0.35	Ring breathing II
689	691 m	1.04	0.19	γPh I
685	662 w	14.39	15.93	γPh II
628	628 w	17.48	3.42	$\delta\text{Ph}(\text{X})$ II
619		3.74	10.80	δPh I
567	578 w	0.36	0.22	$\delta\text{Ph}(\text{X})$ I
561		3.14	0.83	$\gamma\text{Ph}(\text{X})$ II
544		1.49	0.40	$\gamma\text{Ph}(\text{X})$ I
519	514 w	9.56	0.01	$\delta\text{Ph}(\text{X})$ II
496	487 w	4.96	1.04	ρNO_2
433	436 w	1.49	0.15	γPh I
413	419 w	0.01	0.02	$\delta\text{Ph}(\text{X})$ I
407		2.16	0.92	$\gamma\text{Ph}(\text{X})$ II
387		0.14	0.72	$\delta\text{Ph}(\text{X})$ II
375		7.15	0.31	$\delta\text{CC}(\text{X})$ I
317		7.00	1.71	γPh I
299		0.05	5.64	$\delta\text{CC}(\text{X})$ II
268		0.02	2.08	$\delta\text{CF}(\text{X})$ I

Table 2 (Continued)

$\nu_{\text{(calculated)}} \text{ (cm}^{-1}\text{)}$	$\nu_{\text{(IR)}} \text{ (cm}^{-1}\text{)}$	IR intensity (kM/mol)	Raman activity (A^{**4}/amu)	Assignments
227		1.52	1.28	$\gamma\text{CC(X) I}$
192		0.93	1.14	$\gamma\text{CO(X) II}$
171		8.44	0.68	$\gamma\text{CC(X) II}$
106		0.93	0.39	$\gamma\text{CF(X) I}$
70		0.51	0.23	τNO_2
57		0.03	0.04	τPh
40		0.07	0.49	τPh
35		0.53	1.94	τPh

(ν) stretching; (δ) in-plane deformation; (γ) out-of-plane deformation; (ρ) rocking; (τ) torsional; (Ph) phenyl; (I) Ph attached to fluorine; (II) Ph attached to nitro group; (v) very; (s) strong; (m) medium; (w) weak; (X) substituent sensitive; subscripts: (as) asymmetric; (s) symmetric.

4. Results and discussion

The observed IR bands with their relative intensities and calculated wavenumbers and assignments are given in Table 2. The most characteristic bands in the spectra of nitro compounds are due to the NO_2 stretching vibrations. In nitro compounds, the asymmetric and symmetric NO_2 stretching vibrations are located in the regions 1661–1499 and 1389–1259 cm^{-1} , respectively [18,19]. Nitrobenzene derivatives display $\nu_{\text{as}}\text{NO}_2$ in the region $1535 \pm 30 \text{ cm}^{-1}$ and 3-nitropyridines at $1530 \pm 20 \text{ cm}^{-1}$ [18,20]. In substituted nitrobenzenes [18,19] $\nu_{\text{s}}\text{NO}_2$ appears strongly at $1345 \pm 30 \text{ cm}^{-1}$, in 3-nitropyridine at $1350 \pm 20 \text{ cm}^{-1}$ and in conjugated nitroalkenes [21] at $1345 \pm 15 \text{ cm}^{-1}$. For the title compound, asymmetric and symmetric NO_2 stretching vibrations are calculated at 1637 and 1432 cm^{-1} and only the symmetric mode is observed as a strong band in the IR spectrum at 1437 cm^{-1} . The NO_2 scissors [18] occur at higher wavenumbers ($850 \pm 60 \text{ cm}^{-1}$) when conjugated to $\text{C}=\text{C}$ or aromatic molecules, according to some investigators [22–24] with a contribution of the νCN which is expected near 1120 cm^{-1} . For nitrobenzene, δNO_2 is reported [18] at 852 cm^{-1} , for $\text{H}_2\text{C}=\text{CHNO}_2$ at 890 cm^{-1} and 1,3-dinitrobenzene at 904 and 834 cm^{-1} . For the title compound the band at 840 cm^{-1} (calculated) is assigned as δNO_2 mode. In aromatic compounds the wagging mode ωNO_2 is assigned at $740 \pm 50 \text{ cm}^{-1}$ with a moderate to strong intensity, a region in which γCH also is active [18]. ωNO_2 is reported at 701 and 728 cm^{-1} for 1,2-dinitrobenzene and at 710 and 772 cm^{-1} for 1,4-dinitrobenzene [18]. For the title compound the band at 762 cm^{-1} in the IR spectrum is assigned as ωNO_2 mode. The HF calculation gives 769 cm^{-1} as the ωNO_2 mode. The rocking mode ρNO_2 is active in the region $540 \pm 70 \text{ cm}^{-1}$ in aromatic nitro compounds [18]. Varsanyi et al. [25] found $70 \pm 20 \text{ cm}^{-1}$ and Suryanarayana et al. [26] $65 \pm 10 \text{ cm}^{-1}$ as the torsion of NO_2 for aromatic compounds. In the present case the rocking mode is observed at 487 cm^{-1} in the IR spectrum. The HF calculations give 496 cm^{-1} as ρNO_2 and 70 cm^{-1} as the torsional mode of nitro group.

Fluorine atoms directly attached to an aromatic ring give rise to bands in the region 1270–1100 cm^{-1} [27]. Many of these compounds including the simpler ones with one fluorine only on the ring absorb near 1230 cm^{-1} [27]. Saxena et al. [28] reported a value 1157 cm^{-1} for polybenzodithiazole and Anto et al. [11]

reported a value 1223 (IR), 1244 cm^{-1} (HF) for 5-methyl-2-(*p*-fluorophenyl)benzoxazole as $\nu\text{C-F}$ stretching mode. For the title compound the stretching mode $\nu\text{C-F}$ is observed in the IR spectrum at 1227 cm^{-1} and the calculated value is 1239 cm^{-1} .

The $\text{C}=\text{N}$ stretching skeletal bands are observed in the range 1672–1566 cm^{-1} [13,19,28,29]. Saxena et al. [28] reported a value of 1608 cm^{-1} for polybenzodithiazole and Klots and Collier [30] reported a value of 1517 cm^{-1} for benzoxazole as $\nu\text{C}=\text{N}$ stretching mode. Yang et al. [31] reported a band at 1626 cm^{-1} in the IR spectrum as $\nu\text{C}=\text{N}$ for the oxazole ring. For substituted benzoxazole derivatives, $\nu\text{C}=\text{N}$ is reported at 1638, 1643 (HF) 1661 (Raman) and 1671 cm^{-1} (IR) [11,12]. For the title compound, the HF calculation give the $\nu\text{C}_{24}=\text{N}_8$ mode at 1663 cm^{-1} and a weak band is observed at 1692 cm^{-1} in the IR spectrum.

Since the identification of all the normal modes of vibration of large molecules is not trivial, we tried to simplify 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 [11,12,32–36]. In the following discussion, the phenyl rings attached with the fluorine and nitro groups are designated as rings I and II, respectively. The modes in the two phenyl rings will differ in wavenumber and 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 [32–34,37].

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 [27]. For 2-mercaptobenzoxazole this mode [38] is reported at 1340 cm^{-1} (Raman) and 1325 cm^{-1} (ab initio calculations). Sandhyarani et al. [39] reported $\nu\text{CN} \sim 1318 \text{ cm}^{-1}$ for 2-mercaptobenzothiazole. For benzoxazole compounds, the authors have reported [11,12] $\nu\text{C}_2\text{N}_8$, at 1332, 1331 (IR), 1315 (Raman) 1315, 1323 cm^{-1} (HF). For the title compound $\nu\text{C}_2\text{N}_8$ mode is observed at 1343 cm^{-1} in the IR spectrum and the calculated value is 1312 cm^{-1} .

As expected the asymmetric C-O-C stretching vibration produce strong band at 1265 cm^{-1} in the IR spectrum [13,19]. The symmetric C-O-C stretching vibration appears as a strong band in the IR spectrum at 1062 cm^{-1} [13,19]. The ab initio calculation give 1281 and 1067 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 [38] and 1269 (Raman), 1263 (IR), 1261 (HF), 1061 (Raman), 1055 (IR), 1060 cm^{-1} (HF) for 5-methyl-2-(*p*-fluorophenyl)benzoxazole [11] and 1261 (IR), 1264 (HF), 1076 (IR), 1066 cm^{-1} (HF) for 5-methyl-2-(*p*-methylaminophenyl)benzoxazole [12]. Fukukawa and Ueda [40] reported the symmetric C–O–C stretch at 1045 cm^{-1} for benzoxazole.

The existence of one or more aromatic rings in structure is normally 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 multiplicity of weak to moderate bands, compared with the aliphatic C–H stretching [41]. Klots and Collier [30] reported the bands at 3085, 3074, 3065 and 3045 cm^{-1} as ν C–H modes for benzoxazole. The C–H modes are reported at, 3023, 3048 cm^{-1} (IR), 3036, 3075 cm^{-1} (Raman) and in the range 3001–3050 cm^{-1} (HF) for 5-methyl-2-(*p*-fluorophenyl)benzoxazole [11], and at 3066, 3031 cm^{-1} (IR) and in the range 2995–3043 cm^{-1} (HF) for 5-methyl-2-(*p*-methylaminophenyl)benzoxazole [12]. In the present case, the ab initio calculation give ν C–H modes in the range 3036–3083 cm^{-1} . The weak bands observed at 3100 and 3087 cm^{-1} in the IR spectrum are assigned as these modes.

For the paradisubstituted light heavy, fluorine attached phenyl ring the ν Ph modes are expected in the range 1280–1620 cm^{-1} and for the trisubstituted phenyl ring these modes are seen in the region 1640–1260 cm^{-1} [18]. For the parasubstituted benzene ring I the ν Ph modes are observed at 1622, 1521, 1416, 1288 cm^{-1} in the IR spectrum and at 1620, 1593, 1508, 1405, 1288 cm^{-1} theoretically. For the trisubstituted benzene ring II, the ν Ph modes are observed at 1601, 1561, 1497 cm^{-1} in the IR spectrum and at 1603, 1572, 1475, 1451, 1249 cm^{-1} theoretically. In the present case the benzoxazole ring stretching vibrations exist in the range 1603–1249 cm^{-1} theoretically [28,42]. Anto et al. [11] reported these modes at 1504, 1433, 1418 cm^{-1} in the Raman spectrum, 1499, 1474, 1412, 1309 cm^{-1} in the IR spectrum as ring stretching vibrations. Klots and Collier [30] reported the bands at 1615, 1604, 1475, 1451 cm^{-1} as fundamental ring vibrations of the benzoxazole ring. Ambujakshan et al. [12] reported bands at 1608, 1517, 1500, 1419 cm^{-1} in the IR spectrum as ring stretching vibrations.

The ring breathing modes for the paradisubstituted benzenes with entirely different substituents [43] have been reported to be strongly IR active with typical bands in the interval 780–840 cm^{-1} . For the title compound, this is confirmed by the strong band in the infrared spectrum at 804 cm^{-1} which finds support from the computational results. Ambujakshan et al. [12] reported a value 792 cm^{-1} (IR) and 782 cm^{-1} (HF) as ring breathing mode.

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} [43]. When all the three substituents are heavy, the frequency appears above 1100 cm^{-1} . In the case of mixed substituents the frequency is expected to appear between 600 and 750 cm^{-1} [43]. For the title compound the phenyl ring II breathing mode is observed at 733 cm^{-1} in the IR spectrum

and at 738 cm^{-1} theoretically as expected. This is in agreement with the results obtained by Ambujakshan et al. [12].

For paradisubstituted benzenes the δ CH modes are seen in the range 995–1315 cm^{-1} and for trisubstituted benzenes these modes are in the range 1290–1050 cm^{-1} [18]. Bands observed at 1162, 1123, 1000 cm^{-1} in the IR spectrum are assigned as δ CH modes. The ab initio calculations give these modes at 1212, 1191, 1160, 1144, 1104, 1056 and 994 cm^{-1} .

The CH out-of-plane deformations are observed between 1000 and 700 cm^{-1} [18]. Generally, the CH out-of-plane deformations with the highest wavenumbers have a weaker intensity than those absorbing at lower wavenumbers. These γ CH modes are observed at 935, 923, 849, 828 cm^{-1} in the IR spectrum. The ab initio calculations give these modes at 994, 987, 975, 931, 924, 853, 834 and 820 cm^{-1} . These results are in agreement with that for previous reports [11,12].

For benzoxazole, Klots and Collier [30] reported the bands at 932, 847 and 746 cm^{-1} as out-of-plane deformations for the benzene ring. According to Collier and Klots [44] the non-planar vibrations are observed at 970, 932, 864, 847, 764, 620, 574, 417, 254, 218 cm^{-1} for benzoxazole and at 973, 939, 856, 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} [44]. 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 [18]. For the title compound, a very strong γ CH is observed at 849 cm^{-1} . Again according to literature [18,27] a lower γ CH absorbs in the neighbourhood $820 \pm 45 \text{ cm}^{-1}$, but is much weaker or infrared inactive. The ab initio calculations give a γ CH at 820 cm^{-1} and no band is experimentally observed for this mode. In the case of trisubstituted benzenes, two γ CH bands are observed at 890 ± 50 and $815 \pm 45 \text{ cm}^{-1}$ in the IR spectrum. The bands observed at 923, 828 cm^{-1} in the IR spectrum and 924, 834 cm^{-1} (HF) are assigned as these modes.

For the title compound the bond lengths C₃–O₉, C₂–N₈ are found to be 1.3566 and 1.3827 Å, while these are, respectively, 1.3436, 1.3739 Å for 2-mercaptobenzoxazole [38], 1.3590, 1.3892 Å for 5-methyl-2-(*p*-methylaminophenyl)benzoxazole [12], 1.3594, 1.3903 Å for 5-methyl-2-(*p*-fluorophenyl)benzoxazole [11]. The bond lengths N₈–C₂₄, O₉–C₂₄, C₂–C₃ are found to decrease to 1.27, 1.3456 and 1.3854 Å from the values 1.3001, 1.3804 and 1.3827 Å observed for 2-mercaptobenzoxazole [38]. For substituted benzoxazole these values are 1.2753, 1.3492, 1.3784 Å [12] and 1.2727, 1.347 and 1.3776 Å [11].

According to Lifshitz et al. [45] for benzoxazole, the bond lengths N₈–C₂₄, C₂₄–O₉, O₉–C₃, C₂–C₁, C₃–C₄, C₂–C₃ and N₈–C₂ are 1.291, 1.372, 1.374, 1.39, 1.4, 1.403 and 1.401 Å, respectively, and the corresponding values for the title compound are 1.27, 1.3456, 1.3566, 1.3872, 1.37, 1.3854 and 1.3827 Å. These changes in bond lengths for the title compound can be attributed to the conjugation of the phenyl ring. In our previous works, the corresponding values are 1.2753, 1.3492,

1.359, 1.3768, 1.3879, 1.3784, 1.3892 Å [12] and 1.2727, 1.347, 1.3594, 1.3884, 1.3777, 1.3776, 1.3903 Å [11] for benzoxazole derivatives.

Purkayastha and Chattopadhyay [46] reported N_8-C_{24} , N_8-C_2 bond lengths as 1.327, 1.4 Å for benzothiazole and 1.3503, 1.407 Å for benzimidazole compounds. For the title compound, we have obtained 1.27 Å as N_8-C_{24} and 1.3827 Å as N_8-C_2 bond lengths. The substitution of fluorine in the phenyl ring shortens the C–C bond lengths $C_{16}-C_{15}$ and $C_{16}-C_{17}$ of the benzene ring. Fluorine is highly electronegative and tries to obtain additional electron density. It attempts to draw it from the neighbouring atoms which move closer together in order to share the electrons more easily as a result. Due to this the bond angle A(15,16,17) is found to be 122.5° in the present calculation which is 120° for normal benzene. Similarly, the bond lengths $C_{16}-C_{15}$ and $C_{16}-C_{17}$ are 1.3812 and 1.3787 Å, respectively, which is 1.3864 Å for benzene [11]. The C–C bond lengths in the phenyl ring I lies between 1.3787 and 1.3935 Å while for phenyl ring II, the range is 1.37–1.3938 Å. The CH bond lengths lies between 1.0729 and 1.0733 Å for Ph I and 1.0702–1.0729 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 [47].

The HF calculations also give shortening of the angles $C_6-C_5-N_{11}$ by 1.4° and $C_4-C_5-N_{11}$ by 2° from 120° at C_5 position and $C_5-N_{11}-O_{26}$ by 2.1° and $C_5-N_{11}-O_{25}$ by 2.4° from 120° at N_{11} position. This reduction in angles reveal the hydrogen bonding with H_{12} and H_{10} which is evident from the enlargement in the angles $C_4-C_5-C_6$ by 3.5° and $O_{26}-N_{11}-O_{25}$ by 4.6°.

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