

Vibrational spectroscopic studies and theoretical calculations of 2-phenyl-4H-3,1-benzoxazin-4-one

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(Received: October 22, 2008; Accepted: December 01, 2008)

ABSTRACT

FT-IR and FT-Raman spectra of 2-phenyl-4H-3,1-benzoxazin-4-one were recorded and analyzed. The vibrational wavenumbers of the title compound have been computed using the Hartree-Fock and B3LYP levels of theory using 6-31G* basis set and compared with the experimental data. The results indicate that B3LYP calculations approximate the observed fundamental wavenumbers much better than the HF results. The first hyperpolarizability value is also reported. The prepared compound was identified by NMR and mass spectra.

Key words: IR, Raman, HF, DFT calculations, Benzoxazin.

INTRODUCTION

2-phenyl-4H-3,1-benzoxazin-4-one also known as benzoylenthranil, is a leading bleach activator and belongs to an interesting class of tricyclic heteroaromatic molecule. It is cost effective, environment-friendly and provides effective bleaching at as low as 40°C¹. Polybenzoxazines exhibit excellent mechanical strength and thermal stability, near-zero shrinkage, no release of volatiles during polymerization, low viscosity, no need of harsh catalysts, and rich molecular design flexibility²⁻⁷. By taking advantage of its design flexibility, several high performance benzoxazines, naphthazoxines, and phthalonitrile and phenylnitrile functional polybenzoxazines, have been developed⁸⁻¹¹. Recently, the synthesis, identification and antiplatelet evaluation of 2-morpholino substituted benzoxazines were reported by

Pritchard *et al.*¹². The use of 1,3-benzoxazines has been important in the development of antimicrobial, antiviral, and antifungal drugs¹³⁻¹⁵. The 2H-1,4-benzoxazin-3-(4H)-one and 3,4-dihydro-2H-1,4-benzoxazine scaffolds have been studied intensively as important heterocyclic systems for building natural^{16,17} and designed synthetic compounds and have been frequently utilized as suitable skeletons for the design of biologically active compounds, ranging from herbicides and fungicides to therapeutically usable drugs. Several benzoxazine derivatives are inhibitors of bacterial histidine protein kinase^{18,19}, 2-oxo-1,4-benzoxazine derivative²⁰ is potentially useful for treating infections caused by *Mycobacterium* sp. 1,4-benzoxazine-3-one derivative²¹ is a potential drug for treating heart disease, myocardial necrosis or arrhythmia and 1,4-benzoxazine derivative²² possesses peroxisome proliferators-activated receptor and could be used

in treating diabetes, hyperlipidemia and other diabetic complications. Eckroth and Squire²³ reported a study of the mechanism of the photoisomerization of 2-phenylisatogen to 2-phenyl-4H-3,1 benzoxazin-4-one. Alagarsamy *et al.*²⁴ reported the synthesis, analgesic, anti-inflammatory and antibacterial activities of some novel 2-phenyl-3-substituted quinazolin-4(3H) ones. 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, FT-Raman and theoretical calculations of the wavenumber values of the title compound are reported.

EXPERIMENTAL

To a solution of anthranilic acid (0.01 mol) dissolved in pyridine (60 ml), benzoyl chloride (0.02 mol) was added. The mixture was stirred for 30 min. at room temperature. This was poured into a beaker containing 5% NaHCO₃ (50 ml) solution. The solid obtained was filtered and recrystallized from ethanol. Purity of compound was checked by TLC, using benzene and ethyl acetate as mobile phase in the ratio of 7:3. Iodine vapour was used as detecting agent. Yield was found to be 80%, Melting point was determined in open capillary tubes on a Thomas Hoover apparatus and was uncorrected, m.p. 120°C. Mass spectra recorded on a Varian Atlas CH-7 mass spectrometer at 70 eV and NMR spectra on a Bruker-Avance 300MHz FT-NMR, solvent CDCl₃, TMS internal standard, the peak assignments were done on the basis of TOCSY, COSY and HSQC(HETCORR) spectra in addition to ¹³C-spectra; proton shifts δ (ppm): H₈, 8.25, H₁₀ 7.83, H₇ 7.69, H₉ 7.58, H₁₆ 8.31, H₁₇ 8.31, H₁₉ 7.59, H₂₀ 7.59, H₂₁ 7.54; ¹³C shifts δ (ppm): C₄ 128.6, C₅ 128.8, C₆ 136.6, C₁ 132.6, C₁₃ 128.3, C₁₂ 128.3, C₁₄ 128.6, C₁₆ 128.6, C₁₈ 127.2, C₂₂ 159.6, C₃ 117.01, C₂ 146.2, C₂₆ 157.1, C₁₁ 130.2; Proton coupling values in Hz: J_{8,9} 8.1, J_{8,10} 1.2, J_{8,7} 0, J_{9,10} 7.5, J_{9,7} 1.2, J_{10,7} 7.8, J_{17,20} 8.7, J_{19,16} 8.7, J_{19,21} 6.9, J_{20,21} 6.9, J_{16,21} 1.5, J_{17,21} 1.5. MS(m/z)223 (M+); Anal. Calculated/found: C 75.33/75.37; H 4.03/3.99; N 6.27/6.3. The FT-IR spectrum was recorded on a DR/Jasco FT/IR-6300 spectrometer with KBr pellets. The FT-Raman spectrum was obtained on a Bruker

RFS 100/S, Germany. For excitation of the spectrum the emission of Nd:YAG laser was used, excitation wavelength 1064 nm, maximal power 150 mW, resolution 4 cm⁻¹, measurement on solid sample.

Computational details

Calculations of the title compound were carried out with Gaussian03 program²⁵ using the HF/6-31G* and B3LYP/6-31G* basis sets to predict the molecular structure and vibrational wavenumbers. The wavenumber values computed contain known systematic errors²⁶ and we therefore, have used the scaling factor values of 0.8929 and 0.9613 for HF and DFT basis sets. The absence of imaginary values of wavenumbers on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy. The assignment of the calculated wavenumbers is aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes^{27,28}.

RESULTS AND DISCUSSION

The observed Raman and IR bands with their relative intensities and calculated wavenumbers and assignments are given in Table 1. The C=N stretching skeletal bands²⁹⁻³² are observed in the range of 1627 -1566 cm⁻¹. For the title compound, the band observed at 1692 cm⁻¹ in the IR spectrum is assigned as ν C=N mode. The HF calculations give the ν C=N mode at 1667 cm⁻¹ and the DFT calculation give this mode at 1608 cm⁻¹. All these results agree with the results of Alagarsamy *et al.*²⁴ and Nanda *et al.*³³. Primary aromatic amines with nitrogen directly on the ring absorb strongly at 1330-1260 cm⁻¹ due to stretching of the phenyl carbon-nitrogen band³⁴. For the title compound the ν CN mode is observed at 1322 cm⁻¹ in the Raman spectrum and the calculated value is 1319 cm⁻¹ (DFT).

The carbonyl stretching wavenumber has been most extensively studied by infrared spectroscopy. This multiply bonded group is highly polar and therefore gives rise to an intense infrared absorption band. The carbon-oxygen double bond is formed by P _{π} -P _{π} bonding between carbon and oxygen. Because of the different electro negativities

Table 1: Calculated vibrational wavenumbers, measured infrared and Raman band positions and assignments for 2-phenyl-4H-3, 1-benzoxazin-4-one

$\nu_{(\text{HF})}$ (cm^{-1})	$\nu_{(\text{DFT})}$ (cm^{-1})	$\nu_{(\text{IR})}$ (cm^{-1})	$\nu_{(\text{Raman})}$ (cm^{-1})	Assignments
3052	3112			$\nu\text{CH I}$ 20a
3051	3108			$\nu\text{CH I}$ 20b
3044	3103			$\nu\text{CH II}$ 20a
3039	3099			$\nu\text{CH II}$ 20b
3026	3087			$\nu\text{CH I}$ 2
3024	3086			$\nu\text{CH II}$ 7b
3015	3076	3060 w	3070 s	$\nu\text{CH I}$ 13
3008	3070	3050 w	3022 w	$\nu\text{CH II}$ 2
3003	3065	3040 m		$\nu\text{CH I}$ 7b
1820	1783	1763 vs	1757 m	$\nu\text{C=O}$
1667	1608	1692 s		$\nu\text{C=N}$
1621	1600	1613 s	1623 vs	$\nu\text{Ph II}$ 8b
1613	1590	1585 sh	1599 vs	$\nu\text{Ph I}$ 8a
1590	1570	1578 s	1574 s	$\nu\text{Ph I}$ 8b
1582	1555			$\nu\text{Ph II}$ 8a
1492	1485	1490 m		$\nu\text{Ph I}$ 19a
1474	1459	1474 s	1476 s	$\nu\text{Ph II}$ 19b
1458	1452	1450 m	1451 w	$\nu\text{Ph II}$ 19a
1442	1439			$\nu\text{Ph I}$ 19b
1320	1319		1322 s	$\nu\text{Ph I}$ 14, νCN
1306	1318	1315 s		$\nu\text{Ph II}$ 3
1272	1303		1300 w	$\delta\text{CH II}$ 14
1238	1299			$\delta\text{CH I}$ 3
1217	1249	1258 s	1259 vs	$\nu\text{C(X)X II}$ 13 νCO
1204	1231	1236 m		$\delta\text{CH I}$ 9a
1197	1195	1183 m	1183 w	$\delta\text{CH II}$ 15
1164	1165			$\delta\text{CH I}$ 9b
1112	1149	1153 w	1157 m	$\delta\text{CH II}$ 9b
1098	1143			$\delta\text{CH II}$
1094	1095	1112 m		$\nu\text{C(X)X II}$ 1
1072	1074			$\nu\text{C(X)X I}$ 7a, Breathing II
1061	1051	1058 m	1064 w	$\delta\text{CH I}$ 15
1039	1020	1027 m	1028 w	νCOC
1015	1012	1018 m		$\delta\text{CH I}$ 18a
1012	982	1012 s	1002 s	$\delta\text{CH II}$ 18b

1009	976	984 m		Breathing I 1
999	970			δ CH I
997	964			γ CH I 5
987	948			γ CH II 5
974	939	929 w		γ CH II 17b
961	919			γ CH I 17a
922	900	882 w		γ CH I 17b
891	865	858 w	858 w	γ CH II 17b
861	840			γ CH II 17a
833	834			γ CH I 10a
797	773		784 w	δ Ph(X) II
789	766	765 s		γ CH I, II 11
775	756		749 w	γ CH I, 11
733	728			δ Ph (X) II 4
703	684		680 w	δ Ph(X) I 12
691	673	684 s		δ Ph I 4
675	667			γ Ph II 4
663	666			γ Ph (X) II 6a
614	610	628 m	618 w	δ C=O
604	607	600 w		δ Ph I 6b
563	564		568 w	δ Ph (X) II 6b
538	530	537 m		γ C=O
516	514		520 w	γ Ph(X) II 16a
472	473	483 w	487 w	γ Ph(X) II 16b
454	449			γ Ph II 18a
425	421	425 w		γ Ph(X) I 16b
405	399			γ Ph I 16a
347	348		358 w	δ Ph (X) I 6a
294	290		305 w	δ CX (X) II
288	289			γ Ph(X) II 7b
254	257		260 w	γ Ph(X) II 9a
182	180		178 w	δ CX (X) I 18b
150	149		136 w	γ CX (X) I 10b
114	114			t Ph I
105	105		97 m	t Ph II
56	54			t Ph II
36	39			t Ph II

v- stretching; δ - in-plane deformation; γ - out-of-plane deformation ; t-torsion; v-very; b-broad; s-strong; w-weak; m-medium; X – substituent sensitive; Ph- phenyl ring;

of carbon and oxygen atoms, the bonding electrons are not equally distributed between the two atoms. The lone pair of electrons on oxygen also determines the nature of the carbonyl group. The most characteristic band of esters arising from the C=O stretching vibration occurring at $1750 \pm 50 \text{ cm}^{-1}$ with a strong to very strong intensity³⁵. For the title compound the $\nu\text{C=O}$ mode is seen as a very strong band at 1763 cm^{-1} in the IR spectrum, 1757 cm^{-1} in the Raman spectrum and at 1783 cm^{-1} (DFT), 1820 cm^{-1} (HF) theoretically. The intensity of this band can increase owing to conjugation or formation of hydrogen bonds. The increase in conjugation, therefore, leads the intensification of IR band. The deviation of the calculated wavenumber in the HF calculation for this mode can be attributed to the underestimation of the large degree of π -electron delocalization due to conjugation in the molecule. The C(=O)O stretching vibration, often considered as the C-O asymmetric stretching, appears strongly at $1255 \pm 60 \text{ cm}^{-1}$, a region in good agreement with that of the $\nu\text{C-O}$ in carboxylic acids ($1250 \pm 80 \text{ cm}^{-1}$)³⁵. The strong band seen at 1258 cm^{-1} in the IR spectrum, 1259 cm^{-1} in the Raman spectrum is assigned as this mode. The O-C stretching vibration appears in the wide range $975 \pm 125 \text{ cm}^{-1}$ with an intensity varying from weak to strong³⁵. The mode is often called the symmetric C-O-C stretching vibration and the band observed at $\sim 1027 \text{ cm}^{-1}$ in both the IR and Raman spectra. Ishida and Ohba³⁶ reported asymmetric and symmetric C-O-C stretching mode at 1240 and 1032 cm^{-1} , respectively.

Since the identification of all the normal modes of vibration of large molecule 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 rings³⁷⁻⁴¹. In the following discussion, the mono substituted phenyl ring and di-substituted phenyl ring are designated as 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 co-ordinates) 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^{37,38,42}. The assignments of the benzene ring vibrations of the title compound in Wilson notation⁴³ is made by referring the case of benzene derivatives with mono substitution and ortho substitution as summarized by Roeges³⁵. 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 stretch⁴⁴. The bands observed at 3040 , 3050 and 3060 cm^{-1} in the IR spectrum are assigned as $\nu\text{C-H}$ modes of the benzene ring. In the Raman spectrum two bands are observed at 3022 and 3070 cm^{-1} . The benzene ring possesses six ring stretching vibrations, of which the four with the highest wavenumbers (8a, 8b, 19a and 19b, occurring respectively near 1600 , 1580 , 1490 and 1440 cm^{-1}) are good group vibrations. In the absence of ring conjugation, the band near 1580 cm^{-1} is usually weaker than that at 1600 cm^{-1} . The fifth ring stretching vibration $\nu\text{Ph 14}$ is active near $1335 \pm 35 \text{ cm}^{-1}$, a region which overlaps strongly with that of the CH in-plane deformation and the intensity is in general, low or medium high^{35,45}. The six ring stretching vibration or ring breathing mode $\nu\text{Ph 1}$ appears as a weak band near 1000 cm^{-1} in mono, 1,3-di and 1,3,5-trisubstituted benzenes. In the otherwise substituted benzenes, however, this vibration is substituent sensitive and difficult to distinguish from the ring in-plane deformation $\delta\text{Ph 12}$. The wavenumber of the vibrational pair 8, 19a in mono substituted benzenes is rather insensitive of substitution⁴⁵. The wavenumber interval for vibration 19a is^{45,46} 1470 - 1515 cm^{-1} and for all mono substituted benzene derivatives 19a have a band between 1477 and 1511 cm^{-1} in the IR spectrum. When the derivatives have substituents of donor character, the wavenumber is found between 1493 and 1511 cm^{-1} and in this group of derivatives the band has higher intensity when a carbon atom is attached directly to the ring. For the title compound the ring breathing mode for phenyl-I is assigned at 976 cm^{-1} theoretically and a band is observed at 984 cm^{-1} in the IR spectrum. The bands observed at 1585 , 1578 , 1490 cm^{-1} in the IR spectrum and at 1599 , 1574 , 1322 cm^{-1} in the Raman spectrum are assigned as phenyl ring stretching modes νPh

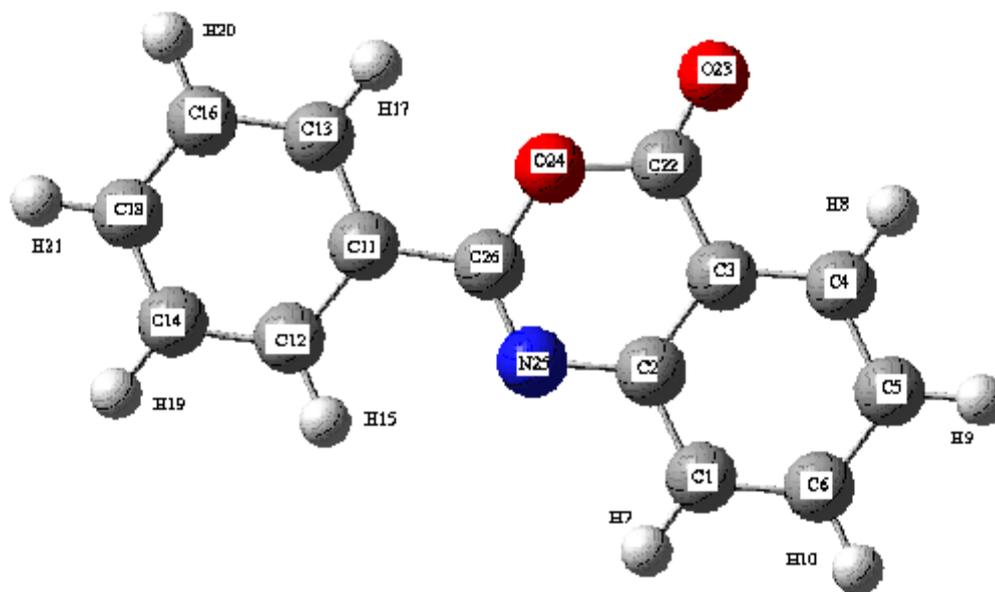
I. In mono substituted benzenes, there should be five CH in-plane bending vibrations 3, 9a, 9b, 15 and 18a. The mode 9a appears between 1165 and 1195 cm^{-1} in the spectra of all mono substituted benzene derivatives, mode 15 is found between 1050 and 1080 cm^{-1} and the intensity of 9a and 18a are the most intense in the IR spectrum^{45,46}. The mode 3 is weak in general for both IR and Raman in the range^{35,45} 1250-1300 cm^{-1} . In the present case, for the phenyl ring I, the bands observed at 1236, 1058, 1018 in IR spectrum, at 1064 cm^{-1} in Raman spectrum and at 1231, 1165, 1051, 1012, 970 cm^{-1} (DFT) theoretically are assigned as δCH I modes. In the case of heavy substituents the out-of-plane CH deformations γCH ^{35,45} of mono substituted benzene derivatives have the modes 5, 17a, 17b, 10a, 11. These modes are expected in the range³⁵ 1000-730 cm^{-1} . Generally, the CH out-of-plane deformations with the highest wavenumbers have a weaker intensity than those absorbing at lower wavenumbers. The stronger γCH band occurring in the region $745 \pm 25 \text{ cm}^{-1}$ (γCH 11 or umbrella mode) tends to shift to lower (higher) wavenumbers with increasing electron donating (attracting) power of the substituent, but seems to be more sensitive to mechanical interaction effects. The lower wavenumber for this umbrella mode are found in the spectra of benzenes substituted with a saturated carbon or a heavy atom such as halogen, sulfur or phosphorus^{45,47-49}. The out-of-plane deformation γCH 11 at 765 cm^{-1} and the out-of-plane ring deformation γPh 4 at 684 cm^{-1} in the IR spectrum form a pair of strong bands characteristics of mono substituted benzene derivatives^{35,49}. In mono substituted benzenes, six modes of vibrations are substituent sensitive, which means that their wavenumbers shift systematically with mass or inductive or mesomeric effects of the substituent. The highest substituent sensitive mode $\nu\text{CX}(\text{X})$ mode 7a appears in the region $1090 \pm 30 \text{ cm}^{-1}$ for mono substituted benzenes^{35,50}. The DFT calculations give 1074 cm^{-1} as this mode. The other substituent sensitive modes are also identified (Table 1). The phenyl ring II stretching vibrations νPh II are also identified. In 1,2-disubstituted benzenes, the role of vibration 14 could be rather different from that played in p- and m-di-substitution, since the change in the direction of the main symmetry axis results in the total symmetry of the vibration. This means that the band

corresponding to the vibration might be very strong both in IR and Raman. Kohlrausch⁵¹ in his fundamental Raman studies of benzene derivatives established a wavenumber between 1250 and 1290 cm^{-1} , more or less independent of substitution in ortho disubstituted benzenes. The strong band observed at around 1258 cm^{-1} in both spectra is assigned to the mode 14 of the phenyl ring II. The fifth ring stretching vibration νPh 14 is active near $1315 \pm 65 \text{ cm}^{-1}$, a region which overlaps strongly that of the δCH mode³⁵. The band is not pure but contains significant contributions from other modes. In ortho disubstitution vibrations 1 and 12 are substituent sensitive⁴⁵. Substituent sensitive modes are assigned at 1249 and 1095 cm^{-1} theoretically (DFT). The sixth ring stretching mode or ring breathing mode νPh 1 is assigned at 1074 cm^{-1} . No bands are experimentally observed for this mode. In o-disubstitution mode 3 appears in general, as a weak band in IR or Raman, provided it can be identified at all⁴⁵. The in-plane CH vibrations³⁵ are seen in the range 1230-1280 cm^{-1} and 1170 – 1000 cm^{-1} . The bands at 1183, 1153, 1012 cm^{-1} in the IR spectrum and at 1300, 1183, 1157, 1002 cm^{-1} in the Raman spectrum are assigned as δCH modes. The DFT calculations give these modes at 1303, 1195, 1149, 1143, 982 cm^{-1} . The out-of-plane CH deformation bands γCH are expected in the range³⁵ 740-990 cm^{-1} . As seen from Table 2, the DFT calculations give wavenumbers at 948, 939, 865, 840, 766 cm^{-1} as the out-of-plane CH deformations of phenyl ring II. In the case of 1,2-disubstitution only one strong absorption in the region $755 \pm 15 \text{ cm}^{-1}$ is observed and is due to the γCH . The out-of-plane ring deformation γPh 4 gives rise to a weak shoulder on the γCH band or coincides with it³⁵. The strong bands observed at 765 cm^{-1} in the IR spectrum is assigned to this mode, which is not pure but contains contribution from the phenyl ring I also. In o-disubstitution the in-phase mode is obtained from the vibration 18a and the out-of-phase one is related to the vibration 9a⁴⁵. In o-disubstitution vibration 18a corresponding to the in-phase mode⁴⁵ appears between 250 and 450 cm^{-1} . Vibration 9a corresponding to the out-of-phase mode is found in the wavenumber interval⁴⁵ 130-270 cm^{-1} . The line of this vibration in the Raman spectrum is generally more intense than the line of vibration 18a.

The HF calculation give shortening of angle $C_2-C_3-C_{22}$ by 1.8° and increase of angle $C_4-C_3-C_{22}$ by 0.8° from 120° at C_3 position. Also at C_2 position, the angle $C_3-C_2-N_{25}$ is increased by 1.5° and $C_1-C_2-N_{25}$ is reduced by 0.6° from 120° . The asymmetry in the exocyclic angles at C_3 and C_2 positions reveal the interaction between phenyl ring II and the substituents. At C_{22} position, the angles $O_{23}-C_{22}-C_3$ is increased by 7.2 and $O_{23}-C_{22}-O_{24}$ is reduced by 1.5° from 120° , which shown the interaction between $C(=O)O$ group with the phenyl ring I. Both of the $C_{26}-N_{25}$ (1.2598 \AA) and $C_{22}-O_{23}$ (1.1813 \AA) bonds show typical double-bond characteristics. However, the C_2-N_{25} bond length (1.3883 \AA) is shorter than the normal C-N single-bond length of about 1.48 \AA . The shortening of this C-N bond reveals the effects of resonance in this part of the molecule⁵². The C-C bond lengths⁵³ lie in the range $1.3809 - 1.3932 \text{ \AA}$ for phenyl ring I and $1.3748 - 1.3974 \text{ \AA}$ for phenyl ring II, while the C-C bond length for benzene is 1.3991 \AA .

To the best of our knowledge, no X-ray crystallographic data of this molecule has yet been established. However, the theoretical results obtained are almost comparable with the reported structural parameters of related molecules.

According to Costa *et al.*⁵⁴ for benzoxazine derivatives, the bond lengths C_2-N_{25} , $N_{25}-C_{26}$, $C_{26}-O_{24}$, $O_{24}-C_{22}$ are 1.3982 , 1.3012 , 1.3622 , 1.3812 \AA , respectively and the corresponding values for the title compound are 1.3883 , 1.2598 , 1.3463 , 1.3625 \AA (HF calculations). The bond angles $C_2-N_{25}-C_{26}$, $N_{25}-C_{26}-O_{24}$, $C_{26}-O_{24}-C_{22}$ of the title compound are 118.2 , 124.5 , 123.3° which is in agreement with the reported values⁵⁴ of 116.3 , 125.3 and 121.0° . For a series of benzoxazin derivatives, Crano *et al.*⁵⁵ reported the bond lengths, $C_2-N_{25} = 1.4$, $C_{26}-N_{25} = 1.2746$, $C_{26}-O_{24} = 1.36 \text{ \AA}$ whereas in the present case, the corresponding values are 1.3833 , 1.2598 , 1.3463 \AA , respectively. Also, the bond angles $C_2-N_{25}-C_{26} = 118.2$, $C_{22}-O_{24}-C_{26} = 123.3^\circ$ are in agreement with the values 117.2 , 1201.1° given by Crano *et al.*⁵⁵. For the benzoxazin moiety of the title compound, the calculated values of the bond lengths $C_{22}-O_{23}$, $C_{22}-O_{24}$, C_2-N_{25} , C_3-C_{22} , C_2-C_3 are 1.1813 , 1.3625 , 1.3883 , 1.4629 , 1.3910 \AA , respectively while the reported values for similar benzoxazin derivatives are 1.2313 , 1.3794 , 1.4203 , 1.4954 , 1.4034 \AA ⁵⁶. For complexes of benzoxazin⁵⁷, the bond lengths $C_{26}-N_{25} = 1.2823$ and $C_{11}-C_{26} = 1.4993 \text{ \AA}$ which are in agreement with the values 1.2598 , 1.4784 \AA , in the present case.



The first hyperpolarizability (β_0) of this novel molecular system is calculated using HF/6-31G* basis set, based on the finite field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry⁵⁸. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the electric field is weak and homogeneous, this expansion becomes

$$E = E_0 - \sum_i \mu_i F^i - \frac{1}{2} \sum_{ij} \alpha_{ij} F^i F^j - \frac{1}{6} \sum_{ijk} \beta_{ijk} F^i F^j F^k - \frac{1}{24} \sum_{ijkl} \gamma_{ijkl} F^i F^j F^k F^l + \dots$$

where E_0 is the energy of the unperturbed molecule, F^i is the field at the origin, μ_i , α_{ij} , β_{ijk} and γ_{ijkl} are the components of dipole moment, polarizability, the first hyper polarizabilities, and second hyperpolarizabilities, respectively. The calculated first hyperpolarizability of the title compound is 2.067×10^{-30} esu, which is 9.17 times that of urea.

In order to investigate the performance and vibrational wavenumbers of the title compound root mean square value (RMS) and correlation coefficient between calculated and observed wavenumbers were calculated. RMS values of wavenumbers were evaluated using the following expression⁵⁹.

$$RMS = \sqrt{\frac{1}{n-1} \sum_i^n (v_i^{calc} - v_i^{exp})^2}$$

The RMS error of the observed Raman bands, IR bands and scaled wavenumbers are found to be 22.17, 24.11 for HF and 18.12, 21.20 for DFT calculations, respectively. The small differences between experimental and calculated vibrational modes are observed. It must be due to the fact that hydrogen bond vibrations present in the crystal lead to strong perturbation of the infrared wavenumbers and intensities of many other modes. Also, we state that experimental results belong to solid phase and theoretical calculations belong to gaseous phase.

CONCLUSION

The FT-IR and FT-Raman spectra of 2-phenyl-4H-3,1-benzoxazin-4-one were studied. The molecular geometry and wavenumbers have been calculated using HF and B3LYP methods and compared with the experimental values. The difference between experimental and calculated wavenumbers comes from the environment of the compound. It is clear that the experimental results belong to solid phase and the theoretical calculations belong to gaseous phase. In fact, it is evident gas state vibration wavenumbers are larger than those of solid state. Moreover, solid states of the compound include a lot of intra- and intermolecular interactions. The calculated first hyperpolarizability of 2-phenyl-4H-3,1-benzoxazin-4-one is found to be 2.067×10^{-30} esu, which is 9.17 times that of urea.

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