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FT-IR and FT-Raman spectra and *ab initio* calculations of 3-{[(2-hydroxyphenyl) methylene]amino}-2-phenylquinazolin-4(3H)-one

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Fourier transform infrared (FT-IR) and Fourier transform (FT) Raman spectra of 3-{[(2-hydroxyphenyl)methylene]amino}-2-phenylquinazolin-4(3H)-one were recorded and analyzed. The vibrational wavenumbers of the title compound were computed using HF/6-31G* and 6-311G* basis sets and compared with experimental data. The assignments of the normal modes are done by potential energy distribution (PED)calculations. The prepared compound was identified by nuclear magnetic resonance (NMR) and mass spectra. Optimized geometrical parameters of the title compound are in agreement with reported structures. Shortening of CN bond lengths reveal the effect of resonance. The simultaneous IR and Raman activations of the C═O stretching mode shows a charge transfer interaction through a π-conjugated path. The first hyperpolarizability, infrared intensities and Raman activities are reported. The phenyl C–C stretching modes are equally active as strong bands in both IR and Raman spectra, which are responsible for hyperpolarizability enhancement leading to nonlinear optical activity.

Supporting information may be found in the online version of this article.

Keywords: quinazoline; IR spectra; Raman spectra; *ab initio* calculations; PED

Introduction

Among a wide variety of nitrogen heterocycles that have been explored for developing pharmaceutically important molecules, the quinazolines have played an important role in medicinal chemistry and subsequently emerged as a pharamacophore.[1] In normal practice, three groups of agents (chemotherapeutic, analgesic and antiinflammatory) are prescribed simultaneously. Compounds possessing all three activities are not common. Quinazolines and quinazoline derivatives exhibit potent antimicrobial[2] and central nervous system activities such as antiinflammatory[3] and anticonvulsant.[4] Compounds containing a fused quinazoline or isoquinoline ring belong to a broad class of compounds that has received a considerable attention over the past years due to their wide range of biological activities.[5,6] Some of the aminoquinazoline derivatives were found to be inhibitors of the tyrosine kinase[7,8] or dihydrofolate reductase enzymes[9,10] and so they work as potent anticancer agents. They are also used to design medicines against hypertension and malaria and to fight infections involving acquired immune deficiency syndrome (AIDS).[11] Quinazolines are frequently used in medicine because of their wide spectrum of biological activities.[12] Antitumor activities are also reported for 2,3-dihydro-2-aryl-4-quinazolines.[13,14] Several quinazoline derivatives have been reported for their antibacterial, antifungal, anti-human immunodeficiency virus (HIV),[15,16] anthelmintic,[17] central nervous system depressant,[18] antitubercular,[19] hypotensive,[20] anticonvulsant,[21] antifibrillatory,[22] diuretic[23] and antiviral activities.[24–26] Some reports have suggested that 2-styrylquinazolin-4-ones[27,28] could be effective inhibitors of tubulin polymerization. The 2,3-disubstituted quinazolones have been predicted to possess antiviral and antihypertensive activities.[29] Synthesis of vascinone, a naturally occurring bioactive alkaloid hav-

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ing a quinazolone system, has been reported recently.[30] Quinazolines are widely used for the extraction and analytical determination of metal ions. Nitraquazone, a quinazoline derivative, has been found to possess potent phosphodiesterase inhibitory activity,[31] which is potentially useful in the treatment of asthma.[32] Alagarsamy *et al*.[33] have reported the synthesis and analgesic, antiinflammatory and antibacterial activities of some novel 2-phenyl-3-substituted quinazolin-4(3H)ones. Nanda *et al*.[34] have reported the antibacterial activity and quantitative structure activity relation (QSAR) studies of some 3arylideneamino-2-phenyl quinozoline-4(3H)-ones. Costa *et al*.[35] reported the synthesis of 4H-3,1-benzoxazines, quinazolin-2-ones, and quinoline-4-ones by palladium-catalyzed oxidative carbonylation of 2-ethynylaniline derivatives. These nitrogen heterocycles can be used as valuable intermediates for the preparation of dyestuffs[35] and pharmaceutical products[36–38] since they exhibit a wide range of biological activities. The three-dimensional (3D) QSAR studies for one large set of quinazoline-type epidermal growth factor receptor (EGF-R) inhibitors were conducted using two types of molecular field analysis techniques: comparative molecular field analysis and comparative molecular similarity indices analysis.[39] A number of reports have shown that a broad class of 4-anilinoquinazolines are potent and highly selective inhibitors of EGF-R phosphorylation.[7,8,40,41] Chen *et al*.[42] reported the intramolecular imidate-amide rearrangement of 2-substituted 4-(chloroalkoxy)quinazoline derivatives. Quantum mechanical studies of the competitive hydration between protonated quinazoline and Li^+, Na^+ and Ca^{2+} ions were reported by Sawunyama and Bailey.[43] Various quinazoline derivatives interrupt pregnancy by 40–50% and show anti-implantation activity and are also used in contraceptive compositions.[44] *Ab initio* quantum mechanical method is at present widely used for simulating the IR spectrum. Such simulations are indispensable tools to perform normal coordinate analysis and modern vibrational spectroscopy is unimaginable without involving them. Besides, very few spectroscopic studies have been reported so far on the heteroaromatic bicyclics. To obtain reliable wavenumber assignments, a detailed vibrational analysis is required. Considering the above facts, in the present study the Fourier transform infrared (FT-IR), Fourier transform (FT) -Raman and theoretical calculations of the wavenumber values of the title compound are reported.

Experimental

Synthesis of the title compound involved three steps: benzoylation with simultaneous cyclization, addition of hydrazine and finally condensation to form a Schiff base. Thus, anthranilic acid was treated with benzoyl chloride in the presence of pyridine to undergo cyclization forming 2-phenyl-4H-benzo[d][1,3]oxazin-4-one, which on condensation with hydrazine hydrate yielded 3-amino-2-phenylquinazolin-4(3H)-one. The latter compound was then treated with suitable substituted benzaldehydes in the presence of ethanol to form the title compound. Synthesis of the title compound, 3-{[(2-Hydroxyphenyl)methylene]amino}-2-phenyl quinazolin-4(3H)-one has been reported elsewhere.[34] In subsequent experiments it was observed that solvent-free synthesis yielded stoichiometric conversion to the product. In this procedure, equimolar amounts of 3-amino-2-phenylquinazolin-4(3H)-one and 2-hydroxybenzaldehyde were triturated in a pestle and mortar and the mixture was transferred into a vial; the vial was heated in an oil bath for 30 min at about 80 °C. The product thus formed was almost pure for subsequent use. However, it was crystallized from an ethanol/benzene 5 : 1 mixture to obtain the crystalline product. Purity of the compound was checked by thin layer chromatography (TLC) using benzene and ethyl acetate as mobile phase in the ratio 7 : 3. Iodine vapor was used as developer. The melting point was determined in open capillary tubes on a Thomas Hoover apparatus and was uncorrected: mp. 166 °C. Mass spectra were recorded on a FAB, JEOL SX 102 mass spectrometer and nuclear magnetic resonance (NMR) spectra on a Bruker–Avance 300 MHz FT-NMR spectrometer (solvent $CDCl_3$, TMS internal standard, the peak assignments done on the basis of total correlation spectroscopy (TOCSY), correlation spectroscopy (COSY) and heteronuclear single quantum correlation (HETCORR) spectra in addition to ^{13}C-spectra). The FT-IR spectrum (Fig. 1) was recorded using a Bruker IFS 28 spectrometer with KBr pellets (number of scans 16, resolution 2 cm^{-1}). The FT-Raman spectrum (Fig. 2) was obtained on a Bruker Equinox 55/s spectrometer with FRA Raman socket, 106/s. For excitation of the spectrum, the emission of a Nd : YAG laser was used (excitation wavelength 1064 nm, laser power 250 mW, resolution 2 cm^{-1}, number of scans 128 and measurement on solid sample).

FAB MS (*m/z*): 342 (M + 1); ^1H-NMR: 6.69 (H-28), 6.9 (H-19), 7.35 (H-26), 7.35 (H-27), 7.4 (H-39), 7.48 (H-38), 7.56 (H-7), 7.6(H-9), 7.6(H-10), 7.81(H-35), 8.36 (H-8), 9.19 (s, 1H. H-C═N), 9.99 (OH, H-bonded), 7.8 Hz (J56); ^{13}C-NMR: 116.42 (C-29), 117.50 (C-21), 119.69 (C-25), 121.46 (C-3), 127.32 (C-5), 127.39 (C-1), 128.00 (C-31), 128.97 (C-2), 130.34 (C-34), 132.5 (C-24), 133.33 (C-36), 134.19 (C-23), 134.84 (C-6), 146.37 (C-4), 153.63 (C-14), 159.14 (C-11), 159.74 (═C(OH), C-20), 164.75 (H–C═N), C-29 quaternary peak not observed; Anal. Calcd. for $C_{21}H_{15}N_3O_2$: C, 73.89%; H, 4.45%; N, 12.31%; found: C, 74.10%; H, 4.45%; N, 12.28%.

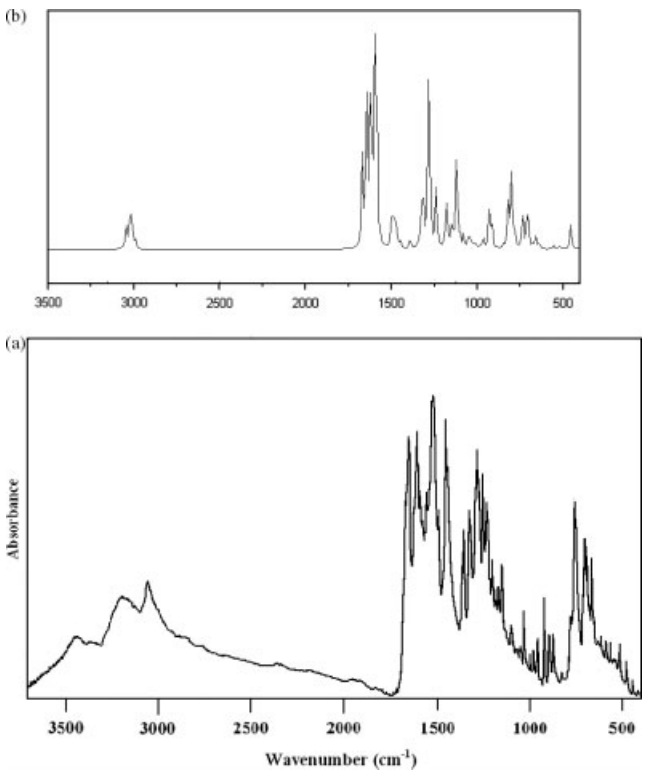

Figure 1. FT-IR spectrum of 3-{[(2-hydroxyphenyl)methylene]amino}-2-phenylquinazolin- 4(3H)-one (a) experimental (b) calculated.

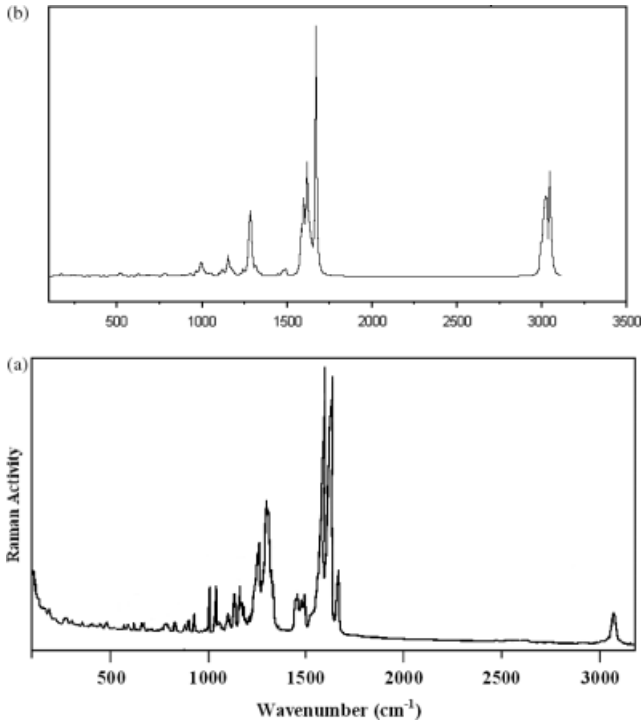

Figure 2. FT-Raman spectrum of 3-{[(2-hydroxyphenyl)methylene] amino}-2- phenylquinazolin-4(3H)-one (a) experimental (b) calculated.

Computational Details

Calculations of the title compound were carried out with the Gaussian03 program[45] using the HF/6-31G* and 6-311G* basis sets to predict the molecular structure and vibrational wavenumbers. The molecular geometry was fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wavenumbers were calculated using the analytic second derivatives to confirm the convergence to minimum on the potential surface. The wavenumber values computed at the Hartree–Fock level contain known systematic errors due to the negligence of electron correlation.[46] 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. 3) are given in Table S1 (Supporting Information). The absence of imaginary wavenumbers on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy. The potential energy distribution (PED) was calculated with the help of GAR2PED software package.[47]

Results and Discussion

IR and Raman Spectra

The observed IR and Raman bands with their relative intensities, scaled wavenumbers and assignments are given in Table 1. The HF calculations give the υOH band at 3615 cm^{-1} with 100% PED, and a strong broad band is observed in the IR spectrum at 3440 cm^{-1}. The in-plane deformation[48] is expected in the region 1400 ± 40 cm^{-1}, and the band at 1452 cm^{-1} in the IR spectrum and at 1450 cm^{-1} in the Raman spectrum is assigned as the in-plane deformation of OH band. The stretching mode of the hydroxyl group with respect to the phenyl moiety $\upsilon C_{21}-O_{40}$ appears at 1271 cm^{-1} in the IR spectrum, 1272 cm^{-1} in the Raman spectrum and the calculated value is 1274 cm^{-1}. This band is expected in the region[49–51] 1220 ± 40 cm^{-1}. El-Shahway *et al.*[52] reported υ(C–O) at 1240 cm^{-1}.

The carbonyl group is contained in a large number of different classes of compounds, for which a strong absorption band due to the C═O stretching vibration is observed in the region[53] 1850–1550 cm^{-1}. If a carbonyl group is part of a conjugated system, then the wavenumber of the carbonyl stretching vibration decreases, the reason being that the double-bond character of the C═O group is less due to the π-electron conjugation being localized. For the title compound, the υC═O mode is seen as a strong band at 1652 cm^{-1} in the IR and at 1656 cm^{-1} in the Raman spectrum. But the electron-releasing effect in the C═O double bond causes a polarizability change during vibration, making the Raman band intensity comparable to that of the IR band. Also, here the intramolecular charge transfer takes place via a conjugated phenyl ring path which makes the phenyl ring stretching mode at 1623 (IR), 1621 (Raman) cm^{-1} simultaneously active in the IR and Raman spectra.[54] The deformation bands of the C═O group are also identified (Table 1).

The C═N stretching skeletal bands[55–57] are observed in the range 1650–1550 cm^{-1}. For the title compound the bands observed at 1662, 1652, 1588 cm^{-1} in the IR spectrum and at 1656 cm^{-1} in the Raman spectrum are assigned as υC═N modes. The HF calculations give these modes at 1669, 1646, 1584 cm^{-1}; these modes are not pure but contain significant contribution from other modes. For conjugated azines the υC═N mode is reported[58] at 1553 cm^{-1}.

For aromatic and unsaturated amines,[53] for ═C–N, two bands are observed at 1360–1250 and 1280–1180 cm^{-1} due to conjugation of the electron pair of the nitrogen with the ring imparting double-bond character to the C–N bond. Primary and secondary aromatic amines absorb strongly in the first region. Primary aromatic amines with nitrogen directly on the ring absorb at 1330–1260 cm^{-1} because of the stretching of the phenyl C–N bond.[50] For the title compound, the υC_4-N_{12} stretching mode is observed at 1232 cm^{-1} in the IR spectrum, 1295 cm^{-1} in the Raman spectrum and at 1288, 1235 cm^{-1} theoretically, as expected. These modes are not pure but contain significant contributions from other modes.

The C–N stretching bands are reported in the range[59] 1100–1300 cm^{-1}. In the present case, the $\upsilon C_{14}-N_{15}$ and $\upsilon C_{11}-N_{15}$ stretching bands are observed at 1283 cm^{-1} in the IR spectrum and at 1286, 1243 cm^{-1} in the Raman spectrum, and at 1283, 1240, 1119 cm^{-1} theoretically. υN–N has been reported at 1115 cm^{-1} by Crane *et al.*,[60] at 1121 cm^{-1} by Bezerra *et al.*[61] and at 1130 cm^{-1} by El-Behery and El-Twigry.[62] The band observed at 967 (HF) and 960 cm^{-1} (IR) is assigned to the $\upsilon N_{15}-N_{16}$ mode.

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 utilized by several workers for the vibrational assignments of molecules containing multiple homoaromatic and heteroaromatic rings.[63–67] In the following discussion, the meta-, mono- and ortho-substituted phenyl rings are designated as PhI, PhII and PhIII, respectively. The modes in the three 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 three rings. For some modes, this splitting is so small that they may be considered as quasi-degenerate, and for

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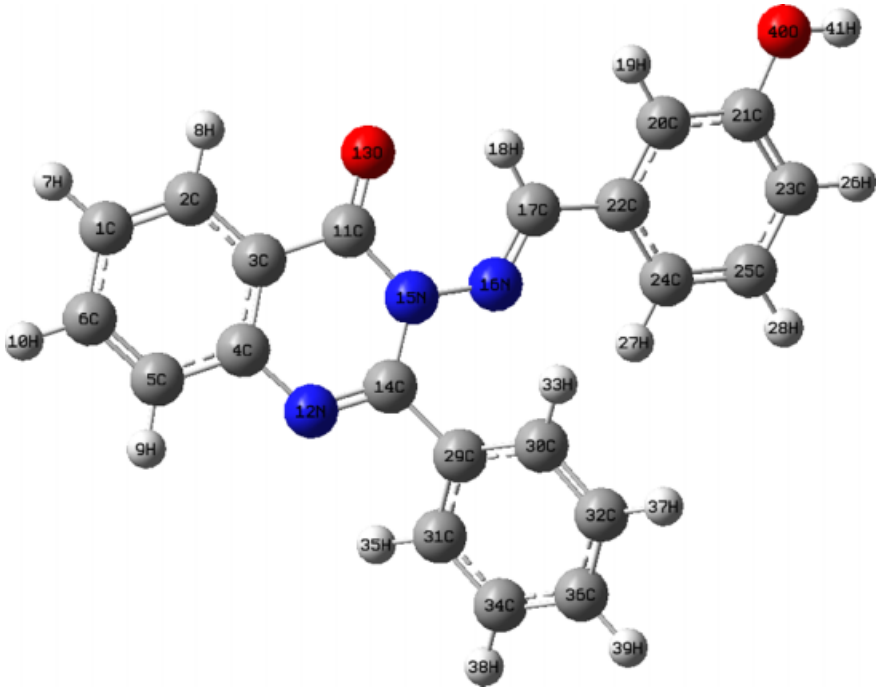

Figure 3. Optimized Geometry of 3-{[(2-hydroxyphenyl)methylene]amino}-2-phenylquinazolin-4(3H)-one. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

other modes a significant amount of splitting is observed. Such observations have already been reported.[65,68,69]

The existence of one or more aromatic rings in a 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 a multiplicity of weak to moderate bands, compared to the aliphatic C–H stretching.[70] In the present case, the HF calculations give υC–H modes of the phenyl rings in the range 2993–3051 cm^{-1}.

Corresponding to the $\upsilon C_{17}–H_{18}$ mode, a strong broad band is observed in the IR spectrum at 3199 cm^{-1} and the HF calculation gives this mode at 3070 cm^{-1} with a PED contribution of 98%. The deformations bands of $C_{17}–H_{18}$ are also identified at 1390 and 1038 cm^{-1}.

The benzene ring possesses six ring-stretching vibrations, of which the four with the highest wavenumbers (occurring near 1600, 1580, 1490, and 1440 cm^{-1}) are good group vibrations. With heavy substituents, the bands tend to shift to somewhat lower wavenumbers. In the absence of ring conjugation, the band at 1580 cm^{-1} is usually weaker than that at 1600 cm^{-1}. In the case of C═O substitution, the band near 1490 cm^{-1} can be very weak. The fifth ring stretching vibration is active near 1315 $\pm$ 65 cm^{-1}, a region that overlaps strongly with that of the CH in-plane deformation. The sixth ring stretching vibration, or the ring-breathing mode, 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.[48] The υPh modes are expected in the region 1615–1270, 1620–1285 and 1620–1260 cm^{-1} for Ph I, PhII and PhIII rings, respectively.[48] The υPh modes are observed at 1517, 1452, 1245, 1132 cm^{-1} in the IR spectrum, 1602, 1489, 1450, 1243, 1129 cm^{-1} in the Raman spectrum, 1630, 1596, 1491, 1465, 1243, 1240, 1123 cm^{-1} theoretically for ring PhI; at 1588, 1522, 1443, 1203, 1188 cm^{-1} in the IR spectrum, 1516, 1443, 1204, 1188 cm^{-1} in the Raman spectrum and 1617, 1584, 1501, 1449, 1224, 1190, 1078 cm^{-1} theoretically for ring Ph II and at 1623, 1579, 1490, 1283, 1232, 1153 cm^{-1} in the IR spectrum, 1621, 1572, 1470, 1295, 1286, 1156 cm^{-1} in the Raman spectrum and 1623, 1578, 1478, 1467, 1288, 1283, 1240, 1235, 1154 cm^{-1} theoretically for ring Ph III. Due to aromatic ring vibrations, quinazolines[55] absorb strongly at 1635–1610, 1580–1565, and 1520–1475 cm^{-1}.

In ortho disubstitution, the ring-breathing mode has three wavenumber intervals depending on whether both substituents are heavy; or one of them is heavy, while the other is light; or both of them are light. In the first case, the interval is 1100–1130 cm^{-1}; in the second case 1020–1070 cm^{-1}; while in the third case it is between[49] 630 and 780 cm^{-1}. The ring-breathing modes of the phenyl rings are assigned at 1013, 999, 992 cm^{-1} (HF) by PED calculations. The in-plane and out-of-plane CH deformations of the phenyl ring are expected above and below 1000 cm^{-1}, respectively.[48] Generally, the CH out-of-plane deformations with the highest wavenumbers have a smaller intensity than those absorbing at lower wavenumbers. Most of the deformation bands of the CH vibrations of the phenyl rings are not pure but contain significant contributions from other modes (Table 1). The IR bands in the region 1841–2861 cm^{-1} and their large broadening support the intramolecular hydrogen bonding.[71]

Geometrical parameters and first hyperpolarizability

To the best of our knowledge, no X-ray crystallographic data of this molecule have yet been established. However, the theoretical results obtained are almost comparable with the reported structural parameters of the parent quinazoline molecules. The carbon–oxygen (phenolate) $C_{21}–O_{40}$ distance of 1.3765 ´Å is in agreement with the average distance of 1.362 ´Å found among phenols.[72] The experimental N–N bond length of hydrazine[73] is reported at 1.449 ´Å and the electron diffraction N–N bond length

Table 1. Calculated vibrational wavenumbers (scaled, in cm^{-1}), measured infrared and Raman band positions (in cm^{-1}) and assignments for 3-{[(2-hydroxyphenyl)methylene]amino}-2-phenylquinazolin-4(3H)-one

HF/6-311G*			HF/6-31G*					
$\upsilon_{(HF)}$ (cm^{-1})	IR intensity	Raman activity	$\upsilon_{(HF)}$ (cm^{-1} cm^{-1})	IR intensity	Raman activity	$\upsilon_{(IR)}$ (cm^{-1})	$\upsilon_{(Raman)}$ (cm^{-1})	Assignments of normal modes with PED(%)[a]
3653	83.10	151.09	3615	86.86	168.31	3440 sbr		$\upsilon O_{40}H_{41}$(100)
3045	1.89	20.86	3070	2.46	21.17	3199 sbr		$\upsilon C_{17}H_{18}$(98)
3029	3.46	71.93	3051	2.93	74.60	3056 s	3063 w	$\upsilon C_{24}H_{27}$(93), $\upsilon C_{25}H_{28}$(6)
3025	15.31	210.29	3047	13.27	213.40			υC_2H_8(60), υC_5H_9(23) υC_1H_7 (12)
3022	3.49	164.69	3045	4.96	140.94			$\upsilon C_{30}H_{33}$ (69), $\upsilon C_{31}H_{35}$ (16)
3021	8.08	55.93	3043	4.37	48.49			υC_5H_9 (66), υC_2H_8 (27)
3019	22.64	9.66	3042	15.29	25.28			$\upsilon C_{31}H_{35}$ (72), $\upsilon C_{30}H_{33}$ (19)
3006	2.26	62.20	3029	1.33	59.70			$\upsilon C_{20}H_{19}$(98)
3001	23.35	206.26	3023	17.55	210.29			υC_1H_7 (57), υC_6H_{10} (24) υC_2H_8 (11)
3000	53.42	146.59	3023	43.80	147.49			$\upsilon C_{36}H_{39}$ (46), $\upsilon C_{34}H_{38}$ (20), $\upsilon C_{32}H_{37}$ (19)
2994	26.59	114.69	3016	20.69	115.50			$\upsilon C_{25}H_{28}$ (77), $\upsilon C_{23}H_{26}$ (16)
2988	17.51	114.51	3010	14.65	113.64			$\upsilon C_{32}H_{37}$ (46), $\upsilon C_{34}H_{38}$ (46)
2984	8.19	82.44	3006	7.60	85.44			υC_6H_{10} (64), υC_1H_7 (29)
2975	0.09	49.48	2998	0.09	50.12			$\upsilon C_{36}H_{39}$ (50), $\upsilon C_{32}H_{37}$ (24) $\upsilon C_{34}H_{38}$ (23)
2971	16.27	100.42	2993	13.52	100.07			$\upsilon C_{23}H_{26}$ (82), $\upsilon C_{25}H_{28}$ (16)
1649	103.36	1116.24	1669	131.73	1025.74	1662 s		$\upsilon N_{16}C_{17}$ (61), $\delta N_{16}H_{18}C_{17}$ (11) $\delta C_{22}H_{18}C_{17}$ (11)
1627	355.58	121.05	1646	283.31	91.82	1652 vs	1656 s	$\upsilon C_{11}O_{13}$ (27), $\upsilon N_{12}C_{14}$ (21)
1612	41.22	218.70	1630	37.22	232.23			υ Ph I (51), δ CCC I (10)
1606	217.62	91.99	1623	225.69	92.25	1623 m	1621 m	υ Ph III (53)
1599	53.10	366.47	1617	52.30	373.52			υ Ph II (46)
1582	120.58	284.86	1601	199.19	309.42	1606 s	1609 vs	$\upsilon N_{12}C_{14}$ (17), $\upsilon C_{11}O_{13}$ (14)
1578	237.66	78.18	1596	176.00	40.88		1602 s	υ Ph I (40)
1567	169.78	223.16	1584	227.36	227.07	1588 m		$\upsilon N_{12}C_{14}$ (18), υ Ph II(40)
1559	68.85	8.84	1578	8.68	42.78	1579 m	1572 vs	υ Ph III (61)
1487	40.80	1.13	1501	37.87	1.64	1522 s	1516 w	δ CHC II (63), υ Ph II (29)
1478	30.73	19.11	1491	33.48	21.96	1517 s	1489 w	δ CHC I (52), υ Ph I (29)
1466	51.28	29.99	1478	62.32	33.66	1490 m		δ CHC III (48), υ Ph III (28)
1453	9.91	2.24	1467	8.86	1.68		1470 w	δ CHC III (36), υ Ph III (25)

Table 1. (*Continued*)

HF/6-311G*			HF/6-31G*					
$\upsilon_{(HF)}$ (cm^{-1})	IR intensity	Raman activity	$\upsilon_{(HF)}$ (cm^{-1} cm^{-1})	IR intensity	Raman activity	$\upsilon_{(IR)}$ (cm^{-1})	$\upsilon_{(Raman)}$ (cm^{-1})	Assignments of normal modes with PED(%)[a]
1452	0.82	1.66	1465	1.55	1.46	1452 s	1450 w	δ CHC I (22), υ Ph I (29), δ OH(32)
1434	12.56	6.85	1449	13.81	7.61	1443 s	1443 w	δ CHC II(57), υ Ph II (26)
1383	21.18	1.58	1390	18.47	2.11			$\delta C_{17}H_{18}$(56)
1331	8.77	12.55	1344	6.50	11.55	1357 m	1355 w	δ CHC II (83)
1316	78.37	17.93	1326	63.63	16.15	1324 m	1328 w	δ CHC I (50)
1306	77.74	42.39	1316	85.74	42.78		1317 w	δ CHC I (36), δ CHC III (36) δ QRing (30)
1278	142.27	143.30	1288	129.14	201.79		1295 s	υC_4N_{12} (14), υ Ph III (27) δ CHC III (12)
1274	151.26	99.12	1283	180.44	113.00	1283 s	1286 s	$\upsilon C_{14}N_{15}$ (19), υ Ph III (13) $\upsilon C_{11}N_{15}$ (10)
1263	62.19	270.41	1274	69.39	202.75	1271 s	1272 w	$\upsilon C_{21}O_{40}$ (25), δ CCC I (16) $\upsilon C_{17}C_{22}$ (13), δ CHC I (11)
1229	15.22	5.64	1243	52.74	13.79	1245 s	1252 m	υ Ph I (37)
1224	82.12	1.69	1240	31.28	9.41		1243 m	υ Ph III (17), υ Ph I (13), $\upsilon C_{11}N_{15}$ (16)
1222	34.73	3.27	1235	27.98	4.87	1232 s		υ Ph III (14), υC_4N_{12} (11) δ CHC III (22)
1205	3.97	0.74	1224	6.13	2.00	1203 m	1204 w	υ Ph II (53), δ CHC II (27)
1177	26.49	23.05	1190	6.89	8.71	1188 m	1188 w	δ CHC II (76), υ Ph II (14)
1175	61.73	12.45	1180	72.73	19.88		1178 w	$\delta C_{21}H_{41}O_{40}$ (15) δ CHC II (28)
1158	34.40	11.73	1167	12.49	27.77	1171 m	1169 w	δ CHC I (42)
1146	6.51	90.60	1154	1.49	55.30	1153 m	1156 m	δ CHC I (17), δ CHC III (16), υ Ph III (13)
1138	27.16	17.76	1149	28.42	38.32			$\upsilon C_{11}N_{15}$ (10), υ Ph II (24)
1123	3.79	8.06	1147	14.75	19.87			υ Ph II (43), δ CHC II (20)
1110	108.70	18.23	1123	150.54	17.92	1132 w	1129 m	$\delta C_{21}H_{41}O_{40}$ (29), υ Ph I (44)
1107	27.50	20.50	1119	24.53	21.47			$\upsilon C_{14}N_{15}$ (11), υ Ph III (24) δ CHC III (15)
1091	22.67	11.29	1101	23.78	12.65	1100 w	1098 w	δ CCC III (18), υ Ph III (25) δ CHC III (10)
1066	13.82	0.81	1079	21.17	1.01			υ Ph I (42), δ CHC I (27)
1064	2.06	0.05	1078	0.32	0.15	1075 w		υ Ph II (36), δ CHC II (24)
1032	24.92	17.56	1063	0.31	0.92		1069 w	γCH III(84),

Table 1. (*Continued*)

HF/6-311G*			HF/6-31G*					
$\upsilon_{(HF)}$ (cm^{-1})	IR intensity	Raman activity	$\upsilon_{(HF)}$ (cm^{-1} cm^{-1})	IR intensity	Raman activity	$\upsilon_{(IR)}$ (cm^{-1})	$\upsilon_{(Raman)}$ (cm^{-1})	Assignments of normal modes with PED(%)[a]
								τ CCCC III (14)
1025	0.04	0.70	1056	0.19	1.02		1057 w	γCH II (80), τ CCCC II (18)
1021	0.02	0.59	1049	29.28	19.11	1052 w	1044 w	$\gamma H_{18}N_{16}C_{22}C_{17}$ (41), γCH I (26) $\tau N_{15}N_{16}C_{17}H_{18}$ (13) $\tau N_{15}N_{16}C_{17}C_{22}$ (13)
1011	4.55	2.55	1038	6.20	2.09			γCH I(66), $\gamma H_{18}N_{16}C_{22}C_{17}$ (15)
1010	2.55	0.12	1032	2.72	0.20	1034 m	1033 m	γCH III (85)
1009	0.31	0.70	1029	0.91	3.17			γCH II (89)
1009	1.46	2.72	1024	4.46	2.05			δ CCC II (29), υ Ph II (46)
1002	8.30	30.54	1013	9.86	29.54			υ Ph III (60), δ CH III (17)
986	3.57	28.22	999	2.03	34.89	1002 w	1000 m	δ CCC II (49), υ Ph II (11)
980	1.75	50.29	992	1.73	44.81			δ CCC I (60), υ Ph I (31)
964	2.68	32.58	982	2.53	9.50	981 w		γCH II (74)
957	17.92	21.87	967	19.48	32.58	960 m		$\upsilon N_{15}N_{16}$ (12), $\upsilon C_{11}N_{15}$ (11)
922	1.81	0.21	943	3.54	0.67			γCH I (85)
920	63.65	5.53	936	18.60	0.76			γCH I (69), τ CCCC I (15)
911	4.90	1.17	930	6.47	2.99			γCH III (77)
908	38.28	3.78	927	53.13	6.23	923 m	924 w	υ Ph I (25), $\upsilon C_{21}O_{40}$ (13) $\upsilon C_{17}C_{22}$ (13)
904	15.33	0.42	913	42.79	5.82			δ CCC III (21), $\delta N_{15}N_{16}C_{17}$ (12) $\upsilon N_{15}N_{16}$ (12) δ Qring (30)
869	1.25	3.18	882	1.34	5.48	896 m	896 w	γCH II (99)
841	3.02	2.74	848	4.89	2.32	875 m	877 w	δ CCC III (13), $\delta N_{15}N_{16}C_{17}$ (10)
812	4.28	3.16	831	3.92	2.41	828 w	827 w	τ QRing (36), $\gamma O_{13}C_3N_{15}C_{11}$ (19) τ CCCC III (15)
805	64.35	0.59	822	63.10	1.53			γCH I (65), τ CCCC I (17)
796	45.79	0.89	807	42.56	0.56			γCH III(56)
788	86.70	2.27	802	98.13	1.28	795 w	799 w	τ CCCC II (16), γCH II (13) γCH III (12), $\gamma C_{14}C_{30}C_{31}C_{29}$ (10)
774	34.18	16.70	781	37.46	15.70	781 m	776 w	$\delta N_{16}C_{22}C_{17}$ (12), $\delta N_{16}H_{18}C_{17}$ (12) $\delta C_{22}H_{18}C_{17}$ (12) $\upsilon C_{21}O_{40}$ (10), υ Ph I (10)
720	51.68	1.07	735	68.79	0.73	751 s	759 w	τ CCCC III (25), γQRing (28) τ QRing (14)
705	10.85	4.06	713	22.53	4.60			τ CCCC II (36),

Table 1. (*Continued*)

HF/6-311G*			HF/6-31G*					
$\upsilon_{(HF)}$ (cm^{-1})	IR intensity	Raman activity	$\upsilon_{(HF)}$ (cm^{-1} cm^{-1})	IR intensity	Raman activity	$\upsilon_{(IR)}$ (cm^{-1})	$\upsilon_{(Raman)}$ (cm^{-1})	Assignments of normal modes with PED(%)[a]
								γCH II (24)
702	23.71	1.25	710	14.82	2.35		709 w	τ CCCC II (17), δ CCC III (13)
694	41.00	1.83	703	43.46	0.50	702 s		τ CCCC I (46), τ CCCC II (13)
								$\gamma C_{17}C_{20}C_{24}C_{22}$ (10)
689	6.67	2.43	696	1.79	7.03	692 m	692 w	$\gamma O_{13}C_3N_{15}C_{11}$ (22) τ CCCC I (19)
670	9.66	9.89	675	10.00	8.71		668 w	δ CCC II (35), δ CCC III (18)
654	18.11	0.616	659	19.08	0.71	666 m	656 w	$\delta NC_{29}C_{14}$ (22), τ CCCC II (18), δ QRing (36), δ CCC III (14)
635	8.93	3.94	639	9.85	3.15			δ CCC I (39), δ CCC III (13)
620	0.31	8.18	626	0.38	7.52	630 w		δ CCC II (83)
609	0.35	0.98	611	0.87	0.46	615 w	618 w	$\gamma O_{40}C_{20}C_{23}C_{21}$ (38) τ CCCC I (22)
								$\gamma C_{17}C_{20}C_{24}C_{22}$ (20)
579	0.56	3.07	584	0.54	2.86	588 w	588 w	δ CCC III (43), δ QRing (34) δ CCC II (13)
550	8.27	0.55	556	7.21	0.98	566 w	567 w	τ CCCC III (49), γCH III (14), τ Qring (19)
521	3.03	4.72	524	3.01	4.60			δ CCC I (59)
514	3.08	12.55	517	2.83	11.73	512 w	514 w	δ QRing (44)
502	1.09	2.78	505	1.20	2.81			τ CCCC II (26)
								$\gamma C_{14}C_{30}C_{31}C_{29}$ (16)
475	1.11	0.80	480	0.78	0.98	476 w	478 w	τ CCCC I (25), τ CCCC III (10) δ QRing(30)
465	1.04	0.48	467	0.57	0.44			τ CCCC I (35), τ CCCC II (11)
452	34.76	0.72	454	28.83	0.61			τ CCCC III (20) $\delta N_{15}N_{16}C_{17}$ (17)
448	7.37	0.73	452	13.58	1.11	444 w	446 w	τ CCCC III (29), τ CCCC II (13)
416	0.55	1.71	418	0.46	1.84			τ CCCC II (84)
384	5.80	2.20	387	5.49	1.74		403 w	$\delta CO_{40}C$ (40), $\delta CN_{16}N_{15}$ (36) $\delta C_3O_{13}C_{11}$ (12) $\delta N_{15}O_{13}C_{11}$ (12)
371	2.68	1.72	375	3.27	1.87			$\gamma N_{16}C_{11}C_{14}N_{15}$ (21) τ CCCC III (16), τ CCCC I (13)
350	3.61	2.32	353	3.43	2.62		351 w	$\delta C_{20}O_{40}C_{21}$ (16) $\delta C_{23}O_{40}C_{21}$ (16) τ CCCC III (13)
322	4.65	2.16	324	5.74	2.68			τ CCCC III (28), τ QRing (12)
279	3.62	1.07	283	190.99	4.56		299 w	$\tau C_{20}C_{21}O_{40}H_{41}$ (88)
274	171.17	4.38	281	4.13	1.27		272 w	τ CCCC II (21), δ QRing (44)

Table 1. (*Continued*)

HF/6-311G*			HF/6-31G*			$\upsilon_{(IR)}$ (cm^{-1})	$\upsilon_{(Raman)}$ (cm^{-1})	Assignments of normal modes with PED(%)[a]
$\upsilon_{(HF)}$ (cm^{-1})	IR intensity	Raman activity	$\upsilon_{(HF)}$ (cm^{-1} cm^{-1})	IR intensity	Raman activity			
262	3.49	5.62	264	3.44	5.31		265 w	$\upsilon C_{14}C_{29}$ (21), δ CCC II (21)
242	28.83	4.59	245	22.77	5.36			$\gamma N_{16}C_{11}C_{14}N_{15}$ (32) τ CCCC I (15), τ QRing (20)
238	3.37	1.42	238	5.60	1.30			τ CCCC I (71)
210	6.82	4.41	210	7.77	5.84		217 w	τ QRing (26) $\tau CN_{15}N_{16}C_{17}$ (26)
197	0.58	2.42	199	0.68	2.40			$\delta CC_{17}C$ (35), $\delta CN_{16}N_{15}$ (24), δ Qring (13)
172	4.66	7.39	171	5.52	9.00		183 w	$\tau C_5C_4C_3C_{11}$ (11) $\tau C_2C_3C_4N_{12}$ (11) $\tau CNN_{16}C_{17}$ (20)
157	3.42	2.66	156	4.26	3.10		152 w	$\tau CNN_{16}C_{17}$ (30), $\tau NNC_{17}H_{18}$ (20)
130	0.57	1.79	130	0.54	2.13		129 w	τ QRing (44), τ CCCC III (13)
84	1.83	2.12	86	2.22	2.32			τ QRing (16), $\delta CC_{17}C$ (20)
84	3.01	3.29	82	3.35	3.80			$\tau CNN_{16}C_{17}$ (23), $\tau N_{16}C_{17}CC$ (17), $\tau H_{18}C_{17}CC$ (17), $\delta N_{12}C_{29}C_{14}$ (10) $\delta N_{15}C_{29}C_{14}$ (10)
55	0.76	0.94	55	0.73	1.06			τ QRing (25), $\gamma C_{14}CCC$ (12), $\gamma C_{29}N_{12}N_{15}N_{14}$ (15), $\gamma N_{16}C_{11}C_{14}N_{15}$ (10)
51	0.72	8.38	50	0.88	10.32			$\tau N_{12}C_{14}CC$ (42), $\tau N_{15}C_{14}CC$ (42), $\delta N_{15}N_{16}C_{17}$ (13)
35	0.24	4.42	35	0.32	4.50			$\tau N_{12}C_{14}CC$ (23), $\tau N_{15}C_{14}CC$ (23), $\delta N_{15}N_{16}C_{17}$ (19), $\delta N_{12}C_{29}C_{14}$ (10), $\delta N_{15}C_{29}C_{14}$ (10)
26	1.54	2.85	26	1.65	3.64			τ QRing (31), $\tau N_{15}N_{16}C_{17}H_{18}$ (15), $\tau N_{15}N_{16}C_{17}C_{22}$ (15) $\tau N_{12}C_{14}CC$ (13), $\tau N_{15}C_{14}CC$ (13), $\gamma N_{16}C_{11}C_{14}N_{15}$ (12)
18	0.12	1.81	17	0.18	2.26			$\tau CNN_{16}C_{17}$ (52), $\delta N_{15}N_{16}C_{17}$ (14), $\gamma N_{16}C_{11}C_{14}N_{15}$ (12)

υ, Stretching; δ, in-plane bending; γ, out-of-plane bending; τ, torsion; s, strong; m, medium; w, weak; v, very; br, broad; QRing, quinazoline ring. Meta, mono and ortho substituted phenyl rings are designated as PhI, PhII and PhIII.

[a] PED, potential energy distribution, only contribution larger than 10% were given.

of tetramethylhydrazine[74] is reported at 1.401 ´Å. Kostava *et al.*[75] calculated the $N_{15}-N_{16}$ bond length in the range 1.318–1.357 ´Å for different molecules. In the present case, the $N_{15}-N_{16}$ bond length is 1.3892 ´Å, which is somewhere between the length of an N–N single bond (1.45 ´Å) and an N=N double bond (1.25 ´Å).

For the title compound, the bonds $C_{17}=N_{16}$ = 1.2708, $C_{14}=N_{12}$ = 1.2805, and $C_{11}=O_{13}$ = 1.2302 ´Å show typical double bond characteristics. However, the C_4-N_{12} = 1.3871, $C_{11}-N_{15}$ = 1.3939 and $C_{14}-N_{15}$ = 1.4037 ´Å bond lengths are shorter than the normal C–N single bond length of about 1.48 ´Å.

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The shortening of the C–N bonds reveal the effects of resonance in this part of the molecule.[76] The difference between the length of CN bonds are similar to the values of reported quinazoline derivatives[77] and this situation can be attributed to the difference in hybridization of the different carbon atoms. For a quinazoline derivative, Costa *et al*.[35] reported $C_4-N_{12} = 1.3954$, $C_{14}-N_{15} = 1.3904$ and $C_{11}-N_{15} = 1.4174$ ´Å. Gai *et al*.[78] reported $C_{11}-N_{15}$, $C_{14}-N_{15}$, C_4-N_{12}, C_3-N_{11}, and C_4-C_3 as 1.3703, 1.4623, 1.4043, 1.4823 and 1.3903 ´Å, respectively, for a quinazoline derivative. In the present case, the corresponding values are 1.3939, 1.4037, 1.3871, 1.4555, 1.3897 ´Å, respectively. For the title compound, the HF calculations give the bond angles $C_{11}-N_{15}-N_{16} = 123.7$, $C_{11}-N_{15}-C_{14} = 121.5$, $N_{16}-N_{15}-C_{14} = 114.3$, $O_{13}-C_{11}-N_{15} = 121.4$, $O_{13}-C_{11}-C_3 = 122.9$, $N_{15}-C_{11}-C_3 = 115.6$, $C_4-C_3-C_2 = 120.5$, $C_4-C_3-C_{11} = 119.1$, $C_2-C_3-C_{11} = 120.4$, $C_3-C_4-C_5 = 119.7$, $C_3-C_4-N_{12} = 120.8$, $C_5-C_4-N_{12} = 119.4^\circ$, whereas the corresponding reported values[78] are 120.3, 121.0, 118.0, 121.8, 122.7, 115.5, 119.7, 120.6, 119.6, 120.0, 118.6, and 121.2°.

The dihedral angles are $C_2-C_3-C_{11}-N_{15} = -178.6^\circ$ and $C_{11}-N_{15}-C_{14}-C_{29} = -174.9^\circ$. This indicates that the phenyl ring III and the quinazoline moiety of the title compound are in tilted positions. Also, the dihedral angles $C_{32}-C_{30}-C_{29}-C_{14}$, $C_{29}-C_{14}-N_{12}-C_4$ and $C_{29}-C_{14}-N_{15}-C_{11}$ are 175.0, 177.8 and −174.9°, respectively, which shows the phenyl ring II and the quinazoline moiety are in different planes. The $N_{16}=C_{17}$ moiety is essentially planar as seen from the torsion angles $N_{16}-C_{17}-C_{22}-C_{20} = 177.8$ and $N_{16}-C_{17}-C_{22}-C_{24} = 2.1^\circ$. The $N_{12}=C_{14}$ ring moiety is slightly twisted from the phenyl ring III ($C_3-C_4-N_{12}-C_{14} = -2.1$ and $C_5-C_4-N_{12}-C_{14} = 179.0^\circ$) and more twisted from the phenyl ring II ($N_{12}-C_{14}-C_{29}-C_{30} = -133.3$ and $N_{12}-C_{14}-C_{29}-C_{31} = 41.4^\circ$) as is evident from the torsion angles.

For a quinazoline derivative, Krishnakumar and Muthunatesan[79] reported the bond lengths $N_{12}-C_{14}$, $C_{14}-N_{15}$, $C_{11}-C_3$, C_3-C_2, C_2-C_1, C_1-C_6, C_6-C_5, C_5-C_4 as 1.311, 1.362, 1.427, 1.414, 1.380, 1.415, 1.380, and 1.416 ´Å. In the present study, the corresponding values are 1.2805, 1.4037, 1.4535, 1.3981, 1.3754, 1.4014, 1.376, and 1.3967 ´Å, respectively. The HF calculations give the bond angles $N_{12}-C_{14}-N_{15}$, $C_{14}-N_{15}-C_{11}$, $N_{15}-C_{11}-C_3$, $C_{11}-C_3-C_2$, $C_3-C_2-C_1$, $C_2-C_1-C_6$, $C_1-C_6-C_5$, $C_6-C_5-C_4$ as 121.9, 121.5, 115.6, 120.4, 119.6, 119.9, 120.8, 119.5°, respectively, whereas the corresponding reported values are 127.7, 116.2, 123.4, 124.4, 119.5, 120.3, 120.9 and 126.1°, respectively.[79]

The three bond angles around C_{11} atom are not equal to 120° each. It is seen that the $N_{15}-C_{11}-O_{13}$ bond angle (121.4°) is considerably greater than the $N_{15}-C_{11}-C_3$ angle (115.6°). This observation is similar to that in the structures of hydrazones reported earlier,[80] which is explained as due to a decrease the repulsion between the lone pairs present in N_{15} and O_{13} atoms. The central part of the molecule adopts a completely extended double bonded conformation. It can be confirmed by the $C_{11}-O_{13}$ bond length (1.2302 ´Å) which is considerably longer than the standard C=O bond length 1.21 ´Å and $N_{15}-C_{11}$ bond length (1.3939 ´Å) which is shorter than the standard N–C single bond length (1.47).[80]

Analysis of organic molecules having conjugated π-electron systems and large hyperpolarizability using infrared and Raman spectroscopies has evolved as a subject of research.[81] The potential applications of the title compound in the field of nonlinear optics demands the investigation of its structural and bonding features contributing to the hyperpolarizability enhancement, by analyzing the vibrational modes using the IR and Raman spectra. The ring stretching bands at 1623, 1579, 1283, 1245, 1153 cm^{-1} observed in IR have their counterparts in Raman at 1621, 1572, 1286, 1252, 1156 cm^{-1}, respectively, and their relative intensities in IR and Raman spectra are comparable.

The first hyperpolarizability (β_0) of this novel molecular system was 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 because of Kleinman symmetry.[82]

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

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

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 hyperpolarizibilites, respectively. The calculated first hyperpolarizability of the title compound is 0.92×10^{-30} esu, which is comparable with the reported values of similar quinazoline derivatives,[83] and experimental evaluation of this data is not readily available. We conclude that the title compound is an attractive object for future studies of nonlinear optical (NLO) properties.

In order to investigate the performance and vibrational wavenumbers of the title compound, the root mean square (RMS) values and correlation coefficients between calculated and observed wavenumbers were calculated (Fig. 4). RMS values of wavenumbers were evaluated using the following expression.[84]

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

The RMS error of the observed Raman bands is 9.89 and 17.56 and that for IR bands is 20.96 and 28.52, for HF/6-31G* and 6-311G* basis, respectively. 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 3-{[(2-hydroxyphenyl)methylene]amino}-2-phenylquinazolin-4(3H)-one were studied. The molecular geometry and the wavenumbers were calculated using HF/6-31G* basis, and the normal modes are assigned by PED calculations. Optimized geometrical parameters of the title compound are in agreement with the reported

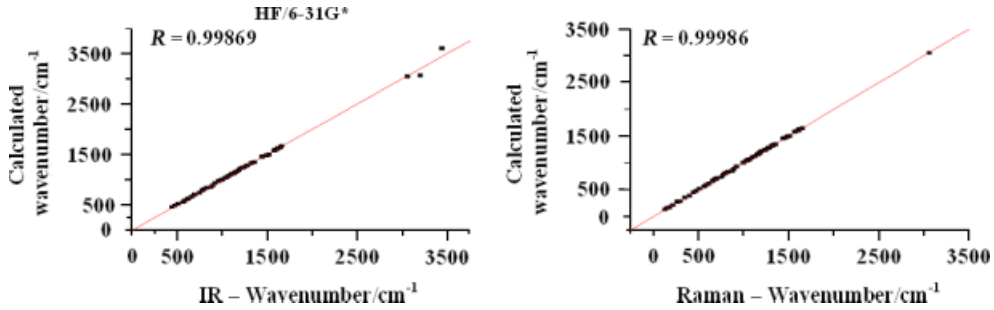

Figure 4. Correlation graph. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

values. Analysis of the phenyl ring modes shows C–C stretching mode is equally active as strong bands in both IR and Raman, which can be interpreted as the evidence of intramolecular charge transfer via conjugated path, which is responsible for hyperpolarizability enhancement leading to nonlinear optical activity. The simultaneous IR and Raman activation of the C=O stretching mode shows a charge transfer interaction through a π-conjugated path.

Supporting information

Supporting information may be found in the online version of this article.

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