

Vibrational spectroscopic studies and computational study of quinoline-2-carbaldehyde benzoyl hydrazone

S.R. Sheeja^a, Neema Ani Mangalam^a, M.R. Prathapachandra Kurup^a, Y. Sheena Mary^b, K. Raju^b, Hema Tresa Varghese^{c,1}, C. Yohannan Panicker^{d,1,*}

^a Department of Applied Chemistry, Cochin University of Science and Technology, Kochi, Kerala 682 022, India

^b Department of Physics, University College, Trivandrum, Kerala, India

^c Department of Physics, Fatima Mata National College, Kollam, Kerala 691001, India

^d Department of Physics, TKM College of Arts and Science, Kollam, Kerala 691005, India

ARTICLE INFO

Article history:

Received 15 November 2009

Received in revised form 6 March 2010

Accepted 10 March 2010

Available online 16 March 2010

Keywords:

FT-IR

DFT

Hydrazone

Hyperpolarizability

ABSTRACT

FT-IR spectrum of quinoline-2-carbaldehyde benzoyl hydrazone (HQb-H₂O) was recorded and analyzed. The synthesis and crystal structure data are also described. The vibrational wavenumbers were examined theoretically using the Gaussian03 package of programs using HF/6-31G(d) and B3LYP/6-31G(d) levels of theory. The data obtained from vibrational wavenumber calculations are used to assign vibrational bands obtained in infrared spectroscopy of the studied molecule. The first hyperpolarizability, infrared intensities and Raman activities are reported. The calculated first hyperpolarizability is comparable with the reported values of similar derivatives and is an attractive object for future studies of non-linear optics. The geometrical parameters of the title compound obtained from XRD studies are in agreement with the calculated values. The changes in the C–N bond lengths suggest an extended π -electron delocalization over quinoline and hydrazone moieties which is responsible for the non-linearity of the molecule.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Hydrazides and acylhydrazones are nowadays of considerable technical and commercial importance [1]. This is connected with their wide use as drugs, photo-thermochromic compounds and precursors for organic synthesis [2–4]. In the case of acylhydrazones the presence of the carbonyl oxygen atom promotes the formation of a chelate binding center [3]. Hydrazones and their metal complexes possess pronounced biological and pharmaceutical activities as antitumor [5–7], antimicrobial [8], antituberculosis [9] and antimalarial agents [10]. Hydrazones play an important role in improving the antitumor selectivity and toxicity profile of antitumor agents by forming drug carrier systems employing suitable carrier proteins [11]. They are also employed as extracting agents in spectrophotometric determination of some ions [12–14] and spectrophotometric determination of some species in pharmaceutical formulations [15], as well as used in catalytic processes [16,17] and waste water treatment [18]. Hydrazones, such as pyridoxal isonicotinoylhydrazone, salicylaldehyde benzoylhydrazone and 2-pyridyl carboxaldehyde-2-thiophene carboxalde-

hyde hydrazone, act as orally effective drugs for the treatment of iron overload diseases or genetic diseases β -thalassemia [19,20]. Metal complexes of hydrazones have found applications in various chemical processes like non-linear optics, sensors etc. [21], and have been used in the separation and concentration of palladium and platinum in road dust [22]. Quinolines are heterocyclic compounds, which are worth to study for many reasons, chief among them being their prevalence among biologically active molecules [23]. Derivatives of quinoline have been widely used in the synthesis of antibacterial, antihypertensive and antifungal drugs [24]. These molecules possess non-centrosymmetry and hence they are widely used in the synthesis of molecules having non-linear responses [24,25]. As for molecular design of new non-linear optical materials based on quinoline, the pyridine ring can be thought of as an acceptor group within the molecule, with the benzene ring as a donor. Increasing the acceptor character of the pyridine ring and/or increasing the donor character of the benzene ring would, therefore, substantially increase the non-linearity of this class of compounds [26]. Hydrazones have found wide applications in synthetic chemistry [27], to be used as indicators. Hydrazones are now being used extensively in detection and quantitative determination of several metals, for the preparation of compounds having diverse structures, analytical chemistry for the identification and isolation of carbonyl compounds [28]. The hydrazones have been used for different purposes such as herbicides, insecticides,

* Corresponding author.

E-mail address: cyphyp@rediffmail.com (C.Y. Panicker).

¹ Temporary address: Research Centre, Department of Physics, Mar Ivanios College, Trivandrum, Kerala, India.

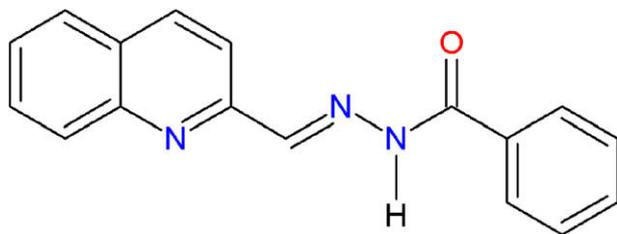


Fig. 1. Structure of hydrazone.

nematocides, redenticides and plant growth regulators [29]. The hydrazones are also important for their use as plasticizers and stabilizers for polymers [30], polymerization initiators and antioxidants [31]. More recently, 8-hydroxyquinoline aluminum has been widely used as the emissive and electron transporting material in organic light emitting devices [32,33]. El-Sonbati et al. [34] reported the supramolecular structures and stereo-chemical versatility of azoquinoline containing novel rare earth metal complexes. Computational method is at present widely used for simulating IR spectra. Such simulations are indispensable tools to perform normal coordinate analysis so that modern vibrational spectroscopy is unimaginable without involving them. Non-linear optics deals with the interaction of applied electromagnetic fields in various materials to generate new electromagnetic fields, altered in wave-number, phase, or other physical properties [35]. Organic molecules able to manipulate photonic signals efficiently are of importance in technologies such as optical communication, optical computing, and dynamic image processing [36,37]. In this context, the dynamic first hyperpolarizability of the title compound is also calculated in the present study. The first hyperpolarizability (β_0) of this novel molecular system is calculated using B3LYP/6-31G(d) method, 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 symmetry [38]. 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. In the present work, the synthesis, crystal structure data and vibrational spectroscopic analysis of quinoline-2-carbaldehyde benzoyl hydrazone (HQb-H₂O) is reported. The structure of the hydrazone is given in Fig. 1.

2. Experimental

All the chemicals and solvents used for the syntheses were of analytical grade. Benzhydrazide (Sigma Aldrich) and quinoline-2-carbaldehyde (Sigma Aldrich) were used as received. The title compound is prepared by protocol reported by Mangalam et al. [39]. Benzhydrazide (0.136 g, 1 mmol) dissolved in methanol (10 cm³) was added to a hot solution of quinoline-2-carbaldehyde (0.157 g, 1 mmol) in the same solvent (20 cm³). Two drops

of glacial acetic acid were added to the reaction mixture. Then the reaction mixture was refluxed for 4 h and cooled to room temperature. The pale yellow product formed was filtered off and washed with methanol and dried over P₄O₁₀ *in vacuo*. Yield – 89%, m.p. 143 °C. Elemental Anal. Found (Calcd)%: C, 67.81 (67.54); H, 4.86 (5.33); N, 14.40 (13.90) for C₁₇H₁₃N₃O·1.5H₂O.

Elemental analyses were carried out using a Vario EL III CHNS analyzer at SAIF, Kochi, India. IR spectrum (Fig. 2) was recorded on a Thermo Nicolet AVATAR 370 DTGS model FT-IR Spectrophotometer in the range 4000–400 cm⁻¹ with KBr pellets and ATR technique at SAIF, Kochi, India.

Colorless block shaped crystals of the hydrazone, suitable for X-ray diffraction studies, were grown from a solution of mixture of DMF and ethanol (1:1v/v). The lattice is monoclinic in nature with *P*2₁/*n* symmetry. The crystal data and structural refinement parameters are given in Table 1. The data were collected using Oxford Diffraction Xcalibur-S diffractometer, equipped with graphite-monochromated Mo K α (λ = 0.71073 Å) radiation at the National Single Crystal X-ray Facility, IIT Bombay, Mumbai, India. The intensity data were collected at 150(2)K by the ω / q -scan mode. The cell refinement was done using the CrysAlis RED software [40]. The structure was solved by direct methods with the program SHELXS-97 and refined by full matrix least squares on F^2 using SHELXL-97 [41]. The graphical tool used were Diamond version 3.1f [42] and mercury [43]. Full crystallographic data (cif file) relating to the crystal structure have been deposited with the Cambridge Crystallographic Data Centre as CCDC 743681.

The ORTEP diagram of the compound is given in Fig. 3.

The molecule (numbering of atoms, according to Fig. 3) as a whole is roughly planar with a maximum dihedral angle of 4.82(11)° between the rings formed by the atoms C₁, C₂, C₃, C₄, C₅, C₆ and C₁₂, C₁₃, C₁₄, C₁₅, C₁₆, C₁₇ respectively. The C₁₁–O₁ bond length of 1.228(3) Å indicates the molecule exists in the keto form in the solid-state. The C₁₀–N₂ bond length of 1.279(2) Å confirms its significant double-bond character. The values of the N₂–N₃ and N₃–C₁₁ bond distances of 1.379(2) and 1.362(3) Å, respectively, indicate significant delocalization of π -electron density over the hydrazone portion of the molecule. The torsion angle values, –179.54(19)° and 1.9(3)° attained by N₃–N₂–C₁₀–C₉ and N₂–N₃–C₁₁–O₁, suggest the existence of the ligand in *trans* configuration along the C₁₀–N₂ bond and in *cis* form along the C₁₁–N₃ bond [44–46]. The existence of C₁₀–N₂ bond in *trans* configuration, rules out the possibility of intramolecular N₃–H \cdots N₁ hydrogen bonding. The packing of molecules in the crystal lattice is shown in Fig. 4.

The unit cell is viewed down the 'a' axis. The molecules are arranged in a zig-zag manner in the unit cell. An interesting feature of the crystal packing is the formation of a supramolecular chain mediated by a network of hydrogen bonds (Fig. 5).

The residual water molecule in the crystal lattice interconnects adjacent molecules in the lattice through intermolecular hydrogen bonds. Finally, these chains are linked into highly ribbed 3D array by extensive hydrogen bonding interactions. The orientation of the molecules in the crystal lattice is in such a manner that π ·· π stacking interactions are present between Cg (2) (C₁, C₂, C₃, C₄, C₅, C₆) and Cg(3) (C₁₂, C₁₃, C₁₄, C₁₅, C₁₆, C₁₇) at an average distance of 3.8931(14) Å. In addition, C₁₁–O₁··Cg (2) interaction is also observed with O₁··Cg distance of 3.9025(19) Å and C₁₁··Cg distance of 3.481(2) Å. The molecules in the adjacent layers within the unit cell are held together by these interactions, which reinforce the packing. The significant bond parameters and interaction parameters are given in Tables 2 and 3 respectively.

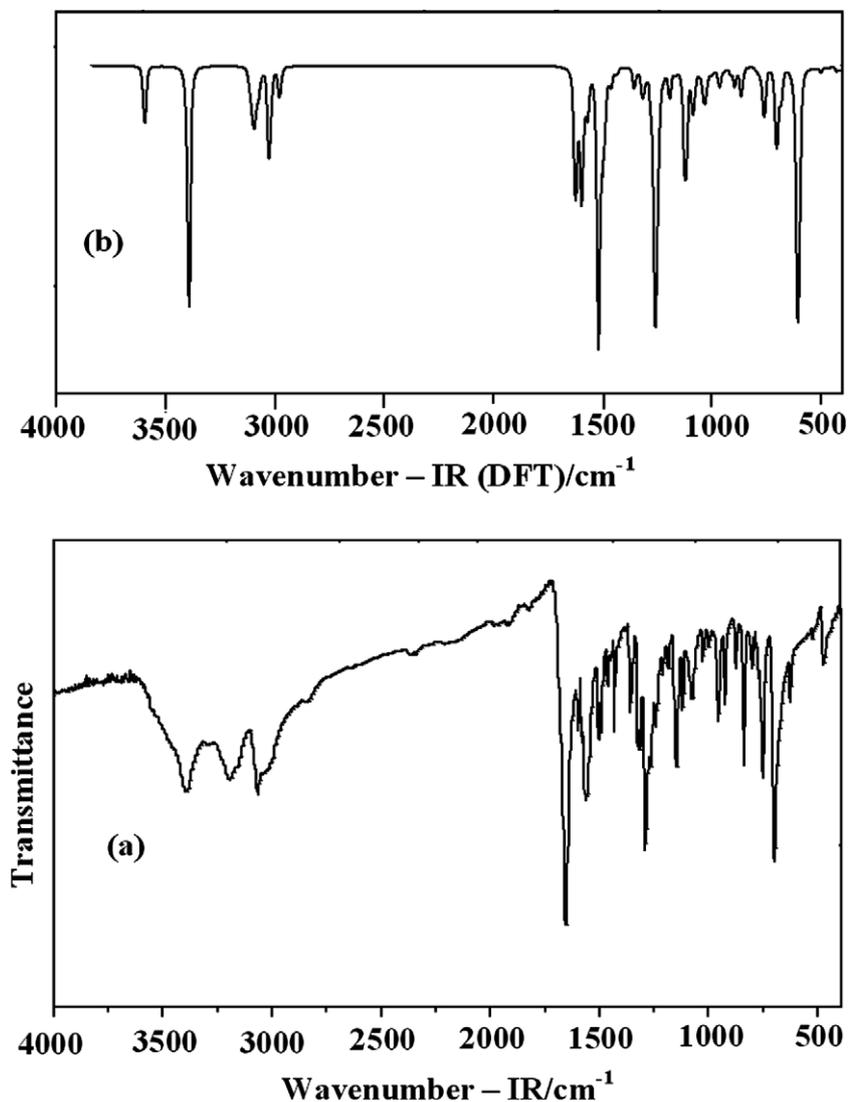


Fig. 2. IR spectrum (a) experimental (b) theoretical (DFT).

3. Computational details

Calculations of the title compound were carried out with Gaussian03 program [47] using the HF/6-31G(d) and B3LYP/6-31G(d) levels of theory to predict the molecular structure and vibrational wavenumbers. The wavenumber values computed contain known systematic errors [48] and we therefore, have used the scaling factor values of 0.8929 and 0.9613 for HF and DFT levels of theory. Parameters corresponding to optimized geometry of the title compound (Fig. 6) are given in Table 4. 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 [49,50].

4. Results and discussion

The observed IR bands with their relative intensities and calculated (scaled) wavenumbers and assignments are given in Table 5.

The NH stretching vibration [51] appears strongly and broadly in the region $3390 \pm 60 \text{ cm}^{-1}$. In the present study, the NH stretching band has split to a doublet, $3395, 3294 \text{ cm}^{-1}$ in the IR spectrum

owing to the Davydov coupling between the neighboring units. A similar type of splitting observed in acetanilide [52,53] and N-methylacetamide [54] in the stretching band is attributed to the Davydov splitting. The splitting of about 101 cm^{-1} in the IR spectrum is due to the strong intermolecular hydrogen bonding. The CNH vibration in which N and H atoms move in opposite direction of carbon atom in the amide moiety appears at 1523 (IR) , $1518 \text{ cm}^{-1} \text{ (DFT)}$ and the CNH vibration in which N and H atoms move in the same direction of carbon atom in the amide group appear at 1260 (IR) and at $1256 \text{ cm}^{-1} \text{ (DFT)}$ [55–57]. The NH rock in the plane is observed at 1210 cm^{-1} in IR and at 1221 cm^{-1} theoretically [57]. The out-of-plane wagging of NH [51] is moderately active with a broad band in the region $790 \pm 70 \text{ cm}^{-1}$ and the band at 875 (IR) , $865 \text{ cm}^{-1} \text{ (DFT)}$ is assigned as this mode. Panicker et al. [58] reported NH deformation bands at $1538, 1220 \text{ cm}^{-1}$ in IR spectrum and at $1538, 1223 \text{ cm}^{-1}$ theoretically.

The CN stretching vibration [51] coupled with δNH , is moderately to strongly active in the region $1275 \pm 55 \text{ cm}^{-1}$. El-Shahawy et al. [57] observed a band at 1320 cm^{-1} in the IR spectrum as this νCN mode. In the present case, the $\nu\text{C}_{32}\text{—N}_{20}$ band is observed at 1358 cm^{-1} in the IR spectrum and at 1353 cm^{-1} theoretically. This mode is not pure, but contains significant contribution from in-plane CH mode.

Table 1
Summary of crystal data and structure refinement for HQb·H₂O.

Formula	C ₁₇ H ₁₅ N ₃ O ₂
Formula weight	293.32
Color; shape	Colorless, block
Temperature, <i>T</i> (K)	150(2)
Wavelength (Mo Kα) (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Lattice constants	
<i>a</i> (Å)	6.4221(4)
<i>b</i> (Å)	32.7824(18)
<i>c</i> (Å)	7.0736(4)
α (°)	90.00
β (°)	104.047(6)
γ (°)	90.00
Volume, <i>V</i> (Å ³)	1444.69(15)
<i>Z</i>	4
Calculated density, ρ (Mg m ⁻³)	1.349
Absorption coefficient, μ (mm ⁻¹)	0.091
<i>F</i> (0 0 0)	616
Crystal size (mm ³)	0.23 × 0.18 × 0.15
θ range for data collection	3.03–25.0
Limiting indices	−6 ≤ <i>h</i> ≤ 7; −38 ≤ <i>k</i> ≤ 35; −8 ≤ <i>l</i> ≤ 8
Measured/unique data	9072/2546 [<i>R</i> _(int) = 0.064]
Observed data [<i>I</i> > 2σ(<i>I</i>)]	1416
Data/restraints/parameters	2540/0/211
Final <i>R</i> indices	<i>R</i> ₁ = 0.0475, <i>wR</i> ₂ = 0.0680
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1179, <i>wR</i> ₂ = 0.0806

The carbonyl stretching C=O vibration [51,59] is expected in the region 1715–1680 cm⁻¹ and in the present study this mode appears at 1655 cm⁻¹ in the IR spectrum. The DFT calculations give

this mode at 1624 cm⁻¹. The δ C=O in-plane deformation and the out-of-plane deformation γ C=O are expected in the regions 625 ± 70 and 540 ± 80 cm⁻¹, respectively [51]. The bands observed at 750 and 625 cm⁻¹ in the IR spectrum are assigned as these mode. The theoretically calculated values are 756 and 626 cm⁻¹. Lv et al. [60] reported the stretching vibrations ν C=N at 1506 cm⁻¹ and ν C=O at 1601, 1539 cm⁻¹. The C=N stretching skeletal bands [61–63] are observed in the range 1627–1566 cm⁻¹. For the title compound the band calculated at 1617 cm⁻¹ is assigned as C=N stretching mode and a weak band is observed in the IR spectrum at 1622 cm⁻¹.

The ν N–N has been reported at 1115 cm⁻¹ by Crane et al. [64], at 1121 cm⁻¹ by Bezerra et al. [65] and at 1130 cm⁻¹ by El-Beheery and El-Twigry [66]. The band observed at 1118 cm⁻¹ in IR, 1118 cm⁻¹ in DFT is assigned to the N₁₉–N₂₀ stretching mode in the present case.

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 for the vibrational assignments of vibrations containing multiple homo- and heteroaromatic rings [67–70]. In the following discussion, the mono and ortho substituted phenyl rings are designated as PhI and PhII, respectively. The modes in the two phenyl rings will differ in wavenumber, and the magnitude of splitting will depend in the strength of the interaction between the different parts (internal coordinates) of the two rings. For some modes, the splitting is so small that they may be considered as quasi-degenerate, and for other modes a significant amount of splitting is observed. Such observations have already been reported [67–71].

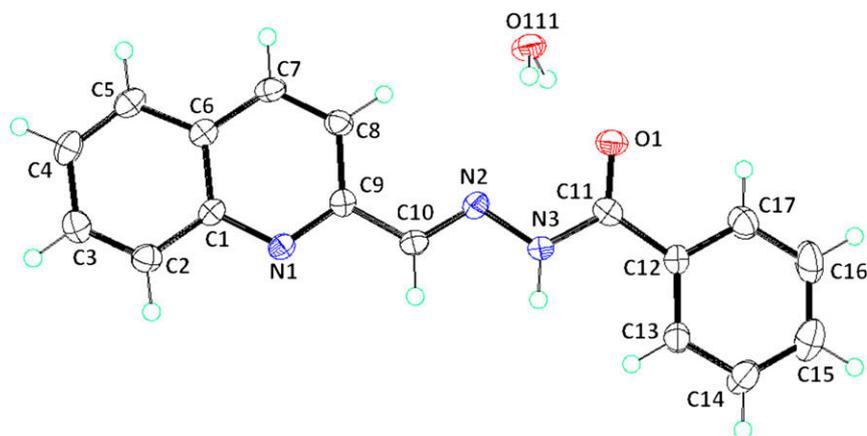


Fig. 3. ORTEP diagram of the molecule.

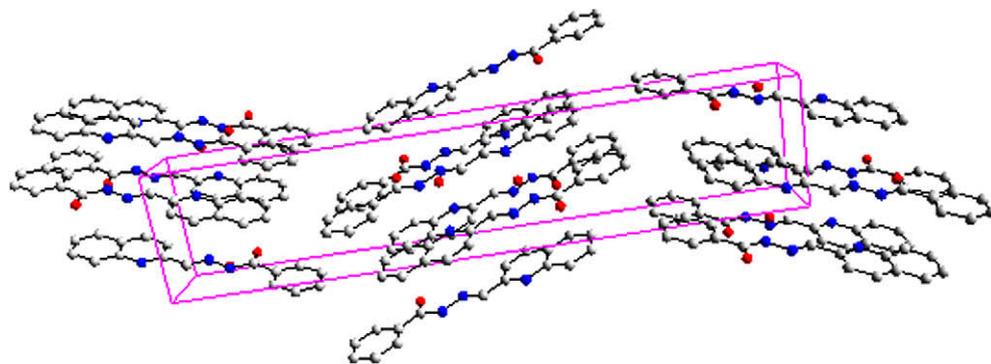


Fig. 4. Unit cell packing diagram of quinoline-2-carbaldehyde benzoyl hydrazone monohydrate viewed along the 'a' axis. Hydrogen atoms are excluded for clarity.

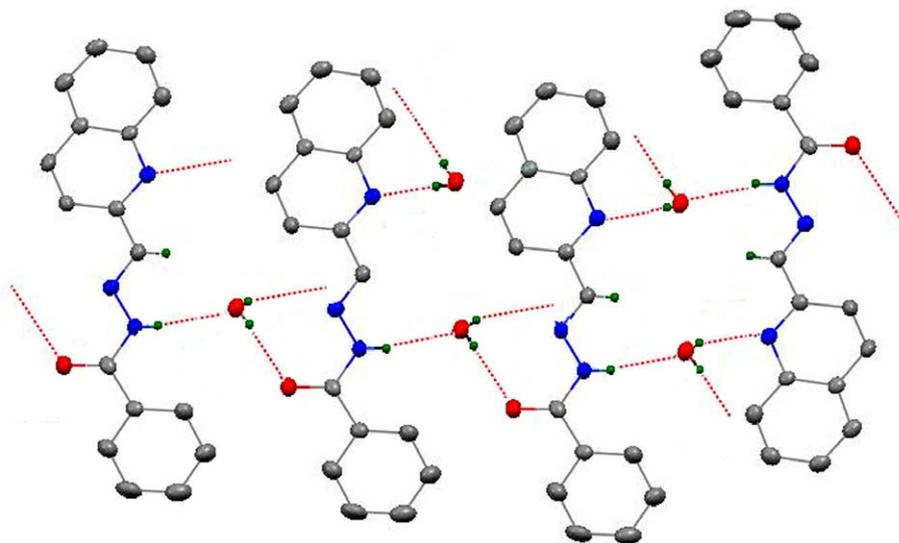


Fig. 5. Supramolecular chain stabilized by hydrogen bonding between the hydrazone and the water molecule.

Table 2
Selected bond lengths (Å) and bond angles (°) of HQb-H₂O.

Bond lengths (Å)		Bond angles (°)	
C ₁₀ –N ₂	1.279(2)	C ₁₀ –N ₂ –N ₃	115.50(19)
C ₁₁ –O ₁	1.228(3)	N ₂ –N ₃ –C ₁₁	118.1(2)
N ₂ –N ₃	1.379(2)	N ₃ –C ₁₁ –O ₁	121.9(2)
C ₁₁ –N ₃	1.362(3)	C ₉ –C ₁₀ –N ₂	119.9(2)
C ₉ –C ₁₀	1.460(3)	N ₃ –C ₁₁ –C ₁₂	117.0(2)
C ₁₁ –C ₁₂	1.495(3)		

Table 3
Interaction parameters of the title compound.

Hydrogen bonding				
D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)
N ₃ –H(3 N)...O ₁₁₁ ^a	0.91(3)	2.00(3)	2.879(3)	161.4(18)
O ₁₁₁ –H ₁₁₁ ...O ₁	0.92(3)	1.91(3)	2.796(2)	161(2)
O ₁₁₁ –H ₂₂₂ ...N ₁ ^b	0.84(3)	2.14(3)	2.948(3)	160(3)
C(5)–H(5)...O(1) ^c	0.95	2.54	3.367(3)	145
C(10)–H(10)...O(111) ^a	0.95	2.41	3.224(3)	144
C(13)–H(13)...O(111) ^a	0.95	2.48	3.416(3)	167
Short-ring interaction				
Cg(I)–Res(I)...Cg(J)	Cg–Cg (Å)	α (°)	β (°)	γ (°)
Cg(2) [1]...Cg(3) ^b	3.8931(14)	4.82	20.70	25.52
Pi-ring interactions				
Y–X(I)–Res(I)...Cg(J)	X...Cg (Å)	Y–X...Cg	Y...Cg	
C(11)–O(1) [1]...Cg(2) ^d	3.9025(19)	61.19(12)	3.481(2)	

Note: Equivalent position codes: a = 1 + x, y, z; b = 1 – x, –y, 2 – z; c = –x, –y, 1 – z; d = 1 – x, –y, 1 – z.

Cg(2) = C1, C2, C3, C4, C5, C6; Cg(3) = C12, C13, C14, C15, C16, C17.

For substituted benzenes, the CH stretching modes are expected in the region 3105–3000 cm^{−1} [51]. There are five CH stretching modes for mono substituted benzenes. According to selection rules all five bands are allowed in the IR spectrum [55]. The calculated values are 3116, 3103, 3091, 3079, 3069 cm^{−1} and only one band is observed in the IR spectrum at 3193 cm^{−1}. For ortho substituted benzene, νCH modes are observed at 3095, 3080, 3067 cm^{−1} in the IR spectrum and at 3109, 3094, 3080, 3066 cm^{−1} (DFT) theoretically. The benzene ring possesses six ring stretching vibrations, of which the four with the highest wavenumbers occurring respec-

tively near 1600, 1580, 1490 and 1440 cm^{−1} are good group vibrations [51]. 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 is active near 1335 ± 35 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 [51,55]. The sixth ring stretching vibration or ring breathing mode appears as a weak band near 1000 cm^{−1} in mono substituted benzenes [51]. The bands observed at 1593, 1560, 1493, 1449, 1328 cm^{−1} and 1601, 1542, 1504, 1461, 1431, 1380, 1313 cm^{−1} in IR spectrum are assigned as νPh stretching modes of PhI and PhII, respectively. As seen from Table 5, the DFT calculations give these modes in the range 1603–1313 cm^{−1}. These vibrations are expected in the region 1620–1300 cm^{−1} [51]. Some modes are not pure, but contain significant contributions from other modes. For the title compound the ring breathing mode of the mono substituted benzene is assigned at 996 cm^{−1} in the IR spectrum and at 995 cm^{−1} theoretically.

The CH out-of-plane deformations of the phenyl ring [51] are observed between 1000 and 700 cm^{−1}. Generally the CH out-of-plane deformations with the highest wavenumbers have weaker intensity than those absorbing at lower wavenumbers. In the present case, the γCH vibrations are observed at 956, 837, 801, 791, 773, 750 cm^{−1} in the IR spectrum and at 992, 975, 959, 931, 863, 849, 793, 791, 774, 756 cm^{−1} theoretically. The γCH at 774 cm^{−1} and the out-of-plane ring deformation at 698 cm^{−1} form a pair of strong bands characteristics of mono substituted benzene derivatives [72]. In the case of 1,2-disubstituted phenyl ring one strong vibration in the region 755 ± 35 cm^{−1} is observed and is due to γCH. This is confirmed by the strong band at 750 cm^{−1} in the IR spectrum. This band is not pure but contains significant contribution from δC=O mode.

In ortho disubstituted benzene rings, the ring breathing mode has three wavenumber intervals according to 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 it is 1020–1070 cm^{−1}, while in the third case [55] it is 630–780 cm^{−1}. In the present case, the band at 760 cm^{−1} given by DFT is assigned as the ring breathing mode of ortho substituted phenyl ring.

Quinolines and isoquinolines have three bands near 1600 cm^{−1} and five bands in the range 1500–1300 cm^{−1} [73]. Chowdhury et al. [74] reported the in-plane skeletal deformation bands of

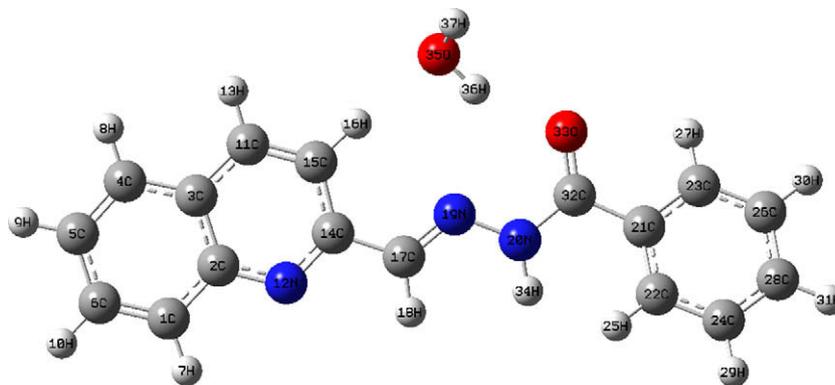


Fig. 6. Optimized geometry of the molecule.

Table 4
Geometrical parameters of the title compound, atom labeling according to Fig. 6.

Bond lengths (Å)	Bond lengths (Å)		Bond angles (°)		Dihedral angles (°)			
	DFT	XRD	DFT	XRD	DFT	XRD	DFT	XRD
C ₁ –C ₂	1.4211	1.4063	A(2,1,6)	120.3	120.2	D(6,1,2,3)	0.0	0.7
C ₁ –C ₆	1.3806	1.3673	A(2,1,7)	117.6	119.9	D(6,1,2,12)	–179.9	–179.1
C ₁ –H ₇	1.0841	0.95	A(6,1,7)	122.1	119.9	D(7,1,2,3)	180.0	
C ₂ –C ₃	1.435	1.4163	A(1,2,3)	119.4	119.1	D(7,1,2,12)	0.1	
C ₂ –N ₁₂	1.3725	1.3743	A(1,2,12)	118.8	118.2	D(2,1,6,5)	0.0	0.1
C ₃ –C ₄	1.421	1.4123	A(3,2,12)	121.8	122.6	D(2,1,6,10)	180.0	
C ₃ –C ₁₁	1.4245	1.4143	A(2,3,4)	118.9	119.0	D(7,1,6,5)	–180.0	
C ₄ –C ₅	1.382	1.3623	A(2,3,11)	117.5	117.0	D(7,1,6,10)	0.0	
C ₄ –H ₈	1.0863	0.95	A(4,3,11)	123.6	124.0	D(1,2,3,4)	–0.1	–1.4
C ₅ –C ₆	1.4206	1.4023	A(3,4,5)	120.5	120.7	D(1,2,3,11)	–180.0	178.5
C ₅ –H ₉	1.0853	0.95	A(3,4,8)	118.9	119.6	D(12,2,3,4)	179.9	178.4
C ₆ –H ₁₀	1.0852	0.95	A(5,4,8)	120.6	119.6	D(12,2,3,11)	–0.0	–1.7
C ₁₁ –H ₁₃	1.0861	0.95	A(4,5,6)	120.5	120.0	D(1,2,12,14)	–180.0	–179.3
C ₁₁ –C ₁₅	1.377	1.3543	A(4,5,9)	120.1	120.0	D(3,2,12,14)	0.1	0.9
N ₁₂ –C ₁₄	1.3401	1.3273	A(6,5,9)	119.5	120.0	D(2,3,4,5)	0.0	1.2
C ₁₄ –C ₁₅	1.4285	1.4143	A(1,6,5)	120.4	121.0	D(2,3,4,8)	–179.9	
C ₁₄ –C ₁₇	1.4619	1.4603	A(1,6,10)	120.1	119.5	D(11,3,4,5)	179.9	–178.6
C ₁₅ –H ₁₆	1.0901	0.95	A(5,6,10)	119.4	119.5	D(11,3,4,8)	–0.0	
H ₁₆ –O ₃₅	2.104		A(3,11,13)	119.2	119.9	D(2,3,11,13)	179.7	
C ₁₇ –H ₁₈	1.0945	0.95	A(3,11,15)	120.4	120.1	D(2,3,11,15)	–0.1	0.7
C ₁₇ –N ₁₉	1.2934	1.2792	A(13,11,15)	120.3	119.9	D(4,3,11,13)	–0.2	
N ₁₉ –N ₂₀	1.3751	1.3792	A(15,14,17)	122.0	121.8	D(4,3,11,15)	–180.0	–179.5
N ₁₉ –H ₃₆	2.4765		A(2,12,14)	118.6	117.9	D(3,4,5,6)	–0.0	–0.3
N ₂₀ –C ₃₂	1.3826	1.3623	A(12,14,15)	123.6	122.9	D(3,4,5,9)	–180.0	
N ₂₀ –H ₃₄	1.0161	0.922	A(12,14,17)	114.4	115.3	D(8,4,5,6)	180.0	
C ₂₁ –C ₂₂	1.407	1.3833	A(11,15,14)	118.0	119.4	D(8,4,5,9)	–0.0	
C ₂₁ –C ₂₃	1.4058	1.3813	A(11,15,16)	121.7	120.3	D(4,5,6,1)	–0.0	–0.3
C ₂₁ –C ₃₂	1.4905	1.4953	A(14,15,16)	120.3	120.3	D(4,5,6,10)	–180.0	
C ₂₂ –C ₂₄	1.3978	1.3853	A(15,16,35)	175.9		D(9,5,6,1)	180.0	
C ₂₂ –H ₂₅	1.0859	0.95	A(14,17,18)	115.3	120.0	D(9,5,6,10)	–0.0	
C ₂₃ –C ₂₆	1.3956	1.3813	A(14,17,19)	121.3	119.9	D(3,11,15,14)	0.1	1.1
C ₂₃ –H ₂₇	1.0838	0.95	A(18,17,19)	123.4	120.0	D(3,11,15,16)	179.6	
C ₂₄ –C ₂₈	1.3999	1.3703	A(17,19,20)	118.4	115.5	D(13,11,15,14)	–179.7	
C ₂₄ –H ₂₉	1.085	0.95	A(17,19,36)	139.0		D(13,11,15,16)	–0.2	
C ₂₆ –C ₂₈	1.4009	1.3814	A(20,19,36)	102.2		D(2,12,14,15)	–0.1	1.1
C ₂₆ –H ₃₀	1.0849	0.95	A(19,20,32)	119.1	118.1	D(2,12,14,17)	–179.9	–179.0
C ₂₈ –H ₃₁	1.0852	0.95	A(19,20,34)	120.1	120.1	D(12,14,15,11)	–0.1	–2.1
C ₃₂ –O ₃₃	1.2525	1.2283	A(32,20,34)	120.6	121.8	D(12,14,15,16)	–179.5	
O ₃₃ –H ₃₆	1.9717		A(22,21,23)	119.3	118.7	D(17,14,15,11)	179.7	178.0
O ₃₅ –H ₃₆	0.9851	0.923	A(22,21,32)	123.3	124.3	D(17,14,15,16)	0.3	
O ₃₅ –H ₃₇	0.9741	0.843	A(23,21,32)	117.3	117.0	D(12,14,17,18)	1.2	
			A(21,22,24)	120.2	120.4	D(12,14,17,19)	–178.7	178.7
			A(21,22,25)	120.8	119.8	D(15,14,17,18)	–178.6	
			A(24,22,25)	118.9	119.8	D(15,14,17,19)	1.5	–1.3
			A(21,23,26)	120.3	120.9	D(11,15,16,35)	–157.8	
			A(21,23,27)	118.4	119.5	D(14,15,16,35)	21.6	
			A(26,23,27)	121.3	119.5	D(15,16,35,36)	–17.2	
			A(22,24,28)	120.1	120.5	D(15,16,35,37)	–136.4	
			A(22,24,29)	119.8	119.7	D(14,17,19,20)	–179.9	–179.1
			A(28,24,29)	120.1	119.7	D(14,17,19,36)	–8.5	
			A(23,26,28)	120.1	120.0	D(18,17,19,20)	0.2	
			A(23,26,30)	119.8	120.0	D(18,17,19,36)	171.6	
			A(28,26,30)	120.1	120.0	D(17,19,20,32)	178.2	179.7

(continued on next page)

Table 4 (continued)

Bond lengths (Å)	DFT	XRD	Bond angles (°)	DFT	XRD	Dihedral angles (°)	DFT	XRD
			A(24,28,26)	119.9	119.5	D(17,19,20,34)	3.1	
			A(24,28,31)	120.0	120.2	D(36,19,20,32)	4.0	
			A(26,28,31)	120.1	120.2	D(36,19,20,34)	-171.2	
			A(20,32,21)	116.2	117.0	D(17,19,36,33)	-175.4	
			A(20,32,33)	121.9	121.9	D(17,19,36,35)	15.2	
			A(21,32,33)	122.0	121.1	D(20,19,36,33)	-3.1	
			A(32,33,36)	122.3		D(20,19,36,35)	-172.5	
			A(16,35,36)	95.8		D(19,20,32,21)	178.0	-178.2
			A(16,35,37)	129.7		D(19,20,32,33)	-3.1	1.9
			A(36,35,37)	108.0	104.0	D(34,20,32,21)	-6.9	
			A(19,36,33)	74.3		D(34,20,32,33)	172.0	
			A(19,36,35)	124.6		D(23,21,22,24)	-1.0	0.1
			A(33,36,35)	158.9		D(23,21,22,25)	176.4	
						D(32,21,22,24)	-179.6	179.2
						D(32,21,22,25)	-2.2	
						D(22,21,23,26)	1.3	0.1
						D(22,21,23,27)	-178.7	
						D(32,21,23,26)	180.0	-179.1
						D(32,21,23,27)	0.0	
						D(22,21,32,20)	-23.9	-1.1
						D(22,21,32,33)	157.2	178.9
						D(23,21,32,20)	157.5	178.0
						D(23,21,32,33)	-21.4	-2.1
						D(21,22,24,28)	0.1	-0.2
						D(21,22,24,29)	179.4	
						D(25,22,24,28)	-177.4	
						D(25,22,24,29)	2.0	
						D(21,23,26,28)	-0.6	0.0
						D(21,23,26,30)	179.5	
						D(27,23,26,28)	179.4	
						D(27,23,26,30)	-0.5	
						D(22,24,28,26)	0.6	0.2
						D(22,24,28,31)	-179.9	
						D(29,24,28,26)	-178.7	
						D(29,24,28,31)	0.8	
						D(23,26,28,24)	-0.4	-0.1
						D(23,26,28,31)	-179.9	
						D(30,26,28,24)	179.5	
						D(30,26,28,31)	0.0	
						D(20,32,33,36)	-0.5	
						D(21,32,33,36)	178.4	
						D(32,33,36,19)	2.0	
						D(32,33,36,35)	157.4	
						D(16,35,36,19)	-6.9	
						D(16,35,36,33)	-157.7	
						D(37,35,36,19)	128.1	
						D(37,35,36,33)	-22.6	

2,2'-biquinoline at 526, 472, 508, 624, 829 869 cm^{-1} and out-of-plane CH deformations at 737, 785, 938 cm^{-1} and the ring vibrations at 1245, 1383, 1434, 1470, 1593, 1621 cm^{-1} in the Raman spectrum and 760 cm^{-1} as the ring breathing mode. For 2-benzoylpyridine the ring breathing mode is reported at 1002 cm^{-1} , stretching mode of C=O at 1659 cm^{-1} and in-plane C=O deformation band at 568 cm^{-1} [75]. For 8-hydroxyquinoline, the ring deformation bands are reported at 422, 470, 487, 542, 705 cm^{-1} in the IR spectrum, 422, 472, 489, 514, 548, 578, 636 cm^{-1} in the Raman spectrum [76]. The in-plane and out-of-plane CH vibrations are reported in the range 739–868 cm^{-1} and 1141–1259 cm^{-1} and the ring stretching vibrations in the range 1347–1630 cm^{-1} [76] which are in agreement with our results.

Corresponding to $\text{C}_{11}\text{--H}_{13}$, $\text{C}_{15}\text{--H}_{16}$, $\text{C}_{17}\text{--H}_{18}$ stretching modes, bands are observed at 3077, 3043, 2984 cm^{-1} in the IR spectrum and at 3078, 3025, 2978 cm^{-1} theoretically.

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 [56]. For the title compound, the $\nu_{\text{C}_2\text{--N}_{12}}$ mode is observed at 1289 cm^{-1} in the IR spectrum and at 1276 cm^{-1} theoretically. The C–N stretching bands are expected [77] in the range 1100–1300 cm^{-1} . In the present case $\nu_{\text{C}_{14}\text{--N}_{12}}$ mode stretching band is calculated to be at 1304 cm^{-1} theoretically.

5. Geometrical parameters and first hyperpolarizability

The experimental N–N bond length of hydrazone [78] is reported as 1.449 Å and the electron diffraction N–N bond length of tetramethylhydrazone [79] is reported at 1.401 Å. Kostova et al. [80] calculated N–N bond length of 3,5-pyrazoledicarboxylic acid molecules with different methods and found the bond length varying from 1.318 to 1.357 Å. In the present case, the N–N bond length is 1.3756 Å (DFT), 1.3792 Å (XRD) which is somewhere between the length of an N–N single-bond (1.45 Å) and an N=N double-bond (1.25 Å).

Both of the $\text{C}_{17}\text{--N}_{19}$ = 1.2934 Å (DFT), 1.2792 Å (XRD) and $\text{C}_{32}\text{--O}_{33}$ = 1.2525 Å (DFT), 1.2283 Å (XRD) bonds show typical double-bond characteristics. However, the bond lengths $\text{C}_2\text{--N}_{12}$ = 1.3725 Å (DFT), 1.3743 Å (XRD), $\text{C}_{14}\text{--N}_{12}$ = 1.3401 Å (DFT), 1.3273 Å (XRD) and $\text{C}_{32}\text{--N}_{20}$ = 1.3826 Å (DFT), 1.3623 Å (XRD) are shorter than the normal C–N single-bond length of about 1.48 Å. The shortening of the C–N bond lengths reveal the effects of resonance in this part of the molecule [81]. At C_{21} position, the angles $\text{C}_{25}\text{--C}_{21}\text{--C}_{32}$ is reduced by 2.7° (DFT), 3° (XRD) and $\text{C}_{22}\text{--C}_{21}\text{--C}_{32}$ is increased by 3.3° (DFT), 4.3° (XRD) from 120°, and this asymmetry of exocyclic angles reveals the interaction between O_{33} and the mono substituted phenyl ring.

Table 5

Calculated vibrational wavenumbers (scaled), measured infrared band positions and assignments for quinoline-2-carbaldehyde benzoyl hydrazone.

HF/6-31G(d)			B3LYP/6-31G(d)			$\nu_{(IR)}$ (cm ⁻¹)	Assignments
$\nu_{(HF)}$ (cm ⁻¹)	IR intensity	Raman activity	$\nu_{(DFT)}$ (cm ⁻¹)	IR intensity	Raman activity		
3664	148.44	100.74	3597	71.41	95.12		νOH
3504	269.82	146.72	3394	285.76	222.84		νOH
3435	24.94	170.52	3388	14.51	531.23	3395 s, 3294 sbr	νNH
3044	5.77	134.39	3116	8.79	155.24	3193 s	νCH I
3038	17.71	175.66	3109	23.18	206.86		νCH II
3032	52.35	102.90	3103	22.34	249.22		νCH I
3030	19.80	195.39	3094	38.19	268.60	3094 sh	νCH II
3022	37.15	212.43	3091	24.42	104.44		νCH I
3019	27.67	69.04	3080	24.04	157.23	3080 sh	νCH II
3010	31.13	118.46	3079	2.54	104.41		νCH I
3008	7.98	100.12	3078	2.22	72.52	3077 s	ννC ₁₁ H ₁₃
3006	4.90	74.19	3069	11.91	37.17		νCH I
3000	4.75	36.62	3066	1.81	39.81	3067 sh	νCH II
2995	0.24	38.57	3025	131.18	110.65	3043 sh	νC ₁₅ H ₁₆
2947	31.55	42.11	2978	42.59	50.10	2984 sh	νC ₁₇ H ₁₈
1698	1.13	1986.27	1624	132.84	10.93	1655 s	νC=O
1652	296.07	203.94	1617	37.69	1062.39	1622 w	νC=N
1638	8.89	264.84	1603	8.80	2827.47	1601 w	νPh I, νC=C
1617	46.66	94.58	1597	30.62	1846.21	1593 m	νPh Im
1613	9.53	187.39	1595	114.70	57.12		ρH ₂ O
1590	159.17	14.58	1584	23.92	1297.35		νC ₁₁ C ₁₅ , νPh II
1586	210.27	34.87	1569	53.39	245.68	1560 w	νPh I
1577	0.72	28.62	1537	0.83	13.56	1542 sh	νPh II
1550	360.70	2.12	1518	313.50	240.36	1523 sh	δNH
1505	60.00	30.76	1504	94.84	333.83	1504 w	νPh II
1499	22.83	2.99	1491	50.90	6.79	1493 m	νPh I
1476	14.47	85.20	1464	22.78	349.57	1461 w	νPh II
1450	5.47	3.46	1447	2.88	3.92	1449 w	νPh I
1437	14.08	94.53	1434	7.53	189.28	1431 w	νPh II
1365	15.66	255.70	1370	0.46	862.83	1380 w	νPh II
1353	21.72	490.05	1353	27.61	49.81	1358 m	δC ₁₇ H ₁₈ , νC ₃₂ N ₂₀ ,
1341	0.79	15.29	1336	0.56	10.72		δCH I
1321	37.43	28.30	1319	14.75	283.41	1328 m	δC ₁₅ H ₁₆ , νPh I
1308	8.26	188.19	1315	20.19	369.71	1313 m	δC ₁₅ H ₁₆ , νPh II
1282	272.64	26.26	1304	9.93	759.57		δC ₁₇ H ₁₈ , νC ₁₄ N ₁₂
1274	270.81	111.47	1276	30.30	13.77	1289 s	νC ₂ N ₁₂
1238	6.32	72.44	1256	409.29	1075.31	1260 m	δNH
1234	50.69	32.48	1242	26.07	375.04	1240 w	δCH II
1195	2.71	14.87	1221	5.50	261.24	1210 w	ρNH
1189	19.87	4.09	1192	32.91	45.07		δCH I
1168	1.42	11.07	1178	1.90	7.55	1185 w	δCH II
1151	9.30	12.71	1174	0.43	63.82		δCH I
1137	159.26	9.03	1164	5.52	34.01	1145 m	δCH II
1134	13.72	18.67	1126	55.14	70.50		νCC(X) II
1105	51.06	11.07	1118	131.11	275.37	1118 m	νNN
1086	8.31	0.24	1084	62.73	55.94	1077 m	νCC(X) I
1079	30.96	1.86	1055	6.43	1.27		δCH I
1068	0.06	0.69	1033	61.57	83.06	1040 w	δCH I
1053	0.06	1.51	1021	6.98	65.34	1028 w	νPh I
1041	40.98	10.44	1011	1.25	20.29	1014 w	δCH II
1038	0.57	0.21	1004	3.74	8.37	1001 w	νC ₁₄ C ₁₇
1021	4.77	1.96	995	8.07	118.09	996 w	Ring breath I
1020	9.64	0.50	992	0.00	0.32		γCH II
1002	38.15	31.47	975	1.62	2.04		γCH I
994	0.84	4.43	964	26.59	18.42		γ C ₁₇ H ₁₈
994	4.38	61.65	959	2.79	0.73	956 m	γCH II
988	1.13	8.57	941	3.32	1.51		νC ₂₁ C ₃₂
942	1.63	0.90	931	1.50	5.06		γCH I
924	21.38	3.67	913	8.35	5.26	923 m	δPh II
916	8.00	3.11	893	22.99	4.95		γ C ₁₁ H ₁₃
891	57.39	0.08	865	14.70	32.26	875 m	ωNH
889	0.92	3.62	863	21.57	1.16		γCH II
864	19.65	12.34	849	1.38	7.61	837 m	γCH I
824	4.07	3.22	793	5.77	10.58	801 w	γCH I
818	2.47	5.21	791	0.55	4.93	791 w	γCH II
785	76.11	4.30	774	10.37	9.87	773 W	γCH I
770	18.97	5.37	760	53.87	4.94		Ring breath II
758	6.02	47.43	756	5.48	107.36	750 s	γCH II, δC=O
731	198.72	4.35	703	98.52	8.92	698 s	γPh I, II
707	2.95	0.75	691	1.98	0.30		γPh I, Ph II
698	0.68	0.57	684	15.56	1.19		γPh(X) I
682	35.10	2.17	681	22.52	1.43	683 w	δPh(X) II
626	7.76	2.91	628	7.16	6.24		δPh(X) I, II

(continued on next page)

Table 5 (continued)

HF/6-31G(d)			B3LYP/6-31G(d)			$\nu_{\text{IR}} \text{ (cm}^{-1}\text{)}$	Assignments
$\nu_{\text{HF}} \text{ (cm}^{-1}\text{)}$	IR intensity	Raman activity	$\nu_{\text{DFT}} \text{ (cm}^{-1}\text{)}$	IR intensity	Raman activity		
626	0.60	4.54	626	2.17	6.88	625 w	$\gamma\text{C=O}$
604	198.70	1.47	610	21.67	2.47		δCNC
601	89.35	2.07	605	265.92	4.82		$\gamma\text{Ph(X) M}$
583	84.76	2.25	595	53.17	4.10		$\delta\text{C=C-C}$
554	14.88	1.58	545	1.26	1.57		$\gamma\text{Ph(X) II}$
523	0.57	14.36	523	2.72	27.88	523 w	$\gamma\text{Ph(X) I}$
510	10.74	6.39	501	6.04	10.02		$\gamma\text{C=C-C}$
502	4.64	0.99	486	2.45	1.30		$\delta\text{Ph(X) I}$
466	4.01	1.20	466	2.43	1.64	470 w	$\delta\text{Ph(X) II}$
427	11.19	2.50	428	8.27	1.48	427 w	$\gamma\text{Ph II}$
418	0.31	0.29	409	0.58	1.21	415 w	$\gamma\text{Ph M}$

ν – stretching, δ – in-plane bending, γ – out-of-plane bending, s – strong, m – medium, w – weak, v – very, br – broad; sh – shoulder; mono and ortho substituted phenyl rings are designated as PhI and PhII; X – substituent sensitive.

According to Noveron et al. [82] for complexes of benzamide, the bond lengths $\text{C}_{32}\text{—O}_{33} = 1.2253$, $\text{C}_{32}\text{—N}_{20} = 1.3703$, $\text{C}_{32}\text{—C}_{21} = 1.4943$, $\text{C}_{21}\text{—C}_{22} = 1.3923$, $\text{C}_{21}\text{—C}_{23} = 1.3933$ and $\text{N}_{20}\text{—H}_{34} = 0.773$ Å. In the present case, the corresponding values given by DFT calculation are 1.2525, 1.3826, 1.4905, 1.407, 1.4058, 1.0161 Å and the XRD values are 1.2283, 1.3623, 1.4953, 1.3833, 1.3813 and 0.922 Å. For some benzamide complexes [83] the bond lengths for $\text{C}_{32}\text{—O}_{33} = 1.2445$, $\text{C}_{32}\text{—N}_{20} = 1.3646$, $\text{C}_{32}\text{—C}_{21} = 1.4816$ Å respectively, while in the present case, the corresponding values are 1.2525, 1.3826, 1.4905 Å (DFT) and 1.2283, 1.3623, 1.4953 Å (XRD). The C=O and C—N bond lengths [84] in benzamide, acetamide and formamide are, respectively, 1.2253, 1.2203, 1.2123 Å and 1.3801, 1.3804, 1.3683 Å. According to literature [85–88] the changes in bond length in C=O and C—N are consistent with the following interpretation: that is, hydrogen bond decreases the double-bond character of C=O and increases the double-bond characteristics of the C—N bond. The values of the angles $\text{C}_{23}\text{—C}_{21}\text{—C}_{32} = 117.3^\circ$ (DFT), 117.0° (XRD) and $\text{C}_{21}\text{—C}_{32}\text{—O}_{33} = 122.0^\circ$ (DFT), 121.1° (XRD) are smaller than those of benzaldehyde [89] 121.0° and 123.6° . These differences are ascribed to the steric repulsion between H25 and H34 atoms.

In the present case, the dihedral angles $\text{C}_{22}\text{—C}_{21}\text{—C}_{32}\text{—O}_{33}$ was determined to be 157.2° (DFT) and 178.9° (XRD). On the contrary, the equilibrium structure of benzaldehyde is planar [81]. The steric repulsion in the present case is also considered to cause the non-planar skeleton. The $\text{C}_{21}\text{—C}_{32}$ bond length 1.4905 Å (DFT), 1.4953 Å (XRD) is larger than the corresponding length of benzaldehyde (1.4794 Å) by 0.0111 Å [89].

The $\text{C}_{32}\text{—N}_{20}$ bond is twisted from the monosubstituted phenyl ring, as is evident from the torsion angles $\text{N}_{20}\text{—C}_{32}\text{—C}_{21}\text{—C}_{23} = -23.9^\circ$ (DFT), -1.1° (XRD) and $\text{N}_{20}\text{—C}_{32}\text{—C}_{21}\text{—C}_{22} = 157.5^\circ$ (DFT), 178.0° (XRD). The $\text{C}_2\text{—N}_{12}$ ring moiety is slightly twisted from the disubstituted phenyl ring ($\text{C}_3\text{—C}_2\text{—N}_{12}\text{—C}_{14} = 0.1^\circ$ (DFT), 0.9° (XRD) and $\text{C}_1\text{—C}_2\text{—N}_{12}\text{—C}_{14} = -180.0^\circ$ (DFT), -179.3° (XRD) as is evident from the torsion angles.

For quinoline derivatives, Krishnakumar et al. [90] reported the bond lengths $\text{N}_{12}\text{—C}_{14} = 1.45$ Å, $\text{C}_{14}\text{—C}_{15} = 1.53$ Å, $\text{C}_{15}\text{—C}_{11} = 1.53$ Å, $\text{C}_{11}\text{—C}_3 = 1.51$ Å, $\text{C}_3\text{—C}_2 = 1.42$ Å, $\text{C}_2\text{—N}_{12} = 1.39$ Å, $\text{C}_3\text{—C}_4 = 1.39$ Å, $\text{C}_4\text{—C}_5 = 1.39$ Å, $\text{C}_5\text{—C}_6 = 1.4$ Å, $\text{C}_6\text{—C}_1 = 1.39$ Å, $\text{C}_1\text{—C}_2 = 1.4$ Å, $\text{C}_{15}\text{—H}_{16} = 1.09$ Å, $\text{C}_{11}\text{—H}_{13} = 1.09$ Å, $\text{C}_4\text{—H}_8 = 1.08$ Å, $\text{C}_6\text{—H}_{10} = 1.08$ Å, $\text{C}_1\text{—H}_7 = 1.08$ Å. For the title compound, the corresponding values are 1.3401, 1.4285, 1.377, 1.4245, 1.435, 1.3725, 1.421, 1.382, 1.4206, 1.3806, 1.4211, 1.0901, 1.0861, 1.0863, 1.0852, 1.0841 Å (DFT) and 1.3273, 1.4143, 1.3543, 1.4143, 1.4163, 1.3743, 1.4123, 1.3623, 1.4023, 1.3673, 1.4063, 0.95, 0.95, 0.95, 0.95 and 0.95 Å. The reported values of bond angles [90] $\text{C}_{11}\text{—C}_3\text{—C}_2 = 119.1^\circ$, $\text{C}_1\text{—C}_2\text{—C}_3 = 118.6^\circ$, $\text{C}_2\text{—C}_3\text{—C}_4 = 118.8^\circ$, $\text{C}_3\text{—C}_4\text{—C}_5 = 123^\circ$ are in agreement with our calculated values in the present case. For quinolinium derivatives Atalay et al. [91] re-

ported the dihedral angles $\text{C}_{14}\text{—N}_{12}\text{—C}_2\text{—C}_1 = 180.0^\circ$, 179.1° , $\text{C}_6\text{—C}_1\text{—C}_2\text{—N}_{12} = -180.0^\circ$, 179.5° , $\text{C}_5\text{—C}_4\text{—C}_{13}\text{—C}_{11} = 180.0^\circ$, 179.9° , $\text{C}_{15}\text{—C}_{11}\text{—C}_3\text{—C}_4 = -180.0^\circ$, 179.9° , $\text{N}_{12}\text{—C}_2\text{—C}_3\text{—C}_4 = 180.0^\circ$, -179.3° and $\text{C}_1\text{—C}_2\text{—C}_3\text{—C}_{11} = 180.0^\circ$, -179.3° theoretically. The corresponding experimentally reported values are -175.5° , 179.2° , -176.7° , 178.9° , 179.9° and 176.1° [92]. For the title compound, we have obtained -180.0° , -179.9° , 179.9° , -180.0° , 179.9° , -180.0° theoretically and -179.3° , -179.1° , -178.6° , -179.5° , 179.4° and 178.5° experimentally. For the title compound, the bond angles and bond lengths are in agreement with the values reported by Atalay et al. [91] and Baraczyriski et al. [92].

Using the x , y and z components, the magnitude of the dynamic first hyperpolarizability can be calculated by $\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$. The complete equation for calculating the magnitude of the dynamic first hyperpolarizability from the Gaussian03 output is given as follows [93].

$$\beta = \left[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2 \right]^{1/2}$$

To calculate the dynamic first hyperpolarizability, the origin of the Cartesian coordinate system was chosen as the centre of mass of the compound. The calculated first hyperpolarizability of the title compound in an electric field of value 0.001 a.u. is 14.03×10^{-30} esu. The C—N distances in the calculated molecular structure vary from 1.2934 to 1.3826 Å which are intermediate between those of a C—N single-bond (1.48 Å) and a C=N double-bond (1.28 Å). Therefore, the calculated data suggest an extended π -electron delocalization over quinoline and hydrazone moieties [94,95] which are responsible for the non-linearity of the molecule. Honeybourne et al. [94] and Bader et al. [95] reported a hyperpolarizability value equal to 1.794×10^{-30} esu for 8-hydroxyquinolinium picrate. We conclude that the title compound is an attractive object for future studies of non-linear optical properties.

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 (Fig. 7). RMS values of wavenumbers were evaluated using the following expression [96].

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

The RMS error of the observed IR bands is found to be 35.24 for HF method and 13.11 for DFT method. 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.

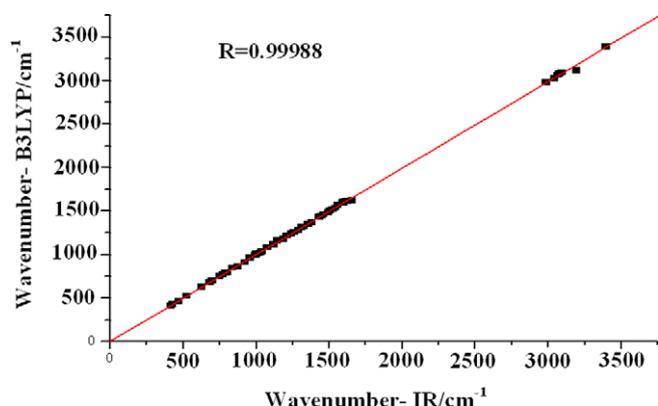


Fig. 7. Correlation graph between experimental and theoretical (DFT) wavenumbers.

6. Conclusion

The synthesis, crystal structure data, and FT-IR spectrum of quinoline-2-carbaldehyde benzoyl hydrazone were reported. The molecular geometry and wavenumbers were calculated using HF/6-31G(d) and B3LYP/6-31G(d) basis. Optimized geometrical parameters of the title compound are in agreement with the crystal structure data obtained from XRD studies. The extended π -electron delocalization over quinoline and hydrazone moieties is responsible for the non-linearity of the molecule. The first hyperpolarizability, infrared intensities and Raman activities are reported. The calculated first hyperpolarizability is comparable with the reported values of similar derivatives and is an attractive object for future studies of non-linear optics. An interesting feature of the crystal packing is the formation of a supramolecular chain mediated by a network of hydrogen bonds.

References

- [1] E. Schmidt, *Hydrazine and Its Derivatives: Preparation, Properties, Applications*, second ed., Wiley, New York, 2001.
- [2] P.V. Bernhardt, P. Chin, D.R. Richardson, *J. Biol. Inorg. Chem.* 6 (2001) 801.
- [3] V. Kogan, V. Zelentsov, G. Larin, V. Lhukov, *Complexes of Transitional Metals with Hydrazones*, Nauka, Moscow, 1990.
- [4] U. Ragnarsson, *Chem. Soc. Rev.* 30 (2001) 205.
- [5] N. Terzioğlu, A. Gurosy, *Eur. J. Med. Chem.* 38 (2003) 781.
- [6] M.T. Cocco, C. Congiu, V. Lilliu, V. Onnis, *Bioorg. Med. Chem.* 14 (2006) 366.
- [7] J. Easmon, G. Puerstinger, T. Roth, H.H. Fiebig, M. Jenny, W. Jaeger, G. Heinisch, J. Hofmann, *Int. J. Cancer* 94 (2001) 89.
- [8] P. Vicini, F. Zani, P. Cozzini, I. Doytchinova, *Eur. J. Med. Chem.* 37 (2002) 553.
- [9] J. Patole, U. Sandbhor, S. Padhye, D.N. Deobagkar, C.E. Anson, A. Powell, *Bioorg. Med. Chem. Lett.* 13 (2003) 51.
- [10] A. Walcourt, M. Loyevsky, D.B. Lovejoy, V.R. Gordeuk, D.R. Richardson, *Int. J. Biochem. Cell Biol.* 36 (2004) 401.
- [11] F. Kratz, U. Beyer, T. Roth, N. Tarasova, P. Coltery, F. Lechenault, A. Cazabat, P. Schumacher, C. Unger, U. Falken, *J. Pharm. Sci.* 87 (1998) 338.
- [12] S. Sivaramaiah, P.R. Reddy, *J. Anal. Chem.* 60 (2005) 828.
- [13] S.H. Babu, K. Suvadhan, K.S. Kumar, K.M. Reddy, D. Rekha, P. Chiranjeevi, *J. Hazard. Mater.* 120 (2005) 213.
- [14] S.A. Berger, *Microchem. J.* 47 (1993) 317.
- [15] A.A. El-Emam, F.F. Belal, M.A. Moustafa, S.M. El-Ashry, D.T. El-Sherbiny, S.H. Hansen, *Il Farmaco* 58 (2003) 1179.
- [16] M.S. Niasari, A. Amiri, *Appl. Catal. A. Gen.* 290 (2005) 46.
- [17] P. Pelagatti, M. Carcelli, C. Pelizzi, M. Costa, *Inorg. Chim. Acta* 342 (2003) 323.
- [18] M.G. El-Meligy, S. El-Rafie, K.M. Abu-Zied, *Desalination* 173 (2005) 33.
- [19] T.B. Chaston, D.R. Richardson, *Am. J. Hematol.* 73 (2003) 200.
- [20] P.V. Bernhardt, P. Chin, P.C. Sharpe, J.Y.C. Wang, D.R. Richardson, *J. Biol. Inorg. Chem.* 10 (2005) 761.
- [21] M. Bakir, I. Hassan, T. Johnson, O. Brown, O. Green, C. Gyles, M.D. Coley, *J. Mol. Struct.* 688 (2004) 213.
- [22] X. Ge, I. Wendler, P. Schramel, A. Ketrup, *React. Funct. Polymer* 61 (2004) 1.
- [23] M.K. Jain, S.C. Sharma, *Organic Chemistry*, Shoban Lal Nagin Chand and Co., Educational Publishers, New Delhi, 2001.
- [24] A.G. Mac Diarmid, A.J. Epstein, in: S.A. Jenekhe, K.J. Wynne (Eds.), *Photonic and Optoelectronic Polymers*, American Chemical Society, Washington, DC, 1997.
- [25] A.J. Epstein, *Mater. Res. Soc. Bull.* 22 (1997) 16.

- [26] G. Purohit, G.C. Joshi, *Indian J. Pure Appl. Phys.* 41 (2003) 992.
- [27] A.V. Xavier (Ed.), *Frontiers in Bioinorganic Chemistry*, VCH, 1985.
- [28] M. Fabian, G. Palmer, *Biochemistry* 40 (2001) 1867.
- [29] I. Pozdnyakova, P.W. Stafsheide, *Biochemistry* 40 (2001) 13728.
- [30] U. Kuehn, S. Warzeska, H. Pritzko, R. Kramer, *J. Am. Chem. Soc.* 123 (2001) 8125.
- [31] K.D. Karlin, J. Zubieta, *Biochemistry Chemical and Inorganic Perspectives*, Adenine Press Guilderland, New York, 1983.
- [32] H.D. Burrows, M. Fernandes, J.S. de Melo, A.P. Monkman, S. Navaratnam, *J. Am. Chem. Soc.* 125 (2003) 15310.
- [33] G.M. Credo, D.L. Winn, S.K. Buratto, *Chem. Mater.* 13 (2001) 1258.
- [34] A.Z. El-Sonbati, R.M. Issa, A.M.A. El-Gawad, *Spectrochim. Acta A* 68 (2007) 134.
- [35] Y.R. Shen, *The Principles of Nonlinear Optics*, Wiley, New York, 1984.
- [36] P.V. Kolinsky, *Opt. Eng.* 31 (1992) 1676.
- [37] D.F. Eaton, *Science* 253 (1991) 281.
- [38] D.A. Kleinman, *Phys. Rev.* 126 (1962) 1977.
- [39] N.A. Mangalam, S. Sivakumar, S.R. Sheeja, M.R.P. Kurup, E.R.T. Tiekink, *Inorg. Chim. Acta* 362 (2009) 4192.
- [40] CrysAlis CCD and CrysAlis RED Versions 1.171.29.2 (CrysAlis 171. NET), Oxford Diffraction Ltd., Abingdon, Oxfordshire, England, 2006.
- [41] G.M. Sheldrick, *Acta Crystallogr. A* 64 (2008) 112.
- [42] K. Brandenburg, *Diamond Version 3.1f*, Crystall Impact GbR, Bonn, Germany, 2008.
- [43] C.F. Macrae, P.R. Edgington, P. McCabe, E. Pidcock, G.P. Shields, R. Taylor, M. Towler, J. van de Streek, *J. Appl. Crystallogr.* 39 (2006) 453.
- [44] V. Suni, M.R.P. Kurup, M. Nethaji, *Spectrochim. Acta A* 63 (2006) 174.
- [45] M. Joseph, V. Suni, M.R.P. Kurup, M. Nethaji, S.G. Bhat, *Polyhedron* 23 (2004) 3069.
- [46] R.P. John, A. Sreekanth, M.R.P. Kurup, A. Usman, I.R. Razak, H.K. Fun, *Spectrochim. Acta A* 59 (2003) 2349.
- [47] M. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *Gaussian03, Revision C.02*, Gaussian, Inc., Wallingford, CT, 2004.
- [48] J.B. Foresman, in: E. Frisch, (Ed.), *Exploring Chemistry with Electronic Structure Methods: A Guide to Using Gaussian*, Gaussian Inc., Pittsburgh, PA, 1996.
- [49] P. Flukiger, H.P. Luthi, S. Portmann, J. Weber, *MOLEKEL 4.3*, Swiss Center for Scientific Computing, Manno, Switzerland, 2000.
- [50] S. Portmann, H.P. Luthi, *Chimia* 54 (2000) 766.
- [51] N.P.G. Roeges, *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*, Wiley, New York, 1994.
- [52] J. Edler, R. Pfister, V. Pouthier, C. Falvo, P. Hamm, *Phys. Rev. Lett.* 93 (2004) 106405.
- [53] J. Edler, P. Hamm, *A.C. Scott, Phys. Rev. Lett.* 88 (2002) 067403.
- [54] J. Edler, P. Hamm, *Phys. Rev. B* 69 (2004) 214301.
- [55] G. Varsanyi, *Assignments of Vibrational Spectra of Seven Hundred Benzene Derivatives*, Wiley, New York, 1974.
- [56] N.B. Colthup, L.H. Daly, S.E. Wiberly, *Introduction to Infrared and Raman Spectroscopy*, third ed., Academic Press, Boston, 1990.
- [57] A.S. El-Shahawy, S.M. Ahmed, N.K. Sayed, *Spectrochim. Acta A* 66 (2007) 143.
- [58] C.Y. Panicker, H.T. Varghese, T. Tansani, *Turk. J. Chem.* 38 (2009) 1.
- [59] M. Barthes, G. De Nunzio, G. Ribet, *Synth. Met.* 76 (1996) 337.
- [60] Y. Lv, J. Zhang, W. Cao, J.C. Juan, F. Zhang, Z. Xu, *Spectrochim. Acta A* 68 (2007) 382.
- [61] I. Yalcin, E. Sener, T. Ozden, A. Akin, *Eur. J. Med. Chem.* 25 (1995) 705.
- [62] R. Saxena, L.D. Kandpal, G.N. Mathur, *J. Polym. Sci. Part A: Polym. Chem.* 40 (2002) 3959.
- [63] R.M. Silverstein, F.X. Webster, *Spectrometric Identification of Organic Compounds*, sixth ed., Wiley, Singapore, 2003.
- [64] L.G. Crane, D. Wang, L.M. Sears, B. Heyns, K. Carron, *Anal. Chem.* 67 (1995) 360.
- [65] A.C.S. Bezerra, E.L. de Sa, F.C. Nart, *J. Phys. Chem. B* 101 (1997) 6443.
- [66] M. El-Behery, H. El-Twigry, *Spectrochim. Acta A* 66 (2007) 28.
- [67] C.Y. Panicker, K.R. Ambujakshan, H.T. Varghese, S. Mathew, S. Ganguli, A.K. Nanda, C. Van Alsenoy, *J. Raman Spectrosc.* 40 (2009) 527.
- [68] V.S. Madhavan, H.T. Varghese, S. Mathew, J. Vinsova, C.Y. Panicker, *Spectrochim. Acta* 72 (2009) 547.
- [69] C.Y. Panicker, H.T. Varghese, K.C. Mariamma, K. John, S. Mathew, J. Vinsova, C. Van Alsenoy, Y.S. Mary, *J. Raman Spectros.* doi:10.102/jrs2492.
- [70] C.Y. Panicker, H.T. Varghese, L. Ushakumari, T. Ertan, I. Yildiz, C.M. Granadeiro, H.I.S. Nogueira, Y.S. Mary, *J. Raman Spectros.* doi:10.1002/jrs2471.
- [71] J.H.S. Green, *Spectrochim. Acta* 24 (1968) 1627.
- [72] S. Higuchi, H. Tsuyama, S. Tanaka, H. Kamada, *Spectrochim. Acta A* 30 (1974) 463.
- [73] G. Socrates, *Infrared Characteristic Group Frequencies*, Wiley-Interscience, New York, 1980.

- [74] J. Chowdhury, M. Ghosh, T.N. Misra, *Spectrochim. Acta A* 56 (2000) 2107.
- [75] J. Chowdhury, M. Ghosh, *J. Colloid Interf. Sci.* 277 (2004) 121.
- [76] J. Chowdhury, M. Ghosh, T.N. Misra, *J. Colloid Interf. Sci.* 228 (2000) 372.
- [77] S. Kundoo, A.N. Banerjee, P. Saha, K.K. Chattopadhyay, *Mater. Lett.* 57 (2003) 2193.
- [78] N. Kohata, T. Fukuyama, K. Kuchitsu, *J. Phys. Chem.* 86 (1982) 602.
- [79] V.A. Naumov, O.A. Litvinov, H.J. Geise, J. Dillen, *J. Mol. Struct.* 99 (1983) 303.
- [80] I. Kostova, N. Peica, W. Keifer, *J. Raman Spectrosc.* 38 (2007) 2.
- [81] H. Arslan, U. Florke, N. Kulcu, G. Binzet, *Spectrochim. Acta A* 68 (2007) 1347.
- [82] J.C. Noveron, A.M. Arif, P.J. Stang, *Chem. Mater.* 15 (2003) 372.
- [83] W.H. Sun, W. Zhang, T. Gao, X. Tang, L. Chen, Y. Li, X. Jin, *J. Organomet. Chem.* 689 (2004) 917.
- [84] H. Takeuchi, M. Sato, T. Tsuji, H. Takashima, T. Egawa, S. Konaka, *J. Mol. Struct.* 485–486 (1999) 175.
- [85] E.D. Stevens, *Acta Crystallogr. B* 34 (1978) 544.
- [86] T. Otterson, *Acta Chim. Scand. A* 29 (1975) 939.
- [87] Q. Gao, G.A. Jeffrey, J.R. Ruble, R.K. McMullan, *Acta Crystallogr. B* 47 (1991) 742.
- [88] J.L. Katz, B. Post, *Acta Crystallogr.* 13 (1960) 624.
- [89] K.B. Borisenko, C.W. Bock, I. Hargittai, *J. Phys. Chem.* 100 (1996) 7426.
- [90] V. Krishnakumar, N. Prabavathi, S. Muthunatesan, *Spectrochim. Acta A* 69 (2008) 853.
- [91] Y. Atalay, D. Avcı, A. Basoglu, *Spectrochim. Acta A* 71 (2008) 760.
- [92] P. Barczynski, A. Komasa, M. Ratajczak, A. Katrusiak, B. Brzezinski, *J. Mol. Struct.* 791 (2006) 106.
- [93] K.S. Thanthiriwatte, K.M.N. de Silva, *J. Mol. Struct.* 617 (2002) 169.
- [94] C.L. Honeybourne, R.J. Ewen, K.J. Alkins, in: R.A. Hann, D. Bloor (Eds.), *Inorganic Materials for Non-linear Optics*, Royal Society of Chemistry, Burlington House, London, 1989.
- [95] M.M. Bader, T. Hamada, A. Kakuta, *J. Am. Chem. Soc.* 114 (1992) 6475.
- [96] L. Ushakumari, H.T. Varghese, C.Y. Panicker, T. Ertan, I. Yildiz, *J. Raman Spectrosc.* 39 (2008) 1832.