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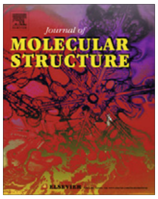

Experimental and theoretical study of 4-cyanobenzaldehyde isonicotinoyl-hydrazone monohydrate

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ABSTRACT

The molecular geometry, vibrational frequencies, gauge-including atomic orbital (GIAO) ^{1}H and ^{13}C chemical shift values of 4-cyanobenzaldehyde isonicotinoyl-hydrazone monohydrate in the ground state have been calculated by using the Hartree–Fock (HF) and density functional method (DFT/B3LYP) with 6-31++G(d,p) basis set. Furthermore, this structure has been confirmed by IR, ^{13}C and ^{1}H spectroscopy. The results of the optimized molecular structure are presented and compared with the experimental X-ray diffraction. The computed vibration frequencies are used to determine the types of molecular motions associated with each of the experimental bands observed. ^{13}C and ^{1}H NMR data were calculated by means of the methods of GIAO, CSGT, and IGAIM. Calculated chemical shift values are compared with the experimental 4-cyanobenzaldehyde isonicotinoyl-hydrazone monohydrate.

1. Introduction

Tuberculosis (TB) has reemerged and infecting three million deaths annually [1], due to the advent of multi drug resistant strains and the association of the tuberculosis with human immunodeficiency virus infection in AIDS [2]. Therefore, the search for new drugs for tuberculosis is of the utmost importance. Treatment regimens for tuberculosis are based on long-term basis with combined chemotherapy [3]. Isoniazid (isonicotinoylhydrazine), a bactericidal drug that acts both intracellular in the macrophages and extracellular in the necrotic tissue, is main drug used in combination with other drugs for the treatment of tuberculosis [4]. The calculation of NMR parameters is a recent, but extremely rapidly progressing area of quantum chemistry [5]. During the past decade, numerous ab initio methods have been developed, implemented, and tested, and several theoretical overviews [6–8] and routinely applicable implementations of methods are currently available [9–11]. Recently, the ab initio and density functional theory (DFT) have become a powerful tool in the investigation of chemical shift and molecular structure [14,15].

The aim of the present work is to describe and characterize the molecular structure, experimental and theoretical vibration properties and chemical shifts on 4-cyanobenzaldehyde isonicotinoyl-hydrazone monohydrate crystalline-structure. A number of papers have recently been appeared in the literature concerning the calculation of NMR chemical shift (c.s.) by quantum-chemistry methods [16–22]. These papers indicate that geometry optimization is a crucial factor in an accurate determination of computed NMR chemical shift. Moreover, it is known that the DFT (B3LYP) method adequately takes into account electron correlation contributions, which are especially important in systems containing extensive electron conjugation and/or electron lone pairs. However, considering that, as molecular size increases, computing-time also increases. It was proposed that the single-point calculation of magnetic shielding by DFT methods was combined with a fast and reliable geometry-optimization procedure at the molecular mechanics level [18].

Several methods used with ab initio calculations are now available for calculating nuclear shielding. The gauge-including atomic orbital (GIAO) [9–11], individual gauges for atoms in molecules (IGAIM) [13], and continuous set of gauge transformations (CSGT) [12] methods are three of the most common approaches for calculating nuclear magnetic shielding tensors. The GIAO has been shown to provide results that are often more accurate than those calculated with other approaches, at the same basis set size [25]. In most cases, in order to take into account correlation effects, post-Hartree–Fock calculations of organic molecules have been performed using: (i) Møller–Plesset perturbation methods, which are highly time consuming and hence applicable only to small

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molecular systems, and (ii) density functional theory (DFT) methods, which usually provide significant results at a relatively low computational cost [26]. In this regard, DFT methods have been preferred in the study of large organic molecules [27], metal complexes [28] and organometallic compounds [29] and for GIAO ^{13}C c.s. calculations [25] in which cases the electron correlation contributions were not negligible.

In the previous work, the crystal structure of the title compound was studied experimentally [26]. To best of our knowledge, no theoretical results exist for the title compound. In this study, the IR (KBr pellets), ^{1}H and ^{13}C (in the DMSO solvent) of the title compound are analyzed. Besides, the geometrical parameters, and GIAO [9–11], CSGT [12], IGAIM [16] ^{1}H and ^{13}C chemical shifts of the title compound have been calculated in the ground state by using the HF and DFT (B3LYP) method with 6-31++G(d,p) basis set. A comparison of the experimental and theoretical spectra can be very useful in making correct assignments and understanding the basic chemical shift-molecular structure relationship. And so, these calculations are valuable for providing an insight into molecular analysis.

2. Computational details and experimental procedure

The molecular structures of 4-cyanobenzaldehyde isonicotinoyl-hydrazone monohydrate in the ground state (in vacuum) are optimized HF and B3LYP with 6-31++G(d,p) basis set. Then vibrational frequencies for optimized molecular structures were calculated. The vibrational frequencies for these species were scaled by 0.8929 and 0.9613 respectively. The geometry of the title compounds, together with that of tetramethylsilane (TMS), was fully optimized. ^{1}H and ^{13}C NMR chemical shifts were calculated within GIAO, CSGT and IGAIM approach [23,24] applying B3LYP and HF methods [27] with 6-31++G(d,p) [28] basis set. The theoretical chemical shift values of ^{1}H and ^{13}C were obtained by subtracting the GIAO, CSGT and IGAIM isotropic magnetic shielding (IMS)

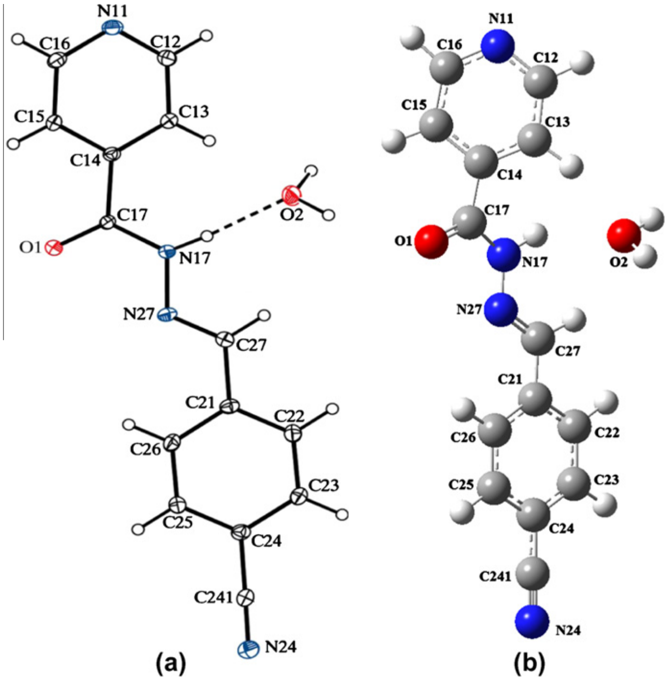

Fig. 1. (a) The experimental geometric structure of the title compound ($C_{15}H_{12}N_4O{\cdot}H_2O$) [26], (b) the theoretical (with B3LYP) geometric structure of the title compound ($C_{15}H_{12}N_4O{\cdot}H_2O$).

Table 1
Optimized and experimental geometries of the ground state of the title compound.

Parameter	Experimental [26]	Calculated [6-31++G(d,p)]	
		HF	B3LYP
Bond lengths (Å)			
C16—C15	1.383(3)	1.385	1.394
C16—N11	1.344(3)	1.323	1.341
C16—H	0.950	1.076	1.088
C15—C14	1.392(3)	1.387	1.400
C15—H	0.950	1.073	1.084
C14—C13	1.386(4)	1.387	1.401
C14—C17	1.505(3)	1.507	1.511
C13—C12	1.387(3)	1.387	1.398
C13—H	0.950	1.074	1.085
C12—N11	1.336(3)	1.320	1.338
C12—H	0.950	1.076	1.088
C17—O1	1.224(3)	1.194	1.221
C17—N17	1.356(3)	1.364	1.386
N17—N27	1.383(3)	1.354	1.357
N17—H	0.900	1.000	1.019
N27—C27	1.279(3)	1.256	1.287
C27—C21	1.473(4)	1.477	1.465
C27—H	0.950	1.083	1.096
C26—C25	1.372(4)	1.379	1.388
C26—C21	1.399(4)	1.396	1.409
C26—H	0.950	1.073	1.085
C25—C24	1.398(3)	1.395	1.410
C25—H	0.950	1.074	1.085
C24—C23	1.397(3)	1.388	1.405
C24—C241	1.445(4)	1.445	1.434
C23—C22	1.386(4)	1.386	1.392
C23—H	0.950	1.074	1.085
C22—C21	1.393(4)	1.390	1.406
C22—H	0.950	1.076	1.087
O2 H2A	0.950	0.944	0.967
Bond angles (°)			
C15—C16—N11	123.5(2)	123.5	123.7
C15—C16—H	118.2	120.2	120.2
N11—C16—H	118.2	116.3	116.1
C16—C15—C14	118.7(2)	118.5	119.1
C16—C15—H	120.7	121.1	121.5
C14—C15—H	120.7	120.4	119.4
C15—C14—C13	118.3(2)	118.2	117.6
C15—C14—C17	117.9(2)	118.2	116.8
C13—C14—C17	123.7(2)	123.5	125.6
C14—C13—C12	118.8(2)	118.4	118.7
C14—C13—H	120.6	121.8	122.6
C12—C13—H	120.6	119.7	118.7
C13—C12—N11	123.6(2)	123.6	124.0
C13—C12—H	118.2	120.1	120.0
N11—C12—H	118.2	116.3	116.1
C16—N11—C12	117.0(2)	117.8	116.9
C14—C17—O1	121.1(2)	121.1	121.3
C14—C17—N17	114.6(2)	114.5	115.9
O1—C17—N17	124.3(2)	124.4	122.8
C17—N17—N27	118.5(2)	119.3	119.3
C17—N17—H	128.6	120.6	121.7
N27—N17—H	112.3	119.2	119.0
N17—N27—C27	115.5(2)	119.2	117.6
N27—C27—C21	119.0(2)	120.8	120.7
N27—C27—H	120.5	122.1	121.9
C21—C27—H	120.5	117.1	117.5
C25—C26—C21	120.3(2)	120.2	120.5
C25—C26—H	119.8	120.5	120.6
C21—C26—H	119.8	119.4	118.9
C26—C25—C24	120.2(2	120.0	120.2
C26—C25—H	119.9	120.3	120.3
C24—C25—H	119.9	119.7	119.5
C25—C24—C23	119.9(2)	120.2	119.7
C25—C24—C241	119.2(2)	119.8	120.2
C23—C24—C241	121.0(2)	119.9	120.1
C24—C23—H	120.2	120.0	119.7
C22—C23—H	120.2	120.5	120.5
C23—C22—C21	120.3(2)	120.7	120.9
C23—C22—H	119.8	119.3	119.4
C21—C22—H	119.8	120.0	119.6
C27—C21—C26	121.5(2)	121.6	121.8

Table 1 (*continued*)

Parameter	Experimental [26]	Calculated [6-31++G(d,p)]	
		HF	B3LYP
C27—C21—C22	119.0(2)	119.0	119.2
C26—C21—C22	119.6(2)	119.4	119.0
C15—C16—N11	123.5(2)	123.5	123.7
Torsion angles (°)			
N11—C16—C15—C14	1.8(4)	−1.0	−0.2
C15—C16—N11—C12	0.2(4)	−0.1	−0.1
C16—C15—C14—C13	−2.2(4)	1.3	0.4
C16—C15—C14—C17	179.6(2)	179.4	179.8
C15—C14—C13—C12	0.9(4)	−0.2	−0.3
C17—C14—C13—C12	179.0(2)	177.9	−179.6
C15—C14—C17—O1	25.7(4)	−31.9	−7.7
C15—C14—C17—N17	−153.1(2)	−0.2	171.9
C13—C14—C17—O1	−152.4(3)	146.1	171.6
C13—C14—C17—N17	28.8(3)	−34.3	−8.8
C14—C13—C12—N11	1.1(4)	−0.7	−0.1
C13—C12—N11—C16	−1.6(4)	1.0	0.2
C14—C17—N17—N27	176.7(2)	178.7	179.3
O1—C17—N17—N27	−2.1(4)	−1.7	−1.1
C17—N17—N27—C27	179.0(2)	173.1	178.5
N17—N27—C27—C21	179.9(2)	179.4	180.0
N27—C27—C21—C26	−11.6(4)	0.2	0.0
H—C27—C21—C22	168.0(3)	0.4	0.0
C21—C26—C25—C24	1.0(4)	0.0	0.0
C25—C26—C21—C27	176.8(3)	180.0	179.9
C25—C26—C21—C22	−2.8(4)	0.0	0.0
C26—C25—C24—C23	1.7(4)	0.0	0.0
C26—C25—C24—C241	−179.5(3)	180.0	180.0
C25—C24—C23—C22	−2.5(4)	0.0	0.0
N11—C16—C15—C14	1.8(4)	−1.0	−0.2
C15—C16—N11—C12	0.2(4)	−0.1	−0.1
C16—C15—C14—C13	−2.2(4)	1.3	0.4
C16—C15—C14—C17	179.6(2)	179.4	179.8
C15—C14—C13—C12	0.9(4)	−0.2	−0.3
C17—C14—C13—C12	179.0(2)	177.9	−179.6
C15—C14—C17—O1	25.7(4)	−31.9	−7.7
C15—C14—C17—N17	−153.1(2)	−0.2	171.9
C13—C14—C17—O1	−152.4(3)	146.1	171.6
C13—C14—C17—N17	28.8(3)	−34.3	−8.8
C14—C13—C12—N11	1.1(4)	−0.7	−0.1
C13—C12—N11—C16	−1.6(4)	1.0	0.2
C14—C17—N17—N27	176.7(2)	178.7	179.3
O1—C17—N17—N27	−2.1(4)	−1.7	−1.1
C17—N17—N27—C27	179.0(2)	173.1	178.5

values [29,30]. For instance, the average ^{13}C IMS of TMS were taken into account for the calculation of ^{13}C c.s. of any X carbon atom, and so c.s. can be calculated using the following equation: $CS_x = IMS_{TMS} - IMS_x$. All the calculations were performed by using Gauss-View molecular visualization program [31] and Gaussian 03W program package on personal computer [32].

4-Cyanobenzaldehyde isonicotinoyl-hydrazone monohydrate was obtained experimentally by the procedure [26] as follows. Isonicotinoylhydrazine (10 mmol) and 4-cyanobenzaldehyde (10 mmol) in tetrahydrofuran (20 ml) was heated under reflux for 4 h. The solution was cooled and the solvent was removed under reduced pressure; the residue was washed successively with cold ethanol and recrystallized from ethanol [26]. NMR (DMSO-d_6):3.406(2H, s, H_2O), 7.832 (2H, d, $J = 5.5$ Hz, H13 and H15), 7.928 (4H, m, H22, H23, H25 and H26), 8.512 (1H, s, H27), 8.800 (2H, d, $J = 5.5$ Hz, H12 and H16), 12.31 (1H, s, NH); δ(C) 162.39, 150.80, 147.53, 140.5, 138.90, 133.25, 128.29, 122.03, 119.06, 112.67. IR (KBr pellets, cm^{-1}):3481.27 (OH), 3165.12 (NH), 2223.77 (C≡N), 1666.38 (C=O), 1299.93 (C—N). The FTIR spectra were recorded using Shimadzu 8201 spectrometer with KBr technique, in the region 4000–400 cm^{-1} that was calibrated by polystyrene. The ^{1}H and ^{13}C NMR spectra were obtained on Varian ^{UNITY} INOVA 500 MHz NMR Spectrometer at 500 and 125 MHz, respectively, using DMSO(d_6) as solvent and TMS as internal standard.

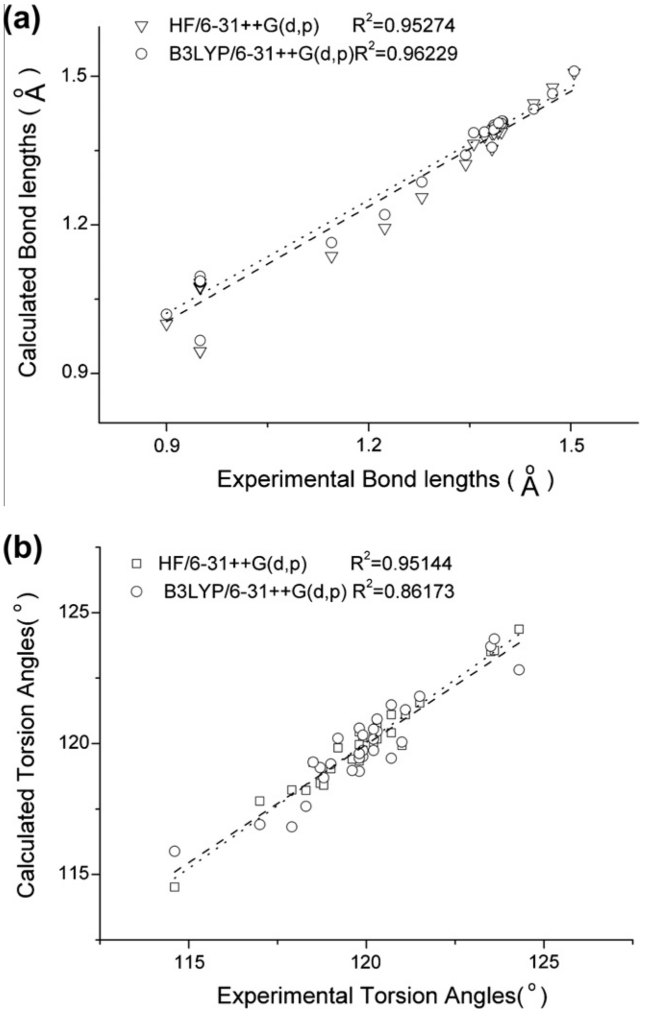

Fig. 2. (a) Correlation graphs of calculated and experimental molecular bond lengths of the title compound. (b) Correlation graphs of calculated and experimental molecular bond angles of the title compound.

3. Results and discussion

3.1. Geometrical structure

Molecular structure of 4-cyanobenzaldehyde isonicotinoyl-hydrazone monohydrate was determined by Wardell et al. [26]. The geometric structure of the title compound is shown in Fig. 1a and b. The optimized parameters (bond lengths and angles, and dihedral angles) of the title compound have been obtained at the HF and B3LYP methods with the basis set. These results are listed in Table 1 and compared with the experimental data of the title compound. Geometrical parameter of the title molecule indicates that hydrazone part between C14 and C21 is effectively planar and atoms are in trans-positions. Rings of the molecule are twisted away from the hydrazone plane [26]. Geometric properties of substituted-benzaldehyde isonicotinoyl-hydrazone are similar to that of 4-cyanobenzaldehyde isonicotinoyl-hydrazone monohydrate [33–35]. In the present subject parameters of 4-cyanobenzaldehyde isonicotinoyl-hydrazone monohydrate bonds (lengths and angles) optimized by HF, B3LYP methods with 6-31++G(d,p) as the basis set are listed in Table 1. Calculated data are compared with experimental crystal structure data of the title compound. Correlation indicates that, both calculation with HF and B3LYP give agreement with experimental values (Fig. 2).

Table 2
Comparison of the observed and calculated vibrational spectra of the title compound ($C_{15}H_{12}N_4O{\cdot}H_2O$).

Assignments	FT-IR (cm^{-1}) KBr	Scaled frequencies (6-31++G(d,p)) (cm^{-1}) and Rel. intensity (km/mol)			
		HF	Rel. intensity	B3LYP	Rel. intensity
ν(H—O—H) str.	3481	3947	0.08003806	3914	0.176925074
ν(H—O—H) str.	3323	3834	0.033205229	3800	0.049635638
ν(N17—H) str.	3165	3493	0.0908663	3491	0.200009532
ν(rings C—H) str.	–	3300	0.002373689	3229	0.008969576
ν(rings C—H) str.	–	3296	0.000747571	3225	0.003179972
ν(rings C—H) str.	–	3283	0.006645109	3215	0.009969053
ν(rings C—H) str.	–	3280	0.00383211	3209	0.003936204
ν(rings C—H) str.	–	3274	0.001435834	3209	0.000547794
ν(rings C—H) str.	3076	3259	0.014354219	3184	0.018837179
ν(rings C—H) str.	–	3250	0.007959626	3180	0.03917278
ν(rings C—H) str.	3051	3250	0.014318989	3169	0.051881196
ν(rings C—H) str.	3000	3177	0.012679233	3078	0.042664025
ν(C241—N24) asym. str.	2224	2388	0.068930679	2330	0.163734323
ν(C17—O1) str.	1666	1758	0.272159945	1761	0.55313509
ν(N27—C27) str.	–	1702	0.011754873	1676	0.016518449
ν(N27—C27 + Ph ring C—C) str.	1604	1610	0.005556389	1650	0.047259163
ν(Pyr. ring C—C) str.	1577	1606	0.007618549	1640	0.009399703
ν(Ph ring C—C) str. + β(N17—H + H—O—H) bend.	1552	1652	0.0778391	1594	0.083315057
β(N17—H) bend.	1504	1639	0.209221839	1581	0.737347995
β(Ph ring C—H) bend.	1552	1577	0.026732577	1561	0.077833561
β(Pyr. ring C—H) bend.	–	1568	0.002460841	1528	0.049354029
ν(rings C—C)str. + β(rings C—H) bend.	–	1460	0.010952823	1447	0.003619591
ν(rings C—C)str. + β(rings C—H) bend.	–	1458	0.014130693	1445	0.037442781
β(C27—H) bend.	1409	1421	0.036621612	1420	0.066368063
ρ(Pyr. ring C—H)rock	1358	1368	0.001762279	1362	0.013107297
ρ(Ph ring C—H)rock	1300	1348	0.002909597	1339	0.003919196
ν(Pyr. ring C—C) sym. str.	1280	–	–	1300	0.0514837
ν(C14—C17—N17) asym. str.	–	1308	1	1276	1
β(Pyr. ring C—H) bend.	–	1241	0.000984308	1250	0.050976843
β(Pyr. ring C—H) bend.	1174	1224	0.014997947	1200	0.001837778
ν(N17—N27) str.	1151	1215	0.093162995	1172	0.484820876
β(Ph ring C—H) bend.	–	1201	0.003898593	1139	0.040266983
β(Pyr. ring C—H) bend.	–	1175	0.047544745	1122	0.026276888
ν(Pyr. ring C—C + N17—N27) str.	1072	1090	0.005891926	1100	0.042434031
ν(Pyr. ring C—C + C17—N17) str.	1059	1074	0.003917699	1085	0.024992836
β(Ph ring C—C) bend.	–	1060	0.000304924	1032	0.006430939
β(Ph ring C—C) bend. + τ(Ph ring C—H)	1010	–	0	1012	0.003486499
τ(H—C16—C15—H)	1005	–	0	1010	0.001934285
τ(H—C26—C25—H)	–	1024	0.000628812	1004	0.001872188
τ(H—C22—C23—H + C27—H)	962	–	0	966	0.019260384
β(N17—N27—C27) bend.	921	–	0	934	0.036040864
ω(Pyr. ring C—H) wag.	881	–	0	903	0.001193676
ω(H—C26—C25—H) wag.	–	960	0.014080263	865	0.001207321
ν(Ph ring C—C) str. + ω(Pyr. ring C—H) wag.	852	890	0	857	0.029340973
ω(H—C22—C23—H) wag.	835	874	0.02217392	846	0.040897045
ω(Pyr. ring C—C and C—H) wag.	795	807	0.016281781	805	0.017821882
ν(Ph ring C—C and C24—C241) str.	754	758	0.001667386	757	0.004573187
τ(Ph ring C—C)	–	750	0.000148023	735	0.000646476
ω(Pyr. ring H—C16—N11—C12—H) wag.	702	737	0.011549105	717	0.009216182
β(Pyr. ring C and N) bend.	690	695	0.04248882	692	0.102346435
β(Pyr. ring C—C) bend.	–	688	0.001745161	682	0.002854064
β(Ph ring C—C) bend.	663	673	0.001696507	677	0.003737455
τ(N17—H)	–	627	0.086239243	642	0.195084729
ω(Ph ring C—H) wag.	–	577	0.004159905	572	0.040306733
β(C24—C241—N24) bend.	557	561	0.002894042	564	0.000642323
ω(rings C—H) wag.	503	505	0.002570153	509	0.000217535
ω(rings C—H) wag.	480	486	0.001592025	496	0.004320648
β(N17—N27—C27) bend.	453	459	0.000198382	475	0.001194467
τ(Ph ring C—C)	422	451	5.69646E−05	434	0.000260251
τ(Pyr. ring C—C)	–	388	–	397	–

3.2. Assignments of the vibration modes

Based on optimized geometries, the calculation of vibrational frequencies were performed by the same methods and basis set as. These calculations of the title compound were compared to the experimental results. The bands calculated in the measured region 4000–400 cm^{-1} arise from the vibrations of O—H stretching, N–H symmetric stretching, rings C—H stretching, C≡N stretching, C═O stretching and the internal vibrations, etc. of the title compound. Experimentally observed infrared spectrum of title compound by using KBr pellets, are found; 3481.27 cm^{-1} (OH), 3165.12 cm^{-1} (NH), 2223.77 cm^{-1} (C≡N), 1666.38 cm^{-1} (C═O), 1299.93 cm^{-1} (C—N). The vibrational bands assignments have been made by using Gauss-View molecular visualization program [32]. Theoretical and experimental results of the title compound are shown in Table 2. Infrared spectrum of title compound indicates that N—H stretching, 3493 cm^{-1} (HF), 3491 cm^{-1} (B3LYP), C≡N stretching 2388 cm^{-1} (HF), 2330 cm^{-1} (B3LYP), C═O stretching

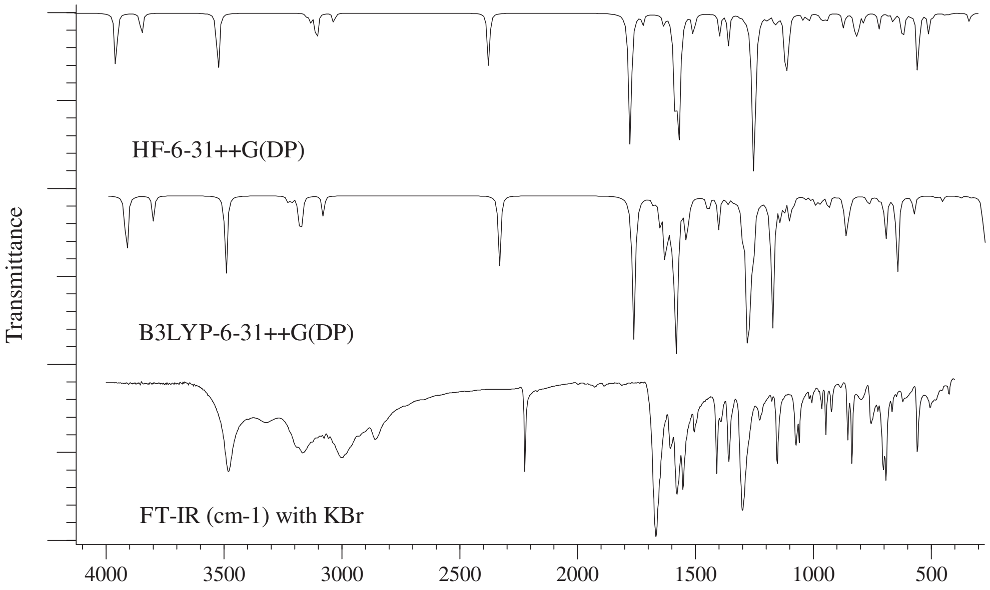

Fig. 3. FT-IR spectrum and simulated (HF, B3LYP) IR spectra of the title compound ($C_{15}H_{12}N_4O{\cdot}H_2O$).

Table 3
Theoretical and experimental ^{13}C and ^{1}H isotropic chemical shifts (with respect to TMS all values in ppm) for the title compound ($C_{15}H_{12}N_4{\cdot}H_2O$).

Atom	NMR(DMSO-d_6)		HF/6-31++G(d,p)			B3LYP/6-31++G(d,p)		
			GIAO	IGAIM	CSGT	GIAO	IGAIM	CSGT
H(N17)	12.315	12.31[a]	11.83	9.97	11.71	11.12	9.25	10.99
H(C16)	8.800	8.80[a]	10.04	9.59	10.11	9.32	8.87	9.40
H(C12)	8.800	8.80[a]	9.76	9.41	9.92	9.05	8.70	9.91
H(C27)	8.512	8.52[a]	9.39	9.03	9.74	8.67	8.31	9.03
H(C22)	7.928	7.94[a]	8.20	8.30	8.59	7.45	7.58	7.87
H(C26)	7.928	7.94[a]	9.79	9.71	9.98	9.08	9.00	9.27
H(C25)	7.928	7.94[a]	8.82	8.70	8.98	8.11	7.98	8.26
H(C23)	7.928	7.94[a]	8.70	8.57	8.86	7.99	7.85	8.14
H(C15)	7.832	7.83[a]	9.53	8.80	9.34	8.82	8.08	8.63
H(C13)	7.832	7.83[a]	8.97	8.17	9.07	8.26	7.45	8.35
H(O29)	3.406	–	2.92	2.71	3.60	2.20	1.99	2.87
H(O30)	3.406	–	2.92	2.63	3.58	2.21	1.91	2.88
C17	162.39	161.9[a]	162.2	161.97	164.81	144.66	144.50	147.26
C12	150.80	150.4[a]	154.4	150.44	156.10	136.83	132.93	138.54
C16	150.80	150.4[a]	156.1	152.51	158.21	138.54	135.05	140.71
C27	147.53	146.0[a]	144.16	142.06	148.63	126.64	126.50	131.11
C14	140.65	140.2[a]	143.74	145.89	146.13	126.22	128.41	128.62
C21	138.90	138.4[a]	144.90	140.79	146.41	127.36	123.27	128.88
C25	133.25	132.8[a]	137.61	134.58	139.96	120.12	117.00	122.41
C23	133.25	132.8[a]	136.43	133.72	139.03	118.92	116.24	121.52
C26	128.29	127.8[a]	130.53	126.59	132.53	113.04	109.08	115.00
C22	128.29	127.8[a]	132.45	128.72	135.51	114.95	111.17	117.98
C15	122.03	121.5[a]	128.3	123.63	130.81	110.81	106.06	113.27
C13	122.03	121.5[a]	121.97	118.75	123.61	104.47	101.21	106.15
C32	119.06	118.6[a]	120.29	116.80	125.38	102.77	99.33	107.88
C24	112.67	112.2[a]	119.08	115.34	121.18	101.38	97.80	103.67

[a] Taken from literature Ref. [26].

1758 cm^{-1} (HF), 1761 cm^{-1} (B3LYP) can be assigned clearly. Calculated infrared intensity (Rel. intensity) allows determination of the strength of the transition. Note that experimental IR spectra are generally reported in either percent transmission or absorbance unit. Apparently, these mentioned data can be seen in Fig. 3. In Hartree–Fock, all the vibrational frequencies are overestimated and they are in agreement within 10–20% error for the average of overall frequencies [36,37]. This overestimation depends on type of the vibrational mode and the wave number range. In general, the DFT methods have relatively close wave numbers to experimental values. According to the different molecular structures with many electrons, this statement can be changed. In our results, as it can be seen in Fig. 3 and Table 2, the simulated infrared spectra are, in general, closer to the experimental IR spectrum.

3.3. Assignments of the chemical shift values

DFT and HF methods differ in that no electron correlation effects are taken into account in HF. DFT methods treat the electronic energy as a function of the electron density of all electrons simultaneously and thus include electron correlation effect. Particular consideration was given for the investigation of the influence of the level that is used in the geometry optimization on the final value of the title compound when GIAO, CSGT and IGAIM ^{13}C and ^{1}H c.s. calculations were performed. One of the GIAO, CSGT or IGAIM ^{13}C and ^{1}H c.s. calculations is sufficient for comparison. But the others support the result. Thus, GIAO, CSGT and IGAIM ^{13}C and ^{1}H c.s. calculations have been carried out using the B3LYP method with 6-31++G(d,p) basis set for the optimized geometry. The results of these calculations and the experimental ^{13}C and ^{1}H chemical shift values are tabulated in Table 3. The theoretical ^{13}C and ^{1}H chemical shift values (with respect to TMS) of the title compound are generally compared to the experimental ^{13}C and ^{1}H chemical shift values. The ^{1}H chemical shift values (with respect to TMS) have been calculated to be 11.83–2.63 ppm with HF level and 11.12–1.91 ppm with B3LYP level. These variations are observed experimentally between 12.31 and 3.41 ppm. These values are depicted in Table 3, and so the accuracy ensures reliable interpretation of spectroscopic parameters. In the title compound nitrogen atom which shows electronegative property, and so N17—H atom contribute to the downfield resonance and has chemical shifts 12.31 ppm. Besides, chemical shifts for rings-H 8.800–7.832 ppm and H—O—H 3.406 ppm. These chemical shifts have been obtained to be 11.83 ppm (N17—H), 8.17–11.83 ppm (rings-H) 2.63 ppm (H—O—H) for HF calculations and 11.12 ppm (N17—H), 9.40–7.45 ppm (rings-H) 2.88 ppm (H—O—H) for B3LYP calculations. Furthermore, the ^{13}C chemical shift values (with respect to TMS) are observed to be 162.39–112.67 ppm range and found to be 164.81–119.08 ppm range by HF level and 147.26–97.80 ppm range. As can be seen from Table 3, theoretical ^{1}H and ^{13}C chemical shift results of the title compound are generally closer to the experimental chemical shift data.

The correlation between the experimental and calculated chemical shifts obtained by the HF and B3LYP methods is shown in

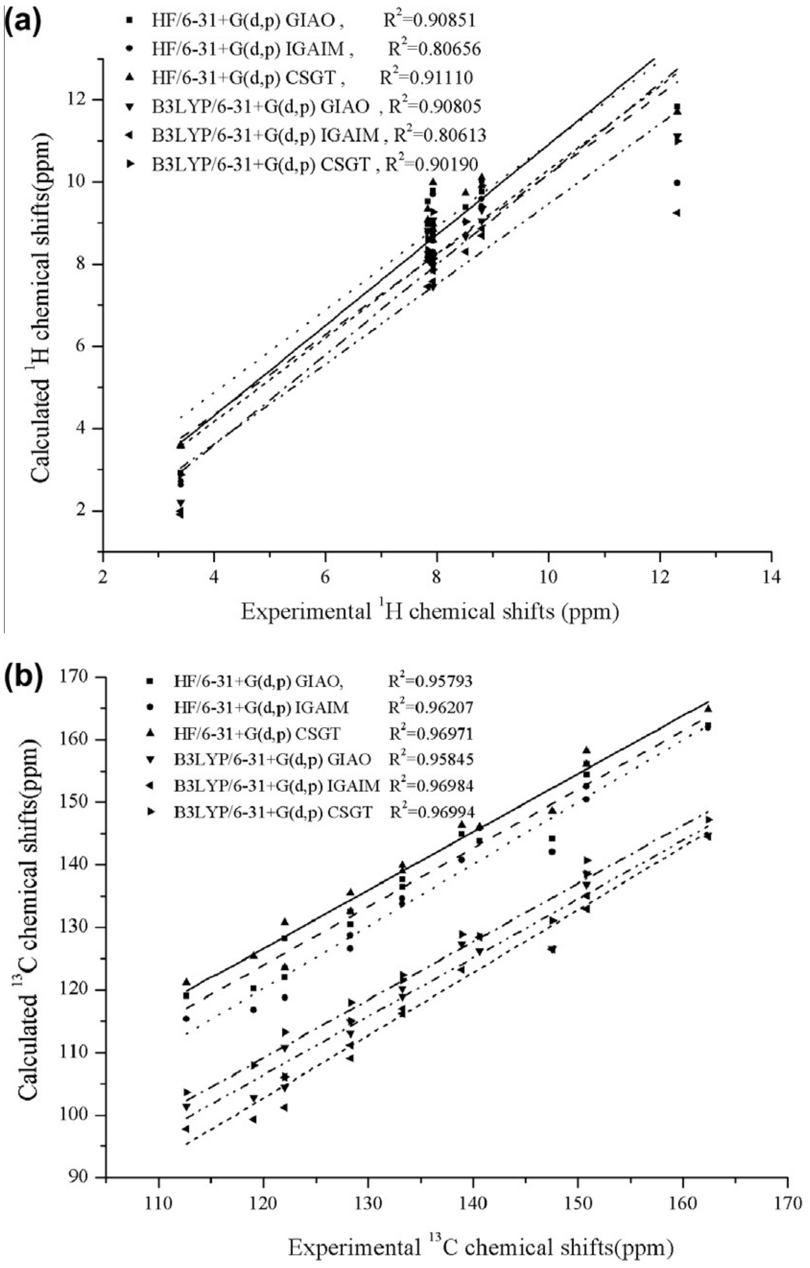

Fig. 4. (a) Correlation graphics of calculated and experimental ^{1}H chemical shift values of the title compound ($C_{15}H_{12}N_4O{\cdot}H_2O$). (b) Correlation graphics of calculated and experimental ^{13}C chemical shift values of the title compound ($C_{15}H_{12}N_4O{\cdot}H_2O$).

Fig. 4. Owing to our calculations, B3LYP method correlated for chemical shifts are much closer to experimental data (Table 3, Fig. 4).

4. Conclusions

In this study, the results of experimental and the HF and DFT level of theory with 6-31++G(d,p) basis set are reported. Computed and experimental geometric parameters, vibrational frequencies, and chemical shifts of the title compound have been compared with each other. It has noted that experimental results belong to the solid phase in the atmospheric conditions. Compared experimental, theoretical calculations belong to the gaseous phase in the vacuum. Therefore experimental and theoretical result has slightly different values.

To fit the theoretical frequency results with experimental ones for HF and B3LYP levels, the data have been multiplied. Results with multiplied factors seemed to be in good agreement with experimental ones. The B3LYP levels, which have electron correlation component, shown better fit to the experimental ones than those of HF levels in terms of evaluate bond angles, vibrational frequencies, and chemical shifts. Comparison of the experimental and theoretical results can be very useful for understanding molecular structure analysis.

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