Indian J Phys (May 2014) 88(5):439–448
DOI 10.1007/s12648-013-0439-5

ORIGINAL PAPER

Theoretical investigation of phenazine derivatives by using ab initio calculations

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Received: 21 October 2013 / Accepted: 13 December 2013 / Published online: 5 January 2014

Abstract: Objective of present study is to compute molecular structures, vibrational frequencies and chemical shifts of phenazine derivatives using density functional theory and Hartree–Fock methods and to compare these results with experimental data. Intramolecular *N*–H···*N* interactions have been investigated for stabilization of the molecular conformations. Comparisons of theoretical and experimental data exhibit good correlation confirming the reliability of methods employed in this work. Moreover, frontier orbitals and molecular electrostatic potential have been visualized and calculations of the energy band gaps have been interpreted. According to the results of these investigations, we can say that DFT calculations are significantly stable in electronic structures, spectral, frontier orbitals and electrostatic potential analysis for both the phenazine derivatives.

Keywords: Phenazine derivatives; Density functional theory; Hartree–Fock; IR spectra; HOMO–LUMO gap

PACS Nos.: 31.15.E−; 07.57.−c; 07.10.−h

1. Introduction

Phenazine is a dibenzo annulated pyrazine and parent substance of many dyestuffs, such as eurhodines, toluylene red and it is also called azophenylene, dibenzopyrazine and acridizine. Many phenazine compounds are found in nature and are produced by bacteria. Natural phenazine products have been implicated in virulence and competitive fitness of the producing organisms [1, 2]. Phenazine derivatives constitute basis of some antitumor agents, bactericides, fungicides [3–8]. These compounds, a nitrogen-containing heterocyclic redox agent are also a group of antibiotic agents. Many phenazine derivatives have been identified and described and these compounds can be produced in ways, namely biosynthesis and chemosynthesis [9]. Biosynthesis of phenazine is regulated by nutrient depletion, high cell density and conversion of the bacterium to the biofilm form [10–13]. Chemical synthesis has also been used to prepare various synthetic phenazines [14]. Besides, phenazine derivatives have been also chosen to reduce the use of chemical pesticides in agriculture [15]. Biopesticides, phenazine compounds, can be used either alone or in combination with pesticides to lower the doses of chemicals needed to obtain a profitable crop yield.

Conformationally flexible molecules can have interesting applications in non-linear optics and molecular motors. For example, effects of dipole orientations on nonlinear optical properties of oxo-bridged dinitroaniline systems have been investigated by some researchers [16]. They have found that the best conformation is where the nitroaniline dipoles are arranged parallel to each other in the same plane. In another study, Nijamudheen et al. [17] have studied role of supramolecular interactions by a supramolecular rotor designed based on a phosphonate cavitand. In our study, molecular structures and chemical shifts of *N*-methyl-2-(10-methylphenazin-5(10H)-yl)aniline (*phenazine1*) and *N*-butyl-2-(10-methylphenazin-5(10H)-yl)aniline (*phenazine2*), have been calculated at DFT and HF methods with 6-31 G(*d*) basis sets. Geometrical parameters have been compared with X-ray analysis results of

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hydrochloride salts of the isomeric structure *phenazine1* and vibrational frequencies for *phenazine2* compound are in agreement with experimental results [18]. Furthermore, frontier orbitals and molecular electrostatic potential are visualized and energy band gaps are interpreted for the title compounds. Similar studies on various compounds have been experimentally and reported by density functional theory approach in the recent past [19, 20].

2. Methods of calculations

All computations were performed by using Gaussian 09 package program with molecular visualization program [21, 22] on the personal computer in the framework of Hartree–Fock and density functional theory methods at 6-31 G(*d*) basis set. Cartesian representation of theoretical force constants was computed at optimized geometry under C_1 point group. Transformation of the force field and subsequent normal coordinate analysis including the least square refinement of scaling factors, calculations of potential energy distribution (PED) and prediction of IR intensities were analyzed by Vibrational Energy Distribution Analysis (VEDA-4) program [23]. Chemical shifts of ^{1}H and ^{13}C NMR in $CHCl_3$ (chloroform solvent)-polarizable continuum (PCM) model were calculated by GIAO method [24] using the same set levels of the theory, routinely used for NMR chemical shift calculations on fairly large molecules [25, 26]. In chemical shift calculations tetramethylsilane (TMS) was used as reference molecule. So, the theoretical values of chemical shift of ^{1}H and ^{13}C were obtained by subtracting the GIAO isotropic magnetic shielding (IMS) values [27, 28].

3. Results and discussion

3.1. Conformer analysis and optimized structures

In order to investigate all possible conformers of phenazine1 compounds, a detailed potential energy surface (PES) scan in τ_1(C5–N2–C14–C15) and τ_2(C14–C15–N3–C20) dihedral angles have been performed by changing the dihedral angles every 20° for 360° rotation, a total of 88 steps, around the bond (simultaneously for both dihedral angles). The change in potential energy values as a function of the dihedral angle is shown in Fig. 1. Minimal energy structure (relative energy value of 0 kcal/mol) has been optimized at B3LYP/6-31 G(*d*) and HF/6-31 G(*d*) level of calculations, respectively. After the optimizations, total energies are obtained as lower values, −937.82 and −1,055.77 a.u, at Restricted-

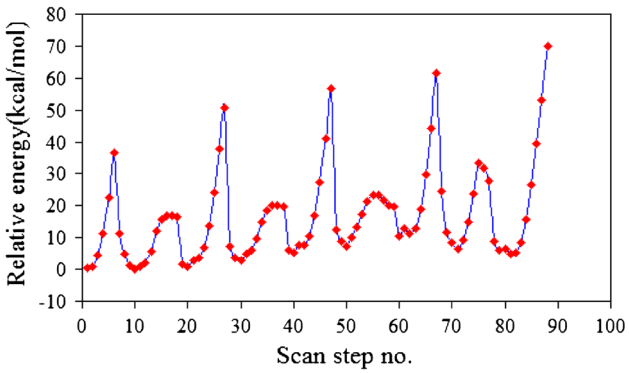

Fig. 1 Potential energy surface scan in essential dihedral angles τ_1[C5–N2–C14–C15] and τ_2[C14–C15–N3–C20] of *Phenazine1* with DFT method

B3LYP calculation method for *Phenazine1* and *Phenazine2*, respectively. Calculated and experimental optimized structure parameters for *phenazine1* are summarized in Table 1, in accordance with the atom numbers shown in Fig. 2. Since the X-ray analysis results are obtained from the hydrochloride salts of the isomeric structure *phenazine1* [18], calculated optimized structure parameters (bond lengths, bond angles and torsion angles) have been compared with those of *phenazine1* compound in Table 1. Besides, computed values for bond lengths and bond angles are compared with experimental results of phenazine crystals crystallized from acetonitrile [29]. Calculated results eventually show a good agreement with the experimental ones for *Phenazine1*. Largest differences between calculated and experimental parameters are 0.123 Å (R-HF), 0.134 Å (R-B3LYP) for bond lengths and 4.20° (R-HF), 2.90° (R-B3LYP) for bond angles and 31.1° (R-HF), 34.5° (R-B3LYP) for dihedral angles. Since the intramolecular *N*–H···*N* interaction stabilizes molecular conformation, results of calculations on intramolecular *N*–H···*N* hydrogen-bonding interactions are given in Table 2. In mononuclear unit, an intramolecular *N*–H···*N* hydrogen-bonding interaction between NH_2 group attached to the triazole ring and the non-coordinating N atom of pyridine has been observed in a previous study [30] and also Feng et al. [31] have carried out a similar study about a triazole derivative compound. Structural optimizations have been also performed with M06-2X/6-31 G(*d*) level [32, 33] at DFT method. M06-2X functional is known to be effective in incorporating long-range dispersion forces, so calculations at this level provide an estimate of such forces as well [34]. Dispersion forces are generally weaker than the forces associated with hydrogen bonding, but dispersion interactions play a major role in the stabilization of large biomolecules in which these interactions are abundant [35–37].

Table 1 Experimental values and theoretical geometric parameters for the optimized structures of *Phenazine1* at DFT and HF method

Bond length (Å)	Exp. [18]	Exp. [29]	DFT method 6-31G(*d*)	HF method 6-31G(*d*)	Bond length (Å)	Exp. [18]	Exp. [29]	DFT method 6-31G(*d*)	HF method 6-31G(*d*)
C6–C1	1.396	1.352	1.400	1.391	C12–C13	1.386	1.424	1.396	1.382
C5–C6	1.384	1.426	1.395	1.381	C13–N2	1.408	1.342	1.416	1.409
C5–C4	1.410	1.438	1.416	1.403	C12–H12	0.950		1.084	1.073
C5–N2	1.419	1.341	1.417	1.411	C7–N1	1.454		1.448	1.440
C11–C12	1.388	1.351	1.401	1.393	C7–H7(A,B,C)	0.980		1.102	1.090
C10–C11	1.386	1.416	1.387	1.374	C14–N2	1.437		1.436	1.427
C6–H6	0.950		1.084	1.072	C15–N3	1.460		1.380	1.380
C4–N1	1.387		1.409	1.404	C20–N3	1.488		1.448	1.443
C8–N1	1.397		1.407	1.402	N3–H	0.920		1.010	0.994

Bond angles (°)	Exp. [18]	Exp. [29]			Bond angles (°)	Exp. [18]	Exp. [29]		
C4–C5–N2	119.4	121.73	118.5	117.8	N2–C13–C8	119.2	121.56	118.5	117.9
C6–C5–N2	120.7	119.74	122.1	122.8	C13–N2–C5	120.25	116.72	119.3	118.3
C6–C5–C4	119.9	118.53	119.4	119.4	C12–C13–N2	121.0	119.70	122.2	122.8
C13–C12–C11	120.7	120.49	120.9	120.8	C13–N2–C14	117.37		119.7	120.4
C5–C6–C1	120.8	120.44	120.8	120.7	N1–C7–H7(A)	109.5		109.2	109.2
C2–C1–C6	119.7	120.94	119.9	119.9	H7(A)–C7–H7(B)	109.5		108.0	107.7
C10–C11–C12	119.5	120.85	119.9	119.9	N1–C4–C3	123.0		122.6	123.1
C5–C6–H6	119.6		119.1	119.6	N1–C4–C5	119.2		118.3	117.6
C9–C8–N1	122.6		122.6	123.2	N1–C8–C13	119.2		118.3	117.5
C15–C14–N2	120.5		120.2	121.0	N1–C7–H7(B)	109.5		109.2	109.2
C14–C15–N3	119.26		119.8	119.8	H7(A)–C7–H7(C)	109.5		108.4	108.5
C4–N1–C8	121.6		118.8	117.4	C16–C15–N3	119.4		122.3	122.0
C4–N1–C7	119.1		119.9	119.9	N3–C20–H20(C)	109.5		108.5	108.3

Torsion angles (Å)	Exp. [18]			Torsion angles (Å)	Exp. [18]		
C4–C5–C6–C1	1.3	0.4	0.00	N1–C8–C13–C12	−175.9	−175.6	−175.8
N2–C5–C6–C1	179.8	179.5	179.7	C9–C8–C13–N2	−177.8	−178.1	−177.7
C5–C6–C1–C2	0.9	1.2	1.4	N1–C8–C13–N2	2.4	3.7	4.1
C1–C2–C3–C4	−0.8	−1.3	−1.3	C6–C5–N2–C13	176.3	161.1	154.6
C2–C3–C4–N1	−176.1	−175.5	−175.7	N2–C14–C19–C18	178.8	179.7	179.4
C6–C5–C4–N1	175.7	176.0	176.5	N2–C14–C15–C16	−179.2	−179.3	−179.1
N2–C5–C4–N1	−2.3	−3.1	−3.3	C19–C14–C15–N3	−179.0	−178.2	−178.0
C6–C5–C4–C3	−3.8	−2.4	−2.0	N2–C14–C15–N3	2.3	2.2	2.6
N2–C5–C4–C3	178.2	178.5	178.2	C17–C16–C15–N3	179.0	177.9	177.8
N1–C8–C9–C10	176.3	175.2	175.3	C14–C15–N3–C20	−132.6	−167.1	−163.7
C13–C8–C9–C10	−3.5	−2.9	−2.8	C12–C13–N2–C5	−176.1	−161.2	−154.9
C11–C12–C13–N2	−179.8	−179.8	−179.8	C12–C13–N2–C14	−21.5	−6.3	−16.2

3.2. Vibrational analysis

In Table 3, results of selected vibrational frequencies (IR spectra) for *Phenazine2* compound are given together with experimental data obtained from [18] and calculated IR spectra of this molecule are shown in Fig. 3. For computed frequencies, scale factors of 0.8929 and 0.9614 are used for HF and B3LYP, respectively [38]. Also, calculated IR

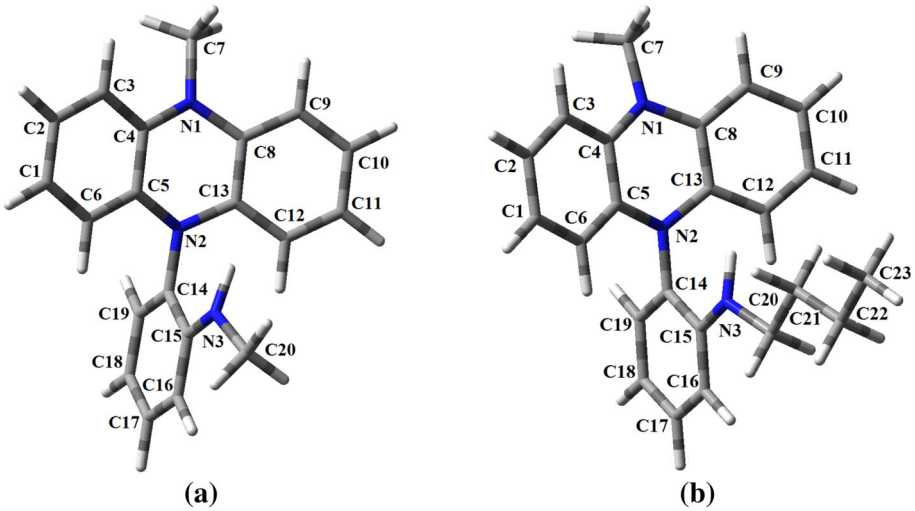

Fig. 2 The molecular structures of (**a**) *Phenazine1* and (**b**) *Phenazine2*

Table 2 Theoretical geometric parameters for intramolecular *N*–H···*N* hydrogen-bonding interaction

Parameters	Experimental[a] *Phenazine1*	Calculated					
		DFT method 6-31G(*d*) G(B3LYP)		DFT method 6-31G(*d*) (M06-2X)		HF method 6-31G(*d*)	
		Phenazine1	*Phenazine2*	*Phenazine1*	*Phenazine2*	*Phenazine1*	*Phenazine2*
N3–H (Å)	0.92	1.010	1.011	1.007	1.013	0.994	0.995
H···*N2* (Å)	2.32	2.412	2.414	2.372	2.379	2.415	2.409
N3···*N2* (Å)	2.815	2.830	2.830	2.784	2.809	2.828	2.827
∠*N3*–H···*N2* (°)	113.0	103.8	103.7	103.5	104.4	104.2	104.5

[a] Taken from Ref. [18]

spectra of *Phenazine2* at DFT and HF method have been presented in Fig. 3 for the comparison. Assignments corresponds to selected vibrational modes in tables are obtained by using VEDA 4 program. IR spectrum has shown bands including the intense C=C and C=N stretching at 1,472–1,284 cm^{-1} in a recent study by Nansathit et al. [9] about synthesis, isolation and antimicrobial activities of phenazine-1-carboxylic acid, other phenazine derivative. These stretching modes are computed at ∼1,353–1,250 and ∼1,446–1,261 cm^{-1} through DFT(B3LYP) and HF method, respectively. As shown in Fig. 3(a), 3(b) and Table 3, we note that by and large C–H stretching modes of CH_2 and CH_3 groups are determined at highest frequency range (∼3,027–2,829 cm^{-1}) with high percent of PED for both methods. Besides, aromatic C–H stretching are calculated as ∼3,081, 3,035 cm^{-1} in basic phenazine group by using DFT and HF method, respectively. Calculated results show a good agreement with the experimental ones for *Phenazine2* compound.

3.3. NMR spectral analysis

Experimental and calculated ^{1}H and ^{13}C NMR chemical shifts (with respect to TMS) for *Phenazine1* and *Phenazine2* are given in Table 4. Theoretical results are computed in $CHCl_3$ (chloroform) solvent and solvent-free by using Polarizable Continuum Model (PCM). Experimental chemical shifts of *Phenazine1* and *Phenazine2* in $CDCl_3$ (deuterated chloroform) solvent have been obtained from the literature [18]. In chemical shifts computations, more electronegative property if N atoms polarizes the electron distribution in its bond to adjacent carbon atoms and decreases electron density at bridge for our title molecules, therefore calculated chemical shifts are higher. Since mean absolute

Table 3 The experimental and selected theoretical scaled wavenumbers (in cm^{-1}) using B3LYP and HF/6-31 G(*d*) along with their relative intensities (km mol^{-1}) and potantial energy distribution (PED %) of *Phenazine2*

Assignments based on PED (≥ 10 %) (DFT/B3LYP method)	Experimental FTIR [18]	Calculated			
		B3LYP/6-31G(d)		HF/6-31G(d)	
		Scaled frequencies	IR intensity (km/mol)	Scaled frequencies	IR intensity (km/mol)
$\nu[N_3–H]$ (100)	3,415.04	3,461.88	21.19	3,446.88	25.49
$\nu[C–H]_{asym}$Phz (97)	3,061.20	3,080.63	38.75	3,034.92	57.41
$\nu[C–H]_{asym}$ (Me′ + Me″) (97)		2,990.63	53.77	3,027.20	31.20
$\nu[C–H]_{asym}$ Me′ (66) + $\nu[C–H]_{asym}$ Me″ (19)	2,956.53	2,958.95	39.80	3,016.87	48.89
$\nu[C–H]_{asym}$ Me′ (87)	2,926.24	2,922.82	44.12	2,914.28	100.67
$\nu[C_7–H]_{sym}$ Me″ (99)	2,870.50	2,879.31	83.09	2,850.17	56.84
$\nu[C–H]_{sym}$ Me′ (99)		2,856.84	53.25	2,829.29	79.09
ν[C–C] (34)	1,679.12	1,603.72	76.65	1,607.77	38.95
ν[C–C] (35) + δ[CCC] (10)	1,607.09	1,570.96	20.85	1,594.49	66.2
δ[HCC] (18) + δ[HNC] (13)	1,508.90	1,511.47	115.02	1,523.39	167.03
δ[HCC] (15)	1,483.23	1,473.87	420.91	1,482.62	482.1
$\nu[N_1–C]$ (22)	1,363.07	1,352.67	172.84	1,446.04	56.86
δ[HCC] (12) + $\nu[N_1–C]$ (11) + ν[C–C] (11)	1,337.11	1,312.56	105.91	1,349.45	261.55
ν[C–C] (19)	1,288.32	1,277.72	282.48	1,298.45	113.22
$\nu[N_2–C]$ (12) + δ[HCC] (12)	1,268.31	1,249.76	108.34	1,261.47	85.14
δ[HCC] Phz (13)		1,220.13	18.30	1,231.68	80.82
δ[HCC] (88) + $\tau[HCN_3C]$ (10)	1,160.73	1,151.50	14.51	1,182.79	75.58
$\tau[HCN_3C]$ (32) + δ[HCC] (11)	1,143.21	1,143.62	5.09	1,124.46	19.99
$\nu[N_3–C]$ (15) + δ[CCC] (Me′ + Me″) (12)	1,131.65	1,123.48	13.00	1,091.06	55.63
δ[HCC] Phz (16) + ν[C–C] Phz (12)	1,052.62	1,044.06	20.18	1,032.84	44.23
τ[HCCC] Phz (63)		867.22	5.63	930.96	0.42
τ[HCCC] (10) + τ[CCCC] (10)	737.59	722.55	15.92	838.94	10.28
δ[CCC] (48)		624.24	15.34	621.43	14.53
$\gamma[N_1CCC]$ (14) + τ[CCCC] (10)		553.18	14.10	553.85	15.79

Phz Phenazine, *Me′* Methylene, *Me″* Methyl, ν stretching, δ bending, γ out of plane bending, τ torsion modes

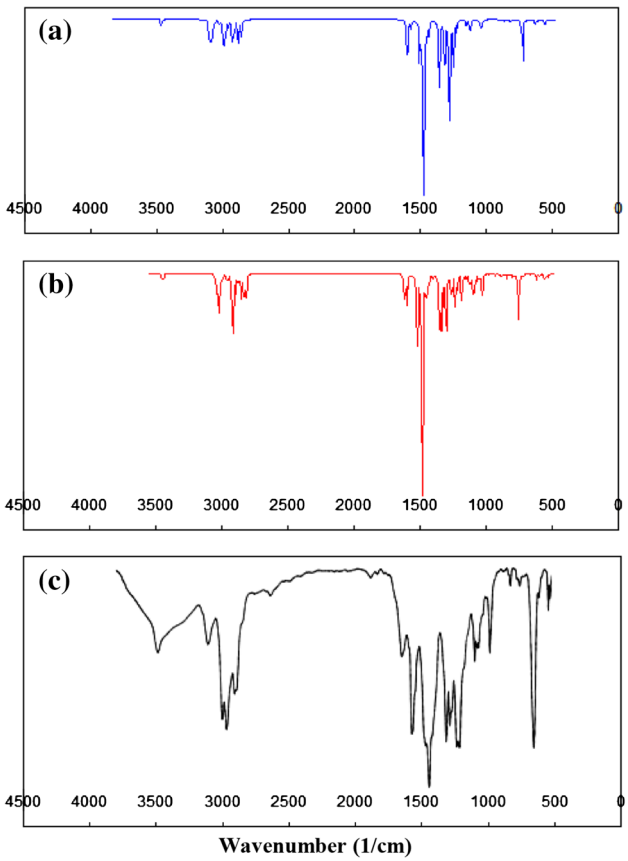

Fig. 3 Calculated IR spectra of *Phenazine2* at (**a**) DFT and (**b**) HF method respectively and (**c**) represents the experimental spectra taken from Ref. [18]

error (MAE) is a quantity used to measure how close the predictions are to eventual outcomes in statistics, MAE values and the correlation values (R^2) between experimental and calculated frequencies are shown in Table 5. Although the correlation coefficients are very close for both methods, MAE results have also shown that the DFT calculations are generally in better agreement with experimental data than HF method. For minimum MAE values between calculated and experimental data, we compute average value of 136 ppm for aromatic carbons (C4, C5, C8 and C13) that is adjacent to nitrogen atoms in phenazine structure of the both compounds with DFT method (B3LYP). ^{1}H-NMR data are reported between 7.80 and 8.70 ppm consistent with presence of signals for aromatic protons while ^{13}C-NMR spectra show the peaks between 120.00 and 131.50 ppm indicating presence of aromatic carbons for phenazine-5,10-dioxide in the study similar to the previous made by Nansathit et al. [9].

3.4. Frontier molecular orbitals (FMO) and electrostatic potential analysis

Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important parameters for quantum chemistry. We can determine the way the molecule interacts with other species; hence, they are called the frontier orbitals. HOMO, which can be thought as the outermost orbital containing electrons, tends to give these electrons such as an electron donor. On the other hand, LUMO can be thought as innermost orbital containing free places to accept electrons [39]. Owing to interaction between HOMO and LUMO orbital of a structure, transition state of π–π* type is observed with regard to molecular orbital theory [40]. Therefore, while energy of the HOMO is directly related to ionization potential, LUMO energy is directly related to electron affinity. 3D plots and energy difference between HOMO and LUMO of *Phenazine1* are shown in Fig. 4. HOMO–LUMO energy gaps of *Phenazine2* are also computed 97.2, 240.1 kcal mol^{-1} with DFT and HF approach, respectively. It is noted that energy gaps have minimal values at DFT frontier and second frontier calculations for the both compounds. Besides, 3D plot painted according to values of electrostatic potential for *Phenazine1* is shown in Fig. 5. The molecular electrostatic potential (MEP) is related to the electronic density and a very useful descriptor for determining sites for electrophilic attack and nucleophilic reactions as well as hydrogen–bonding interactions [41, 42]. Molecular electrostatic potential, $V(r)$ is defined in terms of interaction energy between electrical charge generated from electrons and nuclei of molecules and a positive test charge (a proton) located at any given point $r(x,y,z)$ in the vicinity of a molecule [43, 44]. Minimum $V(r)$ is calculated as −0.0144 a.u around aromatic carbons at DFT (B3LYP) method. However, this result is determined as −0.0134 a.u for the HF method.

4. Conclusions

In this study, some theoretical results are used to clarify the identification of *Phenazine1* and *Phenazine2* compounds. Optimized molecular structures (bond lengths, bond angles and torsion angles), selected vibrational frequencies including Infrared intensities, corresponding vibrational spectra interpreted with the aid of normal coordinate analysis based on scaled density functional force field have been analyzed utilizing HF/6-31 G(*d*) and DFT-B3LYP/6-31

Table 4 The experimental and calculated chemical shifts (ppm) using B3LYP and HF/6-31 G(*d*) for *Phenazine1* and *Phenazine2* with the GIAO method

Atoms	Experimental (ppm) [18] *Phenazine1* (solvent: $CDCl_3$)	Calculated GIAO method				Experimental (ppm) [18] *Phenazine2* (solvent:$CDCl_3$)	Calculated GIAO method			
		HF/6-31G(*d*) basis set		B3LYP/6-31 G(*d*) basis set			HF/6-31 G(*d*) basis set		B3LYP/6-31 G(*d*) basis set	
		Solvent: none	Solvent: $CHCl_3$	Solvent: none	Solvent: $CHCl_3$		Solvent: none	Solvent: $CHCl_3$	Solvent: none	solvent: $CHCl_3$
C11	117.5	119.72	119.60	114.68	114.39	117.5	119.87	119.60	114.67	114.39
C12	111.8	112.02	111.97	105.33	105.20	111.8	114.69	113.99	105.32	105.18
C13	131.1	136.60	136.57	131.46	131.60	131.1	135.64	135.81	131.65	131.75
C8	129.6	136.59	136.53	130.48	130.69	129.6	136.20	136.37	130.60	130.81
C9	111.2	111.87	112.18	105.74	106.00	111.2	111.33	111.82	105.74	106.02
C10	120.7	120.13	120.16	115.14	115.07	120.7	120.26	120.23	115.10	115.07
C4	129.6	136.24	136.41	130.10	130.49	129.6	136.55	136.49	130.25	130.63
C5	131.1	135.59	135.79	131.24	131.45	131.1	136.67	136.61	131.27	131.45
C6	111.8	114.70	113.98	107.33	106.67	111.8	111.95	111.87	107.46	106.79
C1	117.5	119.90	119.61	115.01	114.55	117.5	119.70	119.59	115.00	114.55
C2	120.7	120.33	120.26	115.06	114.93	120.7	120.06	120.12	115.11	115.01
C3	111.2	111.35	111.84	105.60	105.92	111.2	111.87	112.20	105.55	105.89
C7	30.2	31.79	31.64	32.15	32.00	31.6	31.81	31.65	32.06	31.90
C14	121.7	121.01	120.68	116.66	116.33	121.7	120.81	120.54	116.63	116.36
C15	146.9	150.44	150.95	139.72	140.13	146.9	150.21	150.64	139.46	139.79
C19	136.9	135.16	134.76	125.91	125.47	136.9	135.12	134.75	125.85	125.45
C16	110.9	106.71	106.99	103.98	104.29	110.9	107.12	107.35	104.47	104.74
C18	125.5	113.89	113.41	111.16	110.63	125.5	113.74	113.31	111.11	110.65
C17	129.2	131.78	132.17	123.47	123.71	129.2	131.77	132.13	123.42	123.65
C20	29.7	28.83	28.59	29.67	29.41	43.3	40.34	40.14	44.29	44.10
C21						29.9	29.13	29.07	32.92	32.82
C22						20.3	19.83	19.65	23.44	23.24
C23						14.0	15.21	15.02	15.79	15.57
H6	6.82	6.485	6.468	5.509	5.488	6.82	6.131	6.177	5.549	5.526
H11	6.63	6.786	6.896	6.137	6.206	6.63	6.865	6.956	6.142	6.213
H12	6.82	6.111	6.162	5.368	5.384	6.82	6.506	6.490	5.405	5.420
H9	7.33	6.609	6.781	5.803	5.942	7.33	6.611	6.791	5.828	5.970
H10	7.16	6.954	7.079	6.310	6.397	7.16	6.984	7.105	6.311	6.401
H1	6.63	6.865	6.954	6.196	6.246	6.63	6.784	6.896	6.218	6.270
H2	7.16	6.987	7.105	6.337	6.416	7.16	6.952	7.079	6.334	6.416
H3	7.33	6.612	6.793	5.824	5.963	7.33	6.609	6.781	5.833	5.973
H7-A	3.01	3.032	3.088	2.773	2.821	3.01	3.000	3.069	2.773	2.822
H7-B	3.01	2.999	3.068	2.748	2.807	3.01	3.033	3.089	2.741	2.801

Table 4 continued

Atoms	Experimental (ppm) [18] *Phenazine1* (solvent: $CDCl_3$)	Calculated GIAO method				Experimental (ppm) [18] *Phenazine2* (solvent:$CDCl_3$)	Calculated GIAO method			
		HF/6-31G(*d*) basis set		B3LYP/6-31 G(*d*) basis set			HF/6-31 G(*d*) basis set		B3LYP/6-31 G(*d*) basis set	
		Solvent: none	Solvent: $CHCl_3$	Solvent: none	Solvent: $CHCl_3$		Solvent: none	Solvent: $CHCl_3$	Solvent: none	solvent: $CHCl_3$
H7-C	3.01	2.768	2.880	2.512	2.600	3.01	2.770	2.882	2.504	2.593
H19	6.82	7.869	7.897	7.158	7.173	6.82	7.868	7.901	7.160	7.181
H16	5.82	6.839	6.993	6.448	6.578	5.82	6.830	6.977	6.410	6.535
H18	6.41	6.971	7.047	6.681	6.728	6.41	6.958	7.039	6.660	6.714
H17	6.34	7.757	7.894	7.200	7.296	6.34	7.735	7.873	7.167	7.267
H(N3)	4.45	2.797	2.885	3.371	3.486	4.45	2.643	2.706	3.222	3.309
H20-A	2.79	2.423	2.479	2.535	2.564	3.12	2.955	3.009	2.790	2.826
H20-B	2.79	2.891	2.922	2.794	2.815	3.12	2.513	2.571	3.038	3.081
H20-C	2.79	2.641	2.753	2.585	2.707	–	–	–	–	–
H21-A						1.55	1.064	1.114	1.704	1.686
H21-B						1.55	1.479	1.443	1.400	1.451
H22-A						1.36	1.279	1.317	1.500	1.524
H22-B						1.36	1.260	1.294	1.484	1.514
H23-A						0.85	0.856	0.853	0.959	0.956
H23-B						0.85	1.138	1.136	1.138	1.135
H23-C						0.85	0.913	0.906	0.908	0.908

Table 5 Correlation factors between experimental and calculated values

	Correlation values (R^2)		Mean absolute error (MAE)	
	DFT method *6-31 G(d)*	HF method *6-31 G(d)*	DFT method *6-31 G(d)*	HF method *6-31 G(d)*
Phenazine1 Bond length (Å)	0.9805	0.9825	0.039	0.036
Phenazine1 Bond Angles (°)	0.9419	0.9019	0.885	1.166
Phenazine1 Torsion angles (Å)	0.9959	0.9959	3.825	3.854
Phenazine2 Frequencies (cm^{-1})	0.9994	0.9974	17.22	31.37

Phenazine1	Solvent-free	In $CHCl_3$	Solvent-free	In $CHCl_3$	Solvent-free	In $CHCl_3$	Solvent-free	In $CHCl_3$
^{13}C NMR chemical shifts (ppm)	0.9825	0.9813	0.9828	0.9820	3.00	3.09	4.63	4.76
^{1}H NMR chemical shifts (ppm)	0.8830	0.8847	0.8568	0.8576	0.52	0.50	0.69	0.65
Phenazine2	Solvent-free	In $CHCl_3$	Solvent-free	In $CHCl_3$	Solvent-free	In $CHCl_3$	Solvent-free	In $CHCl_3$
^{13}C NMR chemical shifts (ppm)	0.9918	0.9915	0.9914	0.9908	2.73	2.80	4.36	4.42
^{1}H NMR chemical shifts (ppm)	0.9401	0.9417	0.9333	0.9347	0.45	0.43	0.56	0.53

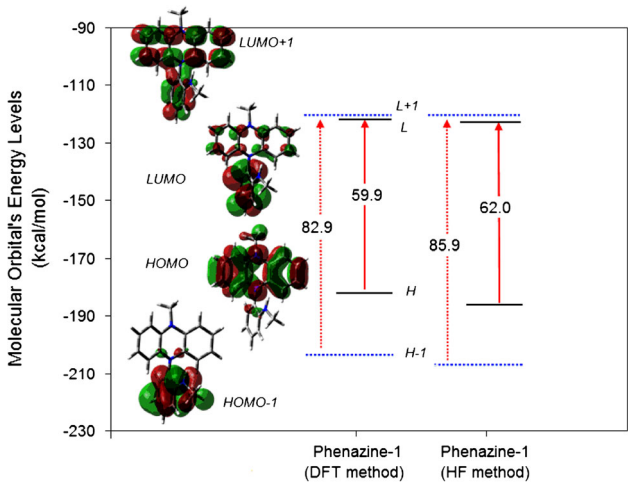

Fig. 4 3D plots and energy diagrams of the HOMO–LUMO and second frontier orbital's obtained from DFT(B3LYP) and HF method for *Phenazine1*

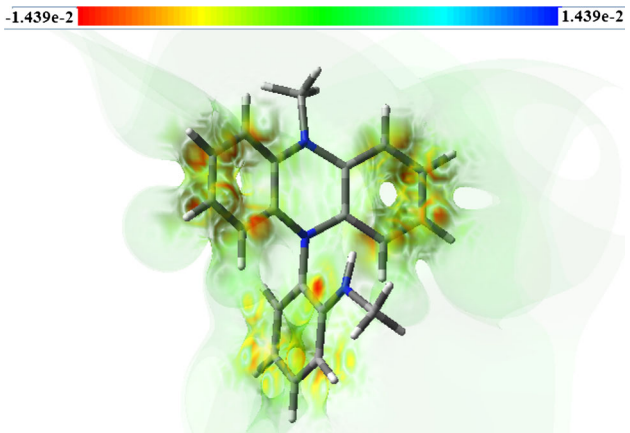

Fig. 5 3D plot painted according to values of electrostatic potential for *Phenazine1*

G(*d*) methods. It has been found that optimized molecular structures and vibrational frequencies show a good agreement with available experimental results and DFT-B3LYP computations are found to be superior to HF ones. Moreover, not only are HOMO and LUMO orbitals visualized and interpreted but also energy band gap are investigated for identification of the compounds. The energy band gap reveals that DFT frontier and second frontier calculations are more stable results for both compounds. This study not only shows the way to the characterization of *N*-methyl-2-(10-methylphenazin-5(10H)-yl)aniline (phenazine1) and *N*-butyl-2-(10-methylphenazin-5(10H)-yl)aniline (phenazine2) molecules but also helps to researchers for the future studies in technology and industry.

Acknowledgments The authors gratefully acknowledge the Karamanoglu Mehmetbey University Scientific Research Projects (BAP) Coordinating Office for support (Grant No 07-M-13).

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