Volume 26 Number 1, 2017 Природните науки в образованието

From the Research Laboratories В изследователските лаборатории

SYNTHESIS AND CHARACTERIZATION OF COMPOUND PMPA USING NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY AND OPTIMIZED MOLECULAR STRUCTURES CALCULATED USING THE DFT/B3LYP METHOD WITH THE 3-21G** BASIS SET COMBINED WITH THE Co^{II} COMPLEX

^{1,4}Mohammad Mahdi Akbarzadeh, ²Khirollah Mehrani, ³Shahriar Ghammamy, ⁴Vahideh Hadigheh Rezvan *IBuilding Chemical Engineering, Tehran – Iran*

IBuilding Chemical Engineering, Ienrah – Iran 2Islamic Azad University – Iran 3Imam Khomaini International University – Iran 4Ardabil Branch, Islamic Azad University – Iran

Abstract. In this study, the Schiff base complex of Co^{II} derived from reaction between Benzene-1,2-diamine, Acetophenone, and 1H-Pyrrole-2-carbaldehyde have been synthesized. All the complexes have been characterized on the basis of elemental analysis and spectral studies. All the complexes are light in color and stable to atmosphere. Elemental analysis shows ML₂ stoichiometry for the complex. IR spectral data indicates coordination through NH pyrrole and azomethine nitrogen groups. Electronic spectral data suggests a polymeric octahedral structure for the Co^{II} complex. The structural characterization of Schiff base and cobalt complexes were carried out on the basis of their melting point, solubility, elemental analyses, conductivity measurements, FT-IR, ¹H NMR, ¹³C NMR, DEPT 90, and HETCOR spectroscopy studies. Molecular geometries, vibrational frequencies, and NMR frequencies of the title compounds in the ground state are calculated using the Hartree-Fock (HF) and density functional theories (DFT/B3LYP), and GIAO methods with the 3-21G** basis set and compared with the experimental data. The calculated results show that the optimized geometries can reproduce the crystal structural parameters, and the theoretical vibrational frequencies show good agreement with the experimental values. The calculated Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energies show that charge transfer occurs within the molecule. The geometries and normal modes of vibrations obtained from DFT/3-21G** calculations are in good agreement with the experimentally observed data.

Keywords: 1H-Pyrrole-2-carbaldehyde, HETCOR, DEPT 90, DFT/B3LYP, ¹³C-¹³C COSY

Introduction

The compounds containing azomethine (-C=N-) group are known as Schiff bases, are formed by condensation of primary amines with carbonyl compounds such as aldehydes or ketones (Royer et al., 2005). Schiff bases are characterized by the -N=CH- (imine) group, which is important in elucidating the mechanism of transamination and racemization reactions in biological systems (Jaeger et al., 1979). Literature review shows that Schiff bases show bacteriostatic and bactericidal activities (Tarafder et al., 2000; Sakiyan et al., 2004) Antibacterial, antifungal, antitumor, and anticancer activities have been reported in a number of studies, and are active against a wide range of organisms (e.g., C. albicans, E. coli, S. aureus, B. polymyxa, and P. viticolaetc.) (Aiad & Negm, 2009a; 2009b; Chohan et al., 2010). Schiff based reagents are becoming increasingly important in the pharmaceutical, dye (Aksuner et al., 2009) and plastic industries (Gupta et al., 2006), as well as for Liquid Crystal Display technology and mechanistic investigations of drugs used in pharmacology, biochemistry, and physiology (Pardridge, 2009; Fricker, 2006; Chen & Rhodes, 1996). However, despite extensive scientific reports on synthesis, characterization, and crystalline structure of the transition metal-salen complexes, few reports have been published on the use of salen molecules as ionophoresin ion-selective studies (Sadeghi et al., 2006; Fatibello-Filho et al., 2007).

A series of transition metal ions form complexes with schiff bases (Gupta & Sutar, 2008; Cozzi, 2004; Chohan et al., 2001), aromatic hydrazones (Sridhar et al., 2001; 2002; Pouralimardan et al., 2007) like *o*-hydroxy 5-methyl salicylidinehydrazone, 2-hydroxy-4-methylacetophenone phenyl hydrazine, *o*-hydroxy 5-methyl acetophenone phenyl hydrazone, *o*-hydroxy 4-methoxysalicylidine phenyl hydrazone, *o*-hydroxy 5-methyl salicylidine phenyl hydrazone, *o*-hydroxy 5-methyl salicylidine phenyl hydrazone, *o*-hydroxy 5-methyl salicylidine phenyl hydrazone (Karabatsos & Taller, 1963; Garcia-Herbosa et al., 1994; Metwally et al., 2012; Sacconi, 1954) hydroxamic acid (Gibson & Magrath, 1969) and *a*-mercapto-2-amino phenyl acetohydroxamic acid (Rudzka et al., 2005; Gould et al., 1978; Puerta & Cohen, 2002).

In this paper, we have synthesized (N¹Z,N²Z)-N¹-((1H-Pyrrol-2-yl)methylen)-N²-(1-phenylethylidene)ethane-1,2-diamine (PMPA) chelating agent and used to synthesize metal chelates with Co^{II} transition metal (Fig. 1).These metal chelates were characterized by analytical, thermal, infrared and ¹H NMR, ¹³C NMR, DEPT 90, and HETCOR spectroscopy.

Herein, we report the synthesis and molecular structure of LM type of $[Co(C_{19}H_{17}N_3)_2]Cl_2$.

To the best of our knowledge, no theoretical Hartree-Fock (HF) or Density Functional Theory (DFT) calculations or detailed Vibrational infrared (IR) and NMR analyses have been performed on the molecule structure.

DFT calculations are known to provide excellent vibrational wave numbers scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and an harmonicity effects (Scott & Radom, 1996;





Stephens et al., 1994; Sinha et al., 2004; Halls et al., 2001; Kim & Jordan, 1994). DFT is the best method compared to the ab initio method for computation of molecular structure, vibrational wave number, and energies of molecules (Mole et al., 1996; Eichkorn et al., 1997). In this work, by using the DFT/B3LYP and GIAO methods (Aliev et al., 2009; Cimino et al., 2004; Dybiec & Gryff-Keller, 2009), we calculated the vibrational and [¹H], [¹³C], [¹⁵N] NMR wave numbers of (N¹Z,N²Z)-N¹-((1H-Pyrrol-2-yl)methylen)-N²-(1-phenylethylidene)ethane-1,2-diamine and molecular geometric parameters. These calculations are available for providing insight into vibrational spectra and molecular parameters.

Calculations were carried out using the GAMESS program (Bode & Gordon, 1998). The images of the structures and Molecular Orbitals (MOs) were obtained using the MOLDEN program (Schaftenaar & Noordik, 2000).

HOMO represents the ability to donate an electron. On the other hand, LUMO as an electron acceptor, represents the ability to obtain an electron. The HOMO and LUMO energies are calculated by the DFT at 3-21G** method (Scuseria, 1999; Zandler & D'Souza, 2006; Zhang & Musgrave, 2007).

Experimental

Materials and methods

All reagents and solvents employed were commercially available and used as received without further purification. The FT-IR spectra were recorded from KBr pellets in the range of 4000 - 400 cm⁻¹ on a NEXUS 670 spectrometer. The ¹H and ¹³C NMR, DEPT 90 and HETCOR spectra were measured on an Avance-300 Bruker instrument (300 MHz) in CDCl₃/TMS. The C and H microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer.

Computational method

A careful examination of the structures, computed using different ab initio and DFT methods pointed out that theB3LYP method in conjunction with the 3-21G** basis set, was an efficient level for performing geometry optimization. Therefore, all the molecular structures were optimized with the DFT (B3LYP) levels at the 3-21G** basis set (Fig. 2; Table 1). Vibrational frequencies for the optimized molecular structures of the title compounds were calculated using the DFT/B3LYP method with the 3-21G** basis set and compared with experimental data (Fig. 3; Table 2).

Entry	Calculated (ppm)			Experimental (ppm)				
¹³ C NMR	CH₃	CH ₂	СН	С	CH_3	CH ₂	СН	С
C _{2B}	22	-	-	-	42.187	-	-	-
C _{3D}	-	-	108	-	-	-	110.089	-
C _{2D}	-	-	111.8	-	-	-	110.49	-
C _{4D}	-	-	118.3	-	-	-	114.214	-
C _{2C}	-	-	123.6	-	-	-	115.48	-

 Table 1. Spectra ¹³C NMR compound PMPA

				r		-		
C _{5C}	-	-	123.6	-	-	-	116.527	-
C _{3C}	-	-	128.6s	-	-	-	116.795	-
C _{4C}	-	-	128.6	-	-	-	117.584	-
C _{3A}	-	-	128.9	-	-	-	118.79	-
C _{5A}	-	-	128.9	-	-	-	120.307	-
C _{2A}	-	-	129.2	-	-	-	123.281	-
C _{6A}	-	-	129.2	-	-	-	126.885	-
C _{4A}	-	-	131	-	-	-	128.354	-
C _{1D}	-	-	-	132.7	-	-	-	131.06
C _{1A}	-	-	-	134	-	-	-	134.708
C _{1C}	-	-	-	140	-	-	-	137.523
C _{6C}	-	-	-	144	-	-	-	141.432
C _{1B}	-	-	-	165	-	-	-	146
C _{5D}	-	-	151	-	-	-	148.323	-

Table 2. Theoretically computed energies (a.u.), zero-point vibrational energies (kcal mol $^{-1}$), rotational constants (GHz), entropies (cal mol $^{-1}$ K $^{-1}$) (Boyer, 1970) for compound PMPA at the B3LYP/3-21G**

Entry	Ea (Thermal)	CVb	Sc
Endy	kcal mol-1	cal mol ⁻¹ K ⁻¹	cal mol ⁻¹ K ⁻¹
Total	205.053	73.327	137.718
Translational	0.889	2.981	42.862
Rotational	0.889	2.981	34.722

Zero-point correction	0.308687 (Hartree/Particle)	
Thermal correction to Energy	0.326772	
Thermal correction to Enthalpy	0.327717	
Thermal correction to Gibbs Free Energy	0.262283	
Sum of electronic and zero- point Energies	0.609596	
Sum of electronic and thermal Energies	0.627681	
Sum of electronic and thermal Enthalpies	0.628625	
Sum of electronic and thermal Free Energies	0.563191	

Mohammad Mahdi Akbarzadeh, Khirollah Mehrani, Shahriar Ghammamy, Vahideh Hadigheh Rezvan

^aEnergy; ^bConstant Vibration; ^cStandard.



Fig. 2. FT-IR spectrum in (KBr) disk of compound PMPA in the range of 4000-400 cm⁻¹ on a NEXUS 670 spectrometer

In addition, NMR frequencies for the optimized molecular structures of the title compounds were calculated using the DFT/B3LYP methods with the 3-21G**(6D, 7F) standard basis set, and compared with the experimental data (Xing et al., 2008; , Han et al., 2009). All calculations were performed using the Gaussian 03 program package on a Windows 7 Ultimate Operating system.



Fig. 3. FT-IR spectrum in (KBr) disk of complex [Co(C19H17N3)2]Cl2.2H2O in the range of 4000-400 cm⁻¹.

Synthesis of ligand $(N^1Z, N^2Z)-N^1-((1H-pyrrol-2-yl)methylen)-N^2-(1-phenyle-thylidene)ethane-1,2-diamine$

 $(N^{1}Z,N^{2}Z)-N^{1}-((1H-Pyrrol-2-yl)methylen)-N^{2}-(1-phenylethylidene)ethane-1,2 diamine was synthesized from benzene-1,2-diamine 11.2 g, acetophenone 5 g, and 1H-Pyrrole-2-carbaldehyde 5.1 g. The reaction mixture was stirred in ethanol (120 ml) at 90 °C for 24 h and then cooled to room temperature, followed by concentrating the resulting mixture to a yellow solid product. Boiling point of the solution was measured 79 °C.$

 $[C_{10}H_{17}N_{2}];$ **IR** (KBr, cm⁻¹):

Calcd., 3136.78 (N-H), 2906.63, 2914.98 (=C-H),1647.32 (C=N),881.709, 961.619, 794.219, 801.525 (C-H, OPP), 3346.43 (C-H, SP²), 3176.74, 3158.23 (C-H, SP³), 1458.21 (C=C), 1548.02, 1647.32, 1755.62 (N-H, C-N);

IR (KBr, cm⁻¹):

Found: 3133.70 m (N-H), 2857.57 w, 2748.89 w (=C-H), 1616.4 s (C=N), 1030.08 m, 880.0 w, 742.52 m (C-H, OPP), 3084.47 w (C-H, SP²), 2969.15 w, 2997.43 w (C-H, SP 3)..168 m (C=C), 1574.77 m (N-H, C-N);

¹**H NMR** (300MHz, CDCl₃): δ 9-10 ppm (s, 1 H, NH), 8-9 (s, 1 H, =C-H), 6-8 (m, 12 H, Ar-H) phenyl group and hetroaromatic groups (Fig. 4);



Fig. 4. Chemical structure of compound PMPA with bonds numbered hydrogen atoms

¹³C NMR (300 MHz CDCl₃): δ 42 ppm (-CH₃), 70-80 (CDCl₃), 100-145 (Phenyl group and hetroaromatic group), 146 (Ph-C=N), 148 (=C-H);

For $C_{10}H_{17}N_{2}$

anal. Calcd: C, 79.41; H, 5.96; N, 14.62 %

Found: C, 79.56; H, 5.84; N, 14.64 %

Mol. Wt.: 287.36, found: 287.41 MW

Exact Mass: 287.14 m/e: 287.14 (100.0 %), 288.15 (20.7 %), 289.15 (2.0 %), 288.14 (1.1 %).

Synthesis of Complex $[Co(C_{10}H_{17}N_3)_2]Cl_22H_2O$

The Schiff base PMPA 4.3 g was dissolved in acetonitrile (20 ml) to which an acetonitril solution (120 ml) of $[CoCl_2]6H_2O$ 1.2 g was added by stirring. The mixture was stirred for 3 h and then cooled to room temperature followed by concentrating the resulting mixture to an orange solid product.

 $[C_{38}H_{32}CoN_{6}]$; **IR** (KBr, cm⁻¹):

Found: 3412 m (N-H), 2804.85 s, 2715.05 m (=C-H), 1603.53 m, 1031.37 m, 967.86 w (C=N), 1085.64 w (C-H, OPP), 3000.74 s (C-H, SP ²), 2914.89 s (C-H, SP ³), 1444.98 w, 1501.34 m (N-H, C-N);



Fig. 5. 1H NMR spectrum (in the magnetic field 300 MHz, solvent CDCl3) of the synthesized ligands PMPA in the range δ 6-8 ppm with hydrogen atoms positions

For C₃₈H₃₂CoN₆ anal. Calcd: C, 72.26; H, 5.11; Co, 9.33; N, 13.31 % Found: C, 72.24; H, 5.18; Co, 9.31; N, 13.28 % Mol. Wt.: 631.63, found: 631.59 MW **Exact Mass**: 631.2 m/e: 631.20 (100.0 %), 632.21 (41.5 %), 633.21 (8.4 %), 632.20 (2.2 %), 634.21 (1.3 %)

Structure elucidation

The structures of both compounds were determined using FT-IR, ¹H NMR, and ¹³C NMR spectroscopy (including DEPT 90 and HETCOR).

 $2D[^{13}C], [^{1}H]$ HETCOR experiments: $2D[^{13}C], [^{1}H]$ HETCOR spectra were measured according to the Van Rossum et al. (1997) method. The pulse sequence for the $2D[^{13}C][^{1}H]$ HETCOR experiment is shown in Fig. 5.

Results and discussion

IR Spectral Studies

All spectral data were consistent with the assigned structure of the compounds. The IR spectra of the ligand give a broad band at 3133.70 cm⁻¹ assignable to v (NH) stretching vibration.

The ligands show strong band in the 1616.43 cm⁻¹ region due to C=N, which is assignable to the Schiff bases appearing in both synthesized ligands Fig. 6.



Fig. 6. Chemical structure of compound PMPA with bonds numbered carbon atoms

Vibrations due to v (C=N) and v (N-H) were found in range of 1616.43 and 3133.70 cm⁻¹ for ligands, and from 1603.53 and 3412.95 cm⁻¹ for complexes, respectively. This decrease in the frequency of C=N and increase in frequency of N-H for the complex indicates complication. From the infrared spectra of complexes, it is clear that there is no doublet peak in the region of 700-950 cm⁻¹, which indicates the connected nature of the ligand.

As seen in Fig. 7, this band is shifted to a lower frequency in the complex, indicating the coordination through azomethine nitrogen. It is found from the IR spectra of the complexes that there is a wide and strong band at 620-800 cm⁻¹ for (M-N) bonding Fig. 7.



Fig. 7. 13C NMR spectra (in the magnetic field 300 MHz, solvent chloroform-*d*) related to the structure of the synthesized PMPA

Metal ligand vibrations are generally observed in the far-IR region and usually provide valuable information regarding the bonding of ligand to the metal-ions.

These bands will give valuable information regarding bonding modes of ligand to metal ions in the complexes.

NMR spectral studies

Further evidence for the formation of target compounds was obtained from the ¹H NMR spectra, which proved to be a diagnostic tool for positional elucidation of the proton. Assignments of the signals are based on the chemical shift and intensity pattern Fig. 8.

A single peak in the range δ 8.6-8.75 ppm indicated the proton of the CH=N group. All the Schiff bases showed negative test for aldehyde, ¹H NMR spectra exhibited a single peak at near δ 8.4 ppm due to the proton of azomethine (Fig. 9).

The NH peak, which appears as a singlet at δ 10.136 ppm in the ligand is absent in all the complexes, which shows the deprotonation of the ligand. The signal at δ 10.136 ppm is assigned to proton NH of the ligand.

The aromatic protons at δ 6-8 (m, Ar-H) shift down field in the complexes. The signal at δ 2.642 (s, 3H) is assigned to the protons of the methyl group of acetophenone. Thus, ¹H NMR spectral observation supplements the assigned geometry.



Mohammad Mahdi Akbarzadeh, Khirollah Mehrani, Shahriar Ghammamy, Vahideh Hadigheh Rezvan

Fig. 8. ¹³C NMR spectra PMPA (in the magnetic field 300 MHz, solvent CDCl₃) related to the structue of the synthesized ligand (a) Positions of the carbon ato ms in the range δ 110 – 125 ppm; (b) Positions of the carbon atoms in the range δ 125 – 150 ppm

Synthesis and Characterization of Compound...



Fig. 9. DEPT 90 spectra (in the magnetic field 300 MHz, solvent CDCl₃) related to the structure (Blinka et al., 1984) of the synthesized logand PMPA: (a) position carbon atom C_{2B}; (b) The position disappearance of carbon atoms in Spectra DEPT 90

The characteristic resonance peaks in the ¹³C NMR spectra of the ligand PMPA, are given in the experimental section (Table 3) (Fig. 10). The carbon atoms of the phenyl group and hetroaromatic groups appear in the expected aromatic region ranging from δ 105-145 ppm.

A peak signal appearing at δ 42.187 ppm is the characteristic of the carbons (C_{2B}) of -CH₃ (Fig. 11).

Table 3. Theoretical frequencies in cm⁻¹ calculated by DFT/3-21G** method for compound PMPA

Observed values	DFT/3-21G**	Approximate assignments	
3133.70 w	3136.78	N-H symmetric stretching	
2857.57 w	2906.63	(-H stratching (aldohyda)	
2748.89 w	2914.98		
1616.40 m	1647.32	C=N stretching	
-	1054.34	(C-H In plane) stretching	
1030.08m	881.709		
880.0w	961.619	(CLLOPP) stratsking	
742.52m	794.219	(C-H OPP) stretching	
-	801.525		
3084.47 w	3346.43	(C-H SP ²) stretching	
2969.15 w	3176.74	(CIICD3) stratskips	
2997.43 w	3158.23	(C-H SP ²) stretching	
1410.68 w	1458.21	C=C bending	
-	1548.02		
1574.77m	1647.32	(C-N , N-H)	
-	1755.62		

A sharp signal at δ 148.323 ppm due to the characteristics of =C-H (C_{5D}) carbon was in accordance with all the proposed structure (Fig. 12).

In the spectrum of DEPT 90, disappearance of the peak area (C_{1B}) 146 ppm, (C_{6C}) 141.432 ppm, (C_{1C}) 137.523 ppm, (C_{1A}) 134.708 ppm, (C_{1D}) 131.060 ppm proton is not related to the fourth type of carbon.

In addition, taking the spectrum DEPT 90 of the composition PMPA, the absence of ethanol solvent was approved (Fig. 13).

An additional confirmation of signal assignments in principal PMPA structures was done based on the HETCOR spectrum (Fig. 14a). ¹H-¹³C COSY is the hetero nuclear correlation spectroscopy. This spectrum was interpreted using established carbon-proton correlations (Kilpelaeinen, 1994). The cross peaks mean correlation between a proton and a carbon (Fig. 14b-d).





Mohammad Mahdi Akbarzadeh, Khirollah Mehrani, Shahriar Ghammamy, Vahideh Hadigheh Rezvan





Fig. 10. HETCOR spectra (in the magnetic field 300 MHz, solvent CDCl₃) compound: (a) PMPA; (b) Position =C-H in the range δ 146-150 ppm; (c) Position -CH₃ in the range δ 41-43 ppm; (d) In the range δ 95-135 ppm; (e) ¹³C-¹³C COSY (Correlation Spectroscopy) (Zhang & Brüschweiler, 2004) of compound PMPA in the range δ 106-132 ppm; (f) In the range δ 114-124 ppm







Fig. 12. Calculated 13C NMR of (N1Z,N2Z)-N1-((1H-Pyrrol-2-yl)methylen)-*N*2-(1-phenylethylidene) ethane-1,2-diamine PMPA, at the DFT/3-21G**.



Fig. 13. Calculated 15N NMR of (N1Z,N2Z)-N1-((1H-Pyrrol-2-yl)methylen)-*N*2-(1-phenylethylidene)ethane-1,2-diamine at the DFT/3-21G**



Fig. 14. The atomic orbital compositions of the frontier molecular orbital for compound PMPA, [C19H17N3] at the DFT/3-21G*

¹³C-¹³C COSY (Correlation spectroscopy)

¹³C-¹³C COSY is used for clearly indicate correlation with coupled carbons. A point of entry into a COSY spectrum is one of the keys to predict information from it successfully. Relation of Coupling carbons is determined by cross peaks (correlation peaks) and in the COSY spectrum. In other words, Diagonal peaks by lines are coupled to each other.

Figure 14c indicates that there are correlation peaks between carbon C_{2C} and $C_{3,5C}$ as well as between $C_{3,5C}$ and $C_{3,5,2A}$. This means the $C_{3,5C}$ coupled to C_{2C} and $C_{3,5,2A}$. In Figure 14c indicates that there are correlation peaks between carbon C_{4A} and C_{2A} as well as between C_{2A} and C_{6A} . This means the C_{2A} coupled to C_{4A} and C_{6A} .

Figure 14e,f indicates that there are correlation peaks between carbon $C_{3,5A}$ and C_{2A} . Also there are correlation peaks between carbon C_{4A} and C_{4C} as well as between C_{4C} and C_{6A} . This means the C_{4C} coupled to C_{4A} and C_{6A} (Simpson, 2012; Rienstra et al., 1998; Olsen et al., 2003; Omichinski et al., 1991).

Molecular geometry

The ONIOM (B3LYP/3-21G**) optimized structure of the ligand PMPA and the binding energies obtained at the B3LYP/3-21G** level are shown in Table 4.

Table 4. Theoretical and experimental IR spectral data (cm $^{-1}$) of compound PMPA at the DFT/3-21G**

Bond lengths	DFTa/3-21G**	Bond angles	DFT/3-21G**	
C1-C2	1.39516	C1-C2-C3	120.00865	
C2-C3	1.39471	C2-C3-C4	119.99413	
C3-C4	1.39543	C3-C4-C5	119.99402	
C4-C5	1.39482	C4-C5-C6	120.00471	
C5-C6	1.39514	C5-C6-C1	120.00002	
C6-C1	1.39483	C6-C1-C2	119.99843	
C6-C12	1.54	C6-C12-C13	109.47238	
C12-C13	1.50715	C6-C12-N36	109.4767	
C12-N36	1.50713	C13-C12-N36	111.80195	
N36-C17	1.54	C12-N36-C17	110.62903	
C17-C18	1.39516	N36-C17-C18	119.99721	
C18-C20	1.39471	C17-C18-C20	120.00863	
C20-C23	1.39543	C18-C20-C23	119.99416	
C23-C21	1.39483	C20-C23-C21	119.99394	
C21-C19	1.39514	C23-C21-C19	120.00475	

C19-C17	1.39483	C21-C19-C17	120.00001	
C18-N35	1.54	C19-C17-N36	120.00431	
N35-C27	1.32591	C19-C17-C18	119.99848	
C27-C39	1.47	C17-C18-N35	119.98082	
C39-C29	1.3918	C20-C18-N35	120.01051	
C29-C31	1.40185	C18-N35-C27	122.71598	
C31-C30	1.43487	N35-C27-C39	122.72008	
C30-N37	1.40175	C27-C39-C29	125.60775	
N37-C39	1.3918	C39-C29-C31	108.41367	
-	-	C29-C31-C30	107.18577	
		C31-C30-N37	107.18724	
		C30-N37-C39	108.41766	
-	-	N37-C39-C27	125.59659	

Mohammad Mahdi Akbarzadeh, Khirollah Mehrani, Shahriar Ghammamy, Vahideh Hadigheh Rezvan

^a Density Functional Theory

The values of the total energy for PMPA from the DFT and B3LYP calculation by employing the 3-21G** basis set are found to be 0.30090845 a.u and 0.262283 a.u, respectively.

Figures 15 - 17 show comparative representations of theoretical ¹H, ¹³C, and ¹⁵N NMR spectra, respectively (Mäki et al., 2005).

Vibrational spectroscopy is extensively used in organic chemistry for the identification of functional groups of organic compounds, the study of molecular conformations, and reaction kinetics *etc*. The observed and calculated data of the vibrational spectrum of PMPA are given in Table 2. The comparative graph of calculated vibrational frequencies by DFT method at 3-21G** basis sets for the PMPA are given in Table 2.

Prominent peaks around 3346.43 and 1647.32 cm⁻¹ in the FT-IR spectra are attributed to v N-H and v C=N modes, respectively. The in plane bending vibration and out of plane bending vibrations of the aromatic C–H group are characterized by bands in the ranges1196.43, 1169.39, 1162.86, 1158.73, 1157.39, and 1139.7 cm⁻¹, respectively.



Fig. 15. System adopted in the theoretical study: (a) compound PMPA; (b) Numbering compound PMPA using DFT/3-21G** level.

The HOMO-LUMO energy of the PMPA was calculated at the B3LYP/3-21G** level and is shown in Fig. 18.

HOMO (DFT) E _{HOMO}= -14.31737 a.u (First excited state) LUMO (DFT) E _{LUMO} = -0.20621 a.u (First excited state)

 $\Delta E = LUMO-HOMO = 14.11116 a.u$ (Ground state)

Mohammad Mahdi Akbarzadeh, Khirollah Mehrani, Shahriar Ghammamy, Vahideh Hadigheh Rezvan



Fig. 16. Theoretical calculated infrared spectra (Klähn et al., 2005; Langhoff, 1996) of compound PMPA, [C19H17N3] (top to bottom, frequencies in cm⁻¹, intensities in arbitrary units)



Fig. 17. 1H NMR Spectrum (in the magnetic field 300 MHz, solvent chloroform-*d*) of the synthesized compound (Huynh et al., 2005) PMPA

It reveals that the energy gaps reflect the chemical activity of the molecule. LUMO as an electron acceptor represents the ability to obtain an electron, while HOMO represents the ability to donate an electron.

The LUMO of nature, (i.e.m heterocyclic ring) is delocalized over the whole C-C and C-N bond. This electronic absorption corresponds to the transition from the ground to the first excited state, and is mainly described by one electron excitation from the highest occupied molecular or orbital LUMO.

Conclusions

A series of novel porphyrin hetero-aromatic were synthesized and structurally characterized by ¹H NMR, ¹³C NMR, DEPT 90, HETCOR, and IR spectroscopy. The hetero-aromatic are coordinated with Co^{II} ion through N-H and azomethine nitrogen.



Fig. 19. Ball & Stick models and system adopted in the study (Nakano et al., 1983; Masonjones et al., 2014; Merritt & Murphy 1994) for complex $[Co(C_{19}H_{17}N_3)_2]$ Cl_2H_2O at DFT/3-21G** level, (Solvent Accessible Surface: Translucent)



Fig. 20. Ball & Stick models and system adopted in the study for complex $[Co(C_{19}H_{17}N_3)_2]Cl_2.2H_2O$ at DFT/3-21G** level, (Solvent Accessible Surface: Translucent)(Connolly Molecular Surface: Dots) (Connolly, 1993).

The HETCOR spectrum is correlated ¹³C nuclei with directly attached protons. ¹H-¹³C coupling is one bond. If a line does not have cross peak, this means that the carbon atom has no attached proton. The structure of (N¹Z,N²Z)-N¹-((1H-Pyrrol-2-yl)methylen)-N²-(1-phenylethylidene)ethane-1,2-diamine geometry was compared with optimized parameters obtained by means of ab initio calculations with the 3-21G** basis set (Figs. 19, 20).

The geometries and normal modes of vibration obtained from DFT/3-21G** calculations are in good agreement with the experimentally observed data. The HOMO and LUMO levels of PMPA have been studied with DFT/3-21G** level. Moreover, NMR frequencies for the optimized molecular structures of the title compounds were calculated using these DFT/B3LYP methods with the 3-21G**(6D,7F) standard basis set, and where then compared with experimental data.

Acknowledgments. The authors would like to thank the laboratory staffs at Islamic Azad University, Ardabil Branch for the support during the period of this research.

REFERENCES

- Aiad, I.A.& Negm, N.A. (2009a). Some Schiff base surfactants as steel-corrosion inhibitors. J. Surfact. Deterg., 12, 313 – 319.
- Aiad, I.A. & Negm, N.A. (2009b). Some corrosion inhibitors based on Schiff base surfactants for mild steel equipments. J. Disp. Sci. & Technology, 30, 1142 – 1147.
- Aksuner, N., Henden, E., Yilmaz, I. & Cukurovali, A. (2009). A highly sensitive and selective fluorescent sensor for the determination of copper(II) based on a Schiff base. *Dyes & Pigments*, 83, 211–217.
- Aliev, A.E., Courtier-Murias, D. & Zhou, S. (2009). Scaling factors for carbon NMR chemical shifts obtained from DFT B3LYP calculations. J. Mol. Str.: THEOCHEM, 893, 1–5.
- Blinka, T.A., Helmer, B.J. & West, R. (1984). Polarization transfer NMR spectroscopy for silicon-29: the INEPT and DEPT techniques. *Adv. Organometallic Chem.*, 23, 193 – 218.
- Bode, B.M. & Gordon, M.S. (1998). Macmolplt: a graphical user interface for GAMESS. J. Mol. Graphics & Modelling, 16, 133 138.
- Boyer, T.H. (1970). Quantum zero-point energy and long-range forces. Ann. Phys., 56, 474-503.
- Brüschweiler, R. (2004). Theory of covariance nuclear magnetic resonance spectroscopy. J. Chem. Phys., 121, 409 414.
- Chen, H. & Rhodes, J. (1996). Schiff base forming drugs: mechanisms of immune potentiation and therapeutic potential. *J. Mol. Med.*, 74, 497 – 504.
- Chohan, Z.H., Munawar, A. & Supuran, C.T. (2001). Transition metal ion complexes of Schiff-bases: synthesis, characterization and antibacterial properties. *Metal-Based Drugs*, *8*, 137 – 143.
- Chohan, Z.H., Sumrra, S.H., Youssoufi, M.H. & Hadda, T.B. (2010). Metal based biologically active compounds: design, synthesis, and antibacterial/antifungal/ cytotoxic properties of triazole-derived Schiff bases and their oxovanadium (IV) complexes. *Eur. J. Med. Chem.*, 45, 2739 – 2747.
- Cimino, P., Gomez-Paloma, L., Duca, D., Riccio, R. & Bifulco, G. (2004). Comparison of different theory models and basis sets in the calculation of¹³C NMR chemical shifts of natural products. *Magn. Reson. Chem.*, *42*, S26 – S33.

- Connolly, M.L. (1993). The molecular surface package. J. Mol. Graphics, 11, 139–141.
- Cozzi, P.G. (2004). Metal–salen Schiff base complexes in catalysis: practical aspects. *Chem. Soc. Rev.*, 33, 410–421.
- Dybiec, K. & Gryff-Keller, A. (2009). Remarks on GIAO-DFT predictions of ¹³C chemical shifts. *Magn. Reson. Chem.*, 47, 63 66.
- Fatibello-Filho, O., Dockal, E.R., Marcolino-Junior, L.H. & Teixeira, M.F.S. (2007). Electrochemical modified electrodes based on metal salen complexes. *Anal. Lett.*,40, 1825 – 1852.
- Eichkorn, K., Weigend, F., Treutler, O. & Ahlrichs, R. (1997). Auxiliary basis sets for main row atoms and transition metals and their use to approximate Coulomb potentials. *Theor. Chem. Accounts*, 97, 119 – 124.
- Fricker, S.P. (2006). The therapeutic application of lanthanides. *Chem. Soc. Rev.* 35, 524–533.
- Garcia-Herbosa, G., Munoz, A., Miguel, D. & Garcia-Granda, S. (1994). Cyclopallated complexes of 2-acetylpyridine phenylhydrazone: a terdentate C,N,N' donor ligand. *Organometallics*, 13, 1775 – 1780.
- Gibson, F. & Magrath, D.I. (1969). The isolation and characterization of a hydroxamic acid (aerobactin) formed by Aerobacter aerogenes 62-1. Biochim. et Biophys. Acta (BBA) – Gen, Subjects, 192, 175 – 184.
- Gould, W.D., Cook, F.D. & Bulat, J.A. (1978). Inhibition of urease activity by heterocyclic sulfur compounds. *Soil Science Society of America Journal*, 42, 66–72.
- Gupta, K.C. & Sutar, A.K. (2008). Catalytic activities of Schiff base transition metal complexes. *Coordination Chem. Rev.*, 252, 1420 – 1450.
- Gupta, K.V., Singh, A.K. & Gupta, B. (2006). A cerium (III) selective polyvinyl chloride membrane sensor based on a Schiff base complex of *N*, *N'*-bis [2-(salicylideneamino)ethyl]ethane-1,2-diamine. *Anal. Chimica Acta*, 575, 198–204.
- Halls, M.D., Velkovski, J. & Schlegel, H.B. (2001). Harmonic frequency scaling factors for Hartree-Fock, S-VWN, B-LYP, B3-LYP, B3-PW91 and MP2 with the Sadlej pVTZ electric property basis set. *Theor. Chem. Accounts, 105*, 413–421.
- Han, J., Xing, Y., Wang, C., Hou, P., Bai, F., Zeng, X., Zhang, X. & Ge, M. (2009). Two complexes (Cu, Zn) with 1,10-phenanthroline and a tridentate amino-Schiff-base: crystal structures, spectra, thermogravimetric analyses and superoxide dismutase activity. J. Coordination Chem., 62, 745 – 756.
- Huynh, M.H., Hiskey, M.A., Chavez, D.E., Naud, D.L. & Gilardi, R.D. (2005). Synthesis, characterization, and energetic properties of diazido heteroaromatic high-nitrogen C-N compound. *J. Am. Chem. Soc.*, *127*, 12537 12543.

- Jaeger, D.A., Broadhurst, M.D. & Cram, D.J. (1979). Electrophilic substitution at saturated carbon. 52: a model for the proton transfer steps of biological transamination and the effect of a 4-pyridyl group on the base-catalyzed race-mization of a carbon acid. *J. Am. Chem. Soc.*, 101, 717–732.
- Karabatsos, G.J. & Taller, R.A. (1963). Structural studies by nuclear magnetic resonance V: phenylhydrazones. J. Am. Chem. Soc., 85, 3624 3629.
- Klähn, M., Schlitter, J. & Gerwert, K. (2005). Theoretical IR spectroscopy based on QM/MM calculations provides changes in charge distribution, bond lengths, and bond angles of the GTP ligand induced by the ras-protein. *Biophys. J.* 88, 3829 – 3844.
- Kilpelaeinen, I., Sipilae, J., Brunow, G., Lundquist, K. & Ede, R.M. (1994). Application of two-dimensional NMR spectroscopy to wood lignin structure determination and identification of some minor structural units of hard- and softwood lignins. J. Agric. Food Chem., 42, 2790 – 2794.
- Kim, K. & Jordan, K.D. (1994). Comparison of density functional and MP2 calculations on the water monomer and dimer. J. Phys. Chem., 98, 10089–10094.
- Langhoff, S.R. (1996). Theoretical infrared spectra for polycyclic aromatic hydrocarbon neutrals, cations, and anions. J. Phys. Chem., 100, 2819 2841.
- Mäki, J., Tähtinen, P., Kronberg, L. & Klika, K.D. (2005). Restricted rotation/tautomeric equilibrium and determination of the site and extent of protonation in bi-imidazole nucleosides by multinuclear NMR and GIAO-DFT calculations. *J. Phys. Org. Chem.*, 18, 240 – 249.
- Masonjones, S.R., Masonjones, H.D., Malone, M.C., Williams, A.H., Beemer, M.M. & Waggett, R.J. (2014). Styrofoam-and-velcro: an alternative to balland-stick models. J. Microbiology & Biology Educ., 15, 295 – 296.
- Merritt, E.A. & Murphy, M.E.P. (1994). *Raster 3D* version 2.0: a program for photorealistic molecular graphics. *Acta Cryst.*, *50*, 869 873.
- Metwally, M.A., Khalifa, M.E. & Koketsu, M. (2012). Thiocarbohydrazides: synthesis and reactions. *Amer. J. Chem., 2,* 38–51.
- Mole, S.J., Zhou, X. & Liu, R. (1996). Density functional theory (DFT) study of enthalpy of formation - 1: consistency of DFT energies and atom equivalents for converting DFT energies into enthalpies of formation. J. Phys. Chem., 100, 14665 – 14671.
- Nakano, H., Sangen, O. & Yamamoto, Y. (1983). Drawing of ball and stick type molecular models with hidden line elimination. J. Chem. Educ., 60, 98.
- Olsen, R.A., Struppe, J., Elliott, D.W., Thomas, R.J. & Mueller, L.J. (2003). Through-bond ¹³C-¹³C correlation at the natural abundance level: refining dynamic regions in the crystal structure of vitamin-D_{3 with solid-state NMR}. *J. Am. Chem. Soc.*, *125*, 11784 – 11785.
- Omichinski, J.G., Clore, G.M., Sakaguchi, K., Appella, E. & Gronenborn, A.M. (1991). Structural characterization of a 39-residue synthetic peptide containing

the two zinc binding domains from the HIV-1 p7 nucleocapsid protein by CD and NMR spectroscopy. *FEBS Lett.*, 292, 25 - 30.

- Pardridge, W.M. (2009). Recent developments in peptide drug delivery to the brain. *Pharmacology & Toxicology*, 71, 3 10.
- Pouralimardan, O., Chamayou, A.-C., Janiak, C. & Hosseini-Monfared, H. (2007). Hydrazone Schiff base-manganese (II) complexes: synthesis, crystal structure and catalytic reactivity. *Inorganica Chimica Acta*, 360, 1599 – 1608.
- Puerta, D.T. & Cohen, S.M. (2002). Elucidating drug-metalloprotein interactions with tris(pyrazolyl)borate model complexes. *Inorg. Chem.*, 41, 5075 – 5082.
- Rienstra, C.M., Hatcher, M.E., Mueller, L.J., Boqin, Fesik, S.W. & Griffin, R.G. (1998). Efficient multispin homonuclear double-quantum recoupling for magic-angle spinning NMR: ¹³C-¹³C correlation spectroscopy of U-¹³C-erythromycin A. J. Am. Chem. Soc., 120, 10602 – 10612.
- Royer, L., De, S.K & Gibbs, R.A. (2005). Iodine as a novel and efficient reagent for the synthesis of a-aminonitriles by a three-component condensation of carbonyl compounds, amines, and trimethylsilyl cyanide. *Tetrahedron Lett.*, 46, 4595 – 4597.
- Rudzka, K., Arif, A.M. & Berreau, L.M. (2005). Chemistry of a Ni(II) acetohydroxamic acid complex: formation, reactivity with water, and attempted preparation of zinc and cobalt analogues. *Inorg. Chem.*, 44, 7234 – 7242.
- Sacconi, L. (1954). Chemical reactions of complexes VII: reaction of hydrazides and aromatic o-oxy- and o-aminoaldehydes and ketones with nickel acetate. J. Am. Chem. Soc., 76, 3400 – 3402.
- Sadeghi, S., Fathi, F., Esmaelli, A.A. & Naeimi, H. (2006). Novel triiodide ion-selective polymeric membrane electrodes based on some transition metal–Schiff base complexes. *Sensors & Actuators B: Chem.*, 114, 928 – 935.
- Sakiyan, I., Loğoğlu, E., Arslan, S., Sari, N. & Şakiyan, N. (2004). Antimicrobial activities of N-(2-hydroxy-1-naphthalidene)-amino acid(glycine, alanine, phenylalanine, histidine, tryptophane) Schiff bases and their manganes (III) complexes. *Biometals*, 17, 115 – 120.
- Schaftenaar, G. & Noordik, J.H. (2000). Molden: a pre- and post-processing program for molecular and electronic structures. J. Computer-Aided Mol. Design, 14, 123 – 134.
- Scott, A.P. & Radom, L. (1996). Harmonic vibrational frequencies: an evaluation of Hartree-Fock, Møller-Plesset, quadratic configuration interaction, density functional theory, and semiempirical scale factors. J. Phys. Chem., 100, 16502 – 16513.
- Scuseria, G.E. (1999). Linear scaling density functional calculations with Gaussian orbitals. J. Phys. Chem. A., 103, 4782 – 4790.
- Simpson, J.H. (2012). Organic structure determination using 2-D NMR spectroscopy: a problem-based approach. Amsterdam: Elsevier.

- Sinha, P., Boesch, S.E., Gu, C., Wheeler, R.A. & Wilson, A.K. (2004). Harmonic vibrational frequencies: scaling factors for HF, B3LYP, and MP2 methods in combination with correlation consistent basis sets. *J. Phys. Chem. A., 108*, 9213 – 9217.
- Stephens, P.J., Devlin, F.J., Chabalowski, C.F. & Frisch, M.J. (1994). Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. J. Phys. Chem., 98, 11623 – 11627.
- Sridhar, S.K., Saravanan. M. & Ramesh, A. (2001). Synthesis and antibacterial screening of hydrazones, Schiff and Mannich bases of isatin derivatives. *Eur. J. Med. Chem.*, 36, 615 – 625.
- Sridhar, S.K., Pandeya, S.N., Stables, J,P. & Ramesh, A. (2002). Anticonvulsant activity of hydrazones, Schiff and Mannich bases of isatin derivatives. *Eur. J. Pharm. Sci.*, 16, 129 – 132.
- Tarafder, M.T.H., Ali, M.A., Saravanan, N., Weng, W.Y., Kumar, S., Umar-Tsafe, N. & Crouse, K.A. (2000). Coordination chemistry and biological activity of two tridentate ONS and NNS Schiff bases derived from S-benzyldithiocarbazate. *Transition Metal Chem.*, 25, 295 – 298.
- Van Rossum, B-J., Förster, H. & de Groot, H.J.M. (1997). High-field and highspeed CP-MAS ¹³C NMR .hetero nuclear dipolar-correlation spectroscopy of solids with frequency-switched Lee-Goldburg homonuclear decoupling. J. Magn. Reson., 124, 516 – 519.
- Xing, Y.H., Aoki, K., Bai, F.Y., Zhang, Y.H. & Zhang, B.L. (2008). Synthesis and structure of di-μ-oxo-bistripyrazolylborato dioxo vanadium (V) complex with lattice of diacetonitrile. *J. Chem. Cryst.*, *38*, 327 331.
- Zandler, M.E. & D'Souza, F.(2006). The remarkable ability of B3LY-P/3-21G^(*) calculations to describe geometry, spectral and electrochemical properties of molecular and supramolecular porphyrin–fullerene conjugates. *Comt. R. Chim.*, *9*, 960–981.
- Zhang, F. & Brüschweiler, R. (2004). Indirect covariance NMR spectroscopy. J. Am. Chem. Soc., 126, 13180 – 13181.
- Zhang, G. & Musgrave, C.B. (2007). Comparison of DFT methods for molecular orbital eigenvalue calculations. J. Phys. Chem. A., 111, 1554 1561.

Mr. Mohammad Mahdi Akbarzadeh (corresponding author)

Faculty of Sciences Islamic Azad University Science and Research Branch P.O. Box 14778-93855 Tehran, Iran E-mail: mehdiakbarzadeh10@yahoo.com