Journal of Molecular Structure 1062 (2014) 44–47

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Synthesis, FT-IR, NMR and DFT analysis of a new salophen based on diaminophenazine moiety

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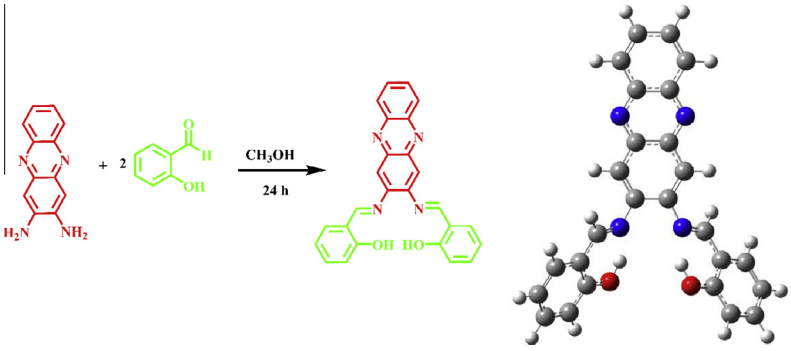
HIGHLIGHTS

- A new salophen was synthesized based on a phenazine moiety.
- Geometry of prepared salophen was examined by DFT method at B3LYP/631G(d) level.
- IR and NMR spectra were calculated by DFT method using camB3LYP/6311+G(d) level.
- RMS errors for the NMR and IR are 0.75 ppm and 94.9 cm^{-1} respectively.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 December 2013
Received in revised form 7 January 2014
Accepted 7 January 2014
Available online 17 January 2014

Keywords:
Diaminophenazine
Salophen
DFT calculation

ABSTRACT

As a rigid diamine, diaminophenazine was prepared by the condensation of 1,2-phenylene diamine and characterized by FT-IR and EI mass spectroscopy. Then, a new salophen was synthesized based on a phenazine moiety, by the condensation of salicylaldehyde and synthesized diamine. The prepared salophen was characterized by FT-IR and ^{1}H NMR spectroscopy. The geometry of the prepared salophen was examined by density functional theory (DFT) method at B3LYP/6-31G(d) level. Also, due to the structure of salophen, IR and NMR spectra of the more stable isomers were calculated by DFT method using camB3LYP/6-311+G(d) level and compared with the experimental results. Also, root mean square (RMS) errors observed between the experimental and calculated results for the NMR and IR were 0.75 ppm and 94.9 cm^{-1}.

1. Introduction

Schiff base ligands are known as "privileged ligands" due to simple preparation by the condensation of primary amines and an aldehyde. Salens, as one class of Schiff base ligands, were prepared by the condensation of salicylaldehyde derivatives and 1,2-diamines [1,2]. Salen-type ligands are known as multipurpose and tunable chelate ligands [3]. One interesting feature of salen-type ligands is their facile variation of electronic and steric properties [4]. For example, different substituents can be placed on the phenol rings that change steric properties of the respective salen [5]. These compounds and their transition metal complexes, because of unique properties, are interesting and used in many fields of chemical research such as biochemistry, luminescence [6–8], sensor and catalysis [8–12]. These compounds act as an initiator [13] or homogenous catalyst [14] for many reactions including: polymerization [15,16], cyclization, ring opening, epoxidation of alkenes [17], oxidation and other reactions [1,4,18–21]. For example, Coletti et al. reported the synthesis of some salophen

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http://dx.doi.org/10.1016/j.molstruc.2014.01.012

and salen oxo vanadium complexes that were used for sulfide oxidation; also, Tong et al. reported the synthesis of luminescent host systems based on binuclear platinum(II) and zinc(II) complexes based on salophen ligands [7].

In recent years, quantum mechanics computation has largely been developed by the progress of computers. These methods are used for predicting and confirming structural, thermodynamical, electronical, and molecular properties such as equilibrium structure, UV–Vis spectra, charge distribution, FT-IR and NMR spectra. Among various methods, density functional theory (DFT) is the most popular method that is widely used for computational works [22–26]. Salens can adopt several isomers contributing to tautomerism. Computational methods can be used for structural studies of salens.

In this work, a new salophen containing phenazine moiety was synthesized and characterized by various spectroscopic methods. Also, DFT method was used to study different probable salophen structures. Then, the main structure of salophen was confirmed according to stabilization energy. Computational data were compared to the experimental results, showing a good correlation.

2. Results and discussion

2.1. Synthesis and characterization of 2,3-diaminophenazine (1)

2,3-Diaminophenazine (1) was synthesized by the condensation of 2 mmol of 1,2-phenylene diamine in the presence of $FeCl_3$ at room temperature. Fig. 1 shows FT-IR spectra related to compounds (1) and (2). FT-IR spectrum of compound (1) showed two peaks at 3394 and 3188 cm^{-1} and a peak at 1633 cm^{-1} that were assigned to NH_2 and C=N group, respectively. Peaks at 1505 and 1552 cm^{-1} were assigned to C=C vibrations; also C—N vibration appeared at 1240 cm^{-1}.

Fig. 3 shows E.I. mass spectrum of 2,3-diaminophenazine (1). According to this image, molecular ion peak appeared in $m/z = 210$ due to the rigid structure of compound (1), molecular ion peak known as the base peak. Also, elemental analysis was measured and the experimental result showed a good agreement with the calculated one.

2.2. Geometry and molecular properties

Different isomers related to salophen are depicted in Fig. 4. Table 1 shows stabilization energy of different salophen isomers. According to the calculated energy, the main isomer was more stable than tautomers 1 and 2. So, the main isomer as the predominant product was selected and examined by computational IR and NMR.

Table 1
Stabilization energy of different salophen isomers.

Isomer	Method	Energy (kCal/mol)
Main isomer	camB3LYP/6-311+G(d)	0
Tautomer 1	camB3LYP/6-311+G(d)	3.926
Tautomer 2	camB3LYP/6-311+G(d)	6.473

2.3. Synthesis and characterization of salophen (2)

Salophen (2) was synthesized by the condensation of 1 mmol of 2,3-diaminophenazine and 2 mmol of salicylaldehyde. The prepared compound was investigated by FT-IR and ^1H NMR spectroscopy. Fig. 2 shows FT-IR spectrum of compound (2). This spectrum showed a broad peak at 3433 cm^{-1} which was assigned to OH group and a peak at 1630 cm^{-1} was related to C=N group; also C=C peak appeared in 1505 cm^{-1}. Computational IR spectrum of compound (2) was calculated by DFT method using camB3LYP/6-311+G(d) level and compared with the experimental results in Table 2. RMS errors between the calculated and experimental results of IR spectrum were 94.9. So, the computational result confirmed the experimental result of FT-IR spectroscopy.

The synthesized salophen was characterized by ^1H NMR spectroscopy. Fig. 5 shows ^1H NMR spectrum of compound (2). According to this image, protons related to OH group showed 2 different peaks at 12.90 and 13.56 ppm; also aromatic hydrogens appeared in the range of 7.09–8.50 ppm. NMR spectrum of compound (2) was also examined by DFT method at camB3LYP/6-311+G(d) level. Table 3 shows computational results of salophen (2). Computational results showed a good correlation with the experimental result, indicating 2 peaks for OH groups. RMS errors for NMR spectrum were 0.75 ppm.

3. Experimental

3.1. Materials

1,2-Phenylene diamine, salicylaldehyde, $FeCl_3$, methanol and dimethyl sulfoxide (DMSO) were purchased from Merck and Sigma–Aldrich chemicals Company. DMSO, as the solvent, was dried over barium oxide and then distillated. Also 1,2-phenylene diamine was purified by sublimation.

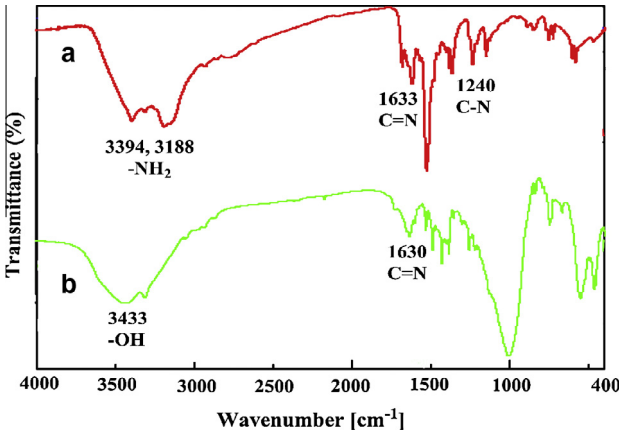


Fig. 1. FT-IR spectra related to; (a) compound (1) and (b) compound (2).

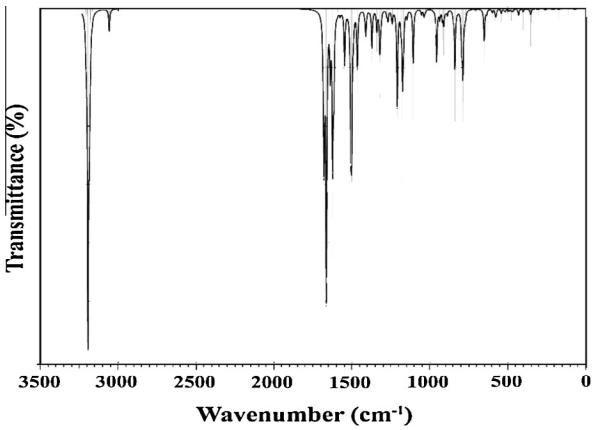


Fig. 2. Calculated IR spectrum of salophen (2).

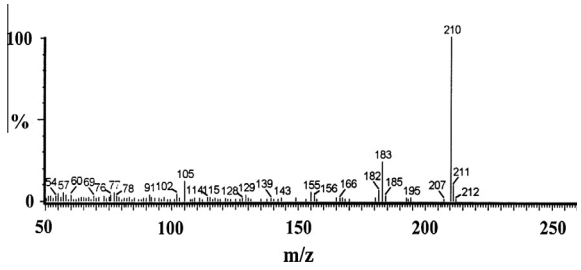


Fig. 3. Mass spectrum of 2,3-diaminophenazine (1).

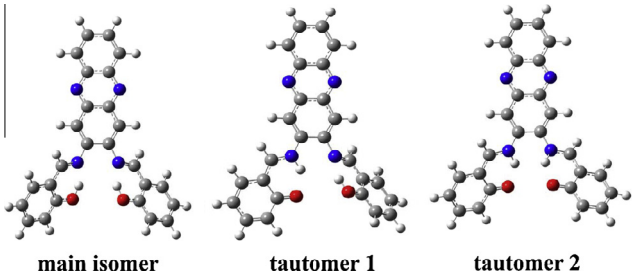


Fig. 4. Different salophen isomers.

Table 2
Calculated and experimental FT-IR spectra.

Functional group	camB3LYP/6-311+G(d) (cm^{-1})	Experimental (cm^{-1})
OH	3217	3433
C=N	1623	1630
C=C	1501	1505
C=C	1546	1552
C—N	1246	1257
C—O	1005	956

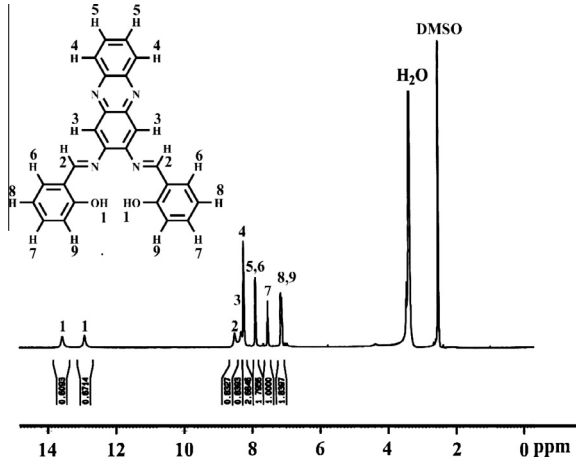


Fig. 5. ^{1}H NMR spectrum of salophen (2).

3.2. Techniques

FT-IR spectra were recorded using a Jasco-680 FT-IR spectrophotometer (Japan) with KBr pellet. Vibration bands were reported as wavenumber (cm^{-1}). The band intensities were classified as weak (w), medium (m), strong (s), broad (br) and shoulder (sh). ^{1}H NMR (500 MHz) spectra were obtained in deuterated dimethylsulfoxide (DMSO-d_6) on a Bruker Avance 500 MHz instrument (Bruker, Rheinstetten, Germany). Chemical shifts are given in the δ scale and in parts per million (ppm). Proton resonances are designated as singlet (s), doublet (d), triplet (t) and multiplet (m). UV–Vis absorption spectra were obtained in DMSO (ca. $\times 10^{-5}$ mol/L) on a JASCO-570, UV–Vis spectrometer. EI mass spectrum was measured by Micromass LCT time-of-flight (TOF) mass spectrometer in dithranol matrix and elemental analysis was also performed by Malek-Ashtar University of Technology, Tehran, Iran.

Table 3
Computational results related to ^{1}H NMR spectrum of salophen (2).

H atom	camB3LYP/6-311+g(d) (ppm)	Experimental (ppm)
H_1	11.41	13.46
H_1	10.46	12.80
H_2	9.15	8.60
H_2	9.00	8.60
H_3	8.42	8.31
H_3	8.33	8.31
H_4	8.10	8.24
H_4	8.06	8.24
H_5	8.06	8.19
H_5	7.99	8.19
H_6	7.85	7.88
H_6	7.73	7.88
H_7	7.67	7.52
H_7	7.64	7.52
H_8	7.07	7.13
H_8	7.03	7.13
H_9	7.03	7.10
H_9	6.98	7.10

3.3. Computational study

DFT calculations with Becke's three-parameter hybrid exchange functional (B3) and the correlation functional of Lee, Yang, and Parr (LYP) were performed on a personal computer using Gaussian 09. Geometry optimization of E,E isomer and the related tautomers, without any symmetry restriction, was performed by DFT method using B3LYP/6-31G(g) level. Then, in order to access energy and the calculated IR spectra, frequency calculation was performed at camB3LYP/6-311+G(d) level of DFT method. Also, the calculated NMR spectra were achieved by NMR calculation at the same level of frequency computations. RMS errors were calculated for IR and NMR spectra using the following expression [27].

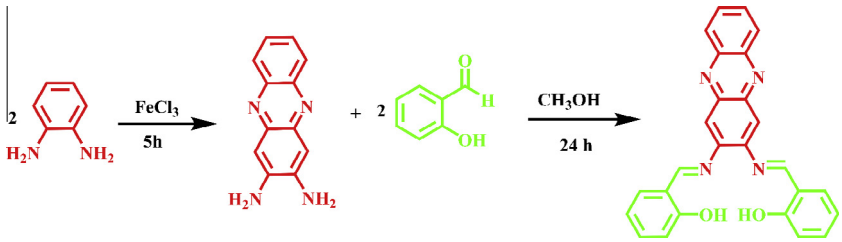
$$\mathrm{RMS} = \sqrt{\frac{1}{n-1}\sum_i^n \left(\nu_i^{\mathrm{calcu}} - \nu_i^{\mathrm{exp}}\right)^2} \quad (1)$$

3.4. 2,3-Diaminophenazine synthesis (1)

2,3-Diaminophenazine was prepared according to the procedure reported in the literature [28]. 6 mL of 0.08 mol/L aq $FeCl_3$ solution was added into 30 mL of a 0.02 mol/L aqueous 1,2-phenylene diamine solution with fast stirring at ambient temperature. A quick color change from purple-black to reddish-brown was observed upon the addition of $FeCl_3$. After 5 h, white precipitate was formed. The solid was washed many times with deionized water, and then separated by centrifugation and sublimated to achieve compound 1 as a white crystal. Yield = 98%; mp > 300 °C. FT-IR (KBr, cm^{-1}) ν: 3394 (s), 3313 (s), 3188 (w), 1692 (m), 1633 (m), 1531 (s), 1478 (s), 1383 (m), 1371 (m), 1240 (m), 1149 (m), 891 (w), 834 (m), 772 (m), 750 (m). EI/MS m/z ($C_{12}H_{10}N_4$): M^+, 210. Anal. Calc. for $C_{12}H_{10}N_4$ (%): C 68.56, H 4.79, N 26.65; found: C 68.42, H 4.71, N 26.59.

3.5. Salophen synthesis (2)

In a 25 mL round-bottom flask, 0.21 g (1 mmol) of 2,3-diaminophenazine (1) and 0.244 g (2 mmol) of salicylaldehyde were added to 10 mL absolute methanol and refluxed with stirring for 24 h.



Scheme 1. Synthesis of salophen.

Then, the resulted precipitate was filtered and washed with methanol to give a light brown precipitate of salophen (2). Purity of salophen (2) was assigned by TLC. Yeild = 77%; FT-IR KBr (cm^{-1}) *v:* 3433 (br), 3301 (m), 3043 (w), 1630 (m), 1530 (w), 1487 (w), 1429 (w), 1384 (m), 1257 (w), 1010 (s), 750 (w), 555 (m), 466 (m); ^{1}H NMR (500 MHz, DMSO-d_6): δ = 13.56 (br, 1H, OH), 12.90 (br, 1H, OH), 8.50 (s, 2H, CH═N), 8.31 (s, 2H, Aromatic H), 8.24 (s, 2H, Aromatic H) 8.17 (s, 2H, Aromatic H), 7.88 (s, 2H, Aromatic H), 7.52 (t, 2H, Aromatic H), 7.13 (m, 2H, Aromatic H) ppm, 7.10 (m, 2H, Aromatic H) ppm; UV–Vis (DMSO): λ = 273, 406, 521 nm (see Scheme 1).

4. Conclusion

Here, for the first time, a rigid diamine was synthesized and characterized by FT-IR and E.I. mass spectroscopy. Then a new salophen was prepared by the condensation of the prepared diamine and salicylaldehyde. The synthesized salophen was characterized by FT-IR and ^{1}H NMR spectroscopy. Also DFT calculations were performed for geometry optimization and structural analysis of the prepared salophen. Computational studies confirmed and showed a good correlation with the experimental result.

Acknowledgements

We gratefully acknowledge the partial financial support from the Research Affairs Division Isfahan University of Technology (IUT), Isfahan. Further partial financial support of Iran Nanotechnology Initiative Council (INIC), National Elite Foundation (NEF) and Center of Excellency in Sensors and Green Chemistry (IUT) is also gratefully acknowledged.

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