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Synthesis and Some Quantum Chemistry Study of Symmetrical Schiff-base Containing Dithio Group

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The reaction between *bis*-(2-aminophenyl) disulfide and 4-phenyl azo salicylaldehyde yields a symmetrical Schiff-base N,N´-[dithio *bis*-(*ortho*-phenylene) *bis*-(4-azophenyl) salicylaldehyde]. This compound has been characterized by spectral methods. Geometric parameters for this Schiff-base compound and its corresponding dianion has been calculated by using AM1 semi-empirical quantum mechanical method. The most stable conformer and the charge density for all coordination sites have been determined by theoretical calculations.

Key Words: Schiff base, Theoretical calculation, AM1, Dithio Schiff base.

INTRODUCTION

The Schiff-base derived from salicylaldehyde (Salens) polydentate ligands are known to form stable complexes with transition metal ions[1-4]. Schiff-bases show important in the pharmaceutical, dye and plastic industries as well as for liquid-crystal technology and mechanistic investigation of drugs used in pharmacology, biochemistry and physiology[5]. We have recently reported the successful use of some Schiff-base compounds in construction of poly vinyl chloride powder (PVC)- based membrane selective sensors[6-9] for Ni^{2+}, Ag^{+}, Fe^{3+} and Cd^{2+}. In some of recently works we studied the Schiff bases as nonlinear optical materials[10-13].

The interaction between *bis*-(2-aminophenyl) disulfide and 4-phenyl azo salicylaldehyde yields a symmetrical Schiff-base N,N´-[dithio *bis*-(*ortho*-phenylene) *bis*-(4-azophenyl) salicylaldehyde] (Fig. 1). The electronic structure of this compound has been investigated by some theoretical calculations. Computational quantum chemistry study may be used as an analytical instrument in structural analysis. All calculations were carried out by using HyperChem program package[14] with AM1[15] semi-empirical quantum chemistry method in high level.

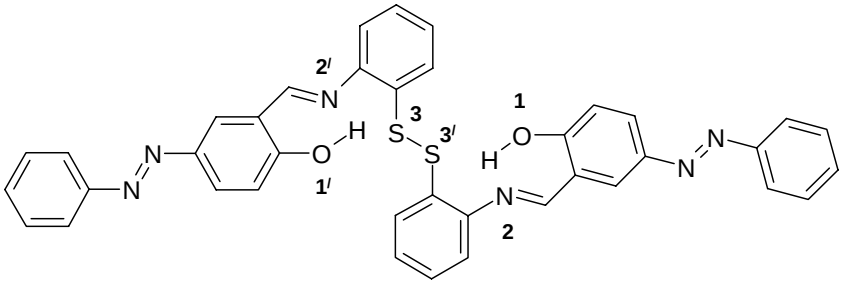

Fig. 1. Structure of N,N´-[dithio *bis*-(*ortho*-phenylene) *bis*-(4-azophenyl) salicylaldehyde]

EXPERIMENTAL

All solvents were dried and purified before use according to published procedure[16]. The other materials were used without further purification, a mixture of 0.001 mol of *bis*-(2-aminophenyl) disulfide in 10 mL CH_2Cl_2 and 0.002 mol of 4-phenyl azo salicylaldehyde in 10 mL CH_2Cl_2 was refluxed for 8 h. The reaction mixture changed from deep yellow to orange. The precipitate was collected and washed with cold absolute ethanol. This product was recrystallized with a solution of 50: 50 ethyl acetate and ethanol and orange crystalline N,N´-[dithio *bis*-(*ortho*-phenylene) *bis*-(4-azophenyl) salicylaldehyde] was obtained: Yield 67%; m.p. 199-200ºC. Anal. (%) calcd. for $C_{38}H_{28}N_6O_2S_2$: C, 68.67; H, 4.21; N, 12.65. Found: C, 68.43; H, 4.11; N, 12.34. The structure of Schiff-base was confirmed by ^{1}H NMR, ^{13}C NMR, UV-Vis, FT-IR and mass spectrometry. FT-IR spectra of 4-phenyl azo salicylaldehyde and Schiff-base reveals that the absorption band of CO group 1668 cm^{-1} disappeared and a new absorption band 1623 cm^{-1} due to (C=N) group appeared upon the condensation. ^{1}H NMR (Bruker AM 400, DMSO with TMS as internal standard), δ: 13.01 (2H, s, OH), 8.4 (2H, s, CH=N) and 7.00-7.32 (24H, d, phenyl). UV-Vis spectral data (DMF as solvent): λ_{max} = 365 nm.

Quantum chemistry calculations

The geometry of N,N´-[dithio *bis*-(*ortho*-phenylene) *bis*-(4-azophenyl) salicylaldehyde] was optimized on AM1 semi-empirical calculation, using HypeChem 5.00 Molecular visualization and Simulation Program[14]. The geometry of mentioned Schiff-base and its corresponding dianion were optimized and the charge densities on the coordination sites were determined. This method has been widely used to predict coordination sites[17]. Fig. 2 shows the calculated net charges on N(1), N(1´), O(1), O(1´), S(3) and S(3´) atoms in the structure of N,N´-[dithio *bis*-(*ortho*-phenylene) *bis*-(4-azophenyl) salicylaldehyde] Schiff-base compound.

The N(1), N(1´), O(1) and O(1´) coordination atoms have negative charges (-0.191, -0.190, -0.264 and -0.264), but S(3) and S(3´) atoms have positive charges (0.103, 0.103), Fig. 2.

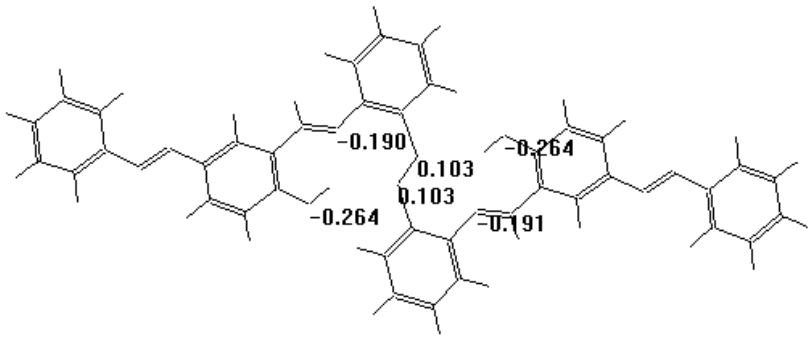

Fig. 2. AM1 calculated net charges on N(1), N(1´), O(1), O(1´), S(3) and S(3´) atoms in the structure of N,N´-[dithio *bis*-(ortho-phenylen) *bis*-(4-azophenyl) salicylaldehyde] Schiff-base compound

The optimized structure of N,N´-[dithio *bis*-(*ortho*-phenylene) *bis*-(4-azophenyl) salicylaldehyde] Schiff-base dianion was shown in Fig. 3.

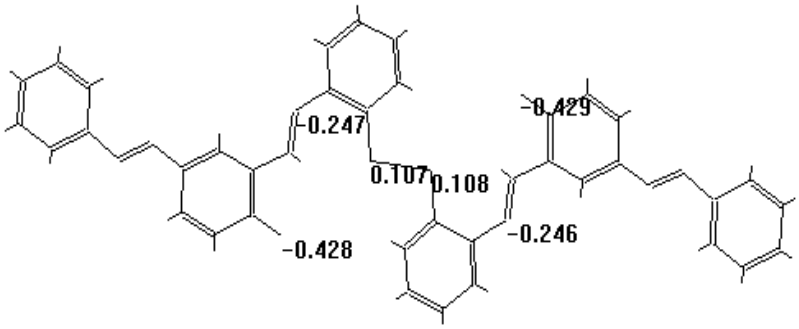

Fig. 3 AM1 calculated net charges of dianion on coordination sites for of N,N´-[dithio *bis*-(*ortho*-phenylene) *bis*-(4-azophenyl) salicylaldehyde] Schiff-base

Figs. 2 and 3 show, the N(1), N(1´), O(1) and O(1´) are active sites of this ligand for binding to the metal ions, but S(3) and S(3´) atoms have not any role in the coordination property of this tetradentate Schiff base. AM1 Mulliken populations in the N and O coordination atoms of N,N´-[dithio *bis*-(*ortho*-phenylene) *bis*-(4-azophenyl) salicylaldehyde] Schiff-base and its dianion are given in Table-1. The Mulliken population analysis shows an increasing in the population of P_x and P_z on the N(1) and N(1´) atoms and an increasing in the population of S, P_x and P_z on the O(1) and O(1´) atoms. These results indicates that the coordination sites of two nitrogen atoms and two oxygen atoms possess different character in generation of the Schiff base complexes with metal ions.

TABLE-1
CALCULATED MULLIKEN POPULATIONS FOR N(1), N(1´), O(1) AND O(1´) ATOMS OF N,N´-[DITHIO *bis*-(*ortho*-PHENYLENE) *bis*-(4-AZOPHENYL) SALICYLALDEHYDE] SCHIFF-BASE AND CORRESPONDING DIANION

Atomic orbital	Ligand				Anion			
	N(1)	N(1´)	O(1)	O(1´)	N(1)	N(1´)	O(1)	O(1´)
S	1.6900	1.6903	1.8561	1.8561	1.6860	1.6859	1.9151	1.9151
P_x	0.9780	0.9781	1.1993	1.1995	1.1155	1.1150	1.5333	1.5355
P_y	1.3443	1.3419	1.3463	1.3472	1.2158	1.2165	1.4907	1.4889
P_z	1.1783	1.1853	1.8618	1.8607	1.2289	1.2290	1.4892	1.4888

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