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Synthesis and Characterization of Two Novel Bidentate N,O-Coordinated Schiff-base Compounds

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Two new mono azo Schiff-base ligands 5-[((4-methyl phenyl) azo)-N-(2-aminopyridine) salicylaldimine] (S_1) and 5-[((4-methyl phenyl) azo)-N-(2-amino-1,2-dicyanomalonitrile) salicylaldimine] (S_2), were reported by the reaction of suitable precursor ligands with 2,6-diaminopyridine and 1,2-diamino dicyano ethylene. Elemental analysis, ^{1}H-NMR, ^{13}C-NMR, UV, FT-IR and G.C. mass spectroscopy methods characterized the prepared compounds. Some theoretical calculations on the nonlinear optical properties of these Schiff base ligands by AM1 semiempirical method (Austin Model 1) have also been investigated.

Key Words: Schiff base ligand, Coordination chemistry, 2,6-diaminopyridine and 1,2-diamino dicyanoethylene and NLO property.

INTRODUCTION

The Schiff base of Salen type is able to form complexes with a wide variety of metal centres, ranging from soft to hard ions[1–3]. Schiff base and its metal complexes find interest in organic chemistry and bioorganic chemistry[4]. In recent years considerable interest has been shown in the preparation of compounds with nonlinear optical property (NLO), which finds application in dye laser technology and optical devices[5–6]. Organic molecules and polymers have been intensively studied with respect to their potential applications as nonlinear optical media. The interest for nonlinear optical materials has been stimulated by the expectation of lower cost, faster optical response and higher versatility to adjusting the structure for their nonlinear optical properties.

Quantum chemistry calculations have been shown to be useful in the description of the relationship among the electronic structures of the molecular systems and nonlinear optical response[9, 10].

We have reported some azo Schiff base compounds with NLO properties elsewhere[7, 8]. However, to our knowledge, there are no experimental or theoretical studies concerning the NLO properties of 5-[((4-methyl phenyl) azo)-N-(2-aminopyridine) salicylaldimine] (S_1) and 5-[((4-methyl phenyl) azo)-N-(2-amino-1,2-dicyanomalonitrile) salicylaldimine] (S_2) Schiff base compounds [Fig. 1]; so we prepared these compounds and then we did some theoretical calculations about

the properties of S_1 and S_2 Schiff base ligands. We optimized the structures and showed the rate of theoretical NLO property, the lengths of bonds and the symmetry for molecular orbital of two of S_1 and S_2 compounds.

EXPERIMENTAL

All solvents were dried and purified before use by standard methods being used according to literature[11]. Salicylaldehyde, 4-methyl aniline, 1,2-dicyanomalonitrile and 2,6-diaminopyridine were used without further purification (reagent grade, Merck or Fluka).

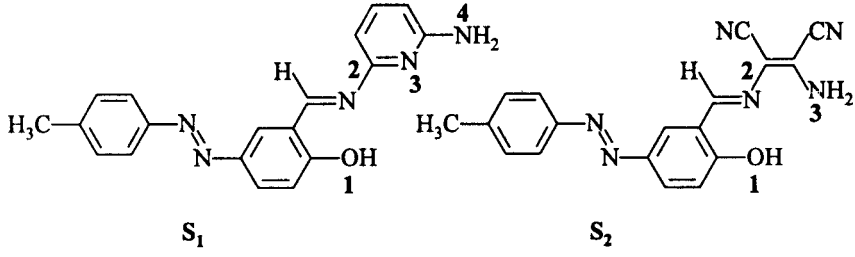

Fig. 1. Structures of Schiff bases

Syntheses

Both Schiff bases S_1 and S_2 were purified using standard procedure[11] involving reaction of the appropriate salicylaldiminato precursor ligand with the corresponding diamine (1 : 1 molar ratio) in ethanol. The coloured imines were purified by recrystallization from ethanol (yields 67–75%).

The analytical results and some physical properties of the isolated S_1 and S_2 Schiff base ligands have been shown in Table-1.

TABLE-1
SOME IMPORTANT PHYSICAL PROPERTIES AND ANALYTICAL RESULTS FOR S_1 AND S_2 SCHIFF BASE LIGANDS

Compound	Formula weight g/mol	Colour	m.p. (°C)	Yield (%)	% Analysis: Calcd. (Found)		
					C	H	N
$C_{19}H_{17}N_5O$	331	Orange	238	46	68.88 (68.60)	5.13 (5.12)	21.14 (20.90)
$C_{18}H_{14}N_6O$	330	Brown	251	54	65.45 (65.30)	4.24 (4.15)	25.45 (25.10)

Elemental analyses were performed on a Perkin-Elmer analyzer, ^{1}H-NMR and ^{13}C-NMR spectra were prepared on a Bruker AM 400 MHz, and UV-Vis spectra were reported with a Beckman DU-7000 spectrometer. FT-IR spectra were reported on a Shimadzu DR-8001.

Spectral data for S_1 ligand: IR ν_{max} (KBr)/cm^{-1}: 3372, 3115, 1540 and 1617 cm^{-1}. ^{1}H-NMR (Bruker AM 400 MHz, $CDCl_3$ solvent with TMS as an internal standard), δ 2.4 (3H, S, CH_3), 6–7.8 (7H, d, phenyl), 10.0 (1H, S, OH), 7.8–8 (1H, d, CH=N), 3.4–3.7 (3H, s, pyridine). ^{13}C-NMR (100 MHz, $CDCl_3$), δ: 15.0,

19.0, 20.0, 54.0, 58.0, 119.0, 120.0, 122.0, 128.0, 130.0, 131.5, 140.0, 145.0, 150.0, 162.0, 198.0. Electronic spectra (DMF as a solvent): λ_{max} = 373 n.m. G.C. mass spectral data: M/Z (331, 329, 210, 106, 91 and 65).

Spectral data for S_2 ligand: IR ν_{max} (KBr)/cm^{-1}: 3375, 3172, 1537 and 1610 cm^{-1}. ^{1}H-NMR (Bruker AM 400 MHz, $CDCl_3$ solvent with TMS as an internal standard), δ 2.38 (3H, s, CH_3), 6.6–8.1 (8H, s, phenyl), 8.25–8.30 (1H, s, CH=N), 11.1 (1H, s, OH). ^{13}C-NMR (100 MHz DMSO), δ: 20.0, 79.0, 102.0, 112.5, 115.0, 117.0, 121.0, 122.0, 124.0, 127.0, 128.0, 140.0, 142.0, 150.0, 152.0, 155.0. Electronic spectra (DMF as a solvent): λ_{max} = 349 nm. G.C. mass spectral data: M/Z (330, 331, 211, 157, 119, 91, 65 and 39).

Theoretical section

In recent years much effort has been focussed on the development of organic materials for nonlinear optics (NLO) use[12, 13]. These compounds have advantages, such as low cost and ease of processing, which make them very attractive to the industry.

In these materials, the second-order nonlinear optical properties are of special interest, because they produce important effects, such as second-harmonic generation. Based on these effects, important applications in optoelectronics[14], photonics and optical data storage have been developed[15].

Method of calculations

The theoretical second-order properties of S_1 and S_2 were calculated, using AM_1 semi-empirical-self-consistent field-molecular orbital (SCF-MO) method by MOPACK 6.0 program package[16]. S_2 Schiff base compound is attractive for second-order NLO property, because S_2 compound has one CH_3 group as electron donating and two CN groups as electron-withdrawing groups in the structure. The calculated NLO property (β) for S_1 and S_2 Schiff base compounds are given in Table-2.

TABLE-2
NLO PROPERTY (β) FOR S_1 AND S_2 SCHIFF BASE COMPOUNDS

Schiff base	μ^a, Debye	$\beta_\mu \times 10^{-30}$ esu[b]
S_1		1.617
	μ_x, –0.93	
	μ_y, –3.072	
	μ_z, 0.014	
	μ, 3.213	
S_2		2.638
	μ_x, 0.336	
	μ_y, 3.134	
	μ_z, –1.424	
	μ, 3.459	

[a]Dipole moments [b]First hyperpolarizability.

The net charges of some coordination atoms in the structures of S_1 and S_2 Schiff base compounds have been shown in Fig. 2.

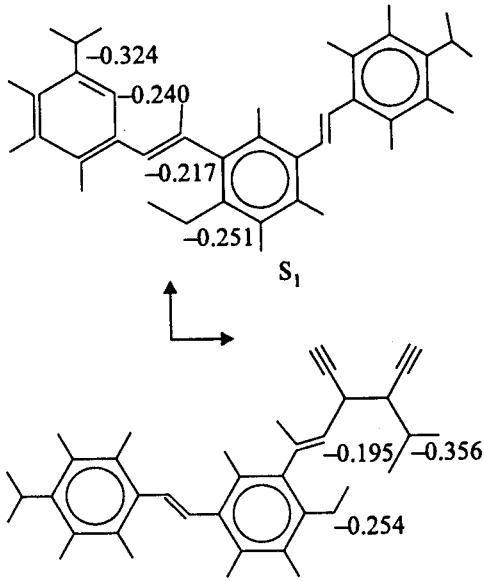

Fig. 2. Some net charge on coordinating atoms in the structures of S_1 and S_2 compounds

Conclusion

Two bidentate N,O-coordination atoms Schiff base ligands S_1 and S_2 have been prepared very easily by condensation of precursor ligands and suitable amines, confirmed the structures by the absence of (C=O) stretching and presence of strong (C=N) stretching bands for both S_1 and S_2 Schiff base compounds. This conclusion is also supported by the elemental analysis, ^{1}H-NMR, ^{13}C-NMR, UV, FT-IR and G.C. mass spectroscopy methods.

Also, according to the theoretical investigations both S_1 and S_2 Schiff base ligands have NLO property and the following conclusions can be drawn.

(1) The cyanide groups and also the number of double bonds play an important role in charge-transfer processes, in which the NLO property in the S_2 Schiff base compound is larger than S_1 Schiff base compound.

(2) Both S_1 and S_2 Schiff base ligands are bidentate ligands ($O_{(1)}$ and $N_{(4)}$ coordination atoms for S_1, $O_{(1)}$, and $N_{(3)}$ coordination atoms for S_2).

(3) The paper is developed for the synthesis and theoretical study of some Schiff base molecules for their NLO properties and the results will be helpful in the simulation and design of new organic NLO compounds.

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Effect of Deposited Stannous Chloride on the Flame-Retardancy Imparted to Cotton Fabric

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The effect of stannous chloride as a non-durable finish on the flammability of 100% cotton fabric (cotton woven construction, weighing 178 g/m^2) has been investigated. The laundered bonedried weighed fabrics were impregnated with suitable concentrations of aqueous stannous chloride solutions by means of squeeze rolls and dried at 65°C for 4 h. Afterwards they were cooled in a desiccator, weighed with analytical precision and kept under ordinary conditions before the fulfilment of the vertical flame test. The optimum add-on values to impart flame retardancy expressed in g anhydrous salt per 100 g fabric was about 5.0–7.71 g. The results with the impartation of stannous chloride into the cotton fabric are in favour of Free Radical Theory and also Vapour Phase Theory[1-3].

Key Words: Flammability, Flame-retardancy, Char length.

INTRODUCTION

As far as the domestic environment is concerned, residental fires annually kill between 15 and 20 thousand people in the United States alone[1]. It is noteworthly that the elderly are at greater risk of fatality due to clothing fires. While deaths due to ignition of clothing are obviously linked with the flammability of textile material, there are other hazards caused by fires. It is stated that over half of the fatalities were due to the combined effects of smoke and toxic gases[2]. These days the need for reduced flammability in various textiles has been increased by governmental legislations in many countries. Hence the incorporation of flame-retardants into consumer products such as fibres, fabrics, plastics etc. has gained great importance.

It is noticeable that the flame-retarding component[3,4] is intended to prevent a small fire from rapidly developing into a major catastrophe[1]. Therefore a flame-retarded material is believed to be combustible in the harsh ignition circumstances.

It is mentionable that the value of chemicals sold for use as flame-retardants in Europe in 2003 was forecast by the split of income between the three main categories[5-7]: phosphorus-based chemicals 38%, inorganic compounds including $Mg(OH)_2$, $ZnSnO_3$, Sb_2O_3 and borates 36% and halogen-based organics 26%. The