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Synthesis and Non-linear Optical Properties of Two New Tridentate Mono Azo Schiff-Base Compounds

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In the present work, two dissymmetric tridentate mono azo Schiff base ligands 5-((4-methyl phenyl)azo)-N-(N,N-dimethyl ethylamine) salicylaldimine and 5-((4-nitrophenyl) azo)-N-(N,N-dimethyl ethylamine) salicylaldimine were prepared by the reaction of precursor ligands with appropriate N,N-dimethyl ethylamine and characterized by FTIR, ^{1}H NMR, ^{13}C NMR, C, H and N elemental analyses and UV-Vis spectroscopy methods. In the other part of this work, some theoretical calculations were done on the structures by semi-empirical and *ab-initio* methods using AM1, PM3 and MINDO/1 Hamiltonians and the geometries of two synthesized tridentate ligands were optimized and then the non-linear optical properties of these ligands were characterized by theoretical calculations.

Key Words: NLO property, Salicylaldehyde, Schiff-base, Theoretical methods.

INTRODUCTION

Schiff-base ligands are one of the oldest classes of ligands in coordination chemistry and these compounds have been used extensively for coordination with transition and main group metal ions[1]. Also Schiff-base compounds have been studied in great details for various applications in chemistry[2–10]. On the other hand, N-donor ligands is an active field of chemical research and there are very reports of this type of Schiff-base ligands.

The interest in non-linear optics has grown tremendously in recent years, primaryily because of the telecommunication industry, need for high-bandwidth optical switching and processing devices to service the information and data transmission needs of the computer age and of the proliferation of sophisticated laser tools[11–13].

Quantum chemical calculations have made an important contribution to the understanding of the electronic polarization underlying the molecular non-linear optical (NLO) processes[14, 15]. Recently, there have been some reports that the NLO of organic compounds might increase by staggering of aromatic donor and acceptor subunits[16, 17].

With the above considerations in mind, we have designed and synthesized two new tridentate Schiff-base compounds, characterized their structures and studied the structures by using with AM1, PM3 and MINDO/1 semi-empirical methods. The calculated NLO property (β) for 5-((4-nitro phenyl)azo)-N-(N,N-dimethyl ethylamine)salicylaldimine ligand is 122.5 times of that of urea[16].

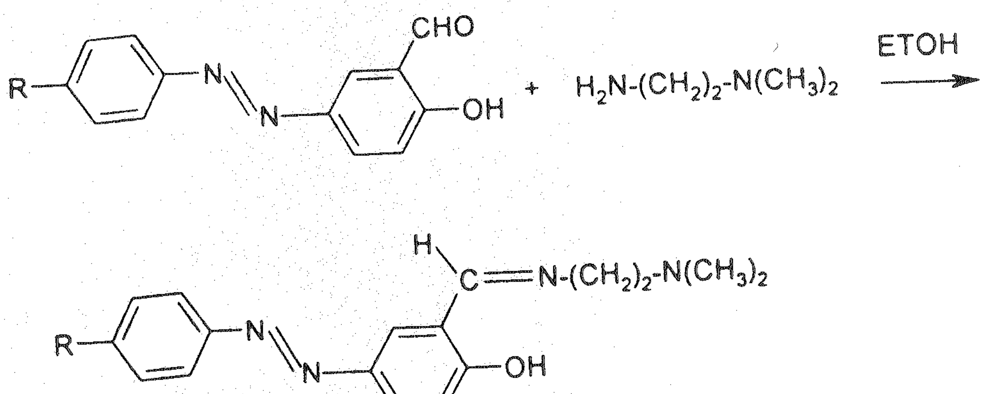
EXPERIMENTAL

All of the chemicals and solvents were of analytical reagent grade and were obtained commercially from Merck. The solvents were purified by standard methods. Two precursor ligands, 5-((4-methyl phenyl)azo)salicylaldehyde and 5-((4-nitro phenyl)azo)salicylaldehyde were synthesized according to previous procedure.

Elemental analyses for C, H and N were performed using a Perkin-Elmer analyzer. Infrared (FTIR) spectra were recorded using KBr discs on an FTIR Shimadzu Dr-8001 in the range of 4000–400 cm^{-1}. ^{1}H and ^{13}C NMR spectra were taken in DMSO on a Bruker Spectrospin Avance 400 MHz ultra shield spectrometer and chemical shifts are indicated in ppm relative to tetramethylsilane (TMS). The UV-Vis spectra were recorded with a Beckman DU-7000 spectrometer and mass spectra were recorded on a Finnigenmat G C-MSDS spectrometer model 8430.

Synthesis of Schiff-base compounds

The tridentate Schiff-base ligands, 5-((4-methyl phenyl)azo)-N-(N,N-dimethyl ethylamine)salicylaldimine **(a)** and 5-((4-nitro phenyl)azo)-N-(N,N-dimethyl ethylamine)salicylaldimine **(b)** were prepared in high yields (45–55%) *via* condensation of ethanolic solution of the appropriate precursor ligands with 1-amino-2-(N,N)-dimethylamine according to **Scheme-1**[18].



R	Schiff base
CH_3	a
NO_2	b

Scheme-1

a = 5-((4-methyl phenyl)azo)-N-(N,N-dimethyl ethylamine) salicylaldimine
b = 5-((4-nitro phenyl)azo)-N-(N,N-dimethyl ethylamine) salicylaldimine

A solution of 1.00 mmol of 1-amino 2-(N, N) dimethylamine in 10 mL absolute ethanol were added to a solution of 1.00 mmol of each precursor ligand in 10 mL absolute ethanol to give clear yellow or red solutions which were gently refluxed for about 9 h. Then evaporated the solvent and obtained two Schiff-base compounds, and then recrystallized the precipitates from ethanol and ethyl acetate (1 : 1 v/v). Some physical properties for two asymmetric tridentate 202 and 203 Schiff-base compounds have been shown in Table-1.

TABLE-1
SOME IMPORTANT PHYSICAL PROPERTIES OF SCHIFF-BASE LIGANDS

Compound	Formula weight (g/mol^{-1})	Colour	m.p. (°C)	Elemental analyses Calcd. (Found)			Yield (%)	Molar conductivity (DMF)
				C	H	N		
$C_{18}H_{22}N_4O$ (a)	310	Yellow	93	69.67 (69.0)	7.9 (6.9)	18.06 (17.8)	45	73.0
$C_{17}H_{19}N_5O_3$ (b)	341	Red	182^d	59.82 (59.3)	5.57 (5.2)	20.52 (20.1)	55	47.5

^{d}Decompose

Inspection of the FTIR spectra of precursor ligands and corresponding tridentate Schiff-base ligands reveals that the absorption band of keto group ν(CO) (1671–1660 cm^{-1}) disappeared and new absorption bands (1633–1615 cm^{-1}) for **a** compound and (1624–1620 cm^{-1}) for **b** compound due to ν(C=N) group appeared upon condensation, while the bands due to ν(OH) group in precursor ligands and corresponding Schiff-base compound lie at about 3450 cm^{-1}.

^{13}C NMR and ^{1}H NMR spectral data (Table-2) for Schiff base compounds in $CDCl_3$ solvent were taken on a Bruker spectrospin Avance 400 MHz Ultra Shield spectrometer and chemical shifts are indicated in ppm relative to TMS.

TABLE-2
^{1}H AND ^{13}C NMR DATA FOR SCHIFF-BASE LIGANDS

	Compounds	
	a	b
^{1}H NMR (ppm)	14.21 (br, 1H,OH)	14.33 (br, 1H, OH)
	8.65 (s, 1H, iminic)	7.027 (br, 1H, iminic)
	2.19 (s, 6H, aliphatic)	2.24 (s, 6H, aliphatic)
	2.49 (s, 3H, aliphatic)	2.60 (s, 2H, aliphatic)
	2.53 (s, 2H, aliphatic)	3.81 (s, 2H, aliphatic)
	3.70 (s, 2H, aliphatic)	7.04–8.45 (s, 2H, aliphatic)
	6.80–7.96 (d, 5H, aromatic)	
^{13}C NMR (ppm)	(4C, aliphatic)	(3C, aliphatic)
	21.32, 45.519	45.46, 55.79
	52.517, 58.989	59.176
	(10C, aromatic)	(10C, aromatic)
	116.46, 121.35	110.18, 117.43
	122.35, 126.56	119.79, 122.90
	130.18, 131.47	124.64, 127.07
	140.53, 142.518	130.18, 144.37
	150.56, 171.68	148.03, 165.33
	(1C, iminic)	(1C, iminic)
	166.64	155.97

Theoretical background

The configuration interaction method with Sum-Over-State method is used to compute the first hyperpolarizability. In this method, the formula for calculating β is shown below[19]:

$$\beta_{total} = (-(\omega_1 + \omega_2); \omega_1, \omega_2) = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

where β is the first hyperpolarizability tensor respectively, which represents the second-order NLO property of the molecule. Donor-acceptor substituted aromatic compounds, as large π-conjugated systems substituted with both strong electron donor and acceptor groups appear most suitable to show high second-order NLO properties[20].

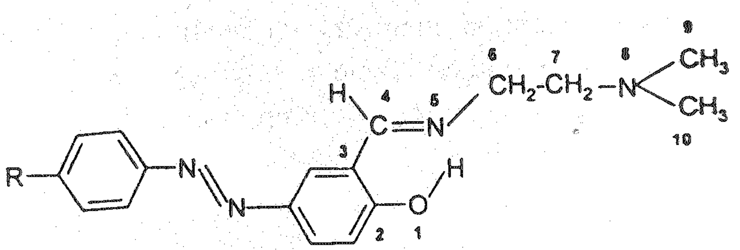
Calculation procedure: Calculations using *ab-initio* method by Cussian 94 package[21] and semi-empirical methods using MOPAC 7.0 program package[22] and the geometry optimization have been carried out at the DFT levels using the three-parameter fit of the exchange correlations potential suggested by (B3LYP)[23].

The semi-empirical methods used were MINDO/1[24, 25], AM1[26] and PM3[27].

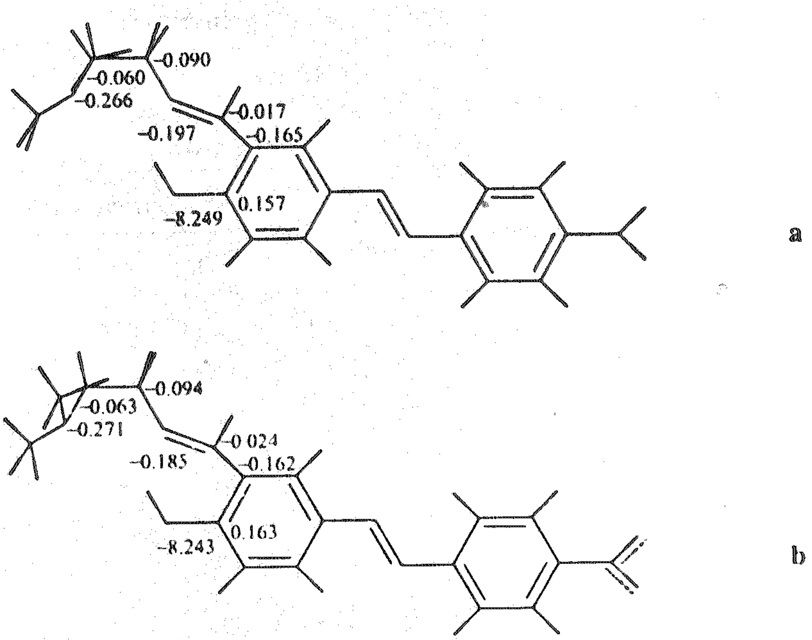
Some important calculated bond lengths, bond angles and the net charge on coordination sites of 202 and 203 Schiff-base compounds **(Scheme-2)** have been shown in Tables 3 and 4 and also the calculated net charge of some important atoms of Schiff-base compounds have been shown in **Scheme-3.**

TABLE-3
SOME IMPORTANT CALCULATED BOND LENGTHS (Å) AND BOND ANGLES (°) OF SCHIFF-BASE LIGANDS

	Method of calculation							
Bond length (Å)	AM1		PM3		MNDO/1		*Ab-initio*	
	a	b	a	b	a	b	a	b
$O_{(1)}\text{-}C_{(2)}$	1.365	1.364	1.350	1.348	1.350	1.348	1.364	1.363
$C_{(2)}\text{-}C_{(3)}$	1.407	1.413	1.411	1.414	1.428	1.429	1.410	1.412
$C_{(3)}\text{-}C_{(4)}$	1.471	1.472	1.463	1.463	1.485	1.486	1.470	1.471
$C_{(4)}\text{-}N_{(5)}$	1.285	1.285	1.296	1.296	1.289	1.289	1.285	1.285
$N_{(5)}\text{-}C_{(6)}$	1.436	1.436	1.463	1.463	1.464	1.454	1.436	1.436
$C_{(6)}\text{-}C_{(7)}$	1.544	1.544	1.530	1.530	1.552	1.552	1.543	1.543
$C_{(7)}\text{-}N_{(8)}$	1.453	1.454	1.492	1.492	1.472	1.472	1.453	1.453
Bond angle (°)								
$O_{(1)}\text{-}C_{(2)}\text{-}C_{(3)}$	125.26	125.19	123.97	124.02	125.09	125.15	125.20	125.22
$C_{(2)}\text{-}C_{(3)}\text{-}C_{(4)}$	123.45	123.28	122.53	122.47	124.75	124.61	123.40	123.39
$C_{(3)}\text{-}C_{(4)}\text{-}N_{(5)}$	122.06	122.75	119.18	119.07	121.12	120.94	122.11	122.52
$N_{(5)}\text{-}C_{(6)}\text{-}C_{(7)}$	120.87	120.91	121.96	121.97	122.22	122.31	120.90	120.91
$C_{(7)}\text{-}N_{(8)}\text{-}C_{(9)}$	112.97	112.97	110.48	110.57	112.87	112.92	112.96	112.96
$C_{(9)}\text{-}N_{(8)}\text{-}C_{(10)}$	113.79	113.65	111.51	111.55	113.46	113.56	113.72	113.69



Scheme-2



Scheme-3. Calculated net charges for some of the important atoms for **a** and **b** Schiff-base compounds

The amount of calculated first order non-linear optical properties (β) for tridentate ligands are shown in Table-4.

Table-4 indicates that monoazo Schiff-base compound (**b**) shows a good second-order non-linear optical response, because it has a strong donor and strong acceptor groups in delocalized π-system.

TABLE-4
NON-LINEAR OPTICAL PROPERTIES CALCULATED BY AM1 SEMI-EMPIRICAL METHOD FOR MONO AZO SCHIFF-BASE COMPOUNDS

Compound	μ^a, deby	$\beta^b\mu \times 10^{-30}$ esu
a	μ_x 2.342	−3.422
	μ_y 1.960	
	μ_z −0.283	
	μ 3.067	
b	μ_x 4.715	17.161
	μ_y 1.625	
	μ_z 1.816	
	μ 5.308	

$^a\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$ $^b\beta = (\beta_{zxx} + \beta_{zyy} + \beta_{zzz})$

Also, the ability of quantum chemistry for predicting coordination sites of Schiff-base ligands can be studied. Table-5 shows the molecular orbital of the anionic from of the tridentate Schiff-base compounds.

From Table-5, one can deduce that the MO more likely to combine with the metal orbital are Ψ_{57}, Ψ_{53} and Ψ_{50} for 202 ligand and Ψ_{53}, Ψ_{56} and Ψ_{59} for 203 tridentate Schiff-base ligand that are located mainly on the $O_{(1)}$, $N_{(5)}$ and $N_{(8)}$ atoms[29]. The calculated net charges on some of important atoms for **a** and **b** tridentate Schiff-base ligands are shown in **Scheme-3.**

TABLE-5
MOLECULAR ORBITALS OF ANIONIC FORM OF MONO AZO TRIDENTATE SCHIFF-BASE LIGANDS

MO	Symmetry	E (eV)	Contribution of AO to the MO		
			$O_{(1)}$	$N_{(5)}$	$N_{(8)}$
		a			
Ψ_{50}	σ	–8.7971	0.0000	0.0000	0.97251
Ψ_{51}	π	–8.3265	0.0000	0.0000	0.00000
Ψ_{52}	π	–7.8233	0.2321	0.0000	0.00000
Ψ_{53}	σ	–7.2410	0.0000	0.5978	0.00000
Ψ_{54}	π	–7.0151	0.0000	0.0000	0.00000
Ψ_{55}	π	–6.6956	0.0000	0.0000	0.00000
Ψ_{56}	π	–6.5350	0.0000	0.0000	0.00000
Ψ_{57}	σ	–6.2929	0.9594	0.0000	0.00000
Ψ_{58}	π	–6.1064	0.0000	0.0000	0.00000
Ψ_{59}	π	–6.0173	0.0021	0.0000	0.00000
Ψ_{60} (HOMO)	π	–3.9620	0.0047	0.0000	0.00000
		b			
Ψ_{53}	σ	–14.8913	0.0000	0.0000	0.97380
Ψ_{54}	π	–14.8763	0.0000	0.0000	0.00000
Ψ_{55}	π	–14.8172	0.0000	0.0000	0.00000
Ψ_{56}	σ	–14.7283	0.9419	0.0000	0.00000
Ψ_{57}	π	–14.5042	0.0000	0.0000	0.00000
Ψ_{58}	π	–14.4136	0.0000	0.0000	0.00000
Ψ_{59}	σ	–14.3651	0.0000	0.4675	0.00000
Ψ_{60}	π	–13.8996	0.0000	0.0000	0.00000
Ψ_{61}	π	–13.7369	0.0000	0.0000	0.00000
Ψ_{62}	π	–13.6370	0.0000	0.0000	0.00000
Ψ_{63}	π	–13.4980	0.0000	0.0000	0.00000
Ψ_{64} (HOMO)	π	–11.7370	0.0000	0.0000	0.00000

RESULTS AND DISCUSSION

Two Schiff-base compounds presented in this paper were obtained from easily available starting materials in good yields.

The molecular structures and electronic properties of these compounds were investigated by some semi-empirical methods (AM1, PM3, MINDO/1) and by *ab-initio* calculations.

Materials with non-linear optical properties (NLO) are of great interest for the development of photonic devices and these compounds have strong donor and acceptor groups. So, compound **b** must show a good response for (NLO) property because the NO_2 group is a good and strong acceptor group and dimethyl group is a good donor group. With the above considerations in mind, we designed and synthesized tridentate Schiff base ligands. However, it seems that the subsistent requires a special attention in designing of the NLO Schiff-base compounds.

According to the calculations (Table-5 and **Scheme-3**), we can make prediction of the coordination atoms in the structure of a ligand; so tridentate Schiff base ligands are in the range of tridentate unsymmetrical mono-azo Schiff-base ligands and O(1), N(5) and N(8) atoms are coordinated with transition metal ions.

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