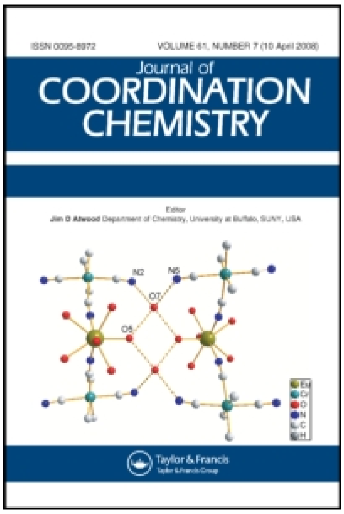

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Synthesis, characterization and theoretical study of the structure and second-order nonlinear optical properties of two new Monoazo Schiff-base compounds

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SYNTHESIS, CHARACTERIZATION AND THEORETICAL STUDY OF THE STRUCTURE AND SECOND-ORDER NONLINEAR OPTICAL PROPERTIES OF TWO NEW MONOAZO SCHIFF-BASE COMPOUNDS

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We describe the syntheses, characterization and theoretical investigation of two new monoazo Schiff-base ligands 5-[(4-methylphenyl)azo]-*N*-(2′-hydroxyphenyl)salicylaldimine (SB1) and 5-[(4-nitrophenyl)azo]-*N*-(2′-hydroxyphenyl)salicylaldimine (SB2). AM1 semiempirical calculations were used to study the structures, electronic properties and second-order nonlinearity of these compounds. Theoretical calculations are useful for describing the relationship between the electronic structure of molecular systems and their nonlinear optical (NLO) response. Second-order NLO calculations and comparison of the NLO properties of these ligands with others reveal that the presence of an NO_2 group enhances the second-order NLO properties of the ligands.

Keywords: Schiff-base ligands; AM1; PM3; MNDO; Nonlinear optical materials

INTRODUCTION

Quantum chemical calculations are useful for describing the relationship between electronic structures of molecules and their nonlinear optical (NLO) response [1,2]. Organic molecules and polymers have been studied intensively with respect to their potential applications as NLO media [3–6].

Materials with NLO properties are of great interest for the development of photonic devices such as electro-optic modulators, frequency generators and optical switches [7].

Quantum chemical calculations have been used to relate the electronic properties of molecular systems and their NLO response [8–10]. The length of bonding conjugation, the strength of donor and acceptor groups linked to phenyl groups, and the lowest

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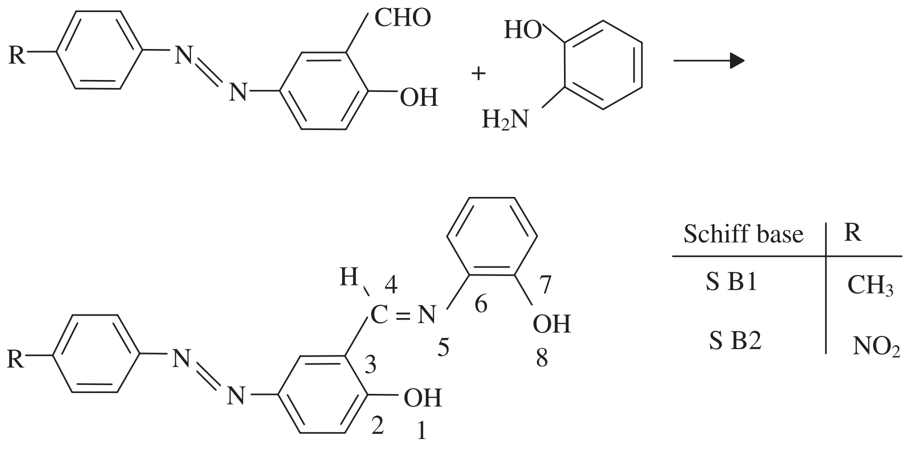

Schiff base	R
S B1	CH_3
S B2	NO_2

SCHEME 1

energy electronic absorption maximum have been considered among the parameters for optimization of the first hyperpolarizability [11–13].

In this work two new monoazo Schiff-base ligands were synthesized by condensation of two different precursor ligands with 2-aminophenol (Scheme 1). The electronic properties of the two new Schiff-base ligands 5-[(4-methylphenyl)azo]-*N*-(2′-hydroxyphenyl)salicylaldimine (SB1) and 5-[(4-nitrophenyl)azo]-*N*-(2′-hydroxyphenyl)salicylaldimine (SB2) and their monoanions were investigated by using SCF-MO methods.

EXPERIMENTAL

Materials

Salicylaldehyde, 4-nitroaniline and 2-aminophenol (reagent grade, Merck) and 4-methylaniline (reagent grade, Fluka) were used without further purification. The solvents ethanol, chloroform and DMF were dried and distilled before use by standard methods.

Preparation and Characterization of Schiff-base Ligands

We reported the preparation of some monoazo Schiff-base ligands in our previous work [14,15]. The SB1 and SB2 Schiff-base ligands were synthesized by combining equimolar amounts of precursor ligand and 2-aminophenol in suitable boiling solvents. Precursor ligands were prepared by standard methods [16]. The two Schiff-base ligands were prepared in high yields (65–72%) by condensation of the appropriate precursor ligand with 2-aminophenol in 1:1 ethanol:chloroform and the mixtures were refluxed for 4 h. The imines prepared were filtered and washed several times with solvent and dried in vacuum at 80°C. Then the imines were readily purified by recrystallization from ethanol. ^1H and ^{13}C NMR spectroscopy, UV–Vis spectroscopy and microanalyses were used to characterize the ligands SB1 and SB2. UV–Vis spectra were recorded with a Beckman DU-7000 spectrometer; FTIR spectra were measured on a

TABLE I Some important physical properties of SB1 and SB2 Schiff-base compounds

Schiff base	*Formula*	*Color*	*Yield (%)*	*MW (g/mol^{-1})*	*C, H and N analyses Exp.(Theor.)*			*mp (°C)*
					C	*H*	*N*	
SB1	$C_{20}H_{17}N_4O_4$	Orange	54	331	72.3(72.50)	4.9(5.13)	12.5(12.68)	228
SB2	$C_{19}H_{14}N_4O_4$	Red	49.5	362	62.7(62.98)	3.8(3.86)	15.2(15.46)	170

Shimadzu DR-8001 spectrometer; C, H and N microanalyses were accomplished on a Perkin Elmer analyzer; and ^{1}H and ^{13}C NMR spectra were obtained on a Bruker Avance DRX 500 MHz.

Spectral Data for SB1 Ligand

IR ν_{max}(KBr)/cm^{-1}: 3450, 3030, 1570, 1550 and 1620. ^{1}H NMR (Bruker AM 400, DMSO with TMS as an internal standard), δ: 1.57 (3H, s, CH_3), 7.1 (2H, d, phenylazo), 7.32 (2H, d, phenylazo), 7.00–7.15 (2H, d, salicylidene), 6.98–7.50 (1H, d, salicylidene), 13.02 (2H, s, OH), 8.5 (1H, s, CH=N), 7.01–7.12 (4H, d, phenylimine). ^{13}C NMR ($CDCl_3$, 100 MHz), δ: 21.00, 130.12, 119.30, 118.10, 111.80, 110.12, 117.15, 136.00, 120.12, 109.27, 155.23, 142.11, 135.17, 107.21, 115.17, 116.39, 102.12, 122.12, 152.12, 111.12. UV–vis spectral data (DMF as solvent): $\lambda_{max} = 345$ nm, $\varepsilon = 1.399$.

Spectral Data for SB2 ligand

IR ν_{max}(KBr)/cm^{-1}: 3375, 3120, 1545, 1552, and 1637. ^{1}H NMR (Bruker AM 400, DMSO with TMS as an internal standard), δ: 6.98 (2H, d, phenylazo), 7.11 (2H, d, phenylazo), 6.94 (2H, d, salicylidene), 7.13 (1H, d, salicylidene), 12.98 (2H, s, O–H), 8.3 (1H, s, HC=N), 6.6–8 (4H, d, phenylimine). ^{13}C NMR spectral data: δ: 109.00, 114.85, 117.10, 131.12, 119.17, 100.35, 143.10, 137.98, 129.95, 107.3, 113.74, 114.39, 109.88, 117.87, 109.25, 113.25, 135.10, 142.15, 133.24. UV–vis spectral data (DMF as solvent): $\lambda_{max} = 375$ nm, $\varepsilon = 0.876$.

Some physical properties of SB1 and SB2 Schiff-base ligands are shown in Table I.

Calculations

Methodology

The molecular geometry for SB1 and SB2 was fully optimized by using AM1, PM3 and MNDO semiempirical methods. The Austin Model 1 (AM1) was the semiempirical theory produced by Dewar's group [17] and designed to eliminate the problems with MNDO [18] that were considered to arise from a tendency to overestimate repulsion between atoms separated by distances approximately equal to the sum of their van der Waals radii. The strategy adopted was to model the core term using Gaussian functions. PM3 [19] is also based on MNDO (the name derives from the fact that it is the third parameterization of MNDO, with AM1 being considered the second).

Geometry optimization calculations were performed on the systems, using atoms with MOPAC atomic partial charges, and the results are presented in Table II.

TABLE II Some selected bond lengths (Å) and bond angles (°) for SB1 and SB2 Schiff-base ligands and their dianions from MOPAC using AM1, PM3 and MNDO Hamiltonian

	SB1			*SB1 dianion*	*SB1*			*SB1 dianion*
	AM1	*PM3*	*MNDO*	*AM1*	*AM1*	*PM3*	*MNDO*	*AM1*
O1–C2	1.373	1.366	1.352	1.252	1.372	1.364	1.353	1.246
C2–C3	1.411	1.408	1.409	1.466	1.411	1.409	1.419	1.472
C3–C4	1.470	1.470	1.469	1.473	1.470	1.470	1.474	1.472
C4–N5	1.291	1.292	1.294	1.294	1.291	1.292	1.291	1.295
N5–C6	1.407	1.432	1.430	1.400	1.408	1.412	1.418	1.394
C6–C7	1.418	1.411	1.414	1.462	1.418	1.410	1.423	1.460
C7–O8	1.379	1.366	1.369	1.265	1.379	1.367	1.370	1.264
O1–C2–C3	117.12	117.02	117.35	124.18	117.11	117.02	117.36	124.31
C2–C3–C4	119.78	120.32	120.21	116.62	119.00	120.10	121.21	116.37
C3–C4–N5	121.19	120.43	120.39	121.80	120.89	119.98	119.44	121.25
C4–N5–C6	123.20	123.01	123.34	125.38	122.05	122.26	122.33	125.35
N5–C6–C7	125.86	124.98	124.87	125.76	125.16	124.78	124.99	125.56
C6–C7–O8	123.38	122.97	123.11	123.64	123.35	123.64	123.71	123.64

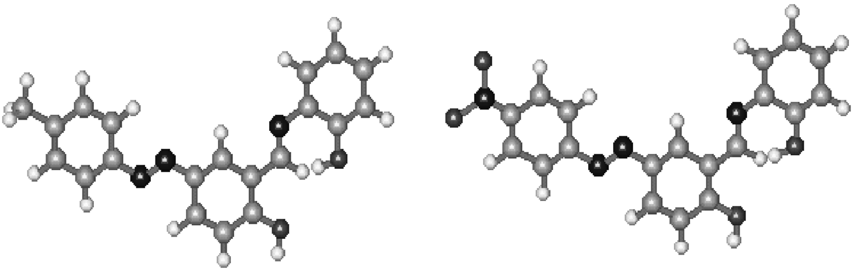

FIGURE 1 Optimized geometry for SB1 and SB2 Schiff-base compounds by the AM1 semiempirical method.

MOPAC 6.0 was used exclusively for the work presented here [20]. A comparison of some selected bond lengths, bond angles and partial charges on important atoms of SB1 and SB2 is presented in Table II and the optimized geometry for SB1 and SB2 compounds by the AM1 semiempirical method is shown in Fig. 1.

We used the three semiempirical methods AM1, PM3 and MNDO for the calculations and compared the ΔH formation of SB1 and SB2 obtained with the three methods and a variety of geometries. AM1, PM3 and MNDO calculations of the first hyperpolarizability (β) for organic compounds have been reported [21,22], leading us to conclude that the AM1 semiempirical method is a suitable method for optimization of the SB1 and SB2 structures.

Table I shows that except for the O1–C2 bond, the remaining bonds show insignificant variation upon anion formation. The O1–C2 bond of the SB1 dianion shows a decrease of 0.121 Å compared with the corresponding ligand (0.126 Å for the SB2 dianion ligand). However the angles of coordination show a large variation compared with the bond distances. This is because of the movement of the C = N group of the imine and might be related to the repulsion of the oxygen and nitrogen lone pair electrons.

TABLE III Partial charges for O(1), N(5) and O(8) atoms in SB1 and SB2 Schiff-base compounds

Atom	*SB1*			*SB2*		
	AM1	*PM3*	*MNDO*	*AM1*	*PM3*	*MNDO*
O(1)	−0.249	−0.229	−0.243	−0.242	−0.226	−0.239
N(5)	−0.334	−0.360	−0.239	−0.252	−0.318	−0.228
O(8)	−0.263	−0.228	−0.252	−0.263	−0.227	−0.251

Calculation of the NLO Properties of SB1 and SB2 Ligands

A finite-field method for calculation of polarizabilities has been developed based on both energy expansion and dipole moment expansion. This procedure is implemented in the MOPAC semiempirical program. Values and components of the dipole moment (μ) and hyperpolarizability (β_μ) are calculated as an extension of MOPAC.

The components of the molecular second-order polarizability tensors (β_{ijk}) were obtained by using the sum-over-states (SOS) expression [17,18]. β_μ is its projection in the direction of the dipole moment and is usually sampled by electronic field-induced second harmonic generation (EFISH) experiments. β_μ is calculated by using the following expression:

$$\beta_\mu(-2\omega_\mathrm{I};\omega,\omega) = (\mu_x\beta_x + \mu_y\beta_y + \mu_z\beta_z)/(\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

Our aim was to determine the NLO properties of the SB1 and SB2 Schiff-base ligands and calculations regarding second-order NLO were performed based on the finite-field method [23] using the POLAR Keyword. AM1 eigenvalues and the contribution of the atomic orbital to some frontier MOs of the anionic form of these Schiff-base ligands are presented in Table IV. Calculated molecular hyperpolarizabilities for SB1 and SB2 are given in Table V.

RESULTS AND DISCUSSION

Up to now organic molecules investigated as second-order NLO materials have contained electron-donating and electron-withdrawing groups linked through an intervening π-backbone. The NO_2 group is a strong acceptor and CH_3 is a donor group. Hence, the SB1 ligand has a large dipole moment and is a suitable NLO material.

Table III indicates the partial charges for all coordination sites O(1), N(5) and O(8) for these monoazo Schiff-base compounds. Table IV indicates the molecular orbital of the anionic forms of SB1 and SB2 ligands. The MOs more likely to combine with the transition metal orbital for the SB1 ligand are Ψ_{53}, Ψ_{55} and Ψ_{59}. In this ligand Ψ_{53} and Ψ_{59} have σ symmetry and the symmetry of Ψ_{55} is π, suggesting that the coordination sites for SB1 would have different properties. For SB2, Ψ_{64} has σ symmetry and Ψ_{55} and Ψ_{63} have π symmetry; therefore the coordination sites O(1), N(5) and O(8) possess different characters in generation of the Schiff-base complexes.

TABLE IV Molecular orbitals of the dianionic form of the SB1 and SB2 Schiff-base ligands

			Contribution of the AO to the MO		
MO	*Symmetry*	*E(eV)*	*O(1)*	*N(5)*	*O(8)*
SB1 Schiff base					
Ψ_{52}	π	−5.3301	0.0000	0.0000	0.0006
Ψ_{53}	σ	−5.2822	0.9536	0.0001	0.7679
Ψ_{54}	π	−4.3773	0.0002	0.0000	0.0000
Ψ_{55}	σ	−4.3085	0.0000	0.4253	0.0008
Ψ_{56}	π	−4.0567	0.0000	0.0001	0.0004
Ψ_{57}	π	−4.0495	0.0003	0.0000	0.0001
Ψ_{58}	π	−3.7725	0.0001	0.0002	0.0000
Ψ_{59}	π	−2.7754	0.0002	0.0003	0.0007
Ψ_{60}	π	−2.3966	0.0001	0.0000	0.0003
Ψ_{61}	π	−1.6823	0.0000	0.0000	0.0001
$\Psi_{62(\mathrm{HMOO})}$	π	−0.7206	0.0001	0.0002	0.0000
SB2 Schiff base					
Ψ_{56}	π	−6.2008	0.0000	0.0000	0.0002
Ψ_{57}	π	−5.8358	0.0000	0.0000	0.0000
Ψ_{58}	π	−5.6735	0.0000	0.0000	0.0000
Ψ_{59}	π	−5.1378	0.0000	0.0000	0.0000
Ψ_{60}	σ	−5.1111	0.7649	0.0051	0.0000
Ψ_{61}	σ	−4.8673	0.0000	0.0000	0.8277
Ψ_{62}	π	−4.6942	0.0008	0.0001	0.0004
Ψ_{63}	π	−4.3741	0.0001	0.0090	0.0002
Ψ_{64}	π	−3.3049	0.0000	0.0000	0.0021
Ψ_{65}	π	−2.9719	0.0003	0.0000	0.0004
Ψ_{66}	π	−2.4544	0.0065	0.0025	0.0018
$\Psi_{67(\mathrm{HOMO})}$	π	−1.2795	0.0002	0.0002	0.0060

TABLE V Nonlinear optical behaviors for SB1 and SB2 Schiff-base compounds

Compound	μ *(debye)*	$\beta_\mu \times 10^{-30}$*(esu)*
SB1	$\mu_x = 0.69$ $\mu_y = 2.37$ $\mu_z = 0.00$ $\mu = 2.47$	1.996
SB2	$\mu_x = 3.92$ $\mu_y = 4.96$ $\mu_z = 0.01$ $\mu = 6.33$	13.815

CONCLUSIONS

We have designed and synthesized two monoazo Schiff-base compounds, and their first hyperpolarizabilities have been calculated. Table V shows that the NLO property of SB2 is greater than that of the SB1 ligand, meaning that the NO_2 group is an important factor for polarization effects in the structure of SB2. The OH group does not have an important role in the NLO properties of these Schiff-base compounds [15].

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