Syntheses, Structures and Second-order Nonlinear Optical Behavior of (*E*)-*N*-(4-Nitrobenzylidene)-3,4-dimethylaniline and (*E*)-*N*-(3-Nitrobenzylidene)-3,4-dimethylaniline

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(*E*)-*N*-(4-Nitrobenzylidene)-3,4-dimethylaniline (**1**) and (*E*)-*N*-(3-nitrobenzylidene)-3,4-dimethylaniline (**2**) have been synthesized, and their crystal structures have been determined by X-ray diffraction analysis. Linear optical characteristics have been evaluated experimentally using UV/Vis spectroscopy and theoretically using the configuration interaction (CI) method. The maximum one-photon absorption (OPA) wavelengths of the studied compounds are shorter than 450 nm, giving rise to good optical transparency in the visible and near IR regions. The *ab initio* quantum-mechanical calculations (finite field second-order Møller-Plesset perturbation theory) of the investigated molecules have been carried out to compute the electric dipole moment (μ) and the first hyperpolarizability (β) values. The *ab initio* results suggest that the title compounds might have microscopic second-order nonlinear optical (NLO) behavior with non-zero values.

Key words: X-Ray Diffraction, UV/Vis Spectroscopy, Electric Dipole Moment, First Hyperpolarizability, Configuration Interaction

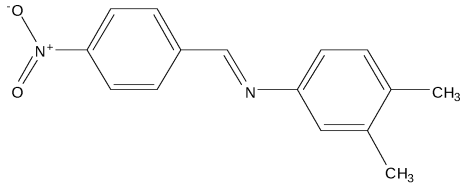
Introduction

Molecular materials with quadratic nonlinear optical (NLO) properties are currently attracting considerable interest [1, 2]. Progress has been made in finding new organic molecules with large second-order polarizability β. Among the materials producing NLO effects, organic materials are of considerable importance owing to their synthetic flexibility, large hyperpolarizabilities, ultra-fast response times, and high laser damage thresholds, compared to inorganic materials. Up to now, several hundreds of donor- and acceptor-substituted systems which show NLO properties have been reported. However, owing to difficulties in getting transparent, good quality crystals of considerable size only some of them could be used for applications as in modulators, second harmonic generators and optical wave guides [3].

The effect of electron donor or acceptor substituents on the first hyperpolarizability of Schiff bases has received a great deal of attention in recent years [4, 5]. Benzylideneanilines are an important class of Schiff bases which have been widely used in coordination, medicinal and biological chemistry. Recently, the thermochromism, photochromism and NLO properties of these compounds have found applications in modern technologies. Because of the structural characteristics of the Schiff base products (*i. e.*, electron donor and acceptor groups connected to a π-conjugated chain), it could be said that they will have potential as NLO or electro-optical materials [6, 7].

Conjugated organic molecules containing both donor and acceptor groups are of great interest for molecular electronic devices. Second-order NLO organic materials that contain stable molecules with large molecular hyperpolarizabilities in non-centrosymmetric packing are of great interest for device applications [8], but according to a statistical study, the overwhelming majority of achiral molecules crystallizes centrosymmetrically [9].

The aim of our present study is twofold: to characterize the newly synthesized Schiff bases shown in Fig. 1 having donor and acceptor substituents with spectroscopic (UV/Vis) and crystallographic techniques, and to compute the electric dipole moments μ and first hyperpolarizabilities β by an *ab initio* finite



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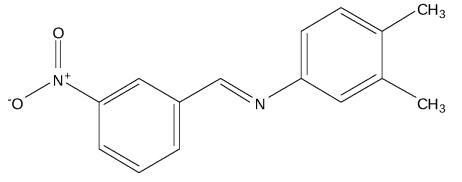

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Fig. 1. Formulae of **1** and **2**.

field second-order Møller-Plesset perturbation (FF MP2) method. Our interest is not only to predict μ and β values of the title molecules, but also to investigate the effect of the nature and the position of the substituents on the microscopic NLO response with quantum-mechanical calculations.

Results and Discussion

UV/Vis spectroscopy studies

Utilizing obtained data by UV/Vis spectroscopy studies, it is possible to determine the optimal working wavelengths of second-order NLO regions. Albert *et al.* [10] have reached the conclusion that with the correct substitution of the push-pull system in the porphyrin ring, characterized by strong intramolecular $\pi \rightarrow \pi^*$ charge transfer transitions found through UV/Vis spectral analysis, some specific electronic and structural properties of this system could produce high NLO responses. Zhou *et al.* [11] have found that the λ_{max} results of novel *para*-phenylenealkyne macrocycles are not improved with the odd number of units, even with 10 units, the value of λ_{max} being 360 nm. Although the λ_{max} was estimated to be shorter than 450 nm in a large enough sample, a strong increase in the hyperpolarizability value is obtained.

The UV/Vis spectra of **1** and **2** have been recorded in the range of 190 – 1100 nm. The maximum absorption wavelengths (λ_{exp}) obtained from the UV/Vis spectral analyses in tetrahydrofuran (THF) for **1** and cyclohexane for **2** are listed in Table 1. The two compounds have three absorption bands in the near UV/Vis region below 450 nm. As seen in Table 1, there is no absorption above 450 nm, *i. e.* both molecules remain transparent above 450 nm. The absence of the absorption above 450 nm in the visible regime might enable the achievement of microscopic NLO response with non-zero values.

	λ_{max}	λ_{exp}
1	410.12	420
	321.74	328
	243.33	242
2	404.56	398
	314.56	348
	239.02	220

Table 1. Calculated (λ_{max}, nm) and measured (λ_{exp}, nm) maximum UV/Vis absorption wavelengths of **1** and **2**.

Description of the crystal structures

The crystal structures of the title molecules **1** and **2** (Fig. 1) have been determined. Both compounds crystallize in centrosymmetric space groups. Their molecular structures in the solid state are shown in Fig. 2. The two molecules are not planar. For **1**, the two Schiff base moieties (C1–C7, O1, O2, N1) [planar with a maximum deviation of 0.070(1) Å for the O1 atom] and (N2, C8–C15) [planar with a maximum deviation of 0.049(1) Å for the C14 atom] are inclined at an angle of 9.97(6)°. Similarly, for **2**, the two Schiff base moieties (C1–C7, O1, O2, N2) [planar with a maximum deviation of 0.026(1) Å for the O1 atom] and (N1, C8–C15) [planar with a maximum deviation of 0.027(1) Åfor the C14 atom] are inclined at

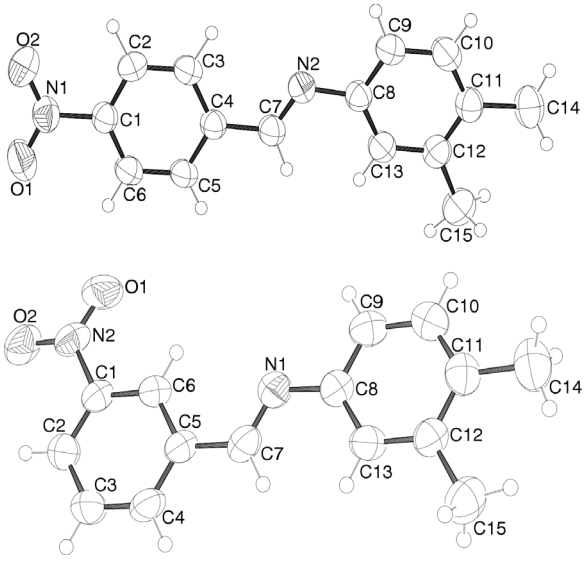

Fig. 2. The molecular structures of **1** (top) and **2** (bottom) in the solid state (displacement ellipsoids are drawn at the 50 % probability level; H atoms are presented as spheres of arbitrary radii).

Table 2. Calculated all static β components and β_{tot} ($\times 10^{-30}$ esu) values of **1** and **2**.

Compound	β_{xxx}	β_{xxy}	β_{xyy}	β_{yyy}	β_{xxz}	β_{xyz}	β_{yyz}	β_{xzz}	β_{yzz}	β_{zzz}	β_{tot}
1	13.043	1.152	−0.776	−0.381	−0.013	0.002	−0.002	−0.013	−0.008	−0.001	12.277
2	1.813	−0.839	0.271	−0.464	−0.093	0.015	0.032	−0.042	0.004	0.001	2.423

an angle of 4.13(5)°. The torsion angles C2–C1–N1–O2 [3.0(2)°] and C6–C1–N1–O1 [2.9(2)°] for **1** and C6–C1–N2–O1 [1.5(2)°] and C2–C1–N2–O2 [0.4(2)°] for **2** indicate a slight deviation of the nitro groups from the plane of their benzene ring.

Examination of the bond lengths in **1** and **2** suggests that there is an extended series of at least partially conjugated π bonds through the entire molecules. Except for the N1–C1 (for **1**), N2–C1 (for **2**) bonds connecting the nitro and phenyl groups, all the other bonds between non-H atoms show $\pi+\sigma$ character. The bond length C4–C7, N2–C8 for **1** and C5–C7, N1–C8 for **2** are shorter than typical single σ bonds, and in good agreement with related compounds in the literature [12]. The bond lengths C4–C7, C7–N2, N2–C8 (for **1**) and C5–C7, C7–N1 and N1–C8 (for **2**) in the chains are similar for both compounds. The C_{sp^2}–N bonds associated with the nitro groups are clearly single bonds, while the bond length C7–N2 for **1** and C7–N1 for **2** are the same (1.254(1) Å), and show a partial double bond character [12, 13] which is also evidence for conjugation. In the phenyl ring, bond lengths lie close to that of the standard arene C–C bonds, at 1.39 Å, but with one being much shorter [C1–C6 1.369(2) Å for **1** and C1–C2 1.360(2) Å for **2**] and one being much longer [C2–C3 1.403(2) Å for **1** and C2–C3 1.393(2) Å for **2**] than this average [14]. The quinoid character of the phenyl ring in these molecules is actually rather typical for rings bearing electron donor and acceptor substituents in para positions, and this feature is considered important in potential NLO compounds [15].

Computational results and discussion

A computational approach allows the determination of molecular NLO properties as an inexpensive way to design molecules by analyzing their potential before synthesis. In addition to the well-known empirical rules to estimate qualitatively the microscopic nonlinear response in organic molecules, especially *ab initio* MP2 calculations allow a more accurate prediction of the NLO activity.

It can be very helpful in the investigation of NLO materials to check, apart from NLO responses, also the spectroscopic absorbance at the appropriate wavelength. Thus, the wavelengths obtained by UV/Vis spectral analysis can be helpful in planning the synthesis of promising NLO materials [16]. Since it is necessary to know the transparency region, the electronic absorption spectral studies of compounds designed to possess NLO properties are important. In this paper, the vertical transition energies from the ground state to each excited state have been computed, giving one-photon absorption (OPA), *i. e.*, the UV/Vis spectrum. The calculated wavelengths (λ_{max}) for the maximum OPA of **1** and **2** are shown in Table 1. Both molecules have three OPA peaks in their spectrum. As can be seen from Table 1, the optical spectra exhibit three relatively intense bands involving $\pi \rightarrow \pi^*$ transitions centered between 244 and 411 nm for **1** and between 240 and 405 nm for **2**. The values of all absorption maxima for both molecules are located in the UV region with wavelengths shorter than 450 nm, implying a good optical transparency in the visible region. It is also seen from Table 1 that our computations on UV/Vis absorption wavelengths are reasonably in accord with the experimental values.

Table 3. The *ab initio*-calculated electric dipole moments μ (Debye) and dipole moment components for **1** and **2**.

Compound	μ_x	μ_y	μ_z	μ
1	6.073	1.728	−0.001	6.314
2	2.952	4.632	0.214	5.497

It is shown that **1** and **2** have large non-zero μ values (see Table 3). Because the studied compounds are polar molecules with non-zero dipole moments, these μ values in Table 3 yield non-zero β_{tot} values. The higher dipole moment values are associated, in general, with a larger projection of β_{tot} quantities [17]. The dipoles may oppose or enhance one another or, at least, bring the dipoles into or out of the required net alignment necessary for NLO properties such as β_{tot} values [18]. Therefore, the μ values in Table 3 may be responsible for enhancing and decreasing the β_{tot} values in Table 2. Methyl and nitro groups are effective donor-acceptor substituents for enhancing the static first hyperpolarizabilities of **1** and **2**. These donor (-CH_3) and acceptor (-NO_2) groups thus affect the second-order optical nonlinearity. β_{tot} values of the

title molecules largely depend on the positioning of substituents. The β_{tot} value for **1** with a nitro group in a *para* position is much larger than that of the value for **2** with a nitro group in a *meta* position (see Table 2). It is important to stress that in these β_{tot} investigations we do not take into account the effect of the field on the nuclear positions, *i. e.* we evaluate only the electronic components of β_{tot}.

Conclusions

1 and **2** have been synthesized for the study of their second-order optical nonlinearities. Their structures have been investigated by X-ray diffraction measurements. We have presented computational studies showing that the title compounds possess second-order NLO behavior. In order to test the microscopic second-order nonlinearity, the electric dipole moments and first hyperpolarizabilities of **1** and **2** have been calculated using an *ab initio* methodology with a 6-311+G(d,p) basis set in the FF approach. In the computations of all these properties, the MP2 perturbation theory has provided adequate electron correlation effects. With *ab initio* FF MP2 computations, it is also possible to predict the β_{tot} value accurately for a given molecular structure. The non-zero μ values of the examined Schiff bases show that **1** and **2** have microscopic first hyperpolarizabilities with non-zero values obtained by the numerical second-derivative of the electric dipole moment according to the applied field strength. The computational results also reveal that the substituent positions play a significant role regarding the NLO properties of both compounds. The OPA characterizations of **1** and **2** have been obtained both theoretically (CI method) and experimentally (UV/Vis spectroscopy). According to the results on the linear optical behavior, the values of electronic transition wavelengths are estimated to be shorter than 450 nm, implying good optical transparency in the visible and near-IR region (450 – 900 nm), in good agreement with the experimental results.

Experimental Section

Reagents and techniques

3-Nitrobenzaldehyde, 4-nitrobenzaldehyde, 3,4-dimethylaniline and ethanol were purchased from Merck (Germany). CNH analyses were performed on a Leco CHNS-932 analyzer. Infrared absorption spectra were obtained with a Perkin Elmer BX II spectrometer on KBr discs. UV/Vis spectra were measured using a Perkin Elmer Lambda 2 series spectrophotometer with 1.0 cm quartz cells.

Table 4. Crystal structure data for **1** and **2**.

Compound	**1**	**2**
Formula	$C_{15}H_{14}N_2O_2$	$C_{15}H_{14}N_2O_2$
Formula weight	254.28	254.28
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$
Crystal dimension, mm^3	$0.06 \times 0.08 \times 0.50$	$0.06 \times 0.18 \times 0.30$
a, Å	9.403(1)	15.548(2)
b, Å	10.369(1)	6.130(1)
c, Å	13.392(2)	27.403(6)
β, deg	95.30(1)	93.40(2)
V, Å^3	1300.1(1)	2607.2(3)
Z	4	8
$D_{calcd.}$, g cm^{-3}	1.30	1.30
μ(MoK_α), mm^{-1}	0.1	0.1
F(000), e	536	1072
$2\theta_{max}$, deg	52.8	52.8
hkl range	$\pm 11, +12, +16$	$\pm 19, +7, +34$
Refl. indep. / obs. ($I \geq 2\sigma(I)$)	2649 / 2636	2642 / 2635
Ref. parameters	215	172
max ($\Delta/sigma$)	0.001	0.003
R ($I \geq 2\sigma(I)$)/Rw (all data)	0.062 / 0.119	0.061 / 0.125
Goodness-of-fit on F^2	1.037	1.035
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.27 / −0.29	0.14 / −0.21

*Preparation of compounds **1** and **2***

(*E*)-*N*-(4-Nitrobenzylidene)-3,4-dimethylaniline (**1**) was prepared by condensation of 4-nitrobenzaldehyde (0.02 mol) and 3,4-methylaniline (0.02 mol) in 75 mL of ethanol. The reaction mixture was stirred for 3 h, and then placed in a freezer for 6 h. The yellow precipitate was collected by filtration, and then washed with cold ethanol. – $C_{15}H_{14}N_2O_2$ (254.28): calcd. C 70.85, H 5.95, N 11.02; found C 70.14, H 5.26, N 10.74. – IR (KBr, cm^{-1}): ν = 3058 w, 2911 – 2878 m, 1638 s (C=N), 160 – 1522 s (C=C), 1348 s (C–N). Compound **2** was synthesized analogously. – $C_{15}H_{14}N_2O_2$ (254.28): calcd. C 70.85, H 5.95, N 11.02; found C 70.38, H 5.12, N 10.94. – IR (KBr, cm^{-1}): ν = 3052 w, 2912 m, 1598 s (C=N), 1510 s (C=C), 1333 s (C–N).

X-Ray structure determination

The data collection for both compounds was performed on an Enraf-Nonius diffractometer employing graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). Data reduction and corrections for absorption and crystal decomposition (0.7 %) of **1** and (1.1 %) of **2** were achieved using the Nonius Diffractometer Control Software [19]. The structures were solved by SHELXS-97 [20] and refined with SHELXL-97 [21]. All non-hydrogen atom parameters were refined anisotropically. H atoms for **1** were located in their

idealized positions with C–H distances in the range 0.93 – 0.96 Å. The positions of H atoms for **2** were refinded freely. The details of the X-ray data collection, structure solution and structure refinements are given in Table 4. The molecular structures with the atom numbering scheme are shown in Fig. 2 [22].

CCDC 743294 and 743295 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Theoretical calculations

As the first step of electric dipole moment and static first hyperpolarizability calculations, the geometries have been optimized in the *ab initio* restricted and unrestricted Hartree-Fock levels for **1** and **2**, respectively. Then, the electric dipole moments and first hyperpolarizability tensor components of the investigated compounds have been calculated using the FF MP2 method at 6-311+G(d, p) polarized and diffused basis set level, which has been found to be more than adequate for obtaining reliable trends in the hyperpolarizability values. All μ and β computations have been performed using GAUSSIAN98W [23] on an Intel Pentium IV 1.7 GHz processor with 512 MB RAM and Microsoft Windows as the operating system.

We report β_{tot} (total first hyperpolarizability) values for the examined compounds. The components of the first hyperpolarizability and the complete equation for calculating the magnitude of the first hyperpolarizability from GAUSSIAN98W output are described in ref. [18].

Since the β values of GAUSSIAN98W outputs are reported in atomic units (a. u.), the calculated β values have been converted into electrostatic units (esu) (1 a. u. = 8.6393×10^{-33} esu). To calculate the electric dipole moments and the hyperpolarizabilities, the origin of the cartesian coordinate system (x, y, z) = (0, 0, 0) has been chosen at the centers of mass of **1** and **2**.

Besides, the $\pi \rightarrow \pi^*$ transition wavelengths (λ_{max}) of the lowest-lying electronic transition for **1** and **2** have been calculated by the electron excitation configuration interaction using the CIS/6-31G method in GAUSSIAN98W.

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