

Quantum chemical study on the electronic structure and second-order nonlinear optical properties of salen-type Schiff bases

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Abstract

Semi-empirical (ZINDO-SOS), time-dependent density functional theory and ab initio quadratic response function (DDRPA) calculations on a series of donor–acceptor substituted salen-type Schiff bases are used to aid in the design of dyes with useful optical nonlinearities (molecular quadratic hyperpolarizabilities β_{vec}). 4-Phenylazo-2-phenyliminomethylphenols **1** are calculated to be less suitable as nonlinear optical materials than the isomeric 5-phenylazo-2-phenyliminomethylphenols **2**. The largest hyperpolarizabilities are predicted for compounds with an acceptor-containing phenylazo and a donor-substituted phenyliminomethyl moiety. The calculations also clearly indicate the intramolecular charge transfer nature of the first $\pi\pi^*$ -transition in the investigated Schiff bases.

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1. Introduction

Aromatic Schiff bases, especially those derived from reaction of salicylic aldehydes with aromatic amines (salen-type Schiff bases), form complexes with a variety of metal ions [1,2]. Among the various possible applications of these complexes [3–7], their nonlinear optical properties for the design of materials in modern communication technology [8–13] are of fundamental importance [14,15]. Besides the experimental determination of macroscopic optical nonlinearities of Schiff base derivatives [16] by the powder technique [17], or their molecular hyperpolarizabilities [18] by electric field induced second

harmonic generation (EFISH) [19,20], quantum chemical procedures for the calculations of NLO properties [12,21–26] also have been applied to a series of donor–acceptor substituted Schiff bases [18,27]. Recently, we reported on the synthesis, spectroscopic characterization and semi-empirical AM1 calculations of arylazo substituted salen-type Schiff base ligands [28,29]. Here we present a semi-empirical and ab initio computational study of a series of such salen-type Schiff bases **1–4** (Scheme 1) with special emphasis on the influence of the nature (donor vs acceptor) and position of substituents on molecular quadratic hyperpolarizabilities (β_{vec}).

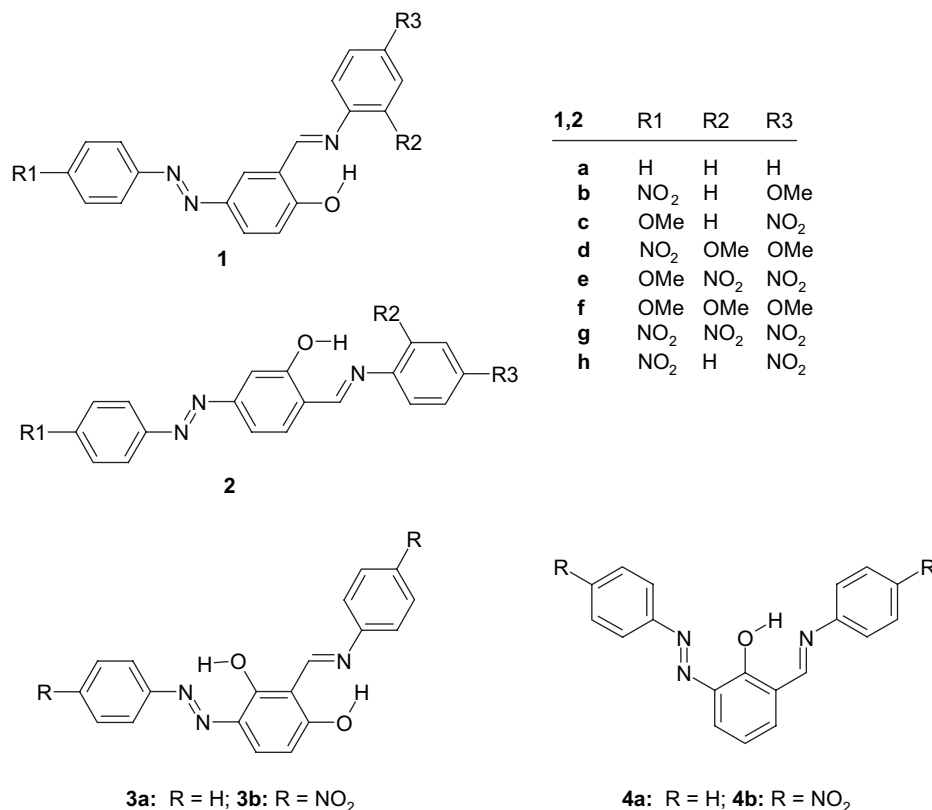
2. Computational details

The geometries of all Schiff bases **1–4** (Scheme 1) were optimised using the semi-empirical AM1 Hamiltonian

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Scheme 1. Structures of the investigated Schiff bases.

[30,31]. For several selected derivatives (**1a–e**, **2a–e**) geometry optimisation was also done with Becke's three parameter hybrid density functional theory – HF procedure [32] using the Lee–Yang–Parr correlation functional [33] and the 6-31G(d) basis set (B3LYP/6-31G(d)) [34]. Electronic excitation energies and hyperpolarizabilities were obtained by the semi-empirical ZINDO procedure [35,36]. In addition, for **1a–c** and **2a–c**, time-dependent density functional theory (TDDFT [37,38], B3LYP/6-31G(d)) and ab initio HF quadratic response function (double direct random phase approximation, DDRPA) calculations [39,40] with Ahlrichs' VDZ basis [41], were used to obtain electronic excitation energies and hyperpolarizabilities, respectively.

3. Results and discussion

The intramolecular hydrogen bond in **1–4** considerably restricts the conformational freedom. Thus, in **3**, only one single rotamer is possible; the orientation of the azo group with respect to the central aromatic ring in both **1** and **2** leads to two conformers ($\tau_1 = \tau(\text{C3–C4–N=N}) \sim 0^\circ$ and $\tau_1 \sim 180^\circ$, for atom numbering, see

Scheme 1). For molecules with $\text{R}^2 \neq \text{H}$, each one of these two rotamers leads to two structures depending on the orientation of R^2 . Compounds **4a,b** may also exist in 4 different conformations (Scheme 2). We will discuss the influence of these conformations on calculated hyperpolarizabilities and electronic transition energies in detail for **1d**, **2d**, and **4a**. Besides the effect of different conformations, other key structural alterations have also been found to influence calculated β -values [42]. Consequently, to address this possibility, we compare ZINDO-SOS calculated quadratic hyperpolarizabilities of **1a–e** and **2a–e** obtained with AM1 and B3LYP/6-31G(d), respectively, geometries.

3.1. Electronic excitation energies

Electronic excitation energies (wavelengths λ/nm), oscillator strengths f , and nature of the respective excited state (principal CI-coefficients) calculated by the TDDFT method for **1a–c** and **2a–c** are summarised in Table 1.

For all derivatives, the calculations predict a very small intensity (low oscillator strength f) for the longest wavelength transition in line with its $n\pi^*$ -character. Experimentally, for **1b** and **1d** the UV/vis maxima were

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