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Geometrical effect on the first hyperpolarizability of thiophene-substituted stilbene derivatives

Patrizia Calaminici [a,*], Andreas M. Köster [a], Karl Jug [b], David Gray [c], Werner Blau [c]

[a] *Departamento de Quimica, CINVESTAV, Avenida Instituto Politécnico Nacional 2508, A.P. 14-740, Mexico, DF 07000, Mexico*
[b] *Theoretische Chemie, Universität Hannover, Am Kleinen Felde 30, 30167 Hannover, Germany*
[c] *Physics Department, Trinity Collage, Dublin 2, Ireland*

This manuscript is dedicated to Prof. Annick Goursot for her important work in the development and applications within Density Functional Theory methods.

Abstract

This paper presents dipole moment (μ), static mean polarizability (α) and mean first hyperpolarizability (β) of thiophene-substituted stilbene derivatives calculated in the framework of density functional theory. The calculations were performed using a finite field approach implemented in the density functional program ALLCHEM. All-electron type basis sets optimized for the calculation of the polarizabilities and hyperpolarizabilities using a local exchange-correlation functional were employed. The molecular structures have been fully optimized using the semiempirical program MSINDO. The calculated mean first hyperpolarizability trends are in agreement with the experimental trends obtained from hyper-Rayleigh scattering technique. This work shows that the increased of hyperpolarizability of the studied thiophene-substituted stilbene derivatives is due to a geometrical effect of their *trans* and *cis* isomers.
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1. Introduction

In the last years, the interest in the design and synthesis of new organic materials with second-order nonlinear optical (NLO) properties has grown considerably because of their potential applications in optical computing, telecommunications and optical signal processing (see, for example, Refs. [1–6] and references therein). Heteroaromatic compounds containing thiophene have attracted a significant interest in the design of novel push–pull structures due to the fact that their NLO properties are superior to those of the corresponding stilbene-based systems. The literature about linear and NLO properties of thiophene compounds is very rich and it would be here not appropriate to review all of it. For a brief introduction on this topic, we address the reader to Ref. [6] and references therein. In particular, it was observed that the replacement of a benzene ring with a thiophene ring drastically increases the magnitude of second-order optical nonlinearity. An explanation of this increasing of hyperpolarizability is suggested in the literature as follows: *the thiophene ring introduces more electron delocalization in donor–acceptor compounds than the stilbene compounds* [6].

However, as it was also pointed out by Breitung et al., the differences in aromatic delocalization energies must not be the only reason which influence the NLO properties for these systems [7]. In particular, the work of Breitung et al. shows that in addition to electronic factors, steric effects also play an important role for larger hyperpolarizability in heteroaromatic analogues of donor–acceptor stilbene compounds.

In this work we present a density functional study of the NLO properties of two new heteroaromatic ring analogues of donor–acceptor stilbene–thiophene compounds [8]. The calculated mean first hyperpolarizabilities are compared with the experimental β values measured recently by hyper-Rayleigh Scattering (HRS) measurements in one of our laboratories. Our results reveal that the relative orientation on the substituted thiophene ring effects the hyperpolarizability of these compounds. This study suggests that the geometrical effect is responsible for the higher hyperpolarizability observed in the compound containing thiophene.

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2. Experimental section

Hyper-Rayleigh scattering (HRS) was used to measure the first hyperpolarizability β of the molecules in solution. This method was chosen as the molecules investigated were not dipolar materials, so ruling out the more traditional Electrical Field Induced Second Harmonic (EFISH) method [9,10].

The experimental set-up [11] illustrated in Fig. 1 used a Nd^{3+}:YAG active/passive mode-locked laser emitting 30 ps pulses at 1064 nm with a repletion rate of 10 Hz and an energy of a few mJ. The use of diffraction from a 1 mm pin hole has enabled a smooth pseudo-gaussian beam profile to be obtained in the far field. This means that the laser beam can be tightly focused with less likelyhood of optical break down. The intensity was controlled with a rotating half-wave plate and polarisers with a filter to remove the residual second harmonic generation (SHG) from the half-wave plate. The reference was taken from a back reflection from the filter on to a fast photodiode. The sample was held in a 5 cm cell whose center is at the focus of the laser beam. The scattered SHG is collected and any fundamental residual is removed. This is then sent to a monochrometer and photomultiplier tube assembly. The monochrometer determines if any background fluorescence is present. A BOXCAR averager collects the data which is synchronized with the stepper motor control of the half-wave plate and then sent to the computer. The experiment was calibrated with pNA (4Nitro-aniline) and DR1 (Dispersed Red 1). The pNA to calibrate β and the DR1 to show the presence of fluorescence [12].

The calibration samples were prepared in acetone and the samples were prepared in methanol, both filtered to 0.5 μm to reduce the parasitic SHG effect from impurities.

3. Computational details

The structures of the studied compounds were fully optimized. For the optimization of the molecular structures, we used the semiempirical program MSINDO [13–15] which is based on a modification of the SINDO1 [16] program.

The quality of the structural results from MSINDO has been proven in previous works on azabenzenes [17] and azoles [18]. The bond length alternation in simple aromatic and heteroaromatic systems like the here studied stilbene derivatives is usually well reproduced by MSINDO. This was also confirmed for the here studied systems by some reference optimizations with the Density Functional Theory (DFT) code deMon2k [19]. The DFT polarizabilities and hyperpolarizabilities with MSINDO optimized structures are in good agreement with the corresponding pure DFT calculations. On the other hand, the combination of semiempirical structure optimization and DFT polarizability calculation results in a significant reduction of computational cost.

All presented calculations of μ, α and β have been carried out using the DFT program ALLCHEM [20]. The DFT polarizabilities and hyperpolarizabilities were calculated via the finite field method described in reference [21]. The calculations were performed using the exchange-correlation contributions proposed by Vosko et al. [22].

In a previous work, we observed that gradient corrected functionals are not really beneficial for the calculation of α and β, if DFT optimized basis sets are used [21]. In order to verify this observation for the here discussed stilbene derivatives, polarizability and hyperpolarizability calculations with the generalized gradient approximation (GGA) proposed to Perdew and Wang [23] and Perdew [24] (PW86) were performed, too.
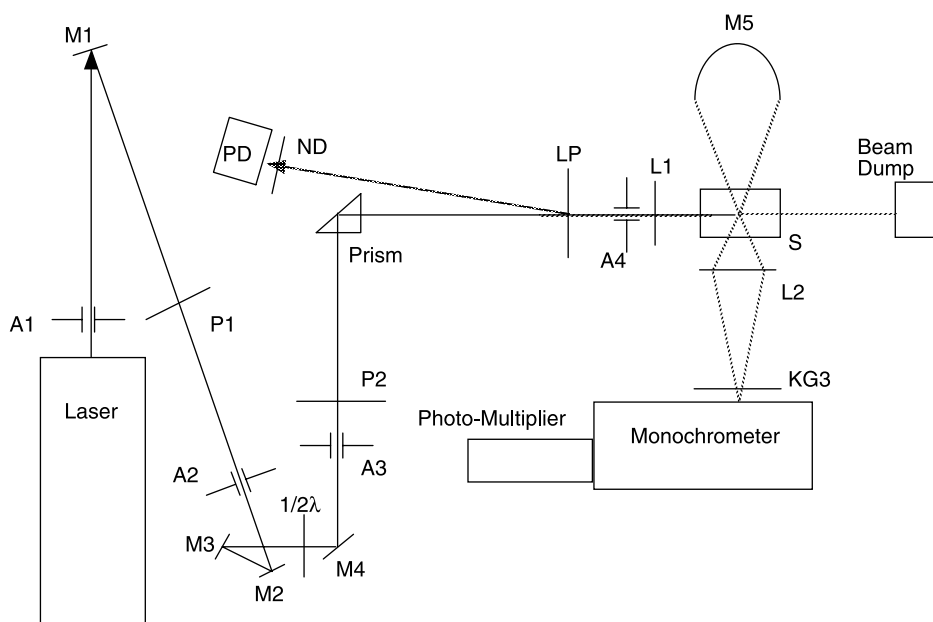

Fig. 1. HRS experiment. A, aperture; M, mirrow; PD, photo-diode; ND, neutral density filter; 1/2λ, half-wave plate; P, polarisier; LP, long pass filter; L, lens; S, sample; KG3, IR blocking filter.

The minmax self-consistent field (SCF) convergence criterion [25] was set to 10^{-9} a.u. in all calculations. For the calculation of α and β, a field strength of 0.0032 a.u. was used.

It is well known that a general characteristic required for basis sets to perform well for polarizability calculations is that they should contain diffuse functions [26]. An economical strategy for constructing these kinds of basis sets is to augment valence basis sets of reasonable good quality with additional polarization functions [27–30]. We have chosen as valence basis a triple zeta basis set (TZVP) which was optimized for local DFT calculations [31]. These basis sets were then augmented with field-induced polarization (FIP) functions due to Zeiss et al. [28]. They derived the FIP function exponents from an analytic analysis of the field-induced charges in hydrogen orbitals. For H, C, O and S atoms, the exponents of the first- and second-order Gaussian-type FIP functions [32] have already been reported in Table I of reference [21]. These basis sets, e.g. TZVP augmented with first-order FIP functions, proved to be most appropriate for the determination of α and β with density functional methods (see, for example, Refs. [17,18,21] and references therein).

4. Results and discussion

The structures of the studied systems are illustrated in Fig. 2. Compound **1** (Fig. 2a) consists a π-conjugated stilbene backbone, with a methoxy MeO donor and COHPh$_2$ acceptor group at the 4,4'-positions. For this compound the first hyperpolarizability has been measured by the HRS techniques described above and an experimental first hyperpolarizability value of 1620.38 a.u. was reported. Compound **2** (Fig. 2b) is a compound analogue to compound **1** in which the benzene ring connected to the acceptor group is replaced with a thiophene ring. For this compound an experimental β value of 2083.35 a.u. was found. Thus, the replacement of a benzene ring by a thiophene ring increases the magnitude of the first hyperpolarizability by more than 450 a.u. in the experiment. This is in agreement with the general observation that the substitution of benzene rings with thiophene rings in donor–acceptor substituted stilbene derivatives increases the second-order nonlinearities.

For the calculation of β, the z-axis is oriented in the direction of the permanent dipole moment of the molecule.
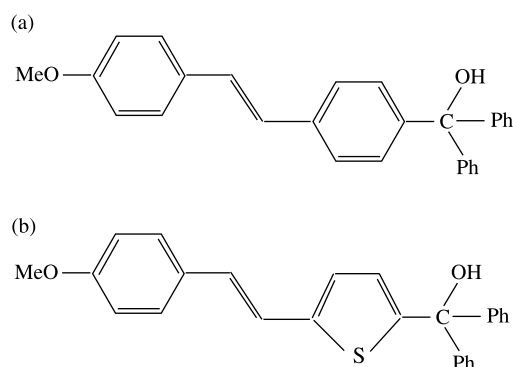

Fig. 2. Structures of the studied compounds.

Table 1
Dipole moment μ (Debye), mean polarizability $\bar{\alpha}$ (a.u.) and mean first hyperpolarizability $\bar{\beta}$ (a.u.) of the studied *trans* compounds. The experimental β values are also given

Compound[a]	μ	$\bar{\alpha}$	$\bar{\beta}$	$\beta_{Exp.}$
Compound **1**	0.55	414.58	2592.51	1620.38
Compound **2**	1.20	408.09	2493.55	2083.35

[a] Geometrical parameters are available upon request.

The mean polarizability was calculated from the polarizability components as:

$$\bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}), \tag{4.1}$$

and the mean first hyperpolarizability from the calculated β components as:

$$\bar{\beta} = \frac{3}{5}\sum_i \beta_{iiz}. \tag{4.2}$$

The DFT calculated static dipole moment, mean polarizability and mean first hyperpolarizability of the *trans* isomers of the studied compounds are listed in Table 1. The experimental values of β are also listed, for comparison.

For compound **1**, a first hyperpolarizability of 2592.51 a.u. is obtained. The calculated dipole moment is 0.55 Debye and the static mean polarizability is 414.58 a.u., respectively. For compound **2**, a β value of 2493 a.u., a dipole moment of 1.20 Debye and a static mean polarizability of 408.09 a.u. have been calculated, respectively.

The two *trans* isomers were also optimized with the DFT code deMon2k using the DZVP basis sets and the VWN functional. No significant differences to the MSINDO optimized structures were found. In order to demonstrate the reliability of our computational approach, i.e. MSINDO structure optimization followed by VWN property calculations, we repeated the calculations of μ, $\bar{\alpha}$ and $\bar{\beta}$ with the gradient corrected PW86 functional using the VWN optimized structures. For compound **1**, a β value of 2561.56 a.u., a dipole moment of 0.56 Debye and a static mean polarizability of 412.68 a.u. were calculated, respectively, whereas for compound **2**, a β value of 2473.91 a.u., a dipole moment of 1.19 Debye and a static mean polarizability of 410.06 a.u. were found, respectively. Moreover, calculations of μ, $\bar{\alpha}$ and $\bar{\beta}$ were also performed with the PW86 functional for both compounds considering the geometries obtained from the semiempirical optimizations. For compound **1**, we obtained values of 0.55 Debye, 414.77 and 2578.83 a.u. for μ, α, and β, respectively, whereas for compound **2**, 1.18 Debye, 412.36 and 2470.01 a.u. were obtained. These results made us confident that our hybrid method (semiempirical optimization in combination with DFT property calculation) is appropriate for our study.

Our discussion will be focused mostly on the mean first hyperpolarizability results since the main objective of this work is to compare the theoretical mean first hyperpolarizability values with those recently measured by the HRS technique described above. Table 1 shows that the calculated

first hyperpolarizabilities of compounds **1** and **2** are about 26 and 20% higher of the corresponding measured second-order nonlinearities, respectively. The theoretical results show us that our calculations are in the right ball-park, however we notice two unusual behaviors. First, the difference between the calculated and experimental β values is larger than the difference we would have expected based on our previous work [21] in which we have estimated average errors of 10% in the hyperpolarizability. This study was based on a representative set of molecules including aliphatic and aromatic hydrocarbons. Second, the calculated β values show a different trend with respect to the experimental one. Since the calculated trend is opposite to the experimental observation that thiophene substituted compounds have larger hyperpolarizabilities, it is evident that some other effects needed to be consider in order to be able to make a fair comparison between theoretical and experimental β values.

In fact, the measured samples are a mixture of *cis* and *trans* isomers and therefore tending to average the experimental results to a middle of the road value. Therefore, the geometries of the *cis* isomers of compounds **1** and **2** have been optimized, too, and the β values have been calculated with the aim to calculate the averaged first hyperpolarizabilities of the *trans* and *cis* isomers of each studied compound.

The optimized structures of the *cis* isomers of compounds **1** and **2** are depicted in the top and in the bottom of Fig. 3, respectively.

For the *cis* isomer of compound **1**, a first hyperpolarizability of 435.18 a.u. was obtained. Thus, the averaged β value of the *cis* and *trans* isomers of compound **1** is around 1561.13 a.u. and differs of about 4% from the experimental value.
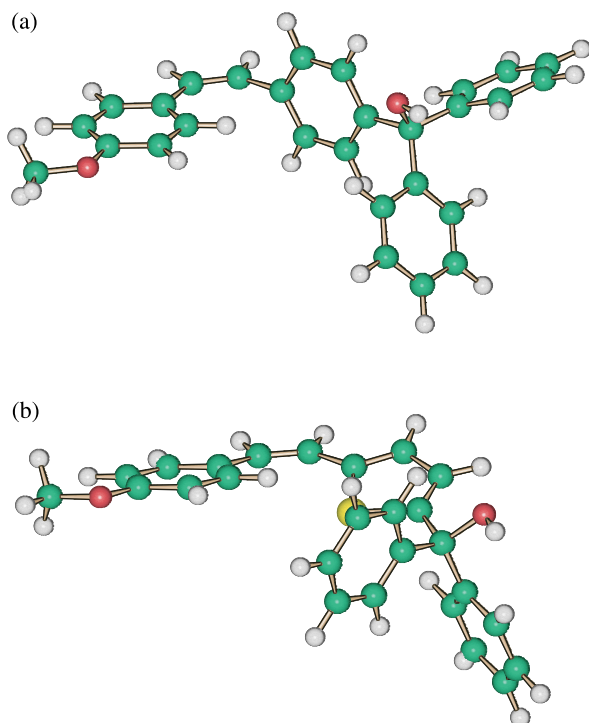

Fig. 3. Optimized structures of the *cis* isomers of the studied compounds.

For the *cis* isomer of compound **2**, a β value of 1234.75 a.u. was found. The averaged β value for this compound results to 1863.87 a.u. and differs by about 10% from the experimental β value.

For both compounds we note that the agreement between calculated and the experimental β values is within our estimated error bounds. Moreover, the calculated average β values have the same trend as the experimental one. Thus, the geometrical arrangement of the studied *cis* isomers resulted to be a crucial point for reproducing the experimental trend of the first hyperpolarizability. However, no solvent and vibrational effects are included in our calculations. As Fig. 3 shows, in the *cis* structure of compound **1** the two benzene rings of the stilbene backbone are almost perpendicular to each other. This geometrical effect breaks the conjugation and therefore a small first hyperpolarizability value is expected. Instead, the *cis* structure of compound **2** shows that the benzene and the thiophene rings are lying almost in the same plane. This geometrical conformation favors the conjugation and therefore the first hyperpolarizability of the *cis* isomer of the thiophene substituted stilbene is considerably larger compared to the *cis* structure of the pure stilbene. Consequently, the averaged first hyperpolarizability is larger for the compound containing the thiophene ring.

From these considerations we conclude that the larger first hyperpolarizability value of the thiophene substituted reported stilbene is due to a geometrical effect in the *cis* isomer. It is very likely that this explains the general increase of second-order nonlinearities in thiophene-substituted stilbene derivatives.

5. Conclusions

In this paper, calculations of dipole moments, static polarizabilities and first hyperpolarizabilities of new thiophene-substituted stilbene derivatives have been reported. The calculations have been performed in the framework of density functional theory and by employing specially designed basis sets for this level of theory. The calculated first hyperpolarizability values have been compared with the experimental β values measured via hyper-Rayleigh Scattering technique. The molecular structures have been fully optimized with the semiempirical program MSINDO. It was proved that these geometries are reliable as those obtained from DFT optimizations. The combination of semiempirical optimized structures and density functional property calculations results in a considerably saving of computer time. We have shown that the combination of MSINDO optimization with DFT hyperpolarizability calculation can quantitatively predict static first hyperpolarizabilities for large molecules like the presented thiophene-substituted stilbene derivatives. It was proved that the inclusion of gradient corrections are of minor influence for the calculations of μ, α and β. The calculated β values agree well with the experimental values. It was shown that the substitution of a benzene ring with a thiophene ring increases the magnitude of second-order nonlinearities due to the high contribution of the β value of the *cis* isomer of the compound containing the thiophene ring. This is the first work in which is

clearly shown that the increase of magnitude of first hyperpolarizability observed in thiophene ring introduces more electron delocalization in donor–acceptor compounds than the stilbene compounds and it represents a further proof to the fact that steric effects may play an important role for larger β values in heteroaromatic analogues of donor–acceptor stilbene compounds.

Acknowledgements

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