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Experimental and theoretical investigation of optical nonlinearities in (nitrovinyl)-1*H*-pyrazole derivative

Y. Dwivedi^a, L. de Boni^a, P.J. Gonçalves^b, L.M. Mairink^c, R. Menegatti^c, T.L. Fonseca^b, S.C. Zilio^{a,*}

^a Instituto de Física de São Carlos, Universidade de São Paulo, Caixa Postal 369, 13560-970 São Carlos, SP, Brazil ^b Instituto de Física, Universidade Federal de Goiás, Caixa Postal 131, 74001-970 Goiânia, GO, Brazil ^c Faculdade de Farmácia, Universidade Federal de Goiás, Caixa Postal 131, 74001-970 Goiânia, GO, Brazil

HIGHLIGHTS

- Nonlinear optical properties of newly synthesized (nitrovinyl)-1Hpyrazole explored.
- ▶ fs Z-scan technique used for 2PA cross-section spectrum in 460–780 nm range.
- 2PA exhibits two bands with crosssections of 58 (520 nm) and 67 GM (690 nm).
- Experimental β_{HRS} (45 × 10⁻³⁰ cm⁵/ esu) estimated by ps hyper-Rayleigh scattering.
- ► Theoretical calculations (MP2/6-311+G(d) yield similar value $40 \pm 2 \times 10^{-30} \text{ cm}^5/\text{esu}.$

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Reaction mechanism to achieve (nitrovinyl)-1*H*-pyrazole structure exhibiting 58 and 67 GM absorption cross-section at 520 and 690 nm wavelengths, respectively and first hyper polarizability 45×10^{-30} cm⁵/esu.



ABSTRACT

This work reports on the optical nonlinearities of a newly synthesized pyrazole derivative, namely (*E*)-1-(4-chlorophenyl)-4-(2-nitrovinyl)-1*H*-pyrazole. The Z-scan technique with femtosecond laser pulses was used to determine the two-photon absorption (2PA) cross-section spectrum, which presents a maximum of 67 GM at 690 nm. We have combined hyper-Rayleigh scattering (HRS) experiments and second-order Møller–Plesset perturbation theory (MP2) calculations to study the first hyperpolarizability (β_{HRS}). It was found that the MP2/6-311+G(d) model, taking into account solvent and dispersion effects, provides the β_{HRS} value of 40 × 10⁻³⁰ cm⁵/esu for the compound, in good agreement with the experimental result of 45 ± 2 × 10⁻³⁰ cm⁵/esu.

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Introduction

Pyrazole is an important heterocyclic compound whose derivatives are used in a number of applications in medicine, going from analgesia to antibacterial activities [1–3]. Such molecule is a member of the azole family that also includes imidazoles, oxadiazoles, oxazoles and thiazoles [4]. It contains a ring structure composed of three carbon and two nitrogen atoms, whose presence as a lone pair produces a conjugated system that points to the possibility of molecular nonlinear optical (NLO) activity. Currently, new pyrazole derivates has been designed and synthesized in order to explore their central pharmacological activity, in vivo hypnotic and analgesic profile and potential antipsychotic properties [5–7]. Additionally, optical properties of a number of pyrazole derivatives were already reported in literature [8–13]. The UV absorption spectra

^{*} Corresponding author. Tel./fax: +55 16 3373 8085. E-mail address: zilio@ifsc.usp.br (S.C. Zilio).

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and dissociation constants of some 1-phenyl-5-substituted pyrazoles were studied by Tabak et al. [13], while Ovejero et al. investigated the luminescence characteristics of pyrazole ligands bonded to Au(I) metal centers or AuL metal fragments (L = Cl, PPh₃, Hpz) [14]. In this study we focus on determining the nonlinear optical (NLO) properties of a novel derivative of pyrazole, which appear to be promising for NLO applications.

The nonlinear behavior of these molecules is important for several applications and can be adjusted, to some extent, by changing the asymmetric polarization through the inclusion of different donor-acceptor groups at the terminal positions of a π -conjugated bridge [15–17]. Indeed, Miller et al. have studied NLO properties of various bisubsituted pyrazol derivatives and reported large first hyperpolarizabilities values for 1,3 and 1,4 substitutions, and dramatically lower for 1,5-substituted derivatives [8]. In this case the NLO activity is analyzed using the push-pull strategy, where the conjugated segment is capped by an electron-donor group on one side and an electron-acceptor group on the other side. Other NLO properties such as fluorescence following one- and two-photon absorption (2PA) in 3-(1,1-dicyanoethenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole crystal using 1064 and 532 nm wavelengths [18]. One of the reasons for the search of materials with large 2PA is the wide range of potential applications such as two-photon fluorescence imaging, optical limiting, optical data storage, phototherapy and up-conversion lasing [9,19-22]. These also show that the preparation of pyrazole-based materials with large NLO could be important for several technological applications.

The present investigation reports on the synthesis of a novel pyrazole derivative, which contain a ring structure, composed of three carbon and two nitrogen atoms, whose presence as a lone pair produces a conjugated system that points to the possibility of molecular NLO activity. The NLO characterization in dimethyl sulfoxide (DMSO) solvent by means of femtosecond 2PA and hyper Rayleigh scattering (HRS) with picoseconds pulse trains. The first technique provides the imaginary part of the third order nonlinear optical susceptibility while the second provides the first hyperpolarizability, a second order effect of the optical molecular polarizability. In this case, in order to make an appropriate comparison between theoretical and experimental results, correlated first hyperpolarizability calculations have been performed accounting for solvent and frequency dispersion effects.

Experimental section

Synthesis of (nitrovinyl)-1H-pyrazoles

High purity reagents and solvents, including ammonium acetate and nitromethane, were purchased from Acros Organics Company and distilled prior using. The melting point was determined with a Marte[®] 284594 apparatus. The *E* configurations of double bonds were determined through NMR data, recorded by using a Bruker Avance III spectrometer, operating at 500.13 MHz to proton frequency. The samples for NMR measurements were prepared in CDCl₃ containing 1% tetramethylsilane as an internal standard. Splitting patterns are designated as follows: s, singlet; d, doublet. The infrared (IR) spectra was obtained with a Perkin-Elmer spectrometer 400 N FT-IR in KBr plates. The progress of the reaction was monitored by thin-layer chromatography (TLC), which was performed on 2.0×6.0 cm aluminum sheets precoated with silica gel 60 (Merck) to a thickness of 0.25 mm. The developed chromatograms were observed under ultraviolet light (254-265 nm) and treated with iodine vapor. For column chromatography, we used Merck silica gel (70-230 mesh).

As illustrated in Fig. 1, the synthesis of (E)-1-(4-chlorophenyl)-4-(2-nitrovinyl)-1-phenyl-1*H*-pyrazole, which for simplicity will

be named as compound (2), was carried out through the reaction between aldehydes and nitromethane, and catalyzed by ammonium acetate, at reflux temperature, for 12 h [23]. The typical procedure to produce it is as follows: in a 50 mL round-bottom flask, 5 mmol of 1-(4-chlorophenyl)-1H-pyrazole-4-carbaldehyde, named as compound (1), were added to a stirred solution of ammonium acetate 1.25 mmol in dry nitromethane 25 mL. The reaction mixture was refluxed for 12 h, then was allowed to cool and was poured into water. The precipitate was filtrated to vacuum, dried and the crude product was purified by chromatography on silica, using 50:50 *n*-hexane-CH₂Cl₂ as mobile phase. The compound (2) was obtained in 72% of yield, as a yellow solid, with a melting point of 146 °C and retardation factor Rf = 0.92 (*n*-hexane/ethyl acetate 7:3). The main infrared bands and NMR data obtained are briefly summarized as follows: IR_{max} (KBr) cm⁻¹: 3139 (C-H), 1552 and 1325 (NO₂), 970 (C=C trans); ¹H NMR (500.13 MHz) CDCl₃ ():8.17 (1H, s, H-5), 8.00 (1H, d, J = 13.5 Hz, H-β), 7.96 (1H, s, H-3), 7.65 (2H, d, *J* = 8.9 Hz, H-2' and 6'), 7.52 (1H, d, J = 13.5 Hz, H- α), 7.47 (2H, d, J = 8.9 Hz, H-3' and 5'); ¹³C NMR (125.76 MHz) CDCl₃ (): 140.7 (C-3), 137.3 (C-1'), 135.9 (Cα), 133.3 (C-4'), 129.8 (2 C-3' and 5'), 129.2 (C-β), 128.3 (C-5), 120.4 (2 C- 2' and 6'), 115.4 (C-4).

NLO measurements

Dimethyl sulfoxide (DMSO) of spectroscopic grade was used as solvent for compound **(2)**. Solutions with different concentrations were prepared and ultrasonicated for 10 min. before performing the experiments. Transparent solutions of light pale yellow and yellow/red colors were achieved. The absorption spectra in the UV/Vis region were measured with a Shimadzu UV-1800 spectrometer, with sample concentration of 6×10^{18} molecules per cm³ (1 × 10² mol L⁻¹). Both linear and nonlinear measurements were done in fused silica cuvettes with a 2 mm optical path.

The 2PA cross-section spectrum was obtained with the openaperture Z-scan technique [24,25] using 120-fs pulses from an optical parametric amplifier pumped by a commercial Ti:Sapphire chirped pulse amplifier (775 nm and 1 kHz repetition rate), allowing wavelength tuning from 450 to 800 nm. To improve the Gaussian profile of the laser beam spatial filtering was used. The beam waist at the focus was measured to be 15–17 μ m, and the laser pulse energies range from 50 to 100 nJ, depending on the excitation wavelength. The details of the Z-scan experimental setup were already discussed in Ref. [26]. The experimental Z-scan curves



Fig. 1. Synthesis of (*E*)-1-(4-chlorophenyl)-4-(2-nitrovinyl)-1-phenyl-1*H*-pyrazole (2).

were fitted using the expression for the normalized energy transmittance, T(z), given as [24,25]:

$$T(z) = \frac{1}{\sqrt{\pi}q_0(z,0)} \int_{-\infty}^{\infty} \ln[1+q_0(z,t)e^{-t^2}]dt,$$
(1)

where $q_0(z,t) = \beta I_0(t)L(1 + z^2/z_0^2)^{-1}$, *L* is the optical path, z_0 is the Rayleigh length, *z* is the sample position, and I_0 is the pulse irradiance. By fitting the Z-scan curve with Eq. (1) one obtains the 2PA coefficient β . The 2PA cross-sections can be determined using the relationship $\delta = hv\beta/N$, where hv is the excitation energy, and *N* is the number of molecules per cm³. Usually, δ is expressed in Goeppert-Mayer (GM) units, being 1 GM = 1 × 10⁻⁵⁰ cm⁴ s molecule⁻¹ - photon⁻¹ [27].

For the measurement of first hyperpolarizability, HRS experiments were carried out with picosecond infrared (1064 nm) pulse trains composed by approximately 20 pulses of 70 ps separated by 13 ns, delivered by a Q-switched and mode-locked Nd:YAG laser. To improve the detection, the scattering point is located between a spherical mirror and a telescope, and the signal is collected by a photomultiplier with a response time of 3 ns at FWHM. A reference signal for the laser intensity is collected by a PIN detector with a response time of 1 ns. The value of the first hyperpolarizability was determined by using the external approach with p-NA (solute) in DMSO (solvent) as reference. Detailed description of the experimental arrangement can be found in Ref. [28].

Quantum chemical calculations

Initially, the ground-state geometry was fully optimized in gasphase and in DMSO without any symmetry constraint using the second-order Møller–Plesset perturbation theory (MP2) method with the 6-311G(2d) basis set. To calculate the solvent effects we have employed the self-consistent reaction field (SCRF) approach with the polarizable continuum model within the integral equation formalism (IEFPCM) [29], as implemented in the GAUSSIAN 09 package [30]. DMSO is an appropriated description of solvent effects.

The excitation energies were obtained using the TD-DFT approach [31] in combination with the CAM-B3LYP (CAM-B3LYP: Coulomb-attenuating method applied to B3LYP) of Yanai et al. [32]. This long-range corrected functional improves the asymptotic behavior of the exchange interaction, which provides a reliable description of the charge-transfer excited-states. Following a previous work [33], we have adopted in the TD-DFT calculations the 6-311+G(2d,p) basis set.

The static and dynamic components of the first hyperpolarizability were calculated analytically using the time-dependent Hartree–Fock (TDHF) approach [34]. A standard wavelength of 1064 nm was considered in dynamic property calculations. At the MP2 level, the calculations of the static properties were performed numerically through the finite field (FF) method using field strengths of order 0.001 a.u. To estimate the correlated dynamic results, we have employed the multiplicative correction scheme used in the literature [35]:

$$\beta_{\rm MP2}(-2w; w, w) \approx \beta_{\rm MP2}(0; 0, 0) \times \frac{\beta_{\rm TDHF}(-2w; w, w)}{\beta_{\rm TDHF}(0; 0, 0)}$$
(2)

The first hyperpolarizability reported here is the quantity related to the hyper-Rayleigh scattering intensity for plane polarized incident light, given by [36]:

$$\beta_{HRS}(-2w; w, w) = \sqrt{\langle \beta_{ZZZ}^2 \rangle + \langle \beta_{ZZZ}^2 \rangle}$$
(3)

The first hyperpolarizability calculations were performed with the 6-311+G(d) basis set that provides a compromise between

computational cost and reliability for a number of organic molecules. Both electronic properties and geometry optimization calculations were performed using the GAUSSIAN 09 electronic structure package [30].

Results and discussion

Two-photon absorption

As shown in Fig. 2, the one-photon absorption (1PA) spectrum of compound (**2**) contains two absorption bands at 258 and 350 nm. The values of absorbance and the concentration were used to estimate the ground-state absorption cross-section, σ_g , from the relation $\alpha_g = N\sigma_g$, where α_g is the ground-state absorption coefficient and *N* is the molecular concentration. The value of absorption cross-section obtained for compound (**2**) was found to be 5.94×10^{-16} cm² at 354 nm.

TD-CAM-B3LYP calculations indicate that the absorption bands originate from $\pi \rightarrow \pi^*$ transitions. In gas-phase, the TD-CAM-B3LYP results give the lower transition energy of 4.14 eV (299 nm) and the higher one of 5.39 eV (230 nm). In DMSO, the IEFPCM-TD-CAM-B3LYP model predicts transition energies of 3.78 eV (328 nm) and of 5.25 eV (236 nm), respectively. These findings show that the solvent effects lead to very large red shift of -0.36 eV (29 nm) for the lower energy band when going from gas-phase to DMSO. For the higher energy band the corresponding red shift is smaller and is predicted to be -0.14 eV (6 nm).

For the compound (2), the CAM-B3LYP functional predicts an absolute energy value that is underestimated in 22 nm, as compared with experimental result of 350 nm (lower energy band) in DMSO. Our TD-DFT calculations also indicate that the lower energy band corresponds to HOMO \rightarrow LUMO excitation whereas the higher one originates from a HOMO \rightarrow LUMO + 1 excitation. The shape of the frontier orbitals involved in the electronic transitions is illustrated in Fig. 3. One can see that the HOMO orbital is delocalized over the compound but its major part is localized on the benzene and pyrazole rings. Upon excitation, the shape of the LUMO orbital is characterized by an intramolecular charge transfer from benzene ring (with a contribution of the Cl atom) to NO₂ group, including some atoms of the pyrazole ring. The LUMO + 1 orbital is delocalized over the benzene and pyrazole ring.

The 2PA cross-section spectrum of compound **(2)** in the wavelength range of 510–750 nm is also depicted in Fig. 2. They were



Fig. 2. Linear absorption spectrum (solid line) and 2PA cross-section (open circles) spectra of compound (**2**) in DMSO solution.

extracted by fitting the Z-scan normalized transmittance curves with Eq. (1) for several excitation wavelengths, as shown by the dashed lines of Fig. 4a. These Z-scan signatures present a decrease in the normalized transmittance on the z position, which indicates the existence of a 2PA process.

Comparing the 1PA and 2PA spectra depicted in Fig. 2, one can see that the absorption bands appear at nearly the same energy. Similar to the 1PA spectrum, 2PA also exhibits two bands with cross-section of ~58 and 67 GM ($1 \text{ GM} = 1 \times 10^{-50} \text{ cm}^4 \text{ s}$ photon⁻¹) at 520 and 690 nm, respectively. Recalling the symmetry selection rule, in case of molecules without center of symmetry, i.e. noncentrosymmetric molecules, the parity of the electronic states is not well-defined and the same transition is simultaneously allowed for 1PA and 2PA. This is distinct from centrosymmetric molecules, in which the selection rules are exclusive for 1PA and 2PA. The allowed transitions are shown in Fig. 4b.

First hyperpolarizability

As already mentioned, the first order hyperpolarizability was measured in picosecond hyper Rayleigh scattering experiments. In HRS, the intensity of the scattered light is proportional to the quadratic of the incident light intensity, according to the expression [37]:

$$\mathbf{I}(2\omega) = \mathbf{G} \cdot \left(\rho_{sv} \beta_{sv}^2 + \rho_{st} \beta_{st}^2\right) \mathbf{I}^2(\omega) \tag{4}$$

where $I(\omega)$ and $I(2\omega)$ are, respectively, the irradiance of the incident light and the light scattered at the double of the frequency of the incident light. The molecular density (ρ) and first hyperpolarizability (β) of the solvent and solute are represented as ρ_{sv} , ρ_{st} and β_{sv} , β_{st} , respectively. Keeping the solvent density constant and varying the solute density, a linear behavior with angular coefficient $G\beta_{st}^2$, obtained by plotting $I(2\omega)/I^2(\omega)$ against ρ_{st} , is expected.



Fig. 3. Representation of the molecular orbitals for compound (2) in DMSO.



Fig. 4. (a) Experimental open aperture Z-scan curves of (2) obtained upon excitation with different wavelengths at identical power. The dashed lines are the theoretical fits obtained by using Eq. (1). (b) Energy level diagram for compound (2) and pathways for optical transitions.

Since the molecule under study partially absorbs at 532 nm, the light scattered should be corrected by the factor $10^{A/b}$, where *A* is absorbance at 532 nm and *b* is the optical path of the sample. The HRS data acquired for compound (**2**) in DMSO solution, given by Eq. (4), and the behavior of $I(2\omega)/I^2(\omega)$ as a function of the concentration are depicted in Fig. 5.

The first hyperpolarizability can be calculated by taking the ratio between the angular coefficient (α) of the reference and compound (**2**), and using the known first hyperpolarizability of the reference (which for pNA in DMSO is $26.2 \times 10^{-30} \text{ cm}^5/\text{esu}$) according to:

$$\beta_{\text{sample}} = \sqrt{\frac{\alpha_{\text{sample}}}{\alpha_{\text{reference}}}} \beta_{\text{reference}}$$
(5)

Using Eq (5), we obtained the first hyperpolarizability of compound (2) in DMSO ass $(45\pm2)\times10^{-30}\,cm^5/esu.$

We compare the MP2/6-311+G(d) results for the static and dynamic first hyperpolarizabilities of compound (2) obtained in the gas-phase and in DMSO with the experimental value. In the gasphase, the static result for β_{HRS} is of 12.40 × 10⁻³⁰ cm⁵/esu. This value represents around of 28% of the experimental result in DMSO, indicating that the MP2 result obtained in gas-phase for β_{HRS} is only in qualitative agreement with the measured value. It is found here that the addition of the solvent polarization effects have a marked influence on the first hyperpolarizability and is crucial to



Fig. 5. HRS signal obtained for (**2**) in DMSO for different solution concentrations and with the signal corrected by its absorbance. The inset shows the linear dependence between the quadratic coefficient and the concentrations of (**2**) in DMSO with and without (black star) corrections for the absorption on 532 nm.

improve the agreement with the experiment. In fact, the static β_{HRS} value estimated in solution is of 37.05×10^{-30} esu, which is approximately three times larger than the value obtained in gasphase. In addition, the frequency dispersion effects induced by an incident beam lead to an increase of β_{HRS} by 7% compared to the static values. Thus, the dynamic MP2 result in solution for β_{HRS} is of 40×10^{-30} cm⁵/esu. Comparing the theoretical and experimental β_{HRS} values, we find that the theoretical β_{HRS} in DMSO is underestimated in only 12%.

Conclusions

In summary, a novel organic compound namely (*E*)-1-(4-chlorophenyl)-4-(2-nitrovinyl)-1*H*-pyrazole was synthesized and its nonlinear optical properties were investigated using 2PA and HRS measurements, as well *ab initio* calculations at the MP2 level with the 6-311+G(d) basis set. It is found that this molecule is non-linear active with 2PA cross-sections of ~58 and 67 GM at 520 and 690 nm, respectively. The MP2 results show that the role of the solvent is crucial to meet the concordance with experiment. Dispersion effects increase the static β_{HRS} value around 7%. The solution dynamic MP2 result for β_{HRS} is estimated to be 40×10^{-30} cm⁵/ esu. This theoretical value of β_{HRS} is in good agreement with the measured value of $45 \pm 2 \times 10^{-30}$ cm⁵/esu.

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