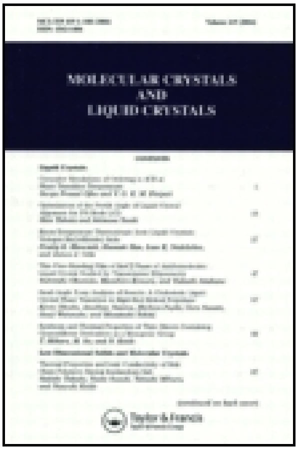

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Jacek Nizioł [a], Ewa Gondek [b], Ivan V. Kityk [c], Zacaria Essaidi [d] & Bouchta Sahraoui [d]

[a] Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Kraków, Poland

[b] Institute of Physics, Cracow University of Technology, Cracow, Poland

[c] Institute of Physics, Jan Dlugosz University in Czestochowa ul. Armii Krajowej, Częstochowa, Poland

[d] POMA - Laboratory of Optical Properties of Materials and Applications, University of Angers, Angers Cedex, France

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Theoretical and Experimental Studies of NLO Properties of New Carbazole Derivatives

Jacek Nizioł[1], Ewa Gondek[2], Ivan V. Kityk[3], Zacaria Essaidi[4], and Bouchta Sahraoui[4]
[1]Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Kraków, Poland
[2]Institute of Physics, Cracow University of Technology, Cracow, Poland
[3]Institute of Physics, Jan Dlugosz University in Czestochowa ul. Armii Krajowej, Częstochowa, Poland
[4]POMA – Laboratory of Optical Properties of Materials and Applications, University of Angers, Angers Cedex, France

In this article we report theoretical calculations and experimental findings concerning linear optical and nonlinear optical properties of three model azo-carbazole derivative dyes. The goal of the work was to answer to what extent theoretical modeling can predict actual properties of a series of these dyes. Theoretical calculations were based on MM+, AM1 and PM3 models. Experimental data were obtained through UV-vis spectroscopy and electro-optic method.

Keywords: azo-carbazole dyes; Pockels effect; poling; quadratic electro-optical Kerr effect

INTRODUCTION

Azo-carbazoles are a kind of dyes which has potential for practical applications. Their chemical properties have already been reviewed in a number of publications [1]. Their applicability in the field of nonlinear optics has also been demonstrated [2,3].

Azo-carbazoles themselves rarely are film forming materials. Typically these dyes are used in blends with an appropriate host polymer. To render the dye molecule compatible with the host polymer it is

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Address correspondence to Jacek Nizioł, Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, al.Mickiewicza 30, Kraków 30-059, Poland. E-mail: gjniziol@cyf-kr.edu.pl

custom to modify the dye by substituting a side group bearing chemical function adapted to the chosen host polymer.

In this article we tried to find to what extent theoretical calculation can predict spectral and nonlinear optical properties of modified in a systematic way, azo-carbazoles.

MATERIALS

Three dyes were synthesised -*3-(2′-chloro-4′-nitrophenylazo-)carbazole* [abbrev. CNPA-C], *3-(2′-chloro-4′-nitrophenylazo-)N-ethylcarbazole* [abbrev. CNPA-EC] and *3-(2′-chloro-4′-nitrophenylazo)-N-(β-chlorethyl)-carbazole* [abbrev. CNPA-ClEC]. The choice reflected logic – no side group, aliphatic substitution, chlorinated aliphatic substitution. Their schematic structures are shown in Figure 1. The azo-carbazole dyes were

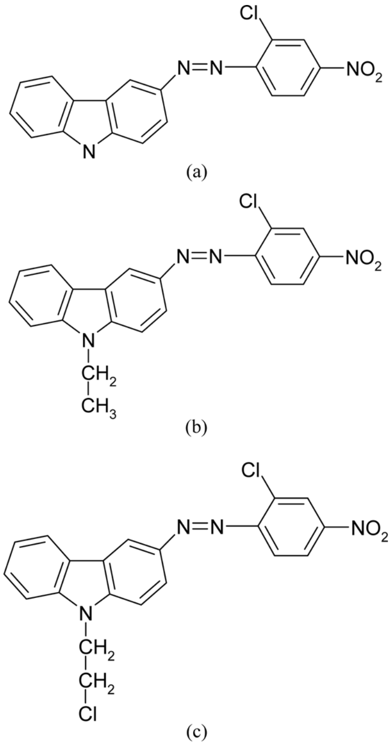

FIGURE 1 Schematic structures of synthesised dyes (a) *3-(2′-chloro-4′-nitrophenylazo-)carbazole* CNPA-C, (b) *3-(2′-chloro-4′-nitrophenylazo-)N-ethylcarbazole* CNPA-EC, (c) *3-(2′-chloro-4′-nitrophenylazo)-N-(β-chlorethyl)-carbazole* CNPA-ClEC.

synthesised by coupling reaction between carbazole or its derivatives and diazonium salts of aromatic amines in a biphasic system. Further details of this procedure have been already described in [4]. All chemicals used, were purchased from Aldrich or Fluka and used as received.

THEORETICAL CALCULATIONS

Calculations of optical absorption spectra, static dipole moments and molecular nonlinear optical properties constants have been performed using the molecular dynamic and quantum-chemical package Hyperchem 7.5. Geometrical optimization has been done using (MM+) force field method (all-atom force-field model). Together with semi-empirical Allinger method (AM1) and PM3 methods this model is known to be the most general and frequently used one for molecular mechanic calculations developed principally for organic molecules. Occupied and unoccupied molecular orbitals have been also taken into account. Configuration interactions determining the most valuable excited states were considered up to the 14 eV.

The intensity of spectral optical absorption I(ω) is determined by (1):

$$I(\omega) \approx \omega \sum_{k=1}^{n} \sum_{i=x,y,z} \frac{\left| \left\langle \Psi_{ji}^{*} \middle| i\hbar \vec{\nabla}_{r} \middle| \Psi_{ki} \right\rangle \right|^{2}}{\hbar^{2} (\omega - \omega_{jk})^{2} + (\Gamma/2)^{2}} \tag{1}$$

where Ψ_j and Ψ_k^* are wave function of j-th and k-th energy levels, $i\hbar\vec{\nabla}_r$ is a transition dipole momentum operator of molecule, $\hbar\omega_{jk} = (E_j - E_k)$ is the energy difference between the ground and excited state, ω is the frequency of incident elelctromagnetic wave.

Taking into account that the integration is performed over the space volume the intensity of spectral absorption reads by (2):

$$I(\omega) \approx \omega \sum_{k=1}^{n} \sum_{i=x,y,z} \frac{\left| (\mu)_{jk}^{i} \right|^{2}}{(\omega - \omega_{jk})^{2} + (\Gamma/2\hbar)^{2}} \tag{2}$$

Molecular nonlinear hyperpolarizabilities γ_{klij} have been calculated using the model with so-called multilevel excitation. They are expressed by (3).

$$\gamma_{klij} = \gamma_{mn} = K \sum_{g=1}^{N} \frac{\left|\mu_i^{(g)}\right| \left|\mu_j^{(g)}\right| \left|M_k^{(g)} - M_k^{(0)}\right| \left|M_l^{(g)} - M_l^{(0)}\right|}{\left(E_g^2 - 4E^2 + H^2\right)} \tag{3}$$

where: $k, l, i, j = x, y, z$ or 1,2,3; $m, n = 1,2,3,4,5,6$ ($1 \equiv xx$, $2 \equiv yy$, $3 \equiv zz$, $4 \equiv yz$, $5 \equiv xz$, $6 \equiv xy$), $K = 7{,}457 \cdot 10^{-38}$, g-number of transition from ground state, E_g-transition energy, $\mu_i^{(g)}$-transition dipole component, $M_k^{(g)}$-excited state dipole component, $M_k^{(0)}$-ground (reference) dipole component H-damping.

Values of molecular nonlinear hyperpolarizabilities β were obtained from Eq. (4):

$$\beta_{kij} = \beta_{kl} = 12\pi^2 K \sum_{g=1}^{N} \frac{E_g^2 \left|\mu_i^{(g)}\right| \left|\mu_j^{(g)}\right| \left(\mathrm{M}_k^{(g)} - \mathrm{M}_k^{(0)}\right)}{(E_g^2 - 4E^2 + H^2)(E_g^2 - E^2 + H^2)} \tag{4}$$

where: $i,j,k, = x,y,z$ or $1,2,3$; $1 = 1,2,3,4,5,6$; $K = 5{,}21073 \cdot 10^{-31}$, g-number of transition from ground state, E_g-transition energy, $\mu_i^{(g)}$-transition dipole component, $M_k^{(g)}$-excited state dipole component, $M_k^{(0)}$-ground (reference) dipole component H-damping.

EXPERIMENTAL

Absorption spectra were measured in solutions. Solvents ranged from the least polar cyclohexane to the most polar acetonitrile. Blend samples in PMMA containing studied molecules were prepared by spin-coating from solution in dimethylethane. Once dried, they were oriented by corona-poling, all under identical conditions – the sample thermostated at 100°C, 7 keV applied to within 5 minutes plus two minutes until the temperature didn't reach the ambient. Since their chemical affinity to the host matrix was similar, it was supposed, that interaction with the surrounding polymer chain was also similar. Then, the macroscopic NLO susceptibilities $\chi^{(2)}$ and $\chi^{(3)}$ should remain in same ratio as do β and γ.

To measure $\chi^{(2)}$ and $\chi^{(3)}$ reflection electro-optic method was used, adapted from [5]. This method relies on phase sensitive detection of the intensity of reflected laser beam. If the sample is subjected to a modulated electric field superimposed on a constant field, frequency dependent variation of reflected laser beam is given by (1).

$$\Delta I(\omega) = const \cdot E_{AC}\left(\chi_{333}^{(2)} - 2E_{DC}\chi_{3333}^{(3)}\right) \tag{1}$$

where *const* – geometrical factor depending on refractive indices, incidence angle, sample thickness and laser beam intensity. If Boltzman-type orientation for poled samples is accepted, all other components of susceptibility tensor can be estimated. Schematic representation of the experimental setup is shown in Figure 2.

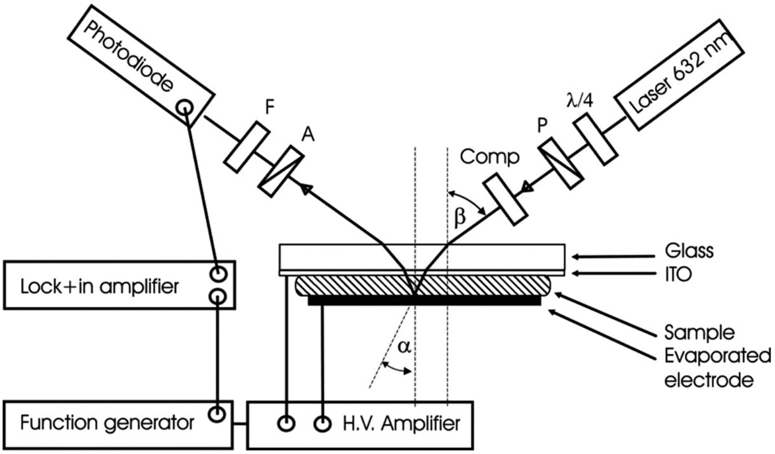

FIGURE 2 Experimental setup for simultaneous determination of second and third-order susceptibilities in poled polymer films. F – laser wavelength interference filter, P – polarizer, A – analyzer, Comp- Soleil-Babinet compensator.

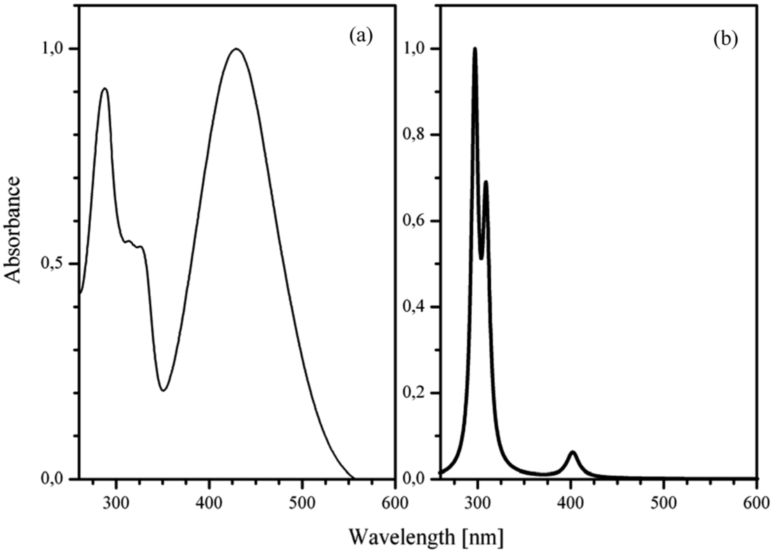

FIGURE 3 Absorption spectra of *3-(2′-chloro-4′-nitrophenylazo-)carbazole* [CNPA-C], in cyclohexane (a), calculated (b).

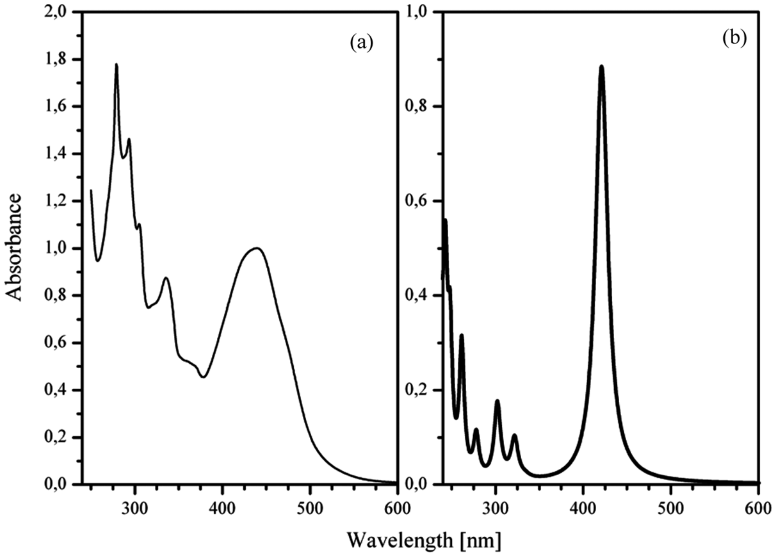

FIGURE 4 Absorption spectra of *3-(2′-chloro-4′-nitrophenylazo-)N-ethylcarbazole* [CNPA-EC] in cyclohexane (a), calculated (b).

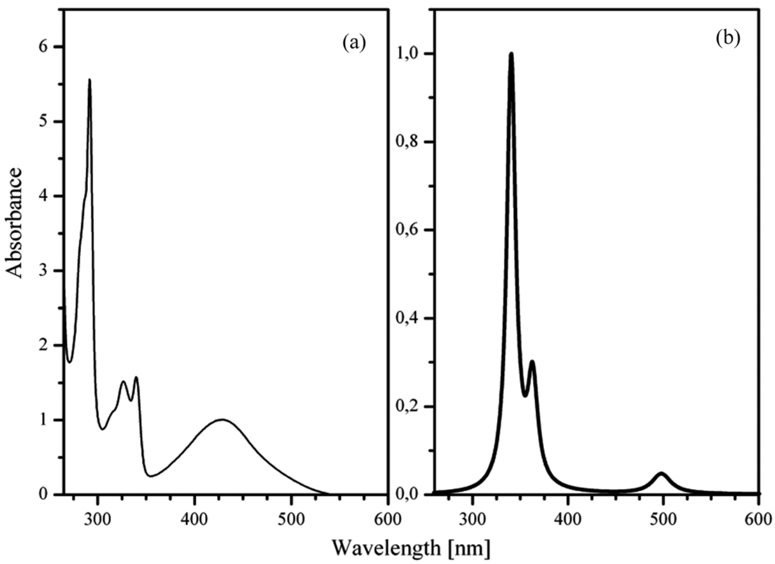

FIGURE 5 Absorption spectra of *3-(2′-chloro-4′-nitrophenylazo)-N-(β-chlorethyl)-carbazole* [CNPA-ClEC] in cyclohexane (a), calculated (b).

TABLE 1 Calculated Values of Nonlinear Molecular Susceptibilities β and γ and Measured Macroscopic Nonlinear Susceptibilities $\chi^{(2)}$ and $\chi^{(3)}$. Calculated Statictic Dipole Moment were as Follows: CNPA-C-1,94 D, CNPA-EC 12,094 D, CNPA-ClEC 2,069 D

Molecule	β[a.u.]	$\gamma[\mathrm{m}^5 \cdot \mathrm{V}^{-2}]$	$\chi^{(2)}_{333}$ [m/V]	χ^{2}_{333} $[\mathrm{m}^2 \cdot \mathrm{V}^{-2}]$	$\beta/\chi^{2}_{333}[\times 10^{11}]$	$\gamma/\chi^{2}_{333}[\times 10^{-16}]$
CNPA-C	1.94	$5{,}80 \cdot 10^{-37}$	$5{,}2 \cdot 10^{-13}$	$1{,}2 \cdot 10^{-21}$	37	4,8
CNPA-EC	1955	$5{,}90 \cdot 10^{-37}$	$7{,}8 \cdot 10^{-11}$	$1{,}7 \cdot 10^{-21}$	250	3,5
CNPA-ClEC	243	$4{,}90 \cdot 10^{-36}$	$0{,}9 \cdot 10^{-11}$	$1{,}6 \cdot 10^{-20}$	270	3,1

RESULTS AND DISCUSSION

Recorded in cyclohexane solution and theoretically predicted spectra are presented in Figures 3–5. As one can see, higher order transitions correspond well in experimental and calculated spectra. However, in all cases calculated transition between fundamental and first excited state (lying most rightwards) fits very poor to experimental data. Absorption due to this transition, situated in the vicinity of 500 nm plays important role in practice because 532 nm is the most often used laser line in many techniques.

Results of both numerical and experimental findings of molecular and bulk hyperpolarizabilities are collected in Table 1. Numbers in two last columns are ratio of calculated β, γ and measured $\chi^{(2)}_{333}$, $\chi^{(2)}_{3333}$ subsequently. One can see that for three studied molecules, these values are in pretty good agreement. It suggests that adopted theoretical models may be used in future to estimate nonlinear susceptibilities of alkyl-substituted azo-carbazoles prior to synthetic work.

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