

## THEORETICAL SIMULATION OF THE THIRD ORDER NONLINEAR OPTICAL PROPERTIES OF SOME SELECTED ORGANOMETALLICS COMPLEXES.

A. Migalska-Zalas

Institute of Physics, J. Dlugosz Academy of Czestochowa, PL-42217, Aleja Armii Krajowej 13/15, Czestochowa, Poland

Theoretical calculations of the third order nonlinear optical coefficient as well as theoretical simulation of UV-VIS absorption spectra for a new alkynyl-ruthenium complexes bearing terminal hydrogen-bonding receptors was presented. The proposed theoretical approach rely on geometry optimisation and corresponding quantum chemical calculations based on semi-empirical ZINDO /1 method within a framework of the restricted Hartree-Fock approach. The theoretically calculated absorption spectral positions are blue shifted in comparison to the experimental spectra for all compounds what is connected with the strong solvent effect. The theoretical calculation show that the second - order hyperpolarizabilities  $\gamma$  depends from the wavelength of incident electromagnetic radiation. A substitution of the different groups at the end of back side group causes the substantial changes of both absorption spectra as well as nonlinear optical coefficients. We show a dramatic enhancement of the molecular cubic hyperpolarizability in these systems for several wavelength of incident light beam. Comparison of theoretical results with the experimental data is presented.

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### 1. Introduction

Since the first investigation of nonlinear optical properties of organometallic molecules many new substances have been found<sup>1, 2, 3,4</sup>. Most of the research now concentrates on materials with two or more  $\pi$ -electrons rings because they are superior with regard to the molecular hyperpolarizabilities. In organometallics, the metal- ligand bonding look forward to point large molecular hyperpolarizability because of the transfer of the electrons between the metal and the conjugated system. Organometallics may have a wide use in optoelectronics including intergrated optics, optical switching, telecommunications<sup>5, 6, 7</sup>. The optimization of the nonlinear properties of organic materials need in first order the study of molecular nonlinearities.

In this paper, we present the theoretical quantum chemical calculation of UV spectra and second order frequency-dependent molecular hyperpolarizability a novel series of donor-acceptor ruthenium chromophores possessing the chemical formula presented in the Table1.

The performance of the UV-VIS spectra is necessary to have an idea about the further modifications of the materials. The quantum chemical calculations give important information concerning the origin of the observed spectra and information for desirable changes of the chemical content using appropriate substituent. Moreover, information about nonlinear optical properties of the investigated molecules may be crucial.

Especially attention will be devoted to the delocalisation of  $\pi$  electrons along the molecular backbone influence of different substituent on the output of third order optical properties and a spectral shift of UV absorption.

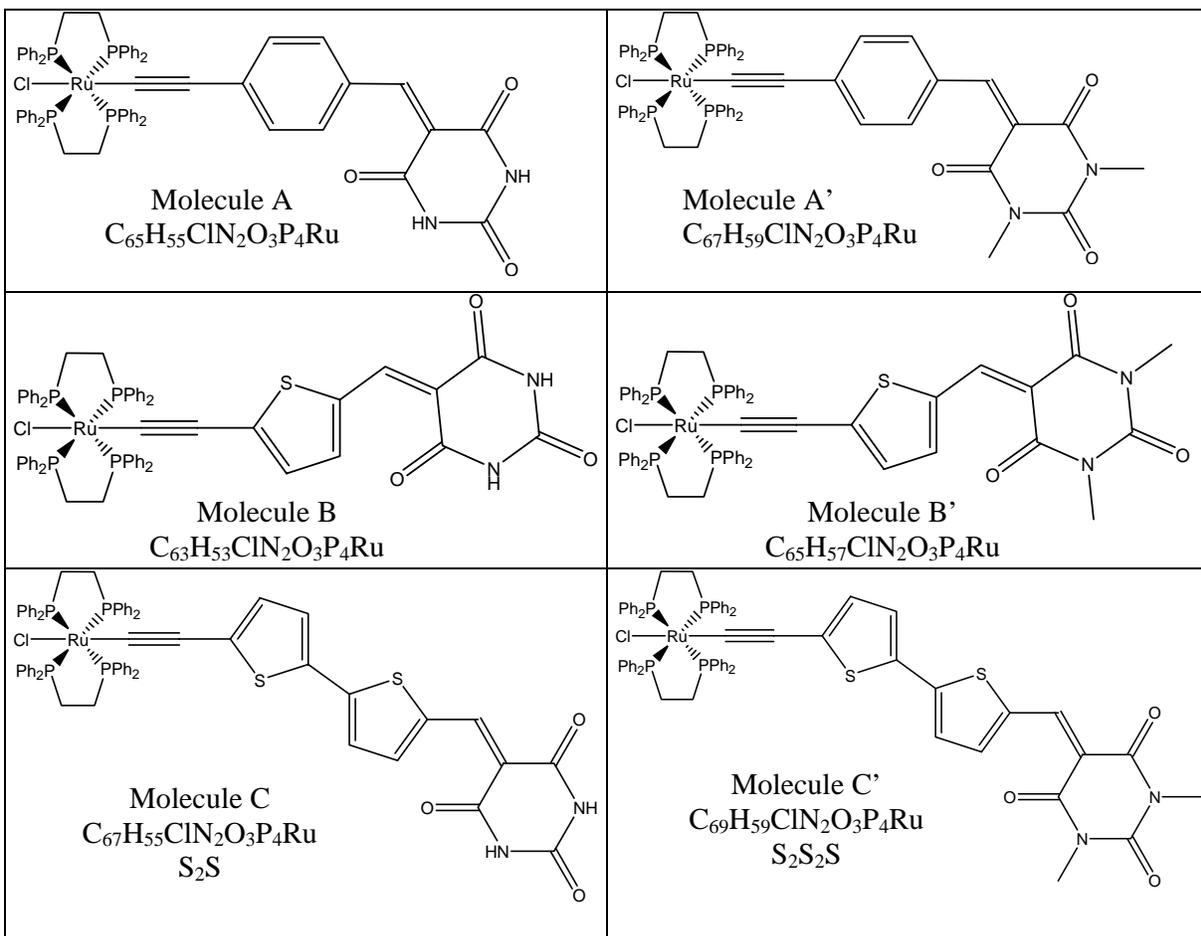
The synthetic methodologies employed for the preparation of the new ruthenium derivatives have been adapted from previously reported procedures in the reference [8]<sup>8</sup>.

## 2. Theoretical simulation

For theoretical simulations of absorption spectrum the six kind of different chromophores (molecules indicated by: A, A', B, B', C, C' – Table 1.) were considered.

Initially geometry optimization (searching of the total energy minimum) for the molecule was performed. The MM<sup>+</sup> molecular force field method was used for total energy minimization and for building of the molecular optimized geometry<sup>9, 10</sup>. All quantum chemical calculations were performed by semi-empirical ZINDO/1 method within a framework of the restricted Hartree-Fock approach and convergence limit up to 10<sup>-6</sup> eV after 500 iterations was achieved. The ZINDO/1 method was optimized as a universal semi-empirical method for calculating energy states in molecules containing transition metals (3d and 4d). The electronic spectra were calculated by the configuration interaction (CI) method with the maximum excitation energy up to 9 eV. Local perturbation were considered only within a framework of the isolated molecule. The influence of the intermolecular electron vibration interactions is not taken into account. Therefore deviations from the experimental data will give information concerning the observed intra-molecular and intermolecular interactions.

Table 1. Chemical formula of the investigated molecules: A, A', B, B', C, C'.



The intensity of absorption was expressed by the formula presented in ref<sup>11</sup>:  
The values of second order hyperpolarizability may be expressed in terms of the different energy levels from  $g$  to  $n$ , of the molecule.

$$\gamma_{ijkl} = K \sum_{g=1}^n \frac{|\mu_i^{(g)} \mu_j^g \langle M_k^{(g)} - M_k^{(0)} | M_l^{(g)} - M_l^{(0)} \rangle|}{(E_g^2 - (2\hbar\omega)^2 + H)} \quad (1)$$

where  $\mu_i^{(g)}, \mu_j^{(g)}$  are the transition dipole moment between the high occupied molecular orbital (HOMO) and the excited state,  $|M_k^{(g)} - M_k^{(0)}|$  - difference between the excited (configuration interaction (CI) level) state dipole moment and ground state one,  $E_g$  - transition energy from the ground to excited state,  $\hbar\omega$  is the energy of an incident laser photon,  $H$  determines the line shape broadening,  $n$  is a number of excited state. Indices  $i, j, k, l = x, y, z$  are defined as laboratory Coordinate Cartesian system where  $x$  - axis corresponds to the longest axes of the molecule.

In a present work we calculated only  $\gamma_{xxxx}$ , because the maximal output of nonlinear signal were observed usually for the diagonal tensor component, where the  $x$ - direction corresponds to polarizations direction of the photo inducing beam. The calculated values of the nonlinear optical hyperpolarizabilities are presented in Figure 2. and in the Table 3.

### 3. Results and discussion

The experimental spectra were performed with a cell thickness of about 1 cm and very weak concentration ( $\sim 10^{-5}$  mol/l). The spectra showed that all these compounds absorb in a weak zone inter 200 nm and 230 nm. We can observe that all these compounds exhibit no measurable absorption at 532 nm what is very important in order to avoid resonance effect in experiment. The calculated and measured spectral positions of the molecules are presented in Table 2.

The position of the two first peaks: I, II, of the calculated spectra are shifted to the region of smallest wavelengths with respect to experimental peaks positions (peaks: 1, 2) about 5-20 nm.

For longer wavelength (peaks: III, IV and 3, 4) we have larger divergence what is connected with the right side of molecule which plays an important role in the vibration system. The second reason of disagreement between the theoretical and experimental results of absorption spectra could be a quantum chemical calculations without taking into account interaction between molecule and solvent polarity<sup>12</sup>.

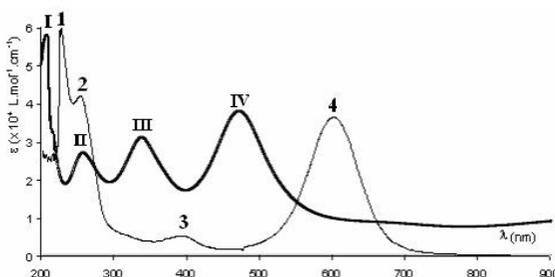


Fig. 1. Theoretical and experimental spectra for compound A (thin line experiment, bold line theory).

Table 2. Calculated and measured spectral positions for the principal.

Complex	$\lambda_1$ (nm) (exp.)	$\lambda_1$ (nm) (cal.)	$\lambda_2$ (nm) (exp.)	$\lambda_2$ (nm) (cal.)	$\lambda_3$ (nm) (exp.)	$\lambda_3$ (nm) (cal.)	$\lambda_4$ (nm) (exp.)	$\lambda_4$ (nm) (cal.)
A	227	208	254	259	375	338	588	476
A'	228	209	253	260	363	339	571	475
B	227	206	256	242	397	386	606	468
B'	227	211	255	243	390	378	593	468
C	228	212	252	249	438	366	681	465
C'	228	224	253	261	429	309	655	451

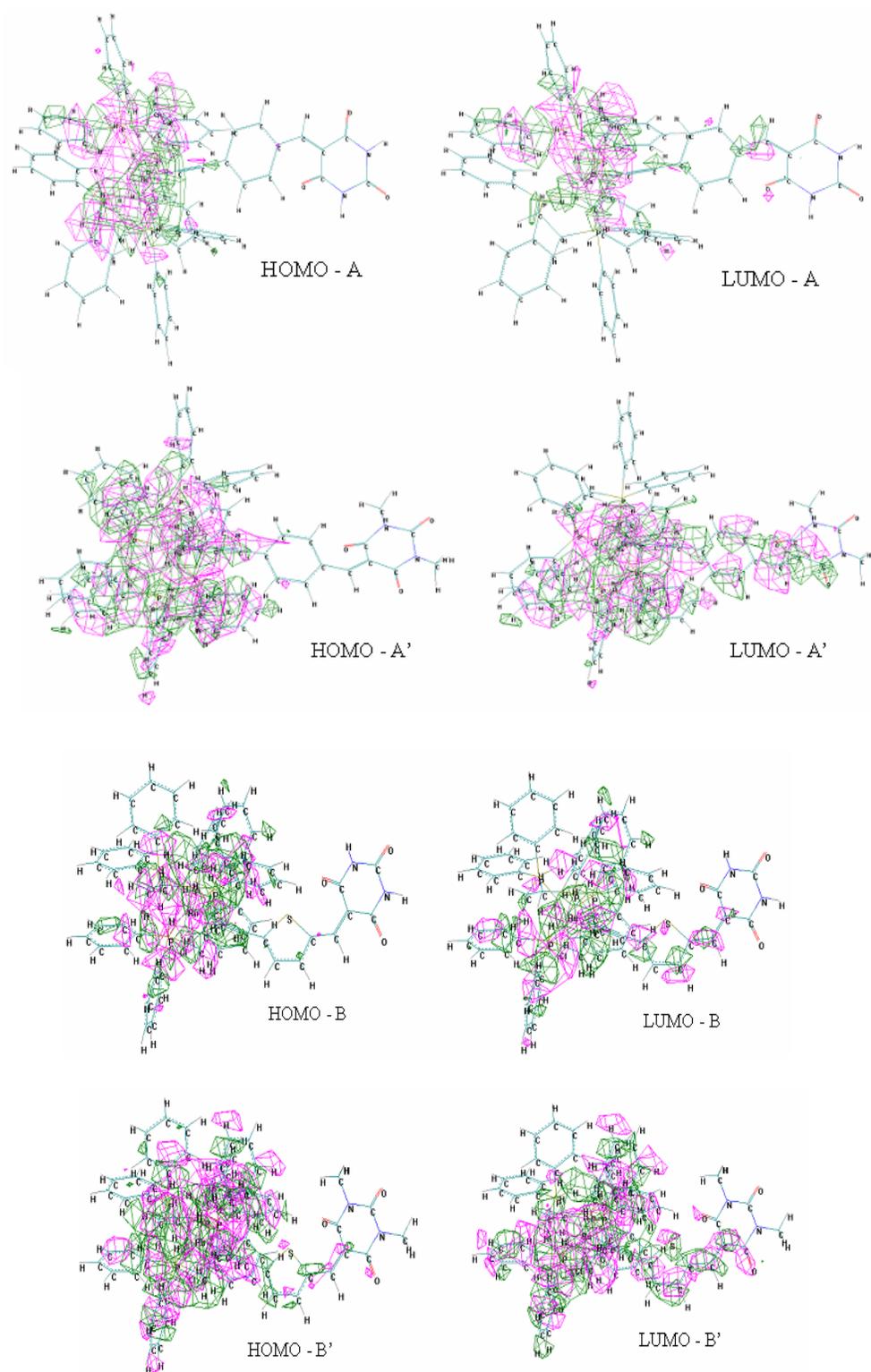


Fig. 2. ( b ). Electrostatic potential distribution HOMO and LUMO for compounds B, B'.

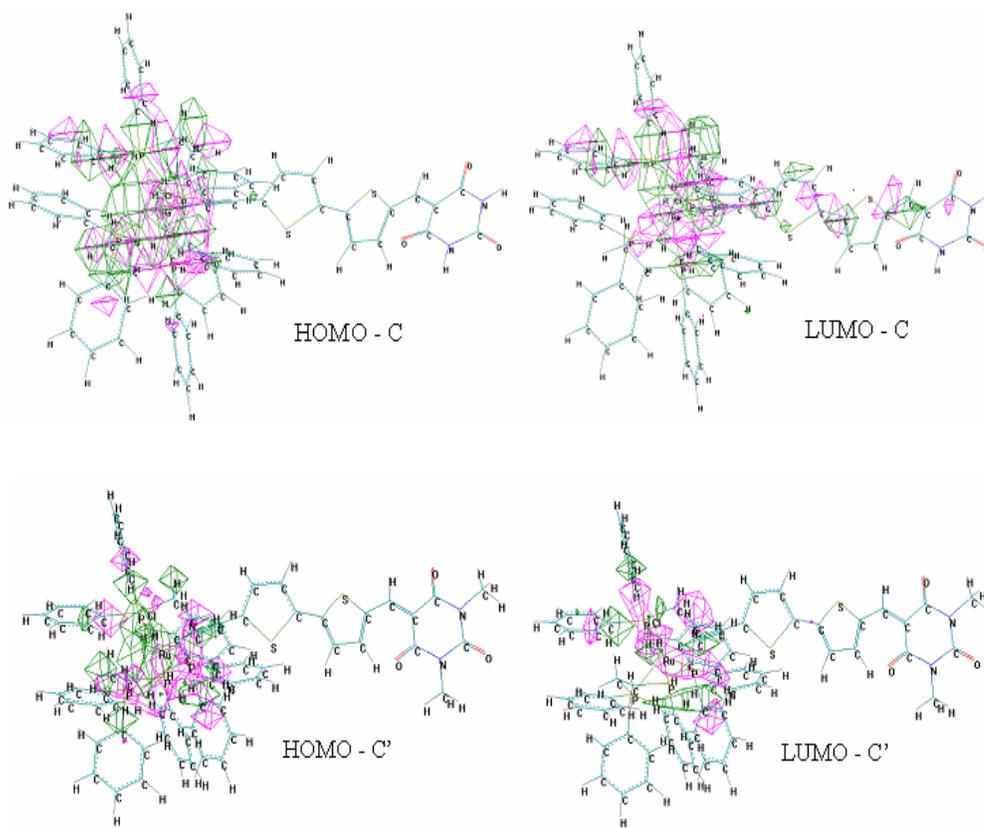


Fig. 2. ( c ). Electrostatic potential distribution HOMO and LUMO for compounds C,C'.

Fig. 2. (a, b, c) present the calculated molecular orbital wavefunctions corresponding to the HOMO and LUMO orbitals.

The mother, left-side part of the molecule is the same, therefore these structural fragments do not essentially contribute in relays of optical properties. We should point out the fragments contributing to the obtained results and we present only the largest contributions connected with influence the MO wave functions. In this case main role belongs to the fragments that are placed on right side of the molecule containing hexagons and pentagons rings. The presented contours (figure 2.(a, b, c)) show how the small change of the backside group, chemical bonds may change the total molecular charge density contributions. We reveal relatively high uniformity of the side chemical groups for compound and large total dipole momentum. The latter leads to enhancement of total molecular asymmetry. Another important parameter is a difference between the ground and excited dipole moments. In Figure 2. (a, b, c) the electronic contributions playing dominant role in the observed nonlinear optical susceptibilities are shown. This asymmetry in the ground and excited state topology plays important role in the observed nonlinear optical properties. A higher charge delocalization is observed for compound A' and B' possessing methyllic group in backside chemical chain. At the same time, the joined methyllic group in molecule C' compensates the gradients of the charge density distribution. Therefore, the right backside groups of the molecule plays a central role in determining of the electron charge density non-centrosymmetry that influences the second-order nonlinear optical properties described by third rank polar tensor.

Figure 3. presents dispersion of the molecular second order hyperpolarizabilities for the investigated molecules. The data were obtained using formula 1. We can see that the results strongly depend on the incident light wavelengths. Frequency-dependent hyperpolarizabilities to possibly used in investigations of propriety of particles different materials change with change of wavelength incident light.

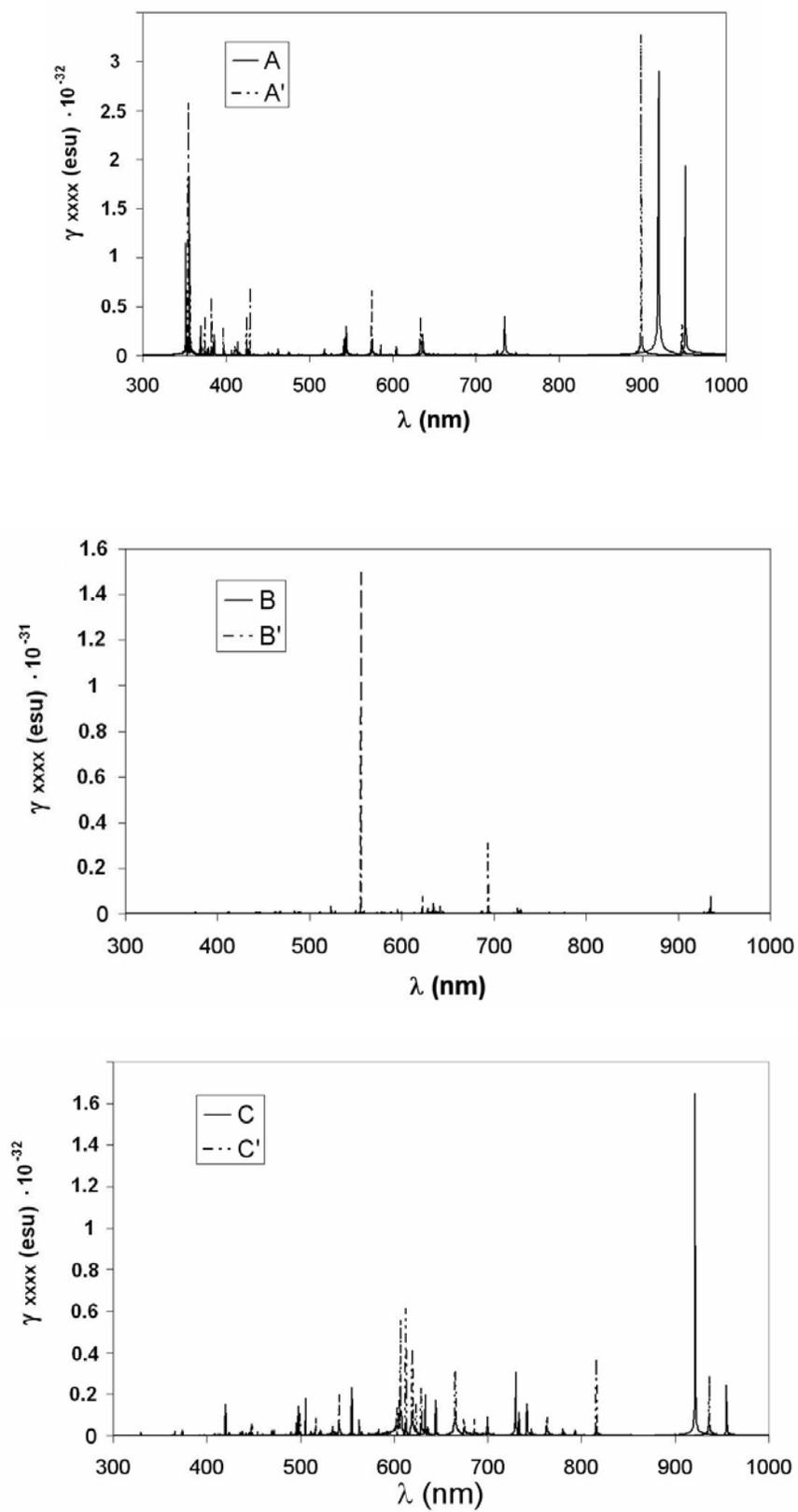


Fig. 3. Dispersion of the molecular third order polarizabilities  $\gamma(-\omega, \omega, \omega, \omega)$  for the investigated molecules (A, A', B, B', C, C').

The main goal of the present work is to investigate the influence of the small modifications in side group (particularly methyl group) on the output on the second order nonlinear optical properties. We can see that the adjunction of methyl group to the end side group lead to a drastic increase of nonlinear coefficient for compounds: A', B' but in molecule C' possessing two pentagon rings causes an opposite effect what is connected with the difference between ground and excited dipole moments described above.

To check the above semi empirical results we compare our theoretical calculations with experiment. Deviations from the experimental and theoretical data give information concerning the observed intramolecular and intermolecular interactions.

We present the measured hyperpolarizabilities  $\gamma_{xxxx}$  (exp) and the calculated one  $\gamma_{xxxx}$  (cal) as well as molecular  $\chi_{xxxx}^{<3>m}$  and electronic  $\chi_{xxxx}^{<3>el}$  component of second-order susceptibility for the various organometallic molecules (Table 3.). The second-order susceptibility and hyperpolarizabilities  $\gamma_{xxxx}$  (exp) are measured and deduced from degenerate four wave mixing (DFWM) technique at fundamental wavelength of 532 nm described in ref. [13]<sup>13</sup>. As you know two essential local effects contribute to the nonlinearities in isotropic media submitted to such laser pulses: deformations of electronic cloud and molecular reorientation (translations, rotations and vibrations). Consequently, one can consider  $\chi^{<3>}$  as being composed of two contributions corresponding to these mechanisms:  $\chi_{ijkl}^{<3>} = \chi_{ijkl}^{<3>el} + \chi_{ijkl}^{<3>m}$ . Taking advantage of different spatial symmetries involved in the  $\chi^{<3>}$  tensor, we can discriminate different physical mechanisms contributing to  $\chi^{<3>}$ .

The proposed theoretical approach is apply only for separate molecule without taking into account inter and intra molecular interaction, molecule - molecule and molecule - solvent.

Taking under attention the different mechanism of formation of nonlinearity in experiment and introduced in calculations we can compare the only trend of changes of non-linear coefficient collected in Table 3. However the comparison of calculated and measured hyperpolarizability is very interesting and may provide some information about intramolecular interactions.

From calculation it results that molecule B' is best candidate from among studied molecules for the nonlinear experimental investigation using laser wavelength close to 532 nm. The maximally achieved second order hyperpolarizability was obtained for the mentioned compound is  $\gamma_{xxxx}$  (cal.) =  $14.98 \times 10^{-32}$  (esu) at  $\lambda_{(max)} = 556$  nm.

Table 3. Values of calculated and measured nonlinear optical properties.

Compounds	$\chi_{xxxx}^{<3>el} \times 10^{-20}$ [m <sup>2</sup> V <sup>-2</sup> ]	$\chi_{xxxx}^{<3>m} \times 10^{20}$ [m <sup>2</sup> V <sup>-2</sup> ]	$\gamma_{xxxx}$ (esu) (cal.) ( $\lambda = 532$ nm)	$\gamma_{xxxx}$ (esu) (exp.) ( $\lambda = 532$ nm)	$\gamma_{xxxx}$ (cal.) maximal and $\lambda$ for which was obtained	
					$\gamma_{xxxx}$ (esu)	$\lambda_{(max)}$ (nm)
Molecule A	0.41	-0.07	$2.32 \times 10^{-35}$	$1.14 \times 10^{-31}$	$2.85 \times 10^{-32}$	919
Molecule A'	0.38	-0.07	$2.27 \times 10^{-35}$	$1.07 \times 10^{-31}$	$3.26 \times 10^{-32}$	898
Molecule B	0.66	-0.19	$0.55 \times 10^{-35}$	$1.64 \times 10^{-31}$	$0.75 \times 10^{-32}$	935
Molecule B'	0.57	-0.18	$2.94 \times 10^{-35}$	$1.35 \times 10^{-31}$	$14.98 \times 10^{-32}$	556
Molecule C	4.12	-1.11	$0.35 \times 10^{-35}$	$11.14 \times 10^{-31}$	$1.64 \times 10^{-32}$	921
Molecule C'	4.21	-1.49	$8.24 \times 10^{-35}$	$10.29 \times 10^{-31}$	$0.61 \times 10^{-32}$	612

The largest second-order hyperpolarizability  $\gamma_{xxxx}$  (exp) is measured for compounds C and C' what is connected with the large electronic contribution to the observed results. (see table 3. first column). We can expect that for these two molecules (C, C') including two thiophen rings in added group the inter and intra molecular electron vibration interactions plays a key role in the observed nonlinearities what is not taken into account in suggested theoretical calculations. Received experimental results contrary to theoretical suggest that better non-linear optical proprieties possess the compounds without added methylic groups yet differences are small in limits of error.

As you know the greatest problem associated with non-linear optical compounds is connected not only with ideal molecules but also the incorporation of these molecules to form ideal macroscopic samples for non-linear optics. So the preparation of the samples play a key role in the obtained non-linear optical properties of the samples, what can be the reason of any disagreement between experimental and theoretical data.

The reason of this could be also simply attributed to the possible errors in quantum –chemical methods, but we cannot rule out a strong influence of the solvent effect.

#### 4. Conclusions

We have theoretically investigated contribution of the backside group to the output of the nonlinear coefficient as well as a UV spectra for a new series of alkynyl ruthenium chromophores. The theoretical results for the molecule agree roughly with experimental data taking into consideration, of course a dispersion of the absorption fundamental edge caused by the intermolecular interactions. We have shown that the right side chemical radicals play essential role in the observed nonlinearities. We have found that the two tiophen rings in molecule C, C' stimulates increasing NLO coefficient. Essential role in this case belongs to inter and intra molecular electron vibration interactions.

The comparison of measured and calculated by quantum chemical ZINDO/1 method absorption spectra manifests rather good agreement for the first two picks. For longer wavelength we have the larger divergence. We have found that the reason of any disagreement between the theoretical and experimental results of absorption spectra is due to vibration and intermolecular contributions on the optical properties.

The presented calculations data showed how change the values of nonlinear optical coefficient in dependence of wavelength what is very important for nonlinear optics molecular engineering. The data thus obtained provide valuable insight into the origin of the hyperpolarizability and help to synthesize molecules with optimal properties.

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