Synthesis and non-linear optical properties of some novel nickel derivatives

G. Soras b, N. Psaroudakis b, G.A. Mousdis a, M.J. Manos c, A.J. Tasiopoulos c, P. Aloukos d,e,g, S. Couris d,e,*, P. Labéguerie e,f, J. Lipinski b, A. Avramopoulos i,j, M.G. Papadopoulos l,**

a Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vas. Constantinou Ave., 116 35 Athens, Greece
b Institute of Organic and Pharmaceutical Chemistry, National Hellenic Research Foundation, 48 Vas. Constantinou Ave., 116 35 Athens, Greece
c Department of Chemistry, University of Cyprus, 1678 Nicosia, Cyprus
d Department of Physics, University of Patras, 26504 Patras, Greece
e Institute of Chemical Engineering and High Temperature Chemical Processes (ICEHT), Foundation for Research and Technology-Hellas (FORTH), P.O. Box 1414, 26504 Patras, Greece
f Institute of Physical and Theoretical Chemistry, Wroclaw Technical University, PL-50370 Wroclaw, Poland
g Université de Toulouse, LAPLACE, UPS-Bat 3R2, 118 rue de Narbonne, 31062 Toulouse Cedex 9, France
h Université de Pau et des Pays de l’Adour-IPREM, ECP-UMR CNRS 5254, Hélioparc, 2 av. du président Angot, 64053 Pau Cedex 09, France
i Institute of Organic and Pharmaceutical Chemistry, National Hellenic Research Foundation, 48 Vas. Constantinou Ave., 116 35 Athens, Greece
j Department of Informatics and Computer Technology, Lamia Institute of Technology, 3rd Km Old National Road, 35100 Lamia, Greece

A R T I C L E   I N F O
Article history:
Received 1 March 2010
In final form 21 April 2010
Available online 26 April 2010

Keywords:
Non-linear optical properties
Nickel derivatives
Z-scan technique
Third-order susceptibility \( \chi^{(3)} \)
Hyperpolarizabilities
GRINDOL
DFT

A B S T R A C T
The synthesis of a new nickel complex with an extended multi-sulfur dithiolene ligand \( \text{Ni}^{(\text{etodddt})_2} \) \((\text{etodddt} = 4,5-(1,4-oxathiane-2,3-diyldithio)-1,3-dithiole)\) is described. It is characterized analytically and spectroscopically. The structure of the compound is determined by single crystal X-ray crystallography. Its redox potentials are determined using cyclic voltammetry and are compared with similar dithiolene complexes. Several other nickel derivatives are synthesized: bis(5,6-dihydro-1,4-dithiine-2,3-dithiole) nickel \((\text{Ni}^{(\text{dddt})_2})\) and bis(6,7-dihydro-5H-[1,4]dithiepine-2,3-ddithiole) nickel \((\text{Ni}^{(\text{pddt})_2})\). The non-linear optical response of the synthesized dithiolenes is measured in the visible \((532 \text{ nm})\) and in the infrared \((1064 \text{ nm})\) using the Z-scan technique with picosecond laser pulses. Both the refractive and absorptive parts of the third-order susceptibility \( \chi^{(3)} \) are determined and the second-order hyperpolarizabilities \( \gamma \) of the dithiolene are determined and compared between them and with other reported in the literature. The second hyperpolarizabilities of the synthesized metal derivatives are calculated by employing a series of computational approaches, involving density functional theory and a semi-empirical method. The first strong transition of the derivatives is attributed mainly to HOMO–LUMO pair connected with the intramolecular charge transfer \( \pi \rightarrow \pi^* \). Similar trends are observed between the experimental and the theoretical second hyperpolarizabilities, although the former are much larger due to resonance enhancement. The reported analysis demonstrates the complementarity of both experimental and theoretical results. It is shown that modest substitution of \( \text{Ni}^{(\text{SCH})_4} \) for example substitution of four H atoms by two \( \text{S}_2\text{C}_2\text{H}_4 \) groups, leads to a very large increase of the second hyperpolarizability.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The interest of the scientific community toward metal 1,2-dithiolene has been increasing continuously during the past decades. There are numerous applications of these complexes in fields as diverse as non-linear optics [1], conductivity and superconductivity [2], laser Q-switching [3], and biochemistry [4], molecular metals and superconductors [5]. In fact, the high degree of electron delocalization, which involves both the organic framework and the metal center [6], confers to dithiolene complexes of d8 metal ions peculiar molecular properties, such as planarity, high thermal and photochemical stabilities, and intense vis-near-IR absorption, along with the ability to carry a molecular charge, which, depending on the nature of the central metal ion and of the dithiolene ligand, can vary reversibly between 2− and 2+. It may also assume fractional values in nonintegral oxidation state (NIO) salts. Overlapping of dithiolens and strong electronic interactions between the units, are conditions to obtain electronic properties, such as conductivity or even unusual magnetic behavior [7]. This delocalization could be enhanced by a suitable choice of a group attached to the core. This group affects the frontier orbitals and thus the related optical and electrochemical properties and can also promote cooperative properties by mediating intermolecular interactions. In addition the metal atom could be a carrier of magnetic properties. Among them the metal complexes of 5,6-dihydro-1,4-dithiin-2,3-dithiol (dddt) [8] are the most important, due to similarities...
with the BEDT-TTF. BEDT-TTF [9] permitted the synthesis of radical cation salts with a quasi two-dimensional character, gave more than 750 superconductors [10] and raised their critical temperature at 14.2 K [11]. In this paper the synthesis of a new nickel 1,2-dithiolene, similar to (dddt), containing an ethylene-thioxo group, is described and its properties are compared with the properties of dddt and pdtt Ni analogues. (Fig. 1, Scheme 1). In that context, the non-linear optical response of the synthesized dithiolenes has been also assessed experimentally by means of the Z-scan technique using picosecond laser pulses in the visible (532 nm) and in the infrared (1064 nm). Both the refractive and imaginary parts of the third-order susceptibility \( \chi^{(3)} \) have been determined and the second-order hyperpolarizability \( \gamma \) has been obtained for each dithiolen. The linear and non-linear optical properties (L&NLO) of the synthesized metal derivatives, Ni(pdtt)\(_2\), Ni(etodddt)\(_2\), Ni(dddt)\(_2\) have also been calculated by employing a series of computational methodologies. These include density functional theory (DFT) and a semi-empirical approach based on a modified NDO method. Several DFT computations have been performed by employing the broken symmetry solution. The former a modified NDO method. Several DFT computations have been performed by employing the broken symmetry solution. The former approach is known to provide reasonable NLO properties [12], and especially second hyperpolarizabilities, to systems which are characterized as singlet diradicals like the synthesized metal derivatives of the present study [13]. We have also computed the UV–Vis spectrum of the metal derivatives, by employing DFT theory, in order to describe the nature of the observed transitions, which govern the NLO response of the considered derivatives. The computational work connects the NLO properties with the electronic structure. In addition the complementarity between the experimentally and theoretically determined hyperpolarizabilities is discussed.

2. Results and discussion

2.1. Synthesis

We prepared the thione 3 by a 2 step method without isolation of the intermediate compound with a total yield of about 50% according to the Scheme 2 (Fig. 1). First we prepared the 1,2 dibromomethane 2, by bromination of the thioxane in CH\(_2\)Cl\(_2\). Evaporation of the solvent under vacuum gave the crude product 2 that was used immediately. The naphthoquin displacement reaction of (Bu\(_4\)N\(_2\))Zn(dmit)\(_2\) with 2 gave the thione 3. An attempt to increase the yield by using the sodium salt of dmit gave only traces of the product. The thione 3 was converted to ketone 4 by treatment with Hg(CH\(_2\)COO)\(_2\) in CH\(_2\)Cl\(_2\)/CH\(_3\)COOH [14]. Deprotonation of ketone 4 with a base (MeONa) in MeOH and addition of NiCl\(_2\)\(\cdot\)H\(_2\)O and Bu\(_4\)NB metanolic solutions leads to the formation in situ of the Ni dithiolate salt 5. The neutral salt 6 can be obtained by oxidation with TCNO or iodine (Scheme 3, Fig. 1).

Elemental analyses were obtained on a Perkin Elmer 2400 Series II elemental analyser. Melting points were determined in open-end capillaries using a Buchi melting point apparatus (pat. 320–388) at a ramp rate 120 (a.u.) without calibration. Solution 1H NMR spectra were recorded on Mercury 200, Varian Unity 300, Bruker Avance 400 and Varian Inova 500 spectrometers operating at (1H) 199.99, 299.91, 400.13, 499.99 MHz. Chemical shifts are reported in ppm downfield of TMS. FTIR spectra were obtained by a Bruker equinox 55 and UV–Vis spectra obtained by the Perkin Elmer, UV/Vis/Nir Lambda 19 spectrometer.

2.1.1. 2,3-Dibromo-1,4-oxathiane (2)

The starting material 2,3-dibromo-1,4-oxathiane was prepared according to the literature by bromination (5 ml, 0.1 mol) of 1,4-oxathiane (5 g, 0.05 mol) The product is sensitive and it was used immediately to the next step. [15].

2.1.2. 4,5-(1,4-Oxathiane-2,3-diylithio)-1,3-dithiol-2-thione (3)

2,3-dibromo-1,4-oxathiane was dissolved in 200 ml aceton and 24 g (0.025 mol) of (Bu\(_4\)N\(_2\))Zn(dmit)\(_2\) were added in 200 ml aceton. The solution was left to stir at room temperature for 3 days. Then the solution was filtered and the solvent was evaporated. The resulting dark-brown sticky residue was purified by column chromatography in silica gel using CH\(_2\)Cl\(_2\) as eluent. Yellow-brown crystals were produced (7 g, 48%); mp: 143 °C; UV–Vis (CH\(_2\)Cl\(_2\), nm): 294; 1H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 5.46 (1H, d, CH), 4.62 (1H, d, CH), 4.46 (1H, hex, CH\(_2\)), 4.08 (1H, oct, CH\(_2\)), 3.31 (1H, hept, CH\(_2\)), 2.41 (1H, hex, CH\(_2\)); IR data (\(\nu\), cm\(^{-1}\)): 2962, 2925, 2904, 2857, 1487, 1446, 1398, 1325, 1296, 1226, 1186, 1064, 1031, 1014, 958, 928, 904, 859, 812, 733, 714, 667, 619, 565.

2.1.3. 4,5-(1,4-Oxathiane-2,3-diylthio)-1,3-dithiol-2-one (4)

Thione 3 (1g, 0.003 mol) was dissolved in a mixture of dichloromethane (100 ml) and acetic acid (30 ml). Then mercury acetate (1.96 g, 0.006 mol) was added and the solution was left to stir at room temperature for 30 min in the dark. The white solid precipitate was removed by filtration in vacuo and the filtrate was washed with water. The organic phase was dried with magnesium stearate and discolored with charcoal. The solvent was evaporated in order to give white-yellow crystals (0.55 g, 65%); mp: 155–157 °C; UV–Vis (CH\(_2\)Cl\(_2\), nm): 294; 1H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 5.46 (d, 1H), 4.62 (d, 1H), 4.46 (m, 1H), 4.08 (m, 1H); CH\(_2\)): 3.31 (hept, 1H), 2.41 (hex, 1H); IR data (\(\nu\), cm\(^{-1}\)): 2947, 2920, 2904, 2860, 1753,
2.1.4. Tetrabutylammonium bis[4,5-(1,4-oxathiane-2,3-diyldithio)-1,3-dithiole] nickel, Bu4N[Ni(etodddt)2] (6)

The compound 5 (55 mg, 0.068 mmole) was dissolved in PhCN (8 ml), heated and filtered. TCNQ (90 mg) was dissolved in CH2Cl2 (8 ml) heated and filtered. The two filtrates were united and re- fluxed for 40 min. The solution left to stand at room temperature for 24 h. The dark solid was filtered and washed with CH2CN. (36 mg, 0.063 mmole 93%), mp: > 300°C (decomp); UV–Vis (CH2Cl2, nm): 1150, 604, 394; IR data (v, cm⁻¹): 2934, 2921, 2867, 2850, 2716, 1473, 1446, 1374, 1316, 1291, 1258, 1220, 1178, 1135, 1075, 1012, 957, 921, 863, 732, 658, 622, 572. Analysis for C12H12NiO2S10 Calc. C: 25.39, H: 2.13. Found, C: 24.98, H: 2.10%.

2.1.5. Bis[5,6-(1,4-oxathiane-2,3-diyldithio)-1,3-dithiole] nickel, Ni(etodddt)2 (6)

The compound 5 (55 mg, 0.068 mmole) was dissolved in PhCN (8 ml), heated and filtered. TCNQ (90 mg) was dissolved in CH2Cl2 (8 ml) heated and filtered. The two filtrates were united and re- fluxed for 40 min. The solution left to stand at room temperature for 24 h. The dark solid was filtered and washed with CH2CN. (36 mg, 0.063 mmole 93%), mp: > 300°C (decomp); UV–Vis (CH2Cl2, nm): 1150, 604, 394; IR data (v, cm⁻¹): 2934, 2921, 2867, 2850, 2716, 1473, 1446, 1374, 1316, 1291, 1258, 1220, 1178, 1135, 1075, 1012, 957, 921, 863, 732, 658, 622, 572. Analysis for C12H12NiO2S10 Calc. C: 25.39, H: 2.13. Found, C: 24.98, H: 2.10%.

2.1.6. Tetrabutylammonium bis[5,6-dihydro-1,4-dithiine-2,3-dithiole] nickel, Bu4N[Ni(dddt)2] (6)

The compound 5 (55 mg, 0.068 mmole) was dissolved in PhCN (8 ml), heated and filtered. TCNQ (90 mg) was dissolved in CH2Cl2 (8 ml) heated and filtered. The two filtrates were united and re- fluxed for 40 min. The solution left to stand at room temperature for 24 h. The dark solid was filtered and washed with CH2CN. (36 mg, 0.063 mmole 93%), mp: > 300°C (decomp); UV–Vis (CH2Cl2, nm): 1150, 604, 394; IR data (v, cm⁻¹): 2934, 2921, 2867, 2850, 2716, 1473, 1446, 1374, 1316, 1291, 1258, 1220, 1178, 1135, 1075, 1012, 957, 921, 863, 732, 658, 622, 572. Analysis for C12H12NiO2S10 Calc. C: 25.39, H: 2.13. Found, C: 24.98, H: 2.10%.

2.1.7. Bis[5,6-dihydro-1,4-dithiine-2,3-dithiole] nickel, [Ni(dddt)2] [17] and bis[6,7-dihydro-5H-1,4-dithiepine-2,3-dithiole] nickel, [Ni(pddt)2] [18]

The compounds were prepared by oxidation with TCNQ in PhCN-ACN following the same procedure as described above for the Ni(etodddt)2.

3. Cyclic voltammetry

The electrochemistry of the complex 5 was investigated by cyclic voltammetry using 1.0 mM solutions in CH2Cl2 with 0.1 M Bu4NPF6, and scan rate 100 mV/s (vs ferrocene with Ag/AgCl as reference electrode and Pt as working electrode). As expected, the cyclovoltamograms of the new metal complex exhibits two 1e reversible oxidation peaks redoxwaves at E1/2 = −0.945 V vs. Ag/AgCl (−1.000 V vs Ferrocene), −0.160 V vs Ag/AgCl (−0.215 V vs ferrocene) and an irreversible at 0.523 V vs Ag/AgCl (0.468 V vs Ferrocene). These oxidations correspond to the equilibrium

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>E1/2 (−2−1) (V)</th>
<th>E1/2 (−1−0) (V)</th>
<th>E1/2 (0+1) (V)</th>
<th>E2−E1 (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(etodddt)2</td>
<td>−0.945</td>
<td>−0.160</td>
<td>0.523</td>
<td>0.785</td>
</tr>
<tr>
<td>Ni(dddt)2</td>
<td>−0.625</td>
<td>−0.042</td>
<td>0.907</td>
<td>0.583</td>
</tr>
<tr>
<td>Ni(pddt)2</td>
<td>−0.690</td>
<td>0.080</td>
<td>0.920</td>
<td>0.770</td>
</tr>
<tr>
<td>Ni(dddt)2</td>
<td>−0.745</td>
<td>0.058</td>
<td>0.875</td>
<td>0.803</td>
</tr>
<tr>
<td>Ni(pddt)2</td>
<td>−0.690</td>
<td>0.300</td>
<td>0.875</td>
<td>0.900</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Formula</th>
<th>C12H12NiO2S10</th>
<th>M</th>
<th>567.61</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/K</td>
<td>100(2)</td>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P1</td>
<td>µ (A)</td>
<td>5.005(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>α (°)</td>
<td>7.9139(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(°)</td>
<td>12.5972(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(°)</td>
<td>72.851(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(°)</td>
<td>78.564(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>V (A°)</td>
<td>87.099(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Z</td>
<td>467.31(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dc (g cm⁻³)</td>
<td>2.017</td>
</tr>
<tr>
<td></td>
<td></td>
<td>µ (mm⁻¹)</td>
<td>2.161</td>
</tr>
<tr>
<td>µ range for data</td>
<td></td>
<td>3.45–28.50</td>
<td></td>
</tr>
<tr>
<td>Reflections</td>
<td></td>
<td>2357</td>
<td></td>
</tr>
<tr>
<td>Data/parameters</td>
<td></td>
<td>1824/124</td>
<td>0.0350</td>
</tr>
<tr>
<td>Rmin</td>
<td></td>
<td>0.0417</td>
<td></td>
</tr>
<tr>
<td>Final R indices*</td>
<td></td>
<td>R1 = 0.0968</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>R2 = 0.0951</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(All data)</td>
<td>0.1006</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Largest diffraction peak and hole/e (Å⁻¹)</td>
<td>1.004 and −0.782</td>
</tr>
</tbody>
</table>

* R1 = Σ||F0|| − |F1|| / Σ||F0||, R2 = (Σ|w(F2)|²) / (Σ|w(F0)|²) ¹/₂.
placed in calculated, ideal positions and refined as riding on their respective C atoms. The programs used were CRYSA LIS CCD [21] for data collection, CRYSA LIS RED [21] for cell refinement and data refinement and WINGX [23] for crystallographic calculations. Unit cell parameters and structure solution and refinement data are listed in Table 2.

Compound 6 crystallizes in the triclinic space group P1. A labeled ball and stick representation of the compound is given in Fig. 2 and selected bond lengths and angles from the crystal structure determination are shown in Tables 3 and 4, respectively. Compound 6 contains one Ni²⁺ ion linked with the two vicinal exocyclic sulfur atoms of the two chelating ligands. The Ni atom is thus tetra-coordinate and has a square planar geometry. The outer rings adopt a chair conformation preventing the formation of stack with short intermolecular contacts. The packing motive of the crystal structure down the b-axis, shown in the Fig. 3, reveals a parallel alignment of the molecules.

The closest Ni–Ni distance is 5.0051(2) Å, which is the length of the a axis. The Ni–S bond lengths are 2.1295(8) [Ni–S1] and 2.125(1) [Ni–S2] Å, whereas the S–C and C=C bond distances are 1.701(3)–1.823(4) Å and 1.391(5) Å, respectively. The distances of the C atoms (C4, C6) to the two O split sites (O1A and O1B) range between 1.409(8) and 1.608(8) Å. These bond distances of the compound lie within the range observed for other neutral dithiolenes [22–25].

5. Measurements

5.1. Basic definitions

The third-order non-linear optical response of the Ni(pddt)₂, Ni(dddt)₂ and Ni(etodddt)₂ dithiolenes has been investigated by means of the Z-scan technique [26] employing 35 ps laser pulses from a mode-locked Nd:YAG laser operating at a repetition rate from 1 to 10 Hz at its fundamental i.e. at 1064 nm. In order to check for possible cumulative thermal effects due to the laser repetition rate, measurements were performed both at a repetition rate of 1 and 10 Hz. However, the obtained Z-scans were identical within the experimental precision suggesting that no such thermal effects were occurring. In addition, measurements were performed using an Optical Kerr Effect setup. The temporal response of the OKE signal of all dithiolenes studied here and the solvents used, was found to be limited by the laser pulse duration, i.e. 35 ps, suggesting that no thermal effects were contributing to the observed non-linear optical response. Moreover, in order to evaluate the strength of resonance effects on the non-linear optical response occurring in particular when the dithiolenes were excited in the infrared namely at 1064 nm, where the characteristic strong π → π* transition occurs, measurements were also performed at 532 nm where no (strong) resonances are present.

The Z-scan technique has been chosen for the study of the NLO response of the synthesized dithiolenes because it allows for the simultaneous determination of the magnitude and the sign of the non-linear refraction and absorption response of a sample. This is attained by measuring the transmittance of the sample as it moves along the propagation direction of a focused Gaussian laser beam in two different ways. Initially, the transmittance is measured just after the sample, by totally collecting the transmitted laser beam, e.g. by means of a large diameter lens (i.e. “open” aperture Z-scan). From this measurement, the non-linear absorption coefficient β
can be deduced by fitting the “open” aperture Z-scan recording with the following equation [26]:

\[
T = \frac{1}{\sqrt{\pi}} \frac{\beta L_{\text{eff}}}{Z_0^2} \int_{-\infty}^{+\infty} \ln \left[ 1 + \frac{\beta L_{\text{eff}}}{Z_0^2} \exp(-t^2) \right] dt,
\]

where \( T \) is the normalized transmittance, \( L_{\text{eff}} = (1 - \exp(-a_0L))/a_0 \) is the effective thickness of the sample, \( a_0 \) is the linear absorption coefficient of the sample at the laser excitation wavelength, \( L \) is the sample thickness and \( b_0 \) is the on-axis irradiance at the focus.

The second-order hyperpolarizability \( \gamma \) is obtained according to the following relation:

\[
\gamma = \frac{\Delta \phi_0}{\phi_0^{\text{on-axis}}}.
\]

The on-axis non-linear phase shift \( \Delta \phi_0 \) can be deduced.

With the parameters \( \gamma \) and \( \beta \) known, the real and imaginary parts of the third-order non-linear susceptibility (i.e. \( \Re \chi^{(3)}(3) \) and \( \Im \chi^{(3)}(3) \)) can be easily obtained using the following relations:

\[
\Re \chi^{(3)}(\text{esu}) = \frac{10^{-6}}{480 \pi^2} \, \text{c} \, \text{m}^2 \, \text{W}^{-1},
\]

\[
\Im \chi^{(3)}(\text{esu}) = \frac{10^{-6}}{36 \pi^2} \, \text{b} \, \text{cm} \, \text{W}^{-1},
\]

where \( c \) is the speed of light in cm s\(^{-1}\) and \( \omega \) is the fundamental frequency in cycles s\(^{-1}\). Since the third-order susceptibility \( \chi^{(3)} \) is a concentration dependent quantity, characterizing the non-linear optical response of a material, often, the second-order hyperpolarizability \( \gamma \) is obtained according to the following relation:

\[
\gamma = \frac{\chi^{(3)}}{\text{NL}^4},
\]

where \( N \) is the number of molecules per unit volume and \( L = (n_2 + 2)/3 \) is the Lorenz–Lorentz local field correction factor. The second-order hyperpolarizability \( \gamma \) is a molecular constant independent of the concentration and indicates the nonlinearity per molecule. More details about the experimental setup and the analysis procedure and the limitations of the Z-scan technique can be found elsewhere [26].

5.2. Spectra

The spectra of tetrabutylammonium bis[4,5-(1,4-oxathiane-2,3-diyldithio)-1,3-dithiole] nickel 5 in various solvents and in thin film, shows a strong broad absorption at 1150 nm which is assigned to a \( \pi \rightarrow \pi^* \) transition [2b_{1u} \rightarrow 3d_{3g}] [27]. There are also bands at 604 nm and 394 nm which are assigned to a \( \pi \rightarrow \text{Ni} \) and \( \text{Ni} \rightarrow \pi \) transitions, respectively [28]. The spectra of thin film has the characteristic long wave transition red shifted to 1240 nm. In case of bis[4,5-(1,4-oxathiane-2,3-diyldithio)-1,3-dithiole]nickel 6 the same bands appear.

In Fig. 4, the UV–Vis-NIR absorption spectra of the experimentally investigated dithiolenes dissolved in CS\(_2\) or DMF are shown. The solutions of Ni(dddt)\(_2\) and Ni(etodddt)\(_2\) in DMF were found to be rather unstable, e.g. changing colour shortly after their preparation, while when dissolved in CS\(_2\), although less soluble than in DMF, solutions were found quite stable. All prepared samples were routinely checked by means of a Perkin-Elmer 900 spectrophotometer in order to ensure that no photodegradation or any other change has occurred at the solution.

The spectra of the present dithiolenes were found to exhibit: (i) a very strong absorption band in the region 900–1200 nm, arising from a low-energy \( \pi \rightarrow \pi^* \) transition and (ii) a relatively lower absorption band lying in the region 300–400 nm, assigned to the S → M charge transfer band [29]. The positions and the intensity of the bands varied with the type and/or the number of the rings and the charge state of the dithiolene as a result of a complex interplay of the relative energies of the ligand \( \pi \) system. As a result, it is in principle possible to tune the position of the absorption band to a desired wavelength in order to obtain an optimum trade-off between near resonance and low absorption, as required in many NLO devices. The lower energy band shows a solvochromeic effect. This absorption is strongly depended from the solvent polarity, as the polarity increase we have a bathichromic shift. In the case of Ni(etodddt)\(_2\) the band is shifted from 1037 for DMSO to 938 for CH\(_3\)Cl\(_2\) while in thin film the peak appears at 923 nm. (Fig. 5). Between the two strong absorption bands already discussed, a relatively low absorption exists in the visible and near-IR region (400–900 nm) for all these complexes, providing a broad transparent window which is of great importance for e.g. optical limiting
applications. It has to be noticed that this transparency window is broader than that exhibited by phthalocyanines (500–700 nm) for example, suggesting that dithiolene complexes can have a superior optical limiting performance than that of phthalocyanine complexes.

In Table 5, the wavelength $\lambda_{\text{max}}$, where the low-energy $\pi-\pi^*$ transition occurs, and the corresponding extinction coefficient $\epsilon_{\text{max}}$ of the investigated dithiolene and the solvent used are presented. As can be easily seen from this table and the UV–Vis-NIR spectra of Fig. 4, an important shift of the $\lambda_{\text{max}}$ of about 30 and 60 nm occurs towards shorter wavelengths going from Ni(dddt)$_2$ to Ni(etodddt)$_2$ and Ni(pddt)$_2$, while the corresponding extinction coefficients of Ni(dddt)$_2$ and Ni(etodddt)$_2$ are about 4 and 5 times larger than that of Ni(pddt)$_2$. It is evident, that the possibility of shifting the positions of the characteristic strong IR absorption peak is very important for potential NLO applications of dithiolenes as e.g. saturable absorbers, optical limiters, etc.

5.3. NLO properties

In Figs. 6 and 7, few typical Z-scan recordings are shown of some Ni(dddt)$_2$ and Ni(pddt)$_2$ solutions in CS$_2$ and DMF, respectively, obtained under 532 (Figs. 6 and 7a) and 1064 nm (Figs. 6 and 7b) laser excitation. In Fig. 6a, the “open”, “closed” and “divided” Z-scans of a 0.314 mM solution of Ni(dddt)$_2$ in CS$_2$, excited at 532 nm with an intensity of 1.75 GW/cm$^2$ are shown. As can be seen, while the non-linear absorption was barely observable in this case, significant non-linear refraction was apparent. In addition, the corresponding “divided” Z-scan exhibited the typical configuration of a pre-focal valley followed by a post-focal peak, indicative of self-focusing situation, corresponding to a positive sign refractive nonlinearity. Similarly, Fig. 7a shows the respective Z-scans of a 1.07 mM solution of Ni(pddt)$_2$ in DMF, as measured at 532 nm using an incident intensity of 7.52 GW/cm$^2$. Basically, as can be seen, a similar behavior was found, with the exception that the non-linear absorption of Ni(pddt)$_2$ was larger than that of Ni(dddt)$_2$. However, this is partly attributed to the much higher intensity used in the latter case. The Ni(etodddt)$_2$ has also exhibited a similar behavior with the other two dithiolenes at 532 nm. In general, the dithiolenes Ni(dddt)$_2$ and Ni(etodddt)$_2$ were found to exhibit much weaker non-linear absorption at 532 nm compared to that of Ni(pddt)$_2$. In fact, the non-linear absorption of Ni(dddt)$_2$ and Ni(etodddt)$_2$ was becoming apparent only at high laser intensities, where, however, the non-linear refraction was saturated not allowing for the determination of the non-linear optical parameters within Z-scan assumptions and restrictions. Therefore, measurements have been performed only at relatively low and moderate intensities where saturation phenomena were not shown. As a general conclusion, it can be affirmed that all three dithiolenes, under 532 nm excitation, were found to exhibit self-focusing behavior (i.e. $\Re\chi^{(3)}>0$) and positive non-linear absorption (i.e. $\Im\chi^{(3)}>0$) when this last was sizeable. At this point, it should be noticed that both solvents (i.e. CS$_2$ and DMF) used had non-linear optical response above certain incident intensity. In order to account for contributions on the observed non-linear optical response of the solutions arising from the solvents, they were always measured after the measurement of each dithiolene solution.

<table>
<thead>
<tr>
<th>Dithiolene complex</th>
<th>Solvent used</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\epsilon_{\text{max}}$ (mol$^{-1}$ L cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(pddt)$_2$</td>
<td>DMF</td>
<td>940</td>
<td>6719</td>
</tr>
<tr>
<td>Ni(etodddt)$_2$</td>
<td>CS$_2$</td>
<td>1009</td>
<td>32,496</td>
</tr>
<tr>
<td>Ni(dddt)$_2$</td>
<td>CS$_2$</td>
<td>1039</td>
<td>25,663</td>
</tr>
</tbody>
</table>

Fig. 6. Z-scans of (a) 0.314 and (b) 0.067 mM solutions of Ni(dddt)$_2$ in CS$_2$, at 532 nm, 1.75 GW/cm$^2$ and 1064 nm, 0.62 GW/cm$^2$, respectively.
under the same experimental conditions. So, in all cases whereas the solvent exhibited some response, this was accounted appropriately for the determination of the non-linear optical response of the solute, i.e. the dithiolene.

In Figs. 6 and 7b some representative Z-scans of the Ni(dddt)$_2$ and Ni(pddt)$_2$ dithiolenes are shown obtained under 1064 nm excitation. As can be seen from the shape of the “divided” Z-scans, in all cases, a pre-focal peak followed by a post-focal valley was observed, indicating self-defocusing behavior, corresponding to negative sign non-linear refraction. In addition, the “open” aperture Z-scans were found to exhibit a peak (i.e. increase of the transmission as the incident intensity was increasing), revealing saturable absorption like behavior, corresponding to negative sign absorptive nonlinearity ($\text{Im} \chi^{(3)} < 0$). This last finding is a direct consequence of the resonant conditions occurring under 1064 nm excitation, due to the strong $\pi \rightarrow \pi^*$ transition $(2b_{1u} \rightarrow 3b_{2g})$ located in this spectral region. In order to avoid saturation effects, the laser intensity used was low enough for all measurements performed at the infrared. In fact, the incident laser energies used were lower than 0.2 $\mu$J for Ni(etoddtd)$_2$ and Ni(dddt)$_2$ and lower than 0.8 $\mu$J for Ni(pddt)$_2$.

Subsequently, the variation of the non-linear optical parameters as a function of the concentration of the dithiolenes was studied. In that respect, the concentration dependence of the determined real part of the third-order susceptibility $\chi^{(3)}$ of the dithiolenes studied is presented in Fig. 8 at both excitation wavelengths investigated.

As shown, good linear correlations were found in all cases, the magnitude of the real part increasing linearly with concentration. A similar behavior was found for the imaginary part of the third-order susceptibility $\chi^{(3)}$. It is interesting to notice here, the very sharp variation of $\text{Re} \chi^{(3)}$ with concentration, found in the case of dithiolenes Ni(etoddtd)$_2$ and Ni(dddt)$_2$, compared to the much slower variation found for Ni(pddt)$_2$. This situation reflects nicely the fact that the laser excitation wavelength (i.e. 1064 nm) is getting closer to the strong $\pi \rightarrow \pi^*$ transition. In particular, in the case of Ni(etoddtd)$_2$ and Ni(dddt)$_2$, this transition occurring at 1009 and 1039 nm, respectively, is in full one photon resonance with the excitation laser light. It is therefore a unambiguous case of resonant enhancement. Obviously, this enhancement is less effective in the case of Ni(pddt)$_2$, since in this dithiolene the $\pi \rightarrow \pi^*$ transition occurs at 940 nm, i.e. about 120 nm far away from the laser excitation wavelength. A similar resonant situation occurs for 532 nm laser excitation, due to the $n \rightarrow \pi^*$ transition present at this spectral region. From the slopes of the linear fits shown in the graphs of Fig. 8, the real and the imaginary parts of the second-order hyperpolarizability $\gamma$ were obtained. Table 6 summarizes the above results. For completeness, the absorbances of 0.1 mM solution of each dithiolene contained in 1 mm cell, at the excitation wavelength (i.e. 532 or 1064 nm) and at the wavelength ($\lambda_{\text{max}}$), where the characteristic IR peak occurs, are also included. The effect of resonance enhancement at 1064 nm is obvious by simple comparison of the hyperpolarizability values at 532 and 1064 nm.
In Table 7 the second-order hyperpolarizability (γ) values of a series of dithiolenes, involving those which are studied in this work and several other similar to them, are presented. The cited γ values, when they were not reported straightforwardly, have been calculated from the reported data, i.e. from the reported values of the third-order susceptibility and the concentration when they were available [33–37]. The names of the dithiolene complexes were kept as they were given in these reports. As can be seen, the present results are in general in very good agreement with other results obtained using similar duration laser excitation, all reported values being of the order of 10⁻³⁰ esu, exhibiting significant increase due to resonant enhancement as the excitation wavelength approaches the characteristic IR band of the dithiolene complexes.

In some recent studies [30,31], investigating the effect of the laser pulse duration on the non-linear absorption of some dithiolene complexes, namely [(CH₃)₄N][Ni(dmit)₂] and [(C₆H₅)₄N][Ni(dmit)₂], using the Z-scan technique and employing 1 and 15 ns laser pulses at 1053, and 40 ps pulses at 1064 nm, saturable absorption like behavior was found under 1 ns and 40 ps laser excitation, corresponding to negative Imγ(3) in agreement with the results of the present work. Similarly, another work [32] investigating the non-linear absorption of some [M(Ph₃timdt)₂] (M = Pd, Pt) dithiolenes at 1064 nm, under 8 ns and 35 ps laser pulses, has also concluded to the same results, reporting saturable absorption behavior under ps excitation, again in agreement with the present work. In another study [33], reporting on the synthesis and the measurement of the third-order optical nonlinearity of some cadmium and zinc dithiolene complexes, namely the (Me₄N)₂[Cd(dmit)(Sph)₂] and (Me₄N)₂[Zn(dmit)(Sph)₂], by a FWM technique, using 15 ps, 532 nm laser excitation, the second-hyperpolarizabilities of these complexes were determined and found to be of the order of 10⁻³⁰ esu, in reasonable agreement with the current results.

Recently, the measurements of the non-linear optical properties of some cuprate dithiolene complexes have been reported [34], investigated by the Z-scan technique, using picosecond laser pulses at 532 and 1064 nm. Although the characteristic strong IR absorption bands, observed in the case of nickel dithiolenes at about 1000 nm, are occurring at about 500 nm in this case, the reported results are qualitatively in excellent agreement with the results of the present work. In fact, for excitation at 352 nm, i.e. in resonance with the strong absorption band, saturable absorption behavior (i.e. Imγ(3) < 0) and negative refractive nonlinearity (i.e. Reγ(3) < 0) have been observed, while under 1064 nm excitation, the “open” Z-scans revealed a clear valley, suggesting positive Imγ(3).

In another recent study [36], investigating the third-order optical nonlinearity of another Ni dithiolene complex ([Pt(N(N-dmit)₂)] with similar absorption spectrum with the presently studied dithiolenes, identical results have been reported. In fact, using the Z-scan technique and employing 1064 nm, 40 ps laser pulses, strong saturable absorption (i.e. Imγ(3) < 0) and negative non-linear refraction (see e.g. Fig. 3 of [36]) indicated by a pre-focal peak followed by a post-focal valley, suggesting self-defocusing behavior (i.e. Reγ(3) < 0) has been also reported, in full accord with the present results.

### 6. Calculations

#### 6.1. Computational methods

The computation of the static (hyper)polarizabilities has been performed by employing density functional theory and a semi-empirical approach. Two functionals were used in the calculations: (i) the PW91LYP using the aug-cc-pVTZ basis set for Ni, C, S, H, O atoms [37], and (ii) the BHHandHLYP [38], employing the 6-31G* basis set for C, S, H, O [39], while for Ni a quasirelativistic effective core pseudopotential was employed (ECP28MWB (SDD) [40]). The second functional has been proven to provide reliable values of the second hyperpolarizability for a series of Ni compounds [12].

The DFT (hyper)polarizabilities have been computed numerically by the finite field method. A Romberg approach has been applied in order to remove the higher order contaminations [41]. A number of field strengths of the magnitude 2mF, where m = 1,2,3,4 and a base field (F) of 0.001 a.u. were used. The GAUSSIAN 03 software [38] has been employed for the DFT calculations.

The semi-empirical approach, employed for the calculation of non-linear electric properties, via finite field formalism of Kurtz et al. [42] involves a locally modified NDO-like method (GRINDOL program) in which the one-electron Hamiltonian matrix elements are calculated from semi-theoretical formulae derived from the Heisenberg equation of motion [43,44]. Literature values have been used for the one-center integrals of Ni and the Slater-type exponents for atomic orbitals [45–47].

All the geometrical structures presented in this paper have been optimized by using the B3LYP/6-31G* and B3LYP/SDD methods.

#### 6.2. Structural data

The structures of the Ni(pdtt)₂, Ni(etoddt)₂, Ni(dddt)₂ were optimized by employing the B3LYP functional and two different types of basis sets for C,S,NiH: (i) The 6-31G set and (ii) An effective core potential for C,S,Ni with a suitable basis set developed by...
the Stuttgart Dresden group (SDD) [40]. For the above three nickel derivatives, there are available experimental data. In all three cases the optimized structures are in satisfactory agreement with the available experimental data. We, therefore, comment on the comparison of the experimental and theoretical data for Ni(pddt)₂ in order to avoid the presentation of too many numerical data (Fig. 9). The optimized structure of Ni(dddt)₂ and Ni(etodddt)₂ are given as supplementary material.

Bond distances of Ni(pddt)₂. The biggest discrepancy is observed for S₄-C₅, where the difference between the theoretical (with either method) and the experimental technique is approximately 0.1 Å. The two theoretical methods give results which are very close.

Bond angles of Ni(pddt)₂. The two computational methods give results which have small differences. The biggest discrepancy between the theoretical and the experimental values is for the angle < S₃C₁C₂. This is approximately 4.6°.

6.3. Charge analysis

Analysis and understanding of the electronic structure is of great importance for the rationalization of the L&M properties. Thus, we performed some analysis of the charge of Ni, which is connected with its oxidation state and the diradical character of the considered derivatives [13,48]. The total atomic charges have been computed by employing the Natural Bond Orbital Analysis (NBO) [49]. The metal of Ni(C₆H₄S₅O)₂ [Ni(etodddt)₂] is donating electrons (1.23e). The NBO analysis shows that the 3d orbital of Ni is occupied by 8.3 electrons, while the occupation of the 4s and 4p orbitals is too low, 0.45 and 0.04 electrons, respectively. The charge excess over the d⁸ configuration of Ni atom indicates a charge transfer from the ligands to the Ni atom leading to a weak covalent bond [13]. The S atoms connected with Ni carry a negative charge (average value: -0.23e).

The previous picture is also valid for the Ni(pddt)₂ and Ni(dddt)₂ derivatives. It is observed that Ni for Ni(pddt)₂, carries a positive charge of 1.23 (1.19)e, while the 3d orbital is occupied by 8.3 (8.3) electrons, and the 4s orbital by 0.44 (0.46) electrons. In parenthesis the corresponding values for Ni(pddt)₂ are being given. The S atoms bonded to Ni, carry a negative charge of 0.26e and 0.19e for Ni(pddt)₂ and Ni(pddt)₂, respectively. The previous observations for the electron population of Ni are in agreement with those reported in the literature [13,50]. The charges we calculated are typical for Ni(II).

6.4. Spectral characteristics

For all the considered compounds intense low energy transitions appear in the near infrared region. This finding has been further confirmed by employing the TDDFT method, which is known to be a powerful tool for the qualitative description of the electronic transitions in molecules [51–53]. All the calculations were done in the presence of solvents, applying the Polarizable Continuum Model (PCM) model [54].

For Ni(etodddt)₂ the functionals B3LYP and PW91LYP have been employed. The 6-31G** basis set was used for C, S, H, O and Ni atoms. It was found that for Ni(etodddt)₂, employing either the B3LYP or PW91LYP functionals, a strong low energy transition occurs at 958.3/990.4 (999) nm and 968.3/996.1 (976) nm, computed in the presence of the acetonitrile and dichloromethane solvents, respectively.

The first strong absorption for Ni(pddt)₂, employing the B3LYP functional, occurs at 838.9 (929–931) nm, computed in the presence of the acetonitrile solvent, while for Ni(pddt)₂, the first strong electronic transition takes place at 1071.3 (1064) nm, computed in the presence of dimethylsulfoxide solvent. In parenthesis the experimental values are quoted. Overall a reasonable agreement between experiment and theory is noted.

Our calculations show that the electronic transition is mainly associated with the HOMO–LUMO pair, as shown in Fig. 10 for the case of the isolated Ni compound. It is observed that the intramolecular charge transfer (π → π⁺) over the ligands (S,C), describes the first and strong UV–Vis transition, similar to what was found for other studied metal complexes [12,50,55]. The metal d orbital (dₓz) contributes to LUMO to a minor extent only [55]. Our calculation show that in the presence of the solvent the HOMO–LUMO gap is equal (in a.u.) to 0.05 (1.36) for Ni(etodddt)₂. In parenthesis the corresponding value in eV is given.

6.5. Polarizabilities

In Table 8 we present the static, electronic polarizabilities of Ni(SCH)₄, Ni(pddt)₂, Ni(dddt)₂ and Ni(etodddt)₂ derivatives. This table shows the evolution of the average polarizability, α and average second hyperpolarizability as a function of the structure. In addition, the x component, which is the dominant one, will be presented. We consider Ni(SCH)₄ as the unit from which the other molecules of interest are built. We start our analysis from the polarizability. The first structural change we consider is that which is involved in the transition from Ni(SCH)₄ to Ni(pddt)₂. We observe that α(Ni(pddt)₂)−α(Ni(SCH)₄) = 3.75 × 10⁻²³ esu, computed with the RPW91LYP/aug-cc-pvTZ method. By employing GRINDOL, the previous difference takes the value 3.54 × 10⁻²³ esu. The corresponding difference, for the αₓ component, takes the value 3.1 × 10⁻²³ (4.1 × 10⁻²³) esu, at the UBHandHLYP/SDD[6-31G*] level. In parenthesis the GRINDOL value is given.

Subsequently we compare the properties of Ni(pddt)₂ and Ni(dddt)₂. They differ by two CH₂ groups: α(Ni(pddt)₂)−α(Ni(SCH)₄) = 3.75 × 10⁻²³ esu, computed with the RPW91LYP/aug-cc-pvTZ method. By employing GRINDOL, the previous difference takes the value 3.54 × 10⁻²³ esu. The corresponding difference, for the αₓ component, takes the value 3.1 × 10⁻²³ (4.1 × 10⁻²³) esu, at the UBHandHLYP/SDD[6-31G*] level. In parenthesis the GRINDOL value is given.

Fig. 9. Bond lengths and angles of the optimized Ni(pddt)₂ compound. The data were computed by employing the B3LYP/6-31G (first row) and B3LYP/SDD (second row) methods. In square brackets the experimental data of the crystal structure are quoted [67].
Fig. 10. The HOMO and LUMO of the Ni(C₆H₆S₅O)₂ compound computed by employing the UHF/6-31G** method.

Table 8
Static (hyper)polarizabilities and \( y \), a parameter describing the diradical character, of a series of derivatives.\(^a\) All (hyper)polarizabilities are given in esu.

<table>
<thead>
<tr>
<th>Compound (^a)</th>
<th>( x_{xx}(\times 10^{-21}) )</th>
<th>( x(\times 10^{-21}) )</th>
<th>( \gamma_{xxx}(\times 10^{-30}) )</th>
<th>( \gamma(\times 10^{-30}) )</th>
<th>( y )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.91(^c)</td>
<td>2.81(^c)</td>
<td>6.85(^c)</td>
<td>1.76(^c)</td>
<td>0.318</td>
</tr>
<tr>
<td></td>
<td>3.29(^d)</td>
<td>2.94(^d)</td>
<td>28.10(^d)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 Ni(dddt)(_2)</td>
<td>8.01(^c)</td>
<td>6.35(^c)</td>
<td>43.61(^c)</td>
<td>33.84(^c)</td>
<td>0.705</td>
</tr>
<tr>
<td></td>
<td>6.39(^d)</td>
<td>6.69(^d)</td>
<td>43.36(^d)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.77(^e)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 Ni(pddt)(_2)</td>
<td>7.43(^c)</td>
<td>6.17(^c)</td>
<td>29.82(^c)</td>
<td>22.51(^c)</td>
<td>0.632</td>
</tr>
<tr>
<td></td>
<td>6.46(^d)</td>
<td>6.93(^d)</td>
<td>32.84(^d)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.77(^e)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 Ni(etoddt)(_2)</td>
<td>10.0(^c)</td>
<td>8.03(^c)</td>
<td>63.97(^c)</td>
<td>45.27(^c)</td>
<td>0.704</td>
</tr>
<tr>
<td></td>
<td>8.48(^d)</td>
<td>9.04(^d)</td>
<td>75.05(^d)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>11.96(^e)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) The B3LYP/SDD optimized geometry was employed to all calculations.
\(^b\) The values were calculated with the UHF/6-31G** method [12].
\(^c\) Values computed by using the GRINDOL method.
\(^d\) The UBHandHLYP/SDD(Ni) 6-31G*(C,S,H,O) method was used.
\(^e\) Values computed by employing the RPW91LYP/aug-cc-pVTZ method.
The properties of Ni(etoeddtt)₂ are compared with those of Ni(dddt)₂. They differ by two 6-membered rings, each one of those involves one sulfur and one oxygen atom. We observe that \( \langle \alpha \rangle_{\text{Ni}(\text{etoeddtt})} - \langle \alpha \rangle_{\text{Ni}(\text{dddt})} = 2.35 \times 10^{-23} \) esu (RPW91LYP/aug-cc-pVTZ). The corresponding difference for the \( \alpha_{\text{xx}} \) component is \( 3.19 \times 10^{-23}, 1.99 \times 10^{-23} \), and \( 2.09 \times 10^{-23} \) esu, for RPW91LYP/aug-cc-pVTZ, GRINDOL and UBHandHLYP/SDD (6-31G*), respectively.

In summary, we note that among the three employed methods, UBHandHLYP, RPW91LYP and GRINDOL, the more satisfactory results are given by the first one, because it provides broken symmetry solutions \([13,48]\). However, all three methods give rather similar polarizability values \( \gamma_{\text{xxxx}} \) (Table 8).

### 6.6. Hyperpolarizabilities

The computed static, electronic second hyperpolarizabilities of the considered derivatives, by employing the UBHandHLYP and GRINDOL methods, are given in Table 8. Hyperpolarizability results using the RPW91LYP will not be presented, since this method does not give symmetry broken solutions and the calculated values are most likely wrong (e.g. they follow the wrong trend). It is observed that the semi-empirical GRINDOL values are close to the UBHandHLYP ones \( \gamma_{\text{xxxx}} \) (Table 8). This is significant, considering that the computational cost of the former approach is much lower than that of the latter. It has been found that at the UBHandHLYP level, \( \gamma_{\text{xxxx}}(\text{Ni}(\text{etoeddtt})_2) \approx \gamma_{\text{xxxx}}(\text{Ni}(\text{dddt})_2) = 1.73 \text{ esu} \) \( (1.47) \) in parenthesis. The CH₂ groups decrease the second hyperpolarizability of the resulting compound \( \gamma_{\text{xxxx}}(\text{Ni}(\text{dddt})_2) \). This can be seen by employing both UBHandHLYP and GRINDOL. These methods predict that \( \gamma_{\text{xxxx}}(\text{Ni}(\text{dddt})_2) \approx \gamma_{\text{xxxx}}(\text{Ni}(\text{dddt})_2) = 0.76 \text{ esu} \) \( (0.68) \). In parenthesis the GRINDOL value is given.

In summary, it is noted that the employed methods, UBHand HLYP and GRINDOL, give similar values \( \gamma_{\text{xxxx}} \) (except for \( \gamma_{\text{xxxx}} \) of 1, Table 8) and the same trends, that is for \( P = \gamma_{\text{xxxx}} \) and \( P(4) > P(2) > P(3) \). Concerning the discrepancy between the GRINDOL and UBHand HLYP values for \( \gamma_{\text{xxxx}} \) of 1, we note that the latter approach gives a more reliable estimate \([48]\). The failure of GRINDOL for \( \gamma_{\text{xxxx}} \) of 1 is, perhaps, surprising, considering the good performance of this method for computing \( \alpha_{\text{xx}} \) and \( \chi \) of 1–4 and \( \gamma_{\text{xxxx}} \) of 2–4 \( (\text{Table 8}) \) and it may be due to the employed, by the method, set of parameters.

In order to check the diradical character of the considered compounds, we employ the parameter \( \gamma_{\text{xx}} \) \([12]\). The value of this parameter is given for the considered singlet diradical systems in Table 8. It is observed that although \( \gamma_{\text{xxxx}}(\text{Ni}(\text{dddt})_2) \) and \( \gamma_{\text{xxxx}}(\text{Ni}(\text{dddt})_2) \) have approximately the same diradical character, their hyperpolarizability values, differ remarkably. Thus, addition of two six-membered rings, involving sulfur and oxygen atoms, did not have any significant effect on the diradical character.

### 6.7. Comparison between experimental and theoretical results

In this section we will compare the theoretical and experimental second hyperpolarizability results obtained in this study and we will discuss a number of issues which arise when such comparisons are taking place. So, at first, as can be seen from the values presented in Tables 6 and 8, there is a large difference between the calculated values of the second hyperpolarizabilities and the experimentally determined ones. Although there are several factors which may be invoked to rationalize such differences between experimentally and theoretically obtained hyperpolarizability results, the most important factor here is the laser pulse duration. When the non-linear optical response of a system is studied, the laser pulse duration is a key parameter since it controls the physical processes which will take place \( \text{e.g. electronic response, nuclear contributions, vibrational contributions, orientational effects, libration, population re-distribution and formation of population gratings, etc.} \) \([56–59]\), and which will define the response of the system. The measurement and the analysis of the time-resolved response of the system provides then evidence and further insight about what mechanism(s) is(are) responsible for the non-linear optical response \([57]\). This is usually clarified by considering different physical mechanisms and convoluting them in order to reproduce the experimentally obtained temporal evolution \( \text{see e.g. Refs. [60–62]} \). In that context it is evident, that use of different duration laser pulses will result in principle, to different values of the hyperpolarizability, reflecting the different underlying processes which are taking place and respond with different characteristic times. For example, when ultra fast laser pulses \( \text{e.g.} 40–100 \text{ fs} \) are employed, and the system’s response \( \text{e.g.} \text{ Kerr signal, DFWM signal, etc.} \) is limited by the laser pulse duration, it is usually accepted that it is the pure electronic response that is revealed. However, when ns laser pulses are used, several other processes can occur, as \( \text{e.g. processes related with the photophysical characteristics of the medium as population of the triplet states through inter-system crossing, etc., which are much slower (compared to the pure electronic response) and correspond to nonlinearities which are several orders of magnitude larger than that associated with the electronic response and are usually described as transient nonlinearities. Measurements performed under picosecond excitation, correspond, in general, to nonlinearities which can contain contributions arising not only from the pure electronic response of a system, but from nuclear and vibrational motions, libration, re-orientational effects, etc. This situation has been described and discussed in detail in the case e.g. of the non-linear optical response of fullerenes, where experimentally determined values using ns, ps and fs lasers were found to span over several orders of magnitude \([63]\). On the other hand, the theoretical calculations of the NLO properties, usually take into account only the electronic contribution, while the vibrational contribution is neglected, because \( i \) it is very hard to compute for large molecules and \( ii \) in frequency dependent properties, the electronic contribution, usually, is much larger.

Another source of difficulty when comparing experimental and theoretical results are possible one-, two- or more-photon resonant enhancements that can occur in experimental work \([64–66]\), while theoretical calculations are frequently performed at the static limit. In that respect, the dithiolenes studied in this work provide a very good example. So, by inspecting their absorption spectrum \( \text{Fig. 4} \) and taking into account the large absorption cross-section of their characteristic strong IR band \( \text{Table 5} \), it becomes evident that one- and two-photon processes are to be expected upon infrared laser excitation. Consequently, the experimental hyperpolarizabilities could be resonantly enhanced \([64]\). As a matter of fact, this is exactly what happens in the case of 1064 nm excitation of the studied dithienoles. The large difference of the absolute magnitudes between experimental and theoretical results found here should most probably due to large extent to these resonant enhancements. However, despite the above issues and the discrepancies often observed on the determination of the absolute magnitude of the nonlinearities, comparisons between experimental and theoretical results can be very useful as they provide information about the trends of the non-linear response and can be also refined accordingly in order to provide a better insight on the evaluation of the contributions of the physical mechanisms which are responsible for the non-linear optical response. In fact, the two approaches are indeed complementary. It
is pleasing to note that both experimental and theoretical results show the same trend. So, $\text{Ni(pddt)}_3$ and $\text{Ni(etoddt)}_2$ were found to exhibit both experimentally and theoretically the lowest and the largest hyperpolarizabilities, respectively.

7. Conclusions

In summary, a new nickel dithiolate complex with an extended multisulfur ligand has been synthesized. Comparison of the new complex with analogous complexes having smaller ligands, shows comparable electrochemical and non-linear optical properties. By employing a series of computational methods the (hyper)polarizabilities and the UV–vis spectrum of the synthesized nickel derivatives have been computed. It has been shown that the experimentally observed strong transition is mainly characterized as an intramolecular charge transfer over the ligands. All the computed absorption wavelengths computed by the TDDFT approach are in a satisfactory agreement with the experimental ones. It has been shown that a modest substitution of Ni(SCH)$_4$, for example substitution of four H atoms by two S$_2$C$_2$H$_4$ groups, leads to a very large increase of the second hyperpolarizability. The pre-computed absorption wavelengths computed by the TDDFT approach gives, in general, satisfactory polarizability and second hyperpolarizability values.

The discrepancy between the experimental and the theoretical second hyperpolarizabilities is most probably, mainly, due the resonance enhancement of the former property values. However, both experimental and theoretical values follow the same trend: $\gamma(4) > \gamma(2) > \gamma(3)$. The discussed comparison between the above sets of values demonstrates their complementarity. The determined nonlinearities are remarkably large and confirm the potential of this class of materials for several applications. The new complex may be used, for example, for the preparation of conducting radical salts and as efficient non-linear optical material (e.g. as an optical limiter). In fact, further studies are in progress in our group in order to determine the efficiency of the optical limiting of this and similar complexes.

Acknowledgment

This work was partially supported through a PENED 2003 grant by the Greek General Secretariat for Research and Technology/Ministry of Development. For computing time provided by the Barcelona Supercomputer centre and by the National Science Foundation through teragrid resources are gratefully acknowledged.

References


http://www.theochem.uni-stuttgart.de/pseudopotentials/clickpot.html.