Theor Chim Acta (1993) 87: 175–194

Theoretica
Chimica Acta

Intramolecular charge transfer in 5-phenyl-3H-1,2-dithiole-3-thione and 5-phenyl-3H-1,2-dithiole-3-one derivative molecules for quadratic nonlinear optics

Alain Botrel[1], Bertrand Illien[1], Péter Rajczy[1,*], Isabelle Ledoux[2], and Joseph Zyss[2]

[1] Laboratoire de Physicochimie Analytique et Théorique, Ecole Nationale Supérieure de Chimie de Rennes (E.N.S.C.R.), avenue du Général Leclerc, F-35700 Rennes, France

[2] Département d'Electronique Quantique et Moléculaire, FRANCE TELECOM, Centre National d'Etudes des Télécommunications, Paris B, 196, avenue Henri Ravera, BP107, F-92225-Bagneux Cedex, France

Received February 25, 1993/Accepted April 29, 1993

Summary. This paper deals with the theoretical and experimental studies of new sulfur-containing NLO chromophores: 5-phenyl-3H-1,2-dithiole-3-thione and 5-phenyl-3H-1,2-dithiole-3-one derivatives; ground-state and first $^1(\pi\pi^*)$ excited states characteristics are determined within the framework of MNDO-PM3 and CNDO/S-CI methods. These results are confronted with the NLO response of these molecules. The intramolecular charge transfer is identified and its contribution to the quadratic nonlinear susceptibility estimated and shown to be the main feature. Theoretical and experimental solvent effects on $\pi \rightarrow \pi^*$ absorption bands are discussed. MNDO-PM3 finite-field first-order hyperpolarizabilities are compared to EFISH measurements. A preliminary CNDO/S parametrization of the sulfur atom in thio-carbonyl compounds is proposed and shown to be adequate for the description of electronic spectra.

Key words: 5-Phenyl-3H-1,2-dithiole-3-(one or thione) – Hyperpolarizability – Dipole moment – Charge transfer – Solvent effect

1 Introduction

The large scale development of theoretical and experimental studies, at the microscopic and macroscopic scale, of the nonlinear optical (NLO) properties of organic materials has for the past twenty years been driven by some specific advantages of these materials with respect to inorganic ones: high NLO efficiency, processability, strong flexibility of the molecular structure, short time NLO response in parametric and to some extent in resonant regimes [1–3]. Incorporation and orientation of

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Correspondence to: A. Botrel

[*] *Permanent address*: Department of Atomic Physics, Roland Eötnös University, Budapest, Hungary

NLO molecules inside amorphous polymers has lead to the elaboration of electro-optic modulators with a low half-wave voltage and a very broad ($>$ 40 GHz) bandpass, then opening the way to various applications in the field of optical communications and optical signal processing devices [4, 5].

However, highly nonlinear organic compounds present a significant limitation in terms of their UV-visible transparency-efficiency trade-off. The presence of strong absorption bands, related to large intramolecular charge transfers (ICT), prevents highly conjugated organic materials from being used in the blue or near UV spectral range, and subsequently limits their potential for applications such as frequency doubling of laser diodes for laser disk storage. A nonlinearity-transparency trade-off criterion [6] has been introduced in the molecular selection process following from the application of "molecular engineering" guidelines.

Among the various attempts at increasing the transparency of nonlinear organic materials, introduction of sulfur atoms in the molecular structure opens interesting perspectives. Sulfur can be used, in alkylthio derivatives, leading to donor groups almost as efficient as the amino group, with the additional benefit of a spectral blue shift on the order of 50 nm with respect to the maximal absorption wavelength (λ_{max}) of the corresponding amino derivatives [7, 8]. The sulfonyl group has also been investigated as an acceptor group [9], also evidencing very large blue shifts of λ_{max} (up to 70 nm with respect to the NO_2 group). An additional advantage of the sulfonyl group lies in its ability to be substituted by two different moieties of the sulfur atom, contrary to more classical groups such as nitro or cyano ones. This feature brings in additional synthetic flexibility for building "multifunctional" molecules or polymers.

Sulfur atoms can also be inserted inside the conjugated part of the molecule, in order to partially interrupt the electronic interaction between the donor and the acceptor substituents involved in the ICT process [7, 10, 11]. However, S is found to disconnect the endgroups too drastically: the price for the increase of transparency leads to a dramatic decrease of β as compared to equivalent molecules without sulfur atoms at intermediary positions in the conjugated path.

Another strategy on the way to new species of interest for their transparency and hyperpolarizability optimization is based on 3H-1,2-dithiole-3-one and 3H-1,2-dithiole-3-thione derivatives. These molecules contain a disulfide group forming, with three additional carbon atoms, an heterocyclic moiety displaying a weak aromatic character [12, 13] with one carbonyl oxygen atom or one thio-carbonyl sulfur atom linked to one of the carbons of the dithiolic ring. We report herein on the NLO properties of 5-phenyl-3H-1,2-dithiole-3-thione and 5-phenyl-3H-1,2-dithiole-3-one derivatives.

The electro-attractive effect of 3H-1,2-dithiole-3-one and 3H-1,2-dithiole-3-thione groups has been investigated using electrochemical methods [14]. Hammett's constants deduced from voltammetric measurements indicate that the "dithiolthione" or "dithiolone" moieties present a strong electron-acceptor character, comparable to that of the cyano group. Such moieties are therefore interesting candidates to interact with electron donors through a conjugated bridging system, so as to promote the ICT at the origin of strong first-order hyperpolarizability (β) values. It must be pointed-out that an additional electron charge transfer occuring within the dithiolic ring may also occur, as deduced from the spectroscopic data [15]. The dithiolic system is therefore more polarizable than most usual electron acceptors. Another advantage of these groups lies in the possibility, similar to that provided by sulfones, of grafting two different functions on the C_4 or C_5 atoms of the cycle.

Quantum mechanical descriptions of the β hyperpolarizability [16–18] evidence the necessity to maximize the following parameters:

– the difference $\Delta\mu$ between the dipole moments in the ground state μ_g and in the first excited state μ_e;

– the value of the oscillator strength f characterizing the transition between the ground state and the first excited state.

For a large number of nonlinear molecules exhibiting a strong intramolecular charge transfer, the frequency-dispersion of the first-order hyperpolarizability β can be described following the two-level model proposed by Oudar [17]:

$$\beta = [3e^2\hbar^2 Wf\Delta\mu]/[2m[W^2 - (2\hbar\omega)^2][W^2 - (\hbar\omega)^2]]$$

where W is the energy difference between the ground state and the ICT level and ω the laser fundamental frequency. This expression has been generalized in the case of anisotropic 2-D systems [19].

The purpose of this study is to present a thorough description of the electronic structure of some dithiolic derivatives, based on quantum chemical semiempirical calculations. Theoretical β values are then inferred and compared to experimental ones as measured by the Electric Field Induced Second Harmonic (EFISH) generation technique. Comparison of these experimental results with semiempirical ones gives explanations of the nature of the ICT involved in the NLO response of the molecules.

Theoretical and experimental studies of molecules belonging to the 5-phenyl-3H-1,2-dithiole-3-thione and 5-phenyl-3H-1,2-dithiole-3-one series will be detailed.

Determination of the molecular conformations of the ground state has been carried-out in the framework of the PM3 method [20] based on the NDDO approximations and well adapted to the calculations of heats of formation, molecular geometries, dipole and multipole moments, and force constants. These approximations are used here in the framework of the MOPAC 6.0 program [21].

The main features of the first excited states, such as energy levels, charge transfers or dipole moments have been determined within the CNDO/S scheme whereby relevant extensions accounting for solvent effects have been introduced [22, 23]. Moreover, the reparametrization proposed by Jacques et al. [24] for the oxygen atom in carbonyl groups was extended to the sulfur atom in thio-carbonyl groups. The 60 lowest-energy single excited configurations are used for the configuration interaction procedure. Using this approach, we will also discuss the influence of the medium on W, f and $\Delta\mu$.

2 Parametrization of the sulfur atom for all thio-carbonyl compounds through the CNDO/S method

Jacques et al. [24] have pointed-out the inadequacy of the CNDO/S parametrization for the oxygen atom belonging to a carbonyl group; this technique is unable to correctly reproduce the features of the visible-UV absorption spectra. They have proposed a modification of the empirical $\beta^0(\mathrm{O})$ parameters. The new adopted value ($\beta^0(\mathrm{O}) = -30\,\mathrm{eV}$) leads to a better description of the spectral characteristics of molecules containing carbonyl groups.

First calculations carried-out with usual CNDO/S parameters [25] on thiocarbonyl compounds having evidenced similar discrepancies with experimental spectroscopic data, it appears here also necessary to reassess the parameters β^0 (s, p and d) of sulfur atoms in thio-carbonyl compounds.

Four "model" molecules with geometries optimized by the PM3 method, as given in Table 1, have been selected. The torsional angles obtained being close to zero or very small, a planar geometry have been adopted for all molecules (apart from methyl hydrogen atoms).

All the calculations have been made with 60 singly-excited configurations with electronic transition energies smaller than 6 eV.

As the modification of the parametrization has little influence in the case of these molecules on $n \rightarrow \pi^*$ transitions, we mainly focus in this study on $\pi \rightarrow \pi^*$ transitions. The initial ratio $\beta^0_{(s,p)}/\beta^0_{(d)} = 5$ has been conserved for all parameters sets tested. The results are presented in Table 2. In every case these transitions always correspond to one dominant configuration, of weight higher than 0.95.

In order to improve the agreement with various experimental data, the parameters β^0 values must be located between -32 and -37 eV for s and p electrons, and between -6 and -7 eV for d electrons.

The following values are then proposed:

$$\beta^0_{(s,p)}(\mathrm{S}) = -35\,\mathrm{eV} \quad \text{and} \quad \beta^0_{(d)}(\mathrm{S}) = -7\,\mathrm{eV}$$

Then, we have assessed the influence of this revised parametrization on the characteristics of the thio-carbonyl bonds, on the one hand, and on the M.O. energy levels on the other hand.

Table 3 shows that the new parametrization leads to a decreased of the conjugation. These results are consistent with the evolution observed in the case of the carbonyl bond C = O [24]: the increase in $|\beta^0|$ results in a decreased

Table 1. Molecular geometries: PM3 results

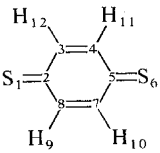
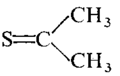
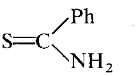
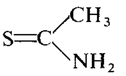
Dithioparabenzoquinone 	$d_{1-2} = 1.58$ Å $d_{2-3} = 1.46$ Å $d_{3-4} = 1.34$ Å $d_{3-12} = 1.10$ Å	1-2-3 = 122.5° 2-3-12 = 120.8° 12-3-4 = 116.7°
Thioacetone  $S{=}C(CH_3)_2$	$d_{C-S} = 1.58$ Å $d_{C-C} = 1.49$ Å $d_{C-H} = 1.10$ Å	S–C–C = 123.4°
Phenylthioamide  $S{=}C(Ph)NH_2$	$d_{C-S} = 1.64$ Å $d_{C-N} = 1.37$ Å $d_{C-Ph} = 1.48$ Å $d_{N-H} = 0.99$ Å	S–C–N = 119.9° S–C–Ph = 123.9° C–N–H = 119.6° C–N–H = 121.1°
Thioacetamide  $S{=}C(CH_3)NH_2$	$d_{C-S} = 1.63$ Å $d_{C-N} = 1.37$ Å $d_{C-C} = 1.50$ Å $d_{C-H} = 1.10$ Å $d_{N-H} = 0.99$ Å	S–C–N = 122.0° S–C–C = 122.5°

Table 2. Influence of $\beta°(S)$ on the lowest singlet–singlet transition energy $\Delta E\,^1(\pi\pi^*)$

Compound	ΔE_{exp} (eV)	Calculated ΔE (eV)						Symmetry[a]
		$\beta°(S)$ in eV						
		(s,p)	− 20	− 25[b]	− 30	− 35	− 40	
		(d)	− 4	− 5[b]	− 6	− 7	− 8	
Dithioparabenzoquinone	3.43		2.97	3.17	3.37	3.56	3.75	B_{1u}
Thioacetone	5.66		4.07	4.68	5.09	5.58	5.80	A
Phenylthioamide	4.32		3.63	3.87	4.12	4.29	4.44	A′
Thioacetamide	4.73		3.85	4.16	4.62	4.93	5.17	A′

[a] The group notations are those corresponding to our choice of the coordinate systems
[b] Usual CNDO/S parameters (s,p and d) [25]

Table 3. C=S bond characteristics as a function of $\beta°(S)$

$\beta°(S)$ in eV		Net π-electron charges and π-bond orders
− 25	− 5	$0.19 \quad C\overset{0.800}{=\!=}S \quad -0.23$
− 30	− 6	$0.18 \quad C\overset{0.820}{=\!=}S \quad -0.20$
− 35	− 7	$0.17 \quad C\overset{0.836}{=\!=}S \quad -0.18$
− 40	− 8	$0.15 \quad C\overset{0.850}{=\!=}S \quad -0.16$

conjugation. In the case of the thio-carbonyl compounds, the search for a closer agreement with the experimental results of the electronic transition energies requires an increase in the $|\beta^0|$ values, thereby evidencing the excessively polar character of the C = S bond as described by the initial β^0 parameters of sulfur atom.

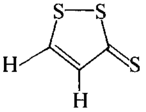
There is, moreover, an empirical relation derived from the Koopman's theorem between the ionization potentials (IP_i) provided by photoelectron spectroscopy and the calculated molecular orbital energies ε_i [26]:

$$IP_i = b - a\varepsilon_i$$

Based on the available experimental values for the 3H-1,2-dithiole-3-thione molecule [27], we have correlated the potentials IP_i and the energies ε_i calculated with the CNDO/S method for the different β^0 parameters values of the sulfur thio-carbonylic atoms. The results are presented in Table 4. The modification of the β^0 parameters of sulfur atom has little effect on the ε_i energy values and the correlation between experimental and calculated values remains satisfactory in all cases (the linear regression coefficients are near to 0.99). The best values are obtained for $\beta^0 = (-25, -5)$ in the cases of the third and the fifth M.O., and $\beta^0 = (-40, -8)$ for the three other ones, the chosen parametrization $(-35, -7)$ then corresponding to an average value.

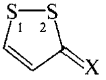
Finally, we checked that the modification of the parametrization of the other sulfur atoms (different from sulfur atoms in thio-carbonyl group) of the 3H-1,2-dithiole-3-thione molecule does not modify significantly the lowest transition

Table 4. Linear correlation between calculated MO energies and experimental ionization potential (IP_i) values for the 3H-1,2-dithiole-3-thione molecule ($IP_i = b - a\varepsilon_i$ with regression coefficient r)



IP_i in eV	Calculated MO energies ε_i				Nature of the MO
	$\beta°$(S) in eV				
	s p d − 25, − 25, − 5	*s p d* − 30, − 30, − 6	*s p d* − 35, − 35, − 7	*s p d* − 40, − 40, − 8	
8.42	− 8.88 − 9.09	− 8.91 − 9.04	− 8.93 − 8.96	− 8.87 − 8.96	π, n
10.52	− 11.09	− 11.07	− 11.06	− 11.05	π
10.79	− 11.49	− 11.61	− 11.72	− 11.84	π
12.42	− 12.80	− 12.81	− 12.77	− 12.75	σ
12.79	− 12.85	− 12.97	− 13.09	− 13.17	σ
Linear correlation results	$a =$ 1.09 $b =$ − 1.54 $r =$ 0.994	$a =$ 1.07 $b =$ − 1.31 $r =$ 0.993	$a =$ 1.05 $b =$ − 1.07 $r =$ 0.991	$a =$ 1.02 $b =$ − 0.81 $r =$ 0.986	

Table 5. Calculated CNDO/S-CI energies for the lowest $\pi \rightarrow \pi^*$ transition of the 3H-1,2-dithiole-3-one and 3H-1,2-dithiole-3-thione molecules as a function of sulfur atoms parametrization



(X = O, S)

3H-1,2-dithiole-3-one		3H-1,2-dithiole-3-thione		
$\beta°$(S1, S2) (eV)	ΔE(eV)	$\beta°$(S of C═S) (eV)	$\beta°$(S1, S2) (eV)	ΔE(eV)
− 25, − 5	4,41	− 35, − 7	− 25, − 5	3.75
− 35, − 7	4,34	− 35, − 7	− 35, − 7	3.55

energies. The results for the 3H-1,2-dithiole-3-one and 3H-1,2-dithiole-3-thione molecules given in Table 5 show that the observed variations (0.07 and 0.20 eV respectively) do not require to take this modification into account, as the values remain in agreement with the proposed reparametrization for the single carbonylic oxygen atoms.

The following values for the β^0 parameters of the sulfur atoms of thio-carbonyl group are finally adopted:

$$\beta^0_{(s)} = \beta^0_{(p)} = -35.0\,\text{eV}$$

$$\beta^0_{(d)} = -7.0\,\text{eV}$$

3 Application to the study of the derivatives of 3H-1,2-dithiole-3-one and of 3H-1,2-dithiole-3-thione

The first four molecules studied are sketched in Table 6.

3.1 *Molecular geometries*

The available geometrical data [28] are

- on the one hand, the experimental determinations (crystallographic data) for the molecules (III) and (IV), the 4-methyl-5-(2-pyrazinyl)-3H-1,2-dithiole-3-one(A), the 4-methyl-5-(2-pyrazinyl)-3H-1,2-dithiole-3-thione(B) and the 4-methyl-5-[2-(2-pyrazinyl)vinyl)]-3H-1,2-dithiole-3-thione(C) molecules that are listed in Table 7;
- on the other hand, the theoretical determinations carried out through the Hückel technique by application of Julg's formulae linking bond orders to bond lengths [29, 30], to the 3H-1,2-dithiole-3-thione(D) and the 3H-1,2-dithiole-3-one(E) species [31].

In all cases, the rings are found almost planar and except for compound (III), the dihedral angles between the 5-atoms rings and the 6-atoms rings are near 0°. For molecule (III), measurements lead to an angular value close to 30°.

Since this theoretical study has been carried-out on isolated molecules, we decided to choose a geometry optimization using the semiempirical method PM3.

Table 6. Studied compounds

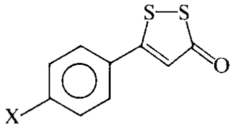
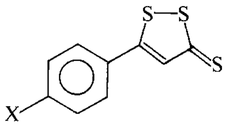
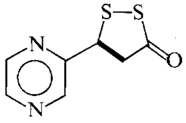
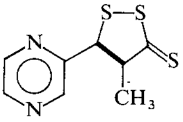
5-(*p*-"X" phenyl)-3H-1,2-dithiole-3-one molecules	5-(*p*-"X" phenyl)-3H-1,2-dithiole-3-thione molecules
 X = H(I) X = OMe(II)	 X = H(III) X = OMe(IV)

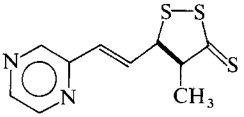
Table 7. Compounds with available geometries



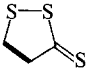
A



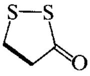
B



C



D



E

The planarity of the 5 and 6-atoms rings having been proved separately, the (other) bond angles and bond lengths are optimized on the planar molecule; the energetic optimization on the dihedral angle between the two rings always leads to a zero angular value. The results obtained for the four molecules studied are presented in Tables 8a and b.

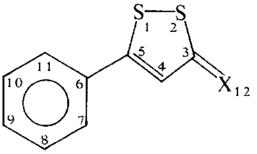
If one compares the calculated geometrical parameters (bond lengths and bond angles) to the available experimental values in the case of compound (III), one notices that the maximal difference is 0.03 Å for the bond lengths (except in the case of the bond C_3–S_{12}: 1.66 Å with 1.57 Å as the calculated value) and often lower than 1° for angles, the differences being most probably due to intermolecular interactions within the crystal.

3.2 Ground states

In Table 9, the experimental and calculated values of ground state dipole moments μ_g as well as the atomic net $\sigma + \pi$ and π-electron charges of the (I)–(IV) molecules are detailed. The theoretical values were obtained through the PM3 method.

Agreement between experimental [32] and calculated dipole moments is satisfactory and consistent with their relative magnitudes. Therefore, a reliable theoretical determination of these moments is possible when experimental determination is not available. It is also useful in the search for new NLO molecules.

Table 8a. Atom numbering conventions and calculated geometries of (I), (III) molecules (PM3 method)



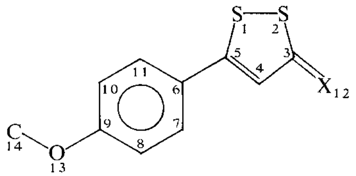
Compound (I)

$d_{1-2} = 2.072$ Å $d_{5-6} = 1.461$ Å (1–5–4) = 117.3°
$d_{2-3} = 1.850$ Å $d_{3-12} = 1.206$ Å (5–1–2) = 95.8°
$d_{3-4} = 1.475$ Å (1–2–3) = 96.2° (4–5–6) = 122.9°
$d_{4-5} = 1.351$ Å (2–3–4) = 110.3° (5–6–7) = 119.8°
$d_{1-5} = 1.765$ Å (3–4–5) = 120.4°
6-atoms ring: 1.389 Å $\leqslant d_{C-C} \leqslant$ 1.400 Å; 119.3° $\leqslant$ (C–C–C) $\leqslant$ 120.5°

Compound (III)

$d_{1-2} = 2.071$ Å $d_{5-6} = 1.458$ Å (1–5–4) = 116.6°
$d_{2-3} = 1.770$ Å $d_{3-12} = 1.573$ Å (5–1–2) = 94.2°
$d_{3-4} = 1.445$ Å (1–2–3) = 97.8° (4–5–6) = 122.7°
$d_{4-5} = 1.363$ Å (2–3–4) = 110.9° (5–6–7) = 119.9°
$d_{1-5} = 1.576$ Å (3–4–5) = 120.5°
6-atoms ring: 1.388 Å $\leqslant d_{C-C} \leqslant$ 1.400 Å; 119.2° $\leqslant$ (C–C–C) $\leqslant$ 120.5°

Table 8b. Atom numbering conventions and calculated geometries of (II), (IV) molecules (PM3 method)



Compound (II)

$d_{1-2} = 2.071$ Å	$d_{3-12} = 1.205$ Å	$(1–5–4) = 117.3°$
$d_{2-3} = 1.851$ Å	$d_{9-13} = 1.375$ Å	$(5–1–2) = 95.8°$
$d_{3-4} = 1.475$ Å	$d_{13-14} = 1.410$ Å	$(4–5–6) = 123.0°$
$d_{4-5} = 1.351$ Å	$(1–2–3) = 96.2°$	$(5–6–7) = 119.7°$
$d_{1-5} = 1.767$ Å	$(2–3–4) = 110.2°$	$(9–13–14) = 117.4°$
$d_{5-6} = 1.458$ Å	$(3–4–5) = 120.5°$	

6-atoms ring: 1.383 Å $\leqslant d_{C-C} \leqslant$ 1.407 Å; 119.3° $\leqslant$ (C–C–C) $\leqslant$ 120.8°

Compound (IV)

$d_{1-2} = 2.071$ Å	$d_{3-12} = 1.575$ Å	$(1–5–4) = 116.6°$
$d_{2-3} = 1.770$ Å	$d_{9-13} = 1.375$ Å	$(5–1–2) = 94.1°$
$d_{3-4} = 1.444$ Å	$d_{13-14} = 1.410$ Å	$(4–5–6) = 122.8°$
$d_{4-5} = 1.364$ Å	$(1–2–3) = 97.8°$	$(5–6–7) = 119.8°$
$d_{1-5} = 1.758$ Å	$(2–3–4) = 111.0°$	$(9–13–14) = 117.5°$
$d_{5-6} = 1.456$ Å	$(3–4–5) = 120.5°$	

6-atoms ring: 1.383 Å $\leqslant d_{C-C} \leqslant$ 1.407 Å; 119.3° $\leqslant$ (C–C–C) $\leqslant$ 120.9°

Preliminary analysis of the electronic distribution of these molecules and of their geometry (in the ground state) shows an alternation in the net π-electron charge signs and in the length (alternated double and single bonds) of the C_6–C_5, C_5–C_4, C_4–C_3, and C_3–X_{12} bonds.

For example, we have: 1.21 Å in the C_3–O_{12} bond, 1.48 Å, 1.35 Å and 1.46 Å in the C_3–C_4, C_4–C_5, and C_5–C_6 bonds respectively in the compounds (I) and (II); 1.57 Å in the C_3–S_{12} bond, 1.44 Å, 1.36 Å and 1.46 Å in the same C–C bonds in the case of the compounds (III) and (IV).

This result, obtained in the absence of solvatation effects, indicates a possible influence of the medium polarity on this type of molecule.

Substitution by the methoxy group does not bring any noticeable change to the electronic structure of dithiolic moiety side of the molecule. The replacement of the oxygen atom O_{12} ("dithiole-3-one") by the sulfur atom S_{12} ("dithiole-3-thione") leads to significant variations in the $(\sigma + \pi)$-electron charges of the S_2 and C_3 atoms (0.14 and -0.42 respectively), but the net π-electron charges are only moderately modified (0.07 and -0.16 respectively).

Sketches of the relative orientations of the ground state dipole moments calculated within PM3 method for compounds (I)–(IV) are presented in Fig. 1.

It should be noted that putting a 3H-1,2-dithiole-3-thione group in place of a 3H-1,2-dithiolone-3-one increases the dipole moment and changes its direction by about 10 degrees (see (I) → (III) and (II) → (IV)). In a similar way, replacement of

Table 9. Calculated net $\sigma + \pi$ and π-electron charges, calculated and experimental (see Ref. [27]) dipole moments for the ground state of (I)–(IV) molecules

Atoms	Molecule (I)		Molecule (II)		Molecule (III)		Molecule (IV)	
	$\sigma + \pi$	π	$\sigma + \pi$	π	$\sigma + \pi$	π	$\sigma + \pi$	π
S_1	0.115	0.107	0.108	0.105	0.123	0.149	0.115	0.147
S_2	− 0.038	0.092	− 0.042	0.090	0.105	0.165	0.103	0.162
C_3	0.273	0.222	0.276	0.224	− 0.158	0.060	− 0.153	0.062
C_4	− 0.273	− 0.105	− 0.282	− 0.116	− 0.196	− 0.067	− 0.205	− 0.077
C_5	− 0.081	0.023	− 0.068	0.029	− 0.097	0.010	− 0.083	0.017
C_6	− 0.056	− 0.044	− 0.100	− 0.084	− 0.056	− 0.045	− 0.101	− 0.085
C_7	− 0.075	0.020	− 0.038	0.044	− 0.073	0.022	− 0.036	0.046
C_8	− 0.102	0.001	− 0.145	− 0.050	− 0.101	0.002	− 0.145	− 0.050
C_9	− 0.075	0.028	0.124	0.072	− 0.073	0.030	0.126	0.075
C_{10}	− 0.101	0.003	− 0.188	− 0.082	− 0.101	0.003	− 0.188	− 0.081
C_{11}	− 0.070	0.015	− 0.027	0.050	− 0.071	0.023	− 0.027	0.050
O_{12}–S_{12}	− 0.240	− 0.370	− 0.241	− 0.372	− 0.028	− 0.351	− 0.035	− 0.357
O_{13}	–	–	− 0.186	0.106	–	–	− 0.185	0.108
C_{14}	–	–	0.050	0.012	–	–	0.049	0.012
μ_{exp} (D)	4.30		5.14		4.93		5.89	
μ_{cal} (D)	4.19		4.89		4.70		5.73	

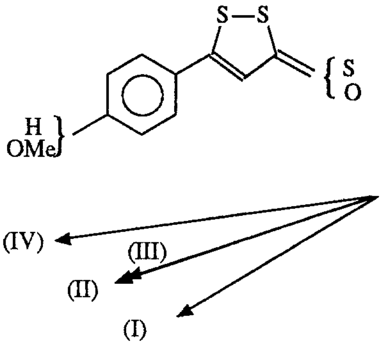


Fig. 1. Relative ground state dipole moments orientations (PM3)

the para-hydrogen atom by a methoxy group in the phenyl ring increases the modulus of the dipole moment and changes its direction by about 10 degrees (see (I) → (II) and (III) → (IV)).

3.3 *Lower excited states*

In Tables 10a and b we have gathered the CNDO/S-CI results obtained for the energies of the first singlet–singlet electronic transitions, the oscillator strengths and other features of these transitions (character and weight of the main configurations). The available experimental values are also given for comparison.

Table 10a. Experimental and CNDO/S-CI calculated singlet–singlet transition energies of 5-(*p*-"X" phenyl)-3H-1,2-dithiole-3-one ((I) and (II))

Compound	Energy (eV) ΔE_{exp} (in dioxane)	ΔE_{cal}	Oscillator strength	Orbital configuration	Weight (%)	Transition character
I		3.65	0.000	27 → 31	62	$\sigma \rightarrow \pi^*$
				27 → 33	25	$\sigma \rightarrow \pi^*$
				27 → 36	11	$\sigma \rightarrow \pi^*$
	3.65	4.23	0.341	30 → 31	77	$\pi \rightarrow \pi^*$
				29 → 31	14	$\pi \rightarrow \pi^*$
		4.33	0.010	29 → 34	48	$\pi \rightarrow \sigma^*$
				30 → 34	35	$\pi \rightarrow \sigma^*$
				29 → 35	10	$\pi \rightarrow \sigma^*$
	4.40	4.51	0.666	29 → 31	79	$\pi \rightarrow \pi^*$
				30 → 31	15	$\pi \rightarrow \pi^*$
II		3.67	0.000	33 → 37	62	$\sigma \rightarrow \pi^*$
				33 → 39	25	$\sigma \rightarrow \pi^*$
				33 → 42	12	$\sigma \rightarrow \pi^*$
	3.97	4.20	0.695	36 → 37	88	$\pi \rightarrow \pi^*$
				35 → 37	5	$\pi \rightarrow \pi^*$
				35 → 39	1	$\pi \rightarrow \pi^*$
		4.26	0.009	35 → 40	77	$\pi \rightarrow \sigma^*$
				36 → 40	15	$\pi \rightarrow \sigma^*$
		4.37	0.378	35 → 37	86	$\pi \rightarrow \pi^*$
				36 → 37	6	$\pi \rightarrow \pi^*$
				35 → 39	3	$\pi \rightarrow \pi^*$

Table 10b. Experimental and CNDO/S-CI calculated singlet–singlet transition energies of 5-(*p*-"X" phenyl)-3H-1,2-dithiole-3-thione ((III) and (IV))

Compound	Energy (eV) ΔE_{exp} (in dioxane)	ΔE_{cal}	Oscillator strength	Orbital configuration	Weight (%)	Transition character
III		1.68	0.000	29 → 31	76	$n \rightarrow \pi^*$
				29 → 32	14	$n \rightarrow \pi^*$
	2.83	3.53	0.690	30 → 31	94	$\pi \rightarrow \pi^*$
		4.20	0.002	30 → 34	72	$\pi \rightarrow \sigma^*$
				28 → 34	20	$\pi \rightarrow \sigma^*$
	3.92	4.37	0.601	28 → 31	94	$\pi \rightarrow \pi^*$
IV		1.69	0.000	35 → 37	76	$n \rightarrow \pi^*$
				35 → 39	18	$n \rightarrow \pi^*$
	2.83	3.51	0.799	36 → 37	94	$\pi \rightarrow \pi^*$
		3.99	0.005	36 → 40	58	$\pi \rightarrow \sigma^*$
				34 → 40	30	$\pi \rightarrow \sigma^*$
	3.58	4.22	0.540	34 → 37	94	$\pi \rightarrow \pi^*$

The two bands experimentally observed for three of the four compounds (for compound (II) there is only a single band) have no particular assignment. In all cases the theoretical calculations evidence two bands for which the $\pi \rightarrow \pi^*$ character is unambiguously defined: 4.23 and 4.51 eV, 4.20 and 4.37 eV, 3.53 and 4.37 eV, and 3.51 and 4.22 eV respectively for the compounds (I), (II), (III), and (IV). The transition of the lowest calculated energy presents a $\sigma \rightarrow \pi^*$ character (compounds I and II) which takes a $n \rightarrow \pi^*$ character for the compounds (III) and (IV). In the latter case, the transition is mainly (76%) described by the one-electron excitation from a molecular orbital (29 for (III) and 35 for (IV)) mainly located on the sulfur atom S_{12} and confined within the molecular plane (lone pairs of the sulfur electrons), towards a molecular orbital (31 for (III) and 37 for (IV)) having a complete π^* character.

The fourth band evidenced by calculation corresponds to a $\pi \rightarrow \sigma^*$ type for all compounds (4.33, 4.26, 4.20 and 3.99 eV, respectively) with a mixture of several configurations in all cases.

We are particularly interested in the two bands with high oscillator strengths and exhibiting the $\pi \rightarrow \pi^*$ character listed for each of the molecules studied. We note in particular that for the "dithiolone" molecules (compounds (I) and (II)), the calculated values of the electronic transition energy for these two bands are very close to each other (0.17 eV for example for the molecule (II)) and that they are characterized by a mixing of the same configurations with different weights. This could explain the experimental observation of a single band in the case of compound (II).

For compounds of the "dithiolethione" series, the two $\pi \rightarrow \pi^*$ bands, whose energy values are more clearly differentiated, correspond to a predominant one-electron excitation:

$$30 \rightarrow 31\ (94\%) \text{ and } 28 \rightarrow 31\ (94\%) \text{ for compound (III)}$$

$$36 \rightarrow 37\ (94\%) \text{ and } 34 \rightarrow 37\ (94\%) \text{ for compound (IV)}$$

We have analyzed the charge transfer that may contribute to these $\pi \rightarrow \pi^*$ transitions for the four compounds studied by arbitrarily "cutting" the molecule into two fragments in the middle of the C_5–C_6 bond.

The $\pi \rightarrow \pi^*$ transition of weaker energy does not present any marked characteristics of a charge transfer. The excitation produces a variation of π-electron charge between the left part of the molecule (atoms 6–11 for (I) and (III), atoms 6–11, 13 and 14 for (II) and (IV) and the right part of the molecule (atoms 1–5 and atom 12) which is slightly positive ($+0.11$ to $+0.27$) for the molecules (I), (III) and (IV), and corresponds to an evolution towards a less polarized electronic distribution. The same variation is slightly negative (-0.15) for the molecule (II).

The second $\pi \rightarrow \pi^*$ absorption band presents, on the contrary, a relatively important charge transfer character for compounds (I), (III) and (IV) as demonstrated in Fig. 2 giving the intramolecular charge transfer between the left (donor, D) and right (acceptor, A) parts of these molecules: -0.40, -0.39 and -0.45, respectively. Molecule (II), once again constitutes a special case (weak transfer of -0.15 and -0.11, for the two $\pi \rightarrow \pi^*$ bands). The interpenetration of the two very closely related bands prevents any further analysis.

Additionally, we have investigated the participation of the disulfide group (S_1 and S_2) of the heterocycle in the two $\pi \rightarrow \pi^*$ transitions. For this purpose, we have studied the electronic transfer between these two atoms and the rest of the

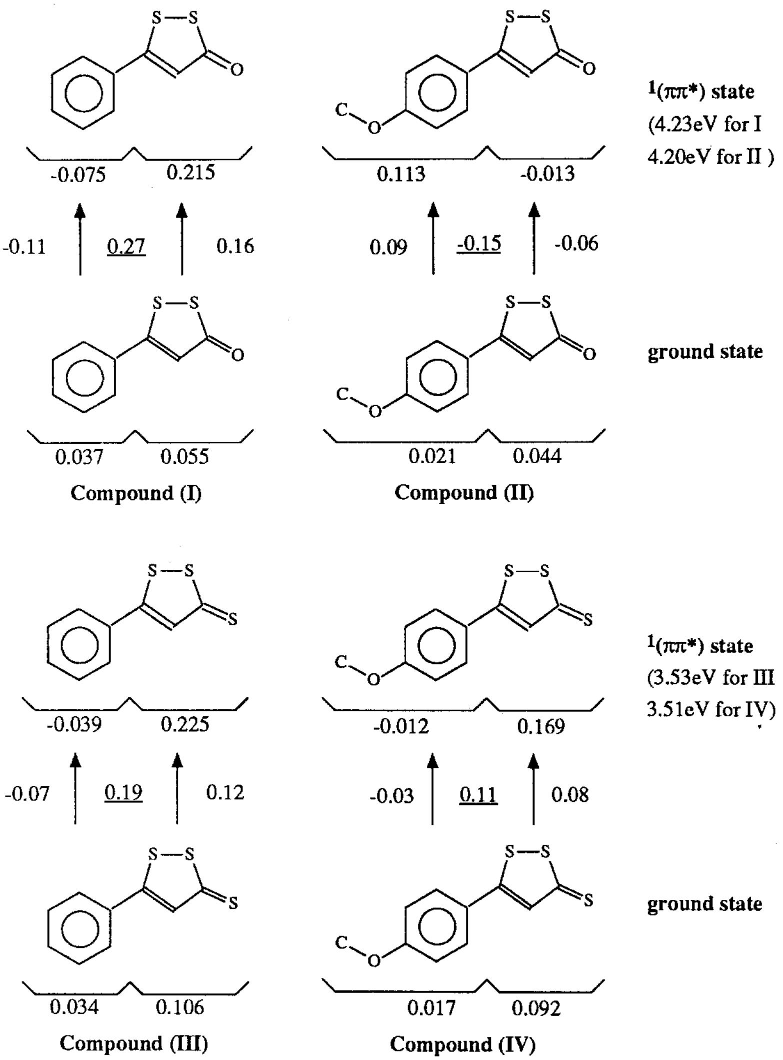


Fig. 2a. Intramolecular charge transfer (changes in net π-electron charges) for the first lowest π → π* transition energy of (I)–(IV) molecules

molecule. We have noticed in all cases a significant π-electron loss on the two sulfur atoms:

– first π → π* transition	– 0.97	– 0.26	– 0.61	– 0.47
– second π → π* transition	– 0.55	– 1.17	– 0.66	– 0.77

for compounds (I), (II), (III) and (IV) respectively.

The charge transfer is mainly oriented towards the C_3 and C_5 atoms for the "dithiolone" molecules and towards C_3, C_5 and S_{12} for the "dithiolthione" molecules. It is most probably the almost unique contribution to the lowest-energy band of dithiole-3-thiones, the corresponding transition energy being exactly the same

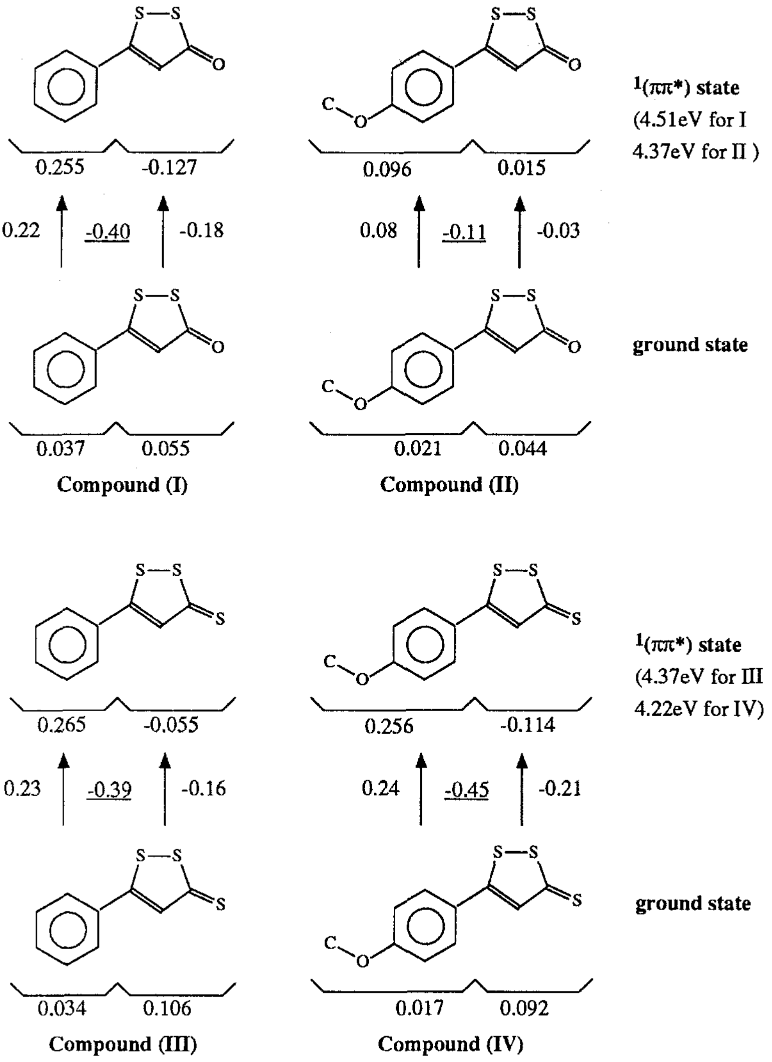


Fig. 2b. Intramolecular charge transfer (changes in net π-electron charges) for the second lowest $\pi \rightarrow \pi^*$ transition energy of (I)–(IV) molecules

(experimental values) or almost exactly the same (calculated values) for compounds (III) and (IV) (this comparison is not possible for "dithiolone" molecules: a single $\pi \rightarrow \pi^*$ band is observed for compound (II)). Therefore, the contribution of an ICT between the phenyl ring and the 3H-1,2-dithiole-3-thione moiety to this transition is probably negligible.

Thus it appears that the two S_1 and S_2 atoms act in competition with the previous charge transfer between the right and left parts of the molecule. A more systematic study of these compounds is under study on other compounds of these series.

Regarding the assignment of the experimentally observed bands, it is reasonable to infer that they correspond to the calculated $\pi \rightarrow \pi^*$ transitions (high oscillator strength values) even if a systematic discrepancy exists between the calculated and observed ΔE values.

These results can be completed by the analysis of the differences $\Delta\mu$ between the dipole moments of the excited states (essentially the $^1(\pi\pi^*)$ states) and of the ground state. The CNDO/S-CI calculated values are collected in Table 11. We have also given, for comparison, the experimental ΔE $^1(\pi\pi^*)$ values in a nonpolar (dioxane) and a strongly polar (acetonitrile) solvent.

In the case of the $^1(\pi\pi^*)$ excited state of weaker energy, the calculated $\Delta\mu$ are weak for the compounds (I), (III) and (IV) and slightly negative in the case of the first two ones. Once again molecule (II) constitutes an exception ($\mu_e > \mu_g$ and $\Delta\mu > 2$ D).

These results are correlated with the data obtained from the previous analysis of the (weak) variation (positive or negative) of the π-electronic distribution between the right and left parts of the molecule during excitation.

For the higher $^1(\pi\pi^*)$ energy state, an inverse evolution ($\mu_e > \mu_g$) is observed, which is consistent with the character of the significant charge transfer (negative) associated with this transition, at least for compounds (I), (III) and (IV). These results are consistent with the experimental spectroscopy data: a slightly negative solvatochromism is observed for the lowest energy band of compound (I), (III) and (IV), whereas a slightly positive solvatochromism is evidenced, in the same molecules, for the second electronic $\pi \rightarrow \pi^*$ transition.

Regarding this last state and except for molecule (II), we have established that the $\Delta\mu$ values calculated for the three other molecules are in agreement with the order of experimental static first-order hyperpolarisability β values determined from experimental data using a quantum two-level model. These values are listed in Table 13:

$$\Delta\mu\,(\mathrm{IV}) > \Delta\mu\,(\mathrm{III}) > \Delta\mu\,(\mathrm{I}) \quad \text{and} \quad \beta\,(\mathrm{IV}) > \beta\,(\mathrm{III}) > \beta\,(\mathrm{I})$$

This is consistent with the predictions of the two-level model (see Ref. [17]), where β is a linear function of $\Delta\mu$, assuming similar oscillator strengths for all molecules mentioned here.

Table 11. Calculated CNDO/S-CI values ($\Delta\mu$, ΔE) and experimental values (ΔE in dioxane and acetonitrile) for the two first excited states $^1(\pi\pi^*)$

Compound	Calculated CNDO/S-CI values		Experimental values	
	$\Delta\mu = \mu_e - \mu_g$ (Debye)	ΔE (eV)	ΔE in dioxane (eV)	ΔE in acetonitrile (eV)
I	− 0.30	4.23	3.65	3.66
	3.79	4.51	4.40	4.38
II	2.18	4.20	3.97	3.95
	3.17	4.37		
III	− 0.80	3.53	2.83	2.86
	5.82	4.37	3.92	3.91
IV	0.31	3.51	2.83	2.86
	6.52	4.22	3.58	3.54

This second $\pi \rightarrow \pi^*$ absorption band which corresponds to the strongest ICT inside the nonlinear molecules seems the most appropriate for correlation with NLO data.

3.4 *Solvent effects on the $\pi \rightarrow \pi^*$ bands of weaker energies*

In order to refine the description of the observed $\pi \rightarrow \pi^*$ bands, we performed CNDO/S and CNDO/S-CI calculations on the four previous molecules while taking into account the solvent effect represented by the function $f(\varepsilon)$ of a virtual charge model [22, 23].

The results are listed in Table 12.

With respect to the first $\pi \rightarrow \pi^*$ band, we notice, in all cases, an increase of the electronic transition energy when the medium polarity increases: this hypsochromic shift characterizes a negative solvatochromism. This $\Delta E\ ^1(\pi\pi^*)$ variation is very weak for compound (II).

The second band is characterized by a generally inverted effect. The calculated variation (decrease of $\Delta E\ ^1(\pi\pi^*)$ value) being characteristic of a positive solvatochromism.

In the case of compound (II), a weak bathochromic effect appears for $f(\varepsilon)$ values in the range 0–0.2, but the energy slightly increases for $f(\varepsilon) > 0.2$. Such a behaviour has already been observed for some $\pi \rightarrow \pi^*$ transitions in merocyanine type compounds [23].

These results are quite consistent with the experimental spectroscopic data given in Table 11. Spectroscopic data are measured in two solvents of different polarities characterized by the $d(\varepsilon, n)$ function [33]:

$$\text{dioxane } (d(\varepsilon, n) = 0.034) < \text{acetonitrile } (d(\varepsilon, n) = 0{,}711)$$

Table 12. Calculated (CNDO/S-CI) excitation energy and $\Delta\mu = \mu_e - \mu_g$ values of the two first singlet excited states $^1(\pi\pi^*)$ of (I)–(IV) molecules as a function of $f(\varepsilon)$

$f(\varepsilon)$	ΔE (eV)	oscillator strength	$\Delta\mu$ (D)	ΔE (eV)	oscillator strength	$\Delta\mu$ (D)
		Compound (I)			Compound (II)	
0	4.23	0.341	– 0.30	4.20	0.695	2.18
	4.51	0.666	3.79	4.37	0.378	3.17
0.2	4.25	0.304	– 0.10	4.21	0.775	3.28
	4.45	0.703	3.92	4.34	0.309	2.71
0.5	4.30	0.189	0.80	4.22	0.849	4.90
	4.39	0.791	4.10	4.36	0.211	0.85
		Compound (III)			Compound (IV)	
0	3.53	0.690	– 0.80	3.51	0.799	0.31
	4.37	0.601	5.82	4.22	0.540	6.52
0.2	3.54	0.689	– 0.83	3.53	0.799	0.22
	4.35	0.614	5.73	4.21	0.550	6.29
0.5	3.59	0.653	– 1.05	3.58	0.780	– 0.25
	4.32	0.644	5.29	4.19	0.578	5.65

The study of the solvatochromism of the $\pi \rightarrow \pi^*$ absorption bands can be completed by the comparison of the dipole moments of the ground state and of the relevant excited state for different values of the function $f(\varepsilon)$. It is generally admitted that an increase in the dipole moment of a polar solute during excitation ($\mu_e > \mu_g$) leads to a stabilization of the excited state relatively to the ground state when the medium polarity increases, leading consequently to a bathochromic effect. On the contrary, a decrease of dipole moment ($\mu_e < \mu_g$) leads to the inverse effect. However, it is important to note that the observed effects must be strong enough to corroborate this rule.

In the case of the results obtained for molecules (I) and (IV), if an overall coherence is noticed, the weakness of some variations makes analysis difficult. However, we note that the second $^1(\pi\pi^*)$ band, for which we have previously established a charge transfer character (in the framework of our model), always corresponds to a bathochromic shift in agreement with the variation of the dipole moment during the electronic transition ($\mu_e > \mu_g$). It should be noted, in particular, that when the difference (positive) $\Delta\mu = \mu_e - \mu_g$ increases with the medium polarity, the differences observed in transition energies $\Delta(\Delta E)$ are relatively important (case of the compound (I)), whereas the inverse evolution results in a relatively weaker bathochromic effect (compounds (III) and (IV) in particular). Concerning the first band, the calculation evidences, on the whole, an hypsochromic shift (ΔE increases) in agreement with the $\Delta\mu$ values (negative or very weak) for the compounds (I), (III) and (IV).

The minor influence of this polarity change on the two calculated $\pi \rightarrow \pi^*$ bands of the compound (II) can be once again explained by the very close values of the corresponding electronic transition energies.

3.5 First-order hyperpolarizabilities: Comparison between theory and experiment

The use of the PM3 Hamiltonian (in the MPOAC 6.0 package) for the calculation of geometries and electronic distributions of the ground states of the four molecules studied here allows for the calculation of the hyperpolarizabilities with a finite-field method [18] based on both an energy expansion and a dipole moment expansion (an electric field gradient of 0.001 a.u. is used) [34].

For information we give (see Table 13) the values obtained for the first-order hyperpolarizabilities of molecules (I) to (IV). Experimental determination of β values was performed using the standard EFISH technique [35] operating at 1.34 μm. The laser source is a Q-switched, mode-locked Nd^{3+}:YAG laser with measurements made in acetone.

There is a good agreement between calculated (β^{PM3}) and experimental "two-level quantum" values ($\beta(0)$) with a linear regression coefficient of 0.994. However, we noticed that β^{PM3} values are always greater than $\beta(0)$ values. Matsuzawa and Dixon [36] also observed these discrepancies with compounds substituted by thiol or thiomethyl groups.

The results discussion is not relevant to this paper as it would require a more systematic study of hyperpolarizabilities (both experimental and theoretical values) for this type of compounds.

It must be pointed out that for compounds (I) and (III) the experimental β values are quite large as compared to classical monosubstituted benzene derivatives ($\beta = 2.10^{-30}$ esu for nitrobenzene at 1.06 μm). These interesting performances

Table 13. Calculated (PM3 method) and experimental second-order hyperpolarizabilities.
(a) calculated hyperpolarizability coefficients with PM3 method
(b) experimental hyperpolarizability coefficients determined at 1.34 μm
(c) static hyperpolarizability $\beta(0)$, deduced from (b) using the quantum two-level model based equation [17]:

$$\beta(0) = \beta(\omega)(1 - (2\lambda_{\max}/\lambda)^2)(1 - (\lambda_{\max}/\lambda)^2)$$

λ: laser fundamental wavelength (here 1.34 μm)
$\lambda_{\max}$: Wavelength of the charge transfer band (here, the second for compounds (I), (III), (IV) and the single one for (II)).

Our choice of the second $\pi \rightarrow \pi^*$ band is in agreement with its charge transfer character leading to larger $\Delta\mu$ values than these values calculated for the first transition (compounds (I), (III), (IV))

Compound	β^{PM3} (a) $\times 10^{-30}$ e.s.u.	$\beta(\omega)$ (b) $\times 10^{-30}$ e.s.u.	$\beta(0)$ (c) $\times 10^{-30}$ e.s.u.
I	4.6	4.8	3.8
II	12.8	12.9	9.2
III	12.6	11.3	8.1
IV	25.8	21.8	15.0

cannot be accounted for by a very large electron-acceptor character of the 3H-1,2-dithiole-3-one or 3H-1,2-dithiole-3-thione moiety, in view of their Hammett's constants as determined by electrochemical methods [14]. This could more probably result from the electronic charge transfer, as evidenced by both the theoretical results and the spectral data, within the dithiolic ring itself.

In the case of compounds (II) and (IV), the role of the methoxy group becomes predominant, leading to a strong enhancement of hyperpolarizabilities $\beta(\omega)$ and $\beta(0)$ as compared to compounds (I) and (III). However the enhancement factor is not as large as observed for more classical benzenic derivatives [1] (e.g. *p*-methoxy nitrobenzene with respect to nitrobenzene, the enhancement factor being at least 7 in this case). This could be related to the predominance of the intracyclic ICT within the dithiolic ring of these compounds, as previously evidenced by charge transfer analysis (see Sect. 3.3).

Conclusion

The initial results of our study gives a description of the electronic structure of the ground and excited states of molecules in 5-phenyl-3H-1,2-dithiole-3-one and 5-phenyl-3H-1,2-dithiole-3-thione series, allowing for a comparison of some of their respective structural, electronic and spectral properties in relation to NLO properties. However, it appears difficult to correlate directly some NLO data (like the β coefficient) with one particular electronic property. For example, the classification of the molecules in terms of decreasing $\Delta\mu$ values of the second $\pi \rightarrow \pi^*$ band is the following:

$$(IV) > (III) > (I) > (II)$$

This order is not in full agreement with the corresponding classification of the β values. The values of the dipole moment of the ground state modulates this classification, and the interpenetration of the excited configurations does not allow, in some cases, to unambiguously characterize an electronic state. On the other hand, the experimental $\beta(0)$ values are deduced from measurements performed at 1.34 μm, using a classical two-level model. In fact, both experimental and theoretical spectroscopic studies show two excited states which can contribute to the first-order hyperpolarizability β. Therefore, a three-level model could be slightly more appropriate to describe the NLO behaviour of these molecules, although the $\beta(0)$ given in Table 13 are already in good agreement with the calculated values from the PM3 method.

Properties must be taken as a whole to be analyzed: from this perspective the theoretical study of a greater number of molecules of the "one" and "thione" series should permit to refine over this study, while adding to the experimental data available for comparison with calculated first-order hyperpolarizabilities.

Acknowledgements. We wish to thank Professor A. Darchen (Laboratoire de Physicochimie Analytique et Théorique de l'E.N.S.C.R.) for providing the four products and the C.R.I. (Centre de Ressources Informatiques) for the effective technical assistance.

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