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Theoretical and experimental studies of electronic effects and second-order nonlinear optical properties of some benzenecarbothioates and benzenecarbodithioates

Alain Botrel[1], André Darchen[1], Brigitte Negroni[1], Isabelle Ledoux[2], 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, URA CNRS 250,
FRANCE TELECOM, Centre National d'Etudes des Télécommunications, Paris B,
196 avenue Henri Ravera, BP107, F-92225 Bagneux Cedex, France

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Abstract. The relative nonlinear efficiency of some conjugated ester, thioester and dithioester molecules was investigated by quantum chemical semi-empirical methods. The results of calculations on ground and excited states properties and on "finite-field" hyperpolarizabilities β allowed to select the best compounds for quadratic nonlinear optics. Some of these molecules were synthesized and the theoretical results were confronted with the experimental NLO response obtained by β EFISH measurements. It was concluded from this analysis that the dithioester substituent represents an interesting electron-accepting group for applications in nonlinear optics and can be used instead of the nitro group.

Key words: Thioesters – Dithioesters – Charge Transfer – Hyperpolarizability

1 Introduction

Recent works [1–4] have shown that the thiocarbonyl group exhibits high electron-accepting efficiency compared to well-known nitro or cyano substituents. Thus, these molecules can be regarded as new interesting materials for quadratic nonlinear optics, so as to design either dipolar or octupolar [5–9] molecules, for various applications in the field of optical signal processing: electro-optic modulation, frequency doubling, parametric interaction. "Optimized" organic materials for quadratic NLO are made of acentric molecules exhibiting a large difference between the ground- and excited-state dipole moments as well as a high transition moment in the electronic transition involved in the nonlinear interaction [10–12]. On the other hand, for frequency doubling, the materials should be transparent not only at the fundamental wavelength but also at its second harmonic wavelength. For example, frequency doubling of infrared semi-conductor lasers for optical information storage (typical fundamental wavelength around 850 nm) requires nonlinear materials that are transparent in the blue wavelength region. However, the first-order hyperpolarizability β increases with the absorption wavelength of the electronic transition (corresponding to electronic intramolecular charge transfer) involved in the nonlinear process, resulting in a bathochromic shift of the

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Correspondence to: A. Botrel

edge of the absorption spectrum. Thus, the larger hyperpolarizability and the wider transparency range of visible wavelength conflict with each other, and a "transparency/nonlinear" trade-off has to be found [13] for a proper optimization of frequency-doubling materials.

The aim of this work is to present a theoretical evaluation of electronic and nonlinear optical properties of some conjugated thio and dithioesters, and to show that the thiocarbonyl group exhibits a good NLO efficiency as compared to the nitro substituent. We have used quantum chemical semi-empirical methods for the determination of ground- and excited-state properties and for the calculation of first-order hyperpolarizability β of these molecules, in order to facilitate the design of such compounds for specific applications in nonlinear optics. We have studied the related ester compounds in order to analyse the relative electronic effects of carbonyl and thiocarbonyl groups. Then, we have synthesized some molecules of these series and the reliability of this calculation procedure was assessed particularly by comparison with experimental β EFISH measurements.

2 Studied molecules and theoretical results

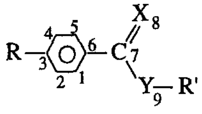
For the semi-empirical calculations we have selected the methyl and phenyl benzoates, thiobenzoates and dithiobenzoates sketched in Chart 1.

2.1 Molecular geometries

The geometries of isolated molecules were optimized with the semi-empirical method PM3 [14] (MOPAC 6.0 program [15]). The main results are presented in Table 1.

We have added the results concerning the methyl *p*-*t*-butylbenzenecarbodithioate for which X-ray data were available [16]. For this molecule, a relatively good agreement between calculated geometrical parameters (bond lengths and bond angles) and experimental values is observed. The main difference is found for the dihedral angle between the plane of the functional group and the plane of the aromatic ring: the experimental value is near 24° when the calculated one is near 50°.

Chart 1. Studied molecules and numbering of atoms



Compounds	**R**	**X**	**Y**	**R'**
methyl benzenecarboxylate (**Ia**)	H	O	O	CH_3
methyl p-N,N-dimethylaminobenzenecarboxylate (**Ib**)	$(CH_3)_2N$	O	O	CH_3
phenyl benzenecarboxylate (**IIa**)	H	O	O	C_6H_5
phenyl p-N,N-dimethylaminobenzenecarboxylate (**IIb**)	$(CH_3)_2N$	O	O	C_6H_5
O-methyl benzenecarbothioate (**IIIa**)	H	S	O	CH_3
O-methyl p-N,N-dimethylaminobenzenecarbothioate (**IIIb**)	$(CH_3)_2N$	S	O	CH_3
O-phenyl benzenecarbothioate (**IVa**)	H	S	O	C_6H_5
O-phenyl p-N,N-dimethylaminobenzenecarbothioate (**IVb**)	$(CH_3)_2N$	S	O	C_6H_5
methyl benzenecarbodithioate (**Va**)	H	S	S	CH_3
methyl p-N,N-dimethylaminobenzenecarbodithioate (**Vb**)	$(CH_3)_2N$	S	S	CH_3
phenyl benzenecarbodithioate (**VIa**)	H	S	S	C_6H_5
phenyl p-N,N-dimethylaminobenzenecarbodihioate (**VIb**)	$(CH_3)_2N$	S	S	C_6H_5

Table 1. Geometrical characteristics of studied molecules: bond lengths in Å, angles in degrees

ESTERS (PM3 CALCULATIONS)

	Ia	Ib	IIa	IIb
6-atoms ring	$1.390 \le d \le 1.399$ $119 \le \theta \le 121$	$1.383 \le d \le 1.405$ $118 \le \theta \le 121$	$1.390 \le d \le 1.400$ $\theta \approx 120$	$1.383 \le d \le 1.405$ $119 \le \theta \le 121$
D_{6-7}	1.488	1.485	1.489	1.485
D_{7-8}	1.217	1.218	1.217	1.217
D_{7-9}	1.367	1.369	1.371	1.373
$D_{9-R'}$	1.412	1.412	1.389	1.388
(1-6-7-8)	178	179	177	170
(7-8-9-10)			178	179

THIOESTERS (PM3 CALCULATIONS)

PLANAR MOLECULES

	IIIa	IIIb	IVa	IVb
6-atoms ring	$1.388 \le d \le 1.402$ $\theta \approx 120$	$1.383 \le d \le 1.410$ $118 \le \theta \le 121$	$1.388 \le d \le 1.403$ $\theta \approx 120$	$1.382 \le d \le 1.412$ $119 \le \theta \le 121$
D_{6-7}	1.482	1.472	1.490	1.477
D_{7-8}	1.627	1.633	1.628	1.634
D_{7-9}	1.363	1.365	1.357	1.360
$D_{9-R'}$	1.412	1.412	1.390	1.391

NON-PLANAR MOLECULES

	IIIa	IIIb	IVa	IVb
6-atoms ring	$1.388 \le d \le 1.398$ $\theta \approx 120$	$1.384 \le d \le 1.406$ $118 \le \theta \le 121$	$1.388 \le d \le 1.400$ $119 \le \theta \le 121$	$1.384 \le d \le 1.405$ $119 \le \theta \le 121$
D_{6-7}	1.483	1.477	1.487	1.479
D_{7-8}	1.617	1.624	1.611	1.617
D_{7-9}	1.363	1.363	1.366	1.369
$D_{9-R'}$	1.411	1.412	1.399	1.400
(1-6-7-8)	136	146	124	146
(7-9-10-11)			95	98

DITHIOESTERS (PM3 CALCULATIONS)

PLANAR MOLECULES

	Va	Vb	VIa	VIb
6-atoms ring	$1.388 \le d \le 1.404$ $\theta \approx 120$	$1.381 \le d \le 1.412$ $119 \le \theta \le 121$	$1.388 \le d \le 1.405$ $\theta \approx 120$	$1.381 \le d \le 1.411$ $118 \le \theta \le 121$
D_{6-7}	1.473	1.461	1.478	1.466
D_{7-8}	1.597	1.603	1.598	1.603
D_{7-9}	1.762	1.768	1.761	1.769
$D_{9-R'}$	1.801	1.802	1.769	1.769

NON-PLANAR MOLECULES

	Va	Vb	VIa	VIb
6-atoms ring	$1.390 \le d \le 1.401$ $\theta \approx 120$	$1.383 \le d \le 1.406$ $118 \le \theta \le 121$	$1.389 \le d \le 1.399$ $\theta \approx 120$	$1.385 \le d \le 1.405$ $118 \le \theta \le 121$
D_{6-7}	1.473	1.468	1.481	1.472
D_{7-8}	1.587	1.593	1.584	1.583
D_{7-9}	1.754	1.759	1.751	1.765
$D_{9-R'}$	1.802	1.801	1.769	1.768
(1-6-7-8)	133	146	121	131
(7-9-10-11)			178	95

METHYL p-t-BUTYLBENZENECARBODITHIOATE

	crystallographic data	PM3 calculations
6-atoms ring	$1.377 \le d \le 1.392$ $117 \le \theta \le 122$	$1.387 \le d \le 1.401$ $118 \le \theta \le 122$
D_{6-7}	1.485	1.475
D_{7-8}	1.630	1.586
D_{7-9}	1.724	1.752
$D_{9-R'}$	1.788	1.801
(1-6-7-8)	156	131

But because of the weak calculated rotational barrier of the functional group ($<5\ \mathrm{kcal\,mol^{-1}}$ for all the molecules) and other X-ray results showing that aromatic thioesters have coplanar C(S)OR′ group and phenyl ring [17], we have also applied theoretical calculations to planar isolated molecules.

On the other hand, we can notice that the calculated dihedral angle clearly decreases when the R substituent is a donor group for all the thio and dithioester molecules.

2.2 *Theoretical investigation of the nonlinear optical properties of the studied molecules*

One of the main factors which have been identified to play an important role on the NLO response of a molecule is its ability to promote charge transfer transitions between the donor and acceptor substituents. The higher this transfer is, the greater are the difference $\overrightarrow{\Delta\mu}$ (between the dipole moments in the ground state $\vec{\mu}_g$ and in the first excited state $\vec{\mu}_e$) and the oscillator strength f characterizing the transition.

The main features of the first singlet–singlet electronic transitions, such as excitation energy, charge transfer, oscillator strength and $\Delta\mu$ values ($\Delta\mu = \|\overrightarrow{\Delta\mu}\| = \|\vec{\mu}_e - \vec{\mu}_g\|$), were determined using the CNDO/S method which offers the advantage of routine calculations on large molecules containing elements of the third row, such as sulfur atom; another interest in this method is the possibility to extensively account for solvent effects [18, 19] and to introduce a new parametrization for oxygen atom in carbonyl groups [20] and sulfur atom in thiocarbonyl groups [3].

In this work, the new parametrization was used, excited states were generated from the ground state occupied and virtual orbitals through a configuration interaction procedure between the 60 lowest energy singly excited configurations, and the bicentric electron integrals were computed using the Nishimoto–Mataga approximation [21].

With the aim of checking influence of solvent polarity on electronic properties of the studied molecules, we have used CNDO/S-CI method taking into account the solvent effect represented by the function $f(\varepsilon)$ [18, 19]. The calculations were applied to some molecules. For example, with respect to the first $\pi \rightarrow \pi^*$ band of Vb dithioester, we noticed an insignificant variation of the electronic transition energy (less than 0.1 eV) when $f(\varepsilon)$ increases from 0 to 0.5. This result was consistent with the corresponding experimental spectroscopic data: $\Delta E^1(\pi\pi^*)$ variation less than 0.2 eV when going from cyclohexane [22] to chloroform [23] solution. Because of this lack of solvatochromism, which results in slight variations of spectroscopic properties and hence of hyperpolarizabilities, we have not carried on this study.

In order to compare the efficiencies of ester, thioester, dithioester and nitro groups, theoretical calculations were also achieved for the *N,N*-dimethyl-*p*-nitroaniline (DMNA).

In Chart 2, we have gathered the CNDO/S-CI results obtained for the two first $\pi \rightarrow \pi^*$ transitions of the planar molecules: singlet electronic transition energies, oscillator strengths, weights of the main configurations, $\Delta\mu$ (the modulus of the dipole moment difference between the excited state and the ground state) and π-electronic intramolecular charge transfer (ICT) associated with these transitions.

After analysis of the first calculations, the ester molecules were divided into three fragments (I, II, III) for the determination of ICT values as indicated in Fig. 1.

The change in net π-electronic transition was calculated according to

$$\mathrm{ICT} = (Q_e^{\mathrm{II}} - Q_g^{\mathrm{II}}) - [(Q_e^{\mathrm{I}} - Q_g^{\mathrm{I}}) + (Q_e^{\mathrm{III}} - Q_g^{\mathrm{III}})],$$

where Q^i is the sum of net π-electron charges of the fragment i (g = ground state, e = excited state). In Chart 2 the direction of transfer is represented by an arrow topped by its value.

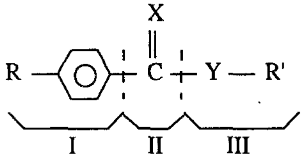


Fig. 1. Cutting up of the molecules Ia to VIb for the calculation of intramolecular charge transfer

The calculations for thio and dithioesters (molecules III to VI) revealed that the excitation produced a relatively important charge transfer between the left part of the molecule and the thiocarbonyl group for the first π → π* transition of compounds substituted with a donor group ($\mathrm{III_b}$, $\mathrm{IV_b}$, $\mathrm{V_b}$ and $\mathrm{VI_b}$). For the molecules without donating substituent the same transfer was clearly and normally less important (thioester IIIa) or appeared to occur between the right part of the molecule and the thiocarbonyl group (dithioesters IVa, Va and VIa). For the molecules containing $N(CH_3)_2$ substituent the rather high values of the calculated oscillator strength for the first π → π* band (in the range 0.63–0.85) confirmed the previous observation. For all the molecules the lowest-energy transition π → π* was mainly described by a one-electron excitation with weight of the predominant configuration in the range 86–96%.

The second π → π* transition was mainly characterized by an electronic transfer between the right moiety (OR′ or SR′ substituent) and the C=S group, except for the thioesters IIIa, IIIb and IVa. In the case of compounds IVb, Va, b and VIa, b the oxygen or sulfur atoms of OR′ and SR′ group act in competition with the dimethylamino group as a donor substituent.

This analysis was completed by a comparison between the $\overrightarrow{\Delta\mu}$ which were found to display relatively high values for compounds with donor substituent (IIIb, IVb, Vb and VIb) in the case of the first $^1(\pi\pi^*)$ excited state (5.42, 5.86, 6.04 and 4.65D, respectively), $\overrightarrow{\mu_g}$ and $\overrightarrow{\mu_e}$ being almost parallel (angles in the range 8–18°). This result was consistent with the charge transfer character of the corresponding transition. For R = H compounds the calculations gave lower $\Delta\mu$ values, in agreement with a more restricted charge transfer except for molecules IVa and VIa which were characterized by $\Delta\mu = 13.64D$ and $8.17D$, respectively but with $\left(\widehat{\overrightarrow{\mu_e}, \overrightarrow{\mu_g}}\right) = 71°$ and 78°, respectively, because of an ICT inside the thio and dithioester groups. The increase of ICT (between the left and the right parts of these molecules) and $\Delta\mu$ values when substituting H by the donor group $N(CH_3)_2$ is associated to an increase of the oscillator strength of this first transition. The results obtained for the second π → π* transition showed a strong decrease of the oscillator strength values, the lowering of which being due to the vanishing of π-electronic charge transfer between the donor and the acceptor group (C(S)OR′ or C(S)SR′) through the conjugated aromatic ring.

The previous analysis was applied to the case of the non-planar geometries (molecules III′ to VI′ – see Chart 3). The calculations evidenced firstly an expected increase of the first π → π* singlet–singlet transition energies with a concomitant decrease of oscillator strength values for all the molecules with the donor substituent,

Chart 2. Calculated transition energies, oscillator strengths, main configurations, $\Delta\mu$ and ICT values for the first $^1(\pi\pi^*)$ states of studied molecules (planar geometries)

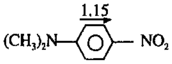
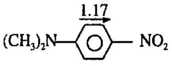
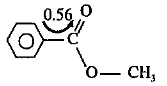
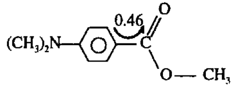
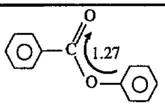
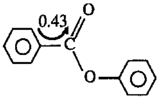
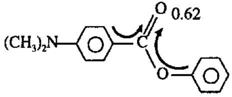
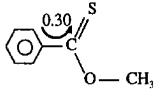
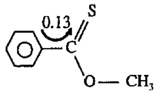
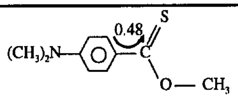
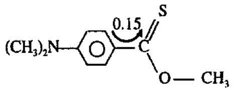
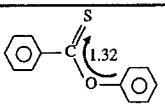
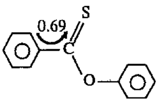
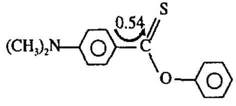
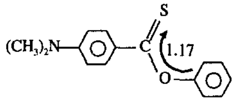
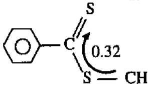
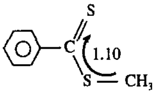
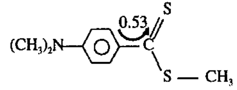
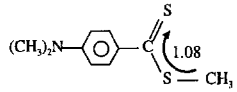
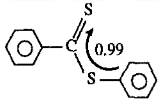
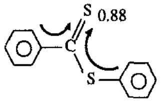
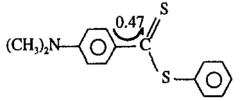
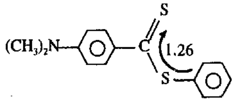
compounds	ΔE (eV)	oscillator strength	orbital configuration	weight (%)	$\Delta\mu$ (D)	ICT
DMNA	4.58	0.48	32 —> 33	94	10.77	
	5.66	0.13	31 —> 33 32 —> 34 31 —> 35	55 31 12	10.38	
Ia	5.51	0.43	25 —> 27 26 —> 27	72 18	4.07	
Ib	4.98	0.61	35 —> 36	94	6.04	
IIa	5.13	0.30	37 —> 38	83	14.99	
	5.56	0.31	34 —> 38	77	1.52	
IIb	4.92	0.75	46 —> 47 45 —> 47	55 36	3.45	
IIIa	4.43	0.63	25 —> 27	86	2.58	
	4.56	0.12	24 —> 27 25 —> 28 25 —> 27	45 32 10	1.40	
IIIb	4.04	0.85	34 —> 36	96	5.42	
	5.85	0.56	32 —> 36 34 —> 37 33 —> 36	61 12 11	3.49	
IVa	4.87	0.21	35 —> 38	86	13.64	
	5.82	0.20	33 —> 38 36 —> 39 33 —> 42	45 31 11	5.86	

Chart 2. (Continued)

IVb	4.05	0.79	45 —> 47	96	5.86	
	4.87	0.15	44 —> 47	88	13.12	
Va	4.27	0.41	25 —> 27	86	1.38	
	4.77	0.33	24 —> 27 23 —> 27	72 16	5.75	
Vb	3.99	0.75	34 —> 36	96	6.04	
	4.63	0.14	33 —> 36	81	5.83	
VIa	4.09	0.19	36 —> 38	90	8.17	
	4.51	0.55	35 —> 38	83	3.53	
VIb	3.99	0.63	45 —> 47	96	4.65	
	4.22	0.38	44 —> 47	88	8.80	

this lowering being due to the torsion angles between the phenyl ring and the acceptor group (in the range 34–43°). However, the charge transfer calculated with the ($\sigma + \pi$) electron charges (because of the difficulty in determining the purely π-electronic charge distribution for these twisted molecules[1]), along with $\Delta\mu$ and f values derived from CNDO/S-CI results lead to similar conclusions as for planar molecules.

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[1] In order to verify the consistency of these results with respect to the previous analysis, we have calculated the charge transfer for planar molecules with π and ($\sigma + \pi$) electron charges. The results were quite identical.

This set of results confirms the dominant role of the first excited state $^1(\pi\pi^*)$ properties in these molecules and emphasizes the potential interest of the thio and dithioester groups as acceptors in the design of molecules for second harmonic generation.

Chart 3. Calculated transition energies, oscillator strengths, main configurations, $\Delta\mu$ and ICT values for the first singlet excited states with a predominant $\pi \rightarrow \pi^*$ character of studied molecules (non-planar geometries)

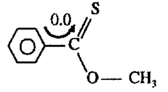
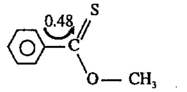
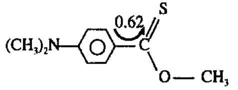
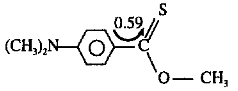
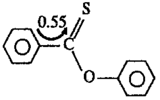
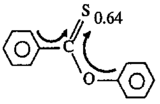
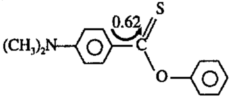
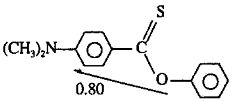
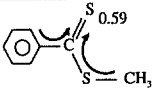
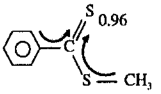
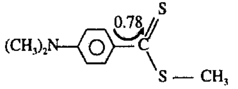
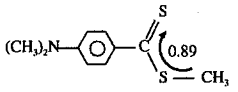
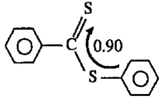
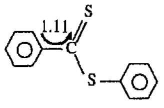
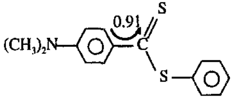
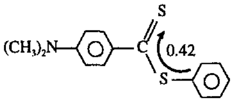
compounds	ΔE (eV)	oscillator strength	orbital configuration	weight (%)	Δμ (D)	ICT
III'a	4.62	0.02	24 —> 27 25 —> 28 26 —> 28 24 —> 29	31 22 16 12	0.34	
	4.73	0.57	25 —> 27 26 —> 31	67 12	3.67	
III'b	4.35	0.73	34 —> 36 35 —> 36	66 29	6.03	
	5.88	0.44	33 —> 36 34 —> 37	50 31	5.64	
IV'a	4.94	0.52	36 —> 38	72	4.66	
	5.77	0.15	32 —> 38 34 —> 38	50 18	2.71	
IV'b	4.37	0.71	45 —> 47 46 —> 47	81 13	6.05	
	5.28	0.11	44 —> 47 46 —> 51 46 —> 47	40 18 13	12.19	
V'a	4.46	0.34	25 —> 27	83	2.92	
	4.81	0.17	24 —> 27 23 —> 27	67 09	4.95	
V'b	4.19	0.54	34 —> 36	90	7.11	
	4.70	0.17	33 —> 36	77	5.04	

Chart 3. (Continued)

VI'a	4.33	0.23	36 —> 38	85	6.68	
	4.75	0.27	35 —> 38	81	8.35	
VI'b	4.30	0.45	45 —> 47	88	7.88	
	4.72	0.13	44 —> 47	53	2.25	

The electronic properties of thio and dithioester groups were also compared with those of ester and nitro groups. The geometries of DMNA and methyl- and phenyl-benzenecarboxylate molecules were optimized with PM3 method and found to be planar.

Firstly, we notice that a direct comparison between molecule IIb and related sulfur-containing compounds is not possible because of the two-dimensional character of the charge transfer associated to this ester. Secondly, the calculation of ground- and excited-state properties of molecule Ib showed a clear decrease of f values and a more slight decrease of ITC values (0.61 and 0.46, respectively) with respect to the similar thio and dithioesters. These results confirm the higher electron-withdrawing character of thio substituents compared to carbonyl group.

On the other hand, most of the materials investigated so far for their NLO properties contain nitro substituent as acceptor moiety. Our CNDO/S-CI calculations for the first $\pi \rightarrow \pi^*$ transition of *N*,*N*-dimethyl-*p*-nitroaniline gave higher values of charge transfer and dipole moment differences but a clearly lower oscillator strength (1.15, 10.8, 0.48, respectively – see Chart 2) and a calculated (PM3) ground-state dipole moment ($\sim 7D$) higher than the corresponding ester values (3.1–5.2D for the planar molecules). This enhancement of $\| \vec{\mu}_g \|$ may cause the antiparallel arrangement of the dipoles when the molecule crystallizes, resulting in a zero value for the first-order hyperpolarizability $\chi^{(2)}$ when measured in the solid state.

In order to complete this theoretical study of the relative ability of nitro, ester, thioester and dithioester acceptor groups to promote charge transfer transition and to classify the potential interest of the corresponding compounds for nonlinear optics, we calculated the hyperpolarizability β values with a finite-field method [11] based on both energy and dipole moment expansions. The results obtained with the use of the PM3 Hamiltonian (in the MOPAC 6.0 package) and an electric field gradient of 0.001 a.u. [24] are gathered in Table 2.

Firstly, we noticed the strong increase of hyperpolarizability β values for $N(CH_3)_2$ group-containing compounds as compared to molecules without donor substituent: for instance, in the case of planar $R' = CH_3$ derivatives, $\beta = 7$ (Ib), 25 (IIIb), 36 (Vb) and $\beta = 1$ (Ia), 2 (IIIa), 5 (Va) ($\times 10^{-30}$ esu), respectively.

Table 2. Calculated (PM3 method) first-order hyperpolarizabilities ($\times 10^{-30}$ esu)

Compounds	Planar molecules	Non-planar molecules
DMNA	8	-
Ia	1	-
IIa	2	-
IIIa	2	1
IVa	4	1
Va	5	3
VIa	7	7
Ib	7	-
IIb	11	-
IIIb	25	14
IVb	32	14
Vb	36	21
VIb	47	13

Secondly, the calculations also revealed that the thio and dithioester groups with $N(CH_3)_2$ substituent were more efficient than the ester and nitro groups in terms of β enhancement in these compounds (β calculated values for the first ones were 3 to 6 times larger than β values for the second ones):

$$C(O)OCH_3 < NO_2 \ll C(S)OCH_3 < C(S)SCH_3.$$

This classification was in agreement, on the one hand with the expected order for the moieties NO_2 and $C(O)OCH_3$ (although the β_{PM3} values are closely related in the case of DMNA and Ib), and on the other hand, with the previous characteristics of the first $\pi \rightarrow \pi^*$ transition determined for all these molecules ($\Delta\mu$, ICT, f), the lower oscillator strength calculated for the dithioester molecule being compensated by higher $\Delta\mu$ and ICT values.

In order to verify these previous theoretical results and to confirm that some of these organic molecules may display nonlinear responses which make them attractive for applications in NLO, we synthesized six $R' = CH_3$ and $R = H$ or $R = N(CH_3)_2$ related compounds. We have not taken phenylbenzoate molecules into account because of the difficulty in synthesizing and in substituting these compounds with noncentrosymmetric groups.

3 Experimental

3.1 Syntheses

NMR spectra were obtained on a JEOL FX 90 Q instrument at 89.55 MHz for proton spectra in $CDCl_3$ solutions, and shifts are referenced to TMS internal standard. All the chemical shifts (δ) are in parts per million (ppm) and coupling constants are in Hertz (Hz) units. Melting points are not corrected.

Methylbenzenecarboxylate (*Ia*)

A mixture of 8.6 ml (74 mmol) of benzoyl chloride, 50 ml of anhydrous methanol and 0.9 g (7.3 mmol) of *p*-*N*,*N*-dimethylaminopyridine was stirred at 25°C for 1 h. Then the methanol was evaporated under reduced pressure. After addition of water, the solution was extracted with ethyl ether. The combined extracts were washed with water until neutral pH and dried ($MgSO_4$). The solvent was removed at reduced pressure to yield 8.26 g (82%) of a colorless liquid: ^1H RMN 3.91 (s, 3H), 7.49 (m, 3H), 8.03 (d, 2H).

Methyl(p-N,N-dimethylamino)benzenecarboxylate (Ib)

In a flask equipped with a magnetic stirrer and a reflux condenser, 10 g (59.3 mmol) of *p-N,N*-dimethylaminobenzenecarboxylic acid was placed. 40 ml of thionyl chloride was added dropwise with stirring. When the addition was completed, the mixture was still stirred for 1 h. It was cooled at room temperature, then the excess thionyl chloride was evaporated under reduced pressure [25]. To the residue were added 40 ml of anhydrous methanol and 0.6 g (4.9 mmol) of *p-N,N*-dimethylaminopyridine [26]. The solution was stirred at 25°C for 1 h, then poured onto 100 ml of ice-cold NaOH ($\sim 1\,M$). The solid was collected by filtration, washed with cold water and dried. Recrystallization from ether petroleum gave 5.2 g (49%) of a white solid: m.p. = 104°C; ^{1}H RMN 3.01 (s, 6H), 3.84 (s, 3H), 6.62 (d, $J = 8.8$, 2H).

O-methylbenzenecarbothioate (IIIa)

In a flask equipped with a magnetic stirrer and a reflux condenser, 1 g (7.3 mmol) of methylbenzenecarboxylate Ia, and 1 equivalent of Lawesson's reagent [27] in 20 ml of anhydrous toluene were placed. The solution mixture was heated at reflux until no more ester could be detected (TLC), then was filtered. The filtrate was cooled at room temperature. The toluene was evaporated under reduced pressure. The residue was placed on a silica gel column chromatography. After elution with petroleum ether and then with ether/petroleum ether (10/90), the first colored fraction was collected. The solvent was removed to yield 0.6 g (54%) of a yellow liquid: ^{1}H RMN 4.29 (s, 3H), 7.46 (m, 3H), 8.20 (d, $J = 9.9$, 2H).

O-methyl(p-N,N-dimethylamino)benzenecarbothioate (IIIb)

The above procedure was repeated by using 1 g (5.6 mmol) of methyl(*p-N,N*-dimethylamino)benzenecarboxylate Ib. Yellow crystals were obtained and recrystallized from petroleum ether to yield 0.7 g (67%) of a yellow solid: m.p. = 134°C; ^{1}H RMN 3.03 (s, 6H), 4.23 (s, 3H), 6.56 (d, $J = 9.2$, 2 H), 8.13 (d, $J = 9.2$, 2H).

Methylbenzenecarbodithioate (Va) [28]

In a two-necked flask equipped with a magnetic stirrer and a reflux condenser and under dry nitrogen, 10 g (64 mmol) of phenyl bromide and 1.3 equivalent of magnesium turning in 35 ml of anhydrous THF were placed. The reaction mixture was stirred for 3 h at room temperature. After decantion from the remaining magnesium, 1 equivalent of pure CS_2 was added dropwise while maintaining the initial temperature, and the mixture was stirred for 1 h. 1.2 equivalent of methyl iodide was added and the solution was stirred for 1 h at room temperature. Ice water was then added and the organic products were extracted with ether. The combined extracts were washed with water until neutral pH and dried ($MgSO_4$). The solvent was distilled, the residue was subjected to a silica gel column chromatography and eluted with petroleum ether. The red colored fractions were collected, the solvent was removed to yield 7.9 g (73%) of a red liquid: ^{1}H RMN 2.76 (s, 3H), 7.43 (m, 3H), 7.99 (m, 2H).

Methyl(p-N,N-dimethylamino)benzenecarbodithioate (Vb)

The above procedure was repeated by using 10 g (50 mmol) of *N,N*-dimethyl-4-bromoaniline. Solvent evaporation yields 6.87 g (65%) of a red solid after recrystallization from petroleum ether: m.p. = 133°C; ^{1}H RMN 2.75 (s, 3H), 3.04 (s, 6H), 6.58 (d, $J = 9.2$, 2H), 8.14 (d, $J = 9.2$, 2H).

3.2 Experimental methods

The ground-state dipole moments were measured by a classical method based on the Guggenheim law [29]. The values were determined in chloroform and tetrachloromethane solutions. The latter ones, being measured in a nonpolar solvent, are more realistic. They are given in Table 3. The former ones were used for β determinations. First hyperpolarizabilities β were obtained from EFISHG measurements [30] which were performed on a Q-switched Nd/YAG laser emitting at 1.06 μm with measurements made in chloroform.

4 Results and discussion

Table 3 shows experimental and PM3 calculated (for planar and non-planar geometries) values of ground state dipole moment μ_g and first hyperpolarizability β.

Firstly, we can notice that the μ_g values deduced from calculations of planar molecules are in good agreement with experimental values except for compound IIIb. In all the cases the planar and nonplanar geometries are very close in energy ($\Delta H_f < 5\,\mathrm{kcal\,mol^{-1}}$) and, for the discussion, we will consider these two conformations.

Secondly, results obtained on β show a close agreement between the relative magnitudes of calculated and experimental values for ester molecules. In particular, Table 3 clearly shows a strong enhancement of experimental β values upon substitution by the dimethylamino donor group. On the other hand, EFISH measurements again evidence that the thio and dithioester groups are better electron acceptors than the ester group: $\beta^{\mathrm{EFISH}} = 20, 41, 5\,(\times 10^{-30}$ esu), respectively, for molecules with $R = N(CH_3)_2$. The direct comparison between experimental values of compounds Ib, IIIb, Vb and *N,N*-dimethyl-*p*-nitroaniline molecule is difficult because of the different experimental conditions used for EFISH measurements. For example, β EFISH measurements performed for DMNA in acetone solution give 12×10^{-30} esu at 1.9 μm (laser fundamental wavelength) [31] and 26×10^{-30} esu at 1.06 μm [32]. In the first case, the thio and dithioester groups can be considered as more efficient than the nitro group at enhancing β. But in the last one, only the dithioester group gives better β values. When we consider the calculated PM3 values, the dithio and thioester molecules with $R = N(CH_3)_2$ are seen to be better than the nitro group for β enhancement of these benzene derivatives.

Table 3. Experimental and calculated (PM3) ground state dipole moments and first-order hyperpolarizabilities

Compounds	μ_g exp (D)	μ_g calcd (D)		$\beta_\mu^{\mathrm{EFISH}}$ ($\times 10^{-30}$ esu)	β_μ calcd ($\times 10^{-30}$ esu)		$\beta(0)$ ($\times 10^{-30}$ esu)	
		Planar	*Non-planar*		*Planar*	*Non-planar*	*Planar*	*Non-planar*
DMNA	6.4 [a]	7.01	-	See text	8	-	12 [b]	-
Ia	1.9	1.99	-	1	1	-	-	-
IIIa	2.9	3.04	2.93	2	2	1	-	-
Va	2.4	1.97	1.93	~0	5	3	-	-
Ib	3.2	3.14	-	5	7	-	4	-
IIIb	3.8	5.26	3.59	20	25	14	12	13
Vb	4.9	4.44	2.62	41	36	21	25	26

[a] Experimental data taken from ref. 31

[b] Experimental data taken from ref. 33

Here, we used a finite-field method to calculate values for the hyperpolarizabilities at zero frequency. In a relevant comparison between these calculated values with those obtained from measurements, the experimental values must be extrapolated to zero frequency. The corresponding $\beta(0)$ values were deduced from EFISH $\beta(2\omega)$ values using the quantum two-level model based equation [10]

$$\beta(0) = \beta(2\omega)/F(\lambda_{\mathrm{max}}, \lambda) = \beta(2\omega)\left[1 - \left(\frac{2\lambda_{\mathrm{max}}}{\lambda}\right)^2\right]\left[1 - \left(\frac{\lambda_{\mathrm{max}}}{\lambda}\right)^2\right],$$

where λ is the laser fundamental wavelength (here 1.06-μm), and λ_{max}. the wavelength of the charge transfer band. The validity of this model is restricted to systems in which a $\pi \rightarrow \pi^*$ band with a large one-dimensional transfer character is predominant, leading to large $\Delta\mu$ values. This requirement seems satisfactorily fulfilled in the case of molecules Ib, IIIb and Vb. The dispersion functions $F(\lambda_{\mathrm{max}}, \lambda)$ were determined using the CNDO/S-CI results obtained for the energies of the first singlet–singlet electronic transition for planar and nonplanar geometries when it is necessary. The $\beta(0)$ values for Ib, IIIb, Vb and DMNA molecules are given in Table 3.

The zero-frequency β values partially confirm the previous analysis: as expected, the magnitude of the first-order hyperpolarizability increases upon changing from $C(O)OCH_3$ to $C(S)SCH_3$ group (Ib < IIIb < Vb) but according to these results the NO_2 group is practically equivalent to the thioester. On the other hand, β_{PM3} and $\beta(0)$ (corrected for dispersion enhancement) values obtained for all the compounds show a relatively good agreement if we consider the geometry giving the better agreement between experimental and calculated values of the ground-state dipole moment (Ib: 7 and 4, IIIb: 14 and 13, Vb: 36 and 25 in 10^{-30} esu).

In the two-level model, the component of β tensor along $\vec{\mu}_g$ in a static field can be expressed as [34]:

$$\beta^0_{\mu\mu\mu} = (6\pi^2 \Delta\mu\mu^2_{\mathrm{eg}})/(h^2\omega^2_{\mathrm{eg}}),$$

where $\Delta\mu$ is the modulus of the dipole moment difference between the two levels, μ_{eg} the modulus of the transition dipole moment and ω_{eg} the transition frequency. The validity of this equation is restricted to systems in which $\vec{\mu}$, $\overrightarrow{\Delta\mu}$ and $\vec{\mu}_{\mathrm{eg}}$ are parallel. In the case of molecules Ib, IIIb and Vb the CNDO/S-CI calculations reveal that the directions of $\vec{\mu}_g$ and $\vec{\mu}_e$ are in the range 9–23° and the directions of $\overrightarrow{\Delta\mu}$ and $\vec{\mu}_{\mathrm{eg}}$ in the range 3–15°. Therefore, the previous condition is not completely fulfilled but the deviations being not important we can try to correlate $\Delta\mu$, the oscillator strength f – defined as $(4\pi m\omega\mu^2_{\mathrm{eg}})/(e^2 h)$ – the excitation energy ΔE of the first $\pi \rightarrow \pi^*$ transition and $\beta(0)$ values (see Charts 2 and 3 and Table 3). In our calculations performed on Ib, IIIb (nonplanar) and Vb molecules, $\Delta\mu$ was found to remain almost constant (near 6*D*), a behavior being consistent with the corresponding intramolecular charge transfer observed. By contrast, the oscillator strength f increases and the excitation energy decreases when the ester group is replaced by a thioester group or a dithioester group (0.61, 0.73 and 0.75 for f; 4.98, 4.35 and 3.99 eV for ΔE, respectively). Thus, the reason why β increases with the substitution $C(O)OR \rightarrow C(S)OR \rightarrow C(S)SR$ in these molecules seems to originate primarily from the increase of oscillator strength and from the red shift of the first $\pi \rightarrow \pi^*$ electronic transition.

It is interesting to compare these characteristics with those of DMNA molecule. The data assembled in Chart 2 indicate that the large $\Delta\mu$ value of DMNA compound is widely balanced by the lower oscillator strength (0.48) and by the appreciable blue shift, especially with regard to the Vb molecule (4.58 and 3.99 eV, respectively). Thus, the nitro group can be considered to be equivalent to the thioester group and not so efficient as the dithioester group in its ability to enhance the hyperpolarizability of donor–acceptor para-substituted benzenes. On the other hand, the higher value of ground-state dipole moment of DMNA (6.4*D* exp., 7.01*D* calcd) also reduces the interest of the nitro group at the acceptor site in terms of acentric crystallization. Lastly, an additional advantage of the dithioester group lies in the ability to substitute optically active groups on the carbon atom of the S–CH_3 group, contrary to the more classical group such as nitro one, in order to obtain a single crystal without a center of inversion or to bring in additional synthetic flexibility for building "multifunctional" molecules or polymers.

Finally, thioesters present an attractive ability to be attached on a polymerizable or cross-linkable moiety, thereby opening the way to more transparent and more stable-oriented polymers for nonlinear related applications.

5 Conclusion

We have investigated the electron-withdrawing effect of the ester, thioester and dithioester groups and the NLO properties of related para-substituted benzenes.

Firstly, we have studied with theoretical methods the electronic characteristics of the ground and the first excited states of these molecules and we have predicted and analyzed, with respect to these results, the first-order hyperpolarizability β of these types of compounds.

The dithioester group was found to be a better electron acceptor than the two other ester substitutents and the nitro group.

Some of these compounds were synthesized and ground-state dipole moments and hyperpolarizabilities β were measured. Experimental results confirm the previous analysis and allow to discuss the use of two-level approximation for the extrapolation of EFISH measurements to zero-frequency $\beta(0)$ values in order to compare with the β values calculated by using a theoretical finite-field method.

Finally, both experimental and theoretical studies evidence the better efficiency of dithioester group at enhancing β in these para-substituted benzenes, the methyl benzenecarbodithioate molecule exhibiting, in particular, higher β values than *N*,*N*-dimethyl-*p*-nitroaniline molecule. Therefore, the dithioester group can be used instead of the nitro group with the additional advantages of a better transparency and its ability to be substituted on the R′ carbon atom by an optically active group or a polymerizable unit contrary to the nitro one.

This work also shows that theoretical calculations can provide reliable informations on the electronic properties of ground and excited states of molecules and can help the design of new molecular materials for which NLO efficiency is required.

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