

The first 1,3-dithiol-2-ylidene donor– π –acceptor chromophores containing an azine spacer: synthesis, electrochemical and nonlinear optical properties

Marcial Moreno-Mañas,*^a Roser Pleixats,^a Raquel Andreu,^{a,b} Javier Garín,*^b Jesús Orduna,^b Belén Villacampa,^c Eric Levillain^d and Marc Sallé^d

^aDepartament de Química, Universitat Autònoma de Barcelona, E-08193 Cerdanyola, Spain

^bDepartamento de Química Orgánica-ICMA, Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain. E-mail: jgarin@posta.unizar.es

^cDepartamento de Física de Materia Condensada-ICMA, Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain

^dLaboratoire d'Ingénierie Moléculaire et Matériaux Organiques, UMR CNRS 6501, Université d'Angers, 2 Bd Lavoisier, F-49045 Angers, France

Received 20th September 2000, Accepted 19th October 2000

First published as an Advance Article on the web 30th November 2000

The first *push–pull* 1,3-dithiol-2-ylidene derivatives containing an azine spacer have been prepared in order to evaluate the effect of the azine bridge on the second-order NLO properties of these compounds, which show $\mu\beta(0)$ values lower than those of similar derivatives endowed with ethylenic spacers. The linear and nonlinear optical properties of these compounds have been studied both experimentally and theoretically by TD-DFT and *ab initio* CPHF calculations respectively. Moreover, the *E–Z* photoisomerization of one of these azines is reported.

Introduction

In the search for new nonlinear optical (NLO) chromophores, a great deal of effort has been devoted to the study of donor– π –acceptor compounds.¹ In order to optimise the NLO response of such molecules it is of crucial importance to know the effect of different donors, acceptors and conjugated spacers. The latter are usually polyenic chains, but a recent theoretical report claimed that asymmetrical azines (2,3-diazabutadiene derivatives) endowed with donor and acceptor aryl groups might be excellent candidates for second-order NLO materials.² To the best of our knowledge, there is only one report in the literature on second harmonic generation of an azine derivative (without experimental details),³ although the potential second-order optical nonlinearities of this kind of compound have been referred to by some authors⁴ and the third-order optical nonlinearities of azines and polyazines have been reported both experimentally and theoretically.⁵

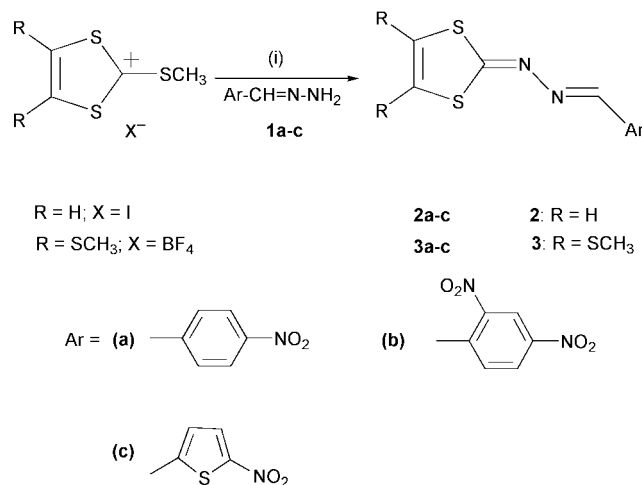
Thus, we reasoned that it would be interesting to study the second-order nonlinear optical responses of *push–pull* asymmetrical azines in order to ascertain the effect of the azine spacer. To that end, we have chosen the 1,3-dithiole moiety as the electron donor group, since it has been shown to act as an efficient donor group in *push–pull* polyenic chromophores giving rise to high first molecular hyperpolarizability (β) values.⁶ This can be ascribed to the fact that the donor moiety can gain aromaticity upon charge separation, due to the contribution of aromatic 1,3-dithiolium canonical forms. A literature search revealed that asymmetrical azine-containing 1,3-dithiole derivatives have not been hitherto described, although one symmetrical derivative⁷ and a few 2-hydrazone-1,3-dithioles are known.^{7,8} We report here on the synthesis and characterisation of compounds **2a–c** and **3a–b** (Scheme 1), and their electrochemical and second-order nonlinear optical properties (EFISH measurements). An analysis of the isomerisation of compound **2c** is also presented. *Ab initio* calculations have been carried out in order to make a structural

assignment of both isomers of **2c** and to study the linear and nonlinear optical properties of the newly prepared derivatives and the effect of the azine spacer when compared to an olefinic spacer.

Results and discussion

Synthesis and characterisation

The targeted asymmetrical azines **2a–c** and **3a–b** were prepared by reaction of 2-methylthio-1,3-dithiolium iodide⁹ or 2,4,5-tris(methylthio)-1,3-dithiolium tetrafluoroborate¹⁰ with hydrazones **1a–c** in the presence of pyridine (see Scheme 1). 2,4-Dinitrobenzaldehyde hydrazone (**1b**) and 5-nitrothiophene-2-carbaldehyde hydrazone (**1c**)¹¹ were prepared from the



Scheme 1 Synthesis of compounds **2a–c** and **3a–b**. Reagents and conditions: (i) pyridine, CH₃OH, 0 °C to rt.

corresponding commercially available aldehydes, by reaction¹² with hydrazine hydrate (two equivalents) in absolute ethanol.

Compound **3c** could not be isolated as a pure product, but as a mixture with 5-nitrothiophene-2-carbaldehyde azine, and all attempts to purify it (recrystallisation and chromatography) failed.

A search of the Cambridge Structural Database System¹³ revealed that all benzaldehyde¹⁴ and substituted benzaldehyde azines^{4b,15} show an (*E,E*) configuration (for NMR-based evidence, see reference 16). Consequently we can expect that derivatives **2a–b** and **3a–b** will also present the (*E*) configuration. This possibility was confirmed by an X-ray diffraction study of single crystals of **2a** which were grown by slow evaporation of its CDCl₃ solution. The poor quality of crystals obtained did not allow an accurate structural determination. Nevertheless, the (*E*) configuration of **2a** was unambiguously established.

On the other hand, structural determination of compound **2c** turned out to be less straightforward, since no single crystals could be obtained and conformational and configurational aspects had to be taken into account. The conformation around the NCH–CS bond was ascertained by ¹H-NMR experiments, through the observation of a positive NOE (9%) on H-3 of the thiophene moiety upon irradiation of the imine-type proton. Thus, **2c** is in the *S,N-cis* conformation, in agreement with the fact that most azomethines derived from five-membered heterocyclic aldehydes retain the *X,N-cis* conformation¹⁷ like the corresponding aldehydes.¹⁸

Unexpectedly, during the purification and characterisation of **2c** we observed by TLC and ¹H-NMR the appearance of a second product when a solution of **2c** in any solvent was exposed to daylight; on the other hand, solutions of **2c** did not evolve when kept in the dark. The signals of the newly formed compound in the ¹H-NMR spectra of the mixtures were the same as those of the original one but shifted and, again, a positive NOE (9%) was observed by irradiating on the shifted signal corresponding to the methyldene proton. Moreover, the infrared and mass spectra of the mixtures were indistinguishable from those of pristine **2c**. These observations along with the previously reported photoisomerization of 2-nitroacetophenone azine¹⁹ led us to think that an *E–Z* isomerization and not a decomposition of the product had taken place. Eventually, both isomers were identified (see below) and it turned out that the synthesised compound was the (*E*)-isomer, which partially isomerizes in solution to the (*Z*)-isomer. We have not been able to isolate the latter from the mixture of both isomers.

The structural assignment of each isomer was possible thanks to theoretical calculations. The relative stabilities of the two species were studied by means of molecular orbital calculations within the Density Functional Theory (DFT). The most commonly used B3LYP²⁰ functional is not adequate for the calculations of optimized geometries of compounds having second-row elements due to the overestimation of bond distances,²¹ and hence we have used the hybrid B3P86 functional²² and the Pople polarized, valence double split, 6-31G* basis set²³ which has proved to be a reliable model chemistry for the study of 1,3-dithiole^{6g} and tetrathiafulvalene (TTF)²⁴ systems.

Geometry optimization of the (*Z*)-isomer revealed the presence of a 1,5-interaction between the thiophene sulfur atom and one of the azine nitrogens (Fig. 1) giving rise to an optimized S–N distance of 2.757 Å, which is substantially less than the sum of van der Waals radii (3.35 Å) and indicative of a weak interaction²⁵ with a covalency ratio $\chi = 0.373$. This result parallels the S–N attractive interaction found in the crystal of a 1,3-dithiole-derived cyanoimine which presents a S–N contact of 2.719 Å (2.722 Å calculated at the B3P86/6-31G* level^{6g}) and reproduces qualitatively the 2.815 Å S–N distance found in the only published X-ray structure of a thiophenecarbaldehyde

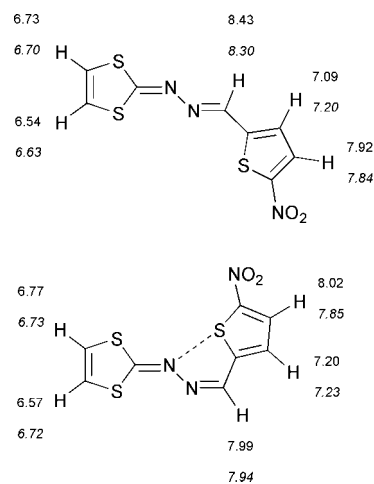


Fig. 1 Proton chemical shifts of the (*E*) and (*Z*) isomers of **2c**: calculated by the GIAO method at the B3P86/6-311+G(2d,p)//B3P86/6-31G* level (plain text) and experimental in CDCl₃ (italics).

azine,²⁶ which adopts a (*Z*) configuration but is reported to be readily and completely converted to the (*E*) form on photolysis. The opposite charges of +0.43 on the sulfur atom and –0.31 on the nitrogen atom involved in the intramolecular contact of **2c** are responsible for this electrostatic interaction that renders the (*Z*)-isomer 0.06 kcal mol^{–1} more stable than the (*E*)-isomer, contrary to compounds **2a–b** and **3a–b**. Nevertheless, this difference in energy is negligible and no conclusion can be drawn about which is the isomer initially formed.

In order to identify these compounds, we considered that the most important experimental differences were found in the ¹H-NMR spectra and hence we took advantage of the ability of *ab initio* methods to predict the different NMR spectra of (*E*) and (*Z*) isomers.²⁷ A recent comparison of the methods used in the calculation of proton chemical shifts²⁸ concluded that DFT methods which include electron correlation are usually superior to HF ones, the best results being obtained using hybrid HF-DFT functionals, and the Gauge-Independent Atomic Orbitals (GIAO)²⁹ method, which is less sensitive to the basis set size than other methods of calculation. Keeping this in mind, we calculated the isotropic shielding values using the GIAO method, the B3P86 functional and the 6-311+G(2d,p) basis set³⁰ using the B3P86/6-31G* geometries. The chemical shifts relative to tetramethylsilane (TMS) were obtained by subtraction of the calculated values from the absolute shielding of TMS calculated using the same model chemistry (31.7376 ppm).

The results of these calculations are shown in Fig. 1. It can be seen that there is an excellent agreement between the calculated values and the experimental data obtained in CDCl₃ with a maximum absolute deviation of 0.17 ppm and a root mean square error of only 0.10 ppm. The proton directly linked to the azine group with a chemical shift of 8.30 ppm (calculated 8.43 ppm) in the (*E*)-isomer and 7.94 ppm (calculated 7.99 ppm) in the (*Z*)-isomer allows the unambiguous characterisation of the product initially formed as the (*E*)-compound which photoisomerizes partially to the (*Z*)-isomer on standing in solution. Solutions of **2c**, either in CHCl₃ or in DMSO, after being kept for one month in daylight, gave *ca.* 1:1 mixtures of the (*E*)- and (*Z*)-isomers.

Electrochemistry

The electrochemical properties of compounds **2a–c** and **3a–b** are summarized in Table 1. Reduction of nitro compounds is facilitated by electron-withdrawing substituents and retarded by electron-donating groups. As a consequence of these two effects, polynitro compounds are reduced in stepwise fashion.³¹ Consequently, the mononitro compounds **2a**, **2c** and **3a** exhibit

Table 1 Oxidation and reduction potentials for compounds **2a–c** and **3a–b**^a

Compound	$E_{\text{red}2}^0/\text{V}$	$E_{\text{red}1}^0/\text{V}$	$E_{\text{ox}1}^0/\text{V}$	$E_{\text{ox}2}^0/\text{V}$
2a	—	-0.88	1.38 ^b	—
2b	-1.06	-0.65	1.46 ^b	—
2c	—	-0.69	1.36 ^b	—
3a	—	-0.87	1.13	1.52
3b	-1.03	-0.63	1.16	1.55

^a $c = 1$ mM; potentials vs. Ag/AgCl in acetonitrile; $n\text{Bu}_4\text{NPF}_6$ (0.2 M); scan rate 0.1 V s^{-1} ; redox potentials were estimated by deconvolution (CONDECON[®]). ^b E_{pa} (irreversible wave).

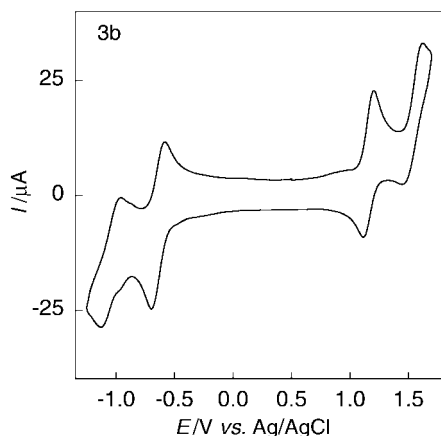
a reversible one-electron process at -0.88 , -0.69 and -0.87 V respectively. Noticeably the thiophene moiety facilitates the reduction of **2c** compared to **2a** and **3a**. Dinitro compounds **2b** and **3b** display two distinct reversible one-electron waves due to the stepwise reduction of the two nitro groups. In acetonitrile with traces of water, an additional irreversible reduction step, due to protons³¹ is observed in the range -1.2 V to -1.5 V.

In the positive direction, voltammograms of compounds **2a**, **2b** and **2c** display one irreversible oxidation wave. This oxidation can be assigned to the dithiafulvene-like group.³² Surprisingly, it is noteworthy that voltammograms of compounds **3a** and **3b** (Fig. 2) exhibit two reversible one-electron redox systems ($E_{\text{ox}2}^0 - E_{\text{ox}1}^0$ close to 0.4). Compared to compounds **2a** and **2b**, we can conclude that the stability of the radical cations **3a**⁺ and **3b**⁺ is due to the presence of the two methylthio (MeS) groups. Although this electrochemical behaviour is unexpected, dithiafulvenes showing one reversible one-electron oxidation waves have already been reported.^{6g}

It is worthy of note that substituents on the dithiole ring have a negligible effect on the reduction potentials ($E_{\text{red}1}^0$) which remain nearly unaltered on passing from compounds **2a** and **b** to **3a** and **b** while the introduction of an additional nitro group causes only a moderate increase in $E_{\text{ox}1}^0$ when comparing **2a** to **2b** and **3a** to **3b**. In other words, the studied compounds behave as isolated dithiole and nitroaryl systems and this fact accounts for the poor conjugation along the azine bridge as demonstrated by theoretical calculations (see below).

Nonlinear optical properties and UV–VIS absorption spectra

The second-order nonlinear optical properties of compounds **2a–c**, **3a** and **3b** were measured in CH_2Cl_2 as solvent using the electric field-induced second harmonic generation (EFISH) technique at 1907 nm. The estimated errors in $\mu\beta$ values are $\pm 10\%$ with the only exception of compound **2a** ($\pm 30\%$) due to both its low solubility and low NLO response. The zero-frequency $\mu\beta$ values were calculated from a two-level dispersion model and are shown in Table 2. These values reveal that

**Fig. 2** Cyclic voltammogram of **3b** (acetonitrile, 10 V s^{-1} , vs. Ag/AgCl).

introduction of methylthio groups (derivatives **3a** and **3b**) results in higher $\mu\beta$ values, in agreement with previous reports concerning the beneficial effect of introducing additional sulfur atoms at the periphery of the dithiole ring.^{6d,6f} As expected,³³ replacement of the benzene ring in **2a** by a thiophene ring (**2c**) also leads to an increase in the molecular hyperpolarizability, since thiophene is less aromatic than benzene³⁴ and, consequently, the formation of quinoidal structures is not as energetically demanding in the former. Nevertheless, this effect is not as large as that caused by introduction of an additional nitro group in the benzene ring. This is noteworthy, since the larger $\mu\beta$ values of compounds **2b** and **3b**, compared to those of **2a** and **3a** respectively, are in contrast to the situation found in a series of dinitrostilbenes, which displayed reduced $\mu\beta$ values when compared with their mononitro analogues.³⁵

The electronic absorption spectra of compounds **2** and **3** show a visible wavelength band (Table 2) which may be assigned to an intramolecular charge-transfer (CT) transition from the donor 1,3-dithiole moiety to the acceptor group, similar to those observed in other similar single-component donor– π –acceptor systems.^{6g} The CT character of this band is supported by its moderate solvatochromism and by theoretical calculations (see below). The introduction of MeS groups^{6d,6f} results in a bathochromic shift of this band, which is consistent with the lower oxidation potentials of compounds **3a–b** compared to **2a–b**. A bathochromic shift is also observed on introduction of additional NO_2 groups^{16c,35} and on replacement of the benzene by a thiophene ring, which suggests that the thiophene moiety provides a more effective conjugation path compared to benzene.

Theoretical calculations

Nonlinear optical properties. In an effort to rationalize the optical properties of these new systems, we have applied quantum chemical methods to their study. Calculations were initially performed using the semiempirical PM3 hamiltonian³⁶ since this method, which we have successfully applied to TTF derivatives,³⁷ usually provides accurate results at a low computational cost. Geometry optimizations on compounds **2a**, **2c** and **3a** afforded planar geometries in agreement with the published solid state structures of benzalazine¹⁴ and 4-substituted benzaldehyde azines.^{4b,15} A completely different result was obtained on compounds **2b** and **3b** possessing a 2-nitro substituent that forces the loss of the planarity giving rise to $\text{C}=\text{N}=\text{N}=\text{C}$ dihedrals of approximately 130° in sharp contrast to the experimental structure of 2-nitrobenzaldehyde azine³⁸ which retains a planar azine group and rotates the aryl groups in order to alleviate the steric tension. The $\mu\beta(0)$ values calculated using the Finite Field (FF) approach and the PM3 give a reasonable prediction of trends in NLO activity, but the absolute $\mu\beta(0)$ values, ranging from 133×10^{-48} esu for **2a** to 234×10^{-48} esu for **3b**, are largely overestimated. This can be related to the reported poor ability of PM3 to predict the NLO activity of molecules with hyperpolarizabilities below 40×10^{-30} esu.³⁹

Considering that Coupled Perturbed Hartree–Fock (CPHF) calculations have succeeded in predicting NLO activities of 1,3-dithiole derivatives for which PM3 failed even in the prediction of the geometry,^{6f} we have performed this type of calculation on compounds **2a–c** and **3a–b** using the HF/6-31G* model chemistry in both geometry optimizations and hyperpolarizability calculations. The optimized geometries of **2b** and **3b** were in this case different to those obtained from PM3 calculations (see Fig. 3). The 1,3-dithiole ring and the azine group are in the same plane while the aryl group is rotated *ca.* 23° out of this plane and the oxygen atoms in the *ortho* nitro group are rotated forming a dihedral angle of *ca.* 27° with the benzene ring. Contrary to PM3 calculations, these geometries

Table 2 Optical properties of compounds **2a–c** and **3a–b**

Compound	Experimental				Calculated		
	λ/nm^a	λ/nm^b	$\mu\beta/10^{-48}$ esu ^c	$\mu\beta(0)/10^{-48}$ esu ^d	μ/D^e	$\mu\beta(0)/10^{-48}$ esu ^e	λ/nm^f
2a	408	402	55	43	6.1	74	404
2b	445	430	165	127	7.3	93	446
2c	449	434	115	84	5.6	56	428
3a	420	408	100	77	5.8	74	399
3b	458	454	197	143	7.0	101	442

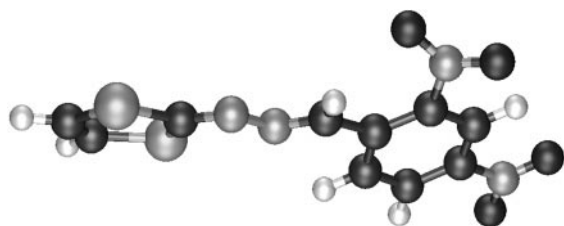
^aIn CH₂Cl₂. ^bIn cyclohexane. ^cMeasured in CH₂Cl₂ at $\lambda=1907$ nm. ^dCalculated using a two-level dispersion model. ^eCPHF/6-31G**/HF/6-31G*. ^fTD-B3LYP/6-31G**/HF/6-31G*.

parallel the X-ray structure of 2-nitrobenzaldehyde azine whose aryl groups form a dihedral angle of 34.2° with the azine plane, with the nitro groups rotated 21.1° with respect to the benzene ring.³⁸

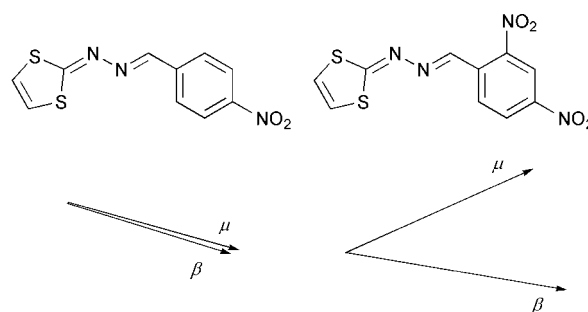
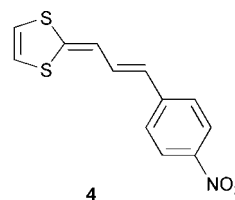
The $\mu\beta(0)$ values calculated by this method are included in Table 2. There is a reasonable agreement between the calculated and the experimental values although the former are underestimated, with the only exception of compound **2a**. However, it should be recalled that the experimental value obtained for this compound suffers from a large uncertainty (see above).

Concerning the effect caused by the introduction of a second nitro group, Marder and co-workers³⁵ observed a decrease in the measured $\mu\beta$ of dinitrostilbenes when compared to nitrostilbenes and concluded that while the total hyperpolarizability β_{tot} was enhanced by the introduction of a second nitro group, there was an important change in the orientation of the dipole moment and hence the projection of β on the dipole moment (β_{vec}) and the measured $\mu\beta$ were reduced. An analogous behaviour is observed for the studied compounds (see Fig. 4). The dipole moment and the total hyperpolarizability of compounds **2a** and **3a** have nearly the same orientation and consequently β_{vec} and β_{tot} have approximately the same value of ca. 12.0×10^{-30} esu (**2a**) and 12.9×10^{-30} esu (**3a**) while the second nitro group in **2b** and **3b** causes a reorientation of μ to form an angle of ca. 33.9° (**2b**) and 31.4° (**3b**) with β_{tot} . The calculated β_{tot} are 15.3×10^{-30} (**2b**) and 16.9×10^{-30} esu (**3b**) while β_{vec} are 12.7×10^{-30} and 14.4×10^{-30} esu respectively. In contrast to dinitrostilbenes the change in the orientation of the dipole moment on passing from compounds **2–3a** to **2–3b** is not large enough to cause a decrease in β_{vec} and this fact together with the increased dipole moment caused by the second nitro group accounts for enhanced $\mu\beta$ values.

Effect of the azine spacer. We have finally calculated the NLO activity of compound **4** (Fig. 5) in order to study the effect caused by the azine group compared to an ethylenic spacer analogue. The CPHF/6-31G* calculation on this compound predicted a $\mu\beta(0)$ value of 235×10^{-48} esu with a dipole moment of 7.4 D. The comparison of the calculations performed on compounds **2a** and **4** reveals that the azine group causes a small decrease in the dipole moment but a large reduction in the second order polarizability with respect to an ethylenic spacer, and therefore is contrary to the prediction of

**Fig. 3** Optimized geometry (HF/6-31G*) of compound **2b**.

unaltered hyperpolarizability made by Glaser and Chen.² Thus, while the reduction of the dipole moment is a desirable effect in the search for molecules giving rise to non centrosymmetrical crystals, in the case of the studied compounds, it is accompanied by a reduction of the hyperpolarizability. In the light of the above comparison, this fact must be due to the electronic structure of the azine bridge. Thus, the essentially planar geometry of azines **2** and **3** suggests conjugation throughout the π -system, and a significant contribution of dipolar charged forms, such as **2a'** (Fig. 6) would be expected to shorten the N–N and lengthen the C=N azine bonds. Nevertheless, comparison with the calculated bond lengths of symmetrically substituted azines **5** and **6** shows that the dithiolenyl and *p*-nitrophenyl halves of **2a** are perturbed very little (less than 0.005 Å) as compared to the corresponding moieties of **5** and **6** respectively. This situation parallels the one described with a series of asymmetrical acetophenone azines, for which there was no evidence of enhanced conjugation compared with their symmetrical counterparts.^{2,3,40} Further evidence of poor conjugation along the azine spacer comes from the calculated charge transfer in the ground state. Thus, the sum of Mulliken charges supported by the dithiolenyl ring in **2a** (+0.378 e) is nearly identical to that calculated for dithiolenyl rings in **5** (+0.369 e) and the second nitro group in **2b** causes only a minor increase in the charge supported by the dithiolenyl ring (+0.396 e) which results in a charge transfer of 0.027 e (0.396–0.369) in the ground state. This charge transfer is small when compared to other 1,3-dithiolenyl- π -acceptor compounds^{6g}

**Fig. 4** Calculated orientation of the dipole moment and hyperpolarizability vectors of compounds **2a** (left) and **2b** (right).**Fig. 5** Structure of compound **4**.

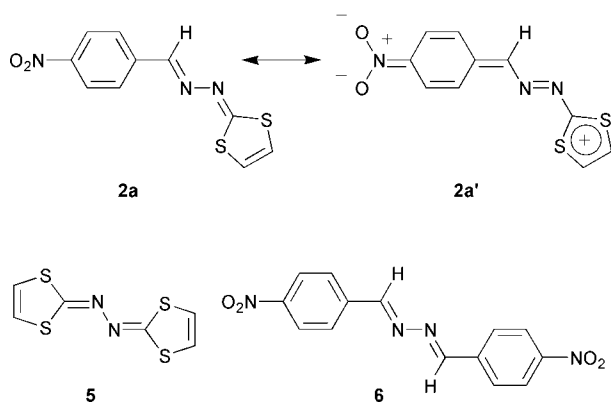


Fig. 6 Structures of **2a** and model compounds **5** and **6**.

and even smaller than that observed in 1,3-dithiol-2-ylidene anthracene compounds for which a poor conjugation was described.⁴¹ These results reinforce the view, proposed by Glaser, that the azine bridge acts as a conjugation stopper.^{2,3}

Electronic absorption spectra. The calculations performed until now involved coupled treatments, in which the hyperpolarizability is calculated as the second numerical (FF) or analytical (CPHF) derivative of the dipole moment with respect to the field. These calculations are usually more accurate numerically than SOS (Sum Over States) procedures, but they are not easily amenable to chemical interpretation due to the lack of information on the excited states responsible for the NLO response.⁴² On the other hand, the precise *ab initio* calculation of excited states involves methods such as CASSCF (Complete Active Space Self Consistent Field) that are not applicable to large molecules due to the large computational resources needed to perform the calculation. The recent implementation of Time-Dependent Density Functional Theory (TDDFT) methods⁴³ using the B3LYP functional allows the calculation of excitation energies of large molecules with a precision comparable to CASSCF at an affordable computational cost.⁴⁴

We have performed TD-B3LYP/6-31G* calculations on the studied compounds that indicate that the lowest energy excitation corresponds to pure HOMO to LUMO transitions with the wavelengths reported in Table 2. These results are in good agreement with the experimental UV-Vis absorption data. As expected, the agreement is better when a non polar medium such as cyclohexane is used in order to minimize the effect of the solvent.

The topologies of the HOMO and the LUMO of **2a** and **2c** are shown in Fig. 7, and according to these calculations the HOMO to LUMO transitions have charge-transfer character since the HOMO resides mainly on the dithiole ring while most of the LUMO density is on the nitrophenyl or nitrothienyl group with a considerable HOMO-LUMO overlap along the azine spacer.

Conclusions

The first push-pull 1,3-dithiol-2-ylidene derivatives containing an azine spacer (**2a-c**, **3a-b**) have been prepared by reaction of nitro-substituted (hetero)aromatic aldehydes with 2-methylthio-1,3-dithiolium salts. Thiophene-derived azine **2c** undergoes a light-induced *E-Z* isomerization, the configuration of each isomer being determined by ¹H-NMR spectroscopy and theoretical calculations. The redox properties, electronic absorption spectra and nonlinear optical properties have been studied. A charge-transfer band is observed for these compounds, whose wavelength is dependent on the nature of the donor and acceptor moieties. Compounds **2** and **3** show

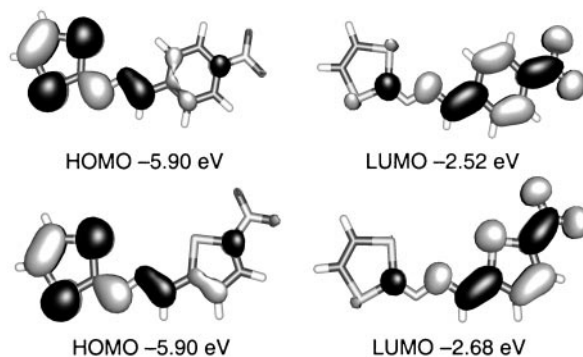


Fig. 7 Electronic density contours of HOMO and LUMO of compounds **2a** (top) and **2c** (bottom) calculated at the B3LYP/6-31G* level.

moderate NLO properties as determined by the EFISH technique ($\mu\beta(0)/10^{-48}$ esu: 36–135). These values are lower than those displayed by similar compounds with ethylenic spacers.

The experimental data are supported by theoretical calculations, which show that this result is mainly due to a decrease of the first molecular hyperpolarizability (β) in the azine derivatives. Moreover, calculated charge-transfer in the ground state and bond lengths show evidence of a poor conjugation across the azine bridge, although the π -system is essentially planar.

Experimental

General remarks

Infrared measurements were carried out in KBr pellets using a Nicolet FT-IR 510 ZDX spectrometer. Melting points were determined with a Kofler apparatus and are uncorrected. ¹H- and ¹³C-NMR spectra were recorded on a Bruker AM250 spectrometer operating at 250 MHz and 62.5 MHz respectively; δ values are given in ppm (relative to TMS) and *J* values in Hz. EI Mass spectra were recorded with an HP 5989 A spectrometer at 70 eV. Elemental analyses were performed by the "Servei d'Anàlisi Química de la Universitat Autònoma de Barcelona". UV-VIS absorption spectra were recorded with a Hitachi U-3400-UV-VIS-NIR spectrophotometer. Cyclic voltammetric experiments have been carried out at 20 ± 0.1 °C with an EGG PAR 273 electrochemical analyzer, in a three-electrode cell (Ag/AgCl reference). The working electrode is a 1 or 2 mm-diameter platinum disk, polished to a mirror finish. Platinum wires were used as the auxiliary electrode. An ohmic drop compensation was applied when necessary. The cell used can be operated either in semi-infinite diffusion or in thin-layer conditions. The one electron processes were checked by TLCV. Molecular orbital calculations were performed on Intel Pentium Pro and Pentium III based computers running under Windows NT 4.0. Semiempirical calculations used the MOPAC 6.0 package program⁴⁵ while HF and DFT calculations were performed with the Gaussian 98w program.⁴⁶ Processing of the results of molecular orbital calculations was achieved with the MOLDEN-3.6⁴⁷ program. EFISH measurements were taken with a non-linear optics spectrometer from SOPRA. The fundamental light source at 1.907 μ m was the first Stokes peak of a hydrogen Raman cell pumped by the 1.064 μ m light of a Q-switched Nd:YAG laser (Quantel YG 781, 10 pps, 8 ns/pulse). That light was passed through a linear polarizer and focused on the EFISH cell. The polarizing dc voltage (parallel to the light polarization) used in this cell was 6 kV. The output light from the cell was passed through an interference filter to select the second harmonic light (0.954 μ m) which was finally detected with an R642 photomultiplier from Hama-

matu. The $\mu\beta$ value of NPP measured in identical conditions is 110×10^{-48} esu.

4-Nitrobenzaldehyde hydrazone (**1a**), 2,4-dinitrobenzaldehyde and 5-nitrothiophene-2-carbaldehyde are commercially available. 2-Methylthio-1,3-dithiolium iodide⁹ and 2,4,5-tris(methylthio)-1,3-dithiolium tetrafluoroborate¹⁰ were prepared as previously described.

General procedure for hydrazones 1b–c

A solution of hydrazine hydrate (0.48 mL, 10 mmol) in 15 mL of absolute ethanol was added dropwise to a stirred solution of the corresponding aldehyde (5 mmol) in 20–25 mL of absolute ethanol. Stirring was continued at room temperature for 3–5 hours. A brown solid was collected by filtration. Evaporation of the filtrate afforded an additional amount of crude product.

2,4-Dinitrobenzaldehyde hydrazone (1b). The collected solid was recrystallised from absolute ethanol, and the filtrate was purified by chromatography (silica gel; CH_2Cl_2 –hexane, 4:1) to afford a light brown solid. (760 mg, 72%). Mp 131 °C. IR (KBr): $\nu = 3477, 3432, 3307, 3199, 3106, 1533, 1332, 1316 \text{ cm}^{-1}$. $^1\text{H NMR}$ (CDCl_3): $\delta = 8.80$ (d, $J = 2.2$ Hz, 1 H), 8.35 (dd, $J = 9.1$ Hz, $J' = 2.2$ Hz, 1 H), 8.29 (d, $J = 9.1$ Hz, 1 H), 8.23 (s, 1 H), 6.33 (s, 2 H).

5-Nitrothiophene-2-carbaldehyde hydrazone (1c). The combined solid products were a mixture of **1c** and 5-nitrothiophene-2-carbaldehyde azine. They were purified by chromatography (silica gel; CH_2Cl_2) to afford a red solid. (667 mg, 78%). Mp 137 °C. Lit.¹¹ mp 142–144 °C. IR (KBr): $\nu = 3427, 3299, 3110, 1564, 1522, 1479, 1441, 1328, 1321 \text{ cm}^{-1}$. $^1\text{H NMR}$ (CDCl_3): $\delta = 7.79$ (d, $J = 4.0$ Hz, 1 H), 7.73 (s, 1 H), 6.89 (d, $J = 4.0$ Hz, 1 H), 5.89 (s, 2 H).

General procedure for 2a–c

A solution of the appropriate hydrazone (1.65 mmol) and pyridine (0.13 mL, 1.65 mmol) in 25 mL of methanol was added dropwise to a stirred suspension of 2-methylthio-1,3-dithiolium iodide (414 mg, 1.5 mmol) in methanol (20 mL) at 0 °C under nitrogen. During the addition the dithiolium salt dissolved completely and an orange to red solid precipitated. Stirring was continued at room temperature for 2–3 hours. The solid was filtered, washed with cold methanol and dried. Recrystallisation from absolute ethanol afforded the desired products. In the case of **2a**, evaporation of the filtrate and chromatography (silica gel; CH_2Cl_2 –hexane, 7:3) gave a second fraction.

4-Nitrobenzaldehyde (1,3-dithiol-2-ylidene)hydrazone (2a). Orange solid. (231 mg, 58%). Mp 197–199 °C. IR (KBr): $\nu = 3110, 1596, 1583, 1526, 1518, 1345, 1332 \text{ cm}^{-1}$. $^1\text{H NMR}$ (CDCl_3): $\delta = 8.34$ (s, 1 H), 8.25 (d, $J = 8.4$ Hz, 2 H), 7.92 (d, $J = 8.4$ Hz, 2 H), 6.68 (d, $J = 7.3$ Hz, 1 H), 6.63 (d, $J = 7.3$ Hz, 1 H). $^{13}\text{C NMR}$ (CDCl_3): $\delta = 153.3, 140.2, 128.7, 124.0, 120.4, 117.0$. MS (EI): m/z (%) = 265 (72) [M^+], 165 (14), 135 (17), 103 (100), 89 (70), 76 (30).

2,4-Dinitrobenzaldehyde (1,3-dithiol-2-ylidene)hydrazone (2b). Orange-red needles. (351 mg, 75%). Mp 168 °C. IR (KBr): $\nu = 3110, 1603, 1575, 1532, 1525, 1484, 1468, 1356, 1338 \text{ cm}^{-1}$. $^1\text{H NMR}$ (CD_3COCD_3): $\delta = 8.91$ (d, $J = 2.2$ Hz, 1 H), 8.84 (s, 1 H), 8.68 (dd, $J = 8.8$ Hz, $J' = 2.2$ Hz, 1 H), 8.53 (d, $J = 8.8$ Hz, 1 H), 7.13 (s, 2 H). $^{13}\text{C NMR}$ (CDCl_3): $\delta = 148.9, 130.6, 127.0, 120.6, 117.7$. MS (EI): m/z (%) = 310 (20) [M^+], 264 (15), 134 (20), 102 (100), 76 (61), 58 (50). $\text{C}_{10}\text{H}_6\text{N}_4\text{O}_4\text{S}_2$ (310.30): calcd. C 38.70, H 1.95, N 18.05, S 20.67; found C 38.94, H 1.82, N 17.95, S 20.88%.

5-Nitrothiophene-2-carbaldehyde (1,3-dithiol-2-ylidene)hydrazone (2c). Red crystalline solid. (195 mg, 48%). Mp 215 °C. IR (KBr): $\nu = 3105, 1575, 1532, 1528, 1496, 1359, 1330 \text{ cm}^{-1}$. $^1\text{H NMR}$ (CDCl_3): $\delta = 8.30$ (s, 1 H), 7.84 (d, $J = 4.4$ Hz, 1 H), 7.20 (d, $J = 4.4$ Hz, 1 H), 6.70 (d, $J = 7.3$ Hz, 1 H), 6.63 (d, $J = 7.3$ Hz, 1 H). MS (EI): m/z (%) = 271 (58) [M^+], 103 (100), 95 (59). $\text{C}_8\text{H}_5\text{N}_3\text{O}_2\text{S}_3$ (271.33): calcd. C 35.41, H 1.86, N 15.49, S 35.45; found C 35.49, H 1.70, N 15.30, S 35.25%.

General procedure for 3a–b

A solution of the appropriate hydrazone (1.65 mmol) and pyridine (0.13 mL, 1.65 mmol) in 25 mL of methanol was added dropwise to a stirred solution of 2,4,5-tris(methylthio)-1,3-dithiolium tetrafluoroborate (492 mg, 1.5 mmol) in methanol (20 mL) at 0 °C under nitrogen. Stirring was continued at room temperature overnight. An orange to brown solid appeared, which was filtered, washed with cold methanol and dried. In the case of **3a** evaporation of the filtrate gave an additional amount of crude product.

4-Nitrobenzaldehyde [4,5-bis(methylthio)-1,3-dithiol-2-ylidene]hydrazone (3a). The combined solids (a mixture of **3a** and 4-nitrobenzaldehyde azine) were purified by chromatography (silica gel; CH_2Cl_2 –hexane, 7:3) to give an orange solid, which can be recrystallised from absolute ethanol. (321 mg, 60%). Mp 148 °C. IR (KBr): $\nu = 1585, 1517, 1505, 1485, 1337 \text{ cm}^{-1}$. $^1\text{H NMR}$ (CDCl_3): $\delta = 8.33$ (s, 1 H), 8.25 (d, $J = 8.8$ Hz, 2 H), 7.91 (d, $J = 8.8$ Hz, 2 H), 2.49 (s, 3 H), 2.46 (s, 3 H). $^{13}\text{C NMR}$ (CDCl_3): $\delta = 174.52, 153.94, 148.85, 129.47, 128.73, 123.91, 18.83$. MS (EI): m/z (%) = 357 (100) [M^+], 327 (21), 184 (10), 182 (49), 118 (41), 91 (96). $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_2\text{S}_4$ (357.48): calcd. C 40.32, H 3.10, N 11.75, S 35.88; found C 40.53, H 3.02, N 11.56, S 36.05%.

2,4-Dinitrobenzaldehyde [4,5-bis(methylthio)-1,3-dithiol-2-ylidene]hydrazone (3b). Recrystallisation from absolute ethanol afforded fine brown needles. (253 mg, 42%). Mp 177 °C. IR (KBr): $\nu = 1605, 1575, 1536, 1526, 1513, 1462, 1435, 1425, 1342 \text{ cm}^{-1}$. $^1\text{H NMR}$ (CD_3COCD_3): $\delta = 8.92$ (d, $J = 2.2$ Hz, 1 H), 8.88 (s, 1 H), 8.69 (dd, $J = 8.8$ Hz, $J' = 2.2$ Hz, 1 H), 8.53 (d, $J = 8.8$ Hz, 1 H), 2.60 (s, 6 H). $^{13}\text{C NMR}$ (CDCl_3): $\delta = 177.61, 149.70, 134.29, 130.61, 129.61, 127.03, 126.20, 120.53, 19.12$. MS (EI): m/z (%) = 402 (53) [M^+], 356 (10), 135 (31), 118 (100), 103 (57), 91 (95). $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_4\text{S}_4$ (402.48): calcd. C 35.81, H 2.50, N 13.92, S 31.87; found C 36.01, H 2.46, N 14.05, S 31.63%.

Acknowledgements

We thank Professor J. Elguero for helpful discussions. Financial support from DGICYT (Projects MAT99-1009-C02-02, PB93-0896 and PB98-0902) is gratefully acknowledged.

References

- 1 For recent reviews see: (a) *Nonlinear Optics of Organic Molecules and Polymers*, ed. H. S. Nalwa and S. Miyata, CRC, Boca Raton, 1997; (b) T. Verbiest, S. Houbrechts, M. Kauranen, K. Clays and A. Persoons, *J. Mater. Chem.*, 1997, **7**, 2175; (c) J. J. Wolff and R. Wortmann, *Adv. Phys. Org. Chem.*, 1999, **32**, 121.
- 2 R. Glaser and G. S. Chen, *J. Comput. Chem.*, 1998, **19**, 1130.
- 3 G. S. Chen, J. K. Wilbur, C. L. Barnes and R. Glaser, *J. Chem. Soc., Perkin Trans. 2*, 1995, 2311.
- 4 (a) R. Centore, B. Panunzi, A. Roviello, A. Sirigu and P. Villano, *Mol. Cryst. Liq. Cryst. A*, 1996, **275**, 107; (b) R. Centore, B. Panunzi and A. Tuzi, *Z. Kristallogr.*, 1996, **211**, 31.
- 5 (a) H. S. Nalwa, T. Hamada, A. Kakuta and A. Mukoh, *Synth. Met.*, 1993, **57**, 3901; (b) H. S. Nalwa, T. Hamada, A. Kakuta and A. Mukoh, *Nonlinear Opt.*, 1993, **6**, 155; (c) H. S. Nalwa, J. Mukai and A. Kakuta, *J. Phys. Chem.*, 1995, **99**, 10766.

- 6 (a) H. E. Katz, K. D. Singer, J. E. Sohn, C. W. Dirk, L. A. King and H. M. Gordon, *J. Am. Chem. Soc.*, 1987, **109**, 6561; (b) M. Blanchard-Desce, I. Ledoux, J. M. Lehn, J. Malthête and J. Zyss, *J. Chem. Soc., Chem. Commun.*, 1988, 737; (c) F. Meyers, J. L. Brédas and J. Zyss, *J. Am. Chem. Soc.*, 1992, **114**, 2914; (d) A. K.-Y. Jen, V. P. Rao, K. J. Drost, K. Y. Wong and M. P. Cava, *J. Chem. Soc., Chem. Commun.*, 1994, 2057; (e) K. Kondo, T. Fujitani and N. Ohnishi, *J. Mater. Chem.*, 1997, **7**, 429; (f) A. I. de Lucas, N. Martín, L. Sánchez, C. Seoane, J. Garín, J. Orduna, R. Alcalá and B. Villacampa, *Tetrahedron Lett.*, 1997, **38**, 6107; (g) A. J. Moore, M. R. Bryce, A. S. Batsanov, A. Green, J. A. K. Howard, M. A. McKerverey, P. McGuigan, I. Ledoux, E. Ortí, R. Viruela, P. M. Viruela and B. Tarbit, *J. Mater. Chem.*, 1998, **8**, 1173; (h) T. T. Nguyen, M. Sallé, J. Delaunay, A. Riou, P. Richomme, J. M. Raimundo, A. Gorgues, I. Ledoux, C. Dhenaut, J. Zyss, J. Orduna and J. Garín, *J. Mater. Chem.*, 1998, **8**, 1185.
- 7 C. Maletzko, W. Sundermeyer, H. Pritzkow, H. Irgartinger and U. Huber-Patz, *Chem. Ber.*, 1991, **124**, 2025.
- 8 (a) R. Mayer and B. Gebhardt, *Chem. Ber.*, 1964, **97**, 1298; (b) S. Hünig, G. Kiesslich, K. H. Oette and H. Quast, *Justus Liebigs Ann. Chem.*, 1971, **754**, 46; (c) G. Scherowsky and J. Weiland, *Justus Liebigs Ann. Chem.*, 1974, 403.
- 9 F. Challenger, E. A. Mason, E. C. Holdsworth and R. Emmott, *J. Chem. Soc.*, 1953, 292.
- 10 A. J. Moore and M. R. Bryce, *Tetrahedron Lett.*, 1992, **33**, 1373.
- 11 E. W. Berndt, H. Van Essen, B. G. Held and R. D. Vatne, *J. Med. Chem.*, 1969, **12**, 371.
- 12 R. L. Hinman, *J. Org. Chem.*, 1960, **25**, 1775.
- 13 F. H. Allen, J. E. Davies, J. J. Galloy, O. Johnson, O. Kennard, C. F. Macrae, E. M. Mitchell, G. F. Mitchell, J. M. Smoth and D. G. Watson, *J. Chem. Inf. Comput. Sci.*, 1991, **31**, 187.
- 14 (a) V. Mom and G. De With, *Acta Crystallogr., Sect. B*, 1978, **34**, 2785; (b) U. C. Sinha, *Acta Crystallogr., Sect. B*, 1970, **26**, 889; (c) M. Burke-Laing and M. Laing, *Acta Crystallogr., Sect. B*, 1976, **32**, 3216.
- 15 (a) J.-L. Galigne and J. Falgueirettes, *Acta Crystallogr., Sect. B*, 1968, **24**, 1523; (b) H. Astheimer, L. Walz, W. Haase, J. Loub, H. J. Muller and M. Gallardo, *Mol. Cryst. Liq. Cryst.*, 1985, **131**, 343; (c) S. V. Sereda, S. V. Shelyazhenko, Yu. A. Fialkov, N. S. Pivovarova and V. A. Mikhailik, *Kristallografiya*, 1992, **37**, 894; (d) S. V. Sereda, M. Yu. Antipin, T. V. Timofeeva and Yu. T. Struchkov, *Kristallografiya*, 1988, **33**, 118; (e) J. Marignan, J. L. Galigne and J. Falgueirettes, *Acta Crystallogr., Sect. B*, 1972, **28**, 93; (f) M. Lewis, C. L. Barnes, B. A. Hathaway and R. Glaser, *Acta Crystallogr., Sect. C*, 1999, **55**, 975.
- 16 (a) E. Arnal, J. Elguero, R. Jacquier, C. Marzin and J. Wylde, *Bull. Soc. Chim. Fr.*, 1965, 877; (b) J. Elguero, R. Jacquier and C. Marzin, *Bull. Soc. Chim. Fr.*, 1968, 713; (c) M. Minabe, Y. Takabayashi, Y. Setta, H. Nakamura, T. Kimura and M. Tsubota, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 3633; (d) For the E-Z isomerism of other aldzines see: P. Freche, A. Gorgues and E. Levas, *Tetrahedron*, 1977, **33**, 2069.
- 17 (a) B. Oussaid, M. Ayad, B. Garrigues, J.-P. Fayet and L. T. Tran, *Can. J. Chem.*, 1992, **70**, 58; (b) For a review on the study of the conformations of acyl groups in heterocyclic compounds and systems structurally related to them see: R. Benassi, U. Folli, L. Schenetti and F. Taddei, *Adv. Heterocycl. Chem.*, 1987, **41**, 75.
- 18 V. N. Sheinker, A. D. Garnovskii and O. A. Osipov, *Russ. Chem. Rev.*, 1981, **50**, 336.
- 19 I. Fleming and J. Harley-Mason, *J. Chem. Soc.*, 1961, 5560.
- 20 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
- 21 B. Ma, J.-H. Lii, H. F. Schaefer III and N. L. Allinger, *J. Phys. Chem.*, 1996, **100**, 8763.
- 22 The B3P86 functional consists of Becke's three parameter hybrid functional²⁰ with the nonlocal correlation provided by Perdew: J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822.
- 23 P. C. Hariharan and J. A. Pople, *Chem. Phys. Lett.*, 1972, **16**, 217.
- 24 (a) N. Terkia-Derdra, R. Andreu, M. Sallé, E. Levillain, J. Orduna, J. Garín, E. Ortí, R. Viruela, R. Pou-Amerigo, B. Sahraoui, A. Gorgues, J.-F. Favard and A. Riou, *Chem. Eur. J.*, 2000, **6**, 1199; (b) R. Viruela, P. M. Viruela, R. Pou-Amerigo and E. Ortí, *Synth. Met.*, 1999, **103**, 1991.
- 25 (a) A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899; (b) R. M. Minyaev and V. I. Minkin, *Can. J. Chem.*, 1998, **76**, 776; (c) A. E. Koziol, R. C. Palenik and G. J. Palenik, *J. Chem. Soc., Chem. Commun.*, 1988, 226.
- 26 J. T. Mague, S. Vang, D. G. Berge and W. F. Wacholtz, *Acta Crystallogr., Sect. C*, 1997, **53**, 973.
- 27 F. Blockhuys, R. Hoefnagels, C. Van Alsenoy, H. J. Geise, T. Jonckers and R. Dommissie, *Tetrahedron Lett.*, 2000, **41**, 555.
- 28 P. R. Rablen, S. A. Pearlman and J. Finkbinder, *J. Phys. Chem. A*, 1999, **103**, 7357.
- 29 (a) R. Ditchfield, *Mol. Phys.*, 1974, **27**, 789; (b) R. Ditchfield, *J. Am. Chem. Soc.*, 1971, **93**, 6287; (c) K. Wolinski, J. F. Hinton and P. Pulay, *J. Am. Chem. Soc.*, 1990, **112**, 8251.
- 30 R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650.
- 31 H. Lund, in *Organic Electrochemistry: an Introduction and a Guide*, 3rd edn., ed. H. Lund and M. M. Baizer, Dekker, New York, 1991, ch. 9.
- 32 (a) P. R. Moses, J. Q. Chambers, J. O. Sutherland and D. R. Williams, *J. Electrochem. Soc.*, 1975, **122**, 608; (b) A. Benahmed-Gasmi, P. Frère, J. Roncali, E. Elandaloussi, J. Orduna, J. Garín, M. Jubault and A. Gorgues, *Tetrahedron Lett.*, 1995, **36**, 2983; (c) D. Lorcy, R. Carlier, A. Robert, A. Tallec, P. Le Maguerès and L. Ouahab, *J. Org. Chem.*, 1995, **60**, 2443; (d) For a comparison of the redox properties of dithiafulvenes and aza-analogues see: D. Lorcy, A. Robert, R. Carlier and A. Tallec, *Bull. Soc. Chim. Fr.*, 1994, **131**, 774.
- 33 (a) V. P. Rao, Y. M. Cai and A. K.-Y. Jen, *J. Chem. Soc., Chem. Commun.*, 1994, 1689; (b) K. Y. Wong, A. K.-Y. Jen, V. P. Rao and K. J. Drost, *J. Chem. Phys.*, 1994, **100**, 6818; (c) P. R. Varanasi, A. K.-Y. Jen, J. Chandrasekhar, I. N. N. Namboothiri and A. Rathna, *J. Am. Chem. Soc.*, 1996, **118**, 12443; (d) I. D. L. Albert, T. J. Marks and M. A. Ratner, *J. Am. Chem. Soc.*, 1997, **119**, 6575.
- 34 B. Y. Simkin, V. I. Minkin and M. N. Glukhovtsev, *Adv. Heterocycl. Chem.*, 1993, **56**, 303.
- 35 B. G. Tiemann, S. R. Marder, J. W. Perry and L.-T. Cheng, *Chem. Mater.*, 1990, **2**, 690.
- 36 (a) J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209; (b) J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 221.
- 37 J. Garín, J. Orduna and R. Andreu, *Synth. Met.*, 1999, **102**, 1531.
- 38 L.-Y. Hsu, C. E. Mordman and D. H. Kenny, *Acta Crystallogr., Sect. C*, 1993, **49**, 394.
- 39 B. Beck and U.-W. Grummt, *J. Phys. Chem. B*, 1998, **102**, 664.
- 40 (a) R. Glaser, G. S. Chen, M. N. Anthamatten and C. L. Barnes, *J. Chem. Soc., Perkin Trans. 2*, 1995, 1449; (b) M. Lewis, C. L. Barnes and R. Glaser, *Can. J. Chem.*, 1998, **76**, 1371.
- 41 A. S. Batsanov, M. R. Bryce, M. A. Coffin, A. Green, R. E. Hester, J. A. K. Howard, I. K. Lednev, N. Martín, A. J. Moore, J. N. Moore, E. Ortí, L. Sánchez, M. Savirón, P. M. Viruela, R. Viruela and T.-Q. Ye, *Chem. Eur. J.*, 1998, **4**, 2580.
- 42 For reviews on the calculation of second order nonlinearities using quantum chemical methods see: (a) D. R. Kanis, M. A. Ratner and T. J. Marks, *Chem. Rev.*, 1994, **94**, 195; (b) J. O. Morley and D. Pugh, in *Nonlinear Optics of Organic Molecules and Polymers*, ed. H. S. Nalwa and S. Miyata, CRC, Boca Raton, 1997, p. 29.
- 43 R. E. Stratmann, G. E. Scuseria and M. J. Fish, *J. Chem. Phys.*, 1998, **109**, 8218.
- 44 (a) M. Petiaou, J. Fabian and P. Rosmus, *Phys. Chem. Chem. Phys.*, 1999, **1**, 5547; (b) S. Hirata, T. J. Lee and M. Head-Gordon, *J. Chem. Phys.*, 1999, **111**, 8904.
- 45 MOPAC 6.0, J. J. P. Stewart, *QCPE Bull.*, 1990, **10**, 455.
- 46 Gaussian 98w, Revision A.7, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1998.
- 47 G. Schaftenaar and J. H. Noordik, *J. Comput. Aided Mol. Design*, 2000, **14**, 123.