Resonance-Enhanced Optical Nonlinearities in Azothiophenes

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The hyperpolarizabilities of a series of donor−acceptor azothiophene dyes have been assessed experimentally for the linear electrooptic effect (LEO) using a solvatochromic technique and theoretically using both a sum-over-states approach at the CNDO/S level and a time-dependent coupled Hartree−Fock approach at the AM1 level. Reasonable correlations have been found between the magnitude of the experimental β_{xxx} values from solvatochromic measurements and those calculated. All the azothiophenes examined possess large values which are substantially greater than those obtained for related azobenzenes. There is substantial resonance enhancement of the hyperpolarizabilities of the phenylazothiophenes when the phenyl ring is replaced by a naphthalene ring because of a lowering of the transition energy between the ground and first excited state. The naphthylazothiophenes have very large hyperpolarizabilities coupled with large dipole moments, which make them ideal candidates for applications in poled polymer films as LEO modulators.

Introduction

Over the past 20 years, many polar organic molecules have been found to exhibit large optical nonlinearities which have been exploited in the areas of both second harmonic generation (SHG) and linear electrooptic modulation (LEO).[1−5] In the former, one major application is concerned with optical data storage where the infrared emission from a semiconductor laser is converted to blue light, enabling up to 4 times as much data to be stored. In the latter, a signal is imposed directly onto a low-energy carrier wave by application of a dc electric field generally at a wavelength of around 1300−1500 nm for applications in telecommunications. Although it is important in SHG applications that the active organic molecule is transparent at the SHG wavelength (to avoid reabsorption of the converted light), this restriction does not apply in LEO applications provided the molecule does not absorb at the carrier wavelength. It is another important requirement, in polymer films applications, that the molecule must have a sufficiently large dipole moment to allow the molecule to be orientated by electric field poling.[1−5]

The most active molecules for both these applications possess a large molecular hyperpolarizability and contain a donor and acceptor group situated at either end of a suitable conjugation path.[1−5] Molecular modeling and theoretical calculations have been employed extensively to assess and screen a large number conjugated organic molecules by calculating their molecular hyperpolarizabilities at several levels of molecular orbital theory.[6−21] The very important nonlinear optical frequency-dependent effects have generally been carried out using a sum-over-states (SOS) approach based on a perturbation formalism derived by Ward.[22] The appropriate formula for the hyperpolarizability relating to the LEO effect (β_{ikj}) is then defined by

$$\beta_{ijk}(\omega) = (-\mathrm{e}^3/2\hbar^2)\sum_{n'n}[(r^i_{gn'}\, r^j_{n'n}\, r^k_{ng} + r^k_{gn'}\, r^j_{n'n}\, r^i_{ng}) \times \{[(\omega_{n'g} + \omega)(\omega_{ng} + \omega)]^{-1} + [(\omega_{n'g} - \omega)(\omega_{ng} - \omega)]^{-1}\} + (r^j_{gn'}\, r^i_{nn'}\, r^k_{ng} + r^j_{gn'}\, r^k_{n'n}\, r^i_{ng})\{[\omega_{n'g}(\omega_{ng} + \omega)]^{-1} + [\omega_{n'g}(\omega_{ng} - \omega)]^{-1}\} + (r^i_{gn'}\, r^k_{n'n}\, r^j_{ng} + r^k_{gn'}\, r^i_{n'n}\, r^j_{ng}) \times \{[(\omega_{n'g} + \omega)\omega_{ng}]^{-1} + [(\omega_{n'g} - \omega)\omega_{ng}]^{-1}\}] \quad (1)$$

where r_{gn} is defined as

$$r_{gn} = \langle\phi_g|\sum r^i(m)|\phi_n\rangle \quad \text{or} \quad \langle g|r^i|n\rangle$$

and $r^i(m)$ is the ith component of the position vector of electron m (of N), $r_{nn} = \langle n|r^i|n\rangle$, ω_{ng} is the eigenvalue of ϕ_n relative to the ground state ϕ_g (the electronic transition energy), e is the magnitude of the electronic charge, and ω is the frequency of the applied radiation field. The indices n and n' may be restricted to run over excited states in increasing energy provided $\langle g|r|g\rangle = 0$, which holds only in the electronic charge centroid system, as we have discussed previously.[9] If the frequency term, ω, is set to zero in the summation, the remaining expression gives a so-called frequency-independent or static field value, β^0.

All 27 components of the second-order tensor are calculated, but usually the hyperpolarizability is expressed either as the vector component, β_x, defined as[9]

$$\beta_x = \beta_{xxx} + (1/3)\sum_{i\neq x}(\beta_{xii} + 2\beta_{iix}) \quad (2)$$

where β_x is aligned to lie along the direction of the molecular dipole moment (x), or as the intrinsic hyperpolarizability, β, defined as

$$\beta = (\beta_x{}^2 + \beta_y{}^2 + \beta_z{}^2)^{1/2} \quad (3)$$

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The value in eq 2 is directly related to the nonlinear coefficients derived both from electric field induced second-harmonic generation in solution and in poled polymer films where molecules are orientated along the direction of their dipole moments by a strong dc field. Because the hyperpolarizability is sometimes greater in a different direction to the dipole moment, the value in eq 3 is often used as a measure of potential hyperpolarizability.

Experimentally, the molecular hyperpolarizability has been measured by electric field induced second-harmonic generation in solution (EFISH),[1,23−25] which gives the vector component defined by eq 2, and by hyper-Raleigh scattering (HRS),[1,26−27] which gives the intrinsic value defined by eq 3. A much simpler method relies on the solvatochromic shifts of polar molecules in two or more solvents of differing dielectric constants.[28] This method, referred to as the two-level model, is only appropriate, however, for molecules that have hyperpolarizabilities that are dominated by the transition of an electron from the ground to the one major excited charge-transfer state only. For SHG, the dominant component of the 27-element tensor reduces to β_{xxx}, and it can be shown[29] that

$$\beta_{xxx}(2\omega) = (3/2\hbar^2) r_{ng}^{\ 2} (r_{nn} - r_{gg}) \omega_{ng}^{\ 2} / (\omega_{ng}^{\ 2} - 4\omega^2)(\omega_{ng}^{\ 2} - \omega^2) \quad (4)$$

where r_{ng} and ω_{ng} are the transition moment and energy, respectively, between the ground and first excited state, r_{gg} and r_{nn} are the dipole moments of the ground and first excited state, respectively, and ω is the frequency of the applied field.

Although not previously reported, a similar approach using the two-level model for the LEO effect in eq 1 leads to the expression

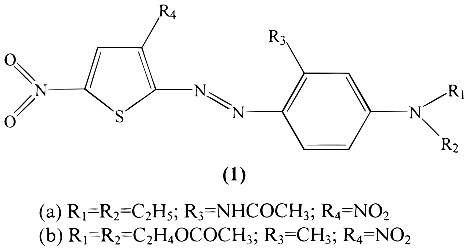
$$\beta_{xxx}(\omega) = (2/\hbar^2) r_{ng}^{\ 2} (r_{nn} - r_{gg}) (3\omega_{ng}^{\ 2} - \omega^2) / (\omega_{ng} - \omega)^2 (\omega_{ng} + \omega)^2 \quad (5)$$

where the terms have the same definition as in eq 4.

At zero applied field, i.e., $\omega = 0$, the relationship between the SHG and LEO effects in eqs 4 and 5 reduces to

$$\beta^0_{xxx}(\mathrm{LEO}) = 4\beta^0_{xxx}(\mathrm{SHG}) \quad (6)$$

The effect of a variation of the applied field (ω) on the experimental and calculated hyperpolarizability of both 4-nitro- and 2-methyl-4-nitroaniline has been systematically explored for second-harmonic generation where there are large resonance enhancement effects.[30] In contrast there have been few studies on the resonance enhancement for the LEO effect with the exception of one theoretical study[31] on the commercial dye[32] 2-((4′-(*N*,*N*-diethylamino)-2′-acetamidophenylazo)-3,5-dinitrothiophene (**1a**), where large effects were calculated to arise from the reciprocal terms of ($\omega_{ng} - \omega$) present in the denominator of eq 1.[31] This study showed that as the energy of the applied field (ω) approached the electronic transition energy (ω_{ng}), the hyperpolarizability was enhanced by several orders of magnitude.[31]

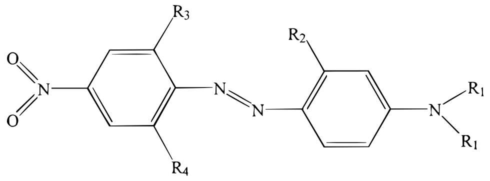


(1)

(a) $R_1=R_2=C_2H_5$; $R_3=NHCOCH_3$; $R_4=NO_2$
(b) $R_1=R_2=C_2H_4OCOCH_3$; $R_3=CH_3$; $R_4=NO_2$
(c) $R_1=R_2=C_2H_4OCOCH_3$; $R_3=H$; $R_4=NO_2$
(d) $R_1=C_2H_5$; $R_2=C_4H_8OCOCH_3$; $R_3=CH_3$; $R_4=COCH_3$
(e) $R_1=R_2=C_2H_4COOCH_3$; $R_3=CH_3$; $R_4=COOC_2H_5$

In SHG applications for data storage, the resonance enhancement effect is rarely utilized because the absorption of active organic molecules must be well removed from the SHG wavelength of around 400 nm. This means in practice that the absorption maximum of any active molecule should not exceed 350 nm to allow for the bandwidth. As the majority of active molecules absorb at wavelengths greater than 300 nm, the scope for resonance enhancement is extremely limited. However, this restriction does not apply to the LEO effect, particularly for telecommunications applications at a transmission wavelength of around 1300−1500 nm, as the absorption of the vast majority of organic molecules is well removed from this region. Molecules that have been currently developed for this application, such as donor−acceptor stilbenes and azobenzenes, typically absorb in the region 450−600 nm, and the important resonant enhancement effects are rarely utilized.

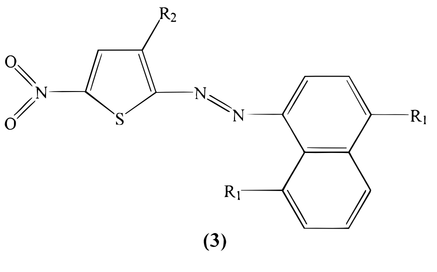
However, we have recently shown both by calculations and by EFISH measurements that azothiophenes, such as 2-(4′-(*N*,*N*-bis(2-acetoxyethyl)amino)-2′-methylphenylazo-3,5-dinitrothiophene (**1b**), do indeed show a much larger resonance enhancement effect over that found for related azobenzenes such as 4-*N*,*N*-dimethylamino-4′-nitroazobenzene (**2a**) partly because of the differences in the absorption maximum, which occurs at 612 nm in the former and 480 nm in the latter.[33] Furthermore, our previous theoretical studies have suggested that a number of heterocyclic azoarenes based on azothiophenes would be expected to possess large molecular hyperpolarizabilities as well as longer wavelength absorption to assist resonance enhancement.[10,34,35]



(2)

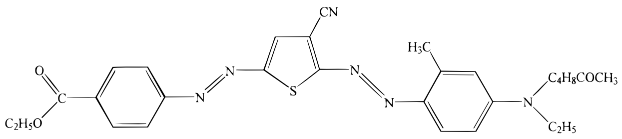
(a) $R_1=CH_3$; $R_2=R_3=R_4=H$
(b) $R_1=C_2H_5$; $R_2=NHCOCH_3$; $R_3=CN$; $R_4=Br$

The present studies have been carried out to therefore extend the previous theoretical work by evaluating the hyperpolarizability of a series of synthetically accessible long wavelength absorption azo dyes based on the phenylazothiophenes **1**, naphthylazothiophenes **3**, bisphenylazothiophenes **4**, naphthylphenylazothiophenes **5**, and the simpler blue azobenzene **2b**. All of the azo dyes were selected because of their potentially



(3)

(a) $R_1=NH(CH_2)_3OCH_3$; $R_2=COCH_3$
(b) $R_1=NH(CH_2)_3OCH_3$; $R_2=NO_2$



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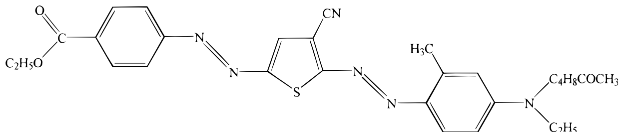

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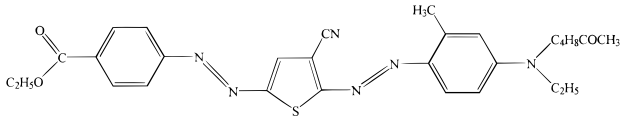

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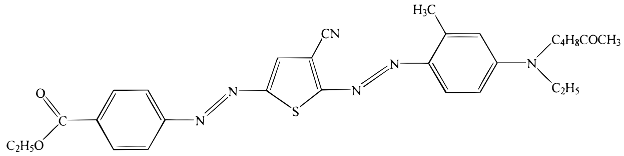
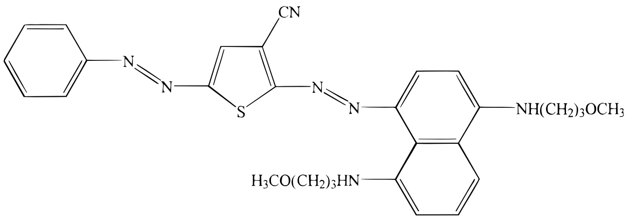
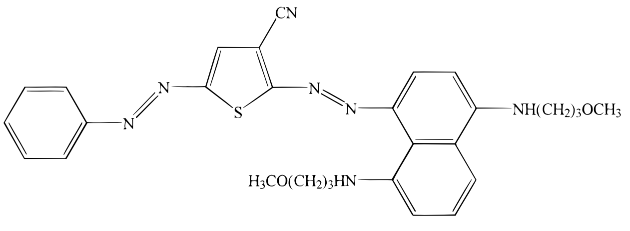


(4/ct)



(5/tc)



(5/cc)

good thermal and photochemical stability and large dipole moments, which should be highly beneficial in poled polymer applications. Furthermore, additional functional groups were placed at the amino substituents in most cases, such as the C_4H_8-$OCOCH_3$ or $C_3H_6OCH_3$ groups, to model the effect of similar groups that would be present in polymeric systems. The experimental evaluation of the β_{xxx} component of the LEO hyperpolarizability of these molecules was carried out using the solvatochromic method given in eq 5, while the theoretical evaluation of β_{xxx}, β_x, and β was carried out using eqs 2 and 3.

Methods of Calculation

Although there have been a considerable number of theoretical studies, and methods developed at various levels of theory, to calculate the nonlinear properties of polar organic systems in terms of their hyperpolarizabilities,[6−21] there have been few studies on the extended azoarenes discussed here partly because of their size, which would preclude the use of ab initio methods. In these studies, the structures of a series of donor−acceptor azoarenes were optimized using the AM1[36] method of the MOPAC package[37] (keywords "prec ef xyz"). Their molecular hyperpolarizabilities were calculated using the CNDOVSB method,[9,10] which is based on an initial configuration interaction treatment of ground- and excited-state wave functions followed by a sum-over-states treatment (SOS) of singly excited states to evaluate all 27 components of the hyperpolarizability tensor for the LEO effect. The β_{xxx}, β_x, and β values were calculated with a parametrization similar to that adopted previously,[10] with the spectroscopic constant, K, of the CNDO/S formulism set at 0.50 and using 80 excited states throughout for the evaluation of the hyperpolarizability to give frequency-dependent values at an applied field of 0.925 eV (1340 nm) and static field (β^0) values at zero frequency as in earlier work.[9,10]

The alternative time-dependent coupled Hartree−Fock method[38] present in the MOPAC program (CPHF or TDHF)[39] was used as an independent assessment of the hyperpolarizability results at zero field, although here the coded LEO expression[39] is not directly comparable to the SOS method and requires multiplication by a factor of 4 using eq 6 to scale the calculated value to that computed by the CNDOVSB procedure. The results from both methods were compared with the experimental values obtained from the solvatochromic measurements (see later). Values of the various hyperpolarizability components are given in units of 10^{-30} cm^5 esu^{-1} throughout.

Solvatochromic Measurements

Equation 5 was used directly to evaluate the major component of the hyperpolarizability tensor. Individual terms shown in the equation were obtained in the following way:

(1) The frequency term ω_{ng} was obtained directly from the measured absorption maximum in dioxane.

(2) The transition moment r_{ng} was taken from the integrated area under the absorption peak using the expression[40]

$$\text{Area} = 2\pi\omega_{ng}N_0\eta r_{ng}2M/3(2.303)\epsilon_0 c\hbar \qquad (7)$$

where M is the concentration (mol/L), N_0 is Avogadro's number, η is the refractive index of the solvent, ϵ_0 is the permittivity of the vacuum, and c is the speed of light in a vacuum.

(3) The ground-state dipole moment used in eq 5 was taken directly from the AM1 results by scaling, as we have found an approximately linear correlation between the calculated values and those determined experimentally, with the former consistently overestimating the latter by around 10% for a wide range of conjugated donor−acceptor systems. For example, the calculated AM1 values for the azothiophene **1b** at 12.6 D overestimates the experimental values of 11.4 D[33] by 10.5%.

(4) The excited-state dipole moment is more difficult to obtain and correlation between theory and experiment is much less satisfactory so that the calculated values are often unreliable and cannot be used. For example, the calculated excited-state dipole moment of 14.1 D obtained for the azobenzene (**2a**) using the AM1 method contrasts markedly with the experimental value of 25.0 D.[41] Following the method described for SHG evaluation,[28] we have evaluated the excited dipole moment, r_{nn}, from the solvatochromic expression[42]

$$(\omega_{ng})_s - \omega_{ng} = A[(\eta^2 - 1)/(2\eta^2 + 1)] + B[(\epsilon - 1)/(\epsilon + 2) - (\eta^2 - 1)/(\eta^2 + 2)] \qquad (8)$$

$$B = (2/4\pi\epsilon_0\hbar a^3)r_{gg}(r_{gg} - r_{nn}) \qquad (9)$$

where $(\omega_{ng})_s$ is the transition energy in a given solvent, ω_{ng} is the transition energy in vacuo (dilute vapor), ϵ is the relative

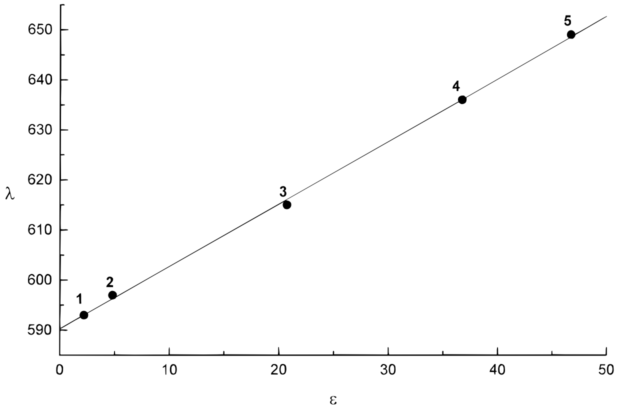


Figure 1. Variation of the absorption maximum (λ, nm) of 4-(*N*,*N*-bis(2-acetoxyethyl)aminophenylazo-3,5-dinitrothiophene (**1c**) with increasing dielectric constant (ϵ) of the solvent (1 dioxan; 2 chloroform; 3 acetone; 4 *N*,*N*-dimethylformamide; 5 dimethyl sulfoxide).

permittivity or dielectric constant of the solvent, η is the refractive index of the solvent, *A* and *B* are constants, and *a* is the radius of a spherical cavity in the solvent occupied by the molecule. *A* can be eliminated by alegebraic manipulation in two or more solvents and *B* evaluated by regression analysis. While the cavity radius *a* can be estimated by various means, we have analyzed the AM1 optimized structures using the SYBYL molecular modeling package[43] and taken 70% of the length of the longest axis to allow for the van der Waals surface on each side of the molecule, as described previously.[28]

In solution, the absorption maxima or transition energies $(\omega_{ng})_s$ of many polar organic molecules in aprotic solvents show an approximately linear relationship to the dielectric constant of the solvent over the range $\epsilon = 2.0-50$, and this is illustrated (Figure 1) for the case of 4-(*N*,*N*-bis(2-acetoxyethyl)aminophenylazo-3,5-dinitrothiophene (**1c**) in dioxane ($\epsilon = 2.2$), chloroform ($\epsilon = 4.8$), acetone ($\epsilon = 20.7$), *N*,*N*-dimethylformamide ($\epsilon = 37.8$), and dimethyl sulfoxide ($\epsilon = 46.7$). At higher dielectric constants the effect saturates and there is only a small increase in absorption maximum in moving to ethylene carbonate ($\epsilon = 89.6$) and then on to *N*-methylacetamide ($\epsilon = 191.3$). As this relationship is essentially linear up to a dielectric constant of 50, the corresponding gas-phase transition energy, ω_{ng}, can be obtained by extrapolation of the data points as previously described.[28] Because the other azothiophenes would be expected to show similar behavior, the gas-phase transition energies, ω_{ng}, were obtained in all these cases by a simple extrapolation of the absorption maxima obtained in dioxane and dimethyl sulfoxide only. However, the 2-(azonaphthyl)-3,5-dinitrothiophene (**3b**) showed anomalous behavior in solvents of high dielectric constants, and the gas-phase value here was obtained by a simple extrapolation from the data in dioxane and chloroform.

Discussion

1. Structure and Electronic Properties. Initial structure optimizations of all the azothiophenes discussed here at the AM1 level produced nonplanar structures where the thiophene ring is twisted from the plane of the phenylazo group. We have reported similar twisted structures for other donor−acceptor azothiophenes[33] and azobenzenes[44] and concluded that unrestrained AM1 optimizations are clearly unsatisfactory for azoarenes of this type because the vast majority are known to be planar.[45] However, if the heavy atoms of the chromophore are constrained to lie in the same plane during the optimization as we have described previously,[33,44] the AM1 method gives sensible geometries for the conjugated atoms of each structure with a typical energy penalty of only 0.5−1.5 kcal mol^{-1} in each case over the nonplanar structures produced from the unconstrained optimization. For example, the calculated C−S, N═N, C−NO$_2$, and C−NR$_2$ bond lengths in the constrained structures of around 1.69, 1.24, 1.46, and 1.38 Å are fully compatible with those found experimentally in related thiophenes and azobenzenes present in the Cambridge Structural Database.[45] Similarly, the calculated C−S−C and Ar−N═N angles of around 94° and 119° are also fully compatible with crystallographic data.[45]

All the structures were calculated using the stable trans conformation at the azo bridge with a torsion angle Ar−N═N−Ar of 180°. The side chains of the azothiophenes **1b**, **1c**, and **1d** at the amino group can adopt a number of different conformations including two where the $-CH_2CH_2OCOCH_3$ groups either add to the general dipole moment of the chromophore or subtract from it. In a previous study,[33] we explored this effect for **1b** and showed that the side chain conformation did have a considerable effect on both the dipole moment and hyperpolarizability. However, in that study, out of numerous possible conformations of the side chains, we selected a number of empirical conformations where the β-carbons of the two $-CH_2CH_2OCOCH_3$ groups were placed below the molecular plane and cis to one another, with E-conformations around the C−O single bond of the ester groups. It has since been brought to our attention[46] that most esters adopt a Z-conformation around the C−O single bond. For this reason we have calculated the closely related azothiophene **1c**, which has been assessed experimentally in these studies, in three Z-conformations (Figure 2) where the O−C═O component of the $-CH_2CH_2OCOCH_3$ group either points toward (1) the left-hand side of the molecule (**1c/1**) to enhance the dipole moment, (2) the right-hand side of the molecule to oppose the dipole moment (**1c/2**), or (3) one points to the left and the other to the right (**1c/3**).

In the *trans*-naphthylazothiophenes **3a** and **3b**, two conformations are possible in principle, where the sulfur atom of the heterocyclic ring (S1) is either cis or trans to the adjacent C2−N═N plane. In practice, the trans arrangement of S1−C2−N═N is not favored in either **3a** or **3b** because of large steric interactions between the substituent present at the 3-position of the thiophene ring and that present at the 8-position of the naphthalene ring which causes each molecule to twist and become nonplanar. Calculations were carried out therefore using the cis arrangement with the torsion angle S1−C2−N═N set at 0°. In the bisphenylazothiophene **4**, there are four possible valid trans conformations at the two azo bridges: these are respectively **4/cc**, where the sulfur atom S1 of the thiophene ring forms two cis arrangements with C5−N═N and C2−N═N, respectively **4/tc** where S1 forms a trans arrangement with C5−N═N and a cis arrangement with C2−N═N; **4/tt**, where S1 forms two trans arrangements with C5−N═N and C2−N═N, respectively; and **4/ct**, where S1 forms a cis arrangement with C5−N═N and a trans arrangement with C2−N═N. The AM1 results indicate that **4/tt** is favored over the other conformers, but because the energy differences among them are relatively small (Table 1), all four possibilities were considered for the subsequent evaluation of their nonlinear properties (see later). Similar conformations are possible also in the related naphthylphenylazothiophene **5**, but only two are favored, **5/tc** and **5/cc**, because of steric clashes between the substituent at the 3-position of the thiophene ring and that present at the 8-position of the naphthalene ring. Again because

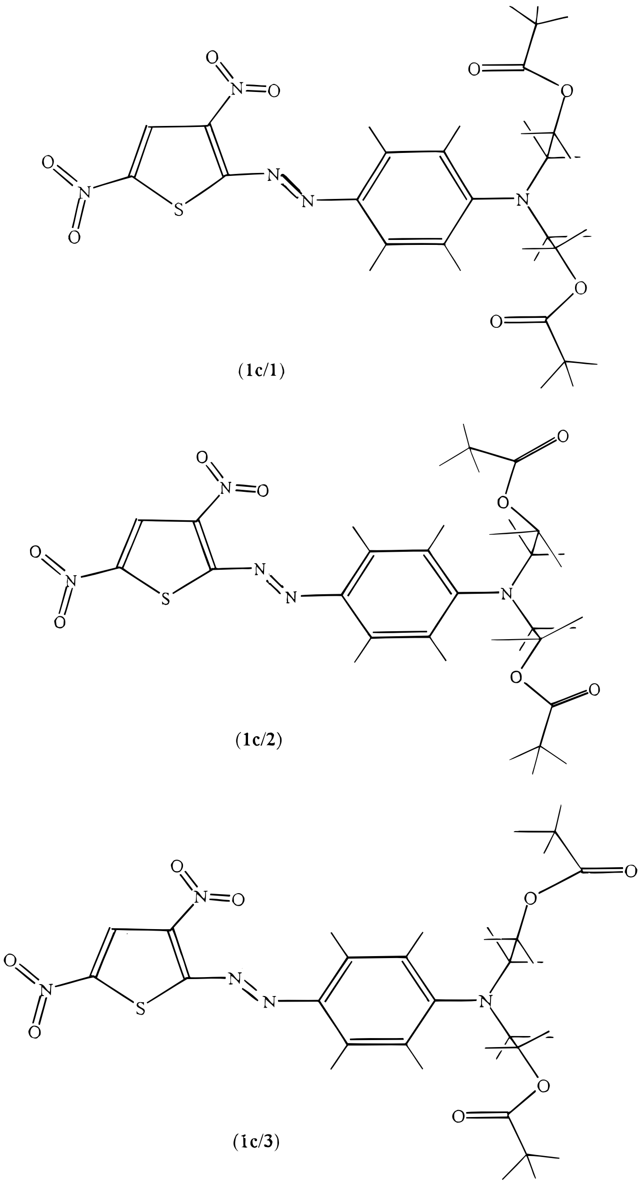


Figure 2. Molecular conformations of the azothiophene dye **1c**.

the energy difference between **5/tc** and **5/cc** is only 1.2 kcal mol^{-1} (Table 1), both structures were considered for further calculations.

Most of the azo dyes are predicted to have substantial dipole moments by both the AM1 and CNDOVSB methods, and although there are significant differences in the magnitude predicted by each method (which arise from the different theoretical approximations adopted), they both show the same trends for the azothiophenes, with **1e** > **1c/1** > **1d** > **1a** (Table 1). Of the molecules considered, the phenylazothiophenes **1** and naphthylazothiophenes **3** have the largest values, followed by the azobenzene **2b**, with the bisazothiophenes **4** and **5** possessing the smallest values. The molecular conformation has a substantial effect on the dipole moment of the phenylazothiophenes **1c**, as we have noted previously for **1b**,[33] with conformer **1c/1** showing roughly twice the value obtained for **1c/2** (12.3 versus 7.40 D at the AM1 level and 14.6 versus 5.83 D at the CNDOVSB level), because of the different orientation of the $-CH_2CH_2OCOCH_3$ groups, which assist the dipole moment in the former and oppose it in the latter. The calculated AM1 result for **1c/1** is comparable to that measured[33] for the closely related azothiophene **1b** at 11.4 D, suggesting that this conformer is preferred over conformers **1c/2** and **1c/3**, in line with the relative stabilities of the three possibilities explored (Table 1). The dipole moment of the bisphenylazothiophene **4** is also dependent on the molecular conformation adopted for calculation with the cis arrangement in **4/cc**, showing a larger value than the corresponding trans arrangement in **4/tt** (7.24 versus 5.07 D, respectively).

TABLE 1: Experimental Absorption Bands, Calculated Heats of Formation, and Dipole Moments for the Phenylazothiophenes 1, Naphthylazothiophenes 3, Bisphenylazothiophene 4, and Naphthylphenylazothiophene 5[a]

	experiment			AM1			CNDOVSB		
structure	λ_a	λ_b	λ_c	ΔH_f	r_{gg}	a	r_{gg}	ω_{ng}	f
1a	626	627	651	72.7	8.43	10.1	5.83	696	0.81
1c/1	591	593	649	−56.8	12.7	11.2	15.1	634	0.80
1c/2				−54.0	7.40		5.82	634	0.80
1c/3				−53.7	9.74		9.60	635	0.80
1d	588	590	640	−33.8	12.1	12.8	13.7	610	0.88
1e	586	589	651	−150.1	13.3	11.2	17.0	606	0.86
2b	547	550	594	108.4	6.80	10.4	4.48	599	0.86
3a	745	748	809	−2.13	10.3	13.9	11.0	752	0.67
3b	797	809	834[b]	41.5	10.0	13.9	8.83	793	0.67
4/tt	639	640	690	13.7	5.07	16.5	5.48	664	1.20
4/cc				16.2	7.24		8.00	668	1.04
4/tc				14.8	5.22		5.45	662	1.19
4/ct				15.0	7.07		8.35	670	1.12
5/tc	787	788	819	136.1	4.60	15.8	4.54	771	0.94
5/cc				137.3	4.61		4.37	776	0.84

[a] λ_a, λ_b, and λ_c are the experimental absorption maxima measured in the gas phase (see text), in dioxane, and in dimethyl sulfoxide, respectively; ΔH_f is the heat of formation (kcal mol^{-1}); r_{gg} is the ground-state dipole moment (in D); a is the cavity radius in (in Å; see text); ω_{ng} is the calculated transition energy (in nm); f is the oscillator strength. [b] Measured in chloroform.

All of the azoarenes absorb at the red end of the visible spectrum and would be expected to show resonance-enhanced values for the hyperpolarizability. The correlation between the calculated transition energies in the gas phase at the CNDOVSB level and the experimental data derived by extrapolation from the spectra in dioxane and dimethyl sulfoxide is reasonably good given the approximations of the method (Table 1). For example, the calculated transition energies for 2-(1-naphthylazo)-3,5-dinitrothiophene (**3a**) and the most stable 2-naphthylazo-5-phenylazothiophene conformer (**5/tc**) at 752 and 771 nm compare favorably with the experimental gas-phase values of 745 and 787 nm, respectively, obtained by extrapolation from the values in dioxane and dimethyl sulfoxide, respectively (Table 1).

2. Experimental and Calculated Hyperpolarizabilities. When conjugated donor−acceptor molecules are excited to the first excited state, charge transfer takes place primarily along the axis of the ground-state dipole moment, which is designated the *x*-axis in this work (see eq 2). It follows that the dominant component of the hyperpolarizability tensor is usually the β_{xxx} component, which can account for up to 80% of the overall value for simple aromatics such as 4-nitroaniline.[6,9,28] A similar trend is found in the calculated results for the azothiophenes **1a** to **1e**, where the β_{xxx} component is a very large proportion both of the final vector hyperpolarizability β_x defined by eq 2 and the intrinsic hyperpolarizability β defined by eq 3, both summed over 80 excited states. For example, in 3,5-dinitro-2-phenylazothiophene (**1a**), the β_{xxx} component amounts to 87% of the β_x value and 82% of the β value. The use of only one excited state in the theoretical evaluation generally results in a substantial overestimation of the β_{xxx} value relative to the experimental data in all cases, and it is clear that more excited states are required at this level of theory to provide reliable calculated results.

TABLE 2: Experimental and Calculated Hyperpolarizabilities of Phenylazothiophenes 1, Naphthylazothiophenes 3, Bisphenylazothiophene 4, and Naphthylphenylazothiophene 5[a]

	experiment		CNDOVSB				AM1
structure	β^0_{xxx}	β_{xxx}	β_{xxx}	β_x	β	β^0	β^0
1a	473.0	775.5	810.7	933.7	986.7	558.1	427.9
1c/1	451.3	697.9	733.5	754.4	771.8	476.1	304.3
1c/2			450.9	630.6	754.5	465.2	301.4
1c/3			745.5	735.1	743.0	457.8	294.2
1d	300.1	461.8	430.8	484.8	524.9	340.6	243.8
1e	316.5	486.2	503.3	536.7	567.6	367.4	223.8
2b	302.5	437.4	380.7	523.6	601.4	400.5	332.0
3a	455.0	960.2	1049.4	1107.4	1149.5	538.8	344.3
3b	632.0	1564.8	1718.2	1737.9	1740.1	751.5	507.3
4/tt	499.7	838.8	525.2	700.2	818.5	482.9	327.1
4/cc			396.7	583.5	707.1	422.5	307.8
4/tc			469.8	628.6	736.0	437.8	324.8
4/ct			219.0	543.3	813.1	479.5	320.4
5/tc	484.4	1131.9	983.4[b]	1273.9[c]	1454.3	620.8	348.6
5/cc			999.7[b]	1240.7[c]	1373.8	583.0	332.3

[a] The tensor components β_{xxx}, β_x and β have been evaluated at 0.925 eV and are defined in eqs 2 and 3, respectively. β^0_{xxx} and β^0 are the corresponding components at zero field (all in units of 10^{-30} cm^5 esu^{-1}). [b] β_{yyy} value (see text). [c] β_y value (see text).

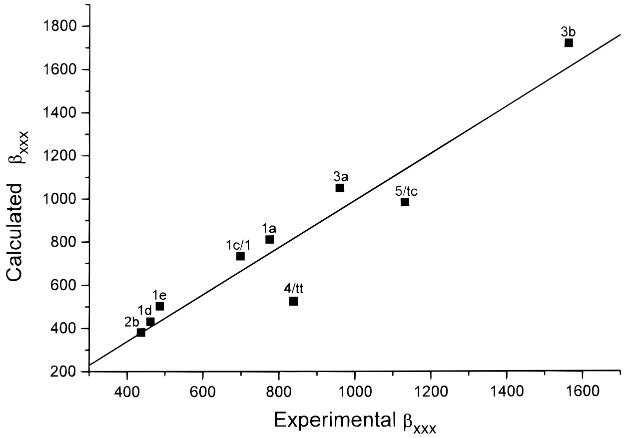


Figure 3. Comparison between the calculated and experimentally determined hyperpolarizabilities of the azo dyes **1**−**5**.

Experimentally, it is difficult to compare the β_{xxx} values obtained by the solvatochromic method with LEO data directly, as none exist. However, it is possible to assess the accuracy of the experimental β_{xxx} values obtained here with results from EFISH experiments, where available, by using eq 6, which shows that the former are expected to be 4 times larger than the latter at zero field frequency. A comparison of the solvatochromic data for the lowest energy conformer of the azothiophene **1c/1** with our previous EFISH data[33] for the closely related azothiophene **1b** at zero field frequency, but now scaled by a factor of 4 (eq 6) gives a β^0_{xxx} value of 451 for the former (Table 2) versus a β^0_x value of 576 ± 68 for the latter.[33] The experimental solvatochromic β^0_{xxx} value is therefore around 78% of the β^0_x value from EFISH measurements and fully in accord with previous studies[28] and strongly suggests that the experimental results on the other azothiophenes are likely to be reliable. Furthermore, a comparison of the experimental β_{xxx} results with the calculated values at 0.925 eV shows an approximately linear relationship (Figure 3).

Overall, there is a good correlation between the solvatochromic and calculated β_{xxx} values of 776 and 811 respectively for **1a** and those for **1e** at 486 and 503, respectively (Table 2, Figure 3). The relative efficacy of these compounds follows the order **1a** > **1c** > **1e** > **1d** by both experiment and calculation. All appear to be superior to the blue azobenzene **2b**, although the calculated values suggest that the vector component of the hyperpolarizability, β_x, for this structure is larger than that calculated for **1d**. Because the transition energy of **1a** is at the longest wavelength of the five phenylazothiophenes studied at 626−651 nm (experimentally) and 696 nm (theoretically), it enjoys the greatest resonance enhancement in the β_x value (Tables 1 and 2). The static field hyperpolarizabilities, β^0, calculated by the CNDOVSB method show trends similar to the frequency-dependent values, with **1a** predicted to possess the largest value; similar trends are obtained with the independent AM1 calculated results although the magnitude of the hyperpolarizability is smaller (Table 2).

The replacement of the phenyl ring in the azothiophene structure by a naphthalene ring would be expected to result in a general enhancement of the hyperpolarizability because of increased conjugation. Our previous calculations in this area are supportive.[34,35] In the experimental examples considered here, the presence of two complex donor groups situated in the 1,5-positions of the naphthalene ring were found to be necessary to facilitate the synthesis of the naphthylazothiophenes **3a** and **3b** from a coupling reaction between 1,5-di(*N*-3-methoxypropyl)aminonaphthalene with diazotized 2-amino-3-acetyl-5-nitrothiophene and 2-amino-3,5-dinitrothiophene, respectively. While the donor at the 4-position of the naphthalene ring is able to conjugate with the azo group at the 1-position and enhance the hyperpolarizability, that at the 8-position cannot and would be expected to exert a small negative effect arising from the inductive effect of the nitrogen atom.

The results show that the naphthalene ring has a pronounced effect on the hyperpolarizability with the experimental β_{xxx} value of 2-(azonaphthyl)-3-acetyl-5-nitrothiophene (**3a**) approximately twice as large as that obtained for the related 2-(azophenyl)-3-acetyl-5-nitrothiophene (**1d**). All the calculated values also reflect these trends with β_{xxx} for **3a** at 1049 and that for **1d** at 503 (Table 2).

The replacement of the acetyl group in **3a** by a second nitro group to give the corresponding 2-(azonaphthyl)-3,5-dinitrothiophene (**3b**) has a very large impact on the hyperpolarizability, with both the experimental and calculated β_{xxx} components of 1565 and 1718, respectively, significantly larger than those obtained for **3a** (Table 2). However, the difference in the intrinsic hyperpolarizabilities, β^0, between **3b** and **3a** is less marked, with the former now only some 1.4 times larger, and it follows that there is a marked resonance enhancement of the hyperpolarizability for this molecule, which absorbs around 800 nm (Table 1). Exactly the same trend is predicted by the AM1 calculations for **3b** and **3a**, although here the magnitude of the hyperpolarizability is smaller, with a β^0 value for the latter of 344 versus the CNDOVSB result of 539 (Table 2).

Although the replacement of a phenyl ring by a naphthalene ring in the azothiophenes (**1**) appears to provide a substantial boost to the nonlinear properties, a similar if smaller enhancement is produced by the simple addition of another donor group to the phenyl ring. For example, a comparison of the β^0 values of the naphthylazothiophene **3b** and phenylazothiophene **1a**, which contains two donor groups, shows that both the molecules have fairly large calculated hyperpolarizabilities of 752 and 558, respectively, using the CNDOVSB method and 507 and 428, respectively, using the AM1 method (Table 2). However, the frequency-dependent hyperpolarizabilities are considerably different, with **3b** around twice as large as **1a**. The major effect of the naphthalene ring, therefore, appears to be a lowering of the transition energy between the ground and first excited state to produce a much longer wavelength absorption, resulting in substantial resonance enhancement.

The two extended azothiophenes **4** and **5** assessed in the current work appear to show few advantages over the naphthylazothiophenes **3a** and **3b**, although the fairly long absorption wavelength of **5** enhances its hyperpolarizability (Table 1). The molecular conformation of **5** has a relatively small effect on the calculated hyperpolarizability, with the largest value found for **5/tc**. However, the calculated results for **4** show a wide variation in the β_{xxx} values depending on the conformation selected for the evaluation (Table 2), with **4/tc** less than half **4/tt**, with values of 219 and 525, respectively. The long conjugation path length in the most stable conformer (**4/tt**) is still insufficient to match the effect of the naphthalene ring in the naphthylazothiophene **3b**, as shown by the experimental β_{xxx} values of 721 and 1288, respectively (Table 2).

In contrast to all the other structures considered here, the largest component of the calculated hyperpolarizability of 3-cyano-2-naphthylazo-5-phenylazothiophene (**5**) is predicted to lie in the transverse direction to the ground-state dipole moment so that the charge-transfer axis on excitation lies mainly in the *y*-direction. This results in a large β_{yyy} component for the most stable conformer (**5/tc**), with values of 1132 obtained by the solvatochromic method and 983 by calculation (Table 2). The overall calculated vector component β_y at 1274 compares very favorably with the β_x values of the naphthylazothiophenes **3a** and **3b** at 1738 and 1107, respectively. This result reflects the similarity of structure between **5** and **3**, where the 3-cyano and 5-phenylazo groups in the thiophene ring have roughly comparable electron-attracting potential to the 3-acetyl and 5-nitro groups in **3a** and the 3,5-dinitro groups in **3b**.

Conclusions

The solvatochromic method appears to give a reasonable account of the magnitude of the hyperpolarizability for the LEO effect by comparison with the calculated values obtained at the CNDOVSB and AM1 levels. All the azothiophenes examined both experimentally and theoretically possess large hyperpolarizabilities, which are greater than those obtained for related azobenzenes. The hyperpolarizabilities of phenylazothiophenes are substantially enhanced when the phenyl ring is substituted by a naphthalene ring because of a lowering of the transition energy between the ground and first excited state. Three of the molecules (**3a**, **3b**, and **5**) appear to show considerable potential for applications in LEO devices.

Experimental Section

The thiophene-based azoarenes were prepared by the diazotization of 2-amino-3,5-dinitrothiophene and subsequent reaction with the appropriate coupling component using literature procedures.[47] Intermediates were either obtained either from Aldrich or supplied from Zeneca. In a typical preparation, 2-amino-3,5-dinitrothiophene (1.89 g, 0.01 mol) was added at 0 °C to a mixture prepared from a solution of sodium nitrite (0.76 g, 0.011 mol) dissolved in concentrated sulfuric acid (9 g) diluted with propionic acid (5 g) and acetic acid (30 g). The resulting solution was stirred 0 °C for 30 min and added to a solution of the coupling component (0.01mol) dissolved in a mixture of concentrated hydrochloric acid (3 g) and crushed ice (65 g). The mixture was stirred for an hour and the azothiophene filtered off, washed, dried, and recrystallized from an appropriate solvent such as toluene.

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