Non-linear optical activity of azo dyes. Conformational effects on the quadratic hyperpolarisability of an azothiophene dye

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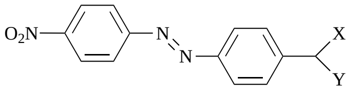
The molecular dipole moment and vector component of the hyperpolarisability of 4-[*N*,*N*-bis(2-acetoxyethyl)amino]phenyl-1-azo-2′-(3′,5′-dinitrothiophene) have been calculated using a semi-empirical approach and the results compared with experimental measurements in solution. The calculated values are found to be highly dependent on the conformation of the bis(2-acetoxyethyl)amino group selected, though experimental results suggest that only certain conformations are preferred under the influence of an applied external electric field. The observed change in the sign of the hyperpolarisability in moving from an applied field to 0.925 to 1.17 eV is well reproduced by the calculations.

Introduction

Orientated organic polymers containing electron-donor and -acceptor groups are currently finding important applications in non-linear optics as electro-optic modulators (EOM) and second harmonic generators (SHG).[1–3] Typical examples are polymers based on azobenzenes such as **1** and C.I. Disperse Red 1 (**2**), which are synthesised from functionalised monomers such as **3**. Copolymerisation with another monomer such as methyl methacrylate then gives an active cross-linked non-linear film.[1] However, when the monomers are processed into polymer films using a strong dc field for orientation either during the polymerisation process or afterwards on the pre-formed polymer near the glass transition temperature, the activity of the resulting cooled polymer film is much less than that expected from the molecular non-linearity. Contributory factors to this reduction include incomplete orientation in the electric field during the poling process coupled with a reorientation of the non-centrosymmetric material by the strong local electrostatic field present in the polymer afterwards on cooling. Factors such as the strength of the poling field, the size of the active molecule and the magnitude of the molecular dipole moment will clearly play an important role in the orientation process.

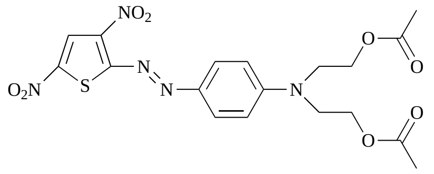


1 X = Y = Me
2 X = Et; Y = C_2H_4OH
3 X = Y = $C_2H_4O_2CCH{=}CH_2$

In the course of research into NLO active dyestuffs, a major goal has been the optimisation of quadratic hyperpolarisability as well as the ground state molecular dipole moment to improve the degree of orientation during poling. Two factors led us to consider azo dyes based on azothiophenes as analogues of the classic azobenzene C.I. Disperse Red 1 (**2**). First, there is an empirical relationship between quadratic hyperpolarisability and bathochromicity of the dye's visible absorbance.[4] While analogous azobenzenes only ever achieve reddish-blue shades, azothiophenes substituted with electronegative groups are blue, tending toward green and might therefore be anticipated to have higher NLO activity. Secondly, molecular orbital calculations on model azothiophenes have suggested that they possess substantial hyperpolarisabilities and fairly large dipole moments.[5]

While there have been a considerable number of theoretical calculations of the molecular first hyperpolarisability of conjugated donor–acceptor organic systems,[5–27] the effect of the side chain conformation of the donor or acceptor group in large molecules containing flexible monomeric chains has received scant attention with the exception of a recent study on methyl 4-(*N*,*N*-dimethylamino)-2′-nitroazobenzene-4′-carboxylate.†,[28]

In the present work, the NLO activity of the commercially available 4-[*N*,*N*-bis(2-acetoxyethyl)amino]phenyl-1-azo-2′-(3′,5′-dinitrothiophene) dye (**4**)[29] has been studied both theoretically and experimentally in solution. During this work, which was carried out under the auspices of a European Community-funded Esprit collaboration,[30] we have encountered a most surprising effect on the calculated NLO activity originating from the conformation of the dipolar but non-conjugated ester substituents present in the side chains of **4**.



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Experimental

Molecular orbital calculations were carried out on empirical conformations of the azothiophene **4** using the AM1[31] and PM3[32] methods of the MOPAC program[33] at the precise level. The conformations selected (see Fig. 1) were as follows where (*i*) the second carbon of each ethyl group was placed below the ring plane with both the ester and carbonyl oxygen atoms pointing away from the thiophene ring (**4a**); (*ii*) a similar conformation, but with the ester and carbonyl oxygen atoms pointing towards the thiophene ring (**4b**); (*iii*) a mixed conformation with the ester and carbonyl oxygen atoms of one group pointing towards the thiophene ring with the other ester and carbonyl oxygen atoms pointing away (**4c**).

A number of other conformations are possible, but the ones selected were considered to be a representative set for the pur-

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† Preferred name: methyl 4-(*N*,*N*-dimethylamino)phenyl-1-azo-4′-(3′-nitrobenzoate).

poses of the present study. The optimised conformations were then used to calculate their molecular hyperpolarisabilities using the CNDOVSB method,[5,6] a sum-over-states procedure (SOS) which has been specifically parametrised for both EOM and SHG applications. As the azothiophene **4** contains considerably more π-electrons than the simpler donor–acceptor arenes considered in earlier studies,[6] 300 excited states were used in the evaluation of the hyperpolarisability with the spectroscopic constant[6] set at 0.46. All 27 components of the tensor are calculated by the CNDOVSB method in the cartesian frame, though the most appropriate quantity for poled polymer films is the vector component, β_x, theoretically defined by eqn. (1)[6] where β_x is aligned to lie along the direction of the molecular dipole moment (μ). A similar expression can be written for β_y which lies in the transverse direction to the dipole moment.

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

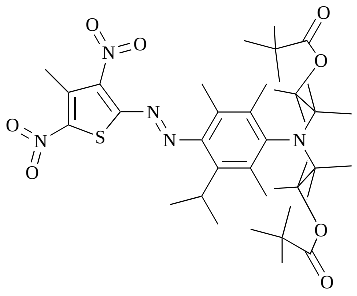
The hyperpolarisability was evaluated at 1.17 eV (1064 nm) and 0.925 eV (1340 nm) and at zero field as in previous work on related structures.[5]

Experimentally, solution measurements were carried out at the same field strengths in chloroform using the electric field induced second harmonic generation technique (EFISH). Details of the experimental set-up have been provided elsewhere.[4]

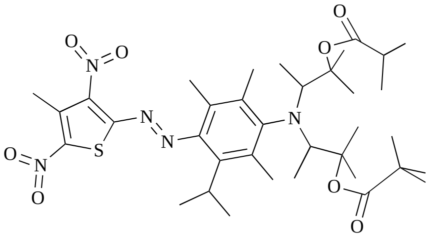
Results and discussion

The structure optimisation of the azothiophene **4a** at both the AM1 and PM3 levels produce a twisted structure where the thiophene ring is approximately orthogonal to the plane of the phenylazo group. Similar results for the thiophene ring are obtained for the other conformers **4b** and **4c** and the unrestrained methods are clearly unsatisfactory for these structures as the vast majority of donor–acceptor azobenzenes are known to be planar.[34] Similar non-planar structures have been reported using the same method of calculation for other azobenzenes.[35] However, if the heavy atoms of the chromophore are constrained to lie in the same plane during the optimisation as we have described previously,[35] the PM3 method gives sensible planar geometries for the conjugated atoms of each of the conformers with an energy penalty of only 1.4 kcal mol^{-1}‡ in each case over the non-planar conformers produced from the unconstrained optimisation. For example, the C–S, N=N and C–NO$_2$ bond lengths of 1.73, 1.25 and 1.49 Å are fully compatible with those found experimentally in related structures present in the Cambridge Structural Database.[34] The nitrogen atom of the dialkylamino group appears to be partially sp^3 hybridised in each case with C–C–N–alkyl torsion angles varying from 9 to 23° depending on the conformer calculated. All three structures appear to be equally valid with a maximum energy difference of *ca.* 0.7 kcal mol^{-1} among them (Table 1).

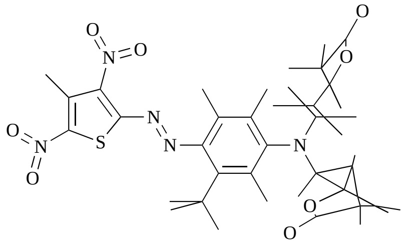
The calculated dipole moments show a surprising variation in magnitude depending on the conformation adopted (see Table 1). The largest value of 13.8 D is obtained for the conformation **4b** where the carbonyl oxygens are pointing in approximately the same direction as the resultant of the electron-attracting nitro groups present in the thiophene ring. The smallest value of 5.40 D is obtained for the alternative conformer **4a** where the carbonyl oxygens are pointing in the opposite direction; the mixed conformer **4c** shows a value between the two extremes. These results appear to correlate well with the experimentally determined value of 11.4 D suggesting that the molecular conformation lies between **4b** and **4c** in the presence of a large electric field.



4a



4b



4c

Fig. 1 Molecular conformations **4a**, **4b** and **4c** of the azothiophene dye

The explanation for the large changes calculated for the three conformers arises in part from the addition or subtraction of the −OCOMe group moment of *ca.* 1.70 D[36] to the dipole moment of *ca.* 10.6 D obtained from a closely related planar azothiophene[37] where the dimethylamino group replaces the bis(2-acetoxyethyl)amino group. When both the carbonyl components of the two −OCOMe groups are pointing towards the nitro groups in the thiophene ring (**4b**, Fig. 1), the contributions of the two groups of *ca.* 3.40 D are approximately additive, whereas in the alternative conformation where they point in the opposite direction (**4a**, Fig. 1), their effect is subtractive.

The calculated transition energies of the conformers show an excellent correlation with the experimental value of 612 nm, but the variation from 606 nm for conformer **4b** to 616 nm for conformer **4c** is unexpected. This arises because the C–C–N–alkyl torsion angle of 19.1° in the former decreases to 13.2° in the latter reflecting more sp^2 character in this case and hence greater overlap of the lone pair electrons and by inference a longer wavelength absorption.

However, the calculated vector component of the hyperpolarisability in the direction of the dipole moment, β_x, shows an astonishing change from 7.9 to 80.3 at zero field and from 89.1 to 657.7 (given in units of 10^{-30} cm^5 esu throughout) at 0.925 e$\nu_{\mathbf{max}}$ (Table 1) with the change in side chain structure from conformer **4a** to conformer **4b**. The large value for the latter arises because the side chain oxygen atoms and nitro groups point in roughly the same direction (Fig. 1) as the charge transfer axis on excitation. In contrast, the side chain oxygen atoms and nitro groups are opposed in conformer **4a** and in this case the dipole moment appears to point in a different direction to the charge transfer axis. As a result, the hyperpolarisability of conformer **4a** appears to be concentrated in the vector component, β_y, which is now the charge transfer axis. Surprisingly

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‡ 1 cal = 4.184 J.

Table 1 Calculated dipole moments, transition energies, oscillator strengths, and hyperpolarisabilities of the azothiophene conformers **4** *versus* experimental data[a]

						$\omega = 0$ eV		$\omega = 1.17$ eV		$\omega = 0.925$ eV	
	$\Delta_f H$/kcal mol^{-1}	μ_g/D	$\delta\mu$/D	λ/nm	f	$\beta_x/10^{-30}$ cm^5 esu	$\beta_y/10^{-30}$ cm^5 esu	$\beta_x/10^{-30}$ cm^5 esu	$\beta_y/10^{-30}$ cm^5 esu	$\beta_x/10^{-30}$ cm^5 esu	$\beta_y/10^{-30}$ cm^5 esu
Calculated data											
1	78.2	7.79	7.89	488	0.88	37.7	−7.91	418.2	−91.1	111.1	−25.0
4a	−85.6	5.40	5.91	613	0.76	7.93	88.7	−66.4	−554.0	89.1	815.2
4b	−86.3	13.8	8.61	606	0.74	80.3	6.52	−522.1	−17.9	657.7	34.1
4c	−85.8	10.1	9.07	616	0.76	85.8	38.0	−524.9	−210.7	846.4	345.6
Experimental data											
1		8.3		480				308			
4		11.4		612		144 ± 17		−677 ± 82		1093 ± 60	

the mixed conformer **4c** shows the largest values of this series probably because the dialkylamino group has a greater overlap with the aromatic rings for reasons given above.

It follows, therefore, that the conformers with the largest dipole moments are likely to be favoured under poling conditions or indeed under measurement conditions using the electric field induced second harmonic (EFISH) technique. The calculated hyperpolarisabilities of conformer **4c**, β_x, are fully consistent with this view with values of −525 at 1.17 eV and 846 at 0.925 eV relative to the experimental EFISH values of −677 ± 82 and 1093 ± 60 at the same field strengths (Table 1).

However, once the field is switched off, the side chain ester group is able to reorientate by simple inversion at the ester oxygen causing a potentially large loss in the prized hyperpolarisability along the induced direction. It is possible, therefore, that the activity of many donor–acceptor organics containing ester groups of the type discussed here and assessed by electric field poling may be substantially less than that expected because of this very large conformational effect at the side chain. This intramolecular conformational relaxation of the aliphatic ester side in **4** is one explanation for the observation of a 30% reduction over one hour in the SHG signal of an 8 μ thick, corona-poled, guest–host film of **4** in poly(methyl methacrylate) after the poling field had been switched off though there may be other explanations for this effect.[38] A further reduction of *ca.* 10% in the signal intensity observed over a much longer period is probably due to whole chromophore reorientation in the non-rigid polymer matrix.

The corresponding calculated and experimental EFISH results for the dimethylamino analogue **1** of C.I. Disperse Red 1 (**2**) gave hyperpolarisabilities of 418.2 and 308 at 1.17 eV together with dipole moments of 7.79 and 8.3 D, respectively (Table 1). Furthermore, as far as the product $\mu\beta_0$ is concerned, the azothiophene **4** is approximately three times larger than C.I. Disperse Red (**2**). Our initial reasons for studying the azothiophene dye are justified therefore on the basis of the much larger dipole moment obtained for (**4**) which should lead to improved poling efficiency though the larger hyperpolarisability in this case may be accentuated by increased resonance effects for the more bathochromic dye.

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