Quadratic Non-linear Optical Properties of Some Donor–acceptor Substituted Thiophenes

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A series of thiophenes and bithiophenes containing combinations of dimethylamino and dimethylhydrazono π-donor and nitro and dicyanovinyl π-acceptor groups was synthesized in order to study their non-linear optical properties. Solution molecular hyperpolarizabilities were determined by a combination of experimental dipole moments and results from the electric field induced second harmonic generation experiment. Values obtained correlate well with those calculated by the CNDOVSB molecular orbital method. The main structure–property relationships deduced from the results are: (*i*) thiophene provides a more efficient electron delocalization pathway than benzene; (*ii*) this increase is proportionately even greater for bithiophene compared with biphenyl; (*iii*) dimethylhydrazono results in twice the hyperpolarizability of dimethylamino in a comparable molecule; and (*iv*) dicyanovinyl is a more effective electron acceptor group than nitro in the thiophenes synthesized and calculated.

Many developments in the future telecommunication and optoelectronic industries will be reliant on the availability of efficient non-linear optical (NLO) materials. The background to the science of organic materials for NLO has been outlined in various texts.[1] A major problem in the search for second-order NLO materials is the optimization of the first hyperpolarizability, β, as given in eqn. (1), where P is the polarization of a

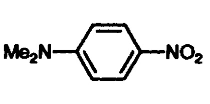
$$P = \alpha E + \beta EE + \gamma EEE + \cdots \qquad (1)$$

molecule in an external field E, α is the static polarizability and β and γ are the first and second hyperpolarizability tensors, respectively. The magnitude of β plays a major part in determining how efficient a given molecule will be in causing quadratic (*i.e.* second-order) NLO effects in the bulk material. Such effects include second harmonic generation (SHG) and the linear electrooptic or Pockels effect. Other things being equal, the higher β is, the more effective the material will be in its chosen application. The main molecular features for high β are a polarizable π-electron framework (X), such as an aromatic ring, substituted by electron donor(s) (D) and acceptor(s) (A) in a non-centrosymmetric fashion.[1] Typically, this results in molecules of the type D–X–A, of essentially rod-like geometry. While this overall design paradigm is now well understood, there is still active interest in the design of more efficient donors, acceptors and conjugating units. Much work has been done where the π-conjugating component is one or more benzene rings or alkene units and combinations of these. Far less has appeared where the benzene ring has been replaced by an aromatic heterocycle, such as thiophene, furan or pyrrole.

We were drawn to molecules based on thiophenes for several reasons. The aromatic resonance energy of the thiophene molecule is less than that of benzene,[2] implying that electron polarization involving charge-separated resonance structures should be easier in the thiophene series and thus lead to higher hyperpolarizability. Molecular orbital calculations of the hyperpolarizabilities β for a series of D,A-substituted benzene, thiophene, furan and pyrrole oligomers indicated that the higher thiophenes would be the most NLO active.[3] Furthermore, polythiophene and thiophene oligomers have been of appreciable interest in third order NLO studies,[4] again implying efficient electron delocalization along the polyheterocycle chain. However, only recently have the second order NLO effects of D,A-substituted thiophenes begun to be reported.[5]

In fact, our own initial studies of the NLO activities of substituted thiophenes were of third-order effects, where cubic hyperpolarizability values, $\gamma(-3\omega;\omega,\omega,\omega)$, were measured by third harmonic generation in solution.[6] This series of molecules included some typical D,A-substituted thiophenes, equally appropriate for study of their quadratic NLO properties. The purpose of the work reported in the current paper was to study the effects of the systematic variations of substituents in a simple series of thiophenes on quadratic hyperpolarizability, β. We report the results of measurements of the ground state dipole moments, the optical absorbance properties and first hyperpolarizability values determined by the Electric Field Induced Second Harmonic generation (EFISH) experiment. Additionally, the NLO data are compared with theoretical values calculated by the CNDOVSB molecular orbital method.[7] Dipole moments and heats of formation calculated by the AM1 MO method[8] are used to help to identify which of several alternative conformations is likely for the conformationally mobile molecules in the series.

The molecules studied are shown as **1**–**7**. *N*,*N*-Dimethyl-*p*-nitroaniline (**1**) is a typical D,A-benzene derivative, much studied in various NLO contexts already. Data for **1** are included here as a baseline from which to compare the novel thiophene derivatives. Molecule **2** is the most obvious thiophene analogue of **1**. We have been interested in easily synthesized π-donor and π-acceptor groups, which simultaneously lead to increased conjugation pathlength in the molecule. Two approaches derive from readily accessible 2-formylthiophenes. Simple condensation with malononitrile gives the dicyanovinyl π-acceptor group. Alternatively, reaction with 1,1-dimethylhydrazine yields a hydrazono π-donor substituent. Introduction of the latter in place of Me_2N in **2** gives nitrothiophene **3**. Molecule **4** exemplifies the former modification, again based on **2**. However, this has only been studied theoretically. Thiophene **5** contains both the hydrazono and dicyanovinyl groups. Bithienyl **6** is a direct analogue of **5** and should reveal the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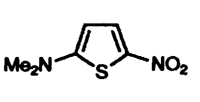
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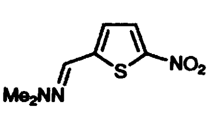
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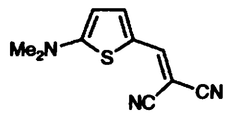
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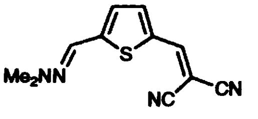
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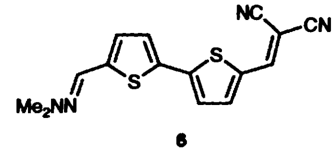
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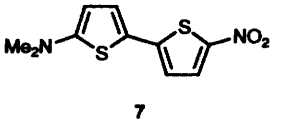
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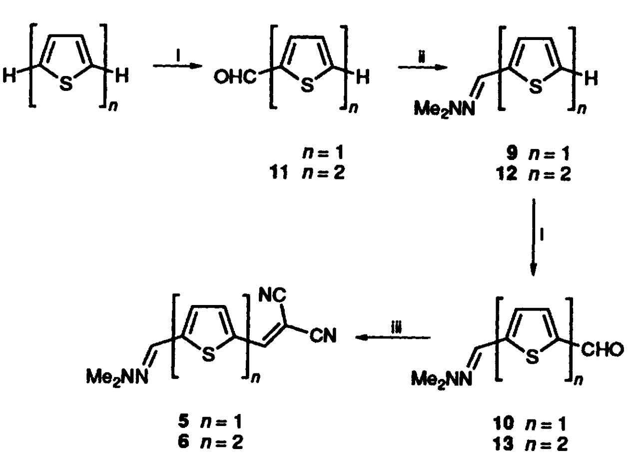
efficiency of more extended thiophene units in increasing β. The recently reported bithienyl derivative 7 is the corresponding bithienyl analogue of 2.[5h]

Results and Discussion

Synthesis.—The general methods used to furnish formylthiophene intermediates and the derived products are summarized in Scheme 1. All reaction steps proceeded uneventfully and do not warrant further comment (see Experimental section).


Scheme 1 *Reagents and conditions: i,* BuLi ($n = 1$) or lithium diisopropylamide ($n = 2$); DMF; H^+; *ii,* Me_2NNH_2; *iii,* $CH_2(CN)_2$

Measurement of Solution Properties.—The Electric Field Induced Second Harmonic Generation (EFISH) technique was used to measure the molecular quadratic hyperpolarizability, β, at a fundamental wavelength of 1.34 μm.[9–11] Neglecting solute–solvent interaction, a mean hyperpolarizability of the solute molecule is derived from the measured macroscopic susceptibility as inferred from the second harmonic signal emitted by a solution of the non-linear molecule in a standard solvent (here acetone). The microscopic susceptibility is given by eqn. (2), where z is aligned along the permanent dipole axis.

$$\gamma^0 = \gamma^e(-2\omega;\omega,\omega,0) + \mu_z\beta_z/5kT \qquad (2)$$

The first term is the scalar part of the cubic hyperpolarizability tensor γ^e. The second term originates from the partial orientation of the permanent dipole moment in the static field. β_z is the z component of the vector part of the quadratic susceptibility tensor β. The orientational contribution is usually assumed to be predominant over the electronic term γ^e. This has already been shown for *p*-nitroaniline derivatives[9] [eqn. (3)].

$$\gamma^0 \approx \mu_z\vec{\beta}_z(-2\omega;\omega,\omega)/5kT \qquad (3)$$

A quadratic hyperpolarizability coefficient projected along z is derived from the EFISH measurements and from the value of the dipole moment μ.

The experimental $\beta(-2\omega;\omega,\omega)$ values are affected by enhancement when the second harmonic frequency is close to the molecular absorption frequencies. A dispersion factor $F(\omega,\omega_{01})$, derived from the two-level model, is used to divide out dispersion enhancement[9] [eqn. (4)], where $E_{01} = \hbar\omega_{01}$.

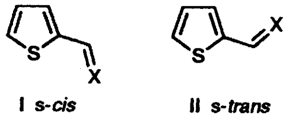
$$F(\omega,\omega_{01}) = E_{01}{}^4/(E_{01}{}^2 - 4\hbar^2\omega^2)(E_{01}{}^2 - \hbar^2\omega^2) \qquad (4)$$

Comparison of the 'static' hyperpolarizabilities $\beta(0) = \beta(-2\omega;\omega,\omega)F(\omega,\omega_{01})$ is then more relevant in terms of intrinsic NLO properties at the molecular level.

Dipole moments are measured separately, preferably in a non-polar solvent (dioxane), using a dipolemeter and applying the Hedestrand method.[12] Reproducibility was *ca.* ±3%.

Results are recorded in Table 1. Errors in the EFISH measurements are estimated to be ±7%, largely due to temperature fluctuations and solvent evaporation during materials handling. The derived β(0) are therefore reproducible within ±10%.

Theoretical Calculation of Molecular Properties.—The calculated ground state gas phase geometries of molecules **1**–**7** were optimized by the AM1 method[8] of the MOPAC package.[13] Starting conformations were constructed in the Sybyl modelling software.[14] Planar geometries were found. In the case of the 2,2′-bithienyl derivatives, the two rings adopt a transoid relationship, as expected. Both the hydrazono and dicyanovinyl groups can access either s-*cis* or s-*trans* conformations with respect the heterocycle S atom, as depicted in **I** and **II**. Thus for **5** and **6** four conformations are possible. For convenience, these are identified in Table 1 by means of the labels shown in **I** and **II**. In all cases, the s-*cis* conformations are slightly lower energy according to the AM1 calculations. Presumably in the s-*trans* conformations, the substituents suffer steric repulsion with the 3-CH of the thiophene rings. Ground state dipole moments were also calculated by AM1 and are recorded in Table 1. Hyperpolarizability values β(0) were calculated with the semiempirical CNDOVSB program[7] for all conformations of **1**–**7** corresponding to energy minima.


I s-*cis* **II** s-*trans*

X = $NNMe_2$ (D) or $C(CN)_2$ (A)

As in previous work, all 27 components of the quadratic hyperpolarizability tensor are calculated by the CNDOVSB method, though the most appropriate quantity is the vector component β theoretically defined in eqn. (5),[7] where β is

$$\beta = \beta_{\mu\mu\mu} + 1/3[\sum_{i \neq \mu}(\beta_{\mu ii} + \beta_{ii\mu})] \qquad (5)$$

aligned to lie along the direction of the molecular dipole moment, μ, and is directly related therefore to the value

Table 1 Experimental and theoretical data for molecules **1–7**

Molecule[a]	Experimental data[b]						Calculated data[c]		
	μ	λ_{max}	$\mu\beta(2\omega)$	$\mu\beta(0)$	$\beta(2\omega)$	$\beta(0)$	μ	$\beta(0)$	$\Delta_f H$
1[d]	6.9	388[e]	180	73	26	10	8.03	10	
2	7.31	442	190	93	26	13	8.22	11	
s-*cis*-Me$_2$NNCH-**3**	6.56	445	330	170	50	25	8.47	31	77.95
s-*trans*-Me$_2$NNCH-**3**							8.3	35	79.09
s-*cis*-CH=C(CN)$_2$-**4**							7.12	27	112.5
s-*trans*-CH=C(CN)$_2$-**4**							8.47	27	113.5
s-*cis*-Me$_2$NNCH,s-*cis*-CH=C(CN)$_2$-**5**	4.78	475	680	300	140	62	6.79	60	153.35
s-*cis*-Me$_2$NNCH,s-*trans*-CH=C(CN)$_2$-**5**							8.19	60	153.72
s-*trans*-Me$_2$NNCH,s-*cis*-CH=C(CN)$_2$-**5**							6.53	70	153.96
s-*trans*-Me$_2$NNCH,s-*trans*-CH=C(CN)$_2$-**5**							8.13	65	154.72
s-*cis*-Me$_2$NNCH,s-*cis*-CH=C(CN)$_2$-**6**	6.06	494	1650	640	270	100	7.55	116	181.61
s-*cis*-Me$_2$NNCH,s-*trans*-CH=C(CN)$_2$-**6**							8.43	104	182.51
s-*trans*-Me$_2$NNCH,s-*cis*-CH=C(CN)$_2$-**6**							7.71	120	182.6
s-*trans*-Me$_2$NNCH,s-*trans*-CH=C(CN)$_2$-**6**							7.98	115	183.36
7[f]	7.95	466[g]			318	54		47	

[a] Numbers refer to structures in text. [b] Dipole moment, μ (Debye); visible spectrum absorption maximum, λ_{max} (nm in methanol unless otherwise noted); first hyperpolarizability at second harmonic frequency and zero field, $\beta(2\omega)$ and $\beta(0)$, respectively (10^{-30} esu); product of dipole moment and first hyperpolarizability, $\mu\beta(2\omega)$ or $\mu\beta(0)$ (10^{-48} esu; acetone solution). [c] Dipole moment, μ (Debye) and heat of formation, $\Delta_f H$ (kcal mol^{-1}; 1 kcal = 4.18 kJ), calculated by AM1; first hyperpolarizability at zero field strength, $\beta(0)$ (10^{-30} esu), calculated by CNDOVSB. [d] Data from M. Barzoukas, D. Josse, J. Zyss, P. F. Gordon and J. O. Morley, *Chem. Phys.*, 1989, **139**, 359. EFISH measurements at ω = 1.06 µm. [e] Ethanol. [f] Data from ref. 5(*h*). EFISH measurements at ω = 1.06 µm. [g] Hexane.

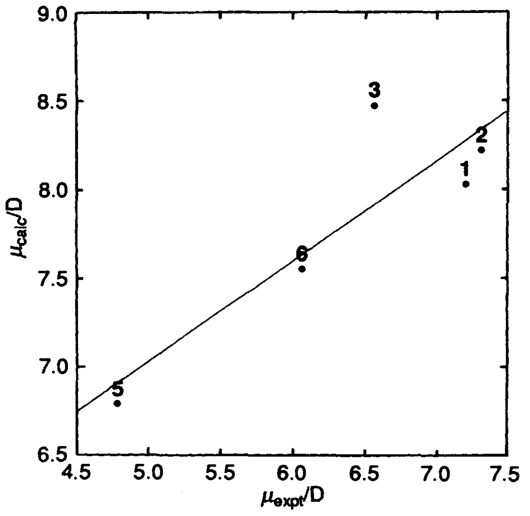


Fig. 1 Plot of calculated *versus* experimental dipole moments (μ/Debye). The straight line corresponds to μ(calc.) = 0.57 µ (expt.) + 4.2.

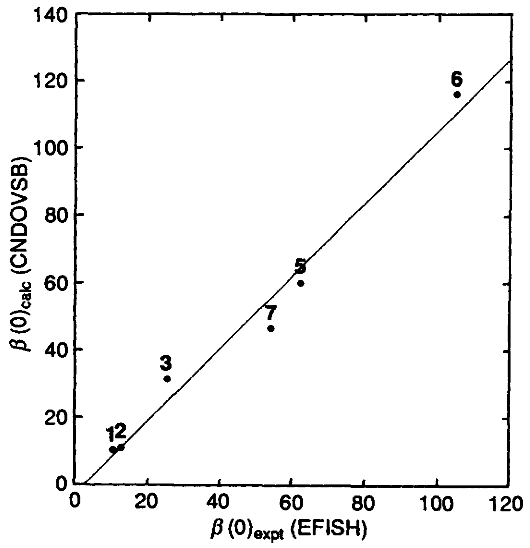


Fig. 2 Plot of calculated *versus* experimental zero field quadratic hyperpolarizabilities [$\beta(0)$; 10^{-30} esu]. The straight line corresponds to $\beta(0)$(calc.) = 1.08 $\beta(0)$(expt.) − 2.5.

obtained from the EFISH experiments. In addition to the frequency-dependent value, $\beta(\omega)$, a static value is also calculated in the absence of the applied frequency to give the quantity $\beta(0)$, free from dispersion enhancement—see above. $\beta(0)$ is an approximate measure of the intrinsic hyperpolarizability of a given molecular system and is used to compare the relative efficacy of one system *versus* another.

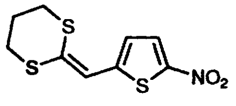
In general, the calculated ground state dipole moments are higher than the experimental values. However, the calculated values which correspond to the lowest energy conformations are most consistent with experiment. The pairs of values are shown plotted in Fig. 1.

The calculated $\beta(0)$ values for the lowest energy conformations are plotted against the experimental $\beta(0)$ values in Fig. 2. A good correlation is observed, indicating that the CNDOVSB program reproduces well experimental hyperpolarizabilities, and can be used predictively with confidence.

Structure–Property Relationships.—Four significant structure–property relationships derive from the results recorded in Table 1.

(*i*) Comparison of β for the *p*-nitroaniline **1** with the corresponding thiophene (**2**) reveals that thiophene provides a more efficient delocalization pathway than benzene. This is consistent with theoretical prediction (Table 1), as well as the intuitive arguments which preceded this work concerning a more easily delocalized π-system in thiophene.

(*ii*) Addition of the imine (–N=CH–) unit to the π-electron conjugating pathway to give hydrazone **3** results in a doubling of β with respect to the comparable dimethylaminothiophene (**2**). At the same time, the optical absorbance maximum is hardly altered. A third analogue with similar absorbance maximum (438 nm) is nitrothiophene **8**, where the donor is a ketene dithioacetal group.[5i] Although the β values are not reported for this compound, the $\mu\beta(0)$ product term is given as 150 × 10^{-48} esu. While this is appreciably higher than the corresponding term for its dimethylamino analogue **2**, it is still



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less than that measured for the dimethylhydrazone **3**. This increased NLO activity, combined with the synthetic ease with which the hydrazono group is introduced into the molecule, suggests that hydrazones could play a wider part as π-donor substituents in the search for higher activity quadratic NLO molecules and materials. Furthermore, it is easy to envisage functionalization of the *N*,*N*-dialkyl substituents to give molecules suitable for inclusion in polymer or Langmuir–Blodgett films. The only report we are aware of where a hydrazono group has been applied to NLO involves (di)nitrophenylhydrazine condensates with various aromatic aldehydes, studied as Langmuir–Blodgett films.[15] However, in these molecules, the hydrazone group is not acting as a simple donor group, as in **3**, **5** and **6**, but rather is part of a more complex chromophore.

(*iii*) Although not experimentally verified, calculation indicates that a corresponding increase in the conjugation pathlength by using dicyanovinyl as acceptor in **4** in place of nitro in **2** also leads to increased β. Others have already noted this improvement experimentally, in several pairs of comparable compounds.[5d,5f] Inclusion of both dicyanovinyl and hydrazono in thiophene **5** results in the expected even higher increase in β with respect to the 'standard' thiophene **2**, by a factor of about five. In the bithienyl series, the hydrazono-dicyanovinyl combination in **6** gives about twice as high β as dimethylamino-nitro in **7**.[5h]

(*iv*) Increasing the conjugation pathlength by this second thiophene group in **6**, compared with monothiophene **5**, gives a further increase in β. Moreover, this increase is proportionately greater than observed for biphenyl analogues. In the latter, the two phenylene rings are constrained by steric interactions to be non-planar, with a torsion angle of about 30°. Deviations from planarity in the bithienyl series are likely to be far less, as evidenced by our own theoretical calculations and X-ray crystal data[16] (although electron diffraction data suggests non-planarity in bithienyl in the gas phase[16]). This result confirms the earlier theoretical predictions of the calculations on thiophene and benzene oligomers.[3]

Overall, these results suggest that thiophenes of the type discussed here could find application in NLO materials. Their strong colour obviates use for SHG, where optical transparency in the technically important green and blue regions of the visible spectrum (400–530 nm) is necessary. However, this limitation does not apply to electro-optic applications such as optical modulation, which rely on the Pockels effect.[1] The combination of appreciable dipole moment as well as hyperpolarizability suggests that functionalized derivatives of these thiophene molecules could find application in electro-optic poled polymers. For example, the $\mu\beta$ value for **6** (637×10^{-48} esu) is significantly higher than that of the azobenzene CI Disperse Red 1 {4-[*N*-ethyl-*N*-(2-hydroxyethyl)amino]-4′-nitroazobenzene; 500×10^{-48} esu}. Derivatives of the latter are commonly used in poled polymer studies. Bithiophene **6** has the advantage of not being photochromic compared with the *cis–trans* photoisomerization possible for azobenzenes. Although the stabilities of the two chromophores are likely to be similar, it is noteworthy that **6** does not contain the reducible azo linkage which could be a significant detrimental feature in subsequent polymer formation and fabrication.

The optical non-linearities of the novel thiophenes discussed here are roughly proportional to λ_{max}, as are other thiophenes and comparable benzene derivatives (Fig. 3). If anything, benzenoid derivatives have marginally higher optical non-linearity than thiophene analogues [as reflected by the $\mu\beta(0)$ product] for a given optical absorption maximum.

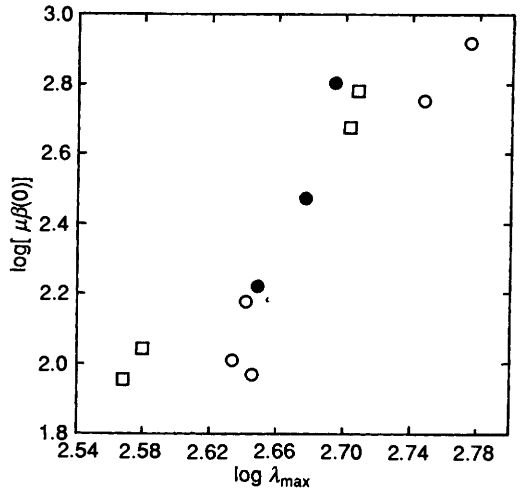

Fig. 3 Plot of $\mu\beta(0)$ *versus* λ_{max} for donor–acceptor substituted benzenes and thiophenes. Data from this study and references 5(*a*), 5(*d*) and 5(*i*). Thiophenes, ○; thiophenecarboxaldehyde dimethylhydrazones, ●; benzenes, □.

The yellow formylthiophene intermediate **10** has SHG activity 50 times that of urea in the Kurtz–Perry powder test.[17] Other aromatic aldehydes have also been noted to be relatively likely to be NLO active in their crystalline phases.[18] However, neither the bithienyl analogue **13** nor thiophenes **2**, **3**, **5** and **6** are SHG active as crystals. They therefore probably crystallize in centrosymmetric space groups. In order to include the active chromogens of these molecules in NLO active materials, further chemical modification would be necessary, *e.g.* for inclusion in materials based on Langmuir–Blodgett or poled polymer films.

The marked solvatochromism of molecule **7** has been noted.[5h] Like this molecule, the novel thiophenes in Table 1 are significantly solvatochromic. A full analysis of this solvatochromism will appear elsewhere.

Experimental

Solution Measurements.—Second-order polarizability measurements were performed using a Q-switched, mode-locked Nd^{3+}:YAG laser emitting at 1.34 µm by the EFISH method. The IR signal delivered by the laser cavity consisted of trains of short pulses separated by 10 ns from each other, the duration of the envelope being 12 ns and the repetition rate 10 Hz. The duration of each short pulse was 160 ps. A small part of the incident beam was split off and sent to a frequency-doubling *N*-(4-nitrophenyl)-L-prolinol (NPP) [(*S*)-(−)-1-(4-nitrophenyl)-pyrrolidine-2-methanol] powder reference, to divide out laser fluctuations. The other part of the beam was polarized vertically and focused into the electroded cell, the visible light being filtered out with a Schott RG1000 filter. The cell windows, in fused silica, formed a wedge of small angle. The active part of the solution was located between two electrodes set 2 mm apart, providing high voltage pulses (up to 10 kV and 2 µs duration) synchronized with the laser signal. The static electric field was oriented vertically. The cell was translated transversally using a stepping motor. The output beam was filtered and if necessary neutral densities were used. The second harmonic was then detected by a photomultiplier. Both second harmonic signals (from NPP and from the solution) were fed into a Boxcar, which takes the ratio of sample to reference signals. The signal was averaged and recorded as a function of time.

For each molecule, the experiment was performed using solutions of increasing concentrations in acetone. In all cases, absorption was found to be negligible at ω and 2ω. The visible light was filtered out and detected by a photomultiplier. The molecules were dissolved in acetone at various mass concentrations x and the solutions placed in a wedge-shaped cell. A high voltage pulse, synchronized with the laser pulse, broke the centrosymmetry of the liquid by dipolar orientation of the molecules. Translation of this cell perpendicular to the beam direction modulated the second harmonic signal into Maker fringes. The amplitude and periodicity of the fringing pattern are related to the macroscopic susceptibility $\Gamma(x)$ and to its coherence length $l_c(x)$. Calibrations were made with respect to the pure solvent. $\Gamma(x)$ is related to the microscopic hyperpolarizabilities of the solvent γ_s and of the dissolved molecule γ_c by eqn. (6); where ρ is the density of the solvent,

$$\Gamma(x) = Nf\rho(\gamma_s/M_s + x\gamma_c/M_c)/(1 + x) \qquad (6)$$

N is the Avogadro number, f the local field factor and M_s and M_c the molecular mass of the solvent and dissolved molecules, respectively.

Dipole moments are deduced from measurements of the dielectric constant (using a WTW DM 01 dipolemeter) and of the refractive index of solutions of increasing concentrations of the molecule.

Calculations.—Starting molecular geometries were based on structures of analogues present in the Cambridge Crystal Structure database and were built in the molecular modelling software Sybyl. These were optimized by the AM1 method, running on a Silicon Graphics work-station. Optimized structures were submitted to the CNDOVSB program for calculation of first hyperpolarizability values. Correlations and derived plots were generated in Statistica.

Synthesis.—BuLi was a commercial material, 2.5 mol dm^{-3} in hexane solvent. All reactions involving organolithium reagents were carried out under an atmosphere of dry nitrogen, in rigorously dried solvents. Standard work-up procedure was used unless otherwise stated and involved extraction into a solvent, separation, washing with water then brine, drying ($MgSO_4$) and solvent removal under reduced pressure to give crude product. Melting points are uncorrected. Yields quoted are unoptimized. Unless otherwise stated, NMR spectra were recorded in $CDCl_3$ solution at 250 MHz and are referenced to Me_4Si. The following were obtained commercially, or from the ICI/Zeneca specimen collection, or synthesized by standard literature routes: thiophene, 2,2′-bithiophene, 2-formylthiophene, 2-bromo-5-nitrothiophene, 5-nitrothiophene-2-carboxaldehyde.

2-Dimethylamino-5-nitrothiophene (**2**). 2-Bromo-5-nitrothiophene (2.08 g, 0.01 mol) was stirred at room temperature for 16 h in ethanolic dimethylamine (20 cm^3, 14 mol) and then evaporated to dryness. The residue was dissolved in chloroform, filtered through silica and evaporated. The residue was recrystallized from water containing 1% ethanol to give the product as needles (0.84 g, 49%) m.p. 134–136 °C (Found: C, 41.5; H, 4.7; N, 16.0; S, 18.3. $C_6H_8N_2O_2S$ requires C, 41.8; H, 4.65; N, 16.3; S, 18.6%); δ_H 3.04 (6 H, s), 5.79 (1 H, d) and 7.78 (1 H, d); *m/z* 172 (M^+); λ_{max}(methanol)/nm 441.

5-Nitrothiophene-2-carboxaldehyde dimethylhydrazone (**3**). A mixture of 5-nitrothiophene-2-carboxaldehyde (3.14 g, 0.02 mol), 1,1-dimethylhydrazine (1.32 g, 0.022 mol) and ethanol (25 cm^3) was refluxed for 2 h. The reaction mixture was cooled, the resulting solid was filtered and washed with ethanol to give crude product (3.05 g) which was recrystallized from toluene to give **3** as a red solid (1.03 g, 26%), m.p. 119–120 °C (Found: C, 42.2; H, 4.5; N, 21.1; S, 16.1. $C_7H_9N_3O_2S$ requires C, 42.3; H, 4.6; N, 21.2; S, 15.9%); δ_H 3.06 (6 H, s), 6.78 (1 H, d), 7.11 (1 H, s) and 7.78 (1 H, d); *m/z* 199 (M^+); λ_{max}(methanol)/nm 443.

Thiophene-2-carboxaldehyde dimethylhydrazone (**9**). Thiophene-2-carboxaldehyde (22.4 g, 0.2 mol) was refluxed for 6 h in an ethanol (200 cm^3) solution of 1,1-dimethylhydrazine (12.0 g, 0.2 mol), hydrochloric acid (2 cm^3) and acetic acid (2 cm^3). The reaction mixture was then evaporated to dryness to give a brown oil which was purified by distillation under reduced pressure to give the title compound as a yellow oil (22.95 g, 75%), b.p. 135–144 °C/19–26 mmHg; δ_H 2.8 (6 H, s), 6.8–7.1 (3 H, m) and 7.35 (1 H, s). This impure material was used without further purification.

5-Formylthiophene-2-carboxaldehyde dimethylhydrazone (**10**). BuLi (0.05 mol) was added dropwise over 30 min at −70 to −65 °C to a solution of dimethylhydrazone **9** (7.7 g, 0.05 mol) in THF (80 cm^3) and stirred at this temperature for 1 h. A solution of DMF (5.8 cm^3, 0.075 mol) in THF (20 cm^3) was added and the temperature was maintained at −50 to −70 °C for 20 min before warming to room temperature. The reaction mixture was then drowned into ice–water (200 cm^3) which contained concentrated hydrochloric acid (20 cm^3). The mixture was filtered and a NaOH solution was added to the filtrates until the solution was faintly alkaline. This was then worked up to give crude product which recrystallized from a mixture of toluene and light petroleum to give the title compound in the form of yellow needles (3.0 g, 33%), m.p. 99–100 °C (Found: C, 53.2; H, 5.8; N, 15.3; S, 17.6. $C_8H_{10}N_2S$ requires C, 52.7; H, 5.5; N, 15.4; S, 17.6%); δ_H 3.28 (6 H, s), 7.05 (1 H, d), 7.27 (1 H, s), 7.65 (1 H, d) and 9.87 (1 H, s); *m/z* 182 (M^+); λ_{max}(chloroform)/nm 390.

5-Dicyanovinylthiophene-2-carboxaldehyde dimethylhydrazone (**5**). Dimethylhydrazone **10** (1.36 g, 0.0075 mol), ammonium acetate (0.1 g) and malononitrile (0.5 g, 0.0075 mol) were refluxed for 1 h in methanol (25 cm^3). The red solution on cooling, filtration and drying under vacuum at 50 °C gave a pure sample of the title compound (1.68 g, 97%), m.p. 193–195 °C (Found: C, 57.2; H, 4.3; N, 24.2; S, 13.4. $C_{10}H_{10}N_4S$ requires C, 57.4; H, 4.4; N, 24.3; S, 13.9%); δ_H 3.09 (6 H, s), 7.0 (1 H, d), 7.2 (1 H, s), 7.6 (1 H, d) and 7.7 (1 H, s); ν_{max}(KBr disc)/cm^{-1} 2215 and 2207; *m/z* 312 (M^+); λ_{max}(methanol)/nm 472.

2,2′-Bithiophene-5-carboxaldehyde (**11**). Toluene (250 cm^3) was azeotroped dry for 1.5 h and cooled to 50 °C and 2,2′-bithiophene (26.09 g, 0.157 mol) and dry DMF (14.57 cm^3, 0.188 mol) were added. $POCl_3$ (15.23 cm^3, 0.172 mol) was then added dropwise during 45 min. The temperature was raised and maintained at 75 °C for 1 h and then stirred for 16 h at room temperature. The orange coloured reaction mixture was added to a saturated NaOAc solution (200 cm^3) and stirred for 0.5 h with ether (400 cm^3). Work-up yielded a crude product (28.02 g) as a brown oil which solidified on cooling. This was then extracted with hexane and the yellow solid was filtered off (13.89 g). This was then recrystallized from methanol–water (8 : 1). Further work-up of mother liquors gave more product as a yellow solid (18.52 g, 61%), m.p. 54.5–56.5 °C (lit.,[19] 58–59 °C) (Found: C, 55.0; H, 3.1; S, 33.1. $C_9H_6OS_2$ requires C, 55.7; H, 3.1; S, 33.0%); δ_H 7.04–7.1 (2 H, m), 7.22–7.46 (3 H, m), 7.68–7.76 (1 H, d) and 9.94 (1 H, s); *m/z* 194 (M^+).

2,2′-Bithiophene-5-carboxaldehyde dimethylhydrazone (**12**). Aldehyde **11** (6.79 g, 0.035 mol) and 1,1-dimethylhydrazine (3.15 cm^3; 2.49 g, 0.035 mol) in methanol (50 cm^3) was refluxed for 3 h. The reaction mixture was cooled to < 5 °C and a small amount of insoluble material was filtered off (0.44 g). The filtrate was then evaporated and the residue was purified by flash chromatography (silica; diethyl ether–hexane gradient). The product was isolated as a yellow oil (7.1 g, 85%) (Found: C, 56.3; H, 5.3; N, 11.9; S, 28.9. $C_{11}H_{12}N_2S$ requires C, 55.9; H, 5.1;

N, 11.8; S, 27.1%). The material was used without further purification.

5′-Formyl-2,2′-bithiophene-5-carboxaldehyde dimethylhydrazone (**13**). BuLi (9.3 cm^3, 0.023 mol) was added dropwise over 10 min to a solution of diisopropylamine (2.35 g, 0.023 mol) in THF (100 cm^3) at −60 to −70 °C and the temperature was maintained at −70 °C for 30 min. A solution of hydrazone **12** (5.0 g, 0.02 mol) in THF (25 cm^3) was added over 10 min at −70 °C to the above mixture and maintained at −70 °C for 1 h. Anhydrous DMF (3.1 g, 0.042 mol) was then added and the reaction mixture was stirred between −70 and −50 °C for 1 h and then allowed to warm to room temp. The mixture was drowned into water (400 cm^3) containing concentrated HCl (20 cm^3) and then concentrated to give a solid precipitate which was dissolved in diethyl ether–dichloromethane and the two-phase mixture was separated. Standard work-up afforded crude product which was purified by flash chromatography (silica; diethyl ether–hexane gradient plus final wash-off with EtOAc) to yield a solid which was recrystallized from methanol to give the title compound (2.92 g, 53%), m.p. 122–124 °C (Found: C, 54.5; H, 4.5; N, 10.5; S, 23.7. $C_{12}H_{12}N_2OS_2$ requires C, 54.5; H, 4.5; N, 10.6; S, 24.2%); ν_{max}(KBr disc)/cm^{-1} 1656; δ_H 3.1 (6 H, s), 6.9 (1 H, d), 7.23–7.35 (3 H, m), 7.7 (1 H, d) and 9.9 (1 H, s); m/z 264 (M$^+$).

5′-Dicyanovinyl-2,2′-bithiophene-5-carboxaldehyde dimethylhydrazone (**6**). Dimethylhydrazone **13** (1.32 g, 0.005 mol), malononitrile (0.36 g, 0.0055 mol) and ammonium acetate (0.1 g) were refluxed for 3 h in methanol (30 cm^3). The deep-red solution was cooled, filtered and dried to yield a crude product which was recrystallized from toluene (1.04 g, 67%), m.p. 212–214 °C (Found: C, 57.8; H, 4.0; N, 17.9; S, 19.8. $C_{15}H_{12}N_4S_2$ requires C, 57.7; H, 3.9; N, 17.9; S, 20.5%); δ_H 2.9 (6 H, s), 7.09 (1 H, d), 7.45 (1 H, s), 7.52 (2 H, d), 7.89 (1 H, d) and 8.5 (1 H, s); ν_{max}(KBr disc)/cm^{-1} 2217 and 2206; λ_{max}(chloroform)/nm 514; (methanol) 492; m/z 312 (M$^+$), isotopic evidence for two sulfur atoms.

Acknowledgements

We thank Simon Allen (ICI Wilton Materials Centre) for powder SHG measurements. This collaboration was supported by funding from ESPRIT Project 2284, Optoelectronics with Active Organic Molecules.

References

1 P. N. Prasad and D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley, New York, 1991; D. S. Chemla and J. Zyss, eds., *Nonlinear Optical Properties of Organic Molecules and Crystals*, vols. 1 and 2, Academic Press, London, 1987; J. Zyss, ed., *Molecular Nonlinear Optics*, Academic Press, 1994.

2 C. W. Bird and G. W. H. Cheeseman, in *Comprehensive Heterocyclic Chemistry*, vol. 4, Pergamon Press, 1984, pp. 28–30.

3 J. O. Morley, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 3009.

4 See, *e.g.*, M.-T. Zhao, B. P. Singh and P. N. Prasad, *J. Chem. Phys.*, 1988, **89**, 5535; D. Fichou, F. Garnier, F. Charra, F. Kajzar and J. Messier, in *Spec. Publ. R. Soc. Chem.* (*Org. Mater. Nonlinear Opt.*), 1989, **69**, 176; H. Thienpont, G. L. J. A. Rikken, E. W. Meijer, W. ten Hoeve and H. Wynberg, *Phys. Rev. Letters*, 1990, **65**, 2141; C. Taliani, A. J. Pal, G. Ruani, R. Zamboni, R. R. Alfano, R. Dorsinville and L. Yang, in SPIE vol. 1599, *Recent Advances in the Uses of Light in Physics, Chemistry, Engineering and Medicine*, 1991, pp. 24–33.

5 (*a*) G. Mignani, F. Leising, R. Meyrueix and H. Samson, *Tetrahedron Lett.*, 1990, **31**, 4743; (*b*) L. Derhaeg, C. Samyn and A. Persoons, in *Organic Molecules for Nonlinear Optics and Photonics*, eds. J. Messier, F. Kajzar and P. Prasad, Kluwer Academic Publishers, 1991, pp. 177–183; (*c*) M. Matsuoka, M. Furukawa, M. Takao, T. Kitao, M. Hamada and K. Nakatsu, *Chem. Lett.*, 1991, 289; (*d*) A. K.-Y. Jen, V. P. Rao, K. Y. Wong and K. J. Drost, *J. Chem. Soc., Chem. Commun.*, 1993, 90; (*e*) V. P. Rao, A. K.-Y. Jen, K. Y. Wong and K. J. Drost, *J. Chem. Soc., Chem. Commun.*, 1993, 1118; (*f*) V. P. Rao, A. K.-Y. Jen, K. Y. Wong and K. J. Drost, *Tetrahedron Lett.*, 1993, **34**, 1747; (*g*) K. J. Drost, V. P. Rao and A. K.-Y. Jen, *J. Chem. Soc., Chem. Commun.*, 1994, 369; (*h*) F. Effenberger and F. Würthner, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 719; (*i*) V. P. Rao, Y. M. Cai and A. K.-Y. Jen, *J. Chem. Soc., Chem. Commun.*, 1994, 1689; (*j*) A. K.-Y. Jen, V. P. Rao, K. J. Drost, K. Y. Wong and M. P. Cava, *J. Chem. Soc., Chem. Commun.*, 1994, 2057.

6 M. G. Hutchings, D. P. Devonald, I. Ferguson, K. Moody, F. Kajzar, J. Messier and C. Sentein, *Chemtronics*, 1991, **5**, 111.

7 V. J. Docherty, D. Pugh and J. O. Morley, *J. Chem. Soc., Faraday Trans. 2*, 1985, **81**, 1179.

8 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.

9 J.-L. Oudar, *J. Chem. Phys.*, 1977, **67**, 446.

10 B. F. Levine and C. G. Bethea, *J. Chem. Phys.*, 1975, **63**, 266.

11 I. Ledoux and J. Zyss, *Chem. Phys.*, 1982, **73**, 203.

12 G. Hedestrand, *Z. Phys. Chem. B*, 1929, **2**, 428.

13 QCPE Program 455 Version 6.0, Department of Chemistry, Indiana University, Bloomington, IN 47405, USA.

14 Sybyl version 6.0 (1992), Tripos Associates Inc., 1699 S. Hanley Road, St. Louis, MO, 63144-2913, USA.

15 D. Lupo, W. Prass, U. Scheunemann, A. Laschewsky, H. Ringsdorf and I. Ledoux, *J. Opt. Soc. Am. B*, 1988, **5**, 300.

16 See ref. 2, p. 32.

17 S. K. Kurtz and T. T. Perry, *J. Appl. Phys.*, 1968, **39**, 3798.

18 M. G. Hutchings, I. Ferguson, S. Allen and J. E. Shearman, *Nonlinear Optics*, 1994, **7**, 157.

19 R. F. Curtis and G. T. Phillips, *Tetrahedron*, 1967, **23**, 4419.

Paper 4/04976D
Received 15*th August* 1994
Accepted 7*th October* 1994