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Novel, highly polarizable thiophene derivatives for use in nonlinear optical applications

Alexander J. Seed Corresponding author[a]; Gregory J. Cross[a]; Kenneth J. Toyne[a]; John W. Goodby[a]
[a] Department of Chemistry, The University, Hull HU6 7RX, UK

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Novel, highly polarizable thiophene derivatives for use in nonlinear optical applications

ALEXANDER J. SEED*, GREGORY J. CROSS, KENNETH J. TOYNE and JOHN W. GOODBY

Department of Chemistry, The University, Cottingham Road, Hull HU6 7RX, UK

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The synthesis of a variety of thiophene-containing materials for use in electro-optic devices requiring highly birefringent materials is reported. The refractive indices were measured with the use of an Abbé refractometer, and from these results the optical anisotropies, polarizabilities and order parameters were determined. The replacement of a phenyl ring by thiophene leads to large enhancements of polarizability. The most significant increases in polarizability anisotropy were observed when the rigid core was a collinear 5,5′-disubstituted-2,2′-dithienyl unit. The changes in the optical properties are discussed in terms of the structural units (thiophene, phenyl, isothiocyanate, nitrile, butylsulfanyl, alkoxy and alkyl moieties) used and their positions with respect to the molecular core.

1. Introduction

For a number of years we have been concerned with establishing relationships between mesogenic structure and the magnitude of the polarizability anisotropy in order to both control and optimize the optical properties of nematic materials for various electro-optic and optoelectronic applications. This work is particularly important in relation to the design of materials for second and third harmonic generation, all-optical switches, holography, ferroelectrics, and antiferroelectrics.

The formulation of liquid crystalline mixtures for displays requires that the mixtures have specific, well defined physical properties such as mesophase range, viscosity, dielectric constants, elastic constants and switching speed. The birefringence [1] is another important physical property that may be tuned by the addition of materials with a high optical anisotropy. In synthesizing such materials we are often confronted by issues such as high melting point and low solubility which are compromised as the birefringence of materials is increased. Colour can also become problematic as materials with large values of birefringence are highly conjugated and absorptions shift toward the visible region with increasing molecular π-conjugation.

In recent studies [2, 3] we have shown that the incorporation of thiophene into the molecular core can substantially increase the optical anisotropy and still provide molecules with relatively low melting points. In this paper we further extend these studies and show that small molecules containing the 5,5′-disubstituted-2,2′-dithienyl unit can be synthesized with exceptionally high values of polarizability and still have very low melting points. An evaluation of the new alkylselanyl moiety is also given with the synthesis of compound **43**.

*Author for correspondence. Present address: Department of Chemistry, Kent State University, Kent, OHIO 44242-0001, USA; e-mail: aseed@kent.edu

2. Experimental

2.1. *Characterization*

^{1}HNMR and ^{13}CNMR spectra were obtained using a JEOL GX NM270 FT NMR spectrometer with tetramethylsilane as internal standard. Infrared spectra were recorded using a Perkin-Elmer 783 spectrometer and mass spectra were recorded using a Finnigan-MAT 1020 GC-MS spectrometer. Ultraviolet spectra were recorded using a Philips PU8720 spectrometer with cyclohexane as solvent (only the major absorption bands are reported).

Thin layer chromatographic analyses were performed using aluminum-backed silica gel plates (Merck 60 F254) and were examined under ultraviolet light. Column chromatography was performed using May and Baker Sorbsil C60 40–60H micron silica gel. The purity of all final products was assessed by HPLC using a Merck–Hitachi HPLC chromatogram incorporating a D6000 interface, a D4000 UV detector (set at 254 nm) and an L6200A Intelligent Pump in conjunction with a Commodore 286 data station. Both normal- and

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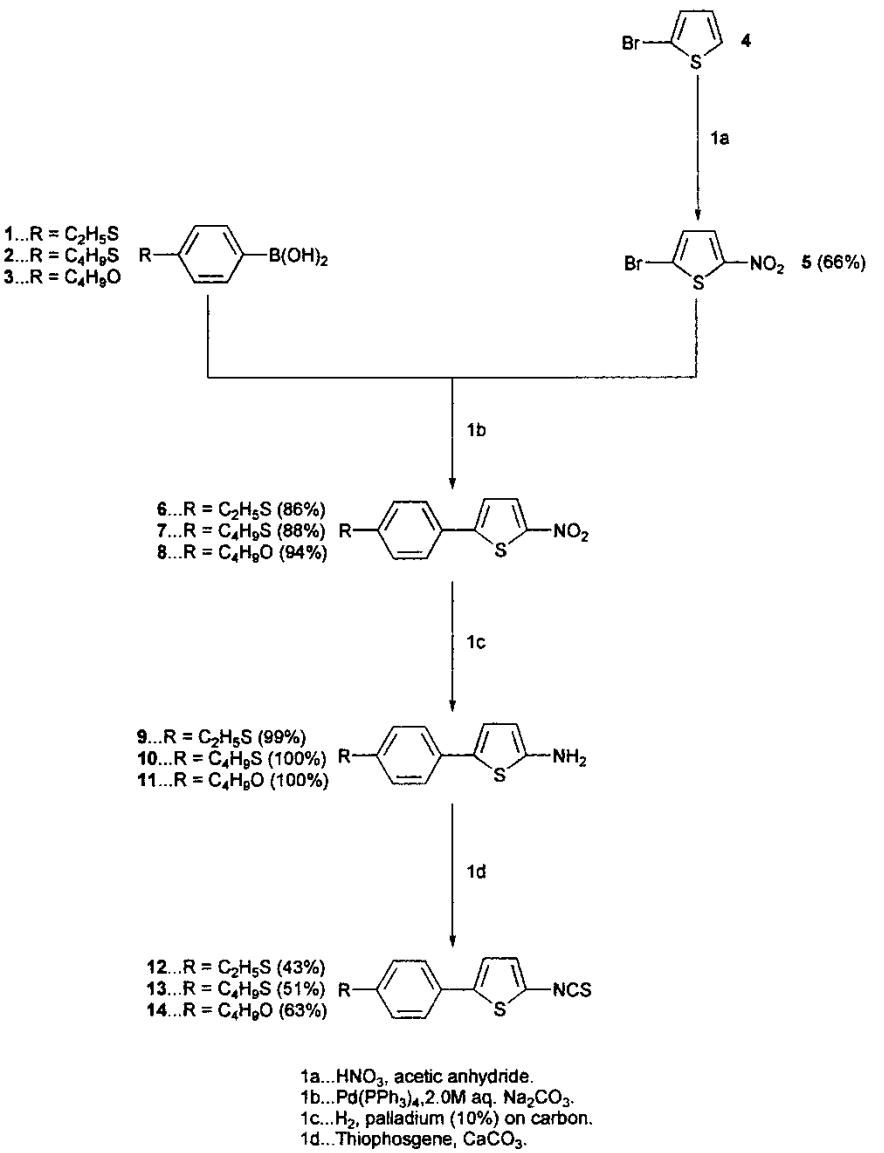
reversed-phase techniques were used with Microsorb Si and C18 columns (the column dimensions were 250 mm × 0.46 mm). Gas chromatography was carried out using a Perkin-Elmer 8320 capillary gas chromatograph equipped with a QC2/BP1-1.0 SGE (12 m) capillary column and flame ionization detector.

The melting points and transition temperatures of the final products (**12**, **13**, **14**, **20**, **24**, **29**, **38**, **43**, **44**, **46**, **49** and **50**) were determined by optical microscopy using a Mettler FP52 heating stage and FP5 temperature control unit in conjunction with an Olympus BH-2 polarizing microscope. Confirmation of the transition temperatures was carried out using differential scanning calorimetry (Perkin-Elmer DSC7 and IBM data station). The heating and cooling rates were $10^{\circ}C\,min^{-1}$ and indium was used for calibration purposes. The virtual $T_{N\text{-}I}$ values of final compounds (none of the compounds exhibited the nematic phase) were determined by the following procedure. Four binary mixtures of known composition (5–47% depending upon the solubility) of the material and a standard nematic host material (E7; Merck UK, Poole, England) of known $T_{N\text{-}I}$ value (60°C) were prepared and the $T_{N\text{-}I}$ transition of each composition was determined by optical microscopy. The $T_{N\text{-}I}$ value for each composition was extrapolated to 100% for the compound being examined using a linear regression computer program which gave an error of $\pm 7^{\circ}C$.



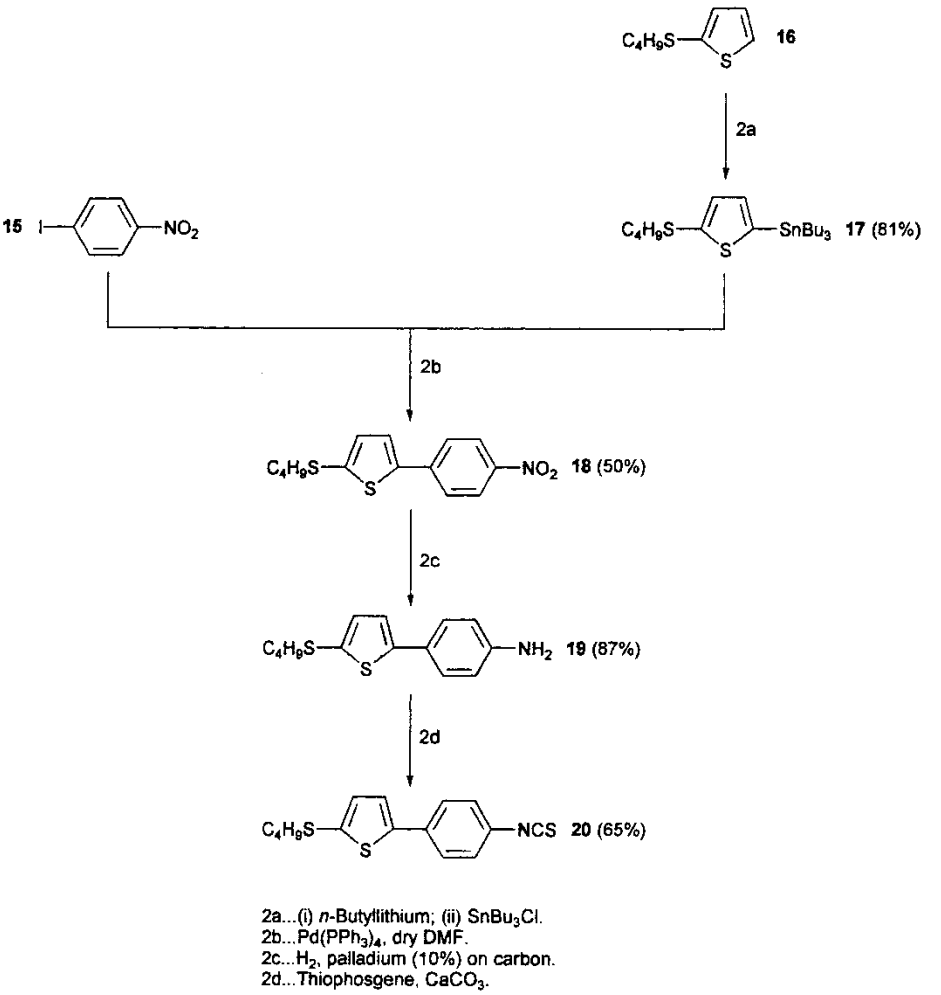
Scheme 1.

The refractive indices of the final compounds (accurate to ± 0.01) were measured using an Abbé refractometer (model 60/HR) at 589 nm (D1 sodium line) in conjunction with a Haake Q silicone oil (Dow-Corning 200/10 CS) bath and Haake F3 temperature control unit as described in a previous paper [4]. The polarizabilities and order parameters were calculated as described in [4] and the associated errors for the polarizabilities and order parameters were ± 1.56 and ± 0.10 respectively.

2.2. *Synthesis*

The nitration of bromothiophene **4** (scheme 1) was carried out using a modification of the method reported by Babasinian [5]. Phenylthienyl compounds **6**, **7** and **8** were synthesized by palladium-catalysed Suzuki cross-coupling [6–10] of the nitrobromothiophene **5** with phenylboronic acids **1**, **2** and **3**, respectively. Biaryl compounds **27** (scheme 4), **36** (scheme 5), **44** (scheme 7), **49** and **50** (scheme 9) were synthesized using the same methodology. Cross-coupling of arylamines and of arylisothiocyanates was avoided due to known complications [11, 12].

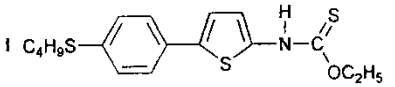
Boronic acid precursors **26** (scheme 4) and **34** (scheme 5) were obtained from appropriate aryl bromides *via* halogen metal exchange (*n*-butyllithium) [13, 14], reaction with trimethyl borate and hydrolysis of the resulting borate esters. Boronic acid **34** turned black upon prolonged storage (>1 week); however, ^{1}H NMR analysis of the boronic acid (and other thienyl boronic acids) revealed that the chemical identity of the material had not changed. The blackened boronic acid was used successfully in subsequent palladium-catalysed cross-coupling reactions. Catalytic hydrogenation of nitro derivatives **6**–**8** gave amines **9**–**11**, respectively, in excellent yields. Because of the anticipated toxicity of these materials, they were not purified at this stage. Amines **19** (scheme 2), **23** (scheme 3), **28** (scheme 4) and **37** (scheme 5) were prepared using the same methodology.



Scheme 2.

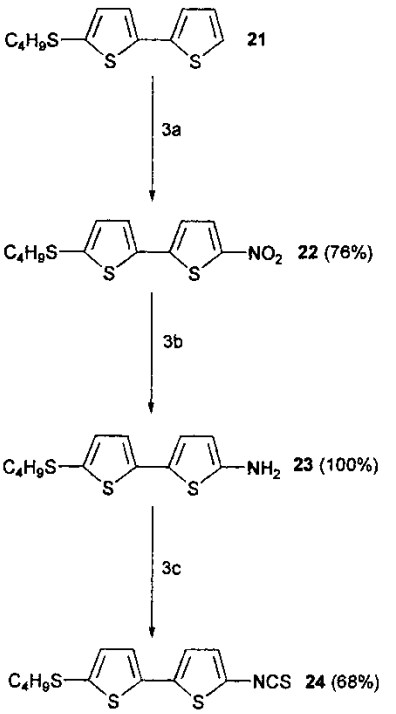
Isothiocyanates **12**–**14** were synthesized from amines **9**–**11**, respectively, using the procedure reported by Dabrowski *et al.* [15]. It was noted that strict temperature control was critical during the addition of the amine; the temperature must be maintained in the range 2–5°C to obtain optimum yields. Isothiocyanates **20** (scheme 2), **24** (scheme 3), **29**(scheme 4) and **38** (scheme 5) were prepared using the same methodology.

During purification of thienylisothiocyanate **13** the compound was crystallized from ethanol. Nucleophilic attack of the solvent at the NCS carbon was observed giving rise to thiocarbamic acid ester **I** (see below). This reaction highlights the electron-withdrawing power of the adjacent thiophene ring which is clearly enhancing the electrophilic character of the NCS carbon. This chemistry is not altogether unexpected and is analogous to the chemistry of isocyanates that are known to react with alcohols to give *N*-carbamates (urethanes). Thiocarbamic acid esters have also been formed when attempting to crystallize 2,3-difluorophenylisothiocyanate derivatives from ethanol [16]. Crystallization of phenylisothiocyanates **20** (scheme 2) and **38** (scheme 5) using the same solvent gave no such reaction.



Cross-coupling of thienylboronic acids under Suzuki conditions is somewhat controversial and has given rise to conflicting results. Independent reports by Seed [2] and others [17] have shown that thienylboronic acids may be coupled in high yields with aryl halides under Suzuki conditions. However, this type of reaction is somewhat unpredictable and in general results in a substantial amount of protodeboronation [18] during the coupling procedure [19]. This is not unexpected, as protodeboronation is facilitated by the electron-withdrawing nature of the sulphur atom in the thiophene ring. In this work we usually chose to use Stille coupling when the metal was required to be situated on the thiophene unit. The Stille methodology avoided the above problems and gave cross-coupled products in good yields. An alternative methodology has recently been reported in the synthesis of aryl–thienyl units, that involves the use of zinc derivatives in place of tin [20]. Such a pathway clearly avoids the use of toxic tin reagents and additional isolation of the metal derivative is avoided in favour of *in situ* coupling. Matharu *et al.* have also described an efficient nickel-catalysed cross-coupling methodology using arylmagnesium halides [21].

Tributylstannylthiophene precursor **17** (scheme 2) was obtained *via* deprotonation of thiophene **16** using *n*-butyllithium and subsequent reaction with tributyltin chloride [13, 14]. Tributyltin derivative **41** (scheme 6) was prepared in a similar manner although LDA was used to deprotonate the thiophene precursor **40**. This modification was found to be essential, as use of the nucleophilic *n*-butyllithium resulted in competitive nucleophilic attack at the selenium and subsequent cleavage of the alkylselanyl chain. Tin derivative **17** was subjected to Stille coupling [22] to give biaryl **18** (scheme 2). Biaryls **43** (scheme 6) and **46** (scheme 8) were obtained using identical Stille coupling.

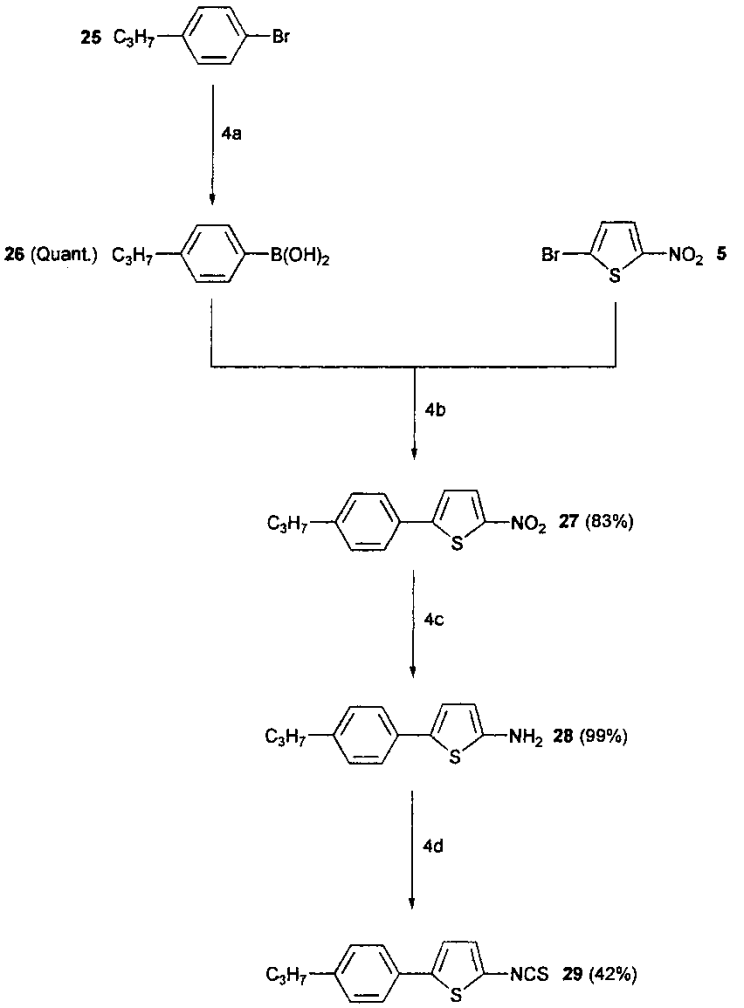


3a...HNO_3, acetic anhydride.
3b...H_2, palladium (10%) on carbon.
3c...Thiophosgene, $CaCO_3$.

Scheme 3.

Acylthiophene **31** (scheme 5) was prepared by standard Friedel–Crafts reaction using propanoic anhydride as the electrophile. Wolff–Kishner reduction [23] of **31** gave alkylthiophene **32** which was then brominated exclusively in the 5-position using NBS [24]. Alkylation of thiophenes may also be effected on a limited scale by deprotonating the heterocycle with *n*-butyllithium and subsequent reaction with an appropriate alkyl bromide/iodide [13, 25].

Selenol **39** (scheme 6) was prepared by reaction of the Grignard derivative of bromothiophene **4** with grey selenium followed by acidification of the resulting selenate. Alkylation of selenol **39** using 1-bromobutane and sodium ethoxide as base [4], gave butylselanylthiophene **40** in excellent yield.



Scheme 4.

3. Results and discussion

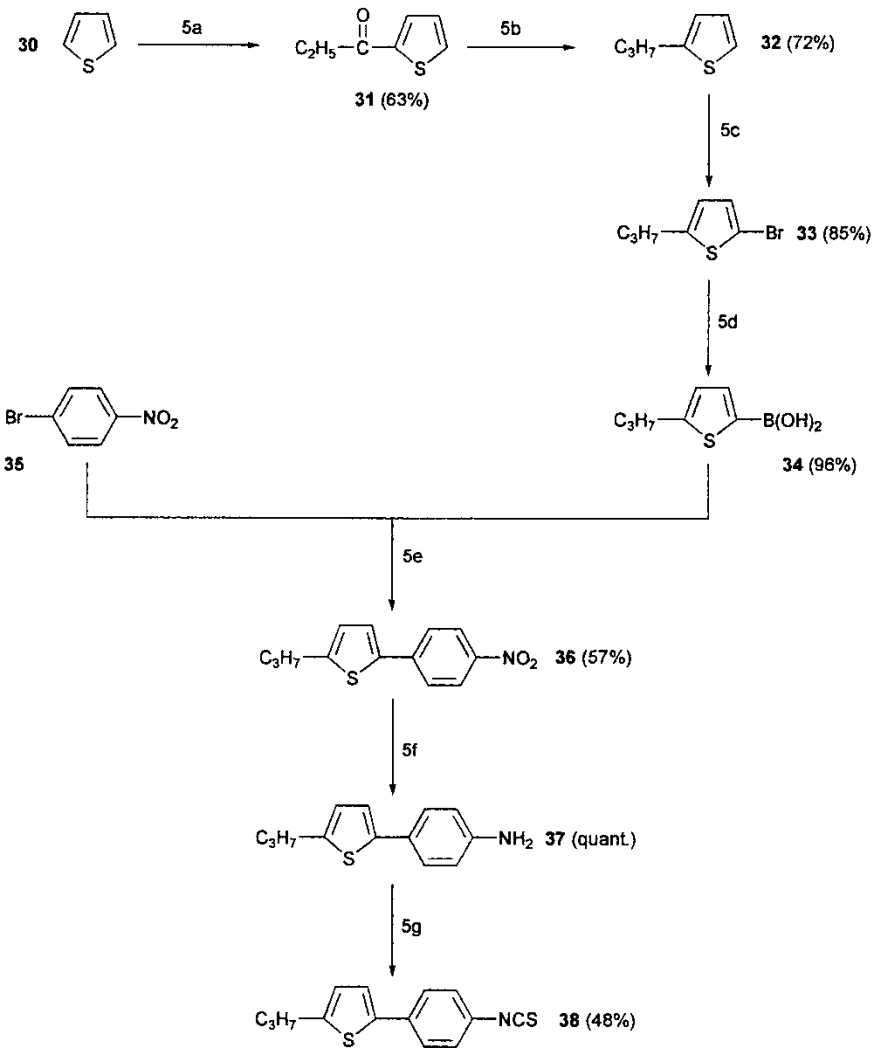
3.1. *Melting points and transition temperatures*

The melting points and transition temperatures of the final products **12**–**14**, **20**, **24**, **29**, **38**, **43**, **44**, **46**, **49** and **50** are given in table 1, and those of literature compounds **51**–**56** [2, 11] are given in table 2.

None of the final products has a nematic phase and virtual values were instead recorded from mixtures in E7. In most studies found in the liquid crystal literature it has been shown that the replacement of a phenyl ring with a 2,5-disubstituted thiophene leads to a reduction in the melting point. In this current study the prediction of melting point is not clear, as exemplified by thiophene-based compounds **13** and **12** which have melting points 3.9°C lower and 14.4°C higher than the parent biphenyl compounds **55** and **56**, respectively. It is of note that the collinear dithienyl compounds **43** and **46** are very low melting and **24** is an oil.

The replacement of an alkoxy with an alkylsulphanyl terminal chain results in a reduction of the melting point of 6.7°C (compare **14** and **13**, respectively). This trend is in accord with all previous work that we have performed on alkylsulfanyl systems [2, 11, 26]. The combination of consistently lower melting points and enhanced polarizabilities (relative to the alkoxy analogues) has made this chain extremely useful in the synthesis of relatively high birefringence materials.

Symmetrical dicyano compound **49** is very high



Scheme 5.

melting and is insoluble in E7. An attempt to lower the melting point and increase the solubility of this type of material was made by introducing a 'bent' 2,5-disubstituted thiophene in place of a phenyl ring (**50**). A reduction in the melting point of 26.2°C was noted although **50** was still insoluble in E7.

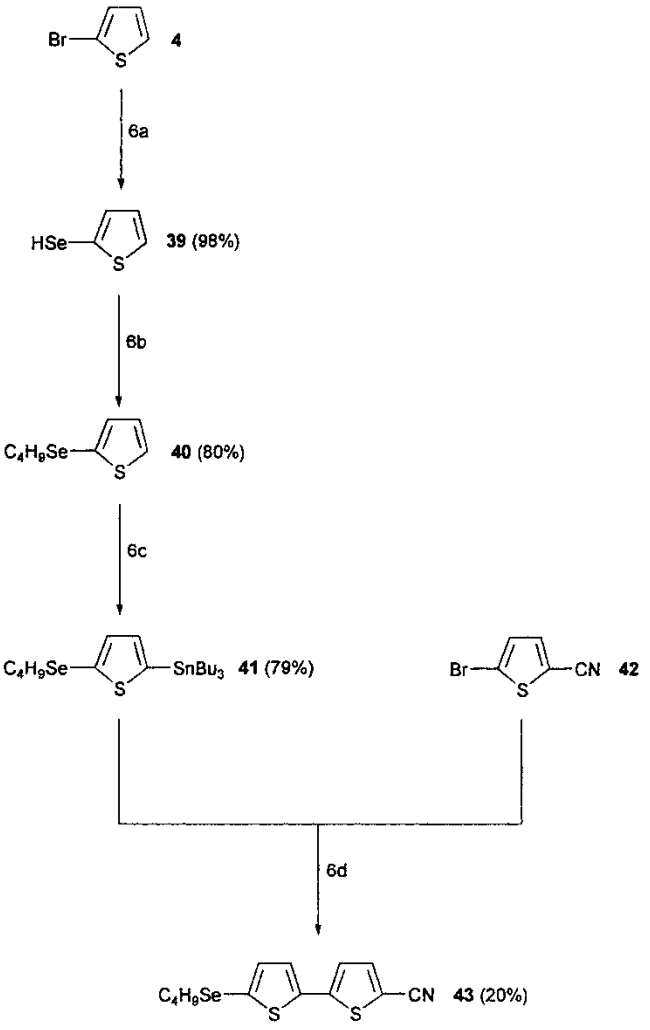
Isothiocyanates **12**–**14**, **29** and **38** possess short temperature range crystal B phases which are formed on cooling from the isotropic liquid. The identity of this phase was made by the observation of the formation of 'twins', crystallites, and platelet mosaics on cooling from the isotropic liquid.

3.2. *Refractive indices, optical anisotropies, polarizabilities and order parameters*

3.2.1. *Polarizabilities*

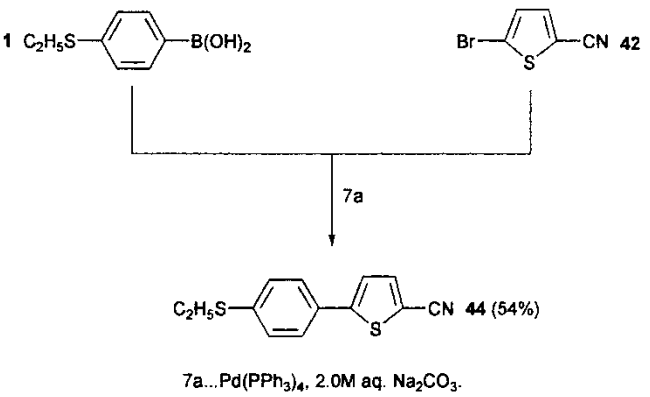
The refractive indices ($n_{\parallel}$ and $n_{\perp}$), optical anisotropies (Δn), polarizabilities ($\Delta\alpha$) and order parameters (S) for the final products **12**–**14**, **20**, **24**, **29**, **38**, **43**, **44** and **46** are given in table 3. Analogous physical properties for literature materials **51**–**56** are given in table 4 [2, 27].

The values for optical anisotropy, polarizability and order parameter at 25°C are important factors for determination of the performance of a particular material in



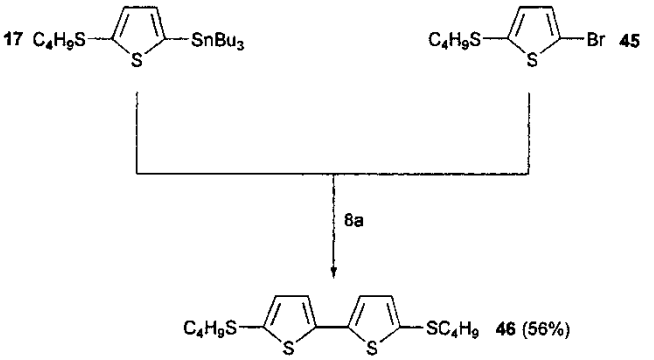
6a...(i) Mg; (ii) grey selenium; (iii) conc. HCl.
6b...1-Bromobutane, NaOEt.
6c...(i) Lithium diisopropylamide; (ii) tributyltin chloride.
6d...$Pd(PPh_3)_4$, dry DMF.

Scheme 6.



7a...$Pd(PPh_3)_4$, 2.0M aq. Na_2CO_3.

Scheme 7.



8a...$Pd(PPh_3)_4$, dry DMF.

Scheme 8.

a device at ambient temperature. However, the following discussion of the physical properties is given with reference to a fixed reduced temperature that takes into account the $T_{N\text{-}I}$ values of the individual compounds.

The trends in refractive indices, and hence the optical anisotropies, are not always obvious. Since the refractive indices are dependent upon both the molecular polarizability and the order parameter, these factors will first be discussed in order to rationalize the observed refractive index measurements.

Replacement of a butoxy with a butylsulphanyl chain (compare compounds **14** and **13**, respectively) results in an increase in the polarizability of 5.07. Similarly, the replacement of a butylsulphanyl chain with a butylselanyl chain (compare **53** and **43**, respectively) results in an increase in polarizability of 6.10. Both of these results are in accord with the increasing polarizability of the heteroatom; static average electric dipole polarizabilities (units of $10^{-24}\,cm^3$) for oxygen, sulfur and selenium are 0.802, 2.90 and 3.77, respectively [28].

Increasing the alkylsulphanyl terminal chain length from 2 to 4 carbon atoms always results in a decrease in polarizability due to the dilution effect of the low polarizability saturated hydrocarbon units; compare isothiocyanates **13** (C4, $\Delta\alpha = 33.23$) and **12** (C2, $\Delta\alpha = 33.85$) and compare nitriles **52** (C4, $\Delta\alpha = 24.10$) and **44** (C2, $\Delta\alpha = 26.52$) [11]. The incorporation of two additional carbons therefore results in reductions in polarizability of 0.62 in the isothiocyanate system and 2.42 in the cyano system. The discrepancies in the magnitude of the numbers between these two systems may be due to differences in packing densities with antiparallel associations being exhibited by the cyano-based systems **52** and **44**.

When one phenyl ring of a biphenyl system is replaced by thiophene, an increase in the polarizability is always observed regardless of whether the left-hand (LH) or right-hand (RH) ring is substituted. Thiophenes

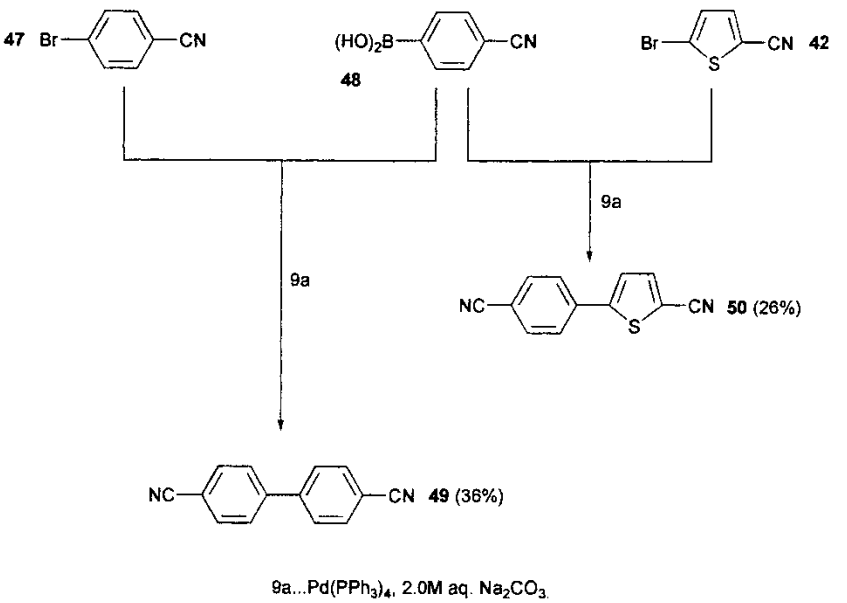
20 (LH, $\Delta\alpha = 34.18$) and **13** (RH, $\Delta\alpha = 33.23$) have polarizabilities 2.12 and 1.17 higher respectively than biphenyl analogue **55** ($\Delta\alpha = 32.06$). The phenylthiophenes with thiophene as the left-hand ring always have polarizabilities higher than when thiophene occupies the right-hand ring; compare also **29** (RH, $\Delta\alpha = 25.66$) and **38** (LH, $\Delta\alpha = 26.60$). This observation has been noted in other studies [2] and may be due to the transition moment acting more along the director when thiophene occupies the left-hand ring. When both rings are replaced with thiophene a broader collinear structure results with the transition moment acting directly along the director, thus giving rise to a considerable increase in the anisotropy of the polarizability; compare dithienyl **24** ($\Delta\alpha = 47.66$) and biphenyl **55** ($\Delta\alpha = 32.06$).

The replacement of a nitrile terminal group with an isothiocyanate always results in a very large increase in the polarizability; compare **24** (NCS, $\Delta\alpha = 47.66$) and **53** (CN, $\Delta\alpha = 28.39$), **13** (NCS, $\Delta\alpha = 33.23$) and **52** (CN, $\Delta\alpha = 24.10$) and compounds **20** (NCS, $\Delta\alpha = 34.18$) and **51** (CN, $\Delta\alpha = 25.12$). The dithienyl systems **24** and **53** (terminal isothiocyanate and cyano, respectively) display a much larger difference in polarizability (19.27) than the analogous isothiocyanato and cyanophenylthiophene systems; **13** and **52** (9.13) and compounds **20** and **51** (9.06). An explanation that may account for this anomaly is found in X-ray studies of various phenylisothiocyanates [29–32]. X-ray studies have shown that the C(aryl)–N–C bond of phenylisothiocyanates varies between 154° and 175°. The extent of conjugation with the aromatic system has a significant effect on increasing the extent of the double bond character of the C(aryl)–N bond. It is therefore possible that the high level of conjugation with the dithienyl system (molecular modelling indicates that the inter-annular torsion angle between the two thiophene rings is smaller, ~10°, than between a phenyl and a thiophene ring, thus enhancing molecular conjugation) places the isothiocyanate much more on-axis than for the less highly conjugated phenylthiophene systems, thus explaining the significantly higher polarizability of dithienylisothiocyanate **24**.

The synthesis of sulphur-containing compounds has been explored at Hull for a number of years and has resulted in the discovery of a variety of materials with exceptionally high molecular polarizabilities [2, 4, 27, 33]. The synthesis of **46** was undertaken in order to evaluate a highly fluid system (two alkylsulphanyl chains expected to impart a low melting point to a symmetrical molecule) that is collinear and has all four heteroatoms situated along the molecular axis. The result was a colourless material with no sensitive functional groups that possessed a very high polarizability ($\Delta\alpha = 26.08$).

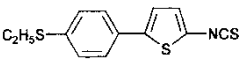
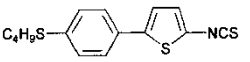
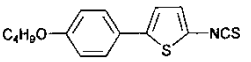
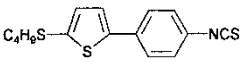
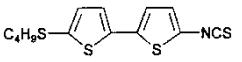
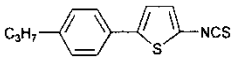
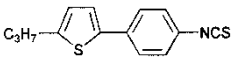
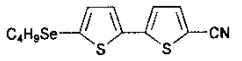
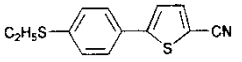
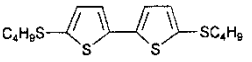
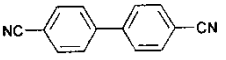
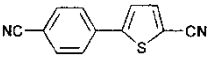
3.2.2. *Order parameters*

Replacement of a butoxy with a butylsulphanyl terminal chain leads to a decrease in the order parameter of 0.07—compare butoxy **14** ($S = 0.67$) with butylsulphanyl **13** ($S = 0.60$)—which is consistent with the increase in molecular breadth of the system. The C–S–C bond angle of the butylsulphanyl chain is smaller than the C–O–C bond angle of the butoxy chain, thus forcing the butylsulphanyl chain to project more



Scheme 9.

Table 1. Phase transition data for experimental compounds.

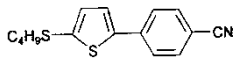
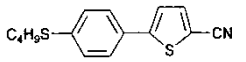
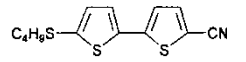
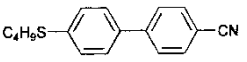
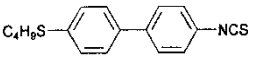
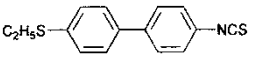
Compound	Structure	Cr		B		N		I
12		•	91.9	•	92.4	[•	16][a]	•
13		•	74.5	•	75.1	[•	19]	•
14		•	81.2	•	84.7	[•	26]	•
20		•	44.2	—	—	[•	−38]	•
24			Oil					
29		•	52.4	•	52.6	[•	20]	•
38		•	78.5	•	80.0	[•	34]	•
43		•	22.8	—	—	[•	−138]	•
44		•	102.9	—	—	[•	11]	•
46		•	28.8	—	—	[•	−98]	•
49		•	239.6	—	—	Insoluble in E7		•
50		•	213.4	—	—	Insoluble in E7		•

[a][ ] Denotes a virtual transition temperature determined from mixtures in E7 (see experimental).

'off-axis' and giving rise to a consequent reduction in the molecular anisotropy. The torsion angle [C(aryl)–C(aryl)–O–C(alkyl)] about oxygen in similar systems is 0° and is a result of the effective 2p–2p overlap of the π-orbitals of oxygen and the benzene ring. Conversely, the torsion angle about analogous sulphur (and selenium) derivatives is widely variable [34–36]. As a result of all of the above, the anisotropic intermolecular forces are reduced, leading to the observation of the smaller order parameter.

Replacement of the butylsulphanyl chain with a butylselanyl chain—compare **53** ($S=0.48$) and **43**

Table 2. Phase transition data for literature compounds.

Compound	Structure	Cr		B		N		I
51		•	32.6	—		[•	−52] [a]	•
52		•	55.7	—		[•	5]	•
53		•	30.3	—		[•	−63]	•
54		•	64.8	—		(•	35.5) [b]	•
55		•	78.4	•	78.6	[•	44]	•
56		•	77.5	•	78.9	[•	43]	•

[a][ ] Denotes a virtual transition determined from mixtures in E7 (see experimental).
[b]( ) Denotes a monotropic transition.

($S=0.96$), respectively—leads to a very surprising large increase in the order parameter (0.48) that is contrary to the above argument. An explanation for this result is unclear.

Increasing the alkylsulphanyl chain length by two carbons leads to an increase in the order parameter for nitrile-based systems—compare **44** (C2, $S=0.53$) and **52** (C4, $S=0.66$)—whereas isothiocyanate-based systems are unchanged—compare **12** (C2, $S=0.60$) and **13** (C4, $S=0.60$). The increase in order parameter for the nitrile system is consistent with the enhanced molecular anisotropy and greater van der Waals forces. The isothiocyanates are unusual in their behaviour and the result may be a reflection of the measurement in the virtual $T_{N\text{-}I}$ value that is higher for the shorter chain compound. The result is also within the margin of experimental error for the calculations of the order parameter.

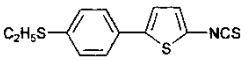
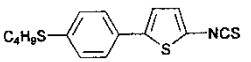
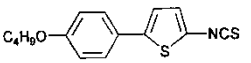
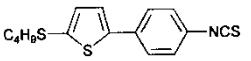
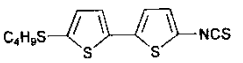
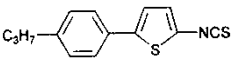
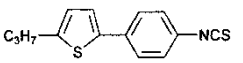
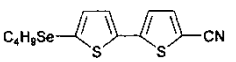
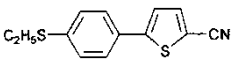
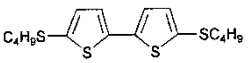
In substituting a single ring of biphenyl isothiocyanate **55** with thiophene, the resulting compound with thiophene in the right-hand ring (**13**) shows a reduction in the order parameter; 0.60: compared with 0.63 for **55** (within experimental error). In contrast, when thiophene replaces the left-hand ring (**20**) the order parameter is substantially larger (0.85) and is just the opposite of the observation made for analogous nitrile-based materials [2]. This result is most unusual and given that isothiocyanates are not known to exhibit antiparallel association, can only be rationalized in terms of the enhanced polarizability observed due to the transition moment being more along the director or to reduced fluctuations. The increased anisotropic molecular polarizability will give rise to increased intermolecular forces, however, given that isothiocyanate **20** is somewhat bent the result is inconsistent with expectations.

Replacement of both phenyl rings with thiophene results in a large decrease in order parameter relative to the biphenyl system. This finding is in line with previous studies on the analogous cyano-based systems and is due to the increased molecular breadth imparted by the two sulphur atoms in the collinear dithienyl system [2].

The replacement of a cyano substituent with an isothiocyanate gives mixed results. Nitriles **52** and **53** ($S=0.66$ and 0.48, respectively) have larger order parameters than the analogous isothiocyanates **13** and **24** ($S=0.60$ and 0.32, respectively). Once again isothiocyanate **20** shows inexplicable behaviour and has a much higher order parameter than corresponding nitrile **51** ($S=0.85$ and 0.56, respectively). This would not be expected if antiparallel association were operating with the nitrile derivatives.

Disulphanyl **46** has a very high order parameter ($S=0.94$) that is consistent with the linear structure,

Table 3. Refractive indices ($n_{\|}$, $n_{\perp}$), optical anisotropies (Δn), polarizabilities ($\Delta\alpha$) and order parameters (S) for experimental compounds.

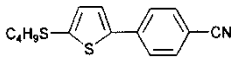
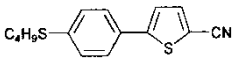
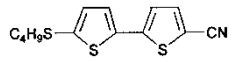
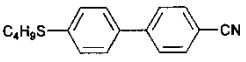
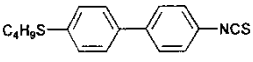
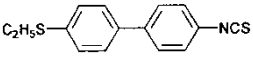
Compound	Structure		$n_{\|}$	$n_{\perp}$	Δn	$\Delta\alpha/10^{-30}\,\mathrm{m}^3$	S
12		Red T	2.06	1.63	0.43	33.85	0.60
		25°C	1.98	1.61	0.37	32.48	0.54
13		Red T	2.00	1.61	0.39	33.23	0.60
		25°C	1.95	1.59	0.35	32.10	0.57
14		Red T	1.94	1.56	0.38	28.16	0.67
		25°C	1.89	1.57	0.32	27.60	0.58
20		Red T	2.20	1.64	0.56	34.18	0.85
		25°C	1.90	1.60	0.30	29.29	0.52
24		Red T	1.93	1.64	0.29	47.66	0.32
		25°C	1.73	1.62	0.11	43.50	0.13
29		Red T	1.99	1.60	0.39	25.66	0.68
		25°C	1.88	1.59	0.29	24.45	0.53
38		Red T	1.94	1.58	0.36	26.60	0.60
		25°C	1.88	1.56	0.32	25.50	0.56
43		Red T	2.12	1.65	0.47	34.49	0.96
		25°C	1.70	1.64	0.06	29.98	0.73
44		Red T	1.93	1.59	0.34	26.52	0.53
		25°C	1.87	1.57	0.30	25.50	0.50
46		Red T	2.08	1.66	0.42	26.08	0.94
		25°C	1.65	1.60	0.05	21.08	0.13

and high molecular polarizability that gives rise to increased van der Waals forces. The measured virtual $T_{\mathrm{N\text{-}I}}$ value is extremely low (−98°C) and since the order parameter is calculated at a similarly low fixed reduced temperature, any material exhibiting liquid crystal phases at such a temperature would be expected to have considerably reduced fluctuations with a corresponding increase in order. A similar argument would account for the high order parameter of **43** ($S=0.96$, $T_{\mathrm{N\text{-}I}}=-138$°C).

3.2.3. *Refractive indices and optical anisotropies*

Now that the trends in polarizability and order parameter have been discussed, it is possible to discuss the trends in the refractive indices and optical anisotropies. Replacement of the butoxy chain with a butylsulphanyl chain (compare **14** with **13**, respectively) results in a small increase in both $n_{\|}$ (0.06) and $n_{\perp}$ (0.05) and an overall increase in Δn (0.01). The increase in $n_{\perp}$ is due to the more off-axis nature of the alkylsulphanyl chain that increases the molecular breadth

Table 4. Refractive indices ($n_{\|}$, $n_{\perp}$), optical anisotropies (Δn), polarizabilities ($\Delta\alpha$) and order parameters (S) for literature compounds.

Compound	Structure		$n_{\|}$	$n_{\perp}$	Δn	$\Delta\alpha/10^{-30}\,\mathrm{m}^3$	S
51		Red T	1.89	1.59	0.30	25.12	0.56
		25°C	1.79	1.57	0.22	23.70	0.44
52		Red T	1.92	1.58	0.34	24.10	0.66
		25°C	1.84	1.56	0.28	23.10	0.56
53		Red T	1.90	1.61	0.29	28.39	0.48
		25°C	1.76	1.59	0.17	26.40	0.30
54		Red T	1.86	1.56	0.30	20.83	0.67
		25°C	1.83	1.55	0.28	19.50	0.63
55		Red T	1.96	1.56	0.40	32.06	0.63
		25°C	1.91	1.56	0.36	30.23	0.59
56		Red T	2.00	1.58	0.42	32.68	0.61
		25°C	1.96	1.58	0.38	30.75	0.58

of the system, whereas the increase in $n_{\|}$ is due to introduction of the much more polarizable sulphur atom that is conjugated with the polarizable core and is the dominant factor in Δn.

Replacement of the butylsulphanyl chain with a butylselanyl chain (compare **53** and **43**, respectively) gives the expected analogous result for both the refractive indices and optical anisotropy.

Increasing the terminal chain length from 2 to 4 carbons might be expected to result in an increase in $n_{\perp}$ due to the increase in molecular breadth, and a decrease in $n_{\|}$ due to the dilution effect of the two extra methylene units. However, in comparing compounds **12** and **44** (ethylsulphanyl chains) with **13** and **52** (butylsulphanyl chains), respectively, the trend in $n_{\perp}$ is observed to be just the opposite, with the shorter chain homologues **12** and **44** having the higher values of $n_{\perp}$. This trend was not altogether unexpected as a study of a homologous series of 4-alkylsulphanyl-4′-isothiocyanatobiphenyls (C2 to C10 chains) showed a *general decrease in $n_{\perp}$ as the chain length increased* [27]. The increase in $n_{\perp}$ is likely to be due to the increase in number density for the short chain homologues when compared with the long chain systems.

Examination of biphenyl compounds clearly shows that the replacement of any one of the phenyl rings with thiophene gives rise to increases in both the values of $n_{\|}$ and $n_{\perp}$. The incorporation of thiophene always results in an increase in $n_{\perp}$ due to the 'bent' nature of the heterocyclic core that pushes the chain even more 'off-axis,' reducing the molecular anisotropy and increasing the lateral transition moment. Again this result is consistent with previous studies [2] regardless of whether thiophene occupies the left-hand ring, the right-hand ring, or both rings (BR); compare, for example, **13** (RHR), **20** (LHR), **24** (BR) and biphenyl **55** with values for $n_{\perp}$ of 1.61, 1.64, 1.64, and 1.56, respectively. Replacement of both rings with thiophene (compare dithienyl **24** with biphenyl **55**) leads to a decrease in $n_{\|}$ (0.03) and an increase in $n_{\perp}$ (0.08). The decrease in $n_{\|}$ must be due to the very low order parameter of **24** ($S=0.32$).

When replacing a cyano substituent with an isothiocyanate, the value of $n_{\|}$ always increases due to the enhanced longitudinal polarizability of the isothiocyanate. In contrast, the angular nature of the isothiocyanate unit also increases the transverse polarizability that is reflected in the values of $n_{\perp}$ which are always increased on substituting a cyano for an isothiocyanate substituent.

4. Experimental

The syntheses of compounds **1** and **2** are described in reference [11] and the syntheses of compounds **21**, **42** and **48** in reference [2]; the preparation of **21** is also described in [2]. The syntheses of compounds **16**, **25**, **31**, **39**, **40** and **49** are described in references [2, 37–41], respectively. Compounds **4**, **15**, **30**, **35** and **47** were purchased from Aldrich Chemical Company.

4.1. *Scheme 1*

4.1.1. *2-Bromo-5-nitrothiophene (**5**)*

A solution of nitric acid (24.0 g, 0.381 mol, 1.42 sp. gr.) in acetic anhydride (50 ml) at 0°C, was added dropwise at −5 to 0°C to a cooled (0°C), rapidly stirred solution of **4** (24.8 g, 0.152 mol) in acetic anhydride (50 ml). At the end of the addition the stirring was continued for 0.5 h and the reaction mixture was refrigerated overnight (GLC and TLC analyses revealed a complete reaction). The mixture was poured into ice-water (400 ml) and the precipitate was filtered off, dissolved in ether (2 × 200 ml), and washed with water until free of acid. The solvent was removed *in vacuo* and the product purified by column chromatography (silica gel, petroleum fraction b.p. 40–60°C/dichloromethane, 5/1) and was crystallized from ethanol/1,2-dimethoxyethane, 10/1, to afford pale yellow crystals which were dried *in vacuo* (P_2O_5, $CaCl_2$). Yield 20.9 g (66%), m.p. 44–46°C (lit[5] 45–46°C), purity (GLC) >99%. ^{1}H NMR ($CDCl_3$) δ 7.10(1H, d), 7.70(1H, d). IR (KBr) ν_{max} 730, 815, 1340, 1400, 1510, 1530, 3110 cm^{-1}. MS *m/z* 209,207(M^+), 151,149(100%), 81.

4.1.2. *2-(4-Ethylsulphanylphenyl)-5-nitrothiophene (**6**)*

Tetrakis(triphenylphosphine)palladium(0) (0.45 g, 0.39 mmol) was added in one portion to a rapidly stirred mixture of **1** (2.01 g, 0.011 mol), **5** (2.0 g, 0.010 mol) and sodium carbonate (9.6 ml, 2.0M, 0.019 mol) in 1,2-dimethoxyethane (100 ml), under dry nitrogen. The reaction mixture was heated under reflux overnight (TLC and GLC analyses revealed a complete reaction) and the product was extracted into ether (2 × 200 ml); the combined ethereal solutions were washed with saturated sodium chloride (300 ml) and dried ($MgSO_4$). The drying agent was filtered off and the solvent removed *in vacuo* before the product was purified by column chromatography (silica gel/petroleum fraction b.p. 40–60°C/dichloromethane, 10/3) to afford a yellow solid. Yield 2.29 g (86%), m.p. 90–91°C. ^{1}HNMR ($CDCl_3$) δ 1.39(3H, t), 3.05(2H, q), 7.21(1H, d), 7.34(2H, d), 7.54(2H, d), 7.90(1H, d). IR (KBr) ν_{max} 725, 810, 1140, 1195, 1320, 1350, 1425, 1485, 1500, 1590, 2920, 2960 cm^{-1}. MS *m/z* 265(M^+,100%), 175, 146, 102, 58.

4.1.3. *2-(4-Butylsulphanylphenyl)-5-nitrothiophene (**7**)*

Compound **7** was prepared in a similar way to that described for the preparation of **6**, using the quantities stated. Quantities: **2** (5.0 g, 0.024 mol), **5** (4.32 g, 0.021 mol), tetrakis(triphenylphosphine)palladium(0) (1.19 g, 1.03 mmol) and sodium carbonate (21.0 ml, 2.0M, 0.042 mol). The product was purified by column chromatography (silica gel, petroleum fraction b.p. 40–60°C/dichloromethane, 5/1) to afford an orange solid. Yield 5.44 g (88%), m.p. 68–69°C. ^{1}H NMR ($CDCl_3$) δ 0.96(3H, t), 1.50(2H, sext), 1.69(2H, quint), 3.00(2H, t), 7.20(1H, d), 7.33(2H, d), 7.53(2H, d), 7.90(1H, d). IR (KBr) ν_{max} 740, 810, 1000, 1335, 1435, 1520, 2960 cm^{-1}. MS *m/z* 293(M^+), 237(100%), 147, 102, 69.

4.1.4. *2-(4-Butoxyphenyl)-5-nitrothiophene (**8**)*

Compound **8** was prepared in a similar way to **6** and **7**. Quantities: **3** (3.38 g, 0.017 mol), **5** (3.31 g, 0.016 mol), tetrakis(triphenylphosphine)palladium(0) (0.91 g, 0.79 mmol) and sodium carbonate (15.8 ml, 2.0M, 0.032 mol). The product was purified by column chromatography (silica gel, petroleum fraction b.p. 40–60°C/dichloromethane, 3/1) and was crystallized from ethanol to afford a pale yellow solid which was dried *in vacuo* (P_2O_5,$CaCl_2$). Yield 4.17 g (94%), m.p. 92–93°C. ^{1}H NMR ($CDCl_3$) δ 1.00(3H, t), 1.51(2H, sext), 1.80(2H, quint), 4.00(2H, t), 6.94(2H, d), 7.12(1H, d), 7.57(2H, d), 7.89(1H, d). IR (KBr) ν_{max} 810, 840, 1010, 1050, 1180, 1325, 1430, 1485, 1510, 1600, 2880, 2980 cm^{-1}. MS *m/z* 277(M^+), 221(100%), 191, 131, 57.

4.1.5. *2-Amino-5-(4-ethylsulphanylphenyl)thiophene (**9**)*

A stirred mixture of **6** (2.11 g, 8.00 mmol) and palladium-on-carbon (10%, 1.66 g), in ethanol (30 ml) and THF (30 ml), was stirred under a hydrogen atmosphere overnight (TLC and GLC analyses revealed a complete reaction). The catalyst was removed by filtration through 'Hyflo Supercel' filter aid and the solvent was removed *in vacuo* to afford a purple solid that was used in the next step without purification. Yield 1.86 g (99%).

4.1.6. *2-Amino-5-(4-butylsulfanylphenyl)thiophene (**10**)*

Compound **10** was prepared in a similar way to that described for the preparation of **9**, using the quantities stated. Quantities: **7** (4.11 g, 0.014 mol) and palladium-on-carbon (10%, 1.90 g). A black solid was obtained which was used in the next step without purification. Yield 3.69 g (100%).

4.1.7. *2-Amino-5-(4-butoxyphenyl)thiophene (**11**)*

Compound **11** was prepared in a similar way to **9** and **10**. Quantities: **8** (2.98 g, 0.011 mol) and palladium-on-carbon (10%, 1.97 g). A purple solid was obtained which was used in the next step without purification. Yield 2.72 g (100%).

4.1.8. *2-(4-Ethylsulphanylphenyl)-5-isothiocyanatothiophene (**12**)*

A solution of **9** (1.86 g, 7.91 mmol) in chloroform (75 ml) was added dropwise to a stirred, cooled (0°C) mixture of water (40 ml), chloroform (20 ml), calcium carbonate (1.17 g, 0.012 mol), and thiophosgene (1.02 g, 8.87 mmol) at 2–5°C. The mixture was heated at 35°C for 1 h and poured into water (50 ml) before separating the two layers. The organic layer was washed with hydrochloric acid (100 ml, 1%) and dried ($MgSO_4$). The drying agent was filtered off and the solvent removed *in vacuo* before the product was purified by column chromatography (silica gel, petroleum fraction (b.p. 40–60°C)/dichloromethane, 5/1). The product was crystallized from hexane to afford white crystals which were dried *in vacuo* ($CaCl_2$). Yield 0.95 g (43%), purity (HPLC) >99%. Transitions (°C) Cr 91.9 B 92.4 [N 16] I. $n_{\|}=1.98$, $n_{\perp}=1.61$, $\Delta n=0.37$, $\Delta\alpha=32.48$, $S=0.54$ at 25°C. $n_{\|}=2.06$, $n_{\perp}=1.63$, $\Delta n=0.43$, $\Delta\alpha=33.85$, $S=0.60$ at $T/T_{\text{N-I}}=0.7815$. ^{1}H NMR ($CDCl_3$) δ 1.35(3H, t), 2.96(2H, q), 6.82(1H, d), 7.00(1H, d), 7.30(2H, d), 7.43(2H, d). IR (KBr) $\nu_{\max}$ 790, 805, 1100, 1450, 1495, 2120, 2920, 2980 cm^{-1}. UV $\lambda_{\max}$ (cyclohexane) 192(34 600 $dm^3\,mol^{-1}\,cm^{-1}$), 198(39 600), 309(41 800) nm. MS *m/z* 277(M^+, 100%), 248, 190, 139, 102, 58.

4.1.9 *2-(4-Butylsulfanylphenyl)-5-isothiocyanatothiophene (**13**)*

Compound **13** was prepared in a similar way to that described for the preparation of **12**, using the quantities stated. Quantities: **10** (3.69 g, 0.010 mol), thiophosgene (1.80 g, 0.016 mol) and calcium carbonate (2.18 g, 0.022 mol). The product was purified by column chromatography (silica gel, petroleum fraction b.p. 40–60°C/dichloromethane, 5/1) and was crystallized from hexane to afford a pale yellow solid which was dried *in vacuo* ($CaCl_2$). Yield 1.56 g (51%), purity (HPLC) >99%. Transitions (°C) Cr 74.5 B 75.1 [N 19] I. $n_{\|}=1.95$, $n_{\perp}=1.59$, $\Delta n=0.35$, $\Delta\alpha=32.10$, $S=0.57$ at 25°C. $n_{\|}=2.00$, $n_{\perp}=1.61$, $\Delta n=0.39$, $\Delta\alpha=33.23$, $S=0.60$ at $T/T_{\text{N-I}}=0.7815$. ^{1}H NMR ($CDCl_3$) δ 0.94(3H, t), 1.47(2H, sext), 1.65(2H, quint), 2.95(2H, t), 6.82(1H, d), 6.99(1H, d), 7.29(2H, d), 7.42(2H, d). IR (KBr) $\nu_{\max}$ 810, 1045, 1100, 1260, 1400, 1450, 1490, 2010, 2920, 2960, 3440 cm^{-1}. UV $\lambda_{\max}$ (cyclohexane) 211(22 150 $dm^3\,mol^{-1}\,cm^{-1}$), 353(25 000) nm. MS *m/z* 305(M^+, 100%), 248, 217, 203, 189.

4.1.10. *2-(4-Butoxyphenyl)-5-isothiocyanatothiophene (**14**)*

Compound **14** was prepared in a similar way to **12** and **13**. Quantities: **11** (2.72 g, 0.011 mol), thiophosgene (2.07 g, 0.018 mol) and calcium carbonate (2.20 g, 0.022 mol). The product was purified by column chromatography (silica gel, petroleum fraction (b.p. 40–60°C)/dichloromethane, 5/1] and was crystallized from hexane to afford white crystals which were dried *in vacuo* ($CaCl_2$). Yield 2.00 g (63%), purity (HPLC) >99%. Transitions (°C) Cr 81.2 B 84.7 [N 26] I. $n_{\|}=1.89$, $n_{\perp}=1.57$, $\Delta n=0.32$, $\Delta\alpha=27.60$, $S=0.58$, at 25°C. $n_{\|}=1.94$, $n_{\perp}=1.56$, $\Delta n=0.38$, $\Delta\alpha=28.16$, $S=0.67$ at $T/T_{\text{N-I}}=0.7815$. ^{1}H NMR ($CDCl_3$) δ 1.00(3H, t), 1.50(2H, sext), 1.80(2H, quint), 3.96(2H, t), 6.80(1H, d), 6.90(1H, d), 6.91(2H, d), 7.40(2H, d). IR (KCl) $\nu_{\max}$ 800, 835, 1040, 1180, 1260, 1290, 1400, 1505, 1610, 2120, 2880, 2940, 3400 cm^{-1}. UV $\lambda_{\max}$ (cyclohexane) 340(17 700 $dm^3\,mol^{-1}\,cm^{-1}$) nm. MS *m/z* 289(M^+), 233(100%), 204, 172, 131.

4.2. *Scheme 2*

4.2.1. *2-Tributylstannyl-5-butylsulphanylthiophene (**17**)*

n-Butyllithium (41.7 ml, 2.5M in hexane, 0.104 ml) was added dropwise to a stirred, cooled (−10°C) solution of **16** (16.3 g, 0.094 mol) in dry THF (200 ml), under dry nitrogen. The reaction mixture was maintained under these conditions for a further 30 min before tributyltin chloride (34.0 g, 0.104 mol) was added dropwise at −10°C. The mixture was allowed to warm to room temperature, then left to stir overnight. The reaction mixture was poured into water (500 ml) and washed with diethyl ether (2 × 200 ml). The combined organic extracts were washed with water (2 × 200 ml) and dried ($MgSO_4$). The drying agent was filtered off and the solvent removed *in vacuo* before the residue was distilled. Yield 35.0 g (81%), b.p. 250°C at 0.5 mm Hg, purity (GLC) >99%. ^{1}H NMR ($CDCl_3$) δ 0.90(12H, t), 1.09(6H, t), 1.33(8H, m), 1.56(8H, quint), 2.82(2H, t), 7.05(1H, d), 7.15(1H, d). IR (film) $\nu_{\max}$ 800, 930, 1070, 1200, 1380, 1470, 2940 cm^{-1}. MS *m/z* 460(M^+), 404(100%).

4.2.2. *2-Butylsulphanyl-5-(4-nitrophenyl)thiophene (**18**)*

Compound **15** (2.4 g, 98.0 mmol) was added in one portion to a stirred mixture of **17** (5.0 g, 0.011 mol) and tetrakis(triphenylphosphine)palladium(0) (0.6 g, 5.2 mmol) in dry DMF (100 ml) under dry nitrogen at room temperature. The mixture was heated at 80°C for

2 h (GLC and TLC analyses confirmed a complete reaction) and allowed to cool before the solvent was removed *in vacuo*. The crude product was purified by column chromatography (silica gel, petroleum fraction b.p. 40–60°C/dichloromethane, 1/1) and was crystallized from hexane to afford a yellow solid which was dried *in vacuo*. Yield 1.7 g (50%), m.p. 47–50°C. ^{1}H NMR ($CDCl_3$) δ 0.95(3H, t), 1.45(2H, sext), 1.65(2H, quint), 2.90(2H, t), 7.15(1H, d), 7.34(1H, d), 7.68(2H, d), 8.23(2H, d). IR (KBr) ν_{max} 750, 780, 840, 1100, 1330, 1420, 1500, 1590, 2940 cm^{-1}. MS *m/z* 293(M^+), 237, 114, 57(100%).

4.2.3. *2-(4-Aminophenyl)-5-butylsulphanylthiophene (**19**)*

Compound **19** was prepared as described for the preparation of **9**, using the quantities stated. Quantities: **18** (1.7 g, 57 mmol) and palladium-on-carbon (10%, 1.1 g). A grey solid was obtained which was used in the next step without purification. Yield 1.3 g (87%).

4.2.4. *2-Butylsulphanyl-5-(4-isothiocyanatophenyl)thiophene (**20**)*

Compound **20** was prepared as described for the preparation of **12**, using the quantities stated. Quantities: **19** (1.3 g, 50 mmol), thiophosgene (0.6 g, 54 mmol) and calcium carbonate (0.8 g, 80 mmol). The product was purified by column chromatography (silica gel, petroleum fraction b.p. 40–60°C) and was crystallized from hexane to afford pale yellow plates which were dried *in vacuo* ($CaCl_2$). Yield 1.00 g (65%), purity (GLC) >99%. Transitions (°C) Cr 44.2 [N −38] I. $n_{\|}=1.90$, $n_{\perp}=1.60$, $\Delta n=0.30$, $\Delta\alpha=29.29$, $S=0.52$ at 25°C. $n_{\|}=2.20$, $n_{\perp}=1.64$, $\Delta n=0.56$, $\Delta\alpha=34.18$, $S=0.85$ at $T/T_{N\text{-}I}=0.7815$. ^{1}H NMR ($CDCl_3$) δ 0.92(3H, t), 1.44(2H, sext), 1.64(2H, quint), 2.84(2H, t), 7.06(1H, d), 7.16(1H, d), 7.22(2H, d), 7.25(2H, d). IR (KBr) ν_{max} 780, 830, 920, 1000, 1100, 1400, 1490, 2040, 2940 cm^{-1}. UV λ_{max} (cyclohexane) 195(42 095 dm^3 mol^{-1} cm^{-1}), 332(28 499) nm. MS *m/z* 305(M^+), 249(100%), 215.

4.3. *Scheme 3*

4.3.1. *5-Butylsulphanyl-5′-nitro-2,2′-dithienyl (**22**)*

Compound **22** was prepared as described for the preparation of **5**, using the quantities stated. Quantities: **21** (1.04 g, 4.09 mmol) and nitric acid (0.26 g, 4.13 mmol, 1.42 sp. gr.). The crude product was purified by column chromatography (silica gel, petroleum fraction (b.p. 40–60°C/dichloromethane, 1/1) and was crystallized from petroleum fraction b.p. 40–60°C to afford a yellow solid. Yield 0.93 g (76%), m.p. 41°C, purity (GLC) >99%. ^{1}H NMR ($CDCl_3$) δ 0.93(3H, t), 1.45(2H, sext), 1.64(2H, quint), 2.89(2H, t), 7.03(2H, 2xd), 7.21(1H, d), 7.84(1H, d). IR (KBr) ν_{max} 730, 800, 810, 1035, 1220, 1325, 1350, 1430, 1490, 1510, 1535, 2870, 2920, 2960, 3100 cm^{-1}. MS *m/z* 299(M^+), 243, 152(100%), 120, 69.

4.3.2. *5-Amino-5′-butylsulphanyl-2,2′-dithienyl (**23**)*

Compound **23** was prepared in a similar way to that described for the preparation of **9**, using the quantities stated. Quantities: **22** (0.88 g, 2.94 mmol) and palladium-on-carbon (10%, 1.82 g). A black solid was obtained which was used in the next step without purification. Yield 0.79 g (100%).

4.3.3. *5-Butylsulphanyl-5′-isothiocyanato-2,2′-dithienyl (**24**)*

Compound **24** was prepared in a similar way to that described for the preparation of **12**, using the quantities stated. Quantities: **23** (0.79 g, 2.94 mol), thiophosgene (0.39 g, 3.39 mmol) and calcium carbonate (0.50 g, 5.0 mmol). The product was purified twice by column chromatography (silica gel, petroleum fraction b.p. 40–60°C/dichloromethane, 5/1] to give a pale yellow oil. Yield 0.61 g (68%), purity (HPLC) >99%. $n_{\|}=1.73$, $n_{\perp}=1.62$, $\Delta n=0.11$, $\Delta\alpha=43.50$, $S=0.13$, at 25°C. $n_{\|}=1.93$, $n_{\perp}=1.64$, $\Delta n=0.29$, $\Delta\alpha=47.66$, $S=0.32$ at $T/T_{N\text{-}I}=0.7815$. ^{1}H NMR ($CDCl_3$) δ 0.92(3H, t), 1.43(2H, sext), 1.62(2H, quint), 2.82(2H, t), 6.75(1H, d), 6.84(1H, d), 6.96(1H, d), 6.99(1H, d). IR (film) ν_{max} 700, 790, 1190, 1420, 1460, 1510, 1950–2220, 2870, 2920, 2960 cm^{-1}. UV λ_{max} (cyclohexane) 212(18 860 dm^3 mol^{-1} cm^{-1}), 356(18 930) nm. MS *m/z* 311(M^+), 254(100%), 69, 57, 45.

4.4. *Scheme 4*

4.4.1. *4-Propylphenylboronic acid (**26**)*

n-Butyllithium (7.0 ml, 10M in hexane, 0.070 mol) was added dropwise at −78°C to a stirred, cooled (−78°C) solution of **25** (13 g, 0.065 mol) in dry THF (120 ml) under dry nitrogen. The reaction mixture was maintained under these conditions for a further 0.5 h (GLC analysis confirmed a complete reaction) before a previously cooled (0°C) solution of trimethyl borate (14.6 g, 0.140 mol) in dry THF (20 ml) was added dropwise at −78°C. The reaction mixture was allowed to warm to room temperature overnight and was stirred for 1 h with hydrochloric acid (100 ml, 10%) before being washed with ether (2 × 200 ml). The combined organic phases were washed with water (200 ml) and dried ($MgSO_4$). The drying agent was filtered off and the solvent removed *in vacuo* to afford a white waxy solid that was used in the next step without purification. Yield 11 g (quantitative). ^{1}H NMR (DMSO-d_6)

δ 0.94(3H, t), 1.61(2H, sext), 2.56(2H, t), 7.16(2H, d), 7.70(2H, d), 7.80(2H, s). IR (KBr) ν_{max} 850, 1190, 1310, 1350, 1420, 1520, 1620, 2890, 2940, 2980, 3330 cm^{-1}. MS *m/z* 164(M^+), 216, 160, 144, 115(100%).

4.4.2. *2-Nitro-5-(4-propylphenyl)thiophene (**27**)*

Compound **27** was prepared in a similar way to that described for the preparation of **6**, using the quantities stated. Quantities: **26** (3.78 g, 0.023 mol), **5** (3.16 g, 0.015 mol), tetrakis(triphenylphosphine)palladium(0) (0.87 g, 0.75 mmol) and sodium carbonate (15.0 ml, 2.0M, 0.030 mol). The crude product was purified by column chromatography (silica gel, petroleum fraction b.p. 40–60°C/dichloromethane, 5/1) and was crystallized from ethanol to afford yellow needles which were dried *in vacuo* (P_2O_5, $CaCl_2$). Yield 3.07 g (83%), m.p. 57–58°C, purity (GLC) >99%. ^{1}H NMR ($CDCl_3$) δ 0.97(3H, t), 1.67(2H, sext), 2.64(2H, t), 7.21(1H, d), 7.26(2H, d), 7.56(2H, d), 7.91(1H, d). IR (KBr) ν_{max} 735, 800, 1040, 1205, 1330, 1355, 1425, 1480, 1505, 2930, 2960 cm^{-1}. MS *m/z* 247(M^+), 218(100%), 172, 128, 115.

4.4.3. *2-Amino-5-(4-propylphenyl)thiophene (**28**)*

Compound **28** was prepared in a similar way to that described for the preparation of **9**, using the quantities stated. Quantities: **27** (2.22 g, 8.99 mmol) and palladium-on-carbon (10%, 1.01 g). A brown solid was obtained which was used in the next step without purification. Yield 1.93 g (99%).

4.4.4. *2-Isothiocyanato-5-(4-propylphenyl)thiophene (**29**)*

Compound **29** was prepared in a similar way to that described for the preparation of **12**, using the quantities stated. Quantities: **28** (1.93 g, 8.89 mmol), thiophosgene (1.18 g, 0.010 mol) and calcium carbonate (1.33 g, 0.013 mol). The crude product was purified by column chromatography (silica gel, petroleum fraction b.p. 40–60°C/dichloromethane, 5/1) and was crystallized twice from petroleum fraction b.p. 40–60°C to afford a pale yellow solid which was dried *in vacuo* ($CaCl_2$). Yield 0.98 g (42%), purity (HPLC) >99%. Transitions (°C) Cr 52.4 B 52.6 [N 20] I. $n_{\|}=1.88$, $n_{\perp}=1.59$, $\Delta n=0.29$, $\Delta\alpha=24.45$, $S=0.53$ at 25°C. $n_{\|}=1.99$, $n_{\perp}=1.60$, $\Delta n=0.39$, $\Delta\alpha=25.66$, $S=0.68$ at $T/T_{N\text{-}I}=0.7815$. ^{1}H NMR ($CDCl_3$) δ 0.95(3H, t), 1.65(2H, sext), 2.60(2H, t), 6.82(1H, d), 6.98(1H, d), 7.19(2H, d), 7.42(2H, d). IR (KBr) ν_{max} 790, 955, 1450, 1510, 2090, 2930, 2960 cm^{-1}. UV λ_{max} (cyclohexane) 210(14 680 dm^3 mol^{-1} cm^{-1}), 222(16 030), 253(8 720), 324(23 350) nm. MS *m/z* 259(M^+), 230(100%), 171, 115, 102.

4.5. *Scheme 5*

4.5.1. *2-Propanoylthiophene (**31**)*

Anhydrous iron(III) chloride (9.13 g, 0.057 mol) was added in one portion to a rapidly stirred mixture of **30** (47.39 g, 0.564 mol) and propanoic anhydride (85.0 g, 0.654 mol) under dry nitrogen (a temperature increase to 112°C was noted) at room temperature. The reaction mixture was allowed to cool and was subsequently stirred at room temperature for 5 h (GLC and TLC analyses revealed a complete reaction) before being diluted with water (200 ml). The crude product was extracted into ether (2 × 200 ml), washed with saturated sodium hydrogen carbonate until free of acid, and dried ($MgSO_4$). The drying agent was filtered off and the solvent removed *in vacuo* before the residue was distilled to give a colourless liquid. Yield 50.00 g (63%), b.p. 106–108°C at 20 mm Hg, purity (GLC) >98%. ^{1}H NMR ($CDCl_3$) δ 1.22(3H, t), 2.94(2H, q), 7.12(1H, dd), 7.62(1H, dd), 7.72(1H, dd). IR (film) ν_{max} 720, 850, 900, 1050, 1225, 1410, 1515, 1710, 2940, 2970 cm^{-1}. MS *m/z* 140(M^+), 111(100%), 83, 57, 49.

4.5.2. *2-Propylthiophene (**32**)*

A mixture of **31** (30.0 g, 0.214 mol), hydrazine hydrate (32.18 g, 55% hydrazine content) and diethylene glycol (200 ml), was heated at 130–160°C for 1 h and water and the excess of hydrazine were distilled off. The mixture was cooled to below 60°C and potassium hydroxide pellets (36.1 g, 0.645 mol) were added. The mixture was then heated at 200°C for 20 min (GLC analysis revealed a complete reaction), cooled, and poured onto crushed ice (200 g) and hydrochloric acid (200 ml, 6.0M). The product was extracted into ether (2 × 200 ml) and dried ($MgSO_4$). The drying agent was filtered off and the solvent removed *in vacuo* before the residue was distilled to give a colourless liquid. Yield 19.5 g (72%), b.p. 44–46°C at 20 mm Hg (lit[23] 158–159°C at 760 mm Hg). ^{1}H NMR ($CDCl_3$) δ 1.00(3H, t), 1.71(2H, sext), 2.80(2H, t), 6.76(1H, dd), 6.90(1H, dd), 7.10(1H, dd). IR (film) ν_{max} 700, 825, 855, 1390, 1445, 1460, 1720, 2890, 2940, 2970 cm^{-1}. MS *m/z* 126(M^+), 111, 98, 97(100%), 53.

4.5.3. *2-Bromo-5-propylthiophene (**33**)*

A stirred solution of **32** (17.7 g, 0.141 mol) and *N*-bromosuccinimide (25.3 g, 0.142 mol) in chloroform (80 ml) and glacial acetic acid (80 ml), was gently heated under reflux for 0.5 h (GLC analysis revealed a complete reaction). The cooled reaction mixture was diluted with water (200 ml) and washed with dichloromethane (2 × 100 ml); the combined organic extracts were washed successively with water (300 ml) and aqueous potassium hydroxide (5% wt/vol, 300 ml) before drying ($MgSO_4$). The drying

agent was filtered off and the solvent removed *in vacuo* before the residue was distilled to give a colourless liquid. Yield 24.6 g (85%), b.p. 93–94°C at 20 mm Hg, purity (GLC) >99%. ^{1}H NMR ($CDCl_3$) δ 0.98(3H, t), 1.67(2H, sext), 2.73(2H, t), 6.55(1H, d), 6.85(1H, d). IR (film) ν_{max} 955, 1040, 1380, 1440, 2920, 2950 cm^{-1}. MS *m/z* 206,204(M^+), 177,175(100%), 96.

4.5.4. *5-Propylthien-2-ylboronic acid (**34**)*

Compound **34** was prepared in a similar way to that described for the preparation of **26**, using the quantities stated. Quantities: **33** (10.0 g, 0.049 mol), *n*-butyllithium (5.0 ml, 10M in hexane, 0.050 mol) and trimethyl borate (10.2 g, 0.098 mol). A black liquid was obtained which was used in the next step without purification. Yield 7.96 g (96%). ^{1}H NMR (DMSO-d_6) δ 0.94(3H, t), 1.62(2H, sext), 2.75(2H, t), 6.92(1H, d), 7.27(1H, d), 7.50(2H, s). IR (film) ν_{max} 650, 690, 800, 1190, 1360, 1450, 2920, 2960, 3200 cm^{-1}. MS *m/z* 170(M^+), 427, 319, 199, 97(100%).

4.5.5. *2-(4-Nitrophenyl)-5-propylthiophene (**36**)*

Compound **36** was prepared in a similar way to that described for the preparation of **6**, using the quantities stated. Quantities: **34** (4.93 g, 0.029 mol), **35** (4.23 g, 0.021 mol), tetrakis(triphenylphosphine)palladium(0) (1.21 g, 1.05 mmol) and sodium carbonate (20.9 ml, 2.0M, 0.042 mol). The crude product was purified by column chromatography (silica gel, petroleum fraction b.p. 40–60°C/dichloromethane, 5/1) to afford a yellow solid. Yield 2.96 g (57%), purity (GLC shows 50% of **35** remaining). ^{1}H NMR ($CDCl_3$) δ 1.02(3H, t), 1.76(2H, sext), 2.84(2H, t), 6.83(1H, d), 7.31(1H, d), 7.70(2H, d), 8.11(2H, d), excluding the signals from **35**. IR (KBr) ν_{max} 740, 800, 840, 1010, 1100, 1340, 1405, 1505, 1600, 2920, 2950 cm^{-1}. MS *m/z* 247(M^+), 203, 171, 157, 75(100%).

4.5.6. *4-(5-Propylthien-2-yl)aniline (**37**)*

Compound **37** was prepared in a similar way to that described for the preparation of **9**, using the quantities stated. Quantities: **36** (1.92 g, 7.77 mmol) and palladium-on-carbon (10%, 1.41 g). A black solid was obtained which was used in the next step without purification. Yield 1.76 g (quantitative).

4.5.7. *2-(4-Isothiocyanatophenyl)-5-propylthiophene (**38**)*

Compound **38** was prepared in a similar way to that described for the preparation of **12**, using the quantities stated. Quantities: **37** (1.76 g, 8.11 mmol), thiophosgene (0.93 g, 8.09 mmol) and calcium carbonate (1.05 g, 0.010 mol). The crude product was purified by column chromatography (silica gel, petroleum fraction b.p. 40–60°C/dichloromethane, 5/1) and was crystallized from hexane to afford white crystals which were dried *in vacuo* ($CaCl_2$). Yield 1.00 g (48%), purity (HPLC) >99%. Transitions (°C) Cr 78.5 B 80.0 [N 34] I. $n_\parallel = 1.88$, $n_\perp = 1.56$, $\Delta n = 0.32$, $\Delta\alpha = 25.50$, $S = 0.56$ at 25°C. $n_\parallel = 1.94$, $n_\perp = 1.58$, $\Delta n = 0.36$, $\Delta\alpha = 26.60$, $S = 0.60$ at $T/T_{N\text{-}I} = 0.7815$. ^{1}H NMR ($CDCl_3$) δ 1.00(3H, t), 1.72(2H, sext), 2.80(2H, t), 6.76(1H, d), 7.13(1H, d), 7.20(2H, d), 7.52(2H, d). IR (KBr) ν_{max} 805, 840, 940, 1470, 1510, 2000, 2040, 2940, 2960 cm^{-1}. UV λ_{max} (cyclohexane) 220(9 550 dm^3 mol^{-1} cm^{-1}), 326(38 400) nm. MS *m/z* 259(M^+), 230(100%), 171, 58, 45.

4.6. *Scheme 6*

4.6.1. *Thiophene-2-selanol (**39**)*

A single crystal of iodine was added to dry crushed magnesium turnings (8.80 g, 0.368 mol) in dry diethyl ether (50 ml) under dry nitrogen at room temperature. As soon as the reaction was initiated a solution of **4** (50.0 g, 0.307 mol) in dry diethyl ether (100 ml) was added at such a rate as to maintain a vigorous reflux. Once the addition was complete the mixture was heated under reflux for a further 1 h before being allowed to cool to room temperature. Powdered grey selenium (28.0 g, 0.360 mol) was added in portions with external cooling (caution: vigorous reaction with foaming). Once the addition was complete the reaction was heated under reflux for a further 1 h, cooled and poured into rapidly stirred ice-water and concentrated hydrochloric acid (200 ml). The organic layer was separated and the aqueous layer washed with diethyl ether (2 × 200 ml). The combined organic washings were stirred for 5 min over magnesium sulphate and the drying agent was filtered off. The solvent was removed *in vacuo* to give a foul-smelling orange oil that was used in the next step (immediately) without purification. Yield 49.0 g (98%).

4.6.2. *2-Butylselanylthiophene (**40**)*

Compound **39** (49.0 g, 0.307 mol) was added dropwise at room temperature, under dry nitrogen, to a stirred solution of ethanolic sodium ethoxide prepared from 7.8 g of sodium (0.339 g atom) in super-dry ethanol (500 ml). Once the addition was complete, 1-bromobutane was added dropwise to the resulting solution at room temperature. The reaction mixture was heated at 80°C for 2 h and the solution allowed to cool to room temperature before the sodium bromide was filtered off. The solvent was removed *in vacuo* and dichloromethane (200 ml) was added. The solution was washed with water (3 × 500 ml) and the organic layer dried ($MgSO_4$). The drying agent was filtered off and

the solvent was removed *in vacuo* before the crude product was distilled to give a colourless liquid. Yield 53.9 g (80%), b.p. 60–65°C at 0.3 mm Hg (lit[40] 120–121°C at 13 mm Hg). ^{1}H NMR ($CDCl_3$) δ 0.80(3H, t), 1.40(2H, sext), 1.65(2H, quint), 2.85(2H, t), 6.95(1H, dd), 7.15(1H, dd), 7.15(1H, dd). IR (film) ν_{max} 700, 840, 960, 1050, 1080, 1200, 1260, 1400, 1460, 2960 cm^{-1}. MS *m/z* 220(M^+, 100%), 163, 57.

4.6.3. *2-Butylselanyl-5-tributylstannylthiophene (**41**)*

Compound **41** was prepared in a similar way to that described for the preparation of **17** except that lithium diisopropylamide was used instead of *n*-butyllithium, using the quantities stated. Quantities: **40** (10.0 g, 0.046 mol), diisopropylamine (5.1 g, 0.050 mol), *n*-butyllithium (22.0 ml, 2.5M in hexane, 0.055 mol) and tributyltin chloride (16.3 g, 0.050 mol). The crude product was distilled to give a colourless liquid. Yield 18.5 g (79%), b.p. 240–250°C at 0.1 mm Hg. ^{1}H NMR ($CDCl_3$) δ 0.90(12H, t), 1.09(6H, sext), 1.33(8H, m), 1.56(8H, quint), 2.85(2H, t), 7.15(1H, d), 7.35(1H, d). IR (film) ν_{max} 700, 840, 930, 1070, 1200, 1260, 1380, 2940 cm^{-1}. MS *m/z* 507(M^+), 450(100%).

4.6.4. *5-Butylselanyl-5′-cyano-2,2′-dithienyl (**43**)*

Compound **43** was prepared in a similar way to that described for the preparation of **18**, using the quantities stated. Quantities: **42** (2.5 g, 0.013 mol), **41** (8.0 g, 0.016 mol) and tetrakis(triphenylphosphine)palladium(0) (0.8 g, 6.5 mmol). The crude product was purified by column chromatography (silica gel, petroleum fraction b.p. 40–60°C/dichloromethane, 1/1) before being distilled and crystallized from hexane to afford a yellow solid which was dried *in vacuo*. Yield 0.86 g (20%), b.p. 230–240°C at 0.5 mm Hg, purity (GLC) >99%. Transitions (°C) Cr 22.8 [N −138] I. $n_\parallel = 1.70$, $n_\perp = 1.64$, $\Delta n = 0.06$, $\Delta\alpha = 29.98$, $S = 0.73$ at 25°C. $n_\parallel = 2.12$, $n_\perp = 1.65$, $\Delta n = 0.47$, $\Delta\alpha = 34.49$, $S = 0.96$ at $T/T_{N\text{-}I} = 0.7815$. ^{1}H NMR ($CDCl_3$) δ 0.92(3H, t), 1.43(2H, sext), 1.70(2H, quint), 2.88(2H, t), 7.09(1H, d), 7.10(1H, d), 7.12(1H, d), 7.51(1H, d). IR (KBr) ν_{max} 800, 870, 1040, 1190, 1250, 1440, 1540, 2220, 2940 cm^{-1}. UV λ_{max} (cyclohexane) 194(17 462 dm^3 mol^{-1} cm^{-1}), 345(19 301) nm. MS *m/z* 327(M^+), 271, 191(100%).

4.7. *Scheme 7*

4.7.1. *2-Cyano-5-(4-ethylsulphanylphenyl)thiophene (**44**)*

Compound **44** was prepared in a similar way to that described for the preparation of **6**, using the quantities stated. Quantities: **1** (2.32 g, 0.013 mol), **42** (2.0 g, 0.011 mol), tetrakis(triphenylphosphine)palladium(0) (0.61 g, 0.53 mmol) and sodium carbonate (10.6 ml, 2.0M, 0.021 mol). The crude product was purified by column chromatography (silica gel, petroleum fraction b.p. 40–60°C/dichloromethane, 1/1) and was crystallized from cyclohexane to afford yellow crystals which were dried *in vacuo* ($CaCl_2$). Yield 1.45 g (54%), purity (HPLC) >99%. Transitions (°C) Cr 102.9 [N 11]. $n_\parallel = 1.87, n_\perp = 1.57, \Delta n = 0.30, \Delta\alpha = 25.50, S = 0.50$, at 25°C. $n_\parallel = 1.93$, $n_\perp = 1.59$, $\Delta n = 0.34$, $\Delta\alpha = 26.52$, $S = 0.53$ at $T/T_{N\text{-}I} = 0.7815$. ^{1}H NMR ($CDCl_3$) δ 1.36(3H, t), 3.00(2H, q), 7.24(1H, d), 7.33(2H, d), 7.51(2H, d), 7.58(1H, d). IR (KBr) ν_{max} 815, 1045, 1100, 1440, 1590, 2220, 3100 cm^{-1}. UV λ_{max} (cyclohexane) 205(18 600 dm^3 mol^{-1} cm^{-1}), 243(8 000), 328(24 100) nm. MS *m/z* 245(M^+,100%), 217, 197, 172, 69.

4.8. *Scheme 8*

4.8.1. *5,5′-Dibutylsulfanyl-2,2′-dithienyl (**46**)*

Compound **46** was prepared in a similar way to that described for the preparation of **18** using the quantities stated. Quantities: **45** (3.0 g, 0.012 mol), **17** (5.0 g, 0.011 mol) and tetrakis(triphenylphosphine)palladium(0) (0.6 g, 5.2 mmol). The crude product was purified by column chromatography (silica gel, petroleum fraction b.p. 40–60°C) before being distilled and crystallized from hexane to afford a colourless solid which was dried *in vacuo*. Yield 2.1 g (56%), b.p. 240–250°C at 0.1 mm Hg, purity (GLC) >99%. Transitions (°C) Cr 28.8 [N −98] I. $n_\parallel = 1.65$, $n_\perp = 1.60$, $\Delta n = 0.05$, $\Delta\alpha = 21.08$, $S = 0.13$ at 25°C. $n_\parallel = 2.08$, $n_\perp = 1.66$, $\Delta n = 0.42$, $\Delta\alpha = 26.08$, $S = 0.94$ at $T/T_{N\text{-}I} = 0.7815$. ^{1}H NMR ($CDCl_3$) δ 0.91(6H, t), 1.42(4H, sext), 1.62(4H, quint), 2.81(4H, t), 6.98(4H, 2xd). IR (KBr) ν_{max} 790, 870, 1200, 1270, 1380, 1430, 1500, 2940 cm^{-1}. UV λ_{max} (cyclohexane) 194(33 179 dm^3 mol^{-1} cm^{-1}), 341(19 718) nm. MS *m/z* 342(M^+, 100%), 285, 229.

4.9. *Scheme 9*

4.9.1. *4,4′-Dicyanobiphenyl (**49**)*

Compound **49** was prepared in a similar way to that described for the preparation of **6**, using the quantities stated. Quantities: **48** (3.62 g, 0.025 mol), **47** (3.89 g, 0.021 mol), sodium carbonate (21.0 ml, 2.0M, 0.042 mol), and tetrakis(triphenylphosphine)palladium(0) (1.21 g, 1.05 mmol). The crude product was purified by column chromatography (silica gel, petroleum fraction b.p. 40–60°C/dichloromethane, 1/1) and was crystallized from ethanol/ethyl acetate, 3/1, to afford a white solid which was dried *in vacuo* (P_2O_5). Yield 1.53 g (36%), purity (HPLC) >99%, m.p. 239.6°C. No virtual nematic transition was recorded as the product was found to be insoluble in E7. ^{1}H NMR ($CDCl_3$) δ 7.69(4H, d), 7.79(4H, d). IR (KBr) ν_{max} 820, 865, 1185, 1400, 1500, 1610,

2240 cm^{-1}. UV λ_{max} (cyclohexane) 272(12 200 dm^3 mol^{-1} cm^{-1}) nm. MS *m/z* 204(M^+), 177, 119, 58(100%), 88.

4.9.2. *2-Cyano-5-(4-cyanophenyl)thiophene (**50**)*

Compound **50** was prepared in a similar way to **6** and **49**. Quantities: **48** (1.76 g, 0.012 mol), **42** (1.87 g, 0.010 mol), tetrakis(triphenylphosphine)palladium(0) (0.57 g, 0.49 mmol) and sodium carbonate (9.9 ml, 2.0M, 0.02 mol). The crude product was purified by column chromatography (silica gel, petroleum fraction b.p. 40–60°C/dichloromethane, 1/1) and was crystallized from cyclohexane/ethyl acetate, 1/1 to afford pale yellow needles which were dried *in vacuo* (P_2O_5). Yield 0.55 g (26%), purity (HPLC) >99%, m.p. 213.4°C. No virtual nematic transition was recorded as the product was found to be insoluble in E7. ^{1}H NMR ($CDCl_3$) δ 7.39(1H, d), 7.64(1H, d), 7.70(2H, d), 7.74(2H, d). IR (KBr) ν_{max} 590, 860, 1445, 1605, 2210, 2230, 3100 cm^{-1}. UV λ_{max} (cyclohexane) 201(16 800 dm^3 mol^{-1} cm^{-1}), 231(7 100), 306(22 300) nm. MS *m/z* 210(M^+, 100%), 139, 74, 69, 63.

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