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The synthesis, phase transitions and optical properties of novel tetrathiafulvalene derivatives with extremely high molecular polarizabilities

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The synthesis of novel unsymmetrically-substituted tetrathiafulvalene derivatives based on lithiation procedures is described. The disubstituted derivatives were synthesized as 1 : 1 *cis/trans*-isomeric mixtures, the compositions of which were established by ^{1}H NMR and ^{13}C NMR spectroscopy. The transition temperatures, refractive indices, birefringence, polarizability and order parameter of each of the mixtures were determined and the values are discussed in comparison with analogous compounds with the tetrathiafulvalene unit replaced by a 1,4-phenylene group. In addition, we describe the synthesis of a number of monosubstituted tetrathiafulvalene derivatives and their associated thermal properties. The isomeric compounds presented in this paper have exceptionally large values of polarizability anisotropy, as compared with their phenyl-containing counterparts.

1. Introduction

Since the discovery of the high electrical conductivity of the donor–acceptor complex of tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) in 1973 by Ferraris *et al.* [1, 2], chemists have sought organic metals based on the tetrathiafulvalene core [3–5]. The superconductivity observed in these systems is due to a combination of the high polarizability of the tetrathiafulvalene molecules and the partial charge transfer between the donor and acceptor molecules, which exist in separate stacks [6, 7]. The high polarizability of tetrathiafulvalene makes derivatives incorporating this core-unit suitable targets for synthesis as high birefringence materials for use as dopants in devices including, for example, all-optical switches, spatial light modulators, electrically controlled birefringence displays and optical interconnects for use in telecommunications.

To date there have been no reports of the synthesis of unsymmetrically-substituted liquid crystalline (LC) tetrathiafulvalene-containing materials, although a number of non-LC unsymmetrically-substituted derivatives have been reported [8, 9]. Many of the symmetrically-disubstituted [10–13] and tetrasubstituted [10, 12, 14–16] tetrathiafulvalene compounds reported in the literature have melting points well in excess of 100°C [12, 13, 17, 18]. The majority of these materials do not form LCs, although a few exceptions are known [12, 13].

Liquid-like alkyl chains of no more than five carbon atoms in length help to lower the melting point, and at the same time are short enough to keep the dilution effect associated with their low polarizability to a minimum [19, 20]. At the same time, highly polarizable sulfur atoms in conjugation with π-systems, such as phenyl rings, tolanes and alkenes, enhance the polarizability but usually at the expense of the melting point [19]. To counteract this effect, an ester linkage was placed between the tetrathiafulvalene core and the π-system of the phenyl ring, in the belief that a combination of reduced conjugation between the two polarizable units and increased planarity of the system (molecular modelling showed that the ester-containing systems were the more planar [21]) would lead to a lowering of the melting points; we expected the $T_{\text{N-I}}$ values to be slightly enhanced (compared with the non-ester-linked parent compounds) due to the increase in the aspect ratio of the molecules.

This paper describes the synthesis of six novel tetrathiafulvalene derivatives using directed lithiation procedures based on the work of Green [22, 23]. The optical anisotropies of these materials have been determined (as described previously [21]) from the refractive indices $n_{\|}$ and $n_{\perp}$ with the use of an Abbé refractometer.

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From these results the polarizabilities and order parameters have been determined using a combination of the Maier–Saupe theory, the Haller derivation [24] and Vuks equation.

2. Experimental

2.1. *Characterization*

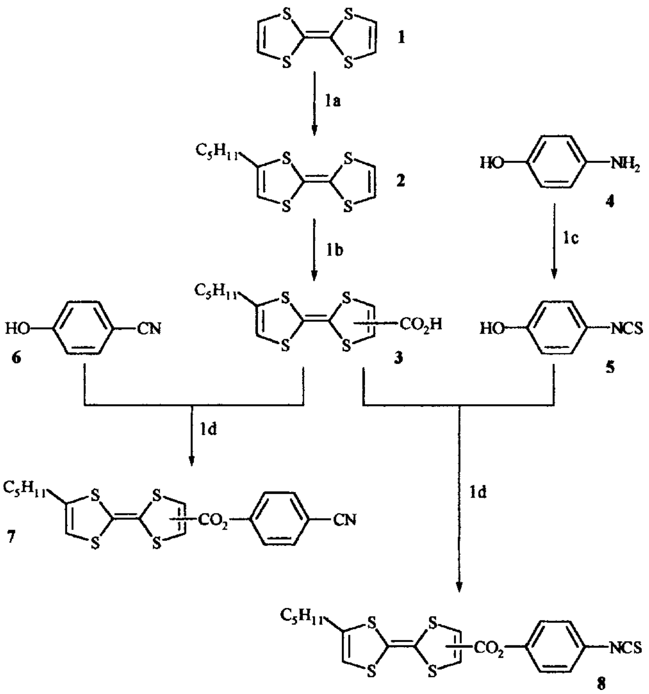
^{1}H NMR and ^{13}C NMR spectra were obtained using a Jeol GX NM270 FT NMR spectrometer with tetramethylsilane as internal standard. Infrared spectra were recorded using a Perkin-Elmer 783 spectrometer, and mass spectra using a Finnigan-MAT 1020 GC-MS spectrometer. Ultraviolet spectra were recorded 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 under gravity 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 chromatograph 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 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 (**7**, **8** and **13–16**) 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 these transitions was obtained using differential scanning calorimetry (Perkin-Elmer DSC7 and IBM data station). The heating and cooling rates were 10°C min^{-1} and indium was used for calibration. The virtual $T_{\text{N-I}}$ values of final compounds that were non-mesogenic were determined by the following procedure. Four binary mixtures of known composition of the material and a standard nematic host material (E7, Merck UK, Poole, England) of known $T_{\text{N-I}}$ value (60°C) were prepared, and the $T_{\text{N-I}}$ transition of each mixture was determined by optical microscopy. The $T_{\text{N-I}}$ value for each composition was extrapolated to 100% for the compound being examined using a linear regression computer program which gave an error of ± 7°C. The refractive indices of the final compounds (accurate to ± 0.001) were measured using an Abbé refractometer (model 60/HR) at 589 nm (D_1 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 [21]. The polarizabilities and order parameters were calculated as described in [19, 21]; their associated errors were ± 1.56 and ± 0.10 respectively.

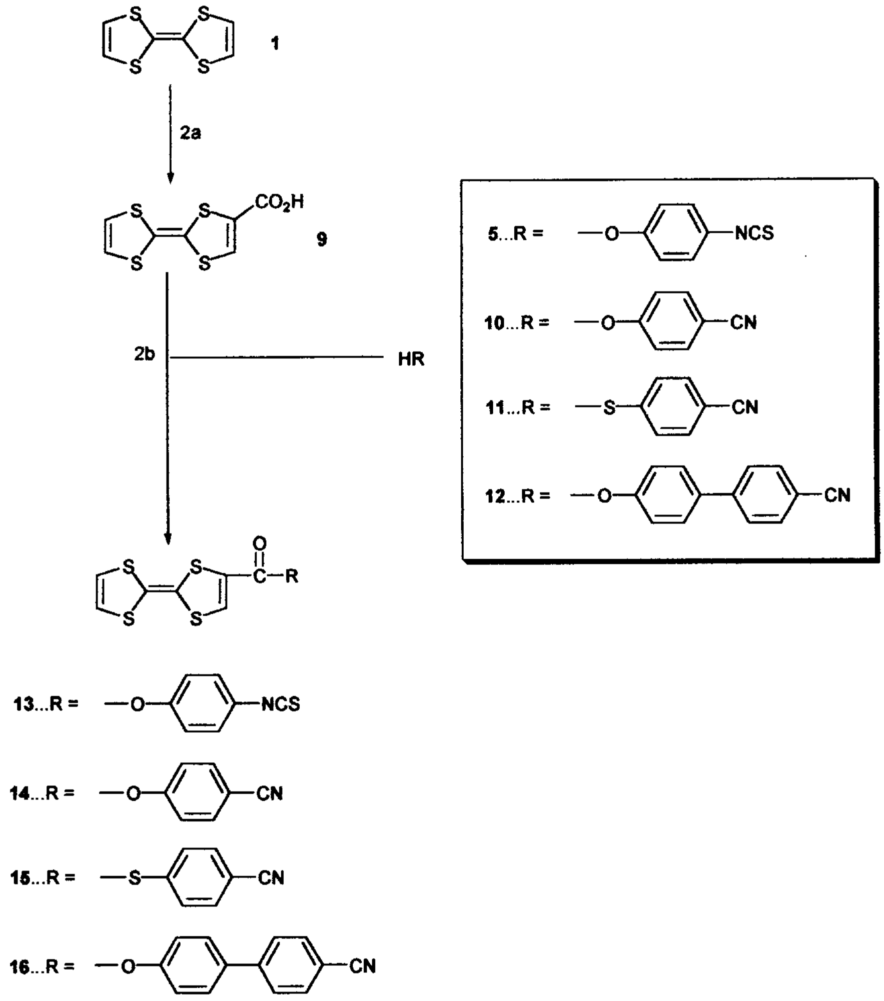
2.2. *Synthesis*

The synthetic routes used to obtain the tetrathiafulvalene derivatives **7**, **8** and **13–16** are depicted in schemes 1 and 2. The preparation of tetrathiafulvalene (**1**) followed the method of Melby *et al.* [25] which gave an excellent overall yield of highly pure tetrathiafulvalene. An improvement in the yield of the intermediate 1,3-dithiolium hexafluorophosphate to 97% (90% by Melby) was noted. Numerous attempts were made to synthesize 2-pentyltetrathiafulvalene (**2**) including the lithiation of tetrathiafulvalene with *n*-butyllithium followed by the addition of 1-iodopentane at – 78°C, with tetrahydrofuran (THF) as solvent; 1-bromopentane was also used unsuccessfully. The mixture of 2-lithiotetrathiafulvalene and 1-iodopentane was left to stir for up to 12 h at – 78°C giving only 20% yields of the desired product which proved to be inseparable from unknown products. It was decided to use hexamethylphosphorous triamide (HMPT) [26] as co-solvent (one part in six of THF) in an attempt to accelerate the



1a¼(i) n-Butyllithium, THF, HMPT; (ii) 1-iodopentane.
1b¼(i) n-Butyllithium; (ii) $CO_{2(s)}$; (iii) $HCl_{(aq)}$.
1c¼Carbon disulfide, *N,N*-dicyclohexylcarbodiimide, pyridine.
1d¼*N,N*-Dicyclohexylcarbodiimide, 4-(*N,N*-dimethylamino)pyridine.

Scheme 1. Synthetic route to the unsymmetrical TTF derivatives **7** and **8**.



2a...(i) n-Butyllithium; (ii) $CO_{2(s)}$; (iii) glacial acetic acid.
2b...*N,N'*-Dicyclohexylcarbodiimide, 4-(*N,N*-dimethylamino)pyridine

Scheme 2. Synthetic route to the monosubstituted TTF derivatives **13–16**.

reaction of the 1-iodopentane with the lithium salt. After seven hours at −78°C, GLC analysis showed that all the tetrathiafulvalene had been consumed, but many product peaks were present. The crude product was purified by column chromatography (twice in petroleum fraction b.p. 40–60°C) to give the product in 30% yield and >99% purity by GLC. Although it was not attempted, it is also likely that the reaction might be further improved by the use of potassium *tert*-butoxide as the base, or chelating/solvating agents such as 1,4-diazabicyclo[2.2.2]octane (DABCO), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) or dimethoxyethane (DME) [27].

The presence of the electron-donating pentyl group in the tetrathiafulvalene system was expected to decrease the acidity of the proton adjacent to the pentyl substituent and therefore to direct further lithiation into the other ring. Monolithiation of 2-pentyltetrathiafulvalene (**2**) was achieved at −78°C using *n*-butyllithium in a procedure similar to that used by Green [22, 23]. At higher temperatures, redistribution of the lithium is known to occur to give multi-lithiated species and unknown products. Subsequent reaction of the lithium salt with solid carbon dioxide [28] gave the acid **3** in 84% yield. Esterification of compound **3** gave compounds **7** and **8**, and their ^{13}C NMR spectra showed that reaction had occurred only in the unsubstituted ring to give an almost 1:1 mixture (composition established from ^{1}H NMR integration of the tetrathiafulvalene signals) of the *cis*- and *trans*-isomers. Compound **5** was prepared in 52% yield using the method reported by Jochims [29]. The esterification of compound **3** with the phenols **5** and **6** (steps 1d) used the method of Hassner and Alexanian [30]; the poor yields of mixtures **7** and **8** obtained were due to recrystallization from large volumes of solvent to ensure the absolute chemical purity of the *cis*/*trans*-isomer mixtures. Attempted separation of the *cis*- and *trans*-isomers of mixtures **7** and **8** failed, using HPLC on both silica and C18 columns with a wide range of solvents including cyclopentane, chloroform, tetrahydrofuran, water and acetonitrile in numerous combinations.

2.2.1. *Tetrathiafulvalene (**1**)*

Compound **1** was prepared as previously described [25]; yield 13.45 g (82%), m.p. 119°C (lit [25] 119–119.5°C), purity (GLC) >99%. ^{1}H NMR ($CDCl_3$) δ 6.32 (4H, s). ^{13}C NMR ($CDCl_3$) δ 110(2C), 119(4C) ppm. IR (KBr) ν_{max} 630, 650, 780, 795, 1250, 1530 cm^{-1}. MS *m*/*z* 204 (M^+, 100%), 159, 146, 102, 76.

2.2.2. *2-Pentyltetrathiafulvalene (**2**)*

n-Butyllithium (1.7 ml, 10.0M in hexanes, 0.017 mol) was added dropwise to a stirred, cooled (– 78°C) solution of compound **1** (3.02 g, 0.015 mol), dry THF (150 ml) and dry HMPT (30 ml) under dry nitrogen at – 78°C. The reaction mixture was maintained under these conditions for a further 45 min before 1-iodopentane (6.70 g, 0.034 mol) was added dropwise at – 78°C. The reaction mixture was maintained under these conditions for a further 7 h (GLC analysis revealed a complete reaction) before being allowed to warm to room temperature (overnight). Water (400 ml) was added and the crude product was extracted into ether (3 × 100 ml) and dried ($MgSO_4$). The solvent and the excess of 1-iodopentane were removed *in vacuo* and the product was purified by column chromatography (twice, silica gel/petroleum fraction b.p. 40–60°C) to give a yellow oil; yield 1.21 g (30%), purity (GLC) >99%. ^{1}H NMR ($CDCl_3$) δ 0.90 (3H, t), 1.30 (4H, m), 1.54 (2H, quint), 2.38 (2H, t), 5.88 (1H, s), 6.29 (2H, 2 × d). IR (film) ν_{max} 640, 740, 780, 795, 1120, 1375, 1455, 1595, 2850, 2920, 2950, 3065 cm^{-1}. MS *m*/*z* 274 (M^+), 146, 102 (100%), 76, 70.

2.2.3. *6- and 7-Pentyltetrathiafulvalene-2-carboxylic acid (**3**)*

n-Butyllithium (1.7 ml, 2.5M in hexanes, 4.3 mmol) was added dropwise to a stirred, cooled (– 78°C) solution of compound **2** (1.07 g, 3.91 mmol) in dry THF (200 ml), under dry nitrogen at – 75 to – 78°C. The mixture was maintained under these conditions for a further 0.5 h (GLC analysis confirmed a complete reaction) before being poured into a stirred slurry of solid carbon dioxide and dry THF. The slurry was left to stir overnight and the solvent was removed *in vacuo* before the residue was dissolved in hot glacial acetic acid. Ice (400 g) was added to the solution and the product was filtered off, washed with water (250 ml) and dried *in vacuo* (KOH, P_2O_5) to afford a dark red solid which was used in the next step without purification; yield 1.05 g (84%), m.p. 128–130°C. ^{1}H NMR ($CDCl_3$) δ 0.91 (3H, t), 1.33 (4H, m), 1.58 (2H, quint), 2.41 (2H, t), 2.99–3.96 (1H, br s), 5.91 (1H, two s), 7.46 (1H, two s). IR (KBr) ν_{max} 1290, 1380, 1420, 1540, 1660, 1730, 2920, 2960, 3200–3600 cm^{-1}. MS *m*/*z* 318 (M^+), 146 (100%), 86, 76, 45.

2.2.4. *4-Isothiocyanatophenol (**5**)*

Compound **5** was prepared as described in [29]; yield 15.77 g (52%), m.p. 40–41°C (lit [29] 40°C), purity (GLC) >99%. ^{1}H NMR ($CDCl_3$) δ 5.14 (1H, s), 6.81 (2H, d), 7.12 (2H, d). IR (KBr) ν_{max} 825, 925, 1100, 1240, 1355, 1445, 1500, 1595, 1610, 2050, 3360 cm^{-1}. MS *m*/*z* 151 (M^+, 100%), 119, 93, 75, 65.

2.2.5. *4-Cyanophenyl 6- and 7-pentyltetrathiafulvalene-2-carboxylate (**7**)*

N,*N*′-Dicyclohexylcarbodiimide (DCC) (0.41 g, 1.90 mmol) was added in one portion to a stirred solution of compound **3** (0.53 g, 1.67 mmol), compound **6** (0.20 g, 1.68 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) (0.03 g, 0.25 mmol) in dry dichloromethane (50 ml) at room temperature. The reaction mixture was stirred at room temperature overnight and the aqueous *N*,*N*′-dicyclohexyl urea filtered off. The filtrate was washed successively with aqueous potassium hydroxide (2 × 200 ml, 5%), water (200 ml), acetic acid (200 ml, 5%), water (200 ml) and dried ($MgSO_4$). The solvent was removed *in vacuo* and the crude product was purified by column chromatography (silica gel/dichloromethane) and crystallization from 1:1 ethanol:ethyl acetate to afford red crystals which were dried *in vacuo* (P_2O_5); yield 0.09 g (13%), purity (HPLC) >99%. Transitions (°C) Cr 120.4 (N 100.0) I. $\Delta n = 0.404$, $\Delta\alpha = 53.48$, $S = 0.55$ at 25°C. $\Delta n = 0.398$, $\Delta\alpha = 52.96$, $S = 0.55$ at $T/T_{N\text{-}I} = 0.7815$. ^{1}H NMR ($CDCl_3$) δ 0.91 (3H, t), 1.32 (4H, m), 1.55 (2H, q), 2.42 (2H, t), 5.92 (1H, two s), 7.30 (2H, d), 7.61 (1H, two s), 7.72 (2H, d). ^{1}H NMR (DMSO-d_6) δ 0.86 (3H, t), 1.28 (4H, m), 1.47 (2H, q), 2.50 (2H, t), 6.43 (1H, two s), 7.51 (2H, d), 7.96 (2H, d), 8.17 (1H, two s). ^{13}C NMR ($CDCl_3$) δ 14(1C), 22(1C), 29(1C), 31(2C), 110(1C), 111(0.5C), 112(0.5C), 116(1C), 118(1C), 122(2C), 126(1C), 134(2C), 136(0.5C), 136(0.5C) 138(2C), 153(1C), 157(1C) ppm. IR (KBr) ν_{max} 715, 840, 1005, 1170, 1195, 1220, 1265, 1285, 1420, 1500, 1600, 1680, 1720, 2240, 2920, 2960 cm^{-1}. UV λ_{max} (cyclohexane) 196 (61 200 dm^3 mol^{-1} cm^{-1}), 232 (19 230), 284 (21 850) nm. MS *m*/*z* 419 (M^+), 173, 131, 69 (100%), 53.

2.2.6. *4-Isothiocyanatophenyl 6- and 7-pentyltetrathiafulvalene-2-carboxylate (**8**)*

Compound **8** was prepared by a similar method to that described for compound **7** using the quantities stated: compound **3** (0.47 g, 1.48 mmol), compound **5** (0.22 g, 1.46 mmol), DMAP (0.37 g, 2.96 mmol), DCC (0.02 g, 0.16 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 petroleum fraction b.p. 40–60°C: ethyl acetate, 2 : 1 to afford red crystals which were dried *in vacuo* (P_2O_5); yield 0.18 g (27%), purity (HPLC) $>$99%. Transitions (°C) Cr 107.0 SmA 115.0 [N 89] I. $\Delta n = 0.425$, $\Delta\alpha = 74.18$, $S = 0.45$ at 25°C. $\Delta n = 0.496$, $\Delta\alpha = 73.48$, $S = 0.53$, at $T/T_{\text{N-I}} = 0.7815$. ^{1}H NMR ($CDCl_3$) δ 0.90 (3H, t), 1.32 (4H, m), 1.55 (2H, q), 2.41 (2H, t), 5.91 (1H, two s), 7.15 (2H, d), 7.25 (2H, d), 7.57 (1H, two s). ^{1}H NMR (DMSO-d_6) δ 0.88 (3H, t), 1.29 (4H, m), 1.49 (2H, q), 2.50 (2H, t), 6.42 (1H, two s), 7.35 (2H, d), 7.52 (2H, d), 8.13 (1H, two s). ^{13}C NMR ($CDCl_3$) δ 14(1C), 22(1C), 29(1C), 31(2C), 111(0.5C), 112(0.5C), 123(2C), 127(4C), 129(1C), 135(0.5C), 135(0.5C) 136(2C), 138(1C), 149(1C), 157(1C) ppm. IR (KBr) $\nu_{\max}$ 840, 980, 1010, 1190, 1255, 1270, 1490, 1495, 1700, 1720, 2000–2200, 2920, 2960 cm^{-1}. UV $\lambda_{\max}$ (cyclohexane) 203 (44 150 dm^3 mol^{-1} cm^{-1}), 225 (37 580), 289 (29 620) nm. MS *m/z* 451 (M$^+$), 273, 173, 115, 69 (100%).

2.2.7. *Tetrathiafulvalene-2-carboxylic acid (9)*

Compound **9** was prepared as described for the preparation of compound **3** using the quantities stated: *n*-butyllithium (2.4 ml in hexane, 2.5M, 6.0 mmol), compound **1** (1.12 g, 5.49 mmol). Water was added to the isolated lithium salt of the acid and the solution was filtered to remove any unreacted lithium-tetrathiafulvalene derivative before being made acidic with hydrochloric acid (1.0M). The product was filtered off under dry nitrogen and crystallized from benzene to afford a dark red solid that was dried *in vacuo* ($CaCl_2$); yield 0.93 g (75%), m.p. 187–188°C (lit [23] 182–184°C). ^{1}H NMR [$(CD_3)_2CO$] δ 2.90 (1H, s), 6.66 (2H, s), 7.64 (1H, s). IR (KBr) $\nu_{\max}$ 730, 1040, 1195, 1305, 1530, 1640, 2500–3080 cm^{-1}. MS *m/z* 248 (M$^+$), 146, 102, 76, 58 (100%).

This compound and compounds **14–16**, were prepared as described for the preparation of compound **7**, using the quantities stated.

2.2.8. *4-Isothiocyanatophenyl tetrathiafulvalene-2-carboxylate (13)*

Quantities: compound **9** (0.50 g, 2.02 mmol), compound **5** (0.28 g, 1.85 mmol), DCC (0.44 g, 2.04 mmol), DMAP (0.10 g, 0.80 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 cyclohexane : ethyl acetate, 1 : 1 to afford a red solid which was dried *in vacuo* (P_2O_5); yield 0.50 g (69%), purity (HPLC) $>$99%. Transitions (°C) Cr 161.4 [N 124] I. ^{1}H NMR ($CDCl_3$) δ 6.35 (2H, 2 × d), 7.08 (2H, d), 7.23 (2H, d), 7.58 (1H, s). ^{1}H NMR (DMSO-d_6) δ 6.84 (2H, 2 × d), 7.40 (2H, d), 7.57 (2H, d), 8.19 (1H, s). ^{13}C NMR ($CDCl_3$) δ 118(1C), 119(1C), 123(2C), 127(3C), 129(1C), 135(2C), 136(1C), 149(1C), 158(1C), 167(1C) ppm. IR (KBr) $\nu_{\max}$ 855, 1190, 1240, 1255, 1495, 1535, 1720, 2120, 2180, 3160 cm^{-1}. UV $\lambda_{\max}$ (chloroform) 284 (39 030 dm^3 mol^{-1} cm^{-1}) nm. MS *m/z* 381 (M$^+$, 100%), 203, 187, 146, 103.

2.2.9. *4-Cyanophenyl tetrathiafulvalene-2-carboxylate (14)*

Quantities: compound **9** (0.75 g, 3.02 mmol), compound **10** (0.29 g, 2.44 mmol), DCC (0.60 g, 2.78 mmol), DMAP (0.12 g, 0.96 mmol). The product was purified by column chromatography (silica gel/dichloromethane) and was crystallized from petroleum fraction b.p. 40–60°C: ethyl acetate, 1 : 5 to afford brown crystals which were dried *in vacuo* (P_2O_5); yield 0.22 g (26%), purity (HPLC) $>$99%. Transitions (°C) Cr 211.4 [N 143] I. ^{1}H NMR (DMSO-d_6) δ 6.79 (2H, 2 × d), 7.52 (2H, d), 7.96 (2H, d), 8.18 (1H, s). IR (KBr) $\nu_{\max}$ 960, 1015, 1215, 1240, 1490, 1530, 1600, 1720, 2230, 3070 cm^{-1}. UV $\lambda_{\max}$ (chloroform) 241 (40 250 dm^3 mol^{-1} cm^{-1}) nm. MS *m/z* 349 (M$^+$, 100%), 203, 187, 146, 102.

2.2.10. *S-4-Cyanophenyl tetrathiafulvalene-2-thiocarboxylate (15)*

Quantities: compound **9** (0.65 g, 2.62 mmol), compound **11** (0.28 g, 2.07 mmol), DCC (0.52 g, 2.41 mmol), DMAP (0.11 g, 0.88 mmol). The crude product was purified by column chromatography (silica gel/dichloromethane) and was crystallized from petroleum fraction b.p. 40–60°C: ethyl acetate, 4 : 1 to afford dark red crystals which were dried *in vacuo* (P_2O_5); yield 0.10 g (13%), purity (HPLC) $>$99%. Transitions (°C) Cr 238.2 [N 133] I. ^{1}H NMR ($CDCl_3$) δ 6.37 (1H, d), 6.43 (1H, d), 7.35 (1H, s), 7.52 (2H, d), 7.67 (2H, d). IR (KBr) $\nu_{\max}$ 880, 1090, 1105, 1510, 1590, 1655, 2230, 3050 cm^{-1}. UV $\lambda_{\max}$ (chloroform) 239 (22 360 dm^3 mol^{-1} cm^{-1}), 277 (29 030) nm. MS *m/z* 365 (M$^+$, 100%), 231, 203, 146, 102.

2.2.11. *4′-Cyanobiphenyl-4-yl tetrathiafulvalene-2-carboxylate (16)*

Quantities: compound **9** (0.38 g, 1.53 mmol), DCC (0.31 g, 1.44 mmol), DMAP (0.06 g, 0.48 mmol), compound **12** (0.24 g, 1.2 mmol). The crude product was purified by column chromatography (silica gel/petroleum fraction b.p. 40–60°C: dichloromethane, 1 : 3) and was crystallized from ethyl acetate to afford red crystals which were dried *in vacuo* (P_2O_5); yield 0.42 g (82%), purity (HPLC) $>$99%. Transitions (°C) Cr 228.5 N 260.3 decomp. ^{1}H NMR ($CDCl_3$) δ 6.36 (3H, m), 7.28 (2H, d), 7.62 (2H, d), 7.67 (2H, d), 7.74 (2H, d). IR (KBr)

ν_{max} 825, 1000, 1180, 1195, 1260, 1490, 1530, 1600, 1710, 2220, 3065 cm^{-1}. UV λ_{max} (chloroform) 216 (32 750 dm^3 mol^{-1} cm^{-1}), 280 (51 490) nm. MS *m*/*z* 425 (M$^+$), 203, 195, 146, 103 (100%).

3. Results and discussion

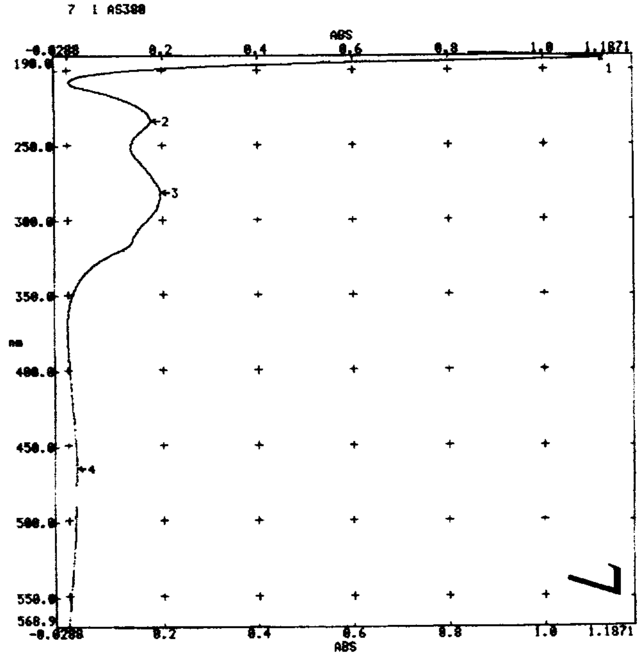
3.1. *Transition temperatures and physical properties*

Both of the unsymmetrically-substituted tetrathiafulvalene mixtures (**7** and **8**) are red and show a small absorption in the blue region of the visible spectrum (see figure 1). The cyano mixture (**7**) absorbs at 471 nm (18 700 dm^3 mol^{-1} cm^{-1}) and the isothiocyanate mixture (**8**) absorbs at 466 nm (18 540 dm^3 mol^{-1} cm^{-1}), emphasizing the high degree of conjugation provided by the TTF unit.

The solubility of both mixtures in the non-polar I eutectic host material is rather low with the cyano mixture being soluble up to 12 wt% and the isothiocyanate mixture being soluble up to 17 wt%. In the E7 polar mixture (Merck UK, England) the solubility of both materials rises to ~25 wt% making their use as dopants quite feasible.

The melting points and transition temperatures of isomer mixtures **7** and **8** are given in table 1. A comparison of tetrathiafulvalenes **7** and **8** with the corresponding systems **17** [31] and **18** [19] (see figure 2), with a phenyl ring in place of the tetrathiafulvalene unit, reveals some remarkable results. The $T_{N\text{-}I}$ values of mixtures **7** and **8** are 45.7°C and 46°C higher than those of compounds **17** and **18**, respectively, and mixture **8** exhibits a smectic A phase up to 115°C after melting at 107.0°C. The nematic phase thermal stabilities of mixtures **7** and **8** are not easy to predict as although the $T_{N\text{-}I}$ values should be higher than those of compounds **17** and **18** because of the huge increase in the polarizability (see later), the situation is complicated by an increase in the length:breadth ratios (for the *trans*-forms of **7** and **8**, compared with **17** and **18**, respectively) and by the bent geometry of the *cis*-compounds (low aspect ratio) which are present in each mixture. The latter issue will additionally complicate the possibility of antiparallel associations.

The greater molecular polarizability (see table 3) and length : breadth ratio of the isothiocyanate group leads to an increase in the clearing point when compared with the cyano mixture. Studies by the authors on phenylthiophene compounds [32] with cyano and butylsulfanyl terminal substituents have shown that clearing points are much lower than for the corresponding biphenyl compounds. This is thought to be in part due to the reduced antiparallel association caused by the nitrile lying over the large sulphur atom of the thiophene ring. It is thus possible that antiparallel association in tetrathiafulvalene systems such as **7** is very weak, and the difference in the clearing points of mixtures **7** and **8** may be mainly due to the enhanced molecular polarizability of mixture **8** combined with the greater aspect ratio.



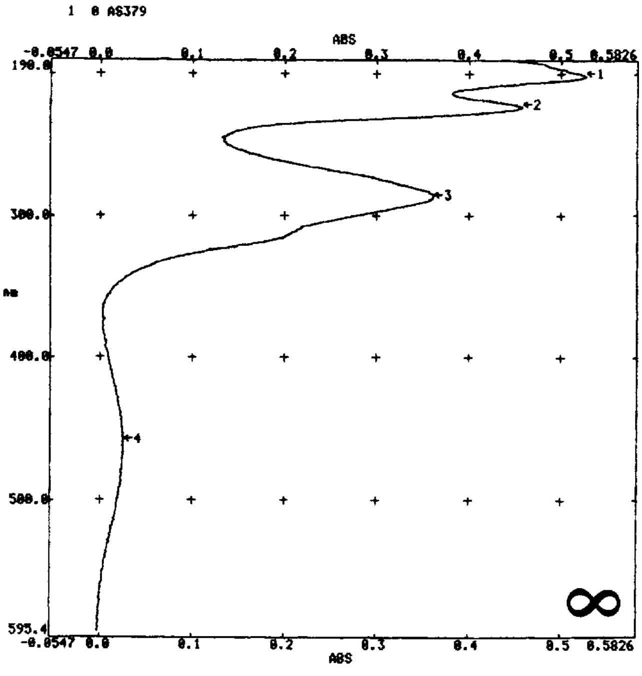
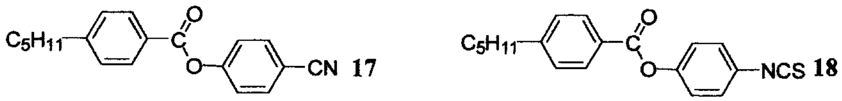


Figure 1. UV spectra of compounds 7 and 8.

The melting points and transition temperatures of the monosubstituted tetrathiafulvalene ester derivatives **13–16** are given in table 2. Compounds **13–15** all have a single phenyl ring and none of these compounds is mesogenic because of the high melting points; the virtual

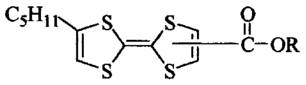


17 Cryst. 60.3 (N 54.3) I

18 Cryst. 90.7 [N 43] I

Figure 2. Phenyl analogues of the isomeric mixtures **7** and **8**.

Table 1. Melting points and transition temperatures of the tetrathiafulvalene ester mixtures **7** and **8**.



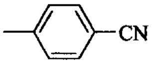
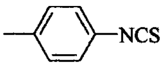
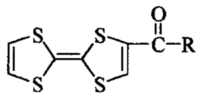
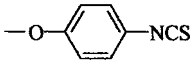
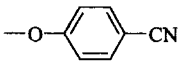
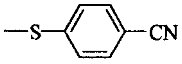
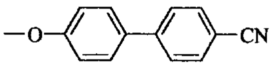
Mixture	*R*	Cr		SmA		N		I
7		•	120.4	—	—	(•	100)	•
8		•	107.0	•	115.0	[•	89]	•

Table 2. Melting points and transition temperatures of the tetrathiafulvalene esters **13**–**16**.



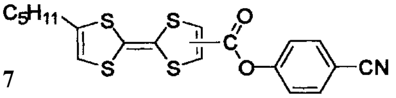
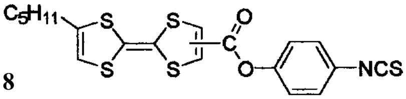
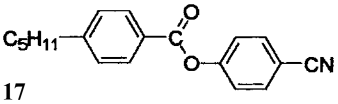
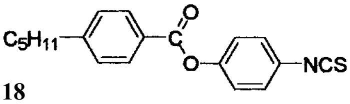
Compound	*R*	Cr		N		I
13		•	161.4	[•	124]	•
14		•	211.4	[•	143]	•
15		•	238.2	[•	133]	•
16		•	228.5	•	260.3	Decomposition

$T_{\text{N-I}}$ values for these compounds are similar. The biphenyl derivative **16** melts at 228.5°C and has an enantiotropic nematic phase, but the compound decomposes at 260.3°C before the clearing point is reached. The incorporation of a benzene ring into the structure of **14** to produce **16** has contributed to an increase in $T_{\text{N-I}}$ value of at least 117°C (before decomposition); the magnitude of this increase is in keeping with that seen for the 4-cyanophenyl and 4′-cyanobiphenyl-4-yl benzoates [33].

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

The optical properties and related parameters for compounds **7**, **8**, **17** and **18** are given in table 3. Values are quoted at a fixed reduced absolute temperature ($T/T_{\text{N-I}} = 0.7815$) [19] to provide a fair comparison of the changes in molecular structure between the systems. Values at 25°C are additionally quoted in § 2 to give the reader an idea of the usefulness of the materials at a

Table 3. The refractive indices, optical anisotropies, polarizabilities and order parameters of mixtures **7** and **8** and compounds **17** and **18** at $T/T_{N\text{-}I} = 0.7815$.

Compound/isomeric mixture	$n_\parallel$	$n_\perp$	Δn	$\Delta\alpha$	S
 **7**	1.822	1.424	0.398	53.0	0.55
 **8**	1.962	1.466	0.496	73.5	0.53
 **17**	1.711	1.516	0.195	13.6	0.72
 **18**	1.795	1.534	0.261	22.4	0.67

standard operating temperature. The following discussion is given with reference to the fixed reduced temperatures only.

The polarizabilities of mixtures **7** and **8** are 39.4 and 51.1 higher than those of compounds **17** and **18**, respectively. In crude quantitative terms these results show that tetrathiafulvalene provides twice the polarizability of a 2,6-naphthalene unit and five times that of 1,4-benzene [19] The extremely high polarizability of the tetrathiafulvalene core has to overcome the greater breadth of the molecule compared with that of benzene. The greater polarizability of **8** compared with **7** is due to the greater polarizability of the isothiocyanate group and the increased aspect ratio. Although the isothiocyanate group is bent (the C–N–C bond angle being roughly 120°), the breadth of the tetrathiafulvalene core shields this bend.

The order parameters of mixtures **7** and **8** are similar to each other and are 0.17 and 0.14 lower than those of compounds **17** and **18**, respectively. The order parameters of the tetrathiafulvalene mixtures would be expected to be lower than those of the corresponding phenyl compounds because the length : breadth ratios are reduced as a result of the broad tetrathiafulvalene core and, more importantly, the presence of the 'bent' *cis*-isomers that will result in a lower intermolecular attraction due to an uneven distribution of the dispersion forces. The fact that the mutual relationships for the order parameters of **7** and **8** and of **17** and **18** are similar indicates that for **7** and **8** the complicated issues of *cis/trans*-mixtures, and possible differences in antiparallel correlations and in the densities of the materials are fortuitously self-cancelling.

For mixtures **7** and **8**, the values of $n_\parallel$ are 0.111 and 0.167 higher than those for compounds **17** and **18**, respectively, due to the huge increase in the longitudinal polarizability on replacing the phenyl ring with tetrathiafulvalene. Surprisingly, the values of $n_\perp$ for mixtures **7** and **8** are 0.091 and 0.068 lower than those of compounds **17** and **18**, respectively. It is probable that the electrons on tetrathiafulvalene are so polarizable that the cyano and ester groups create a very large longitudinal polarizability, but since there is no net lateral dipole arising from the tetrathiafulvalene core itself, the effects of the sulphur atoms in the core may cancel each other out and the electrons may contribute very little to the lateral polarizability. However, the very small value of $n_\perp$ may also arise because of a decreased density, but this is difficult to confirm since we have a mixture of *cis*- and *trans*-forms and the possibility of antiparallel association for mixture **7**. A reduced density would also affect the values of $n_\parallel$, although since they are so large the decrease may be small relative to the decrease in $n_\perp$ and hence be difficult to quantify.

The optical anisotropy of the cyano mixture is 0.098 lower than that of the isothiocyanate mixture, which has a birefringence of 0.496. The greater polarizability of the isothiocyanate group is due to sp^2 hybridization of the nitrogen and sulphur atoms (carbon is sp hybridized in the same way as an allene) and the highly polarizable sulphur nucleus, whereas the cyano group is sp hybridized and the electrons are located closer to the nuclei, thus being less polarizable. Compounds **7** and **8** have optical anisotropies that are 0.203 and 0.235 higher than compounds **17** and **18**, respectively, due to the enhanced polarizability of the tetrathiafulvalene core.

The monosubstituted tetrathiafulvalene derivatives **13–16** were found to be insoluble in the I eutectic host material and only of low solubility in the E7 host material; this poor solubility prevented accurate evaluation of their optical properties but demonstrates their unsuitability as high birefringence additives.

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