JOURNAL OF
Materials
CHEMISTRY

Synthesis and liquid crystal behaviour of tetrathiafulvalenes containing cyanobiphenylyloxy groups

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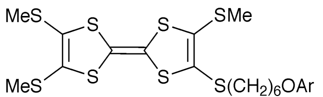
The synthesis and characterization of a series of tetrathiafulvalenes (**1**–**3**) bearing a different number of 4′-cyanobiphenyl-4-yloxy side groups is reported. Compound **3** exhibits a nematic and a smectic A mesophase. In the smectic A phase a peculiar local biaxial order due to the unconventional molecular structure is proposed. A charge-transfer salt derived from **3**, namely **3**·I_5, also shows mesogenic behaviour.

Tetrathiafulvalene (TTF) derivatives[1] have played a pivotal role in the development of organic conductors.[2] The transport properties of these materials are clearly dependent on the molecular architecture in the solid and so a wide variety of substituents has been introduced at the periphery of the TTF core in order to achieve a suitable solid-state organization. In this respect, the most relevant results have been obtained with electrocrystallized bidimensional cation-radical salts which, in some cases, have given rise to organic superconductivity.[3] Given the numerous and subtle factors involved in the electrocrystallization technique, alternative ways of organizing assemblies of TTF derivatives have been developed, such as Langmuir–Blodgett film deposition.[2,4]

Another possible approach is based on the preparation of mesogenic compounds. Surprisingly, although a considerable number of TTF derivatives have so far been synthesized, there are only a few reports describing tetrathiafulvalene derivatives with mesomorphic properties[5–11] and, consequently, it is not yet possible to establish structure–property relationships for this family of compounds. A possible starting point in the search for new liquid-crystalline TTF derivatives lies in the attachment of mesogenic units to the periphery of the TTF core. We envisaged the use of the 4′-alkoxy-4-cyanobiphenyl moiety, which has been successfully used in the preparation of calamitic liquid crystals,[12–14] some of which bear electron-donor units such as thiophene[13] and ferrocene.[14]

In order to study the effect of such moieties on the possible liquid crystal behaviour of new TTF derivatives, we attached a different number of 4′-cyanobiphenyl-4-yloxy side-groups to a TTF unit through flexible spacers. In this article we report the synthesis, characterization and study of the mesomorphic properties of tetrathiafulvalene derivatives **1**, **2** and **3**.



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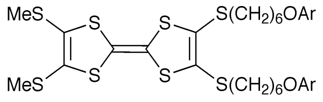

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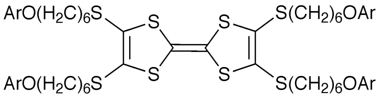

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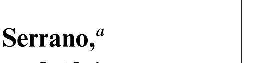


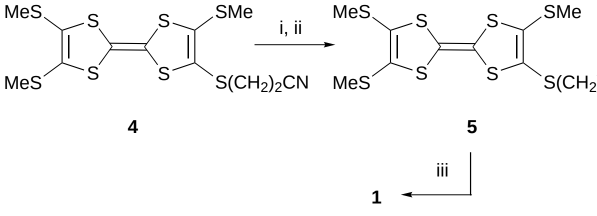
Moreover, the mesogenic behaviour of a charge-transfer salt derived from compound **3** is also described.

Results and Discussion

Synthesis and characterization

The synthetic methodology adopted for the preparation of compounds **1**, **2** and **3** makes use of the previously described tetrathiafulvalenes **4**, **6** and **10**, respectively. As recently shown by Becher,[15,16] the 2-cyanoethylthio moiety is a convenient protecting group for the thiolate anion in TTF chemistry, leading to a variety of alkylthiotetrathiafulvalene derivatives. For the synthesis of **1**, the required ω-bromo compound **5** was prepared by the reaction of the corresponding tetrathiafulvalenethiolate anion, generated *in situ*, added dropwise to a solution of 1,6-dibromohexane in dichloromethane. A subsequent Williamson reaction with the sodium salt of 4-cyano-4′-hydroxybiphenyl afforded compound **1** in good yield (Scheme 1).

The preparation of bromides **9** and **13** required longer syntheses than that described above since the treatment of the corresponding di- or tetra-thiolates (generated from **6** and **10**, respectively, with Bu^{t}OK in DMF) with 1,6-dibromohexane could lead to undesired side reactions giving, for example, cyclization products.[17] Thus, alcohols **7** and **11** were prepared



Scheme 1 *Reagents*: i, CsOH; ii, $Br(CH_2)_6Br$; iii, 4,4′-$HOC_6H_4C_6H_4CN$, NaH

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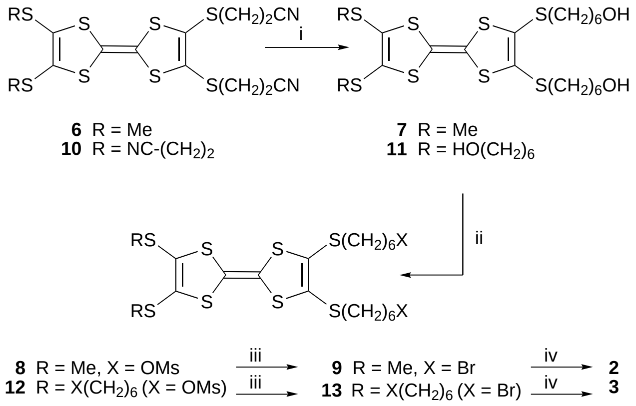

Scheme 2 *Reagents*: i, Bu^{t}OK, Br(CH$_2$)$_6$OH; ii, MeSO$_2$Cl, NEt$_3$; iii, LiBr; iv, 4,4′-HOC$_6$H$_4$C$_6$H$_4$CN, NaH

and converted into the required bromides *via* the corresponding mesylates, with yields ranging from good to excellent. In a similar way to the synthesis of **1**, a twofold or fourfold Williamson reaction gave tetrathiafulvalenes **2** and **3** respectively (Scheme 2).

The target compounds were characterized by IR, elemental analysis, ^{1}H and ^{13}C NMR, and mass spectrometry. All the compounds studied in EI$^+$ mode showed very intense molecular ion peaks and the characteristic fragmentation pattern of the TTF system. High molecular weight ($m/z > 900$) derivatives were analyzed by LSIMS$^+$. Moreover, single crystals of the monosubstituted TTF derivative **1** were grown from an ethyl acetate–pentane mixture, allowing an X-ray diffraction study[18] to be performed. The small size of the needles obtained, associated with the high number of independent atoms in the unit cell (two independent molecules per unit cell), meant that an accurate structural determination could not be obtained. Nevertheless, the main crystallographic features of **1** are undoubtedly found in the occurrence of fully extended conformations, in which both the cyanobiphenyl and TTF fragments of two different molecules are located face to face, without evidence of intermolecular interactions.

Mesogenic behaviour

Microscopy study. Tetrathiafulvalene **3**, bearing four mesogenic groups attached to the central TTF core, is the only derivative in this series which shows mesomorphic properties. When studied by polarizing microscopy compound **3** shows monotropic liquid crystal behaviour. On cooling the isotropic liquid a nematic phase appears with a characteristic schlieren texture. On cooling the sample further a transition to a smectic A phase, with a fan-shaped texture, is observed. On further cooling, crystallization does not occur, but the sample solidifies into a glassy state. Thus, a glass that retains the structure of the S$_A$ phase is obtained.

DSC study. By comparing the DSC results with the microscopic observations, a more detailed view of the thermal behaviour of this compound can be obtained. The different scans are shown in Fig. 1. The crystalline substance was heated at a rate of 10 °C min^{-1} (scan A). During the melting process rich polymorphism was detected. In the first cooling (scan B) a peak at *ca.* 92 °C is observed, corresponding to the I→N transition, followed by a shoulder (N→S$_A$ transition). Upon further cooling, the monotropic S$_A$ mesophase undergoes a glass transition ($T_g = 23$ °C) to give a frozen (S$_{glass}$) phase. Crystallization does not take place, even on prolonged storage of the sample at low temperature, and in the subsequent heating (scan C), the S$_{glass}$→S$_A$ transition is observed at 23 °C, followed by a peak corresponding to the S$_A$→N and N→I transitions. At a lower scanning rate (1 °C min^{-1}, scan D) separation of these overlapped transitions is achieved, revealing that they occur at 91.5 and 92.2 °C, respectively.

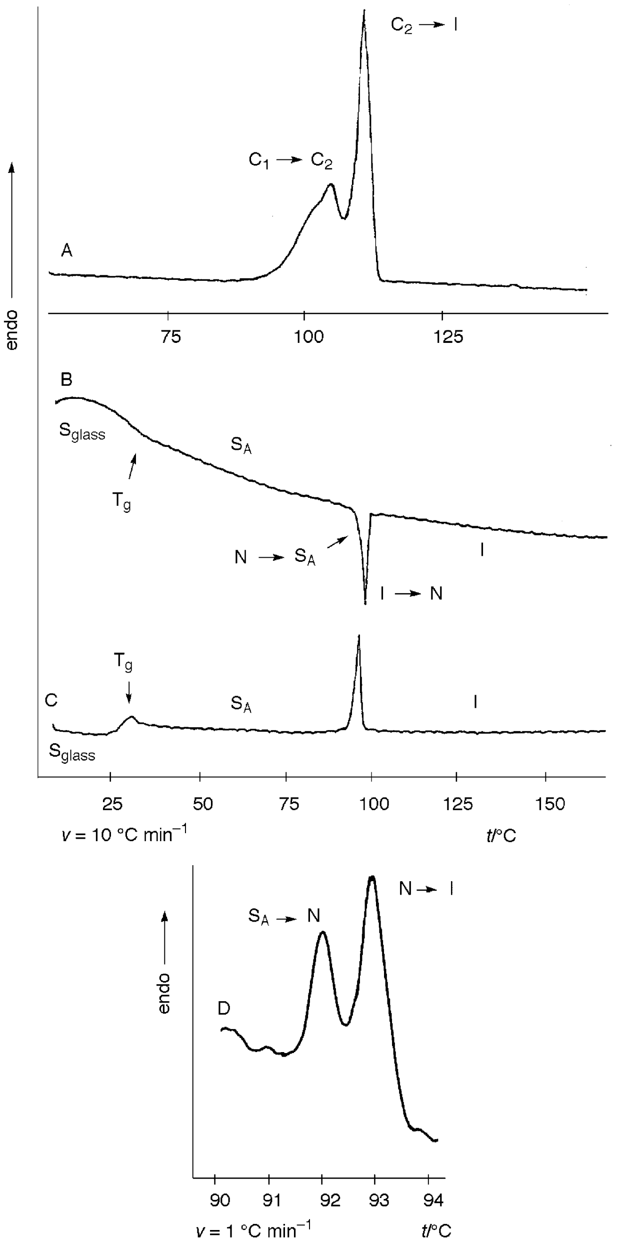

Fig. 1 DSC curves of compound **3**

X-Ray diffraction study. An X-ray diffraction study was carried out on the frozen monotropic mesophase of compound **3** at room temperature. A sample of the compound was placed in a Lindemann glass capillary, heated in an oven at a temperature high enough to give the isotropic liquid and then quickly cooled to 25 °C. The X-ray photograph obtained by irradiating this sample is shown along with a schematic drawing in Fig. 2 and 3 respectively.

From the pattern it can be deduced that the molecules within the sample adopt a preferential orientation, as revealed by the presence of diffraction arcs instead of the rings expected from a non-oriented powder sample. This spontaneous orientation has been described by other authors,[19] and arises from a *wall* effect that favours an alignment of the molecular axes parallel to the internal surface of the glass capillary (planar orientation).

Two regions can be distinguished in the pattern:

At small angles, two pairs of spots are observed in the

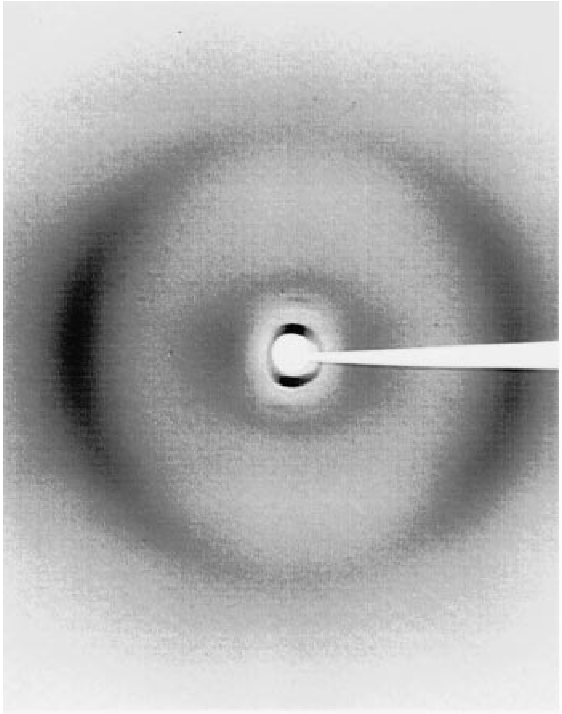

Fig. 2 X-Ray photograph of **3**

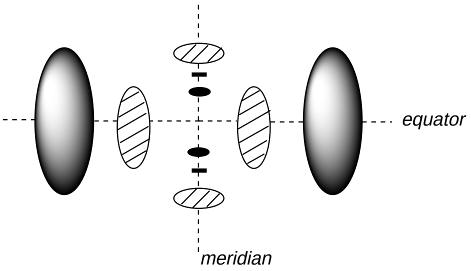

Fig. 3 Schematic drawing of photograph in Fig. 2

direction of the capillary axis (vertical direction in Fig. 3, also called the *meridian*), the first of which is much stronger than the second. These maxima are related to the lamellar order and correspond, respectively, to the first and second order reflection from the smectic layers. Using Bragg's law, these reflections give a layer spacing of 34 Å.

At large angles, a pair of diffuse arcs are observed which are centred in the plane perpendicular to the capillary axis (horizontal direction in Fig. 3, also called the *equator*). This maximum is related to the short-range order within the smectic layer and, using Bragg's law, allows an estimation of the mean intermolecular distance. This distance is about 4.4 Å, a value typical of those found in calamitic mesophases (*i.e.* formed by rod-like molecules).

This kind of pattern is consistent with a smectic A mesophase. The broadness and diffuseness of the large-angle maximum exclude the existence of long-range order within the layers, which allows us to rule out other more organized smectic mesophases.

It is interesting to note that the presence of the second order reflection from the smectic layers is not usual in most classical liquid crystals. High-order reflections only tend to appear when the molecule contains heavy atoms (for instance metals or, in this case, sulfur) which increase the structure factor at high angles and therefore reinforce the intensity of the diffraction peaks over the whole angular range.[20]

Although the layer spacing in a smectic A mesophase would be expected to be equal to the molecular length, the value measured experimentally is usually smaller than that predicted from molecular models. This is due in most cases to the conformational freedom of the hydrocarbon chains in the mesophase (presence of a number of *gauche* bonds), which reduces the effective length. The molecular length calculated for compound **3** using Dreiding stereomodels, assuming an all-*trans* conformation, is 50 ± 1 Å. The difference of 16 Å found with respect to the layer thickness measured by X-ray diffraction (34 Å) is too large to be accounted for only by the existence of a number *gauche* bonds. Indeed, a difference of 16 Å between the predicted and the experimental values should correspond to a reduction of 8 Å in each chain length, which is not reasonable for a chain of only six carbon atoms. The most plausible explanation is that a phenomenon of interpenetration or interdigitation between molecules of neighbouring layers takes place, a situation that has also been described for the mesophases formed by other molecules with an X- or H-shape.[19,21] Moreover, the presence of the terminal cyano groups is known to favour an antiparallel association of dipoles,[22] that generates structures in which molecules of neighbouring sublayers are interdigitated.

In addition to the diffraction maxima observed at small and large angles that have been described above, and are typically found in the patterns of the smectic A mesophase of rod-like liquid crystals, the X-ray photograph of compound **3** also shows some unusual features. In particular, a diffuse shell with an elliptical shape is seen at middle angles and the intensity of this shell is reinforced in the directions of the meridian and equator. The presence of this scattering indicates that there is some kind of short-range order which is usually absent in a smectic A mesophase.

The scattered intensity centred in the equator corresponds to a distance of 14–15 Å and must be associated with the existence of interactions within the smectic layers. This phenomenon has been reported for liquid crystals formed by transition metal complexes with a dimer structure (two mesogenic organic ligands linked through one or two metal atoms)[19,23] and an H-or X-molecular shape. For **3**, two maxima are found in the equatorial region: the scattering at 4.4 Å corresponds to an average of distances between aliphatic chains and average distance between neighbouring molecules located face-to-face; the scattered intensity at 14–15 Å may correspond to the mean distance between neighbouring molecules placed side-to-side. This large value suggests that the molecule has an X-rather than an H-shape, *i.e.* the four branches of the molecule are not parallel, but radiate outward from the molecular core at an angle. In turn, this is consistent with the interdigitation phenomenon proposed above, as the branches of the molecules in a layer tend to fill the empty spaces between the branches of the molecules in the next layer. This structure corresponds to a local orthorhombic order with dimensions 34, 14.5 and 4.4 Å, for which a reasonable density value of 1.10 g cm^{-3} is calculated. Moreover, the deduced cross-section chain area ($14.5 \times 4.4/2 = 32$ Å^2) is consistent with typical chain areas in mesophases. A schematic drawing of the proposed arrangement is illustrated in Fig. 4. This arrangement involves short-range biaxial order. However, there is no evidence that biaxiality extends to large distances.

The scattered intensity at middle angles centred in the meridian corresponds to a distance of 12–13 Å and is associated with interactions along the director (direction of the molecular axes). Although its origin is more difficult to explain, two possible explanations can be proposed:

In the molecule there are two elements rich in electronic density: the TTF unit and the biphenyl moieties. Therefore, these two parts give rise to strong X-ray scattering, and thus the 12–13 Å maximum could arise from intramolecular interferences between these two kinds of scattering elements. Although the intramolecular distance between the TTF and the biphenyl units measured experimentally in the crystal of **1**

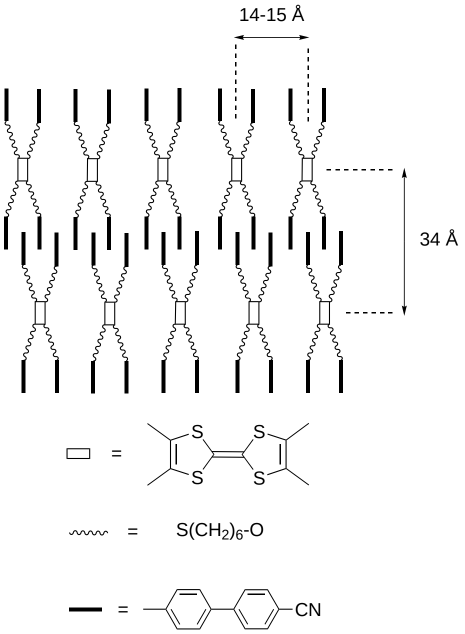

Fig. 4 Schematic drawing of the proposed arrangement in the smectic A mesophase of compound **3**

is 14.5 Å, the conformational disorder of the hydrocarbon chains can account for the slightly smaller value measured in the mesophase.

A mutual shifting of neighbouring molecules inside each layer could take place in the direction of the long molecular axis in such a way that adjacent molecules are parallel but the central TTF units tend to lie on each side of the median plane of the layer at a distance of 6–6.5 Å from that plane. This phenomenon has been found in some liquid crystals formed by dinuclear palladium complexes[23] and, in the case of compound **3**, might be due to the face-to-face location of the cyanobiphenyl and TTF parts of neighbouring molecules, shown in the single-crystal X-ray analysis of compound **1**.

Charge-transfer salts. The electron donor properties of compounds **1–3** were determined by cyclic voltammetry, and all compounds show two one-electron reversible waves ($E_1^{1/2}=0.50$, $E_2^{1/2}=0.82$ V *vs.* SCE, Pt electrode, 100 mV s^{-1}, $CH_2Cl_2/Bu_4{}^nNPF_6$). These redox potentials indicate a good donor ability (for comparison, values for TTF itself under the same conditions are:[24] $E_1^{1/2}=0.40$, $E_2^{1/2}=0.82$ V) so the preparation of charge-transfer salts derived from liquid crystal **3** was attempted in order to obtain new materials showing both conducting and mesomorphic properties.

Electrocrystallization experiments were carried out at constant current (0.05–1 μA) in the presence of linear (I_3^-), tetrahedral (ClO_4^-) and octahedral (PF_6^-) anions in a variety of solvents. However, a radical-cation salt could not be isolated under any of the conditions employed.

Next, the preparation of charge-transfer complexes (CTC) was attempted using a variety of acceptors. Tetracyanoquinodimethane (TCNQ) was used first, but this compound did not form a CTC with compound **3**, a situation which has already been found with other tetrakis(alkylthio)TTF derivatives bearing long[25] or bulky[26] groups. This fact cannot be ascribed to a poor electron donating ability of the donor (see above), but to a size mismatch between the two components.

On the other hand, heating **3** and 2,4,7-trinitrofluoren-9-one (TNF)[27] on the hot stage of a polarizing microscope led to the development of a brown colour in the contact zone. Such behaviour is indicative of charge-transfer, but the complex did not show mesomorphic properties.

Finally, when CH_2Cl_2 solutions of **3** and iodine (excess) were mixed, a black microcrystalline solid was obtained after slow evaporation of the solvent and repeated washings with CCl_4. Elemental analysis revealed the stoichiometry of this complex to be $\mathbf{3}{\cdot}I_{10-x}$ ($x\approx0.4$) which, although not common, has already been reported for a CTC of BEDO–TTF.[28] Moreover, LSIMS$^+$ of the complex shows the molecular ion of **3**(*m*/*z* 1440), thus confirming that the structure of the starting TTF remains unchanged. Despite its non-integer valence, conductivity measurements on pressed pellets showed this complex to be insulating.

Microscopy study and thermogravimetric analysis

On first heating $\mathbf{3}{\cdot}I_{10-x}$, a prolonged melting process was observed between *ca.* 140 and 160 °C. In order to study this phenomenon further, a thermogravimetric study was undertaken. The sample showed a weight loss which reached about 25% of the initial weight at 160 °C. Two experimental facts led us to deduce that the melting process observed may well be explained by a simultaneous loss of iodine and melting of the material. Firstly, the evolved species was identified as iodine by EI$^+$ mass spectrometry [*m*/*z* 254 (M$^{\cdot+}$, 100%), 127 (45%)] and, secondly, pristine compound **3** does not show any weight loss up to 200 °C. Moreover, a $\mathbf{3}{\cdot}I_5$ stoichiometry can be assigned to the complex after heating to 160 °C. On cooling, a phase transition to a very viscous nematic phase with marbled and schlieren textures is observed at 84 °C (Fig. 5). Below this temperature no crystallization occurs and the compound remains as a nematic glass.

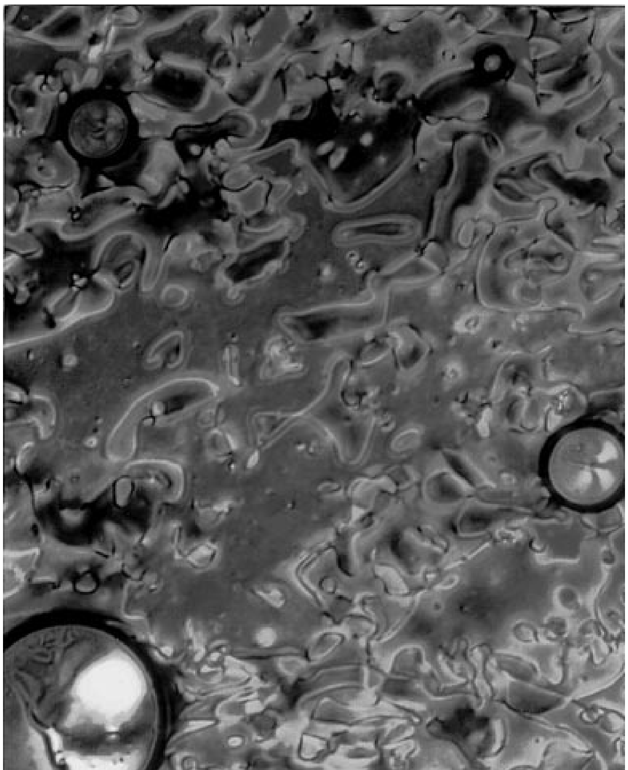

Fig. 5 Microphotograph of the optical texture of the nematic mesophase of compound $\mathbf{3}{\cdot}I_5$ at 78 °C

DSC study

During the first heating an endothermic peak ($\Delta H = 49.3$ J g^{-1}) was observed with an onset at 140 °C, corresponding to the melting process and the aforementioned loss of iodine. In the first cooling cycle, the peak corresponding to the I→N transition was not observed, even when lower scanning rates were used. This result suggests that the enthalpy of this transition is small and, therefore, that the nematic mesophase is very disordered. This is in good agreement with the X-ray diffraction studies discussed below. Upon further cooling neither a crystallization peak nor a glass transition were observed and, in the subsequent heating cycle, the $N_{glass} \rightarrow N$ transition could not be detected either.

X-Ray diffraction study

The X-ray diffraction data are consistent with the nematic nature of the mesophase of complex **3**·I_5. For the X-ray study a sample of the complex was placed in a Lindemann glass capillary, heated in an oven to give the isotropic liquid, and then quickly cooled to room temperature. In contrast to pristine compound **3**, an unoriented pattern was obtained consisting of two diffuse rings, one in the small-angle region and the other in the large-angle region. In a nematic phase the molecules are orientationally ordered but positionally disordered. The two rings arise respectively from end-to-end and side-to-side interferences, and they are diffuse because these positional correlations are short-range, *i.e.* they only extend over a few molecules. Attempts to align the sample by slowly cooling the isotropic liquid into the mesophase under a magnetic field of about 1 T failed, probably due to the high viscosity of the mesophase and its tendency to vitrify. However, the combination of the microscopic observations and the X-ray results unambiguously indicates a nematic phase. A number of sharp spots of weak intensity were detected on the pattern taken after several hours at room temperature, and these are the result of the presence of a small amount of a crystalline phase that forms slowly over prolonged periods of time.

In summary, new TTF derivatives bearing one, two and four 6-(4′-cyanobiphenyl-4-yloxy)hexylthio side-groups have been prepared. Of these, only the more heavily substituted derivative shows mesomorphic properties. Moreover, a charge-transfer salt of this compound also shows a liquid-crystal phase, a promising result in the search for new multi-property materials.

Experimental Section

Techniques

Infrared measurements were carried out using a Perkin-Elmer FT 1600 spectrophotometer. Melting points were determined using a Büchi 510 apparatus. NMR spectra were recorded with a Varian Unity 300 or a Bruker ARX-300 spectrometer. *J* values are given in Hz. Elemental analyses were carried out at the Service Central d'Analyses (CNRS, Vernaison, France). Mass spectra were recorded using a VG-Autospec EBE spectrometer. HRMS-EI$^+$ spectra at 10 000 resolution (peak width at 5% height) were measured using perfluorokerosene as the reference compound. Cyclic voltammetry measurements were performed using a PAR 273 potentiostat. The optical textures of the mesophases were studied with an Olympus BH-Z polarizing microscope equipped with a hot stage and a LINKAM THMS 600 controller. The transition temperatures were determined by differential scanning calorimetry with a Perkin-Elmer DSC-7 instrument. The apparatus was calibrated with indium (156 °C; 28.4 J g^{-1}) as a standard. Thermogravimetric analysis was performed using an STD 2960 simultaneous DTA–TGA apparatus using powdered samples heated under a nitrogen atmosphere. X-Ray diffraction experiments were carried out using a Pinhole camera (Anton-Paar) operating with a Ni-filtered Cu-Kα beam. The samples were held in Lindemann glass capillaries (0.7 mm diameter) and the patterns were collected on photographic film.

Synthesis

Compounds **6**,[15] **4**[16] and **10**[15] were prepared as previously described.

2,3,6-Tris(methylthio)-7-(6′-bromohexylthio)tetrathiafulvalene 5. To a solution of compound **4** (427 mg, 1 mmol) in CH_2Cl_2 (15 ml), kept at 0 °C and under nitrogen, was added a solution of $CsOH{\cdot}H_2O$ (420 mg, 2.5 mmol) in MeOH (5 ml). After stirring for 20 min the resulting solution was added dropwise, at room temperature and under nitrogen, to a solution of 1,6-dibromohexane (0.46 ml, 3 mmol) in CH_2Cl_2 (20 ml). After completion of the addition, the solvent was removed and the crude product was purified by column chromatography on silica gel (CH_2Cl_2–hexane, 1:3) to give an orange–brown oil (440 mg, 80%). MS (EI$^+$) (*m*/*z*): 536 ($M^{\bullet+}$). δ_H ($CDCl_3$) 3.41 (t, *J* 6.7, 2 H), 2.81 (t, *J* 7.1, 2 H), 2.42 (s, 9 H), 1.87 (m, 2 H), 1.65 (m, 2 H), 1.46 (m, 4 H).

2,3-Bis(methylthio)-6,7-bis(6′-hydroxyhexylthio)tetrathiafulvalene 7. Bu^{t}OK (420 mg, 3.75 mmol) was added, under a nitrogen atmosphere, to a solution of compound **6** (700 mg, 1.5 mmol) in dry DMF (25 ml). The brown solution was stirred for 15 min, 6-bromohexan-1-ol (0.43 ml, 3.28 mmol) was added dropwise and the mixture was stirred for 45 min at room temp. The solvent was removed and the resulting oil was taken up in CH_2Cl_2 (40 ml) and washed with water (3 × 75 ml). The organic layer was dried ($MgSO_4$) and the solvent evaporated. The crude product was purified by column chromatography on silica gel (CH_2Cl_2–Et_2O, 1:3) to give a red–orange oil which solidified on standing (536 mg, 64%), mp 65–67 °C. ν/cm^{-1} (Nujol) 3314 (O—H). HRMS (EI$^+$) (*m*/*z*): 560.0152, calc. for $C_{20}H_{32}O_2S_8$: 560.0168. δ_H ($CDCl_3$) 3.65 (t, *J* 6.4, 2 H), 2.83 (t, *J* 6.9, 2 H), 2.44 (s, 3 H), 1.70–1.30 (m, 9 H). δ_C ($CDCl_3$) 127.74, 127.41, 111.09, 109.99, 62.76, 36.14, 32.54, 29.66, 28.23, 25.29, 19.15.

2,3-Bis(methylthio)-6,7-bis(6′-methylsulfonyloxyhexylthio)tetrathiafulvalene 8. A solution of $MeSO_2Cl$ (0.28 ml, 3.6 mmol) in CH_2Cl_2 (10 ml) was added dropwise over 1 h to a solution of compound **7** (504 mg, 0.9 mmol) and NEt_3 (2 ml) in CH_2Cl_2 (30 ml), kept at 0 °C and under nitrogen. The mixture was stirred at room temp. for 20 min and the solvent removed. The crude product was purified by column chromatography on silica gel (CH_2Cl_2) and recrystallization from acetonitrile gave an orange solid (515 mg, 80%), mp 71 °C. HRMS (EI$^+$) (*m*/*z*): 715.9714, calc. for $C_{22}H_{36}O_6S_{10}$: 715.9719. δ_H ($CDCl_3$) 4.24 (t, *J* 6.4, 2 H), 3.02 (s, 3 H), 2.83 (t, *J* 7.1, 2 H), 2.43 (s, 3 H), 1.80–1.63 (m, 4 H), 1.47–1.43 (m, 4 H). δ_C ($CDCl_3$) 127.71, 127.42, 110.77, 110.17, 69.88, 37.35, 36.02, 29.43, 28.97, 27.80, 24.96, 19.14 (Found: C, 36.99; H, 5.09; O, 13.59; S, 44.44. Calc. for $C_{22}H_{36}O_6S_{10}$: C, 36.87; H, 5.03; O, 13.41; S, 44.69%).

2,3-Bis(methylthio)-6,7-bis(6′-bromohexylthio)tetrathiafulvalene 9. A solution of compound **8** (609 mg, 0.85 mmol) and LiBr (370 mg, 4.25 mmol) in acetone (35 ml) was refluxed under nitrogen for 9 h. The mixture was cooled and the solvent removed. The residue was taken up in CH_2Cl_2 (60 ml) and washed with water (3 × 100 ml). The organic layer was dried ($CaCl_2$) and, after evaporation of the solvent, the crude product was purified by column chromatography on silica gel (hexane–CH_2Cl_2, 2:1) to give a red–orange oil (538 mg, 92%). MS (EI$^+$) (*m*/*z*): 684 ($M^{\bullet+}$). δ_H ($CDCl_3$) 3.42 (t, *J* 6.7, 2 H), 2.83 (t, *J* 7.1, 2 H), 2.44 (s, 3 H), 1.90–1.64 (m, 4 H), 1.48–1.44 (m, 4 H).

2,3,6,7-Tetrakis(6′-hydroxyhexylthio)tetrathiafulvalene 11. This was prepared in an analogous way to **7**, using compound **10** (1.088 g, 2 mmol), DMF (35 ml), Bu^tOK (1.792 g, 16 mmol) and 6-bromohexan-1-ol (1.57 ml, 12 mmol). Column chromatography on silica gel (CH_2Cl_2/MeOH 15:1) followed by recrystallization from $CHCl_3$ gave an orange solid (753 mg, 53%), mp 82 °C. *ν*/cm^{-1} (Nujol) 3353 (OH). MS (EI$^+$) (*m/z*): 732 (M$^{\bullet +}$, 100%). δ_H ($CDCl_3$) 3.65 (t, J 6.4, 2 H), 2.83 (t, J 7.2, 2 H), 1.80–1.30 (m, 9 H). δ_C ($CDCl_3$) 127.74, 110.25, 62.77, 36.11, 32.55, 29.74, 28.26, 25.31 (Found: C, 48.58; H, 7.22; O, 9.41; S, 34.93. Calc. for $C_{30}H_{52}O_4S_8$: C, 49.18; H, 7.10; O, 8.74; S, 34.97%).

2,3,6,7-Tetrakis(6′-methylsulfonyloxyhexylthio)tetrathiafulvalene 12. This was prepared in an analogous way to **8**, using compound **11** (400 mg, 0.55 mmol), NEt_3 (2 ml) and $MeSO_2Cl$ (0.43 ml, 5.5 mmol). Column chromatography on silica gel (CH_2Cl_2/MeOH 22:1) afforded a red–orange solid (517 mg, 90%), mp 78 °C. MS (LSIMS$^+$) (*m/z*): 1044 (M$^{\bullet +}$). δ_H ($CDCl_3$) 4.24 (t, *J* 6.34, 2 H), 3.00 (s, 3 H), 2.83 (t, *J* 7.1, 2 H), 1.80–1.44 (m, 8 H). δ_C ($CDCl_3$) 127.70, 109.91, 69.91, 37.33, 35.97, 29.65, 28.91, 27.80, 24.95.

2,3,6,7-Tetrakis(6′-bromohexylthio)tetrathiafulvalene 13. This was prepared in an analogous way to **9**, using compound **12** (522 mg, 0.5 mmol) and LiBr (522 mg, 6 mmol). Column chromatography on silica gel (hexane–CH_2Cl_2, 3:1) afforded an orange oil (320 mg, 65%). MS (LSIMS$^+$) (*m/z*): 980 (M$^{\bullet +}$). δ_H ($CDCl_3$) 3.42 (t, *J* 6.7, 2 H), 2.82 (t, *J* 7.0, 2 H), 1.88–1.40 (m, 8 H).

2,3,6-Tris(methylthio)-7-[6′-(4′-cyanobiphenyl-4-yloxy)hexylthio]tetrathiafulvalene 1. A solution of 4-cyano-4′-hydroxybiphenyl (96.72 mg, 0.496 mmol) in THF (10 ml) was added dropwise, at room temp. and under nitrogen, to a suspension of NaH (80% dispersion in mineral oil, 17.11 mg, 0.570 mmol) in THF (10 ml). After addition of a catalytic amount (*ca.* 5 mg) of tetrabutylammonium iodide, the mixture was stirred for 2 h and then a solution of compound **5** (532 mg, 0.992 mmol) in THF (15 ml) was added dropwise. The mixture was refluxed under nitrogen for 1.5–2 h., cooled, and the solvent was removed. CH_2Cl_2 (70 ml) was added and the solution was washed with water (3 × 100 ml). The organic layer was dried ($CaCl_2$) and the solvent was evaporated to give the crude product, which was purified by column chromatography on silica gel (CH_2Cl_2–hexane, 1:2), followed by recrystallization from EtOAc. An orange solid was obtained (253 mg, 78%), mp 112 °C. *ν*/cm^{-1} (Nujol) 2223 (CN). HRMS (EI$^+$) (*m/z*): 651.0007, calc. for $C_{28}H_{29}NOS_8$: 651.0015. δ_H ($CDCl_3$) 7.72–7.63 (m, 4 H), 7.54 (d, *J* 8.80, 2 H), 6.99 (d, *J* 8.80, 2 H), 4.02 (t, *J* 6.35, 2 H), 2.85 (t, *J* 7.10, 2 H), 2.42 (s, 9 H), 1.81–1.51 (m, 8 H). δ_C ($CDCl_3$) 159.70, 145.23, 132.56, 131.32, 129.62, 128.33, 127.06, 119.09, 115.06, 110.04, 67.89, 36.14, 29.57, 29.04, 28.10, 25.57, 19.17 (Found: C, 51.65; H, 4.35; N, 2.34; O, 2.88; S, 39.36. Calc. for $C_{28}H_{29}NOS_8$: C, 51.61; H, 4.45; N, 2.15; O, 2.46; S, 39.32%).

2,3-Bis(methylthio)-6,7-bis[6′-(4′-cyanobiphenyl-4-yloxy)hexylthio]tetrathiafulvalene 2. This was prepared in an analogous way to compound **1**, using compound **9** (375 mg, 0.547 mmol), NaH (80% dispersion in mineral oil, 38 mg, 1.26 mmol), and 4-cyano-4′-hydroxybiphenyl (213 mg, 1.09 mmol). Column chromatography on silica gel (hexane–CH_2Cl_2, 1:1, then CH_2Cl_2) followed by recrystallization from acetone gave an orange solid (223 mg, 45%), mp 119 °C. *ν*/cm^{-1} (Nujol) 2224 (CN). MS (LSIMS$^+$) (*m/z*): 914 (M$^{\bullet +}$). δ_H ($CDCl_3$) 7.71–7.62 (m, 4 H), 7.53 (d, *J* 8.8, 2 H), 6.98 (d, *J* 8.8, 2 H), 4.01 (t, *J* 6.5, 2 H), 2.85 (t, *J* 7.1, 2 H), 2.42 (s, 3H), 1.85–1.50 (m, 8 H). δ_C ($CDCl_3$) 159.65, 145.16, 132.54, 131.31, 128.20, 128.00, 127.50, 127.03, 119.07, 115.03, 110.04, 67.88, 36.13, 29.60, 29.04, 28.14, 25.55, 19.12 (Found: C, 60.53; H, 5.15; N, 3.17; O, 3.71; S, 28.39. Calc. for $C_{46}H_{46}N_2O_2S_8$: C, 60.39; H, 5.03; N, 3.06; O, 3.50; S, 28.01%).

2,3,6,7-Tetrakis[6′-(4′-cyanobiphenyl-4-yloxy)hexylthio]tetrathiafulvalene 3. This was prepared in an analogous way to compound **2**, using compound **13** (320 mg, 0.325 mmol), NaH (80% dispersion in mineral oil, 50 mg, 1.646 mmol), and 4-cyano-4′-hydroxybiphenyl (279 mg, 1.430 mmol). Column chromatography on silica gel (hexane–CH_2Cl_2, 1:4) followed by recrystallization from $CHCl_3$–pentane gave a pale orange solid (234 mg, 50%), mp 113–115 °C. *ν*/cm^{-1} (Nujol) 2224 (CN). MS (LSIMS$^+$) (*m/z*): 1440 (M$^{\bullet +}$). δ_H ($CDCl_3$) 7.70–7.61 (m, 4 H), 7.52 (d, *J* 8.8, 2 H), 6.98 (d, *J* 8.8, 2 H), 3.99 (t, *J* 6.34, 2 H), 2.81 (t, *J* 7.1, 2 H), 1.87–1.62 (m, 4 H), 1.53–1.49 (m, 4 H). δ_C ($CDCl_3$) 159.66, 145.16, 132.56, 131.35, 128.33, 127.78, 127.04, 119.07, 115.05, 110.08, 67.88, 36.11, 29.60, 29.05, 28.17, 25.58 (Found: C, 68.04; H, 5.63; N, 3.90; O, 5.01; S, 17.73. Calc. for $C_{82}H_{80}N_4O_4S_8$: C, 68.33; H, 5.56; N, 3.89; O, 4.44; S, 17.78%).

We are indebted to DGICYT (PB94–0577) for financial support. A doctoral fellowship to R. A. (DGA) is also gratefully acknowledged.

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Paper 7/08416A*; Received* 21*st November*, 1997