

# Synthesis, Properties and Radical Cation Salts of Non-centrosymmetrical Tetrathiafulvalenes Derived from 1,3,5,7-Tetrathia-s-indacene

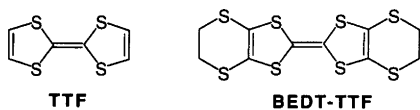
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1,3,5,7-Tetrathia-s-indacene, obtained by reduction of the corresponding bis(trithiocarbonate) with diisobutylaluminium hydride, is oxidized to the monodithiolium salt with  $\text{Ph}_3\text{C}^+\text{PF}_6^-$  to afford, after reaction with trimethyl phosphite, the corresponding 6*H*-1,3,5,7-tetrathia-s-indacen-2-ylphosphonic acid dimethyl ester. This, in turn, reacts with a variety of 1,3-dithiol-2-yliminium salts to afford non-centrosymmetrically substituted tetrathiafulvalenes, the electrochemical properties of which are also reported. Electrocrystallization experiments led to the formation of various semi-conducting radical cation salts. 6*H*-2-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-1,3,5,7-tetrathia-s-indacene (**1a**) forms a salt with  $\text{AsF}_6^-$ , (**1a**)<sub>2</sub>AsF<sub>6</sub><sup>-</sup>, which crystallizes in the triclinic system, space group *P*–1, with *a* = 7.246(6), *b* = 7.797(1), *c* = 15.041(2) Å,  $\alpha$  = 100.73(1),  $\beta$  = 91.44(3),  $\gamma$  = 101.20(3)°, *V* = 817.4 Å<sup>3</sup>. The donor molecules stack in a zig-zag fashion along the *a* axis.

Most recent advances in the area of organic metals and superconductors<sup>1</sup> are based on the so-called unsymmetrical or dissymmetrical tetrathiafulvalenes (TTF). Those expressions were introduced to contrast this particular group of TTFs with their prototypical precursors like the well known tetrathiafulvalene (TTF), tetramethyltetraselenafulvalene (TMTSF) or bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), which all have an *mmm* point



symmetry (Fig. 1). In the case of dissymmetrical TTFs, lacking one of these mirror symmetry elements, several possibilities arise. The absence of *m<sub>p</sub>* concerns non-rigid molecules and will not be discussed further here. In addition, several TTFs lacking the mirror plane *m<sub>L</sub>* have been reported such as dithienotetrathiafulvalene (DT-TTF)<sup>2</sup> and bis(methylthio)tetrathiafulvalenes (BMT-TTF).<sup>3b</sup> Very few of those give rise to characterized radical cation salts.<sup>3a</sup> Note also, that, in solution, such molecules exist together with the centrosymmetrical isomer.<sup>3b</sup> TTFs lacking the *m<sub>1</sub>* mirror plane, such as ethylenedithiotetra-

thiafulvalene (EDT-TTF)<sup>4</sup> or 3,4-dimethyl-3',4'-ethylenedithio-1,5-diselena-1',5'-dithiafulvalene (DMET-TTF),<sup>5</sup> have been intensively investigated and will be described here as non-centrosymmetrical, in contrast with DT-TTF for example. Those molecules proved particularly attractive for their potential to form head-to-tail dimers in the solid state, thus given rise to two-dimensional  $\kappa$ -phases, as previously observed in several superconducting BEDT-TTF salts.

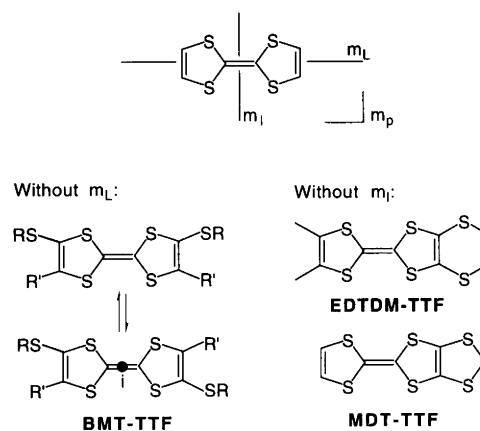
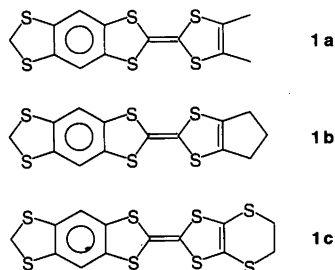


Fig. 1. A symmetry-based description of unsymmetrical TTFs.

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In this paper, we report our recent results on the synthesis of such non-centrosymmetrical TTFs (lacking the  $m_1$  symmetry element), based on 1,3,5,7-tetrathia-*s*-indacene. The large number of sulfur atoms as well as the extended  $\pi$ -system of **1a–c** are expected to enhance

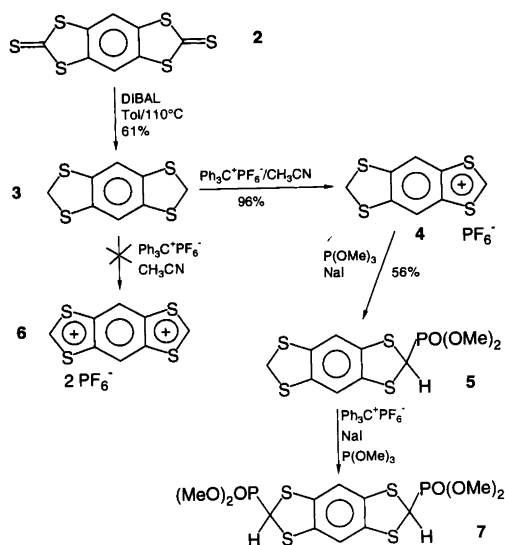


the intermolecular overlap as well as to decrease the intramolecular Coulombic interactions, two trends which should lead to radical cation salts with high conductivity. We will see that this is not always the case and will try to rationalise the origin of such behavior.

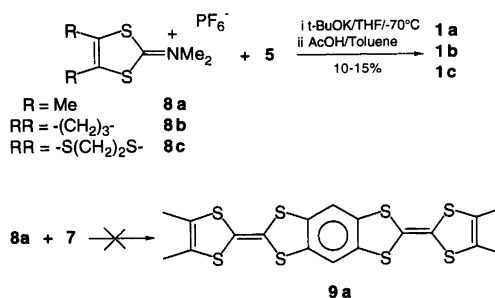
### Results and discussion

In a previous paper, the different procedures for the synthesis of non-centrosymmetrical TTFs have been discussed.<sup>6</sup> The more general and specific one was reported by Lerstrup *et al.* and involves a Wittig–Horner reaction of 1,3-dithiole-2-phosphonate ester anions as nucleophiles with 1,3-dithiol-2-iminium salts as electrophiles.<sup>7</sup> This versatile reaction gives access to several non-centrosymmetrical TTFs<sup>8</sup> and has also been exploited for the synthesis of various bis-<sup>9</sup> and tris-(tetrathiafulvalenes).<sup>10</sup>

2,6-Dihydro-1,3,5,7-tetrathia-*s*-indacene **3** can be prepared by alkylation of the easily prepared benzene-1,2,4,5-tetrathiolate<sup>11</sup> with dibromo- or diiodo-methane. This procedure, however, proved inadequate. A more



Scheme 1.



Scheme 2.

indirect synthetic route involves the reduction of 1,3-dithiole-2-thiones to 2*H*-1,3-dithiols with *i*-Bu<sub>2</sub>AlH (DIBAL) or BH<sub>3</sub>–Me<sub>2</sub>S.<sup>12</sup> Thus, treatment of the bis(thione)<sup>13</sup> **2** with an excess of DIBAL in refluxing toluene afforded **3** in good yield (Scheme 1).

The phosphonate ester **5** has been prepared by an Arbuzov-type reaction of the corresponding dithiolium cation **4** with NaI and P(OMe)<sub>3</sub>. The cation **4** is formed quantitatively from **3** by hydride abstraction with trityl hexafluorophosphate.<sup>14</sup> Note also that all attempts to isolate the bis(dithiolium) salt **6** by treatment of **3** with two or more equivalents of trityl hexafluorophosphate were, in our hands, unsuccessful. The corresponding bis(phosphonate ester) **7** can, however, be prepared from the mono(phosphonate ester) **5**, by successive treatments with Ph<sub>3</sub>C<sup>+</sup>PF<sub>6</sub><sup>–</sup>, NaI and P(OMe)<sub>3</sub>. Reaction of **5** with *t*-BuOK, followed by addition of the 1,3-dithiol-2-iminium salts **8a–c** (Scheme 2) afforded the corresponding non-centrosymmetrical TTFs **1a–c** in low yield (10–20%). In principle, reaction of the bis(phosphonate ester) **7** with two equivalents of an iminium salt such as **8a** should yield the twin TTF **9a**. Twin TTFs have been prepared recently by Müllen *et al.*<sup>15</sup> by a different route, however with alkoxy groups on the two free positions of the central benzene ring in order to increase their solubility. The low yield of the mono reaction (**5** + **8** → **1**) indicates that the yield of the double coupling reaction is so much lower that, under the conditions given, no reasonable quantities of **9a** could be isolated for further characterization and electrocrystallization experiments.

Cyclic voltammetry experiments were conducted on the new non-centrosymmetrical donor molecules **1a–c** in benzonitrile (Table 1). Every one of the new donors exhibits

Table 1. Cyclic voltammetry data for **1a–c** and the reference compounds TMTTF and benzo-dimethyl-tetrathiafulvalene (BDM-TTF), in PhCN, Bu<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>–</sup> 0.1 M, at 100 mV s<sup>–1</sup>, with SCE as reference electrode.

Donor	$E_{1/2}^1/V$	$E_{1/2}^2/V$	$\Delta E/V$
<b>1a</b>	0.40	0.83	0.43
<b>1b</b>	0.41	0.83	0.42
<b>1c</b>	0.51	0.88	0.37
TMTTF	0.24	0.74	0.40
BDM-TTF	0.41	0.88	0.46

Table 2. Electrocrystallization experimental conditions and results.

Donor	Anion	Solvent	Current/ $\mu\text{A}$	Crystals	Stoichiometry <sup>a</sup>	Conductivity <sup>b</sup>
1a	$\text{PF}_6^-$	$\text{CH}_2\text{Cl}_2$	2.0	Needles	2 : 1 <sup>c</sup>	Insulating
1a	$\text{AsF}_6^-$	$\text{Cl}_2\text{CHCH}_2\text{Cl}$	0.5	Flat needles	2 : 1 <sup>d</sup>	Insulating
1b	$\text{PF}_6^-$	$\text{Cl}_2\text{CHCH}_2\text{Cl}$	0.5	Platelets	4 : 1 <sup>d</sup>	SC, 3 S $\text{cm}^{-1}$
1c	$\text{I}_3^-$	$\text{Cl}_2\text{CHCH}_2\text{Cl}$	0.2	Platelets	1 : 1 <sup>d</sup>	Insulating
1c	$\text{AuBr}_2^-$	PhCl	0.2	Platelets	2 : 1 <sup>d</sup>	SC, 50 S $\text{cm}^{-1}$
1c	$\text{AuI}_2^-$	PhCl	0.2	Large platelets	2 : 1 <sup>d</sup>	SC, 400 S $\text{cm}^{-1}$

<sup>a</sup>The ratio donor: anion is indicated. <sup>b</sup>Conductivities were measured by the four-point contacts method, SC = semiconducting behavior. <sup>c</sup>Determined from X-ray crystal structure. <sup>d</sup>Determined from microanalysis.

two reversible, one-electron oxidation waves, as expected for tetrathiafulvalenes. The differences of  $E_{1/2}^1$  values for 1a–c are consistent with the usual substituent effects observed in the TTF family.<sup>16</sup>

Benzodimethyltetrathiafulvalene (BDM-TTF), which, when compared with 1a, lacks only the dithiomethylene group, behaves very similarly, thus demonstrating that this end group as a very limited influence on the donor properties of 1a. This is in agreement with extended Hückel calculations on 1a (Fig. 2), which show that the HOMO of 1a is essentially localized on the  $\text{C}_2\text{S}_4$  moiety of the tetrathiafulvalene. Note, however, that a non-negligible coefficient is observed on the sulfur atoms [S(5), S(6)] of the outer dithiomethylene fragment. Thus, one can expect that, in 1a cation radical salts, any short intermolecular contacts involving those sulfur atoms could lead to a sizeable delocalization.

Electrocrystallization experiments were conducted with

Table 3. Positional parameters in  $(1a)_2\text{AsF}_6$  and their estimated standard deviations.

	x	y	z	$B_{\text{eq}}^a$
As	0.00	0.00	0.00	3.48(2)
F(1)	0.096(6)	0.2223(4)	0.0291(3)	6.6(1)
F(2)	0.123(1)	0.0125(7)	0.0946(4)	15.4(2)
F(3)	0.1959(8)	0.0453(7)	-0.0528(4)	13.5(2)
S(1)	0.2520(2)	-0.0835(2)	0.31487(8)	3.37(3)
S(2)	0.1777(2)	-0.3540(2)	0.42649(8)	3.29(3)
S(3)	0.2315(2)	-0.0461(2)	0.60644(8)	3.31(3)
S(4)	0.3045(2)	0.2266(2)	0.49284(8)	3.27(3)
S(5)	0.3935(2)	0.7573(2)	0.8002(1)	4.25(3)
S(6)	0.3072(2)	0.4842(2)	0.91286(9)	4.33(3)
C(1)	0.2292(7)	-0.1280(6)	0.4234(3)	3.0(1)
C(2)	0.2526(7)	0.0015(6)	0.4989(3)	2.92(9)
C(3)	0.1737(6)	-0.4307(6)	0.3095(3)	3.0(1)
C(4)	0.2087(7)	-0.3052(7)	0.2582(3)	3.3(1)
C(5)	0.3113(6)	0.3064(6)	0.6107(3)	2.8(1)
C(6)	0.2740(6)	0.1761(6)	0.6636(3)	2.8(1)
C(7)	0.2728(6)	0.2273(6)	0.7585(3)	2.6(1)
C(8)	0.3114(7)	0.4042(7)	0.7968(3)	3.2(1)
C(9)	0.3531(7)	0.5362(6)	0.7427(3)	3.1(1)
C(10)	0.3516(6)	0.4889(6)	0.6499(3)	2.6(1)
C(11)	0.4350(9)	0.7068(7)	0.9108(4)	4.7(1)
C(12)	0.1316(7)	-0.6268(7)	0.2778(4)	3.7(1)
C(13)	0.2163(7)	-0.3373(7)	0.1588(3)	3.9(1)

<sup>a</sup> $B_{\text{eq}} = 4/3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab \cos \gamma B(1,2) + ac \cos \beta B(1,3) + bc \cos \alpha B(2,3)]$ .

1a–c in the presence of various anions (see Table 2). A full X-ray analysis was carried out for the salt  $(1a)_2\text{AsF}_6$ . It crystallizes in the triclinic system, space group  $P-1$ . The  $\text{AsF}_6^-$  anions are located at inversion centers and the 1a molecules in general positions in the unit cell (Fig. 3). Positional parameters are given in Table 3, bond lengths and angles in Table 4. The geometry of 1a is consistent with that of TMTTF, for example, in the analogous  $(\text{TMTTF})_2\text{X}$  salts.<sup>17</sup> While the TTF moiety of 1a is fully planar, the methylene group of the outer dithiole ring is twisted by  $29.5(3)^\circ$  out of the plane of the TTF moiety (Fig. 4). Similar puckering was also observed in the structure of salts of bis(methylenedithio)tetrathiafulvalenes like  $(\text{BMDT-TTF})_2\text{SbF}_6$  ( $31.3^\circ$ )<sup>18</sup> as well as, albeit to a lesser extent, in the salt of the non-centrosymmetrical methylenedithiotetrathiafulvalene (MDT-TTF),  $(\text{MDT-TTF})_2\text{AuI}_2(11^\circ)$ .<sup>19</sup>

The structure consists of stacks of centrosymmetrical

Table 4. Bond distances and angles in  $(1a)_2\text{AsF}_6$  ( $\text{\AA}$ ,  $^\circ$ )

Distances			
S(1)–C(1)	1.737(4)	S(6)–C(11)	1.808(5)
S(1)–C(4)	1.743(4)	C(1)–C(2)	1.354(6)
S(2)–C(1)	1.738(4)	C(3)–C(4)	1.345(6)
S(2)–C(3)	1.748(4)	C(3)–C(12)	1.482(6)
S(3)–C(2)	1.730(4)	C(4)–C(13)	1.475(6)
S(3)–C(6)	1.750(4)	C(5)–C(6)	1.394(5)
S(4)–C(2)	1.742(4)	C(5)–C(10)	1.405(5)
S(4)–C(5)	1.763(4)	C(6)–C(7)	1.409(5)
S(5)–C(9)	1.744(4)	C(7)–C(8)	1.363(6)
S(5)–C(11)	1.811(5)	C(8)–C(9)	1.420(6)
S(6)–C(8)	1.744(4)	C(9)–C(10)	1.376(6)
Angles			
C(1)–S(1)–C(4)	96.4(2)	C(3)–C(4)–C(13)	126.2(4)
C(1)–S(2)–C(3)	96.4(2)	S(4)–C(5)–C(6)	115.6(3)
C(2)–S(3)–C(6)	95.7(2)	S(4)–C(5)–C(10)	122.8(3)
C(2)–S(4)–C(5)	95.6(2)	C(6)–C(5)–C(10)	121.5(4)
C(9)–S(5)–C(11)	95.1(2)	S(3)–C(6)–C(5)	116.9(3)
C(8)–S(6)–C(11)	95.4(2)	S(3)–C(6)–C(7)	123.3(3)
S(1)–C(1)–S(2)	113.8(2)	C(5)–C(6)–C(7)	119.7(4)
S(1)–C(1)–C(2)	123.1(3)	C(6)–C(7)–C(8)	119.0(4)
S(2)–C(1)–C(2)	123.1(3)	S(6)–C(8)–C(7)	123.3(3)
S(3)–C(2)–S(4)	116.2(2)	S(6)–C(8)–C(9)	115.6(3)
S(3)–C(2)–C(1)	122.2(3)	C(7)–C(8)–C(9)	121.1(4)
S(4)–C(2)–C(1)	121.6(3)	S(5)–C(9)–C(8)	116.3(3)
S(2)–C(3)–C(4)	116.4(3)	S(5)–C(9)–C(10)	122.9(3)
S(2)–C(3)–C(12)	116.3(3)	C(8)–C(9)–C(10)	120.8(4)
C(4)–C(3)–C(12)	127.3(4)	C(5)–C(10)–C(9)	117.9(4)
S(1)–C(4)–C(3)	117.0(3)	S(5)–C(11)–S(6)	109.0(2)
S(1)–C(4)–C(13)	116.9(3)		

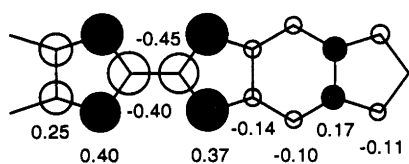


Fig. 2. Atomic coefficients in the HOMO of **1a**.

dimers of **1a**, along the *a* axis (Fig. 4). This structural organization is often encountered with non-centrosymmetrical molecules, e.g., in (EDTDM-TTF)<sub>2</sub>PF<sub>6</sub><sup>20</sup> or (DMET)<sub>2</sub>PF<sub>6</sub>.<sup>5</sup> Note that, in (**1a**)<sub>2</sub>AsF<sub>6</sub>, the methyl groups of one of the two molecules fit nicely into the cavity defined by the puckered methylenedithio end group of the other molecule. Thus, the displacement along the longitudinal molecular axis, relative to an exact face-to-face superposition of the TTF moieties of the molecules, amounts to 1.22 Å, as compared with that observed in the regular (TMTTF)<sub>2</sub>X stack (1.30–1.45 Å, double-bond over ring overlap). If we consider the latter values to optimize the π–π overlap, the interlocking of the two **1a** molecules within the dimer forces a relatively short longitudinal displacement, and hence, leads to a poorer overlap between the TTF HOMOs.

The organic stack is slightly dimerized with plane-to-plane distances of 3.58 and 3.64 Å. Those values are slightly larger than those observed in the analogous (TMTTF)<sub>2</sub>PF<sub>6</sub> salt (3.52, 3.62 Å). This dimerization is enhanced by the large longitudinal displacement between dimers which, in this case, amounts to 1.77 Å.

Some S–S interstack contacts are also identified, but S–S distances (3.79, 3.85, 3.92 Å) largely exceed the accepted value for van der Waals S–S contacts (3.6 Å), excluding sizeable two-dimensional character.

In conclusion, all those geometrical features point

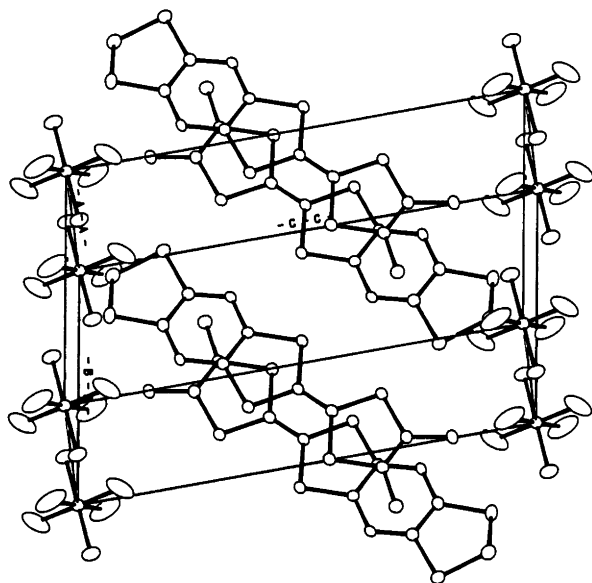


Fig. 3. A view of the unit cell of (**4a**)<sub>2</sub>AsF<sub>6</sub>.

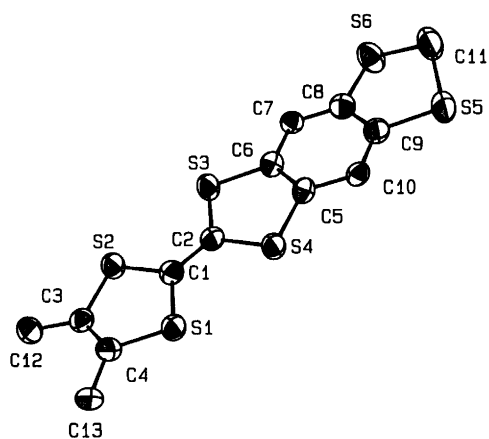


Fig. 4. ORTEP drawing and numbering scheme for **1a** in (**1a**)<sub>2</sub>AsF<sub>6</sub>. Atoms are drawn with 50% probability ellipsoids.

toward a dimerized stack, with little, if any, interstack interaction. This structure may explain the observed insulating character of the investigated compound.

Similarly the semiconductive behavior of the other crystalline salts of **1b** or **1c** (Table 1) suggests that, in those compounds also, the intermolecular overlaps remain insufficient for extended delocalization.

### Experimental

The solvents THF and Et<sub>2</sub>O were freshly distilled from Na–benzophenone before use. Melting points are uncorrected. <sup>1</sup>H NMR spectra were recorded on a Jeol PMX60

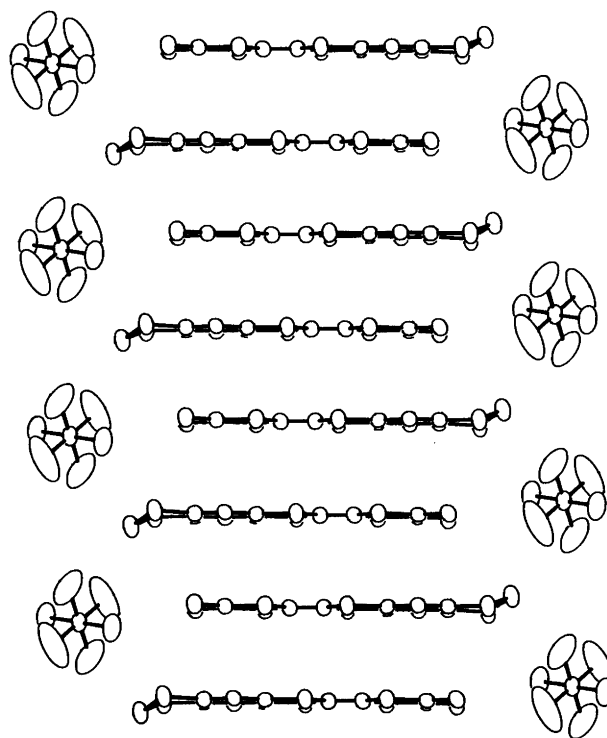


Fig. 5. A view of the stack in (**1a**)<sub>2</sub>AsF<sub>6</sub>.

spectrometer. Mass spectra were obtained by chemical ionization and elemental analyses were performed at the *Institut de Chimie des Substances Naturelles*, Gif/Yvette, France and at the Microanalysis Laboratory, at the University of Copenhagen.

**2,6-Dihydro-1,3,5,7-tetrathia-s-indacene (3).** A suspension of 1,3,5,7-tetrathia-s-indacene-2,6-dithione<sup>13</sup> **2** (5.8 g, 20 mmol) in toluene (200 ml) was heated to reflux. The heating source was removed and DIBAL (25% in toluene, 94 ml, 0.14 mol) was added dropwise over 1 h. External heating became necessary towards the end of the addition in order to maintain gentle reflux for a further 3 h. After being cooled to room temperature, the clear solution was treated dropwise (foam!) with aq. NaOH (40%, 40 ml). The organic phase was washed with NaOH (40%) and dried on MgSO<sub>4</sub>. Evaporation afforded a white crystalline product which was further recrystallized from toluene (2.8 g, 61%), m.p. 196–198°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 4.65 (s, 4 H, CH<sub>2</sub>), 7.29 (s, 2 H, Ar).

**6H-1,3,5,7-Tetrathia-s-indacen-2-ium hexafluorophosphate (4).** To a solution of **3** (4.56 g, 20 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (300 ml) was added a solution of trityl hexafluorophosphate (8.14 g, 21 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (300 ml). After 30 min, Et<sub>2</sub>O (600 ml) was added to precipitate the salt. Filtration and washing with Et<sub>2</sub>O afforded **4** as a red powder (7.2 g, 96%). Anal. C<sub>8</sub>H<sub>5</sub>PF<sub>6</sub>S<sub>4</sub>: C, H. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.0 (s, 2 H, CH<sub>2</sub>), 6.1 (s, 1 H, CH), 6.9 (s, 2 H, Ar).

**Dimethyl 6H-1,3,5,7-tetrathia-s-indacene-2-ylphosphonate (5).** A suspension of **3** (0.46 g, 2 mmol) in dry CH<sub>3</sub>CN, cooled to 0°C, was treated with a solution of Ph<sub>3</sub>C<sup>+</sup>PF<sub>6</sub><sup>-</sup> (1 g, 3 mmol) in CH<sub>3</sub>CN (10 ml). After 30 min, P(OMe)<sub>3</sub> (0.5 ml, 3 mmol) was added followed by NaI (0.8 g, 3 mmol). The solution was warmed to 40°C for 30 min and evaporated and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The concentrated CH<sub>2</sub>Cl<sub>2</sub> solution was chromatographed on silica gel, eluting with CH<sub>2</sub>Cl<sub>2</sub> to remove Ph<sub>3</sub>CH and then with AcOEt to elute **5**. Evaporation afforded 0.65 g, quantitative yield. The crude product can be purified by dissolution in CHCl<sub>3</sub> (50 ml) and treatment with Et<sub>2</sub>O until cloudiness (35 ml). Cooling to 5°C afforded **5** (7.7 g, 56%) as a white crystalline material, m.p. 136–138°C. Anal. C<sub>10</sub>H<sub>11</sub>O<sub>3</sub>PS<sub>4</sub>: C, H. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.7 (d, *J* = 10 Hz, 6 H, OMe), 4.4 (s, 2 H, CH<sub>2</sub>), 4.8 (d, *J* = 4 Hz, 1 H, CH-P), 7.0 (s, 2 H, Ar).

**Dimethyl 1,3,5,7-tetrathia-s-indacene-2,6-diylldiphosphonate (7).** A suspension of crude **5** (0.65 g, 2 mmol) in dry CH<sub>3</sub>CN (40 ml) was cooled to 0°C and treated with a solution of Ph<sub>3</sub>C<sup>+</sup>PF<sub>6</sub><sup>-</sup> (1 g, 3 mmol) in CH<sub>3</sub>CN (10 ml). After stirring for 30 min, P(OMe)<sub>3</sub> (0.5 ml, 3 mmol) and NaI (0.8 g, 3 mmol) were added and the solution was warmed to 40°C for 30 min. The white precipitate of **7** was filtered off and washed with a small amount of CH<sub>3</sub>CN, quantitative yield. The product is

insoluble in common solvents (CH<sub>3</sub>CN, toluene, THF or AcOEt) but can be recrystallized, albeit with some decomposition, in EtOH–H<sub>2</sub>O (200 ml) to afford **7** (0.36 g, 40%), m.p. 242–243.5°C. Anal. C<sub>12</sub>H<sub>16</sub>O<sub>6</sub>P<sub>2</sub>S<sub>4</sub>: C, H, S.

**2-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-6H-1,3,5,7-tetrathia-s-indacene (1a).** The general procedure for the synthesis of non-centrosymmetrically substituted TTFs has been reported.<sup>6,7,9</sup> Only extra details are reported here.

To a solution of the phosphonate ester **5** (0.52 g, 1.5 mmol) in THF (25 ml) at –70°C was added a solution of *t*-BuOK (0.22 g, 1.9 mmol) in THF (10 ml) and then the iminium salt **6a** (0.6 g, 1.9 mmol). The temperature was raised 0°C, Et<sub>2</sub>O was added and the precipitate was filtrated off. The solution was then concentrated, diluted with toluene and treated dropwise with AcOH (1 ml). Filtration through a short silica gel column and recrystallization from toluene afforded **1a** as orange crystals (0.07 g, 13%) m.p. > 300°C. Anal. C<sub>13</sub>H<sub>10</sub>S<sub>6</sub>: C, H, S. MS-CI: *m/z* 358 (*M*<sup>+</sup>), 179 (*M*<sup>2+</sup>).

**2-(4,5-Trimethylene-1,3-dithiol-2-ylidene)-6H-1,3,5,7-tetrathia-s-indacene (1b).** As above, from **5** (0.52 g, 1.5 mmol), *t*-BuOK (0.22 g, 1.9 mmol) and the iminium salt **6b** (0.80 g, 2.4 mmol). Yield 0.08 g, 11%, m.p. > 300°C. Anal. C<sub>14</sub>H<sub>10</sub>S<sub>6</sub>: C, H, S. MS-CI: *m/z* 370 (*M*<sup>+</sup>).

**2-(1,3-dithiolo[4,5-b][1,4]dithiin-2-ylidene)-6H-1,3,5,7-tetrathia-s-indacene (1c).** As above, from **5** (0.52 g, 1.5 mmol), *t*-BuOK (0.22 g, 1.9 mmol) and the iminium salt **6c** (1.02 g, 2.06 mmol), finely ground before use. Yield 0.096 g, 15%, m.p. > 300°C. Anal. C<sub>13</sub>H<sub>8</sub>S<sub>8</sub>: C, H, S. MS-CI: *m/z* 420 (*M*<sup>+</sup>).

**Electrochemical measurements.** Cyclic voltammograms were recorded using a PAR 273 potentiostat with Pt as the working and auxiliary electrodes, and SCE as the reference electrode *n*-Bu<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup> was used as the supporting electrolyte in benzonitrile.

**Electrocrystallization experiments.** Solvents were distilled prior to use and dried on activated basic aluminium oxide. Electrocrystallizations were conducted at constant current in the solvent indicated (Table 2) in a three-compartment cell (*V* = 30 ml), using platinum electrodes (*Ø* = 1 mm, *L* = 2 cm), with the indicated anions as tetrabutylammonium salts as electrolytes. Crystals were harvested on the anode after one to two weeks and washed with a small amount of solvent.

**Crystal structure determination of (1a)<sub>2</sub>AsF<sub>6</sub>.** C<sub>13</sub>H<sub>10</sub>S<sub>6</sub>(AsF<sub>6</sub>)<sub>0.5</sub>, *M*<sub>r</sub> = 453.035, triclinic, *a* = 7.246(6), *b* = 7.797(1), *c* = 15.041(2) Å, α = 100.73(1), β = 91.44(3), γ = 101.20(3)°, *V* = 817.4 Å<sup>3</sup> (determined by least-squares refinement of the angular coordinates of 25 accurately centered reflections with θ varying from 6 to 12°); Mo-Kα radiation, λ = 0.71069 Å, space group *P*-1, *Z* = 2, *D*<sub>calc</sub> =

1.841 g cm<sup>-3</sup>; crystal dimensions: 0.3 × 0.21 × 0.03 mm<sup>3</sup>;  $\mu = 18.285 \text{ cm}^{-1}$ ,  $F(0,0,0) = 455$ .

Enraf-Nonius CAD4-F diffractometer,  $\omega/2\theta$  mode with  $\omega$  scan width  $1 + 0.35 \text{ tg}\theta$ , graphite-monochromated Mo-K $\alpha$ , 4008 measured reflections ( $1 \leq \theta \leq 26^\circ$ ,  $h, \pm k, \pm l$ ), 3208 unique reflections, giving 2103 reflections with  $I > 3\sigma(I)$ . Intensity control every hour showed averaged loss of 0.1% in 52 h of X-ray exposure time. Empirical absorption correction from data from a  $\psi$  scan was applied. Residual electron density amounts to  $1.1 \text{ e } \text{Å}^{-3}$ .

The structure was solved by direct methods (MULTAN<sup>21</sup>). Hydrogen atoms were included in structure factor calculations at ideal positions, but not refined. All atoms (except H) were refined anisotropically to  $R = 0.044$  and  $R_w = 0.065$ , GOF = 1.52. Scattering factors were taken from *International Tables for X-Ray Crystallography* and all computer programs are from the Enraf-Nonius Structure Determination Package.<sup>22</sup>

Atomic coordinates (1 page), structure factors and thermal parameters (12 pages) are available from the authors on request.

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