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A novel array in extended tetrathiafulvalenes (TTF): the 'H' shape

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Abstract

The highly extended, cross-conjugated and sulfur rich π-electron donor **2a** was synthesized and characterized introducing the 'H' shape as a new approach in the tetrathiafulvalene (TTF) array. © 2000 Elsevier Science Ltd. All rights reserved.

Since its discovery,[1] tetrathiafulvalene (TTF) still remains one of the most studied systems in the field of molecular materials because of its ability to reach electrically (super)conducting cation radical salts or charge transfer complexes.[2] Among the wide variety of chemical modifications performed on the TTF skeleton,[3] the synthesis of highly extended and sulfur rich systems has recently received particular attention.[4] Thus, bis(1,4-dithiafulven-6-yl) TTFs have proved to be efficient in the enhancement of the dimensionality of the related materials since they afford interesting 2D electroconducting cation radical salts.[5]

With this aim, we have previously reported the synthesis and electrochemical properties of new π-donors **1**.[6] Thus, the bidimensional 'T' shape of such compounds is of particular interest resulting in: (i) the enhancement of the extended, cross-conjugated π-system which may induce favourable intermolecular interactions in the stacking mode of related materials due to the lowering of the charge density; (ii) the accumulation of sulfur atoms allowing multi intra- and interchain S···S contacts that would increase the dimensionality of the corresponding salts; (iii) the easier access to highly oxidized states which may provide organic salts of unusual stoichiometries.

Focusing our efforts in this field, we have designed new π-donor **2a** endowed with a typical H-shaped character prone to improve the above properties of T-shaped compounds **1** and we report here its straightforward synthesis (R=SPent).

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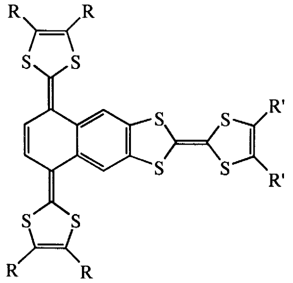
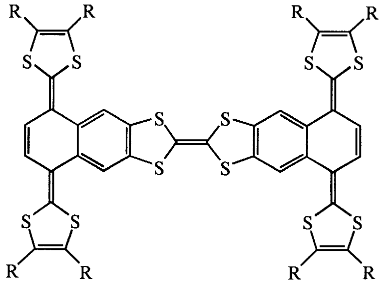


1



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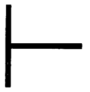
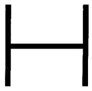
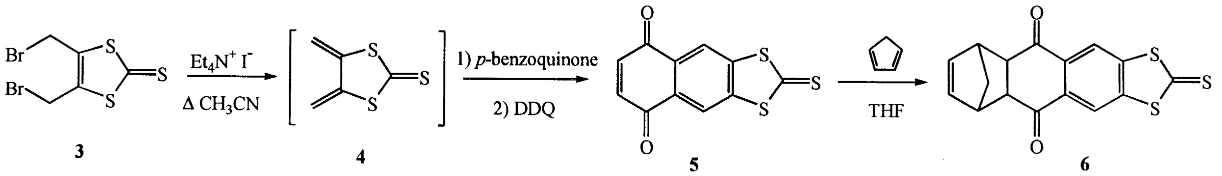


: " T " shape



: " H " shape

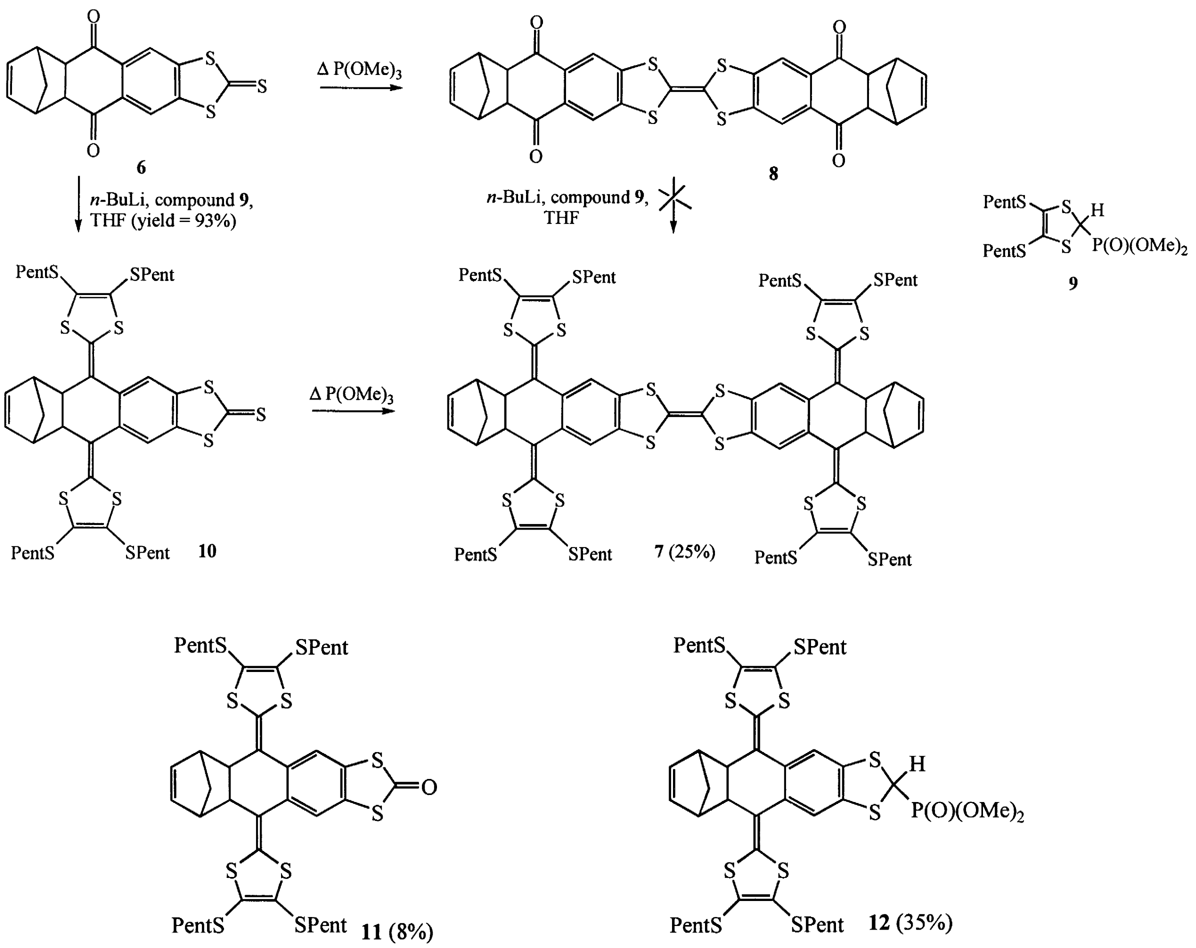
The synthesis of target TTF **2a** started from 4,5-bis(bromomethyl)-2-thioxo-1,3-dithiole **3**[7] which was easily obtained by transformation of the corresponding diol[8] with PBr_3 in 94% yield. The following reductive elimination was carried out using $Et_4N^+ I^-$ and the resulting transient diene **4** was condensed with *p*-benzoquinone affording the Diels–Alder cycloadduct (Scheme 1). The aromatization into compound **5** was finally induced by subsequent treatment with DDQ. Because of its low solubility, and in order to allow further Horner–Wadsworth–Emmons (HWE) olefinations by diminishing the electron-accepting character of this precursor **5**,[6a] we submitted the raw material to a [4+2] cycloaddition with cyclopentadiene in THF according to Yamashita's methodology.[9] Compound **6** was obtained in 59% yield (calculated from **3**) after purification by silica gel column chromatography (CH_2Cl_2).



Scheme 1.

At this stage, the first route investigated to reach precursor **7** used the classical self-coupling reaction of **6** in $P(OMe)_3$ at 80°C (Scheme 2). Nevertheless, the low yield observed for this reaction and the poor solubility of the resulting TTF **8** prevented the fourfold subsequent olefinations with the phosphonate anion of **9**[10] to occur. The second synthetic strategy started from the 'HWE' reaction of both carbonyl functionalities of **6** which was carried out using an excess (3 equivalents) of reagent **9** in the presence of *n*-BuLi. The bis-olefinated product **10** could be isolated as an analytically pure compound in 93% yield after precipitation with MeOH. The following $P(OMe)_3$ self-coupling reaction of thione **10** was studied under different experimental conditions. The best result was obtained using $P(OMe)_3$ diluted in toluene (0.028 M L^{-1}) at 140°C for 4 h. We observed that the expected precursor **7** was accompanied with the oxo derivative **11** which could result from the transformation of the thioxo functionality,[11] and the corresponding phosphonate **12** arising from the conversion of the thione under high dilution according to a mechanism previously described.[12] These three compounds were easily separated by silica gel column chromatography to successively afford H-shaped **7** (petroleum ether/CH_2Cl_2 7/3, 25% yield), then the oxo derivative **11** (petroleum ether/CH_2Cl_2 7/3, 8% yield) and finally, the phosphonate **12** (petroleum ether/EtOAc 1/1, 35% yield).

The ^1H NMR spectrum of **7** showed the presence of both *cis* and *trans* isomers in the ratio 64/36.[13] This structure was also supported by its FAB^+ mass spectrum which exhibited: (i) the molecular ion peak



Scheme 2.

whose isotopic distribution is in agreement with the calculated pattern; and also (ii) two peaks related to both successive eliminations of cyclopentadiene at m/z=1692 and m/z=1626, respectively (Fig. 1). In accordance with our previous investigations on compounds **1**,[6] the corresponding *retro* Diels–Alder reactions were cleanly performed from **7** upon refluxing in *o*-dichlorobenzene to give the analytically pure H-shaped TTF **2a** in quantitative yield whose structure is confirmed by ^{1}H NMR and MALDI–TOF mass spectrometry.

The cyclic voltammogram of **7** suggests an electrochemically induced loss of cyclopentadiene molecules at the second oxidation step, further cycling corresponding to the deprotected compound **2a**. It should also be noted that, as expected, the first reversible oxidation peak of **2a** (E^1_{ox}=0.31 V/ vs Ag/AgCl, 1 mM in CH_2Cl_2-*n*-Bu_4NPF_6 (0.1 M), Pt electrode, v=100 mVs^{-1}) arises at a value close to that of the T-shaped compound **1a** (R=R′=SMe, E^1_{ox}=0.27 V).[6a] Complementary experiments are now in progress to specify the electrochemical behaviour and the different oxidation states of **7** and **2a** during the CV study.

Compound **2a** readily reacts with TCNQ upon simple grinding of the solids[14] to form an electroconducting charge transfer complex presenting a metallic appearance. Further experiments are now under-way to isolate single crystals of this charge transfer complex and to prepare cation radical salts by chemical or electrochemical oxidations.

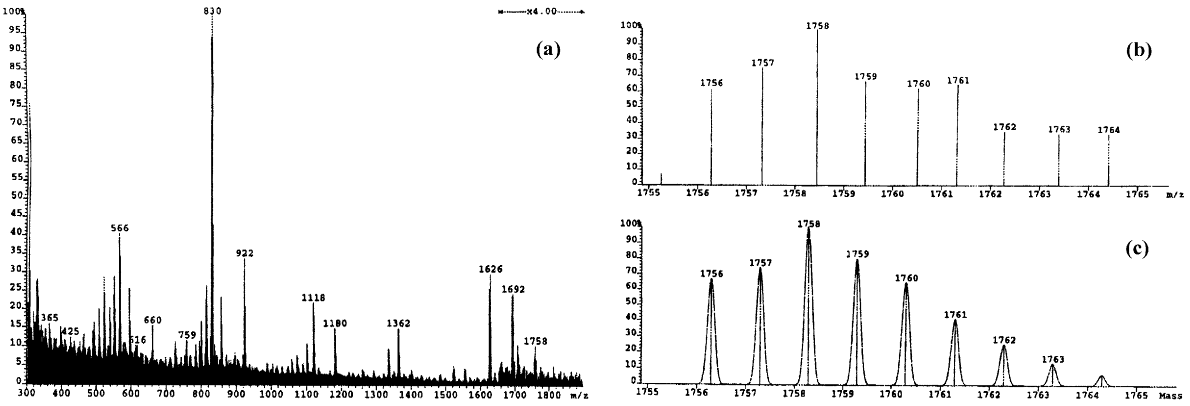


Fig. 1. Mass spectrum (FAB^+) of compound **7** (a), theoretical (b) and experimental (c) spectra

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13. All new compounds gave satisfactory spectroscopic data. **8**: Red powder, MS *m/z* (I%) EI*:* 464 ($M^{+\cdot}-2C_5H_6$, 100), 306 (10), 264 (19), 232 (14), 188 (7), 66 (20). **7**: Orange crystals, ^1H NMR ($CDCl_3$) δ : 0.89 and 0.92 (2t, 24H, CH_3, ^3J=7.0 Hz), 1.20–1.80 (2m, 52H, $CH_3\text{-}(CH_2)_3-$, $CH\text{-}CH_2$), 2.60–2.96 (m, 16H, CH_2S), 3.06 (br s., 4H, =C-CH-C*H*), 3.33 (br s.,

4H, =C-C*H*-CH), 5.41 (2dd, 4H, H-C=C-H, ^{3}J=1.5 Hz and ^{3}J=1.5 Hz), 7.13 (64%) and 7.15 (36%) (2s, 4H, =CH arom); ^{13}C NMR (CDCl$_3$) δ *:* 14.65 (CH$_3$), 22.89 (CH$_3$-*C*H$_2$), 30.09 and 30.16 (CH$_3$-(CH$_2$)$_2$-*C*H$_2$-), 31.36 and 31.41 (CH$_3$-CH$_2$-*C*H$_2$-), 36.88 (CH$_2$S), 47.71 (=C-*C*H-CH), 48.97 (=C-CH-*C*H), 50.40 (=C-CH-CH-*C*H$_2$), 111.97 and 112.66 (cent. C=C), 119.23 (S-C=*C*H-C), 124.67 (S$_2$*C*=C-C), 126.79 and 127.01 (S$_2$C=CS$_2$), 128.75 (S$_2$C=*C*-C), 134.81 (H-C=C-H), 134.93, 135.09, 135.19 (S-*C*=CH-*C* *cis*/*trans*); calcd for $C_{84}H_{108}S_{20}$ (1759.024): C, 57.35; H, 6.19; S, 36.46. Found: C, 57.40; H, 6.25; S, 36.60%. **2a**: Dark red crystals, mp: 162–165°C (*o*-C$_6$H$_4$Cl$_2$); ^{1}H NMR (C$_6$D$_6$, 340 K) δ : 0.85–1.00 (m, 24H, CH$_3$), 1.20–1.80 (m, 48H, CH$_3$-(C*H*$_2$)$_3$-), 2.87 and 2.91 (2t, 16H, CH$_2$S, ^{3}J=7.3 Hz), 6.46 (s, 4H, H–C=C–H), 7.75 (s, 4H, S–C=CH–C); MS *m/z* MALDI–TOF (DHB matrix): simulated: 1626.2, exp. 1628.5 max. (M+2H)$^+$; calcd for $C_{74}H_{96}S_{20}$ (1626.828): C, 54.63; H, 5.94. Found: C, 54.41; H 5.81%.

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