

Tetrathiafulvalene- and Dithiafulvene-Substituted Mesitylenes, New π -Donor Molecules with 3-Fold Symmetry and the Formation of an Unprecedented New Class of Electroactive Polymers

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Abstract: Novel π -donor molecules with 3-fold symmetry are built on the 1,3,5-benzene core, substituted with three identical moieties, i.e. $-\text{CH}=\text{CH}(\text{TTF})$ (**8**) (TTF = tetrathiafulvalene), $-\text{CH}_2\text{S}((\text{TTF})\text{Me}_3)$ (**9**), 1,4-dithiafulven-6-yl (**10a,b**), and 6-methyl-1,4-dithiafulven-6-yl (**11a,b**). Cyclic voltammetry experiments demonstrate that oxidation of **10a,b** gives rise to the precipitation of an electroactive polymer on the electrode, while **9** can be reversibly oxidized to **9³⁺** and **9⁶⁺**. Electrocrystallization of **9** in the presence of $\text{TBA}_2(\text{Mo}_6\text{Cl}_{14})$ affords crystals of $(\text{9}^{2+})\cdot\text{Mo}_6\text{Cl}_{14}^{2-}$, whose magnetic properties are investigated by EPR. **10a** crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 3.986(1)$ Å, $b = 21.312(2)$ Å, $c = 20.473(2)$ Å, $\beta = 94.24(1)^\circ$, and $Z = 4$. **11a** crystallizes in the monoclinic system, space group $P2_1/a$, with $a = 10.919(4)$ Å, $b = 17.175(2)$ Å, $c = 11.481(1)$ Å, $\beta = 97.86(2)^\circ$, and $Z = 4$. Columns of planar molecules of **10a** are exquisitely interlocked to create a dense ($d_{\text{calcd}} = 1.61$ g cm⁻³) solid whereas no stacking pattern is observed in the structure of the nonplanar, puckered molecule **11a** ($d_{\text{calcd}} = 1.44$ g cm⁻³). MO calculations demonstrate that, because of their meta orientation, the three dithiolyidene fragments in **10a** and **11a** are nearly independent.

Introduction

The scope of this paper consists of the synthesis of new π -donor molecules with 3-fold symmetry and their electrochemical and structural characterization. The creation of aesthetical, highly symmetrical molecular objects has long motivated hard-earned synthetic achievements.¹ In the case of conjugated systems, high symmetry leads to the degeneracy of the frontier orbitals and hence to the possibility of a stable triplet ground state, a prerequisite for the generation of ferromagnetic materials.² The strategy for the production of intermolecular ferromagnetic interactions in organic solids, originally designed by McConnell in 1963,³ and further extended to ionic charge-transfer salts in 1967,⁴ stipulates that in order to achieve ferromagnetic behavior the donor or acceptor component needs to have at least one pair of degenerate HOMOs or LUMOs. This condition is often fulfilled in transition metal complexes but very rarely in organic molecules, except when they belong to a point group of higher symmetry, i.e. C_3 or higher. This theoretical background led to the development of several other models, particularly by Breslow,⁵ Torrance,⁶ Wudl,⁷ and Miller,⁸ who adapted the McConnell mechanism to cation- or anion-radical salts.

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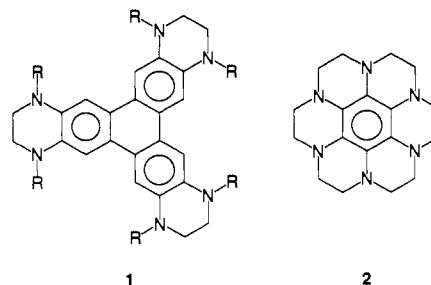
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The need for molecules with a degenerate frontier orbital has encouraged the preparation of numerous π -donor molecules with 3-fold symmetry. Following the discovery of a triplet ground state in hexamethoxytriphenylene by Parker and Bechgaard,¹³ Breslow reported the preparation of several amino derivatives like **1** or **2**, which are much easier to oxidize than the methoxy



analog. Dications of these very electron-rich donors were isolated with organic as well as inorganic anions,^{5c,14,15} and some of them indeed exhibit a triplet ground state. However, all the materials reported so far proved to present antiferromagnetic ordering.

Bulk ferromagnetism was observed in organometallic metal-locene-based $[\text{Cp}^*_2\text{Fe}](\text{TCNE})$ ⁹⁻¹¹ and $[\text{Cp}^*_2\text{Mn}](\text{TCNQ})$ ¹² charge-transfer complexes in particular. The latter are made of parallel mixed stacks of alternating cation and anion radicals.

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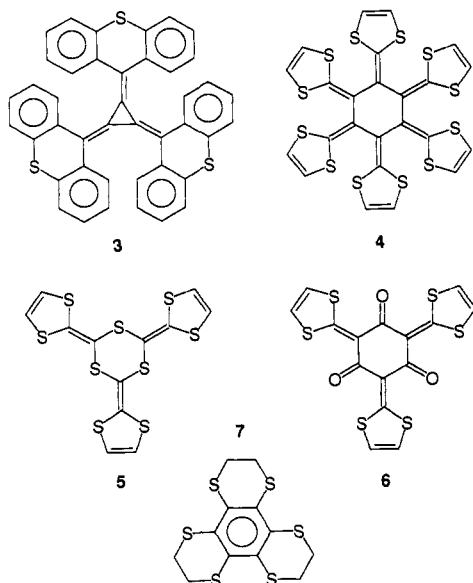
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Torrance reported true ferromagnetic behavior in a polymeric material obtained by oxidation of the 1,3,5-triaminobenzene with iodine, thus giving a polyaniline analog with local 3-fold symmetry.¹⁶ The saturation magnetization of the best sample, however, represented only 2 mol % (based on monomer) of possible spins in the polymer. The preparation of this material was improved,¹⁷ but its magnetic behavior proved irreproducible.

From a practical point of view, and according to the Torrance model, it was then necessary to prepare 3-fold symmetry donor molecules with enough electron-donating ability to be oxidized to stable dicationic species. Several sulfur-based donor molecules of 3-fold symmetry like **3**,¹⁸ **4**,¹⁹ **5**,²⁰ **6**,²¹ or **7**²² have been reported

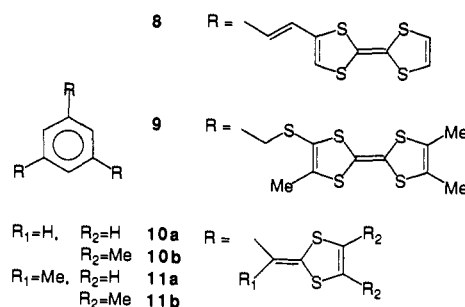


by now. However, complex electrochemical behaviors were observed for example in the cases of **3**–**5**, as a likely consequence of conformational rearrangements upon oxidation. Besides, **7** oxidizes at high potentials only (over 1 V vs SCE). Finally, in **6**, two reversible, one-electron oxidation waves were found to be separated by only 0.15 V, an indication of a moderate interaction between the three redox dithiole rings.

Given that small, flat and highly conjugated molecules such as **6** or **7** proved difficult to oxidize up to the di- or tricationic species, we sought an efficient means to decrease their intramolecular Coulombic repulsions. This can be achieved in TTF chemistry by synthesizing either the so-called extended TTFs or the coupled TTFs. Extended TTFs have been prepared in which the two dithiole rings are separated by long conjugated spacers like butadiene,²³ acetylene,²⁴ or *p*-phenylene²⁵ moieties. Increasing the separation between the two dithiole rings allows the

molecules to be oxidized directly to the dication at a single potential. Besides, two tetrathiafulvalenyl groups have been coupled across organic spacers such as $-\text{Ar}-$,²⁶ $-\text{CH}=\text{CH}-$, $\text{Ar}-\text{CH}=\text{CH}-$,²⁷ $-(\text{CH}_2)_n-$,²⁸ $-\text{S}(\text{CH}_2)_n\text{S}-$ ²⁹ or main-group elements ($-\text{Hg}-$,³⁰ $-\text{S}-$,³¹ $-\text{Se}-$,³¹ $-\text{Te}-$,³² $-\text{SiMe}_2-$,³⁰ or $-\text{PPH}-$ ^{30,33}). In those coupled TTFs, the two redox moieties are nearly independent and oxidize to the monocation at the same potential. Coulombic through-space interactions may, in some cases, split the first two-electron oxidation wave into two one-electron waves, when the TTFs are close enough to interact, either by construction^{30,31} (short tetrahedral spacers) or by folding.²⁹

A combination of those two approaches is used in this paper to prepare π -donor molecules which may adopt 3-fold symmetry in the solid state.³⁴ Three types of molecules are investigated with the common feature of being derived from a common central core, a 1,3,5-trisubstituted benzene. In **8** and **9**, three coupled



TTFs are expected to be nearly independent, and the molecules should oxidize easily to the tricationic state. **10a,b** and **11a,b** are derived from the extended TTFs construction principle, and significant electron delocalization is anticipated. Note however that because of the meta orientation of the dithiolyldene fragments, these molecules are unprecedented and their electrochemical behavior is particularly interesting.

In addition, we report that molecules **10a,b**, derived from the triformylbenzene, undergo a polymerization process upon oxidation to afford a new kind of electroactive polymer. As expected, the introduction of methyl substituents on the active sites of **10a,b** to give **11a,b** results in a drastic inhibition of the polymerization process. The differences in electrochemistry and polymerization behavior between **10a,b** and **11a,b** will be discussed and related to differences in the structural and electronic properties of both classes of molecules.

Experimental Section

General Information. Solvents (Et₂O, THF) were freshly distilled under argon over sodium and benzophenone before use. Melting points are uncorrected. ¹H NMR spectra were recorded on a Jeol-PMX60

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(34) In fact, such molecules are targeted to present a quasi-3-fold symmetry. The precise molecular configuration achieved by the corresponding radical cations in the solid state obviously will depend on the nature and structure of the counter anions.

spectrometer, with TMS as the internal standard. Mass spectra were obtained by chemical ionization, and elemental analyses were performed at the Institut des Substances Naturelles, CNRS, Gif/Yvette, France.

1,3,5-Tris(hydroxymethyl)benzene (13). 13 was prepared from 12 as previously described,³⁵ mp 75–78 °C (lit.³⁵ 75–77 °C). ¹H NMR: δ_{H} 4.53 (s, 6 H, CH₂), 7.16 (s, 3 H, Ar).

1,3,5-Tris(bromomethyl)benzene (14). A 100-mL round-bottomed flask was equipped with a stir bar, 1,3,5-tris(hydroxymethyl)benzene (13) (2.00 g, 12.3 mmol), and concentrated HBr (57 mL), and the mixture was refluxed for 30 min. After an oil had formed, the solution was cooled with ice and the oil crystallized. The solution was filtered and the solid washed with water and dried under vacuum. The crude solid was then dissolved in CH₂Cl₂, the solution dried over MgSO₄ and filtered, and the solvent removed under vacuum affording a white solid. Yield: 3.6 g (83%, before recrystallization). The solid was then recrystallized in cyclohexane, providing large white crystals, mp 94–99 °C (lit.^{36,37} 93 °C). Anal. Calcd for C₉H₉Br₃: C, 30.30; H, 2.52. Found: C, 30.99; H, 2.73. ¹H NMR (CDCl₃): δ_{H} 4.43 (s, 6 H, CH₂), 7.33 (s, 3 H, Ar).

1,3,5-Triformylbenzene (15). 1,3,5-tris(hydroxymethyl)benzene (13) (3.4 g, 20 mmol) was suspended in CH₂Cl₂ (200 mL), and solid pyridinium chlorochromate (13 g, 60 mmol) was added. After 30 min of stirring, the thick reaction mixture was diluted with a little acetone, and further stirring for 2 h gave a more homogeneous suspension. The precipitated chromium salts were filtered off and washed with CH₂Cl₂, and the organic phase was washed with HCl (1 M, 2 × 100 mL), H₂O (100 mL), K₂CO₃ (1 M, 100 mL), H₂O (100 mL) and NaCl (1 M, 100 mL) and finally dried over MgSO₄. Filtration through a short silica gel column (eluant CH₂Cl₂) and recrystallization from AcOEt afforded 2.5 g of white crystals, mp 155–159 °C (lit.^{35,36} 155.5–160 °C). ¹H NMR (CDCl₃): δ_{H} 8.66 (s, 3 H, Ar), 10.23 (s, 3 H, CHO).

1,3,5-Tris((triphenylphosphonium)methyl)benzene Tribromide (16). 16 was prepared from 14 according to ref 35 and was used directly in the following reaction (see below).

1,3,5-Tris(2-(tetrathiafulvalenyl)ethenyl)benzene (8). To a suspension of 16 (11.4 g, 10 mmol) in a 1:1 mixture of THF/CH₃CN (50 mL) at –70 °C was added dropwise BuLi (2.5 M in hexanes, 12 mL, 30 mmol), followed by formyltetrathiafulvalene (7 g, 30 mmol). The dark red mixture was stirred to room temperature. The filtered dark red precipitate (4 g, 53%) proved to be insoluble in all usual solvents and was not further investigated.

1,3,5-Tris(((4,3',4'-trimethyltetrathiafulvalen-3-yl)thio)methyl)benzene Tribromide (18). To a solution of 14 (1 g, 2.83 mmol) in chloroform (25 mL) was added the mesoionic 2-(*N,N*-dimethylamino)-5-methyl-1,3-dithiolium-4-thiolate³⁰ (17). The resulting orange solution was stirred at room temperature for 1 h, during which an oil formed. The mixture was evaporated to dryness, leaving a brittle, light yellow foam. This solid was collected, yielding 9.8 g (100% yield if considered as a solvate with two CHCl₃ molecules, see the microanalysis). Anal. Calcd for C₂₇Br₃H₃₆N₃S₉(CHCl₃)₂: C, 29.77; Br, 20.49; H, 3.27; N, 3.59; S, 24.67. Found: C, 29.5; Br, 21.1; H, 3.2; N, 3.30; S, 24.8. ¹H NMR (DMSO-*d*₆): δ_{H} 2.23 (s, 9 H, Me), 3.53 (s, 18 H, NMe₂), 4.10 (s, 6 H, CH₂), 7.20 (s, 3 H, Ar).

1,3,5-Tris(((4,3',4'-trimethyltetrathiafulvalen-3-yl)thio)methyl)benzene (9). 4,5-Dimethyl-1,3-dithiolium iodide^{25b,38} (13.4 g, 52 mmol) was stirred with P(OMe)₃ (6.8 mL, 55 mmol) in CH₃CN (90 mL) for 2 h. Evaporation of the solvent afforded 2-(dimethoxyphosphoryl)-4,5-dimethyl-2*H*-1,3-dithiole (19b) as an air-sensitive oil, which was used directly. The phosphonate ester 19b was then dissolved in THF (200 mL) and further reacted with a THF solution of *t*-BuOK (5.85 g, 55 mmol), the reaction mixture being kept below –60 °C. After 5 min, 18·(CHCl₃)₂ (9.8 g, 8.5 mmol) was added in one portion and the mixture was stirred while allowing the temperature to reach –10 °C. Ether (250 mL) was added to precipitate the salts, which were removed by filtration. The ether/THF solution was then concentrated to a deep orange oil, which was dissolved in toluene (100 mL). Concentrated acetic acid was added until the solution became permanently red. The solution stood overnight, after which the precipitated orange product was filtered off. Yield: 1.85 g (23% yield, calculated on 18) (mp 228–229 °C). Anal. Calcd for C₃₆H₃₆S₁₅: C, 45.55; H, 3.79; S, 50.66. Found: C, 45.59; H, 3.45; S, 49.01. ¹H NMR: δ_{H} 1.76 (s, 9 H, Me), 1.93 (s, 18 H, Me), 3.80

(s, 6 H, CH₂), 7.03 (s, 3 H, Ar). MS *m/z*: 949 (M⁺, 100), 705 (M⁺ – Me₃(TTF), 22), 673 (M⁺ – (Me₃(TTF))S, 65), 277 ((Me₃(TTF))S, 75).

1,3,5-Tris(1,4-dithiafulven-6-yl)benzene (10a). 1,3-Dithiolium tetrafluoroborate (10 g, 50 mmol) was suspended in acetone and treated with a solution of NaI (25 g, 50 mmol) in acetone. After stirring the solution for 1 h, the yellow precipitate of the iodide was filtered off, washed with acetone, and dried (quantitative yield). The iodide (2.31 g, 10 mmol) was suspended in CH₃CN (50 mL), and P(OMe)₃ (1.5 mL, 12.5 mmol) was added. After 1 h of stirring, the colorless solution was evaporated off to afford 19a as a slightly red oil. It was further dissolved in dry THF and cooled at –60 °C. *t*-BuOK (1.2 g, 11 mmol) dissolved in THF was added, followed by 1,3,5-triformylbenzene (15) (0.4 g, 2.7 mmol). After the solution was stirred to room temperature for 2 h, the reaction mixture was evaporated and the residue extracted with toluene. Recrystallization from toluene afforded 10a as yellow needles, mp 160–165 °C. Yield: 135 mg (12%). Anal. Calcd for C₁₈H₁₂S₆: C, 51.38; H, 2.87; S, 45.73. Found: C, 51.90; H, 2.95; S, 45.27. ¹H NMR (CDCl₃): δ_{H} 6.30 (s, 3 H, CH=C), 6.56 (s, 6 H, CH=CH), 6.93 (s, 3 H, Ar).

1,3,5-Tris(2,3-dimethyl-1,4-dithiafulven-6-yl)benzene (10b). 10b was prepared as above from 4,5-dimethyl-1,3-dithiolium iodide (2.6 g, 10 mmol), P(OMe)₃ (1.5 mL, 12 mmol), *t*-BuOK (1.3 g, 11 mmol), and 1,3,5-triformylbenzene (15) (0.4 g, 2.7 mmol). Yield: 0.29 g (21%) (mp 232–234 °C). Anal. Calcd for C₂₄H₂₄S₆: C, 57.09; H, 4.79; S, 38.11. Found: C, 57.39; H, 4.88; S, 37.80. ¹H NMR (CDCl₃): δ_{H} 1.93 (s, 18 H, Me), 6.36 (s, 3 H, CH=C), 6.83 (s, 3 H, Ar).

1,3,5-Tris(6-methyl-1,4-dithiafulven-6-yl)benzene (11a). 11a was prepared as above from 1,3-dithiolium iodide (11.5 g, 50 mmol), P(OEt)₃ (8.6 mL, 50 mmol), BuLi (2.5 M in hexanes, 20 mL, 50 mmol), and 1,3,5-triacetylbenzene (20) (2.45 g, 12 mmol). After chromatographic separation on silica gel with toluene, a yellow oil was obtained, which crystallized upon standing. Recrystallization from CH₃CN afforded 11a as white needles, mp 157–158 °C. Yield: 2.8 g (50%). Anal. Calcd for C₂₁H₁₈S₆: C, 54.50; H, 3.92; S, 41.77. Found: C, 54.50; H, 3.73; S, 41.31. ¹H NMR (CDCl₃): δ_{H} 2.06 (s, 9 H, Me), 6.2 (dd, *J*_{HH} = 6.4 Hz, CH=CH), 7.16 (s, 3 H, Ar). MS *m/z*: 463 (M⁺, 100).

1,3,5-Tris(2,3,6-trimethyl-1,4-dithiafulven-6-yl)benzene (11b). 11b was prepared as above from 4,5-dimethyl-1,3-dithiolium iodide (5.16 g, 20 mmol), P(OMe)₃ (2.5 mL, 20 mmol), *t*-BuOK (2.25 g, 20 mmol), and 1,3,5-triacetylbenzene (20) (1 g, 5 mmol). The reaction mixture was stirred at room temperature overnight. After extraction in CH₂Cl₂ and flash chromatography with CH₂Cl₂, the first fraction was recrystallized from toluene. As seen by MS, the product also contains some monoacetyl bis-fulvalenyl derivative which could be removed by reduction to the alcohol with LiAlH₄ in refluxing Et₂O and a second recrystallization in toluene. Yield: 0.66 g (25%) (mp 205–209 °C). Anal. Calcd for C₂₇H₃₀S₆(C₆H₅CH₃)_{0.6}: C, 61.92; H, 5.79; S, 31.79. Found: C, 62.24; H, 5.78; S, 31.73. ¹H NMR (CDCl₃): δ_{H} 1.85 (s, 9 H, Me), 1.93 (s, 9 H, Me), 2.06 (s, 9 H, Me), 7.23 (s, 3 H, Ar). MS *m/z*: 547 (M⁺, 100), 432 (5).

Electrochemical Measurements. Cyclic voltammograms were recorded using a PAR 273 potentiostat with Pt working (1 mm²) and auxiliary (1 cm²) electrodes, a SCE reference electrode, and (*n*-Bu)₄N⁺PF₆[–] as the supporting electrolyte. Solvents were dried on basic aluminium oxide before use.

Electrocrystallization Experiments. Experiments were conducted at 40 °C, in CH₂Cl₂/DMF (4:1) or in butyronitrile, dried over basic aluminium oxide. A constant current density of 0.3 μ A cm^{–2} was used. Crystals grown on the anode were collected after 2 weeks and washed with a small amount of solvent. Anal. Calcd (found) for (9²⁺)₂Mo₆Cl₁₄^{2–}, C₃₆H₃₆S₁₅Mo₆Cl₁₄: C, 21.39 (22.20); H, 1.79 (1.91); S, 23.79 (23.12).

X-ray Diffraction Studies. Colorless crystals of 10a and 11a were mounted on the end of a glass rod. The Enraf-Nonius Structure Determination Package³⁹ was used for data collection, data processing, and structure solution. The unit cell parameters were determined from a least-square refinement of the angular settings of 25 well-centered reflections. Crystallographic data and additional details regarding data collection and refinement for 10a and 11a are given in Table I. *Lp* correction was applied and no absorption correction was carried out. The structures were solved by direct methods with MULTAN 11/82⁴⁰ and refined by full-matrix least-squares (on *F*²) anisotropically, with hydrogen atoms, found from a difference Fourier map, included in structure factor

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Table I. Crystallographic Data for 10a and 11a

	10a	11a
chem. formula	C ₁₈ H ₁₂ S ₆	C ₂₁ H ₁₈ S ₆
fw	420.68	462.76
temp, K	293	293
space group	P2 ₁ /c	P2 ₁ /a
a, Å	3.986(1)	10.919(4)
b, Å	21.312(2)	17.175(2)
c, Å	20.473(2)	11.481(1)
β , deg	94.24(1)	97.86(2)
V, Å ³	1734.4	2131.
Z	4	4
d_{calcd} , g cm ⁻³	1.61	1.44
μ , cm ⁻¹	7.55	6.2
diffractometer	Enraf-Nonius CAD4-F	
λ , Å	0.71073	
monochromator	graphite	
crystal size, mm	0.21 × 0.09 × 0.08	0.30 × 0.15 × 0.06
octants collected	$h, k, \pm l$	$\pm h, k, l$
max h, k, l	4, 25, 24	13, 21, 14
2 θ range, deg	2, 52	2, 52
collection method	ω -2 θ	ω -2 θ
no. of data collected	3987	4558
no. of unique data	2463	4181
no. of data used	1943	1723
($I > 3\sigma(I)$)		
no. of variables	217	244
R, R_w	0.032, 0.041	0.038, 0.050
max peak on final	0.27	0.23
diff Four. map, e/Å ³		
goodness of fit	1.132	1.04

calculations and not refined ($B_H = 1.3 B_C$). A non-Poisson contribution weighting scheme, of the form $w = 4R_o^2/[\sigma^2(I) + (pF_o)^2]$ was applied, with $p = 0.04$ and 0.07 for **10a** and **11a**, respectively. Bond distances and angles for **10a** and **11a** are given in Tables II and III, respectively.

ESR Experiments. ESR spectra were recorded on a Varian X-band spectrometer (frequency 9.3 GHz) equipped with an Oxford ESR 900 helium cryostat.

Extended Hückel Calculations.⁴¹ Single- ζ calculations have been conducted, and the following parameters (H_{ii}) and orbital exponents (ζ) have been used. S: 3s, $H_{ii} = -20.0$ eV, $\zeta = 1.817$; 3p, $H_{ii} = -13.3$ eV, $\zeta = 1.817$. C: 2s, $H_{ii} = -21.4$ eV, $\zeta = 1.625$; 2p, $H_{ii} = -11.4$ eV, $\zeta = 1.625$. H: 1s, $H_{ii} = -13.6$ eV, $\zeta = 1.3$.

Results and Discussion

Synthesis. The preparation of **8**, **9**, **10a,b**, and **11a,b** critically depends upon the ease of access to several mesitylene derivatives (Scheme I). Thus, a modification of the Storck procedure³⁵ for reduction of the trimethyl ester of 1,3,5-benzenetricarboxylic acid (**12**) with LiAlH₄ and THF allows for the preparation of 1,3,5-tris(hydroxymethyl)benzene (**13**) in 80% yield. The latter is in turn converted in 83% yield to 1,3,5-tris(bromomethyl)benzene (**14**) by boiling in concentrated HBr. Several preparations of 1,3,5-triformylbenzene (**15**) have been reported so far. They include the reduction of 1,3,5-benzenetricarbonyl chloride by the Rosenmund reduction³⁷ or with LiAl(O-*t*-Bu)₃H,³⁶ the hydrolysis of 1,3,5-tris(dibromomethyl)benzene,⁴² the oxidation of 1,3,5-tris(bromomethyl)benzene,³⁷ in three or two steps, and the direct formation of the benzene ring from HC(CHO)₃.⁴³ Since none of these procedures appeared really convincing, we sought an alternative procedure, involving the oxidation of the readily available triol **13**. We found that the latter can be oxidized directly to the trialdehyde **15** by reaction with a slight excess of pyridinium chlorochromate⁴⁴ in CH₂Cl₂.

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Table II. Bond Distances and Angles in 10a (Å, deg)

Distances			
S(1A)-C(8A)	1.753(3)	C(1)-C(7A)	1.448(5)
S(1A)-C(9A)	1.747(4)	C(2)-C(3)	1.392(5)
S(1B)-C(8B)	1.758(3)	C(3)-C(4)	1.402(4)
S(1B)-C(9B)	1.737(4)	C(3)-C(7B)	1.457(5)
S(1C)-C(8C)	1.760(4)	C(4)-C(5)	1.393(5)
S(1C)-C(AC)	1.738(4)	C(5)-C(6)	1.401(4)
S(2A)-C(8A)	1.768(3)	C(5)-C(7C)	1.467(4)
S(2A)-C(10A)	1.727(4)	C(7A)-C(8A)	1.341(5)
S(2B)-C(8B)	1.762(3)	C(7B)-C(8B)	1.346(5)
S(2B)-C(10B)	1.726(4)	C(7C)-C(8C)	1.333(5)
S(2C)-C(8C)	1.770(3)	C(9A)-C(10A)	1.314(5)
C(2C)-C(10C)	1.727(4)	C(9B)-C(10B)	1.325(6)
C(1)-C(2)	1.397(4)	C(9C)-C(10C)	1.319(5)
C(1)-C(6)	1.397(4)		
Angles			
C(8A)-S(1A)-C(9A)	96.0(2)	C(1)-C(2)-C(3)	122.2(3)
C(8B)-S(1B)-C(9B)	96.2(2)	C(2)-C(3)-C(4)	117.7(3)
C(8C)-S(1C)-C(9C)	96.2(2)	C(2)-C(3)-C(7B)	125.4(3)
C(8A)-S(2A)-C(10A)	96.7(2)	C(4)-C(3)-C(7B)	116.9(3)
C(8B)-S(2B)-C(10B)	96.0(2)	C(3)-C(4)-C(5)	122.2(3)
C(8C)-S(2C)-C(10C)	96.4(2)	C(4)-C(5)-C(6)	117.9(3)
C(2)-C(1)-C(6)	118.1(3)	C(4)-C(5)-C(7C)	124.5(3)
C(2)-C(1)-C(7A)	116.7(3)	C(6)-C(5)-C(7C)	117.6(3)
C(6)-C(1)-C(7A)	125.1(3)	C(1)-C(6)-C(5)	121.8(3)
C(1)-C(7A)-C(8A)	132.0(3)	S(1C)-C(8C)-S(2C)	112.1(2)
C(3)-C(7B)-C(8B)	130.2(3)	S(1C)-C(8C)-C(7C)	127.1(3)
C(5)-C(7C)-C(8C)	129.8(3)	S(2C)-C(8C)-C(7C)	120.8(3)
S(1A)-C(8A)-S(2A)	112.2(2)	S(1A)-C(9A)-C(10A)	117.9(3)
S(1A)-C(8A)-C(7A)	127.7(3)	S(1B)-C(9B)-C(10B)	117.1(3)
S(2A)-C(8A)-C(7A)	120.1(3)	S(1C)-C(9C)-C(10C)	117.7(3)
S(1B)-C(8B)-S(2B)	112.5(2)	S(2A)-C(10A)-C(9A)	117.2(3)
S(1B)-C(8B)-C(7B)	127.0(3)	S(2B)-C(10B)-C(9B)	118.1(3)
S(2B)-C(8B)-C(7B)	120.5(3)	S(2C)-C(10C)-C(9C)	117.7(3)

8 has been prepared by the procedure used very recently for the analogous para-dimeric compound (Scheme II).²⁷ It involves the Wittig reaction of 1,3,5-tris((triphenylphosphonium)methyl)benzene tribromide (**16**),³⁵ prepared from 1,3,5-tris(bromomethyl)benzene (**14**) and triphenylphosphine, with 3 equiv of formyltetrathiafulvalene. The latter was prepared in 80% yield from (TTF)Li by reaction with *N*-methylformanilide instead of DMF as proposed earlier.⁴⁵ However, in our hands, the yield of the Wittig reaction was poor and the product appears very insoluble, thus preventing further characterization.

This route was therefore modified for the synthesis of derivatives of higher solubilities. This was achieved by using a more flexible spacer. Specifically, the synthesis of a wide variety of coupled TTFs, of general formula (TTF)SCH₂YCH₂S(TTF) (Y = Ar (*o*, *m*, *p*) or (CH₂)_{*n*}), has been recently described²⁹ and the procedure developed for their preparation can be extended to the trisubstituted derivative **9** (Scheme III). It involves the alkylation of the mesoionic compound **17** with 1,3,5-tris(bromomethyl)benzene (**14**) to the tris(2-(dimethylamino)-1,3-dithiolium) salt **18**. We have recently demonstrated that these iminium salts react with the anions formed from the phosphonate esters **19a,b** to give unsymmetrical tetrathiafulvalenes.²⁹ Accordingly, the tris(tetrathiafulvalene) molecule **9** was prepared from **19b** in 23% yield. It is slightly soluble in common solvents and can be recrystallized from toluene.

The Wittig-Horner reagents **19a,b** have been extensively used for the synthesis of extended TTFs by reaction with various conjugated dialdehydes like 1,2- or 1,4-diformylbenzene,⁴⁶ 5-diformylfuran (or thiophene or *N*-methylpyrrole),⁴⁷ or with various formyltetrathiafulvalenes.⁴⁸ A similar synthetic procedure is employed here with 1,3,5-triformylbenzene (**15**), affording **10a,b** in good yield (Scheme IV). Since these molecules appear particularly reactive upon oxidation (see below), we looked for

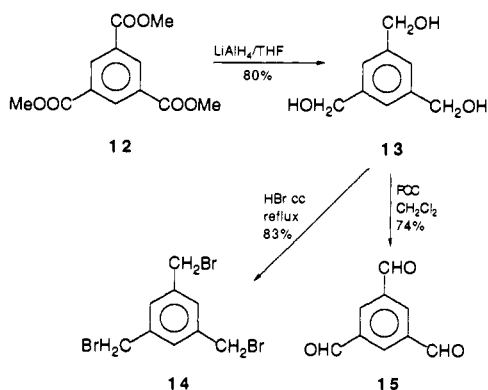
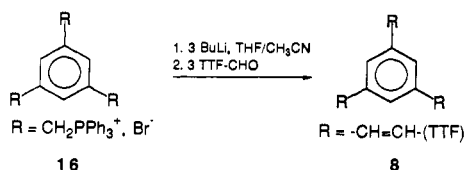
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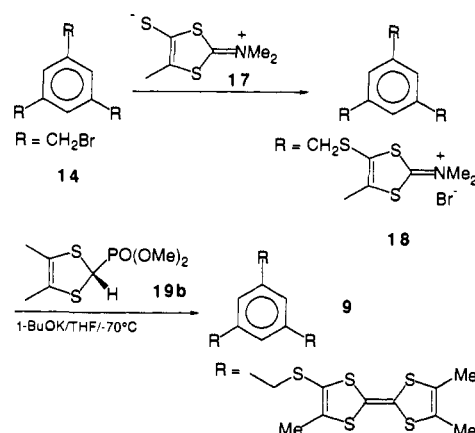
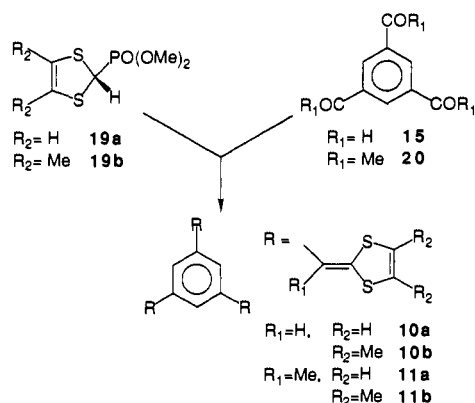
Table III. Bond Distances and Angles in **11a** (Å, deg)

Distances			
S(1A)–C(8A)	1.762(5)	C(2)–C(3)	1.408(6)
S(1A)–C(9A)	1.753(6)	C(3)–C(4)	1.395(6)
S(1B)–C(8B)	1.753(5)	C(3)–C(7B)	1.490(7)
S(1B)–C(9B)	1.733(6)	C(4)–C(5)	1.394(7)
S(1C)–C(8C)	1.764(5)	C(5)–C(6)	1.379(6)
S(1C)–C(9C)	1.717(6)	C(5)–C(7C)	1.495(6)
S(2A)–C(8A)	1.767(5)	C(7A)–C(8A)	1.333(6)
S(2A)–C(10A)	1.710(6)	C(7A)–C(11A)	1.515(8)
S(2B)–C(8B)	1.775(5)	C(7B)–C(8B)	1.339(6)
S(2B)–C(10B)	1.730(6)	C(7B)–C(11B)	1.506(7)
S(2C)–C(8C)	1.770(5)	C(7C)–C(8C)	1.337(7)
S(2C)–C(10C)	1.734(6)	C(7C)–C(11C)	1.511(7)
C(1)–C(2)	1.382(6)	C(9A)–C(10A)	1.309(8)
C(1)–C(6)	1.395(6)	C(9B)–C(10B)	1.309(8)
C(1)–C(7A)	1.488(6)	C(9C)–C(10C)	1.308(8)

Angles			
C(8A)–S(1A)–C(9A)	95.5(3)	C(6)–C(1)–C(7A)	118.8(4)
C(8B)–S(1B)–C(9B)	96.3(3)	C(1)–C(2)–C(3)	121.2(4)
C(8C)–S(1C)–C(9C)	96.0(3)	C(2)–C(3)–C(4)	118.4(4)
C(8A)–S(2A)–C(10A)	96.4(3)	C(2)–C(3)–C(7B)	120.1(4)
C(8B)–S(2B)–C(10B)	95.9(3)	C(4)–C(3)–C(7B)	121.3(4)
C(8C)–S(2C)–C(10C)	95.9(3)	C(3)–C(4)–C(5)	121.0(4)
C(2)–C(1)–C(6)	118.7(4)	C(4)–C(5)–C(6)	119.0(4)
C(2)–C(1)–C(7A)	122.5(4)	C(4)–C(5)–C(7C)	120.3(4)
C(3)–C(7B)–C(8B)	123.4(4)	C(6)–C(5)–C(7C)	120.6(4)
C(3)–C(7B)–C(11B)	117.2(4)	C(1)–C(6)–C(5)	121.6(4)
C(8B)–C(7B)–C(11B)	119.4(3)	C(1)–C(7A)–C(8A)	123.8(5)
C(5)–C(7C)–C(8C)	123.0(4)	C(1)–C(7)–C(11A)	115.8(4)
C(5)–C(7C)–C(11C)	117.7(4)	C(8A)–C(7A)–C(11A)	120.3(4)
C(8C)–C(7C)–C(11C)	119.3(4)	S(2A)–C(8A)–C(7A)	122.5(4)
S(1A)–C(8A)–S(2A)	112.0(3)	S(1B)–C(8B)–S(2B)	112.1(3)
S(1A)–C(8A)–C(7A)	125.5(4)	S(1B)–C(8B)–C(7B)	126.9(4)
		S(2B)–C(8B)–C(7B)	120.9(4)
		S(1C)–C(8C)–S(2C)	112.0(3)
		S(1C)–C(8C)–C(7C)	121.9(4)
		S(2C)–C(8C)–C(7C)	126.1(4)
		S(1A)–C(9A)–C(10A)	117.4(5)
		S(1B)–C(9B)–C(10B)	117.9(5)
		S(1C)–C(9C)–C(10C)	118.7(5)
		S(2A)–C(10A)–C(9A)	118.3(4)
		S(2B)–C(10B)–C(9B)	117.9(4)
		S(2C)–C(10C)–C(9C)	117.4(5)

Scheme I**Scheme II**

an efficient way to stabilize them. This was achieved by using 1,3,5-triacetylbenzene (**20**) instead of the triformyl analog **15** in the reaction with the 2-phosphoryl-1,3-dithiole esters **19a,b**, thus affording **11a,b** in good yield. As expected, ketones were not as

Scheme III**Scheme IV**

reactive as aldehydes and the reaction times had to be increased in order to carry out the reaction to completion.

Comparison of the X-ray Structures of 10a and 11a. **10a** crystallizes in the monoclinic system, space group $P2_1/c$; the molecule is located in the general position (Figure 1). All bond lengths and angles (Table II) are normal except the values of the angles around the substituted carbon atoms of the central phenyl ring, which are lower than the corresponding angles in the unsubstituted ones. The molecule exhibits a slight distortion from planarity. Out-of-plane twisting of the dithiole rings A, B, and C away from the planar central six-membered ring amounts to 8.2(5), 11.0(3), and 6.1(7)°, respectively. The five-membered rings adopt an envelope conformation, except ring B, which is planar. Of particular interest is the observation that the essentially planar molecules **10a** stack on top of each other along the a axis (Figure 2). This columnar pattern is very unusual for neutral π -donor molecules and is likely to be a consequence of the highly symmetrical shape of the molecule, which allows adjacent stacks to fit nicely into each other. However, intermolecular distances are in the expected range, indicating that the cohesion of the structure is mainly due to van der Waals interactions.

11a crystallizes in the monoclinic system, space group $P2_1/a$, with the molecule located in the general position (Figure 3). As

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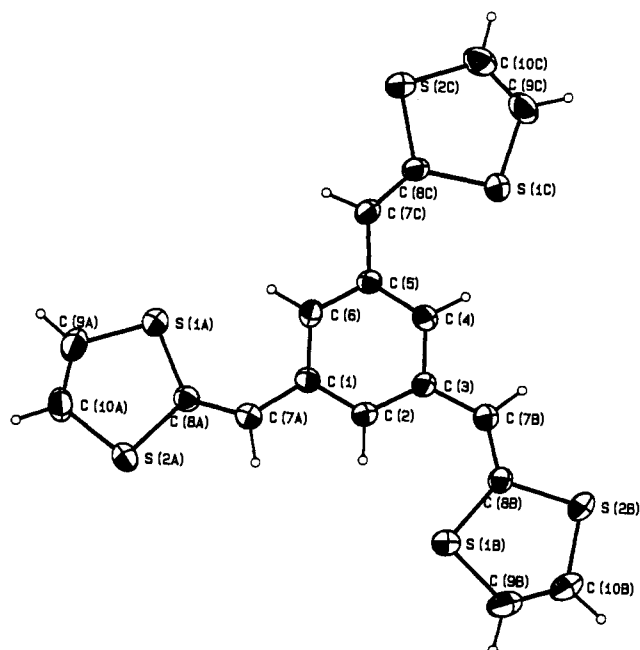


Figure 1. ORTEP drawing and numbering scheme for **10a**. Thermal ellipsoids are drawn at the 50% probability level.

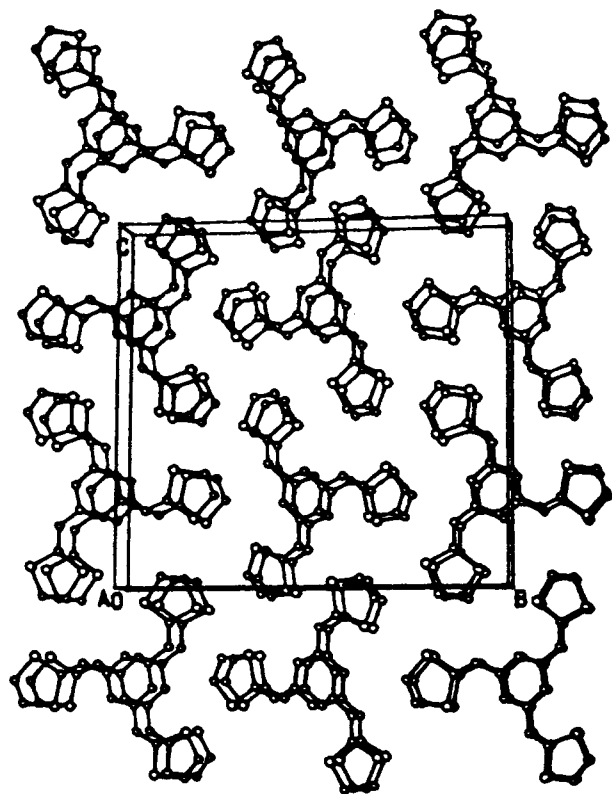


Figure 2. Stacking pattern and interstack locking in **10a**, as viewed along the *a* axis.

in **10a**, bond lengths and angles (Table III) are normal and a similar distortion of the central phenyl ring is observed. Due to the steric bulk of the methyl groups, the three dithioliydene fragments A, B, and C are twisted out of the plane of the central phenyl ring by as much as 46.2(1), 38.7(1), and 44.8(1) $^\circ$, while the five-membered dithiole rings remain planar. Note, however, that the rotation sign is not the same for the three fragments. In principle there exists the possibility to obtain a helical molecule presenting two enantiomers (the right- and left-handed helices). However, while two of these fragments have their methyl groups up, the methyl group of the third one is down. These strong

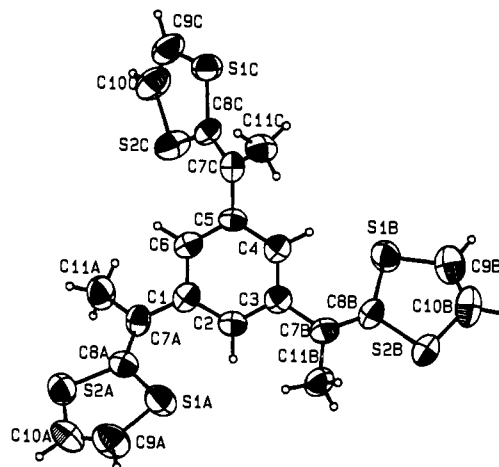


Figure 3. ORTEP drawing and numbering scheme for **11a**. Thermal ellipsoids are drawn at the 50% probability level.

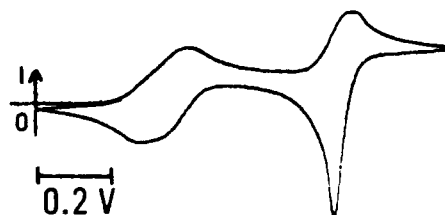


Figure 4. Cyclic voltammogram of **9** in CH_2Cl_2 , at a scan speed of 100 mV/s.

distortions from planarity probably also result in the lower density of **11a** (1.44 g cm^{-3}) as compared to that of **10a** (1.61 g cm^{-3}). Indeed the latter value is typical of molecular crystals with those elements (C, H, S), for example, TTF ($d_{\text{calcd}} = 1.68 \text{ g cm}^{-3}$)⁴⁹ or BEDT(TTF) ($d_{\text{calcd}} = 1.786 \text{ g cm}^{-3}$).⁵⁰ Of particular interest is the presence of a network of short intermolecular S...H distances in **11a**. In fact every sulfur atom of **11a** is engaged in such attractive contacts^{51,52} with hydrogen atoms of the neighboring molecules, with S...H distances less than the sum of the van der Waals radii (3.0 Å). On the contrary, in **10a**, only one short intermolecular contact is identified. Thus, it appears that the high density of **10a** is a signature of the perfect, closest packing of the molecules in the crystal, while in **11a** the highly unsymmetrical, puckered molecules are mainly held together by a set of directional S...H interactions.

Electrochemical Behavior of 9 and Electrocrystallization. A cyclic voltammogram of **9** (Figure 4) exhibits two oxidation waves at $E_{\text{ox}} = 0.40$ and 0.83 V , the second one distorted by adsorption processes at the electrode, as commonly observed with such large donor molecules. It appears similar to that of a single TTF molecule substituted with three methyl and one thiobenzyl groups, which oxidizes at 0.27 and 0.81 V vs SCE.²⁹ This voltammogram points toward the simultaneous oxidation of the three TTFs to form 9^{3+} , followed by simultaneous oxidation to 9^{6+} , as also postulated for a recently described analog.⁵² However, the slight broadening of the first wave ($\Delta E = 100 \text{ mV}$) may indicate a small through-space Coulombic interaction between the three redox groups, also observed in the analogous coupled TTFs.²⁹ Such through-space interactions, if any, remain however very weak. Indeed, only the close proximity of the three redox moieties

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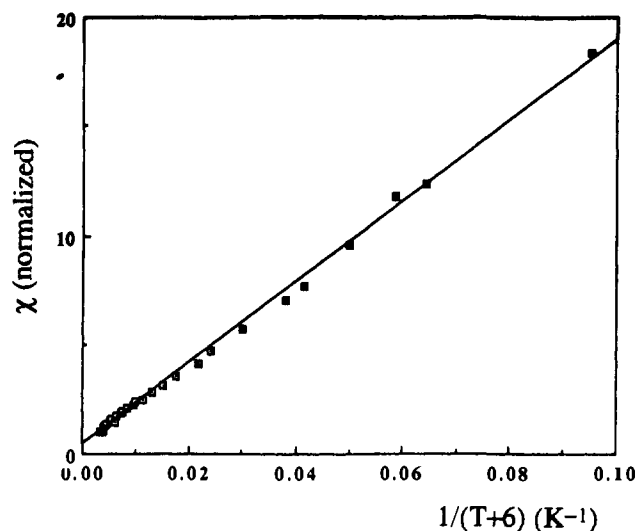


Figure 5. Temperature variation of the spin susceptibility in $(9^+)\cdot\text{Mo}_6\text{Cl}_{14}$.

in the tertiary phosphine $\text{P}(\text{TTF})_3$,⁵³ results in enough through-space interaction to make possible the observation of stepwise oxidations to the mono-, di-, and trication, $\text{P}(\text{TTF})_3^{3+}$.

In order to prepare cation-radical salts of this new donor, electrocrystallization experiments were conducted with several anions, including PF_6^- or ClO_4^- and larger molecular metal cluster anions such as $\text{Mo}_6\text{X}_{14}^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$)^{54a-c} or $\text{Re}_6\text{Q}_5\text{Cl}_9^-$ ($\text{Q} = \text{S}, \text{Se}$).^{54d-g} No precipitation occurs at the electrode with PF_6^- or ClO_4^- , indicating high diffusion of the generated cation-radical species into the solution. Small, black needlelike crystals were obtained with $(\text{Bu}_4\text{N}^+)_2/\text{Mo}_6\text{Cl}_{14}^{2-}$. The limited size of the crystals did not allow however a full X-ray structural determination. Microanalysis favors a 1:1 stoichiometry, i.e. $(9^{2+})\cdot\text{Mo}_6\text{Cl}_{14}^{2-}$. Thus, in this salt, only two of the three TTFs would be oxidized to the cation radical, affording then a mixed-valence salt.

EPR experiments were conducted on a small single crystal from 293 to 4 K. A single Lorentzian line is observed at $g = 2.0070$, a typical value for such organic radicals. Upon cooling, the line width increases slightly from 7 G up to 9 G at 100 K, where a plateau is observed down to 20 K. The complex temperature variation of the paramagnetic susceptibility (Figure 5) can be fitted satisfactorily with $\chi = \chi_0 + C/(T - \theta)$, with $\theta = -6$ K. Thus, in the low-temperature region ($T < 40$ K), the susceptibility follows a Curie-Weiss law with $\theta = -6$ K. At higher temperatures, a temperature-independent contribution χ_0 , attributable to delocalized electrons, adds to the Curie-Weiss susceptibility. A rough estimate of the proportion of spins involved in this temperature-independent magnetism can be deduced from the χ_0 value. In fact, the typical Curie susceptibility for such compounds amounts to $\approx 10^{-3}$ emu cgs/mol, while a temperature-independent susceptibility, as found in many TTF-based radical cations,⁵⁵ does not exceed $(4-5) \times 10^{-4}$ erg/mol. Thus we can estimate the proportion x of spins at 300 K involved in the Curie-Weiss susceptibility to be $2x/(1-x) = 0.6/0.4$, that is, $x = 43\%$.

Electrocrystallization experiments are being actively pursued

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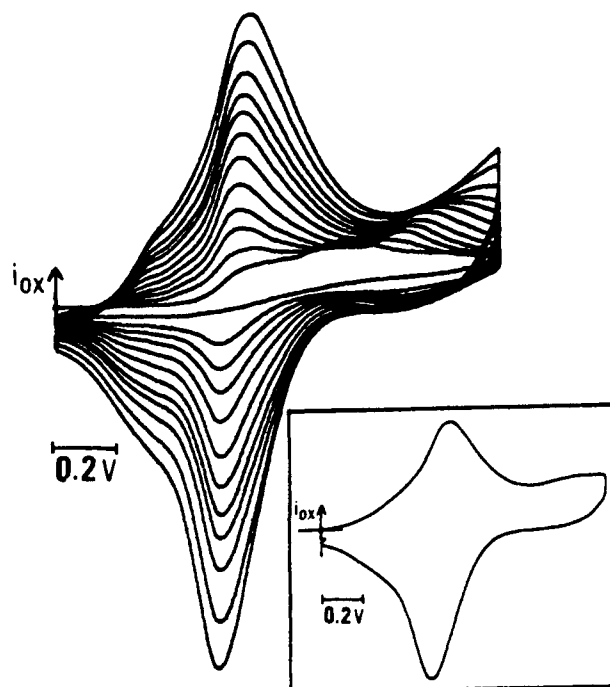
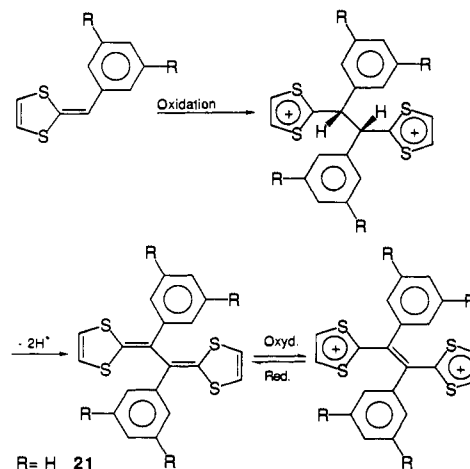


Figure 6. Successive cyclic voltammograms of **10a** in CH_3CN , at a scan speed of 100 mV/s. Every fifth cycle has been represented. In insert: cyclic voltammogram of the modified electrode after 80 cycles, in an electrolyte solution in the absence of the donor molecule **10a**.

Scheme V



in order to isolate larger crystals of $(9^{2+})\cdot\text{Mo}_6\text{Cl}_{14}^{2-}$ suitable for an X-ray structure analysis.

Electropolymerization of 10a,b. The cyclic voltammogram of **10a** is shown on Figure 6. The initial fully irreversible scan modifies upon successive scans to develop a steadily increasing reversible wave with $E_{1/2}(\mathbf{10a}) = 0.55$ V (in CH_3CN) and $E_{1/2}(\mathbf{10b}) = 0.45$ V (in CH_2Cl_2). This behavior is characteristic of the deposition at the electrode of an insoluble material with an added reversible redox functionality. We postulate that, upon oxidation, the dithiolylylene fragments of **10a,b** undergo an intermolecular dimerization (Scheme V). A similar reaction has previously been reported for "monomeric" analogs^{47a,56} (Scheme V, $\text{R} = \text{H}$), to yield the corresponding extended TTF **21**. Note that the presence of the two hydrogen atoms on the double bond is necessary to allow the elimination of two H^+ species and the subsequent formation of the extended TTF moiety. Thus, it is likely that when the trimeric dithiolylylene compounds **10a,b** are subjected to successive oxidation-reduction scans, a polymeric

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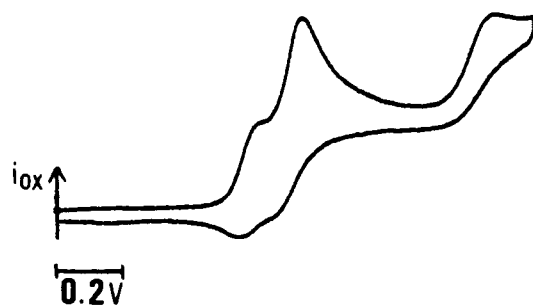


Figure 7. Cyclic voltammogram of **11b** in CH_3CN , at a scan speed of 100 mV/s.

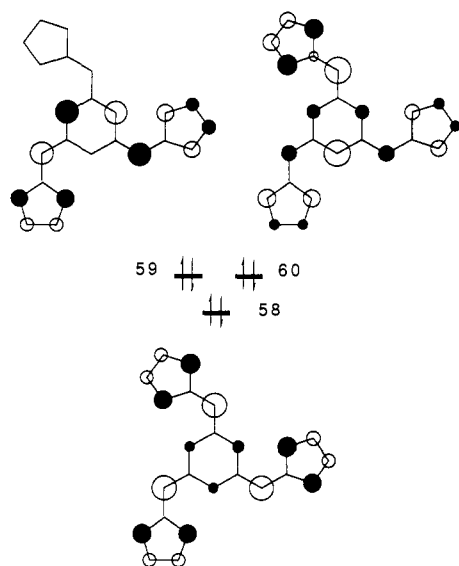
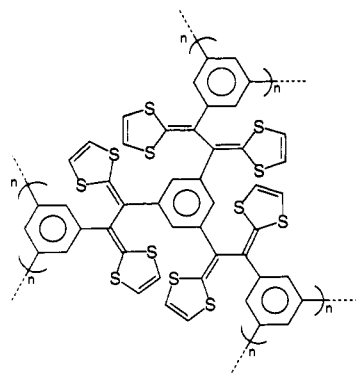


Figure 8. Atomic coefficients in the three highest occupied orbitals of **10a** (orbitals no. 58, 59, and 60). The radii of circles are approximately proportional to the coefficient of the considered molecular orbital on each atom.

Scheme VI



network, including those extended TTF electroactive fragments, develops at the electrode. This network may ideally be considered as a central benzene ring surrounded by three extended TTF functionalities in the 1, 3, and 5 positions (Scheme VI).

The material deposited at the electrode is further characterized by carrying out a cyclic voltammetry experiment with this modified

electrode immersed in an electrolyte solution without donor molecules. Note, as shown in the insert of Figure 6, that the deposited film still exhibits a reversible oxidation wave at $E_{1/2} = 0.55$ V vs SCE. The potential of this polymerization process to yield linear soluble polymers is being examined and will be reported separately.

In **11a,b**, it was expected that the methyl substituents located on the double bonds will stabilize the oxidized dithiolyldiene moieties and introduce sufficient steric effects to inhibit the polymerization process. A cyclic voltammogram of **11b** is shown in Figure 7. In CH_3CN , **11a,b** both exhibit three, nonreversible oxidation waves. This behavior is not modified upon repeated scanning, indicating the lack of polymerization. In CH_2Cl_2 , **11a** exhibits a completely different voltammogram. After an initial irreversible oxidation wave, the electrode is rapidly passivated and the current intensity drops to zero.

Extended Hückel Calculations. Extended Hückel calculations were conducted on **10a**, with an arbitrary perfect 3-fold symmetry. As expected from the symmetry of the molecule, the HOMO is degenerate (Figure 8). Also, a third orbital is located only 80 meV below the first two degenerate orbitals. Actually, one can describe this molecule as composed of three fragment orbitals located on each dithiolyldiene group. These three fragment orbitals ψ_A , ψ_B , and ψ_C interact only slightly with each other, giving rise to a bonding ($\psi_A + \psi_B + \psi_C$) and two degenerate ($\psi_A - \psi_B$ and $\psi_C - (\psi_A + \psi_B)$) orbitals. A high electronic density is observed on the C7a, C7b, and C7c positions in the three highest occupied orbitals. Thus, in the oxidized molecule, those sites are expected to be particularly reactive, as otherwise demonstrated in the course of the electrochemical studies. In order to evaluate the modifications introduced in this MO scheme by the twisting of the dithiolyldiene fragments observed in **11a**, similar calculations were conducted after rotating by 45 and 90° the three dithiolyldiene groups above the central benzene ring. The MO diagram remains essentially the same. However, because of the decreasing overlap, the three HOMOs become fully degenerate.

Conclusion

Several molecules of 3-fold symmetry have been prepared and electrochemically and crystallographically characterized. For those molecules bearing three TTF moieties, each redox unit behaves independently and cation radical salts can be grown electrochemically. The behavior of the dithiolyldiene derivatives strongly depends on the presence of a substituent on the C7 position. The lack of any substituent makes the molecules (**10a,b**) unstable toward oxidation, giving access to an unprecedented class of extraordinary electroactive polymers.

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Supplementary Material Available: Tables of crystallographic data, positional and displacement parameters, and bond distances and angles (20 pages); tables of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.