

Hetero-analogues of Hückel Degenerate Systems and Related Compounds: Preparation of Thienyl-substituted Fulvalene and Electron-donating Tetrathiafulvalene Vinyllogues and Conductive Complexes¹

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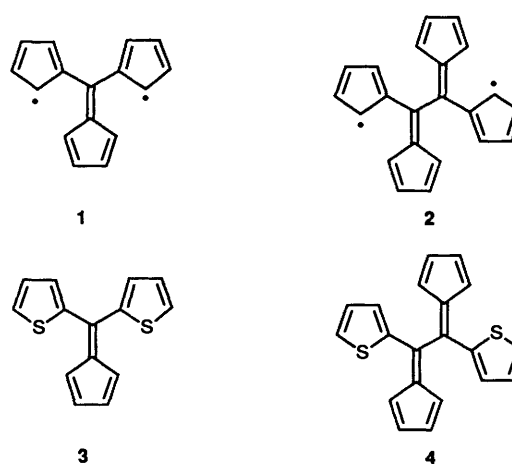
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1,4-Bis[6-(2-thienyl)fulven-6-yl]benzene **9** has been prepared as a model of the six-fold Hückel HOMO-degenerate tetracyclopentadienylideneethane biradical vinyllogue. This extended dithienylfulvalene **9** was reduced reversibly to the dianion. Attempted preparation of other dithienyl-substituted extended fulvalenes **4** and **8** are described. Attempted preparation of dithiolylidenedithienylethane **17** gave only the monocondensed products **22** and **24**. An attempted preparation of the vinylene analogue **18** from the dithienylbutenedione **12** gave, instead, the unexpected products **25**, **26** and **27**. Thus, compound **18** was prepared *via* the cyclopentadiene cycloadduct **30**. The phenylene analogue **19** was prepared from 1,4-dithenoylbenzene **15**. The extended tetrathiafulvalenes **18** and **19** were found to be good electron donors. The nonplanar vinylene-TTF **18** formed conductive CT complexes with TCNQ and iodine. The outcome of these studies are discussed.

Molecules which possess degenerate MO's are of both theoretical and practical interest.² Interesting magnetic properties would be expected for those which possess partially filled degenerate HOMO orbitals. Those with high-lying degenerate MO's would have additional properties inherent to the high-energy MO electrons. Many hydrocarbon systems with such degenerate orbitals are known, among which the trimethylenemethane³ and tetramethyleneethane⁴ biradicals have been probably most extensively investigated. However, almost all of these systems are radicals in the neutral states, and thus are expected to have only a fleeting existence. It occurred to us that it would be worthwhile to try to prepare and study the properties of a series of hetero analogues where the radical sites of degenerate hydrocarbons are replaced by hetero atoms. Such hetero analogues should be generally stable, and are, in a classical sense, isoelectronic with the closed shell (poly)anions derived from degenerate hydrocarbon radicals, although hetero atoms are generally regarded as isoelectronic with double bonds.

The replacement of carbon atoms of hydrocarbon frameworks by hetero atoms should affect the MO's of the resultant systems, and it would be too optimistic to expect that such degeneracy would be retained even in the corresponding hetero analogues. To a first approximation however, it would appear likely that some properties associated with these hydrocarbons would be reflected in the corresponding hetero analogues. For example, for hydrocarbons which have high-lying π -degenerate HOMO's, the corresponding hetero analogues would be expected to have π -electrons with high energy levels. In other words, such hetero analogues may constitute good candidates as π -electron donors.

Recently, Dowd⁵ pointed out that the hydrocarbon biradicals **1** and **2** should have five- and six-fold degenerate HOMO's respectively in the Hückel approximation. They may be viewed as derivatives of trimethylenemethane and tetramethyleneethane biradicals confined in conjugated ring systems. It was later pointed out though that AM1-CI calculations on nonplanar compounds **1** and **2** predicted them to have triplet and singlet ground state respectively.⁶ It kindled our interest in preparing and studying the properties of hetero analogues of these systems. The dithia analogue **3** of the biradical **1** was prepared recently.⁷ We therefore decided to prepare and study properties of a dithia analogue **4** of the

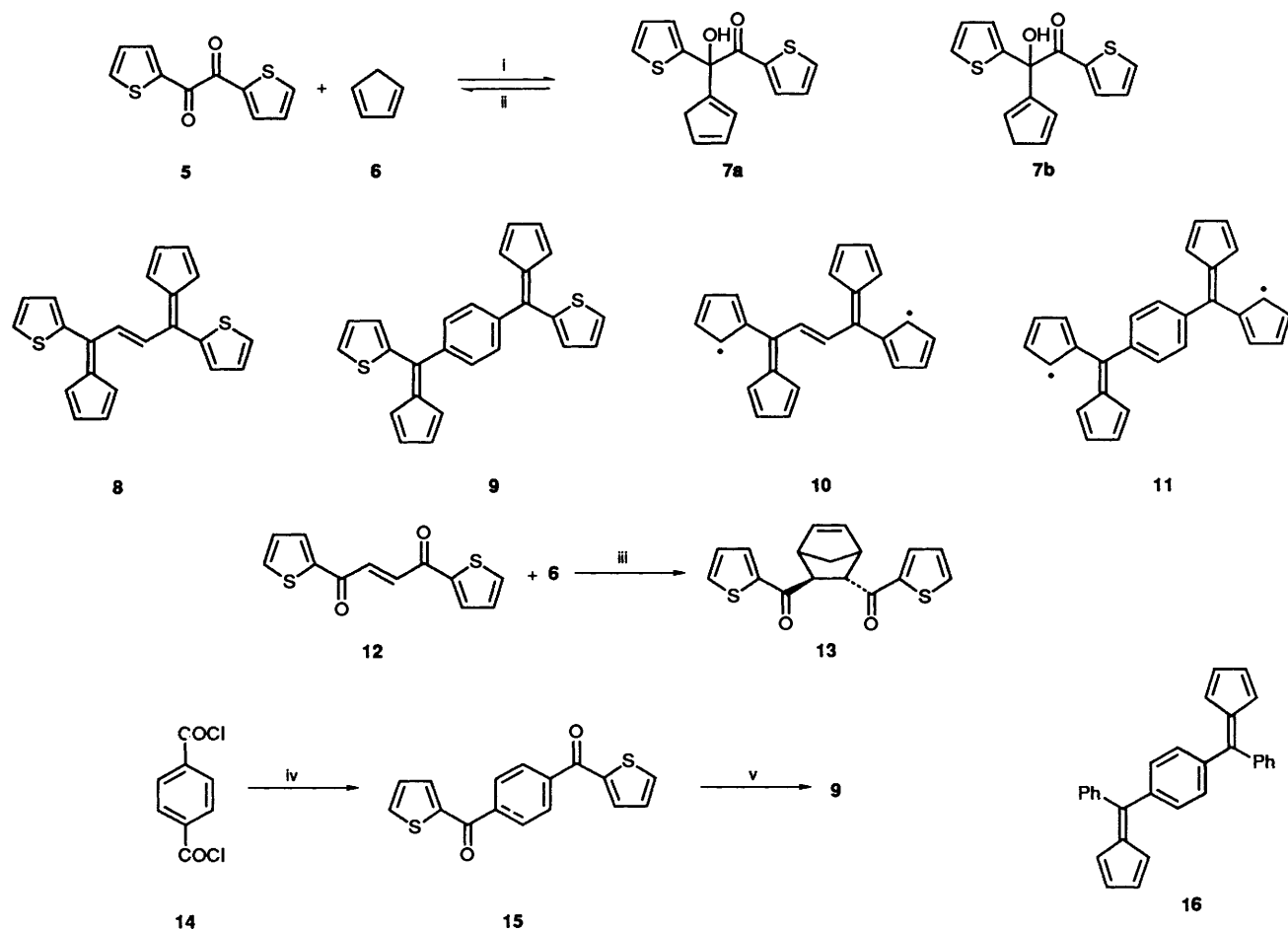


Scheme 1

Hückel six-fold degenerate biradical **2**. We report here attempts at preparation of the dithia analogue **4** and its vinyllogues, and successful preparation of the phenylene analogue **9**. Also reported here are syntheses of the closely related dithienyl-tetrathiafulvalene vinyllogues **18** and **19** together with their electron-donating properties as well as the results for electroconductive complex formation for one of them.

Results and Discussion

Synthesis.—Attempts to prepare the dithia analogue **4** by diethylamine-catalysed condensation between the diketone **5** and cyclopentadiene **6** failed, the reaction stopping at the stage of addition of one molecule of cyclopentadiene to the diketone. This product was probably a mixture of two isomers **7a** and **7b**, but it was not stable enough to obtain a pure sample for elemental analysis. The structural assignment was, therefore, based solely on the spectral properties of the compound (see Experimental section). The use of a stronger base such as sodium hydride resulted in complex products. The adduct **7** regenerated the diketone **5** on treatment with triethylamine, and complex products resulted on treatment of the adduct with toluene-*p*-sulfonic acid.

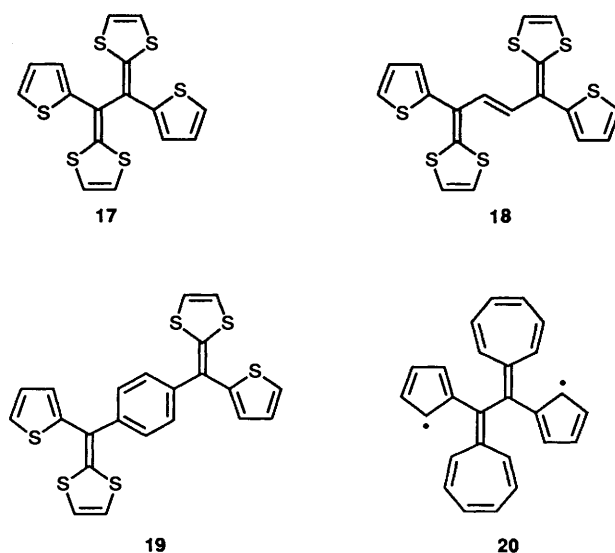


Scheme 2 Reagents and conditions: i, Et_2NH ; ii, Et_3N , iii, Et_3N or heat; iv, thiophene/ AlCl_3 ; v, 6/ KOtBu

In order to avoid the problems of steric hindrance which probably prevented the desired reaction, we turned our attention to the preparation of the vinyllogues of 4, and selected compounds 8 and 9 as our next targets. Hückel calculation showed that the corresponding hydrocarbon biradicals 10 and 11 still retain the characteristic six-fold HOMO degeneracy at the same energy level ($\alpha + 0.618\beta$). It was further found that any conjugated spacer groups could be inserted between the two dicyclopentadienylidene moieties of the biradical 2 without affecting the HOMO degeneracy. This feature was independently pointed out recently by others in more generalised ways.⁸

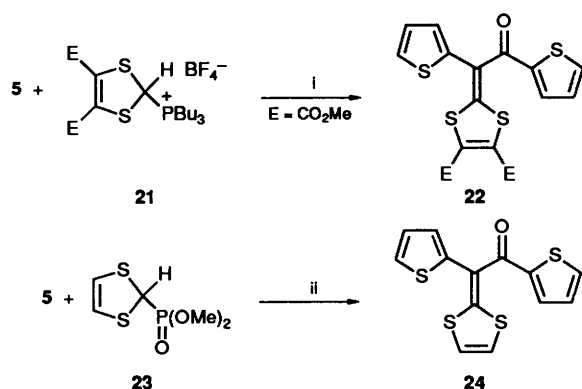
Treatment of the dithienylbutanedione 12 with cyclopentadiene 6 in the presence of triethylamine gave only the Diels-Alder cycloadduct 13, but with sodium hydride as the base, complex products resulted. No further condensation of the adduct 13 with cyclopentadiene under these conditions took place. 1,4-Dithienylbenzene 15, prepared in 65% yield by Friedel-Crafts acylation of thiophene with terephthaloyl chloride 14, was allowed to react with cyclopentadiene in the presence of potassium *tert*-butoxide to give the desired dithienylfulvalene 9 in 43% yield. A closely related diphenyl analogue 16 was prepared very recently.⁹

In connection with the work described above, we were interested in preparing and studying the properties of the corresponding dithienyl-substituted tetrathiafulvalenes (TTF) 17, 18 and 19. Replacement of the cyclopentadienylidene groups with 1,3-dithiol-2-ylidene, it was reasoned, would raise the HOMO energy levels and provide compounds useful as strong electron donors. In a classical sense, these systems may be regarded as isoelectronic with the dianions derived from



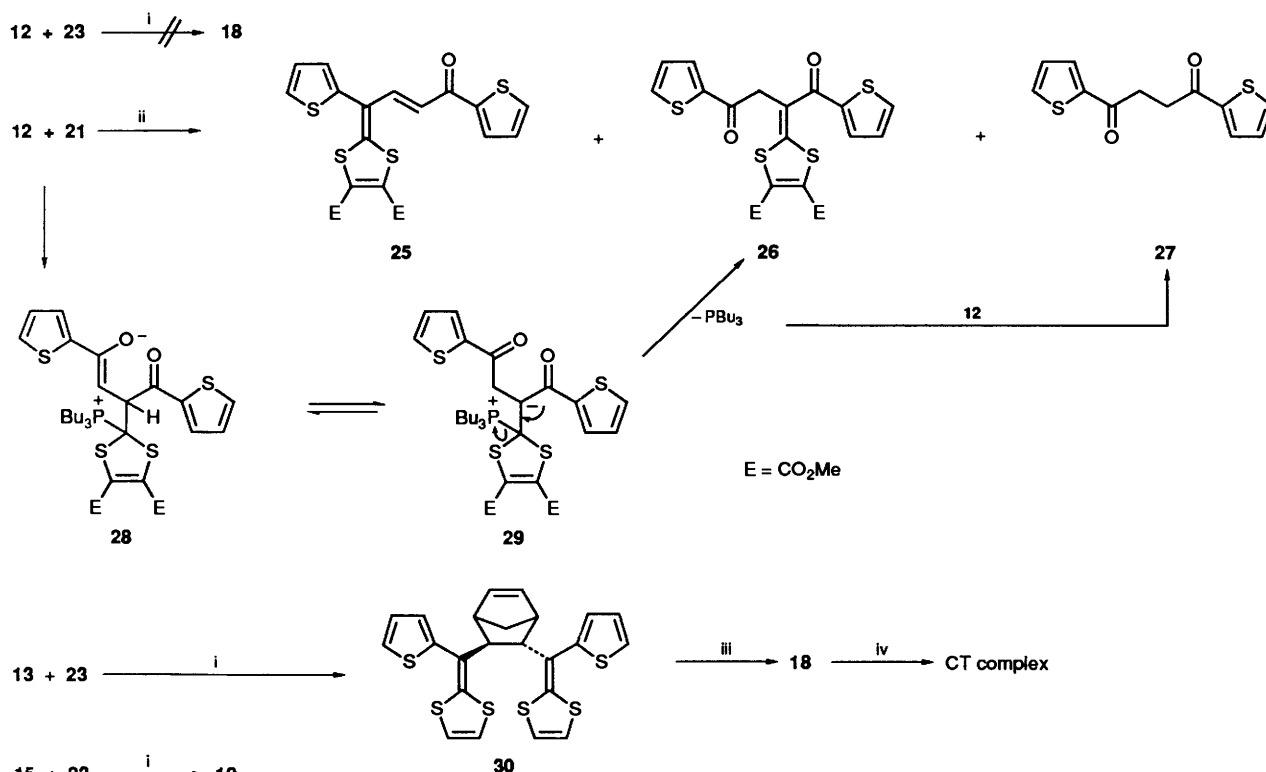
heptafulvalene biradicals, e.g. 20 although the latter is no longer HOMO degenerate even in a Hückel approximation.

When the diketone 5 was treated with the dithiolylium phosphonium salt 21 in the presence of triethylamine, the monocondensation product 22 was formed in 97% yield. Treatment of the diketone with the anion derived from the dithiolylium phosphonate 23 similarly gave the monocondensation product 24 (57%). Further treatment of the monocondensation products 22 and 24 with the ylide derived from the phosphonium salt 21 or with the anion of the phosphonate 23

Scheme 3 Reagents: i, Et_3N ; ii, BuLi

resulted in recovery of the starting materials. The failure of the preparation of the double condensation products in these reactions may be due either to steric hindrance or to inactivation of the carbonyl carbon atom by the strongly electron-donating dithiole ring. In support of the latter possibility, the IR carbonyl absorptions of the dithiolydene ketones **22** and **24** appear at 1580 and 1560 cm^{-1} , respectively, showing that the carbonyl group is strongly polarised.

On reaction, the dithienylbutenedione **12** and the anion generated from the dithiolyphosphonate **23** failed to give the desired compound **18**, instead, complex products resulted. Neither was success attendant upon an attempted double Wittig condensation of **12** and the dithiolyphosphonium salt **21** in the presence of triethylamine, only the monocondensation product **25** (6%), the Michael adduct **26** (51%), and the butenedione **27** (1%) being isolated. Assignment of structure to the Michael adduct **26** was based on its spectral properties (see Experimental section) and on the presence of two carbonyl groups and a methylene group. As suggested in Scheme 4, it is likely that the Michael product **26** was formed by a sequence consisting of ylide attack at the conjugated position β to the carbonyl group,

Scheme 4 Reagents and conditions: i, BuLi ; ii, Et_3N ; iii, heat; iv, TCNQ or I_2

prototropy of the adduct **28**, and elimination of tributylphosphine from the resulting zwitterion **29**. Tributylphosphine thus formed should react with the butenedione **12** to give the reduction product **27**. Tributylphosphine is known to reduce dibenzoyl ethylene,¹⁰ and it was confirmed that the butenedione **12** was reduced to the butenedione **27** (10%) when treated with tributylphosphine.

In order to protect the reactive double bond, the butenedione **12** was converted into the cyclopentadiene cycloadduct **13** in 90% yield, the latter then being allowed to react with the anion derived from the phosphonate **23**. This reaction gave the double condensation product **30** (67%), which, when heated neat at 180°C , underwent thermal retro-Diels-Alder fragmentation to give the desired dithienylvinylene-TTF **18** in 73% yield.

A further target compound, the phenylene-TTF **19** was readily prepared in 86% yield in a straightforward manner, by Wittig-Horner condensation of 1,4-dithienylbenzene **15** with the anion of the phosphonate **23**.

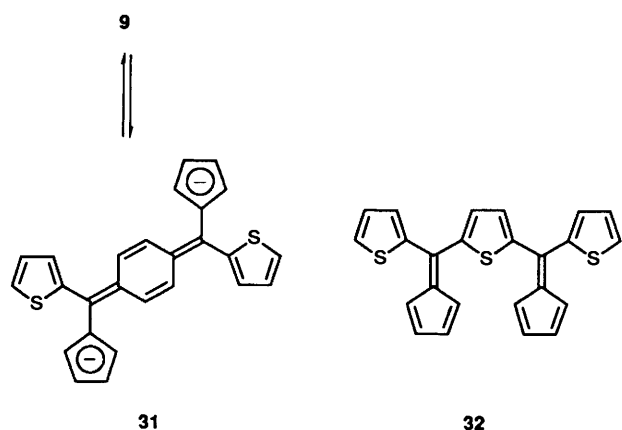
Calculation, Electrochemical and Conductive Properties, and Discussion.—Table 1 lists the HOMO and LUMO energy levels of the compounds described here as calculated by PM3-MNDO method. These calculations show that the HOMO levels of the TTF vinylogues are raised considerably in comparison with the corresponding fulvalene vinylogues. It is noteworthy that the HOMO level of the vinylene-TTF **18** almost parallels that of TTF itself. According to these calculations, the molecule of neutral **18** takes a nonplanar conformation, in which the thiophene plane is almost orthogonal (87°) to the dithiole plane, with a dihedral angle of 20° between the ethylene and the dithiole planes. In a molecule of **19**, both the thiophene and the benzene planes are almost orthogonal to the dithiole plane with dihedral angles of 87 and 78° respectively.

The electron-accepting and -donating properties of the fulvalene **9** and TTF's **18** and **19** were evaluated by cyclic voltammetry (CV). The fulvalene **9** is reduced reversibly by a two-electron process to the dianion probably corresponding to

Table 1 HOMO and LUMO energies (eV) of extended fulvalenes and TTF's (PM3-MNDO)^a

Compound	HOMO	LUMO
4	-9.19	-1.24
8	-8.72	-1.64
9	-9.15	-1.22
17	-8.13	-0.81
18	-7.95	-1.06
19	-8.32	-0.54
TTF	-7.99	-0.62

^a MOPAC Ver. 5.00 (QCPE No. 445), J. J. P. Stewart, *QCPE Bull.*, 1989, 9, 10; T. Hirano, *JCPE Newsletter*, 1989, 1, 36; Revised as Ver. 5.01 by J. Toyoda for OS/2 Personal Computers (NEC PC-9801), *JCPE Newsletter*, 1990, 2, 34.



Scheme 5

31 with a half-wave potential of -1.63 V (*vs.* Ag/Ag⁺; DMF). This interpretation was supported by the charge distribution as calculated by PM3 on the dianion of **9**. In the neutral molecule of **9**, the dihedral angles of the thiophene and the benzene planes against the cyclopentadienylidene plane are 84 and 59° respectively. This molecule flattens somewhat on going to the dianion (85 and 8°), and the charge density on one cyclopentadiene unit amounts to -1.10 while the corresponding value for neutral **9** is -0.06 . No oxidation peak for **9** was observed by CV. Kawase *et al.*¹¹ recently reported the preparation of a related thienyl-substituted fulvalene **32**, which also is reversibly reduced to the dianion.

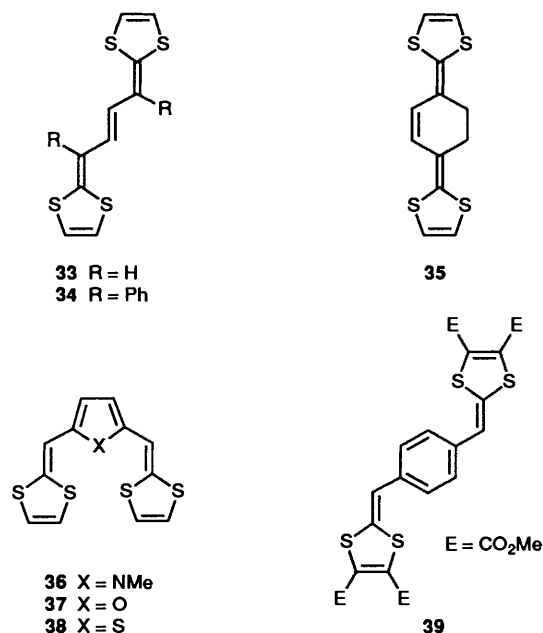
The extended TTF's described here were found to be good electron donors. The vinylene-TTF **18** is oxidised reversibly by a two-electron process to the dication at a half-wave potential of 0.02 V (*vs.* Ag/Ag⁺; MeCN), while the phenylene-TTF **19** undergoes a reversible and an irreversible single-electron oxidation with a half-wave potential of 0.04 and a peak potential of 0.23 V respectively (*vs.* Ag/Ag⁺; DMF). The first half-wave potentials of the two-stage redox process of TTF under identical conditions are 0.02 (in MeCN) and -0.08 V (in DMF). Therefore, these dithienyl-TTF vinyllogues are good electron donors. Moreover, these results also show that PM3 calculations correctly predicted the order of the oxidation potentials of these compounds.

The vinylene-TTF **18** formed charge-transfer complexes with tetracyanoquinodimethane (TCNQ) and iodine. The component ratio were 1:1.8–1.9 for TCNQ and 1:1.2 for iodine based on elemental analyses if allowance is made for $\pm 0.5\%$. Two-probe conductivity measurements on compressed powder pellets showed conductivities of 1.6×10^{-2} (TCNQ complex) and 3.1×10^{-2} (I₂ complex) S cm⁻¹ respectively. The IR absorption of the nitrile group of the TCNQ complex appears at 2205 cm⁻¹, which indicates that charge transfer is 50%

Table 2 Oxidation potentials^a and conductive properties of extended TTF's

Compound No.	$E_1^{1/2}/V$	$E_2^{1/2}/V$	Reference electrode	Complex ^b (TCNQ)
18	0.02	0.02	Ag/Ag ⁺	10 ^{-2c}
19	0.04	0.23 ^d	Ag/Ag ⁺	no
33 ^{14a}	0.22	0.22	Ag/AgCl	no
34 ^{14a}	0.28	0.28	Ag/AgCl	?
35 ^{14a}	0.23	0.23	Ag/AgCl	10 ^{-1e}
36 ^{14b,c}	0.20 ^{14b}	0.38	SCE	no
37 ^{14b,c}	0.32 ^{14b}	—	SCE	10 ^{-5c}
38 ^{14b,c}	0.39 ^{14b}	0.49	SCE	no
39 ^{14d}	0.88 ^d	1.08 ^d	SCE	?
TTF ^{14a}	0.34	0.71	Ag/AgCl	2.5 ^e

^a Measured in acetonitrile with the exception of **19** and **39** which were measured in DMF. ^b Numerals show conductivity in unit of S cm⁻¹, no indicates no complex formation, ? means no statement given concerning complex formation. ^c Two-probe compressed powder. ^d Irreversible oxidation. ^e Four-probe compressed powder.



complete.¹² The TCNQ complex is moderately soluble in common organic solvents such as dichloromethane and acetonitrile. When acetonitrile solutions of the phenylene-TTF **19** and TCNQ were mixed, electronic absorption spectrum of the resultant solution showed a weak CT band in the 600–900 nm region which, on magnification, was almost superimposable with that of the **18**-TCNQ complex. However, it appeared that the equilibrium is shifted far to the dissociated state, and it was not possible to isolate the complex.

Until recently, it was generally considered that only planar donor-acceptor pairs are expected to show good electric conductivity.¹³ Several planar extended TTF analogues, devoid of substituent(s) α to the dithiole rings, with a variety of spacer groups have been prepared.^{13a,14} Structures and pertinent electrochemical properties of such planar TTF vinyllogues and one nonplanar compound closely related to our vinylene-TTF **18** are shown in Table 2. Among the compounds listed, the α,α' -unsubstituted compound **33** showed only a transient colour change when mixed with TCNQ.^{14a} It appears that the α,α' -diphenyl analogue **34** did not form a CT complex with TCNQ.^{14a} Comparison with these data suggests that the sulfur atoms in the almost orthogonally placed thienyl groups of **18** play an important role in the complex formation and probably in conductivity. Unfortunately, no X-ray crystallographic data are available at present to evaluate the role of the sulfur atoms.

Although direct comparison of these values is inappropriate due to the variation in conditions of measurements, it is worthy to note that nonplanar molecules such as **18** can form complexes with considerable conductivities. Formation of conductive CT complexes from nonplanar donors were reported recently.^{15,16} These reports as well as the findings described above would suggest that planarity may not be taken as an important factor in designing components for conductive complexes. Lastly, we would like to suggest that it would be worthwhile to try to analyse the spin properties of the dianion and the dications described above.

Experimental

M.p.s (uncorrected) were determined on a Yanagimoto hot-stage apparatus. UV and IR (KBr) spectra were recorded with a Shimadzu UV-260 and a Hitachi 345 spectrophotometer respectively. Only pertinent IR peaks are given. Unless otherwise stated, ¹H (90 MHz) and ¹³C (22.5 MHz) NMR spectra were recorded with a JEOL JNM-FX-90Q spectrometer on solutions in deuteriochloroform (tetramethylsilane internal standard). *J* Values are given in Hz. Mass spectra (electron impact; 70 eV) were measured with a Shimadzu GCMS-QP1000EX spectrometer. Cyclic voltammograms were recorded with a BAS 100 electrochemical analyser with glassy carbon working electrode, Pt-wire counter electrode, Ag/Ag⁺ (0.01 mol dm⁻³ AgClO₄) reference electrode, and Et₄NClO₄ (0.1 mol dm⁻³) as supporting electrolyte in dry solvents at room temperature, with a scan rate of 100 mV s⁻¹; the system was deoxygenated in measurements of reduction potential; under these conditions, the half-wave potentials of ferrocene (Fc⁰/Fc⁺ couple) were 0.08 (MeCN) and 0.00 V (DMF). Chromatographic separations were performed with Nakarai silica gel 60 or Merck Kieselgel 60 PF₂₅₄. Yields are based on isolated products with sufficient purity. In spectrum assignments, the symbols Th and Cp represent thienyl and cyclopentadienyldiene respectively.

Reaction of Di-2-thienyl Diketone with Cyclopentadiene.—A solution of di-2-thienyl diketone¹⁷ **5** (2.0 g, 9 mmol), cyclopentadiene **6** (2.97 g, 45 mmol) and diethylamine (94 mm³, 0.9 mmol) in methanol (25 cm³) was stirred at room temperature for 3.5 h under nitrogen. The solvent was removed under reduced pressure, and the residue was dissolved in dichloromethane. The solution was washed successively with dilute hydrochloric acid, aq. sodium hydrogen carbonate, and water, dried (Na₂SO₄), and concentrated. The residue was chromatographed (silica/CH₂Cl₂) to give a mixture of 2-(cyclopenta-1,3-dienyl)- and 2-(cyclopenta-1,4-dienyl)-2-hydroxy-1,2-di(2-thienyl)ethan-1-one **7** (1.72 g, 66%) as pale yellow solid, m.p. 59–64 °C. This unstable product could not be purified further; $\nu_{\max}/\text{cm}^{-1}$ 3460 (OH) and 1635 (C=O); δ_{H} 2.78–3.43 (2 H, m, CH₂), 5.14 and 5.20 (total 1 H, s, OH), 6.36–6.63 (3 H, m, CpH-H), 6.88–7.08 (3 H, m, Th-3,4-H and CO-Th-4-H), 7.23–7.32 (1 H, dd + dd, Th-5-H) and 7.59–7.70 (2 H, m, CO-Th-3,5-H); δ_{C} 41.3 and 41.5 (each t, CH₂), 79.3 and 79.7 (each q, C-2) and 190.6 (C=O); *m/z* 288 (M⁺, 1%), 270 (M – H₂O, 11), 242 (13), 177 (M – ThCO, 18) and 111 (ThCO⁺, 100).

trans-5,6-Di(2-thienyl)bicyclo[2.2.1]hept-2-ene 13.—(a) A solution of dithienylbutenedione **12** (m.p. 196–197 °C, lit.,¹⁸ 188–189 °C; 500 mg, 2.0 mmol) and cyclopentadiene **6** (0.7 cm³, 8.4 mmol) in benzene (10 cm³) was heated under reflux for 1.5 h. The solvent was removed under reduced pressure and the resulting solid was recrystallised from ethanol to give the adduct **13** (567 mg, 90%) as colourless needles, m.p. 156 °C (Found: C, 65.2; H, 4.6. C₁₇H₁₄O₂S₂ requires C, 64.9; H, 4.5%; $\nu_{\max}/\text{cm}^{-1}$

1640 (C=O); δ_{H} 1.52 (1 H, dd, *J* 8.7 and 1.5, 7-H), 1.96 (1 H, br d, *J* 8.7, 7-H), 3.19 (1 H, br s, 1-H), 3.42 (1 H, br s, 4-H), 3.78 (1 H, dd, *J* 4.6 and 1.5, 6-H), 4.28 (1 H, dd, *J* 4.6 and 3.6, 5-H), 6.02 (1 H, dd, *J* 5.5 and 3.0, 3-H), 6.41 (1 H, dd, *J* 5.5 and 3.0, 2-H), 7.04–7.16 (2 H, m, Th-4-H), 7.52–7.65 (2 H, m, Th-5-H) and 7.75–7.84 (2 H, m, Th-3-H); δ_{C} 47.7 (t), 48.7 (d), 49.2 (d), 50.0 (d), 52.0 (d), 128.1 and 128.3 (Th-4,4'), 132.1 and 132.5 (Th-5,5'), 133.4 and 133.8 (Th-3,3'), 134.8 (C-2 or 3), 137.2 (C-3 or 2), 144.2 and 144.4 (Th-2,2'), 192.0 (C=O) and 193.7 (C=O); *m/z* 314 (M⁺, 21%), 203 (M – ThCO, 27), 111 (ThCO⁺, 100), 83 (Th⁺, 13) and 66 (CpH₂⁺, 34). (b) When a solution of **12** (150 mg, 0.6 mmol), **6** (0.25 cm³, 3.0 mmol), and triethylamine (9 mm³, 0.06 mmol) in methanol was stirred at room temperature for 2 days under nitrogen, compound **13** (18%) was again isolated.

1,4-Di(2-thienyl)benzene 15.—A solution of terephthaloyl chloride **14** (10 g, 49.2 mmol) in dichloromethane (20 cm³) and then thiophene (12 cm³, 148 mmol) were added successively to a stirred and cooled suspension of aluminium chloride (16.4 g, 123 mmol) in dichloromethane (70 cm³). The mixture was vigorously stirred at room temperature for 4 h and then poured into ice-water. The solid was collected and recrystallised from xylene to give pale yellow needles of the title compound **15** (9.6 g, 65%), m.p. 227 °C (Found: C, 64.75; H, 3.65. C₁₆H₁₀O₂S₂ requires C, 64.4; H, 3.4%; $\nu_{\max}/\text{cm}^{-1}$ 1620 (C=O); δ_{H} 7.20 (2 H, dd, *J* 4.9 and 3.8, Th-4-H), 7.68 (2 H, dd, *J* 3.8 and 1.2, Th-3-H), 7.78 (2 H, dd, *J* 4.9 and 1.2, Th-5-H) and 7.97 (4 H, s, Ar-H); *m/z* 298 (M⁺, 18%), 215 (M – Th, 9), 187 (M – ThCO, 12), 111 (ThCO⁺, 100) and 83 (Th⁺, 8).

1,4-Bis[6-(2-thienyl)fulven-6-yl]benzene 9.—Cyclopentadiene **6** (0.3 cm³, 3.6 mmol) and potassium *tert*-butoxide (75 mg, 0.67 mmol) were added to a suspension of 1,4-di(2-thienyl)benzene **15** (100 mg, 0.34 mmol) in THF (10 cm³). The mixture was stirred at room temperature for 23 h under nitrogen, poured into water, and extracted with dichloromethane. The extract was washed with water, dried (Na₂SO₄), and concentrated. Recrystallisation from dichloromethane gave the title compound **9** (57 mg, 43%) as reddish orange needles, m.p. 193–195 °C (decomp.) (Found: C, 79.1; H, 4.4. C₂₆H₁₈S₂ requires C, 79.1; H, 4.6%; $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 228 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 18 900), 266 (14 600) and 361 (38 400); $\nu_{\max}/\text{cm}^{-1}$ 1565, 1410, 1360, 770 and 700; δ_{H} 6.08–6.18 (2 H, m, Cp-H), 6.50–6.69 (4 H, m, Cp-H), 6.75–6.85 (2 H, m, Cp-H), 7.06–7.18 (4 H, m, Th-3,5-H), 7.42 (4 H, s, Ar-H) and 7.55 (2 H, dd, *J* 4.5 and 1.9, Th-5-H); δ_{C} 123.3, 125.0, 127.5, 130.5 (Cp–C's), 130.9 (Ar), 132.1, 132.9, 133.4 (Th–C's), 141.7 (s), 143.0 (s) and 143.7 (s); *m/z* 394 (M⁺, 100%) and 235 (M – Th – C₆H₄, 22).

2-(4,5-Dimethoxycarbonyl-1,3-dithiol-2-ylidene)-1,2-di(2-thienyl)ethan-1-one 22.—A mixture of di-2-thienyl diketone **5** (200 mg, 0.9 mmol), the phosphonium salt¹⁹ **21** (1.1 g, 2.2 mmol), and triethylamine (1.0 cm³) in THF (10 cm³) was stirred at room temperature under nitrogen. After 3.5 h, the mixture was concentrated under reduced pressure and the residue was recrystallised from acetonitrile to give the title compound **22** (371 mg, 97%) as yellow needles, m.p. 209–210 °C (Found: C, 48.25; H, 2.8. C₁₇H₁₂O₅S₄ requires C, 48.1; H, 2.85%; $\lambda_{\max}(\text{EtOH})/\text{nm}$ 203 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 18 400), 225 (16 500), 302 (5870) and 406 (25 400); $\nu_{\max}/\text{cm}^{-1}$ 1740 (CO₂Me), 1710 (CO₂Me) and 1580 (C=O); δ_{H} 3.84 (3 H, s, Me), 3.92 (3 H, s, Me), 6.88–6.92 (2 H, m, Th-3,5-H), 7.10 (1 H, dd, *J* 3.6 and 1.3, CO-Th-3-H), 7.22 (1 H, dd, *J* 5.1 and 3.6, CO-Th-4-H), 7.47 (1 H, dd, *J* 3.6 and 2.5, Th-4-H) and 7.61 (1 H, dd, *J* 5.1 and 1.3, CO-Th-5-H); δ_{C} 53.4 (Me), 113.3 (C-2), 127.6, 128.5, 129.4, 130.1 (Th–C's and CO-Th–C's), 130.7 (SC=CS), 133.0, 133.4, 137.5, 142.5 (Th–C's), 159.8 (CO₂Me), 160.3 (CO₂Me), 165.2 (S–C–S) and 177.5 (C=O); *m/z* 424 (M⁺, 91%) and 111 (ThCO⁺, 100).

2-(1,3-Dithiol-2-ylidene)-1,2-di(2-thienyl)ethan-1-one **24**.—A hexane solution of butyllithium (1.59 mol dm⁻³; 1.2 cm³, 1.91 mmol) was added into a stirred solution of the dithiolyphosphonate²⁰ **23** (370 mg, 1.74 mmol) in THF (20 cm³) at -78 °C under nitrogen. After 30 min di-2-thienyl diketone **5** (190 mg, 0.85 mmol) in THF (2 cm³) was added to the solution, and the mixture was stirred for a further 1 h at this temperature. The mixture was then allowed to warm gradually to room temperature and stirred further for 5 h. The solution was concentrated under reduced pressure and diluted with water. The product was extracted with dichloromethane, and the extract washed with water, dried (Na₂SO₄), and concentrated. The residue was solidified by addition of acetonitrile and recrystallised from acetonitrile to give the title compound **24** (150 mg, 57%) as yellow plates, m.p. 155 °C (Found: C, 50.9; H, 2.4. C₁₃H₈OS₄ requires C, 50.6; H, 2.6%); $\nu_{\max}/\text{cm}^{-1}$ 1560 (C=O); δ_{H} 6.83–6.99 (4 H, m, Th-3,5-H and dithiole-H), 7.08 (1 H, dd, *J* 3.5 and 1.3, CO-Th-3-H), 7.21 (1 H, dd, *J* 5.3 and 3.5, CO-Th-4-H), 7.42 (1 H, dd, *J* 3.6 and 2.5, Th-4-H) and 7.58 (1 H, dd, *J* 5.3 and 1.3, CO-Th-5-H); δ_{C} 111.7 (C-2), 120.1 (SC=CS), 125.9 (SC=CS), 127.4, 128.2, 128.7, 129.8, 131.9, 132.2, 139.8, 143.7 (Th-C's and CO-Th-C's), 171.9 (S-C-S) and 176.1 (C=O); *m/z* 308 (M⁺, 92%), 280 (21), 197 (M - ThCO, 17), 153 (18), 111 (ThCO⁺, 100) and 83 (Th⁺, 15).

Reaction of Dithienylbutenedione 12 with the Phosphonium Salt 21.—A solution of dithienylbutenedione **12** (1.0 g, 4.0 mmol), the phosphonium salt **21** (5.1 g, 10.0 mmol) and triethylamine (4.0 cm³, 28.7 mmol) in THF (50 cm³) was stirred at room temperature for 8 h under nitrogen. The solvent was removed under reduced pressure and the residue was separated by chromatography (silica/CH₂Cl₂) to give the compounds shown below: 4-(4,5-dimethoxycarbonyl-1,3-dithiol-2-ylidene)-1,4-di(2-thienyl)but-2-en-1-one **25** (97 mg, 6%), orange needles, m.p. 166 °C (from MeCN) (Found: C, 50.6; H, 3.0. C₁₉H₁₄O₅S₄ requires C, 50.6; H, 3.1%); $\lambda_{\max}(\text{EtOH})/\text{nm}$ 203 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 19 000), 232 (22 800), 282 (11 000), 305 (10 900) and 430 (27 100); $\nu_{\max}/\text{cm}^{-1}$ 1725 (CO₂Me), 1710 (CO₂Me), 1620 (C=C) and 1560 (C=O); δ_{H} 3.81 (3 H, s, Me), 3.88 (3 H, s, Me), 6.52 (1 H, d, *J* 14.4, 3-H), 7.02–7.27 (3 H, m, Th-3,5-H and CO-Th-3-H), 7.59–7.45 (3 H, m, Th-4-H and CO-Th-4,5-H) and 7.68 (1 H, d, *J* 14.4, 2-H); δ_{C} 53.3 (Me), 117.5 (C-4), 121.0 (C-2), 127.5 (Th-5), 127.7 (Th-3), 128.0 (Th-4), 128.5 (CO-Th-4), 131.3 (CO-Th-5), 131.5 (SC=CS), 132.4 (SC=CS), 133.3 (CO-Th-3), 137.6 (Th-2), 138.9 (C-3), 145.8 (CO-Th-2), 147.8 (S-C-S), 159.2 (CO₂Me), 159.4 (CO₂Me) and 181.5 (C=O); *m/z* 450 (M⁺, 12%), 232 [M - C₃S₂(CO₂Me)₂, 100] and 111 (ThCO⁺, 26); 2-(4,5-dimethoxycarbonyl-1,3-dithiol-2-ylidene)-1,4-di(2-thienyl)butane-1,4-dione **26** (952 mg, 51%), yellow needles, m.p. 159 °C (from MeCN) (Found: C, 48.8; H, 2.75. C₁₉H₁₄O₆S₄ requires C, 48.9; H, 3.0%); $\lambda_{\max}(\text{EtOH})/\text{nm}$ 204 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 18 900), 264 (15 300), 288 (14 800) and 400 (24 800); $\nu_{\max}/\text{cm}^{-1}$ 1720 (CO₂Me), 1705 (CO₂Me), 1670 (C=O) and 1575 (C=O); δ_{H} 3.85 (3 H, s, Me), 3.91 (3 H, s, Me), 4.52 (2 H, s, CH₂), 7.00 (1 H, dd, *J* 5.0 and 3.9, Th-4-H), 7.20 (1 H, dd, *J* 5.0 and 3.8, Th-4'-H), 7.39 (1 H, dd, *J* 3.9 and 1.1, Th-3-H), 7.52 (1 H, dd, *J* 5.0 and 1.1, Th-5-H), 7.74 (1 H, dd, *J* 5.0 and 1.2, Th-5'-H) and 7.88 (1 H, dd, *J* 3.8 and 1.2, Th-3'-H); δ_{C} 43.0 (C-3), 53.4 (Me), 112.7 (C-2), 127.7, 128.5 (Th-4,4'), 131.8, 132.6, 134.5 (Th-3,3',5,5'), 139.1 (SC=CS), 141.9, 142.7 (Th-2,2'), 159.2 (CO₂Me), 160.4 (S-C-S), 160.8 (CO₂Me), 179.9 (C-1) and 187.2 (C-4); *m/z* 466 (M⁺, 100%), 355 (M - ThCO, 100) and 111 (ThCO⁺, 95); 1,4-di(2-thienyl)butane-1,4-dione **27** (9 mg, 1%), m.p. and mixed m.p. 136–137 °C, lit.¹⁸ 130–131 °C; $\nu_{\max}/\text{cm}^{-1}$ 1650 (C=O); δ_{H} 3.38 (4 H, s, CH₂), 7.13 (2 H, dd, *J* 5.0 and 3.8, Th-4-H), 7.63 (2 H, dd, *J* 5.0 and 1.2, Th-5-H) and 7.81 (2 H, dd, *J* 3.8 and 1.2, Th-3-H); *m/z* 250 (M⁺, 14%), 139 (M - ThCO, 17) and 111

(ThCO⁺, 100); and the phosphonium salt **21** (2.24 g, 44% recovery).

1,4-Di(2-thienyl)butane-1,4-dione **27** from the Butenedione **12**.—A solution of the dithienylbutenedione **12** (100 mg, 0.4 mmol) and tributylphosphine (0.13 cm³, 0.48 mmol) in THF (10 cm³) was stirred at room temperature for 10 h under nitrogen. Hydrochloric acid (10%; 1 cm³) was added and after 5 min, the solvent was removed under reduced pressure. Ethanol was added to the residue and the resultant solid was collected to give the dithienylbutanedione **27** (10 mg, 10%), identical with an authentic sample.¹⁸

trans-5,6-Bis[1-(1,3-dithiol-2-ylidene)-2-thienylmethyl]bicyclo[2.2.1]hept-2-ene 30.—A hexane solution of butyllithium (1.6 mol dm⁻³; 14 cm³, 22.4 mmol) was added to a stirred solution of the dithiolyphosphonate **23** (4.3 g, 20 mmol) in THF (50 cm³) at -78 °C under nitrogen. After 30 min, a solution of dithienylbornene **13** (1.6 g, 5.1 mmol) in THF (10 cm³) was added to the mixture. The mixture was stirred at -78 °C for 1.5 h, allowed to warm gradually to room temperature, and then stirred further for 13 h. The solvent was removed under reduced pressure, water was added to the residue, and the product was extracted with dichloromethane. The extract was washed with water, dried (Na₂SO₄), and concentrated, and acetonitrile was added to the residue. The resulting solid was recrystallised from acetonitrile to give the title compound **30** (1.65 g, 67%) as pale yellow needles, m.p. 164–165 °C (decomp.) (Found: C, 56.5; H, 3.9. C₂₃H₁₈S₆ requires C, 56.7; H, 3.7%); $\nu_{\max}/\text{cm}^{-1}$ 1560, 720 and 645; δ_{H} 1.05–1.26 (2 H, m, 7-H), 2.47 (1 H, dd, *J* 5.9 and 1.3, 6-H), 2.73 (1 H, br s, 1-H), 2.95 (1 H, br s, 4-H), 3.06 (1 H, dd, *J* 5.9 and 3.0, 5-H), 5.50 (1 H, dd, *J* 5.7 and 2.6, 3-H), 5.96–6.28 (5 H, m, 2-H and dithiole-H), 6.80 (1 H, dd, *J* 3.5 and 1.1, Th-3-H), 6.96–7.14 (3 H, m, Th-4,3',4'-H) and 7.25–7.42 (2 H, m, Th-5,5'-H); δ_{C} 46.1 (C-7), 47.8, 48.8 (C-5,6), 51.4, 51.9 (C-1,4), 117.4 (Th-C=), 118.2 (SC=CS), 118.3 (SC=CS), 119.0 (SC=CS), 119.1 (SC=CS), 126.3, 126.7, 127.2, 127.5, 127.6 (Th-3,3',4,4',5,5'), 134.7, 137.4 (C-2,3), 140.3, 140.4 (Th-2,2'), 142.1 and 142.5 (S-C-S); *m/z* 486 (M⁺, 1%) and 420 (M - CpH₂, 100).

1,4-Di(1,3-dithiol-2-ylidene)-1,4-di(2-thienyl)but-2-ene **18**.—The norbornene derivative **30** (300 mg, 0.62 mmol) was heated neat at 180 °C for 30 min. Recrystallisation from toluene gave the vinylene-TTF **18** (190 mg, 73%) as orange needles, m.p. 179–180 °C (Found: C, 51.6; H, 2.9. C₁₈H₁₂S₆ requires C, 51.4; H, 2.9%); $\lambda_{\max}(\text{MeCN})/\text{nm}$ 228 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 23 930), 420 (40 490) and 442 (46 670); $\nu_{\max}/\text{cm}^{-1}$ 1535, 1490 and 700; $\delta_{\text{H}}([\text{C}_6\text{H}_6]\text{-DMSO})$ 6.03 (2 H, s, 2- and 3-H), 6.66 (2 H, d, *J* 6.6, dithiole-H), 6.68 (2 H, d, *J* 6.6, dithiole-H), 7.05 (2 H, dd, *J* 3.5 and 1.3, Th-3-H), 7.16 (2 H, dd, *J* 5.0 and 3.5, Th-4-H) and 7.65 (2 H, dd, *J* 5.0 and 1.3, Th-5-H); δ_{C} 117.4 (C-1,4), 118.3 (SC=CS), 119.0 (C-2,3), 126.0, 127.2, 127.6 (Th-3,4,5), 140.2 (S-C-S) and 140.9 (Th-2); *m/z* 420 (M⁺, 100%), 317 (M - C₃H₂S₂ - H, 25) and 285 (M - C₃H₂S₂ - S - H, 17).

1,4-Bis[1-(1,3-dithiol-2-ylidene)-2-thienylmethyl]benzene **19**.—The phosphonate anion was generated as described above from the phosphonate **23** (1.78 g, 8.38 mmol) and a hexane solution of butyllithium (1.55 mol dm⁻³; 5.9 cm³, 9.22 mmol) in THF (20 cm³). A suspension of 1,4-di(2-thienyl)benzene **15** (1.0 g, 3.35 mmol) in THF (10 cm³) was then added to the solution. After 1 h at -78 °C, the mixture was stirred at room temperature for 6.5 h. The mixture was concentrated under reduced pressure, water was added to the residue, and the solid which separated out was recrystallised from DMF to give the title compound **19** (1.35 g, 86%) as pale yellow needles, m.p. 173–174 °C (Found: C, 56.05; H, 3.15. C₂₂H₁₄S₆ requires C, 56.1; H, 3.0%); $\lambda_{\max}(\text{MeCN})/\text{nm}$ 240 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 14 740)

and 351 (21 250); $\nu_{\max}/\text{cm}^{-1}$ 1540, 1495, 800, 680 and 645; δ_{H} 6.30 (2 H, d, J 6.7, dithiole-H), 6.41 (2 H, d, J 6.7, dithiole-H), 6.83 (2 H, dd, J 3.7 and 1.3, Th-3-H), 7.02 (2 H, dd, J 5.0 and 3.7, Th-4-H), 7.25 (2 H, dd, J 5.0 and 1.3, Th-5-H) and 7.40 (4 H, s, Ar-H); δ_{C} 118.3 (SC=CS), 118.4 (SC=CS), 118.9 (Ar-C=), 124.0 (Th-3), 124.9 (Th-4), 127.2 (Th-5), 130.2 (Ar), 142.2 (Th-2) and 144.7 (Ar-1,4); m/z 470 (M^+ , 100%) and 235 (M^{2+} , 12).

TCNQ Complex of 18.—The vinylene-TTF **18** (50 mg, 0.12 mmol) was added to a solution of TCNQ (50 mg, 0.24 mmol) in dichloromethane (15 cm^3). The solution was stirred for 5 min at room temperature, concentrated to ca. 5 cm^3 , and the precipitate which separated out was collected, and washed with cold dichloromethane to give the TCNQ complex (51 mg) as black powder, m.p. 156–160 °C (decomp.) (Found: C, 60.0; H, 2.4; N, 13.2%); these values correspond to composition of 1:1.8–1.9 for **8**: (TCNQ); $\lambda_{\max}(\text{MeCN})/\text{nm}$ 224, 393, 438, 666, 680, 743, 760 and 842.

Iodine Complex of 18.—A solution of iodine (35 mg, 0.14 mmol) in dichloromethane (3 cm^3) was added to a solution of the vinylene-TTF **18** (50 mg, 0.12 mmol) in dichloromethane (5 cm^3). The resultant solid was collected and washed with dichloromethane to give the iodine complex (78 mg, 97%) as black powder, m.p. > 300 °C (Found: C, 29.7; H, 1.7%); these values correspond to composition of 1:1.2 for **8**: I_2 ; $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 231, 294, 365, 421, 444, 687 and 837.

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