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1,3-Dithiol-2-ylidene Derivatives of 1,3-Indanedione

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Abstract: The synthesis is described of a series of mono-, bis-, and tris(1,3-dithiol-2-ylidene) derivatives **7**, **9** and **10** starting from 1,3-indanedione. Cyclic voltammetric data establish that the π–electron donor ability of these molecules increases in the sequence **7** < **9** < **10**, which is consistent with stabilisation of the cationic species by the presence of additional 1,3-dithiole units. The X-ray crystal structure of a complex (**7a**)$_2$·TCNQ is reported. Short intramolecular S···O contacts are observed within moiety **7a**. The mean planes of **7a** and TCNQ are almost parallel forming planar layers within which ribbons of TCNQ molecules are intercalated by double ribbons of molecule **7a** all stretched along the *x* direction. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Dithioles; Electron donors; Complexes; X-ray crystal structure

INTRODUCTION

1,3-Dithiol-2-ylidene derivatives,[1] of which tetrathiafulvalene (TTF) **1** is the archetype, represent a major family of molecules for the formation of organic molecular crystals which possess interesting solid state properties, *e.g.* electronic conduction in derived charge-transfer complexes.[2] In this context, the key feature of the 1,3-dithiole ring is its ability to stabilise a cation by heteroaromatic 6π delocalisation.[3] Additionally, the planarity (or near planarity) of many 1,3-dithiol-2-ylidene derivatives favours the formation of ordered stacks, dimers or sheets in the solid state structure, with intermolecular interactions facilitated by short S···S contacts.[4]

A major research effort has been directed towards variations on the TTF framework in the search for new families of organochalcogen π-donor molecules. Representative compounds are vinylogous TTF derivatives **2** and extended analogues,[5] compound **3**,[6] and compound **4**.[7] We now report the synthesis and redox properties of new 1,3-dithiol-2-ylidene derivatives of 1,3-indanedione **5**, and the X-ray crystal structure of a complex of compound **7a** and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ).

RESULTS AND DISCUSSION

We recognised that sequential reactions of 1,3-indanedione offered the possibility of producing an interesting series of mono-, bis-, and tris(1,3-dithiol-2-ylidene) derivatives (Scheme). The reaction of 2-methylsulfanyl-1,3-dithiolium cation salts **6a**[8] and **6b**[9] with the anion of 1,3-indanedione, under conditions described previously for analogous reactions of other β-dicarbonyl compounds,[10] afforded **7a** and **7b** in good yields. In the next step, reaction of **7a** with one equivalent of the anion of phosphonate ester reagent **8a**[8] gave bis(1,3-dithiol-2-ylidene) derivative **9a** in 71% yield, which subsequently reacted with a second equivalent of the anion to give the tris(1,3-dithiol-2-ylidene) system **10a** in 60% yield. Analogous reactions of **7b** with **8b**[9] gave **9b** and hence **10b** in good yields.

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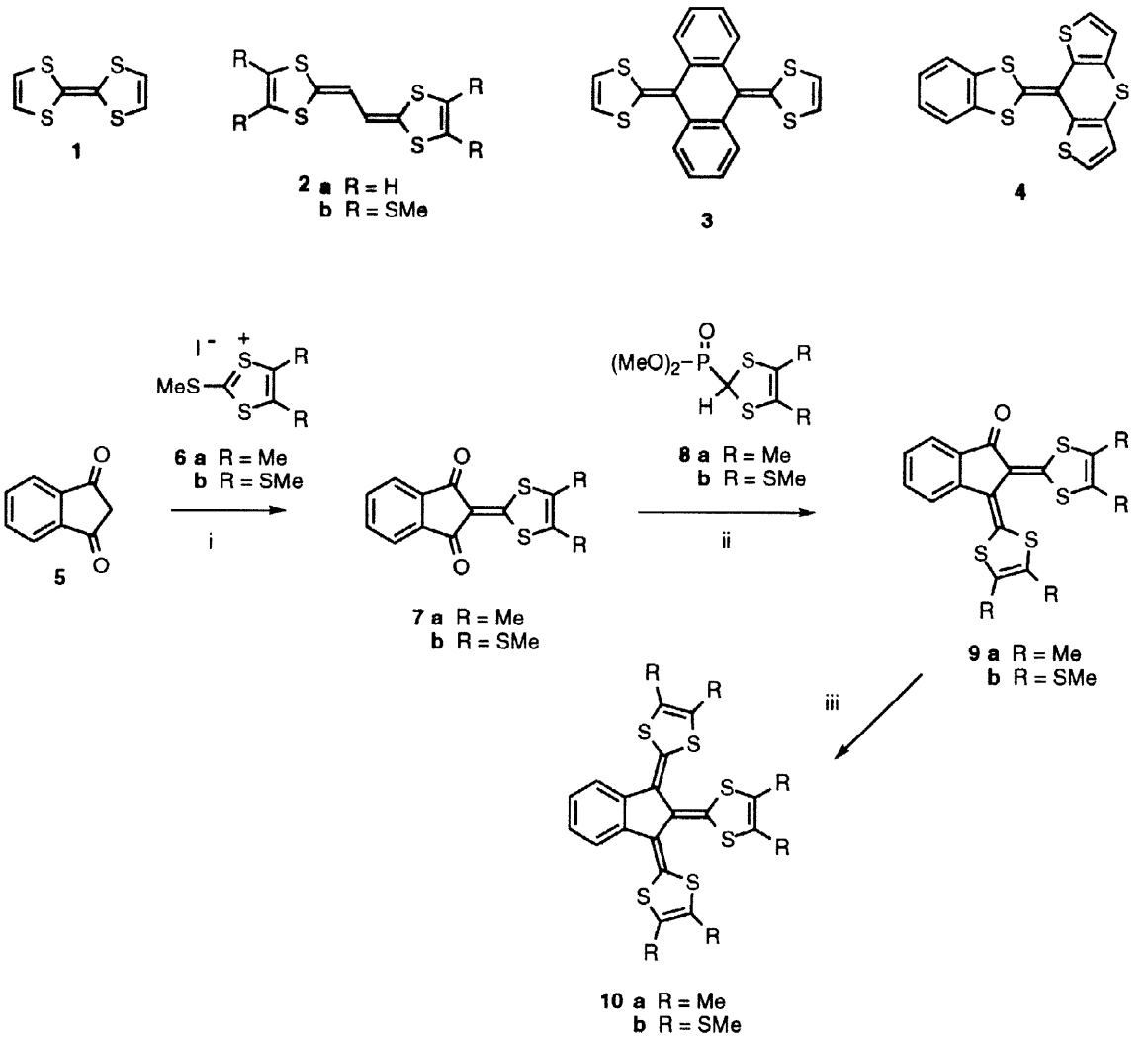


Scheme: *Reagents and Conditions*: i, NaOEt, EtOH, reflux, then compound **6**; ii, compound **8** (1 equiv.), *n*-BuLi, -78 °C, then compound **7**; iii, compound **8** (1 equiv.), *n*-BuLi, -78 °C, then compound **9**.

Spectroscopic and solution electrochemical data have been obtained on compounds **7**, **9** and **10**. The IR spectra show a strong absorption peak at the following frequencies: **7a** (1661 cm^{-1}), **7b** (1646 cm^{-1}), **9a** (1650 cm^{-1}) and **9b** (1642 cm^{-1}). These data are consistent with a conjugated carbonyl group, possibly further shifted to lower frequency by a weak intramolecular 1,5-S···O interaction[11] [as observed in the X-ray crystal structure of (**7a**)$_2$·TCNQ discussed below]. The lower frequency values for **9a** and **9b**, compared to **7a** and **7b**, respectively, are explained by increased electron donation into the whole π-system from the additional 1,3-dithiole ring. The solution electronic absorption spectra in acetonitrile of compounds **7**, **9** and **10** revealed an absorption maximum in the λ_{max} 420-430 nm region (Table 1). For the bis- and tris(1,3-dithiole) derivatives **9** and **10** an additional, weaker band at longer wavelength (480-490 nm) was also observed, arising from the extended π-delocalisation which accompanies an increase in the number of dithiole rings in the molecule.

Cyclic voltammetric data are also collated in Table 1. The data for compounds **7a** and **7b** are notably different: the former compound shows an irreversible oxidation wave at E^{ox} = +1.27 V, and the latter a

reversible wave at $E^{1/2}$ = +1.14 V (E^{ox} +1.18 V). Oxidation at these potentials is consistent with the generation of a radical cation of a 1,3-dithiol-2-ylidene moiety[5d,8,12] with the potentials considerably anodically shifted by the strongly electron-withdrawing indanedione unit. The cathodic shift and the reversibility of this process for compound **7b** was not predictable: in the TTF series and for π-extended analogues, methylsulfanyl groups usually decrease the π-donor ability, relative to methyl groups.[13] It is possible that in **7a** there is a stronger intramolecular S···O interaction than in **7b** which perturbs the oxidation process. The data for **9a** and **9b** are similar to each other; the substituents on the dithiole rings exert little effect in these systems. Following the precedent of other bis(1,3-dithiol-2-ylidene)ethane systems,[5,9] *e.g.* compound **2b**,[5c] the first oxidation processes for compounds **9a** and **9b** occur at considerably lower potentials. A second irreversible oxidation to yield the dicationic species 9^{2+} is also observed. In respect of the first oxidation, compounds **9** behave very similarly to compounds **2**: the small anodic shift for the second wave of **9** (60 mV compared to **2b**) and the irreversibility of this wave for compounds **9**, could be explained by steric effects preventing planarity of the dication of the bis(1,3-dithiol-2-ylidene)ethane moiety of **9**, and/or an electronic effect of the carbonyl substituent (an intramolecular 1,5-S···O interaction may also play a role here). Molecular modelling studies of compound **9a** gave an energy-minimised structure (Figure 1) in which the planes of dithiole rings A and B form dihedral angles of 7° and <1°, respectively, with the plane of the indane ring system, suggesting that steric effects are not important. For compounds **10a** and **10b** the situation is different: steric hindrance will certainly prevent coplanarity of the three 1,3-dithiole units, as observed in an X-ray crystal structure of tetrakis(1,3-dithiol-2-ylidene)cyclopentanone.[14] In the energy-minimised structure for **10b** (Figure 1) the planes of dithiole rings A, B and C form dihedral angles of 11°, 34° and 11°, respectively, with the indane plane. The effect of this is that the first oxidation process for **10**, which based on literature precedents[5a,14] is assigned as a two-electron wave, arises from simultaneous oxidation of the 1,3-dithiole units A and C. However, the subsequent wave to yield the trication radical species, which is ascribed to the substantially out-of-plane (non-conjugated) 1,3-dithiole unit C, is anodically shifted by *ca.* 1.0 V and is an irreversible process. The first oxidation for **10a** occurs at a lower potential than for **10b**, suggesting that the anomalous substituent effect for compounds **7** and **9** (especially seen for compounds **7**) is due to the presence of the carbonyl group(s).

We note that Yamashita *et al.* have reported that compound **11** undergoes an irreversible oxidation at E^{ox} = +0.62 V in PhCN *versus* Ag/AgCl; the irreversibility was ascribed to a chemical reaction occurring during the CV experiment.[12c] In the light of our studies reported herein, it seems likely that the irreversible oxidation of **11** is a consequence of the methylene group in that compound.

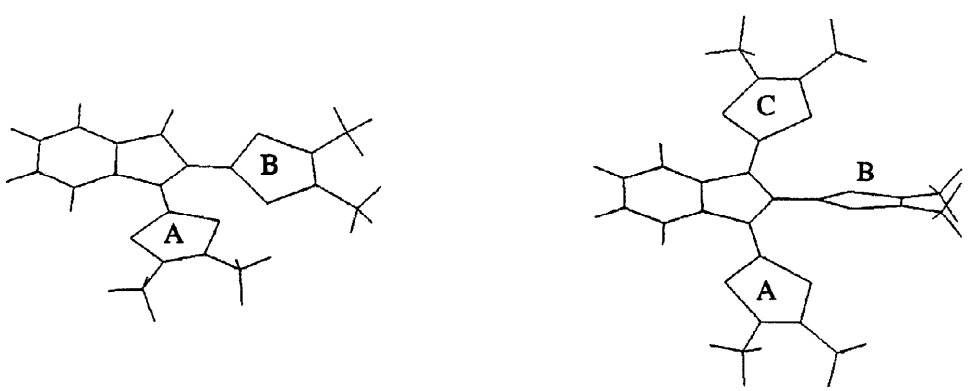


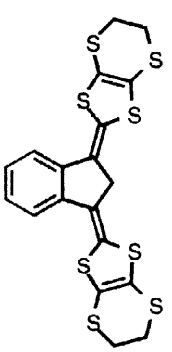
Fig. 1. Energy-minimised structures of compound **9a** (left) and compound **10a** (right).

Table 1 Electronic absorption maxima[a] and cyclic voltammetric data[b]

Compound	λ_{max}/nm	$E_1^{1/2}$/V	$E_2^{1/2}$/V	E_3^{ox}/V
2b	404, 423	+0.50	+0.63	–
7a	422	+1.27[c]	–	–
7b	426	+1.14	–	–
9a	420, 490	+0.48	+0.69[c]	–
9b	418, 485	+0.47	+0.69[c]	–
10a	416, 488	+0.15 (2e)		+1.25[c]
10b	418, 490	+0.35 (2e)		+1.23[c]
11	–	+0.62[c,d]	–	–

[a] In MeCN solution, 20 °C; [b] in dry MeCN solution, *vs.* Ag/AgCl (see Experimental section for further details); [c] irreversible wave, the value stated is for E^{ox}; [d] data taken from ref. 12c, PhCN, *vs.* Ag/AgCl.

A crystalline complex of compound **7a** with TCNQ was isolated from acetonitrile solution, and its X-ray crystal structure was determined. The asymmetric unit of the complex (**7a**)$_2$·TCNQ contains one molecule of **7a** occupying a general position and half of a TCNQ molecule (situated at an inversion centre) (Figure 2). The bond distances in **7a** are in good agreement with those found in neutral 2-(1,3-dithiol-2-ylidene)cyclopent-4-ene-1,3-dione **12**[15] and 2-(4,5-ethylenedithio-1,3-dithol-2-ylidene)1,3-indanedione **13**;[16] the molecule is planar, but for a 5° twist around the C(7)-C(16) bond. Thus the intramolecular S···O distances (average 2.94 Å) are shorter than the 'standard' van der Waals contact (3.45 Å)[17] and characteristic of weak donor-acceptor interactions.[17] The geometry of the TCNQ molecule is indicative of a neutral[19] rather than negatively charged species.[20] The crystal packing (Figure 3) can be described as triple ribbons of molecules, linked by weak C-H···O and C-H···N hydrogen bonds in a **7a**/TCNQ/**7a** pattern. Molecules of **7a**, related *via* the y translation form a stack through partial overlap between their donor and acceptor parts (interplanar separation *ca.* 3.6 Å). The TCNQ molecule is sandwiched between benzene rings of two **7a** molecules, forming with them the angle of 13° and interplanar separations of *ca.* 3.5 Å. Although these overlaps can give rise to significant π-π* interactions,[21] (**7a**)$_2$·TCNQ can be best described as a molecular complex with minor intermolecular charge-transfer interactions.



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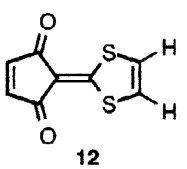

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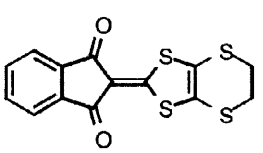

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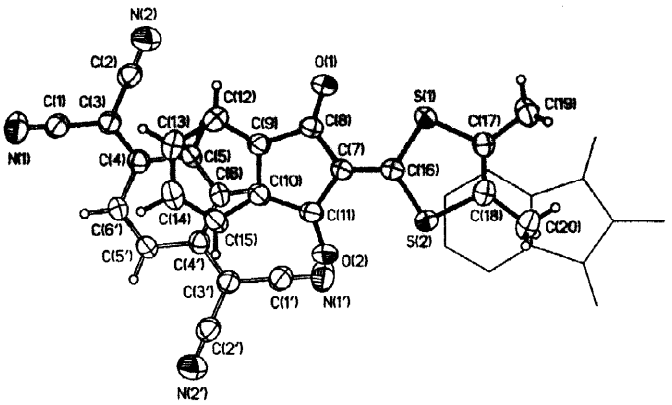

Fig. 2. Molecular overlap in the crystal of (**7a**)$_2$·TCNQ, showing molecules of TCNQ (primed atoms are inversion-related), **7a** and part of its translation equivalent (thin lines). Thermal ellipsoids shown at 50% probability level.

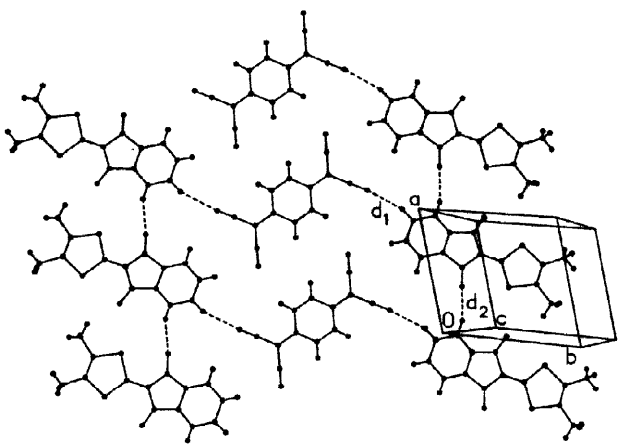

Fig. 3. Molecular layer in the crystal of (**7a**)$_2$·TCNQ; projection on the (0 1 $\bar{4}$) plane, showing hydrogen bonds N(2)...H(14) d_1 = 2.47(3), O(1)...H(15) d_2 = 2.26(3) Å for idealised H positions.

CONCLUSIONS

Sequential reactions of 1,3-indandione have been developed to yield the mono-, bis-, and tris(1,3-dithiol-2-ylidene) derivatives **7**, **9** and **10**, respectively. The redox properties are consistent with the generation of the oxidised species $\mathbf{7}^{+\cdot}$, $\mathbf{9}^{+\cdot}$ and $\mathbf{10}^{2+}$, and for compounds **9** and **10** a second oxidation process leading to the species $\mathbf{9}^{2+}$ and $\mathbf{10}^{3+\cdot}$ is also observed. The X-ray crystal structure of the complex (**7a**)$_2$·TCNQ reveals interesting structural features, notably, the existence of relatively short intramolecular S···O contacts within moiety **7a**, and planar layers of **7a** and TCNQ within which ribbons of TCNQ molecules are intercalated by double ribbons of molecules **7a**. This work should stimulate further studies on new 1,3-dithiol-2-ylidene derivatives and their charge-transfer complexes.

EXPERIMENTAL

General Methods. Elemental analyses were performed on a Carlo-Erba Strumentazione instrument. ^{1}H NMR spectra were obtained on Bruker AC 250 spectrometer operating at 250.133 MHz. ^{13}C NMR spectra were recorded on a Varian VXR 400S spectrometer operating at 100.6 MHz. Mass spectra were recorded on a

VG7070E spectrometer operating at 70 eV. Infra-red spectra were recorded on a Perkin-Elmer 1615 FTIR spectrometer operated from a Grams Analyst 1600, in the solid phase. Melting points were obtained on a Kofler hot-stage microscope apparatus and are uncorrected. All reagents were of commercial quality and solvents were dried, where necessary, using standard procedures. All reactions were performed under an inert atmosphere of argon in pre-dried glassware. Cyclic voltammetric data were measured with iR compensation using a BAS 100 electrochemical analyser. The experiments were carried out with 5 mL of a *ca.* 10^{-4} M solution of the compound in acetonitrile containing 0.2 M tetrabutylammonium hexafluorophosphate (Fluka, puriss, electrochemical grade) as the supporting electrolyte, at scan rate 100 mV s^{-1}. The potentials were measured *versus* a platinum wire quasi-reference electrode and corrected *versus* ferrocene/ferrocene$^+$ as $E^{1/2}$ = +0.36 V by adding ferrocene to the studied solution after the experiment, and referenced *versus* Ag/AgCl. For the molecular modelling studies the structural set up was performed with Insight II, version 95.0 (Biosym/MSI Technologies, Inc. San Diego, CA, USA). Structures were generated using the Builder module of Insight. Energy simulations were performed with the DISCOVER program, Version 2.9.7 on a Silicon Graphics Indigo 2 computer, using the consistent valence force field (CVFF) function. A non-bonded cut-off distance of 18 Å with a switching distance of 2 Å was employed. The non-bonded pair list was updated every 20 cycles and a dielectric constant of 1 was used in all calculations. Energy minimisation was conducted by means of the method of steepest descents without Morse or cross terms, until the derivative of energy with respect to structural perturbation was less than 1.0 kcal/Å; then the method of conjugate gradients, without Morse or cross terms until the derivative of energy with respect to structural perturbation was less than 0.1 kcal/Å; and finally the method of conjugate gradients, with Morse and cross terms until the final derivative of energy with respect to structural perturbation was less than 0.1 kcal/Å.

2-[4,5-Dimethyl-1,3-dithiol-2-ylidene]-1,3-indanedione 7a. A stirred mixture of 1,3-indanedione (5.0 g, 34 mmol) and sodium ethoxide [from sodium (0.9 g, 39 mmol)] in dry ethanol (100 mL) was refluxed for 0.5 h. Salt **6a**[8] (11.7 g, 34 mmol) was added as a suspension in dry ethanol (20 mL) and the mixture was refluxed for a further 4 h. After cooling, the solvent was evaporated *in vacuo*, water (100 mL) was added and the residue was extracted with dichloromethane (3 x 75 mL). The combined extracts were dried ($MgSO_4$), filtered, and the solvent removed *in vacuo*. Column chromatography of the residue (silica, eluent dichloromethane) afforded compound **7a** as a bright yellow solid (9.8 g, 90%) mp. > 250 °C; δ_H ($CDCl_3$) 7.76 and 7.58 (both 2 H, AA'XX', *J* 7.0 Hz), 2.31 (6 H, s); ν_{max}/cm^{-1} 1661 (C=O), 1591, 1490, 1334, 1158, 928, 724, 651; *m/z* (EI) (%) 274 (100) (M^+), 146 (20), 120 (40). Analysis calculated for $C_{14}H_{10}O_2S_2$: C, 61.3; H, 3.7; S. 23.4. Found: C, 61.5; H, 3.8; S, 23.0%.

2-[4,5-Bis(methylsulfanyl)-1,3-dithiol-2-ylidene]-1,3-indanedione 7b was prepared analogously to **7a** from **6b** (3.0 g, 9.1 mmol), 1,3-indanedione (1.2 g, 8.2 mmol) and sodium ethoxide (8.4 mmol) in ethanol (100 mL). After refluxing for 4 h, work-up and purification on a silica column (eluent dichloromethane/hexane 1:1 v/v), followed by recrystallisation from dichloromethane/hexane, yielded **7b** as a yellow solid (1.8 g, 65%) mp. 183-185 °C; $\delta_H(CDCl_3)$ 7.8-7.6 (4 H, m), 2.58 (6 H, s); $\delta_C[CDCl_3, Cr(acac)_3]$ 187.4, 166.6, 140.2, 133.2, 129.3, 121.8, 113.5, 13.0; ν_{max}/cm^{-1} 1646 (C=O), 1586, 1500, 1440, 1327, 1209, 1156, 1033, 969, 756, 725, 647; *m/z* (EI) 338 (100) (M^+), 323 (35), 189 (15), 135 (62). Analysis calculated for $C_{14}H_{10}O_2S_4$: C, 49.7; H, 3.0. Found: C, 49.8; H, 2.9 %.

1,2-Bis(4,5-dimethyl-1,3-dithiol-2-ylidene)-3-indanone 9a. Phosphonate ester **8a**[8] (0.56 g, 2.3 mmol) was dissolved in anhydrous THF (100 mL) and to this solution *n*-BuLi (1.6 M in hexane, 1.4 mL, 2.3 mmol) was added at -78°C. After stirring for 30 min a solution of compound **7a** (0.60 g, 2.2 mmol) in THF (20 mL) was

added. The temperature was maintained at -78 °C for 2 h and then allowed to warm to room temperature overnight. The solvent was evaporated *in vacuo* to yield a red solid. This was extracted into dichloromethane (100 mL), washed with water (2 x 50 mL), dried ($MgSO_4$), evaporated and then chromatographed on a neutral alumina column (eluent: hexane/dichloromethane 2:1 v/v) to yield **9a** as a red solid (0.60 g, 71%) mp. >250°C (from dichloromethane/hexane); $\delta_H(CDCl_3)$ 7.71-7.18 (4 H, m), 2.25 (3 H, s), 2.18 (3 H, s), 2.12 (3 H, s), 2.10 (3 H, s); ν_{max}/cm^{-1} 1650 (C=O), 1592, 1457, 1337, 1156, 1088, 759, 712, 652; *m/z* (EI) 388 (100) (M^+), 274 (80), 230 (40), 149 (94). Analysis calculated for $C_{19}H_{16}OS_4$: C, 58.7; H, 4.2. Found: C, 58.9; H, 4.10 %.

1,2-Bis[4,5-di(methylsulfanyl)-1,3-dithiol-2-ylidene)]-3-indanone 9b was prepared analogously to **9a** from phosphonate ester **8b**[9] (0.23 g, 0.74 mmol) and compound **7b** (0.25 g, 0.74 mmol). Work-up and purification as described for **9a** gave **9b** as a red solid (0.24 g, 62% yield) mp. >250°C (from dichloromethane/hexane); $\delta_H(CDCl_3)$ 7.70-7.24 (4 H, m), 2.48 (6 H, s), 2.47 (6 H, s), ν_{max}/cm^{-1} 1642 (C=O), 1590, 1450, 1333, 1241, 1100, 758, 730; *m/z* (EI) 516 (100) (M^+), 122 (30), 106 (42). Analysis calculated for $C_{19}H_{16}OS_8$: C, 44.2; H, 3.1. Found: C, 44.2; H, 3.3 %.

1,2,3-Tris(4,5-dimethyl-1,3-dithiol-2-ylidene)indane 10a was prepared analogously to **9a** using phosphonate ester **8a** (0.28 g, 1.15 mmol) and compound **9a** (0.45 g, 1.15 mmol). Work-up and purification, as described for **9a**, afforded **10a** as a yellow solid (0.35 g, 60%) which slowly darkened on exposure to air. Mp. >250°C (from dichloromethane/hexane); $\delta_H(CDCl_3)$ 7.38 (2 H, m), 7.19 (2 H, m), 2.06 (12 H, s), 2.04 (6 H, s); ν_{max}/cm^{-1} 1600, 1585, 1444, 1330, 1287, 1080, 802, 760; *m/z* (EI) 502 (100) (M^+), 318 (30), 251 (28). Analysis calculated for $C_{24}H_{22}S_6$: C, 57.3; H, 4.4 %. Found: C, 56.9; H, 4.3 %. Compound **10a** was also prepared directly from **5** and **8a** (2 equivalents) in 40% yield.

1,2,3-Tris[4,5-di(methylsulfanyl)-1,3-dithiol-2-ylidene]indane 10b was prepared analogously to **10a** using reagent **8b** (0.23 g, 0.74 mmol) and compound **9b** (0.25 g, 0.74 mmol). Work-up and purification as described for **10a** yielded **10b** as a yellow solid (0.44 g, 85%) mp. 140-142°C (from dichloromethane/hexane); $\delta_H(CDCl_3)$ = 7.38-7.24 (4 H, m), 2.48 (6 H, s), 2.46 (12 H, s); ν_{max}/cm^{-1} 1595, 1558, 1490, 1444, 1356, 1090, 777; *m/z* (CI) 695 (100), (M^++1), 278 (15), 139 (30). Analysis calculated for $C_{24}H_{22}S_{12}$: C, 41.5; H, 3.2 %. Found: C, 41.4; H, 3.2 %. Compound **10b** was also prepared directly from **5** and **8b** (2 equivalents) in 38% yield.

Complex (7a)$_2$·TCNQ. Cooling of an equimolar solution of **7a** and TCNQ in dry acetonitrile from reflux to room temperature yielded small amounts of greenish-black blocks of (**7a**)$_2$·TCNQ of suitable quality for a single crystal X-ray diffraction study. Analysis calculated for $C_{40}H_{24}N_4O_4S_4$: C, 63.8; H, 3.2; N, 7.4 %. Found C, 63.4; H, 3.2; N, 7.2 %. These blocks were hand-picked from the major product **7a**·TCNQ complex (1:1 stoichiometry) which was obtained as green plate-like crystals. Analysis calculated for $C_{26}H_{14}N_4O_2S_2$: C, 65.3; H, 2.9; N, 11.7 %. Found: C, 65.4; H, 3.1, N, 11.4 %] and yellow crystals of unreacted **7a**.

X-Ray Crystallographic data for (7a)$_2$·TCNQ: The experiment was performed on a Siemens R3m/V four-circle diffractometer at room temperature, computations with SHELXTL-Plus programmes.[22] Crystal data: $C_{40}H_{24}N_4O_4S_4$, M = 752.9, triclinic, a = 7.751(2), b = 8.347(2), c = 14.049(2) Å, α = 92.50(2), β = 96.44(2), γ = 103.30(2)°, V = 876.7(3) Å^3, space group $P\bar{1}$, Z = 1, D_c = 1.43 g cm^{-3}, graphite-monochromated Mo-Kα radiation ($\bar{\lambda}$ = 0.71073 Å), μ = 3.21 cm^{-1}. 4362 unique reflections with $2\theta \leq 60°$ were measured by the Wyckoff (limited ω) scan technique and corrected for absorption (on real crystal shape). The structure was solved by direct methods and refined by full matrix least-squares against |F| of 3210 reflections with $I > 2\sigma(I)$

(non-hydrogen atoms in anisotropic approximation, H atoms in isotropic one) to R = 0.047, wR = 0.055 and goodness-of-fit 1.62, residual max. Δρ 0.34 min., –0.27 eÅ^{-3}. Structural data have been deposited at the Cambridge Crystallographic Data Centre.

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