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An in depth study of the formation of new tetrathiafulvalene derivatives from 1,8-diketones

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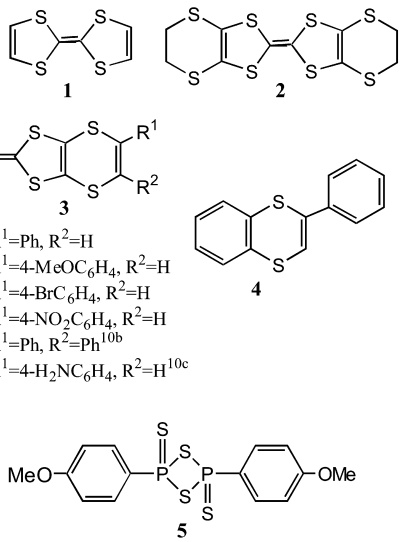
Abstract—A detailed study of the reactions of phosphorus pentasulfide and Lawesson's reagent with a series of 4,5-bis($RCOCH_2S$)-1,3-dithiole-2-thiones (R=Ph, 4-$MeOC_6H_4$, 4-Br C_6H_4, Me) has been carried out. These reactions lead to fusion of either an unsaturated 1,4-dithiin ring or a thiophene to the dithiole; the former in higher yield, while the latter is a significant product in the reactions with Lawesson's reagent; as well as small amounts of minor products. A mechanistic rationalization of these products is discussed in some detail. The new fused dithioles have been converted to novel series of fused TTF derivatives.

1. Introduction

There has been continued interest in the synthesis of derivatives of tetrathiafulvalene, TTF **1**. This is due to the metallic behaviour of its radical cation salts with mono anions and charge transfer complexes with electron acceptors such as TCNQ, which exhibit semi-conducting, conducting and superconducting properties. It has been established that the physical properties of the radical cation salts depend on the electronic and structural features of TTF derivatives.[1] The most widely studied derivative, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) **2**, has yielded some salts which show superconducting properties, including κ-(BEDT-TTF)Cu[$N(CN)_2Br$] which has the highest critical temperature, T_c=12.8 K, for an organic superconductor.[2] In recent years, the electron-donating property of TTF has led to the synthesis of various analogues with different potential applications such as chromophores for dyes, nonlinear optics, synthetic light-harvesting systems, liquid crystals,[3] dendrimers,[4–6] phthalocyanines,[4,5] polymers,[7] and supramolecular switches.[8] Obviously, such a wide range of application possibilities requires the synthesis of TTF derivatives bearing versatile functional groups.



To improve the conducting properties, efforts have been aimed at (i) extension of the conjugation of the molecule to delocalize the charges formed in the charge transfer salts and (ii) introduction of hydrogen bonding groups to produce specific attractive interactions with the anions in the derived radical cation salts.[1b] So far, extension of conjugation has been achieved in the centre of the molecule,[1b] but, there are just a few examples of the introduction of conjugation at the peripheral ethylene bridges,[9] and they are achieved with conventional methods which have limited applications.

Keywords: 1,8-diketone ring formation; 1,4-dithiin; thiophene; BEDT-TTF; TTF.
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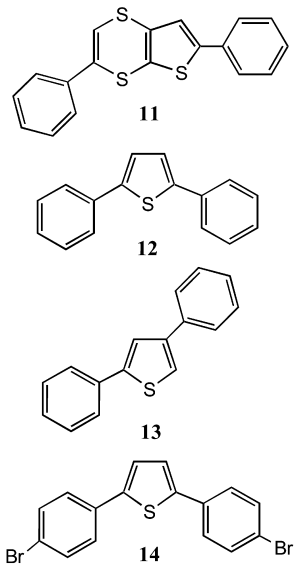
Recently, we have reported a convenient method of synthesizing fused 1,4-dithiin ring systems with various functional groups (**3**, **4**).[10] This method has allowed conjugation to be introduced into the peripheral ethylene bridges of the BEDT-TTF system. As far as we are aware this is the best method available to synthesize molecules with substituted 1,4-dithiin rings fused to tetrathiafulvalene,[11] and it has potential to find convenient applications with other ring systems to generate various fused 1,4-dithiin heterocycles.[10a] Installation of functional groups such as 4-$CH_3OC_6H_4$ and 4-BrC_6H_4 to the periphery of a fully conjugated BEDT-TTF will provide easy access to the construction of more complex systems.

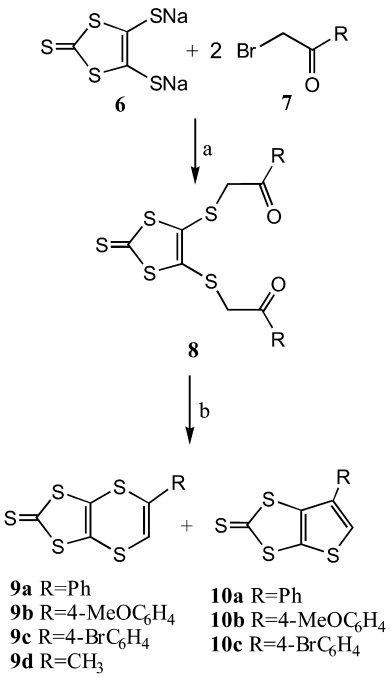
2. Results and discussion

2.1. Synthesis of fused 1,4-dithiins and thiophenes; 1,8-diketone ring formation reaction

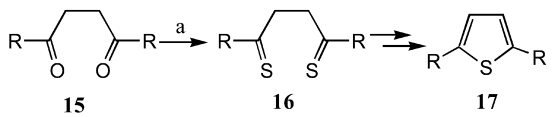


Cyclization of 1,8-diketones **8**, obtained from the reaction of readily available dithiolate **6**[12] with α-haloketones **7**, is the crucial step of this study. The 1,8-diketones were prepared in dry THF or EtOH at room temperature under nitrogen atmosphere, and were then subjected to the 1,8-diketone ring formation reaction[10] using either Lawesson's reagent (LR) **5** or P_4S_{10} in refluxing dry toluene under nitrogen atmosphere, until the consumption of the starting material was complete (Scheme 1). With both LR and P_4S_{10}, the reaction resulted in the formation of a fused six-membered 1,4-dithiin ring **9** and a fused five-membered thiophene ring **10** along with various side products **11**–**14**. The thiophenes **10** are probably derived from **9** by loss of a sulfur atom.

It is well established that both LR and P_4S_{10} are useful reagents for both conversion of ketones to thiones[13] and formation of thiophenes **17** from 1,4-diketones **15**.[14] Even in the latter case, the initial reaction is conversion of a 1,4-diketone to a 1,4-dithione **16**, which subsequently



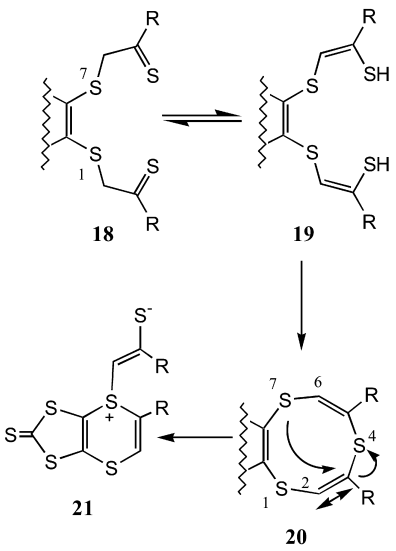
Scheme 1. (a) THF (dry), N_2, rt, overnight; (b) LR or P_4S_{10}, toluene, reflux overnight (LR), 3 h (P_4S_{10}).



Scheme 2. LR, toluene, reflux, overnight.

undergoes in situ cyclization to give thiophene **17** (Scheme 2). Although the 1,8-diketone ring closure reaction to form 1,4-dithiin and thiophene is an unusual reaction of LR and P_4S_{10} we suggest that initial reaction of 1,8-diketones, as in the case of 1,4-diketones, is the formation of 1,8-dithione **18** intermediates, which is very likely to be in equilibrium with its corresponding dienedithol **19** and can form the nine-membered ring **20**. This highly unstable ring then rearranges to a six-membered ring as a zwitterion **21** (Scheme 3).

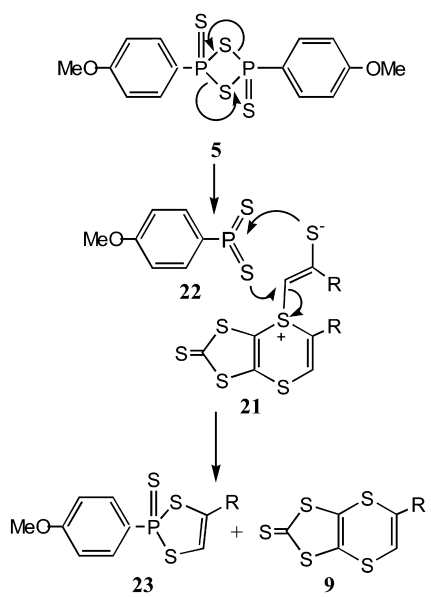
The side products **12**–**14** isolated from the cyclization reactions provide further evidence to our prediction. On the other hand, one may claim that an attack from one of the exocyclic sulfur atoms to the thiocarbonyl carbon may result in the same products, although it can be understood easily that such an attack is very difficult since the exocyclic sulfur atoms are so hindered and in conjugation with a double bond. The possibility of such a nucleophilic attack was investigated, using computational chemistry, from the hindered exocyclic sulfur atoms to the thiocarbonyl carbons, that is from S1 to C5 or from S7 to C3 of **18** (Scheme 3). The conformational analysis of **18** with the MMFF method showed that the distances between S1–C5 and S7–C3 are too long that such a nucleophilic attack is not possible. On the other hand, the analysis indicated that 1,8-dithione **18** is in equilibrium with its corresponding dienedithiol form **19**, and the dithiol forms were found to be more stable than the dithione forms. This means the tautomeric equilibrium favours the dithiol form **19**. We predict that the elimination of H_2S from the dithiol **19** gives the nine-membered ring **20**.



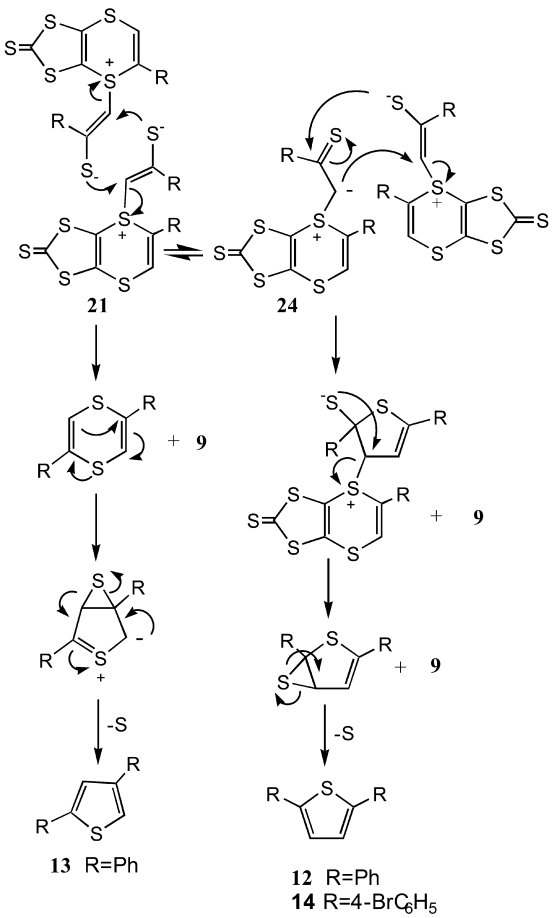
Scheme 3. Proposed mechanism for the formation of nine-membered ring and its rearrangement to six-membered ring.

The molecular modelling studies of **20** indicated that the distances from S1 to C5 and from S7 to C3 are both 3.46 Å. This makes the rearrangement possible by attacking from the sulfurs S1/S7 to the corresponding carbons C5/C3 to produce the zwitterion **21**. The semiempirical PM3 calculations predicted that the activation energy for such an attack is 35.526 kcal/mol, including zero point energy correction, which can be overcome easily under the reflux conditions in toluene. As expected, formation of the zwitterionic intermediate **21** is an endothermic reaction with ΔH_{rxn}=29.435 kcal/mol. Following Hammond's postulate, therefore, the predicted structure of the transition state resembles that of the intermediate **21**. A detailed study of semiempirical calculations is in preparation and will be published elsewhere.

Our initial assumption[10a] was that the zwitterion **21** gave a



Scheme 4. 1,4-Dithiin formation.



Scheme 5. Proposed mechanism for thiophene side products.

cyclic reaction with the decomposition product **22** of LR, which is the actual reagent for replacing oxo groups with thioxo groups rather than undecomposed LR **5** itself,[15] to free the fused 1,4-dithiin molecule **9** and give the 2-phospha-1,3-dithiole-2-thione **23** (Scheme 4). Unfortunately, we have never isolated any product such as **23** to prove this mechanism. On the other hand, our latest results have indicated that other mechanisms for decomposition of the zwitterion are in operation, which can explain the generation of the side products. The zwitterion **21** reacts with a second zwitterion following two different mechanisms (Scheme 5). In one case, the two enethiolate side chains (which could in principle react as nucleophiles through S or the β-carbon) react together forming two C,S bonds to give a 1,4-dithiin which can lose sulfur to give 2,4-disubstituted thiophene **13**, while in the second case the two β-carbons bond and one thiolate S attacks the α-carbon of the other side chain forming a thiiranothiophene which loses sulfur to give 2,5-thiophenes **12** and **14**. Unfortunately, in the other case, where R=CH_3, such side products could not be isolated.

Moreover in one reaction (R=Ph), an interesting by-product, 3,6-diphenylthieno[2,3-*b*][1,4]dithiin **11**, was isolated and its structure was established by X-ray diffraction analysis (Fig. 1). A possible explanation for the mechanism

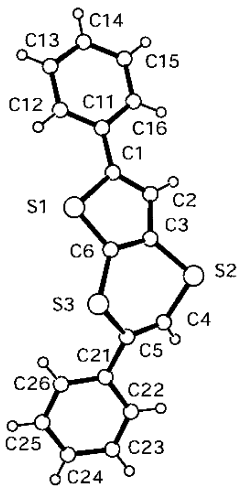
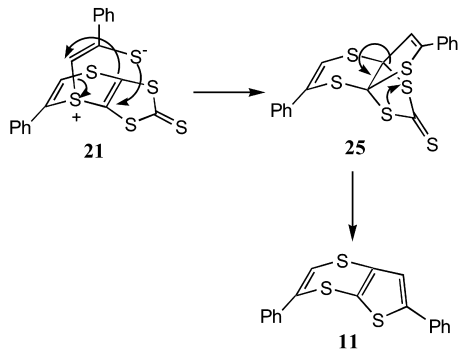


Figure 1. X-Ray diffraction analysis of **11**.

is that the zwitterion **21** decomposes by the enethiolate fragment bonding to the double bond at the fusion of the ring system (Scheme 6). The resultant tetra-cyclic intermediate **25** then rearranges to give the bicyclic product **11** with loss of carbon disulfide and sulfur. Surprisingly, such a product could only be isolated where the side groups were phenyl.



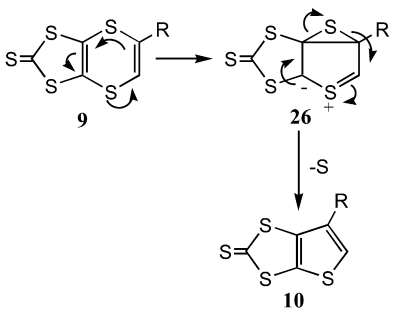
Scheme 6. Proposed mechanism for thienodithiin side product.

2.2. Yields

Although the 1,8-diketone ring formation reaction with LR and P_4S_{10} gave 1,4-dithiin **9** as a main product in all cases, it appears that the thiophene **10** is the second major product in many cases, even though it could not be obtained at all in some reactions such as with P_4S_{10} where R=Ph or CH_3 and with LR where R=CH_3 (Table 1). Their formation possibly follows the rearrangement of the dithiin ring **9**, which leads to the formation of the tetracyclic intermediate **26**, from which loss of sulfur produces the fused thiophenes **10** (Scheme 7).

Table 1. Yields form LR and P_4S_{10} reactions

	P_4S_{10}		LR	
	9 (%)	**10** (%)	**9** (%)	**10** (%)
a	49	–	40	17
b	45	15	30	27
c	40	2	35	18
d	52	–	5	–

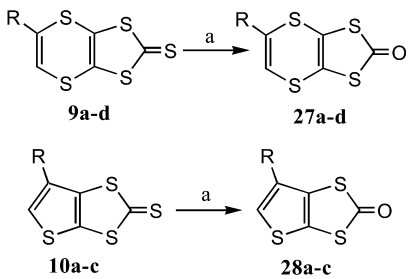


Scheme 7. Formation of thiophene from dithiin.

It appears that carrying out the 1,8-diketone ring formation reaction with P_4S_{10} improves the yield of the major product, 1,4-dithiin (Table 1). On the other hand, reaction with LR improves the yield of the thiophene product, though it remains the minor product. It appears that the reaction time is an important factor here, since both reagents follow a similar mechanism.[15] Our results indicate that the reactions with P_4S_{10} are complete in ca. 3 h while the reactions with LR require overnight reflux, which means a longer reaction time causes the 1,4-dithiin ring to lose a sulfur atom to form the thiophene (Scheme 7). When the reaction of 1,8-diketone, where R=CH_3, was carried out with LR, little formation of 1,4-dithiin, 5%, was observed. However, when the reaction was conducted with P_4S_{10}, a much higher yield of 1,4-dithiin was isolated, 52%.

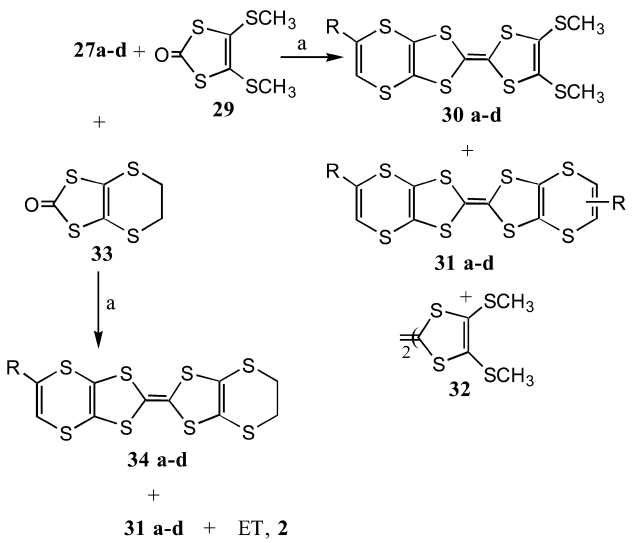
2.3. Coupling reactions

Couplings of the 1,4-dithiins **9a-d** and the thiophenes **10a-c** to give new fused TTF derivatives were carried out employing the well-established procedure in the literature.[16] Initially, the thione sulfur atoms of all the dithiins and the thiophenes were converted to oxygen with mercuric acetate to obtain **27** and **28**, respectively (Scheme 8).

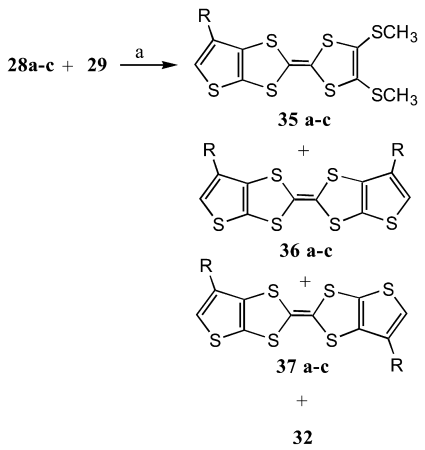


Scheme 8. (a) $Hg(OAc)_2$, AcOH/$CHCl_3$, rt, 1 h.

Oxo compound **27** was coupled with the readily available 4,5-di(methylsulfanyl)-1,3-dithiol-2-one **29**[17] in neat triethyl phosphite at 110°C under a nitrogen atmosphere, which yielded a mixture of four compounds (Scheme 9). A successful column chromatography resulted in the separation of the cross-coupled organosulfur donor **30** (20–25%), a *cis* and *trans* mixture of self-coupled material **31** and the tetrasubsituted TTF **32**. Couplings of the 1,4-dithiins **27** were also carried out with the unsubstituted bicyclic oxo compound **33** (Scheme 9), employing the same reaction conditions. Column chromatography of the reaction mixture gave four compounds; cross-coupled organosulfur donor **34**



Scheme 9. (a) $(EtO)_3P$, N_2, 3 h, 110°C.

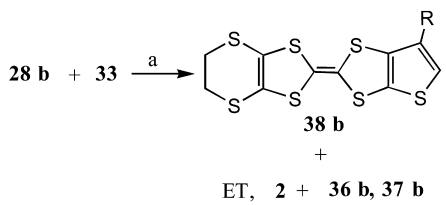


Scheme 10. (a) $(EtO)_3P$, N_2, 3 h, 110°C.

(15–20%), a *cis* and *trans* mixture of self-coupled **31**, and ET **2**.

Cross-coupling products of fused thiophenes **28** were obtained by performing the reaction with 4,5-di(methylsulfanyl)-1,3-dithiol-2-one **29** in triethyl phosphite at 110°C under nitrogen atmosphere, which produced a mixture of four compounds (Scheme 10). A successful column chromatography achieved their separation as the cross-coupled TTF derivatives **35** (19–22%), a *cis* and *trans* mixture of **36** and **37**, respectively, and the tetrasubstituted TTF **32**.

Coupling of **28** was also carried out with the oxo compound **33** under the usual coupling conditions, which resulted in the synthesis of **38** (20%) along with ET **2** and the isomeric mixture of **36** and **37** (Scheme 11).



Scheme 11. (a) $(EtO)_3P$, N_2, 3 h, 110°C.

2.4. Cyclic voltammetry (CV) measurements

Oxidation potentials of the new organosulfur donors **30**, **34** and **35** prepared in the coupling reactions, were measured by cyclic voltammetry, and are compared with data for ET **2** (Tables 2 and 3). The CV measurements in Tables 2 and 3 were carried out in acetonitrile containing $NaClO_4$ or dichloromethane containing $TBABF_4$, respectively. The CV measurements of ET were also performed separately in these two solutions. Placing a double bond at the bridgehead of ET as in the series **34** leads to an increase in the two oxidation potentials for these donors by ca. 0.15 V (for E_1) and by ca. 0.2 V (for E_2). Apart from the extra conjugation possible, the fully unsaturated six-membered ring is likely to be flexed about the S–S axis, while in ET, this ring adopts an envelope conformation in which just one carbon from the ethylene bridge is out of plane. Compared with series **34**, replacing the remaining $-CH_2CH_2-$ bridge by two methyl groups as in series **30**, leads to a significant reduction in the oxidation potentials, so that they both lie just less than that of ET itself. In these compounds the S–Me bonds are likely to lie perpendicular to the best of plane of the donor molecule, in contrast to ET. When a sulfur atom is removed from the dithiin ring in this latter series to give series **35**, which have the fused thiophene instead, then the oxidation potential rise again, typically by ca. 0.1 V for E_1 and ca. 0.2 V for E_2. Nevertheless, all these donors are candidates for formation of radical cation salts and charge transfer salts.

Table 2. CV measurements of **30a-d** in ca. 1 mM MeCN solutions, $NaClO_4$ (0.1 M), vs Ag/AgCl, 100 mV s^{-1}

	$E^1_{1/2}$ (V)	$E^2_{1/2}$ (V)	ΔE
30a	0.49	0.63	0.14
30b	0.50	0.63	0.13
30c	0.47	0.72	0.25
30d	0.42	0.66	0.24
ET	0.50	0.77	0.27

Table 3. CV measurements of **34a-d** and **35a-c** in ca. 1 mM CH_2Cl_2 solutions, $TBABF_4$ (0.1 M), vs Ag/AgCl, 115 mV s^{-1}

34a	0.66	0.96	0.30
34b	0.60	0.95	0.35
34c	0.68	1.00	0.32
34d	0.64	0.99	0.24
35a	0.59	0.86	0.27
35b	0.51	0.83	0.32
35c	0.62	0.94	0.32
ET	0.51	0.85	0.34

3. Conclusion

In this study, reaction mechanisms of formation of 1,4-dithiins and thiophenes from the reactions of diketones with LR and P_4S_{10} have been investigated. Using this reaction as a tool, various TTF analogues have been prepared and their CV properties have been presented. It has been demonstrated that 1,8-diketone ring formation reaction can be applied to

the preparation of various dithiin and thiophene analogues, which could be particularly important for material chemistry.

4. Experimental

4.1. General

Melting points are uncorrected. NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as the internal standard for ^1H (200 MHz) or solvent as the internal standard for ^{13}C (67.8 MHz) unless otherwise stated. Mass spectra were recorded at an ionising voltage of 70 eV. Chromatography was performed on flash silica gel (Merck) and TLC was carried out on 0.2 mm silica gel plates. All reagents and solvents were commercial grade (Aldrich) and purified according to established convention.

4.1.1. 2-[5-(2-Oxo-2-phenylethylsulfanyl)-2-thioxo-1,3-dithiol-4-ylsulfanyl]-1-phenylethanone (8a). To the solution of dianion **6** (2.00 g, 8.26 mmol) in dry THF (100 mL), under a N_2 atmosphere and in an ice bath, was added 2-bromoacetophenone **7a** (3.29 g, 16 mmol) dissolved in dry THF (80 mL) dropwise from a dropping funnel, and the mixture was left stirring overnight at room temperature. The solvent was then evaporated in vacuo and the residue was extracted with dichloromethane (3×100 mL), dried over Na_2SO_4, filtered and the solvent was evaporated in vacuo. The crude product was recrystallized from ethanol to give the title compound **8a** (2.57 g, 72%) as an orange powder, mp 89–92°C. [Found: C, 52.55; H, 2.94. $C_{19}H_{14}O_2S_5$ requires C, 52.53, H, 3.22%]; ν_{max}(Nujol) 1670 (C═O), 1050 (C═S) cm^{-1}; δ_H 7.92 (4H, d, J=7.6 Hz, Ar), 7.50 (6H, m, Ar), 4.41 (4H, s, SCH_2CO); δ_C 210.4, 192.3, 137.1, 134.9, 134.1, 128.9, 128.5, 43.1 (SCH_2); m/z (FAB, NOBA Matrix) 435 (M^++1); m/z (EI) 434 (M^+).

The following were similarly prepared.

4.1.2. 1-(4-Methoxyphenyl)-2-{5-[2-(4-methoxyphenyl)-2-oxoethylsulfanyl]-2-thioxo-1,3-dithiol-4-ylsulfanyl} ethanone (8b). The crude product was crystallized from ethanol to give the title compound **8b** (2.85 g, 70%) as orange needles, mp 98–100°C. [Found: C, 51.27, H, 3.44. $C_{21}H_{18}O_4S_5$ requires C, 51.01; H, 3.64%]; ν_{max}(Nujol) 1660 (C═O), 1080 (C═S) cm^{-1}; δ_H 7.90 (4H, d, J=8.8 Hz, Ph), 6.90 (4H, d, J=8.8 Hz, Ph), 4.31 (4H, s, SCH_2CO), 3.87 (6H, s, OCH_3); δ_C 210.8 (C═S), 190.8 (C═O), 164.2, 137.2, 130.9, 127.9, 114.1, 55.6 (OCH_3), 42.9 (SCH_2); m/z (EI) 494 (M^+).

4.1.3. 1-(4-Bromophenyl)-2-{5-[2-(4-bromophenyl)-2-oxoethylsulfanyl]-2-thioxo-1,3-dithiol-4-ylsulfanyl} ethanone (8c). The crude product was crystallized from ethanol to give the title compound **8c** (3.08 g, 63%) as an orange powder, mp 140–143°C. [Found: C, 52.91, H, 2.63. $C_{19}H_{12}Br_2O_2S_5$ requires C, 52.7, H, 2.77%]; ν_{max}(Nujol) 1680 (C═O), 1060 (C═S) cm^{-1}; δ_H (DMSO) 7.90 (4H, d, J=8.5 Hz, Ar), 7.75 (4H, d, J=8.5 Hz, Ar), 4.69 (4H, s, SCH_2CO); δ_C (DMSO) 210.7 (C═S), 192.6 (C═O), 144.0, 133.7, 131.7, 130.4, 127.9, 42.7; m/z (FAB, NOBA matrix) 592 (M^+).

4.1.4. 1-[5-(2-Oxopropylsulfanyl)-2-thioxo-1,3-dithiol-4-ylsulfanyl]propan-2-one (8d). The crude product was crystallized from ethanol to give the title compound **8d** (1.84 g, 72%) as an orange powder, mp 75–78°C. [Found: C, 34.90, H, 3.3. $C_9H_{10}O_2S_5$ requires C, 34.8, H, 3.22%]; ν_{max}(Nujol) 1700 (C═O), 1060 (C═S) cm^{-1}; δ_H 3.78 (4H, s, SCH_2CO), 2.30 (6H, s, CH_3); δ_C 207.0 (C═S), 200.8 (C═O), 138.3, 46.3 (SCH_2), 28.7 (SCH_3); m/z (FAB, NOBA matrix) 310 (M^+).

4.1.5. 5-Phenyl[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-thione (9a). (a) A mixture of **8a** (1.00 g, 2.30 mmol) and Lawesson's reagent **5** (1.10 g, 2.71 mmol) was boiled under reflux in dry toluene (25 mL) under a N_2 atmosphere until the starting material was consumed. After 4 h, toluene evaporated under reduced pressure and the residue was separated by column chromatography, eluting with hexane/CH_2Cl_2 (2/1) to give **11** (yellow powder, 0.11 g, 15%), **13**[20,21] (yellow powder, 49 mg, 9%), the title compound **9a** (yellow powder, 0.28 g, 40%) and **10a** (light brown powder, 0.1 g, 17%) in order of elution.

(b) A mixture of **8a** (0.50 g, 1.15 mmol) and phosphorus pentasulfide (0.55 g, 1.23 mmol) was boiled under reflux in dry toluene (20 mL) under a N_2 atmosphere until the starting material was consumed (1 h). The precipitate was filtered off, and toluene was evaporated under reduced pressure. The residue was separated by column chromatography eluting with hexane/CH_2Cl_2 (2/1) to give **12**[18,19] (yellow powder, 22 mg, 8%) and the title compound **9a** (yellow powder, 0.17 g, 49%) as first and second fractions, respectively.

Compound **9a**. Mp 145–148°C. [Found: C, 44.14, H, 1.98. $C_{11}H_6S_5$ requires C, 44.29, H, 2.01%]; ν_{max}(Nujol) 1080 (C═S) cm^{-1}; δ_H 7.54 (2H, m, Ar), 7.39 (3H, m, Ar), 6.66 (1H, s, ═CH); δ_C 213.8 (C═S), 142.4, 134.9, 129.7, 129.3, 128.9, 128.7, 127.3, 117.6; m/z (FAB, NOBA Matrix) 298 (M^+); m/z (EI) 298 (M^+).

4.1.6. 6-Phenylthieno[2,3-*d*][1,3]dithiole-2-thione (10a). Mp 210–212°C. [Found: C, 49.34, H, 2.38. $C_{11}H_6S_4$ requires C, 49.62, H, 2.25%]; δ_H 7.57 (2H, m, Ph), 7.44 (3H, m, Ar), 7.28 (1H, s, thiophene); δ_C 214.6 (C═S), 136.3, 129.2, 128.8, 128.6, 126.5, 125.7, 125.2, 115.5; m/z (FAB, NOBA Matrix) 267 (M^++1).

4.1.7. 3,6-Diphenylthieno[2,3-*b*][1,4]dithiin (11). Mp 117–119°C. [Found: C, 66.39, H, 3.36. $C_{18}H_{12}S_3$ requires C, 66.60, H, 3.70%]; δ_H 7.52 (4H, m, Ar), 7.35 (6H, m), 7.01 (1H, s, thiophene), 6.65 (1H, s, dithiin); δ_C 138.0, 136.0, 133.0, 131.0, 128.9, 128.8, 128.6, 128.0, 127.7, 126.8, 125.7, 125.5, 121.0, 118.0; m/z (EI) 324 (M^+); m/z (LSI) 324 (M^+), 290 (M^+-H_2S), 247 (M^+−Ph), 203 (M^+−PhCS).

The following were similarly produced.

4.1.8. 5-(4-Methoxyphenyl)[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-thione (9b). The residue was separated by column chromatography eluting with hexane/CH_2Cl_2 (2/1) to give the title compound **9b** as a first fraction (yellow powder, 0.2 g, 30% with LR and 0.3 g, 45% with P_4S_{10}) and **10b**[10a,d] as a second fraction (0.16 g, 27% with LR and

0.09 g, 15% with P_4S_{10}). **9b** Mp 88–90°C. [Found: C, 44.16, H, 2.51. $C_{12}H_8OS_5$ requires C, 43.90, H, 2.43%]; δ_H (270 MHz) 7.42 (2H, d, J=9.0 Hz, Ar), 6.90 (2H, d, J=9.0 Hz, Ar), 6.65 (1H, s, =C*H*), 3.82 (3H, s, OCH_3); δ_C 213.9 (*C*=S), 160.8, 142.6, 129.1, 128.8, 127.3, 115.0, 114.3, 55.4 (OCH_3); *m*/*z* (FAB, NOBA matrix) 328 (M^+).

4.1.9. 5-(4-Bromophenyl)[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-thione (9c). The residue was separated by column chromatography eluting with hexane/CH_2Cl_2 (2/1) to give **14** (yellow powder, 6.6 mg,10% with P_4S_{10}), the title compound **9c** (yellow powder, 0.22 g, 35% with LR and 0.26 g, 40% with P_4S_{10}) and **10c** (light brown powder, 0.1 g, 18% with LR and 12 mg, 2% with P_4S_{10}) in order of elution.

Compound **9c**. Mp 150–152°C. [Found: C, 35.24; H, 1.56. $C_{11}H_5BrS_5$ requires C, 35.0, H, 1.32%]; ν_{max}(KBr) 1059 (C=S) cm^{-1}; δ_H (270 MHz) 7.52 (2H, d, J=8.8 Hz, Ar), 7.41 (2H, d, J=8.8 Hz, Ar), 6.68 (1H, s, =C*H*); δ_C 214.6 (*C*=S), 141.2, 133.9, 132.1, 129.3, 128.8, 124.1, 118.4; *m*/*z* (EI) 377 (M^+).

4.1.10. 6-(4-Bromophenyl)thieno[2,3-*d*][1,3]dithiole-2-thione (10c). Mp 120–123°C. [Found: C, 38.62; H, 1.36. $C_{11}H_5BrS_4$ requires C, 38.26, H, 1.45%]; ν_{max}(KBr) 1050 (C=S) cm^{-1}; δ_H (270 MHz) 7.58 (2H, d, J=8.6 Hz, Ar), 7.42 (2H, d, J=8.6 Hz, Ar), 7.28 (1H, s, =C*H*); δ_C 213.7 (*C*=S), 148.6, 139.2, 132.4, 131.7, 132.4, 128.1, 127.1, 115.9; *m*/*z* (EI) 345 (M^+).

4.1.11. 2,5-Di(bromophenyl)thiophene (14). Mp 155–157°C. [Found: C, 48.55, H, 2.32. $C_{16}H_{10}Br_2S$ requires C, 48.73, H, 2.53%]; δ_H 7.49 (8H, 2×d, J=10.2, 9.1 Hz, Ar), 7.25 (2H, s, thiophene); δ_C 143 (q*C*) 133 (q*C*) 132 (*C*H), 127 (*C*H), 125 (*C*H), 122 (q*C*). HRMS (EI): M^+, found 393.8852. $C_{16}H_{10}Br_2S$ requires 393.8849.

The following was similarly produced.

4.1.12. 5-Methyl[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-thione (9d). Orange powder, 0.40 g, 52% with LR and 38 mg, 5% with P_4S_{10}, mp 100–102°C. [Found: C, 30.62, H, 1.40. $C_6H_4S_5$ requires C, 30.50, H, 1.69%]; ν_{max}(Nujol) 1061 (C=S) cm^{-1}; δ_H 6.19 (1H, s, =C*H*), 2.19 (3H, s, CH_3); δ_C 213.8 (*C*=S), 138 (q*C*), 128.4 (q*C*), 116.8 (*C*H), 22.3 (*C*H_3); *m*/*z* (FAB, NOBA matrix) 236 (M^+).

4.1.13. 5-Phenyl[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-one (27a). A mixture of **9a** (0.50 g, 1.67 mmol) dissolved in $CHCl_3$ (20 mL), mercuric acetate (1.33 g, 4.18 mmol) and glacial acetic acid (10 mL) was stirred at room temperature for 1 h. The mixture was filtered through celite and the filtrate was extracted with sodium carbonate solution (2×50 mL) and water (2×50 mL). The organic layer was dried over sodium sulphate, filtered and the solvent was evaporated under reduced pressure to give the title compound **27a** (0.37 g, 90%) as a white powder, mp 105–108°C. [Found: C, 46.51, H, 1.98. $C_{11}H_6OS_4$ requires C, 46.80, H, 2.12%]; ν_{max}(Nujol) 1665 (C=O) cm^{-1}; δ_H (270 MHz) 7.55 (2H, m, Ar), 7.38 (3*b* H, m, Ar), 6.64 (1H, s, =C*H*); δ_C 191.9 (*C*=O), 142.0, 135.2, 129.6, 128.8, 128.6, 127.4, 125.4, 117.0; *m*/*z* (EI) 282 (M^+).

The following were similarly produced.

4.1.14. 5-(4-Methoxyphenyl)[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-one (27b). White powder (0.42 g, 90%), mp 146–148°C. [Found: C, 46.51, H, 2.65. $C_{12}H_8O_2S_4$ requires C, 46.15, H, 2.56%]; ν_{max}(Nujol) 1670 (C=O) cm^{-1}; δ_H (270 MHz) 7.50 (2H, d, J=9.0 Hz, Ar), 6.90 (2H, d, J=9.0 Hz, Ar), 6.50 (1H, s, =C*H*), 3.83 (3H, s, OCH_3); δ_C 192.0 (*C*=O), 160.7, 142.3, 128.9, 127.6, 119.4, 114.5, 114.2, 114, 55.4; *m*/*z* (EI) 312 (M^+).

4.1.15. 5-(4-Bromophenyl)[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-one (27c). White powder (0.40 g, 85%), mp 135–137°C. [Found: C, 36.71; H, 1.23. $C_{11}H_5BrOS_4$ requires C, 36.56, H, 1.38%]; ν_{max}(Nujol) 1660 (C=O) cm^{-1}; δ_H 7.50 (2H, d, J=8.7 Hz, Ar), 7.40 (2H, d, J=8.7 Hz, Ar), 6.60 (1H, s, =C*H*); *m*/*z* (EI) 361 (M^+).

4.1.16. 5-Methyl[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-one (27d). White powder (0.41 g, 93%), mp 73–76°C. [Found: C, 32.60; H, 1.63. $C_6H_4OS_4$ requires C, 32.72, H, 1.81%]; δ_H 6.17 (1H, s, =CH), 2.20 (3H, s, CH_3); δ_C 195.0 (C=O), 137.7 (qC), 119.0 (qC), 116.7 (CH), 107.0 (qC), 22.2 (CH_3); *m*/*z* (EI) 220 (M^+).

4.1.17. 6-Phenylthieno[2,3-*d*][1,3]dithiol-2-one (28a). A mixture of **10a** (0.20 g, 0.75 mmol) dissolved in $CHCl_3$ (20 mL), mercuric acetate (0.60 g, 1.9 mmol) and glacial acetic acid (6.25 mL) was stirred at room temperature for 1 h. The mixture was filtered through celite and the filtrate was extracted with sodium carbonate solution (2×50 mL) and water (2×50 mL). The organic layer was dried over sodium sulphate, filtered and the solvent was evaporated under reduced pressure to give the title compound **28a** (0.13 g, 70%) as a white powder, mp 113–115°C. [Found: C, 52.51, H, 2.78. $C_{11}H_6O_2S_3$ requires C, 52.59, H, 2.79%]; δ_H (270 MHz) 7.52 (2H, m, Ar), 7.38 (3H, m, Ar), 7.34 (1H, s, =C*H*); δ_C 193.4 (*C*=O), 146.1 (q*C*), 129.8 (q*C*), 128.6 (*C*H), 127.8 (*C*H), 126.8 (*C*H), 116.9 (*C*H); *m*/*z* (EI) 251 (M^+).

The following were similarly produced.

4.1.18. 6-(4-Methoxyphenyl)thieno[2,3-*d*][1,3]dithiol-2-one (28b). White powder, 70 mg, 35%, mp 185–187°C. [Found: C, 48.50, H, 2.75. $C_{11}H_5BrOS_3$ requires C, 48.64, H, 2.70%]; δ_H (270 MHz) 7.54 (2H, d, J=9.0 Hz, Ar), 7.14 (1H, s, =C*H*), 6.91 (2H, d, J=9.0 Hz, Ar), 3.84 (3H, s, OCH_3); δ_C 194.6 (*C*=O), 159.2 (q*C*), 142.7 (*q*C), 127.2 (q*C*), 126.8 (*C*H), 122.9 (*C*H), 114.7 (*C*H), 55.4 (OCH_3); *m*/*z* (EI) 296 (M^+).

4.1.19. 6-(4-Bromophenyl)thieno[2,3-*d*][1,3]dithiol-2-one (28c). White powder, 0.16 g, 84%, mp 158–160°C. [Found: C, 39.92, H, 1.65. $C_{11}H_5BrOS_3$ requires C, 40.12, H, 1.52%]; δ_H (270 MHz) 7.53 (2H, d, J=8.5 Hz, Ar), 7.39 (2H, d, J=8.5 Hz, Ar), 7.29 (1H, s, =C*H*); δ_C 191.5 (*C*=O), 144.6 (q*C*), 132.4 (*C*H), 131.8 (q*C*), 128.3 (q*C*), 127.1 (*C*H), 122.5 (q*C*), 117.3 (*C*H); *m*/*z* (FAB, NOBA matrix) 330 (M^++1).

4.1.20. 2-[4,5-Di(methylsulfanyl)-1,3-dithiol-2-ylidene]-5-phenyl[1,3]dithiolo[4,5-*b*][1,4]dithiin (30a). A mixture

of oxo compounds **27a** (0.22 g, 0.8 mmol) and **29** (0.13 g, 0.9 mmol) was heated in freshly distilled $(EtO)_3P$ (20 mL) under N_2 atmosphere at 110°C for 3 h. The precipitate was filtered and $(EtO)_3P$ was distilled off under reduced pressure. The precipitate was characterized as **31a** and the residue was separated by column chromatography eluting with hexane/CH_2Cl_2 (2/1). The first three fractions were characterized as **32** (32 mg, 19%), the title compound **30a** (47 mg, 22%) and more **31a** (76 mg, 18%). The desired cross-coupling product **30a** was recrystallized from ethanol to give bright yellow needles, mp 54–56°C. [Found: C, 41.35, H, 2.43. $C_{16}H_{12}S_8$ requires C, 41.70, H, 2.60%]; δ_H (270 MHz) 7.44 (2H, s, Ar), 7.28 (3H, s, Ar), 6.52 (1H, s, =C*H*), 2.35 (6H, s, CH_3); δ_C 142.3, 135.4, 129.3, 128.9, 128.7, 128.7, 128.6, 127.2, 118.6, 19.3 (*C*H_3); *m/z* (EI) 460 (M^+). **31a** Light brown powder. [Found: C, 49.24, H, 2.07. $C_{22}H_{12}S_8$ requires C, 49.60, H, 2.25%]; δ_H (270 MHz) 7.53 (4H, m, Ar), 7.37 (6H, m, Ar), 6.61 (2H, s, =C*H*); δ 142.4, 135.4, 129.4, 128.8, 127.2, 121.4, 121.2, 118.6; *m/z* (EI) 532 (M^+).

The following were similarly produced.

4.1.21. 2-[4,5-Di(methylsulfanyl)-1,3-dithiol-2-ylidene]-5-(4-methoxyphenyl)[1,3]dithiolo[4,5-*b*][1,4]dithiin (30b). The residue was separated by column chromatography eluting with hexane/CH_2Cl_2 (1/1). The middle fraction gave the title compound **30b** as bright yellow needles (78 mg, 23%, recrystallized from ethanol), mp 110–118°C. [Found: C, 41.45, H, 2.52. $C_{17}H_{14}OS_8$ requires C, 41.60, H, 2.85%]; δ_H (270 MHz) 7.50 (2H, d, *J*=9.0 Hz, Ar), 6.87 (2H, d, *J*=9.0 Hz, Ar), 6.45 (1H, s, =C*H*), 3.80 (3H, s, OCH_3), 2.40 (6H, s, 2×CH_3); δ_C 149.9, 142.4, 128.8, 128.6, 127.8, 121.4, 116.6, 116.0, 114.2, 114.1, 55.4 (O*C*H_3), 19.3 (S*C*H_3); *m/z* (EI) 490 (M^+); *m/z* (FAB, NOBA matrix) 490 (M^+). **31b** (third fraction) Yellow powder (31 mg, 15%). [Found: C, 48.50, H, 2.58. $C_{24}H_{16}O_2S_8$ requires C, 48.64, H, 2.70%]; δ_H (270 MHz) 7.49 (2H, d, *J*=8.8 Hz, Ar), 6.87 (2H, d, *J*=8.8 Hz, Ar), 6.46 (1H, s, =C*H*); δ_H (DMSO-d_6, 270 MHz) 7.54 (2H, d, *J*=8.8 Hz, Ar), 6.98 (2H, d, *J*=8.8 Hz, Ar), 7.05 (1H, s, =C*H*); HRMS (EI): M^+, found 591.8928. $C_{24}H_{16}O_2S_8$ requires 591.8916.

4.1.22. 5-(4-Bromophenyl)-2-[4,5-di(methylsulfanyl)-1,3-dithiol-2-ylidene][1,3]dithiolo[4,5-*b*][1,4]dithiin (30c). The residue was separated by column chromatography eluting with hexane/CH_2Cl_2 (2/1). The first fraction gave the title compound **30c** as yellow needles (80 mg, 25%, recrystallized from ethanol), mp 153–155°C. [Found: C, 35.60, H, 2.04. $C_{16}H_{11}BrS_8$ requires C, 35.25, H, 2.22%]; δ_H 7.50 (2H, d, *J*=8.6 Hz, Ar), 7.40 (2H, d, *J*=8.6 Hz, Ar), 6.61 (1H, s, =C*H*), 2.40 (6H, s, CH_3). HRMS (EI): M^+, found 537.7820. $C_{16}H_{11}BrS_8$ requires 537.7809. **31c** (third fraction) Yellow powder (41 mg, 16%). [Found: C, 38.26, H, 1.45. $C_{22}H_{10}Br_2S_8$ requires C, 38.45, H, 1.53%]; δ_H (DMSO-d_6, 270 Hz) 7.57 (2H, d, *J*=7.2 Hz, Ar), 7.54 (2H, d, *J*=7.2 Hz, Ar), 7.24 (1H, s, =C*H*); *m/z* (EI) 690 (M^+).

4.1.23. 2-[4,5-Di(methylsulfanyl)-1,3-dithiol-2-ylidene]-5-methyl[1,3]dithiolo[4,5-*b*][1,4]dithiin (30d). Orange powder (80 mg, 20%), [Found: C, 33.26, H, 2.21. $C_{11}H_{10}S_8$ requires C, 33.16, H, 2.51%]; δ_H 6.09 (1H, s, =C*H*), 2.10 (9H, s, 3×CH_3); δ_H 137.9 (q*C*), 127.3 (q*C*), 120.1 (q*C*), 117.3 (*C*H), 114.3 (q*C*), 22.2 (*C*H_3), 19.3 (2×S*C*H_3); *m/z* (EI) 398 (M^+).

4.1.24. 2-(5,6-Dihydro[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-5-(4-methoxyphenyl)[1,3]dithiolo[4,5-*b*][1,4]dithiin (34b). A mixture of **27b** (0.10 g, 0.32 mmol) and **33** (0.10 g, 0.48 mmol) was heated in freshly distilled $(EtO)_3P$ (20 mL) under N_2 atmosphere at 110°C for 3 h. The precipitate was filtered and $(EtO)_3P$ was distilled off in vacuo. The residue was separated by column chromatography eluting with hexane/CH_2Cl_2 (1/1). The second fraction gave the title compound **34b** as an orange powder (31 mg, 20%), mp 165–167°C. [Found: C, 41.66, H, 2.51. $C_{17}H_{12}OS_8$ requires C, 41.80, H, 2.46%]; δ_H (270 MHz) 7.47 (2H, d, *J*=8.7 Hz, Ar), 6.87 (2H, d, *J*=8.7 Hz, Ar), 6.72 (1H, s, =C*H*), 3.81 (3H, s, CH_3); HRMS (EI): M^+, found 487.8659. $C_{17}H_{12}OS_8$ requires 487.8653.

The following were similarly produced.

4.1.25. 2-(5,6-Dihydro[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-5-(4-bromophenyl)[1,3]dithiolo[4,5-*b*][1,4]dithiin (34c). The residue was separated by column chromatography eluting with hexane/CH_2Cl_2 (2/1). The second fraction gave the title compound **34c** as an orange powder (29 mg, 18%), mp 173–175°C. [Found: C, 35.48, H, 1.56. $C_{16}H_9BrS_8$ C, 35.75, H, 1.67%]; δ_H (270 MHz) 7.48 (2H, d, *J*=6.7 Hz, Ar), 7.4 (2H, d, *J*=6.7 Hz, Ar), 6.61 (1H, s, =C*H*) 3.30 (4H, s, 2×CH_2); HRMS (EI): M^+, found 537.7586. $C_{16}H_9BrS_8$ requires 537.7632.

4.1.26. 2-(5,6-Dihydro[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-5-methyl[1,3]dithiolo[4,5-*b*][1,4]dithiin (34d). The residue was separated by column chromatography eluting with hexane/CH_2Cl_2 (2/1). The second fraction gave the title compound **34d** as an orange powder (27 mg, 15%), mp 207–210°C. [Found: C, 33.25, H, 1.99. $C_{11}H_8S_8$ requires C, 33.33, H, 2.02%]; δ_H (270 MHz) 6.53 (1H, s, =C*H*), 3.23 (4H, s, 2×CH_2), 2.11 (3H, s, CH_3); HRMS (EI): M^+, found 395.8393. $C_{11}H_8S_8$ requires 395.8391.

4.1.27. 2-[4,5-Di(methylsulfanyl)-1,3-dithiol-2-ylidene]-6-phenylthieno[2,3-*d*][1,3]dithiole (35a). A mixture of oxo compounds **28a** (0.12 g, 0.48 mmol) and **29** (0.15 g, 0.72 mmol) was heated in freshly distilled $(EtO)_3P$ (20 mL) under N_2 atmosphere at 110°C for 3 h. The precipitate was filtered and $(EtO)_3P$ was distilled off under reduced pressure. The residue was separated by column chromatography eluting with hexane/CH_2Cl_2 (2/1). The first fraction gave **35a** as bright yellow needles (0.04 g, 20%, recrystallized from ethanol), mp 145–147°C. [Found: C, 45.10, H, 2.53. $C_{16}H_{12}S_7$ requires C, 44.85, H, 2.80%]; δ_H (270 MHz) 7.43 (2H, m, Ar), 7.35 (3H, m, Ar), 7.05 (1H, s, =C*H*), 2.44 (6H, s, 2×CH_3); δ_C 129.0 (*C*H), 128.0 (*C*H), 125.2 (*C*H), 116.2 (*C*H), 19.2 (*C*H_3); HRMS (EI): M^+, found 427.8986. $C_{16}H_{12}S_7$ requires 427.8984.

The following were similarly produced.

4.1.28. 2-[4,5-Di(methylsulfanyl)-1,3-dithiol-2-ylidene]-6-(4-methoxyphenyl)thieno[2,3-*d*][1,3]dithiole (35b).

$(EtO)_3P$ was distilled off under reduced pressure and the mixture was separated by column chromatography eluting with hexane/CH_2Cl_2 (2/1). The second fraction gave the title compound **35b** as an orange powder (35 mg, 19%), mp 157–160°C. [Found: C, 44.14, H, 2.98. $C_{17}H_{14}OS_7$ requires C, 44.54, H, 3.05%]; δ_H (270 MHz) 7.40 (2H, d, J=8.7 Hz, Ar), 6.92 (2H, d, J=8.7 Hz, Ar), 6.88 (1H, s, =C*H*), 3.83 (3H, s, OCH_3), 2.44 (6H, s, 2×SCH_3); δ_H 126.7, 122.9, 114.5, 114.4, 55.4 (OCH_3), 19.2 (2×SCH_3); HRMS (EI): M^+, found 457.9103. $C_{17}H_{14}OS_7$ requires 457.9089. **36b+37b** (mixture, third fraction, 30 mg, 16%). [Found: C, 54.65, H, 3.19. $C_{24}H_{16}O_2S_6$ requires C, 54.54, H, 3.03%]; δ_H (270 MHz) 7.53 (4H, d, J=8.9 Hz, Ar), 6.93 (4H, d, J=8.9 Hz, Ar), 7.16 (2H, s, =C*H*), 7.14 (2H, s, =C*H*), 3.83 (6H, s, OCH_3); *m/z* (EI) 528 (M^+).

4.1.29. 6-(4-Bromophenyl)-2-[4,5-di(methylsulfanyl)-1,3-dithiol-2-ylidene]thieno[2,3-*d*][1,3]dithiole (35c). The mixture was separated by column chromatography eluting with hexane/ethyl acetate (7/3). The second fraction gave the title compound **35c** as a light orange powder (40 mg, 22%), mp 208–210°C. [Found: C, 38.05, H, 2.39. $C_{16}H_{11}S_7Br$ requires C, 37.86, H, 2.17%]; δ_H (THF-d_8, 270 MHz) 7.54 (2H, d, J=7.8 Hz, Ar), 7.47 (2H, d, J=7.8 Hz, Ar), 7.36 (1H, s, =C*H*), 2.57 (6H, s, 2×SCH_3); δ_C (THF-d_8) 133 (*C*H), 127.4 (*C*H), 18.9 (S*C*H_3); HRMS (EI): M^+, found 507.8057. $C_{16}H_{11}S_7Br$ requires 507.8068.

4.1.30. 2-[6-(4-Methoxyphenyl)thieno[2,3-*d*][1,3]dithiol-2-ylidene]-5,6-dihydro[1,3]dithiolo[4,5-*b*][1,4]dithiin (38b). The precipitate, which was characterized as ET **2**, was filtered and the mixture was separated by column chromatography eluting with hexane/CH_2Cl_2 (2/1). The first and the second fractions gave ET and the title compound **38b**, respectively, and the third fraction gave a mixture of **36b** and **37b**. **38b** (37 mg, 20%) Light yellow powder, mp 177–179°C. [Found: C, 44.85, H, 2.59. $C_{17}H_{12}OS_7$ requires C, 44.73, H, 2.63%]; δ_H (270 MHz) 7.54 (2H, d, J=8.7 Hz, Ar), 7.13 (1H, s, =C*H*), 6.92 (2H, d, J=8.7 Hz, Ar), 3.83 (3H, s, OCH_3), 2.07 (4H, brs, 2×CH_2); *m/z* (EI) 456 (M^+).

4.2. X-Ray analyses of 11

$C_{18}H_{12}S_3$, M_r=324.9, monoclinic, a=30.4496(4) Å, b=6.0673(8) Å, c=8.1449(10) Å, β=95.16(1)°, V=1498.6 Å^3, Cc, Z=4, D_c=1.43 g cm^{-3}, μ(Mo Kα)=4.8 cm^{-1}, T=150 K, R(int)=0.048, 1484 independent reflections, final $R1$=0.093 for 1297 reflections with $F>4\sigma(F)$. Very thin crystals were grown from toluene. Data was collected by the EPSRC X-ray crystallography service, using a Enraf Nonius FAST system. The structure was solved with SHELXS-97[22] and refined with SHELXL-97.[23] Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 214528. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Rd, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or email: deposit@ccdc.cam.ac.uk).

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