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4,5-Diformyl-1,3-dithiol-2-ylidene substituted ethanals or ethanones and vinylogs of tetraformyltetrathiafulvalene from acetylenedicarbaldehyde and 3-thioxo-1,2-dithioles

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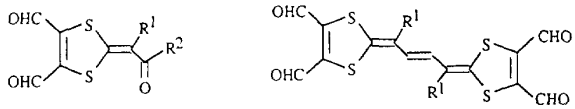
Summary – The cycloaddition of 3-thioxo-1,2-dithioles onto mono-(diEt)-acetal of acetylenedicarbaldehyde gives stable thials or thiones **5′**. The thials are readily converted into **2** by dimerization with loss of sulfur, and the *trans*-configuration at the central C=C bond is demonstrated by UV-visible spectroscopy. For thiones or thials **5(′)**, the conversion of the C=S to C=O group with mercuric acetate-acetic acid leads to trialdehydes **1**. The X-ray structure and spectroscopic studies reveal a *δ-cis* conformation in all our X=S or X=O compounds due to S···S or S···O 1,5-interactions.

cycloaddition / but-2-ynedial / 3-thioxo-1,2-dithiole / intramolecular interaction / TTF

The ability of tetrathiafulvalene (TTF) derivatives to furnish monodimensional (1D) electroconductive salts is now well established [1]. In order to suppress the metal-insulator transitions at low temperature, which are intrinsic to such systems, the design and syntheses of new π-electron donors capable of forming cation-radical salts with higher dimensionality have been intensively studied [2]. Recent efforts include increasing the spatial extension of the donor molecules and/or enriching them with sulfur atoms in order to decrease any coulombic repulsions between charged or polycharged species, and to increase the number of intra- and inter-chain S···S contacts in the corresponding cation-radical salts [3].

In this context, we have recently developed a general synthetic strategy for obtaining new S-rich and spatially extended π-donors, *ie* the bis- and tetrakis-1,4-dithiafulven-6-yl TTFs [4], dihydro-TTFs [4] and vinylogs of TTFs [5]. This strategy involves Wittig-type olefination of polyformyl (di-, tri- or tetra-) TTF derivatives with phosphoranes or phosphonate anions bearing 1,3-dithiol-2-ylidene moieties [6].

In view of the synthetic usefulness of polyaldehydic building blocks in TTF and 1,3-dithiole chemistry, we herein report the full details of the synthesis and characterization of the title compounds **1** and **2**, which are shown in figure 1. Subsequent to our preliminary reports on the synthesis of tetraformyl TTF [7] and TSeF [8], and the title compounds [9], we have found these



1 **2**

Fig 1

species to be excellent precursors to S-rich and spatially extended π-donors.

As shown in figure 2, the common key-step for the preparation of **1** and **2** is the cycloaddition of 3-thioxo-1,2-dithioles **3** to an electrophilic alkyne [10], such as the acetylenedicarbaldehyde (ADCA) **4** or its monoacetal **4′** [11], the latter being easier to handle. The thials **5′** generated in this way can be readily converted into either **1** or **2** *via* standard procedures.

Cycloaddition of 4 or 4′ with 3

In our preliminary experiments, we studied the cycloaddition of **4** [11a] to **3b** [12] in HCO_2H-free dichloromethane, for comparison with the similar reaction employing dimethyl acetylenedicarboxylate [10]. The cycloaddition reaction involving ADCA occurs at much milder conditions (instantaneous at −10 to −20°C)

* Correspondence and reprints

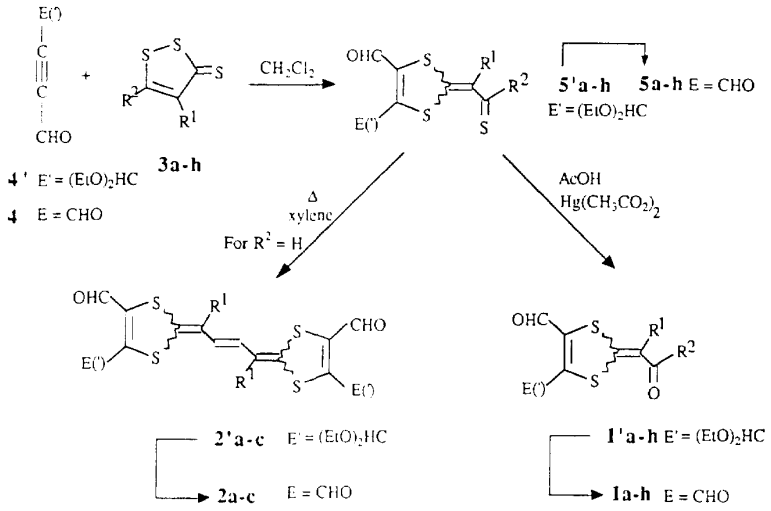


Fig 2. **a**: $R^1 = R^2 = H$; **b**: R^1 = Ph, R^2 = H; **c**: R^1 = pMe-Ph, R^2 = H; **d**: $R^1 = R^2$ = Me; **e**: R^1 = H, R^2 = Ph; **f**: R^1 = H, R^2 = pMeO-Ph; **g**: R^1 = H, R^2 = pBr-Ph; **h**: R^1 = H, R^2 = α-thienyl.

than that with dimethyl acetylenedicarboxylate (3 h at 20°C). In order to avoid a further [4+2] cycloaddition of ADCA to the thial **5b**, it is necessary to slowly add a slightly less (5%) than a molar equivalent of ADCA dissolved in CH_2Cl_2 to a cooled (−10°C) CH_2Cl_2 solution of **3b**.

Given the difficulties inherent in the preparation of acid-free solutions of ADCA (best yields are *ca* 40% from the corresponding bisacetal), we preferred to use the monoacetal **4'** as the starting electrophilic alkyne. Of course, the latter is less electrophilic than the dialdehyde ADCA. For instance, its reaction with **3b** requires 30 min at 20°C for completion, and here too, it is necessary to use a slight excess (10%) of **3** in order to prevent any further cycloaddition of **4'** with the product enethial **5'**.

This cycloaddition reaction is quite general and has been carried out with all of the 3-thioxo-1,2-dithioles **3a–h** listed in figure 2. The corresponding thials **5'a–c** (R^2 = H) and thiones **5'd–h** ($R^2 \neq$ H) were obtained as quite stable solids after evaporation of CH_2Cl_2 and treatment with diethyl ether. They consisted of nearly equal amounts of (*Z*) and (*E*) isomers, and could be stored at 0°C for long periods without any decomposition; yields in **5'** from **4'**: **a** 57%, **b** 71%, **c** 60%, **d** 79%, **e** 75%, **f** 80%, **g** 72%, **h** 65%.

Access to polyformyl vinylogs of TTF 2' and 2

As previously reported in related derivatives [10b], thials **5'a–c** (R^2 = H) dimerize with the loss of sulfur by simply refluxing in xylene solution (N_2 atmosphere), whereas thioketones **5'd–h** do not. A straightforward preparation of **2'a–c** avoiding any prior isolation of **5'** consists of mixing **4'** and **3** (10% excess) in xylene under nitrogen and then refluxing the resulting solution. Compounds **2'** were isolated by SiO_2 column chromatography (CH_2Cl_2 eluent) in 70–80% yields. Depending on the R^1 substituents, compounds **2'** are formed as a mixture of geometric isomers, but with a *trans*-configuration at their central ethylenic linkage (*vide infra*).

The deacetalization was best carried out by Coppola's method [13] using Amberlyst-15 (in acetone/water); the yields are good (80% for **2b** and **2c**) to fair (30% for **2a**). In all cases, only one isomer could be detected in the product, indicating that the central C=C bond in the acetal precursors must have been presented in a single isomeric configuration (either *trans* or *cis*). Since our attempts to grow single crystals suitable for X-ray structure determination were unsuccessful, we were unable to unambiguously assign the configuration of the central C=C bond. Therefore, we decided to use comparative UV-vis spectroscopy by using tetraester **6** as the reference compound.

No truly convincing arguments have been presented so far to assign the configuration of the C=C bond in the tetraester **6** obtained by refluxing dimethyl acetylenedicarboxylate and 3-thioxo-1,2-dithiole [14]. We could chemically ascertain the configuration to be *trans*, since the same compound is produced in one step from fumaric aldehyde or the aldehyde **7** [15] from the corresponding mono(diMe)acetal by bis- or mono-olefination with P-ylids **8** [16] (fig 3).

As expected, the comparison of the electronic spectra of derivatives **2a** and **6**, which differ only by their aldehyde or ester functional groups, reveals a very similar conjugated framework with a slight bathochromic effect for the CO_2Me derivative with respect to the CHO one (fig 4 and table I columns 1 and 2).

By making the same comparison for **2b** and **2c** (table I, columns 3 and 4) the very similar data found are indicative of the occurrence of similar conjugated systems. We could thus conclude that both compounds possess the *trans* configuration at their central CH=CH bond. Moreover, the Ph and *p*-Me-Ph substituents do not significantly modify the degree of conjugation with respect to **2a**, suggesting that their π-system must not interact with that of the rest of molecule. The Ph and *p*-MePh planes are therefore not lying in the same

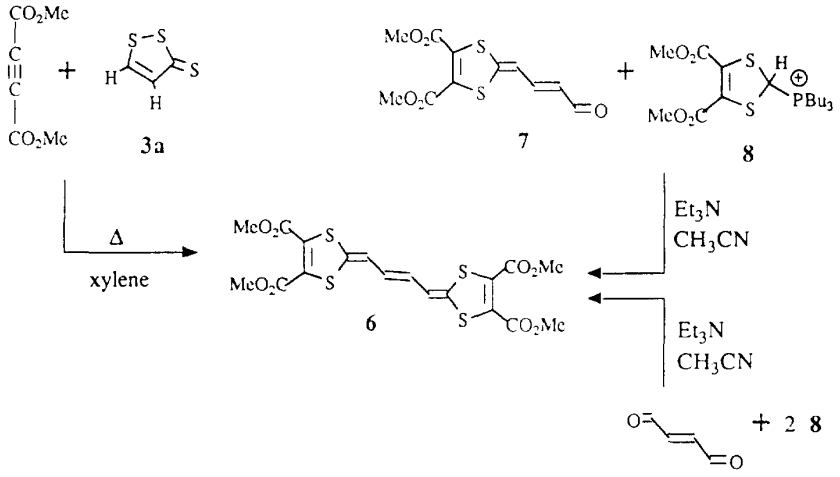


Fig 3

Table I. Comparison of electronic spectra of **2a–c** and **6** in THF.

	6	**2a**	**2b**	**2c**
	R = CO_2Me	R = CHO	R = CHO	R = CHO
	R^1 = H	R^1 = H	R^1 = Ph	R^1 = *p*Me-Ph
λ_1 (nm)	418	413	415	415
λ_2 (nm)	396	391	397	398

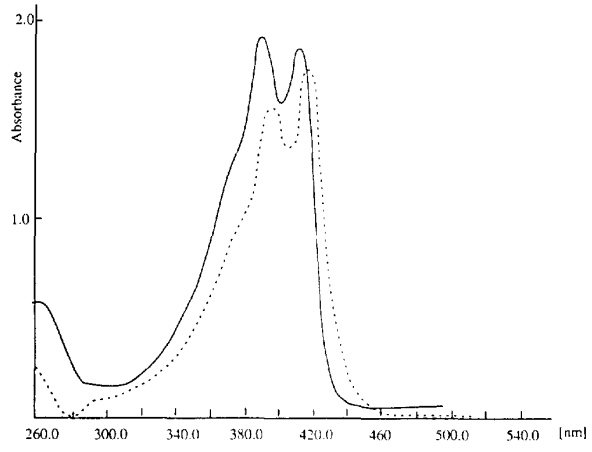


Fig 4. Electronic spectra in THF; solid line for compound **2a**, broken line for compound **6**.

plane as the rest of the molecule. This assumption is in agreement with the results obtained by Kobayashi with vinylogs of TTF substituted with α-thienyl groups, which show that thienyl groups are nearly perpendicular to the 1,3-dithiole ring [17].

The presence of single isomer in **2a–c** was also supported by the formation of one product only, by reacting **2b** or **2c** with hydrazine hydrate in DMF. The corresponding bis-pyridazino derivatives **9b** and **9c** (fig 5) were obtained, whose ^1H NMR spectra exhibit an AX pattern (^5J = 1 Hz) for the CH=N-N=CH units.

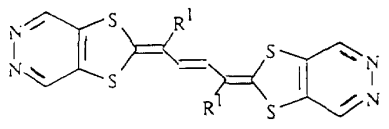


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Fig 5. 9b, R^1 = Ph; **9c**, R^1 = *p*-MePh.

Access to 4,5-diformyl-1,3-dithiol-2-ylidene ethanals and ethanones

The C=S in compounds **5′a–h** was readily converted into a C=O group by use of mercuric acetate/acetic acid in chloroform as the solvent [18]. Upon refluxing **5′** with the mercuric acetate reagent in the presence of a small amount of water, a black inorganic solid precipitates (HgS). Compounds **1′** can be isolated as yellow solids after usual work-up. By performing the same reaction at room temperature, *gem*-diacetate **10**, instead of **1′**, was isolated (fig 6). The *gem*-diacetate undergoes a slow hydrolysis on standing in air, which can be accelerated by adding formic acid dropwise. These results can be rationalized by the mechanistic pathway represented in figure 6. In the first step, soft–soft Hg-S interaction favors the intermolecular contact between **5′** and $Hg(OAc)_2$ allowing their coordination, which is followed by $S^{2-}/2\ AcO^-$ exchange and loss of HgS. Subsequently, hydrolysis (or acidolysis) of *gem*-diacetate **10** gives rise to the expected C=O derivatives **1′**. Note that, in contrast to the *gem*-diacetate functionality, the acetal group is not hydrolyzed (or acidolyzed)

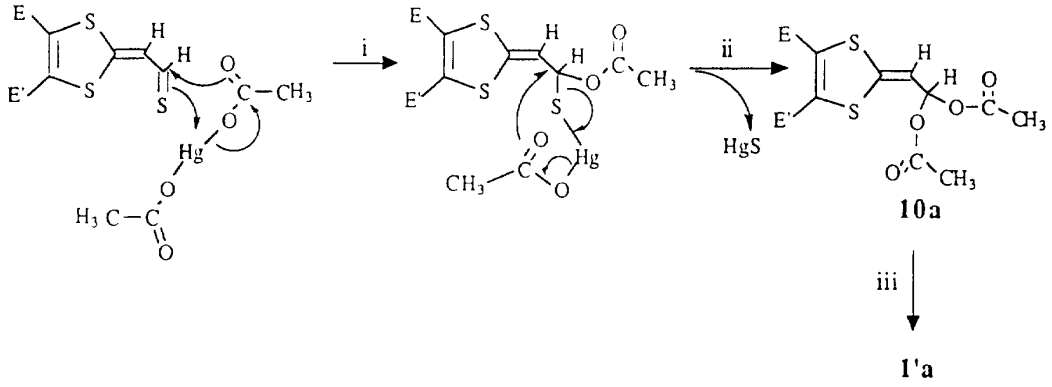


Fig 6. Mechanistic pathway for the conversion of C=S into C=O promoted by $Hg(OAc)_2$-AcOH-$CHCl_3$; (i) soft–soft interaction between Hg and the sulfur of thiocarbonyl; (ii) exchange of S^{2-} by two AcO^- with loss of HgS; (iii) acidolysis of **10**.

by water, acetic acid or dilute formic acid under these conditions.

Generally, monoacetals **1′** obtained as yellow solids were not purified, and were directly subjected to the $E' \rightarrow E$ deacetalization. This was best carried out by treatment with anhydrous formic acid at 20°C. In the case of more stable aromatic ketones **1e–h**, nearly instantaneous conversions were observed by using concentrated $HCO_2H/CHCl_3$ solutions (1/1 vol). For the more sensitive aldehydes **1b,c** more dilute formic acid solutions (1/3 vol) were used and hence longer periods (8 h at rt) were required for completion of the reaction. The highly acid-sensitive derivative **1a** undergoes total degradation even under low concentration conditions, and the conversion **1a′** → **1a** could only be performed by Coppola's method using Amberlyst 15 [13], resulting in a relatively poor yield (20%). Table II summarizes the overall yields of **1** from the monoacetal of acetylenedicarbaldehyde **4′**. They can be regarded as fairly good since they correspond to three successive steps.

Table II. Overall yields in 1 from 4′.

R^1	H	Ph	pMePh	Me	H	H	H	H
R^2	H	H	H	Me	Ph	pMeOPh	pBrPh	α-Thienyl
1	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**
% yield	20*	51	55	56	67	63	61	33

* Best yields; **1a** appears as acid-sensitive and poorly stable.

Structural features of thials 5′ and oxo-derivatives 1 and 1′

Like trithiapentalene [19], and related oxygenated compounds [20], the thials or thioketones **5** and **5′**, and their oxygenated analogs **1** and **1′** are endowed with intramolecular S···S (S···O) 1,5-bonding interactions, implying a much more favored *δ-cis* conformation (fig 7).

The evidence for such a preferred *δ-cis* conformation in all of our compounds (X=S or X=O) in the solid state and in solution could be afforded by X-ray diffraction studies and by spectroscopic studies, respectively.

First, in agreement with the exceptional stability of our thials **5**(′) [21], the X-ray crystal structure of

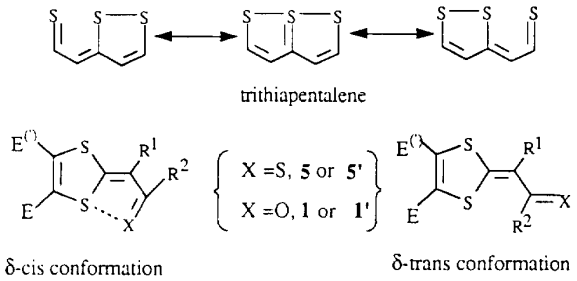


Fig 7. Structural features in **5**(′) and **1**(′).

compound **5′b** revealed a *δ-cis* conformation for the two independent molecules present in the unit cell (fig 8).The three S atoms are in the same plane and very strong S···S bonding 1,5-interactions are observed with the $S_1 \cdots S_2$ and $S_4 \cdots S_5$ lengths of 2.914 (2) Å and 2.932 (2) Å, which are between 3.60 (*ie*, twice the Van der Waals radius of S) and 2.04 Å (the value of a S-S single bond length [22]).

Second, similar kind of internal bonding 1,5-interaction was also found in ketone **1g** [8] with an S···O length of 2.570 Å, between the sum of S and O van der Waals radii (1.8 + 1.5 = 3.3 Å) and the S-O single bond length (1.75 Å) [23]. Note that such an internal interaction may be partly responsible for the lower electrophilicity of the aldehydic carbonyl functionalities. For example, in our attempts at the Wittig-olefination of compound **1a–c**, only the two vicinal aldehyde groups on the 1,5-dithiole ring, could be readily olefinated [5a].

We have also undertaken comparative spectroscopic studies on compounds **7**, **11** [14] and **1a** by ^1H NMR ($CDCl_3$) as well as IR (solid in KBr, or solution in various solvents). The main results are collected in tables III and IV. These also agree with the occurrence of strong S···O 1,5-interactions forcing the *δ-cis* conformation in compounds **1**(′).

Thus, in the ^1H NMR, the presence of weak $^3J_{ab}$ coupling (close to 1.5 Hz) in **11** and **1a** is indicative of *δ-cis* conformation, which can be contrasted with the

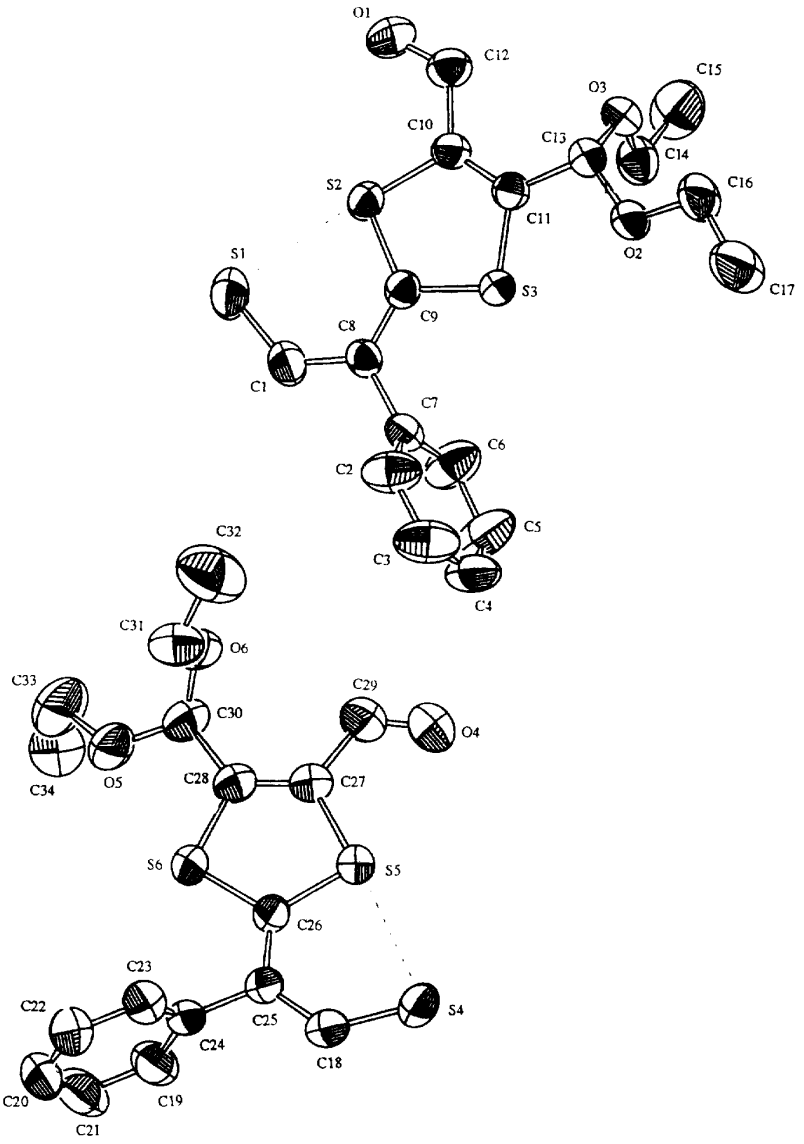


Fig 8. ORTEP view of **5'b**.

larger $^3J_{ab}$ coupling (8 Hz) found in **7**, in which an S···O bonding 1,5-interaction is not possible.

In agreement with previous studies by Mollier *et al* on ketones related to **1** [24], IR spectra also confirm the above conclusions. For example, while the strong peak at 1 664 cm^{-1} in **7** is indicative of a free CHO group without any S···O bonding, the corresponding peaks in **11** and **1a** are less intense and are shifted to 1 625 and 1 635 cm^{-1} as a consequence of intramolecular S···O bonding. Such a decrease in frequency is comparable to that found in other related 1,3-dithiol-2-ylidene ethanones. In table III, the conjugated CH=O group of **7** and the vicinal conjugated groups of **1a** absorb near 1 660 cm^{-1} and are not interacting with S.

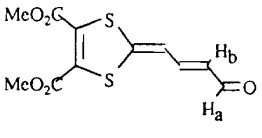
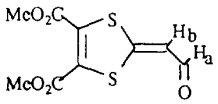
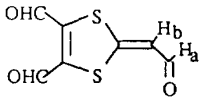
The CHO frequencies of compounds **1** are collected in table IV. These were sometimes difficult to assign because of their possible overlap with those of the aromatic core in the case of aromatic ketones. However, their assignment is possible based on the solvent effects, as reported by Mollier *et al* [24].

All of these results clearly indicate a *δ-cis* conformation in compounds **5**(') and **1**(') resulting from S···S and S···O 1,5-internal interactions. These compounds can actually be regarded as hybrid systems between open and closed resonance contributions. This concept agrees with i) the C=X (X=S or O) reactivity observed here and elsewhere (Wittig reactions) [5a]; ii) the lowering of the electrophilicity with respect to a free C=X group, which is often observed; and iii) the good stability of the thials **5**(').

Conclusion

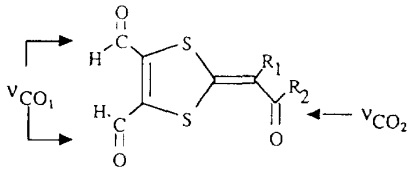
The principal results presented here include a straightforward access to 4,5-diformyl-1,3-dithiol-2-ylidene

Table III. Comparative ^{1}H NMR and IR data for **7**, **11** and **1a**.

	 **7**	 **11**	 **1a**
^{1}H NMR ($CDCl_3$)	δH_a = 9.6 ppm $^3J_{Ha-Hb}$ = 8 Hz	δH_a = 9.48 ppm $^3J_{Ha-Hb}$ = 1.8 Hz	δH_a = 9.5 ppm (1H) $^3J_{Ha-Hb}$ = 1.5 Hz
IR (KBr) 1 800–1 500 cm^{-1}	$\nu_{C=O}$ Ester 1 719–1 709 strong $\nu_{C=O}$ Aldehyde 1 664 strong $\nu_{C=C}$ 1 594 strong 1 570 medium 1 525 medium	$\nu_{C=O}$ Ester 1 739–1 707 strong $\nu_{C=O}$ Aldehyde 1 635 medium $\nu_{C=C}$ 1 577 medium	$\nu_{C=O}$ Aldehyde vic 1 662–1 665 strong $\nu_{C=O}$ Aldehyde 1 625 medium $\nu_{C=C}$ 1 555 medium

ethanals or ethanones involving cycloaddition reaction of 3-thioxo-1,2-dithioles onto acetylenedicarbaldehyde mono-(diEt)-acetal as the key step. The X-ray diffraction and spectroscopic (IR and ^{1}H NMR) study has provided evidence for S···S or S···O 1,5-interactions in compounds **5**(′) and **1**(′), forcing them to adopt a *δ-cis* conformation in the solid state and in solution. All of the new compounds prepared here are of immense synthetic value in the field of TTF chemistry, as has been reported previously [5]. This will be detailed in a forthcoming full paper.

Table IV. IR data of ν_{CO_1} and ν_{CO_2} bands of compounds **1** in KBr.



R_1	R_2	Compound	ν_{CO_1} (strong)	ν_{CO_2} (medium)
H	H	**1a**	1 662–1 652	1 625
Ph	H	**1b**	1 663–1 657	1 630
p-MePh	H	**1c**	1 667–1 655	1 625
Me	Me	**1d**	1 666–1 654	1 604
H	Ph	**1e**	1 660–1 665	1 573
H	*p*-MeOPh	**1f**	1 573 (broad)	1 566
H	*p*-BrPh	**1g**	1 667–1 648	1 570
H	Thienyl	**1h**	1 653 (broad)	1 580

Experimental section

High resolution mass spectra were recorded by P Guénot (Centre de Mesure Physique de l'Ouest, Rennes). The chemical shift are expressed in ppm towards tetramethylsilane as internal reference, and the coupling constants are in Hz. Absorption wave numbers in IR are expressed in cm^{-1}. Elemental analysis results were obtained from the CNRS (Centre d'analyse, Vernaison).

4,5-Disubstituted-1,3-dithiole-2-ylidene ethanethials or ethanethiones **5**(′)

• *Aldehyde-acetal* **5′**

A solution of 1.56 g (10 mmol) of monoacetal of ADCA **4′** in 10 mL of CH_2Cl_2 was added to the 3-thioxo-1,2-dithioles **3** (11 mmol) in 40 mL of CH_2Cl_2. The reaction mixture was stirred for 30 min at room temperature. The black oil obtained after evaporation of the solvent was crystallized by addition of ether. The crude solids were collected by filtration, washed with Et_2O (5 mL) and recrystallized from Et_2O to furnish **5′** as black or green needles, which were a mixture of *Z* and *E* isomers.

5′a, $R^1 = R^2$ = H, yield 57%: mp 98°C (dec).

IR ($CHCl_3$) 1 665 (C=O).

^{1}H NMR ($CDCl_3$) 10.78 and 10.72 (2d, 1H, *J* = 6.8 Hz, CHS), 10.12 and 10.10 (2s, 1H, CHO), 7.80 (d, 1H, S_2C=CH), 5.94 and 5.81 (2s, 1H, acetal), 3.65 (m, 4H, 2 CH_2), 1.24 (m, 6H, 2 CH_3).

5′b, R^1 = Ph, R^2 = H [5-(diethoxymethyl)-2-(1-phenyl-2-thioxoethylidene)-1,3-dithiole-4-carbaldehyde], yield 71%: mp 110°C; $C_{17}H_{18}O_3S_3$, M^+ calc 366.0418, found 366.0415. Anal calc: C 55.70, H 4.95, O 13.09, S 26.24; found: C 55.91, H 4.98, O 13,23, S 26.07.

IR ($CHCl_3$) 1 665 (C=O), 1 580 (arom).

^{1}H NMR ($CDCl_3$) 10.67–10.61 (2s, 1H, CHS), 10.23 and 10.18 (2s, 1H, CHO), 7.44 (m, 5H, H arom), 5.97 and 5.90 (2s, 1H, acetal), 3.67 (m, 4H, 2 CH_2), 1.25 (m, 6H, 2 CH_3).

^{13}C NMR ($CDCl_3$) 203.33 and 203.48 (C=S), 182.64 and 181.60 (HC=O), 159.71 and 158.76 (S_2C), 151.23 and 151.06 (S-*C*[acetal]=C-S), 134.02 and 132.16 (S-C=*C*[CHO]-S), 136.34 and 135.73 (S_2C=*C*), 140.76, 129.60, 128.84, 128.64 (arom).

5′c, R^1 = *p*-Me-Ph, R^2 = H, yield 60%: mp 90-92°C; $C_{18}H_{20}O_3S_3$, M^+ calc 380.05745, found 380.0579.

IR ($CHCl_3$) 1 670 (C=O), 1 585 (arom).

^{1}H NMR ($CDCl_3$) 10.66 and 10.60 (2s, 1H, CHS), 10.23 and 10.18 (2s, 1H, CHO), 7.28 and 7.31 (2s, 4H, H arom), 5.97 and 5.90 (2s, 1H, acetal), 3.67 (m, 4H, 2 CH_2), 2.44 and 2.42 (2s, 3H, CH_3-Ph), 1.25 (m, 6H, 2 CH_3).

5′d, $R^1 = R^2$ = Me, yield 79%: mp 133–134°C; $C_{13}H_{18}O_3S_3$, M^+ calc 318.04180, found 318.0413.

IR (KBr) 1 655 (C=O).

^{1}H NMR ($CDCl_3$) 10.18 and 10.13 (2s, 1H, CHO), 6.03 and 5.83 (2s, 1H, acetal), 3.70 (m, 4H, 2 CH_2), 2.83 (s, 3H, Me), 2.46 and 2.40 (2s, 3H, CH_3), 1.26 (m, 6H, 2 CH_3).

5'e, R^1 = H, R^2 = Ph, yield 75%: mp 87–90°C; $C_{17}H_{18}O_3S_3$, M^+ calc 366.0418, found 366.0415.

IR (KBr) 1 670 (C=O), 1 580 (arom).

^{1}H NMR ($CDCl_3$), 10.21 and 10.20 (2s, 1H, CHO), 8.10 and 8.09 (2s, 1H, =CH), 7.55 (m, 5H, H arom), 6.01 and 5.89 (2s, 1H, acetal), 3.70 (m, 4H, 2 CH_2), 1.30 (m, 6H, 2 CH_3).

5'f, R^1 = H, R^2 = pMeO-Ph, yield 80%: mp 120–121°C; $C_{18}H_{20}O_4S_3$, M^+ calc 396.0523 found 396,0530; anal calc: C 54.52, H 5.08, O 16.13, S 24.25; found: C 54.20, H 5.05, O 16.34, S 23.66.

IR ($CHCl_3$) 1 665 (C=O), 1 600 (arom).

^{1}H NMR ($CDCl_3$), 10.18 and 10.17 (2s, 1H, CHO), 8.08 and 8.12 (2s, 1H, =CH), 7.9–6.9 (AA'BB', 4H, arom), 5.97 and 5.86 (2s, 1H, acetal), 3.82 (s, 3H, MeO), 3.7 (m, 4H, 2 CH_2), 1.30 (m, 6H, 2 CH_3).

5'g, R^1 = H, R^2 = *p*-Br-Ph, yield 72%: mp 128°C; $C_{17}H_{17}O_3S_3Br$ anal calc: C 45.24, H 3.24, O 10,78, S 21.59; found: C 45.55, H 3.75, O 11.20, S 21.48.

IR ($CHCl_3$) 1 665 (C=O), 1 580 (arom).

^{1}H NMR ($CDCl_3$), 10.19 and 10.12 (2s, 1H, CHO), 8.14 and 8.13 (2s, 1H, =CH), 7.60 (AA'BB', 4H, arom), 6.15 and 5.90 (2s, 1H, acetal), 3.82 (s, 3H,MeO), 3.80 (m, 4H, 2 CH_2), 1.20 (m, 6H, 2 CH_3).

5'h, R^1 = H, R^2 = α-thienyl, yield 65%: mp 110–111°C; $C_{15}H_{16}O_3S_4$, M^+ calc 371.99823 found 371.9979.

IR ($CHCl_3$) 1 660 (C=O).

^{1}H NMR ($CDCl_3$), 10.21 and 10.20 (2s, 1H, CHO), 8.13 and 8.12 (2s, 1H, =CH), 7.60 (m, 2H, thienyl), 7.10 (m, 1H, thienyl), 6.00 and 5.85 (2s, 1H, acetal), 3.7 (m, 4H, 2 CH_2), 1.2 (m, 6H, 2 CH_3).

• *Dialdehyde* **5**

■ *Method A: by action of ADCA* **4** *onto* **3**

A neutral solution of ADCA **4** (1.4 mmol) in CH_2Cl_2 is added under nitrogen and in the dark to a solution of **3e** or **3f** in CH_2Cl_2 (10 mmol) cooled to −10°C. The thiones **5e** or **5f** precipitated immediately as black solids and are recrystallized from CH_3CN.

■ *Method B: by formolysis of monoacetal* **5'**

A $CHCl_3$ solution (5 mL) of **5'e** or **5'f** (0.5 mmol) was treated with 10 mL of pure formic acid (99%). The precipitate was filtered off and washed with methanol and Et_2O.

5e, R^1 = H, R^2 = Ph, yield 75%: mp 210°C; $C_{13}H_8O_2S_3$, M^+ calc 292.3995, found 292.4008.

IR (KBr) 1 670 (C=O), 1 580 (arom).

^{1}H NMR (DMSO-d_6), 10.30 (s, 2H, CHO), 8.50 (s, 1H, =CH), 7.40 (m, 5H, arom).

5f, R^1 = H, R^2 = pMeO-Ph, yield 80%: mp 185°C; $C_{14}H_{10}O_3S_3$, M^+ calc 321.9792 found 321.9799; anal calc: C 52.15, H 3.12, O 14.88, S 29.83; found: C 51.80, H 3.10, O 15.05, S 29.96.

IR ($CHCl_3$) 1 665 (C=O), 1 600 (arom).

^{1}H NMR (DMSO-d_6), 10.55 and 10.53 (2s, 2H, CHO), 8.67 (s, 1H, C=CH), 7.50 (AA'BB', 4H, arom), 3.83 (s, 3H, MeO).

^{13}C NMR (DMSO-d_6), 207.38 (C=S), 184.21, 183.02 (HC=O), 159.04 (S_2C), 146.35, 142.33 (S-*C*=*C*-S), 162.38, 137.77, 129.52, 113.80 (arom), 119.46 (S_2C=C), 55.02 (MeO).

4,5-Disubstituted-1,3-dithiole-2-ylidene ethanals or ethanones **1**(')

• *Aldehyde-acetal* **1'**

A solution of 4 mmol of mercuric acetate in 10 mL of glacial acetic acid was added to compounds **5'** (4 mmol) in 40 mL of $CHCl_3$ and the reaction mixture was refluxed 1.5 h. After cooling, the black precipitate was removed by centrifugation and the solution was washed with water, sodium bicarbonate (1 M) and water, and then dried over $MgSO_4$. Evaporation *in vacuo* affords **1'** as an orange-colored oil which was directly acidolysed (*vide infra*). By treatment with Et_2O, compounds **1'e** and **1'f** were isolated as yellow solids which darken at rt.

1'e mixture of *Z* and *E* isomers, R^1 = H, R^2 = Ph, yield 78%: mp 148–150°C; $C_{17}H_{18}O_4S_2$, M^+ calc 350.0646, found 350.0643.

IR (KBr) 1 663 (C=O), 1 585 (arom), 1 570 (C=O).

^{1}H NMR (60 MHz) ($CDCl_3$), 10.20 and 10.10 (2s, 1H, CHO), 7.50 (m, 6H, arom and C=CH), 5.90 and 5.80 (2s, 1H, acetal), 3.80 (m, 4H, CH_2), 1.30 (m, 6H, CH_3).

1'f mixture of *Z* and *E* isomers, R^1 = H, R^2 = *p*MeO-Ph, yield 79%: mp 85°C; $C_{18}H_{20}O_5S_2$, M^+ calc 380.0752, found 380.0744.

IR (KBr): 1 665 (C=O), 1 590 (arom), 1 570 (C=O).

^{1}H NMR (60 MHz) ($CDCl_3$), 10.20 and 10.10 (2s, 1H, CHO), 8.1–7.1 (AA'BB',4H, arom), 7.40 and 7.30 (2s, 1H, C=CH), 5.97 and 5.86 (2s, 1H, acetal), 3.86 (s, 3H, MeO), 3.80 (m, 4H, CH_2), 1.30 (m, 6H, CH_3).

• *Dialdehyde* **1**

■ *Formolysis of* **1'b–d**

A $CHCl_3$ solution (40 mL) of **1'b–d** (4 mmol) was treated with 10 mL of pure formic acid and the reaction mixture was stirred for 12 h at room temperature. The solution was washed with water, sodium bicarbonate (1 N) and water. After drying ($MgSO_4$), the solvent was removed *in vacuo* and the residue chromatographed on a silica column (dichloromethane eluent).

■ *Formolysis of* **1'e–h**

A $CHCl_3$ solution (10 mL) of **1'e–h** (4 mmol) was treated with 15 mL of pure formic acid (99%). The ketones **1e–h** precipitated; they were filtered off and washed with methanol and recrystallized from CH_3CN.

1a, R^1 = R^2 = H, yield 35% from **5'a**: mp 188–190°C; $C_7H_4O_3S_2$, M^+ calc 199.9601 found 199.9608; anal calc: C 41.98, H 2.01, found: C 42.22, H 2.30.

^{1}H NMR ($CDCl_3$) 10.41 (s, 1H, CHO), 10.37 (s, 1H, CHO), 9.54 (d, 1H, J = 1.5 Hz, CHO), 6.72 (d, 1H, J = 1.5 Hz, S_2C=CH).

^{13}C NMR ($CDCl_3$) 183.84 (dd, ^1J = 179 Hz, ^2J = 4, HC-*C*HO), 179.10 (d, ^1J = 189 Hz, *C*HO), 178.90 (d, ^1J = 191 Hz, *C*HO), 155.36 (d, ^2J = 6 Hz, =*C*S_2), 149.34 (d, ^2J = 35 Hz, =*C*-CHO), 145.85 (d, ^2J = 36 Hz, =*C*-CHO), 109.74 (dd, ^1J = 167 Hz, ^2J = 26, =*C*H-CHO).

1b, R^1 = Ph, R^2 = H, yield 72% from **5'b**: mp 115°C; $C_{13}H_8O_3S_2$, M^+ calc 275.9914 found 275.991, anal calc: C 56.50, H 2.91, O 17.36, found: C 55.61, H 2.98, O 17.19.

^{1}H NMR ($CDCl_3$) 10.10 (s, 2H, 2 CHO), 9.50 (s, 1H, CHO), 7.50 (m, 5H, arom).

1c, R^1 = *p*Me-Ph, R^2 = H, yield 92% from **5'c**: mp 132°C; $C_{14}H_{10}O_3S_2$, M^+ calc 290.0071, found 290.0090, anal

calc: C 57.91, H 3.47, O 16.53, found: C 58.14, H 3.50, O 16.59.

^{1}H NMR ($CDCl_3$) 10.38 and 10.39 (2s, 2H, 2 CHO), 9.46 (s, 1H, CHO), 7.28 (AA'BB', 4H, arom), 2.41 (s, 3H, Me).

^{13}C NMR ($CDCl_3$) 185.48 (HC-*C*HO), 179.65 (*C*HO), 178.19 (*C*HO), 152.35 (=*C*S_2), 149.52 (=*C*-CHO), 145.13 (=*C*-CHO), 139.16, 132.80, 130.37, 128.10 (arom), 124.67 (=*C*Ph-CHO), 23.6 ($PhCH_3$).

1d, $R^1 = R^2$ = Me, yield 71% from **5'd**: mp 204°C; $C_9H_8O_3S_2$, M^+ calc 277.9914, found 277.9921.

^{1}H NMR ($CDCl_3$) 10.40 and 10.35 (2s, 2H, 2 CHO), 2.34 (s, 3H, Me), 2.17 (s, 3H, Me).

1e, R^1 = H, R^2 = Ph, yield 89% from **5'e**: mp 206°C; $C_{13}H_8O_3S_2$, M^+ calc 275.9914, found 275.9911; anal calc: C 56.50, H 2.90, O 17.36, S 23.20, found: C 56.47, H 2.80, O 17.38, S 23,49.

^{1}H NMR (DMSO-d_6) 10.48 (s,2H, 2 CHO), 8.04 (s, 1H, H CH=C), 7.78 (m, 5H, arom).

1f, R^1 = H, R^2 = *p*MeO-Ph, yield 79% from **5'f**: mp 264°C; $C_{14}H_{10}O_4S_2$, M^+ calc 306.002, found 306.0017, anal calc: C 54.88, H 3.29, found: C 54.68, H 3.57.

^{1}H NMR (DMSO-d_6) 10.47 (s, 2H, 2 CHO), 7.86 (s, 1H, CH=C), 8.05–7.05 (AA'BB', 4H, arom), 3.85 (s, 3H, MeO).

1g, R^1 = H, R^2 = *p*Br-Ph, yield 85% from **5'g**: mp 251°C; $C_{13}H_7O_3S_2Br$, M^+ calc 355.9003/^{81}Br, found 355.8999/^{81}Br, anal calc: C 43.95, H 1.99, S 18.05, found: C 43,98, H 2.05, S 18.09.

^{1}H NMR (DMSO-d_6) 10.47 (s, 2H, 2 CHO), 8.03 (s, 1H, CH=C), 7.95–7.76 (AA'BB', 4H, arom).

1h, R^1 = H, R^2 = α-thienyl, yield 51% from **5'h**: mp 229°C; $C_{11}H_6O_3S_3$, M^+ calc 281.9462, found 281.9470, anal calc: C 46.79, H 2.14, 0 16.99, found: C 46.14, H 2.23, O 16,90.

^{1}H NMR (DMSO-d_6) 10.45 (s, 2H, 2 CHO), 8.02 (d, J = 3.8 Hz, 1H, thioph), 7.98 (d, J = 4.9 Hz, 1H, thioph), 7.26 (dd, J = 4.9 Hz and J = 3,8 Hz, 1H, thioph).

^{13}C NMR (DMSO-d_6) 183.3 (*C*HO), 182.7 (*C*HO), 177.6 (*C*=O), 148.3 (=*C*-CHO), 145.8 (=*C*-CHO), 154.6 (=*C*S_2), 144.3, 134.6, 131.5, 134.6 (thioph), 107.5 (S_2C=*C*H).

• gem-*Diacetate* **10a** *or* **10c**

A solution of 1 mmol of mercuric acetate in 5 mL of glacial acetic acid was added to compounds **5'a** or **5'c** (1 mmol) in 20 mL of CH_2Cl_2. The reaction mixture was stirred for 20 min, and the precipitate was removed by centrifugation. The solution was washed with water, sodium bicarbonate (1 M) and water, dried over $MgSO_4$ and finally evaporated. **10a** (after adding a drop of Et_3N) or **10c** were obtained as orange-colored oils which gave **1'a** or **1'b** on treatment with a diluted CH_2Cl_2 solution of formic acid.

10a: mixture of (*Z*) and (*E*) isomers,

^{1}H NMR ($CDCl_3$) 9.85 and 9.75 (2s, 1H, CHO), 7.10 and 7.05 (2d, 1H, J = 7 Hz, *gem*-diacetate), 5.78 (s, 1H, acetal), 5.50 (d, 1H, J = 7 Hz, S_2C=CH), 3.60 (m, 4H, 2 CH_2), 2.00 (s, 6H, CH_3CO), 1.20 (m, 6H, CH_3).

IR ($CHCl_3$) 1 760 (C=O acetyl), 1 660 (C=O aldehyde).

10c: mixture of (*Z*) and (*E*) isomers,

^{1}H NMR ($CDCl_3$) 9.86 and 9.83 (2s, 1H, CHO), 7.23 (s, 1H, H *gem*-diacetate), 7.16 (s, 4H, H arom), 5.70 and 5,63 (2s, 1H, acetal), 3.56 (m, 4H, 2 CH_2), 2.33 (s, 3H, CH_3-Ph), 2.03 (s, 3H, CH_3CO), 1.2 (m, 6H, CH_3).

Vinylogs of TTFs

• *Aldehyde-acetals* **2'**

A xylene (anhydrous, 50 mL) solution of 16.2 mmol of dithiolethione **3** and 16 mmol of monoacetal of ADCA was refluxed under nitrogen (**2a**: 1 h; **2b**: 4 h; **2c**: 3 h). After evaporation of the solvent, the residual oil was chromatographed over silica gel (CH_2Cl_2). Compounds **2'** were obtained as red solids.

2'a; R^1 = H, yield 75%: mp = 110°C; $C_{22}H_{28}O_6S_4$ anal calc: C 51.13, H 5.46, S 24.30, found: C 51.02, H 5.46, S 24.30.

IR (nujol) 1 660 cm^{-1} (C=O).

^{1}H NMR ($CDCl_3$) 9.86 and 9.84 (2s, 2H, CHO), 5.82 (m, 4H, CH=CH), 5.69 (s, 2H, acetal), 3.60 (m, 8H, CH_2), 1.24 (m, 12H, CH_3).

2'b; R^1 = Ph, yield 78%: mp 270°C; $C_{34}H_{36}O_6S_4$, M^+ calc 668.0868, found 668.0888, anal calc: C 61.05, H 5.42, O 14.35, S 19.17 ; found: C 61.31, H 5.41, O 14.19, S 18.56.

IR (nujol) 1 660 cm^{-1} (C=O).

^{1}H NMR ($CDCl_3$) 9.90–9.85 (2s, 2H, CHO), 7.31 (m, 10H, phenyl), 5.90 (s, 2H, CH=C), 5.62 (s, 2H, acetal), 3.62 (m, 8H, CH_2), 1.21 (m, 12H, CH_3).

2'c; R^1 = *p*-Me-Ph, yield 78%: mp 84°C.

IR (nujol) 1 660 cm^{-1} (C=O).

^{1}H NMR ($CDCl_3$) 9.95 and 9.78 (2s, 2H, CHO), 7.24 (m AA'BB', 8H, phenyl), 5.81 (s, 2H, CH=C), 5.61 (s, 2H, acetal), 3.60 (m, 8H, CH_2), 2.43 (s, 6H, Me), 1.13 (m, 12H, CH_3).

• *Tetraaldehydes* **2**

A mixture of **2'** and Amberlyst 15 (0.5 g per mmol of **2'**) in acetone was stirred at room temperature for 1 h. The green solution was filtered off, the solvent was evaporated and the residue was chromatographed over silica gel (CH_2Cl_2) and the green solids were recrystallized from CH_2Cl_2.

2a; R^1 = H, yield 30%: mp > 300°C; $C_{14}H_8O_4S_4$, M^+ calc 367.9305, found 367.9292.

IR (nujol) 1 660 cm^{-1} (C=O).

^{1}H NMR (DMSO-d_6) 10.26 and 10.25 (2s, 4H, CHO), 6.16 (m, 4H, CH=CH).

^{13}C NMR (DMSO-d_6) 182.34 (d, ^1J = 195 Hz, 2 *C*HO), 181.98 (d, ^1J = 195 Hz, 2 *C*HO), 148.65 (d, ^2J = 35 Hz, 2 =*C*-CHO), 147.62 (d, ^2J = 35 Hz, 2 =*C*-CHO), 127.08 (s, 2 =*C*S_2), 126.63 (d, ^1J = 155 Hz, 2 *C*=C-CS_2), 117.42 (d, ^1J = 182 Hz, 2 C=C).

2b; R^1 = Ph, yield 78%: mp 270°C; $C_{26}H_{16}O_4S_4$, M^+ calc 519.9931, found 519.9946, anal calc: C 59.97, H 3.09, O 12.29; found: C 59.78, H 3.01, O 12.18.

IR (nujol) 1 670 cm^{-1} (C=O).

^{1}H NMR (DMSO-d_6) 10.14–10.10 (2s, 4H, CHO), 7.33 (m, 10H, phenyl), 5.80 (s, 2H, HC=C).

^{13}C NMR (DMSO-d_6) 178.27 (2 *C*HO), 178.24 (2 *C*HO), 149.27 (2 =*C*-CHO), 148.57 (2=*C*-CHO), 137.60, 129.73, 129.68, 128.93 (arom), 129.48 (2 *C*=C-CS_2), 128.35 (2 =*C*S_2), 127.59 (2 C=C).

2c; R^1 = *p*-Me-Ph, yield 77%: mp 272°C; $C_{28}H_{20}O_4S_4$, M^+ calc 548.0244, found 548.0230, anal calc: C 61.28, H 3.67, O 11.66; found: C 61.32, H 3.53, O 11.85.

IR (nujol) 1 670 cm^{-1} (C=O).

^{1}H NMR (DMSO-d_6) 10.14 and 10.09 (2s, 4H, CHO), 7.13 (m AA'BB', 8H, phenyl), 5.82 (s, 2H, CH=C), 2.43 (s, 6H, Me).

^{13}C NMR (DMSO-d_6) 178.31 (2 *C*HO), 178.27 (2 *C*HO), 149.30 (2 =*C*-CHO), 148.60 (2=*C*-CHO), 138.89, 134.67, 130.42, 128.73 (arom), 129.67 (2 *C*=C-CS_2), 127.96 (2 =*C*S_2), 127.61 (2 C=C), 21.45 ($PhCH_3$).

• *Bis-pyridazino derivative* **9**

An excess of $N_2H_4 \cdot H_2O$ was dropped into a solution of 0.3 mmol of **2b–c** in CH_2Cl_2 (10 mL). The yellow precipitate was filtered off, washed with CH_2Cl_2 and recrystallized from THF.

9b; R^1 = Ph: mp 286°C; $C_{26}H_{16}N_4S_4$, M^+ calc 512.0257, found 512.0248.

^{1}H NMR (DMSO-d_6) 9.19 (d, ^5J = 1 Hz, 1H, CH=N), 9.08 (d, ^5J = 1 Hz, 1H, CH=N), 7.42 (m, 10H, phenyl), 5.85 (s, 2H, CH=CH).

9c; R^1 = *p*-Me-Ph: mp 300°C; $C_{28}H_{20}N_4S_4$, M^+ calc 540.0570, found 540.0555.

^{1}H NMR (DMSO-d_6) 9.22 (d, ^5J = 1 Hz, 1H, CH=N), 9.11 (d, ^5J = 1 Hz, 1H, CH=N), 7.30 (m AA'BB', 8H, phenyl), 5.92 (s, 2H, CH=CH), 2.41 (s, 6H, Me).

X-ray structure determination

All measurements were made on a Rigaku AFC6S diffractometer with graphite monochromated Mo$K\alpha$ radiation.

Cell constants and an orientation matrix for data collection, obtained from a least squares refinement using the setting angles of 24 carefully centered reflections in the range $33.74 < 2\theta < 37.22°$ correspond to a triclinic cell (table V).

The data were collected at a temperature of 24 ± 1°C using the $\omega - 2\theta$ scan technique to a maximum 2θ value of 50.1°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.34° with a take-off angle of 2.8°. Scans of $(1.37 + 0.30 \tan \theta)°$ were made at a speed of 4.0°/min (in omega). The weak reflections ($I < 4.0\sigma(I)$) were rescanned (maximum of 2 rescans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to backround counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 400.00 mm.

Of the 6 802 refections which were collected, 6 430 were unique (R_{int} = 0.026). The intensities of three representative reflections which were measured after every 150 reflections declined by −2.60%. A linear correction factor was applied to the data to account for this phenomenon.

The linear absorption coefficient for Mo$K\alpha$ is 4.0 cm^{-1}. An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.94 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by the direct method. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 4 329 observed reflections ($I > 3.00\sigma(I)$) and 414 variable parameters and converged with unweighted and weighted agreement factors of:

$$R = \Sigma \mid (\mid F_o \mid - \mid F_c \mid) \mid / \Sigma \mid F_o \mid = 0.047$$

$$Rw = [(\Sigma w(\mid F_o \mid - \mid F_c \mid)^2 / \Sigma F_o^2]^{1/2} = 0.051$$

The standard deviation of an observation of unit weight was 1.97. The weighting scheme was based on counting statistics and included a factor (p = 0.03) to weight the intense reflections. Plots of Σ w $(\mid F_o \mid - \mid F_c \mid)^2$ *versus* $\mid F_o \mid$, reflection order in data collection, $\sin\theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.42 and −0.29 e$^-$/Å^3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber. Anomalous dispersion effects were included in F_{calc}; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer. All calculations were performed using the TEXSAN crystallographic software package of the Molecular Structure Corporation.

Table V. Crystal data for compound **5'b**.

Empirical formula	$C_{17}S_3O_3H_{18}$
Formula weight	365.50
Crystal system	Triclinic
Lattice parameters	a = 10.808 (2) Å
	b = 17.912 (4) Å
	c = 9.798 (2) Å
	α = 102.16 (2)°
	β = 90.82 (2)°
	γ = 79.05 (2)°
	V = 1 819.9 (6) Å^3
Space group	$P\bar{1}$
Z value	4
D_{calc}	1.334 g/cm^3
F (000)	764
μ (Mo$K\alpha$)	4.0 cm^{-1}
Radiation	Mo$K\alpha$
Scan	$\omega - 2\theta$
$2\theta_{max}$	50.1°
Reflections measured	Total 6 802
	Unique 6 430 (R_{int} = 0.026)
Reflections observed	
($I > 3\sigma(I)$)	4 329
Variable	414
Reflection/parameter ratio	10.46
Residuals	R = 0.047
	Rw = 0.051

Supplementary material

X-ray characterization data for **5'b** including tables of distances and angles, fractional atomic coordinates, thermal parameters; calculated and observed structure factors (25 pages) have been deposited with the British Library, Document Supply Center at Boston Spa, Wetherby, West Yorkshire, LS23 7BQ, UK, as supplementary publication N° = SUP 90391 and are available on request from the Document Supply Centre.

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