Pergamon

Tetrahedron, Vol. 53, No. 30, pp. 10441-10450, 1997
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0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00655-8

Cycloaddition of $Bu_3P{\bullet}CS_2$: Formation of Extended bis- and tris-1,3-Dithiolanes and Dithiolane-Containing Polymers

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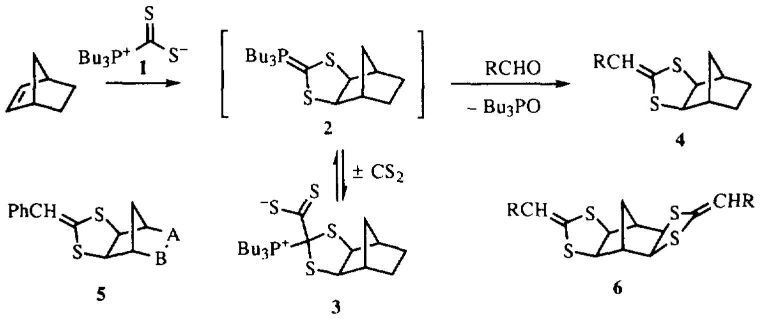
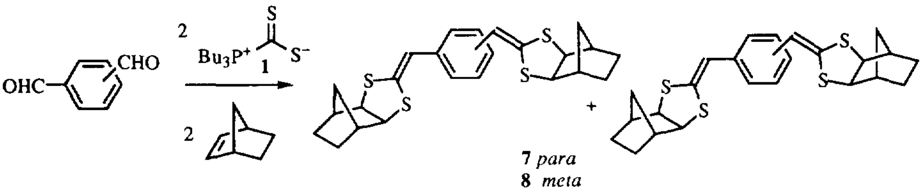
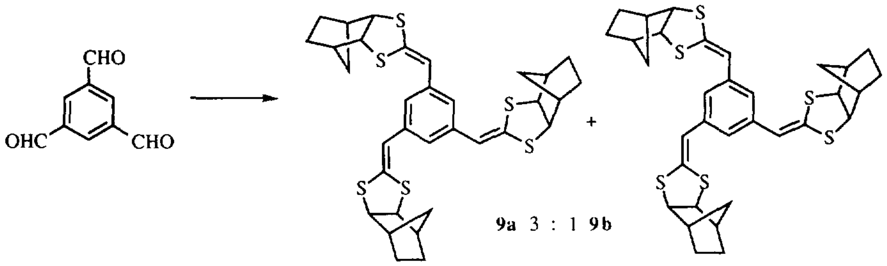
Abstract: Reaction of the tri-*n*-butylphosphine/carbon disulfide adduct **1** with norbornene and aromatic di- and trialdehydes gives the bis- and tris-dithiolanes **7-9** resulting from Wittig reaction of **2**. In the same reaction, norbornadiene diester **10** reacts only on the unsubstituted double bond to give bis-dithiolanes **11** and **12**, while norbornadiene itself reacts on both double bonds to give novel dithiolane-containing polymers **13-15**. In the bis-dithiolane **16** derived from reaction of **1**, norbornene and phthalaldehyde, the groups interact leading to cyclisation so that only the spiroindane isomer **17** is obtained and its X-ray crystal structure is presented. In the reaction of **1**, **10** and phthalaldehyde the initial product **21** can be observed but it similarly cyclises upon acid catalysis to afford **22**. By treatment of **21** with HBF_4 followed by Et_3N the opposite stereoisomer **23** is mainly obtained in addition to **22**.

In a recent paper[2] we described the reaction of the readily formed crystalline adduct **1** of tri-n-butylphosphine and CS_2 with strained C=C double bonds such as that in norbornene to afford the unusual zwitterionic adduct **3**. Although stable in the solid state, this dissociates significantly in solution by loss of CS_2 to generate the phosphorane **2**, so that performing the reaction in the presence of an aldehyde affords the Wittig product **4** directly. The reaction was extended to a variety of other bicyclo[2.2.1]alkenes to give **5** and to norbornadiene to give **6**. We now report that by using di- and tri-aldehydes, a range of extended and polymeric 1,3-dithiolanes can be obtained.

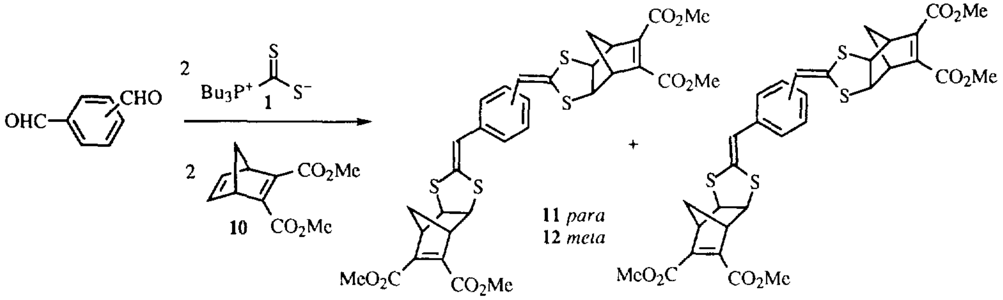


Reaction of two equivalents of both **1** and norbornene with terephthalaldehyde in CH_2Cl_2 at RT for 24 h gave the expected product **7** which could be filtered off directly from the reaction mixture in 82% yield. Use of isophthalaldehyde likewise afforded the *meta* isomer **8** albeit in a lower yield of 34%. By using a 3:1 ratio of **1** and norbornene to mesitaldehyde the trifunctional product **9** was similarly obtained. These compounds all gave satisfactory analytical and spectroscopic data and their ^{13}C NMR spectra formed a highly consistent pattern (Table 1). It is clear that the aldehyde functions in all three cases react independently and so both **7** and **8** exist as mixtures of isomers which do not differ spectroscopically. In **9** the two isomers were formed in the statistically expected 3:1 ratio and this could be confirmed since some ^{13}C NMR signals did differ between the two isomers.





The norbornadiene diester **10**, readily obtained by cycloaddition of DMAD with cyclopentadiene, reacted only on the unsubstituted double bond with **1** and either terephthalaldehyde or isophthalaldehyde to give **11** and **12** respectively. Again these were formed as 1:1 mixtures of isomers and in this case some of the ^{13}C NMR signals did differ between the isomers of **12** (Table 1).



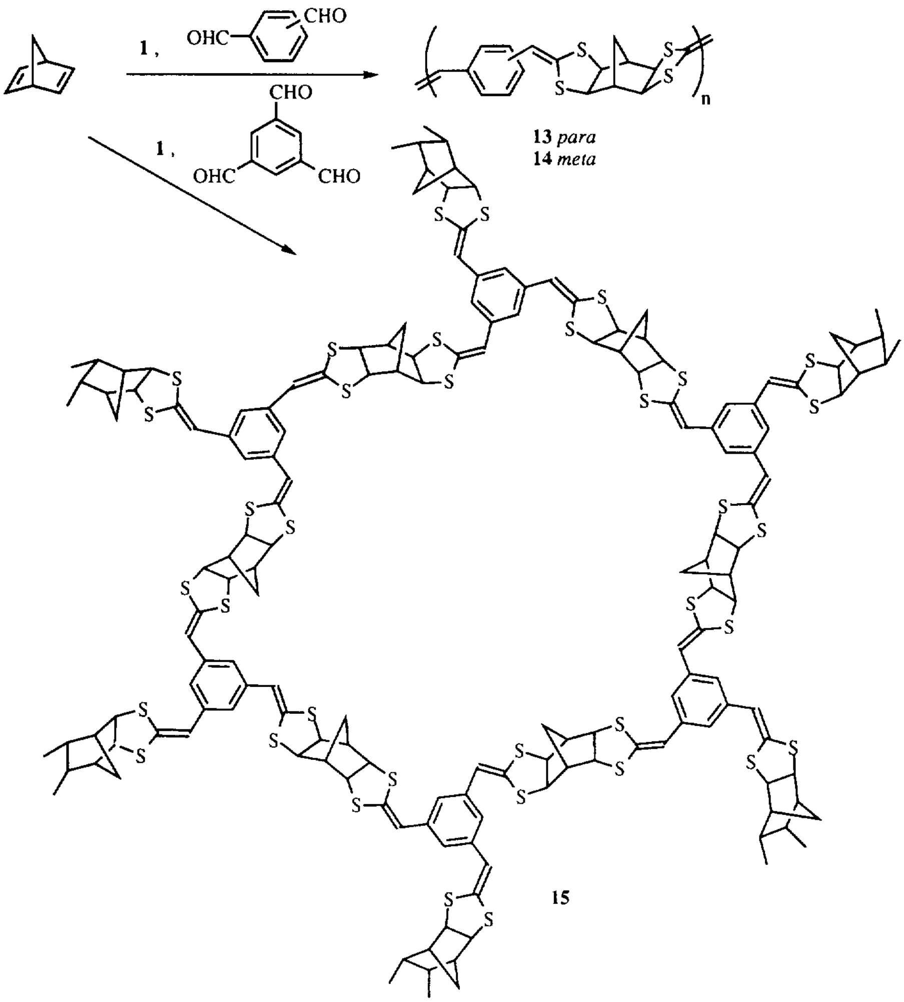
The reaction could readily be extended to the formation of novel dithiolane-containing polymers by using norbornadiene. Thus, reaction of norbornadiene (0.5 equiv.) with **1** and either terephthalaldehyde or isophthalaldehyde in CH_2Cl_2 at RT gave the linear polymers **13** and **14** which could be filtered off as pale yellow and white powders, respectively. The reaction with mesitaldehyde similarly afforded a polymer which has the

Table 1: ^{13}C NMR Spectra of **7–9**, **11**, **12** and **21**, δ_C

	C-1, C-7	C-2, C-6	C-4	C-8, C-9	C-10	$=\underline{C}H-$	$-C_6H_4-$ or $-C_6H_3-$ signals	CO_2Me
7	45.5, 45.3	63.8, 57.4	139.2	28.0, 27.7	32.3	115.4	135.0 (4ry), 127.6 (4 CH)	
8	45.6, 45.4	63.8, 57.4	139.8	28.0, 27.7	32.3	115.4	137.4 (4ry), 128.2 (CH), 127.0 (CH), 125.4 (2 CH)	
9a	45.6, 45.34	63.8, 57.4	139.8	28.0, 27.7	32.3	115.6	137.3 (4ry), 124.9 (2 CH), 124.75* (CH)	
9b	45.6, 45.28	63.8, 57.4	139.8	28.0, 27.7	32.3	115.5	137.3 (4ry), 124.82* (3 CH)	
11	53.9, 53.8	60.2, 54.2	139.7	144.9, 144.3	41.3	117.1	134.9 (4ry), 127.7 (4 CH)	164.19, 164.14, 52.1
12*	54.00, 53.96	60.2, 54.2	140.2	145.0, 144.4	41.4	117.33	137.04 (4ry), 128.3 (CH), 127.1 (CH), 126.1 (2 CH)	164.25, 164.19, 52.1
	53.92, 53.8	60.2, 54.2	140.2	145.0, 144.4	41.4	117.26	137.01 (4ry), 128.3 (CH), 126.9 (CH), 126.0 (2 CH)	164.25, 164.19, 52.1
21 (maj)	54.13, 54.10	59.1, 55.1	141.77	144.9, 144.5	41.6	115.3	135.48 (4ry), 128.3 (2 CH), 126.82 (2 CH)	164.26, 164.18, 52.3‡
(min)	53.9 (2 C)	59.1, 55.1	141.73	144.8, 144.3	41.6	115.3	135.43 (4ry), 128.2 (2 CH), 126.78 (2 CH)	164.26, 164.13, 52.3‡

* Assignments may be interchanged. ‡ Two signals: 52.30, 52.28 equal size.

idealised structure **15**. All three materials were insoluble in any common solvent and so no accurate estimation of their molecular weight has been possible. The *para* polymer **13** melted with decomposition at 317 °C and a DSC study showed a well defined glass transition (T_g 263 °C) while the *meta* isomer **14** melted at 250–260 °C and no glass transition was apparent, and **15** had a mp of >300 °C. Elemental analysis for **13** and **14** gave results in reasonable agreement with expectation, while for **15** the results indicated the presence of Bu_3PO to an extent of 20%, either in the form of unreacted end groups or in the free state entrapped within the polymer structure.



13 *para*
14 *meta*

15

Treatment of phthalaldehyde with **1** and norbornene as before gave a crystalline product in 64% yield, but analytical and spectroscopic examination clearly showed that this was an isomer of the expected product **16**. In particular, the expected symmetry was absent and all 24 carbon atoms in the molecule gave separate signals in the ^{13}C NMR spectrum. The expected –CH= signals were absent in both ^{1}H and ^{13}C spectra and had apparently been replaced by a quaternary carbon (δ_C 75.6) and a CH_2 group (δ_C 53.6, δ_H 4.13 and 4.09 [AB pattern]). The structure was revealed by a single crystal X-ray structure determination to be the spiro-indane **17** (Figure 1).

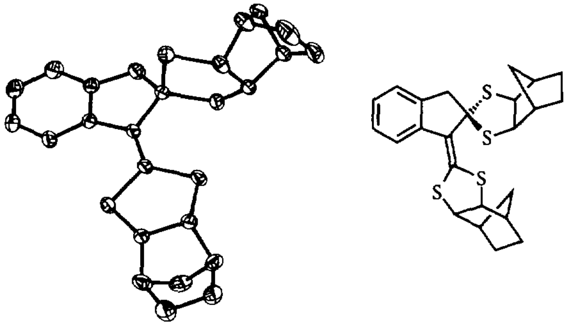
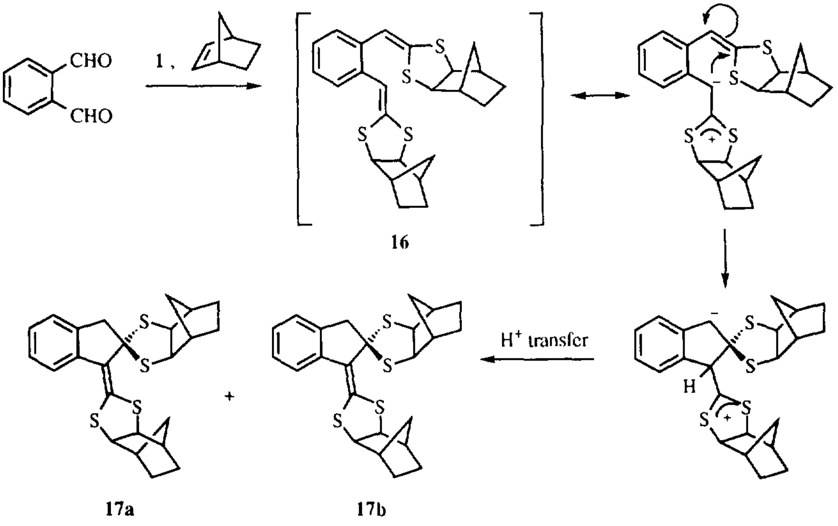


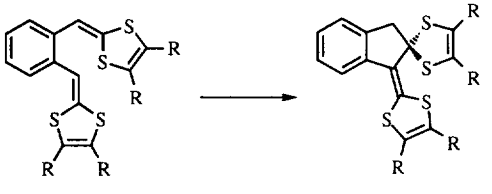
Figure 1: X-Ray structure of **17** (enantiomer **17a** shown)

The dithiolane rings are *exo* with respect to each norbornane unit and the configuration about the spiro centre is fixed, *i.e.* the C_1 bridge is always away from the other dithiolane moiety and towards the indane CH_2. However, the second bicyclic part of the structure is disordered and the compound exists as a 3:1 mixture of the forms **17a** and **17b** which are (*E*) and (*Z*) isomers about the double bond and at the same time, because of the symmetry, enantiomers. Because of the space group symmetry, the crystal contains equal proportions of the two forms with the occupancy at two of the four sites in the unit cell being 75% **17a** and 25% **17b** and at the other two sites 75% **17b** and 25% **17a**.

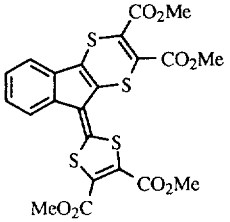
The formation of **17** can be rationalised by assuming that the expected product **16** is first formed as for the *para* and *meta* isomers **7** and **8**. In these compounds, and thus presumably in **16** also, the double bonds are significantly polarised [**7** δ_C 139.2 (CS_2) and 115.4 (–CH=)]. This can result in the mode of reaction shown below in which attack by the nucleophilic carbon of one double bond at the electrophilic carbon of the other leads to ring-closure and only a proton transfer, which probably occurs intermolecularly in solution, is then required to give **17**.



While our work was in progress, Gorgues, Bryce and coworkers reported a similar process in which the bis(alkylidenedithioles) **18** were transformed into the corresponding spiroindane derivatives **19** either by acid catalysis[3] or electrochemically.[4] The spectroscopic properties of **19** [$R_2 = (CH_2)_4$] are in good agreement with those of **17** [δ_C 71.8 (CS_2), 58.9 (CH_2), δ_H 4.06 (CH_2)]. Despite the apparent similarity however, there are distinct differences between the two processes. Thus the compounds **18** could be isolated, and only underwent slow cyclisation to **19** under acidic or electro-oxidative conditions. The mechanism was shown to involve acid catalysis and thus to proceed by initial protonation of one –CH= carbon to give a dithiolium salt which could then suffer nucleophilic attack from the other alkylidenedithiole group. A mechanism involving one-electron oxidation was proposed some time earlier by Lakshmikantham and coworkers[5] for the conversion of **18** (R = CO_2Me) into **20** in high yield upon treatment with bromine. In both these previous studies the involvement of intermediates containing the stable 6π dithiolium cation system might be thought of as favouring the observed reactions. However from the present results it appears that this delocalisation may actually reduce the reactivity, as the much more ready occurrence of cyclisation in the case of **16** (complete cyclisation in neutral solution at RT) may be due to no such 6π delocalised system being possible for the dithiolane rings.

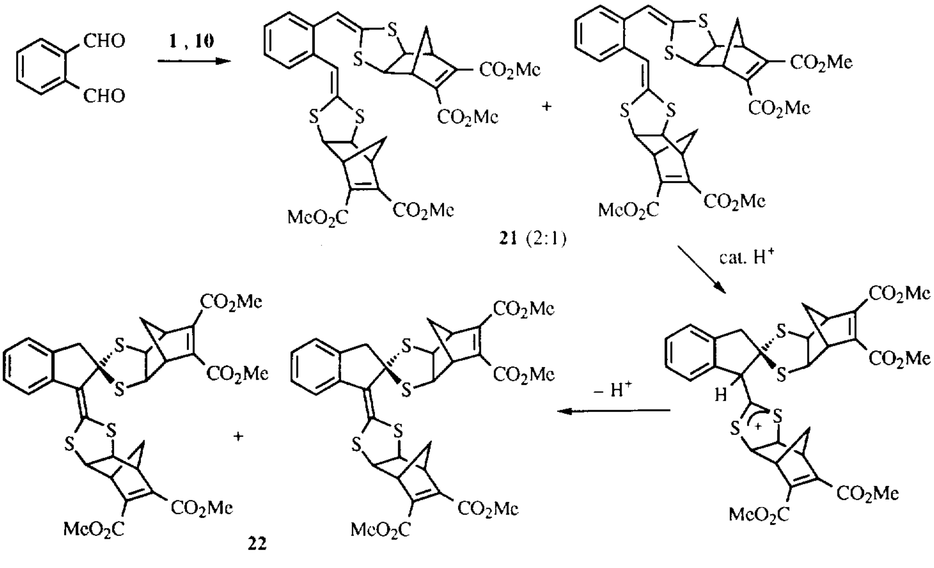


18 **19**



20

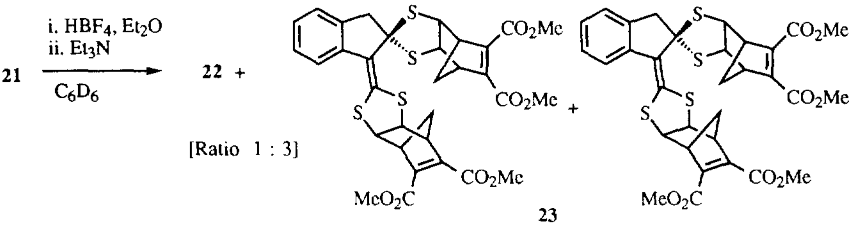
Further insight into the mechanism of the cyclisation was gained from the reaction of the norbornadiene diester **10** with **1** and phthalaldehyde. In this case the initial non-cyclised product **21** could be isolated and characterised spectroscopically. It is interesting to note that, as for the *meta* isomer **12**, the compound consisted



21 (2:1)

22

of two isomers which could be distinguished spectroscopically, but these were now formed in a 2:1 ratio. Clearly the proximity of the two aldehyde groups has allowed the direction of attack at the second group to be influenced by that at the first, although we are not able to predict which is the favoured isomer. Attempted purification of **21** by column chromatography on silica led to rapid cyclisation and **22** was obtained which had spectroscopic properties in good agreement with **17** including ^{13}C NMR signals at δ_C 79.1 (4ry) and 54.8 (CH_2). The cyclisation proceeded slowly over a period of hours in $CDCl_3$ and was thus amenable to a kinetic study using NMR. In this we attempted to demonstrate that cyclisation of **21** to **22** involved intermolecular proton transfer and would thus show a second order dependence on the concentration of **21** if the proton transfer was rate-determining or a first order dependence if it was not. In the event rather inconsistent results were obtained leading to the suspicion that the process was being catalysed by a trace of HCl present in the chloroform. This was readily confirmed by the observation that in d_6-benzene **21** showed no tendency to cyclise and was unchanged after several hours. To demonstrate the requirement for acid catalysis further, anhydrous HBF_4 in ether was added to a solution of **21** in d_6-benzene causing immediate precipitation of a dark red oil. Upon addition of excess triethylamine this redissolved and the spectrum showed that cyclisation had occurred. Very interestingly however, the product was now mainly the opposite stereoisomer to that obtained using SiO_2 or $CDCl_3$, compound **23**. The ratio of **23**:**22** was ca. 3 : 1 and the assignment of structure **23** to the major isomer is based on the much smaller differentiation of the $C\underline{H}S$ protons of the spiro-fused bicyclic unit as compared to either **22** or **17**, consistent with them being oriented away from the other bicyclic unit which makes them non-equivalent. Why the cyclisation of **21** should give exclusively **22** when catalysed by SiO_2 or traces of HCl in $CDCl_3$ but mainly the apparently more sterically hindered isomer **23** by treatment with HBF_4 followed by Et_3N is not entirely clear. It seems possible that the cyclised dithiolanylium salt leading to **23** is less soluble than that leading to **22** and so is selectively precipitated out, but further work is clearly required to explain these results fully.



Experimental

General

All NMR spectra were recorded on solutions in deuteriochloroform unless otherwise stated. ^1H spectra were recorded at 300 MHz and ^{13}C spectra at 75 MHz on a Bruker AM300 instrument with tetramethylsilane as internal reference. IR spectra were recorded on a Perkin Elmer 1420 instrument. Low and high resolution mass spectra were obtained on an AEI-Kratos MS-50 mass spectrometer using electron impact at 70 eV. Elemental analyses for C and H were performed on a Carlo-Erba 1106 analyser. Melting points were determined on a Reichert hot-stage microscope and are uncorrected. Column chromatography was performed using BDH silica gel for flash chromatography (particle size 40-63 µm).

Reactions of terephthalaldehyde, isophthalaldehyde and mesitaldehyde with **1** *and norbornene.*
a. 1,4-Phenylenebis(4-methylenyl-3,5-dithiatricyclo[5.2.1.0^{2,6}]decane) **7**.

A solution of tri-*n*-butylphosphoniodithioformate **1**[2] (4.0 g, 14 mmol), norbornene (1.32 g, 14 mmol) and terephthalaldehyde (0.94 g, 7 mmol) in dry CH_2Cl_2 (30 cm^3) was stirred at room temperature for 24 h. The resulting white solid was filtered off and washed with ether to give the *title compound* (82%) as colourless crystals, mp 238–240 °C (from toluene) (Found: C, 65.3; H, 5.9. $C_{24}H_{26}S_4$ requires C, 65.1; H, 5.9%); ν_{max} /cm^{-1} 1560, 1404, 1306, 1290, 1247, 1223, 1176, 1114, 928, 837, 780, 760 and 683; δ_H 7.35 (4 H, s), 6.50 (2 H, s), 4.05 and 3.75 (4 H, AB pattern of d, *J* 8, 2), 2.40 (4 H, m), 1.98 (2 H, half AB pattern, *J* 12), 1.7–1.6 (4 H, m) and 1.35–1.17 (6 H, m); δ_C see Table 1; *m/z* 442 (M$^+$, 8%), 255 (5), 189 (30), 173 (20), 147 (22), 134 (22), 120 (30), 92 (100) and 76 (73).

b. 1,3-Phenylenebis(4-methylenyl-3,5-dithiatricyclo[5.2.1.0^{2,6}]decane) **8**.

Reaction was carried out as in *a.* using isophthalaldehyde in place of terephthalaldehyde. After 24 h, the resulting white solid was filtered off and washed with ether to give the *title compound* (34%) as colourless crystals, mp 176–178 °C (from toluene) (Found: C, 64.8; H, 5.7. $C_{24}H_{26}S_4$ requires C, 65.1; H, 5.9%); ν_{max} /cm^{-1} 1587, 1550, 1310, 1293, 1180, 932, 890, 804 and 690; δ_H 7.35–7.1 (4 H, m), 6.50 (2 H, m), 4.03 and 3.73 (4 H, AB pattern of d, *J* 8, 2), 2.38 (4 H, m), 1.97 (2 H, half AB pattern, *J* 12), 1.7–1.55 (4 H, m) and 1.30–1.15 (6 H, m); δ_C see Table 1; *m/z* 442 (M$^+$, 100%), 348 (17), 316 (10), 222 (28), 190 (35), 133 (20), 93 (30) and 66 (60).

c. 1,3,5-Benzenetris(4-methylenyl-3,5-dithiatricyclo[5.2.1.0^{2,6}]decane) **9**.

Reaction was carried out as in *a.* using mesitaldehyde (0.73 g, 4.5 mmol) in place of terephthalaldehyde. After 4 days the solvent was remove *in vacuo* and the residual dark red oil was pre-absorbed onto silica gel and purified by flash-column chromatography (SiO_2, CH_2Cl_2 - light petroleum, 3:7) yielding the *title compound* (0.91 g, 47%) as an off-white solid, mp 215–218 °C (Found: C, 63.5; H, 6.3. $C_{33}H_{36}S_6$ requires C, 63.4; H, 5.8%); ν_{max} /cm^{-1} 1590, 1575, 1470, 1390, 1330, 1310, 1200, 940, 895, 825, 790 and 715; δ_H 7.15 and 7.14 (3 H, 2 s, Ar-H), 6.48 (3 H, s, C=C<u>H</u>), 4.03 (3 H, d, *J* 8) and 3.72 (3 H, dd, *J* 8 and 2) (2-H and 6-H), 2.37 (6 H, s, 1-H and 7-H), 1.97 (3 H, d, *J* 11, 10-H *syn*), 1.59 (6 H, m, 8-H and 9-H), 1.23 (9 H, m, 8-H, 9-H and 10-H *anti*); δ_C See Table 1; *m/z* 624 (M$^+$, 37%), 530 (6), 474 (7), 456 (28), 442 (100), 368 (6), 348 (11), 340 (10), 316 (9), 279 (6), 263 (8), 222 (13), 190 (15), 171 (11) and 149 (20).

Reactions of terephthalaldehyde and isophthalaldehyde with **1** *and* **10**.

d. 1,4-Phenylenebis(4-methylenyl-8,9-bis(methoxycarbonyl)-3,5-dithiatricyclo[5.2.1.0^{2,6}]dec-8-ene) **11**.

A solution of **10**[6] (1.50 g, 7.20 mmol), **1** (2.00 g, 7.18 mmol) and terephthalaldehyde (0.48 g, 3.58 mmol) in CH_2Cl_2 (25 cm^3) was stirred at room temperature for 40 h. The solvent was removed *in vacuo* yielding a yellow oil which partially solidified with time. The solid was suspended in diethyl ether, filtered off, washed with ether and dried. Recrystallisation (toluene) yielded the *title compound* (0.34 g, 14%) as sandy coloured crystals, mp 184-186 °C (Found: C, 57.6; H, 4.2. $C_{32}H_{30}O_8S_4$ requires C, 57.3; H, 4.5%); ν_{max} /cm^{-1} 1740, 1720, 1635, 1585, 1480, 1455, 1360, 1285, 1250, 1180, 1120, 1040, 1000, 880, 820 and 770; δ_H 7.31 (5 H, s, Ar-H), 6.53 (2 H, s, =C<u>H</u>), 4.29 (2 H, d, *J* 8, C<u>H</u>S), 4.00 (2 H, dd, *J* 8,2, C<u>H</u>S), 3.794, 3.790 (12 H, 2 s, 4xMe), 3.32 (4 H, d, *J* 2, 1-H and 7-H), 2.12 (2 H, d, *J* 10, 10-H), 1.84 (2 H, d, *J* 10, 10-H); δ_C see table 1; *m/z* 670 (M$^+$, 15%), 488 (21), 402 (11), 368 (11), 306 (68), 236 (10), 220 (100), 182 (5), 153 (22) and 122 (15).

e. 1,3-Phenylenebis(4-methylenyl-8,9-bis(methoxycarbonyl)-3,5-dithiatricyclo[5.2.1.0^{2,6}]dec-8-ene) **12**.

Reaction as in *d.* using isophthalaldehyde in place of terephthalaldehyde gave, after flash-column chromatography (SiO_2, CH_2Cl_2), the *title compound* (0.33 g, 14%) as a pale yellow foam, mp 93–95 °C (Found: C, 57.1; H, 4.5. $C_{32}H_{30}O_8S_4$ requires C, 57.3; H, 4.5%); ν_{max} /cm^{-1} 1730, 1640, 1580, 1470, 1450, 1350, 1285, 1220, 1180, 1120, 1045, 1000, 850, 815 and 790; δ_H 7.3 (2 H, m, Ar-H), 7.2 (2 H, m, Ar-H), 6.56 (2 H, s, =C<u>H</u>), 4.30 (2 H, dt, *J* 8, 2, C<u>H</u>S), 4.01 (2 H, dd, *J* 8, 2, C<u>H</u>S), 3.80 (6 H, s, 2xMe), 3.79 (6H, s, 2xMe), 3.33 (2 H, br s, 1-H and 7-H), 2.13 (2 H, m, 10-H), 1.85 (2 H, dm, *J* 10, 10-H); δ_C see table 1; *m/z* 670 (M$^+$, 4%), 488 (54), 306 (100), 248 (26), 203 (7), 178 (6), 153 (38), 119 (10) and 103 (19).

Reactions of terephthalaldehyde, isophthalaldehyde and mesitaldehyde with **1** *and norbornadiene.*

f. p-Polymer **13**.

Reaction was carried out as in *a*. using **1** (4.0 g, 14 mmol), norbornadiene (0.64 g, 7 mmol) and terephthalaldehyde (0.94 g, 7 mmol). After stirring at RT for 24 h the resulting pale yellow solid was filtered off and washed with ether to give the *title polymer* (1.95 g, 80%) as a yellow powder, mp (dec.) 317 °C, T_g 262 °C from DSC (Found: C, 58.05; H, 3.8. $(C_{17}H_{14}S_4)_n$ requires C, 58.9; H, 4.1%); ν_{max} /cm^{-1} 1678, 1598, 1568, 1540, 1312, 1164, 935, 850 and 785.

g. m-Polymer **14**.

Reaction was carried out as in *a*. using **1** (4.0 g, 14 mmol), norbornadiene (0.64 g, 7 mmol) and isophthalaldehyde (0.94 g, 7 mmol). After stirring at RT for 24 h the resulting white solid was filtered off and washed with ether to give the *title polymer* (1.84 g, 76%) as a colourless powder, mp (dec.) 250–260 °C (Found: C, 57.35; H, 4.0. $(C_{17}H_{14}S_4)_n$ requires C, 58.9; H, 4.1%); ν_{max} /cm^{-1} 1684, 1585, 1560, 1312, 1162, 932, 890, 816 and 690.

h. Polymer **15**.

Reaction was carried out as in *a*. using **1** (1.55 g, 5.6 mmol), norbornadiene (0.26 g, 2.8 mmol) and mesitaldehyde (0.30 g, 1.85 mmol). After stirring the mixture at RT for 3 days, the resulting yellow precipitate was filtered off, washed with dichloromethane, and dried *in vacuo* to give the *title polymer* (0.56 g, 32%) as a yellow powder, mp: underwent progressive decomposition above 320 °C but did not melt below 400 °C (Found: C, 58.2; H, 4.6; S, 31.5. $(C_{45}H_{36}S_{12}\cdot 0.25\ Bu_3PO)_n$ requires C, 58.2; H, 5.5; S, 32.0%); ν_{max} /cm^{-1} 1680, 1555, 1450, 1370, 1310, 1280, 1140, 1020, 920, 865, 800, 770 and 735.

Reactions of phthalaldehyde with **1** *and norbornene or* **10**.

i. 1-(3,5-Dithiatricyclo[5.2.1.0^{2,6}]decane-4-ylidene)indane-2-spiro-4'-(3',5'-dithiatricyclo[5.2.1.0^{2,6}]decane) **17**.

Reaction was carried out as in *a*. using phthalaldehyde in place of terephthalaldehyde. After stirring at RT for 24 h the resulting pale yellow solid was filtered off and washed with ether to give the *title compound* (64%) as colourless crystals, mp 194–196 °C (from toluene) (Found: C, 65.6; H, 6.2; M, 442.0892. $C_{24}H_{26}S_4$ requires C, 65.1; H, 5.9%; *M*, 442.0917); ν_{max} /cm^{-1} 1600, 1540, 1305, 1180, 1095, 1040 and 975; δ_H 7.87 (1 H, m), 7.25–7.05 (3 H, m), 4.13 and 4.09 (2 H, AB pattern, *J* 4), 3.95 (2 H, s), 3.92 (2 H, s), 2.5–2.35 (3 H, m), 2.26 (2 H, s), 2.00 (1 H, half AB pattern, *J* 12), 1.7–1.6 (4 H, m) and 1.3–1.2 (6 H, m); δ_C 140.9, 139.8, 134.9, 131.6 (all 4ry), 126.7, 126.3, 124.1, 123.5 (all CH), 75.6 (4ry), 68.5, 68.2, 61.2, 60.2 (all CH), 53.6 (CH$_2$), 45.5, 45.4, 44.53, 44.50 (all CH), 32.9, 32.4, 27.82, 27.78, 27.4 and 27.3 (all CH$_2$); *m/z* 442 (M$^+$, 22%), 348 (8), 316 (10), 284 (100), 254 (75), 222 (28), 190 (13), 158 (35), 146 (18), 134 (12) and 66 (50).

j. 1-(8,9-Bis(methoxycarbonyl)-3,5-dithiatricyclo[5.2.1.0^{2,6}]dec-8-ene-4-ylidene)indane-2-spiro-4'-(8',9'-bis(methoxycarbonyl)-3',5'-dithiatricyclo[5.2.1.0^{2,6}]dec-8-ene) **22**.

Reaction was carried out as in *d*. using phthalaldehyde in place of terephthalaldehyde. After 38 h the solvent was removed *in vacuo* yielding a yellow oil which partially solidified with time. The solid was suspended in diethyl ether, filtered, washed with ether and dried yielding *1,2-phenylenebis(4-methylenyl-8,9-bis(methoxycarbonyl)-3,5-dithiatricyclo[5.2.1.0^{2,6}]dec-8-ene)* **21** (contaminated with traces of tributylphosphine oxide and sulphide) δ_H 7.40 (2 H, m Ar-H), 7.23 (2 H, m, Ar-H), 6.58 and 6.56 (2 H, 2 x s, =C<u>H</u>), 4.20 (2 H, m, C<u>H</u>S), 4.05 (2

H, m, C<u>H</u>S), 3.81 and 3.78 (12 H, 2 x s, Me), 3.35, (2 H, m, 1-H/7-H), 3.27 (2 H, m, 1-H/7-H), 2.17 and 2.11 (2 H, 2 x dt, *J* 10, 1, 10-H) and 1.86 (2 H, d of quintets, *J* 10, 2);δ_C see Table 1.

Purification by flash-column chromatography (SiO_2, CH_2Cl_2) yielded the *title spiro compound* **22** (1.05 g, 44%) as a yellow solid, mp 190–191 °C (from methanol) (Found: C, 57.1; H, 4.3. $C_{32}H_{30}O_8S_4$ requires C, 57.3; H, 4.5%); ν_{max} /cm^{-1} 1765, 1740, 1640, 1560, 1485, 1350, 1280, 1220, 1180, 1125, 1060, 1010, 865 and 805; δ_H 7.87 (1 H, d, *J* 8) 7.28-7.22 (1 H, m), 7.16 (2 H, d, *J* 5), 4.43 and 4.40 (2 H, AB pattern of d, *J* 8, 2), 4.24 and 4.18 (2 H, AB pattern of d, *J* 8, 2), 4.09 (2 H, d, *J* 3), 3.84 (3 H, s), 3.82 (9 H, s), 3.43 (1 H, q, *J* 2), 3.38 (1 H, q, *J* 2), 3.25 (2 H, t, *J* 1), 2.68 (1 H, dt, *J* 10, 1), 2.09 (1 H, dt, *J* 10, 1), 2.02 (1 H, d of quintets, *J* 10, 2) and 1.86 (1 H, d of quintets, *J* 10, 2); δ_C 164.73, 164.66, 164.57, 164.4 (all C=O), 144.9, 144.5, 144.4, 144.1, 140.8, 139 0, 137.2, 133.8 (all 4ry), 127.3, 127.2, 124.2, 123.9 (all CH), 79.1 (4ry), 65.2, 64.7, 57.9, 57.4, 54.4, 54.3, 53.4, 53.3 (all CH), 54.8 (CH_2), 52.4, 52.3 (OMe) and 43.1, 41.8 (CH_2); *m/z* 670 (M^+, 47%), 488 (23), 430 (15), 402 (7), 368 (21), 306 (10), 279 (12), 248 (80), 222 (100), 220 (88), 216 (45), 204 (18), 192 (27), 166 (76) and 149 (62).

k. *Isomer* **23**.

A solution of **21** (ca. 30 mg) in C_6D_6 (0.5 cm^3) was treated with tetrafluoroboric acid in ether (excess) which led to immediate precipitation of a dark red oil. Triethylamine (excess) was added leading to dissolution of the oil to give a clear yellow solution. This was evaporated to dryness and its ^1H NMR spectrum recorded in $CDCl_3$ showed a 1 : 3 mixture of **22**; δ_H as above and *the isomer* **23**; δ_H 7.93 (1 H, d, *J* 8), 7.20-7.10 (3 H, m), 4.23 and 4.18 (2 H, AB pattern of d, *J* 8, 2), 4.10 (2 H, d, *J* 2), 3.90 (2 H, s), 3.82 (12 H, s), 3.43 (1 H, q, *J* 2), 3.38 (1 H, q, *J* 2), 3.30 (2 H, q, *J* 1.5), 2.93 (1 H, d, *J* 10), 2.13 (1 H, d, *J* 10), 1.98 (1 H, d of m, *J* 10) and 1.89 (1 H, d of m, *J* 10).

X-Ray structure determination of **17**.

Crystal data: $C_{24}H_{26}S_4$, M_r = 442.69, monoclinic, space group $P2_1/c$, a = 6.1272(12), b = 19.254(2), c = 18.0075(11) Å, β = 96.08(2) °, V = 2112.4(5) Å^3, Z = 4, ρ_{calcd} = 1.392 g cm^{-3}, R_1 = 0.0878, wR_2 = 0.1659 for all 5386 unique data and 329 parameters [R_1 = 0.0491, wR_2 = 0.1271 for 2569 data with $I > 2\sigma(I)$]. Data were recorded at 293±2 K using a FAST TV area detector diffractometer and Mo-Kα radiation. The structure was solved by direct methods (SHELX) and refined using full-matrix least squares methods in SHELX-93. Hydrogen atoms were included in calculated positions but their U_{iso} values were refined. Atomic coordinates, bond lengths and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

We thank Professor Martin Bryce, University of Durham for the sulfur analysis and E.P.S.R.C. for their generous support (Research Grant No. J38895).

References and Notes

1. To receive any correspondence regarding the X-ray structure determination.
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(*Received in UK* 7 *March* 1997; *revised* 3 *June* 1997; *accepted* 5 *June* 1997)