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The 1,2,3-Thiadiazole Route to New Vinylogue Tetrathiafulvalenes

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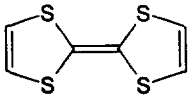
Abstract: Cleavage of 1,4-dithiafulvene-substituted 1,2,3-thiadiazoles with base and dimerisation of the resulting alkyne-1-thiolate gives new tetrathiafulvalene-type vinylogue extended π-donors in a one pot reaction. The solvent-/base-system used (acetonitrile/NaH) was optimised for the synthesis of 1,3-dithiole-2-thiones *via* this route. Efficient synthesis of the important 4-formyl-1,3-dithiol-2-thione and its coupling to 2,6(7)-bisformyltetrathiafulvalene is presented. Preparation of a number of new 1,4-dithiafulvenes are reported.

INTRODUCTION

There is a long standing interest in the chemistry and properties of the 1,3-dithiole ring system in modern material chemistry due to its unusual redox-chemistry.[1] Especially the focus has been centered on derivatives of tetrathiafulvalene (TTF) **(1)** containing two 1,3-dithioles in conjugation, since the finding of metallic conductivity and low temperature superconductivity in radical cation salts of tetrathiafulvalene derivatives.[2] Compared to the large number of tetrathiafulvalene derivatives which have been synthesised only a limited number of the so called extended tetrathiafulvalenes, where the 1,3-dithiole rings are separated by a conjugating spacer group, have been prepared.[2] The parent system is the vinylogue extended tetrathiafulvalene **(2)**. The majority of preparations used to make extended systems such as **(2)** involve multistep reactions. Recently a low temperature superconducting radical cation salt of a derivative of **(2)**, has been prepared.[3] Therefore, alternative synthetic routes to such compounds are of interest.



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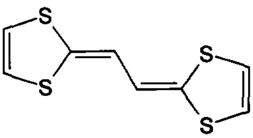

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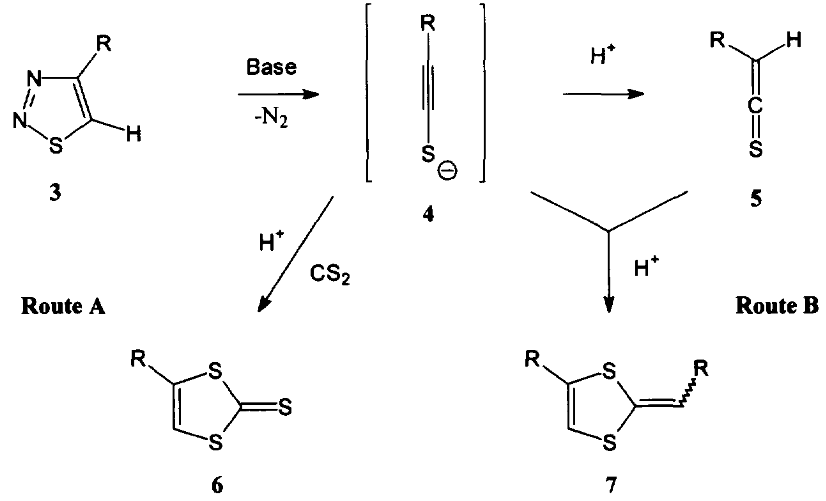
It is well known that alkyne-1-thiolates (**4**) can be generated from 1,2,3-thiadiazoles (**3**),[4] and that these alkyne-1-thiolates (**4**) can lead to either 4-substituted 1,3-dithiole-2-thiones (**6**),[5] a major starting material in tetrathiafulvalene-chemistry, or 1,4-dithiafulvenes (**7**)[4a,4b,6,7,8] depending on the reaction conditions. The direct synthesis of 4-substituted 1,3-dithiole-2-thiones *via* this route has been known for almost two decades, as has the similar route from 1,2,3-selenadiazoles to 1,3-thiaselenole-2-thiones.[9,10] However, as an entry into tetrathiafulvalene-chemistry, this route seems to be overlooked.[2]

1,4-Dithiafulvenes have also been prepared by photolytic cleavage of 1,2,3-thiadiazoles via a carbenic dipolar intermediate.[11] Similarly, 1,3-dithiole-2-thiones have been generated by thermolytic cleavage of 1,2,3-thiadiazoles in CS_2 also via a carbenic dipolar intermediate. This route is limited to ring annelated 1,2,3-thiadiazoles.[12]

In the base-mediated ring opening reactions an alkyne-1-thiolate (**4**) is generated from 1,2,3-thiadiazoles (**3**) after proton abstraction and expulsion of nitrogen (Scheme 1). Upon protonation, the alkyne-1-thiolate (**4**) can rearrange to a thioketene (**5**). Reaction of alkyne-1-thiolate (**4**) with the thioketene (**5**) leads to 1,4-dithiafulvenes (**7**).[4] If CS_2 is present the alkyne-1-thiolate (**4**) undergoes cycloaddition leading to 1,3-dithiole-2-thione (**6**).[8] When the 1,2,3-thiadiazoles are substituted in the 4-position, the resulting 1,4-dithiafulvenes (**7**) consists of a mixture of diastereomers. It has been shown that the reaction favours formation of the *cis*-isomer, though acid catalyses causes isomerisation to the more stable *trans*-isomer[6]. The corresponding 1,2,3-selenadiazoles were found to behave similarly[6].



Scheme 1. General scheme for the base promoted ring opening of 1,2,3-thiadiazoles

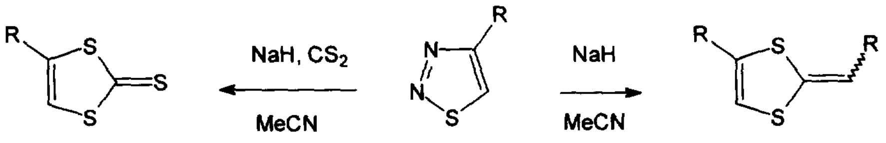
In general 1,2,3-thiadiazoles are readily available *via* the Hurd-Mori synthesis from acylhydrazones of methyl ketones upon treatment with thionylchloride, though other methods are known.[13]

In the syntheses of 1,3-dithiole-2-thiones (**6**), the alkyne-1-thiolate is first generated and then CS_2 is added (route A). This leads to the formation of 1,4-dithiafulvenes (**7**) along with **6**, which besides lowering the yield often are difficult to separate from the 1,3-dithiole-2-thiones. The ratio of 1,4-dithiafulvalene to 1,3-dithiole-2-thione depends on the rate of addition of CS_2. Normally CS_2 cannot be present during the addition of base due to precipitation of base-CS_2 adducts, though it was reported that 1,3-thiaselenole-2-thione could be prepared from 1,2,3-selenadiazole when the reaction was performed in DMF/CS_2 with potassium *tert*-butoxide as the base.[10]

In the present work we demonstrate that using acetonitrile/CS_2 with NaH as base is an excellent base/solvent system for performing these reactions (route A). The presence of CS_2 supresses concomitant formation of the fulvenes. The yields ranged from good to excellent. For example, the 4-phenyl-1,3-dithiole-2-thione was isolated in 89% yield without formation of fulvene using this procedure.[14] Furthermore we found this route to be efficient for the synthesis of 4-formyl-1,3-dithiole-2-thione, which hitherto was difficult to prepare,[15] and thus the unknown 2,6(7)-bisformyltetrathiafulvalene could be prepared.[16]

Adapting the procedure for 4-(1,4-dithiafulven-6-yl)-substituted 1,2,3-thiadiazoles, the fulvene product obtained from the cycloaddition (route B) represents a new type of vinylogue tetrathiafulvalene.

RESULTS AND DISCUSSION



6 **3** **7**

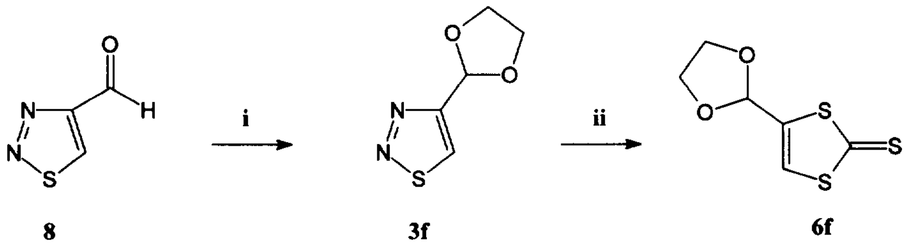
Route A	**Route B**
6a, R = *p*-C_6H_4CN, 57%	**7a**, R = *p*-C_6H_4CN, 94 %
6b, R = *p*-$C_6H_4NO_2$, 98%	**7b**, R = *p*-$C_6H_4NO_2$, 75%
6c, R = 5-cyano-thien-2-yl, 74%	**7c**, R = 5-cyano-thien-2-yl, 76%
6d, R = 2-thienyl, 75%	**7d**, R = 2-thienyl, 43%
6e, R = 3-thienyl, 83%	**7e**, R = 3-thienyl, 50%
6f, R = 1,3-dioxolan-2-yl, 98%	**7g**, R = 2-pyridyl, 83%

Scheme 2. The 4-substituted 1,3-dithiole-2-thiones and 2,6-substituted 1,4-dithiafulvalenes synthesised from 4-substituted 1,2,3-thiadiazoles.

Using the acetonitrile/NaH procedure, a number of thiadiazoles were subjected to these ring opening conditions leading either to the corresponding 1,3-dithiole-2-thiones **(6)** (route A) or the 1,4-dithiafulvenes **(7)** (route B) (scheme 2).

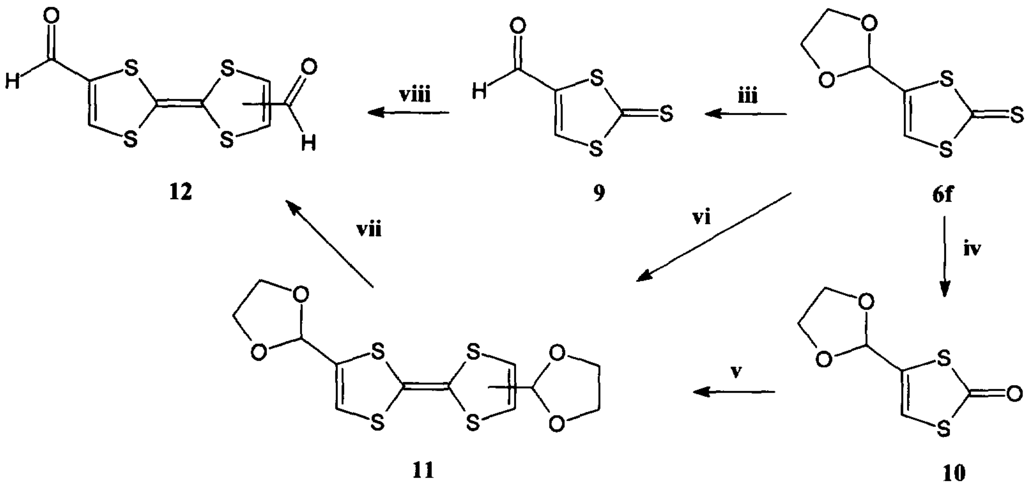
Both types of reactions give fair yields in most cases. As indicated above, it is important to note that no fulvenes were detected in the syntheses of 1,3-dithiole-2-thiones **(6)** using this procedure (route A). In the case of 4-pyridyl-substitution, fulvene **(7g)** was the sole product obtained with CS_2 present. Formation of **(7g)** may be the result of tautomeric stabilization of the negatively charged thioketene by the pyridine nitrogen.

Thiadiazole **(3f)** was prepared from the readily available 4-formyl-1,2,3-thiadiazole **(8)** (scheme 3),[17] and when treated with NaH/acetonitrile and CS_2 it gave the 1,3-dithiol-2-thione **(6f)** in excellent yield.



Scheme 3. The synthesis of (1,3-dioxolan-2-yl)-1,3-dithiole-2-thione. i) Ethylene glycol, toluene, *p*-toluene sulfonic acid; 75 %. ii) NaH, MeCN, CS_2; 98%.

This sequence opens an efficient route to the hitherto not readily available 4-formyl-1,3-dithiole-2-thione **(9)** and subsequently the unknown 2,6(7)-bisformyltetrathiafulvalene **(12)**.[16] Preparation of 2,6(7)-bisformyltetrathiafulvalene **(12)** could be acheived by several routes all starting from 1,3-dioxolan-2-yl-1,3-dithiole-2-thione **(10)** (Scheme 4). Hydrolysis of the acetal group to 4-formyl-1,3-dithiole-2-thione **(9)** followed by coupling with $Co_2(CO)_8$ gave **(12)**. Coupling of acetal **(6f)** with $Co_2(CO)_8$ to the 2,6(7)-bisacetaltetrathiafulvalene **(11)** followed by hydrolysis of the acetal-group also afforded **(12)**. Transchalcogenation of acetal **(6f)** afforded **(10)** and subsequent reaction with $P(OEt)_3$ gave **(11)** which produced **12** on hydrolysis. All steps except for the coupling steps gave fair yields, and all reactions were readily scaled up.



Scheme 4. Synthetic routes to 2,6(7)-bisformyltetrathiafulvalene. iii) H^+, acetone, H_2O; 90%. iv) $Hg(OAc)_2$, MeCN; 83%. v) $P(OEt)_3$, 120°C, 4 hrs.; 30%. vi) $Co_2(CO)_8$, toluene, 100°C, 1 hour; 26%. vii) H^+, MeOH; 89%. viii) $Co_2(CO)_8$, toluene, 100°C, 1 hour; 15 %.

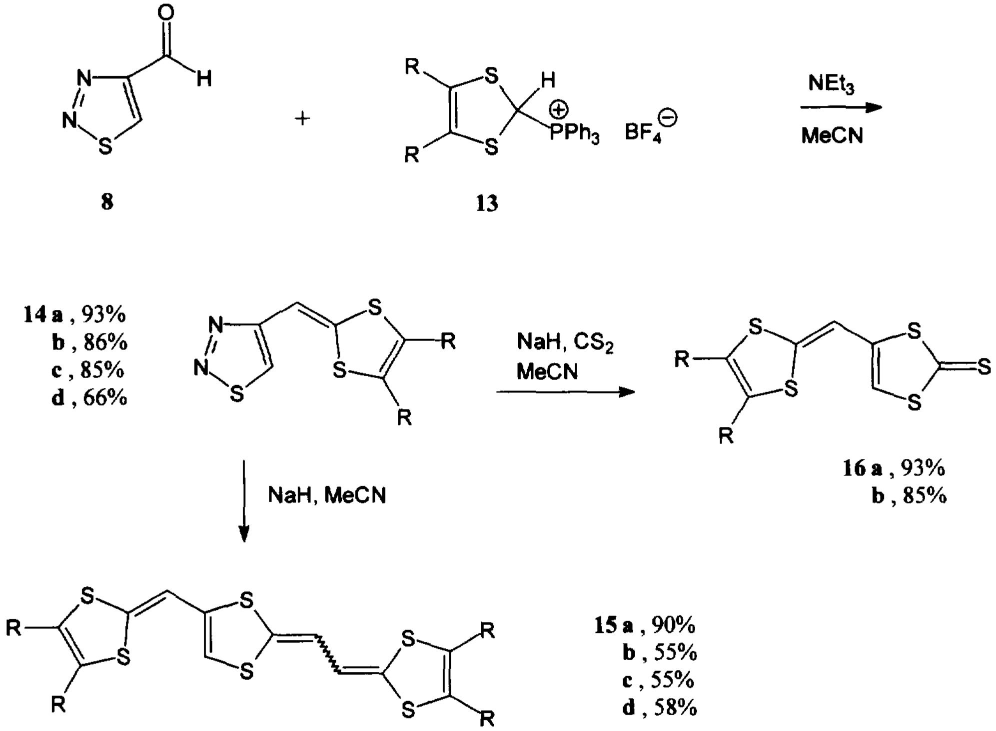
Vinylogue tetrathiafulvalenes

The facility of the reactions described above and the clean formation of fulvenes via route B suggested that 4-(1,4-dithiafulvenyl) substituted 1,2,3-thiadiazoles might give new vinylogue tetrathiafulvalenes by a similar cycloaddition route.

The 4-(1,4-dithiafulvenyl) substituted 1,2,3-thiadiazole **(14)** system was readily obtained from 4-formyl-1,2,3-thiadiazole **(8)** by a Wittig-reaction (Scheme 5). The phosphorous ylid is generated by proton removal from the corresponding dithiolyl phosphonium salt.

The reaction sequence using a benzo-annelated and ethylendithio-substituted fulvenyl group **(14a)** and **(14b)** worked satisfactory in the 1,3-dithiole-2-thione syntheses (route A) giving the new fulvenes **(16a)** and **(16b)**, wheras route B resulted in the formation of the extended tetrathiafulvalenes **(15a)** and **(15b)**. These latter products were very insoluble and characterisation was difficult. Nevertheless, the mass spectra of **(15a)** and **(15b)** indicated isolation of the expected compound.

Soluble products were obtained by substitution with bis-*p*-methyl-benzylthio and bis-phenethylthio groups in the 4,5-positions on the fulvenyls **(14c)** and **(14d)**. This gave the soluble compounds **(15c)** and **(15d)** in fair yields allowing full characterization. This method represents a short and facile route to an extended tetrathiafulvalene system. The extended tetrathiafulvalenes all gave dark coloured products upon treatment with iodine.



Scheme 5. The syntheses of fulvenyl vinylogue extended tetrathiafulvalenes. The substituents are **a)** R = (-CH=CH-), **b)** R = ($-SCH_2-$), **c)** R = $-SCH_2C_6H_4$-*p*-CH_3, **d)** R = $-SCH_2CH_2C_6H_5$.

EXPERIMENTAL

Melting points recorded on a Büchi apparatus are uncorrected. NMR spectra were recorded on a Bruker AC 250 Mhz. Mass Spectra were obtained on a Varian Mat 311A by Electrical Ionisation or by Fast Atom Bombardment. Plasma Desorption Mass Spectra were obtained on a Bioion 10 K. Elemental analyses; University of Copenhagen, Microanalytical Department.

4-(*p*-Cyanophenyl)-1,2,3-thiadiazole (3a):

p-Cyanoacetophenon (12.34 g, 85 mmol) and ethylcarbazate (8.85 g, 85 mmol) was dissolved in toluene (70 ml) with a catalytic amount of *p*-toluenesulfonic acid in a Dean-Stark apparatus. The solution was refluxed until no more water condensed or the starting materials disappeared according to TLC (appr. 3hrs.). The cooled slurry was added a little petroleum ether and it was then filtered. Washing with petroleum ether gave *p*-cyanoacetophenon ethoxycarbonylhydrazon (18.55 g, 80 mmol).

This (17.34 g, 75 mmol) was added to $SOCl_2$ cooled on a water-ice bath. The water-ice bath was removed taking precaution of the HCl gas evolved allowing the solution to warm to room temperature and standing overnight. Residual $SOCl_2$ was evaporated under waterpump vacuum. The residue was dissolved in $MeCl_2$, washed with water twice and filtered through silica. Evaporation gave 4-(*p*-cyanophenyl)-1,2,3-thiadiazole **(3a)** 63% (9.30 g, 50 mmol). Recrystallisation from ethylacetate gave off-white plates melting at 161-163°C. Anal. calcd. for $C_9H_5N_3S$ (187.22) C 57.74 H 2.69 N 22.44 S 17.12. Found C 57.56 H 2.81 N 22.65 S 16.97. ^1H NMR ($CDCl_3$/TMS): δ = 8.83 (1H,s), 8.19 (2H,d), 7.81 (2H,d). MS (EI): m/z = 187 (M^+), 159, 115,114.

4-(*p*-Nitrophenyl)-1,2,3-thiadiazole (3b):

p-Nitroacetophenon (3.30 g, 20 mmol) and ethylcarbazat (2.08 g, 20 mmol) was dissolved in 50 ml EtOH with a catalytic amount of *p*-toluenesulfonic acid and left overnight. It was then filtered to give *p*-nitroacetophenon ethoxycarbonylhydrazon (4.63 g, 18 mmol). This (3.77 g, 15 mmol) was treated as described above to give 4-(*p*-nitrophenyl)-1,2,3-thiadiazole **(3b)** 74% (2.50 g, 12 mmol). Recrystallisation from ethylacetate gave pale yellow crystals subliming at 192-194°C. Anal. calcd. for $C_8H_5N_3O_2S$ (207.21) C 46.37 H 2.43 N 20.28 S 15.47. Found C 46.48 H 2.47 N 20.08 S 15.44. ^1H NMR ($CDCl_3$/TMS): δ = 8.84 (1H,s), 8.38 (2H,d), 8.26 (2H,d). MS (EI): m/z = 207 (M^+), 191, 179, 163, 149.

4-(2-Cyanothien-5-yl)-1,2,3-thiadiazole (3c):

2-Acetyl-5-cyanothiophen (5.0 g, 33 mmol) was reacted as described above to give 2-acetyl-5-cyanothiophen (7.54 g, 32 mmol). This (7.11 g, 30 mmol) was treated as above to give 4-(2-cyanothien-5-yl)-1,2,3-thiadiazole **(3c)** 86% (5.18 g, 22 mmol). Recrystallisation from ethylacetate gave pale yellow needles melting at 139°C. Anal. calcd. for $C_7H_3N_3S_2$ (193.24) C 43.51 H 1.56 N 21.74 S 33.18. Found C 43.58 H 1.65 N 21.51 S 32.59. ^1H NMR (DMSO-d_6/TMS): δ = 9.77 (1H,s), 8.07 (1H,d), 7.97 (1H,d). MS (EI): m/z = 193 (M^+), 165, 121.

4-(2-Thienyl)-1,2,3-thiadiazole (3d):

2-Acetylthiophene (3.16 g, 25 mmol) was reacted as described above to give 2-acetylthiophene ethoxycarbonylhydrazon (5.27 g, 25 mmol). This (4.24 g, 20 mmol) was treated as above to give 4-(2-thienyl)-

1,2,3-thiadiazole **(3d)** 49% (1.65 g, 10 mmol). Recrystallisation from cyclohexane gave pale yellow needles melting at 67°C. Anal. calcd. for $C_6H_4N_2S_2$ (168.23) C 42.84 H 2.40 N 16.65. Found C 42.76 H 2.32 N 16.55. ^{1}H NMR ($CDCl_3$/TMS): δ = 8.50 (1H,s), 7.64 (1H,m), 7.41 (1H,m), 7.13 (1H,m). MS (EI): m/z = 168 (M^+), 140, 96, 69, 45.

4-(3-Thienyl)-1,2,3-thiadiazole (3e):

3-Acetylthiophene (12.6 g, 100 mol) was reacted as described above to give 3-acetylthiophene ethoxycarbonylhydrazon (17.7 g, 83 mmol). This (17.0 g, 80 mmol) was treated as above to give 4-(3-thienyl)-1,2,3-thiadiazole **(3e)** 46% (7.35 g, 44 mmol). Recrystallisation from cyclohexane gave off-white plates melting at 63°C. Anal. calcd. for $C_6H_4N_2S_2$ (168.23) C 42.84 H 2.40 N 16.65. Found C 42.76 H 2.51 N 16.49. ^{1}H NMR ($CDCl_3$/TMS): δ = 8.51 (1H,s), 7.97 (1H,m), 7.62 (1H,m), 7.44 (1H,m). MS (EI): m/z = 168 (M^+), 140, 96, 69, 45.

4-(1,3-Dioxolan-2-yl)-1,2,3-thiadiazole (3f):

4-Formyl-1,2,3-thiadiazole **(8)** (11.4 g, 0.10 mol) dissolved in toluene and ethylene glycol (6.2 ml, 6.9 g, 0.11 mol) with a catalytic amount of *p*-toluenesulfonic acid was refluxed in a Dean-Stark apparatus until the reaction was finished as evidenced by TLC (5-6 hrs. or overnight). Most of the toluene was evaporated and the residue filtered through a short column of silica using $MeCl_2$ as the eluent. Evaporation and recrystallisation from ethylacetate/petroleum ether(65-70°C) gave 4-(1,3-dioxolan-2-yl)-1,2,3-thiadiazole **(3f)** 75% (11.90 g, 75 mmol). White needles; mp 48-49°C. Anal. calcd. for $C_5H_6N_2O_2S$ (158.17) C 37.96 H 3.82 N 17.71 S 20.26. Found C 37.88 H 3.61 N 17.65 S 20.35. ^{1}H NMR ($CDCl_3$/TMS): δ = 8.65 (1H,s), 6.46 (1H,s), 4.16 (4H,m). MS (EI): m/z = 130 (M^+-N_2), 129, 115, 102, 73.

4-(2-Pyridyl)-1,2,3-thiadiazole (3g):

2-Acetyl-pyridine (2.42 g, 20 mmol) was treated as above to give 2-acetyl-pyridine ethoxycarbonylhydrazon (3.89 g, 19 mmol). This (3.11 g, 15 mmol) was reacted as described above to give 4-(2-pyridyl)-1,2,3-thiadiazole **(3g)** 83% (2.15 g, 13 mmol). Recrystallisation from cyclohexane gave off-white plates melting at 86°C. Anal calcd. for $C_7H_5N_3S$ (163.20) C 51.52 H 3.09 N 25.75 S 19.64. Found C 51.81 H 3.17 N 25.45 S 20.05. ^{1}H NMR ($CDCl_3$/TMS): δ = 9.23 (1H,s), 8.67 (1H,d), 8.46 (1H,d), 7.86 (1H,m), 7.33 (1H,m). MS (EI): m/z = 163 (M^+), 135, 108, 78.

4-(*p*-Cyanophenyl)-1,3-dithiole-2-thione (6a):

4-(*p*-Cyanophenyl)-1,2,3-thiadiazole **(3a)** (1.87 g, 10 mmol) was dissolved in a mixture of dry MeCN (30 ml) and CS_2 (2 ml). Subsequently NaH (0.1 g 60% mineral oil dispersion, 2.5 mmol) was added. After 2 hrs the product was filtered off and washed with a little MeCN to give 4-(*p*-cyanophenyl)-1,3-dithiole-2-thione **(6a)**

57% (1.34 g, 5,7 mmol). Recrystallisation from toluene/petroleum ether (65-70°C) gave yellow needles melting at 204-205°C. Anal. calcd. for $C_{10}H_5NS_3$ (235.34) C 51.04 H 2.14 N 5.95 S 40.87. Found C 51.13 H 2.09 N 6.18 S 40.61. ^{1}H NMR ($CDCl_3$/TMS): $\delta = 7.73$ (2H,d), 7.52 (2H,d), 7.26 (1H,s). MS (EI): m/z = 235 (M^+), 191, 159, 146, 115, 114.

4-(*p*-Nitrophenyl)-1,3-dithiole-2-thione (6b):

4-(*p*-Nitrophenyl)-1,2,3-thiadiazole **(3b)** (207 mg, 1.0 mmol) was dissolved in a mixture of 1:1 MeCN/$MeCl_2$ (10 ml) and CS_2 (0.5 ml). Subsequently NaH (0.01 g 60% mineral oil dispersion, 0.25 mmol) was added and the solution was left overnight. Next day a little MeOH was added followed by filtration and washing with MeOH. This gave 4-(*p*-nitrophenyl)-1,3-dithiole-2-thione **(6b)** 98% (251 mg, 0.98 mmol). Recrystallisation from ethylacetate gave yellow crystals melting at 222-223°C. Anal. calcd. for $C_9H_5NO_2S_3$ (255.32) C 42.34 H 1.97 N 5.49 S 37.77. Found C 42.37 H 2.02 N 5.38 S 37.26. ^{1}H NMR ($CDCl_3$/TMS): $\delta = 8.29$ (2H,m), 7.58 (2H,m), 7.31 (1H,s). MS (EI): m/z = 255 (M^+), 149, 133, 121, 89.

4-(2-Cyanothien-5-yl)-1,3-dithiole-2-thione (6c):

4-(2-Cyanothien-5-yl)-1,2,3-thiadiazole **(3c)** (1.93 g, 10 mmol) was dissolved in a mixture of dry MeCN (50 ml) and CS_2 (2 ml). Subsequently NaH (0.4 g 60% mineral oil dispersion, 10 mmol) was added. After 1 hour the product was poured on water, filtered off and washed with a little MeCN to give 4-(2-cyanothien-5-yl)-1,3-dithiole-2-thione **(6c)** 74% (1.82 g, 7.5 mmol). Recrystallisation from toluene gave yellow needles melting at 224°C. Anal. calcd. for $C_8H_3NS_4$ (241.36) C 39.81 H 1.25 N 5.80. Found C 39.58 H 1.28 N 5.87. ^{1}H NMR (DMSO-d_6/TMS): $\delta = 8.08$ (1H,d), 7.99 (1H,d), 7.51 (1H,s). MS (EI): m/z = 241 (M^+), 165, 121.

4-(2-Thienyl)-1,3-dithiole-2-thione (6d):

4-(2-Thienyl)-1,2,3-thiadiazole **(3d)** (841 mg, 5 mmol) dissolved in a mixture of dry MeCN (15 ml) and CS_2 (1.5 ml) was added NaH (0.04 g 60% mineral oil dispersion, 1 mmol) and refluxed overnight under N_2. The cooled solution was poured on water (5 ml), filtered and washed with a little MeOH to give 4-(2-thienyl)-1,3-dithiole-2-thione **(6d)** 75% (811 mg, 3.7 mmol). Recrystallisation from toluene/petroleum ether (65-70°C) gave yellow plates melting at 102°C. Anal. calcd. for $C_7H_4S_4$ (216.35) C 38.86 H 1.86. Found C 38.94 H 1.80. ^{1}H NMR ($CDCl_3$/TMS): $\delta = 7.33$ (1H,m), 7.08 (1H,m), 7.04 (1H,m), 6.99 (1H,s). MS (EI): m/z = 216 (M^+), 140, 96, 69, 45.

4-(3-Thienyl)-1,3-dithiole-2-thione (6e):

4-(3-Thienyl)-1,2,3-thiadiazole **(3e)** (3.36 g, 20 mmol) dissolved in a mixture of dry MeCN (50 ml) and CS_2 (6 ml) was added NaH (0.8 g 60% mineral oil dispersion, 20 mmol) and refluxed overnight under N_2. The cooled solution was poured on water (10 ml), filtered off and washed with a little MeOH to give 4-(3-thienyl)-

1,3-dithiole-2-thione **(6e)** 83% (3.60 g, 16.6 mmol). Recrystallisation from cyclohexane gave yellow needles melting at 104°C. Anal. calcd. for $C_7H_4S_4$ (216.35) C 38.86 H 1.86. Found C 39.29 H 2.03. ^{1}H NMR ($CDCl_3$/TMS): δ = 7.40 (1H,m), 7.33 (1H,m), 7.18 (1H,m), 7.02 (1H,s). MS (EI): m/z = 216 (M^+), 140, 96.

4-(1,3-Dioxolan-2-yl)-1,3-dithiole-2-thione (6f):

4-(1,3-Dioxolan-2-yl)-1,2,3-thiadiazole **(3f)** (3.34 g 21 mmol) was dissolved in a mixture of dry MeCN (70 ml) and CS_2 (1.8 ml). NaH (0.1 g 60% mineral oil dispersion, 2.5 mmol) was added and after 30 min. the solution was poured on water (100 ml) and extracted with Et_2O (3x60 ml). The ether was evaporated and the product filtered through a column of silica using $MeCl_2$ as the eluent. Evaporation gave 4.25 g 4-(1,3-dioxolan-2-yl)-1,3-dithiole-2-thione **(6f)** 98% (4.25 g, 20.6 mmol); mp 63°C. Further crystallisation in toluene/petroleum ether (65-70°C) is possible giving long yellow needles. Anal. calcd. for $C_5H_6N_2O_2S$ (206.29) C 34.93 H 2.93 S 46.62. Found C 35.03 H 2.96 S 46.81. ^{1}H NMR ($CDCl_3$/TMS): δ = 7.11 (1H,s), 5.78 (1H,s), 3.90 (4H,m). MS (EI): m/z = 206 (M^+), 134, 73.

2,6-Bis(*p*-cyanophenyl)-1,4-dithiafulvene (7a):

4-(*p*-Cyanophenyl)-1,2,3-thiadiazole **(3a)** (374 mg, 2 mmol) was dissolved in dry MeCN (20 ml) and NaH (0.04 g 60% mineral oil dispersion, 1 mmol) was added. After stirring for 2 hrs. 5 ml of MeOH was added. Filtration and washing with MeCN gave 2,6-bis(*p*-cyanophenyl)-1,4-dithiafulvene **(7a)** 94% (300 mg, 0.94 mmol). Recrystallisation from toluene/petroleum ether (65-70°C) gave yellow needles; mp >250°C. Anal. calcd. for $C_{18}H_{10}N_2S_2$ (318.41) C 67.90 H 3.17 N 8.80 S 20.14. Found C 67.76 H 3.18 N 8.61 S 20.04. ^{1}H NMR (DMSO-*d*$_6$/TMS): δ = 7.86 (4H,m), 7.73 (2H,d), 7.71 (1H,s), 7.48 (2H,d), 6.89 (1H,s). MS (EI): m/z = 318 (M^+), 191, 159, 146, 115, 114.

2,6-Bis(*p*-nitrophenyl)-1,4-dithiafulvene (7b):

4-(*p*-Nitrophenyl)-1,2,3-thiadiazole **(3b)** (207 mg, 1 mmol) dissolved in a 1:1 mixture of MeCN/$MeCl_2$ (10 ml) was added NaH (0.01 g 60% mineral oil dispersion, 0.25 mmol) and refluxed for 2 hrs. The product was filtered off and washed with MeCN. This gave 2,6-bis(*p*-nitrophenyl)-1,4-dithiafulvene **(7b)** 75% (134 mg, 0.37 mmol). Recrystallisation from large volume of ethylacetate gave red crystals; mp >250°C. Anal. calcd. for $C_{16}H_{10}N_2O_4S_2$ (358.39) C 53.62 H 2.81 N 7.82. Found C 52.82 H 2.82 N 7.64. ^{1}H NMR (DMSO-*d*$_6$/TMS): δ = 8.31 (2H,d), 8.27 (2H,d), 7.87 (1H,s), 7.84 (2H,d), 7.57 (2H,d), 7.04 (1H,s). MS (EI): m/z = 358 (M^+), 342, 328, 312, 282, 165, 121.

2,6-Bis(2-cyanothien-5-yl)-1,4-dithiafulvene (7c):

4-(2-Cyanothien-5-yl)-1,2,3-thiadiazole **(3c)** (579 mg, 3 mmol) dissolved in dry MeCN (10 ml) was added NaH (0.4 g 60% mineral oil dispersion, 10 mmol) and left overnight. The solution was poured on MeOH, filtered and washed with a little MeOH to give 2,6-bis(2-cyanothien-5-yl)-1,4-dithiafulvene **(7c)** 76% (381 mg, 1.15 mmol). Recrystallisation from large volume of ethylacetate gave an orange material; mp >250°C. Even after prolonged vacuum all the solvent did not come off. Anal. calcd. for $C_{14}H_6N_2S_4$ (330.45) C 50.89 H 1.83 N 8.48 S 38.81. Found C 50.86 H 1.57 N 8.57 S 38.81 (corr. 0.22 mole ethyl acetate). ^{1}H NMR (DMSO-*d*$_6$/TMS): δ = 7.97 (1H,d), 7.93 (1H,d), 7.64 (1H,s), 7.43 (1H,d), 7.29 (1H,s), 7.09 (1H,d). MS (EI): m/z = 330 (M^+) 165, 121.

2,6-Bis(2-thienyl)-1,4-dithiafulvene (7d):

4-(2-Thienyl)-1,2,3-thiadiazole **(3d)** (1.68 g, 10 mmol) dissolved in dry MeCN (40 ml) was added NaH (0.2 g 60% mineral oil dispersion, 5 mmol) and left overnight. The solution was added MeOH (15 ml), then filtered and washed with MeOH to give 2,6-bis(2-thienyl)-1,4-dithiafulvene **(7d)** 43% (610 mg, 2.18 mmol). Recrystallisation from toluene/petroleum ether (65-70°C) gave yellow needles melting at 194-196°C (dec.). Anal. calcd. for $C_{12}H_8S_4$ (280.44) C 51.40 H 2.88. Found C 51.76 H 3.11. ^{1}H NMR (CDCl$_3$/TMS): δ = 7.24-7.20 (2H,m), 7.07-6.91 (4H,m), 6.56 (1H,s), 6.42 (1H,s). MS (EI): m/z = 280 (M^+), 172, 140, 96.

2,6-Bis(3-thienyl)-1,4-dithiafulvene (7e):

4-(3-Thienyl)-1,2,3-thiadiazole **(3e)** (840 mg, 5 mmol) dissolved in dry MeCN (25 ml) was added NaH (0.8 g 60% mineral oil dispersion, 20 mmol) and left overnight. The solution was added MeOH (5 ml), then filtered and washed with MeOH to give 2,6-bis(3-thienyl)-1,4-dithiafulvene **(7e)** 50% (350 mg, 1.25 mmol); yellow needles; mp 173°C. Further crystallisation in toluene/petroleum ether (65-70°C) is possible. Anal. calcd. for $C_{12}H_8S_4$ (280.44) C 51.40 H 2.88. Found C 51.28 H 2.93. ^{1}H NMR (CDCl$_3$/TMS): δ = 7.33-7.08 (6H,m), 6.56 (1H,s), 6.41 (1H,s). MS (EI): m/z = 280 (M^+), 140, 108, 96.

2,6-Bis(2-pyridyl)-1,4-dithiafulvene (7g):

4-(2-Pyridyl)-1,2,3-thiadiazole **(3g)** (163 mg, 1 mmol) dissolved in dry MeCN (3 ml) was added NaH (0.04 g 60% mineral oil dispersion, 1 mmol) and left overnight. The solution was filtered and washed with a little MeCN to give 2,6-bis(2-pyridyl)-1,4-dithiafulvene **(7g)** 83% (112 mg, 0.41 mmol). Recrystallisation from cyclohexane gave dark yellow needles melting at 148°C. Anal. calcd. for $C_{14}H_{10}N_2S_2$ (270.37) C 62.19 H 3.73 N 10.36 S 23.72. Found C 62.05 H 3.76 N 10.33 S 23.29. ^{1}H NMR (CDCl$_3$/TMS): δ = 8.72 (1H,d), 8.60 (1H,d), 7.68 (1H,m), 7.56 (1H,m), 7.51 (1H,d), 7.16 (1H,m), 7.13 (1H,s), 7.05 (1H,d), 6.95 (1H,m), 6.66 (1H,s). MS (EI): m/z = 270 (M^+), 167, 135.

4-Formyl-1,3-dithiole-2-thione (9):

4-(1,3-Dioxolan-2-yl)-1,3-dithiole-2-thione **(6f)** (2.06 g, 10 mmol) was dissolved in 35 ml acetone and 2M H_2SO_4 (15 ml) was added. The solution was heated (45-50°C) for 1 hour and then poured on water (50 ml) followed by extraction into ether (2x50 ml). The ether fase was transferred to a short column (silica/$MeCl_2$) and eluted ($MeCl_2$). Evaporation gave 4-formyl-1,3-dithiole-2-thione **(9)** 90% (1.45 g, 9.0 mmol). Recrystallisation from toluene/petroleum ether (65-70°C) gave yellow crystals melting at 83°C. $C_4H_2OS_3$ (162.24). ^{1}H NMR ($CDCl_3$/TMS): $\delta = 9.55$ (1H,s), 8.02(1H,s).

4-(1,3-Dioxolan-2-yl)-1,3-dithiole-2-one (10):

4-(1,3-Dioxolan-2-yl)-1,3-dithiole-2-thione **(6f)** (2.06 g, 10 mmol) dissolved in MeCN (30 ml) was added $Hg(OAc)_2$ (4.3 g, 13 mmol). The mixture was stirred at 40-45°C for 30 min., whereupon the cooled solution was poured on a short column (silica/$MeCl_2$) and the product eluted ($MeCl_2$). This was washed with aqueous Na_2CO_3 then dried ($MgSO_4$) and evaporated to give 4-(1,3-dioxolan-2-yl)-1,3-dithiole-2-one **(10)** 83% (1.60 g, 8.4 mmol). Recrystallisation from ether/petroleumether gave white crystals melting at 30-31°C. Anal. calcd. for $C_6H_6O_3S_2$ (190.23) C 37.88 H 3.18 S 33.71. Found C 38.02 H 3.22 S 33.34. ^{1}H NMR ($CDCl_3$/TMS): $\delta =$ 6.85 (1H,s), 5.73(1H,s), 4.03 (4H,m). MS (EI): m/z = 190 (M^+), 161, 130, 73.

2,6(7)-Bis(1,3-dioxolan-2-yl)-1,4,5,8-tetrathiafulvalene (11):

Method 1:

4-(1,3-Dioxolan-2-yl)-1,3-dithiole-2-one **(10)** (0.82 g, 4.3 mmol) was dissolved in 2 ml $P(OEt)_3$ and heated to 120°C for 4 hrs. while stirrng under N_2. The cooled solution was then poured on a column of silica in cyclohexane. First the $P(OEt)_3$ was eluted with cyclohexane and then the product with $MeCl_2$. Evaporation and crystallisation in ether/petroleums ether gave 2,6(7)-bis(1,3-dioxolan-2-yl)-1,4,5,8-tetrathiafulvalene **(11)** 30% (0.23 g, 0.66 mmol) yellow crystals; mp 210-211°C.

Method 2:

4-(1,3-Dioxolan-2-yl)-1,3-dithiole-2-thione **(6f)** (1.64 g, 8 mmol) was dissolved in dry toluene (15 ml) and degassed for 5 min. with N_2. Then Co_2CO_8 (2.0 g, 8.4 mmol) was added while stirring, and the solution was heated to 100°C for 1 hour. The cooled solution was added a little $MeCl_2$ and eluted through a column (silica/$MeCl_2$) with $MeCl_2$. Evaporation gave 2,6(7)-bis(1,3-dioxolan-2-yl)-1,4,5,8-tetrathiafulvalene **(11)** 26% (0.35 g, 1.0 mmol); yellow crystals; mp 210-211°C. Further crystallisation in toluene/petroleum ether (65-70°C) is possible. Anal. calcd. for $C_{12}H_{12}O_4S_4$ (348.46) C 41.36 H 3.47 S 36.80. Found C 41.77 H 3.51 S 35.90. ^{1}H NMR ($CDCl_3$/TMS): $\delta = 6.40$ (1H,s), 5.65 (1H,s), 4.07-3.91 (4H,m). ^{13}C NMR ($CDCl_3$/TMS): $\delta =$ 135.5, 135.3, 118.3, 118.0, 110.8, 110.6, 99.6, 65.3. MS (EI): m/z = 348 (M^+), 276, 204, 146, 88, 73.

2,6(7)-Diformyl-1,4,5,8-tetrathiafulvalene (12):

Method 1:

4-Formyl-1,3-dithiole-2-thione **(9)** (300 mg, 1.9 mmol) was dissolved in dry toluene (15 ml) and degassed for 5 min. with N_2. Then Co_2CO_8 (0.4 g, 1.7 mmol) was added while stirring and the solution was heated to 100°C for 1 hour. The cooled solution was added a little $MeCl_2$ and eluted through a column (silica/$MeCl_2$) with $MeCl_2$. Evaporation gave 2,6(7)-diformyl-1,4,5,8-tetrathiafulvalene **(12)** 15% (40 mg, 0.15 mmol); dark red crystals; mp > 250°C.

Method 2:

2,6(7)-Bis(1,3-dioxolan-2-yl)-1,4,5,8-tetrathiafulvalene **(11)** (9.7 mg, 0.028 mmol) dissolved in 5 ml MeOH was added 1M HCl (1 ml) and slightly heated. The product was then filtrered and washed with first MeOH then petroleum ether. This gave 2,6(7)-diformyl-1,4,5,8-tetrathiafulvalene **(12)** 89% (6.4 mg, 0.025 mg). Recrystallisation from toluene/petroleum ether (65-70°C) gave dark red crystals; mp > 250°C. Anal. calcd. for $C_8H_4O_2S_4$ (260.36) C 36.91 H 1.55. Found C 37.08 H 1.72. ^1H NMR (DMSO-d_6/TMS): δ = 9.55 (1H,s), 8.293 (0.55H,s), 8.287 (0.45H,s). MS (EI): m/z = 260 (M^+), 174, 146, 88, 76.

4,5-Bis(*p*-methyl-benzyl-thio)-1,3-dithiol-2-thione:

Tetraethylammonium bis(1,3-dithiole-2-thione-4,5-dithio) zincate (14.3 g, 0,02 mol) dissolved in MeCN (200 ml) was slowly added *p*-methyl benzylbromid whereupon precipitaion began. After stirring for 30 min. the solvent was evaporated. The precipitate was dissolved in $CHCl_3$ (300 ml) and given aqeous work-up. Recrystallising in EtOH gave 4,5-bis-(*p*-methyl-benzyl-thio)-1,3-dithiol-2-thione 75% (12.0 g, 0.03 mol); mp 86°C. Anal. calcd. for $C_{19}H_{18}S_5$ (406.65) C 56.12 H 4.46. Found C 55.95 H 4.55. ^1H NMR ($CDCl_3$/TMS): δ = 7.10 (8H,s), 3.88 (4H,s), 2.31 (6H,s). MS (EI): m/z = 406 (M^+), 373, 301, 105.

2-Methylthio-4,5-bis(*p*-methyl-benzyl-thio)-1,3-dithiolylium tetraflourborate:

4,5-Bis-(*p*-methyl-benzyl-thio)-1,3-dithiol-2-thione (12.2 g, 30 mmol) in $MeSO_4$ (20 ml) was stirred for 30 min. at 85°C. The solution was cooled and added first Et_2O (5 ml) then HBF_4 (6 ml 54 % ethereal solution). Precipitating with Et_2O, dissolving in $MeCl_2$ and reprecipitating with Et_2O gave 2-methylthio-4,5-bis(*p*-methyl-benzyl-thio)-1,3-dithioleum tetraflourborate 93 % (14.25 g, 28 mmol); mp 114-115°C. Anal. calcd. for $C_{20}H_{21}S_5BF_4$ (508.49) C 47.24 H 4.16. Found C 47.15 H 4.29. ^1H NMR (CD_3CN/TMS): δ = 7.22 (8H,s), 4.22 (4H,s), 3.00 (3H,s), 2.38 (6H,s). MS (FAB): m/z = 421 (M^+ - BF_4), 317, 283.

Methyl 4,5-bis(*p*-methyl-benzyl-thio)-1,3-dithiole-2-yl sulfide:

2-Methylthio-4,5-bis-(*p*-methyl-benzyl-thio)-1,3-dithioleum tetraflourborate (5.08 g, 10 mmol) dissolved in MeCN (30 ml) was added dropwise to a suspension of $NaBH_4$ (0.5 g, 13.2 mmol) in *i*-PrOH (4 ml) on an icebath. When all was added the icebath was removed and the reaction was left stirring for 30 min. The mixture was poored on water and extracted with Et_2O. Drying ($MgSO_4$) and evaporating gave methyl 4,5-bis(*p*-methyl-benzyl-thio)-1,3-dithiole-2-yl sulfid 94% (3.98 g, 9.4 mmol). Yellow oil. Anal. calcd. for $C_{20}H_{22}S_5$ (422.69) C 56.83 H 5.25. Found C 56.95 H 5.42. ^1H NMR ($CDCl_3$/TMS): δ = 7.14 (8H,m), 5.73 (1H,s), 3.86 (4H,s), 2.31 (6H,s), 2.12 (3H,s). MS (EI): m/z = 422 (M^+), 375, 274, 105.

Triphenyl 4,5-bis(*p*-methyl-benzyl-thio)-1,3-dithiole-2-yl phosphonium tetraflouro-borate (13c):

Methyl 4,5-bis(*p*-methyl-benzyl-thio)-1,3-dithiole-2-yl sulfid (2.11 g, 5 mmol) in dry MeCN (50 ml) with PPh_3 (1.8 g, 6.8 mmol) on an icebath was purged with N_2. Then HBF_4 (1 ml 54 % ethereal solution) was added. Precipitation with Et_2O gave triphenyl 4,5-bis(*p*-methyl-benzyl-thio)-1,3-dithiole-2-yl phosphonium tetraflourborate **(13c)** 85% (3.06 g, 4.2 mmol); mp 146-147°C. Anal. calcd. for $C_{37}H_{34}PS_4BF_4$ (724.69) C 61.32 H 4.73. Found C 61.24 H 4.86. ^1H NMR (CD_3CN/TMS): δ = 8.02-7.74 (15H,m), 7.18-7.10 (8H,m), 6.83 (1H,d), 3.70 (4H,m), 2.36 (6H,s). MS (FAB): m/z = 637 (M^+ - BF_4), 531, 375.

Methyl 4,5-bis(phenylethylthio)-1,3-dithiole-2-yl sulfide:

4,5-Bis(phenylethylthio)-1,3-dithiol-2-thione (8.00 g, 20 mmol) in 20 ml $MeSO_4$ was stirred for 30 min. at 80°C. The solution was cooled and added first Et_2O (5 ml) then HBF_4 (4 ml 54 % ethereal solution). Precipitating with Et_2O gives an oil, dissolving in $MeCl_2$ and reprecipitating with Et_2O gave 9.47 g 2-methylthio-4,5-bis-(phenylethylthio)1,3-dithioleum tetraflourborate as a viscous oil. This was taken directly further dissolving in MeCN (30 ml) and adding dropwise to a suspension of $NaBH_4$ (1.5 g, 0.04 mol) in *i*-PrOH (4 ml) on an icebath. When all was added the icebath was removed and the reaction was left stirring for 30 min. The mixture was added water (50 ml) and extracted with Et_2O (2 x 100 ml). Drying ($MgSO_4$), evaporating and recrystallising in ethanol gave methyl 4,5-bis(phenylethylthio)-1,3-dithiole-2-yl sulfid 82% (6.79 g, 0.16 mol); mp 68-69°C. Anal. calcd. for $C_{20}H_{22}S_5$ (422.69) C 56.83 H 5.25. Found C 56.68 H 5.22. ^1H NMR ($CDCl_3$/TMS): δ = 7.25 (10H,m), 5.75 (1H,s), 3.19 (2H,m), 2.94 (2H,m), 2.28 (3H,s). MS (EI): m/z = 422 (M^+), 375, 271, 105.

Triphenyl 4,5-bis(phenylethylthio)1,3-dithiole-2-yl phosphoniumtetraflourborate (13d):

Methyl 4,5-bis-(phenylethylthio)1,3-dithiole-2-yl sulfid (2.36 g, 5.6 mmol) in dry MeCN (75 ml) with PPh_3 (2.0 g, 7.6 mmol) on an icebath was purged with N_2. Then HBF_4 (1 ml 54 % ethereal solution) was added and the reaction mixture was stirred for 30 min. whereupon Et_2O was added. The Et_2O was decanted and redissolving in MeCN and precipitating with Et_2O gave triphenyl (4,5-bis(phenylethylthio)-1,3-dithiole-2-yl) phosphonium tetraflour-borate **(13d)** 89% (3.58 g, 4.9 mmol); mp 162-163°C. Anal. calcd. for $C_{37}H_{34}PS_4BF_4$ (724.69) C 61.32 H 4.73. Found C 61.15 H 4.73. ^{1}H NMR (CD_3CN/TMS): δ = 7.99-7.73 (15H,m), 7.39-7.19 (8H,m), 6.91 (1H,d), 2.87-2.74 (4H,m), 2.00 (4H,m).

4-(Benzo-1,4-dithiafulven-6-yl)-1,2,3-thiadiazole (14a):

4-Formyl-1,2,3-thiadiazole **(8)** (1.14 g, 10 mmol) and triphenyl (benzo-1,3-dithiol-2-yl) phosphonium triflouromethanesulphonate (5.65 g, 10 mmol) was dissolved in MeCN (25 ml) and NEt_3 (2 ml) was added. After stirring for 30 min. MeOH (25 ml) and water (15 ml) was added to give a suspension that was filtered. Washing with MeCN afforded 4-(benzo-1,4-dithiafulven-6-yl)-1,2,3-thiadiazole **(14a)** 93% (2.32 g, 9.3 mmol). Recrystallisation from EtOH gave pale yellow needles melting at 153°C. Anal. calcd. for $C_{10}H_6N_2S_3$ (250.35) C 47.98 H 2.42 N 11.19. Found C 47.98 H 2.44 N 11.16. ^{1}H NMR ($CDCl_3$/TMS): δ = 8.14 (s,1H), 7.30 (2H,m), 7.15 (2H,m), 6.91 (1H,s). MS (EI): m/z = 250 (M^+), 222, 177, 153, 69.

4-(2,3-(Ethylenedithio)-1,4-dithiafulven-6-yl)-1,2,3-thiadiazole (14b):

4-Formyl-1,2,3-thiadiazole **(8)** (1.14 g, 10 mmol) and triphenyl (4,5-(ethylendithio)-1,3-dithiol-2-yl) phosphonium triflouromethanesulphonate (6.05 g, 10 mmol) was dissolved in MeCN (40 ml). NEt_3 (6 ml) was added and stirring for 30 min. gave a thick suspension that was filtered. Washing with MeCN afforded 4-(2,3-(ethylenedithio)-1,4-dithiafulven-6-yl)-1,2,3-thiadiazole **(14b)** 86% (2.50 g, 8.6 mmol). Recrystallisation from EtOH gave yellow needles decomposing at 207°C. Anal. calcd. for $C_8H_6N_2S_5$ (290.45) C 33.08 H 2.08 N 9.64 S 55.19. Found C 33.12 H 2.09 N 9.65 S 55.04. ^{1}H NMR ($CDCl_3$/TMS): δ = 8.07 (1H,s), 6.85 (1H,s), 3.34 (4H,s). MS (EI): m/z = 290 (M^+), 262, 234, 170, 114, 88.

4-(2,3-Bis(*p*-methyl-benzyl-thio)-1,4-dithiafulven-6-yl)-1,2,3-thiadiazole (14c):

4-Formyl-1,2,3-thiadiazole **(8)** (0.35 g, 3.1 mmol) dissolved in 25 ml MeCN with **(13c)** (2.38 g, 3.3 mmol) was added NEt_3 (0.6 ml). After stirring for 1 hour the solution was evaporated and eluted through a column of silica (10% cyclohexane i $MeCl_2$) giving 4-(2,3-bis-(*p*-methyl-benzyl-thio)-1,4-dithiafulven-6-yl)-1,2,3-thiadiazole **(14c)** 85% (1.23 g, 2.6 mmol); mp 101-103°C. Anal. calcd. for $C_{22}H_{20}N_2S_5$ (472.71) C 55.90 H 4.26 N 5.93 S 33.91. Found C 56.47 H 4.34 N 5.82 S 33.36. ^{1}H NMR ($CDCl_3$/TMS): δ = 8.13 (1H,s), 7.17-7.07 (8H,m), 6.74 (1H,s), 3.87 (2H,s), 3.81 (2H,s), 2.30 (3H,s), 2.29 (3H,s). MS (FAB): 472 (M^+), 445, 375, 340.

4-(2,3-Bis-(phenylethylthio)1,4-dithiafulven-6-yl)-1,2,3-thiadiazole (14d):

4-Formyl-1,2,3-thiadiazole **(8)** (0.35 g, 3.1 mmol) dissolved in 25 ml MeCN with **(13d)** (2.38 g, 3.3 mmol) was added NEt_3 (0.6 ml). After stirring for 1 hour the solution was evaporated and eluted through a column of silica (10% cyclohexane i $MeCl_2$) giving 4-(2,3-bis-(phenylethylthio)1,4-dithiafulven-6-yl)-1,2,3-thiadiazole

(14d) 66% (973 mg, 2.1 mmol) as a semicrystaline solid. Anal. calcd. for $C_{22}H_{20}N_2S_5$ (472.71) C 55.90 H 4.26 N 5.93. Found C 55.99 H 4.34 N 5.98. ^1H NMR ($CDCl_3$/TMS): δ = 8.06 (1H,s), 7.31-7.20 (10H,m), 6.82 (1H,s), 3.16-3.05 (4H,m), 2.99-2.92 (4H,m). MS (FAB): 473 (M^+ + H), 472 (M^+), 444, 412.

2,6-Bis(benzo-1,4-dithiafulven-6-yl)-1,4-dithiafulvene (15a):

A suspension of 4-(benzo-1,4-dithiafulven-6-yl)-1,2,3-thiadiazole **(14a)** (250 mg, 1.0 mmol) in dry MeCN (20 ml) was added NaH (0.04 g 60% mineral oil dispersion, 1 mmol) and stirred overnight under N_2. MeOH (30 ml) was added. The orange product was filtered and washed with MeOH to give 2,6-bis(benzo-1,4-dithiafulven-6-yl)-1,4-dithiafulvene **(15a)** 90% (200 mg, 0.45 mmol). Mp > 250°C, the product is very insoluble. $C_{20}H_{12}S_6$ (444.67), MS (PD): m/z = 444.7 (M^+). MS (EI): m/z = 444 (M^+), 412, 362, 331, 330, 222. Peak match: found 443.9282, calc. for $C_{20}H_{12}S_6$ 443.9263. The isotopic pattern of the molecular ion is in agreement with the calculated values.

2,6-Bis(2,3-(ethylenedithio)-1,4-dithiafulven-6-yl)-1,4-dithiafulvene (15b):

A suspension of 4-(2,3-(ethylenedithio)-1,4-dithiafulven-6-yl)-1,2,3-thiadiazole **(14b)** (290 mg, 1 mmol) in dry MeCN (5 ml) was added NaH (0.08 g 60% mineral oil dispersion, 2 mmol) and gently refluxed for 1 hour under N_2. The cooled suspension was then added EtOH (5 ml). The product was filtered and washed with EtOH to give 2,6-bis(2,3-(ethylenedithio)-1,4-dithiafulven-6-yl)-1,4-dithiafulvene **(15b)** 55% (146 mg, 0.28 mmol). Recr.: not possible; mp > 250°C. $C_{16}H_{12}S_{10}$ (524.87), MS (PD): m/z = 524.6 (M^+).

2,6-Bis(2,3-bis-(*p*-methyl-benzyl-thio)-1,4-dithiafulven-6-yl)-1,4-dithiafulvene (15c):

4-(2,3-Bis(*p*-methyl-benzyl-thio)-1,4-dithiafulven-6-yl)-1,2,3-thiadiazole **(14c)** (473 mg, 1 mmol) in dry MeCN (20 ml) under N_2 was added NaH (0.04 g 60% mineral oil dispersion, 1 mmol) and left stirring overnight. MeOH (25 ml) was added. The precipitate was filtered and washed with MeOH. Recrystallisation in ethylacetate/ethanol gave 2,6-bis(2,3-bis-(*p*-methyl-benzyl-thio)-1,4-dithiafulven-6-yl)-1,4-dithiafulvene **(15c)** 55% (246 mg, 0.28 mmol); mp 103°C. Calc. for $C_{44}H_{40}S_{10}$ (889.40) C 59.42 H 4.53. Found C 59.30 H 4.67 ^1H NMR ($CDCl_3$/TMS): δ = 7.12 (16H,M), 5.93-5.67 (4H,m), 3.78 (8H,m), 2.31 (12H,s). MS (FAB): 888 (M^+), 784, 750, 678. The isotopic pattern of the molecular ion is in agreement with the calculated values.

2,6-Bis(2,3-bis-(phenylethylthio)1,4-dithiafulven-6-yl)-1,4-dithiafulvene (15d):

4-(2,3-Bis-(phenylethylthio)1,4-dithiafulven-6-yl)-1,2,3-thiadiazole **(14d)** (473 mg, 1 mmol) in dry MeCN (20 ml) under N_2 was added NaH (0.04 g 60% mineral oil dispersion, 1 mmol) and left stirring overnight. H_2O (100 ml) was added. The solution was extracted into Et_2O (3 x 70 ml). After evaporation it was redissolved in $MeCl_2$, filtered through a short column of silica and treated with activated charcoal. Elution through a column of silica with $MeCl_2$ as the eluent gave 2,6-bis(2,3-bis-(phenylethylthio)1,4-dithiafulven-

6-yl)-1,4-dithiafulvene **(15d)** 58% (257 mg, 0.29 mmol); dark red viscous oil. ^{1}H NMR (CDCl$_3$/TMS): δ = 7,32-7,19 (20H,M), 6.02-5.67 (4H,m), 3,07-2,93 (8H,m). MS (FAB): 888 (M$^+$), 784, 752, 679. The isotopic pattern of the molecular ion was, 888(100), 889(52.9), 890(58.9), 891(34.0), 892(17.2), 893(8.0), 894(3.0), 895(1.2). Calcd. for $C_{44}H_{40}S_{10}$ (889.40): 888(100), 889(57.9), 890(60.9), 891(28.4), 892(16.6), 893(6.5), 894(2.7), 895(0.9).

4-(Benzo-1,4-dithiafulven-6-yl)-1,3-dithiole-2-thione (16a):

A suspension of 4-(benzo-1,4-dithiafulven-6-yl)-1,2,3-thiadiazole **(14a)** (131 mg, 0.5 mmol) in a mixture of dry MeCN (7 ml) and CS_2 (0.5 ml) was added NaH (0.04 g 60% mineral oil dispersion, 1 mmol) under N_2 and stirred overnight. The product was filtered and washed with MeCN to give 4-(benzo-1,4-dithiafulven-6-yl)-1,3-dithiole-2-thione **(16a)** 93% (140 mg, 0.47 mmol). Recrystallisation from toluene/petroleum ether (65-70°C) gave orange plates melting at 209°C. Anal. calcd. for $C_9H_6S_7$ (298.47) C 44.27 H 2.03. Found C 44.18 H 2.08. ^{1}H NMR (CDCl$_3$/TMS): δ = 7.30 (2H,m), 7.19 (2H,m), 6.70 (s,1H), 6.31 (1H,s). MS (EI): m/z = 298 (M$^+$), 222, 177, 111.

4-(2,3-(Ethylenedithio)-1,4-dithiafulven-6-yl)-1,3-dithiole-2-thione (16b):

A suspension of 4-(2,3-(ethylenedithio)-1,4-dithiafulven-6-yl)-1,2,3-thiadiazole **(14b)** (1.45 g, 5 mmol) in dry MeCN (50 ml) and CS_2 (5 ml) was added NaH (0.4 g 60% mineral oil dispersion, 10 mmol) and gently refluxed for 1 hour under N_2. The cooled suspension was poured on water (100 ml). The product was filtered and washed with MeOH to give 4-(2,3-(ethylenedithio)-1,4-dithiafulven-6-yl)-1,3-dithiole-2-thione **(16b)** 85% (1.44 g, 4.3 mmol). Recrystallisation from toluene/petroleum ether (65-70°C) gave dark red plates decomposing at192°C. Anal. calcd. for $C_9H_6S_7$ (338.57) C 31.92 H 1.79 S 66.29. Found C 32.19 H 1.84 S 66.37. ^{1}H NMR (CDCl$_3$/TMS): δ = 6.57 (s,1H), 6.25 (1H,s), 3.34 (4H,s). MS (EI): m/z = 338 (M$^+$), 310, 262, 234,88.

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