Ring fused 1,2,5-thiadiazoles from oximes and trithiazyl trichloride

Charles W. Rees and Tai-Yuen Yue

Department of Chemistry, Imperial College of Science, Technology and Medicine, London, UK SW7 2AY

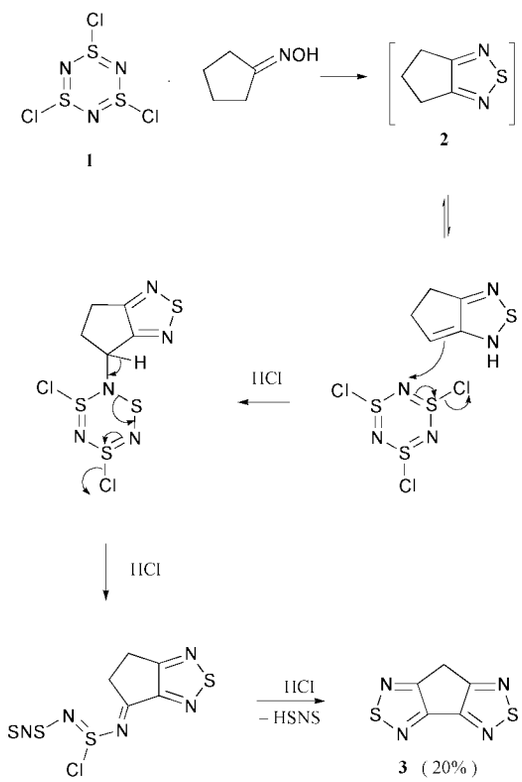
Received (in Cambridge, UK) 18th July 2001, Accepted 20th August 2001
First published as an Advance Article on the web 20th September 2001

Trithiazyl chloride **1** converts the oximes of simple cyclic ketones into fused 1,2,5-thiadiazoles and bis-1,2,5-thiadiazoles in mild one-pot reactions. Cyclopentanone oxime gives the bisthiadiazole **3** (20%) in which all four methylene groups have been functionalised. Indan-1-one oxime **4** gives the thiadiazole **5** (63%), and tetralone oximes **6** and **8** give the bisthiadiazole **7** in low yields (20%) in complex reactions. Benzosuberone oxime **11** however gives only the monothiadiazole **12** (30%) which is not converted further with more trimer **1**. These reactions probably occur by mechanisms analogous to those proposed earlier for the conversion of alkenes, alkynes, active methylene compounds and enamines into 1,2,5-thiadiazoles. Bisthiadiazole **3**, a reactive analogue of fluorene, condenses with *p*-anisaldehyde to give **13** and is oxidised by PCC to the fluorenone analogue **15** in low yield; **15** is formed directly from cyclopentane-1,3-dione with trimer **1**. Ketone **15** condenses with malononitrile and Hünig's base to give the dicyanomethylene derivative **17** (94%) which forms a black metallic 1 : 1 complex with TTF at room temperature.

We have shown that enamines, enamides and 1,2,3-triazoles all react with trithiazyl trichloride **1**, the trimer of N≡S–Cl, to form 1,2,5-thiadiazoles by a combination of C–C–N and S–N components.[1] On mechanistic grounds it seemed that the even more readily available oximes of α-methylene ketones might react similarly and we now show, in a limited investigation, that they do. Our initial reactions of oximes with the trimer **1** proved to be relatively complex and not high yielding. However, some interesting ring systems, not easily accessible otherwise, can be made in this way in one step; further work could extend the scope of the reaction and probably improve the yields.

We started with oximes of very simple cyclic ketones; with unsymmetrical ketones no attempt was made to separate isomeric oximes. Cyclohexanone oxime and the trimer **1** in boiling tetrachloromethane gave a complex mixture from which no pure products could be isolated. Under the same conditions cyclopentanone oxime also gave a complex mixture with a considerable amount of tarry material. Purification by treatment with active charcoal and chromatography on silica gave a colourless solid with *m*/*z* 182, shown by HRMS to be $C_5H_2N_4S_2$. The ^{1}H NMR spectrum showed only a sharp singlet at 4.1 ppm and the ^{13}C NMR spectrum showed two peaks in the aromatic region at 173 and 156 ppm and one peak at 30 ppm. The formula suggests involvement of one cyclopentane ring with the formation of two 1,2,5-thiadiazole rings and the product was considered to have structure **3** (Scheme 1) which is a new fused ring system. This structure was confirmed by some chemistry of **3** which is described below. Although the yield of **3** is low (20%) it is formed in an extensive reaction in which two thiadiazole rings have been created and all four methylene groups of the oxime have been functionalised in one reaction.

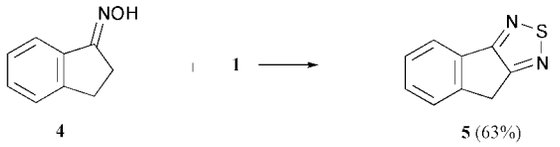
The first step is presumably condensation of the oxime with the trimer to give the monothiadiazole **2**, entirely analogous to the earlier C–C–N + S–N reactions,[1] although product **2** was not observed. The electron withdrawing effect of its thiadiazole ring and the coplanarity of the carbon atoms attached to the heterocyclic ring presumably allow the formation of the enamine tautomer of **2**. This could then react rapidly in the carbocyclic ring with a second molecule of trimer to give the isolated product **3** (Scheme 1) by a mechanism similar to those proposed earlier for the formation of 1,2,5-thiadiazoles from alkenes, alkynes and active methylene compounds.[1,2]



Scheme 1

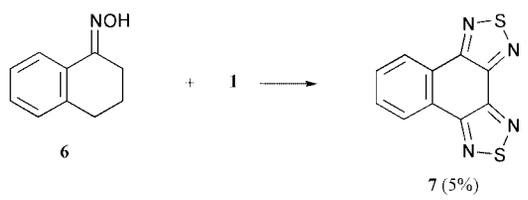
Treatment of indan-1-one oxime **4**, where the second reaction of Scheme 1 is not possible, with the trimer **1** in boiling tetrachloromethane gave the 1,2,5-thiadiazole **5** in much better yield (63%). The spectroscopic properties indicated this structure and agreed with those reported for **5** which has been prepared in lower yield by boiling indan-1-one with tetrasulfur tetranitride in toluene for 24 h (20%)[3] and indan-1-one oxime with tetrasulfur tetranitride in dioxane for 24 h (33%).[4]

 DOI: 10.1039/b106384g

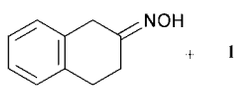


4 5 (63%)

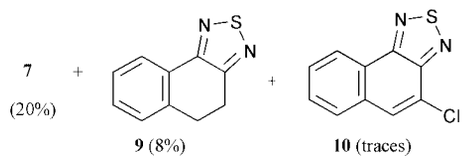
The reactions of 1- and 2-tetralone† oximes with trimer **1** in boiling tetrachloromethane were complex but slightly improved by the addition of pyridine to the reaction mixture. From 1-tetralone oxime **6** only the bisthiadiazole **7** could be isolated, in very low yield (5%); the properties of **7** agreed with those reported for a minor product of reaction of tetrahydronaphthalene and tetrasulfur tetranitride at 140 °C.[5] From 2-tetralone oxime and trimer **1** the same bisthiadiazole **7** was isolated in higher yield (20%) together with the monothiadiazole **9** (8%), which was the same as another product of the tetrahydronaphthalene–S_4N_4 reaction,[5] and traces of a chlorinated product tentatively assigned structure **10**. The position of the chlorine atom is based upon the assumption that compound **10** arises from the chlorination of **9** *via* its enamine tautomer (*cf*. Scheme 1) by the trimer **1**, and dehydrochlorination. A much higher yielding (91%) route to compound **7** is available, however, in the treatment of 1,4-dibromo-2,3-dihydroxynaphthalene with tetrasulfur tetranitride in boiling toluene for 48 h.[6]



6 7 (5%)



8



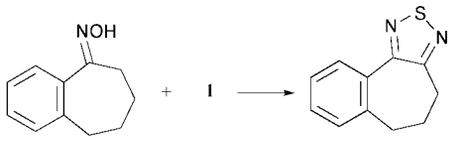
9 (8%) 10 (traces)

When benzosuberone‡ oxime **11** was treated with the trimer **1** under the same conditions as above, the thiadiazole **12** was obtained as a pale yellow oil in 30% yield. Its structure followed from the molecular formula $C_{11}H_{10}N_2S$, from mass spectrometry and HRMS, and ^1H and ^{13}C NMR spectra. Interestingly, no bisthiadiazole adduct of a type analogous to **7** was obtained from this reaction, and the thiadiazole **12** did not give any such bis-adduct on further treatment with **1** (1.5 equiv.) but was recovered almost quantitatively. Presumably the α-methylene protons in the more flexible 7-membered ring are less reactive and the isomeric enamine needed for further reaction is not generated to a significant extent.

In all of the above oxime–trimer reactions the oxime oxygen is lost, probably by dehydration, since no *N*-oxides are observed.

† The IUPAC names for 1- and 2-tetralone are 3,4-dihydronaphthalen-1(2*H*)-one and 3,4-dihydronaphthalen-2(1*H*)-one, respectively.

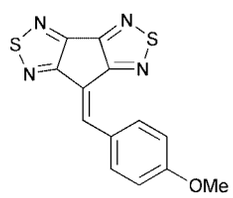
‡ The IUPAC name for suberone is cycloheptanone.



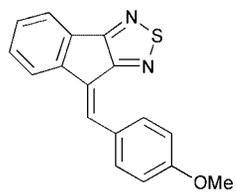
11 12 (30%)

Chemistry of the bisthiadiazole 3

The bisthiadiazole **3** is a new heterocyclic analogue of fluorene; the methylene hydrogens of **3** and, to a lesser extent, **5** should be more acidic than those of fluorene since the heterocyclic rings are electron withdrawing. The methylene chemical shifts of fluorene, **5** and **3** are 3.87, 3.89 and 4.07 respectively. Compound **3** condensed readily with *p*-anisaldehyde and a catalytic amount of piperidine in refluxing benzene to give bright yellow needles (68%) of **13** after 2 h. A strong molecular ion peak at *m/z* and microanalysis indicated the molecular formula $C_{13}H_8N_4OS_2$; the ^1H NMR showed signals for a *p*-disubstituted benzene ring and a singlet at 7.8 ppm for the vinylic hydrogen and the ^{13}C NMR was also consistent with structure **13**. The bright yellow colour presumably results from the extensive electron delocalisation from the methoxy group to the (then 14π) tricyclic system.



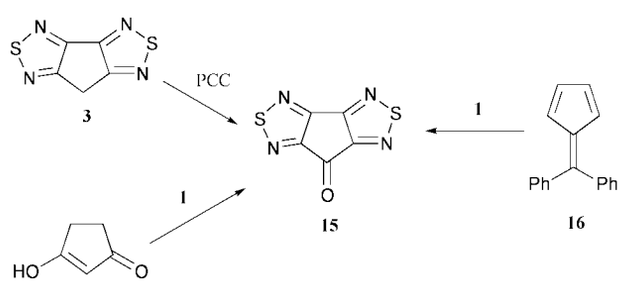
13



14

Condensation of the less activated **5** with *p*-anisaldehyde was slower (TLC monitoring) than **3**, giving only 21% yield of the analogous product **14** after heating under reflux for 5 h. The stereochemistry of **14** was not proved (an NOE study being complicated by overlapping vinylic and aromatic proton signals), but the isomer shown is considered likely to be the more stable.

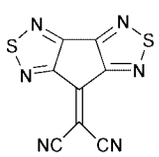
The methylene group of compound **3** was oxidised to the fluorenone analogue **15** by pyridinium chlorochromate and Celite in refluxing benzene, as recommended for the oxidation of fluorene to fluorenone,[7] though the yield was low (14%). The ketone **15** was identical with that formed earlier by treatment of diphenylfulvene **16** with an excess of trimer (21%);[2a] it was also formed by direct treatment of cyclopentane-1,3-dione with trimer in refluxing toluene for 16 h but again only 14% could be isolated from the complex reaction.



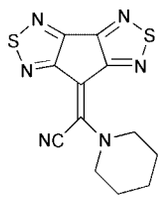
3 15 16

The carbonyl group in **15** is expected to be susceptible to nucleophilic attack. When heated with malononitrile and a catalytic amount of piperidine in benzene it gave orange prisms of the dicyanomethylene derivative **17** (45%). MS and HRMS gave the molecular formula $C_8N_6S_2$ and all the spectroscopic properties indicated the symmetrical structure **17**; ^{13}C NMR showed signals at 110 and 83 ppm respectively for the cyano groups and the carbon attached to them. Concentration of the mother liquor from the recrystallisation of **17** gave a

second product, $C_{12}H_{10}N_6S_2$, as yellow needles for which the ^1H and ^{13}C NMR indicated the product **18** of displacement of a cyano group, activated by the heterocyclic rings, by piperidine. The displacement of similarly activated cyano groups in TCNE[8] and in 9-dicyanomethylenedinitrofluorenes by secondary amines has been reported.[9] In view of this incorporation of piperidine, the condensation of **15** with malononitrile was repeated with the non-nucleophilic Hünig's base as catalyst, and **17** was then obtained as the only product in 94% yield.



17



18

The structural and chemical similarities between the dicyanomethylene compound **17** and TCNE and other electron acceptors such as the dicyanomethylene polynitrofluorenes and tetracyanoquinodimethane suggested that **17** might be a useful electron acceptor in charge-transfer (C-T) complexes with, for example, the donor tetrathiafulvalene (TTF).[10] An acetonitrile solution of TTF was therefore added to an acetonitrile solution of **17** and after 30 min fine black metallic needles, $C_{14}H_4N_6S_6$, mp 208–210 °C, started to separate and this was complete in about 2 h. X-Ray diffraction [11] confirmed that this product was a 1 : 1 complex of **17** and TTF but unlike the conducting C-T complexes of TTF this new complex exhibited no π–π stacking behaviour or electron-transfer from TTF to **17** and was therefore not investigated further.

Thus, we have shown that the reactions of oximes with trimer **1** are relatively complex and low yielding, but they do generate, in one step, ring systems not readily accessible otherwise.§ Further work would be needed to improve yields and explore the scope of these reactions. In the conversion of simple cyclic ketoximes into fused 1,2,5-thiadiazoles and bisthiadiazoles, several methylene groups are being functionalised. Reduction of the thiadiazole rings to diamino compounds,[6,12] for example, could then lead to polyamines such as the possible conversion of cyclopentanone oxime through **3** into 1,2,3,4-tetraaminocyclopentane derivatives.

Experimental

For general details see earlier parts of this series.[1,2]

The oximes were prepared from the ketones with hydroxylamine hydrochloride and pyridine in refluxing ethanol, and their properties agreed with those reported.

7*H*-Cyclopenta[1,2-*c*:3,4-*c*′]bis[1,2,5]thiadiazole 3

To a refluxing solution of cyclopentanone oxime (99 mg, 1 mmol) in CCl_4 (10 ml), a solution of trithiazyl trichloride (489 mg, 2 mmol) in CCl_4 (15 ml) was added dropwise. The mixture was heated under reflux for 16 h. The reaction mixture was cooled to room temperature and filtered through a column containing a short pad of activated charcoal on top of a short pad of silica. The filtrate was concentrated under reduced pressure. Column chromatography of the residue on silica with DCM–light petroleum (1 : 1) afforded the *title compound* (36 mg, 20%) as colourless prisms, mp 148–150 °C (ethanol) (Found: M^+ 181.9721 $C_5H_2N_4S_2$ requires M 181.9722); ν_{max} (Nujol mull)/cm^{-1} 1614w, 1339s, 1188s and 1096s; δ_H (270 MHz; $CDCl_3$) 4.07 (2H, s); δ_C (63 MHz; $CDCl_3$) 172.3, 156.1 and 29.95; *m*/*z* 182 (M^+, 100%), 155 (12, M − HCN), 149 (11, M − HS), 124 (8, M − CNS) and 116 (6, SNCCNS).

8*H*-Indeno[1,2-*c*][1,2,5]thiadiazole 5

To a refluxing solution of indan-1-one oxime **4** (147 mg, 1 mmol) in CCl_4 (10 ml), a solution of trithiazyl trichloride (489 mg, 2 mmol) in CCl_4 (15 ml) was added dropwise. The mixture was heated under reflux for 16 h. The reaction mixture was cooled to room temperature and filtered through a short pad of silica. The filtrate was concentrated under reduced pressure. Column chromatography of the residue on silica with DCM–light petroleum (1 : 1) afforded the title compound (110 mg, 63%) as a colourless solid, mp 74–75 °C (ethanol) (lit.,[3] 72–74 °C); δ_H (270 MHz; $CDCl_3$) 7.95 (1H, dd, *J* 5.7, 3.0), 7.59 (1H, m), 7.48–7.43 (2H, m) and 3.89 (2H, s); δ_C (63 MHz; $CDCl_3$) 168.7, 166.9, 148.9, 133.0, 129.8, 128.0, 126.8, 122.5 and 30.8; *m*/*z* 174 (M^+, 100%), 147 (7, M − HCN), 141 (45, M − HS) and 116 (40, M − CNS).

Reaction of trithiazyl trichloride with 1-tetralone oxime

To a refluxing solution of 1-tetralone oxime **6** (150 mg, 0.93 mmol) and pyridine (664 mg, 8.4 mmol) in CCl_4 (10 ml), trithiazyl trichloride (683 mg, 2.8 mmol) in CCl_4 (15 ml) was added dropwise. The reaction mixture was heated under reflux for 16 h. The reaction mixture was cooled to room temperature and filtered through a short pad of silica. The filtrate was concentrated under reduced pressure and column chromatography of the residue on silica with DCM–light petroleum (1 : 1) afforded naphtho[1,2-*c*:3,4-*c*′]bis[1,2,5]thiadiazole **7** (12 mg, 5%) as colourless needles, mp 206–207 °C (DCM) (lit.,[5] 208–209 °C); *m*/*z* 244 (M^+, 100%) and 217 (2, M − HCN).

Reaction of trithiazyl trichloride with 2-tetralone oxime

To a refluxing solution of 2-tetralone oxime **8** (150 mg, 0.93 mmol) and pyridine (664 mg, 8.4 mmol) in CCl_4 (10 ml), trithiazyl trichloride (683 mg, 2.8 mmol) in CCl_4 (15 ml) was added dropwise over 5 min. The reaction mixture was then quenched with ice-cold water (50 ml). The CCl_4 solution was then washed with water (3 × 30 ml) and dried over anhydrous sodium sulfate. The CCl_4 solution was filtered and the filtrate was concentrated under reduced pressure. Column chromatography of the residue on silica with DCM–light petroleum (1 : 1) afforded a mixture of three compounds. Further purification by preparative TLC with DCM–light petroleum (35 : 65) afforded a least polar fraction of 4-chloronaphtho-[1,2-*c*][1,2,5]thiadiazole **10** in trace quantity as brown needles, mp 93–95 °C (DCM); *m*/*z* 220 (M^+, 100%) and 185 (28, M − Cl); a second fraction of 4,5-dihydronaphtho[1,2-*c*][1,2,5]thiadiazole **9** (15 mg, 8%) as a light yellow solid, mp 26–27 °C (lit.,[5] 29–30 °C); δ_H (250 MHz; $CDCl_3$) 8.04 (1H, m), 7.38–7.31 (3H, m), 3.23 (2H, m) and 3.14 (2H, m); δ_C (63 MHz; $CDCl_3$) 160.3, 156.9, 137.4, 130.1, 129.8, 128.5, 127.5, 125.5, 28.6 and 26.3; *m*/*z* 188 (M^+, 100%) and 116 (17, M − CH_2CNS); and a most polar fraction of naphtho[1,2-*c*:3,4-*c*′]bis[1,2,5]thiadiazole **7** (45 mg, 20%) as colourless needles identical with those above.

5,6-Dihydro-4*H*-benzo[3,4]cyclohepta[1,2-*c*][1,2,5]thiadiazole 12

To a refluxing solution of benzosuberone oxime **11** (175 mg, 1.0 mmol) in CCl_4 (10 ml), a solution of trithiazyl trichloride (734 mg, 3.0 mmol) in CCl_4 (15 ml) was added dropwise. The mixture was heated under reflux for 16 h. The mixture was cooled to room temperature and filtered through a short pad of silica. The filtrate was concentrated under reduced pressure. Column chromatography of the residue on silica with DCM–light petroleum (60 : 40) afforded the *title compound* (61 mg, 30%) as a light yellow oil (Found: M^+ 202.0568. $C_{11}H_{10}N_2S$ requires

§ As we have seen, tetrasulfur tetranitride can sometimes effect the same transformation as the trimer **1** but, being less reactive, it requires more vigorous conditions and the resulting reactions are generally more complex, giving lower yields of 1,2,5-thiadiazoles.

202.0565); ν_{max} (neat)/cm^{-1} 1604s, 1457s, 1405s, 1338s, 1277m, 1252m and 1164; δ_H (270 MHz; $CDCl_3$) 7.82 (1H, m), 7.41–7.26 (3H, m), 3.03 (2H, t, *J* 7.3), 2.69 (2H, t, *J* 6.7) and 2.30 (2H, quintet, *J* 6.7); δ_C (63 MHz; $CDCl_3$) 161.9, 161.0, 139.8, 132.8, 129.7, 129.6, 129.1, 127.0, 32.4, 28.7 and 28.2; *m*/*z* 202 (M^+, 100%), 187 (50), 174 (12), 148 (9) and 116 (19).

Benzocyclohepta[1,2-*c*][1,2,5]thiadiazole **12** (60 mg, 0.3 mmol) and trithiazyl trichloride (110 mg, 0.45 mmol) were dissolved in CCl_4 (10 ml). The mixture was heated under reflux for 16 h. TLC showed no formation of a new product and the mixture was concentrated under reduced pressure. Column chromatography of the residue with DCM–light petroleum (60 : 40) recovered the starting material **12** (53 mg, 88%).

7-*p*-Methoxybenzylidene-7*H*-cyclopenta[1,2-*c*:3,4-*c*′]bis[1,2,5]-thiadiazole 13

7*H*-Cyclopenta[1,2-*c*:3,4-*c*′]bis[1,2,5]thiadiazole **3** (73 mg, 0.4 mmol), anisaldehyde (65 mg, 0.48 mmol) and one drop of piperidine were dissolved in benzene (5 ml). The mixture was heated under reflux for 2 h. The mixture was cooled to room temperature and concentrated under reduced pressure. Column chromatography of the residue on silica with DCM afforded the *title compound* (82 mg, 68%) as bright yellow needles, mp 179–180 °C (ethanol) (Found: C, 51.9; H, 2.4; N, 18.3. $C_{13}H_8N_4OS_2$ requires C, 52.0; H, 2.7; N, 18.65%); ν_{max} (Nujol mull)/cm^{-1} 1600s, 1568m, 1512s, 1268s, 1178s, 1025s and 831s; δ_H (250 MHz; $CDCl_3$) 8.47 (2H, dt, *J* 8.9, 2.5), 7.84 (1H, s, alkene H), 7.05 (2H, dt, *J* 8.9, 2.5) and 3.91 (3H, s, OMe); δ_C (63 MHz; $CDCl_3$) 172.3, 168.2, 162.5, 155.1, 152.9, 136.5, 134.1, 126.8, 116.5, 114.4 and 55.5 (OMe); *m*/*z* 300 (M^+, 100%), 285 (19, M − Me) and 269 (33, M − MeO).

8-*p*-Methoxybenzylidene-8*H*-indeno[1,2-*c*][1,2,5]thiadiazole 14

Indeno[1,2-*c*][1,2,5]thiadiazole **5** (85 mg, 0.5 mmol), anisaldehyde (83 mg, 0.6 mmol) and one drop of piperidine were dissolved in benzene (5 ml). The mixture was heated under reflux for 5 h. The mixture was cooled to room temperature and concentrated under reduced pressure. Column chromatography of the residue on silica with DCM afforded the *title compound* (30 mg, 21%) as light yellow needles, mp 134–135 °C (ethanol) (Found: C, 69.6; H, 4.0; N, 9.45. $C_{17}H_{12}N_2OS$ requires C, 69.8; H, 4.1; N, 9.6%); ν_{max} (Nujol mull)/cm^{-1} 1596s, 1514s, 1346m, 1329m, 1312m, 1262 and 1181s; δ_H (400 MHz; $CDCl_3$) 8.37 (2H, dt, *J* 8.9, 2.5), 7.85 (1H, m), 7.79 (1H, m), 7.41 (1H, s, alkene H), 7.44–7.35 (2H, m), 7.01 (2H, dt, *J* 8.9, 2.5) and 3.88 (3H, s, OMe); δ_C (101 MHz; $CDCl_3$) 166.4, 163.0, 161.1, 148.1, 133.0, 130.9, 129.6, 129.1, 127.9, 127.7, 122.1, 121.9, 120.7, 114.0 and 55.3 (OMe); *m*/*z* 292 (M^+, 66%), 277 (20, M − Me), 260 (100, M − MeOH) and 190 (54, $MeOC_6H_4CHC{=}C{=}NS$).

7*H*-Cyclopenta[1,2-*c*:3,4-*c*′]bis[1,2,5]thiadiazol-7-one 15

Method 1. 7*H*-Cyclopenta[1,2-*c*:3,4-*c*′]bis[1,2,5]thiadiazole **3** (100 mg, 0.5 mmol), pyridinium chlorochromate (1.0 g, 4.6 mmol) and Celite (2.5 g) were mixed in benzene (10 ml) and heated under reflux for 16 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was concentrated under reduced pressure. Column chromatography of the residue on silica with DCM–light petroleum (1 : 1) afforded the *title compound* **15** (15 mg, 14%), mp 140–142 °C, identical with that described earlier.[2a]

Method 2. To a refluxing solution of cyclopentane-1,3-dione (98 mg, 1.0 mmol) in toluene (10 ml), trithiazyl trichloride (489 mg, 2.0 mmol) in toluene (10 ml) was added dropwise and the reaction mixture was heated under reflux for 16 h. The reaction mixture was cooled to room temperature and filtered through a pad of activated charcoal on top of a pad of silica. The filtrate was concentrated under reduced pressure. Column chromatography of the residue on silica with DCM–light petroleum (1 : 1) afforded the title compound **15** (27 mg, 14%) identical with that described above.

7-Dicyanomethylene-7*H*-cyclopenta[1,2-*c*:3,4-*c*′]bis[1,2,5]thiadiazole 17 and 7-(1-cyano-1-piperidinomethylene)-7*H*-cyclopenta[1,2-*c*:3,4-*c*′]bis[1,2,5]thiadiazole 18

7*H*-Cyclopenta[1,2-*c*:3,4-*c*′]bis[1,2,5]thiadiazol-7-one **15** (80 mg, 0.41 mmol) and malononitrile (27 mg, 0.41 mmol) were dissolved in benzene (10 ml) in the presence of a drop of piperidine. The reaction mixture was heated under reflux for 1 h. The reaction mixture was cooled and filtered, and the filtrate was concentrated under reduced pressure. Column chromatography of the residue on silica with DCM–light petroleum (1 : 1) afforded 7-dicyanomethylene-7*H*-cyclopenta[1,2-*c*:3,4-*c*′]bis-[1,2,5]thiadiazole **17** (57 mg, 57%) as yellow prisms, mp 258–260 °C (ethanol) (Found: M^+ 243.9623. $C_8N_6S_2$ requires *M* 243.9626); ν_{max} (Nujol mull)/cm^{-1} 2246w (nitrile) and 1593 (C=N); δ_C (101 MHz; $CDCl_3$) 164.4, 157.5, 141.8, 110.2 (nitrile C) and 83.4 ($C(CN)_2$); *m*/*z* 244 (M^+, 100%), 192 (1, M − SNCCN), 160 (6, M − SNCCN), 116 (19, SNCCNS), 84 (15, SNCCN) and 64 (62, S_2). Concentration of the mother liquor resulted in the separation of 7-(1-cyano-1-piperidinomethylene)-7*H*-cyclopenta[1,2-*c*:3,4-*c*′]bis[1,2,5]thiadiazole **18** (8 mg, 6%) as yellow needles, mp 142–144 °C (ethanol) (Found: M^+ 302.0403. $C_{12}H_{10}N_6S_2$ requires *M* 302.0408); ν_{max} (Nujol mull)/cm^{-1} 2237w (nitrile) and 1591 (C=N); δ_H (400 MHz; $CDCl_3$) 3.95 (4H, t, *J* 5.5), 1.90–1.84 (4H, m), 1.83–1.78 (2H, m); δ_C (101 MHz; $CDCl_3$) 168.8, 166.5, 151.5, 150.8, 124.7, 112.9, 107.1, 53.4, 26.7 and 23.6; *m*/*z* 302 (M^+, 25%), 274 (7), 269 (6, M − HS), 220 (14, M − C_5H_8N) and 83 (100, C_5H_9N).

A similar reaction between 7*H*-cyclopenta[1,2-*c*:3,4-*c*′]-bis[1,2,5]thiadiazol-7-one **15** (58 mg, 0.30 mmol) and malononitrile (20 mg, 0.3 mmol) in refluxing benzene in the presence of 1 drop of Hunig's base afforded 7-dicyanomethylene-7*H*-cyclopenta[1,2-*c*:3,4-*c*′]bis[1,2,5]thiadiazole **17** (68 mg, 94%) identical to that described above.

7-Dicyanomethylene-7*H*-cyclopenta[1,2-*c*:3,4-*c*′]bis[1,2,5]-thiadiazole–tetrathiafulvalene complex

7-Dicyanomethylene-7*H*-cyclopenta[1,2-*c*:3,4-*c*′]bis[1,2,5]thiadiazole **17** (20 mg, 0.08 mmol) in acetonitrile (6 ml) was mixed slowly with a solution of TTF (16.8 mg, 0.08 mmol) in acetonitrile (3 ml). Black needles separated after 30 min, and the solution was allowed to stand for 2 h when precipitation appeared to be complete. The black needles were filtered off and washed with acetonitrile to give the *title compound* (11 mg, 31%) as metallic black needles, mp 208–210 °C (acetonitrile) (Found: C, 37.7; H, 0.8; N, 18.6. $C_{14}H_4N_6S_6$ requires C, 37.5; H, 0.9; N, 18.7%); ν_{max} (Nujol mull)/cm^{-1} 2227w (nitrile) and 1549w (C=N); *m*/*z* (FAB$^+$) 204 (M^+, 100%, TTF).

Acknowledgements

We thank the Commonwealth Scholarship Commission and the British Council for a scholarship to T.-Y. Y., Professor D. J. Williams for X-ray crystallography, MDL Information Systems (UK Ltd) for financial support and the Wolfson Foundation for establishing the Wolfson Centre for Organic Chemistry in Medical Science at Imperial College.

References

1 C. W. Rees and T.-Y. Yue, *J. Chem. Soc., Perkin Trans. 1*, 2001, 662.
2 (*a*) X.-G. Duan, X.-L. Duan, C. W. Rees and T.-Y. Yue, *J. Chem. Soc., Perkin Trans. 1*, 1997, 2957; (*b*) X.-G. Duan and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1997, 2695; (*c*) X.-G. Duan, X.-L. Duan and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1997, 2831.
3 S. Mataka, A. Hosoki, K. Takahashi and M. Tashiro, *Synthesis*, 1979, 524.
4 J. Cho and K. Kim, *J. Chem. Soc., Perkin Trans. 1*, 1993, 2345.

5 V. Bertini, A. De Munno and A. Marraccini, *J. Org. Chem.*, 1972, **37**, 2587.
6 S. Mataka, Y. Ikezaki, K. Takahashi, A. Tori-i and M. Tashiro, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 2221.
7 R. Rathore, N. Saxena and S. Chandrasekaran, *Synth. Commun.*, 1986, **16**, 1493.
8 B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower, *J. Am. Chem. Soc.*, 1958, **80**, 2806.
9 I. F. Perepichka, A. F. Popov, T. V. Artyomova, A. N. Vdovichenko, M. R. Bryce, A. S. Batsanov, J. A. K. Howard and J. L. Megson, *J. Chem. Soc., Perkin Trans. 2*, 1995, 3.
10 J. Ferraris, D. O. Cowan, V. Walatka and J. H. Perlstein, *J. Am. Chem. Soc.*, 1973, **95**, 948.
11 D. J. Williams, unpublished work.
12 M. Prashad, Y. Liu and O. Repic, *Tetrahedron Lett.*, 2001, **42**, 2277 and references therein.