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Synthesis of 1,3,4-thiadiazole oligomers

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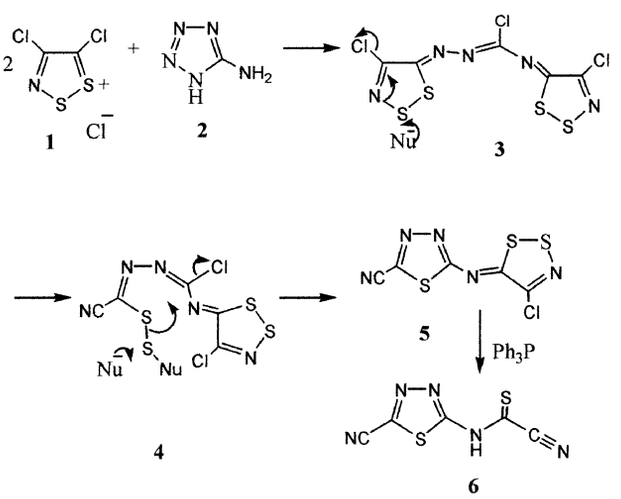
A range of hydrazono chlorides **8**, readily prepared from 5-substituted tetrazoles **7** and Appel salt **1**, are rapidly converted by triphenylphosphine into 5-cyano-1,3,4-thiadiazoles **9** in high yield. These cyanides are converted by azide into the corresponding tetrazoles **10** which with Appel salt give the hydrazono chlorides **11** which are similarly converted by triphenylphosphine into the bi-1,3,4-thiadiazolyls **12a**,**c**,**g**, all in high yield. Repetition of the 3-step sequence (**12** ⟶ **13** ⟶ **14** ⟶ **15**) gives the ter-1,3,4-thiadiazolyls **15a**,**g**.

We have shown that 4,5-dichloro-1,2,3-dithiazolium chloride (Appel salt) **1** reacts with 5-aminotetrazole **2** at both the primary amino group and the heterocyclic ring, to give a modest yield of the red crystalline bis(imino-1,2,3-dithiazole) **3**.[1] Although simple mono(imino-1,2,3-dithiazoles) are usually very stable thermally, the red solution of **3** in warm DMSO (35 °C) slowly faded to yellow over one or two days. This change was complete in 4 h at 50 °C and a new yellow product **5** was isolated; similar results were obtained in DMF (Scheme 1).



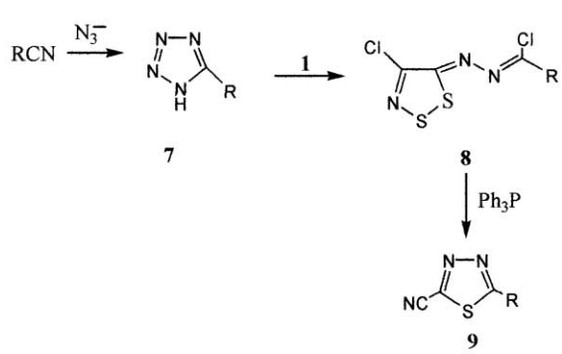
Scheme 1

Evaporation of the solvent, flash chromatography on silica and crystallisation from DCM–light petroleum (60–80 °C) gave fine yellow cubic crystals (25%).

Analysis, spectroscopy and mass spectrometry of the yellow product showed the absence of hydrogen, the presence of a conjugated cyano group and the molecular formula to be $C_5ClN_5S_3$, representing the loss of the elements of SCl_2 from **3**. These data suggested that one of the dithiazole rings had opened, probably under nucleophilic attack by DMSO or DMF since **5** was stable above 50 °C in acetone, DCM, chloroform or ethanol. Attack on sulfur in the appropriate dithiazole ring (arrows in **3**) will generate a cyano group, as usual,[2] and further attack will generate nucleophilic sulfur suitably placed (**4**) to cyclise to a cyano-1,3,4-thiadiazole. This sequence suggested the thiadiazole structure **5** for the yellow product, and this has been confirmed by X-ray crystallography.[1] It is interesting to note that the central "imidoyl" chloride in **3** is inert to intermolecular displacement[1] and therefore considered not to be the first site for nucleophilic attack on **3**; however the corresponding chlorine in intermediate **4** is reactive enough to be displaced intramolecularly as shown (Scheme 1).

We have shown that triphenylphosphine rapidly converts *N*-arylimino-1,2,3-dithiazoles into cyanothioformanilides under mild conditions,[3] and this stronger thiophile should be more effective for the conversion of **3** into **5** by the mechanism of Scheme 1. The red compound **3** was therefore treated with triphenylphosphine in undried DCM; it rapidly gave (30 min, RT) the same yellow product **5** (25%) together with the orange cyanothioformamide **6** (20%). This latter has arisen by the usual opening of the second dithiazole ring in **3** by triphenylphosphine; treatment of **3** with an excess of the phosphine gave **6** (85%) as the sole product. Triphenylphosphine oxide and sulfide were also isolated in almost quantitative yields in agreement with a previously proposed mechanism.[3]

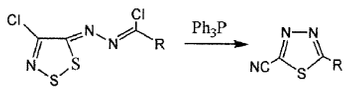
We have also shown the conversion of 5-substituted tetrazoles **7**, where the 5-substituent is inert towards Appel salt **1**, into the hydrazono chlorides **8** by reaction with one equivalent of this salt.[1] On the basis of the mechanism of Scheme 1, these products would be expected to react similarly with triphenylphosphine to give the 1,3,4-thiadiazoles **9**, analogous to **5** but with the second dithiazole imine replaced by the substituent R (Scheme 2). With 2 equiv. of triphenylphosphine in undried



Scheme 2

DCM at RT for 15 min, compounds **8** all gave the corresponding 5-substituted-2-cyano-1,3,4-thiadiazoles **9a**–**h** (Table 1), together with triphenylphosphine oxide and sulfide in high yields, as expected.[3] This transformation provides good support

Table 1 Conversion of hydrazono chlorides **8** into 1,3,4-thiadiazoles **9** with triphenylphosphine



8 **9**

R	9	Yield (%)
C_6H_5	**9a**	82
4-O_2N–C_6H_4	**9b**	92
4-MeO–C_6H_4	**9c**	99
4-NC–C_6H_4	**9d**	72
C_6H_5O	**9e**	75
$ClCH_2CH_2$	**9f**	90
MeS	**9g**	73
2-Thienyl	**9h**	76

for the structures assigned to **8**, and the sequence of reactions shown in Scheme 2 provides a very mild, high-yielding synthesis of 1,3,4-thiadiazoles **9** from nitriles, R–CN, *via* the tetrazoles **7** and dithiazoles **8**.

This new route to 1,3,4-thiadiazoles has the useful feature of directly giving the reactive 2-cyano derivatives **9** which are rare 1,3,4-thiadiazoles, previously made only by multi-step processes.[4] Since the starting cyanide, RCN, is converted into the new cyanide **9** the sequence of Scheme 2 could be repeated to give a series of unsymmetrical thiadiazole oligomers of precisely known structure, with a cyano group at one end and various groups, including strong electron donors, at the other. This sequence of reactions would be somewhat similar to that used by Huisgen *et al.* to convert acyltetrazoles into oligomeric 1,3,4-oxadiazoles.[5] So far we have shown (Table 2) that this route gives high yields of the highly fluorescent dimers **12** (R = Ph, 4-MeOC_6H_4 and MeS) and trimers **15** (R = Ph and MeS). A few such trimers have been made before by classical 1,3,4-thiadiazole ring forming reactions.[6] The structure of **15g** was confirmed by X-ray diffraction;[7] in the crystal the thiadiazole rings are nearly coplanar with the all-*anti* orientation. Well-defined conjugated oligomers related to polythiophenes are important as active compounds in field effect transistors and light-modulating and light-emitting devices with properties that can surpass those of the corresponding polymers.[8]

Experimental

General details

Except where noted, all reactions were protected from moisture by calcium chloride drying tubes, unless carried out under a dry nitrogen atmosphere. Anhydrous magnesium sulfate was used for drying organic extracts, and volatiles were removed under reduced pressure. Ether refers to diethyl ether and light petroleum had bp 60–80 °C. All reactions and chromatography column eluents were monitored by TLC using commercial aluminium-backed thin-layer chromatography (TLC) plates (Merck Kieselgel 60 F_{254}). The plates were observed under UV light at 254 and 350 nm. Flash column chromatography refers to the technique[9] using medium pressure generated by hand bellows or a small air compressor and was used throughout. Dry flash chromatography was carried out with suction using a water pump as described by Harwood.[10] Melting points were determined using a Reichert Kofler hot-stage apparatus. IR spectra were recorded on a Perkin–Elmer 1710FT spectrometer. ^{1}H NMR spectra were recorded on JEOL GSX 270 (at 270 MHz), Bruker AM300WB (at 300 MHz), Bruker RX-400 (at 400 MHz) and Bruker AM500 (at 500 MHz) machines. ^{13}C NMR spectra were recorded on JOEL GSX 270 (at 68 MHz), Bruker AM300WB (at 76 MHz), Bruker RX-400(at 100 MHz) and Bruker AM500 (at 125 MHz) machines. Deuterated solvents were used for homonuclear lock and the signals are referenced to the deuterated solvent peaks. Mass spectra were recorded on a VG micromass 7070E or a VG Autospec "Q" mass spectrometer.

3-Chloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-(4-cyanophenyl)-1,2-diazaprop-2-ene 8d

5-(4-Cyanophenyl)tetrazole [**7**, R = –C_6H_4–CN(4)][11] (1.71 g, 10 mmol) and Appel salt **1** (2.29 g, 11 mmol) in dichloromethane (40 ml) were stirred at room temperature for 4 h. After removal of solvent under reduced pressure the crude product was purified by flash chromatography on silica gel, eluting with dichloromethane–hexane to give the title compound **8d** (2.4 g, 70%) as yellow crystals (Found: C, 37.9; H, 1.1; N, 17.4. $C_{10}H_4Cl_2N_4S_2$ requires C, 38.1; H, 1.3; N, 17.8%); δ_H (500 MHz, $CDCl_3$) 8.21–8.24 (2H, dd, Ar–H), 7.75–7.78 (2H, dd, Ar–H); δ_C (100 MHz, $CDCl_3$) 167.0, 148.2, 144.3, 137.3, 132.4, 129.1, 118.0, 115.4; *m*/*z* 315 (M^+, 65%), 280 (M^+ − Cl, 46), 212 (M^+ − SCl_2, 90), 135, 103, 77.

3-Chloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-methylsulfanyl-1,2-diazaprop-2-ene 8g

5-Methylsulfanyltetrazole (2.0 g, 17.2 mmol) and Appel salt **1** (3.95 g, 19.0 mmol) in dichloromethane (80 ml) were stirred at room temperature for 12 h to give the title compound **8g** (3.50 g, 78%) as yellow crystals (Found: C, 18.2; H, 1.1; N, 16.0. $C_4H_3Cl_2N_3S_3$ requires C, 18.5; H, 1.2; N, 16.15%); δ_H (500 MHz, $CDCl_3$) 2.60 (3H, s, SMe); δ_C (100 MHz, $CDCl_3$) 164.2, 152.7, 143.9, 17.0; *m*/*z* 260 (M^+, 42%), 224 (M^+ − Cl, 53), 157 (M^+ − SCl_2, 62), 151, 135, 103, 77.

3-Chloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-(2-thienyl)-1,2-diazaprop-2-ene 8h

5-(2-Thienyl)tetrazole (**7**, R = 2-thienyl)[12] (1.87 g, 12.3 mmol) and Appel salt **1** (2.82 g, 13.5 mmol) in dichloromethane (20 ml) were stirred at room temperature for 4 h. Work-up as before gave the *title compound* **8h** (3.12 g, 86%) as red crystals, mp 122–123 °C (Found: C, 28.1; H, 0.9; N, 13.9. $C_7H_3Cl_2N_3S_3$ requires C, 28.4; H, 1.0; 14.2%); δ_H (500 MHz, $CDCl_3$) 7.79 (1H, dd, *J* 3.7, 1.4 Hz, Ar–H), 7.56 (1H, dd, *J* 5.1, 1.3 Hz, Ar–H), 7.12 (1H, dd, *J* 5.1, 3.8 Hz, Ar–H); δ_C (100 MHz, $CDCl_3$) 165.5, 144.3, 144.2, 137.7, 132.9, 132.5, 127.9; *m*/*z* 296 (M^+, 30%), 64 (S_2^+, 25).

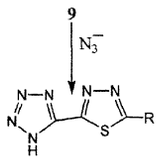
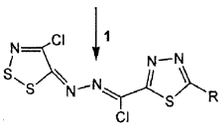
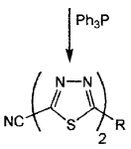
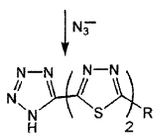
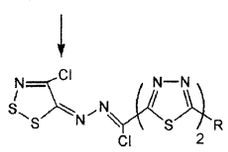
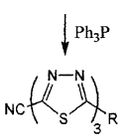
2-Phenyl-1,3,4-thiadiazole-5-carbonitrile 9a

To a solution of 3-chloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-phenyl-1,2-diazaprop-2-ene **8a**[1] (6.46 g, 22 mmol) in dichloromethane (250 ml), triphenylphosphine (12.88 g, 49 mmol) was added portionwise. The reaction mixture was stirred at room temperature for 10 min and evaporated to dryness. The product was purified by flash chromatography on silica gel eluting with dichloromethane to give the *title compound* **9a** (3.43 g, 82%), mp 116–117 °C (Found: C, 58.0; H, 2.6; N, 22.2. $C_9H_5N_3S$ requires C, 57.75; H, 2.7; N, 22.5%); ν_{max} (Nujol)/cm^{-1} 2236 (CN), 1568, 1108, 774 and 733; δ_H (270 MHz, $CDCl_3$) 7.45 (5H, m, Ar–H); δ_C (68 MHz, $CDCl_3$) 172.3, 138.4, 133.0, 129, 128.1, 110.1 (CN); *m*/*z* 187 (M^+, 100%), 135 (61, $PhCNS^+$), 121 (23, $PhCS^+$), 103 (35, $PhCN^+$), 84 (5, $C_2N_2S^+$), 77 (26, $C_6H_5^+$).

2-(4-Nitrophenyl)-1,3,4-thiadiazole-5-carbonitrile 9b

To a solution of 3-chloro-l-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-(4-nitrophenyl)-1,2-diazaprop-2-ene **8b**[1] (100 mg, 0.30 mmol) in dichloromethane (15 ml), triphenylphosphine (173 mg, 0.66 mmol) was added portionwise. The reaction mixture was stirred at room temperature for 10 min and evaporated

Table 2 Repeated sequence of cyanide ⟶ tetrazole ⟶ iminodithiazole ⟶ cyanide

		R					
		C_6H_5	Yield (%)	4-MeO·C_6H_4	Yield (%)	MeS	Yield (%)
	**10**	**a**	86	**c**	100	**g**	97
	**11**	**a**	71	—[a]		**g**	84
	**12**	**a**	83	**c**	59[b]	**g**	85
	**13**	**a**	92		—	**g**	89
	**14**	**a**	90		—	**g**	87
	**15**	**a**	64		—	**g**	79

[a] Not isolated. [b] Yield from **10c**.

to dryness. The product was purified by flash chromatography on silica gel, eluting with dichloromethane–light petroleum (1 : 1) to give the *title compound* **9b** (64 mg, 92%), mp 185 °C (Found: C, 46.2; H, 1.5; N, 24.0. $C_9H_4N_4O_2S$ requires C, 46.55; H, 1.7; N, 24.1%); ν_{max} (Nujol)/cm^{-1} 2246 (CN), 1603, 1522, 1431, 1407, 1352, 1319, 1303, 1239, 1192, 1162, 1100, 990, 872, 854, 757 and 691; δ_H (270 MHz, $CDCl_3$) 8.41 (2H, dd, *J* 1, 5 Hz, Ar–H), 8.22 (2H, dd, *J* 1, 5 Hz, Ar–H); δ_C (68 MHz, $CDCl_3$) 172.2, 138.3, 132.9, 129.6, 128.6, 128.1, 110.1 (CN); *m*/*z* 232 (M^+, 15%), 202 (58, $M^+ - NO$), 160 (9), 148 (7), 136 (28), 118 (100, $OC_6H_4CN^+$), 91 (8).

2-(4-Methoxyphenyl)-1,3,4-thiadiazole-5-carbonitrile 9c

To a solution of 3-chloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-(4-methoxyphenyl)-1,2-diazaprop-2-ene **8c**[1] (2.22 g, 7.00 mmol) in dichloromethane (150 ml), triphenylphosphine (4.01 g, 15.3 mmol) was added portionwise. The reaction mixture was stirred at room temperature for 10 min and evaporated to dryness. The product was purified by flash chromatography on silica gel, eluting with dichloromethane to give the *title compound* **9c** (1.50 g, 99%) as fluorescent needles, mp 132–133 °C (Found: C, 55.4; H, 3.0; N, 19.3. $C_{10}H_7N_3OS$ requires C, 55.3; H, 3.2; N, 19.35%); ν_{max} (Nujol)/cm^{-1} 2240 (CN), 1598, 1515, 1433, 1401, 1318, 1265, 1261, 1176, 1105, 1034, 983, 837, 722 and 625; δ_H (270 MHz, $CDCl_3$) 7.79 (2H, d, *J* 9 Hz, Ar–H), 7.03 (2H, d, *J* 9 Hz, Ar–H), 3.91 (3H, s, Ar–OCH_3); δ_C (68 MHz, $CDCl_3$) 172.0, 163.4, 137.3, 130.4, 120.7, 115.1, 110.3 (CN), 55.6; *m*/*z* 217 (M^+, 90%), 202 (3, $M^+ - CH_3$), 174 (4), 165 (3), 151 (23), 146 (4), 133 (100, $CH_3OC_6H_4CN^+$), 122 (6), 118 (8), 108 (6), 103 (18), 90 (23), 75 (11).

2-(4-Cyanophenyl)-1,3,4-thiadiazole-5-carbonitrile 9d

The hydrazono chloride **8d** (1.2 g, 3.81 mmol) and triphenylphosphine (2.20 g, 8.38 mmol) in dichloromethane (14 ml) were stirred at room temperature for 1 h. After evaporation under reduced pressure the reaction mixture was separated by flash chromatography on silica, with hexanes–ethyl acetate as eluent to give the title compound **9d** (0.58 g, 72%) as crystals (Found: C, 56.2; H, 1.7; N, 26.2. $C_{10}H_4N_4S$ requires C, 56.6; H, 1.9; N, 26.4%); δ_H (500 MHz, $CDCl_3$) 8.17–8.19 (2H, dd, Ar–H), 7.87–7.89 (1H, dd, Ar–H); δ_C (100 MHz, $CDCl_3$) 170.0, 139.5, 133.3, 131.7, 129.0, 117.4, 116.2 (CN), 109.7 (CN); *m*/*z* 212 (M^+, 100%), 135, 121.

2-Phenoxy-1,3,4-thiadiazole-5-carbonitrile 9e

To a solution of 3-chloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-phenoxy-1,2-diazaprop-2-ene **8e**[1] (200 mg, 0.66 mmol) in dichloromethane (20 ml), triphenylphosphine (359 mg, 1.39 mmol) was added portionwise. The reaction mixture was purified by flash chromatography on silica gel, eluting with dichloromethane–light petroleum (bp 60–80 °C) to give the title compound **9e** (100 mg, 75%) as a colourless oil; ν_{max} (Nujol)/cm^{-1} 2238 (CN), 1567, 1525, 1445, 1398, 1358, 1281, 1248, 1198, 1123, 1008, 965, 845 and 637; δ_H (270 MHz, $CDCl_3$) 7.45 (2H, m, Ar–H), 7.29 (3H, m, Ar–H); *m*/*z* 203 (M^+, 2%), 201 (100), 157 (91), 77 (100, $C_6H_5^+$).

2-Chloroethyl-1,3,4-thiadiazole-5-carbonitrile 9f

To a solution of 3,5-dichloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-1,2-diazapent-2-ene **8f**[1] (100 mg, 0.36 mmol) in

dichloromethane (15 ml), triphenylphosphine (199 mg, 0.76 mmol) was added portionwise. The reaction mixture was stirred at room temperature for 10 min and evaporated to an oil. The product was purified by flash chromatography on silica gel, eluting with dichloromethane–light petroleum (bp 60–80 °C) (1 : 1) to give the title compound **9f** (57 mg, 90%) as an unstable colourless oil; ν_{max} (Nujol)/cm^{-1} 2243 (CN), 1702, 1607, 1447, 1397, 1296, 1171, 1120, 1086, 1017, 946 and 656; δ_H (270 MHz, $CDCl_3$) 3.95 (2H, t, *J*, 6 Hz, C*H*$_2$–CH$_2$Cl), 3.70 (2H, t, *J* 6 Hz, –CH$_2$–C*H*$_2$–Cl); *m*/*z* 174 (M$^+$, 86%), 138 (M$^+$ − HCl, 100), 70 (SCCN$^+$, 67), 52 (NCCN$^+$, 23).

2-Methylsulfanyl-1,3,4-thiadiazole-5-carbonitrile 9g

3-Chloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-methylsulfanyl-1,2-diazaprop-2-ene **8g** (2.44 g, 9.38 mmol) and triphenylphosphine (5.42 g, 20.6 mmol) in dichloromethane (160 ml) were stirred at room temperature for 30 min to give the *title compound* (1.08 g, 73%) as a crystalline solid, mp 116–117 °C (Found: C, 30.3; H, 2.3; N, 27.1. $C_4H_3N_3S_2$ requires C, 30.6; H, 1.9; N, 26.7%); δ_H (500 MHz, $CDCl_3$) 2.90 (3H, *s*, SCH_3); δ_C (100 MHz, $CDCl_3$) 173.0, 137.9, 109.8 (CN), 16.6 (SCH_3); *m*/*z* 157 (M$^+$, 100%), 135, 103, 84.

2-(2-Thienyl)-1,3,4-thiadiazole-5-carbonitrile 9h

The hydrazono chloride **8h** (1.61 g, 5.44 mmol) and triphenylphosphine (3.00 g, 11.4 mmol) in dichloromethane (14 ml) were stirred at room temperature for 1 h and chromatographed as before to give the *title compound* **9h** (0.8 g, 76%) as crystals, mp 129–130 °C (Found: C, 43.3; H, 1.3; N, 21.6. $C_7H_3N_3S_2$ requires C, 43.5; H, 1.6; N, 21.7%); δ_H (500 MHz, $CDCl_3$) 7.72 (1H, dd, *J* 3.7, 1.1 Hz, Ar–H), 7.67 (1H, dd, *J* 5.1, 1.1 Hz, Ar–H), 7.21 (1H, dd, *J* 5.0, 3.8 Hz, Ar–H); δ_C (100 MHz, $CDCl_3$) 165.7, 137.2, 132.3, 131.9, 130.0, 128.7, 110.0 (CN); *m*/*z* 193 (M$^+$, 100%), 168 (35), 135, 121.

2-Phenyl-5-(tetrazol-5-yl)-1,3,4-thiadiazole 10a

A mixture of 5-phenyl-1,3,4-thiadiazole-2-carbonitrile **9a** (2.00 g, 11.0 mmol), anhydrous aluminium chloride (1.43 g, 11.0 mmol) and pulverised sodium azide (2.16 g, 33.0 mmol) suspended in tetrahydrofuran (80 ml) was refluxed under nitrogen for 24 h. The reaction mixture was cooled to room temperature and neutralised by the slow addition of 2 M hydrochloric acid (20 ml) (CAUTION! HN_3 was generated, and was removed by the use of a water pump). The tetrahydrofuran layer was separated from the aqueous layer, extraction of the aqueous layer with ethyl acetate (3 × 300 ml) recovered the remaining product. The ethyl acetate extracts were combined with the tetrahydrofuran layer and dried. Evaporation of the solvents gave, after recrystallisation (from ethanol), the title compound **10a** (2.11 g, 86%) as a pale yellow solid, mp 243–245 °C; ν_{max} (Nujol)/cm^{-1} 1570, 1169, 1095, 734 and 689; δ_H (270 MHz, $(CD_3)_2SO$) 8.13 (2H, d, *J* 1 Hz, Ar–H), 7.63 (3H, m, Ar–H); *m*/*z* 230 (M$^+$, 100%), 202 (30, M$^+$ − N$_2$), 188 (34, M$^+$ − N$_3$), 135 (18, PhCNS$^+$), 121 (62, PhCS$^+$), 103 (64, PhCN$^+$), 77 (47, C$_6$H$_5^+$).

2-(4-Methoxyphenyl)-5-(tetrazol-5-yl)-1,3,4-thiadiazole 10c

A mixture of 2-(4-methoxyphenyl)-1,3,4-thiadiazole-5-carbonitrile **9c** (1.00 g, 4.6 mmol), anhydrous aluminium chloride (0.61 g, 4.6 mmol) and pulverised sodium azide (1.70 g, 21 mmol) suspended in tetrahydrofuran (50 ml) was refluxed under nitrogen for 24 h. The reaction mixture was cooled to room temperature and neutralised by the slow addition of 2 M hydrochloric acid (7 ml) (CAUTION! HN_3 was generated, and was removed by the use of a water pump). The tetrahydrofuran layer was separated from the aqueous layer, extraction of the aqueous layer with ethyl acetate (3 × 150 ml) gave the remaining product. The ethyl acetate extracts were combined with the tetrahydrofuran layer and dried. Evaporation of the solvents gave, after recrystallisation (from ethanol), the *title compound* **10c** (1.12 g, 100%) as a pale yellow solid, mp 234 °C (Found: 260.0480. $C_{10}H_8N_6OS$ requires 260.0480); ν_{max} (Nujol)/cm^{-1} 1603, 1402, 1378, 1313, 1263, 1170, 1103, 1084, 1029, 995, 975, 841, 811 and 723; δ_H (270 MHz, $(CD_3)_2SO$) 8.04 (2H, d, *J* 9 Hz, Ar–H), 7.14 (2H, d, *J* 9 Hz, Ar–H) and 3.87 (3H, s, Ar–OC*H*$_3$); δ_C (68 MHz, $(CD_3)_2SO$) 169.9, 162.3, 153.1, 149.9, 130.0, 121.2, 115.0, 55.8 (Ar–OC*H*$_3$); *m*/*z* 260 (M$^+$, 8%), 232 (8, M$^+$ − N$_2$), 217 (36, M$^+$ − HN$_3$), 151 (3), 108 (100, CH$_3$OPh$^+$), 103 (31), 102 (10), 76 (13, C$_6$H$_4^+$), 70 (11).

3-Chloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-(2-phenyl-1,3,4-thiadiazol-5-yl)-1,2-diazaprop-2-ene 11a

To a suspension of 2-phenyl-5-(5-tetrazolyl)-1,3,4-thiadiazole **10a** (1.5 g, 6.5 mmol) in dichloromethane (200 ml) was added 4,5-dichloro-1,2,3-dithiazolium chloride **1** (1.5 g, 7.19 mmol). The mixture was stirred at room temperature for 15 h. Pyridine (0.5 ml, 6.5 mmol) was slowly added and stirred for a further 10 min. A yellow–brown solid was filtered off and washed with dichloromethane to give the title compound **11a**. The filtrate was concentrated *in vacuo* and the product was purified by flash chromatography on silica gel eluting with dichloromethane to give more of the *title compound* **11a** (1.73 g, 71%) as red cubes, mp 158–159 °C (Found: C, 35.9; H, 1.0; N, 18.3. $C_{11}H_5Cl_2N_5S_3$ requires C, 35.3; H, 1.3; N, 18.7%); ν_{max} (Nujol)/cm^{-1} 1553, 1157, 886, 733 and 723; δ_H (500 MHz, DMSO-d$_6$) 8.09–8.11 (2H, *m*, Ar–H), 7.57–7.65 (3H, m, Ar–H); δ_C (100 MHz, DMSO-d$_6$) 169.6, 162.6, 154.6, 142.9, 139.6, 132.4, 129.7, 128.8, 128.3; *m*/*z* 374 (M$^+$, 10%), 310 (24, M$^+$ − S$_2$), 271 (100, M$^+$ − C$_6$H$_5$CN), 187 (73, M$^+$ − C$_6$H$_5$C$_3$N$_3$S), 135 (59, C$_6$H$_5$CNS$^+$), 121 (42, C$_6$H$_5$CS$^+$), 103 (35, PhCN$^+$), 77 (34, C$_6$H$_5^+$), 64 (25, S$^+_2$).

3-Chloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-(2-methylsulfanyl-1,3,4-thiadiazol-5-yl)-1,2-diazaprop-2-ene 11g

2-Methylsulfanyl-5-(tetrazol-5-yl)-1,3,4-thiadiazole **10g** was prepared (97%) from the cyanide **9g**, aluminium chloride and sodium azide exactly as for the other tetrazoles **10**, and was converted directly into **11g**. Compound **10g** (400 mg, 2.00 mmol) and Appel salt **1** (417 mg, 2.00 mmol) in dichloromethane (6 ml) were stirred at room temperature for 6 h to give the *title compound* **11g** (580 mg, 84%) as a red crystalline solid, mp 193–194 °C (Found: C, 20.8; H, 1.4; N, 20.5. $C_6H_3Cl_2N_5S_4$ requires C, 20.9; H, 0.9; N, 20.3%); δ_H (500 MHz, DMSO-d$_6$) 2.84 (3H, s, SMe); δ_C (100 MHz, DMSO-d$_6$) 172.7, 169.5, 162.0, 142.8, 139.1, 16.7; *m*/*z* 344 (M$^+$, 18%), 280 (M$^+$ − S$_2$, 30), 271, 187, 64 (S$^+_2$, 25).

5-Cyano-5′-phenyl-2,2′-bi(1,3,4-thiadiazolyl) 12a

To a suspension of 3-chloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-(2-phenyl-1,3,4-thiadiazol-5-yl)-1,2-diazaprop-2-ene **11a** (1.44 g, 3.85 mmol) in dichloromethane (120 ml), triphenylphosphine (2.22 g, 8.47 mmol) was added portionwise. The reaction mixture was stirred at room temperature for 30 min and evaporated to dryness. The product was purified by flash chromatography on silica gel, eluting with dichloromethane to give the *title compound* **12a** (0.84 g, 83%), mp 245–246 °C (Found: C, 48.6; H, 1.8; N, 25.9. $C_{11}H_5N_5S_2$ requires C, 48.7; H, 1.85; N, 25.8%); ν_{max} (Nujol)/cm^{-1} 2242 (CN), 1568, 1092, 949, 772, 687 and 606; δ_H (500 MHz, DMSO-d$_6$) 8.10–8.13 (2H, m, Ar–H), 7.60–7.67 (3H, m, Ar–H); δ_C (100 MHz, DMSO-d$_6$) 170.7, 157.1, 141.1, 132.0, 129.2, 128.2, 127.9, 110.0 (CN); *m*/*z* 271 (M$^+$, 100%), 187 (5, C$_6$H$_5$C$_3$N$_3$S$^+$), 168 (6), 135 (32, C$_6$H$_5$CNS$^+$), 121 (20, C$_6$H$_5$CS$^+$), 103 (15, PhCN$^+$), 77 (16, C$_6$H$_5^+$).

5-Cyano-5′-(4-methoxyphenyl)-2,2′-bi(1,3,4-thiadiazolyl) 12c

To a suspension of 2-(4-methoxyphenyl)-5-(tetrazol-5-yl)-1,3,4-thiadiazole **10c** (100 mg, 0.38 mmol) in dichloromethane

(30 ml) was added 4,5-dichloro-1,2,3-dithiazolium chloride **1** (96 mg, 0.46 mmol). The mixture was stirred at room temperature for 16 h. Pyridine (0.03 ml, 0.38 mmol) was added and stirred for a further 4 h, and then triphenylphosphine (352 mg, 1.3 mmol) was added and this mixture was stirred for 30 min. The product was purified by flash chromatography on silica eluting with ethyl acetate–dichloromethane (1 : 9) to give the *title compound* **12c** (68 mg, 59%) as yellow–green needles, mp 258–260 °C (Found: C, 47.8; H, 2.1; N, 23.2. $C_{12}H_7N_5OS_2$ requires C, 47.8; H, 2.3; N, 23.3%); ν_{max} (Nujol)/cm^{-1} 2243 (CN), 1598, 1514, 1397, 1316, 1305, 1255, 1175, 1118, 1091, 1024, 981, 949, 843 and 799; δ_H (270 MHz, $CDCl_3$) 8.07 (2H, d, *J* 8 Hz, Ar–H), 7.16 (2H, d, *J* 8 Hz, Ar–H), 3.88 (3H, s, ArOCH_3); *m*/*z* 301 (M^+, 65%), 217 (19, $M^+ - C_2N_2S$), 165 (6, $M^+ - C_4N_4S$), 151 (32), 133 (100, $MeOC_6H_4CN^+$), 122 (10), 108 (12), 103 (15), 90 (22), 88 (10), 70 (24), 63 (13), 52 (16, C_2N_2).

5-Cyano-5′-methylsulfanyl-2,2′-bi(1,3,4-thiadiazolyl) 12g

3-Chloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-(2-methylsulfanyl-1,3,4-thiadiazol-5-yl)-1,2-diazaprop-2-ene **11g** (300 mg, 0.87 mmol) and triphenylphosphine (530 mg, 1.92 mmol) in dichloromethane (10 ml) was stirred at room temperature for 30 min to give the *title compound* **12g** (178 mg, 85%), mp 168–169 °C (Found: C, 29.9; H, 1.5; N, 29.1. $C_6H_3N_5S_3$ requires C, 29.9; H, 1.25; N, 29.0%); δ_H (500 MHz, $CDCl_3$) 2.91 (3H, s, SMe); δ_C (100 MHz, $CDCl_3$) 172.5, 162.4, 156.4, 140.2, 109.5 (CN), 16.7 (SMe); *m*/*z* 241 (M^+, 19%), 177 ($M - S_2$, 32).

3-Chloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-[2-(2-phenyl-1,3,4-thiadiazol-5-yl)-1,3,4-thiadiazol-5-yl]-1,2-diazaprop-2-ene 14a

5-Phenyl-5′-tetrazolyl-2,2′-bi(1,3,4-thiadiazolyl) **13a** was prepared (92%) from the cyanide **12a**, aluminium chloride and sodium azide, as before, and was converted directly into **14a**. Compound **13a** (300 mg, 0.96 mmol) and Appel salt **1** (200 mg, 0.96 mmol) in dichloromethane (6 ml) were stirred at room temperature for 6 h to give the *title compound* **14a** (396 mg, 90%) as a red crystalline solid, mp 266–267 °C (Found: C, 33.8; H, 1.0; N, 21.3. $C_{13}H_5Cl_2N_7S_4$ requires C, 34.1; H, 1.1; N, 21.4%); δ_H (500 MHz, DMSO-d_6) 8.09–8.11 (2H, m, Ar–H), 7.57–7.65 (3H, m, Ar–H); δ_C (100 MHz, DMSO-d_6) 169.6, 162.6, 154.6, 142.9, 139.6, 132.4, 129.7, 128.8, 128.3; *m*/*z* 458 (M^+, 20%), 310 ($M^+ - S_2$, 48), 271 ($M^+ - C_6H_5CN$, 100), 135 ($C_6H_5CNS^+$, 45), 103 ($PhCN^+$, 34), 77 ($C_6H_5^+$, 20).

3-Chloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-[2-(2-methylsulfanyl-1,3,4-thiadiazol-5-yl)-1,3,4-thiadiazol-5-yl]-1,2-diazaprop-2-ene 14g

5-Methylsulfanyl-5′-tetrazolyl-2,2′-bi(1,3,4-thiadiazolyl) **13g** was prepared (89%) from cyanide **12g**, aluminium chloride and sodium azide, as before, and was converted directly into **14g**. Compound **13g** (120 mg, 0.42 mmol) and Appel salt **1** (97 mg, 0.46 mmol) in dichloromethane (6 ml) were stirred at room temperature for 6 h to give the *title compound* **14g** (158 mg, 87%) as a red crystalline solid, mp 224–224 °C (Found: C, 22.5; H, 1.1; N, 22.7. $C_8H_3Cl_2N_7S_5$ requires C, 22.4; H, 0.7; N, 22.9%); δ_H (500 MHz, DMSO-d_6) 2.88 (3H, s, SMe); δ_C (100 MHz, DMSO-d_6), 172.2, 170.7, 164.1, 161.3, 157.6, 142.9, 138.7, 16.9 (SMe); *m*/*z* 428 (M^+, 30%), 64 (S_2^+, 25).

5-Cyano-5″-phenyl-2,2′:5′,2″-ter(1,3,4-thiadiazolyl) 15a

The hydrazono chloride **14a** (217 mg, 0.47 mmol) and triphenylphosphine (273 mg, 1.04 mmol) in dichloromethane (10 ml) were stirred at room temperature for 30 min to give the *title compound* **15a** (108 mg, 64%), mp 308–310 °C (Found: C, 43.5; H, 1.9; N, 27.1. $C_{13}H_5N_7S_3$ requires C, 43.9; H, 1.4; N, 27.6%); δ_H (500 MHz, DMSO-d_6) 8.10–8.13 (2H, m, Ar–H), 7.60–7.67 (3H, m, Ar–H); δ_C (100 MHz, DMSO-d_6) 170.7, 163.0, 157.1, 141.1, 132.0, 129.2, 128.2, 127.9, 110.0 (CN); *m*/*z* 355 (M^+, 100%), 187 ($M^+ - C_6H_5C_3N_3S^+$, 2), 135 ($C_6H_5CNS^+$, 40), 121 ($C_6H_5CS^+$, 27), 103 ($PhCN^+$, 10), 77 ($C_6H_5^+$, 20).

5-Cyano-5″-methylsulfanyl-2,2′:5′,2″-ter(1,3,4-thiadiazolyl) 15g

The hydrazono chloride **14g** (100 mg, 0.23 mmol) and triphenylphosphine (135 mg, 0.51 mmol) in dichloromethane (6 ml) were stirred at room temperature for 30 min to give the *title compound* **15g** (60 mg, 79%) as crystalline solid, mp 264–265 °C (Found: C, 29.7; H, 0.8; N, 30.3. $C_8H_3N_7S_4$ requires C, 29.5; H, 0.9; N, 30.1%); δ_H (500 MHz, DMSO-d_6) 2.89 (s, SMe); δ_C (100 MHz, DMSO-d_6) 172.5, 162.9, 161.4, 159.1, 157.3, 142.4, 110.6 (CN), 16.9 (SMe); *m*/*z* 325 (M^+, 100%), 168 (6), 135, 121.

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