PERKIN 1

Reaction of Herz salts with malononitrile: a general route to (6*H*-1,2,3-benzodithiazol-6-ylidene)malononitriles

Panayiotis A. Koutentis [a] **and Charles W. Rees** [b]

[a] *Department of Chemistry, University of Cyprus, P.O. Box 20537, 1678 Nicosia, Cyprus. E-mail: koutenti@ucy.ac.cy*
[b] *Department of Chemistry, Imperial College of Science, Technology and Medicine, London, UK SW7 2AY. E-mail: c.rees@ic.ac.uk*

Received (in Cambridge, UK) 2nd November 2001, Accepted 3rd December 2001
First published as an Advance Article on the web 3rd January 2002

6-Chloro-1,2,3-benzodithiazolium chlorides **1** (Herz salts) react with malononitrile to afford the highly coloured ylidenes **2** in low to moderate yields. The reaction is general but complex and in the case of the 6-chloro-4-methoxy-1,2,3-benzodithiazolium chloride **1e** the by-products 6-chloro-4-methoxy-1,3-benzothiazole-2-carbonitrile **3**, 6-chloro-4-methoxy-2,3-dihydro-1,3-benzothiazole-2,2-dicarbonitrile **4**, and 4-methoxy-6-thiocyanato-1,3-benzothiazole-2-carbonitrile **5** were also isolated.

The term "Herz reaction" describes the condensation of aromatic amines and disulfur dichloride to give the corresponding 1,2,3-benzodithiazolium chlorides (Herz salts) and their subsequent hydrolysis to afford 2-aminobenzenethiols.[1,2] This transformation and the accompanying *para*-chlorination of the starting aniline have received considerable attention.[3,4] However, although 1,2,3-benzodithiazolium salts have been known for 80 years[5] their chemistry that does not involve degradation of the heterocyclic ring is still surprisingly sparse.

Recently we needed an independent synthesis of (5*H*-naphtho[1,2-*d*][1,2,3]dithiazol-5-ylidene)malononitrile **2i** and were able to prepare it from 1-aminonaphthalene, which gave 5-chloronaphtho[1,2-*d*][1,2,3]dithiazolium chloride when treated with disulfur dichloride; when this Herz compound was treated with malononitrile and 2 equivalents of base it gave the desired target in moderate yield.[6]

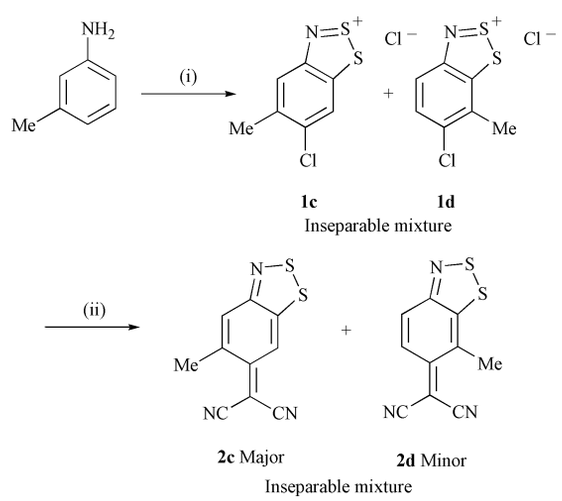
A review of the literature showed that few such condensations with Herz salts had been carried out and that all involved the use of amines. Interestingly these nitrogen based condensation products were found to exhibit antiallergic activities.[7] We now show that the reaction of malononitrile with Herz salts **1** to give ylidenes **2** is general, although moderate to low yielding, and we discuss the identification of other minor products of mechanistic interest.

Results and discussion

The Herz compounds were prepared according to literature procedures (*cf.* refs. 1 and 8) and were washed with DCM to remove soluble impurities and in general were obtained free (by LRMS) of sulfur impurities. Some Herz salts such as the 5-nitro-, 4-chloro-6-methyl- and the 4-phenyl-benzodithiazolium chlorides were either unobtainable or the quality of the salt was so poor that it could not be used. The displacement reaction with malononitrile was quite general and a range of ylidenes was synthesised (Table 1); however, attempts to react diethyl malonate with the Herz salts to generate the analogous ylidenes were unsuccessful.

The reactions were complex (TLC) but the ylidenes could be readily identified by their intense blue–lilac colour in solution; any co-running by-products could be removed from the chromatographed fraction containing the ylidene by one or two recrystallisations from glacial acetic acid to afford analytically pure samples. The naphtho- and the 1,2,5-benzothiadiaza Herz salts gave the best yields (40 and 30% respectively) and it is presumed that the stability added by the fused aromatic ring is the contributing factor.

Interestingly the reaction of 3-monosubstituted anilines with S_2Cl_2 to form Herz salts was reported to result in cyclisation exclusively *para* to that substituent.[9] Whilst 3-methoxyaniline followed this trend, the Herz salts **1c** and **1d** derived from 3-methylaniline gave a mixture of 5-methyl (**2c**) and the more sterically demanding 7-methyl substituted ylidene (**2d**) upon reaction with malononitrile and base (Scheme 1). The mixture

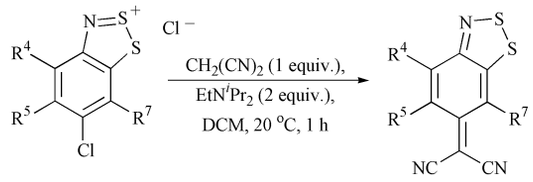


Scheme 1 *Reagents and conditons*: (i) S_2Cl_2, CH_3CO_2H, 90 °C, 8 h; (ii) $CH_2(CN)_2$ (1 equiv.), EtN^iPr_2 (2 equiv.), DCM, 20 °C, 1 h, 5%.

was inseparable but the ^1H and ^{13}C NMR data for the condensation products **2c** and **2d** confirmed their identity. The ratio of **2c** : **2d** was 2 : 1 (by ^1H NMR) after recrystallisation from glacial acetic acid.

In the solid state the ylidenes **2** were lustrous and metallic in appearance. In solution the compounds were deep blue or lilac in colour, with the lowest energy UV absorption band as high as λ_{max} 575 nm (log ε 4.35). This transition shifts further into the red with increasing solvent polarity which suggests intramolecular charge transfer. The ^{13}C NMR data of ylidenes **2**

Table 1 Ylidenes **2** derived from Herz salts **1** by treatment with malononitrile in the presence of Hünig's base



1 **2**

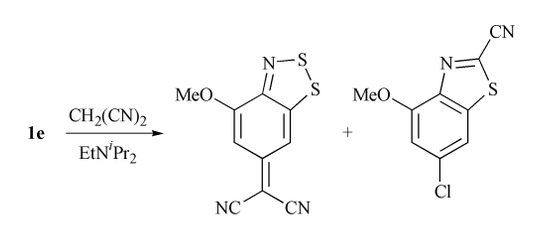
Ylidene	R^4	R^5	R^7	UV–vis λ_{max}/nm (log ε)	^{13}C (ppm) $C(CN)_2$	Yield (%)
2a	H	H	H	575 (4.35)	61.2	11
2b	Me	H	H	569 (4.37)	60.8	16
2c	H	Me	H	N.d.[b]	61.5	5[a]
2d	H	H	Me	N.d.[b]	62.8	5[a]
2e	MeO	H	H	564 (4.33)	60.2	11
2f	H	MeO	H	554 (4.41)	59.7	14
2g	Me	Me	H	569 (4.34)	61.3	13
2h	Me	H	Me	569 (4.34)	62.2	15
2i	–CH=CH–CH=CH–		H	530 (4.41)	61.3	40
2j	=N–S–N=		H	517 (4.35)	63.3	30

[a] The 5- and 7-methyl derivatives **2c** and **2d** were obtained as an inseparable mixture from 3-methylaniline. [b] N.d. = not determined.

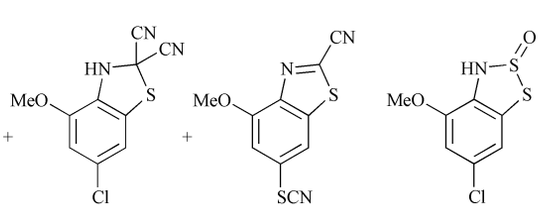
indicated that a considerable negative charge was located on the central carbon of the malononitrile group [60–63 ppm, $C(CN)_2$] indicating the presence of a considerable push–pull effect, the 'push' originating presumably from both sulfurs in the dithiazole ring.

Despite attempts to optimise conditions for the treatment of the Herz salts with malononitrile to give the ylidenes, the yields were poor; variables investigated were reaction time, rate of addition of base, quantity of base, order of addition, reaction solvent (DCM, THF, EtOH) and base (Hünig's base, pyridine, DBU). The only factor that significantly affected the yields of the ylidenes **2** was the quantity of base. If less base was added the yield dropped; a 2 : 1 stoichiometry of base to malononitrile was optimal.

The other products formed during the ylidene synthesis from 4-methoxy-1,2,3-benzodithiazolium chloride **1e** and malononitrile in the presence of Hünig's base were investigated. Apart from the ylidene **2e** (11%), three other compounds were isolated. A fluorescent cream coloured solid was identified as 6-chloro-4-methoxybenzothiazole-2-carbonitrile **3** (24%); a ^{1}H–^{13}C correlation ^{13}C NMR eliminated the possibility of the isomeric benzisothiazole structure. A trace amount of a faint yellow crystalline compound **4** was isolated and tentatively assigned the dicyanomethylene structure, based on the LRMS and on the fact that it readily formed the benzothiazole **3** on standing. The remaining compound was tentatively assigned as 4-methoxy-6-thiocyanatobenzothiazole-2-carbonitrile **5** (5%).



2e **3**



4 **5** **6**

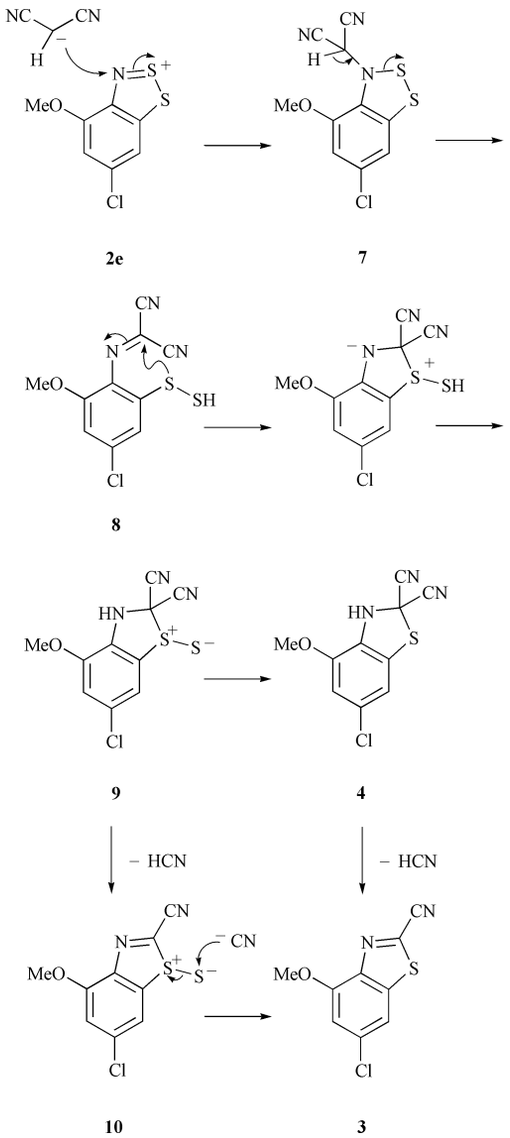
All the standard spectral data were collected for the compound **5** which is isomeric with the ylidene **2e**, $C_{10}H_5N_3OS_2$, as shown by microanalysis and HRMS. However compound **5** is almost colourless and does not show the typical ylidene absorptions in the UV spectrum; its spectrum λ_{max} 303 (log ε 4.06) and 344 nm (3.84) was very similar to that of the benzothiazole **3** λ_{max} 302 (log ε 4.17) and 339 nm (3.78), and both compounds were strongly fluorescent. The LRMS of compound **5** had a relatively intense fragmentation from the parent ion *m*/*z* (EI) 247 (62%) to 218 (100) which was significantly absent in the LRMS of the ylidene **2e**. LSMS confirmed the fragment *m*/*z* (EI) 218 (100%) to come directly from the parent ion. A similar fragmentation was seen from the benzothiazole **3** parent ion *m*/*z* (EI) 224 (54%) to 195 (100). HRMS supported the formula of CHO for this fragment. The IR data show two very different nitrile stretches for **5** at 2231 and 2159 cm^{-1} and the low wavenumber nitrile stretch is in the region for thiocyanates (2170–2135 cm^{-1}).[10] The ^{13}C NMR shows ten separate carbon environments, two of which can be identified as belonging to the two nitriles (112.9 and 109.7 ppm) and one of which is the methoxy carbon resonance (57.3 ppm). The ^{1}H NMR shows the same aromatic substitution pattern as for the benzothiazole **3** and the ylidene **2e**. Like the UV data, the ^{13}C and ^{1}H NMR patterns for the aromatic resonances were closer to the benzothiazole **3** than to the ylidene **2e**. Based on all this we have assigned the compound as the 6-thiocyanato derivative **5**.

A suspicion that 6-chloro-4-methoxy-1,2,3-benzodithiazole 2-oxide **6** (formed by hydrolysis of the corresponding Herz salt **1e**) was the species reacting with the malononitrile to give the by-products **3**, **4** and **5** was eliminated by treating a pure sample of oxide **6** with malononitrile and Hünig's base. TLC analysis was unable to locate any of the above products.

Benzothiazoles have been prepared from Herz salts previously; however, the procedure involved reduction of the heterocyclic dithiazole ring to afford the aminobenzenethiol, which is then cyclised to the benzothiazole.[3] Since under our reaction conditions such a reduction and cyclisation are not feasible an alternative pathway must be operating.

We postulate (Scheme 2) that malononitrile attacks the dithiazolium nitrogen † to afford the adduct **7** which ring opens to the imine **8**. Cyclisation by the highly nucleophilic sulfur followed by proton transfer could yield benzothiazole **9** which

† Broadly similar, alternative, mechanisms initiated by nucleophilic attack at either ring sulfur atom seem somewhat less likely, but cannot be discounted at present.



Scheme 2

could lose sulfur *via* a chain extension mechanism to give **4**. Alternatively loss of HCN from **9** could occur first to give **10** followed by loss of sulfur to afford benzothiazole **3**. It is also possible that cyanide could play a part in the desulfurisation of **9** and **10** thus generating the thiocyanate anions which could displace the activated chlorine atoms, particularly in the starting Herz salt **1**. This could presumably lead to the subsequent formation of benzothiazole **5**.

In conclusion we have demonstrated that the condensation of malononitrile with Herz salts in the presence of base gives highly coloured ylidenemalononitriles in low to modest yields in somewhat complex reactions which can include direct attack of the heterocyclic ring by malononitrile to give various benzothiazole by-products.

Experimental

All reactions and 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. The technique of dry flash chromatography was used throughout for all non-TLC scale chromatographic separations using Sorbsil C60 M40 silica. Petrol refers to light petroleum, bp 60–80 °C.

Melting points were determined using a Reichert Kofler hot-stage apparatus. Solvents used for recrystallisation are indicated after the melting point. UV spectra were obtained using a Perkin-Elmer Lambda II spectrometer and inflections are identified by the abbreviation 'inf'. IR spectra were recorded on a Perkin–Elmer 1710FT spectrometer and strong, medium and weak peaks are represented by s, m and w respectively. ^{1}H NMR spectra were recorded on Bruker RX-400 (at 400 MHz) and Bruker AM500 (at 500 MHz) machines. ^{13}C NMR spectra were recorded on Bruker RX-400 (at 100 MHz) and Bruker AM500 (at 125 MHz) machines. A doublet of sextets is represented by dhex. 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. Microanalyses were performed on a Perkin–Elmer 2400 CHN Analyser.

Reaction of Herz salts with malononitrile

Typical procedure. To a stirred suspension of 6-chloro-1,2,3-benzodithiazol-2-ium chloride **1a**[11] (223 mg, 1 mmol) in DCM (25 ml) at *ca.* 20 °C, malononitrile (66 mg, 1 mmol) was added followed by the addition of Hünig's base (348 μl, 2 mmol). After 1 h TLC indicated a deep blue product and chromatography (DCM) gave *(6H-1,2,3-benzodithiazol-6-ylidene)-propanedinitrile* **2a** (24 mg, 11%) as deep blue prisms, mp 283–285 °C (from glacial acetic acid) (Found: C, 49.7; H, 1.5; N, 19.1. $C_9H_3N_3S_2$ requires C, 49.8; H, 1.4; N, 19.35%); λ_{max}(DCM)/nm 228 (log ε 3.66), 276 inf (3.96), 281 (3.99), 333 inf (4.00), 343 (4.12), 395 (3.23), 551 inf (4.33), 575 (4.35), 619 inf (4.13); ν_{max}(Nujol)/cm^{-1} 3096w, 3068w and 3047w (Ar CH), 2205s (CN), 2175m (CN), 1596s (C=N), 1513s (C=C), 1489s, 1455s, 1407s, 1353m, 1339m, 1245m, 1199w, 1171w, 1150m, 1029m, 985m, 902m, 870m, 838m, 789s, 725m, 649m; δ_H(400 MHz; DMSO-d_6) 7.88 (1H, d, *J* 9.6 Hz, Ar *H*-4), 7.82 (1H, d, *J* 2.0 Hz, Ar *H*-7), 7.50 (1H, dd, *J* 2.0, 9.6 Hz, Ar *H*-5); δ_C(100 MHz; DMSO-d_6) 159.0, 153.2, 152.0, 129.0 (Ar *C*H), 128.2 (Ar *C*H), 116.4 (*C*N), 116.4 (*C*N), 109.8 (Ar *C*H), 61.2 [*C*(CN)$_2$]; *m*/*z* (EI) 217 (M$^+$, 100%), 190 (M$^+$ − CHN, 5), 173 (4), 162 (12), 155 (4), 141 (9), 127 (5), 114 (5), 87 (3), 76 ($C_6H_4^+$, 7), 64 (S_2^+, 9) (Found: M$^+$, 216.9749. $C_9H_3N_3S_2$ requires *M*, 216.9768).

(4-Methyl-6*H*-1,2,3-benzodithiazol-6-ylidene)propanedinitrile 2b

Similar treatment of 6-chloro-4-methyl-1,2,3-benzodithiazol-2-ium chloride **1b**[11] with malononitrile and Hünig's base gave the *title compound* **2b** (16%) as lustrous green–brown solid, mp > 300 °C (from glacial acetic acid) (Found: C, 51.8; H, 2.2; N, 18.0. $C_{10}H_5N_3S_2$ requires C, 51.95; H, 2.2; N, 18.2%); λ_{max}(DCM)/nm 228 (log ε 3.87), 275 inf (3.99), 279 (4.01), 347 (4.14), 395 (3.44), 414 (3.42), 545 inf (4.35), 569 (4.37), 610 inf (4.16); ν_{max}(Nujol)/cm^{-1} 3068w (Ar CH), 2201s (CN), 1603s (C=N), 1507s (C=C), 1432m, 1399s, 1319s, 1253w, 1133m, 1037w, 985m, 904m, 881w, 860w, 840w, 826w, 809m, 736m, 577w; δ_H(400 MHz; DMSO-d_6) 7.70 (1H, d, *J* 2.0 Hz, Ar *H*), 7.31 (1H, m, Ar *H*), 2.53 (3H, d, *J* 1.1 Hz, C*H*$_3$); δ_C(100 MHz; DMSO-d_6) 159.8, 153.2, 152.6, 138.4, 126.5 (Ar *C*H), 116.5 (*C*N), 116.5 (*C*N), 108.7 (Ar *C*H), 60.8 [*C*(CN)$_2$], 18.8 (*C*H$_3$); *m*/*z* (EI) 231 (M$^+$, 100%), 203 (2), 198 (3), 171 (3), 140 (3), 128 (3), 115 (3), 101 (2), 89 (2), 64 (4) (Found: M$^+$, 230.9912. $C_{10}H_5N_3S_2$ requires *M*, 230.9925).

(5-Methyl-6*H*-1,2,3-benzodithiazol-6-ylidene)propanedinitrile 2c and (7-methyl-6*H*-1,2,3-benzodithiazol-6-ylidene)-propanedinitrile 2d

Similar treatment of a mixture of 6-chloro-5-methyl-1,2,3-benzodithiazol-2-ium chloride **1c**[12] and 6-chloro-7-methyl-1,2,3-benzodithiazol-2-ium chloride **1d** with malononitrile and Hünig's base gave a mixture of the *title compounds* **2c** and **2d** (5%) as blue needles, mp > 300 °C (from glacial acetic acid) (Found: C, 52.05; H, 2.0; N, 18.0. $C_{10}H_5N_3S_2$ requires C, 51.95; H, 2.2; N, 18.2%); δ_H(400 MHz; DMSO-d_6) **2c**: 7.82 (1H, s, Ar

H-7), 7.72 (1H, m, Ar *H*-4), 2.56 (3H, d, *J* 0.8 Hz, 5-CH_3); **2d**: 7.79 (1H, d, *J* 9.7 Hz, Ar *H*-4), 7.55 (1H, d, *J* 9.7 Hz, Ar *H*-5), 2.60 (3H, s, 7-CH_3); δ_C(100 MHz; DMSO-d_6) **2c**: 158.9, 151.5, 151.0, 138.4, 127.7 (Ar *C*H), 118.3 (*C*N), 117.8 (*C*N), 111.2 (Ar *C*H), 61.5 [*C*$(CN)_2$], 21.6 (5-*C*H_3); **2d**: 158.0, 153.0, 149.2, 131.5 (Ar *C*H), 126.6 (Ar*C*H), 119.0, 118.1 (*C*N), 117.6 (*C*N), 62.8 [*C*$(CN)_2$], 22.4 (7-*C*H_3); δ_C(100 MHz; DMSO-d_6, DEPT 135) **2c**: 127.7 (Ar *C*H), 111.2 (Ar *C*H), 21.6 (5-*C*H_3); **2d**: 131.5 (Ar *C*H), 126.6 (Ar *C*H), 22.4 (7-*C*H_3); *m*/*z* (EI) 231 (M^+, 100%), 204 ($M^+ - CHN$, 27), 177 [$M^+ - 2(CN)$, 3], 171 (3), 153 (9), 140 (3), 128 (3), 102 (4), 89 (2), 76 (2), 64 (S_2^+, 5) (Found: M^+, 230.9936. $C_{10}H_5N_3S_2$ requires *M*, 230.9925).

(4-Methoxy-6*H*-1,2,3-benzodithiazol-6-ylidene)propanedinitrile 2e

Similar treatment of 6-chloro-4-methoxy-1,2,3-benzodithiazol-2-ium chloride **1e**[12] with malononitrile and Hünig's base gave the *title compound* **2e** (11%) as green needles, mp > 300 °C (from glacial acetic acid) (Found: C, 48.3; H, 2.0; N, 16.7. $C_{10}H_5N_3OS_2$ requires C, 48.6; H, 2.0; N, 17.0%); λ_{max}(DCM)/nm 233 (log ε 3.92), 273 (3.91), 345 (4.05), 436 inf (3.66), 541 inf (4.30), 564 (4.33), 610 inf (4.09); ν_{max}(Nujol)/cm^{-1} 3062w (Ar CH), 2202s and 2183s (CN), 1607s (C=N), 1493s, 1461s, 1423s, 1368m, 1324s, 1266s, 1212m, 1190m, 1169s, 1146m, 1035s, 907m, 844s, 810m, 738s, 662m; δ_H(400 MHz; DMSO-d_6) 7.32 (1H, d, *J* 1.6 Hz, Ar *H*), 6.55 (1H, d, *J* 1.6 Hz, Ar *H*), 3.99 (3H, s, CH_3O); δ_C(100 MHz; DMSO-d_6) 155.1, 155.0, 153.2, 152.4, 116.6 (*C*N), 116.5 (*C*N), 106.0 (Ar *C*H), 102.5 (Ar *C*H), 60.2 [*C*$(CN)_2$], 56.8 (*C*H_3O); *m*/*z* (EI) 247 (M^+, 100%), 232 ($M^+ - CH_3$, 5), 214 ($M^+ - HS$, 16), 204 (24), 186 ($M^+ - CHOS$, 12), 177 (9), 162 (5), 152 (3), 128 (4), 113 (7), 101 (3), 89 (6), 64 (S_2^+, 8) (Found: M^+, 246.9879. $C_{10}H_5N_3OS_2$ requires *M*, 246.9874).

(5-Methoxy-6*H*-1,2,3-benzodithiazol-6-ylidene)propanedinitrile 2f

Similar treatment of 6-chloro-5-methoxy-1,2,3-benzodithiazol-2-ium chloride **1f**[12] with malononitrile and Hünig's base gave the *title compound* **2f** (14%) as green–brown needles, mp > 300 °C (from glacial acetic acid) (Found: C, 48.3; H, 1.9; N, 16.7. $C_{10}H_5N_3OS_2$ requires C, 48.6; H, 2.0; N, 17.0%); λ_{max}(DCM)/nm 228 (log ε 4.08), 275 (3.93), 287 inf (3.80), 377 (3.90), 406 inf (3.68), 536 inf (4.40), 554 (4.41), 599 inf (4.14); ν_{max}(Nujol)/cm^{-1} 3061w (Ar CH), 2201s and 2190s (CN), 1588m (C=N), 1515s, 1503s (C=C), 1454s, 1405s, 1363m, 1301w, 1260s, 1231s, 1181w, 1168w, 1048m, 1007s, 978w, 904w, 868s, 826s, 753m, 725s, 687w, 658w; δ_H(400 MHz; DMSO-d_6) 7.81 (1H, s, Ar *H*), 7.30 (1H, s, Ar *H*), 3.94 (3H, s, CH_3O); δ_C(100 MHz; DMSO-d_6) 160.0, 156.6, 149.4, 145.6, 117.5 (*C*N), 117.1 (*C*N), 109.6 (Ar *C*H), 102.4 (Ar *C*H), 59.7 [*C*$(CN)_2$], 56.5 (*C*H_3O); *m*/*z* (EI) 247 (M^+, 100%), 217 ($M^+ - CH_2O$, 36), 207 (25), 204 ($M^+ - C_2H_3O$, 25), 192 ($M^+ - C_2HNO$, 44), 179 (41), 160 (14), 141 (14), 113 (12), 89 (17), 64 (S_2^+, 17) (Found: M^+, 246.9891. $C_{10}H_5N_3OS_2$ requires *M*, 246.9874).

(4,5-Dimethyl-6*H*-1,2,3-benzodithiazol-6-ylidene)propanedinitrile 2g

Similar treatment of 6-chloro-4,5-dimethyl-1,2,3-benzodithiazol-2-ium chloride **1g** with malononitrile and Hünig's base gave the *title compound* **2g** (13 %) as lustrous green needles, mp 259–266 °C (from glacial acetic acid) (Found: C, 54.0; H, 2.8; N, 17.0. $C_{11}H_7N_3S_2$ requires C, 53.9; H, 2.9; N, 17.1%); λ_{max}(DCM)/nm 228 (log ε 3.97), 280 (3.97), 359 (4.06), 406 (3.54), 428 inf (3.50), 552 inf (4.32), 569 (4.34), 610 inf (4.15); ν_{max}(Nujol)/cm^{-1} 3089w (Ar CH), 2200s (CN), 1577s (C=N), 1504s (C=C), 1396m, 1334s, 1196m, 1165s, 1128w, 1103w, 952w, 913w, 868w, 830m, 743m, 714w, 663m; δ_H(400 MHz; DMSO-d_6) 7.76 (1H, s, Ar *H*-7), 2.52 (3H, s, CH_3), 2.48 (3H, s, CH_3); δ_C(125 MHz; DMSO-d_6) 159.6, 152.5, 150.3, 135.2, 134.2, 118.6 (*C*N), 118.2 (*C*N), 110.2 (Ar *C*H), 61.3 [*C*$(CN)_2$], 17.5 (*C*H_3), 16.4 (*C*H_3); *m*/*z* (EI) 245 (M^+, 100%), 230 ($M^+ - CH_3$, 6), 218 ($M^+ - CHN$, 29), 191 (4), 162 (9), 152 (6), 127 (4), 113 (6), 101 (2), 70 (3), 58 (9) (Found: M^+, 245.0089. $C_{11}H_7N_3S_2$ requires *M*, 245.0081).

(4,7-Dimethyl-6*H*-1,2,3-benzodithiazol-6-ylidene)propanedinitrile 2h

Similar treatment of 6-chloro-4,7-dimethyl-1,2,3-benzodithiazol-2-ium chloride **1h** with malononitrile and Hünig's base gave the *title compound* **2h** (15 %) as lustrous green needles, mp > 270 °C (from glacial acetic acid) (Found: C, 53.9; H, 2.7; N, 17.1. $C_{11}H_7N_3S_2$ requires C, 53.9; H, 2.9; N, 17.1%); λ_{max}(DCM)/nm 229 (log ε 3.86), 276 (3.88), 318 (3.59), 353 (4.19), 408 (3.54), 427 inf (3.50), 545 inf (4.37), 569 (4.34), 606 inf (4.24); ν_{max}(Nujol)/cm^{-1} 2199s (CN), 1607s (C=N), 1511s (C=C), 1493s, 1425s, 1405s, 1392s, 1355w, 1290m, 1214m, 1156w, 1122w, 1059m, 1033w, 962m, 909m, 896w, 880m, 834s, 741w, 722w, 685s, 654m; δ_H(400 MHz; DMSO-d_6) 7.36 (1H, d, *J* 1.2 Hz, Ar *H*-5), 2.57 (3H, s, CH_3), 2.49 (3H, hidden by DMSO, CH_3); δ_C(100 MHz; DMSO-d_6) 158.7, 153.0, 150.3, 136.6, 129.0 (Ar *C*H), 118.2 (*C*N), 117.7 (*C*N), 117.6, 62.2 [*C*$(CN)_2$], 22.5 (*C*H_3), 18.4 (*C*H_3); *m*/*z* (EI) 245 (M^+, 100%), 230 ($M^+ - CH_3$, 8), 217 ($M^+ - CH_2N$, 20), 201 (3), 186 (5), 162 (17), 151 (10), 132 (10), 113 (10), 101 (5), 89 (8), 88 (7), 73 (21), 70 (18) (Found: M^+, 245.0071. $C_{11}H_7N_3S_2$ requires *M*, 245.0081).

(5*H*-Naphtho[1,2-*d*][1,2,3]dithiazol-5-ylidene)propanedinitrile 2i

Similar treatment of 5-chloronaphtho[1,2-*d*][1,2,3]dithiazol-2-ium chloride **1i**[13] with malononitrile and Hünig's base gave the title compound **2i** (40%) as lustrous green–brown needles, mp 285–88 °C (from glacial acetic acid), identical with an authentic sample.

(5*H*-[1,2,5]Thiadiazolo[3,4-*e*][1,2,3]benzodithiazol-5-ylidene)-propanedinitrile 2j

Similar treatment of 5-chloro[1,2,5]thiadiazolo[3,4-*e*][1,2,3]-benzodithiazol-2-ium chloride **1j** with malononitrile and Hünig's base gave the *title compound* **2j** (30%) as graphite grey crystals, mp > 300 °C (from glacial acetic acid) (Found: C, 39.2; H, 0.4; N, 25.4. $C_9HN_5S_3$ requires C, 39.3; H, 0.4; N, 25.45%); λ_{max}(DCM)/nm 232 inf (log ε 3.69), 250 inf (3.86), 264 inf (3.97), 277 (4.02), 291 (4.16), 297 (4.17), 302 (4.24), 341 (3.73), 357 (3.72), 378 (3.72), 493 inf (4.30), 517 (4.35), 555 inf (4.26), 590 inf (3.96); ν_{max}(Nujol)/cm^{-1} 3073w (Ar CH), 2209s (CN), 1549m and 1534m (C=N), 1519s (C=C), 1495m, 1394s, 1354w, 1332w, 1283s, 1212w, 1086m, 973w, 864w, 832m, 806w, 739m, 721w; δ_H(500 MHz; DMSO-d_6) 7.95 (1H, s, Ar *H*); δ_C(125 MHz; DMSO-d_6) 156.8, 152.0, 151.2, 149.3, 144.5, 116.3 (*C*N), 116.2 (*C*N), 108.8 (Ar *C*H), 63.3 [*C*$(CN)_2$]; *m*/*z* (EI) 275 (M^+, 100%), 217 (7), 191 ($M^+ - C_2N_2S$, 2), 159 ($M^+ - C_2N_2S_2$, 3), 137.5 (M^{++}, 3), 91 (8), 70 (5), 64 (S_2^+, 9), 46 (NS^+, 3) (Found: M^+, 274.9411. $C_9HN_5S_3$ requires *M*, 274.9394).

Reaction of 6-chloro-4-methoxy-1,2,3-benzodithiazol-2-ium chloride 1e with malononitrile and Hünig's base

To a stirred suspension of 6-chloro-4-methoxy-1,2,3-benzodithiazol-2-ium chloride **1e** (506 mg, 2 mmol) in DCM (25 ml) at *ca.* 20 °C, malononitrile (132 mg, 2 mmol) was added followed by the addition of Hünig's base (695 µl, 4 mmol). After 12 h TLC indicated several products; the volatiles were removed and chromatography (petrol–DCM, 1 : 1) of the residue gave *6-chloro-4-methoxybenzothiazole-2-carbonitrile* **3** (108 mg, 24%) as cream coloured needles, mp 126–128 °C (from cyclohexane) (Found: C, 48.2; H, 2.4; N, 12.3. $C_9H_5ClN_2OS$ requires C, 48.2; H, 2.2; N, 12.5%); λ_{max}(DCM)/nm 256 (log ε 4.24), 294 inf

(4.11), 302 (4.17), 339 (3.78), 351 inf (3.71); ν_{max}(Nujol)/cm^{-1} 3070m and 3035w (Ar CH), 2228m (CN), 1585s and 1562s (C=N) or (C=C), 1464s, 1424s, 1386s, 1325s, 1270s, 1187w, 1137s, 1097m, 1036s, 908w, 863m, 841s, 794m, 783m, 749w, 640w, 603m; δ_H(400 MHz; DMSO-d_6) 7.86 (1H, d, *J* 1.8 Hz, Ar *H*), 7.16 (1H, d, *J* 1.8 Hz, Ar *H*), 3.98 (3H, s, C*H*$_3$O); δ_C(100 MHz; DMSO-d_6) 154.1, 141.1, 137.9, 135.4, 134.7, 113.7 (Ar *C*H), 113.7 (*C*N), 109.5 (Ar *C*H), 56.6 (*C*H$_3$O); δ_C(100 MHz; DMSO-d_6) 154.1 (dhex, *J* 1.5, 4.3, 6.0 Hz, *C*-4), 141.1 (t, *J* 6.8 Hz, *C*-3a), 137.9 (d, *J* 1.7 Hz, *C*-7a), 135.4 (s, *C*-2), 134.7 (t, *J* 4.3 Hz, *C*-6), 113.7 (dd, *J* 5.3, 176.7 Hz, *C*-5 or *C*-7), 113.2 (s, *C*N), 109.5 (dd, *J* 5.6, 167.1 Hz, *C*-5 or *C*-7), 56.6 (q, *J* 146 Hz, *C*H$_3$O); *m*/*z* (EI) 224 (M$^+$, 54%), 195 (M$^+$ − CHO, 100), 189 (M$^+$ − Cl, 7), 181 (16), 159 (27), 129 (10), 93 (13), 81 (9), 79 (15), 69 (27), 62 (9). Further elution (petrol–DCM, 1 : 3) gave *4-methoxy-6-thiocyanatobenzothiazole-2-carbonitrile* **5** (24 mg, 5%) cream coloured needles, mp 169–172 °C (from cyclohexane–pentane) (Found: C, 48.3; H, 2.0; N, 16.9. $C_{10}H_5N_3OS_2$ requires C, 48.6; H, 2.0; N, 17.0%); λ_{max}(DCM)/nm 303 (log ε 4.06), 344 (3.84); ν_{max}(Nujol)/cm^{-1} 3082w and 3062w (Ar CH), 2231m (CN) and 2159m (SCN), 1620m and 1586s (C=N), 1565s and 1508m (C=C), 1383s, 1327s, 1308m, 1280s, 1270m, 1240m, 1209w, 1146m, 1108w, 1092w, 1041m, 906w, 892w, 848w, 830m, 771w, 744w, 721w; δ_H(400 MHz; DCM-d_2) 7.75 (1H, d, *J* 1.6 Hz, Ar *H*), 7.10 (1H, d, *J* 1.7 Hz, Ar *H*), 4.10 (3H, s, C*H*$_3$O); δ_C(100 MHz; DCM-d_2) 155.6, 143.7, 138.7, 136.7, 127.7, 114.6 (Ar *C*H), 112.9 (*C*N), 109.7 (S*C*N), 109.2 (Ar *C*H), 57.3 (*C*H$_3$O); *m*/*z* (EI) 247 (M$^+$, 62%), 220 (M$^+$ − CHN, 13), 218 (M$^+$ − CH$_3$N, 100), 204 (4), 191 (8), 159 (18), 149 (6), 107 (3), 94 (6), 69 (14) (Found: M$^+$, 246.9908. $C_{10}H_5N_3OS_2$ requires *M*, 246.9874); LSMS: (EI, B/E of *m*/*z* 247) 232 (2%), 218 (100), 204 (2), 191 (13), 159 (7); (EI, B^2/E of *m*/*z* 218) 247 (M$^+$, 100%). Further elution (DCM) gave (4-methoxy-6*H*-1,2,3-benzodithiazol-6-ylidene)propanedinitrile **2e** (54 mg, 11%) as green needles, mp > 300 °C (from glacial acetic acid), identical to that described above. A final elution (DCM) gave *6-chloro-4-methoxy-2,3-dihydrobenzothiazole-2,2-dicarbonitrile* **4** (6 mg, 1%) as faint yellow needles, *m*/*z* (EI) 251 (M$^+$, 3%), 224 (M$^+$ − HCN, 49), 195 (M$^+$ − HCN, –CHO, 100), 189 (M$^+$ − HCN, –Cl, 6), 181 (15), 159 (26), 129 (9), 93 (12), 85 (30), 79 (13), 71 (52), 62 (7).

Acknowledgements

We thank the EPSRC for a Research Studentship (P.A.K.), Mr R. Sheppard for expert help with NMR spectroscopy, MDL Information Sytems (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 W. K. Warburton, *Chem. Rev.*, 1957, **57**, 1011.
2 S. W. Schneller, *Int. J. Sulfur Chem.*, 1976, **8**, 579.
3 L. D. Huestis, M. L. Walsh and N. Hahn, *J. Org. Chem.*, 1965, **30**, 2763.
4 P. Hope and L. A. Wiles, *J. Chem. Soc. (C)*, 1967, 1642.
5 L. Cassella and Co., GP. 360,690/1922 (R. Herz, *Chem. Zentralbl.*, 1922, **4**, 948).
6 P. A. Koutentis and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1999, 111.
7 E. Jacobi, R. Gericke and S. M. Coutts, EP: 0056475/1982 (*Chem. Abstr.*, 1982, **97**, 216192).
8 L. Cassella and Co., BP 17 417/1914 (*Chem. Abstr.*, **1922**, **16**, 500).
9 B. Kh. Strelets, L. S. Éfros and Z. V. Todres, *Chem. Heterocycl. Compd. (Engl. Transl.)*, 1970, **6**, 327; B. Kh. Strelets, L. S. Éfros and Z. V. Todres, *Khim. Geterotsikl. Soedin.*, 1970, **6**, 351 (*Chem. Abstr.*, 1970, **73**, 66507).
10 E. Pretsch, J. Seibel, W. Simon and T. Clerc, *Tables of Spectral Data for Structure Determination of Organic Compounds*, Springer-Verlag, Berlin, 2nd Edition, 1989, p. I–65.
11 L. Cassella & Co., Ger. Pat. 367 345/1915 (*Chem. Abstr.*, 1924, **18**, 991).
12 B. Kh. Strelets, L. S. Éfros and Yu. I. Akulin, *Chem. Heterocycl. Compd. (Engl. Transl.)*, 1976, **12**, 161; B. Kh. Strelets, L. S. Éfros and Yu. I. Akulin, *Khim. Geterotsikl. Soedin.*, 1976, **2**, 183 (*Chem. Abstr.*, 1976, **85**, 32925).
13 R. Shibata and M. Okuyama, *Bull. Chem. Soc. Jpn.*, 1936, **11**, 117.