Chemistry of 4-chloro-5-cyano-1,2,3-dithiazolium chloride

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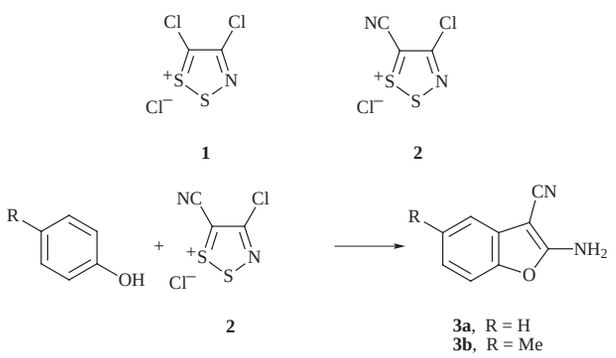
The title compound **2**, modelled on Appel salt **1**, reacts as rapidly as **1** with phenols and anilines; since it lacks a good leaving group at the highly electrophilic C-5 position there is not one low energy reaction pathway, as there is with **1**, and the reactions are complex giving more products in lower yields. With phenols it gives 2-aminobenzofuran-3-carbonitriles **3** resulting from initial nucleophilic attack through the phenolic *ortho*-carbon (Scheme 1). Aniline reacts with **2** largely through nitrogen to give 2-phenyliminopropanedinitrile **7** and the amidine **8**, the bis-anilinomalononitrile **9** and the thioamide **10**, all derived from **7** (Scheme 2). 1,4-Diaminobenzene reacts similarly with **2** to give the mono- and bis-dicyanoimines **22** and **23**, whilst 1,2-diaminobenzene gives the cyclised product 2-aminoquinoxaline-3-carbonitrile **20**. 1,8-Diaminonaphthalene gives the sulfur abstraction product, thiadiazine **24**, and the quinomethane imine **25** and products derived from it (Scheme 7), in keeping with the high reactivity of the naphthalene ring towards electrophilic substitution. In all of these reactions with aromatic amines, salt **2** is acting as an equivalent of NC–$\overset{+\cdot}{\underset{\cdot\cdot}{C}}$–CN (umpolung of malononitrile) whilst with phenols it acts as an equivalent of dicyanocarbene, NC–$\ddot{C}$–CN.

4,5-Dichloro-1,2,3-dithiazolium chloride (Appel salt) **1**[1] has found extensive use in heterocyclic synthesis[2–8] because of the ready displacement of the 5-chlorine atom by nucleophiles, and subsequent attack at either ring sulfur with opening of the dithiazole ring and formation of the latent cyano group. We recently described[9] the synthesis and structure of a number of salts analogous to **1** but with the 5-Cl replaced by non-leaving



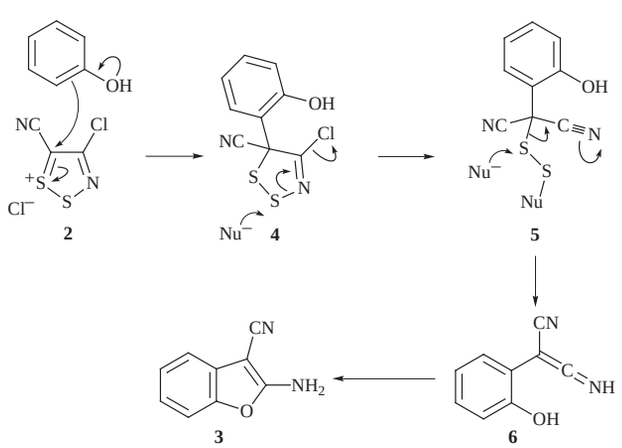
groups, and we questioned how such modified substrates would respond to nucleophilic attack. We describe here some chemistry of the 5-cyano salt **2** which is readily prepared as golden flakes from malononitrile and disulfur dichloride.[9]

Reaction of cyano salt 2 with phenols

Phenols react smoothly as ambident nucleophiles with Appel salt **1**, displacing the 5-Cl atom through *ortho* and *para* ring carbons to give deeply coloured cyclohexadienone derivatives of 1,2,3-dithiazoles in high yield.[1,10] When the cyano salt **2** was treated similarly, in dichloromethane (DCM) at room temperature in the presence of Hünig's base, the reactions were considerably more complex, not surprisingly in view of the absence of a good leaving group at the highly electrophilic 5-position.

Phenol and 4-methylphenol gave low yields of products which, from their spectroscopic properties, appeared to be aminobenzofurancarbonitriles. From mechanistic considerations (see below) the most likely structures were thought to be the 2-amino-3-carbonitriles **3a**,**b** or the isomeric 3-amino-2-carbonitriles. Both parent compounds (R = H) are reported in the literature; the reported melting points for **3a** (lit.,[11] over 270 °C) and the 3-amino-2-carbonitrile isomer (lit.,[12] 154–155 °C) seemed unusually different, and the melting point of our product **3a**, 179–181 °C, was significantly different to both values. The spectroscopic data were insufficient to identify our product conclusively, and so this was proved, by X-ray crystallography,[13] to be 2-aminobenzofuran-3-carbonitrile **3a**.

A possible mechanism for this transformation is shown in Scheme 1. This is based on nucleophilic attack at the 5-position



Scheme 1

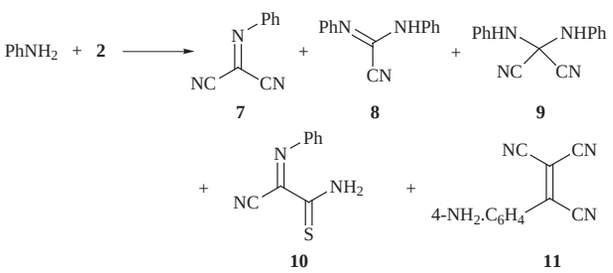
of the salt **2** by phenol through the *ortho*-carbon to give adduct **4**. This is entirely analogous to the reaction of phenol with Appel salt **1**[1,10] but, in the absence of a good leaving group at C-5, the dithiazole ring is attacked further by an external nucleophile at S-2 to cleave the S–N bond and regenerate the nitrile group, to give intermediate **5**. Subsequent nucleophilic attack on **5** could give the ketenimine **6** which would collapse to the observed benzofuran **3**. The nature of the nucleophilic species in Scheme 1 is not known, but the phenol or phenoxide ions or chloride ions are possibilities.

A similar mechanism, but with initial attack by phenol through oxygen would have resulted in the unobserved

3-amino-2-carbonitrile isomers. We were surprised that in this reaction of phenol there was no indication of attack *via* its *para* position, analogous to the reaction with Appel salt.[1,10] It is possible that the early steps of the reaction are reversible and become irreversible only on cyclisation to the furan, or that furan formation actually occurs earlier in the sequence by displacement of the chlorine by the phenolic oxygen in **4**. It may be significant that in these rather complex reactions phenol gave a lower yield (18%) of the benzofuran than did 4-methylphenol (29%), indicating that phenol could have reacted in part through the *para*-position to give unstable or unisolated products.

Reaction of cyano salt 2 with aniline

Primary aromatic amines react very cleanly with Appel salt **1**, displacing the 5-Cl atom to give stable 5-arylimino-4-chloro-1,2,3-dithiazoles in high yield.[1–5] Under the same conditions, *i.e.* addition of aniline to a suspension of the cyano salt **2** in DCM followed by addition of pyridine or Hünig's base, the reaction was much more complex. Five compounds were isolated in low yields (1–21%) and identified (Scheme 2); in order of elution



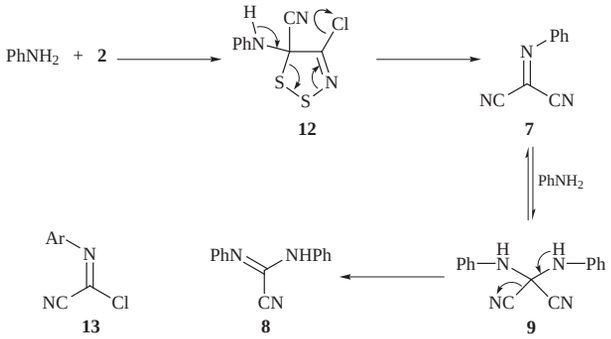
Scheme 2

from the chromatography column these were 2-phenyliminopropanedinitrile **7**,[14] 1-cyano-*N*,*N′*-diphenylformamidine **8**,[15] 2,2-bis(phenylamino)propanedinitrile **9**, 2-cyano-2-(phenylimino)thioacetamide **10**[16] and (4-aminophenyl)ethenetricarbonitrile **11**.[17] Compounds **7**, **8**, **10** and **11** are reported in the literature; whilst sufficient spectral data were available to verify the structures of **7** and **8**, the reported data for **10** and **11** were inconclusive. The structural assignment for the propanedinitrile derivative **9**, $C_{15}H_{12}N_4$, was based on microanalysis and ^{1}H NMR and its ready conversion into cyanoformamidine **8**. Whilst **9** has not been reported, 2,2-bis(4-chlorophenylamino)-propanedinitrile is known and this readily loses HCN in methanolic solution to give the analogous cyanoformamidine.[18] The ^{1}H NMR spectrum of the ethenetricarbonitrile **11** showed a 1,4-disubstituted aromatic ring and a broad N–H proton resonance in the correct integration ratio and its mass spectrum gave a strong parent ion at *m*/*z* 194.

The structural assignment for **10** was confirmed by an independent synthesis from 2-cyanothioacetamide and nitrosobenzene; we were unable to reproduce the reported uncatalysed condensation of these components (lit.,[16] yield 32%) but found that introduction of piperidine gave the thioacetamide **10** in 62% yield.

Mechanism of the aniline reaction

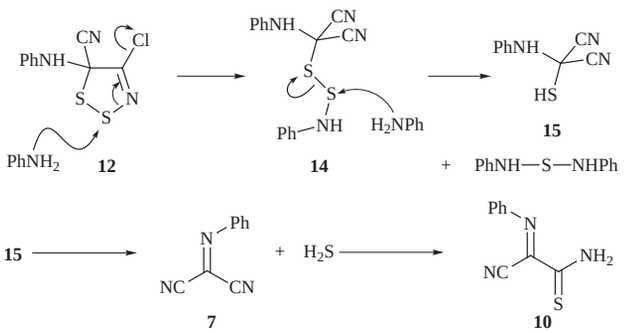
We propose the following mechanistic pathways to explain, as simply as possible, the formation of compounds **7**–**11** from aniline and 4-chloro-5-cyano-1,2,3-dithiazolium chloride **2**. Nucleophilic attack by aniline through nitrogen at C-5 of **2**, in the same way as for **1**,[1–5] would give the adduct **12**, the key intermediate which can suffer various fates. It could (Scheme 3) eliminate HCl and S_2 to afford the first product **7** which would then add more aniline reversibly to give the next product **9** which in turn could undergo a base catalysed elimination of HCN to give the major product **8**. The initial fragmentation



Scheme 3

of intermediate **12** to give **7** is similar to the formation of the analogous imidoyl chlorides **13** in the thermolysis of 5-arylimino-4-chloro-1,2,3-dithiazoles formed from Appel salt.[5]

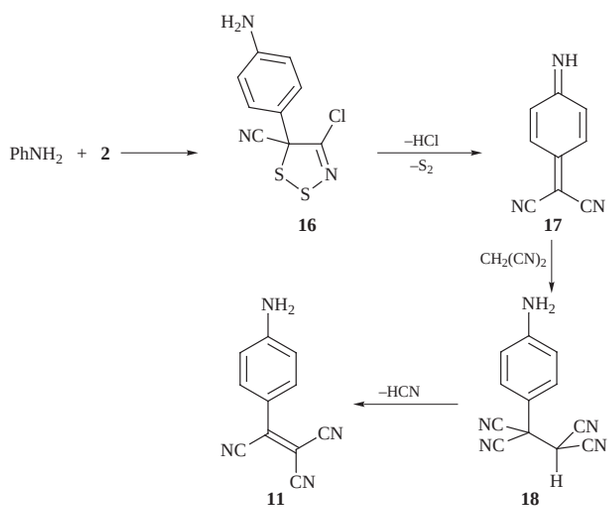
In addition to this fragmentation reaction (Scheme 3), intermediate **12** could also be attacked by aniline at S-2, with ring opening and nitrile formation, to give **14** (Scheme 4); further



Scheme 4

attack at the same sulfur atom would cleave the disulfide bond to give **15**. This sequence of double nucleophilic attack at sulfur is frequently encountered in reactions of the above 5-arylimino-dithiazoles derived from Appel salt.[3,19] Intermediate **15** is isomeric with product **10** and could presumably undergo a base catalysed rearrangement to it, by elimination of H_2S to form **7** and readdition of H_2S to one of the reactive cyano groups (Scheme 4).

Finally, the formation of the remaining (very minor) product, ethenetricarbonitrile **11**, is attributed to a small portion of aniline reacting with **2** through its *para*-position (Scheme 5) to



Scheme 5

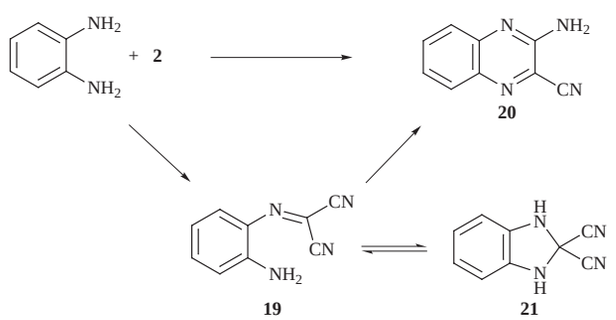
give the intermediate **16**, isomeric with **12**. This intermediate would be expected to lose HCl and S_2 to give the quinomethane imine **17** which, by analogy with quinomethanes,[20] should react

rapidly with any malononitrile present to give the adduct **18** which would lose HCN to give the observed tricyanovinylarene **11** (Scheme 5). It is possible that some malononitrile is formed by hydrolysis of the imine **7** under the experimental conditions. In the reaction of 1,8-diaminonaphthalene with salt **2** (Scheme 7, below) a product **25** was isolated which is exactly analogous to the proposed intermediate **17**. However, it should be pointed out that if any tetracyanoethylene (TCNE) happened to be produced from the cyano salt **2**, product **11** could be formed directly from this and aniline.[21]

Reaction of cyano salt 2 with aromatic diamines

In general, if there are two primary amino groups available for reaction with Appel salt **1** it is possible to isolate the mono- and bis-imino adducts in high yield.[22] If the amino groups are *ortho*, as in 1,2-diaminobenzene, cyclisation can also occur to give benzimidazole-2-carbonitriles *via* the mono-imines.[22]

The reaction of 1,2-diaminobenzene with cyano salt **2** was again much more complex than with **1**, even at low temperature, and chromatography gave only one recognisable product, 3-aminoquinoxaline-2-carbonitrile **20**, in low yield (12%). This was obtained as yellow fluorescent needles with properties in agreement with reported values.[21] Presumably the quinoxaline **20** arose by cyclisation of 2-(2-aminophenylimino)propanedinitrile **19** (Scheme 6) formed exactly as for **7** above (Scheme

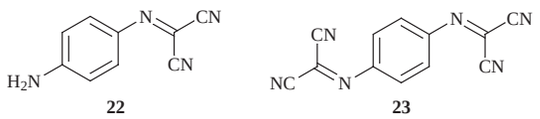


Scheme 6

3). The alternative cyclisation of **19** through the highly electrophilic imine carbon to give **21**, and hence 2-cyanobenzimidazole, was not observed (TLC comparison with the latter) though **21** may be formed reversibly (Scheme 6). This would be the intramolecular version of the formation of **9**, and hence **8**, from aniline (Scheme 3). An analogous cyclisation to give the six- rather than the five-membered ring has recently been reported for a similar reaction, but with dicyanomethylene replacing the dicyanoimine group in **19**.[23]

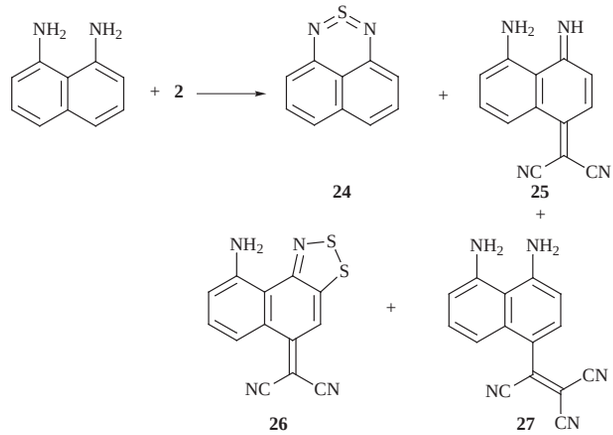
The direct formation of the quinoxaline **20** from 1,2-diaminobenzene has been effected before,[21] in modest yield (31%), by acid catalysed condensation with diiminosuccinonitrile, NC–C(=NH)–C(=NH)–CN, though this reagent is prepared from hydrogen cyanide and cyanogen. Quinoxaline **20** is more readily prepared by condensing benzofuroxan and malononitrile to give its 1,4-di-*N*-oxide (75%) followed by sodium dithionite reduction (87%),[24] but the 1,2-diaminobenzene–cyano salt **2** reaction would provide an attractive route to this versatile intermediate if the (unoptimised) yield were improved. In this last reaction no product analogous to **11**, derived from initial attack of the diamine through carbon, was observed.

Treatment of 1,4-diaminobenzene with one and two equivalents of cyano salt **2** respectively provided a ready source of the mono-dicyanoimine **22** (27%) and the bis-imine **23** (23%). These yields are higher than for the simpler dicyanoimine **7** from aniline, and are comparable with the literature values for the condensation of nitrosobenzene with malononitrile.[14] A wet acetonitrile solution of the orange tetracyano compound **23**, a potential electron acceptor, was hydrolysed back to the mono-



imine **22**. This is not suprising since the imino carbon atoms in **23** must be very electrophilic. This was further indicated by the ^{13}C NMR spectra in which the imino carbon resonance in **23** (109 ppm) is deshielded compared to that in **22** (92 ppm).

The reaction of 1,8-diaminonaphthalene with cyano salt **2** in the presence of Hünig's base (Scheme 7) proved to be cleaner



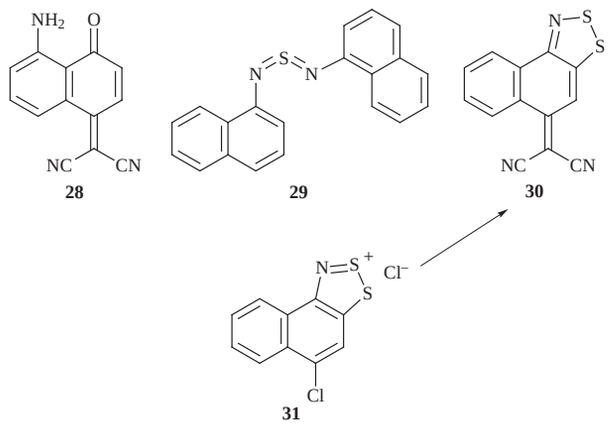
Scheme 7

than any of the previous cyano salt reactions. Elemental sulfur and four organic products were isolated from the reaction run at different temperatures (−78 °C to 20 °C) for different times. At −78 °C two deep blue products, the thiadiazine **24** (18%) and the aminoiminopropanedinitrile **25** (20%) were formed. If the reaction mixture was left for 24 h to reach 20 °C, **25** was no longer present but a third, pink, product, the naphthodithiazole **26** (5%) appeared, and after 72 h at 20 °C there was also a trace of the blue ethenetricarbonitrile **27** (Scheme 7).

Whilst sulfurdiimide **24** was readily identified by comparison with an authentic specimen,[25] the remaining compounds posed solubility and stability problems which made the accumulation of spectral data difficult. The structures **25**–**27** were tentatively assigned on spectroscopic evidence and that of **25**, which is the probable precursor to **26** and **27**, was confirmed by X-ray crystallography.[13] IR spectroscopy identified the primary amino groups in all three compounds, but ^{1}H NMR resonances were very weak and broad; the imine proton resonance in **25** was strong, however. Imine **25** was unstable on silica and during chromatography gave the quinomethane **28**; on treatment with aqueous sulfuric acid at 20 °C, a pure specimen of **25** gave the stable blue quinomethane **28** quantitatively.

Mechanistically, the sulfurdiimide **24** is an obvious product of sulfur capture from the salt **2** or some reaction intermediate derived from it by the diamine, by nucleophilic attack at sulfur as proposed earlier (Scheme 4). The most striking feature of the 1,8-diaminonaphthalene reaction (Scheme 7) is that all the other products are derived from nucleophilic attack by the amino through the *para* carbon; this is entirely in keeping with the enhanced reactivity of the naphthalene ring towards electrophilic substitution. Compounds **25** and **27** are exactly analogous to intermediate **17** and product **11** (Scheme 5) respectively. Dithiazole **26** is a new type of product, not observed for aniline, and it is probably formed from the imine **25** which, though readily hydrolysed, is much longer lived than **17** thus providing the opportunity for further reaction, with a source of disulfur which could be the cyano salt **2** or a ring opened derivative of it. Similar fused dithiazoles have been formed by the same ring construction from quinone oximes and disulfur dichloride.[26]

Products analogous to **25**–**27** (Scheme 7) would be expected from interaction between the cyano salt **2** and 1-aminonaphthalene. However this reaction was as complex as the aniline reaction and only two pure products were obtained in very low yields (5%): di(1-naphthyl)sulfurdiimide **29**[27] and the fused



dithiazole **30**. The former, which is analogous to product **24**, was identified from its reported properties; the latter, analogous to product **26**, was confirmed by its independent formation by treatment of the Herz salt **31** with malononitrile.[28]

In summary, we see that the reactions of simple phenols and anilines with the new cyano salt **2** are more complex than with Appel salt **1** since in the absence of a good leaving group on C-5 there is not one obvious low energy reaction path available; furthermore the initial 1 : 1 adducts are longer lived and hence more subject to attack by external nucleophiles. However the reactions do provide new routes to 2-aminobenzofuran-3-carbonitriles, 3-aminoquinoxaline-2-carbonitriles and various mono- and bis-iminopropanedinitriles (and their derivatives) which could be attractive if the yields were improved. In its reactions with amines, at nitrogen or ring carbon, salt **2** is acting as an equivalent of NC–$\overset{++}{C}$–CN (formally derived by loss of S_2 and $2Cl^-$) in the formation of **7**, **17**, **20**, **22**, **23**, **25** and **30**. However in its reaction with phenols it is acting as an equivalent of dicyanocarbene, NC–$\ddot{C}$–CN (formally derived by loss of S_2 and Cl_2), and a reduction must be involved.

Experimental

General experimental details have been described before.[7,29]

Reaction of 4-chloro-5-cyano-1,2,3-dithiazolium chloride 2 with phenols: 2-aminobenzofuran-3-carbonitrile 3a

To a stirred suspension of the salt **2** (198 mg, 1 mmol) in DCM (20 ml) at 20 °C, phenol (94 mg, 1 mmol) was added followed by the slow addition of Hünig's base (350 µl, 2 mmol). After 24 h the mixture was complex (TLC). The solution was filtered and the filtrate was concentrated under reduced pressure. Chromatography (light petroleum–ether, 3 : 1) of the residue gave the title compound **3a** (28 mg, 18%) as colourless needles, mp 179–181 °C (lit.,[11] over 270 °C) (from cyclohexane) (Found: C, 68.4; H, 4.1; N, 17.5. Calc. for $C_9H_6N_2O$: C, 68.35; H, 3.8; N, 17.7%); λ_{max}(DCM)/nm 253 (log ε 3.85), 285 (3.63); ν_{max}(Nujol)/cm^{-1} 3438s, 3339s and 3204m (NH_2), 2210s (CN), 1647s (C=N), 1582s (C=C), 1463s, 1433m, 1306w, 1273w, 1196m, 1183m, 1047m, 1015m, 967m, 908m, 863w, 733s, 702w; δ_H(270 MHz; $CDCl_3$) 7.37 (1H, dd, *J* 1.5, 7.7, Ar *H*-7), 7.26 (1H, dd, *J* 1.5, 7.7, Ar *H*-4), 7.23 (1H, ddd, *J* 1.5, 7.7, 7.7, Ar *H*-5), 7.12 (1H, ddd, *J* 1.5, 7.7, 7.7, Ar *H*-6), 5.25 (2H, br s, N*H*$_2$, D_2O exchanged); δ_H(270 MHz; DMSO-d_6) 8.21 (2H, br s, N*H*$_2$), 7.38–7.01 (4H, m, Ar *H*); δ_C(68 MHz; DMSO-d_6) 165.95, 147.77, 128.11, 124.15 (Ar *C*H), 121.39 (Ar *C*H), 115.98 (Ar *C*H), 115.38 (*C*N), 109.83 (Ar *C*H), 60.11; *m*/*z* (EI) 158 (M^+, 100%), 140 (1), 131 (M^+ − CHN, 8), 115 (26), 103 (50), 88 (5), 76 ($C_6H_4^+$, 30), 65 (7). Further elution (ether) gave several uncharacterised minor products.

2-Amino-5-methylbenzofuran-3-carbonitrile 3b

To a stirred suspension of the salt **2** (198 mg, 1 mmol) in DCM (20 ml) at 20 °C 4-methylphenol (108 mg, 1 mmol) was added followed by the slow addition of Hünig's base (350 µl, 2 mmol). After 24 h the mixture was complex (TLC). The solution was filtered and the filtrate was concentrated under reduced pressure. Chromatography (light petroleum–ether, 3 : 1) of the residue gave the *title compound* **3b** (50 mg, 29%) as colourless needles, mp 185–189 °C (from cyclohexane) (Found: C, 69.6; H, 4.8; N, 16.1. $C_{10}H_8N_2O$ requires C, 69.8; H, 4.65; N, 16.3%); λ_{max}(DCM)/nm 256 (log ε 4.14), 287 (3.94); ν_{max}(Nujol)/cm^{-1} 3412s, 3334s, 3272s and 3210s (NH_2), 2215s (CN), 1685s, 1651s, 1623s, (C=N), 1589s, 1576s (C=C), 1466s, 1423m, 1303w, 1274w, 1212w, 1188s, 1116w, 1054m, 1007m, 918w, 864m, 789s, 712w, 698w; δ_H(270 MHz; DMSO-d_6) 8.13 (2H, br s, N*H*$_2$), 7.18 (1H, d, *J* 8.1, Ar *H*-7), 7.02 (1H, d, *J* 1.2, Ar *H*-4), 6.84 (1H, dd, *J* 1.3, 8.2, Ar *H*-6), 2.33 (3H, s, C*H*$_3$); δ_C(68 MHz; DMSO-d_6) 166.19, 146.21, 133.40, 128.26, 122.15 (Ar *C*H), 116.33 (Ar *C*H), 115.57 (*C*N), 109.43 (Ar *C*H), 60.18, 20.93 (*C*H$_3$); δ_C(68 MHz; DMSO-d_6 DEPT 135) 122.07 (Ar *C*H), 116.25 (Ar *C*H), 109.36 (Ar *C*H), 20.87 (*C*H$_3$); *m*/*z* (EI) 172 (M^+, 100%), 155 (7), 145 (M^+ − CHN, 8), 129 (4), 117 (14), 102 (3), 90 (8) (Found: M^+, 172.0635. $C_{10}H_8N_2O$ requires *M*, 172.0637). Further elution (ether) gave several uncharacterised minor products.

Reaction of 4-chloro-5-cyano-1,2,3-dithiazolium chloride 2 with aniline

To a stirred suspension of the salt **2** (198 mg, 1 mmol) in DCM (15 ml) at −78 °C, under nitrogen, aniline (108 mg, 1 mmol) was added followed by the slow addition of Hünig's base (350 µl, 2 mmol). The mixture was then allowed to reach *ca.* 20 °C and TLC indicated a complex reaction. The volatiles were removed and chromatography (light petroleum–DCM, 3 : 1) of the residue gave 2-phenyliminopropanedinitrile **7** (8 mg, 5%) as bright yellow needles, mp 60–62 °C (lit.,[14] 63–64 °C) (from benzene–hexane); ν_{max}(Nujol)/cm^{-1} 2238w and 2222m (CN), 1574w, 1546s (C=C), 1482m, 1455s, 1297m, 1207m, 1172m, 1157s, 1103w, 1079w, 1024w, 1000w, 972w, 926w, 852w, 833w, 778s, 734m, 688s, 658w, 619m; δ_H(270 MHz; $CDCl_3$) 7.61–7.48 (5H, m, Ar *H*); δ_C(68 MHz; $CDCl_3$) 146.28 (Ar *C*-1), 133.52 (Ar *C*-4), 130.66 (Ar *C*-3), 123.62 (Ar *C*-2), 113.09 (*C*N), 110.91 [*C*(CN)$_2$], 109.69 (*C*N); *m*/*z* (EI) 155 (M^+, 79%), 129 (M^+ − CN, 8), 103 [M^+ − 2(CN), 100], 92 (3), 77 ($C_6H_5^+$, 41), 65 (9), 51 (31), and further elution (light petroleum–DCM, 3 : 1) gave 1-cyano-*N*,*N*′-diphenylformamidine **8** (23 mg, 21%) as colourless needles, mp 141–142 °C (lit.,[15] 139 °C) (from cyclohexane) (Found: C, 76.1; H, 4.9; N, 18.5. Calc. for $C_{14}H_{11}N_3$: C, 76.0; H, 5.0; N, 19.0%); λ_{max}(DCM)/nm 229 (log ε 4.00), 291 (4.97), 314 (3.94); ν_{max}(Nujol)/cm^{-1} 3341s (NH), 3092w, 3055w and 3029w (Ar CH), 2235w (CN), 1645s and 1603s (C=N), 1591s and 1553s (C=C), 1499s, 1445s, 1330s, 1220m, 1188m, 1073w, 1035w, 1025w, 947w, 907w, 847w, 835w, 783m, 755s, 701s, 692s; δ_H(270 MHz; $CDCl_3$) 7.41–7.16 (10H, m, Ar *H*), 7.05 (1H, br s, N*H*); δ_C(68 MHz; $CDCl_3$) 143.54 (*C*=N), 130.00 (Ar *C*H), 129.40 (Ar *C*), 125.83 (Ar *C*H), 121.53 (Ar *C*H), 110.25 (*C*N); *m*/*z* (CI) 222 (MH^+, 100%), 195 (MH^+ − CHN, 45), 146 (16), 94 (18) (Found: MH^+, 222.1031. $C_{14}H_{11}N_3$ requires *MH*, 222.1031).

Further elution (light petroleum–DCM, 2 : 1) gave *2,2-bis(N-phenylamino)propanedinitrile* **9** (2 mg, 2%) as yellow needles, mp 165–170 °C (from cyclohexane) (Found: C, 72.8; H, 4.6; N, 21.7. $C_{15}H_{12}N_4$ requires C, 72.6; H, 4.8; N, 22.6%); λ_{max}(DCM)/nm 232, 259, 364; δ_H(270 MHz; $CDCl_3$) 7.56–7.03 (10H, m, Ar *H*), 5.49 (2H, br s, N*H*) and 2-cyano-2-(phenylimino)thioacetamide **10** (9 mg, 5%) as orange-red needles, mp 148–149 °C

(lit.,[16] 144–145 °C) (from 1,2-dichloroethane–cyclohexane) (Found: C, 57.3; H, 3.6; N, 22.1. Calc. for $C_9H_7N_3S$: C, 57.1; H, 3.7; N, 22.2%); λ_{max}(DCM)/nm 241 (log ε 3.79), 276 (3.62), 372 (3.94); ν_{max}(Nujol)/cm^{-1} 3377s, 3257s and 3163s (NH_2), 3064w (Ar CH), 2205w (CN), 1610s (C=N), 1595s (C=C), 1488w, 1442m, 1284w, 1206m, 1141m, 1124m, 1074w, 917w, 904w, 803w, 770w, 725m, 703m, 687m, 625s, 605s; δ_H(500 MHz; $CDCl_3$) 8.60 (1H, br s, N*H*, D_2O exchanged), 7.66 (1H, br s, N*H*, D_2O exchanged), 7.54–7.50 (2H, m, Ar *H*), 7.47–7.41 (3H, m, Ar *H*); δ_C(125 MHz; $CDCl_3$) 188.39 (*C*=S), 144.87, 133.46, 130.22 (Ar *C*H), 129.64 (Ar *C*H), 122.12 (Ar *C*H), 109.84 (*C*N); *m*/*z* (EI) 189 (M^+, 92%), 155 ($M^+ - H_2S$, 26), 130 (M^+ − CHNS, 44), 103 ($C_7H_5N^+$, 100), 92 ($C_6H_6N^+$, 19), 77 ($C_6H_5^+$, 66), 65 (11), 60 (41) (Found: M^+, 189.0389. $C_9H_7N_3S$ requires *M*, 189.0361).

A final elution (DCM) gave (4-aminophenyl)ethenetricarbonitrile **11** (2 mg, 1%) as red needles, mp 194–197 °C (lit.,[17] 197–198 °C) (from cyclohexane); ν_{max}(DCM film)/cm^{-1} 3432m, 3349m and 3241m (NH_2), 2214m (CN), 1645s, 1608s, 1548w, 1529w, 1491s, 1457s, 1367m, 1341m, 1296m, 1188s, 991w, 896w, 836w; δ_H(270 MHz; CD_3CN) 7.98 (2H, d, *J* 9.2, Ar *H*), 6.83 (2H, d, *J* 9.2, Ar *H*), 5.97 (2H, br s, N*H*$_2$); *m*/*z* (EI) 194 (M^+, 100%), 167 (M^+ − CHN, 28), 140 [M^+ − 2(CHN), 22], 118 (63), 91 ($C_6H_5N^+$, 13), 76 ($C_6H_4^+$, 10), 65 (13), 52 (15).

Independent synthesis of 2-cyano-2-(phenylimino)thioacetamide 10

To a stirred solution of 2-cyanothioacetamide (100 mg, 1 mmol) in EtOH (10 ml) at *ca.* 20 °C, nitrosobenzene (107 mg, 1 mmol) was added followed by the addition of piperidine (2 drops). The reaction was warmed on a steam bath and after 1 h cooled to *ca.* 20 °C. The volatiles were removed and chromatography of the residue gave the title compound **10** (117 mg, 62%) as orange-red needles, mp 148–149 °C (from 1,2-dichloroethane–cyclohexane), identical with that described above.

3-Aminoquinoxaline-2-carbonitrile 20

To a stirred suspension of the salt **2** (198 mg, 1 mmol) in DCM (15 ml) at −78 °C, under nitrogen, 1,2-diaminobenzene (108 mg, 1 mmol) was added *via* a solid addition tube. This was followed by the addition of Hünig's base (350 µl, 2 mmol) and the mixture was allowed to reach *ca.* 20 °C. TLC indicated a yellow fluorescent product. The volatiles were removed and chromatography (light petroleum–DCM, 1:1) of the residue gave the title compound **20** (20 mg, 12%) as yellow needles, mp 210 °C (lit.,[21] 196–200 °C) (from cyclohexane) (Found: C, 63.7; H, 3.7; N, 32.7. Calc. for $C_9H_6N_4$: C, 63.5; H, 3.5; N, 32.9%); λ_{max}(DCM)/nm 223 (log ε 3.95), 243 (4.01), 255 (4.01), 310 (3.50), 390 (3.43); ν_{max}(Nujol)/cm^{-1} 3412s and 3325m (NH_2), 3133s (Ar CH), 2232m (CN), 1664s (C=N), 1611m, 1563s (C=C), 1490s, 1462s, 1438s, 1374s, 1362s, 1325w, 1254w, 1222m, 1171w, 1144m, 1122w, 1094w, 1013w, 964w, 862w, 761s, 753s; δ_H(270 MHz; DMSO-d_6) 7.84 (1H, dd, *J* 1.5, 8.3, Ar *H*), 7.74 (1H, ddd, *J* 1.5, 7.2, 7.6, Ar *H*), 7.59 (1H, dd, *J* 1.5, 8.5, Ar *H*), 7.47 (1H, ddd, *J* 1.5, 7.2, 7.6, Ar *H*), 7.41 (2H, br s, N*H*$_2$); δ_C(68 MHz; DMSO-d_6) 152.99, 142.88, 135.94, 133.41, 129.00, 125.75, 125.52, 119.37, 115.20 (*C*N); *m*/*z* (EI) 170 (M^+, 100%), 143 (M^+ − CHN, 33), 118 (17), 91 ($C_6H_5N^+$, 13), 84 (13), 76 ($C_6H_4^+$, 6), 66 (13) (Found: M^+, 170.0611. $C_9H_6N_4$ requires *M*, 170.0592).

2-(4-Aminophenylimino)propanedinitrile 22

To a stirred suspension of the salt **2** (198 mg, 1 mmol) in DCM (15 ml) at −78 °C, under nitrogen, 1,4-diaminobenzene (108 mg, 1 mmol) was added *via* a solid addition tube. This was followed by the addition of Hünig's base (350 µl, 2 mmol) and the mixture was allowed to reach *ca.* 20 °C. TLC indicated the presence of a little sulfur, orange and purple products and a strong baseline spot. The volatiles were removed and chromatography (light petroleum–DCM, 3:1) of the residue gave *2-(4-dicyanomethyleneaminophenylimino)propanedinitrile* **23** (2 mg, 1%) as orange crystals, mp 186.5–187 °C (from 1,2-dichloroethane–cyclohexane) (Found: C, 62.3; H, 2.0; N, 36.1. $C_{12}H_4N_6$ requires C, 62.1; H, 1.7; N, 36.2%); λ_{max}(DCM)/nm 228.5 (log ε 3.98), 279 (3.95), 407 (4.12); ν_{max}(Nujol)/cm^{-1} 3111w, 3089m and 3027w (Ar CH), 2244w and 2227m (CN), 1573w, 1518w (C=C), 1486m, 1421w, 1295m, 1209w, 1170s, 1156m, 1117w, 1064w, 1011w, 970w, 860s, 826m, 724w, 662m; δ_H(270 MHz; $CDCl_3$) 7.60 (4H, s, Ar *H*); δ_C(68 MHz; $CDCl_3$) 148.22 (Ar *C*N), 124.63 (Ar *C*H), 113.68 (*C*N), 112.51 (*C*N), 109.03 [*C*(CN)$_2$]; *m*/*z* (EI) 232 (M^+, 100%), 206 (M^+ − CN, 11), 180, [M^+ − 2(CN), 33], 154 [M^+ − 3(CN), 51], 128 [M^+ − 4(CN), 65], 102 [M^+ − 5(CN), 50], 90 (15), 75 (30), 64 (28).

Further elution (light petroleum–DCM, 1:1) gave the *title compound* **22** (46 mg, 27%) as deep red needles, mp 190 °C (from 1,2-dichloroethane–cyclohexane) (Found: C, 63.6; H, 3.6; N, 32.7. $C_9H_6N_4$ requires C, 63.5; H, 3.5; N, 32.9%); λ_{max}(DCM)/nm 277 (log ε 3.62), 443 (4.37); ν_{max}(Nujol)/cm^{-1} 3443s, 3356s, 3265m and 3241s (NH_2), 2224m and 2208w (CN), 1651s, 1613s (C=N), 1546m, 1513m (C=C), 1483s, 1462s, 1356m, 1250m, 1172s, 1160m, 991w, 858w, 843m, 811w, 723w; δ_H(270 MHz; DMSO-d_6) 7.67 (2H, d, *J* 9.0, Ar *H*-1), 7.41 (2H, br s, N*H*$_2$), 6.73 (2H, d, *J* 9.3, Ar *H*-2); δ_C(68 MHz; DMSO-d_6) 156.61 (Ar *C*-4), 134.49 (Ar *C*-1), 130.24 (Ar *C*-3), 115.67 (*C*N), 114.13 (Ar *C*-2), 113.08 (*C*N), 92.37 [*C*(CN)$_2$]; *m*/*z* (EI) 170 (M^+, 100%), 144 (M^+ − CN, 16), 118 [M^+ − 2(CN), 28], 92 [M^+ − 3(CN), 24], 84 (21), 66 (21), 65 (17) (Found: M^+, 170.0595. $C_9H_6N_4$ requires *M*, 170.0592).

2-(4-Dicyanomethyleneaminophenylimino)propanedinitrile 23

To a stirred suspension of the salt **2** (3.66 g, 18.5 mmol) in DCM (40 ml) at −78 °C, under nitrogen, 1,4-diaminobenzene (1 g, 9.25 mmol) was added *via* a solid addition tube. This was followed by the addition of Hünig's base (6.4 ml, 37 mmol) and the mixture was allowed to reach *ca.* 20 °C. TLC indicated the presence of a little sulfur, an orange product and a strong baseline spot. The volatiles were removed and chromatography (light petroleum–DCM, 3:1) of the residue gave the title compound **23** (494 mg, 23%), identical with that described above. Further elution (light petroleum–DCM, 1:1) gave a trace of 2-(4-aminophenylimino)propanedinitrile **22**, identical with that described above.

Reaction of 4-chloro-5-cyano-1,2,3-dithiazolium chloride 2 with 1,8-diaminonaphthalene

To a stirred suspension of the salt **2** (198 mg, 1 mmol) in DCM (15 ml) at *ca.* −78 °C, under nitrogen, 1,8-diaminonaphthalene (158 mg, 1 mmol) was added *via* a solid addition tube. After 15 min stirring, Hünig's base (350 µl, 2 mmol) was added. The mixture became deep blue and copious fumes of hydrogen chloride were evolved. TLC indicated the presence of a little sulfur and two new blue-purple products. After 1 h at −78 °C, chromatography (light petroleum–DCM, 1:1) gave the betaine 1*H*-2λ^4-naphtho[1,8-*cd*][1,2,6]thiadiazin-2-ylium-1-ide **24** (33 mg, 18%) as deep blue plates, mp 145–150 °C decomp. (lit.,[25] 139–141 °C) (from 1,2-dichloroethane–cyclohexane); ν_{max}(Nujol)/cm^{-1} 3027w (Ar CH), 1610m, 1583w, 1563m, 1499w, 1439m, 1353m, 1266m, 1216w, 1167m, 1132m, 1075w, 1063m, 1046m, 1023m, 967w, 887w, 823s, 787w, 764s, 723w, 704s, 617s; δ_H(270 MHz; $CDCl_3$) 6.95 (2H, dd, *J* 1.2, 8.4, Ar *H*), 6.86 (2H, t, *J* 7.2, 8.4, Ar *H*) 6.12 (2H, dd, *J* 1.2, 7.2, Ar *H*); δ_C(68 MHz; $CDCl_3$) 144.49, 137.59, 129.02 (Ar *C*H), 126.54 (Ar *C*H), 125.44, 115.45 (Ar *C*H); *m*/*z* (EI) 186 (M^+, 100%), 159 (M^+ − CHN, 20), 140 (M^+ − NS, 4), 126 ($M^+ - N_2S$, 5), 114 ($M^+ - CN_2S$, 16), 93 (17), 88 (5), 75 (6), 63 (10), 50 (6).

Further elution (DCM) gave *(8-amino-1-imino-1,4-dihydronaphthalen-4-ylidene)propanedinitrile* **25** (44 mg, 20%) as purple needles, mp >300 °C decomp. (from 1,2-dichloroethane–cyclohexane) (Found: C, 70.9; H, 3.8; N, 25.4. $C_{13}H_8N_4$ requires C, 70.9; H, 3.6; N, 25.45%); λ_{max}(DCM)/nm 230 (log ε 4.24), 310 infl (4.02), 365 (4.22), 549 (3.59); ν_{max}(Nujol)/cm^{-1} 3413s and 3270s (NH), 3153w (Ar CH), 2221s (CN), 1606s and 1580m (C=N), 1538s and 1500s (C=C), 1327m, 1301m, 1227w, 1210m, 1177m, 1039m, 1000w, 883w, 870m, 815m, 802w, 754m, 722w, 696w; δ_H(270 MHz; DCM-d_2) 10.11 (1H, br s, N*H*, D_2O exchanged), 7.99 (1H, dd, *J* 1.0, 7.9, Ar *H*), 7.38 (1H, t, *J* 7.9, 8.4, Ar *H*), 7.35 (1H, d, *J* 9.9, Ar *H*), 7.36 (2H, br s, NH_2, D_2O exchanged), 7.03 (1H, dd, *J* 0.9, 8.3, Ar *H*), 6.63 (1H, d, *J* 9.9, Ar *H*); δ_C(76 MHz; DCM-d_2) 166.17 (*C*=NH), 157.15, 150.27, 136.31 (Ar *C*H), 131.33 (Ar *C*H), 129.84, 129.22 (Ar *C*H), 122.81 (Ar *C*H), 116.96 (Ar *C*H), 114.90 (*C*N), 113.71 (*C*N), 111.06, 79.91 [*C*(CN)$_2$]; *m*/*z* (EI) 220 (M^+, 100%), 205 (M^+ − HN, 3), 193 (M^+ − CHN, 65), 165 ($C_{11}H_5N_2^+$, 12), 139 ($C_{10}H_5N^+$, 10), 114 (3), 100 (2), 88 (4), 76 ($C_6H_4^+$, 2), 63 (2) (Found: M^+, 220.0768. $C_{13}H_8N_4$ requires *M*, 220.0749).

If the mixture was left for 24 h at *ca.* 20 °C then chromatography (DCM) gave neither of the above products but gave *(9-amino-5H-naphtho[1,2-d][1,2,3]dithiazol-5-ylidene)propanedinitrile* **26** (14 mg, 5%) as a brown solid, mp >200 °C decomp. (from 1,2-dichloroethane–cyclohexane); λ_{max}(DCM)/nm 239 (log ε 4.12), 332 (3.74), 350 infl (3.68), 535 (4.15); ν_{max}(Nujol)/cm^{-1} 3463m and 3335m (NH_2), 3183w (Ar CH), 2199s (CN), 1613s and 1587m (C=N), 1565s and 1540s (C=C), 1494m, 1456s, 1413s, 1390m, 1327s, 1306s, 1282m, 1222w, 1164w, 1127m, 1071w, 866w, 838m, 801m, 746m, 722w, 704w, 675m; observed proton resonances δ_H(270 MHz; acetone-d_6) 8.33 (1H, dd, *J* 1.0, 7.9, Ar *H*), 7.99 (1H, s, Ar *H*), 7.67 (1H, t, *J* 7.9, 7.9, Ar *H*), 7.43 (1H, dd, *J* 1.0, 7.9, Ar *H*); *m*/*z* (EI) 282 (M^+, 100%), 267 (M^+ − HN, 4), 243 (M^+ − C_2HN, 8), 205 (4), 179, (4), 162 (12), 141 (4), 132 (2), 113 (4), 87 (3), 69 (7), 51 (13) (Found: M^+, 282.0020. $C_{13}H_6N_4S_2$ requires *M*, 282.0034).

If the mixture was left for 72 h at *ca.* 20 °C then chromatography (DCM) gave *1,8-diaminonaphthalen-4-ylethenetricarbonitrile* **27** (2 mg, 1%) as blue needles, mp >200 °C decomp. (from 1,2-dichloroethane–cyclohexane) (Found: C, 69.4; H, 3.1; N, 26.6. $C_{15}H_9N_5$ requires C, 69.5; H, 3.5; N, 27.0%); ν_{max}(Nujol)/cm^{-1} 3416m, 3329m and 3225m (NH), 2207s (CN), 1651s and 1589s (C=N), 1537m (C=C), 1445s, 1329s, 1301s, 1275s, 1218s, 1200m, 1144m, 1073w, 1015w, 968w, 946w, 880w, 829w, 809m, 761s, 653s; observed proton resonances δ_H(270 MHz; DCM-d_2) 7.69 (1H, d, *J* 8.4, Ar *H*), 7.46 (2H, m, Ar *H*), 6.91 (1H, t, *J* 4.3, 4.3, Ar *H*), 6.58 (1H, d, *J* 8.4, Ar *H*); *m*/*z* (EI) 259 (M^+, 100%), 242 (M^+ − H_3N, 11), 233 (M^+ − CN, 19), 216 (M^+ − CH_3N_2, 9), 204 (8), 189 (5), 177 (5), 165 (2), 116 (10), 102 (7), 89 (4), 76 ($C_6H_5^+$, 4), 66 (8) (Found: M^+, 259.0880. $C_{15}H_9N_5$ requires *M*, 259.0858).

(8-Amino-1-oxo-1,4-dihydronaphthalen-4-ylidene)propanedinitrile 28

To a stirred solution of (8-amino-1-imino-1,4-dihydronaphthalen-4-ylidene)propanedinitrile **25** (10 mg, 0.046 mmol) in EtOH (10 ml) at *ca.* 20 °C aqueous sulfuric acid (0.05 M, 5 ml) was added. After 24 h the mixture was diluted with water (20 ml) and extracted with DCM (5 × 10 ml). Then the aqueous fraction was neutralised with aqueous sodium hydrogen carbonate (0.05 M) and extracted with DCM (3 × 10 ml). The organic fractions were combined, dried, filtered and the volatiles were removed. Chromatography (DCM) of the residue gave the *title compound* **28** (10 mg, 99%) as blue needles, mp >250 °C decomp. (from 1,2-dichloroethane–cyclohexane) (Found: C, 68.8; H, 2.8; N, 18.7. $C_{13}H_7N_3O$ requires C, 70.6; H, 3.2; N, 19.0%); λ_{max}(DCM)/nm 228 (log ε 4.14), 279 (3.82), 307 (3.99), 336 (4.07), 565 (3.67); ν_{max}(Nujol)/cm^{-1} 3425s, 3326m and 3295s (NH), 3149w and 3060w (Ar CH), 2223s (CN), 1636s (C=O), 1602s and 1572s (C=N), 1541s and 1506s (C=C), 1323m, 1283s, 1220m, 1170s, 1123w, 1106w, 1051m, 995w, 881w, 842m, 815w, 771w, 755m, 723w, 706w, 696w; δ_H(270 MHz; DCM-d_2) 8.01 (1H, dd, *J* 0.7, 7.7, Ar *H*), 7.69 (1H, d, *J* 10.2, Ar *H*), 7.44 (1H, t, *J* 7.8, 8.5, Ar *H*), 7.02 (1H, dd, *J* 0.9, 8.5, Ar *H*), 7.02 (2H, v br s, NH_2, D_2O exchanged), 6.65 (1H, d, *J* 10.2, Ar *H*); δ_C(76 MHz; DCM-d_2) 185.06 (*C*=O), 155.64, 151.64, 136.32 (Ar *C*H), 134.92 (Ar *C*H), 133.94 (Ar *C*H), 132.16, 124.21 (Ar *C*H), 117.88 (Ar *C*H), 114.46 (*C*N), 113.13 (*C*N), 110.62, 82.75 [*C*(CN)$_2$]; *m*/*z* (EI) 221 (M^+, 100%), 193 (M^+ − CO, 48), 178 (2), 165 ($C_{11}H_5N_2^+$, 8), 149 (4), 139 ($C_{10}H_5N^+$, 8), 113 (3), 100 (2), 88 (3), 76 ($C_6H_4^+$, 3), 63 (3) (Found: M^+, 221.0587. $C_{13}H_7N_3O$ requires *M*, 221.0589).

(5*H*-Naphtho[1,2-*d*][1,2,3]dithiazol-5-ylidene)propanedinitrile 30

To a stirred solution of the salt **2** (1.2 g, 6 mmol) in DCM (50 ml) at *ca.* 20 °C, 1-aminonaphthalene (715 mg, 5 mmol) was added in one portion. After 1 h stirring Hünig's base (1.74 ml, 10 mmol) was introduced. The mixture became hot and copious fumes of hydrogen chloride were evolved. After 12 h the mixture was filtered and the volatiles were removed. Chromatography (light petroleum–DCM, 3:1) of the residue gave di(1-naphthyl)sulfurdiimide **29** (39 mg, 5%) as red needles, mp 80 °C (lit.,[27] 81 °C) (from 1,2-dichloroethane–cyclohexane); δ_H(270 MHz; acetone-d_6) 8.36 (1H, m, Ar *H*), 7.92 (1H, dd, *J* 2.4, 7.0, Ar *H*), 7.81 (2H, d, *J* 8.3, Ar *H*), 7.59 (2H, m, Ar *H*), 7.39 (1H, t, *J* 7.8, 7.8, Ar *H*); *m*/*z* (EI) 314 (M^+, 63), 313 (M^+ − H, 100%), 280 (M^+ − H_2S, 4), 268 (M^+ − NS, 7), 172 (29), 159 (3), 143 (17), 127 (8), 115 (9), 84 (5), 63 (2) (Found: M^+ − H, 313.0799. $C_{20}H_{13}N_2S$ requires *M* − *H*, 313.0799). Further elution (DCM) gave the *title compound* **30** (67 mg, 5%) as lustrous green-brown needles, mp 285–288 °C (from glacial acetic acid) (Found: C, 58.65; H, 1.9; N, 15.6. $C_{13}H_5N_3S_2$ requires C, 58.4; H, 1.9; N, 15.7%); λ_{max}(DCM)/nm 228 (log ε 4.46), 246 infl (4.00), 267 infl (3.72), 289 infl (3.48), 307 infl (3.49), 329 infl (3.76), 345 (4.02), 360 (4.08), 403 (3.57), 428 (3.64), 530 (4.41), 584 infl (4.14); ν_{max}(Nujol)/cm^{-1} 3082w (Ar CH), 2205s and 2189s (CN), 1571s (C=N), 1524s (C=C), 1487m, 1469m, 1431s, 1382m, 1336m, 1303s, 1252m, 1141s, 1092m, 883m, 863w, 844w, 831m, 775m, 761m, 748s, 679m, 652m; δ_H(400 MHz; DMSO-d_6) 8.90 (1H, m, Ar *H*), 8.60 (1H, m, Ar *H*), 7.98 (1H, s, Ar *H*), 7.91 (2H, m, Ar *H*); δ_C(100 MHz; DMSO-d_6) 157.08, 153.58, 151.20, 132.00 (Ar *C*H), 131.24 (Ar *C*H), 127.99, 127.47 (Ar *C*H), 127.14, 125.20 (Ar *C*H), 118.53 (*C*N), 117.32 (*C*N), 110.64 (Ar *C*H), 61.29 [*C*(CN)$_2$]; *m*/*z* (EI) 267 (M^+, 100%), 240 (M^+ − CHN, 4), 196 (M^+ − C_2HNS, 3), 191 (M^+ − CS_2, 6), 164 (M^+ − C_2HNS_2, 12), 152 (5), 149 (3), 139 (9), 133.5 (M^{++}, 3), 120 (5), 107 (3), 91 (4), 77 ($C_6H_5^+$, 5), 69 (3), 64 (S_2^+, 3) (Found: M^+, 266.9926. $C_{13}H_5N_3S_2$ requires *M*, 266.9925).

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