Reaction of tetracyanoethylene with SCl_2; new molecular rearrangements

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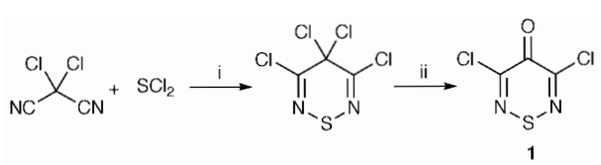
The chloride ion catalysed addition of SCl_2 to TCNE gives the 4-dicyanomethylene-1,2,6-thiadiazine **2** (60%) with two minor products (5%) of extensive molecular rearrangement, the pyrimidine **4** and the pyrroloimidazothiadiazine **5**. Mechanisms proposed for the formation of all three products involve the interaction of SCl_2 with one cyano group and neighbouring group participation by geminal and vicinal cyano groups. The dicyanomethylene thiadiazine **2** reacts further with SCl_2 to give the pyrrolo-1,2,6-thiadiazine **19**. The two chlorine atoms of the pyrroloimidazothiadiazine **5** are successively replaced by pyrrolidine to give the substitution products **20** and **21** in high yield. ^{1}H and ^{13}C NMR spectra show that rotation of the pyrrolidine ring on the thiadiazine is considerably slower than for that on the pyrrole ring, and there is electron delocalisation across the new 14π tricyclic heteroaromatic system.

Derivatives of all six possible thiadiazines have been reported.[1] 1,2,6-Thiadiazine 1,1-dioxides are well known but the unoxidised compounds are rare, particularly 4*H*-derivatives, except for 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one **1**.[2] We have investigated the chemistry of this useful intermediate[3] and the closely related, new, 3,5-dichloro-4-dicyanomethylene-4*H*-1,2,6-thiadiazine **2**, particularly as precursors for fused heterocyclic systems with practical applications as chromophores or as donor–acceptor units in charge transfer complexes. Various heterocyclic dicyanomethylenes have been used as textile dyes, in non-linear optics and as electron transport materials in xerography.[4]

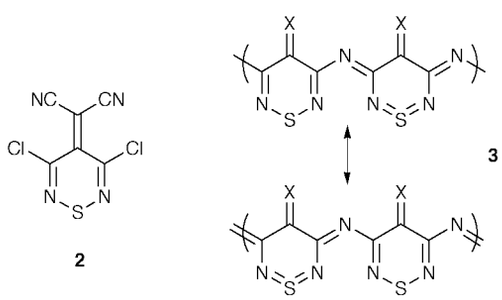
The dichlorothiadiazinone **1** can be prepared from dichlorodicyanomethane and monosulfur dichloride, SCl_2, as shown in Scheme 1, in good yield with no need for chromatography,



Scheme 1 *Reagents and conditions*: i, $Et_4N^+Cl^-$, THF; ii, HCO_2H, 0–20 °C.

and its chlorine atoms can be successively displaced by a range of nitrogen, oxygen and sulfur nucleophiles.[2,3] Many such mono-chloro derivatives of **1** have high fungicidal activity.[5] X-Ray diffraction shows the thiadiazine ring of **1** to be almost planar;[6] Bird calculated his aromaticity index I_A, based upon the statistical evaluation of deviations in peripheral bond orders derived from experimental bond lengths,[7] for this compound. The value of 54 (*cf.* $I_A = 53$ for furan and 100 for benzene) indicated a modestly aromatic ring.

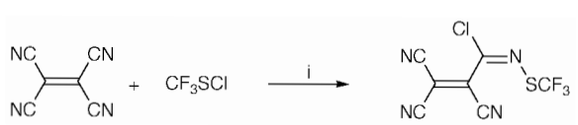
We wished to increase the reactivity of the chlorine atoms in **1** towards nucleophilic displacement particularly by ammonia, since we required a good, large scale synthesis of 3,5-diamino-4*H*-1,2,6-thiadiazin-4-one, or related diamines, as monomers for new conjugated polymers incorporating the repeat unit **3**. Displacement of the first chlorine in **1** occurred readily but the second required the use of liquid ammonia in a pressure vessel or Carius tube. One way of overcoming this problem would be



to replace the 4-keto group of **1** by a more strongly electron withdrawing group, and we therefore decided to synthesise the dicyanomethylene derivative **2**.

Reaction of TCNE with monosulfur dichloride

Our first attempts to prepare **2**, by condensation of **1** with malononitrile under various conditions, were unsuccessful. This reaction also failed when one or both of the chlorine atoms in **1** were first exchanged for morpholine, to reduce the number of electrophilic sites on the thiadiazine ring. An alternative approach to **2** was suggested by the known addition of trifluoromethanesulfenyl chloride to tetracyanoethylene (TCNE) in the presence of a catalytic amount of chloride ion (Scheme 2).[8] Although a second addition of CF_3SCl was not



Scheme 2 *Reagents and conditions*: i, $Et_4N^+Cl^-$, DCM, 20 °C, 5 days.

observed, it seemed possible that SCl_2 might add to TCNE in the same way, followed by cyclisation to give **2** (see later—Scheme 5). The only reported example of the addition of SCl_2 to a dicyanomethylene compound to give a 1,2,6-thiadiazine is shown in Scheme 1. Under similar conditions, SCl_2 and catalytic tetraethylammonium chloride added to cyanogen in THF at −80 °C to give 3,4-dichloro-1,2,5-thiadiazole.[9]

Treatment of TCNE with SCl_2 (2 equiv.) (Scheme 3) did indeed give the desired **2** as the major product (40–60%)

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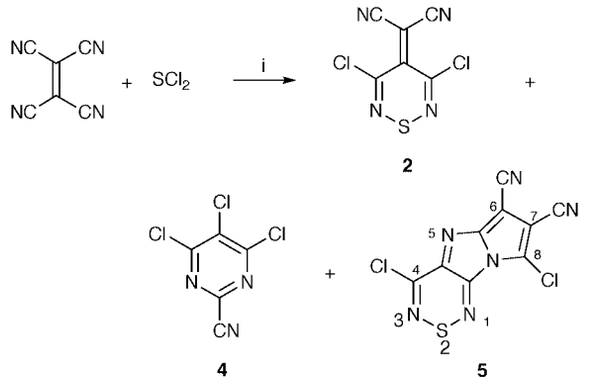
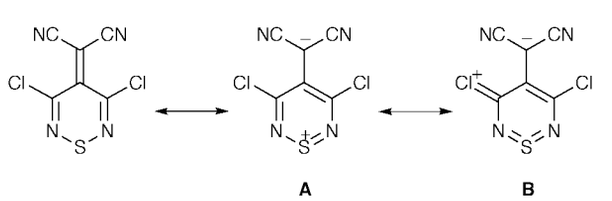


Scheme 3 *Reagents and conditions*: i, $BnEt_3N^+Cl^-$, DCM, 0–20 °C, 72 h.

together with two minor unexpected and somewhat puzzling minor products: 4,5,6-trichloropyrimidine-2-carbonitrile **4** (5%) and 4,8-dichloro-6,7-dicyanopyrrolo[1′,2′ : 1,2]imidazo-[5,4-*c*][1,2,6]thiadiazine **5** (0–5%).[10] The reaction was slow, requiring 72 h at 20 °C for all the TCNE to be consumed. Heating the mixture improved the yield of **5** at the expense of **2**. Using freshly distilled SCl_2 added dropwise at a low temperature under nitrogen gave the highest yield of **2** (60%). The presence of catalytic amounts (1–5%) of chloride ion was essential for the reaction; anhydrous benzyltriethylammonium chloride, or potassium chloride with 18-crown-6, were equally good, affording all three products of Scheme 3. Any remaining TCNE co-ran with **2** on chromatography but was removed by recrystallisation of **2** from cyclohexane.

The thiadiazine **2** was obtained as bright yellow flakes, mp 134–135 °C, that were stable at *ca.* 20 °C in the open atmosphere, but hydrolysed slowly in water. Microanalysis and high resolution mass spectrometry (HRMS) gave the formula $C_6Cl_2N_4S$ and the ^{13}C NMR spectrum showed four carbon resonances, indicating a symmetrical molecule. The presence of a cyano group was supported by an IR band at 2217 cm^{-1} and a carbon resonance at 112.8 ppm. A strong UV absorption at λ_{max} 403 nm (log ε 4.38) suggested the presence of a conjugated or unsaturated cyclic system. An X-ray structure determination[10] confirmed the structure and showed that the thiadiazine ring had a shallow boat conformation unlike the almost planar thiadiazinone **1**. We calculate that the dicyanomethylene derivative **2** has a higher aromaticity index ($I_A = 60$) than **1** in spite of being less planar. We attribute this to a stronger electron withdrawal by the dicyanomethylene group allowing a greater contribution of resonance forms like **A**, and even **B**, to the overall electronic structure (Scheme 4). In agreement with this, the high



Scheme 4

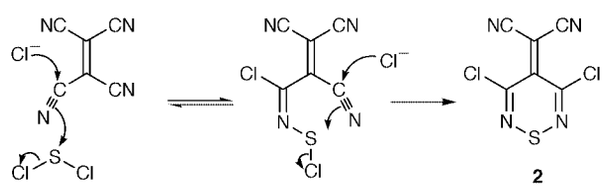
field ^{13}C resonance at 81.8 ppm of the central carbon of the dicyanomethylene group, compared with the analogous resonance at 108.2 ppm for TCNE,[11] indicates that substantial negative charge is located on the dicyanomethylene group of **2**.

Compound **4** was obtained as an orange–brown oil that solidified on standing and sublimed on warming to give colourless needles, mp 64.5–65 °C. Mass spectrometry gave the sulfur-free formula $C_5Cl_3N_3$, indicating six double bond equivalents. The ^{13}C NMR showed four carbon resonances, the signal at 114.1 ppm being attributed to a cyano group, which was supported by an IR absorption at 2270 cm^{-1}; a broad UV band at λ_{max} 252 nm (log ε 4.06) indicated the presence of a conjugated cyclic system. These data led to two structures, the pyrimidine **4** or the other symmetrical isomer 2,4,6-trichloropyrimidine-5-carbonitrile. The latter compound is reported[12] to have mp 119–121 °C and could probably be eliminated from consideration. X-Ray diffraction on single crystals obtained by sublimation confirmed structure **4**.[10]

Compound **5** was obtained as deep red needles or prisms, mp >245 °C with sublimation, that were sparingly soluble in DCM and reacted slowly with DMSO. Microanalysis and HRMS gave the formula as $C_9Cl_2N_6S$, indicating twelve double bond equivalents. The ^{13}C NMR consisted of nine low field resonances two of which, at 111.4 and 111.0 ppm, were tentatively assigned to cyano groups, and supported by stretching bands at 2238 and 2224 cm^{-1} in the IR spectrum. The UV spectrum had a broad band at λ_{max} 501 nm (log ε 3.98), highly structured with many shoulders, suggesting a conjugated, highly rigid system. The fused pyrroloimidazothiadiazine structure **5**, the first example of this ring system, was solved by X-ray crystallography.[10] The ring system of **5** is planar and delocalised and can be considered to be a 14π aromatic system.

Mechanism of formation of 2, 4 and 5

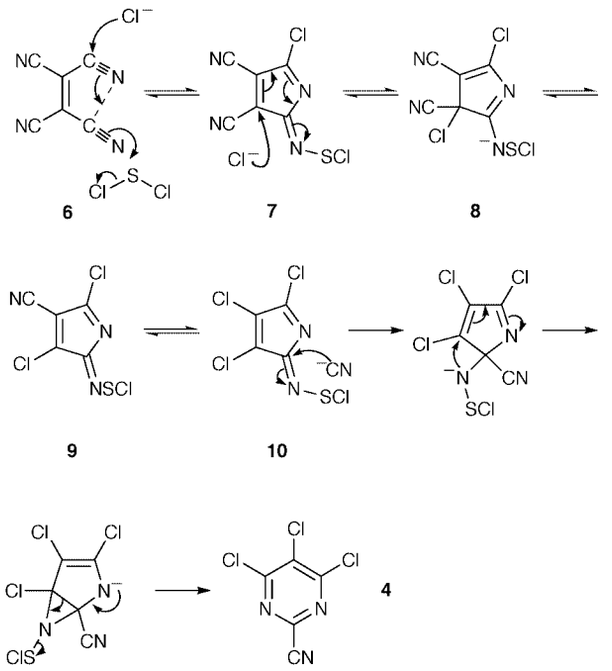
The conversion of TCNE into **2**, **4** and **5** required the presence of both SCl_2 and chloride ions. The formation of **2** in this way was based on analogy with the addition of SCl_2 to dichlorodicyanomethane (Scheme 1) and of CF_3SCl to TCNE (Scheme 2). Addition of SCl_2 to a cyano group is presumably initiated by its coordination to the cyano nitrogen accompanied or followed by nucleophilic addition of chloride ion (Scheme 5). A second



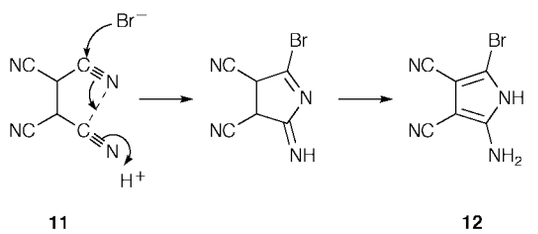
Scheme 5

addition of chloride to a geminal cyano group can then result in cyclisation to the thiadiazine ring. The addition steps are presumably reversible, with the cyclisation driven by the stability of the thiadiazine ring. Addition of the second chloride ion to the alternative (*cis*-vicinal) cyano group and ring closure as before would have generated a 7-membered (antiaromatic) thiadiazepine ring which would be expected to extrude sulfur to give a stable pyridazine; neither of these rings were detected, 6-membered ring formation having dominated, as expected.

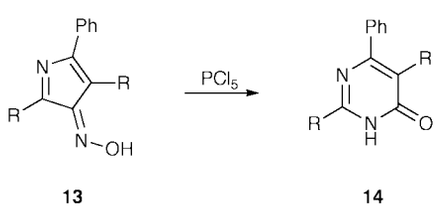
Formation of the two minor products **4** and **5** involves substantial changes in the atom connectivity of TCNE, in unforeseen rearrangement reactions; possible mechanisms for these reactions are suggested in Schemes 6 and 7. In the chloride ion catalysed addition of SCl_2 to TCNE (Scheme 5) it was proposed that a geminal cyano group participated in the reaction of the neighbouring cyano group. A *cis*-vicinal group could also participate but with the developing nitrogen anion now attacking carbon (5-membered ring formation) rather than sulfur (7-membered ring formation), as shown in **6** (Scheme 6). Various examples of such neighbouring group participation in the reactions of α,ω-dicyanides with electrophilic reagents to give heterocycles have been reported,[13] including the addition of hydrogen bromide to tetracyanoethane (arrows in **11**) formed by initial reduction of TCNE by the HBr. At this oxidation level the intermediate can aromatise to give 2-amino-5-bromo-3,4-dicyanopyrrole **12**.[14] The azacyclopentadiene imine **7**, so formed from **6**, with its four electron-withdrawing nitrogens, would be highly electrophilic and subject to successive,



Scheme 6

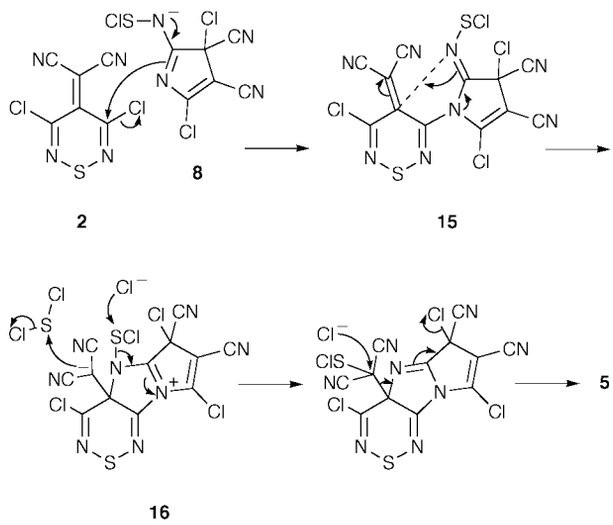


reversible attack by chloride ion and elimination of cyanide ion as shown in **7**→**8**→**9**, ultimately forming the fully chlorinated derivative **10**. This could then undergo a Beckmann-type rearrangement, with the developing carbocation being captured by cyanide to give the observed pyrimidine **4**. A related, classical, Beckmann rearrangement has been observed in the conversion of azacyclopentadiene oximes **13** into pyrimidones **14**



with phosphorus pentachloride.[15] Beckmann carbocation intermediates have been efficiently intercepted by cyanide ions,[16] and by trimethylsilyl cyanide,[17] to give imino nitriles in high yield.

Formation of the pyrroloimidazothiadiazine **5** would appear to have arisen from a combination of the major product **2** with the intermediate **7** proposed as a precursor of the pyrimidine in Scheme 6. We have shown that one of the chlorine atoms in **2** is very readily displaced by nucleophiles;[18] it would therefore be expected to react rapidly with the adducts formed from **7** and chloride ions, such as **8**. The amidine-like ring nitrogen of **8** would be its most nucleophilic centre and would displace a chlorine from **2** as shown (Scheme 7) to give **15** which could collapse to **16**, giving the observed tricyclic system of **5**. It is not known exactly how the dicyanomethylene and other structures are lost from **16** to give the aromatic product **5**, but one possibility is indicated in Scheme 7. In support of this overall

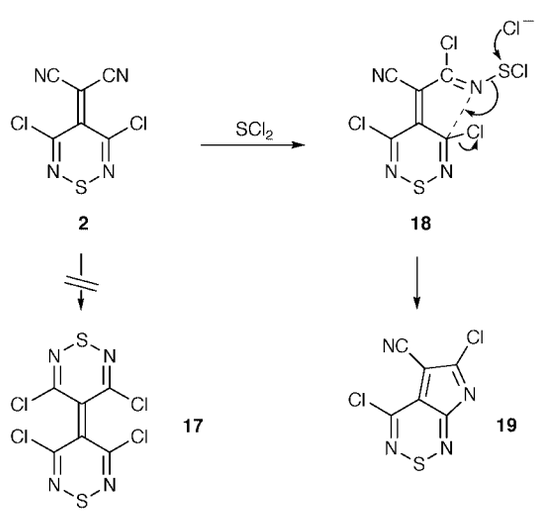


Scheme 7

mechanism, we have shown that other bis-nucleophiles react with thiadiazine **2** with displacement of chlorine and dicyanomethylene to give related polycyclic systems.[18]

Some reactions of compounds 2 and 5

The dicyanomethylene group in thiadiazine **2** might react further with SCl_2 to give the symmetrical dimer **17**; this interesting molecule would be considerably twisted about the carbon–carbon double bond, and a potential precursor for new fused thiadiazines. However, upon treatment of **2** with SCl_2 and benzyltriethylammonium chloride in DCM the only compound isolated was 4,6-dichloro-5-cyanopyrrolo[2,3-*c*][1,2,6]thiadiazine **19** in 20% yield. Compound **19** is a fluorescent yellow crystalline solid, mp 204–206 °C, that decomposes on standing or in solution. HRMS gave the molecular formula $C_6Cl_2N_4S$ and a strong UV absorption at λ_{max} 431 indicated a delocalised system. In the room-temperature conversion of **2** into **19** both SCl_2 and the quaternary ammonium chloride were required. Presumably the first step in the mechanism is the same as that in Scheme 5, giving the intermediate **18** which can now cyclise with displacement of an activated chlorine on the thiadiazine, and possible regeneration of SCl_2, to form the pyrrole ring of **19** (Scheme 8). The decomposition of **19** was not fully explored

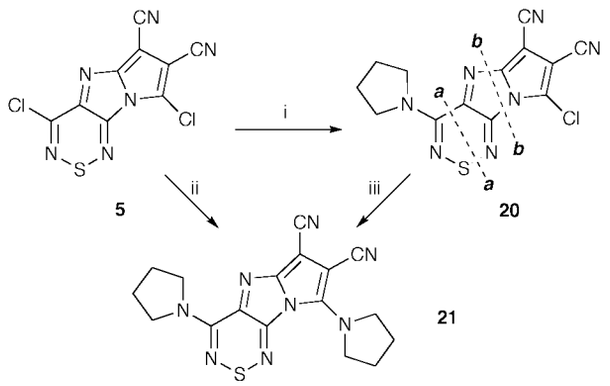


Scheme 8

but LRMS analysis indicated the formation of a new product of molecular weight *m*/*z* (EI) 212 (M^+, 100%). This suggests the hydrolysis of one chlorine, probably the 6-Cl which is activated

to nucleophilic displacement by two "imine" bonds, to give the 6-oxo lactam.

Both chlorine atoms in the pyrroloimidazothiadiazine **5** were, as expected, reactive and could be sequentially displaced by pyrrolidine to give two new highly coloured derivatives: the violet [λ_{max} 551 nm (log ε 4.23)] 8-chloro-6,7-dicyano-4-pyrrolidinopyrrolo[1′,2′ : 1,2]imidazo[5,4-*c*][1,2,6]thiadiazine **20** (93%) and the blue [λ_{max} 609 nm (log ε 4.16)] 6,7-dicyano-4,8-dipyrrolidinopyrrolo[1′,2′ : 1,2]imidazo[5,4-*c*][1,2,6]thiadiazine **21** (96%) (Scheme 9). Compound **20** was also converted



Scheme 9 *Reagents and conditions*: i, pyrrolidine (2 equiv.), DCM, −78 °C to 20 °C, 12 h; ii, pyrrolidine (16 equiv.), DCM, 40 °C, 72 h; iii, pyrrolidine (10 equiv.), DCM, 40 °C, 72 h.

into **21** (82%) under the conditions indicated in Scheme 9. Both products were fully characterised (see Experimental section) and a comparison of their ^{13}C NMR spectra with that of **5** indicated that no skeletal rearrangement of the ring system had occurred during the nucleophilic displacements.

A mass spectrometric analysis of the mono-substituted derivative **20** showed the pyrrolidine to be on the thiadiazine ring. The LRMS of **20** showed fragments at *m*/*z* 201 and 149, confirmed as C_8ClN_5 and C_6ClN_3 respectively by HRMS, derivable from the 8-chloro structure **20** by cleavages ***a*** · · · ***a*** and ***b*** · · · ***b***. Linked scan MS indicated that the ion *m*/*z* 149 was derived directly from *m*/*z* 201 and the parent ion *m*/*z* 329. Similarly a daughter ion scan for the parent ion (329) identified both *m*/*z* 149 and 201 supporting their direct fragmentation from the parent ion. Interestingly the ^{1}H and ^{13}C NMR data showed that rotation of the pyrrolidine ring on the thiadiazine was significantly slower than that of the pyrrolidine ring on the pyrrole. Four carbon resonances were detected for the pyrrolidine in the mono-substituted compound **20** (51.4, 49.3, 27.0 and 24.3 ppm), whilst for the bis-substituted compound **21** the four resonances of the pyrrolidine on the thiadiazine ring had merged into two broad signals (49.5 and 25.4 ppm), and the pyrrolidine on the pyrrole ring showed two sharp signals (51.4 and 25.5 ppm). Presumably replacement of the second chlorine atom by a pyrrolidine ring increases the electron density in the ring system and reduces the amidine-like conjugation between the other pyrrolidine and the thiadiazine ring thus reducing the energy barrier to rotation. This indication of electron delocalisation across the tricyclic 14π aromatic system was also supported by the observed 50 nm red shift of the first UV absorption band on the introduction of each pyrrolidino substituent. The bis-pyrrolidine **21** showed a higher mass impurity *m*/*z* 408 in its mass spectrum which corresponds to a tris-pyrrolidine where one of the cyano groups (probably at C-6) has been replaced by pyrrolidine, but this was not investigated further.

Thus we have synthesised the desired dicyanomethylenethiadiazine **2** in reasonable yield (60%) from TCNE and SCl_2, and the chemistry of **2** will be developed in a forthcoming paper. However, the TCNE–SCl_2 reaction is complicated by the close proximity of all the cyano groups in TCNE which permits their involvement. This neighbouring group participation leads to two minor products, the pyrimidine **4** and the pyrroloimidazothiadiazine **5**. The 4- and 8-chlorine atoms of the latter heteroaromatic system can be successively displaced by pyrrolidine and these "remote" substituents interact quite strongly with each other.

Direct conversion of TCNE into the considerably more complex compounds **2**, **4** and **5** by SCl_2 points the way to the synthesis of various structures from TCNE and other simple electrophilic reagents X^+Y^-.

Experimental

Monosulfur dichloride was freshly distilled from phosphorus trichloride; benzyltriethylammonium chloride was dried over phosphorus pentoxide under reduced pressure. Tetracyanoethylene (TCNE) which is **TOXIC** was prepared according to the literature.[19] All reactions were 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 refers to the fraction bp 60–80 °C.

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[20] was used throughout for all non-TLC scale chromatographic separations using Sorbsil C60 M40 silica.

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 and medium peaks are represented by s and m respectively. ^{1}H NMR spectra were recorded on a JEOL GSX 270 machine (at 270 MHz) and ^{13}C NMR spectra were recorded on a JEOL GSX 270 (at 68 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. Microanalyses were performed on a Perkin-Elmer 2400 CHN Analyser.

3,5-Dichloro-4-dicyanomethylene-4*H*-1,2,6-thiadiazine 2

To a suspension of TCNE (3.0 g, 23.4 mmol) in DCM (50 ml) at 0 °C, under nitrogen, benzyltriethylammonium chloride (53 mg, 1 mol%) was added followed by the slow addition of monosulfur dichloride (3 ml, 47 mmol). The reaction mixture was allowed to reach *ca.* 20 °C and was then monitored (TLC) for 3 days. The volatiles were removed and chromatography (light petroleum–DCM, 5 : 1) of the residue gave *4,5,6-trichloropyrimidine-2-carbonitrile* **4** (242 mg, 5%) as colourless needles, mp 64.5–65 °C (sublimation, 40 °C/10 mmHg); λ_{max}(DCM)/nm 252 (log ε 4.06), 265 inf (3.89), 274 (3.76), 283 (3.55); ν_{max}(Nujol)/cm^{-1} 2420m, 2270w (CN), 1531s and 1505s (C=C), 1462s, 1418s, 1354s, 1314s, 1299s, 1274s, 1255s, 1208m, 1064s, 1056s, 910s, 833s, 818s, 771s, 622s; δ_C(68 MHz; $CDCl_3$) 161.87 (*C*-1), 140.47 (*C*-4/6), 133.97 (*C*-5), 114.13 (*C*-N); *m*/*z* (EI) 207 (M^+, 100%), 172 (M^+ − Cl, 50), 120 ($C_3Cl_2N^+$, 28), 111 ($C_4ClN_2^+$, 13), 94 ($C_2Cl_2^+$, 11), 85 (C_3ClN^+, 26). Further elution (light petroleum–DCM, 1 : 5) gave the *title compound* **2** (2.4 g, 45%) as yellow flakes, mp 134–135 °C (from cyclohexane) (Found: C, 31.1; N, 24.0. $C_6Cl_2N_4S$ requires C, 31.2; N, 24.2%); λ_{max}(DCM)/nm 234 (log ε 3.75), 285 (3.28), 403 (4.38); ν_{max}(DCM film)/cm^{-1} 2217s (CN), 1523s and 1510s (C=C), 1488s, 1290s, 1273m, 1145m, 1083s, 814s, 758s, 713m; δ_C(68 MHz; $CDCl_3$) 139.59, 137.33, 112.80 (*C*N), 81.78 [*C*$(CN)_2$]; *m*/*z* (EI) 230 (M^+, 100%), 204 (M^+ − CN, 2), 195 (M^+ − Cl, 55), 184 (M^+ − NS, 3), 169 (M^+ − CClN, 21), 160 (M^+ − Cl_2, 3), 143

($M^+ - C_2ClN_2$, 4), 134 ($M^+ - CCl_2N$, 21), 123 ($M^+ - CClN_2S$, 4), 114 ($C_6N_3^+$, 3), 108 ($C_4N_2S^+$, 5), 102 ($C_5N_3^+$, 2), 93 ($CClNS^+$, 9), 76 ($C_4N_2^+$, 16), 67 (ClS^+, 42), 58 (CNS^+, 11), 46 (NS^+, 52). A final elution (DCM) gave *4,8-dichloro-6,7-dicyanopyrrolo[1′,2′ : 1,2]imidazo[5,4-c][1,2,6]thiadiazine* **5**, (344 mg, 5%) as red prisms, mp >245 °C sublimation (from 1,2-dichloroethane) (Found: C, 36.8; N, 28.65. $C_9Cl_2N_6S$ requires C, 36.7; N, 28.6%); λ_{max}(DCM)/nm 230 (log ε 4.13), 268 inf (4.44), 276 (4.51), 348 (4.05), 444 inf (3.85), 470 (3.96), 484 (3.97), 501 (3.98), 517 inf (3.90), 539 (3.82), 560 inf (3.55), 585 (3.35); ν_{max}(Nujol)/cm^{-1} 2238w and 2224s (CN), 1607m, 1500s (C=C), 1490s, 1441s, 1413s, 1345s, 1174s, 1084m, 893m, 854m, 819m, 794m, 722m, 677m; δ_C(68 MHz; DMSO-d_6) 149.88 (*C*=N), 144.99 (*C*=N), 144.41 (*C*=N), 141.33 (*C*=C), 117.93 (*C*=C), 111.42 (*C*N), 111.01 (*C*N), 100.41 (*C*=C), 80.22 (*C*=C); *m*/*z* (EI) 294 (M^+, 100%), 268 ($M^+ - CN$, 2), 259 ($M^+ - Cl$, 8), 248 ($M^+ - NS$, 4), 233 ($M^+ - CClN$, 11), 207 ($M^+ - C_2ClN_2$, 3), 201 ($M^+ - CClNS$, 7), 175 ($M^+ - C_2ClN_2S$, 5), 149 ($M^+ - C_3ClN_3S$, 5), 119 ($C_2ClN_2S^+$, 12), 114 ($C_6N_3^+$, 17), 93 ($CClNS^+$, 11), 70 (18), 46 (NS^+, 13).

5-Cyano-4,6-dichloropyrrolo[2,3-*c*][1,2,6]thiadiazine 19

To a stirred solution of 3,5-dichloro-4-dicyanomethylene-4*H*-1,2,6-thiadiazine **2** (101 mg, 0.44 mmol) in DCM (10 ml) under nitrogen at 20 °C, benzyltriethylammonium chloride (100 mg, 1 equiv.) was added followed by the slow addition of monosulfur dichloride (2 ml, 31.8 mmol). After 24 h TLC indicated a new yellow fluorescent product and no starting thiadiazine. Rapid chromatography (DCM) gave the *title compound* **19** (20 mg, 20%) as yellow prisms, mp 204–206 °C (from chloroform–pentane); λ_{max}(DCM)/nm 254, 261 inf, 306, 431; ν_{max}(DCM film)/cm^{-1} 2234m (CN), 1606s, 1563s, 1372m, 1326s, 793m, 759s, 743s, 688m; *m*/*z* (EI) 230 (M^+, 100%), 195 ($M^+ - Cl$, 41), 169 ($M^+ - CClN$, 3), 160 ($M^+ - Cl_2$, 4), 134 ($M^+ - CCl_2N$, 13), 123 ($M^+ - CClN_2S$, 5), 120 (2), 114 ($C_6N_3^+$, 3), 108 ($C_4N_2S^+$, 7), 102 ($C_5N_3^+$, 5), 93 ($CClNS^+$, 18), 76 ($C_4N_2^+$, 39), 67 (ClS^+, 19), 58 (CNS^+, 26), 46 (NS^+, 40) (Found: M^+, 229.9216. $C_6Cl_2N_4S$ requires *M*, 229.9221). The experiment was repeated with the exclusion of either monosulfur dichloride or benzyltriethylammonium chloride and no reaction was observed until the excluded compound was reintroduced.

8-Chloro-6,7-dicyano-4-pyrrolidinopyrrolo[1′,2′ : 1,2]imidazo-[5,4-*c*][1,2,6]thiadiazine 20

To a stirred solution of 4,8-dichloro-6,7-dicyanopyrrolo-[1′,2′ : 1,2]imidazo[5,4-*c*][1,2,6]thiadiazine **5** (95 mg, 0.32 mmol) in DCM (25 ml) at −78 °C, under nitrogen, pyrrolidine (53 µl, 0.64 mmol) was added. The mixture was left to warm to *ca.* 20 °C and after 12 h chromatography (DCM) gave the *title compound* **20** (98 mg, 93%) as violet prisms, mp >280 °C dec. (from 1,2-dichloroethane) (Found: C, 47.6; H, 2.5; N, 29.55. $C_{13}H_8ClN_7S$ requires C, 47.4; H, 2.4; N, 29.8%); λ_{max}(DCM)/nm 230 (log ε 4.45), 289 (4.50), 355 (3.86), 372 (3.85), 531 (4.22), 551 (4.23), 590 inf (3.92); ν_{max}(Nujol)/cm^{-1} 2234m and 2217s (CN), 1593s, 1559s, 1517m, 1448s, 1417m, 1368m, 1344m, 1268m, 1244s, 1156m, 894m, 849s, 829m, 702m; δ_H(270 MHz; DCM-d_2) 4.49 (2H, t, *J* 6.7 Hz, CH_2N), 3.67 (2H, t, *J* 6.8 Hz, CH_2N), 2.14–1.99 [4H, m, 2(CH_2)]; δ_C(125 MHz; DCM-d_2) 150.61 (*C*=N), 149.31 (*C*=N), 141.46 (*C*=N), 134.44 (*C*=C), 114.98 (*C*=C), 112.73 (*C*N), 111.69 (*C*N), 101.17 (*C*=C), 78.85 (*C*=C), 51.44 (*C*H_2N), 49.33 (*C*H_2N), 27.03 (*C*H_2*C*H_2N), 24.25 (*C*H_2*C*H_2N); *m*/*z* (EI) 329 (M^+, 92%), 301 ($M^+ - C_2H_4$, 18), 294 ($M^+ - Cl$, 4), 286 ($M^+ - C_2H_5N$, 3), 274 ($M^+ - C_3H_5N$, 3), 266 ($M^+ - C_3H_4Cl$, 8), 260 ($M^+ - C_4H_3N$, 13), 243 (2), 233 ($M^+ - C_5H_8N$, 2), 225 ($M^+ - C_4H_3ClN$, 7), 202 ($M^+ - C_5H_7N_2S$, 9), 175 ($C_7ClN_4^+$, 2), 164 ($C_7H_6N_3S^+$, 3), 149 ($C_6ClN_3^+$, 4), 123 ($C_5ClN_2^+$, 3), 89 (11), 70 ($C_4H_8N^+$, 100) (Found: M^+, 329.0226. $C_{13}H_8ClN_7S$ requires *M*, 329.0250). LSMS: (EI, *B*/*E* of *m*/*z* 329) 301 (100%), 294 (19), 286 (12), 274 (5), 266 (21), 260 (41), 243 (3), 233 (5), 225 (11), 202 (13), 201 (11), 149 (4), 70 (7); (EI, B^2/E of *m*/*z* 149) 329 (M^+, 25%), 302 (7), 260 (12), 201 (100), 176 (5), 167 (12).

6,7-Dicyano-4,8-dipyrrolidinopyrrolo[1′,2′ : 1,2]imidazo[5,4-*c*]-[1,2,6]thiadiazine 21

Method 1. To a stirred solution of 4,8-dichloro-6,7-dicyanopyrrolo[1′,2′ : 1,2]imidazo[5,4-*c*][1,2,6]thiadiazine **5** (29 mg, 0.10 mmol) in DCM (10 ml) at 20 °C, under nitrogen, pyrrolidine (133 µl, 1.60 mmol) was added. The formation of the mono-pyrrolidino product is observed to occur within 10 min and after heating under reflux for 72 h a new product was observed and no mono-pyrrolidino or starting material remained (TLC). Chromatography (DCM–ether, 3 : 1) gave the *title compound* **21** (35 mg, 96%) as blue needles, mp 257–258 °C (from 1,2-dichloroethane–cyclohexane) (Found: C, 56.3; H, 4.4; N, 30.7. $C_{17}H_{16}N_8S$ requires C, 56.0; H, 4.4; N, 30.8%); λ_{max}(DCM)/nm 232 (log ε 4.32), 302 (4.56), 378 inf (3.71), 401 (3.79), 435 inf (3.61), 567 inf (4.06), 609 (4.16), 647 inf (4.07); ν_{max}(Nujol)/cm^{-1} 2209s (CN), 1600m, 1543s, 1448s, 1417m, 1379m, 1349m, 1319m, 1250m, 889m, 855m, 693m; δ_H(270 MHz; $CDCl_3$) 4.41 [4H, br s, 2(CH_2N)], 3.92 [4H, t, *J* 6.8 Hz, 2(CH_2N)], 2.12–1.98 [8H, m, 4(CH_2)]; δ_C(125 MHz; $CDCl_3$) 149.40 (*C*=N), 144.81 (*C*=N), 142.34 (*C*=N), 139.46 (*C*=C), 133.81 (*C*=C), 115.54 (*C*N), 113.21 (*C*N), 79.61 (*C*=C), 78.34 (*C*=C), 51.35 (*C*H_2N), 49.48 (br, *C*H_2N), 25.54 (*C*H_2*C*H_2N), 25.35 (br, *C*H_2*C*H_2N); *m*/*z* (EI) 364 (M^+, 44%), 310 (3), 262 ($M^+ - C_4H_8NS$, 9), 235 ($M^+ - C_2H_5N$, 5), 143 (8), 133 (11), 105 (100), 89 (40), 70 ($C_4H_8N^+$, 33) (Found: M^+, 364.1217. $C_{17}H_{16}N_8S$ requires *M*, 364.1219).

Method 2. To a stirred solution of 8-chloro-6,7-dicyano-4-pyrrolidinopyrrolo[1′,2′ : 1,2]imidazo[5,4-*c*][1,2,6]thiadiazine **20** (13 mg, 0.04 mmol) in DCM (3 ml) pyrrolidine (33 µl, 0.40 mmol) was added. The mixture was heated under reflux for 72 h until no starting material remained (TLC). Chromatography (DCM) gave the title compound **21** as blue needles (12 mg, 82%), mp 257–258 °C, identical to that described above.

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