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Reaction of tetracyanoethylene with SCl_2: new molecular rearrangements

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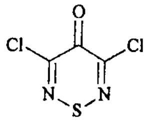
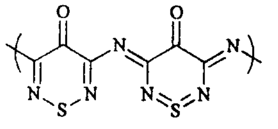
The chloride ion catalysed addition of SCl_2 to TCNE gives the dicyanomethylene-1,2,6-thiadiazine 3 as major product together with two unexpected minor products, pyrimidine 4 and pyrroloimidazothiadiazine 5, whose X-ray crystal structures are described; the products are derived from interaction of SCl_2 with one cyano group with neighbouring group participation by two others.

1,2,6-Thiadiazines which are not oxidised on sulfur are rare.[1] One notable exception is 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one **1** which is readily prepared from dichlorodicyanomethane and SCl_2, followed by hydrolysis with formic acid; the chlorines in **1** can be successively displaced by a range of nucleophiles, the second requiring more vigorous conditions.[2] We needed a large scale synthesis of the 3,5-diamino derivative for incorporation into a conjugated polymer of type **2**. Since the displacement of the second chlorine of **1** by NH_3 required sealed tubes or pressure vessels, we decided to enhance the reactivity of the chlorines by replacing the 4-keto group in **1** by dicyanomethylene to give the monomer **3**.

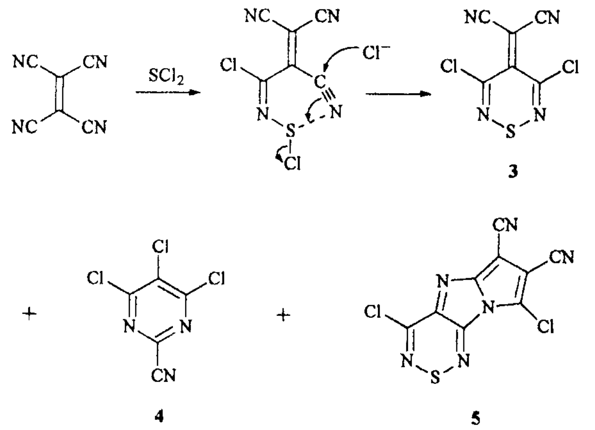


1



2

The dicyanomethylene compound **3** was not formed by condensing the keto compound **1** with malononitrile, but it was formed slowly in up to 60% yield by the addition of SCl_2 to TCNE catalysed by $BnEt_3NCl$, in CH_2Cl_2 at room temperature (Scheme 1). However the formation of **3** was accompanied by the formation of two unexpected and 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** (5%). The dicyanomethylene compound **3** was obtained as bright yellow flakes, mp 134–135 °C, the pyrimidine **4** as colourless, volatile needles, mp 64.5–65 °C, and the pyrroloimidazothiadiazine **5** as deep red needles or prisms, mp > 245 °C with sublimation.



Scheme 1

For the thiadiazinone **1**, which is almost planar,[3] Bird calculated his aromaticity index I_A to be 54,[4] indicating a modestly aromatic compound, *cf.* I_A = 53 for furan and 100 for benzene. The dicyanomethylene analogue **3**, however, has a distinctly non-planar, shallow boat conformation (Fig. 1).† In all four independent molecules in the crystal the N(2)–S(1)–N(6) and C(3)–C(4)–C(5) planes are inclined by *ca.* 25°, thereby distancing the cyano groups from the bulky chloro substituents. Whereas the two C=N bonds in the thiadiazine ring have pronounced double bond character, the C(4)–C(7) linkage is delocalised. Compound **3** has a slightly higher aromaticity index (I_A = 60) than **1**, in spite of being less planar, presumably because the more strongly electron withdrawing group in **3** allows greater contribution from dipolar resonance forms.

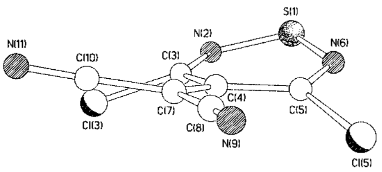


Fig. 1 The molecular structure of **3**. The average S–N, C=N and C(4)–C(7) distances over the four independent molecules are 1.616(7), 1.272(10) and 1.367(10) Å, respectively.

Compounds **4** (Fig. 2) and **5** (Fig. 3) are both planar and delocalised, the latter being the first example of this (14π aromatic) ring system. Crystals of **4** contain two independent molecules which are planar to within 0.031 and 0.071 Å, respectively. The molecules pack with the cyano group of one directed into the π system of the other (Fig. 2), the shortest N···ring centroid distance being 3.22 Å with a C≡N···π angle of 171°. Two polymorphs of **5** were identified; both are monoclinic but one crystallises in a centrosymmetric space group whereas the other is polar. The geometries of the two forms do not differ significantly, being planar to within 0.066 (form 1) and 0.117 Å (form 2), their tricyclic cores having maximum deviations from planarity of only 0.019 and 0.023 Å respectively (Fig. 3). There is distinct bond ordering in the thiadiazine ring and also to a lesser degree in the imidazole, whereas the terminal pyrrole exhibits delocalisation that

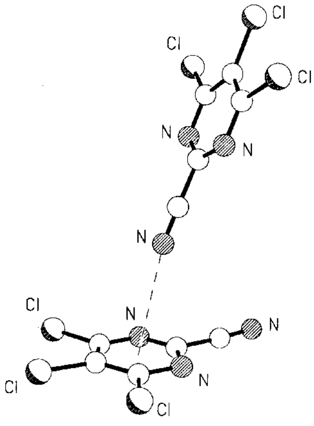


Fig. 2 The molecular structure of **4**.

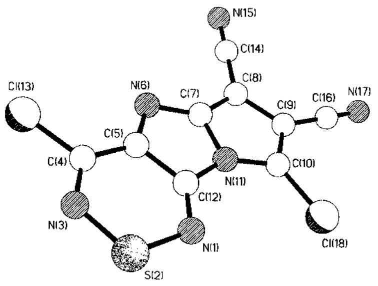
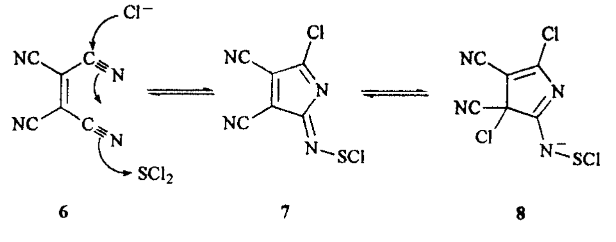


Fig. 3 The molecular structure of **5**.

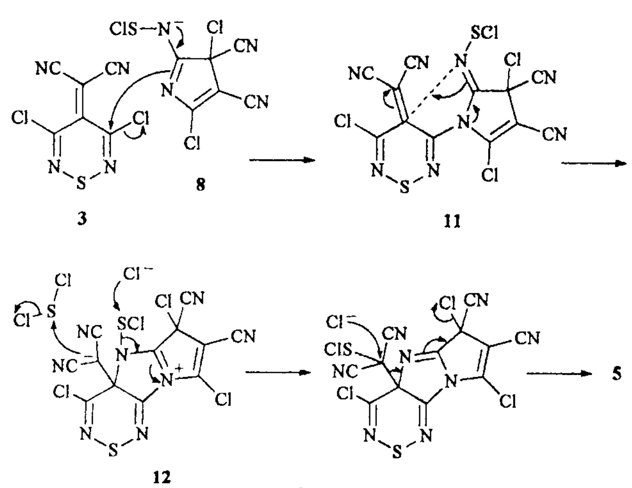
extends from C(8) to C(9) *via* N(11). Despite the differences in packing, both polymorphs contain loosely linked tapes of molecules formed by electrostatic N···Cl interactions.

The formation of **3**, **4** and **5** from TCNE and SCl_2 at room temperature required the presence of chloride ions for a significant rate of reaction; all are presumably initiated by coordination of the electrophilic SCl_2 to a cyanide nitrogen, which activates nucleophilic addition of chloride. This process can be repeated by addition of chloride to a geminal cyano group (Scheme 1), and cyclisation to form the aromatic thiadiazine **3**, which was always the major product. The mechanism of formation of the minor, rearranged, products is much less obvious. However it is possible that a *cis*-vicinal cyano group could also participate in the SCl_2 reaction, with its nitrogen now attacking carbon to form a five-membered ring as shown in **6** (Scheme 2). Various examples of such neighbouring group participation in the reactions of dicyanides with electrophilic reagents have been reported.[5] The intermediate **7**, thus formed, is highly electrophilic and would be subject to successive, reversible attack by chloride ions, ultimately displacing the cyano groups, *via* **8** and **9**, to give the fully chlorinated derivative **10**. This could then undergo a Beckmann-type rearrangement with the developing carbocation being captured by cyanide, in the anhydrous medium, to give the observed pyrimidine **4**. A related, classical, Beckmann rearrangement has been observed in the conversion of analogous azacyclopentadienone oximes into pyrimidones,[6] and Beckmann carbocation intermediates have been efficiently intercepted by cyanide ions.[7]

Formation of **5** could arise by condensation of the major product **3** and the intermediate **7**. One of the chlorine atoms in **3** is very readily displaced by nucleophiles,[8] and it would be expected to react rapidly with the adducts of **7** and chloride ions, such as **8**. The amidine-like nitrogen of **8** would displace a chlorine from **3** (Scheme 3) to give **11**, which could collapse to **12** and finally aromatise to give **5**. It is not known how the dicyanomethylene and other substituents are lost from **12**, but one possibility is shown in Scheme 3. Other bis-nucleophiles react with **3**, displacing a chlorine and the dicyanomethylene to give related polycyclic systems.[8]



Scheme 2



Scheme 3

Thus **3** has been prepared from TCNE and SCl_2, but this reaction is complicated by the involvement of geminal and vicinal cyano groups, after the initial interaction. These neighbouring group interactions lead to the formation of **3** (Scheme 1) or to new molecular rearrangements to give the minor products **4** and **5** (Scheme 2 and 3).

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Notes and references

† *Crystal data* for **3**: $C_6N_4Cl_2S$, M = 231.1, orthorhombic, $Pc2_1b$ (no. 29), a = 10.474(6), b + 10.787(4), c = 31.348(10) Å, V = 3542(3) Å^3, Z = 16 (four independent molecules), D_c = 1.733 g cm^{-3}, μ(Mo-Kα) = 9.20 cm^{-1}, F(000) = 1824, T = 293 K; refined based on F, R = 0.045, Rw = 0.049, 2646 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 50°$], 469 parameters. The polarity of the structure was determined by use of the η parameter, which refined to a value of −0.1(6). For **4**: $C_5N_3Cl_3$, M = 208.4, monoclinic, $P2_1/c$ (no. 14), a = 15.886(4), b = 6.994(2), c = 16.477(2) Å, β = 118.01(2)°, V = 1616.4(5) Å^3, Z = 8 (two independent molecules), D_c = 1.713 g cm^{-3}, μ(Cu-Kα) = 97.4 cm^{-1}, F(000) = 816, T = 293 K; refined based on F, R = 0.053, Rw = 0.055, 1318 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 120°$], 200 parameters. For **5** (form 1): $C_9N_6Cl_2S$, M = 295.1, monoclinic, $P2_1/c$ (no. 14), a = 7.876(2), b = 20.334(10), c = 7.167(2) Å, β = 108.88(2)°, V = 1086.0(7) Å^3, Z = 4, D_c = 1.805 g cm^{-3}, μ(Mo-Kα) = 7.77 cm^{-1}, F(000) = 584, T = 293 K; refined based on F, R = 0.034, Rw = 0.037, 1470 independent observed reflections [$|F_o| > 4\sigma(F_o|)$, $2\theta \leqslant 50°$], 164 parameters. For **5** (form 2): $C_9N_6Cl_2S$, M = 295.1, monoclinic, $P2_1$ (no. 4), a = 6.303(7), b = 14.060(8), c = 6.466(5) Å, β = 105.08(2)°, V = 553.3(9) Å^3, Z = 2, D_c = 1.771 g cm^{-3}, μ(Mo-Kα) = 7.62 cm^{-1}, F(000) = 292, T = 293 K; refined based on F, R = 0.061, Rw = 0.058, 1249 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 60°$], 164 parameters. The polarity could not be assigned. CCDC 182/1524.

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