The chloride ion catalysed addition of $\text{SCl}_2$ 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 $\text{SCl}_2$ 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-one 1 which is readily prepared from dichlorodicyano-methane and $\text{SCl}_2$, 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 $\text{NH}_3$ 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 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).\(^5\) 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](image1.png)

**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 (14\(\pi\) 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 $\pi$ system of the other (Fig. 2), the shortest N···ring centroid distance being 3.22 Å with a $\text{C}_\text{N} \cdots \pi$ 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 (form 2), ca. 25 Å–171°, respectively. The molecules pack with the cyano group of one directed into the $\pi$ system of the other (Fig. 3), the shortest N···ring centroid distance being 3.22 Å with a $\text{C}_\text{N} \cdots \pi$ 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](image2.png)

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

For the thiadiazonine 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).\(^5\) 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.
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 SCl₂ at room temperature required the presence of chloride ions for a significant rate of reaction; all are presumably initiated by coordination of the electrophilic SCl₂ 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 SCl₂ 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. 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, and Beckmann carbocation intermediates have been efficiently intercepted by cyanide ions.

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, 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.

Thus 3 has been prepared from TCNE and SCl₂, 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).

We thank the EPSRC for a Research Studentship (P. A. K.) and the Wolfson Foundation for establishing the Wolfson Centre for Organic Chemistry in Medical Science at Imperial College.

Notes and references

1 Crystal data for 3: C₅N₃Cl₃S, M = 231.1, orthorhombic, P2₁2₁2₁ (no. 29), a = 10.474(6), b = 10.787(4), c = 31.348(10) Å, V = 3542(3) Å³, Z = 16 (four independent molecules), Dₓ = 1.733 g cm⁻³, μ(Mo-Kα) = 9.20 cm⁻¹, F(000) = 1824, T = 293 K; refined based on F, R = 0.0345, Rw = 0.0409, 2646 independent observed reflections [F > 4σ(Fₒ)], 29% > 50%.

4 The polarity could not be assigned. CCDC 182/1524.

Fig. 3 The molecular structure of 5.

Scheme 2

Scheme 3

Notes and references


6 T. Ajello, Gazz. Chim. Ital., 1939, 69, 460; 1940, 70, 504; 1944, 72, 325.


8 P. A. Koutentis and C. W. Rees, unpublished observations.