# Conversion of tetrazoles into hydrazonoyl chlorides. Novel donor–dithiazolium interactions

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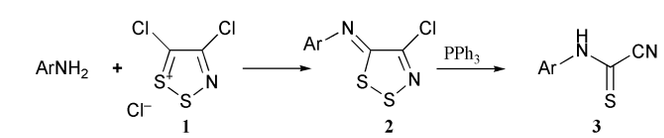
5-Substituted tetrazoles **13**, readily prepared from RCN and aluminium azide, react rapidly with Appel salt **1** at room temperature to give hydrazonoyl chlorides **16** in high yield. 5-Aminotetrazole **4** reacts further to give the extended bis(iminodithiazole) **6** and a minor product **7**. Mechanisms are proposed for these reactions (except for the formation of **7**) which are supported by the smooth conversion of 5-amino-2-substituted tetrazoles **11**, but not 5-amino-1-substituted tetrazoles, into the normal iminodithiazoles **12**. The red bis(imine) **6** rearranges to the yellow 1,3,4-thiadiazole **19** in warm DMSO. The structures of **1**, **6**, **7** and **19** are proved by X-ray crystallography which also reveals the presence in each case of a strong intermolecular 3-centre interaction between the adjacent dithiazole ring sulfur atoms and either oxygen, nitrogen or chlorine donors.

## Introduction

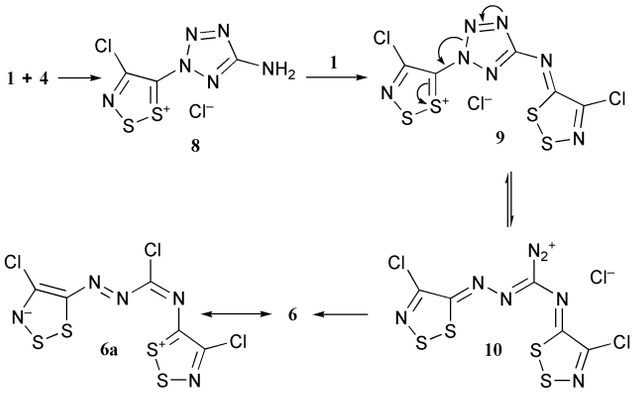
5-Arylimino-4-chloro-1,2,3-dithiazoles **2** are stable yellow crystalline solids reliably prepared in high yields from primary aromatic amines and 4,5-dichloro-1,2,3-dithiazolium chloride **1** ("Appel salt") which itself is readily available in large quantities from chloroacetonitrile and disulfur dichloride.[1] Formation of iminodithiazoles **2** is a general reaction which has been extended to a wide range of aromatic and heteroaromatic amines because of their synthetic versatility.[2] This versatility derives from their reactivity towards inter- and intra-molecular nucleophilic attack at S-1, S-2 and C-5 of the dithiazole ring, largely driven by regeneration of the latent cyano group.[3] Some of these reactions involve the dithiazole ring only, such as treatment with triphenylphosphine in DCM at room temperature to give cyanothioformanilides **3** in high yield,[4] whilst others involve cyclisation onto the adjacent aromatic ring.[2]




## Results and discussion

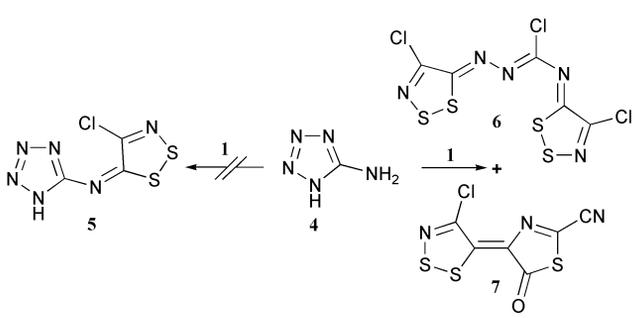
### Reaction of 5-aminotetrazoles with Appel salt[5] 1

We were interested in extending these reactions to aminotetrazoles because of the potential for the extrusion of dinitrogen from the products to generate reactive intermediates.[6] Treatment of 5-aminotetrazole monohydrate **4** with Appel salt (1.1 equiv.) under our standard conditions in DCM at room temperature with pyridine as base, took an entirely different course from that observed with other primary amines, giving none of the corresponding imine **5** ($C_3HClN_6S_2$). Upon mixing **4** and **1** in DCM, nitrogen was evolved from the (complex) reaction mixture from which minor amounts (8 and 1% respectively) of two unexpected products were isolated: **6** ($C_5Cl_3N_5S_4$) as long red needles and **7** ($C_6ClN_3OS_3$) as a maroon powder. The structure of **6** was deduced from analysis, spectroscopy and mechanistic considerations (Scheme 1) and was confirmed by X-ray crystallography. This product was




**Scheme 1**

derived from one equiv. of tetrazole **4** and two equiv of salt **1**, with loss of $N_2$ and 3 HCl; with two to three equiv. of **1** the yields of **6** and **7** rose to 20 and 3% respectively but were not increased further with more Appel salt. The structure of maroon product **7** was more difficult to solve. All the carbons in $C_6ClN_3OS_3$ were in different environments; the ultra-violet maxima at 344 and 376 nm, the infra-red signal at 2220 $cm^{-1}$ for a conjugated cyanide, and mechanistic considerations did not lead to an unambiguous structure. Suitable crystals for X-ray crystallography could not be obtained from either ethyl acetate, ether, ethanol, DCM, chloroform, methanol or pentane, all of which gave powders. Crystals were finally obtained from DMSO, though these, when left in air at room temperature for about 16 hours, reverted to a powder (*vide infra*).

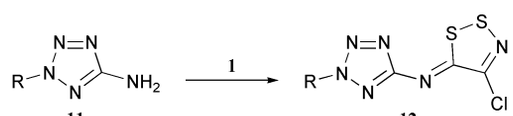


It is possible that the red compound **6** was formed from **1** and **4** *via* the "normal" iminodithiazole **5**, but this seems unlikely since (i) extensive conjugation in **4** renders the exocyclic amino group less nucleophilic than the ring nitrogens and (ii) several other 5-substituted tetrazoles **11**, with substituents inert to the Appel salt, reacted entirely analogously with the salt at N-2 (*vide infra*). We propose therefore (Scheme 1) that **1** and **4** give the 2,5-disubstituted tetrazole **8** which then reacts with more Appel salt to give the 2 : 1-adduct **9**. The strongly electron withdrawing dithiazolium group at N-2 will induce equilibration of **9** with the stabilised diazonium tautomer **10** which with $Cl^-$ would give the isolated covalent trichloro compound **6**.

The central "imidoyl" chloride function of **6** was not readily hydrolysed; heating **6** with aqueous silver nitrate did not give a precipitate of silver chloride. Bimolecular displacement of the chloride would be disfavoured by the electron releasing dithiazole rings, and the structure of **6** does not allow effective stabilisation of the unimolecularly dissociated "nitrilium" chloride by the dithiazole rings.

The conversion of **1** and **4** into **6** as shown in Scheme 1, requires initial nucleophilic attack on **1** by **4** through N-2 of the tetrazole ring to give intermediate **8**. N-2 is the normal site of electrophilic attack on tetrazoles, as in the Huisgen reaction,[7] but with 5-aminotetrazole the regiochemistry is more finely balanced and attack at N-1 is not uncommon.[6] In the present reaction attack by the Appel salt at N-1 analogous to the conversion **8**⟶**9**⟶**10** (Scheme 1) would lead to an unstable *N*-diazonium chloride, or isomeric chloroazide. This could have occurred in the present complex reaction, though it is sterically disfavoured and could not obviously lead to stable covalent products which would survive chromatography.

We investigated this aspect of the proposed mechanism of Scheme 1 by separately blocking the N-1 and N-2 positions of 5-aminotetrazole by *N*-methylation with iodomethane[8] and by *N*-ethoxycarbonylmethylation with ethyl bromoacetate.[9] The 5-amino-2-alkylated tetrazoles **11a**,**b** with N-2 of the ring blocked, reacted with the Appel salt as expected for primary heteroaromatic amines to give the imino-adducts **12a**,**b** in high yield. By contrast, the 5-amino-1-alkylated tetrazoles with Appel salt gave complex reactions with several very minor products only, from which the normal imines, isomeric with **12a**,**b**, could not be isolated. This observation suggests that reaction is probably again occurring at N-2 as well as at the primary amino group, to give *N*-alkylated quaternary salts that are not isolated by column chromatography.

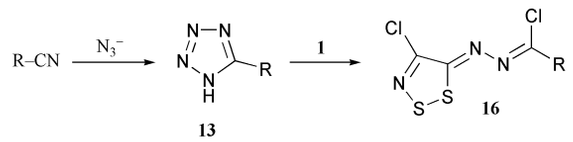



**Reaction of 5-substituted tetrazoles with Appel salt 1**

To extend the scope of this new tetrazole reaction and to support the mechanism of Scheme 1, we investigated the reaction of a series of tetrazoles **13** in which the amino group is replaced by aryl, alkyl, vinyl and phenoxy substituents, all of which are inert to the Appel salt. The tetrazoles (Table 1) were all prepared by azide addition to the appropriate cyanide.[6] The best method involved *in situ* generation of aluminium triazide from aluminium trichloride and sodium azide;[10] these reactions were fast and high-yielding. 5-Phenoxytetrazole was prepared from phenyl cyanate[11] and sodium azide.[12]

The reaction of 5-phenyltetrazole **13a** with Appel salt **1** was typical. A suspension of **13a** in DCM at room temperature was stirred with **1** (1.1 equiv.) for 30 minutes; addition of pyridine (1 equiv.) then gave a clear solution with the evolution of nitrogen and some hydrogen chloride. The yellow product **16a** (87%) was isolated and purified by chromatography. For some of the tetrazoles the addition of pyridine could be omitted if the reaction mixture was stirred for a longer time (12 to 16 hours) at room temperature, these reactions being both cleaner and higher yielding. Analysis and spectroscopy showed that the product, $C_9H_5Cl_2N_3S_2$, from 5-phenyltetrazole retained the phenyl ring and two chlorine atoms. By analogy with the reaction of Scheme 1 and the structure **6**, which was proved by X-ray diffraction, we assigned the hydrazonoyl chloride structure **16a** to this product, and analogous structures to all the products in Table 1. Except for the phenyl **16a**, vinyl **16i** and *p*-nitrophenyl **16j** compounds, they are very soluble in organic solvents, and show two absorption maxima in their UV spectra at 280–300 and 420–450 nm. They are all stable except for the chloroethyl derivative **16h** which decomposed rapidly in the solid state and the phenoxy derivative **16g** which decomposed slowly.

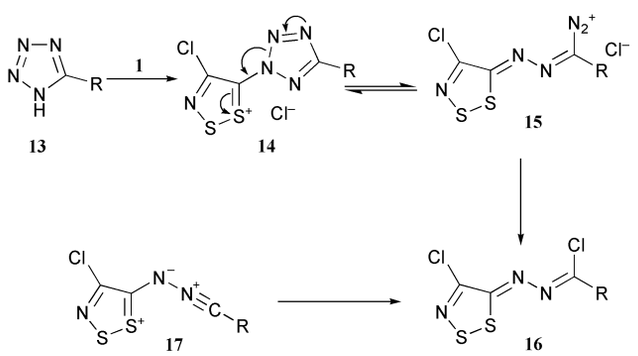
**Table 1** Synthesis of tetrazoles **13** and hydrazonoyl chlorides **16**




| R | **13** | Yield (%) | **16** | Yield (%) |
|---|---|---|---|---|
| $C_6H_5$– | **13a** | 85 | **16a** | 87 |
| 2-$MeOC_6H_4$– | **13b** | 77 | **16b** | 64[a] |
| 3-$MeOC_6H_4$– | **13c** | 82 | **16c** | 83[a] |
| 4-$MeOC_6H_4$– | **13d** | 88 | **16d** | 78[a] |
| 2-$FC_6H_4$– | **13e** | 86 | **16e** | 87 |
| 2-$ClC_6H_4$– | **13f** | 83 | **16f** | 73[a] |
| $C_6H_5O$– | **13g** | 22 | **16g** | 56[a] |
| $ClCH_2CH_2$– | **13h** | 90 | **16h** | 75 |
| $CH_2$=CH– | **13i** | 65 | **16i** | 80 |
| 4-$O_2NC_6H_4$– | **13j**[b] | — | **16j** | 80 |

[a] With pyridine added. [b] Commercial product.

A mechanism for the conversion of the tetrazoles and Appel salt **1** into the hydrazonoyl chlorides **16** is shown in Scheme 2.



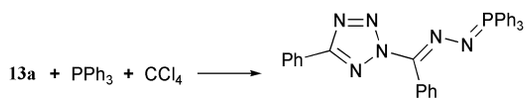

**Scheme 2**

By analogy with the 5-aminotetrazole reactions (Scheme 1) the 1 : 1-adducts **14** should be formed; since, in the absence of the 5-amino group, these cannot react further with **1** they could equilibrate directly with the stabilised diazonium chlorides **15** and hence give the isolated products **16**, analogous to **6**. In the Huisgen reaction with neutral rather than positively charged electron withdrawing groups (*e.g.* benzoyl) on N-2 of the 2,5-disubstituted tetrazole, the dinitrogen is lost in a concerted manner to generate a nitrilimine which then cyclises (*e.g.* to a 1,3,4-oxadiazole). It is also possible that the analogous nitrilimine **17** is formed here and then intercepted by chloride. Similarly a related nitrilimine could be formed by concerted loss of dinitrogen from intermediate **9** in Scheme 1. It has been shown[13] that treatment of 5-phenyltetrazole with tri-

**Table 2** Bond lengths (Å) and angles (°) for **1**

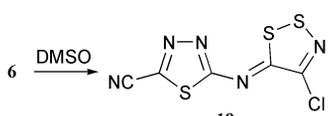
| | | | |
|---|---|---|---|
| S(1)–C(5) | 1.673(4) | S(1)–S(2) | 2.034(2) |
| S(2)–N(3) | 1.615(4) | N(3)–C(4) | 1.319(7) |
| C(4)–C(5) | 1.405(7) | C(4)–Cl(4) | 1.709(4) |
| C(5)–Cl(5) | 1.683(5) | | |
| | | | |
| C(5)–S(1)–S(2) | 92.9(2) | N(3)–S(2)–S(1) | 97.9(2) |
| C(4)–N(3)–S(2) | 115.7(3) | N(3)–C(4)–C(5) | 118.5(4) |
| N(3)–C(4)–Cl(4) | 119.2(4) | C(5)–C(4)–Cl(4) | 122.3(4) |
| C(4)–C(5)–S(1) | 115.0(3) | C(4)–C(5)–Cl(5) | 125.1(4) |
| S(1)–C(5)–Cl(5) | 119.9(3) | | |

phenylphosphine in tetrachloromethane at room temperature gives the intriguing product **18** which is probably formed by an analogous mechanism initiated by similar electrophilic attack of the tetrazole at N-2 by $Ph_3P^+Cl^-$.




**18**

Treatment of the red compound **6** with warm DMSO converted it into a new yellow crystalline compound **19** whose crystal packing provides another example of the interaction between a donor atom of one molecule and the two dithiazole sulfur atoms of another (*vide infra*). The mechanism of this transformation and some of its ramifications such as the rapid, high-yielding conversion of the hydrazonoyl chlorides **16** into simpler 1,3,4-thiadiazoles will be reported later.




**19**

## X-Ray crystallography

As a prelude to our studies of a series of related dithiazole-containing species, we thought that it would be interesting to look at the structure of the simple dithiazole 4,5-dichloro-1,2,3-dithiazolium chloride (**1**),[14] often referred to as the Appel salt.[1] The X-ray analysis of **1** reveals a pattern of bonding within the dithiazole ring (Table 2) that indicates delocalisation that extends around the ring from one sulfur atom to the other (Fig. 1), and indeed there is also evidence for a shortening of the S–S bond length [2.034(2) Å] compared with that normally associated with an S–S single bond. The distance seen here is only marginally longer than that reported for the corresponding separation [2.023 Å] in a fully delocalised dithiole ring,[15] though a shorter distance of 2.007 Å has also been observed.[16] In a fully delocalised dithiadiazole ring an S–S separation of 2.055 Å has been observed.[17] In a recently reported closely related compound 4-chloro-5-perfluorophenyl-1,2,3-dithiazol-2-ium chloride,[18] where the 5-chloride substituent in **1** has been replaced by a $C_6F_5$ ring, the bonding within the dithiazole ring is essentially identical to that seen in **1**. Perhaps a more interesting feature of dithiole salts and related compounds is their behaviour "beyond the molecule". In **1**, there is a short triangular and almost in plane approach [2.932(2) Å to S(1) and 2.974(2) Å to S(2), **a** and **b** in Fig. 1 respectively] of the chloride anion to the two sulfur centres of the dithiazole ring (the chloride lies 0.34 Å out of the ring plane). Approaches of this type by halides are relatively commonplace and have been commented on in a number of early studies of dithiole containing salts by Hordvik *et al.*[19a] who invoked a degree of partial bonding between the halide and the two ring sulfur atoms involving weak triangular three-centre two-electron bonds. In addition to this interaction, in **1** there is also a near-linear side-on approach (**c**) of the chloride anion to the S–S bond, the chloride ion also being positioned over the centre of the dithiazole ring of an adjacent molecule (**d**) at a distance compatible with an electrostatic interaction. Cl ··· ring centroid approaches of this type have also been commented on by Andreasen *et al.*[19b] Interestingly, all three of the aforementioned interactions are also present in the structure of 4-chloro-5-perfluorophenyl-1,2,3-dithiazol-2-ium chloride.[18] In **1**, there is also a short non-bonded Cl ··· Cl contact of 3.163(2) Å (**e**) that is not present in the $C_6F_5$ analogue.

A single crystal structure analysis shows **6** to have a planar structure (Fig. 2), all of the atoms being required to lie within a crystallographic mirror plane. The two dithiazole rings have essentially identical geometries (Table 3), but a pattern of bonding that differs markedly from that seen in **1**. Here, with the exception of the C=N linkages [1.276(3) and 1.278(4) Å] which have pronounced double bond character, all of the bonds are noticeably lengthened compared to their values in **1**, being more consistent with conventional single bonds. The bonds linking the two ring systems show a clear pattern of alternating double or single bond character, though with evidence for a modest degree of delocalisation. A feature of this linking backbone is a substantial contraction of the C(5)–N(6)–N(7) bond angle to 111.9(2)°—and to a lesser degree that for C(8)–N(9)–C(10) [118.6(2)°]—though this is partially compensated for by an enlargement of the N(7)–C(8)–N(9) and a contraction of the N(6)–N(7)–C(8) angles, thereby avoiding too short a contact between S(1) and S(11). The planar molecular geometry results in a short intramolecular contact of 2.597(2) Å between N(7) and S(11) (**a** in Fig. 2), the N(7) ··· S(11)–S(12) angle being 166.70(6)°; a short S(1) ··· S(11) approach is further prevented by enlargements of the S(1)–C(5)–N(6) and

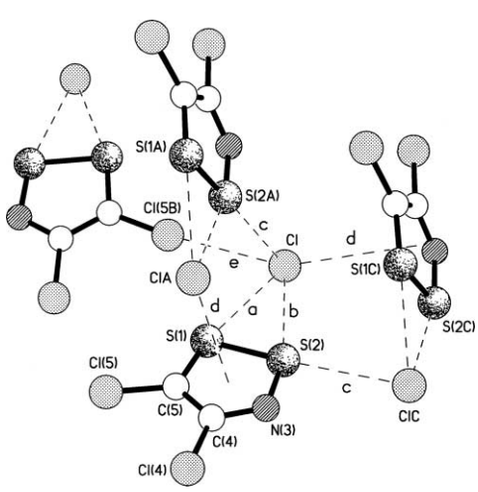



**Fig. 1** The packing of molecules of **1** showing the short non-bonded intermolecular contacts (Å) **a** 2.932(2), **b** 2.974(2), **c** 3.173(2), **d** 3.355(2) and **e** 3.163(2).

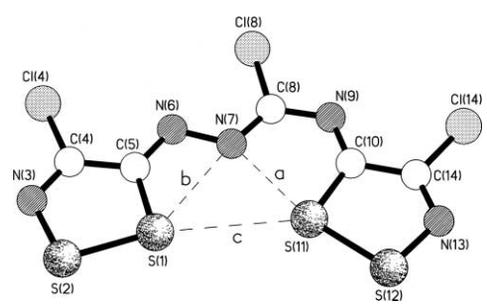



**Fig. 2** The molecular structure of **6** showing the intramolecular S ··· N contacts and the linear approach of one of these to the S–S bond, **a** 2.597(2), **b** 2.835(2) Å; the non-bonded S ··· S separation **c** is 3.353(1) Å.

**Table 3** Bond lengths (Å) and angles (°) for **6**

| | | | |
|---|---|---|---|
| S(1)–C(5) | 1.741(2) | S(1)–S(2) | 2.0852(11) |
| S(2)–N(3) | 1.644(3) | N(3)–C(4) | 1.276(3) |
| C(4)–C(5) | 1.464(3) | C(4)–Cl(4) | 1.709(3) |
| C(5)–N(6) | 1.296(3) | N(6)–N(7) | 1.377(3) |
| N(7)–C(8) | 1.291(3) | C(8)–N(9) | 1.354(3) |
| C(8)–Cl(8) | 1.732(3) | N(9)–C(10) | 1.302(3) |
| C(10)–C(14) | 1.452(3) | C(10)–S(11) | 1.733(2) |
| S(11)–S(12) | 2.0818(10) | S(12)–N(13) | 1.633(3) |
| N(13)–C(14) | 1.278(4) | C(14)–Cl(14) | 1.718(3) |
| | | | |
| C(5)–S(1)–S(2) | 92.62(8) | N(3)–S(2)–S(1) | 97.87(9) |
| C(4)–N(3)–S(2) | 116.2(2) | N(3)–C(4)–C(5) | 121.5(2) |
| N(3)–C(4)–Cl(4) | 119.8(2) | C(5)–C(4)–Cl(4) | 118.7(2) |
| N(6)–C(5)–C(4) | 122.3(2) | N(6)–C(5)–S(1) | 125.9(2) |
| C(4)–C(5)–S(1) | 111.8(2) | C(5)–N(6)–N(7) | 111.9(2) |
| C(8)–N(7)–N(6) | 116.8(2) | N(7)–C(8)–N(9) | 123.3(2) |
| N(7)–C(8)–Cl(8) | 123.2(2) | N(9)–C(8)–Cl(8) | 113.5(2) |
| C(10)–N(9)–C(8) | 118.6(2) | N(9)–C(10)–C(14) | 120.8(2) |
| N(9)–C(10)–S(11) | 128.1(2) | C(14)–C(10)–S(11) | 111.1(2) |
| C(10)–S(11)–S(12) | 93.01(8) | N(13)–S(12)–S(11) | 97.71(9) |
| C(14)–N(13)–S(12) | 115.8(2) | N(13)–C(14)–C(10) | 122.4(2) |
| N(13)–C(14)–Cl(14) | 118.6(2) | C(10)–C(14)–Cl(14) | 119.0(2) |

**Table 4** Bond lengths (Å) and angles (°) for **7**

| | | | |
|---|---|---|---|
| S(1)–C(5) | 1.712(3) | S(1)–S(2) | 2.0570(14) |
| S(2)–N(3) | 1.619(3) | N(3)–C(4) | 1.290(5) |
| C(4)–C(5) | 1.442(5) | C(4)–Cl(4) | 1.706(3) |
| C(5)–C(6) | 1.395(5) | C(6)–N(7) | 1.384(4) |
| C(6)–C(10) | 1.432(5) | N(7)–C(8) | 1.287(4) |
| C(8)–C(11) | 1.436(5) | C(8)–S(9) | 1.733(4) |
| S(9)–C(10) | 1.782(3) | C(10)–O(10) | 1.220(4) |
| C(11)–N(11) | 1.136(5) | S(20)–O(20) | 1.495(3) |
| S(20)–C(21) | 1.765(5) | S(20)–C(22) | 1.767(5) |
| | | | |
| C(5)–S(1)–S(2) | 93.61(12) | N(3)–S(2)–S(1) | 97.27(11) |
| C(4)–N(3)–S(2) | 116.8(2) | N(3)–C(4)–C(5) | 120.4(3) |
| N(3)–C(4)–Cl(4) | 117.2(3) | C(5)–C(4)–Cl(4) | 122.3(3) |
| C(6)–C(5)–C(4) | 128.6(3) | C(6)–C(5)–S(1) | 119.5(2) |
| C(4)–C(5)–S(1) | 111.8(2) | N(7)–C(6)–C(5) | 124.9(3) |
| N(7)–C(6)–C(10) | 115.5(3) | C(5)–C(6)–C(10) | 119.6(3) |
| C(8)–N(7)–C(6) | 109.7(3) | N(7)–C(8)–C(11) | 121.3(3) |
| N(7)–C(8)–S(9) | 119.1(3) | C(11)–C(8)–S(9) | 119.5(3) |
| C(8)–S(9)–C(10) | 87.7(2) | O(10)–C(10)–C(6) | 127.1(3) |
| O(10)–C(10)–S(9) | 124.9(3) | C(6)–C(10)–S(9) | 107.9(2) |
| N(11)–C(11)–C(8) | 178.8(4) | O(20)–S(20)–C(21) | 105.9(2) |
| O(20)–S(20)–C(22) | 106.0(2) | C(21)–S(20)–C(22) | 97.3(2) |

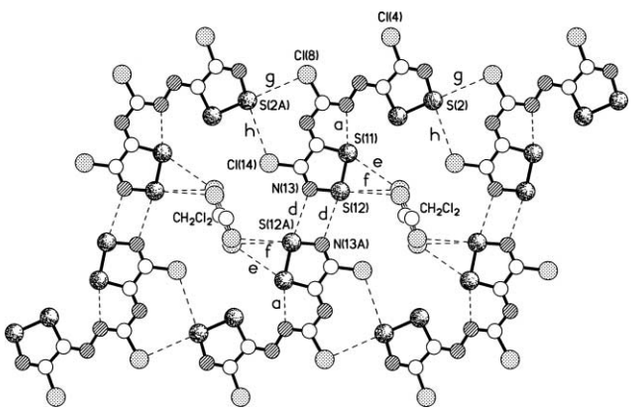



**Fig. 3** Part of one of the tapes present in the structure of **6**, and the short intermolecular contacts **d** 3.035(2), **e** 3.437(7), **f** 3.239(4), 3.286(8), **g** 3.500(1) and **h** 3.565(2) Å.

N(9)–C(10)–S(11) angles relative to their "exterior" counterparts. Centrosymmetrically related pairs of molecules are linked by short S ··· N interactions [3.035(2) Å, **d** in Fig. 3]. This intermolecular S ··· N contact also forms a near linear arrangement with the S(11)–S(12) bond [N ··· S–S angle 172.84(6)°] which extends to include the intramolecular S ··· N contact to N(7) (*vide supra*) thus producing an approximately linear N ··· S–S ··· N geometry. Directly analogous centrosymmetric pairs of linear intermolecular S–S ··· N patterns, with comparable S ··· N distances, are also present in the structures of 4,4′,4″-(1,3,5-triazine-2,4,6-triyl)tris(1,2,3,5-dithiadiazole)[20] and tris(naphtho[2,1-*d*:6,5-*d*′]bis([1,2,3]-dithiazole)) bis(tetrafluoroborate),[21] but were not commented upon by the authors. The dichloromethane molecules included in the crystals of **6**, although partially disordered about the crystallographic $C_2$ axis (and the mirror plane), still play a significant role in cementing the S ··· N linked "dimers" to form the tapes depicted in Fig. 3. The chlorine atoms form a roughly triangular arrangement (**e** and **f** in Fig. 3) with respect to the sulfur atoms of one of the dithiazole rings [based on S(11)], a geometry directly analogous to that seen in **1**. The chlorine atom Cl(8) in one bis(dithiazole) molecule is positioned linearly with respect to the S(1)–S(2) bond of another, though the distance (**g**) is only *ca.* 0.15 Å shorter than the sum of the van der Waals radii (the intermolecular S(2) ··· Cl(14) contact (**h**) is only *ca.* 0.10 Å shorter than the sum of the van der Waals radii). Combinations of linear and triangular approaches of chloride ions to S–S bonds have been discussed previously by Hordvik.[22] Adjacent tapes overlay each other with head-to-tail partial overlap of the dithiazole ring systems; the interplanar separation is 3.36 Å.

In the solid state, **7** is seen to have an almost planar structure (maximum deviation from planarity of 0.06 Å), with the dithiazole ring having a pattern of bonding that is intermediate between that seen in **1** and the essentially localised pattern observed for these rings in **6**. There is a noticeable lengthening of the C=C double bond [1.395(5) Å] linking the dithiazole and 1,3-thiazole ring systems, having a value typical of a C–C aromatic bond and indicating a degree of delocalisation that extends from one ring to the other (Table 4). The C–C and C–S bonds in the 1,3-thiazole ring have lengths typical of single bonds whereas the C=N bond has retained its double bond character. Perhaps of greater interest is the packing of the molecules with respect to the included dimethyl sulfoxide solvent. These assemble in dimeric units wherein the oxygen atoms of a pair of dimethyl sulfoxide molecules form both near-linear (**d**) and triangular (**b** and **c**) O ··· S–S arrangements (Fig. 4) where all of the S ··· O distances are less than 3 Å, and the oxygen atom O(20) lies only 0.18 Å out of the S(1)-containing dithiazole ring plane. This motif can also be considered to include the short non-bonded intramolecular

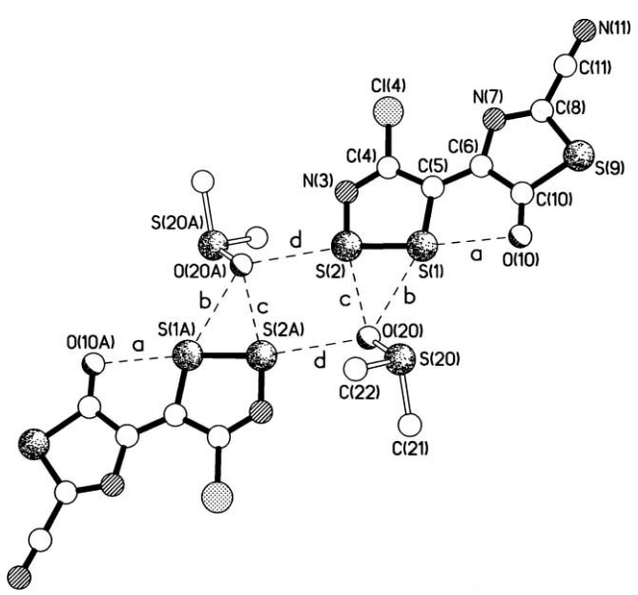



**Fig. 4** The solid-state structure of **7** showing the short intra-molecular contact, **a** 2.614(3) Å, and the intermolecular contacts between centrosymmetrically-related molecules and the DMSO solvent, **b** 2.839(3), **c** 2.711(3), and **d** 2.948(3) Å.

**Table 5** Bond lengths (Å) and angles (°) for **19**

| | | | |
|---|---|---|---|
| S(1)–C(5) | 1.7331(14) | S(1)–S(2) | 2.0767(7) |
| S(2)–N(3) | 1.640(2) | N(3)–C(4) | 1.280(2) |
| C(4)–C(5) | 1.459(2) | C(4)–Cl(4) | 1.708(2) |
| C(5)–N(6) | 1.306(2) | N(6)–C(7) | 1.359(2) |
| C(7)–N(11) | 1.312(2) | C(7)–S(8) | 1.7308(14) |
| S(8)–C(9) | 1.710(2) | C(9)–N(10) | 1.308(2) |
| C(9)–C(12) | 1.430(2) | N(10)–N(11) | 1.359(2) |
| C(12)–N(12) | 1.139(2) | | |
| | | | |
| C(5)–S(1)–S(2) | 92.86(5) | N(3)–S(2)–S(1) | 98.13(5) |
| C(4)–N(3)–S(2) | 115.51(11) | N(3)–C(4)–C(5) | 122.03(13) |
| N(3)–C(4)–Cl(4) | 119.84(11) | C(5)–C(4)–Cl(4) | 118.12(11) |
| N(6)–C(5)–C(4) | 120.55(12) | N(6)–C(5)–S(1) | 127.99(11) |
| C(4)–C(5)–S(1) | 111.46(10) | C(5)–N(6)–C(7) | 117.78(12) |
| N(11)–C(7)–N(6) | 125.74(13) | N(11)–C(7)–S(8) | 113.55(11) |
| N(6)–C(7)–S(8) | 120.69(10) | C(9)–S(8)–C(7) | 86.37(7) |
| N(10)–C(9)–C(12) | 120.86(13) | N(10)–C(9)–S(8) | 115.42(11) |
| C(12)–C(9)–S(8) | 123.72(12) | C(9)–N(10)–N(11) | 111.54(12) |
| C(7)–N(11)–N(10) | 113.12(12) | N(12)–C(12)–C(9) | 179.2(2) |

S(1) ··· O(10) contact (**a**), thus giving an O ··· S–S ··· O pattern similar to the N ··· S–S ··· N arrangement seen in **6**. Triangular S–S ··· O approaches are relatively commonplace and have been considered to represent partial bonding[15] analogous to that seen for halogens. The S ··· O distances seen here [2.711(3) and 2.839(3) Å for **c** and **b** respectively] are at the short end of such interactions, although even shorter contacts of 2.600 and 2.624 Å have been observed in the structure of a related trisulfur-dinitrido salt.[23] Simultaneous end-on and triangular approaches are, however, comparatively rare, with only four examples having been identified,[24] one of which is the above mentioned trisulfur-dinitrido salt. Centrosymmetrically related pairs of molecules stack head-to-tail with partial overlap of the thiazole and dithiazole ring systems with a mean interplanar separation of *ca.* 3.40 Å. These pairs of molecules then stack with their counterparts across an independent inversion centre with the thiazole ring in one pair partially overlaying its counterpart in the next; here the mean interplanar separation is *ca.* 3.46 Å.

The X-ray structure analysis shows **19** to also have an essentially planar structure with a maximum deviation from planarity of 0.09 Å, the small out-of-plane deviation being a consequence of a *ca.* 2° torsional twist about C(5)=N(6). The bond lengths in the dithiazole ring (Table 5) are the same as those observed in **6**, though the N(3)=C(4) linkage is longer, and the S(2)–N(3) bond shorter, than is observed in 5-benzoyloxyimino-4-chloro-5*H*-1,2,3-dithiazole.[25] The C(5)=N(6) and N(6)–C(7) bonds that link the two ring systems are longer and shorter respectively than those associated with localised double and single bonds, thus indicating some delocalisation extending between the two ring systems. The thiadiazole ring exhibits a greater degree of delocalisation than is seen in related systems,[26] and is most noticeable for the N(10)–N(11) bond of 1.359(2) Å, *cf.* a normal single bond distance of *ca.* 1.39 Å. One of the thiadiazole nitrogen atoms N(11) makes a fairly short intramolecular, and approximately linear, approach of 2.625(1) Å to the S(1)–S(2) bond (**a** in Fig. 5). Centrosymmetrically related pairs of molecules abut such that one of the nitrogen atoms of the thiadiazole ring [N(10)] in one molecule is positioned in a triangular relationship with respect to the two sulfur atoms of the dithiazole ring of the other and *vice versa*, the N ··· S distances being (**b**) 3.018(2) Å to S(1) and (**c**) 3.001(2) Å to S(2); the nitrogen atom N(10A) lies 0.38 Å out of the plane of the S(1)-containing dithiazole. This geometry, which is directly analogous to those seen between the S–S bond and chlorine and oxygen in the structures discussed above, has also been commented on by Hordvik and Kjoge,[27] where the two N ··· S distances are both 2.867 Å. Other examples of similar short N ··· S–S contacts are seen in the structures of the cations 1-(1,3,2,4-dithiadiazolium-5-yl)-4-(1,2,3,5-dithiadiazolium-4-yl)-benzene[28] and *p*-bis(1,2,3,5-dithiadiazolium-4-yl)benzene.[29] These "dimer pairs" form continuous stacks with partial dithiazole–thiadiazole overlap with a mean interplanar separation of *ca.* 3.42 Å. Adjacent stacks pack to give a chevron-like pattern (Fig. 6) with the cyano nitrogen atoms N(12) in one stack being directed approximately orthogonally into the C(4) carbon atoms of the next; the N ··· C distance is 3.111(2) Å.

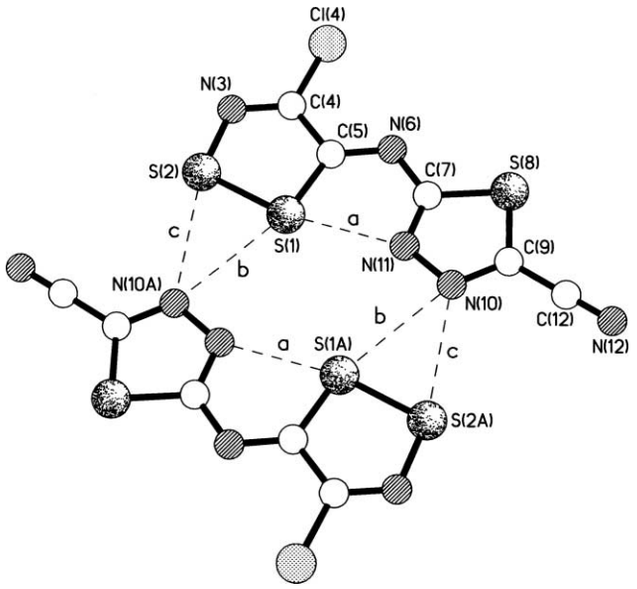



**Fig. 5** The approach of centrosymmetrically-related pairs of molecules in the structure of **19**. The non-bonded contacts are **a** 2.625(1), **b** 3.018(2) and **c** 3.001(2) Å.

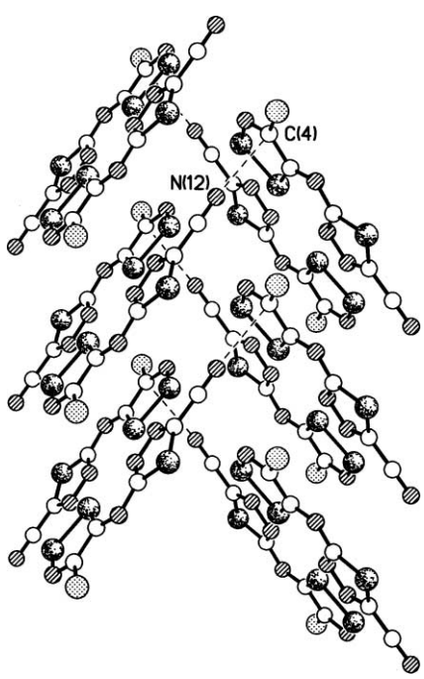



**Fig. 6** The chevron-like pattern produced by adjacent stacked pairs of molecules of **19**. The N(12) ··· C(4) separation is 3.111(2) Å.

## Experimental

Solvents were purified and dried by standard procedures. Light petroleum refers to the fraction boiling between 60 and 80 °C. Flash chromatography was on Merck Kieselgel 60 H. Infra-red absorptions are quoted for medium–strong and strong peaks only. Melting points were measured on a Kofler hot-stage microscope and are uncorrected. Organic layers were dried over $Na_2SO_4$.

### 4,5-Dichloro-1,2,3-dithiazolium chloride 1

4,5-Dichloro-1,2,3-dithiazolium chloride **1** was prepared following the literature method.[1]

**Crystal data for 1 †.** $[C_2NS_2Cl_2][Cl]$, $M = 208.5$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 5.947(1)$, $b = 10.228(1)$, $c = 10.985(1)$ Å, $V = 668.23(7)$ Å$^3$, $Z = 4$, $D_c = 2.072$ g cm$^{-3}$, $\mu$(Cu-K$\alpha$) = 17.4 mm$^{-1}$, $T$ = 173 K, dark brown prisms; 680 independent measured reflections, $F^2$ refinement, $R_1$ = 0.029, $wR_2$ = 0.068, 638 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 130°$], 75 parameters. Though it has crystallised in a chiral space group, *R*-factor tests [$R_1^+ = 0.0296$, $R_1^- = 0.0304$] and the Flack parameter [$x^+ = +0.40(7)$, $x^- = +0.60(7)$] indicate that **1** is a *ca.* 60 : 40 racemic twin. CCDC 180848.

### 3-Chloro-1,4-bis(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-1,2,4-triazabut-2-ene 6 and 4- (4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2-cyano-4*H*-thiazol-5-one 7

To a suspension of 5-aminotetrazole monohydrate **4** (0.50 g, 4.85 mmol) in dichloromethane (30 ml) was added 4,5-dichloro-1,2,3-dithiazolium chloride **1** (3.04 g, 14.5 mmol). The reaction mixture was stirred at room temperature for 5 hours and then pyridine (1.17 ml, 14.55 mmol) was added. A gas was evolved from the reaction mixture, which was stirred until gas evolution ceased. The red slurry was filtered through a short pad of silica gel (C25 mesh), eluting with dichloromethane. The products were purified by flash chromatography on silica gel, eluting with dichloromethane–light petroleum (1 : 2) to give, firstly, the *red compound* **6** (0.35 g, 20%) as needles, mp 218–220 °C (Found: C, 16.6; H, 0; N, 19.2; $C_5Cl_3N_5S_4$ requires C, 16.4; H, 0; N, 19.2%); $\nu_{max}$ (Nujol)/cm$^{-1}$ 1526, 1492, 1422, 1263, 1246, 1158, 1070, 909, 797, 757, 723 and 704; $\lambda_{max}$ (EtOH)/nm 234 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 17230), 276 (12430), 358 (7870), 469 (9450) and 489 (9710); $\delta_C$ (68 MHz, $(CD_3)_2SO$) 162.6, 162.2, 151.5, 148.1 and 143.3; *m*/*z* 363 ($M^+$, 40%), 328 (7, $M^+ - Cl$), 293 (5, $M^+ - Cl_2$), 261 (51, $M^+ - SCl_2$), 226 (91, $M^+ - ClSCl_2$), 168 (73, $M^+ - CCl_3NS_2$), 102 (29, $C_2NS_2^+$), 70 (38), 64 (100, $S_2^+$), 44 (19, $CS^+$) and 32 (35, $S^+$) and, secondly, the *maroon compound* **7** (38 mg, 3%), mp 252–254 °C (Found: C, 27.6; H, 0; N, 15.7; S, 36.9; $C_6ClN_3OS_3$ requires C, 27.6; H, 0; N, 16.1; S, 36.8%); $\nu_{max}$ (Nujol)/cm$^{-1}$ 2220 (conj. CN), 1587, 1462, 1402, 1378, 1276, 1159, 1128, 1067, 901, 841, 773, 725, 685, 646 and 561; $\lambda_{max}$ (EtOH)/nm 344 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 16260) and 476 (3710); $\delta_C$ (68 MHz, $(CD_3)_2SO$) 185.6 (CO), 155.0, 147.5, 135.0, 123.4 and 113.7 (CN); *m*/*z* 261 ($M^+$, 35%), 162 (4, $M^+ - S_2Cl$), 102 (26, $C_2NS_2^+$), 70 (72, $C_2NS^+$), 64 (15, $S_2^+$) and 32 (28, $S^+$).

**Crystal data for 6 †.** $C_5N_5S_4Cl_3 \cdot 0.5CH_2Cl_2$, $M = 407.2$, monoclinic, *C*2/*m* (no. 12), $a = 21.140(5)$, $b = 6.724(2)$, $c = 10.004(3)$ Å, $\beta = 103.22(2)°$, $V = 1384.4(6)$ Å$^3$, $Z = 4$ ($C_s$ symmetry), $D_c = 1.953$ g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 1.45 mm$^{-1}$, $T$ = 293 K, yellow needles; 2410 independent measured reflections, $F^2$ refinement, $R_1 = 0.042$, $wR_2 = 0.106$, 1942 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 120°$], 130 parameters. CCDC 180850.

**Crystal data for 7 †.** $C_6N_3OS_3Cl \cdot Me_2SO$, $M = 339.9$, triclinic, $P\bar{1}$ (no. 2), $a = 8.314(2)$, $b = 9.068(3)$, $c = 9.915(3)$ Å, $\alpha = 112.17(2)$, $\beta = 97.07(2)$, $\gamma = 100.08(2)°$, $V = 666.8(3)$ Å$^3$, $Z = 2$, $D_c = 1.693$ g cm$^{-3}$, $\mu$(Cu-K$\alpha$) = 8.39 mm$^{-1}$, $T$ = 293 K, red blocks; 1774 independent measured reflections, $F^2$ refinement, $R_1 = 0.038$, $wR_2 = 0.102$, 1609 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 113°$], 164 parameters. CCDC 180851.

† CCDC reference numbers 180848–180851. See http://www.rsc.org/suppdata/p1/b2/b202211g/ for crystallographic files in .cif or other electronic format.

### 5-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylimino)-2-methyltetrazole 12a

To a solution of 5-amino-2-methyltetrazole **11a** (300 mg, 3.03 mmol) in dichloromethane (40 ml) was added 4,5-dichloro-1,2,3-dithiazolium chloride **1** (809 mg, 3.88 mmol). The mixture was stirred at room temperature for 30 minutes and then pyridine (0.57 ml, 7.06 mmol) was added. The mixture was stirred for a further 15 minutes and filtered through silica gel (25 mesh), eluting with dichloromethane. The product was purified by flash chromatography on silica gel eluting with dichloromethane to give the *title compound* **12a** (632 mg, 89%) as yellow needles, mp 226–228 °C (Found: C, 20.7; H, 1.2; N, 35.7; $C_4H_3ClN_6S_2$ requires C, 20.5; H, 1.3; N, 35.9%); $\nu_{max}$ (Nujol)/cm$^{-1}$ 1552, 1496, 1174, 1026, 883, 784, 758 and 722; $\delta_H$ (270 MHz, $CDCl_3$) 4.45 (3H, s, N–$CH_3$); $\delta_C$ (68 MHz, $(CD_3)_2SO$) 159.8, 157.4, 141.1 and 40.4 (N–$CH_3$); *m*/*z* 234 ($M^+$, 8%), 206 (3, $M^+ - N_2$), 163 (6, $M^+ - CH_3N_4$), 137 (10), 102 (21), 93 (4), 79 (3), 76 (6), 70 (18), 64 (8, $S^+_2$), 58 (4) and 46 (4).

### Ethyl 5-(4-chloro-5*H*-1,2,3-dithiazol-5-ylimino)tetrazol-2-yl-acetate 12b

To a solution of ethyl (5-aminotetrazol-2-yl)acetate **11b** (0.25 g, 1.46 mmol) in dichloromethane (35 ml) was added 4,5-dichloro-1,2,3-dithiazolium chloride **1** (0.37 g, 1.77 mmol). The mixture was stirred at room temperature for 1 hour and then pyridine (0.24 ml, 2.92 mmol) was added. The mixture was stirred for a further 15 minutes and filtered through silica gel (C25 mesh), eluting with dichloromethane. The product was purified by flash chromatography on silica gel eluting with dichloromethane to give the *title compound* **12b** (0.32 g, 75%) as canary yellow needles, mp 183 °C (Found: C, 27.4; H, 2.4; N, 27.2; $C_7H_7ClN_6O_2S_2$ requires C, 27.45; H, 2.3; N, 27.45%); $\nu_{max}$. (Nujol)/cm$^{-1}$ 1744 (CO), 1564, 1467, 1376, 1241, 1172, 1022 and 881; $\lambda_{max}$ (EtOH)/nm 234 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 16540), 370 sh, 383 (26780) and 399 sh; $\delta_H$ (270 MHz, $(CD_3)_2SO$) 5.90 (2H, s, N–$CH_2$–O) and 4.23 (2H, q, *J* 7 Hz, $CH_2CH_3$) and 1.23 (3H, t, *J* 7 Hz, $CH_2CH_3$); $\delta_C$ (68 MHz, $(CD_3)_2SO$) 166.6, 165.8, 164.6, 147.6, 62.1, 54.1 and 13.9 ($CH_2CH_3$); *m*/*z* 306 ($M^+$, 2%), 278 (4, $M^+ - N_2$), 205 (11, $M^+ - C_3H_5N_2O_2$), 178 (7), 162 (27), 139 (18), 137 (39), 112 (29), 102 (34), 88(3), 87 (55), 85 (36), 76 (10), 71 (26), 64 (21, $S^+_2$), 59 (100), 53 (5) and 44 (16, $CS^+$).

### 3-Chloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-phenyl-1,2,-diazaprop-2-ene 16a

To a suspension of 5-phenyltetrazole **13a** (5.0 g, 34 mmol) in dichloromethane (300 ml) was added 4,5-dichloro-1,2,3-dithiazolium chloride **1** (7.85 g, 37 mmol). The mixture was stirred at room temperature for 12 h. The resulting solution was filtered through silica gel (C25 mesh), eluting with dichloromethane–light petroleum (1 : 3) to give the *title compound* **16a** (8.6 g, 87%) as yellow cubes, mp 145 °C (Found: C, 37.2; H, 1.7; N, 14.4; $C_9H_5Cl_2N_3S_2$ requires C, 37.25; H, 1.7; N, 14.5%); $\nu_{max}$. (Nujol)/cm$^{-1}$ 1619, 1587, 1568, 1465, 1466, 1258, 791 and 684; $\lambda_{max}$ (EtOH)/nm 280 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 13,290) and 418 (9960); $\delta_H$ (270 MHz, $(CD_3)_2SO$) 8.12–8.18 (2H, dd, Ar–H) and 7.21–7.58 (3H, m, Ar–H); $\delta_C$ (68 MHz, $(CD_3)_2SO$) 166.0, 147.6, 142.4, 132.6, 132.3, 128.8 and 128.1; *m*/*z* 289 ($M^+$, 34%), 254 (45, $M^+ - Cl$), 187 (89, $M^+ - SCl_2$), 151 (21, $C_2N_2ClS_2^+$), 135, 103 and 77.

### 3-Chloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-(2-methoxyphenyl)-1,2-diazaprop-2-ene 16b

To a suspension of 5-(2-methoxyphenyl)tetrazole **13b** (80 mg, 0.46 mmol) in dichloromethane (20 ml) was added 4,5-dichloro-1,2,3-dithiazolium chloride **1** (137 mg, 0.66 mmol). The mixture was stirred at room temperature for 3 hours and then pyridine (0.07 ml, 0.91 mmol) was added to the green slurry. The mixture was stirred for a further 30 minutes and filtered through silica gel (C25 mesh) eluting with dichloromethane. The product was

purified by flash chromatography on silica gel eluting with dichloromethane–light petroleum (1 : 2) to give the *title compound* **16b** (93 mg, 64%) as an orange solid, mp 92 °C (Found: 318.9378; $C_{10}H_7Cl_2N_3OS_2$ requires 318.9379); $\delta_H$ (270 MHz, $CDCl_3$) 7.63 (1H, dd, *J* 2 and 6 Hz, Ar–H), 7.50 (1H, t, *J* 6 Hz, Ar–H), 7.04 (2H, m, Ar–H) and 3.92 (3H, s, Ar–$OCH_3$); *m*/*z* 319 ($M^+$, 8%), 284 (16, $M^+ - Cl$), 217 (66, $M^+ - SCl_2$), 188 (18), 90 (80), 84 (14), 64 (81, $S2^+$) and 44 (35, $CS^+$).

### 3-Chloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-(3-methoxyphenyl)-1,2-diazaprop-2-ene 16c

To a suspension of 5-(3-methoxyphenyl)tetrazole **13c** (0.50 g, 2.84 mmol) in dichloromethane (35 ml) was added 4,5-dichloro-1,2,3-dithiazolium chloride **1** (0.65 g, 3.12 mmol). The mixture was stirred at room temperature for 1 hour and then pyridine (0.46 ml, 5.68 mmol) was added to the green slurry. The mixture was stirred for a further 30 minutes and filtered through silica gel (25 mesh), eluting with dichloromethane. The product was purified by flash chromatography on silica gel eluting with dichloromethane–light petroleum (1 : 2) to give the *title compound* **16c** (0.75 g, 83%) as a yellow solid, mp 131 °C (Found: C, 37.5; H, 2.3; N, 13.0; $C_{10}H_7Cl_2N_3OS_2$ requires C, 37.6; H, 2.2; N, 13.2%); $\nu_{max}$ (Nujol)/$cm^{-1}$ 1604, 1566, 1465, 1378, 1262, 1163, 1051, 1038, 965, 894, 867, 788 and 680; $\lambda_{max}$ (EtOH)/nm 279 ($\varepsilon$/$dm^3$ $mol^{-1}$ $cm^{-1}$ 14750); $\delta_H$ (270 MHz, $CDCl_3$) 7.72 (1H, d, *J* 8 Hz, Ar–H), 7.65 (1H, t, *J* 3 Hz, Ar–H), 7.38 (1H, t, *J* 8 Hz, Ar–H), 7.10 (1H, dd, *J* 3 and 8 Hz, Ar–H) and 3.89 (3H, s, Ar–*OCH*$_3$); $\delta_C$ (68 MHz, $CD_3(SO_3)_2$) 165.7, 159.6, 150.2, 144.3, 134.7, 129.7, 121.5, 118.3, 113.9 and 55.5 (Ar–$OCH_3$); *m*/*z* 319 ($M^+$, 44%), 284 (70, $M^+ - Cl$), 217 (79, $M^+ - SCl_2$), 133 (100, $CH_3OC_6H_4CN^+$), 119 (15), 107 (24), 90 (28), 78 (6), 77 (34), 64 (23, $S^+_2$), 50 (13) and 39 (14).

### 3-Chloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-(4-methoxyphenyl)-1,2-diazaprop-2-ene 16d

To a suspension of 5-(4-methoxyphenyl)tetrazole **13d** (0.50 g, 2.84 mmol) in dichloromethane (30 ml) was added 4,5-dichloro-1,2,3-dithiazolium chloride **1** (0.71 g, 3.41 mmol). The mixture was stirred at room temperature for 1 hour and then pyridine (0.46 ml, 5.7 mmol) was added to the slurry. The mixture was stirred for a further 30 minutes and filtered through silica gel (C25 mesh), eluting with dichloromethane–light petroleum (1 : 1). The product was purified by flash chromatography on silica gel eluting with dichloromethane–light petroleum (1 : 2) to give the *title compound* **16d** (0.85 g, 78%) as yellow solid, mp 177 °C (Found: C, 37.6; H, 2.4; N, 13.05; $C_{10}H_7Cl_2N_3OS_2$ requires C, 37.6; H, 2.2; N, 13.2%); $\nu_{max}$ (Nujol)/$cm^{-1}$ 1603, 1585, 1569, 1505, 1464, 1378, 1307, 1267, 1255, 1198, 1173, 1019, 901, 829, 785, 722, 673 and 627; $\lambda_{max}$ (EtOH)/nm 304 ($\varepsilon$/$dm^3$ $mol^{-1}$ $cm^{-1}$ 14070), 410 inf, 425 sh and 446 (8470); $\delta_H$ (270 MHz, $CDCl_3$) 8.10 (2H, d, *J* 9 Hz, Ar–H), 6.93 (2H, d, *J* 9, Ar–H) and 3.90 (3H, s, Ar–*OCH*$_3$); $\delta_C$ (68 MHz, $CD_3(SO_3)_2$) 165.8, 162.9, 148.0, 142.7, 130.1, 114.5, 125.0 and 55.7 (Ar–$CH_3$); *m*/*z* 319 ($M^+$, 28%), 284 (39, $M^+ - Cl$), 217 (77, $M^+ - SCl_2$), 191 (3), 159 (3), 154 (10), 151 (17), 150 (4), 134 (10), 133 (100, $MeOC_6H_4CN^+$), 128 (5), 119 (11), 107 (6), 103 (13), 92 (7), 90 (19), 77 (12), 76 (9), 70 (4), 64 (11, $S^+_2$) and 32 (7, $S^+$).

### 3-Chloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-(2-fluorophenyl)-1,2-diazaprop-2-ene 16e

To a suspension of 5-(2-fluorophenyl)tetrazole **13e** (0.50 g, 3.05 mmol) in dichloromethane (35 ml) was added 4,5-dichloro-1,2,3-dithiazolium chloride **1** (0.95 g, 4.55 mmol). The mixture was stirred at room temperature for 2 hours and then pyridine (0.67 ml, 8.26 mmol) was added. The mixture was stirred for a further 15 minutes and filtered through silica gel (C25 mesh), eluting with dichloromethane. This product was purified by flash chromatography on silica gel eluting with dichloromethane–light petroleum (1 : 2) to give the title compound **16e** (0.94 g, 87%) as yellow needles, mp 128 °C (Found: C, 35.65; H, 1.1; N, 13.55; $C_9H_4Cl_2FN_3S_2$ requires C, 35.2; H, 1.3; N, 13.7%. Found: 306.9208, calculated 306.9208); $\nu_{max}$ (Nujol)/$cm^{-1}$ 1612, 1588, 1572, 1554, 1536, 1512, 1282, 1250, 1219, 1188, 1160, 1108, 1031, 942, 894, 812, 792 and 754; $\delta_H$ (270 MHz, $CDCl_3$) 7.85 (1H, t, *J* 4 Hz, Ar–H), 7.50 (1H, m, Ar–H) and 7.22 (2H, m, Ar–H); $\delta_C$ (68 MHz, $CDCl_3$) 166.3, [161.4 and 159.3 (d, *J* 260 Hz)], 144.9 (d. *J* 7 Hz), 144.2, 133.2 (d, *J* 9 Hz), 131.6, 124.2 (d, *J* 3 Hz), 122.5 (d, *J* 9 Hz) and 116.5 (d, *J* 22 Hz); *m*/*z* 307 ($M^+$, 8%), 272 (12, $M^+ - Cl$), 205 (14, $M^+ - SCl_2$), 156 (6), 153 (15), 139 (7), 107 (13), 95 (20, $C_6H_4F^+$), 64 (35, $S^+_2$) and 44 (73, $CS^+$).

### 3-Chloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-(2-chlorophenyl)-1,2-diazaprop-2-ene 16f

To a suspension of 5-(2-chlorophenyl)tetrazole **13f** (0.50 g, 2.78 mmol) in dichloromethane (35 ml) was added 4,5-dichloro-1,2,3-dithiazolium chloride **1** (0.83 g, 3.99 mmol). The mixture was stirred at room temperature for 30 minutes and then pyridine (0.59 ml, 7.2 mmol) was added. The mixture was stirred for a further 30 minutes and filtered through silica gel (C25 mesh), eluting with dichloromethane. The product was purified by flash chromatography on silica gel eluting with dichloromethane–light petroleum (1 : 2) to give the *title compound* **16f** (0.65 g, 73%) as yellow platelets, mp 143–144 °C (Found: C, 33.6; H, 1.2; N, 12.9; $C_9H_4Cl_3N_3S_2$ requires C, 33.4; H, 1.2; N, 13.0%); $\nu_{max}$(Nujol)/$cm^{-1}$ 1606, 1587, 1518, 1472, 1435, 1287, 1240, 1193, 1067, 904, 899 and 791; $\delta_H$ (270 MHz, $CDCl_3$) 7.67 (1H, dd, *J* 2, and 4 Hz, Ar–H) and 7.40 (3H, m, Ar–H); $\delta_C$ (68 MHz, $CDCl_3$) 166.0, 146.6, 144.2, 133.8, 132.7, 131.7, 131.2, 130.7 and 126.8; *m*/*z* 323 ($M^+$, 2%), 288 (20, $M^+ - Cl$), 221 (32, $M^+ - SCl_2$), 169 (30), 137 (100, $C_6H_4ClCN^+$), 125 (6), 123 (13), 111 (19), 102 (30), 97 (3), 75 (33), 64 (64, $S^+_2$) and 44 (51, $CS^+$).

### 3-Chloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-3-phenoxy-1,2-diazaprop-2-ene 16g

To a suspension of 5-phenoxytetrazole **13g** (200 mg, 1.23 mmol) in dichloromethane (20 ml) was added 4,5-dichloro-1,2,3-dithiazolium chloride **1** (309 mg, 1.48 mmol). The mixture was stirred at room temperature for 6 hours and then pyridine (0.20 ml, 2.46 mmol) was added. The mixture was stirred for a further 30 minutes and filtered through silica gel (C25 mesh), eluting with dichloromethane. The product was purified by flash chromatography on silica gel eluting with dichloromethane–light petroleum (1 : 3) to give the *title compound* **16g** (210 mg, 56%) as a yellow solid, mp 80–82 °C (Found: 306.9222, calculated 306.9222); $\nu_{max}$ (Nujol)/$cm^{-1}$ 1608, 1578, 1378, 1172, 1148, 1062, 1024, 962, 906, 898, 814, 774, 732 and 682; $\delta_H$ (270 MHz, $CDCl_3$) 7.43 (2H, m, Ar–H) and 7.29 (3H, m, Ar–H); $\delta_C$ (68 MHz, $CDCl_3$) 163.8, 153.4, 152.3, 143.8, 129.7, 126.5 and 120.6; *m*/*z* 305 ($M^+$, 16%), 270 (39, $M^+ - Cl$), 228 (18, $M^+ - Ph$), 212 (24, $M^+ - OPh$), 206 ($M^+ - S_2Cl$), 203 (18), 151 (22), 91 (29), 77 (100, $Ph^+$), 65 (22), 51 (43) and 39 (17).

### 3,5-Dichloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-1,2-diazapent-2-ene 16h

To a solution of 5-(2-chloroethyl)tetrazole **13h** (0.50 g, 3.79 mmol) in distilled dichloromethane (35 ml), under nitrogen, was added 4.5-dichloro-1,2,3-dithiazolium chloride **1** (0.87 g, 4.17 mmol). The mixture was stirred at room temperature for 12 hours. The resulting solution was filtered through silica gel (C25 mesh), eluting with dichloromethane. The product was purified by flash chromatography on silica gel eluting with dichloromethane–light petroleum (1 : 1) to give the *title compound* **16h** (0.78 g, 75%) as a yellow solid which

decomposed rapidly; $\delta_H$ (270 MHz, $CDCl_3$) 3.89 (2H, t, *J* 7 Hz, $–CH_2–CH_2–Cl$) and 3.20 (2H, t, *J* 7 Hz, $–CH_2–CH_2–Cl$); $\delta_C$ (68 MHz, $CDCl_3$) 165.1, 149.2, 144.0, 42.4 ($–CH_2–CH_2–Cl$) and 40.0 ($–CH_2–CH_2–Cl$).

### 3-Chloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-1,2-diazapenta-2,4-diene 16i

To a suspension of 5-vinyltetrazole **13i** (0.50 g, 5.21 mmol) in dichloromethane (35 ml) was added 4,5-dichloro-1,2,3-dithiazolium chloride **1** (1.30 g, 6.24 mmol). The mixture was stirred at room temperature for 24 hours. The resulting solution was filtered through silica gel (25 mesh), eluting with dichloromethane. The product was purified by flash chromatography on silica gel eluting with dichloromethane–light petroleum (1 : 1) to give the *title compound* **16i** (1.00 g, 80%) as bronze platelets, mp 105 °C (Found: 238.9150, $C_5H_3Cl_2N_3S_2$ requires 238.9145); $\nu_{max}$ (Nujol)/$cm^{-1}$ 1680, 1606, 1564, 1378, 1288, 1216, 1180, 980, 936, 892, 822, 784, 710 and 694; $\delta_H$ (270 MHz, $CDCl_3$) 6.20 (1H, dd, *J* 7 and 10 Hz, $CH=CH_2$), 6.35 (1H, d, *J* 7 Hz, $CH=CH_aH_b$) and 5.90 (1H, d, *J* 10 Hz, $CH=CH_aCH_b$); *m*/*z* 239 ($M^+$, 22%), 204 (100, $M^+ - Cl$), 151 (16, $M^+ - C_3H_3ClN$), 143 (11), 139 (3), 137 (7, $M^+ - SCl_2$), 125 (4), 115 (5), 102 (11), 85 (5), 70 (9), 64 (70, $S^+{}_2$) and 58 (7, $SCN^+$).

### 3-Chloro-1-(4-chloro-5*H*-1,2,3-dithiazol-5–ylidene)-3-(4-nitrophenyl)-1,2-diazaprop-2-ene 16j

To a suspension of 5-(4-nitrophenyl)tetrazole **13j** (100 mg, 0.52 mmol) in dichloromethane (20 ml) was added 4,5-dichloro-1,2,3-dithiazolium chloride **1** (126 mg, 0.60 mmol). The mixture was stirred at room temperature for 12 hours. The resulting solution was filtered through silica gel (C25 mesh), eluting with dichloromethane. The product was purified by flash chromatography on silica gel eluting with dichloromethane–light petroleum (1 : 3) to give the *title compound* **16j** (140 mg, 80%) as orange needles, mp 225–226 °C (Found: C, 32.3; H, 1.3; N, 16.6; $C_9H_4Cl_2N_4O_2S_2$ requires C, 32.3; H, 1.2; N, 16.7%); $\nu_{max}$ (Nujol)/$cm^{-1}$ 1573, 1558, 1515, 1475, 1376, 1339, 1256, 1041, 892, 860 and 851; $\lambda_{max}$ (EtOH)/nm 283 ($\varepsilon$/$dm^3$ $mol^{-1}$ $cm^{-1}$ 12 110) and 433 (11 690); $\delta_H$ (270 MHz, $(CD_3)_2SO$) 8.61 (2H, dd, *J* 1 and 5 Hz, Ar–H) and 8.43 (2H, dd, *J* 1 and 5 Hz); *m*/*z* 334 ($M^+$, 14%), 299 (14, $M^+ - Cl$), 248 (2, $M^+ - C_2NOS$), 244 (2), 232 (2), 214 (3, $M^+ - NOCNS_2$), 202 (15, $M^+ - NOC_2NS_2$), 118 (12), 102 (25, $C_2NS_2{}^+$) and 64 (100, $S^+{}_2$).

**Crystal data for 19†.** $C_5N_5S_3Cl$, $M = 261.7$, monoclinic, $P2_1/c$ (no. 14), $a = 10.947(3)$, $b = 6.065(2)$, $c = 14.001(4)$ Å, $\beta = 90.48(2)°$, $V = 929.6(4)$ Å$^3$, $Z = 4$, $D_c = 1.870$ g $cm^{-3}$, $\mu$(Mo-K$\alpha$) = 1.05 $mm^{-1}$, $T = 293$ K, yellow plates; 2716 independent measured reflections, $F^2$ refinement, $R_1 = 0.029$, $wR_2 = 0.076$, 2365 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 60°$], 128 parameters. CCDC 180849.

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