ORGANIC HETEROCYCLOTHIAZENES. PART 19.[1] SYNTHESIS OF 1,3,2-DITHIAZOLES USING BIS(CHLOROTHIO)NITRONIUM TETRACHLOROALUMINATE, $[N(SCl)_2][AlCl_4]$†

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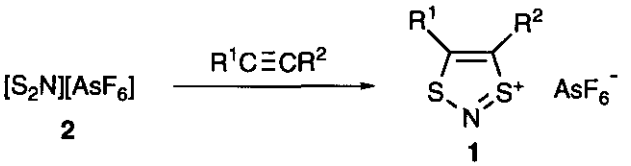
Abstract - Reaction of the readily prepared bis(chlorothio)nitronium tetrachloroaluminate (**4**) with electron-rich arylacetylenes in dichloromethane at room temperature leads to a cycloaddition reaction resulting in 4-aryl-1,3,2-dithiazolium salts (**5**) which when treated *in situ* with base afford 5-aryl-1,3,2-dithiazole-4-thiones (**6**). The scope of this reaction with other alkenes and alkynes is described. No reaction was observed with the electron-deficient 4-nitrophenylacetylene. The conjugated thione (**17**) was also formed in the reaction of an old specimen of salt (**4**) with phenylacetylene. Treatment of salt (**4**) with 1,2-dichloroethylene followed by aniline gave a minor amount of the novel dimer (**20**). The reaction of acetophenone oxime with disulfur dichloride provides a route to the salt (**26**) which on treatment with water or aniline affords 4-phenyl-1,2,3-dithiazol-5-one (**23**) and 4-phenyl-5-phenylimino-1,2,3-dithiazole (**27**) respectively. ^{14}N Nmr studies are shown to be useful in distinguishing between 1,2,3- and 1,3,2-dithiazoles. X-Ray crystal structures are presented for compounds (**17**, **20**, **27**), and 5-anilino-1,3,2-dithiazole-4-thione (**18**).

† Dedicated with admiration and affection to Alan Katritzky on the occasion of his 65th birthday

Introduction

In view of the problems encountered in the synthesis of 1,3,2-dithiazoles described in Part 18 of this series,[1] syntheses based on cycloaddition reactions of reagents containing the SNS unit with C-C multiple bonds were investigated. Interest was stimulated in this approach by the high yielding route to 1,3,2-dithiazolium salts (**1**) provided by treatment of $[S_2N][AsF_6]$ (**2**) with alkynes in liquid SO_2.[2]



$[N(SCl)_2][AsF_6]$

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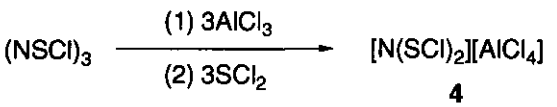


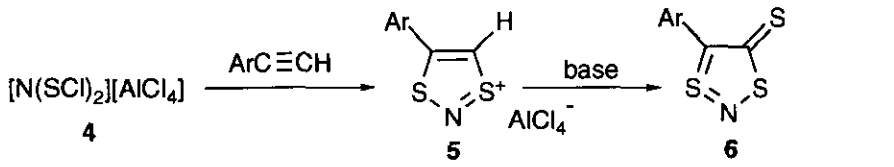
The somewhat hazardous nature of the preparation of $[S_2N][AsF_6]$ **2**[3] and the low solubility of the more readily prepared $[S_2N][SbCl_6]$[4] provided a stimulus for alternative reagents. bis(Chlorothio)nitronium salts, $[N(SCl)_2]^+$, were considered attractive candidates. The hexafluoroarsenate salt (**3**) has been prepared by chlorination of $(S_2N)(AsF_6)$ **2**[5] but this has the problem mentioned above. Therefore our work centred on the much more readily accessible $[N(SCl)_2][AlCl_4]$ **4**, which is prepared in high yield (80%) by treatment of $(NSCl)_3$[6] with aluminium trichloride (3 eq.) in thionyl chloride, followed by addition of sulphur dichloride (3 eq.).[7]

Results and Discussion

5-Aryl-1,3,2-dithiazole-4-thiones (**6**)

Initially we chose to investigate reactions of the salt (**4**) with arylacetylenes since the probable products were salts of the type **5** and, as a result of our previous work,[1] the presence of an active hydrogen on the ring in these salts would be expected to favour base-induced formation of 5-aryl-1,3,2-dithiazole-4-thiones (**6**), several of which

had already been reported.[8,9] Initially an excess of the acetylene was used because addition of chlorine to the acetylene was considered to be a possibility.



7; Ar = Ph
8; Ar=3-$CH_3OC_6H_4$
9; Ar=3,4-$(CH_3O)_2C_6H_3$

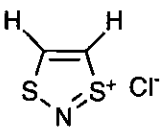
Encouragingly, treatment of $[N(SCl)_2][AlCl_4]$ **4** with phenylacetylene (2.5 eq.) in dichloromethane at room temperature, followed by addition of excess of sulphur (in an attempt to increase the yield of the thione forming reaction) and Hünig's base gave the purple 5-phenyl-1,3,2-dithiazole-4-thione (**7**) (27%) (yield calculated on the basis of one molecule of salt giving one molecule of thione). This product was identical with that previously prepared by the reaction of S_4N_3Cl with a phenylacetylide; the best yield of thione (**7**) (25%) had been obtained by the treatment of sodium phenylacetylide with S_4N_3Cl in liquid ammonia.[9]

Similar treatment of $[N(SCl)_2][AlCl_4]$ **4** with 3-methoxyphenylacetylene[10] (3.1 eq.) and 3,4-dimethoxyphenylacetylene[11] (2.5 eq.), followed by addition of excess of sulphur and Hünig's base gave 5-(3-methoxyphenyl)-1,3,2-dithiazole-4-thione (**8**) (20%) and 5-(3,4-dimethoxyphenyl)-1,3,2-dithiazole-4-thione (**9**) (18%) respectively. These were identical with samples previously prepared by the treatment of the corresponding lithium arylacetylide with S_4N_3Cl in THF at -78°C in yields of 2% and 4% respectively.[8]

On further investigation it was found that addition of sulphur did not increase the yield of the thione and also that the use of one equivalent of alkyne gave similar yields of thiones to those obtained with an excess of alkyne. Thus reaction of salt (**4**) in dichloromethane with phenylacetylene (1 eq.) at room temperature, followed by treatment with triethylamine (3 eq.), afforded the thione (**7**) in 64% yield (on the basis of two molecules of salt affording one molecule of thione). Similar treatment of salt (**4**) with 3,4-dimethoxyphenylacetylene (1 eq.), followed by addition of triethylamine (3 eq.), afforded the thione (**9**) in 56% yield. In larger scale reactions chlorine was seen to be evolved after addition of the acetylene.

These results were valuable to us, since the yields of the arylthiones were of the same order as those for 1,3,2-dithiazolium chloride (**10**), which on treatment with base gave 1,3,2-dithiazole-4-thione (**11**);[1] thus the

cycloaddition reaction of the alkynes with $[N(SCl)_2][AlCl_4]$ **4** is an efficient process, and the comparable yields of thione from one equivalent of alkyne pointed towards an equimolar reaction with evolution of chlorine. However 4-nitrophenylacetylene[11] did not react with $[N(SCl)_2][AlCl_4]$ **4** in dichloromethane at room temperature, and on addition of base none of the analogous thione was observed.



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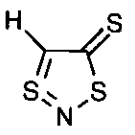

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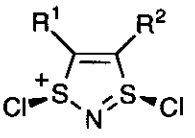

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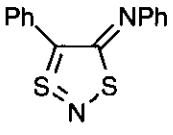
Whilst this investigation was underway, Passmore and co-workers[12] published work showing that bis(chlorothio)nitronium hexafluoroarsenate $[N(SCl)_2][AsF_6]$ **3** underwent symmetry allowed cycloaddition with some alkynes in liquid sulphur dioxide; with acetylene and methylacetylene the corresponding 1,3,2-dithiazolium salts were formed in quantitative yield, although there was no reaction with hexafluorobut-2-yne or acetonitrile. The cycloaddition was thought to proceed via an intermediate cation of type **12** which then loses chlorine to give the aromatised product; our results are entirely consistent with these.

Thus with electron-rich alkynes, $[N(SCl)_2][AlCl_4]$ **4** reacted to give the thiones (**6**), presumably by way of the intermediates (**12**) and (**5**). Treatment of salt (**4**) with phenylacetylene, followed by aniline and, subsequently, triethylamine, gave only thione (**7**) and none of the known imine (**13**).[9] This imine would have been expected if the intermediate (**5**) had undergone *in situ* chlorination and then reacted with aniline, similar to the reaction of 4,5-dichloro-1,2,3-dithiazolium chloride (**14**) with aniline to give the imine (**15**).[13]



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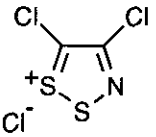

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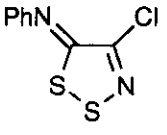

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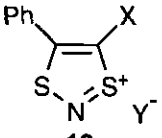


X=Cl,Br

16

Scope of the reaction

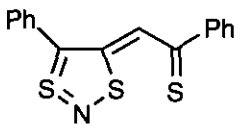
To improve the yield of thiones (**6**), attempts were made to prepare the halogenated intermediate salts of type **16** (which on treatment with hydrogen sulphide would be expected to afford the thione (**7**)) by the use of halogenated alkyne equivalents . Treatment of $[N(SCl)_2][AlCl_4]$ **4** with ß,ß-dibromostyrene[14] (2 eq.) (a 1-bromo-2-phenylacetylene equivalent) in dichloromethane led to a dark-brown reaction mixture, which on addition of aniline gave none of the imine (**13**). On treatment of $[N(SCl)_2][AlCl_4]$ **4** with ß-bromostyrene (mixed isomers) (2 eq.) in dichloromethane, the mixture turned a deep-red colour but no products could be isolated. A similar result was obtained with 1-bromo-2-phenylacetylene[15] and phenylvinyl sulphoxide (a phenylacetylene equivalent). These results showed the salt (**4**) to be generally unreactive towards electron-poor alkenes and alkynes, which was in agreement with its lack of reaction with 4-nitrophenylacetylene. There was also no reaction of the salt (**4**) with the electron-deficient alkynes methyl and ethyl propiolate in dichloromethane. Thus $[N(SCl)_2][AlCl_4]$ **4** and $[N(SCl)_2][AsF_6]$ **3** are less reactive than $[S_2N][AsF_6]$ **2** which does react with electron-poor alkynes, such as hexafluorobut-2-yne.[2] It is believed that the higher reactivity of S_2N^+ relative to $N(SCl)_2^+$ is likely to arise in part from the smaller energy differences between its LUMO and the HOMO's of the alkenes and alkynes.[12]

As an alternative to introducing functionality in the starting alkyne or alkene, *in situ* chlorination of the heterocyclic ring was attempted. Treatment of $[N(SCl)_2][AlCl_4]$ **4** with phenylacetylene (1 eq.), followed by *N*-chlorosuccinimide (5 eq.) to yield an intermediate of type **16**, followed by aniline (3 eq.) and finally Hünig's base, did indeed give the imine (**13**) in reasonable yield (38%). An attempt was made to isolate pure 4-phenyl-1,3,2-dithiazolium chloride, by treatment of the solid obtained from reaction of phenylacetylene and salt (**4**), with THF, which coordinates with aluminium trichloride more strongly than a chloride ion,[16] but this proved unsuccessful.

An unexpected result occurred on repetition of the reaction of phenylacetylene (1.1 eq.) with an old specimen of the salt (**4**) which had been stored in a refrigerator under argon for four months. This led to the expected thione (**7**) (21%), together with a new compound (**17**) which was burgundy coloured in dichloromethane solution. Elemental analysis gave results consistent with the molecular formula $C_{16}H_{11}NS_3$ and mass spectral analysis showed a peak at 313 corresponding to the molecular ion and a large fragmentation peak at 267 for the loss of NS (characteristic of 1,3,2-dithiazoles). The ^{13}C nmr spectrum showed four resonances (187.5, 174.2, 171.5 and 143.1) in addition to those of two phenyl rings. Finally the structure was proved by X-ray crystallographic analysis to be **17**. The 1,3,2-dithiazole ring is seen to be quite unsymmetrical and the system is extensively

delocalised. For comparison the X-ray crystallographic results for 5-anilino-1,3,2-dithiazole-4-thione (**18**)[1] are presented.

The mechanism of formation of **17** is as yet unknown. Treatment of **17** with lead tetraacetate in dichloromethane at 0°C led to destruction of the starting material and none of the corresponding keto derivative was isolated. The corresponding reactions with 3-methoxyphenylacetylene and 3,4-dimethoxyphenylacetylene gave none of the products analogous to **17**.



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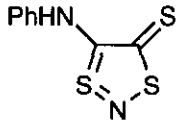

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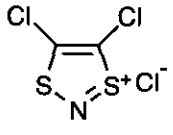

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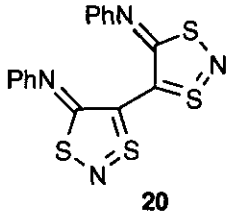

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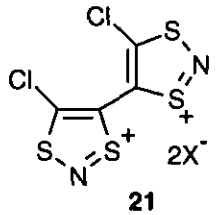

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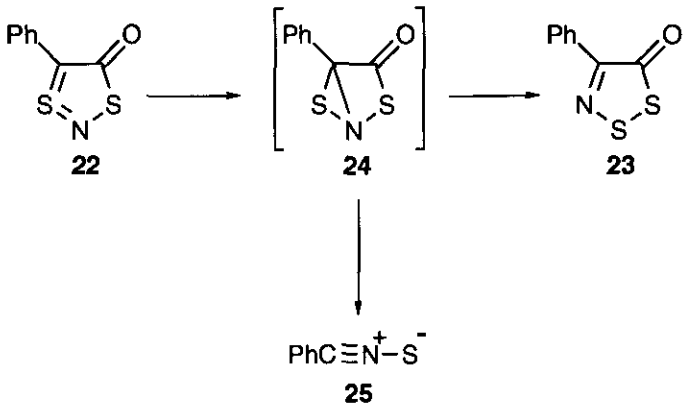
Attempts were made to prepare a clean specimen of the desired 4,5-dichloro-1,3,2-dithiazolium chloride (**19**) using reactions of $[N(SCl)_2][AlCl_4]$ **4**. Because of the hazards associated with dichloroacetylene, trichloroethylene was used as an equivalent, but unfortunately this failed to react with $[N(SCl)_2][AlCl_4]$ **4** at room temperature. Treatment of salt (**4**) with 1,2-dichloroethylene (mixed isomers, 10 eq.) in dichloromethane at room temperature for 90 h, followed by addition of aniline (6 eq.) and then Hünig's base (3 eq.) gave a small amount (6%) of a blue compound. On mass spectral analysis this showed a strong peak at 386 and strong fragmentation peaks corresponding to the loss of NS and PhN; X-ray crystallographic analysis showed its structure to be **20**. This provides an example of cycloaddition of salt (**4**) with an electron-poor alkene; although the mechanism is unclear, an intermediate of type **21** could be envisaged.

Treatment of $[N(SCl)_2][AlCl_4]$ **4** with an excess of acetonitrile (10 eq.) in dichloromethane at room temperature gave no reaction; this is in contrast with the reaction of $[S_2N][AsF_6]$ **2** with acetonitrile to afford 5-methyl-1,3,2,4-dithiadiazolium hexafluoroarsenate.[2]

5-Phenyl-1,3,2-dithiazole-4-thione (**7**)

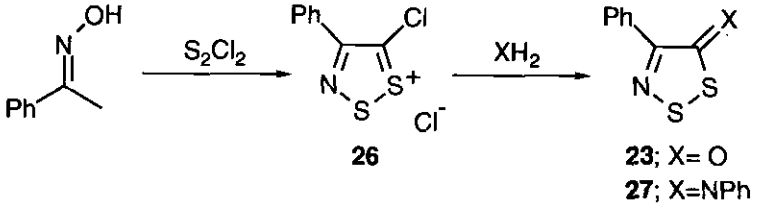
Some chemistry of 5-phenyl-1,3,2-dithiazole-4-thione (**7**) has already been published[9] and in the preceding part[1] reactions of the parent 1,3,2-dithiazole-4-thione (**11**) are described. The availability of the thione (**7**) with the C-5 position blocked by a phenyl group provides an opportunity to study reactions of the thiocarbonyl group in this system without the side reactions which result from the C-5 hydrogen in thione (**11**). We hoped to convert the phenylthione (**7**) into salt (**16**) since treatment of the latter with nucleophiles should provide coupling reactions, ultimately required for polymer formation. Treatment of thione (**7**) with sulphuryl chloride in dichloromethane, followed by aniline (1 eq.) and then Hünig's base gave the imine (**13**) in 21% yield. Treatment of **7** with sulphuryl chloride (1 eq.) and then with sodium nitrate (2 eq.) gave the light sensitive 5-phenyl-1,3,2-dithiazol-4-one (**22**) in good yield (61%). This reaction is presumably also going through **16**, with chloride displacement by the nitrate ion (*cf.* ref. 13). A large scale repetition of the previously reported[9] treatment of thione (**7**) with lead tetraacetate (1.5 eq.) in dichloromethane at -20°C gave 5-phenyl-1,3,2-dithiazol-4-one (**22**) in 94% yield. Exposure of a solution of **22** in tetrachloromethane to laboratory light caused the previously reported photoisomerisation to the 1,2,3-isomer (**23**) in 40% yield; this is thought to proceed *via* the bicyclic intermediate (**24**), and it also gave 3,5-diphenyl-1,2,4-thiadiazole (16%), presumably formed from benzonitrile sulfide (**25**). The ir spectra of the 1,2,3- (**23**) and the 1,3,2-isomers (**22**) in chloroform show strong absorption peaks for the carbonyl groups at 1671 and 1629 cm^{-1} respectively. Similar comparison of the uv spectra show the 1,2,3-isomer (**23**) to have a long wavelength absorption at 365nm compared to that of the 1,3,2-isomer at 429nm.



4-Phenyl-1,2,3-dithiazol-5-one (**23**)

To prepare larger quantities of 4-phenyl-1,2,3-dithiazole derivatives an alternative synthesis was developed. The reaction of acetophenone oxime with an excess of disulphur dichloride, and then reaction of the solid formed with water, gave 4-phenyl-1,2,3-dithiazol-5-one (**23**) in 33% overall yield, presumably *via* the intermediate salt (**26**). Analogous treatment of the solid intermediate with aniline gave the imine (**27**) in 24% overall yield. The imine (**27**) is a bright yellow crystalline solid, the uv spectrum of which shows a long wavelength absorption at 386nm; this is in contrast to the 1,3,2-isomer (**13**) which is a purple oil with a long wavelength absorption in the uv spectrum at 509nm. A similar difference had been observed between the two isomeric bicyclic imines (**28**) and (**29**).[9]

Treatment of 4-phenyl-1,2,3-dithiazol-5-one (**23**) with thionyl chloride or phosphorus pentachloride in refluxing dichloromethane and subsequent treatment of the resulting solid with aniline gave none of the imino compound (**27**), but only recovered starting material. Reaction of 4-phenyl-1,2,3-dithiazol-5-one (**23**) with Lawesson's reagent[17] (2 eq.) in toluene at 80°C led to destruction of the starting material, and gave none of the corresponding thione.



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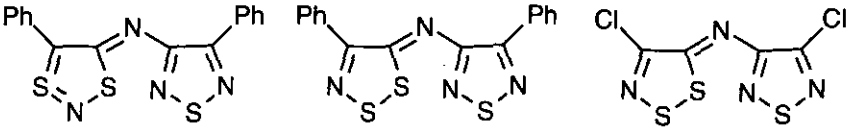
23; X= O
27; X=NPh



28 **29** **30**

X-Ray Studies

The molecular structure of **17** is shown in Figure 1. The dithiazole ring and atom chain extending to C(13) is essentially planar, there being only a *ca.* 4° dihedral angle between the dithiazole and the aromatic [C(8)-C(13)] rings. The aromatic ring attached to C(4) is rotated by *ca.* 50° out of the plane of the heterocyclic ring.

The pattern of bonding in the dithiazole ring is markedly different from that observed in **18** (see below). There is noticeable bond ordering with both the N(2)-S(3) (1.581(3)Å) and S(3)-C(4) (1.678(2)Å) displaying appreciable

double bond character. There is a comcomitant increase in both the S(1)-N(2) (1.674(2)Å) and S(1)-C(5) (1.755(2)Å) bonds. There is a pattern of delocalisation that extends from N(2) via C(4), C(5) to S(7) but noticeably not to C(8) [the C(7)-C(8) bond is quite long (1.489(3)Å)]. There is a short non-bonded S···S contact of 2.661(3)Å between S(1) and S(7) which is accompanied by an enlargement of the sp^2 angle geometry at C(6) [C(5)-C(6)-C(7) angle 124.1(2)°]. It is interesting to note that an essentially linear relationship exists between N(2), S(1) and S(7) (angle 179.5(1)°). The molecules stack in the lattice with the planar portions [S(1)-C(13)] partially overlapping with a mean interplanar separation of ca. 3.5Å. The out of plane aromatic substituent [C(14)-C(19)] is involved in π-π interaction with its symmetry related neighbour (interplanar separation 3.47Å, centroid-centroid distance 3.98Å).

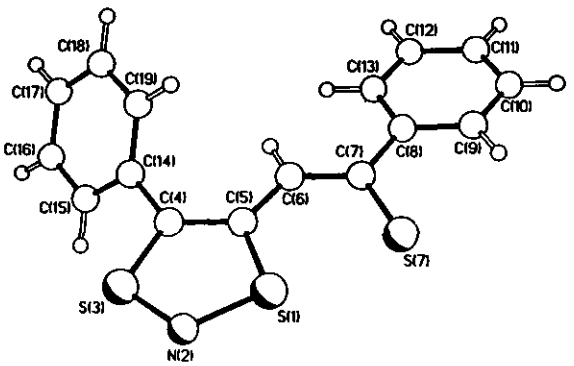


Figure 1 Structure of **17**

Table 1 Selected bond lengths (Å) and angles (°) for **17** with esds in parentheses

S(1)-N(2)	1.674 (2)	S(1)-C(5)	1.755 (2)
N(2)-S(3)	1.581 (3)	S(3)-C(4)	1.678 (2)
C(4)-C(5)	1.403 (4)	C(4)-C(14)	1.477 (4)
C(5)-C(6)	1.406 (3)	C(6)-C(7)	1.378 (4)
C(7)-S(7)	1.700 (3)	C(7)-C(8)	1.489 (3)

N(2)-S(1)-C(5)	97.9(1)	S(1)-N(2)-S(3)	114.2(1)
N(2)-S(3)-C(4)	102.3(1)	S(3)-C(4)-C(5)	113.4(2)
S(3)-C(4)-C(14)	118.1(2)	C(5)-C(4)-C(14)	128.4(2)
S(1)-C(5)-C(4)	112.2(1)	S(1)-C(5)-C(6)	124.1(2)
C(4)-C(5)-C(6)	123.7(2)	C(5)-C(6)-C(7)	124.1(2)
C(6)-C(7)-S(7)	118.3(1)	C(6)-C(7)-C(8)	121.0(2)
S(7)-C(7)-C(8)	120.7(2)		

Compound (**18**) crystallises with two crystallographically independent molecules in the asymmetric unit. The two molecules have essentially identical conformations with a maximum deviation from the least squares fit of *ca.* 0.15Å [for N(6)]. Figure 2 illustrates one of the molecules. In both molecules the dithiazole ring is rotated by*ca.* 32° from the plane of the benzene ring. This rotation is achieved *via* torsional rotations about the C(5)-N(6) and N(6)-C(7) bonds of 0.6 and 32.5° in one molecule and 9.0 and 26.4° in the other.

The bond lengths in the dithiazole ring indicate a marked degree of bond delocalisation. The two S-N bonds are of equal length (mean value 1.627Å) and the two C-S bonds are also of equal length (mean value 1.699Å). The pattern of delocalisation extends to the exocyclic-N, N(6), the C(5)-N(6) bond displaying partial double bond character. The exocyclic C-S bond also displays partial multiple bond character.

There is a noticeable enlargement of the C(5)-N(6)-C(7) angle (129°) from normal sp^2 geometry which probably results from the steric interaction between S(1) and the ortho-proton attached to C(8) of the benzene ring. There is an associated short non-bonded contact of 2.58Å between this proton and S(1).

The molecules are linked in chains *via* the weak N-H···N hydrogen bonds (3.14 and 3.23Å for each independent molecule) between the exocyclic-N in one molecule and the heterocyclic N, N(2), of another. There are accompanying short non-bonded S···S contacts (3.42 and 3.44Å) between the exocyclic S, S(4), and the heterocyclic S, S(1) (Figure 3).

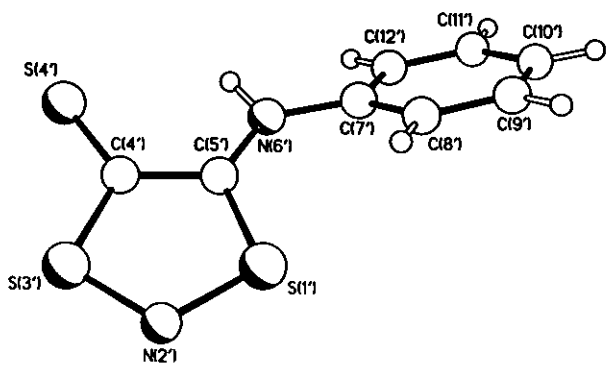


Figure 2 Structure of one of the pair of crystallographically independent molecules of **18**

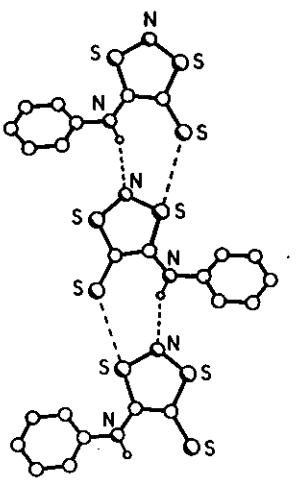


Figure 3 Part of one of the hydrogen-bonded chains of molecules in the crystal of **18**

Table 2 Selected bond lengths (Å) and angles (°) for **18** with esds in parentheses

S(1)-N(2)	1.630 (4)	S(1)-C(5)	1.702 (4)
N(2)-S(3)	1.621 (4)	S(3)-C(4)	1.699 (4)
C(4)-S(4)	1.680 (4)	C(4)-C(5)	1.430 (6)
C(5)-N(6)	1.337 (5)	N(6)-C(7)	1.417 (6)
S(1')-N(2')	1.623 (5)	S(1')-C(5')	1.697 (4)
N(2')-S(3')	1.633 (4)	S(3')-C(4')	1.698 (5)
C(4')-S(4')	1.688 (5)	C(4')-C(5')	1.420 (7)
C(5')-N(6')	1.335 (6)	N(6')-C(7')	1.412 (6)

N(2)-S(1)-C(5)	101.0(2)	S(1)-N(2)-S(3)	112.2(2)
N(2)-S(3)-C(4)	103.1(2)	S(3)-C(4)-S(4)	124.0(3)
S(3)-C(4)-C(5)	110.2(3)	S(4)-C(4)-C(5)	125.7(3)
S(1)-C(5)-C(4)	113.6(3)	S(1)-C(5)-N(6)	126.7(3)
C(4)-C(5)-N(6)	119.6(4)	C(5)-N(6)-C(7)	129.0(4)
N(2')-S(1')-C(5')	101.5(2)	S(1')-N(2')-S(3')	111.8(2)
N(2')-S(3')-C(4')	102.6(2)	S(3')-C(4')-S(4')	124.7(3)
S(3')-C(4')-C(5')	110.8(3)	S(4')-C(4')-C(5')	124.5(3)
S(1')-C(5')-C(4')	113.4(3)	S(1')-C(5')-N(6')	127.0(4)
C(4')-C(5')-N(6')	119.6(4)	C(5')-N(6')-C(7')	129.4(4)

X-Ray crystallographic analysis of **20** confirms the molecule to have the dimeric structure predicted. The structure has crystallographic C_i symmetry about the centre of the two dithiazole rings (Figure 4). The molecule as a whole is essentially planar there being only a *ca.* 5° twist of the phenyl rings relative to the plane of the dithiazoles. The pattern of bonding in the dithiazole ring is again distinctive, differing from that observed in **17** and **18**. The fully delocalised arrangement observed in **18** is almost retained with the exception S(1)-C(5) (1.763(3)Å, *cf.* a mean value of 1.699(6)Å in **18**). This loss of double bond character for S(1)-C(5) is accompanied by a very marked shortening and pronounced double bond character for C(5)-N(6) (1.289(4)Å *cf.* a mean value of 1.336Å in **18**). The planar geometry of the structure gives rise to noticeably short intramolecular contacts between both S(1) and the *ortho*-hydrogen attached to C(8) (2.40Å) and between N(6a) and S(3a) (2.608(5)Å); an essentially linear relationship exists for N(2)-S(3)-N(6a) (176.8°). The molecules pack to form overlapping parallel sheets with a mean intersheet separation of 3.39Å. N(2) and S(3) of the dithiazole ring within one sheet are positioned almost directly above their counterparts in adjacent sheets, with resulting short non-bonded S···N and N···S contacts of 3.45Å (Figure 5).

Table 3 Selected bond lengths (Å) and angles (°) for **20** with esds in parentheses

S(1)-N(2)	1.640 (3)	S(1)-C(5)	1.763 (3)
N(2)-S(3)	1.614 (3)	S(3)-C(4)	1.692 (3)
C(4)-C(5)	1.449 (4)	C(4)-C(4A)	1.406 (5)
C(5)-N(6)	1.289 (4)	N(6)-C(7)	1.399 (4)

N(2)-S(1)-C(5)	100.1(1)	S(1)-N(2)-S(3)	115.4(2)
N(2)-S(3)-C(4)	100.2(1)	S(3)-C(4)-C(5)	115.2(2)
S(3)-C(4)-C(4A)	124.2(3)	C(5)-C(4)-C(4A)	120.7(3)
S(1)-C(5)-C(4)	109.1(2)	S(1)-C(5)-N(6)	132.7(2)
C(4)-C(5)-N(6)	118.2(3)	C(5)-N(6)-C(7)	126.6(3)

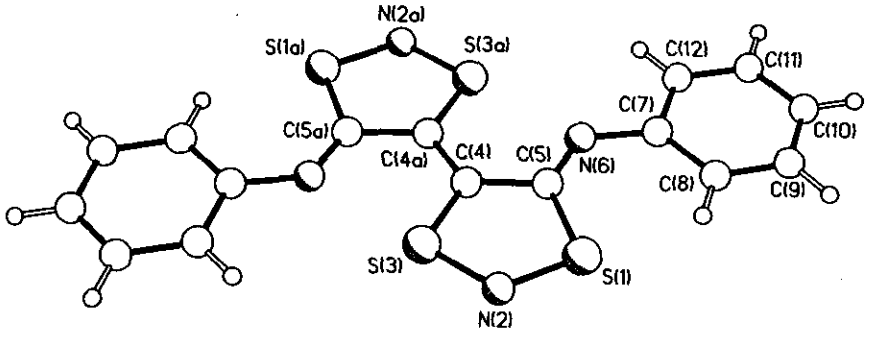


Figure 4 Structure of **20**

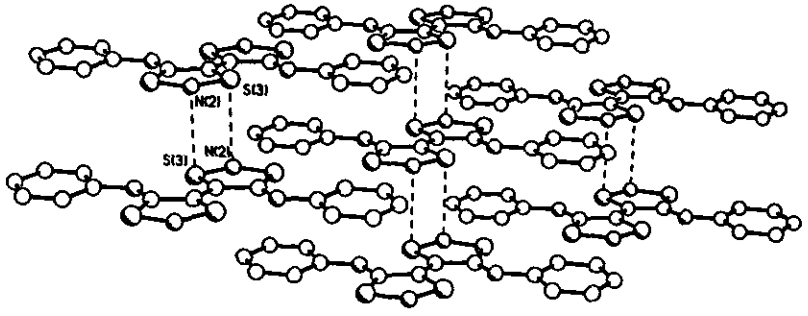


Figure 5 Perspective view of part of the stacked sheets of molecules in the crystals of **20** showing the S···N contacts

Compound (**27**) crystallises with three crystallographically independent molecules in the asymmetric unit. The conformations of the molecules are essentially the same, there being only minor differences in the dihedral angles between the dithiazole ring and the two aromatic rings. The bond lengths and angles are, within statistical

significance, identical for the three molecules (Figure 6). The S-S bond distance [2.062(2)-2.066(2)Å] is comparable with that observed in related systems[13,18,19] and the S-N bond (1.637(3)-1.642(3)Å) is essentially the same as that observed (1.630Å).[18] The most noticeable difference compared with the related 1,2,3-dithiazole (**30**)[18] is a lengthening of the ring C-S bond (1.785(3)-1.792(3)Å cf. 1.736Å in **30**) and a shortening of the exocyclic C-N bond (C(5)-N(6) 1.259(4)-1.273(4)Å *cf.* 1.299Å in **30**). In **30** the longer exocyclic C-N bond distance is a consequence of delocalisation that extends from the dithiazole ring to the thiadiazole, whereas in **27** there is a pronounced pattern of bond ordering. In all three molecules the anilino-ring [(C(7)-C(12)] is oriented essentially orthogonal to the dithiazole ring (dihedral angles 78-84°) whilst the 4-phenyl ring is almost coplanar (dihedral angles 4-15°). Accompanying this latter ring arrangement is a short contact between the hydrogen on the *ortho*-C, C(14), and the anilino-N, N(6). The C···N distances are in the range 2.92-2.95Å and the associated H···N distances are in the range 2.22-2.31Å indicating a significant C-H···N interaction, this is probably the determining factor for the coplanarity of the aromatic and dithiazole rings. Each of the three independent molecules pack in the crystal to form individual parallel stacks that extend in the crystallographic *a* direction, the aromatic ring of one molecule overlying the dithiazole ring of another with interplanar separations that range between 3.4-3.5Å. There are additional inter-stack interactions, these being of two discrete types. The first of these are S···N and N···S as illustrated in Figure 7, the S···N distances being 3.32Å. The other short contact is between one of the S atoms in the molecules of one stack and both S atoms in another (Figure 8); the S···S contacts are between 3.53 and 3.55Å.

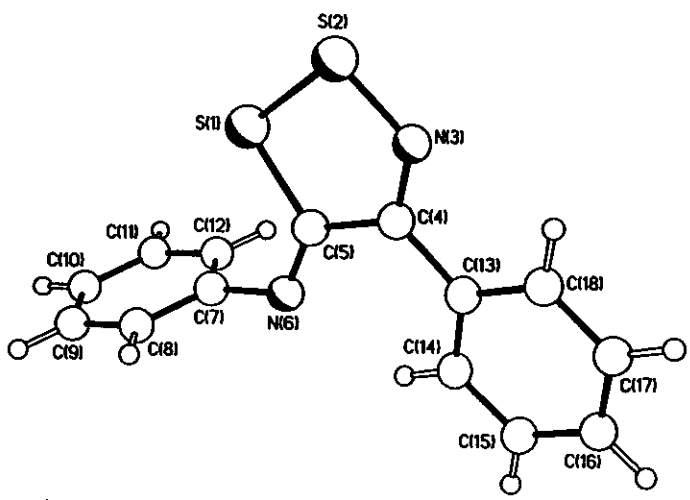


Figure 6 Structure of one of the crystallographically independent molecules of **27**

Table 4 Selected bond lengths (Å) and angles (°) for **27** with esds in parentheses

S(1)-S(2)	2.066 (2)	S(1)-C(5)	1.790 (3)
S(2)-N(3)	1.637 (3)	N(3)-C(4)	1.296 (4)
C(4)-C(5)	1.498 (5)	C(4)-C(13)	1.475 (4)
C(5)-N(6)	1.259 (4)	N(6)-C(7)	1.423 (5)
S(1')-S(2')	2.062 (2)	S(1')-C(5')	1.785 (3)
S(2')-N(3')	1.642 (3)	N(3')-C(4')	1.292 (5)
C(4')-C(5')	1.491 (5)	C(4')-C(13')	1.470 (4)
C(5')-N(6')	1.266 (5)	N(6')-C(7')	1.425 (4)
S(1")-S(2")	2.062 (2)	S(1")-C(5")	1.792 (3)
S(2")-N(3")	1.639 (3)	N(3")-C(4")	1.296 (4)
C(4")-C(5")	1.481 (5)	C(4")-C(13")	1.472 (4)
C(5")-N(6")	1.273 (4)	N(6")-C(7")	1.420 (5)

S(2)-S(1)-C(5)	92.9(1)	S(1)-S(2)-N(3)	98.0(1)
S(2)-N(3)-C(4)	119.6(3)	N(3)-C(4)-C(5)	117.6(3)
N(3)-C(4)-C(13)	119.1(3)	C(5)-C(4)-C(13)	123.3(3)
S(1)-C(5)-C(4)	111.7(2)	S(1)-C(5)-N(6)	122.8(3)
C(4)-C(5)-N(6)	125.6(3)	C(5)-N(6)-C(7)	119.9(3)
S(2')-S(1')-C(5')	92.8(1)	S(1')-S(2')-N(3')	98.1(1)
S(2')-N(3')-C(4')	119.2(2)	N(3')-C(4')-C(5')	117.8(3)
N(3')-C(4')-C(13')	118.2(3)	C(5')-C(4')-C(13')	123.9(3)
S(1')-C(5')-C(4')	112.0(2)	S(1')-C(5')-N(6')	122.8(2)
C(4')-C(5')-N(6')	125.1(3)	C(5')-N(6')-C(7')	119.1(3)
S(2")-S(1")-C(5")	92.6(1)	S(1")-S(2")-N(3")	98.2(1)
S(2")-N(3")-C(4")	118.9(3)	N(3")-C(4")-C(5")	118.3(3)
N(3")-C(4")-C(13")	117.8(3)	C(5")-C(4")-C(13")	124.0(3)
S(1")-C(5")-C(4")	111.9(2)	S(1")-C(5")-N(6")	123.0(3)
C(4")-C(5")-N(6")	125.0(3)	C(5")-N(6")-C(7")	119.1(3)

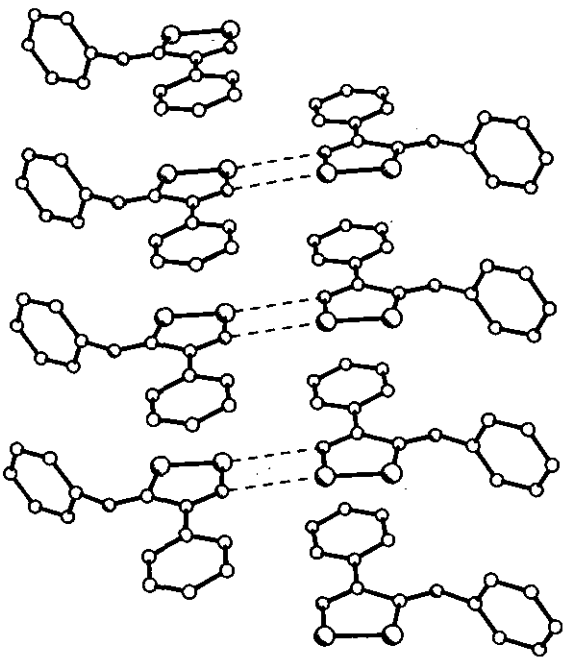


Figure 7 The stacking of molecules of **27** in the crystal showing the inter-stack S···N contacts

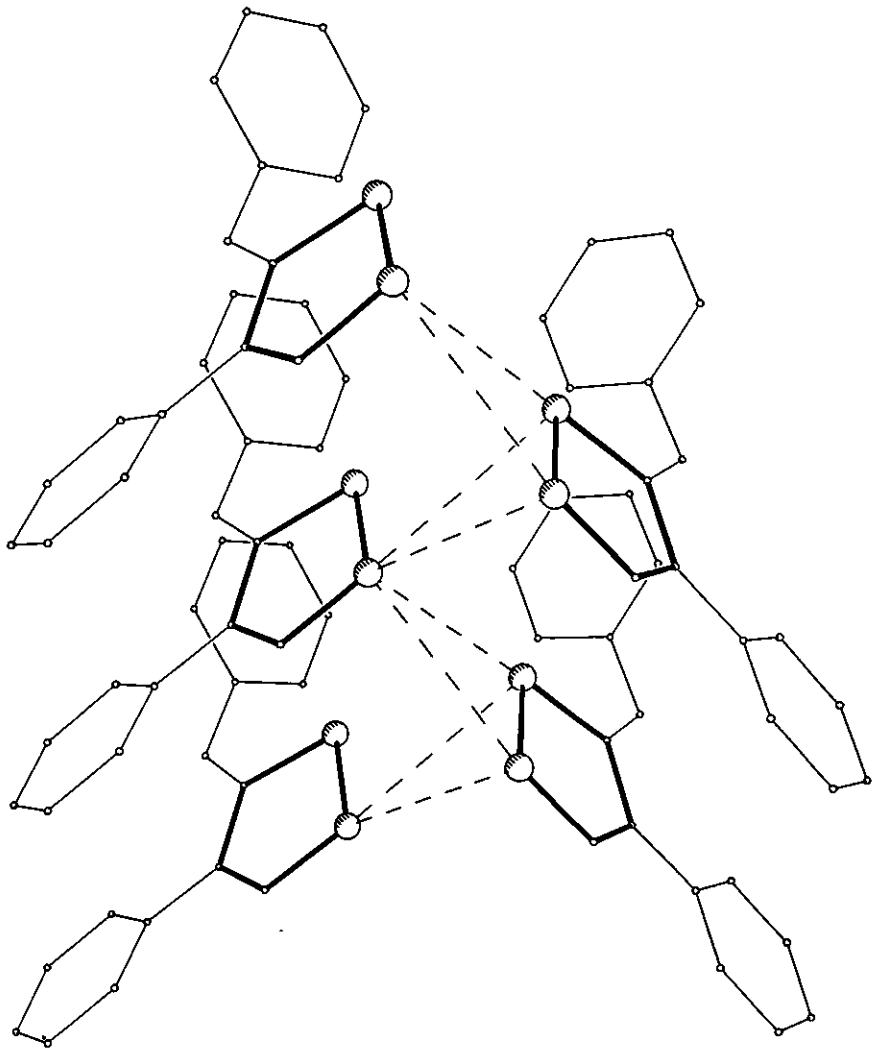


Figure 8 The Chevron-like pattern of adjacent stacks of molecules of **27** showing inter-stack S···S contacts

Table 5 Details of the data collections† and refinements for compounds (**17**, **18**, **20** and **27**)

Compound	**17**	**18**	**20**	**27**
Empirical Formula	$C_{16}H_{11}NS_3$	$C_8H_6N_2S_3$	$C_{16}H_{10}N_4S_4$	$C_{14}H_{10}N_2S_2$
Colour, habit	Purple needles	Bronze needles	Black needles	Yellow Blocks
Crystal size/mm	0.08x0.12x0.38	0.07x0.13x0.83	0.10x0.15x0.50	0.33x0.33x0.50
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a/Å	7.526(2)	9.445(3)	8.717(3)	4.893(2)
b/Å	10.371(2)	20.530(5)	5.721(2)	19.580(5)
c/Å	10.888(2)	9.968(2)	16.120(5)	21.511(8)
α/°	117.40(2)	-	-	68.40(2)
β/°	107.30(2)	95.64(2)	99.61(2)	88.86(2)
γ/°	92.78(2)	-	-	85.98(2)
U/Å	702.9(3)	1923.6(8)	792.6(5)	1911.5(10)
Z	2	8[a]	2[b]	6[c]
M	313.4	226.3	386.5	270.4
D_c/g.cm^{-3}	1.481	1.563	1.619	1.409
Absorption coefficient/mm^{-1}	4.70 (CuKα)	0.72(MoKα)	0.61(MoKα)	0.40(MoKα)
F(000)	324	928	396	840
2θ range/°	0-116	3-50	4-50	3-50
Independent reflections (R_{int}/%)	1893(0.00)	3387(2.56)	1398(1.94)	6728(0.00)
Observed reflections	1741 [F>4.00σ(F)]	2124 [F>4.00σ(F)]	1091 [F>4.00σ(F)]	4551 [F>3.00σ(F)]
Min., Max., transmission	0.387, 0.698	-	-	-
No. of parameters refined	182	235	110	488
Weight G	0.0005	0.0008	0.0007	0.0007
Final R (R')	0.0328(0.0371)	0.0467(0.0463)	0.0335(0.0369)	0.0473(0.0488)
Largest and mean Δ/σ	0.002 and 0.001	0.001 and 0.000	0.026 and 0.006	0.001 and 0.000
Data/parameter ratio	9.6	9.0	9.9	9.3
Largest difference peak, hole/ eÅ^{-3}	0.33, -0.27	0.29, -0.34	0.26, -0.23	0.24, -0.18

a Two crystallographically independent molecules

b The compound has crystallographic C_i symmetry

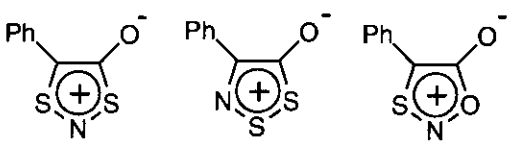
c Three crystallographically independent molecules

† Data for compounds (**18**, **20**, and **27**) measured on a Siemens P4/PC diffractometer with graphite monochromated Mo-Ka radiation (λ=0.71073Å). Data for compound (**17**) measured on Siemens P3/PC diffractometer with graphite monochromated Cu-Ka radiation (λ=1.54178Å). Details in common; W scans, room temperature, weighting scheme $W^{-1}=\sigma^2(F)+GF^2$

^{14}N Nmr Studies

A structural problem associated with the study of organic compounds rich in sulfur and nitrogen is that product characterisation has been largely dependent on the use of X-ray crystallography. Other methods of characterisation are important as alternatives and complements to this, and one obvious approach is the use of ^{14}N nmr spectroscopy.[20] The use of the quadrupolar ^{14}N nucleus (I=1, 99.6% abundant) in nmr experiments due to fast relaxation results in broad resonances and loss of coupling information [compared to the ^{15}N nucleus (I=$^1/_2$, 0.36%)], but allows rapid accumulation and high signal to noise spectra. Important information can be gleaned from the chemical shifts in ^{14}N nmr because although the resonances are broad they are small in comparison to the chemical shift range. Patterns have emerged from the study of chemical shift ranges in sulphur-nitrogen compounds and it has been found that the degree of saturation has a large effect on chemical shifts. Characteristic regions are observed; singly bonded sulphur-nitrogen compounds, such as S_7NH resonate at around 0 ppm; in contrast triply bonded NSF has δ 576ppm. In sulphurdiimides the formal N=S double bonds show signals in the range 250-400 ppm. One interesting observation is that for the 'pseudo-aromatic' compounds such as $(NSCl)_3$ chemical shifts (90-140ppm) intermediate between those of singly and doubly bonded species are seen.[21]

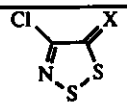
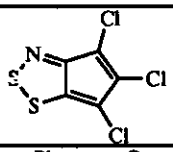
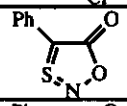
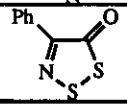
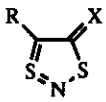
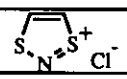
With this in mind we have applied this technique to dithiazoles and similar compounds, especially for the comparison of 1,3,2- and 1,2,3-dithiazoles. Distinguishing the isomers was given added importance by the photoisomerisation of 5-phenyl-1,3,2-dithiazol-4-one(**22**)to 4-phenyl-1,2,3-dithiazol-5-one(**23**).Our results are shown in Table 6.



31 **32** **33**

One of the most striking results was the large difference in chemical shift between the isomeric phenyldithiazolones (**22**)(δ 255ppm) and(**23**)(δ 332ppm); this may possibly be explained by the greater contribution of the mesoionic form **31** to **22** compared to **32** where a lesser contribution to **23** would be expected due to the weaker π overlap across the two adjacent sulphur atoms. The more symmetrical nature of the

Table 6 ^{14}N Nmr data of dithiazoles

Compound		Solvent	Chemical Shift δ (ppm)	Linewidth at half-peak height $\nu_{1/2}$ (Hz)
	X = O **35**	$CDCl_3$	319	315
	X = S **36**	$CDCl_3$	321	365
	**37**	$CDCl_3$	320	420
	**34**	$CDCl_3$	363	560
	**23**	$CDCl_3$	332	487
	R =Ph, X = O **22**	$CDCl_3$	256	320
	R = Ph, X = S **6**	$CDCl_3$	290	460
	R = 3,4-$(MeO)_2C_6H_4$ X = S **9**	$CDCl_3$	282	785
	R = SMe, X= S	$CDCl_3$	276	295
	R = H, X = S **11**	$CDCl_3$	314	155
	**10**	D_2O	372	130

Chemical shifts are relative to anhydrous ammonia at 0°C

nitrogen enviroment in dithiazolone (**22**) led to a narrower line-width. These results can be compared with 4-phenyl-1,3,2-oxathiazol-5-one (**34**)[22] where the contribution of the mesoionic form (**33**) is less than for the above.

There is also a noticeable downfield shift of 25ppm for 5-phenyl-1,3,2-dithiazole-4-thione (**7**) compared to 5-phenyl-1,3,2-dithiazol-4-one (**22**), whilst there is little difference in chemical shifts between the 5-chloro-1,2,3-dithiazol-4-one (**35**)[13], 5-chloro-1,2,3-dithiazole-4-thione (**36**)[13] and the 1,2,3-dithiazole (**37**).[23]

Comparison of the 1,3,2-dithiazolethiones[1] show a chemical shift range between 276 and 314ppm, with electron-releasing substituents in the 5-position being reflected by more upfield signals. The parent 1,3,2-dithiazolethione (**11**) shows a more downfield signal compared to the other dithiazolethiones. The result obtained for 1,3,2-dithiazolium chloride (**10**) in deuterium oxide shows a chemical shift in the expected region[24] and the high symmetry of the salt is reflected in the narrow line-width.

EXPERIMENTAL

For general points see earlier parts of the series. Light petroleum refers to the fraction, bp 40-60°C unless otherwise stated. In reactions involving the formation of thiones yields are calculated on the basis of two molecules of salt giving one molecule of thione, unless a sulphur source was present. ^{14}N Nmr experiments give N chemical shifts relative to anhydrous liquid ammonia at 0°C (δ 0), positive values corresponding to downfield shifts. Nitromethane (δ 380.2) was used as an external reference. Normally 100-300 mg of sample was required and 10 mm nmr tubes were employed. A peak at 309 ppm, attributed to dissolved nitrogen was sometimes observed.

5-Phenyl-1,3,2-dithiazole-4-thione(**7**)[$N(SCl)_2$][$AlCl_4$] **4** (0.589 g, 1.85 mmol) and phenylacetylene (0.215 ml, 1.96 mmol) in dichloromethane (20 ml) were stirred under argon at room temperature; the mixture turned black and evolution of gases was observed. After stirring for 3 h, triethylamine (0.775 ml, 5.58 mmol) was added to the reaction mixture (white fumes evolved) which was protected from light and stirred for a further 2 h. Dry flash column chromatography (30-80% CH_2Cl_2/light petroleum) followed by flash column chromatography (30-80% CH_2Cl_2/light petroleum) gave 5-phenyl-1,3,2-dithiazole-4-thione (**7**) (0.126 mg, 64%) as black needle-like lustrous crystals, mp 99-101°C (lit.,[9] 99-101°C); δ_N(18.06MHz, $CDCl_3$)/($v_{1/2}$(Hz)) 290 (460).

5-(3-Methoxyphenyl)-1,3,2-dithiazole-4-thione (**8**). $[N(SCl)_2][AlCl_4]$ **4** (0.337 g, 1.06 mmol) and 3-methoxyphenylacetylene (0.436 g, 3.30 mmol) in dichloromethane (30 ml) were stirred under argon at room temperature; the mixture turned black and evolution of gases was observed). After stirring for 15 h, Hünig's base (0.410 ml, 2.35 mmol) and sulphur (0.173 g, 5.40 mmol) in dichloromethane (5 ml) were added to the reaction mixture (white fumes evolved) which was protected from light and stirred for a further 2 h. Dry flash column chromatography (20-50% CH_2Cl_2/light petroleum) followed by flash column chromatography (20-50% CH_2Cl_2/light petroleum) gave *5-(3-methoxyphenyl)-1,3,2-dithiazole-4-thione* (**8**) (52 mg, 20%) as black lustrous crystals, mp 109°C (lit.,[8] 108-109°C).

5-(3,4-Dimethoxyphenyl)-1,3,2-dithiazole-4-thione(**9**). $[N(SCl)_2][AlCl_4]$ **4** (0.375g , 1.18 mmol) and 3,4-dimethoxyphenylacetylene (0.208 g, 1.24 mmol) in dichloromethane (15 ml) were stirred under argon at room temperature (reaction turned black and evolution of gas (Cl_2) was observed). After stirring for 2 h, triethylamine (0.495 ml, 3.55 mmol) was added to the reaction mixture (white fumes evolved) which was protected from light and stirred for a further 2 h. Dry flash column chromatography (20-50% CH_2Cl_2/light petroleum) followed by flash column chromatography (20-50% CH_2Cl_2/light petroleum) gave *5-(3,4-dimethoxyphenyl)-1,3,2-dithiazole-4-thione* (**9**) (90 mg, 56%) as black lustrous crystals, mp 144-145°C (lit.,[8] 146-147°C); δ_N(18.06MHz, $CDCl_3$)/($\nu_{1/2}$(Hz)) 285 (785).

4-Phenyl-5-phenylthiocarbonylmethylene-1,3,2-dithiazole (**17**). $[N(SCl)_2][AlCl_4]$ **4** (2.80 g, 8.80 mmol) in dichloromethane (100 ml) was slowly treated with phenylacetylene (1.07 ml, 9.74 mmol) in dichloromethane (20 ml). The reaction immediately turned red-black. After stirring for 3 h, triethylamine (3.75 ml, 0.0269 mol) was added to the reaction mixture (white fumes evolved) which was protected from light and stirred for a further 14 h. Dry flash column chromatography (30-80% CH_2Cl_2/light petroleum) followed by flash column chromatography (30-80% CH_2Cl_2/light petroleum) gave 5-phenyl-1,3,2-dithiazole-4-thione (**7**) (0.191 g, 21%) identical to a previous sample and *4-phenyl-5-phenylthiocarbonylmethylene-1,3,2-dithiazole*(**17**)(0.166 g, 12%) as black needle-like lustrous crystals, mp 154-155°C; Anal. Calcd for $C_{16}H_{11}NS_3$: C, 61.3, H, 3.5; N, 4.5.Found: C, 61.35; H. 3.3; N, 4.3. $\nu_{max}(CHCl_3)/cm^{-1}$ 1601w, 1472s, 1447m, 1385m, 1096w and 651s; λ_{max}(EtOH)/nm(ε) 539 (3.60), 414 (3.76), 355 (3.74) and 252 (4.47); δ_H(270 MHz, $CDCl_3$) 8.17 (1H, s), 7.85-7.79 (2H, m, Ar-H), 7.68-7.59 (5H, m, Ar-H) and 7.40-7.35 (3H, m, Ar-H); δ_C(62.9 MHz, $CDCl_3$) 187.5, 174.2, 171.5, 143.1, 131.1, 129.9, 129.4, 129.3, 128.6, 128.3, 127.9 and 117.1; m/z(210°C) 313

(M^+, 10%), 294 (42), 269 (21), 268 (100), 267 (M^+-NS, 37), 234 (20), 135 (11), 121 ($PhCS^+$, 46), 77 (Ph, 26), 64 (31) and 46 (22).

4-Phenyl-5-N-phenylimino-1,3,2-dithiazole (**13**). (i) $[N(SCl)_2][AlCl_4]$ **4** (0.118 g, 0.372 mmol) and phenylacetylene (43 ul, 0.393 mmol) in dichloromethane (20 ml) were stirred under argon at room temperature; the mixture turned black). After stirring for 3.5 h, *N*-chlorosuccinimide (0.249 g, 1.86 mmol) was added slowly and the reaction was stirred for a further 10 h (yellow-orange reaction). Aniline (0.105 ml, 1.15 mmol) was added to the reaction which immediately turned a red-purple colour and was stirred for an additional 1 h. Dry flash column chromatography (50% CH_2Cl_2/light petroleum) followed by flash column chromatography (20-50% CH_2Cl_2/light petroleum) gave *4-phenyl-5-N-phenylimino-1,3,2-dithiazole* (**13**)[9] (38 mg, 38%) as a violet oil; (Found: M^+, 270.0285, $C_{14}H_{10}N_2S_2$ requires M, 270.0285); $\nu_{max}(CCl_4)/cm^{-1}$ 3065w, 1596w, 1543s, 1486m, 1447w, 936w and 694m; λ_{max}(EtOH)/nm(ε) 509 (3.09), 305 (3.98) and 253 (4.03); δ_H(250 MHz, $CDCl_3$) 8.04-8.00 (2H, m, Ar-H), 7.56-7.41 (6H, m, Ar-H) and 7.17-7.11 (2H, m, Ar-H); m/z(100°C) 270 (M^+, 22%), 224 (M^+-NS, 7), 121 ($PhCS^+$, 100), 77 (Ph, 13) and 51 (7).

(ii) 5-Phenyl-1,3,2-dithiazole-4-thione (**7**) (0.129 g, 0.611 mmol) was titrated with sulphuryl chloride in dichloromethane until the purple colour was dissipated and an orange solid formed. The reaction was stirred for 2 h and then the volatiles were removed *in vacuo*. On addition of dichloromethane followed by aniline, the mixture turned a maroon colour and was stirred for a further 5 h. Flash column chromatography (25-50% CH_2Cl_2/light petroleum) gave 4-phenyl-5-*N*-phenylimino-1,3,2-dithiazole (**13**) (21%) identical with a previously prepared sample.

bis(4-Phenylimino-1,3,2-dithiaz-5-yl) (**20**). 1,2-Dichloroethylene (mixed isomers, 0.512 ml, 4.16 mmol) was added to a suspension of $[N(SCl)_2][AlCl_4]$ **4** (132 mg, 0.416 mmol) in dichloromethane (10 ml) under N_2 at room temperature. The reaction was stirred for 90 h then aniline (0.228 ml, 2.50 mmol) was added and after further stirring for 2 h, Hünig's base (0.220 ml, 1.26 mmol) was added. Flash column chromatography (10% CH_2Cl_2/light petroleum) gave *bis(4-phenylimino-1,3,2-dithiaz-5-yl)* (**20**) (4.5 mg, 6%) as a blue solid; m/z (220°C) 386 (M^+, 58%), 340 (M^+-NS, 100), 237 (75), 191 (56), 159 (44), 88 (97), 77 (Ph, 69) and 51 (35).

5-Phenyl-1,3,2-dithiazol-4-one (**22**). (i) 5-Phenyl-1,3,2-dithiazole-4-thione (**7**) (1.03 g, 4.85 mmol) in dichloromethane (50 ml) was added to a solution of lead tetraacetate (3.28 g, 7.40 mmol) in dichloromethane

(100 ml) protected from light at -20°C over 25 min. The purple colour of the thione was dissipated giving a bright yellow mixture which was purified by dry flash column chromatography (30-80% CH_2Cl_2/light petroleum) affording 5-phenyl-1,3,2-dithiazol-4-one (**22**)[9] (0.891 g, 94%) as a yellow-orange solid, mp 68-70°C; δ_N(18.0δ_N(18.06MHz, $CDCl_3$)/($\nu_{1/2}$(Hz)) 255 (320).

(ii) 5-Phenyl-1,3,2-dithiazole-4-thione (**7**) (46 mg, 0.218 mmol) in dichloromethane (15 ml) under N_2 and protected from light was titrated with sulphuryl chloride in dichloromethane until the purple colour was dissipated yielding a yellow-orange reaction mixture which was stirred for 1 h. The volatiles were removed *in vacuo*. Dichloromethane (10 ml) was added along with sodium nitrate (37 mg, 0.435 mmol) and the reaction was stirred under N_2 protected from light for 20 h. The reaction mixture was adsorbed onto silica and the yellow compound was purified by dry flash column chromatography (30-80% CH_2Cl_2/light petroleum) affording 5-phenyl-1,3,2-dithiazol-4-one **22** (26 mg, 61%), identical to that prepared previously.

4-Phenyl-1,2,3-dithiazol-5-one (**23**). (i) A solution of 5-phenyl-1,3,2-dithiazol-4-one (**22**) (0.891 g, 4.56 mmol) in tetrachloromethane (350 ml) under N_2 was exposed to laboratory light until all the starting material had been consumed. The solvent was removed *in vacuo*. Flash column chromatography (25% CH_2Cl_2/light petroleum) gave 4-phenyl-1,2,3-dithiazol-5-one (**23**)[9] (0.360 g, 40%) as a yellow crystalline solid, mp 49-50°C; (Found: M^+, 194.9813, $C_8H_5NOS_2$ requires M, 194.9813); ν_{max}($CHCl_3$)/cm^{-1} 1671s (C=O), 1445w, 1263w, 702m and 690w; λ_{max}(EtOH)/nm(ε) 365 (4.01) and 249 (3.90); δ_H(270 MHz, $CDCl_3$) 8.16-8.12 (2H, m, Ar-H) and 7.52-7.47 (3H, m, Ar-H); δ_C(62.9 MHz, $CDCl_3$) 189.9 (C=O), 154.8, 130.8, 128.5 and 127.9; δ_N(18.06MHz, $CDCl_3$)/($\nu_{1/2}$(Hz)) 332 (490); m/z(240°C) 195 (M^+, 18%), 167 (M^+-CO, 35), 103 (29), 77 (Ph, 13), 76 (18), 64 (S_2, 100) and 51 (12) and 3,5-diphenyl-1,2,4-thiadiazole (86 mg, 16%) as a colourless solid, mp 89-90°C (lit.,[25] 88-90°C).

(ii) Acetophenone oxime (3.27 g, 0.0242 mol) was slowly added to a cooled solution of disulphur dichloride (25 ml, 0.3 mol) in dichloromethane (40 ml) and the mixture was stirred for 36 h. The mixture was poured onto ice-water (**caution: slowly**), filtered and the mixture was extracted (CH_2Cl_2), the organic phase dried ($MgSO_4$) and the solvent removed *in vacuo*. Flash column chromatography (25% CH_2Cl_2/light petroleum) and recrystallisation (15%CH_2Cl_2/light petroleum) gave 4-phenyl-1,2,3-dithiazol-5-one (**23**) (1.56g, 33%) identical with a previous sample.

4-Phenyl-5-phenylimino-1,2,3-dithiazole (**27**). Acetophenone oxime (3.69 g, 0.0273 mol) was slowly added to a cooled solution of disulphur dichloride (30 ml, 0.37 mol) in dichloromethane (30 ml) and the mixture was stirred for 6 days. Light petroleum (30 ml) was added and the solid formed was filtered off, washed (50% CH_2Cl_2/light petroleum) and dried to give crude 5-chloro-4-phenyl-1,2,3-dithiazolium chloride(**26**)(6.77 g). Crude 5-chloro-4-phenyl-1,2,3-dithiazolium chloride (**26**) (0.664 g, 2.65 mmol) and aniline (0.970 ml, 10.64 mmol) in dichloromethane (50 ml) were stirred under N_2 for 0.5 h. Triethylamine (1.48 ml, 10.62 mmol) was added, the yellow reaction mixture turned brown, and was stirred for a further 2 h. Dry flash column chromatography (25% Et_2O/light petroleum), flash column chromatography (25-33% Et_2O/light petroleum) and then recrystallisation (50% Et_2O/ light petroleum) gave *4-phenyl-5-N-phenylimino-1,2,3-dithiazole* (**27**) (175 mg, 24%) as a golden-yellow crystalline solid, mp 75.5-76.5°C; Anal.Calcd for $C_{14}H_{10}N_2S_2$: C, 62.2, H, 3.7; N, 10.4. Found: C, 61.8; H, 3.4; N, 10.0.(Found: M^+, 270.0285, calculated M, 270.0285); $\nu_{max}(CHCl_3)/cm^{-1}$ 1587m, 1481s, 1443m, 1280m, 1217w, 1185w, 1167w, 1071m, 1024w, 906w, 851m, 841m, 770m, 760m, 689s, 668m and 632s; λ_{max}(EtOH)/nm(ε) 386 (3.85), 266 (3.91) and 216 (3.90); δ_H(250 MHz, $CDCl_3$) 8.24-8.20 (1H, m, Ar-H) and 7.51-7.15 (9H, m, Ar-H); δ_C(62.9 MHz, $CDCl_3$) 165.4, 159.2, 153.2, 132.7, 130.4, 129.9, 129.1, 128.2, 125.7 and 119.0; m/z(120°C) 270 (M^+, 68%), 167 (100), 135 (14), 103 (46), 77(Ph, 25), 76 (13), 64 (84) and 51 (18).

Details of the X-ray data collection and refinements are given in Table 5. All four structures were solved by direct methods and the non hydrogen atoms refined anisotropically. The position of all the hydrogen atoms were located from ΔF maps. Their positions were optimised, assigned isotropic thermal parameters U(H) = $1.2U_{eq}$(C), (N) and allowed to ride on their parent atoms. For compound (**17**) a numerical absorption correction(face indexed crystal) was applied. Refinements were by full-matrix least-squares using the SHELXTL PC program.[26] Additional information available from the Cambridge Crystallographic Data Centre comprises atomic co-ordinates, thermal parameters and the remaining bond lengths and angles.

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