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PEDLER LECTURE*

Organic Poly(sulphur–nitrogen) Chemistry

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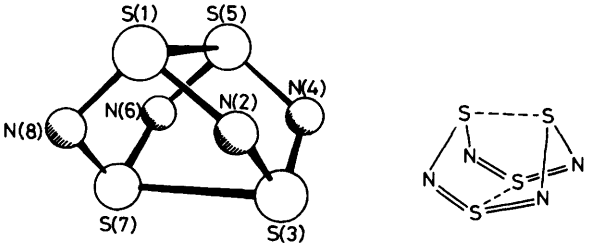
1 Introduction

The starting point for this work was the organic chemistry of the intriguing compound tetrasulphur tetranitride or, more systematically, $1,3\lambda^4\delta^2,5,7\lambda^4\delta^2$-tetrathia-2,4,6,8-tetrazocine (1). S_4N_4 is the best known of a whole family of sulphur nitrides and is one of the most studied of all inorganic heterocyclic compounds,[1] being readily prepared from sulphur dichloride and ammonia as orange crystals (m.p. 178—187 °C decomp.).[2] It may explode when heated, struck, or ground and must be handled with suitable precautions. It was first prepared in 1835,[3] and so is only ten years younger than benzene; its structure, like that of benzene, was not elucidated for over 100 years for the same general reason that it was of an entirely new type. The problem was finally solved by the application of *X*-ray diffraction and electron diffraction techniques, though the fine details of its electronic structure are still debated.



(1)

The atoms of S_4N_4 form a cage structure, with the four nitrogens in a square plane bisecting a tetrahedron of sulphurs, two above and two below the plane (1). The 12π electrons are completely delocalized, all the S–N bonds being of equal

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[1] H. G. Heal, 'The Inorganic Chemistry of Sulphur, Nitrogen and Phosphorus', Academic Press, London, 1980, Chapter 6; H. G. Heal, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 375.
[2] M. Villena-Bianco and W. L. Jolly, *Inorg. Synth.*, 1967, **9**, 98; A. J. Banister, *Inorg. Synth.*, 1977, **17**, 197.
[3] W. Gregory, *Journal de Pharmacie*, 1835, **21**, 315; 1836, **22**, 301.

length (1.62 Å) with bond order 1.65. There is substantial transannular bonding between S(1)–S(5) and S(3)–S(7) which are only 2.58 Å apart (*cf.* the S–S single bond length of 2.06 Å, and the sum of the van der Waals radii of 3.30 Å).

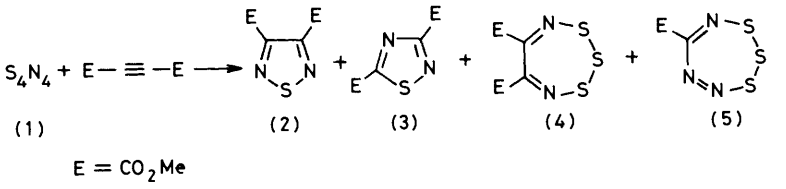
Tetrasulphur tetranitride has a rich and varied inorganic chemistry, undergoing dissociation and addition reactions, oxidations and reductions, and reactions with Lewis acids and bases.[1] So it is not surprising that there have been several investigations of its reactions with organic substrates, as a potential source of organic compounds rich in sulphur and nitrogen. But the scope of these reactions has not yet been fully appreciated since their mechanisms are so poorly understood. They generally give several diverse and unpredictable products in low yields, almost the only exceptions being the formation of 1,2,5-thiadiazoles from S_4N_4 and alkynes,[4] and of cycloadducts from S_4N_4 and strained alkenes, like norbornadiene.[5]

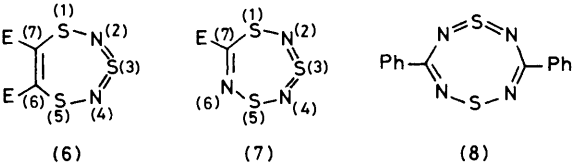
The aims of our work in this area are (i) to lay a foundation of mechanistic understanding of the cycloaddition reactions of S_4N_4 and related species, (ii) to use these species as practical sources of organic compounds rich in sulphur and nitrogen, and (iii) in the longer term to use the new chemistry, particularly of heteroaromatic systems, to modify the structure of the conducting polymer polysulphur nitride, $(SN)_x$, to give much more stable and useful conductors and superconductors.

2 Poly(sulphur–nitrogen) Systems

Our initial search then was for structurally new polyheteroatom species readily derived from S_4N_4, and the first clue to these came in a report of the products formed when S_4N_4 and dimethyl acetylenedicarboxylate (DMAD) were heated in toluene for six hours.[4] Four products were isolated and were claimed to be dimethyl 1,2,5-thiadiazole-3,4-dicarboxylate (2) (60%), dimethyl 1,2,4-thiadiazole-3,5-dicarboxylate (3) (8%), and two other minor but intriguing compounds assigned structures (4) and (5). Compounds (3) and (5) were particularly interesting mechanistically since in their formation the DMAD has been cleaved at the triple bond; but more importantly the two trisulphide structures (4) and (5) did not seem to fit the thermal stability and spectroscopic properties reported for the compounds. Upon reinvestigation[6] we obtained the same four products and confirmed the thiadiazole structures (2) and (3), but *X*-ray crystallography (Figure 1) showed that (4) and (5) were actually dimethyl 1,3,5,2,4-trithiadiazepine-6,7-dicarboxylate (6) and methyl 1,3,5,2,4,6-trithiatriazepine-7-carboxylate (7) respectively. Their seven-membered heterocyclic rings were found to be planar with bonds intermediate in length between single and double bonds. Each ring has ten electrons available to form a π system delocalized over the seven atoms, and further evidence for delocalization came from their long wavelength u.v. absorptions at

[4] S. Mataka, K. Takahashi, Y. Yamada, and M. Tashiro, *J. Heterocycl. Chem.*, 1979, **16**, 1009.
[5] M. R. Brinkman and C. W. Allen, *J. Am. Chem. Soc.*, 1972, **94**, 1550; A. M. Griffin and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1975, **31**, 985; W. L. Mock and I. Mehrotra, *J. Chem. Soc., Chem. Commun.*, 1976, 123.
[6] S. T. A. K. Daley, C. W. Rees, and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1984, 55.





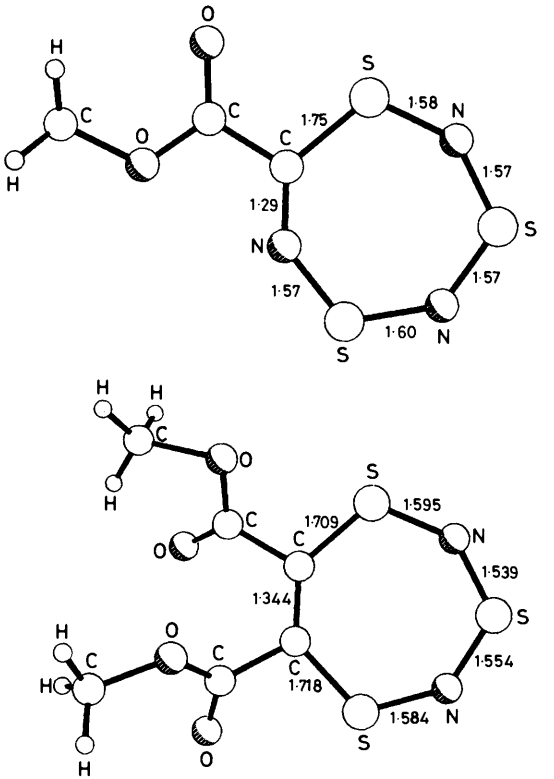
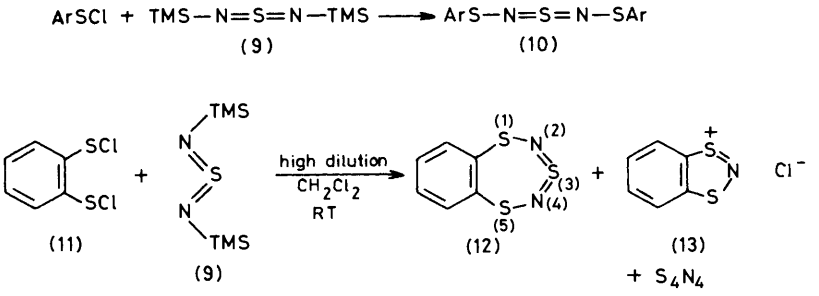


Figure 1 *The molecular structures of* (6) *and* (7) *showing the crystallographic bond lengths* (*in* Å) *for the seven-membered rings*

about 330 nm characteristic of π to π* transitions, and was fully supported by MNDO and *ab initio* MO calculations[7] on the parent trithiadiazepine and trithiatriazepine rings. The thermal stability and chemical inertness towards such reagents as triphenylphosphine and *m*-chloroperbenzoic acid of compounds (6) and (7) were strikingly similar to the properties of diphenyldithiatetrazocine (8), a related eight-membered ring compound reported by Woodward and co-workers in 1981, which also has a 10π electron aromatic ring.[8]

3 Benzotrithiadiazepine

With the ester derivatives (6) and (7) of these new heterocyclic ring systems to hand, it was obviously of interest to try to convert them into the parent compounds, both to explore the chemistry of these and to see if they were still stable without electron-withdrawing substituents compensating for the electron-rich nature of the rings. However, the hydrolysis of diester (6) proved unexpectedly difficult, and since it was available only in very low yield from reactions of S_4N_4 and DMAD, an alternative, more rational, synthesis was required. We first considered the benzo derivative (12) since the combination of a 1,4-bielectrophile based on benzene-1,2-dithiol and a 1,3-binucleophile based on a sulphuridiimide unit (–N=S=N–) looked attractive. Indeed arylsulphenyl chlorides are known to react with bis(trimethylsilyl)sulphurdiimide (9) to give bis(arylsulphenyl)sulphurdiimides (10).[9] Benzene-1,2-dithiol was converted quantitatively into the bis(sulphenyl chloride) (11) with chlorine, and then dilute dichloromethane solutions of this and of the sulphurdiimide (9) were added slowly and synchronously from mechanically driven syringes to a large volume of dichloromethane under nitrogen. This gave the desired 1,3,5,2,4-benzotrithiadiazepine (12) as stable, bright yellow crystals (50%), together with a yellow, water-soluble compound which was identified as 1,3,2-benzodithiazolium chloride (13) (37%) by comparison of its spectral and other properties with those of the corresponding bromide whose structure was proved by *X*-ray crystallography (see below). A small amount of S_4N_4 (5%) was also formed



[7] H. S. Rzepa, unpublished results.
[8] I. Ernest, W. Holick, G. Rihs, D. Schomburg, G. Shohan, D. Wenkert, and R. B. Woodward, *J. Am. Chem. Soc.*, 1981, **103**, 1540.
[9] J. Kuyper and G. B. Street, *J. Am. Chem. Soc.*, 1977, **99**, 7848.

in this reaction; a mechanism for the formation of (13) and S_4N_4 is proposed in Section 7.

The aromatic nature of the benzotrithiadiazepine (12) was supported by its u.v. and n.m.r. spectra,[10] and by an *X*-ray crystal structure determination (Figure 2) which showed the molecules to be planar with a crystallographic two-fold axis passing through S(3) and bisecting the benzene ring.[11] The ring bonds are intermediate in length between single and double bonds, indicating their delocalized nature. In the crystal the molecules pack with parallel overlap, the seven-membered ring of one overlying the six-membered ring of another and *vice versa*; the interplanar separation is small at 3.54 Å.

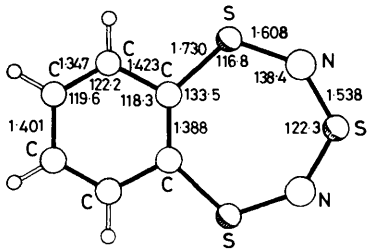


Figure 2 *The molecular structure of* (12) *showing the crystallographic bond lengths* (*in* Å) *and angles* (*in degrees*)

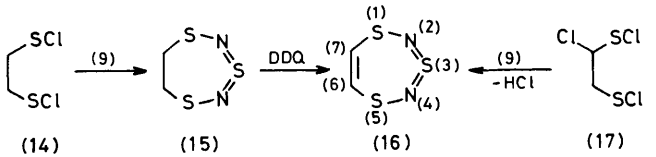
Whilst stable in boiling xylene, (12) is noticeably less stable thermally, and more reactive towards triphenylphosphine and *m*-chloroperbenzoic acid, than the monocyclic diester (6) [or the unsubstituted monocyclic compound (16) to be described later]. This is presumably a consequence of bond alternation in the heterocyclic ring induced by fusion of the benzene ring to it, and *vice versa*. This is clearly seen in the *X*-ray results: although (12) is formally a 14π system, the measured bond lengths show bond alternation in both rings. The C–S bonds are longer (1.73 Å) than the same bonds in the monocyclic compound (16) (1.69 Å) but considerably shorter than the C–S single bonds (1.80 Å) in the dihydro compound (15) which is also described later. In the benzene ring the bond lengths are, starting from the common bond, 1.39, 1.42, 1.35, and 1.40 Å. 7-Methyl-1,3,5,2,4-benzotrithiadiazepine was prepared in the same way as (12), starting from toluene-3,4-dithiol, and it had very similar properties to (12).

4 Trithiadiazepines

The bis(sulphenyl chloride) route to the benzo derivative (12) could not be applied directly to the unsaturated monocyclic compound (16) because of the instability of *Z*-ethene-1,2-dithiol and the problems associated with its chlorination. However,

[10] J. L. Morris, C. W. Rees, and D. J. Rigg, *J. Chem. Soc., Chem. Commun.*, 1985, 396.
[11] R. Jones, J. L. Morris, A. W. Potts, C. W. Rees, D. J. Rigg, H. S. Rzepa, and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1985, 398.

the 6,7-dihydro compound (15) was readily prepared in this way though in low yield: ethane-1,2-dithiol was converted quantitatively into the bis(sulphenyl chloride) (14), with chlorine or sulphuryl chloride, and was treated with the sulphurdiimide reagent (9) in high dilution, as before. This gave 6,7-dihydro-1,3,5,2,4-trithiadiazepine (15) (20%) as a distillable, low-melting orange solid which was dehydrogenated with dichlorodicyanobenzoquinone (DDQ) to give 1,3,5,2,4-trithiadiazepine (16) (70%) as colourless volatile crystals. Since the yield of the cyclization step was so low, this procedure was modified by allowing the chlorination of ethanedithiol to proceed to the trichloride (17) which, on reaction with sulphurdiimide (9) as before, spontaneously lost hydrogen chloride to give the parent trithiadiazepine (16), in 30% overall yield from ethane-1,2-dithiol.



The *X*-ray crystal structure determination of the dihydro compound (15) (Figure 3) shows that the five heteroatoms are almost exactly planar, with the maximum deviation from the plane for these atoms being 0.028 Å for N(2), and the molecule has a crystallographic two-fold axis passing through S(3) and bisecting the C–C bond. The two carbon atoms lie symmetrically 0.47 Å above and below the heteroatom plane such that the methylene hydrogen atoms adopt an

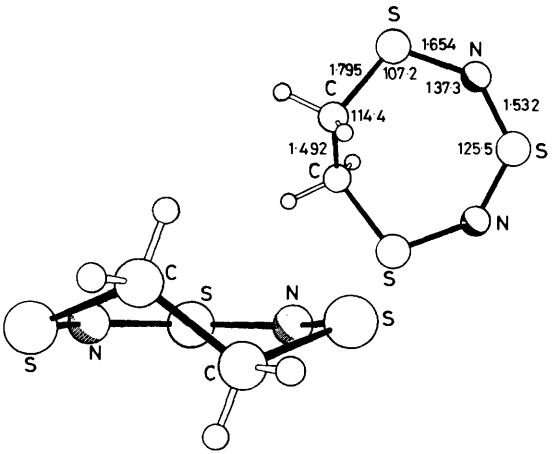


Figure 3 *The molecular structure of* (15) *showing the crystallographic bond lengths* (*in* Å) *and angles* (*in degrees*) *and the view looking down the crystallographic twofold axis showing the planarity of the* S–N–S–N–S *portion of the molecule*

approximately *cis* and *trans* periplanar geometry. The 250 MHz n.m.r. spectrum of (15) at room temperature is a sharp singlet which shows a partially exchange-broadened AA′BB′ spin system only when cooled below 190 K, indicating a low (< 40 kJ mol^{-1}) energy barrier for axial–equatorial hydrogen interconvension. The planarity of the SNSNS unit in (15) presumably enhances its chromophoric activity, giving the orange colour and a long wavelength absorption ($\lambda_{max.}$ 408 nm). Interestingly, the completely delocalized trithiadiazepine (16) is colourless, though its spectroscopic properties[10] and its *X*-ray diffraction analysis (Figure 4)[11] support a fully aromatic structure. The molecule is planar, symmetrical, and has the intermediate bond lengths expected for a 10π aromatic system, and its chemical properties are also in good agreement with this.[10]

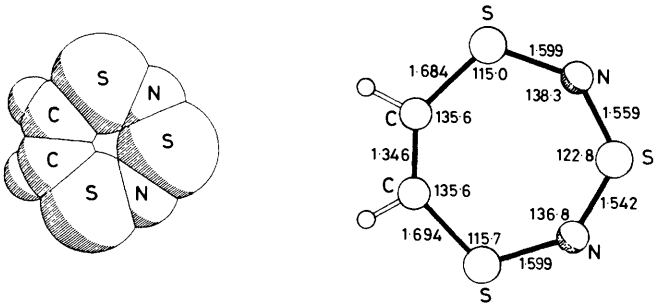


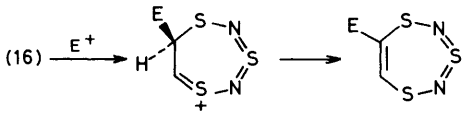
Figure 4 *Space-filling and skeletal representations of the molecular structure of* (16) *showing the crystallographic bond lengths (in* Å*) and angles (in degrees)*

5 Chemistry of Trithiadiazepine

Trithiadiazepine (16) is thermally even more stable than its diester (6), showing that these electron-withdrawing groups are not necessary for its stable existence, but both compounds are rapidly destroyed by irradiation, at 300 nm, in petrol. It is inert to protic and Lewis acids, and to amines but is rapidly decomposed by aqueous sodium hydroxide. It reacts only slowly with triphenylphosphine in boiling toluene or with *m*-chloroperbenzoic acid in boiling dichloromethane. As befits an aromatic structure, it shows no tendency to undergo cycloaddition reactions with a wide range of electron-rich and -poor 2π and 4π components, in striking contrast with S_4N_4 for example.

Trithiadiazepine (16) undergoes some standard electrophilic aromatic substitution reactions at carbon,[10] presumably *via* tetrahedral intermediates which are well stabilized by delocalization of the positive change onto all three sulphur atoms [*e.g.* (18)]. Thus it forms the 6-bromo compound (19, E = Br) (88%) with one equivalent of *N*-bromosuccinimide in acetonitrile at room temperature, and the 6,7-dibromo compound (20), (77%) with an excess of the same reagent. It forms the bright yellow 6-nitro compound (19, E = NO_2) (90%) with copper(II) nitrate trihydrate in acetic anhydride at 0 °C, and the deep yellow 6,7-dinitro compound

(54%) with excess of nitronium tetrafluoroborate in acetronitrile at 10 °C. This introduction of the second, *ortho*, nitro group occurs surprisingly readily, presumably because of the electron-rich nature of the ring. *X*-Ray diffraction of the nitro compounds shows that in the crystalline state a single nitro group is almost co-planar with the ring, indicative of charge delocalization, but in the dinitro compound the two groups are in parallel planes, twisted out of the ring plane by 45°.[12]



(18) (19)

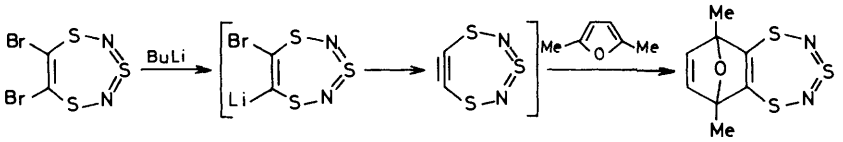
6-Aminotrithiadiazepine would be a key compound, both as a precursor for other derivatives, and in demonstrating the interaction between an electron-releasing substituent and the electron-rich ring. This interaction can be structurally significant with poly(sulphur–nitrogen) compounds; for example, if the phenyl rings in the dithiatetrazocine (8) are replaced by dimethylamino groups the planar aromatic ring transforms into a more stable non-planar structure folded along the S–S axis.[8] Unfortunately we have so far been unable to reduce the 6-nitro compound to the amine. It does not undergo catalytic hydrogenation with a range of palladium and platinum catalysts at various temperatures and pressures since the sulphur-rich ring is an effective catalyst poison.[10] A wide range of chemical reducing agents were no more successful and it is possible that the amine, if formed, is unstable.

Attempts to acetylate or formylate trithiadiazepine (16) have so far failed, possibly because of extensive co-ordination of the Friedel–Crafts catalysts with the many heteroatoms. However, trithiadiazepine (16) was readily converted into its bis(trifluoroacetoxy)thallium derivative [19, E = $Tl(OCOCF_3)_2$] with thallium(III) trifluoroacetate in refluxing acetonitrile. Without isolation, this derivative was transformed into the 6-iodo compound (80%) with aqueous potassium iodide, into the 6-cyano compound compound (85%) with copper(I) cyanide in boiling acetonitrile,[13] and into the 6-methoxycarbonyl derivative (70%) with carbon monoxide and methanol in the presence of palladium chloride, lithium chloride, and magnesium oxide.[14] This last compound (19, E = CO_2Me) is of interest in that it is identical with a minor product previously obtained from the reaction of S_4N_4 with methyl propiolate and assigned an incorrect structure.[4] The formation of methyl trithiadiazepine-6-carboxylate in the S_4N_4 reaction is thus entirely analogous to the formation of diester (6) from S_4N_4 and DMAD, described above.

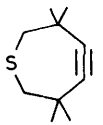
[12] R. Jones and D. J. Williams, unpublished results.
[13] E. C. Taylor, A. H. Katz, and A. McKillop, *Tetrahedron Lett.*, 1984, **25**, 5473.
[14] R. C. Larock and C. A. Fellows, *J. Org. Chem.*, 1980, **45**, 363.

6 Trithiadiazepyne

Metallation of the trithiadiazepine ring by lithium–hydrogen or lithium–bromine exchange proved less useful synthetically, though it has resulted in the generation of 'trithiadiazepyne' (21). Treatment of (16) with n- or t-butyllithium in ether or in petrol containing tetramethylethylenediamine under various conditions gave deep red solutions suggestive of anion formation, but no recognizable products were produced on quenching with electrophiles like iodomethane or methyl chloroformate; the trithiadiazepine (16) was mostly destroyed. The same general picture emerged from similar reactions with 6-bromotrithiadiazepine, though much more starting material could be recovered. However, when the dibromo derivative (20) was treated with n-butyllithium in ether at -65 °C and quenched with 2,5-dimethylfuran the adduct (22) was isolated in good yield (67%) based on the starting material consumed (25%). An analogous adduct was also formed from furan, though in lower yield. It is proposed that metal–halogen exchange gives the *o*-lithiumbromide which eliminates lithium bromide to generate 6,7-didehydro-1,3,5,2,4-trithiadiazepine (trithiadiazepyne) (21). This hetaryne could be a relatively stable one for which it might be possible to get direct spectroscopic evidence. The smallest angle measured at *sp* carbon in an isolable cycloalkyne is 146° in compound (23);[15] the corresponding angle in benzyne is calculated to be 127°.[16] MNDO calculations[7] predict that this angle would be 148° in trithiadiazepyne (21) (Figure 5); the corresponding angle in trithiadiazepine (16) is 135°. This relatively modest ring angle enlargement on formation of the aryne is calculated to be accompanied by a contraction from 115° to 99° in the angles at S(1) and S(5). The C–S bond length is predicted to become shorter by about 0.06 Å in the aryne, and the remaining bond lengths and angles are predicted not to change significantly on formation of the triple bond.



(20) (21) (22)



(23)

[15] A. Krebs and J. Wilke, *Top. Curr. Chem.*, 1983, **109**, 189.

[16] M. J. S. Dewar and W. K. Li, *J. Am. Chem. Soc.*, 1974, **96**, 5569; J. D. Noell and M. D. Newton, *J. Am. Chem. Soc.*, 1979, **101**, 51.

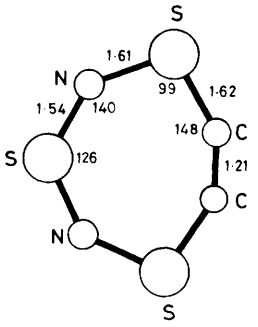
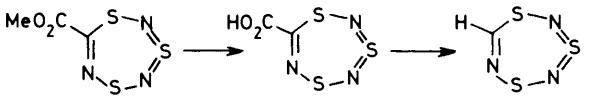


Figure 5 *MNDO calculated geometry of* (21) *showing the calculated bond lengths* (*in* Å) *and angles* (*in degrees*)

7 Trithiatriazepines

As described earlier, the reaction of S_4N_4 with DMAD gave methyl 1,3,5,2,4,6-trithiatriazepine-7-carboxylate (7) as a minor product; the same reaction with di-t-butyl acetylenedicarboxylate gave the corresponding t-butyl ester in similar yield. As yet, these reactions provide the only source of this ring system, and the esters are the only precursors of the parent compound (25). Fortunately the ester (7) can be hydrolysed quantitatively to the acid (24) by careful heating in aqueous hydrochloric acid, and the acid can be equally well decarboxylated under mild conditions, simply by boiling in dioxane for two hours, to give the parent compound (25) as stable, highly volatile, colourless plates. Again the spectral properties of (25) indicate a delocalized structure, very like that of trithiadiazepine (16), and we assume it to be another 10π planar aromatic ring, by analogy with the planar ester (7) which has similar spectroscopic properties. Disorder in the crystal has prevented an *X*-ray analysis of the unsubstituted compound (25). Trithiatriazepine (25) has the same high thermal stability as trithiadiazepine (16), surviving over 20 hours heating in *o*-dichlorobenzene at 180 °C, which is striking for a seven-membered ring containing six hetero-atoms.

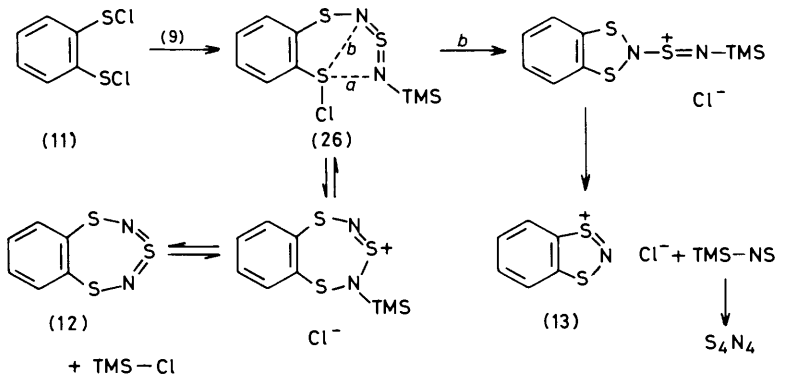


(7) (24) (25)

8 Ring Contraction Reactions

We saw earlier that in the preparation of benzotrithiadiazepine (12) from bis(sulphenyl chloride) (11) and bis(trimethylsilyl)sulphurdiimide (9), a substan-

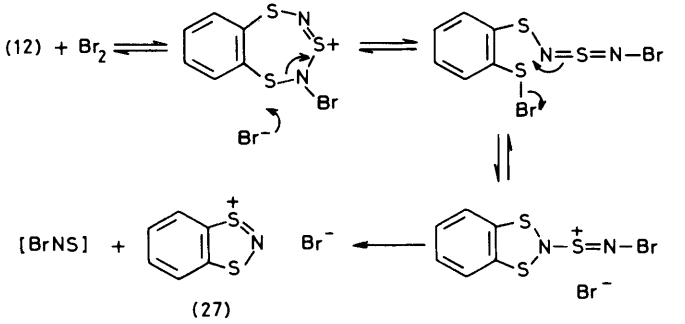
tial amount of benzodithiazolium chloride (13) and a minor amount of S_4N_4 were also produced. The formation of (13) can be explained by competitive ring-closure of the intermediate mono(sulphenyl chloride) (26) as shown in Scheme 1. Cyclization *via* the 'outer' nitrogen atom (path *a*) gives the desired seven-membered heterocyclic ring whilst cyclization *via* the 'inner' nitrogen (path *b*) could lead to compound (13). Alternatively the intermediate (26) could be produced by reaction of benzotrithiadiazepine (12) with the trimethylsilyl chloride generated in the reaction, as shown. Liberation of the reactive intermediate $Me_3Si–N{=}S$ or its isomer $Me_3Si–S{\equiv}N$, could be responsible for the S_4N_4 formed, since this is known to be a tetramer of SN. Although the 1,3,2-dithiazolium ring system was unknown at the time of the above work, the benzodithiazolium chloride (13) has now been prepared by treating benzene-1,2-disulphenyl chloride with trimethylsilyl azide,[17] and the monocyclic ring has also been prepared recently by reaction of acetylene with dithionitronium hexafluoroarsenate.[18]



Scheme 1

A very similar ring contraction was observed on attempted bromination of the benzo compound (12) with bromine in dichloromethane. This gave a red, high-melting, water-soluble crystalline product (56%) which was shown by *X*-ray crystallography to have the intriguing bis(1,3,2-benzodithiazolium)bromide tribromide structure which slowly gave the simple bromide salt (27) on vacuum drying at room temperature. The mechanism for this ring contraction is probably closely related to that of Scheme 1, but with bromine replacing trimethylsilyl chloride (Scheme 2). The chloride (13) and the bromide tribromide had very similar spectroscopic properties, including almost identical u.v. spectra, though the very similar AA′BB′ patterns in their ^1H n.m.r. spectra were separated by 1.2 p.p.m.

[17] G. Wolmershauser, M. Schnauber, and T. Wilhelm, *J. Chem. Soc., Chem. Commun.*, 1984, 573.
[18] G. K. MacLean, J. Passmore, M. J. Schriver, P. S. White, D. Bethell, R. S. Pilkington, and L. H. Sutcliffe, *J. Chem. Soc., Chem. Commun.*, 1983, 807.

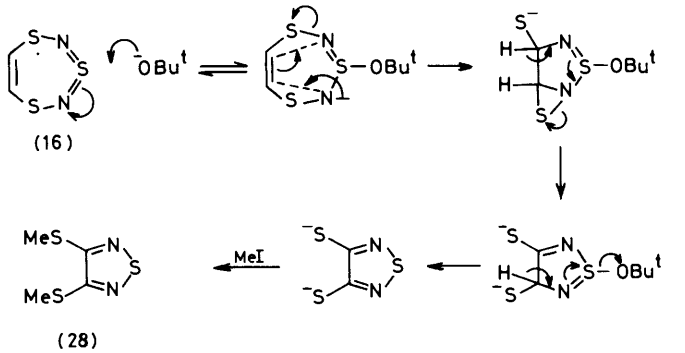


Scheme 2

The characteristic mass spectral fragmentation of trithiadiazepine to give a prominent peak at $M^+ - 46$, for loss of NS, can probably also be attributed to a seven to five ring contraction of this type, leading to the cationic 6π aromatic dithiazolium ring. An alternative seven to five contraction of trithiadiazepines leading to neutral 6π aromatic thiadiazoles was discovered as follows.

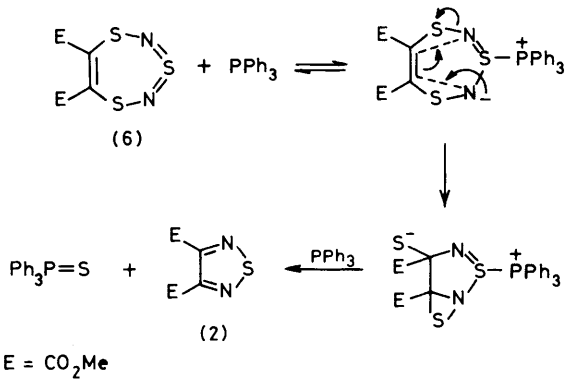
Since 1,3,5,2,4-trithiadiazepine (16) was found to be rapidly decomposed by sodium hydroxide, it was also treated with potassium t-butoxide in dry tetrahydrofuran. An orange salt was precipitated which on addition of iodomethane gave 3,4-bis(methylthio)-1,2,5-thiadiazole (28) (50%). This unexpected product results from a rearrangement in which two of the ring sulphur atoms have become exocyclic. A possible mechanism (Scheme 3) involves reversible coordination of t-butoxide to the most electropositive sulphur, S(3), which could initiate the transformations shown, though the precise sequence of events is speculative.

A similar ring contraction was observed when the trithiadiazepine diester (6) was



Scheme 3

treated with triphenylphosphine, though the two sulphur atoms were now removed from the molecule as triphenylphosphine sulphide, to give dimethyl 1,2,5-thiadiazole-3,4-dicarboxylate (2). This reaction is much slower than that with potassium t-butoxide; thus after heating compound (6) with triphenylphosphine in toluene for five hours only 28% had reacted, but the yield of thiadiazole (2) based on this was high (88%). Again nucleophilic attack on S(3) is proposed as the first step in a generally similar sequence (Scheme 4), with the exocyclic sulphur atoms being abstracted by the triphenylphosphine.



Scheme 4

9 A Monosubstituted Sulphurdiimide

Finally we describe the uncovering of another novel functional group, a monosubstituted sulphurdiimide, RN=S=NH, which proves to be surprisingly stable. This arose in an attempt to prepare a benzotrithiadiazepine, like (12), from a mono- rather than a di-sulphenyl chloride which, if successful, would greatly increase the range of starting materials available to us. It was hoped that treatment of *p*-tolylsulphenyl chloride (29), for example, with bis(trimethylsilyl)-sulphurdiimide (9) would give *N*-(-*p*-tolylsulphenyl)-*N'*-(trimethylsilyl)-sulphurdiimide (30) which could then by cyclization with sulphur dichloride give the benzotrithiadiazepine (31). This cyclization is analogous to the formation of the six-membered ring of 1,3,2,4-benzodithiadiazine (32), albeit in low yield (12%), from *N*-phenyl-*N'*-(trimethylsilyl)sulphurdiimide and SCl_2.[19]

Treatment of sulphenyl chloride (29) with sulphurdiimide (9) gave the desired intermediate (30) but this could not be isolated without chromatography, and when chromatographed on silica the major product was a pale orange crystalline solid, m.p. 53—55 °C. This was slightly air-sensitive in solution but could be stored in a closed vessel for months without decomposition. Its i.r. spectrum showed a characteristic sulphurdiimide stretch at 1120 and an N–H stretch at 3280 cm^{-1},

[19] H. Koenig and R. T. Oakley, *J. Chem. Soc., Chem. Commun.*, 1983, 73.

and the ^{1}H n.m.r. spectrum showed all the *p*-tolyl signals together with a broad singlet at δ 9.7. The mass spectrum had a molecular ion at *m/z* 184 with the major fragment at $M^+ - 47$ which could represent the loss of HNS. These data would fit structure (33) with a terminal *N*–H group on the sulphurdiimide, the trimethylsilyl group having been removed on the silica column. This structure was confirmed by *X*-ray diffraction which showed that in the crystal lattice the SNSN portion is co-planar with the benzene ring and adopts a *cis,trans* conformation, as usual for sulphurdiimides (Figure 6). The C–S bond (1.77 Å) is slightly shorter than a single bond [1.80 Å in 6,7-dihydrotrithiadiazepine (15)]; coupled with the molecular planarity and the u.v. absorption at $\lambda_{max.}$ 364 nm, this indicates some delocalization in the structure, which would presumably contribute to the molecular stability observed. The molecular packing in the crystal also suggests a weak bifurcated hydrogen bond between the terminal *N*–H of one molecule and S(1) and N(2) of another.

We were surprised by the stability of this monosubstituted sulphurdiimide (33) which we expected to be very reactive, particularly by analogy with

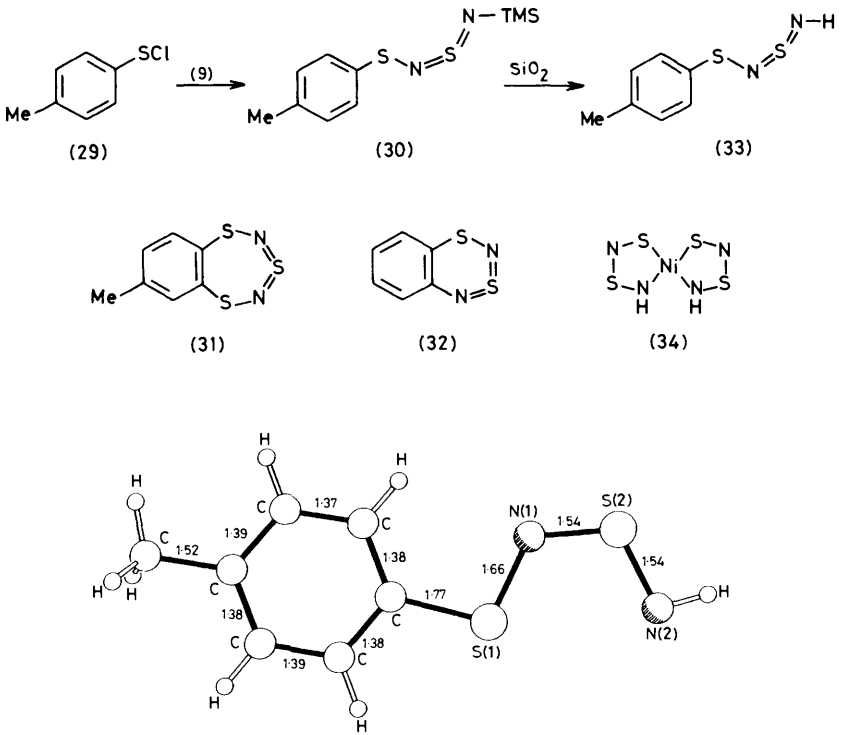


Figure 6 *The molecular structure of* (33) *showing the crystallographic bond lengths* (*in* Å) *and angles* (*in degrees*)

monophenylcarbodiimide.[20] The compound Cl–N=S=N–H has been reported as a highly explosive gas,[21] and very little is known about organic compounds of the type R–N=S=N–H; two such structures have been claimed but they are based on scant evidence. *N*-(Ethylsulphenyl)sulphurdiimide, EtS–N=S=N–H, was said to be a product of the reaction of S_4N_4 with ethylmagnesium bromide,[22] and the structure RO–S–N=S=N–H was proposed for compounds obtained from S_4N_4 and alcohols.[23] A somewhat related functionality is known as a ligand in some transition metal complexes, such as (34).[24]

In this account we have described the new trithiadiazepine and trithiatriazepine ring systems and many of their derivatives, together with other new poly(sulphur–nitrogen) structures. Many of these compounds meet our stated requirements in being stable, readily available, and structurally and chemically novel. With the high ratio of heteroatoms to carbon they stand on the border of inorganic heterocyclic chemistry and, indeed, point the way to new, wholly inorganic, rings. We have not yet achieved the aims set out at the beginning of this account but the stage is now well set for the development of some new heteroaromatic chemistry and its application to the synthesis of stable organic metals.

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[20] T. L. Gilchrist, C. W. Rees, and C. Thomas, *J. Chem. Soc., Perkin Trans. 1*, 1975, 12.
[21] W. Lidy, W. Sundermeyer, and W. Verbeek, *Z. Anorg. Allg. Chem.*, 1974, **406**, 228.
[22] The linear structure is reported without comment by I. Haiduc, 'The Chemistry of Inorganic Ring Systems', Wiley, London, 1970, p. 908, based on the work of A. Meuwsen, *Chem. Ber.*, 1931, **64**, 2301.
[23] W. Gieserich, *Diplomarbeit*, Heidelberg (1954), quoted in M. Goerhing, 'Ergebnisse und Probleme der Chemie der Schwefel-Stickstoff-Verbindungen', Akad. Verlag, Berlin, 1957.
[24] J. D. Woollins, R. Grinter, M. K. Johnson, and A. J. Thomson, *J. Chem. Soc., Dalton Trans.*, 1980, 1910.