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Electron rich 10π and 14π heteroaromatic systems

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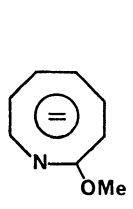
ABSTRACT

The discovery, structure, synthesis, and physical and chemical properties of some novel 10π and 14π heteroaromatic compounds are described. These are the electron-rich 1,3,5,2,4-trithiadiazepine, 1,3,5,2,4,6-trithiatriazepine, 1,3,5,2,4-benzotrithiadiazepine, and 1,3,5,7-tetrathia-2,4,6,8-tetraza-azulene.

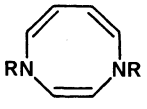
INTRODUCTION

The concept of aromaticity has been one of the most useful generalisations in heterocyclic chemistry, just as in carbocyclic chemistry. It has provided a rational and unifying framework for a wide range of experimental observations, and has stimulated much productive interaction between theory and experiment. One of the major advances in recent years has been the experimental verification of theoretical predictions about the higher π-electron aromatic systems, from [10]annulenes upwards. This development has furnished a modest number of new heteroaromatic ring systems with 10 and 14 π-electrons, though on the whole these have proved to be rather delicate structures, difficult to construct, and usually limited to one or two heteroatoms per ring. In order to sustain 10 or 14 π electrons, large, fully unsaturated rings are necessary with the associated problems of conformational mobility. Alternatively the desired number of π electrons can be achieved in smaller rings either by generating anions or by introducing more heteroatoms, which contribute two electrons to the aromatic system, leading to electron-rich, π-excessive structures.[1] However, the usefulness of the latter approach is limited by the general decrease in stability of aromatic compounds as the number of heteroatoms increases.

Notable landmarks in this area have been the demonstration of the 10π aromatic nature of 2-alkoxyazocine dianions (**1**),[2] 1,4-dihydro-1,4-diazocines (**2**),[3] the azonines (**3**),[4] and 2,7-methanoaza[10]annulene (**4**),[5] and of the 14π aromatic nature of the aza[13]annulenes, e.g. (**5**),[6,7] the dihydroazapyrene (**6**),[8] and the monocyclic aza[14]annulene (**7**).[9] The generation or isolation of such systems which are planar, or nearly so, with delocalised diatropic π-frameworks, together with some related 18π and higher rings, has been an impressive achievement. But as yet there has been relatively little exploration of their chemistry.



(1)
Paquette



(2)
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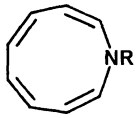
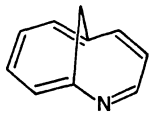
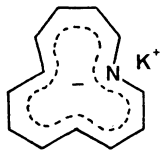


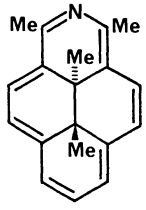
(3)
Anastassiou



(4)
Vogel



(5)
Schröder
Anastassiou



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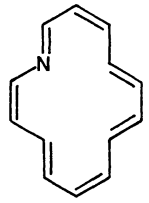
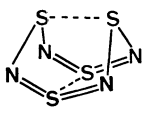
Boekelheide



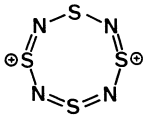
(7)
Schröder

POLY (SULPHUR-NITROGEN) SYSTEMS

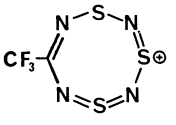
We now wish to describe the chemistry of some new 10π and 14π aromatic compounds which are much richer in heteroatoms (sulphur and nitrogen), are very stable, and are readily available. By virtue of the incorporation of tetravalent sulphur, in sulphurdiimide units, 10 electrons can be sustained over 7-membered rings, thus generating electron-rich aromatic frameworks. Only two similar systems have been reported, the 1,3,5,2,4,6,8-trithiatetrazocine cation (**10**), a minor product of the reaction of trichlorotrithiatriazine with trifluoroacetonitrile,[10] and the 1,5,2,4,6,8-dithiatetrazocine (**11**) formed in low yield from benzamidine and sulphur dichloride.[11] X-Ray diffraction showed that the 8-membered rings in (**10**) and (**11**) are planar, with bond lengths intermediate between single and double bonds. They are isoelectronic with the planar, delocalised 10π dication (**9**)[12] formed by oxidation of tetrasulphur tetranitride (**8**).



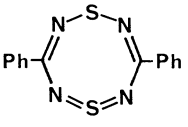
(8) 12π



(9) 10π
Gillespie



(10) 10π
Mews

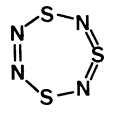


(11) 10π
Woodward

Compound (**11**) is remarkably stable thermally, decomposing only slowly at 220°C; it is also resistant to oxidation by m-chloroperbenzoic acid and is unreactive to stoichiometric amounts of nucleophiles such as benzylamine and butyllithium, though it is hydrolysed to benzamidine with hydrochloric acid or potassium hydroxide. Attempts to prepare the parent compound (**11**, H for Ph) by the same method were unsuccessful, but the reaction of dimethylguanidine with SCl_2 gave the corresponding bis(dimethylamino) derivative which had a very different u.v. spectrum from that of the diphenyl compound. X-Ray diffraction showed that in the bis(dimethylamino) compound the heterocyclic ring was no longer planar but folded about a long $S_{(1)}—S_{(5)}$ bond (2.43 Å), similar to that found in S_4N_4.[11] The very different conformations of these two dithiatetrazocines suggest that there is a delicate energy balance which controls the geometry of the ring. Molecular orbital calculations[13,14] suggest that an increase in electron density in the planar dithiatetrazocine ring would result in population of the strongly antibonding LUMO, thus destabilising the planar structure; folding of the molecule enables the antibonding electron density to be relocated into a weak but stabilising transannular disulphide bond.

10π ELECTRON AROMATIC SYSTEMS

Another way in which the 12π S_4N_4 molecule could be formally converted into a 10π system would be by removal of one sulphur atom, to give trisulphur tetranitride (**12**). Although (**12**) is as yet unknown it could, if planar, be a stable 10π aromatic compound. Successive replacement of the two adjacent nitrogen atoms in (**12**) by trigonal carbon would then produce the potentially 10π ring systems, 1,3,5,2,4,6-trithiatriazepine (**13**) and 1,3,5,2,4-trithiadiazepine (**14**). We have now synthesised both of these and find that they are indeed remarkably stable aromatic systems.



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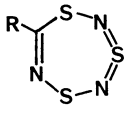

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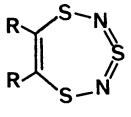
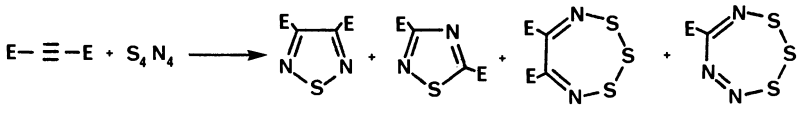
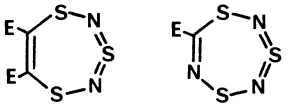


(14)

The first derivatives of these ring systems were discovered in a reinvestigation[15] of an intriguing reaction between S_4N_4 and dimethyl acetylenedicarboxylate (DMAD) in boiling toluene which had been reported[16] to give four products. These were dimethyl 1,2,5-thiadiazole-3,4-dicarboxylate (**15**) (60%), the isomeric dimethyl 1,2,4-thiadiazole-3,5-dicarboxylate (**16**) (8%), and two less polar products to which structures (**17**) and (**18**) were assigned, in 5% and 6% yields respectively. The formation of compounds (**16**) and (**18**) posed



(15) (16) (17) (18)



(19) (20)

a fascinating mechanistic problem since they must arise by cleavage of DMAD at the triple bond; this was not commented upon in the original report.[16] Furthermore the two trisulphide structures (**17**) and (**18**) proposed for the less polar products did not accord with the thermal stability and spectroscopic properties reported for them. Our reinvestigation of this reaction gave the same four products, and led to the formulation of (**17**) as dimethyl 1,3,5,2,4-trithiadiazepine-6,7-dicarboxylate (**19**) and of (**18**) as methyl 1,3,5,2,4,6-trithiatriazepine-7-carboxylate (**20**), these structures being proved by X-ray diffraction analysis (Fig. 1 and 2).[15] Compounds (**19**) and (**20**) fully repaid our interest since the heterocyclic rings were found to be planar, with maximum deviations from their least squares planes of only 0.009 Å for $N_{(6)}$ in (**20**) and 0.019 Å for $C_{(6)}$ in (**19**). Furthermore each ring has 10 electrons available to form a delocalised π system. Initial evidence for extensive π delocalisation in (**19**) and (**20**) was provided by their measured bond

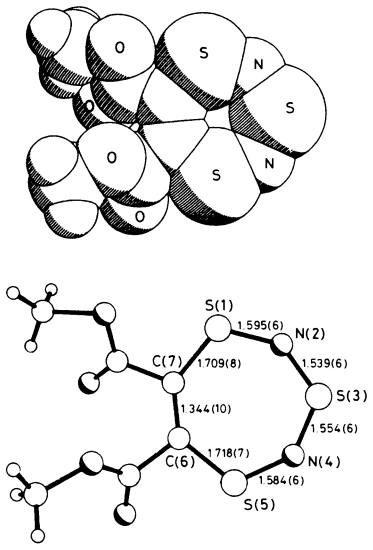


Fig. 1

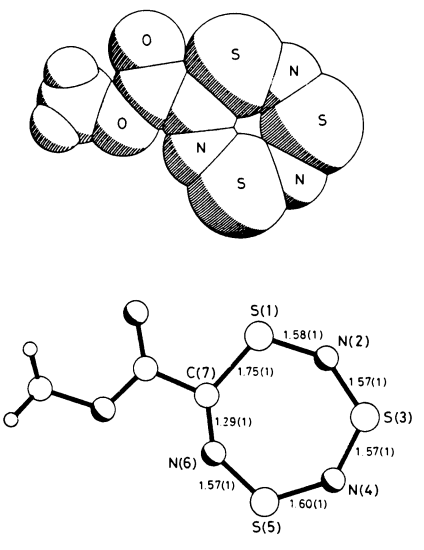


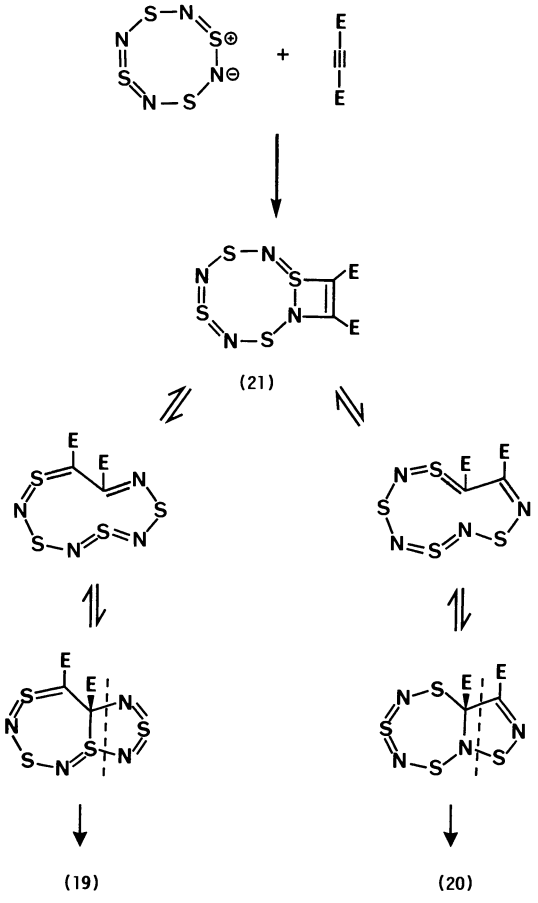
Fig. 2

Space-filling and skeletal representations of the molecular structures of (**19**) and (**20**) showing the bond lengths for the 7-membered rings.

lengths which are intermediate between single and double bond lengths, by their u.v. spectra which exhibit long wavelength absorption at 334 and 332 nm respectively, characteristic of aromatic π to π^* transitions, and by their thermal and chemical stability. All of these properties were highly reminiscent of those of Woodward's dithiatetrazocine (**11**).[11]

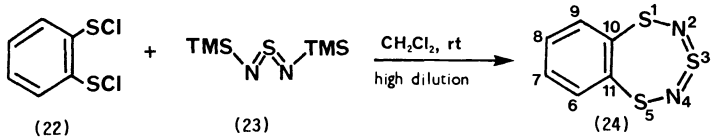
Compounds (**19**) and (**20**) showed no decomposition on boiling in xylene for 24 hours; in boiling decalin (190°C) the trithiadiazepine (**19**) was decomposed in 6 hours, whilst some of the trithiatriazepine (**20**) still remained after 33 hours. Compound (**20**) was also more stable to irradiation at 300 nm than (**19**). Both compounds were strikingly inert towards m-chloroperbenzoic acid and triphenylphosphine, with (**20**) again being the more resistant. The greater stability of (**20**) is understandable in view of the importance of dipolar (S^+-N^-) contributions to these ring structures (see later), since (**20**) has an extra nitrogen site for the negative charge. It is interesting to note that the 7-membered heterocyclic compounds are less polar than the thiadiazoles, in spite of having extra heteroatoms.

Various mechanisms, based on cycloaddition, rearrangement, and fragmentation processes, are possible for the formation of the four heterocyclic products isolated from reaction of S_4N_4 with DMAD. One of the most economical involves initial [2+2] dipolar cycloaddition to give (**21**), followed by ring opening; this is exactly analogous to the reaction of sulphimides with DMAD.[17] The 10-membered ring could then collapse to the 7-5 systems shown which, by retro-cycloadditions, lead to the observed 7-membered ring compounds. The same intermediate (**21**) could also yield the thiadiazoles (**15**) and (**16**) by molecular rearrangements, though the 1,2,5-thiadiazole (**15**) could well result from direct addition of DMAD across $N_{(1)}$—$N_{(3)}$.



Trithiadiazepine

With 10π electrons delocalised over 7 atoms the rings in (**19**) and (**20**) are electron-rich and are presumably stabilised by the ester groups. It was thus of interest to determine the stability of the parent compounds and to see if their chemical properties generally are comparable to those of simpler aromatic species. In view of the low yields and general lack of predictability of the S_4N_4 reactions, rational syntheses were clearly required, and we turned our attention first to the trithiadiazepine ring system (**14**), devising a synthesis for the benzo derivative (**24**).[18] This was based on the reaction of arylsulphenyl chlorides with bis(trimethylsilyl)sulphurdiimide (**23**).[19] Dilute solutions in dichloromethane of benzene-1,2-bis(sulphenyl chloride) (**22**), prepared quantitatively from the dithiol and chlorine, and of the sulphurdiiimide (**23**), were added slowly and synchronously from mechanically driven syringes to a large volume of dichloromethane under nitrogen. This gave 1,3,5,2,4-benzotrithiadiazepine (**24**) as stable, bright yellow crystals (50%). The aromatic nature of (**24**) was supported by its spectral properties [λ_{max} (EtOH) 252 (log ε 4.25), 292 (4.02), 365 nm (3.63); δ_H (250 MHz, $CDCl_3$) AA'BB' multiplet (18 lines detected) δ_A 7.78, δ_B



7.29, $J_{AA'}$ 0.54, $J_{AB'}$ 1.17, $J_{BB'}$ 6.80, J_{AB} 8.70 Hz; δ_C ($CDCl_3$) 121.8, 123.0, 147.2] and confirmed by X-ray diffraction which showed the molecule to be planar with delocalised ring bonds (Fig. 3).[20] This synthetic procedure could not be extended directly to the monocyclic compound because of the instability of Z-ethene-1,2-dithiol and the associated problems of its chlorination. However, ethane-1,2-dithiol was readily and quantitatively converted into the bis(sulphenyl chloride) (**25**) with chlorine (-20°C) or sulphuryl chloride (20°) in tetrachloromethane. Treatment of (**25**) with sulphurdiimide (**23**) in CH_2Cl_2, as above, gave the orange dihydro derivative (**26**) (20%), which was readily dehydrogenated with dichlorodicyanobenzoquinone (DDQ) in boiling dioxane to give the desired 1,3,5,2,4-trithiadiazepine (**27**) (70%) as colourless volatile crystals. In view of the low yield of the cyclisation

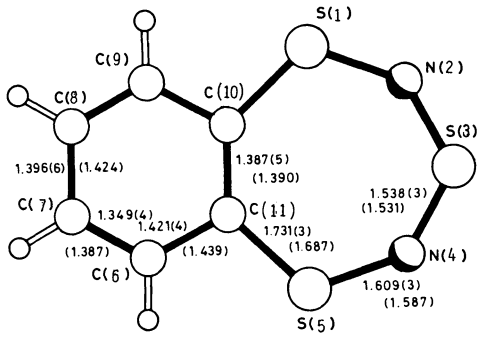


Fig. 3. The molecular structure of (**24**) showing the crystallographic bond lengths with those derived from MNDO calculations given in parentheses. The valence angles in the 7-membered ring at S(3), N(2), S(1), and C(10) are 122.4(2), 138.3(2), 116.9(1), and 135.5(1)° respectively.

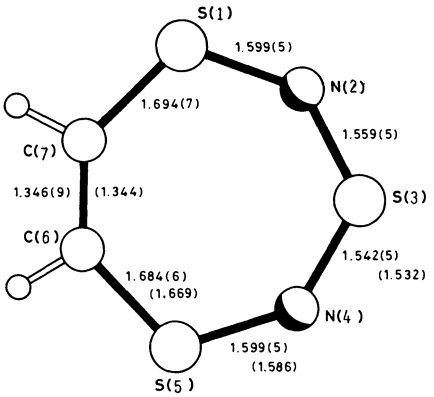
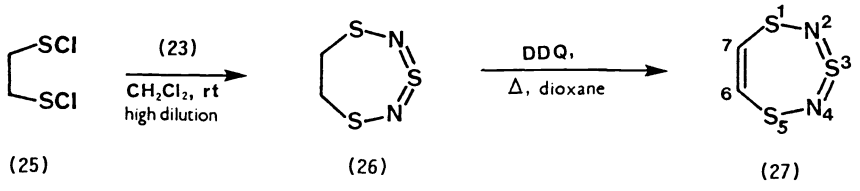
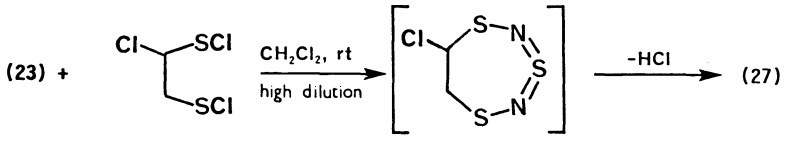


Fig. 4. The molecular structure of (**27**) showing the crystallographic bond lengths with those derived from MNDO calculations given in parentheses. The valence angles starting at S(3) and going clockwise round the ring are: 122.8(3), 138.3(3), 115.0(3), 135.6(5), 135.6(5), 115.7(3), and 136.8(3)° respectively.

step, this procedure was modified by allowing chlorination of ethanedithiol to proceed to the trichloro stage (Cl_2 in CCl_4 at 0°C). Treatment of the trichloride (**28**) with sulphurdiimide (**23**) as before gave the parent trithiadiazepine (**27**), by spontaneous loss of hydrogen chloride, in 30% overall yield from ethanedithiol. The spectroscopic properties of (**27**) [λ_{max} (EtOH) 224 (log ε 3.76), 330 nm (3.64); δ_H (90 MHz, $CDCl_3$), 7.70 (s); δ_C ($CDCl_3$) 127.8] and its X-ray diffraction analysis (Fig. 4) support a fully delocalised structure; the molecule is planar, symmetrical, and has the intermediate bond lengths expected for an aromatic structure. Its chemical properties are equally in accord with this.[18]



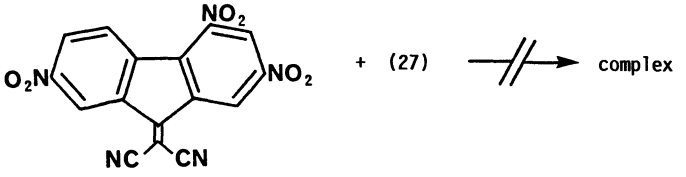
(25) (26) (27)



(28)

Trithiadiazepine (**27**) is thermally stable, being unchanged in boiling 1,2-dichlorobenzene (180°C) for over 2 days. It is thus even more stable than its diester (**19**) and clearly this new, electron-rich system is in no need of electron withdrawing groups for its stability. Compound (**27**) is however rapidly decomposed on irradiation at 300 nm in petrol. It is inert towards protic and Lewis acids (acetic acid, aqueous hydrochloric acid, $AlCl_3$, BF_3) and towards triethylamine and benzylamine, but it is rapidly destroyed by aqueous sodium hydroxide. It is only very slowly consumed by triphenylphosphine in boiling toluene or by m-chloroperbenzoic acid in boiling dichloromethane.

Also in good agreement with its aromatic nature and with the absence of sulphurdiimide reactivity, trithiadiazepine (**27**) shows no tendency to take part in cycloaddition reactions with a range of electron-rich and electron-poor 2π and 4π components. Somewhat surprisingly it also shows no tendency to form charge transfer complexes with picric acid, tetracyanoethylene, or 2,4,7-trinitro-9-fluorenylidenemalononitrile (**29**).

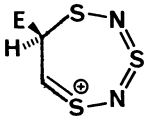


(29)

Trithiadiazepine (**27**) undergoes some standard electrophilic aromatic substitution reactions, irreversibly at carbon, presumably via the well stabilised tetrahedral intermediate (**30**) with the positive charge delocalised over all three sulphur atoms. Thus it forms the 6-bromo compound (**31a**) (88%) with 1 equivalent of N-bromosuccinimide in acetonitrile at room temperature, and the 6,7-dibromo compound (77%) with excess of the same reagent; both are pale cream crystalline solids. It forms bright yellow crystals of the 6-nitro compound (**31b**) (90%) with copper (II) nitrate trihydrate in acetic anhydride at 0°C, and the deep

yellow 6,7-dinitro compound (**32**) (54%) with excess of nitronium tetrafluoroborate in acetonitrile at 10°C. Thus the second nitro group is introduced, adjacent to the first, surprisingly readily. X-Ray diffraction of the nitro compounds shows that in the crystal lattice a single nitro group is almost coplanar with the ring, but when two nitro groups are present these are equally tilted, making angles of 45° with the ring plane. Attempts to acetylate and formylate trithiadiazepine (**27**) have so far failed, possibly because of coordination of the Friedel-Crafts catalysts to the many heteroatoms.

Treatment of (**27**) with thallium (III) trifluoroacetate in refluxing acetonitrile gave the bis(trifluoroacetoxy)thallium derivative (**31c**) which, without isolation, was converted into the pale yellow 6-iodo compound (**31d**) (80%) with aqueous potassium iodide, into the 6-cyano



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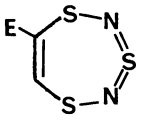
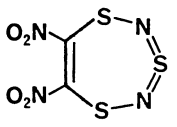


(31)

a; E = Br
b; E = NO_2
c; E = $Tl(OCOCF_3)_2$
d; E = I
e; E = CN
f; E = CO_2Me

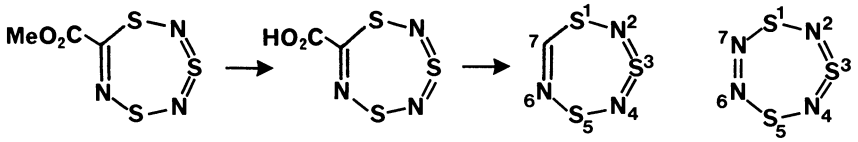


(32)

compound (**31e**) (85%) with copper (I) cyanide,[21] and into methyl trithiadiazepine-6-carboxylate (**31f**) (70%) with carbon monoxide and methanol in the presence of palladium chloride, lithium chloride, and magnesium oxide.[22]

Trithiatriazepine

We saw above that reaction of S_4N_4 with DMAD gave methyl 1,3,5,2,4,6-trithiatriazepine-7-carboxylate (**20**) in low yield (6%) , and a possible mechanism was proposed for this intriguing transformation. We have not yet synthesised this ring system independently but we have increased the yield of (**20**) in the S_4N_4 reaction to 14%. Ester (**20**) can be converted quantitatively into the acid (**33**) by careful heating to 80°C in 5 M hydrochloric acid; and this acid decarboxylates surprisingly readily. Simply boiling in dioxane for 2 h gives stable, highly volatile colourless plates of the parent ring system (**34**) in almost quantitative yield. The acid (**33**) possibly exists as, or in equilibrium with, the zwitterionic form which would presumably decarboxylate readily, like pyridine-2-carboxylic acid.



(20) (33) (34) (12)

The spectral properties of trithiatriazepine (**34**) indicate a 10π delocalised aromatic structure, very like that of trithiadiazepine (**27**). It has a π to π* transition at λ_{max} 327 (log ε 3.54); the ring proton resonates at δ 9.0 and the carbon atom at δ 145, indicative of a diamagnetic ring current. Extensive disorder in the crystal has precluded an X-ray diffraction analysis of the parent compound (**34**) but we assume that the ring is planar, by analogy with ester (**20**) and from the general similarity of their spectral properties.

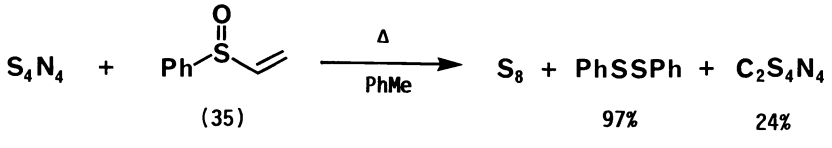
Trithiatriazepine (**34**) has the same high thermal stability as trithiadiazepine (**27**) and the ester (**20**), surviving over 20 hours of heating in 1,2-dichlorobenzene at 180°C. It appears to be slightly less stable kinetically and decomposes slowly in air at room temperature. This may indicate a greater susceptibility to nucleophilic attack at sulphur and perhaps also at the imine-type carbon. The high thermal stability of trithiatriazepine (**34**) and its derivatives, equal to or greater than that of the analogous trithiadiazepines, suggests that the fully inorganic trithiatetrazepine (**12**) might be thermodynamically stable.

14π ELECTRON AROMATIC SYSTEMS

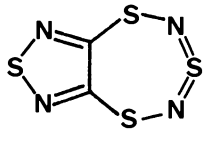
The synthesis and aromaticity of 1,3,5,2,4-benzotrithiadiazepine (**24**) have already been described. Its structure was confirmed by X-ray diffraction; it is planar with a maximum deviation from the least squares plane of 0.032 Å for $S_{(1)}/S_{(5)}$, and has a crystallographic two-fold axis passing through $S_{(3)}$ and bisecting the benzo ring. Although formally a 14π electron system, the measured bond lengths of (**24**) provide evidence of some degree of bond alternation in both rings. The C—S bonds (1.73 Å) are longer than the same bonds in the monocyclic compound (**27**) (1.69 Å) but considerably shorter than the corresponding (single) bonds in the dihydro compound (**26**) (1.80 Å). A pronounced bond alternation is seen in the carbocyclic ring with bond lengths of 1.39, 1.42, 1.35, and 1.40 Å. In agreement with the consequent destabilisation of the aromatic system, benzo compound (**24**) is much more reactive than (**27**) towards triphenylphosphine and m-chloroperbenzoic acid.

Molecules of the benzo compound adopt a parallel stacking geometry in the crystal, the 7-membered ring of one directly overlying the 6-membered ring of another and vice versa. The interplanar separation is quite small at 3.54 Å.

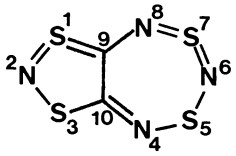
Another, more unusual, 14π system was discovered as follows. S_4N_4 is known to react with alkynes to give predominantly 1,2,5-thiadiazoles, as we saw above with DMAD. These are derived, formally at least, by cycloaddition across $N_{(1)}—N_{(3)}$. The trithiadiazepines could similarly be formed by $S_{(1)}—S_{(5)}$ cycloaddition. In contrast, the stable cycloadducts which are isolated from reaction of S_4N_4 with strained alkenes, such as norbornadiene, result from $S_{(1)}—S_{(3)}$ cycloaddition.[23] In view of this dichotomy we wondered about the reaction of S_4N_4 with "acetylene equivalents"[24] like phenyl vinyl sulphoxide (**35**); would they yield alkene-type products at the alkyne oxidation level, or might they provide a direct route to the parent trithiadiazepine (**27**) which we now had in hand? The reaction of S_4N_4 with acetylene itself had given no significant products.[25] We therefore investigated the



(35)



(36)



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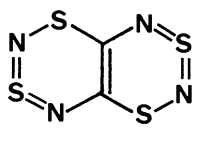

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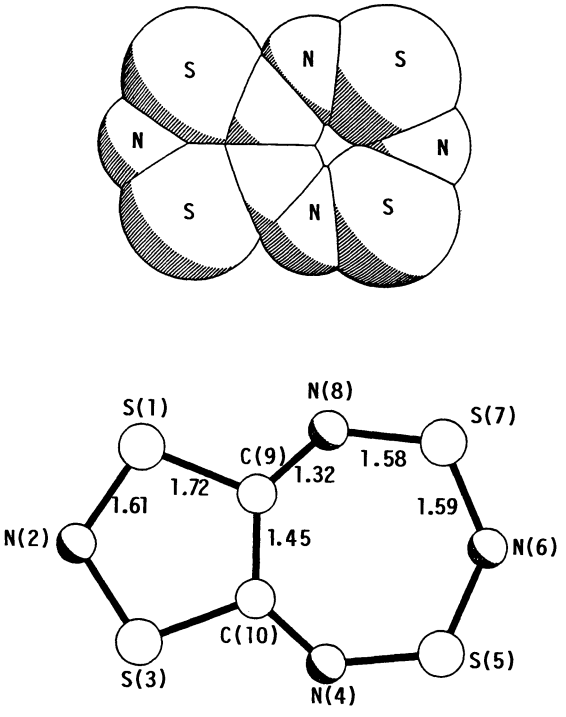
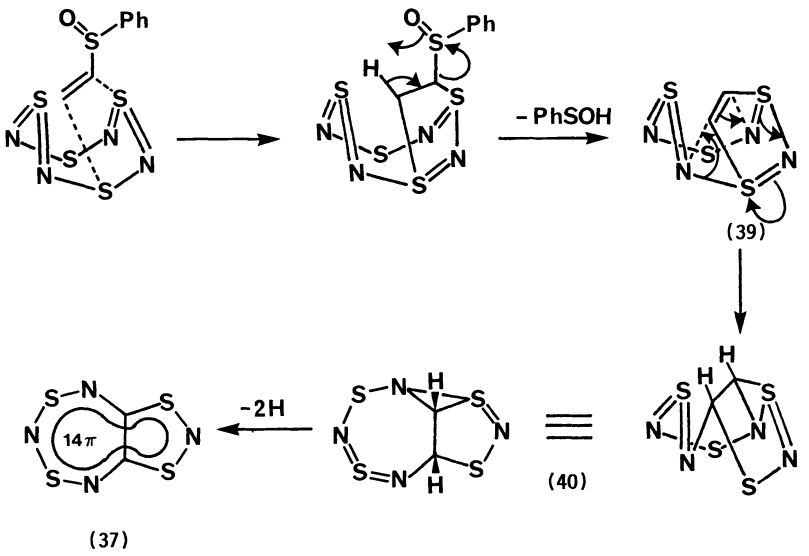


Fig. 5. Space-filling and skeletal representations of the molecular structure of (**37**) showing bond lengths. Angles in the 5-membered ring at S(1), N(2), S(3), C(10) and C(9) are 102°, 114°, 102°, 111° and 111° and in the 7-membered ring at N(4), S(5), N(6), S(7), N(8), C(9) and C(10) are 132°, 119°, 134°, 119°, 132°, 133° and 132° respectively.

reaction of S_4N_4 with phenyl vinyl sulphoxide (**35**) which had proved a good acetylene equivalent in dipolar cycloadditions.[26] When S_4N_4 (2 equiv) was heated with (**35**) (1 equiv) in toluene for 6 hours no trithiadiazepine (**27**) was produced, however; the main products were sulphur, diphenyldisulphide in very high yield, and an entirely new product, $C_2N_4S_4$, as green-black lustrous metallic crystals, formed in modest yield. Acetylene has thus become incorporated into the S_4N_4 structure but with its hydrogen atoms removed; however S_4N_4 is known to be an effective dehydrogenating agent in some instances.[25,27] The thermal stability, deep colour, and u.v. spectrum [λ_{max} 492 (log ε 3.31)] of this product suggested a delocalised aromatic structure and, given its molecular formula, it seemed likely that the alternation of S and N atoms in S_4N_4 had been retained. Thus the 12π cage structure of S_4N_4 could have incorporated a C-C π bond to become a planar 14π system, such as (**36**), (**37**), or (**38**). X-Ray diffraction proved it to be 1,3,5,7-tetrathia-2,4,6,8-tetraza-azulene (**37**) (Fig. 5). The molecules are accurately planar and symmetrical about the $N_{(2)}—N_{(6)}$ axis, with bond delocalisation. All the S—N bonds are about 1.6 Å long, supporting a completely delocalised 14π system. The molecules pack in two arrangements of nearly parallel planes with the smallest interplanar separation being only 3.26 Å. There is a considerable degree of interaction between the molecules in the unit cell.



A possible mechanism for the formation of (**37**) is shown. 1,3-Dipolar cycloaddition of the alkene across $S_{(1)}—S_{(3)}$ followed by thermal elimination of phenylsulphenic acid gives the bicyclic structure (**39**) in which the S_4N_4 cage has been prised open and the 5-membered ring of the final product (**37**) formed. The 7-membered ring of (**37**) can then be formed by the electrocyclic process shown (arrows in **39**). Finally the tricyclic species (**40**) so produced is dehydrogenated, possibly by more S_4N_4, with concomitant aromatising valence isomerism to give (**37**). Surprisingly (**37**), like trithiadiazepine (**27**) and benzotrithiadiazepine (**24**), does not form charge transfer complexes with electron acceptor molecules such as picric acid or trinitrofluorenylidenemalononitrile (**29**).

MOLECULAR ORBITAL CALCULATIONS

MNDO[28] and ab initio[29] molecular orbital calculations have been carried out for the new heterocyclic compounds (**24**), (**27**), (**34**), and (**37**), as well as for the hypothetical molecules (**12**), (**36**), and (**38**), and these are in good general agreement with the experimental observations.

10π systems

Both MNDO and ab initio calculations reveal a distinct pattern of π energy levels characteristic of aromatic systems for trithiadiazepine (**27**), trithiatriazepine (**34**), and trithiatetrazepine (**12**). The MNDO calculated π orbital energies (Fig. 6) show that as the carbon atoms of trithiadiazepine (**27**) are successively replaced by nitrogen atoms the π orbitals of the 10π system become lower in energy. The $4b_2$ orbital achieves the greatest stabilisation, having an energy of -13.12 eV in trithiadiazepine (**27**), falling to -15.63 eV in trithiatetrazepine (**12**).

MNDO π bond orders (Table 1) also support extensive delocalisation in these three molecules. As expected, the 6-7, 2-3, and 3-4 bonds have the most π character, but the remaining four ring bonds have significant π character also, with MNDO π bond orders varying from 0.249 to 0.325.

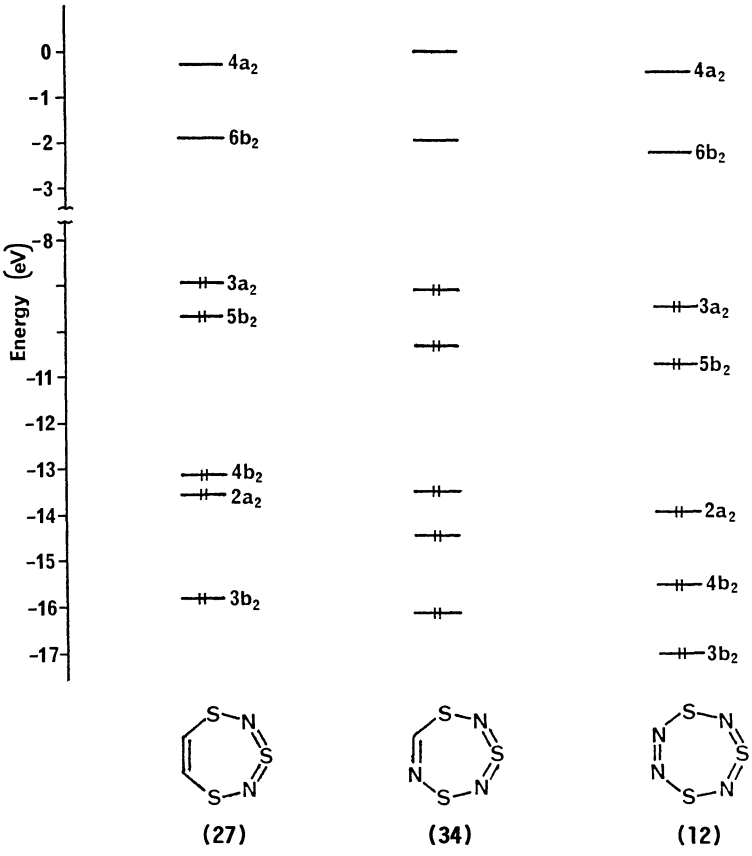


Fig. 6. The MNDO calculated π orbital energies for (**27**), (**34**), and (**12**).

Ab initio and MNDO calculated net atomic charges and dipole moments for (**27**), (**34**), and (**12**) show similar trends. The MNDO results are presented in Table 2. As expected $S_{(3)}$ is the most electropositive centre in each molecule, and thus the most susceptible to nucleophilic attack. In trithiatriazepine (**34**) $N_{(6)}$ effectively withdraws most of the excess electron density from $C_{(7)}$, such that the net atomic charge on carbon falls from -0.217 in trithiadiazepine (**27**) to -0.038 in trithiatriazepine (**34**).

Table 1. MNDO calculated π bond orders of trithiadiazepine (**27**), trithiatriazepine (**34**), and trithiatetrazepine (**12**).

Bond	(27)	(34)	(12)
1-2	0.279	0.249	0.280
2-3	0.597	0.584	0.608
3-4	0.597	0.624	0.608
4-5	0.279	0.301	0.280
5-6	0.307	0.292	0.324
6-7	0.898	0.884	0.880
7-1	0.307	0.325	0.324

Table 2. MNDO calculated net atomic charges and dipole moments(debye).

Atom No.	(27)	(34)	(12)
1	0.324	0.265	0.367
2	-0.591	-0.611	-0.658
3	0.781	0.825	0.861
4	-0.591	-0.656	-0.658
5	0.324	0.474	0.367
6	-0.217	-0.373	-0.140
7	-0.217	-0.038	-0.140
dipole moment	1.524	0.472	1.448

The calculated dipole moment of trithiatriazepine (**34**) (0.472) is considerably less than that of trithiadiazepine (**27**) (1.524), presumably a consequence of its extra nitrogen atom introducing an additional dipole in the molecule in opposition to the net dipole in trithiadiazepine. This accords with the observed trend in the R_f values of these two compounds, trithiatriazepine (**34**) being less polar. However, replacement of the last carbon atom in the 7-membered ring by nitrogen does not further reduce the net dipole, and trithiatetrazepine (**12**) is predicted to have a similar dipole moment (1.448) to trithiadiazepine (**27**) (1.524).

A comparison of ab initio STO-3G and STO-3G* calculated charges for trithiadiazepine (Table 3) shows that the inclusion of d-functions (3G*) produces a significant decrease in the net atomic charges. This suggests that sulphur d-orbitals do make some contribution to the bonding in this 10π system, although dipolar structures are also thought to be important. STO-3G* overlap populations indicate that the largest roles are played by the $S_{(3)}$ $3d_{xy}$ and the $S_{(1)}/S_{(5)}$ $3d_{xz}$ orbitals.

Table 3. Ab initio net atomic charges and dipole moment of trithiadiazepine (**27**).

Atom	STO-3G	STO-3G*
$S_{(1)}/S_{(5)}$	0.334	0.188
$N_{(2)}/N_{(4)}$	-0.560	-0.319
$S_{(3)}$	0.681	0.358
$C_{(6)}/C_{(7)}$	-0.189	-0.114
dipole moment	1.665	1.229

Table 4. MNDO heats of formation (ΔH_f) in kcal/mol and ab initio (3-21G*) RHF total energies ($-\varepsilon_{total}$) in au.

	(**36**)	(**37**)	(**38**)
ΔH_f	170.45	188.21	201.02
$-\varepsilon_{total}$	1874.3713	1874.3448	1874.2835

Table 5. MNDO calculated HOMO and LUMO energies (-ε) of (**36**), (**37**), and (**38**), in eV.

	(**36**)	(**37**)	(**38**)
$-\varepsilon_{LUMO}$	2.33	3.24	3.83
$-\varepsilon_{HOMO}$	9.12	8.25	7.81

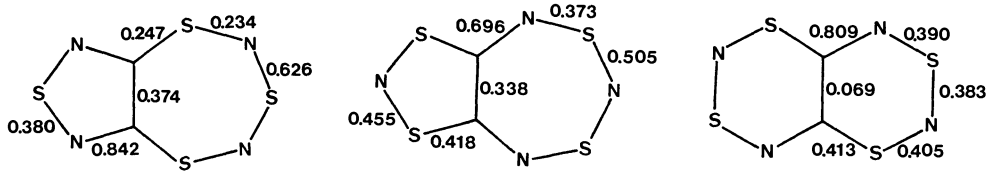
14π systems

Our calculations show that, like trithiadiazepine (**27**), the benzo derivative (**24**) has distinct π energy elevels, supporting its 14π aromatic structure. Lengthening of the C-S bonds in benzotrithiadiazepine (**24**), to 1.73 Å, relative to those in the parent compound (**27**) (1.69 Å), is accompanied by a decrease in the MNDO π bond order to 0.26 in (**24**) from 0.31 in trithiadiazepine (**27**). The pronounced bond alternation in the carbocyclic ring is also reflected in the MNDO π bond orders with values of 0.70, 0.54, 0.77, 0.55, 0.77, and 0.54 starting at $C_{(10)}$ and moving clockwise around the benzo ring.

We now consider 1,3,5,7-tetrathia-2,4,6,8-tetraza-azulene (**37**) and its (unknown) isomers (**36**) and (**38**). MNDO heats of formation and ab initio (3-21G*) RHF total energies for these three isomers (Table 4) lead us to predict that the molecule (**36**) should be the most thermodynamically stable of the three structures. The compound which we have prepared, (**37**), is of intermediate stability; its formation in the reaction of S_4N_4 and phenyl vinyl sulphoxide is presumably favoured by mechanistic factors.

The calculations show that all three molecules have the π-electronic structures expected for 14π aromatic systems; their MNDO HOMO and LUMO energies are indicated in Table 5.

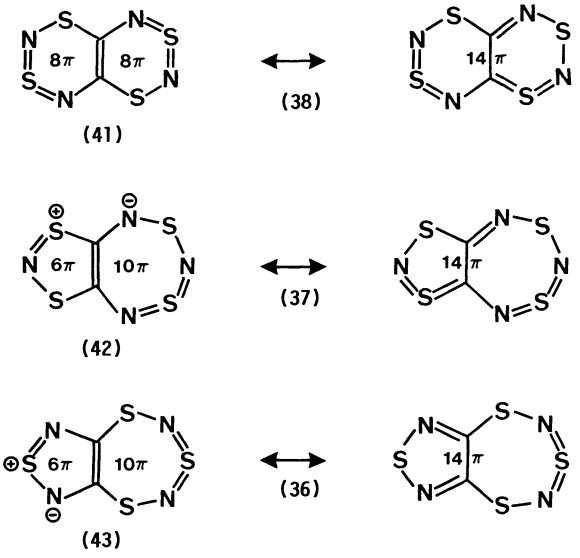
2,4,6,8-Tetrathia-1,3,5,7-tetraza-azulene (**36**) is predicted to have the most tightly bound valence electrons, with a HOMO energy of -9.12 eV.



(36) (37) (38)

Fig. 7. The MNDO calculated π bond orders for (**36**), (**37**), and (**38**).

The MNDO π bond orders (Fig. 7) of these molecules support the existence of delocalised π systems. It is interesting that in the 6-6 isomer (**38**) the central C-C bond has a very low π bond order (0.069) suggesting that resonance forms such as (**41**) with a central double bond make very little contribution to the structure of the molecule. Thus aromatic electron delocalisation around the 14π periphery is preferred over the alternative arrangement of two 8π, formally antiaromatic, rings. The 5-7 systems (**36**) and (**37**), on the other hand, have significant π character in their C-C bonds, indicating that resonance forms such as (**42**) and (**43**), with 6π/10π fused rings, do make important contributions to their structures.



In this Chapter we have described some new classes of heterocyclic compounds, on the borderline of organic and inorganic chemistry. Their novel structures and properties suggest many extensions, some in the direction of useful applications, which we are continuing to explore.

ACKNOWLEDGEMENT

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