Tetrathiatetraza-azulene

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Dedicated with warm regards to Professor Gurnos Jones, a long-time friend and colleague, on the occasion of his 70th birthday

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Abstract

Tetrasulfur tetranitride 1 reacts with phenyl vinyl sulfoxide 3 or sulfone or phenyl vinyl sulfonate to give the planar delocalised 14 P electron aromatic system $1^{\lambda 4\delta 2}$, 3,5,7 $^{\lambda 4\delta 2}$-tetrathia-2,4,6,8-tetraza-azulene 4 as stable dark metallic lustrous crystals. All the sulfur and nitrogen atoms of S_4N_4 have been retained and a C-C P bond incorporated, the 12 P cage structure of S_4N_4 being converted into the planar bicyclic system. A mechanism is proposed for this transformation. The ability of the vinyl component to act as an acetylene equivalent and to suffer dehydrogenation to give the aromatic product appear to be necessary for this type of reaction since more highly substituted sulfoxides lead only to decomposition. Optimum conditions for the reaction of phenyl vinyl sulfoxide with S_4N_4 (3.6 equiv.) in refluxing xylene for 7.5 h give the tetrathiatetraza-azulene 4 in 35%.

Keywords: Tetrathiatetraza-azulene, tetrasulfur tetranitide, phenyl vinyl sulfoxide, phenyl vinyl sulfone, phenyl vinyl sulfonate

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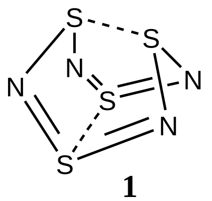
Introduction

The rich and varied inorganic chemistry of tetrasulfur tetranitride, S_4N_4 1 has prompted several studies of its reactions with organic substrates as potential sources of sulfur-nitrogen heterocyclic compounds. However, the scope of its cycloaddition reactions with organic dipolarophiles has not yet been fully explored and the mechanisms of these reactions are poorly understood. For example, S_4N_4 appears to react quite differently with alkenes and with alkynes; it reacts with electron deficient alkynes but not with electron deficient alkenes, and in general it only reacts with alkenes when the double bond is highly strained as in norbornadiene or *trans*-cyclo-octene.[1] The alkyne reactions give predominantly 1,2,5-thiadiazoles[2] together with minor amounts of trithiadiazepines and trithiatriazepines;[2] the major initial process thus appears to be alkyne cycloaddition across N(2)-N(4). The strained alkenes give cycloadducts in high yield which result exclusively from cycloaddition across S(1)-S(3) and S(5)-S(7).[1] This dichotomy led us to consider the reaction of S_4N_4 with alkenes which are acetylene equivalents.[3] These might give alkene-type products at the alkyne oxidation level, or the initial adducts might rearrange to give alkyne-type products. The latter could provide a direct route to the parent trithiadiazepine 2, which is not available from the reaction of S_4N_4 with acetylene itself,[4] but which we have synthesized independently.[5] We therefore investigated the reaction of S_4N_4 with phenyl vinyl sulfoxide 3 which is an effective acetylene equivalent in Diels-Alder[6] and 1,3-dipolar cycloaddition reactions.[7]

Results and Discussion

In a preliminary publication[8] we reported that when S_4N_4 (2 equiv.) was heated with the sulfoxide 3 (1 equiv.) in toluene for 6 h, no trithiadiazepine 2 was formed, the main products were sulfur, diphenyl disulfide (97%), and an entirely new and unexpected green-black crystalline solid with a metallic lustre, mp 142 ^oC (24%), to which the molecular formula $C_2N_4S_4$ was assigned from elemental analysis and the mass spectrum. Its ^{13}C NMR spectrum is a singlet at $\delta 161.8$; the solution i.r. is very simple with only four absorptions above 600 cm^{-1} at 1488, 895, 885, and 625 cm^{-1}, and the u.v. spectrum has long wavelength maxima at 322 (log ε3.35) and 492 nm (3.31), suggesting a highly symmetrical and delocalised structure.



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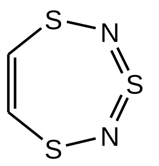

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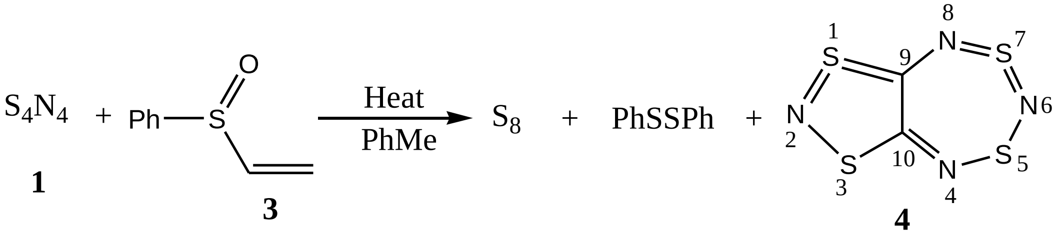

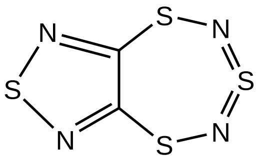

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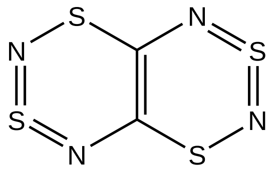

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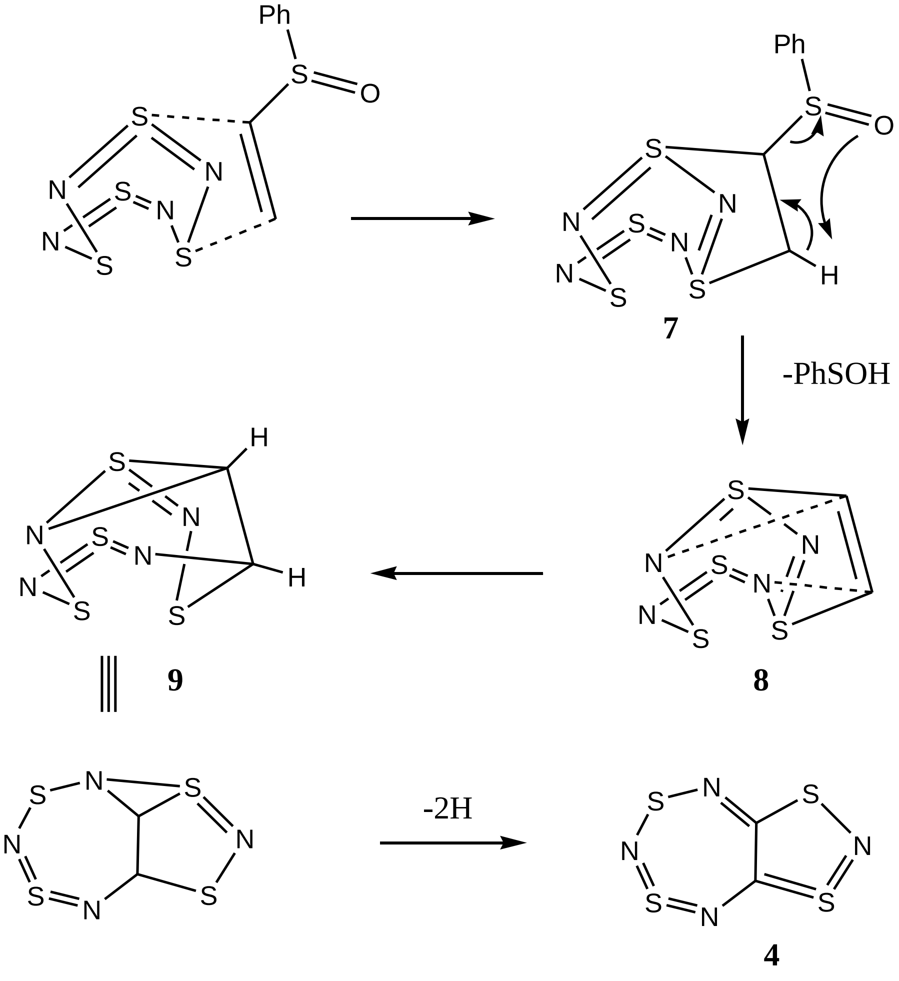
Acetylene has thus become incorporated into the S_4N_4 structure but with its hydrogen atoms removed; however S_4N_4 is known to be able to act as a dehydrogenating agent.[4-9] The thermal stability and spectroscopic properties of the new product suggested an aromatic structure in which the alternating arrangement of sulfur and nitrogen atoms of S_4N_4 had been retained; three possible structures are 4, 5, or 6. A single crystal X-ray analysis showed the product to be $1^{\lambda4\delta2}$,3,5,$7^{\lambda4\delta2}$-tetrathia-2,4,6,8-tetraza-azulene 4. The X-ray analysis showed that compound 4 has two crystallographicaly independent molecules, each of C_{2U}symmetry. They are both planar (the maximum deviation from the least squares plane being 0.027 Å in one case and 0.07 Å in the other) with all the S-N bond lengths close to 1.60 Å, indicating complete delocalisation of the electrons. The S-N bonds are similar in length to those in S_4N_4 (1.62 Å).[1] The molecules pack into two continuous overlapping stacks, each comprising one of the two types of molecule. In one stack adjacent molecules are rotated by 180 with respect to each other, whilst in the other they are rotated by 80 to each other.[8]

The highly delocalised nature of the azulene 4 is further supported by its thermal stability; it remains substantially intact after 7 h at reflux in toluene. However, it is significantly decomposed at reflux in toluene in the presence of either S_4N_4 (20% recovery after 7 h) or phenyl vinyl sulfoxide (42% recovery after 7h), and this presumably contributes to the relatively low yield.

Somewhat surprisingly, the electron rich tetrathiatetraza-azulene 4, does not form charge transfer complexes with electron acceptors like picric acid or 2,4,7-trinitro-9-fluorenylidenemalononitrile.

A possible mechanism for the conversion of S_4N_4 into $C_2N_4S_4$ 4 is shown in Scheme 1. 1.3-Dipolar cycloaddition of the alkene across S(1)-S(3) to give 7 followed by thermal elimination of phenylsulfenic acid gives the bicyclic structure 8 in which the S_4N_4 cage is opened up and the 5-membered ring of the final product 4 generated. The 7-membered ring of 4 can then be formed by the electrocyclic process shown (arrows in 8) and the tricyclic species 9 so produced is dehydrogenated with concomitant aromatising valence isomerisation to give 4. The high yield of diphenyl disulfide formed is uncommon for reactions of phenyl vinyl sulfoxide as an acetylene equivalent, and it may be a direct or indirect consequence of the dehydrogenation process. Either benzenesulfenic acid could perform the dehydrogenation to give diphenyl disulfide and water or, as suggested above, S_4N_4 could be the dehydrogenating agent being itself reduced to $S_4N_4H_4$[1] with this hydride then reducing benzenesulfenic acid to the disulfide. However, the presence of other dehydrogenating agents (manganese dioxide, dichlorodicyanobenzoquinone) did not increase the yield of tetrathiatetraza-azulene 4.



Scheme 1

We hoped to gain some evidence for the formation of the initial cycloadduct 7 by replacing sulfoxide 3 by phenyl vinyl sulfone, which is expected to undergo a similar initial cycloaddition but not an analogous cycloelimination of benzenesulfinic acid. Reaction of this sulfone with S_4N_4 did not give the desired intermediate however but did give a very small amount (4%) of tetrathiatetraza-azulene 4. Presumably there is some elimination of benzenesulfinic acid, even under these mild conditions, indicating the strong driving force for the formation of 4 in which the 12P cage structure of S_4N_4 has incorporated a C-CP bond to become a planar 14P system. Increasing the oxidation level further, we found that phenyl vinylsulfonate, $CH_2=CH-SO_3Ph$,[10] reacted with S_4N_4 at reflux in xylene to give the same product 4 in 16% yield.

We now present the results of further investigations into the reaction of S_4N_4 with phenyl vinyl sulfoxide with a view to improving the yield of tetrathiatetraza-azulene and to gaining a deeper insight into the reaction mechnism, together with attempts to extend the reaction to other ethenyl sulfoxides.

In an attempt to isolate any intermediates that may be formed during the reaction, the lower boiling solvents acetonitrile and THF were substituted for toluene but no reaction was observed in either case.

The reaction was investigated using phenyl vinyl sulfoxide and S_4N_4 (2 equiv.) in boiling xylene (140 ^{o}C) and bromobenzene (156 ^{o}C) at different reaction times. The results, given in Table 1, show that the best yield is obtained in xylene after 7 h at reflux. In water no reaction was observed, other than some decomposition of S_4N_4. At 20 ^{o}C, S_4N_4 is about twice as soluble in dioxan (1.9 g/100 mL) as in benzene (1.0 g/100 mL), suggesting that the reaction might proceed faster in the former solvent than in xylene and bromobenzene. However, when an equimolar mixture of S_4N_4 and phenyl vinyl sulfoxide was heated at reflux in dioxan (bp 98 ^{o}C), a yield of only 5% of the tetrathiatetraza-azulene 4 was obtained.

Having found that with two equiv. of S_4N_4 the best yield of the tetrathiatetraza-azulene 4 was obtained in refluxing xylene after 7.5 h, our attention turned to whether the yield could be improved by using other relative amounts of the two reactants. A series of 7.5 h reactions was performed with xylene as the solvent but varying the amount of S_4N_4. The results are collected in Table 2, and show that a reasonable yield of 35% (the best we obtained) is possible when 3.6 equiv. of S_4N_4 are used.

The addition of Lewis acids to the reactions of S_4N_4 sometimes leads to increased rates and higher yields.[11] A catalytic amount of titanium(IV) chloride was therefore added to the reaction of phenyl vinyl sulfoxide with S_4N_4 (two equiv.) in refluxing xylene. The product $C_2S_4N_4$ 4 did indeed form more quickly than without the catalyst; it was apparent on the TLC plate after 0.5 h rather than the normal 1-1.5 h. However, the yield of 4 isolated was only 5%. A mixture of phenyl vinyl sulfoxide, S_4N_4 (one equiv.) and a large excess of silica gel was heated at reflux in toluene for 23 h. All the S_4N_4 had been consumed but only 3% of 4 could be isolated.

Table 1. The reaction of phenyl vinyl sulfoxide 3 with S_4N_4 (two equiv.) in refluxing xylene or bromobenzene

Solvent	Reaction Time (h)	Yield of (4) (%)	Recovered S_4N_4 (%)
Xylene 140 C	2	12	34
-	4	18	14
-	7.5	22	25
-	15	13	13
Bromobenzene156 C	3	16	6
-	6	13	5

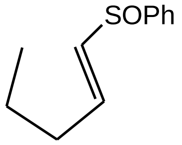
Having examined in detail the reaction of phenyl vinyl sulfoxide with S_4N_4, we looked next at the reactions of more highly substituted vinyl sulfoxides. The aims were to isolate other products which may give evidence of the mechanism of the reaction and to establish the generality of the reaction of ethenyl sulfoxides. In particular, we hoped that by replacing vinylic hydrogen atoms by alkyl groups some of the intermediates on the reaction pathway would be stable enough to be isolated.

Table 2. The reaction of phenyl vinyl sulfoxide 3 with various amounts of S_4N_4 in refluxing xylene for 7.5 h

Number of equivalents of S_4N_4	Yield of (4) (%)	Recovered S_4N_4 (%)
5.0	22	12
3.6	35	18
3.0	30	-
2.0	22	25
0.75	6a	0
0.5	4a	0

1-Cyclopentenyl phenyl sulfoxide 10 and 1-cyclohexenyl phenyl sulfoxide 11 were prepared from cyclopentanone and cyclohexanone respectively and thiophenol.[12] 3-Methyl-2-buten-2-yl phenyl sulfoxide 12 was prepared from 3-methyl-2-butanone and thiophenol in the presence of phosphorus pentoxide to give the alkenyl sulfide,[13] which was readily oxidised with MCPBA in DCM at 0, rather than hydrogen peroxide, to give the sulfoxide (91%). *E*-2-Nitroethenyl phenyl sulfoxide 13,[14] 2,3-bis(phenylsulfinyl)-1,3-butadiene 14[15] and 1,2-propadienyl phenyl sulfoxide 15[16] were prepared by literature methods. Cyclopropyl phenyl sulfide[17] was oxidised to the sulfoxide 16[18] by MCPBA in DCM. Attempted oxidation of benzo[*b*]thiophene and 3-methylbenzo[*b*]thiophene with MCPBA to the sulfoxides gave the 1,1-dioxides 17 (89%) and 18 (49%) respectively. The reactions of these sulfoxides and sulfones are summarised in Table 3.

Table 3. Reactions of sulfoxides and sulfones with S_4N_4



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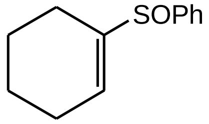

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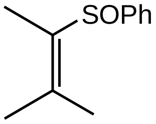

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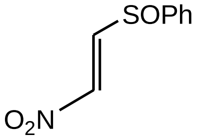

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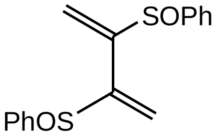

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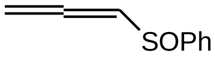

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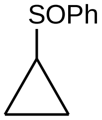

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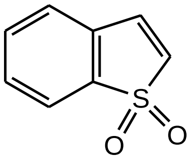

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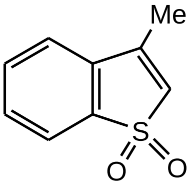

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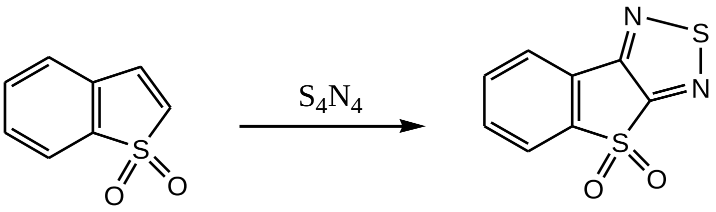
Reactant	Conditions	Result
10	toluene, reflux, 48 h neat, 40 °C, 5 weeks	some decomp. of S_4N_4 some decomp. of S_4N_4
11	toluene, reflux, 5 h xylene, reflux, 6 h	some (38%) decomp. of S_4N_4 complete decomp. of S_4N_4 to S_8 (92%)
12	toluene, reflux, 7 h xylene, reflux, 6 h	no reaction decomp. of S_4N_4 to S_8 (68%)
13	toluene, reflux, 6 h DCM, 25 °C, 23 h	S_8 (32%), 4 (7%), S_4N_4 (21%) no reaction
14	toluene, reflux, 18 h xylene, reflux, 7.5 h	no reaction decomp. to S_8 and PhSSPh
15	toluene, reflux, 3 h	decomp. of sulphoxide
16	xylene, reflux, 6 h	some decomp. of S_4N_4 to S_8
17	toluene, reflux, 23 h	thiadiazole 19(17%)
18	xylene, reflux, 6 h	no reaction

Of the compounds examined, only two gave products which included any of the sulfur and nitrogen atoms of S_4N_4. The first was nitroethenyl phenyl sulfoxide 13 which gave a low yield of tetrathiatetraza-azulene 4; this product probably arises from the loss not only of benzensulfenic acid, but also of nitrous acid (HNO_2). The second was benzo[*b*]thiophene 1,1-dioxide 17 which gave the fused 1,2,5-thiadiazole derivative 19. Oxidation of the sulfur in benzo[*b*]thiophene disrupts the aromaticity and the double bond in the heterocyclic ring becomes more like an alkene. This makes it more reactive, though S_4N_4 is not normally reactive enough to add to unstrained, electron-deficient double bonds. Benzo[*b*]thiophene itself did not react with S_4N_4 in refluxing xylene after 8 h.



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It was apparent that in reactions where the S_4N_4 decomposed, it did so more rapidly than would have been the case in the absence of an ethenyl sulfoxide. For example, S_4N_4 has a half-life of about 8 h in refluxing xylene, while in the reaction of 3-methyl-2-buten-2-yl phenyl sulfoxide 12 with S_4N_4 in refluxing xylene the S_4N_4 had completely decomposed to sulfur within 6 h. Under the same conditions, S_4N_4 (25%) was recovered from the reaction of phenyl vinyl sulfoxide in refluxing xylene after 7.5 h. 1-Cyclopentenyl and 1-cyclohexenyl phenyl sulfoxides also increased the rate at which S_4N_4 decomposed. These differences may be the result of the ability of S_4N_4 to act as a dehydrogenation agent [4-9] since 3 methyl-2-buten-2-yl phenyl sulfoxide and the two cycloalkenyl sulfoxides have allylic hydrogen atoms which can be abstracted, whilst phenyl vinyl sulfoxide does not.

In view of the failure to isolate any products from the reactions of the majority of the vinyl sulfoxides investigated, 1-cyclopentenyl and 1-cyclohexenyl phenyl sulfoxides were tested as potential substituted acetylene equivalents, extending the original idea of Paquette.[6] The two sulfoxides were each treated with anthracene in refluxing xylene, but no reaction was observed even after 24 h.

Experimental Section

General Procedures. Light petroleum refers to the fraction of petroleum ether boiling between 40 °C and 60 °C and was distilled before use. Benzene, toluene, xylene and ethyl ether were dried by standing over sodium wire for several days. Tetrahydrofuran was dried by distillation

from potassium metal under nitrogen. Dichloromethane and tetrachloromethane were dried by distillation from phosporus pentoxide and stored over 4 Å molecule sieves. Tetrasulfur tetranitride was prepared by the method of Jolly[19] and, following the safety recommendations of Banister,[20] the crude product was stored for at least seven days before purification by recrystallisation from benzene. Flash Chromatography refers to the technique described by Still[21] using medium pressure (hand-bellows), and Dry-column Flash Chromatography to the technique described by Harwood.[22] The silica gel employed in both cases was Merck Kieselgel 60 h and the sample mixture was applied to the column preadsorbed onto silica. Preparative thin layer chromatography was carried out using plates coated with silica gel (Merck Kieselgel GF_{254}).
Commercial aluminium-backed thin-layer chromatography plates (Merck Kieselgel 60 F_{254}) were used throughout to check reactions and column eluants. After elution the plates were observed under u.v. light at 254 and 366 nm and/or developed in iodine vapour.
Ultra-violet/visible spectra were recorded using a Pye-Unicam SP800B spectometer. Infra-red spectra were recorded on a Perkin-Elmer 1710 spectrometer.

^{1}H-Nuclear magnetic resonance spectra were recorded on the following machines: Varian EM360 at 60 MHz; Perkin-Elmer R32 or Jeol FX90Q at 90 MHz; Jeol GSX270 at 270 MHz. ^{13}C-Spectra were recorded on a Jeol GSX270 spectrometer at 69 MHz. Chemical shifts are given in parts per million downfield of tetramethylsilane.

Low resolution mass spectra and accurate mass measurements were recorded on an AE1 MS12 mass spectrometer or a VG Micromass 7070B mass spectrometer using electron impact ionisation.

$1^{\lambda 4\delta 2}3,5,7^{\lambda 4\delta 2}$-Tetrathia-2,4,6,8-tetraza-azulene (4). A mixture of phenyl vinyl sulfoxide 3 (143 mg, 0.94 mmol), S_4N_4 (631 mg, 3.42 mmol), and xylene (10 ml) was heated at reflux for 7.5 h. The residue after evaporation *in vacuo* was separated by flash chromatography (10 g silica gel, 1.25% gradient from light petroleum to DCM, 10 mL fractions). Elution with 1.25-3.75% DCM gave diphenyl disulfide (41 mg, 40%); with 5-8.75% DCM gave sulfur, with 10-12.5% DCM gave the title compound 4 (69 mg, 35%) as black/green metallic crystals, mp 141-142 °C; and with 20-21.25% DCM gave S_4N_4 (116 mg, 18%). Compound 4, recrystallised from DCM, had mp 142-143 °C (Found: C, 11.7; N, 26.8. $C_2N_4S_4$ requires C, 11.55; N, 26.9%); λ_{max} (EtOH) 213 (log e 3.54), 230 (3.53), 322 (3.35), and 492 nm (3.31); ν_{max}, ($CHCl_3$) 1488s, 895, 885, and 625 $cm^{-1}$$\nu_{max}$ (KBr) 475s, 460, 310s, and 305s, cm^{-1}; $^{\delta}{}_{C}$ (C_6D_6) 161.8; *m*/*z* 208 (*M*, 100%), 162 (41), 110 (11), 78 (74), 64 (11), and 46 (67).
Reaction of S_4N_4 with phenyl vinyl sulfone. S_4N_4 (398 mg, 2.16 mmol) and phenyl vinyl sulfone (341 mg, 2.03 mmol) were heated at reflux in dry toluene (10 mL) under nitrogen for 7.5 h. The solvent was evaporated and the residue chromatographed on silica to give sulfur (110 mg), tetrathiatetraza-azulene 4 (18 mg, 4%), S_4N_4 (55 mg, 14%), and phenyl vinyl sulfone (112 mg, 33%).

Reaction of S_4N_4 with phenyl vinylsulfonate. A mixture of phenyl vinylsulfonate (183 mg, 1.0 mmol) and S_4N_4 (366 mg, 2.0 mmol) in xylene (10 mL) was heated at reflux for 7 h. The solvent was removed *in vacuo* and the residue was purified by flash chromatography to give sulfur (151 mg) and tetrathiatetraza-azulene 4 (34 mg, 16%).

Thermolysis of tetrathiatetraza-azulene (4). Compound 4 (33 mg, 0.16 mmol) was heated at reflux in dry toluene (10 mL) under nitrogen for 7 h; no significant decomposition was evident by t.l.c. The solvent was evaporated and the residue chromatographed on silica; elution with 20% DCM in petrol gave the tetrathiatetraza-azulene 4 (31 mg, 93% recovery).

Thermolysis of S_4N_4. S_4N_4 (86 mg, 0.47 mmol) was heated at reflux in dry toluene (15 mL) under nitrogen for 7 h, after which time t.l.c. indicated slight decomposition. The solvent was evaporated and the residue chromatographed on silica; elution with 25% DCM in petrol gave S_4N_4 (70 mg, 82% recovery).

Treatment of tetrathiatetraza-azulene (4) with S_4N_4. Tetrathiatetraza-azulene 4 (45 mg, 0.22 mmol) and S_4N_4 (42 mg, 0.23 mmol) were heated at reflux in dry toluene (5 mL) under nitrogen for 7 h. The solvent was evaporated and the residue chromatographed on silica. Elution with petrol gave sulfur (23 mg, 86% based on decomposed S_4N_4 and $C_2S_4N_4$). Elution with 20% DCM in petrol gave tetrathiatetraza-azulene 4 (13 mg, 29% recovery) and elution with 25% dichloromethane in petrol gave S_4N_4 (32 mg, 77% recovery).

Treatment of tetrathiatetraza-azulene (4) with phenyl vinyl sulfoxide 3. Tetrathiatetraza-azulene 4 (45 mg, 0.22 mmol) and phenyl vinyl sulfoxide 3 (36 mg, 0.24 mmol) were heated at reflux in dry toluene (5 mL) under nitrogen for 7 h. The solvent was evaporated and the residue chromatographed on silica. Elution with petrol gave sulfur (28 mg) and with 20% DCM in petrol gave tetrathiatetraza-azulene 4 (19 mg, 42% recovery).

Benzo[*b*]thiophene S,S-dioxide (17). A mixture of benzo[*b*]thiophene (1.34 g, 10 mmol) and MCPBA (80%; 4.32 g, 20 mmol) in DCM (20 mL) was stirred at 0-5 °C for 18 h. The mixture was filtered, diluted with DCM, and washed with saturated sodium bicarbonate (2 x 25 mL), and water (30 mL), then dried ($MgSO_4$) and evaporated. The residue was purified by flash chromatography to give compound 17 (1.49 g, 89%) as a crystalline solid, mp 142-143 °C (lit.[23] 142 °C); $_{vmax}$ ($CHCl_3$) 3 028, 1 306s, 1 220, 1 196, 1 155s, 781, 766, 762, 736, 683, 626, 553, and 525 cm$^{-1\delta}$$_{max}$ (90 MHz; $CDCl_3$) 7.1-7.7 (4H, m), 7.12 (1H, d, *J* 7.5 Hz), and 6.68 (1H, d, *J* 7.5 Hz).

3-Methylbenzo[*b*]thiophene S,S-dioxide (18). A mixture of 3-methylbenzo[*b*]-thiophene (1.34 g, 9.0 mmol) and MCPBA (80%; 3.90 g, 18.0 mmol) in DCM (20 mL) was stirred at 0-4 °C for 15 h, then filtered. The filtrate was washed with saturated sodium bicarbonate (3 x 15 mL), and water (15 ml), dried ($MgSO_4$) and evaporated to give compound 18 (0.86 g, 49%) as crystals, mp 144-145 °C (lit.[23] 143-144 °C).

[1,2,5]Thiadiazolo[3,4-*b*]benzo[*b*]thiophene 8,8-dioxide (19). A mixture of benzo[*b*]thiophene S,S-dioxide 17 (166 mg, 1.0 mmol) and S_4N_4 (184 mg, 1.0 mmol) in xylene (10 mL) was heated at reflux for 10.5 h. The residue after evaporation was purified by flash chromatography to give sulfur and the *title compound*19 (38 mg, 17%) as crystals, mp 150 °C (Found: C, 42.7; H, 1.7; N, 12.5. $C_8H_4N_2O_2S_2$ requires C, 42.85; H, 1.8; N, 12.5%); ν_{max} (CCl_4) 3 074w, 1 592, 1 526s, 1 500s, 1 437, 1 317, 1 299, 1 244, 1 105s, and 871 cm^{-1}; *m/z* 244 (M, 100%), 166 (M - N_2S, 15), 160 (M - SO_2, 19), 148 (M -C_6H_4, 10), 134 (M - $C_6H_4SO_2$, 27), and 64 (SO_2, 16).

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