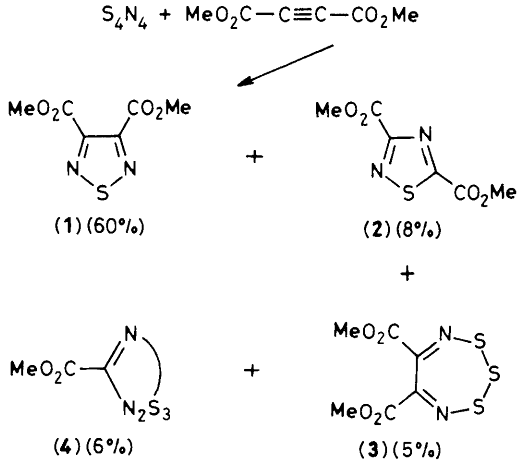
# 1,3,5,2,4-Trithiadiazepines and 1,3,5,2,4,6-Trithiatriazepines, New 10π Heteroaromatic Systems

**Stephen T. A. K. Daley, Charles W. Rees, and David J. Williams**
*Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY, U.K.*

The products of reaction of $S_4N_4$ with dimethyl acetylenedicarboxylate include the trithiadiazepine (**5**) and the trithiatriazepine (**6**) whose planar structures, determined by *X*-ray diffraction, represent two new stable 10π electron aromatic ring systems; these structures correct previous assignments.

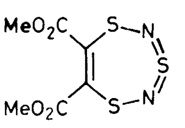
The reaction of tetrasulphur tetranitride, $S_4N_4$, with dimethyl acetylenedicarboxylate (DMAD) in boiling toluene for 6 hours was reported to give the four products shown, with yields, in Scheme 1; only a partial structure was assigned to compound (**4**) and no mechanisms for the formation of the products were proposed.[1] Whilst the thiadiazole structures (**1**) and (**2**) seemed reasonable, the formation and stability of (**3**) and (**4**) were surprising, and the structural evidence presented was not convincing. We therefore repeated the reaction, and obtained four products in yields similar to those reported.



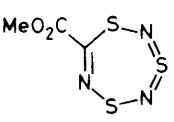
Scheme 1

We agree with structures (**1**) and (**2**), but the spectroscopic data do not support structures (**3**) and (**4**). For example, the u.v. spectra [$\lambda_{max}$(EtOH)274 (log ε 4.26), 334 nm (3.56), and 266 (log ε 4.09), 332 nm (3.40) respectively] indicate highly delocalised structures, the i.r. spectra do not show C=N absorptions, and the mass spectral fragmentation pattern suggests the presence of C–S rather than C–N bonds in (**3**), whilst (**4**) shows no loss of $N_2$ nor of S.

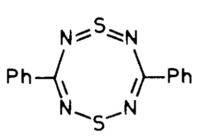
The structures of products previously assumed to be (**3**) and (**4**) were solved by *X*-ray diffraction analysis and found to be dimethyl 1,3$\lambda^4\delta^2$,5,2,4-trithiadiazepine-6,7-dicarboxylate (**5**) and methyl 1,3$\lambda^4\delta^2$,5,2,4,6-trithiatriazepine-7-carboxylate (**6**)



(**5**)



(**6**)



(**7**)

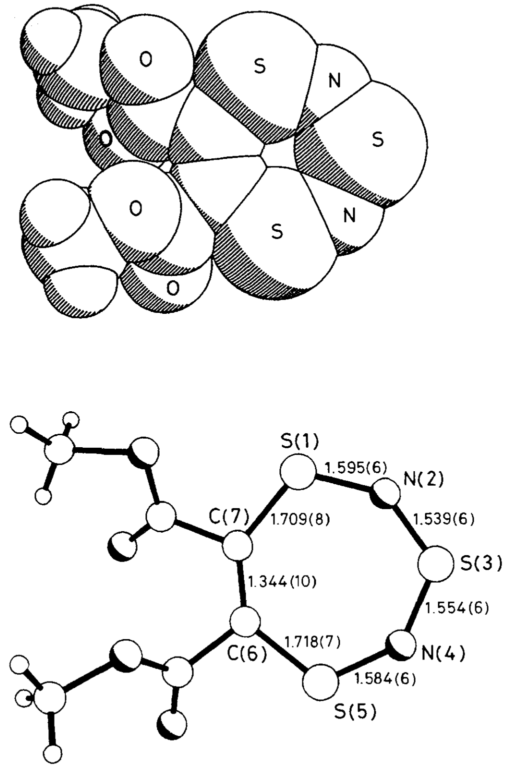


**Figure 1.** Skeletal and space-filling representations of the molecular structure of (**5**) showing the bond lengths for the 7-membered ring.

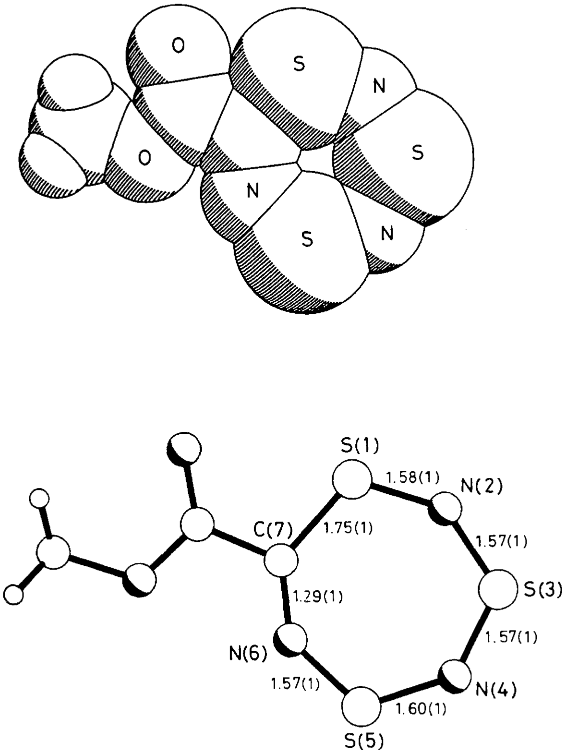


**Figure 2.** Skeletal and space-filling representations of the molecular structure of (**6**) showing the bond lengths for the 7-membered ring.

respectively (Figures 1 and 2).[†] Both rings are planar with maximum deviations from the least squares planes of 0.019 Å [C(6) in (**5**)] and 0.009 Å [N(6) in (**6**)]. They can, by a count of the delocalisable electrons,[2] be considered as 10π aromatic systems. This view is strongly supported by the measured bond lengths, the u.v. spectra, the thermal and chemical stability of the rings, and by MO calculations. The new rings are thus isoelectronic with the cycloheptatrienyl trianion,[3] and are comparable to the trisulphur trinitride anion $S_3N_3^-$,[4] the thiotrithiazyl cation, $S_4N_3^+$,[5] and Woodward's dithiatetrazocine (**7**),[6] all of which are 10π aromatic systems. Indeed the thermal and chemical stability of compounds (**5**), (**6**), and (**7**), are very similar.

The S–N bond lengths in (**5**) and (**6**) (1.54—1.60 Å) (Figures 1 and 2) are all similar and close to those of (**7**) (1.56—1.57 Å), and are nearer to double (1.55 Å) than to single (1.67 Å) bonds. The ring C–C and C–S bonds in (**5**) are very similar in length to the corresponding bonds in thiophene. The planarity of these systems results in greatly enlarged angles at the nitrogen atoms, similar to those in (**7**). The angles are 140 and 138° at N(2) and N(4) in (**5**), and 141, 135, and 140° at N(2), N(4), and N(6) respectively in (**6**).

Compounds (**5**) and (**6**), like (**7**), showed no decomposition on boiling in xylene (138 °C) for 24 hours; in boiling decalin (190 °C) the trithiadiazepine (**5**) was decomposed in 5.5 hours, whilst some of the trithiatriazepine (**6**) still remained after 33 hours. Compound (**6**) was also more stable than (**5**) to irradiation at 300 nm in light petroleum (b.p. 60—80 °C). Compounds (**5**) and (**6**) were strikingly inert to *m*-chloroperbenzoic acid and to triphenylphosphine. Neither reacted significantly with the peracid in boiling dichloromethane; (**5**) was slowly decomposed by triphenylphosphine in boiling toluene, whilst (**6**) survived these conditions.

The greater stability of the trithiatriazepine (**6**) is understandable since dipolar structures will undoubtedly make important contributions to these structures and in (**6**) an extra nitrogen site is available for negative charge. Preliminary RHF MNDO and *ab initio* SCF MO calculations[7] on the unsubstituted ring systems predicted that they would be very similar, planar [10]annulenes with bond lengths and angles in good agreement with the experimental values. The charge distributions show the importance of dipolar structures, though d orbital contributions are significant, and reflect the greater contributions of the structure with negative charge on position 6 when this is occupied by nitrogen.

The formation of compounds (**1**), (**2**), (**5**), and (**6**) from $S_4N_4$ and DMAD can be rationalised by a combination of cycloaddition, rearrangement, and ring cleavage reactions, which for (**2**) and (**6**) involve cleavage of the DMAD triple bond.

Rational syntheses and further chemistry of the trithiadiazepines and trithiatriazepines are under investigation.

---

[†] *Crystal Data:* (**5**), $C_6H_6N_2O_4S_3$, monoclinic, $a$ = 19.676(3), $b$ = 5.798(1), $c$ = 18.646(5) Å, $\beta$ = 94.17(2)°, $U$ = 2122 Å$^3$, space group $C2/c$, $Z$ = 8, $M$ = 266.3, $D_c$ = 1.67 g cm$^{-3}$. (**6**), $C_3H_3N_3O_2S_3$, monoclinic, $a$ = 3.816(2), $b$ = 14.682(9), $c$ = 6.725(6) Å, $\beta$ = 93.43(6)°, $U$ = 376 Å$^3$, space group $Pn$, $Z$ = 2, $M$ = 209.3, $D_c$ = 1.86 g cm$^{-3}$. Data for both compounds were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-$K_\alpha$ radiation and using ω scans. Both structures were solved by direct methods and refined anisotropically to give $R$ values of 0.067 for (**5**) (1224 independent observed reflections $\theta \leqslant 55°$) and 0.067 for (**6**) (588 observed reflections $\theta \leqslant 58°$). The accuracy of these structures was limited by disorder of the ester groups in (**5**) and the poor crystal quality of (**6**). The atomic co-ordinates for this work are available on request from the Director of Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

We thank the S.E.R.C., Esso Chemicals Ltd, and Dr. T. Colclough for support, and Dr. H. S. Rzepa for the MO calculations and valuable discussion.

*Received, 14th September 1983; Com. 1225*

## References

1 S. Mataka, K. Takahashi, Y. Yamada, and M. Tashiro, *J. Heterocycl. Chem.*, 1979, **16**, 1009.
2 H. G. Heal, 'The Inorganic Heterocyclic Chemistry of Sulfur, Nitrogen and Phosphorus,' Academic Press, London, 1980, p. 159.
3 J. J. Bahl, R. B. Bates, W. A. Beavers, and C. R. Launer, *J. Am. Chem. Soc.*, 1977, **99**, 6126.
4 J. Bojes, T. Chivers, W. G. Laidlaw, and M. Trsic, *J. Am. Chem. Soc.*, 1979, **101**, 4517.
5 P. Friedman, *Inorg. Chem.*, 1969, **8**, 692.
6 I. Ernest, W. Holick, G. Rihs, D. Schomburg, G. Shoham, D. Wenkert, and R. B. Woodward, *J. Am. Chem. Soc.*, 1981, **103**, 1540.
7 Dr. H. S. Rzepa, Department of Chemistry, Imperial College of Science and Technology; personal communication.