Electronic and Crystallographic Structures of Trithiadiazepines

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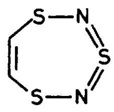
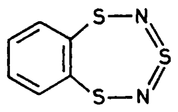
1,$3\lambda^4\delta^2$,5,2,4-Trithiadiazepine (1) and its benzo derivative (2) have planar delocalised 10π and 14π aromatic structures, respectively; in the dihydro compound (3) the five heteroatoms are co-planar, with the approximately *cis* and *trans* periplanar methylene protons rapidly interconverting.

An *X*-ray analysis of dimethyl 1,3,5,2,4-trithiadiazepine-6,7-dicarboxylate revealed a planar geometry for the heterocyclic ring.[1] The parent trithiadiazepine (**1**) and its benzo (**2**) and dihydro (**3**) derivatives have been synthesised[2] and their *X*-ray crystallographic structures are now reported† together with the results of *ab initio*[3a] and MNDO[3b] calculations and the photoelectron spectra of (**1**) and (**2**).

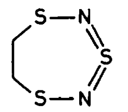
Trithiadiazepines (**1**) and (**2**) (Figures 1 and 2) both have the same striking planarity as the diester,[1] with maximum deviations from their least-squares planes of 0.04 Å [for S(3)] in (**1**) and 0.032 Å [for S(3)] in (**2**). The dihydro derivative (**3**) (Figures 3 and 4) retains a planar S–N–S–N–S portion with a maximum deviation for these atoms of 0.028 Å [for N(2)]. Structure (**1**) is essentially symmetric and structures (**2**) and (**3**) each has a crystallographic two-fold axis passing through the apical sulphur and bisecting the C–C bond. Surprisingly, despite their planar geometry, molecules of (**1**) do not adopt a parallel stacking arrangement in the crystal. Molecules of the benzo derivative (**2**), however, do pack with parallel overlap, the 7-membered ring of one directly overlying the 6-membered ring of another and *vice versa*. The interplanar separation is small at 3.54 Å.



(**1**)



(**2**)



(**3**)

The S–N bond lengths in both the parent (**1**) and the benzo compound (**2**) are, within statistical significance, the same as those observed for the diester,[1] demonstrating again the marked degree of partial double bond character. This delocalisation is supported by *ab initio* and MNDO calculations (Table 1) which show a distinct pattern of π energy levels characteristic of an aromatic system. There is however a

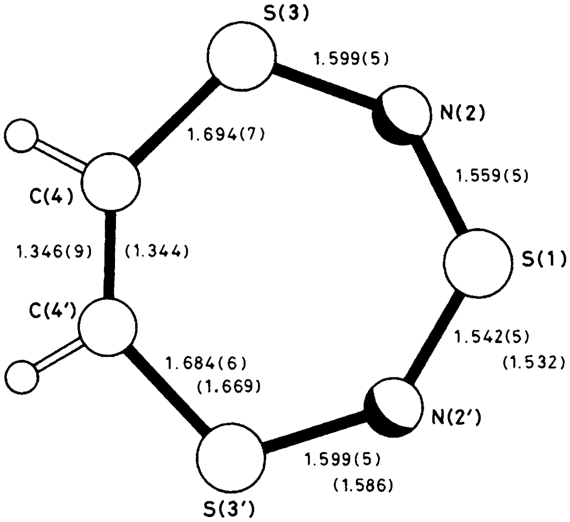


Figure 1. The molecular structure of (**1**) showing the crystallographic bond lengths, with those derived from MNDO calculations given in parentheses. The valence angles starting at S(1) and going clockwise round the ring are: 122.8(3), 138.3(3), 115.0(3), 135.6(5), 135.6(5), 115.7(3), and 136.8(3)° respectively.

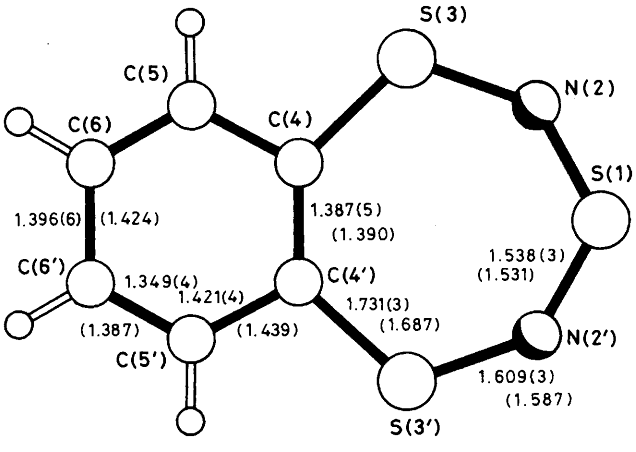


Figure 2. The molecular structure of (**2**) showing the crystallographic bond lengths, with those derived from MNDO calculations given in parentheses. The valence angles in the 7-membered ring at S(1), N(2), S(3), and C(4) are 122.4(2), 138.3(2), 116.9(1), and 133.5(1)° respectively.

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† *Crystal data:* (**1**), $C_2H_2N_2S_3$, monoclinic, $a = 6.883(1)$, $b = 7.693(1)$, $c = 10.521(2)$ Å, $\beta = 96.50(1)°$, $U = 554$ Å^3, space group $P2_1/n$, $Z = 4$, $M = 150.2$, $D_c = 1.81$ g cm^{-3}, $\mu(\text{Cu-}K_\alpha) = 110$ cm^{-1}. (**2**), $C_6H_4N_2S_3$, monoclinic, $a = 12.167(3)$, $b = 9.698(3)$, $c = 7.099(2)$ Å, $\beta = 108.51(2)°$, $U = 794$ Å^3, space group $C2/c$, $Z = 4$, $M = 200.3$, $D_c = 1.68$ g cm^{-3}, $\mu(\text{Cu-}K_\alpha) = 79$ cm^{-1}. (**3**), $C_2H_4N_2S_3$, monoclinic, $a = 9.947(2)$, $b = 8.807(2)$, $c = 7.614(2)$ Å, $\beta = 114.97(2)°$, $U = 605$ Å^3, space group $C2/m$, $Z = 4$, $M = 152.2$, $D_c = 1.68$ g cm^{-3}, $\mu(\text{Cu-}K_\alpha) = 101$ cm^{-1}. Data for all three compounds were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-K_α radiation using ω-scans. Crystals of (**1**) and (**3**) are highly volatile in air and were sealed in Lindemann glass capillary tubes. Structures (**1**) and (**3**) were solved by the heavy-atom method, and structure (**2**) by direct methods. All three structures were refined anisotropically using absorption corrected data to give for (**1**) $R = 0.045$, $R_w = 0.049$ for 623 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $\theta \leqslant 58°$]; for (**2**) $R = 0.032$, $R_w = 0.036$ for 497 reflections ($\theta \leqslant 56°$); and for (**3**) $R = 0.033$, $R_w = 0.040$ for 376 reflections ($\theta \leqslant 58°$), respectively. In (**1**) and (**2**) the hydrogen atom positions were fixed, but in (**3**) they were refined isotropically. The atomic co-ordinates for this work are available on request from the Director of the 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.

Table 1. Comparison between measured vertical ionisation energies (I.E.) and calculated orbital energies ($-\varepsilon$) for 1,3,5,2,4-trithiadiazepine (**1**) (all values in eV).

Band	I.E.	Assignment[a]	$-\varepsilon$(MNDO)[b]	$-\varepsilon$(4-31G)[b]	$-\varepsilon$(3G*)[b]
		$6b_2(\pi)$	1.85	−0.65	−4.75
1	8.58	$3a_2(\pi)$	8.91	8.32	5.31
2	10.00	$5b_2(\pi)$	9.65	9.39	5.90
3	11.42	$13b_1(\sigma)$	10.80	10.72	7.99
	11.67	$4b_2(\pi)$	13.02	13.68	10.87
	12.11	$17a_1(\sigma)$	13.12	12.49	9.49
4	13.06	$2a_2(\pi)$	13.52	13.82	10.98
5	13.99	$16a_1(\sigma)$	13.75	13.50	10.75
	14.32	$12b_1(\sigma)$	14.12	14.21	11.47
6	16.06	$3b_2(\pi)$	15.74	16.43	13.64
		$11b_1(\sigma)$	16.35	16.13	13.57
		$10b_1(\sigma)$	16.55	21.59	18.90
		$15a_1(\sigma)$	17.22	18.78	16.08

[a] Symmetry assignments were based on the *ab initio* orbital basis set. [b] All geometries were optimised at the level of theory indicated in parentheses.

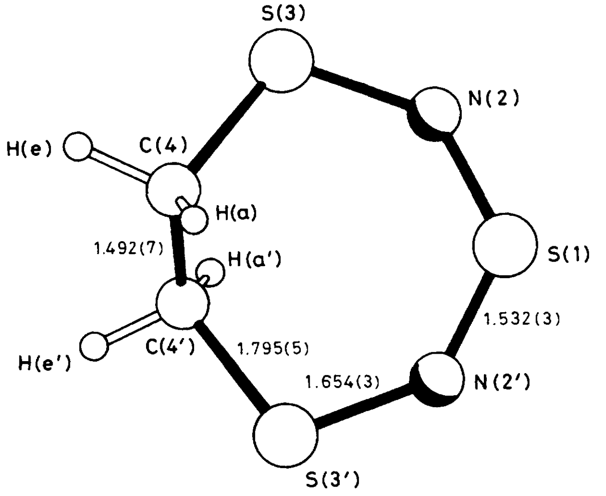

Figure 3. The molecular structure of (**3**) showing the crystallographic bond lengths. The valence angles at S(1), N(2), S(3), and C(4) in the ring are 125.5(2), 137.3(2), 107.2(2), and 114.4(3)° respectively.

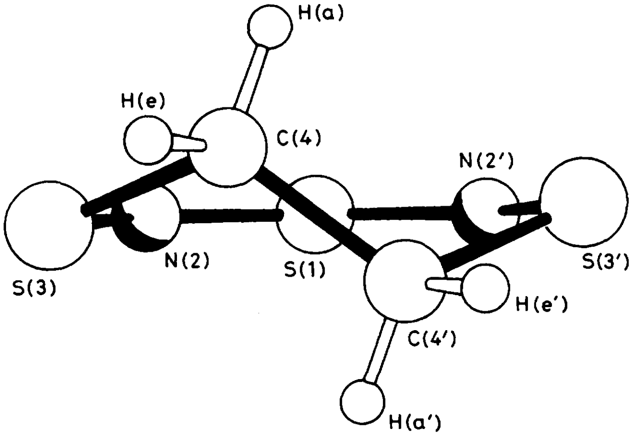

Figure 4. View looking down the crystallographic 2-fold axis in (**3**) showing the planarity of the S–N–S–N–S portion of the molecule and the relative geometric relationships of the hydrogen atoms of the methylene groups.

considerable lengthening and loss of double bond character in the N(2)–S(3) (crystallographic numbering) bond of the dihydro compound (**3**).

An increase in the C–S bond length from 1.684 Å/1.694 Å in the parent (**1**) to 1.731 Å in the benzo compound (**2**), and the accompanying decrease in the MNDO π bond order from 0.307 to 0.260, causes a destabilisation of the aromatic trithiadiazepine system. In accord with this the benzo compound (**2**) is much more reactive than the monocyclic compound (**1**) towards such reagents as triphenylphosphine and *m*-chloroperbenzoic acid.[2] A pronounced bond alternation is also induced in the carbocyclic ring of (**2**), the MNDO π bond orders being 0.700, 0.543, 0.766, and 0.555 for C(4)–C(4'), C(4)–C(5), C(5)–C(6), and C(6)–C(6'), respectively.

As a consequence of the molecular planarity the angles at nitrogen are abnormally large, 137° and 138° in (**1**) and 138° in (**2**), comparable to those in the diester.[1] Interestingly, this enlargement is equally marked in the dihydro compound (**3**) with angles at nitrogen of 137° despite conformational changes in the ring caused by the sp^3 carbon atoms. These two carbon atoms lie symmetrically 0.47 Å above and below the S–N–S–N–S plane such that the methylene hydrogen atoms adopt an approximately *cis* and *trans* periplanar geometry, resulting in an H(e)CCH(e') torsion angle of 31° (Figure 4). The 250 MHz ^1H n.m.r. spectrum of (**3**) at room temperature is a sharp singlet which shows characteristics of a partially exchange-broadened AA'BB' spin system only on cooling below 190 K, indicating a relatively low ($\leqslant$ 40 kJ mol^{-1}) energy barrier for axial–equatorial hydrogen interconversion. The MNDO calculated barrier is 55.6 kJ mol^{-1} whilst a 4-31G//MNDO calculation predicts a barrier of only 13.0 kJ mol^{-1}.

The vertical ionisation potentials of 1,3,5,2,4-trithiadiazepine (**1**), from its He (I)α photoelectron spectrum, are given in Table 1 together with the corresponding valence shell (2p/3p) orbital energies calculated by the MNDO, STO-4-31G, and STO-3G* methods.[3] These ionisations were assigned on the basis of the MNDO calculations since *ab initio* calculations at the 4-31G Koopmans' theorem level can result in spurious σ/π inversions.[3] However, all procedures gave the same relative ordering of the π orbital energies. From the calculations, the HOMO consists predominantly of an out of phase π overlap of sulphur and nitrogen lone pair orbitals. The form of the first photoelectron band, which shows a weak vibrational progression (1490 cm^{-1}) and a stable cation, would accord with ionisation from this largely nonbonding π type orbital. The low first ionisation potential of (**1**) (8.58 eV) indicates that the radical cation should be readily generated. The spin density in this radical cation, obtained from an unrestricted MNDO calculation, has its greatest value (0.23) at carbon. The benzo derivative (**2**) has the even lower first ionisation potential of 7.90 eV.

These results all confirm the fundamentally aromatic nature of the trithiadiazepine ring, in accord with its stability, chemical reactivity, and other spectroscopic properties,[2] notwithstanding its unusually high proportion of heteroatoms.

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