Notes

Evidence for Through-space Interactions between Sulphur and Nitrogen Lone Pairs in 2,2a,4,4a,6,6a-Hexahydro-1,3,5-trithia-7-azacyclopenta[*cd*]-pentalene †

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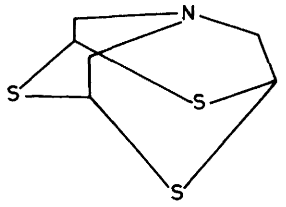
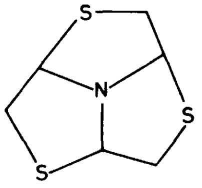
The *X*-ray crystal structure determination of the title compound has revealed a general flattening of the molecule with the nitrogen atom being pulled slightly into the plane defined by the three sulphur atoms. The crystals are rhombohedral, space group *R*3*c*, with a = 7.721(2) Å, α = 105.14(2)°, and Z = 2. The structure was solved by direct methods and refined to a final R = 0.024 (R' = 0.041) for 649 unique reflections. *Ab initio* molecular orbital calculations show that the sulphur and nitrogen lone pairs interact to produce four highest occupied π-type molecular orbitals. The photoelectron spectrum shows only a single broad peak at -1.38×10^{-18} J. This is consistent with the molecular orbital calculations which indicate that there should be three closely spaced transitions in this region from the highest occupied molecular orbitals.

In 1955, Craig *et al.*[1] reported the isolation of the adamantane-type compound (1) where the structural assignment was based on elemental analysis and the i.r. spectrum. Some years later, Fort and Semon [2] showed, using ^{1}H n.m.r. spectroscopy, that the correct structure was (2).

We wish to report the crystal structure of (2) along with its photoelectron spectrum and *ab initio* calculations which give some insight into the electronic nature of this rather unusual molecule.



(1)



(2)

Experimental

Compound (2), 2,2a,4,4a,6,6a-hexahydro-1,3,5-trithia-7-aza-cyclopenta[*cd*]pentalene, was prepared following a literature procedure.[2] The photoelectron spectrum was measured on a Perkin-Elmer PS-16 spectrometer, and was calibrated by the simultaneous introduction of argon into the target chamber. The sample was heated until it became volatile and the spectrum could be measured.

After a preliminary photographic survey, a suitable crystal was mounted on a Picker FACS-I diffractometer equipped with graphite-monochromated Mo-K_α radiation. Cell dimensions and an orientation matrix were determined by a least-squares fit to the co-ordinates of 20 centred reflections with $2\theta \geqslant 35°$. Intensity data were measured using an ω—2θ scan of 2° min^{-1} in 2θ. An initial estimate of the background intensity was made by standing counts of 1/10 scan-time at each end of the scan. However, if the reflection were significant [$I \geqslant 2\sigma(I)$] an analysis of the peak profile was made. Data were collected in the range $5 \leqslant 2\theta \leqslant 60°$ of which those reflections with $I \geqslant 2\sigma(I)$ were considered observed and included in the refinement.

The structure was initially solved in the space group *Cc* by a version of the direct methods program MULTAN-80 modified to run on a PDP8/A computer. The positions of all non-hydrogen atoms were obtained from an *E*-map calculated from the solution with the best 'combined figure of merit'.‡ The resulting structure was then transformed to the rhombohedral space group *R*3*c*. The structure was refined by least-squares techniques minimising the function $\Sigma w(|F_o| - |F_c|)^2$. Scattering factors were taken from International Tables.[3] Those for sulphur were corrected for anomalous dispersion, and weights were derived from counter statistics. After the initial cycles of refinement, the positions of the hydrogens were located in a difference synthesis and were included in the refinement with isotropic thermal parameters. Several least-squares cycles in which the non-hydrogen atoms were refined anisotropically resulted in final residuals of R = 0.024 and R' = 0.041 (0.029 and 0.043 respectively when unobserved reflections were included). A final difference synthesis showed no unexpected features. Refinement of the inverted structure resulted in a final R = 0.029 indicating that the correct enantiomorph had been chosen. The programs used throughout the investigation were those of Larson and Gabe [4] for the PDP8/A computer.

Crystal data are given in Table 1, atomic co-ordinates in Table 2, and bond distances and angles in Table 3.

The molecular orbital calculations were performed using a modified version of the GAUSSIAN 70 program [5] with an STO-3G basis set.

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† *Supplementary data available* (No. SUP 23948, 11 pp.): H-atom co-ordinates, thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

‡ We wish to thank a referee for pointing out the possibility of an incorrect space group.

Table 1. Crystal data *

Molecular formula	$C_6H_9NS_3$
Molecular weight	191.33
Space group	$R3c$
a/Å	7.721(2)
α/°	105.14(2)
U/Å^3	401.1(4)
Z	2
D_c/Mg m^{-3}	1.58
Crystal dimensions (mm)	0.3 × 0.3 × 0.2
No. of unique data	712
No. of observed data [$I \geqslant 2\sigma(I)$]	649
μ/mm^{-1}	0.81

* Estimated standard deviations are given in parentheses.

Table 2. Fractional atomic co-ordinates *

Atom	x	y	z
S	−0.1133(3)	0.1029(3)	−0.3010(3)
N	0	0	0
C(1)	−0.3409(4)	−0.0445(4)	−0.1066(4)
C(2)	−0.1413(4)	0.0834(4)	−0.0790(4)

* Estimated standard deviations are given in parentheses.

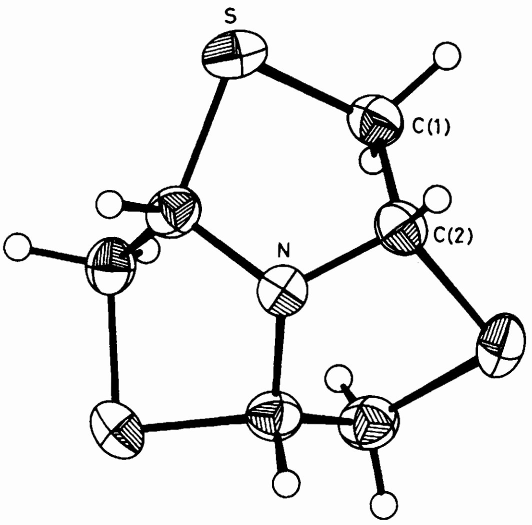

Figure 1. ORTEP plot of (2) showing the atom numbering scheme. Thermal ellipsoids are drawn at 50% probability and the hydrogen atoms are shown with radii of 0.1 Å

Results and Discussion

The first indication that there is a considerable interaction among the sulphur and nitrogen lone pairs comes from an examination of the crystal structure of (2) (Figure 1). The C–N–C bond angles [112.3(1)°] are substantially larger than the expected tetrahedral angles. This has the effect of flattening the structure and of drawing the N atom toward the plane defined by the sulphur atoms, resulting in a nitrogen–sulphur plane distance of 0.952 Å.

In the photoelectron spectrum, a single broad peak was observed centred at -1.38×10^{-18} J (Figure 2). This was ascribed to the transitions from the energetically very similar molecular orbitals formed from the interacting sulphur and nitrogen lone pairs. If the nitrogen and sulphur lone pairs were completely localised and non-interacting, two sharp peaks

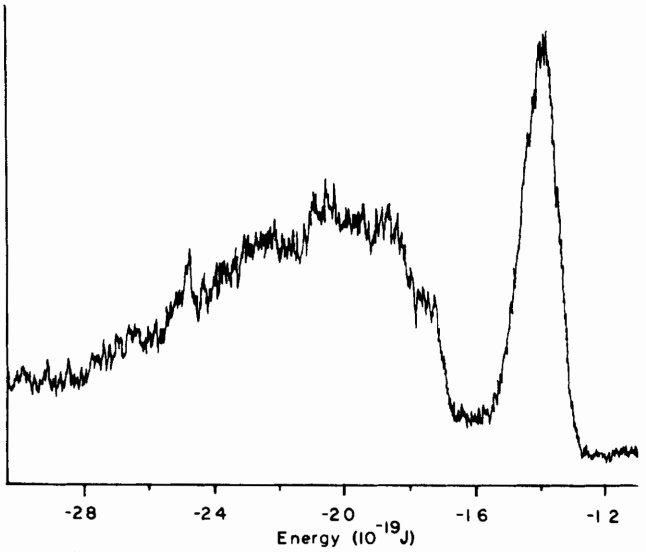

Figure 2. Photoelectron spectrum of (2)

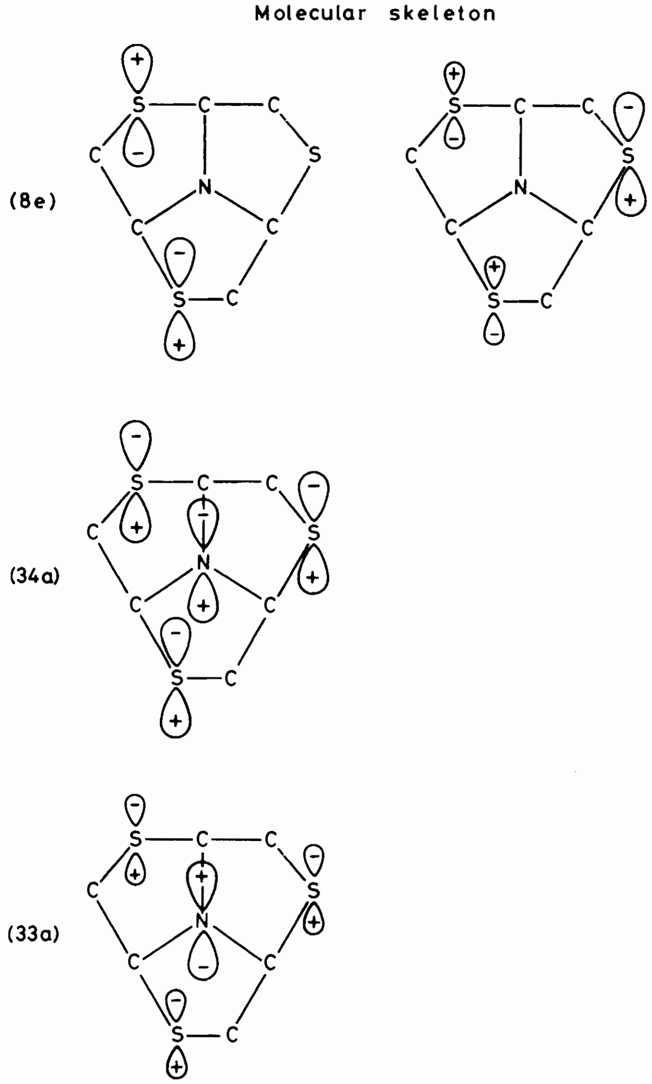

Figure 3. Representations of the four highest occupied molecular orbitals formed from interactions among the lone pairs on the nitrogen and sulphur atoms. Energies: (8e), -1.05×10^{-18}; (34a), -1.13×10^{-18}; (33a) -1.22×10^{-18} J

Table 3. Bond distances (Å) and angles (°) *

S–C(1)	1.807(2)	N–C(2)	1.484(2)
S–C(2)	1.822(2)	C(1)–C(2)	1.523(4)
C(1)–S–C(2)	89.4(1)	S–C(2)–N	106.6(1)
C(2)–N–C(2′)	112.3(1)	S–C(2)–C(1)	113.6(2)
S–C(1)–C(2)	103.2(2)	N–C(2)–C(1)	108.7(2)

* Estimated standard deviations are given in parentheses.

would have been expected, one at *ca.* -1.39×10^{-18} J for a transition from the sulphur orbitals and another at *ca.* -1.43×10^{-18} J for a transition from the nitrogen orbitals.[6] The close proximity of these expected peaks may alone account for the broadness of the observed transition.

From the *ab initio* calculations on (2), it can be seen that the four highest orbitals are predominantly combinations of the p_z orbitals on the nitrogen and sulphur atoms (Figure 3). Since these orbitals are centred on non-bonded atoms, any electronic communication between them is probably a through-space π interaction. The highest occupied molecular orbitals (h.o.m.o.s) are a degenerate set at -1.05×10^{-18} J (8e).* These are composed primarily of $3p_z$ orbitals on the sulphur atoms (75% of the electron density is concentrated in these atomic orbitals). The remaining electron density in these degenerate molecular orbitals is located in the $2p_z$, $3p_x$, and $3p_y$ atomic orbitals on the sulphurs. The next two lower occupied orbitals, at -1.13×10^{-18} and at -1.22×10^{-18} J* are the bonding and antibonding combinations of p_z orbitals on the three sulphur atoms and the nitrogen atom (Figure 3). About 93% of the electron density is concentrated in p_z orbitals in the 'bonding combination' (34a) (*i.e.* with respect to the S–N interaction) and 57% in the antibonding combination (33a).

In summary, the crystal structure indicates that there is some electronic interaction between the sulphur and nitrogen atoms. From the *ab initio* calculations, it appears that this arises from a slight stabilisation arising from the interaction of the p_z lone pair orbitals on these atoms.

Acknowledgements

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* The inclusion of *d* orbitals in the bonding made little difference to the form of the molecular orbitals obtained since CNDO/2 calculations on the molecule indicated that the electron density in *d* orbitals was negligible in the molecular orbitals under consideration. The values of the energies of orbitals composed predominantly of lone pairs on sulphur atoms in the present work is estimated to be a factor of *ca.* 1.3 too low by CNDO/2 calculations, *i.e.* -1.82×10^{-19} J for the h.o.m.o. followed by a degenerate pair at -1.87×10^{-19} J and the last of the set at -1.92×10^{-19} J. This underestimation of orbital energies involving sulphur lone pairs has been noted in previous work (see ref. 7). Conversely, the energies of the same orbitals are over-estimated by the present *ab initio* calculation by a factor of *ca.* 1.2.