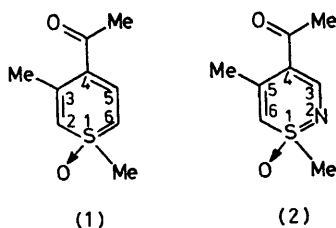


X-Ray Crystal Structures of a Thiabenzene 1-Oxide and its 2-Azathia-analogue

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Summary X-Ray crystal structure analyses of 4-acetyl-1,3-dimethylthiabenzene 1-oxide monohydrate and 4-acetyl-1,5-dimethyl-2-azathiabenzene 1-oxide are reported, and their conformations and bonding structures are compared.

RECENTLY we described the syntheses, properties, and electronic structures of 4-acetylthiabenzene 1-oxides and their 2-azathia analogues.^{1,2} In order to obtain further information regarding the structure and bonding in the thiabenzene 1-oxide system,[†] we have now undertaken X-ray structure analyses of 4-acetyl-1,3-dimethylthiabenzene 1-oxide monohydrate (**1**) and 4-acetyl-1,5-dimethyl-2-azathiabenzene 1-oxide (**2**).



Compound (**1**), $C_9H_{12}O_2S \cdot H_2O$, gives orthorhombic crystals from ethanol-light petroleum (b.p. 30–60 °C), space group $P2_12_12_1$,[‡] $a = 13.902(4)$, $b = 14.949(4)$, $c = 4.893(3)$ Å; $D_m = 1.319(2)$, $D_c = 1.321$ g cm⁻³; $Z = 4$. The structure was solved by the heavy-atom method and refined by least-squares to $R = 0.043$ using 1396 independent reflections. Compound (**2**), $C_8H_{11}NO_2S$, crystallises from ether-hexane in the triclinic space group $P\bar{1}$; $a = 8.418(1)$, $b = 8.987(1)$, $c = 12.342(1)$ Å; $\alpha = 90.12(1)$, $\beta = 96.14(1)$, $\gamma = 84.55(1)^\circ$; $D_m = 1.327(1)$, $D_c = 1.332$ g cm⁻³; $Z = 4$. The structure was solved by the direct method (MULTAN⁴) and refined by block-diagonal least-squares to $R = 0.047$ using 3750 independent reflections. There are two crystallographically independent molecules, (**2A**) and (**2B**), in the unit cell. The difference between (**2A**) and (**2B**) in the bond lengths and angles, however, is small.[§]

The molecular structures of (**1**) and (**2**) are illustrated in Figures 1 and 2, respectively. The six-membered heterocyclic rings of both molecules have similar half-boat conformations with the apex at sulphur. Small differences are found in the degree of the deviation of the sulphur atom [0.43 Å for (**1**), 0.28 Å for (**2A**), and 0.39 Å for (**2B**)] and the twisting of the acetyl group [dihedral angles: 2.2° for (**1a**), 6.7° for (**2A**), and 9.4° for (**2B**)] from planarity of the best plane. The oxygen atom attached to sulphur occupies an axial position and the S-methyl group an

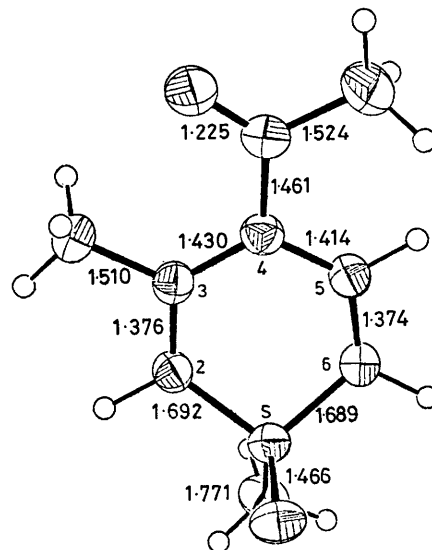


FIGURE 1. Molecular structure of (**1**). Standard deviations of the bond lengths given vary between 0.003 and 0.006 Å (except C-H: 0.04–0.05 Å).

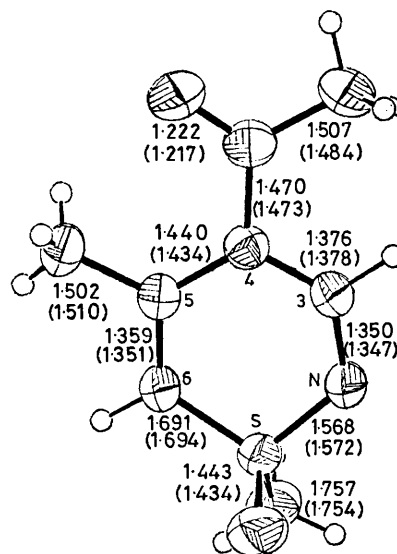


FIGURE 2. Molecular structure of (**2**). Only the molecule of (**2A**) is shown. Bond lengths for (**2A**) are given, with those for (**2B**) in parentheses. Standard deviations vary between 0.002 and 0.003 Å (except C-H: 0.03 Å).

[†] Although the X-ray analysis of 6-benzoyl-3-hydroxy-1-methyl-5-phenylthiabenzene 1-oxide has been reported, it was not a genuine thiabenzene 1-oxide (ref. 3).

[‡] Only one of two possible enantiomers is involved in the unit cell.

[§] 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.

equatorial position. The half-boat conformation seems to be a result of the release of angle strain caused by introduction of the tetrahedral sulphur atom into the planar pentadienyl or azapentadienyl anion system.

The bonding in the two compounds is significantly different. In compound (1) the C(2)–C(3) (1.376 Å) and C(5)–C(6) (1.374 Å) distances are very similar and shorter than C(3)–C(4) (1.430 Å) and C(4)–C(5) (1.414 Å), whereas in compound (2) C(3)–C(4) [1.376 Å for (2A) and 1.378 Å for (2B)] and C(5)–C(6) [1.359 Å for (2A) and 1.351 Å for (2B)] have more double bond character than C(4)–C(5) [1.440 Å for (2A) and 1.434 Å for (2B)]. On the basis of the C(4)–CO [1.461 Å for (1), 1.470 Å for (2A), and 1.473 Å for (2B)] and C=O bond lengths [1.225 Å for (1), 1.222 Å for (2A), and 1.217 Å for (2B)] it seems very likely that the acetyl group of both the heterocycles is involved in the delocalisation of the negative charge, but it is clear that the

delocalisation is relatively small compared with open-chain acyl-stabilized ylides.⁵ Since the S–C bond lengths in (1) (1.692 and 1.689 Å) are intermediate between the single (1.80 Å)^{3,6} and double bond lengths (1.65 Å)^{3,6} and the S–N bond in (2) [1.568 Å for (2A) and 1.572 Å for (2B)] is closer to the S=N (1.53 Å)⁷ rather than to the S–N bond length (1.74 Å),⁷ there is an appreciable contribution from the $p\pi-d\pi$ bonding in the S–C and S–N bonds, with a greater contribution to the latter. These results are in general agreement with the conclusions of the spectroscopic studies.^{1,2}

Finally, the water molecules in (1) are arranged along a two-fold screw axis and linked by hydrogen bonds (2.733 Å); they are also involved in hydrogen bonding (2.812 Å) with the carbonyl oxygen atom of (1).

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