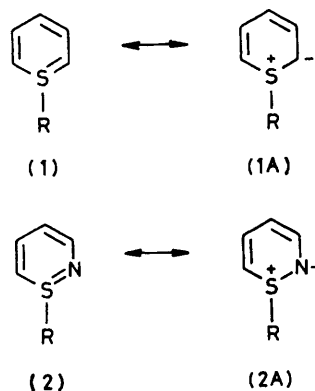


Synthesis and X-Ray Structure of an Azathiabenzene Derivative, a Cyclic Sulphimide

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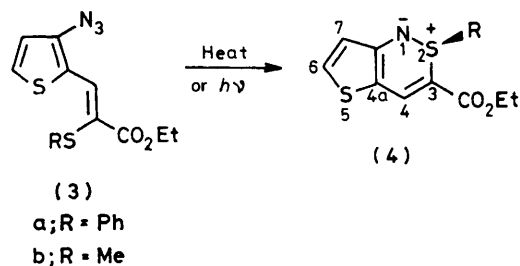
Summary Decomposition of azidothiophens (**3**) gives the thieno[3,2-*c*][1 λ^4 ,2]thiazines (**4**), which are stable cyclic sulphimides, the ylidic nature of (**4a**) being confirmed by its properties and X-ray structure determination; photolysis of the sulphimides (**4**) gives the thieno[3,2-*b*]pyrroles (**6**) suggesting that MeS and PhS undergo very rapid [1,5] sigmatropic shifts.

THIABENZENES (**1**) are highly reactive species better represented by the cyclic sulphonium ylide structure (**1A**).¹ Azathiabenzenes (**2**), which would be expected to be more stable, are almost unknown however,² although the corresponding S-oxides are well described.³ Indeed, few examples of cyclic sulphur–nitrogen ylides, sulphimides, have been reported,^{4,5} although the open-chain analogues are well known.⁵ We now report the synthesis and the first X-ray crystal structure of an azathiabenzene.



In continuation of our work on the decomposition of 3-azidothiophens,⁶ we decided to try to intercept the intermediate nitrene intramolecularly with a suitably positioned

nucleophilic sulphur, and thereby generate a cyclic sulphimide directly. Therefore, 3-azidothiophen-2-carbaldehyde was condensed with ethyl phenylthioacetate in ethanolic sodium ethoxide at -15°C to give the azide (**3a**) (85%), m.p. $106\text{--}108^\circ\text{C}$ (decomp.).[†] The azide (**3b**), m.p. $54\text{--}55^\circ\text{C}$, was similarly prepared (80%).



The azide (**3a**) decomposed in boiling toluene (2.5 h) to give the stable cyclic sulphimide (**4a**) (90%) as orange-red crystals, m.p. $128\text{--}129^\circ\text{C}$, λ_{max} (EtOH) 220 ($\log \epsilon$ 4.15), 262 sh (3.64), 326 (3.93), and 459 (3.63) nm. The cyclic ylide structure was supported by the n.m.r. spectrum which showed quaternary carbon signals at δ 85.5 and 116.2 p.p.m. for C-3 and C-4a respectively, indicating delocalisation of the negative charge from nitrogen to carbon, and was confirmed by an X-ray crystal structure determination (Figure). The S–N bond length of 1.63 Å is within the range for acyclic sulphimides, and is intermediate between the S–N (1.74 Å) and S=N (1.53 Å) distances.⁵

Crystal data: Crystals of (**4a**) are triclinic, $a = 7.740(2)$, $b = 10.109(3)$, $c = 10.524(3)$ Å, $\alpha = 64.92(2)$, $\beta = 88.50(2)$, $\gamma = 71.53(2)^\circ$, $U = 702 \text{ \AA}^3$, space-group $P\bar{1}$, $Z = 2$. Of the 1447 independent reflections ($\theta \leq 50^\circ$) measured on a diffractometer using Cu- K_α radiation, 14 were classified as

[†] Satisfactory analyses and spectral data were obtained for all new compounds.

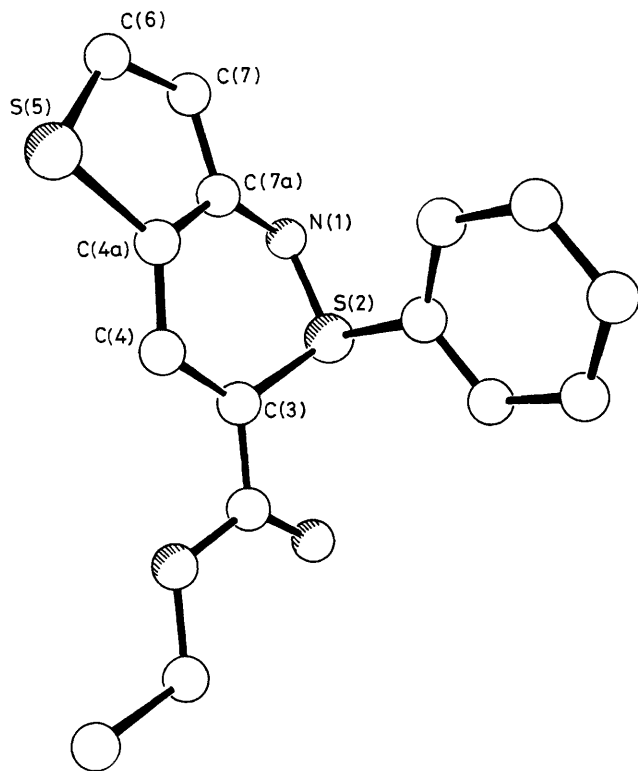
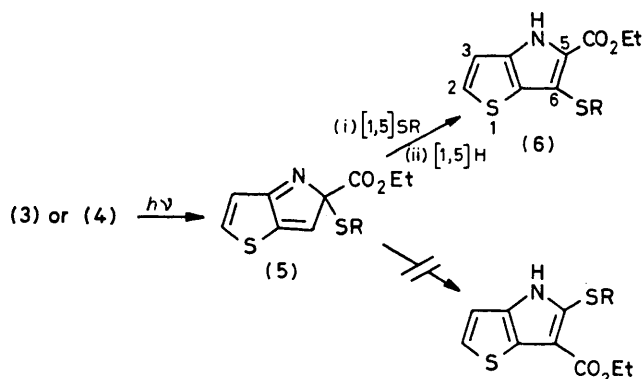


FIGURE. The crystal structure of (4a). Selected bond distances: N(1)–S(2) 1.629(3), S(2)–C(3) 1.762(3), C(3)–C(4) 1.363(6), C(4)–C(4a) 1.406(5), C(4a)–S(5) 1.747(5), S(5)–C(6) 1.709(3), C(6)–C(7) 1.345(6), C(7)–C(7a) 1.425(5), C(7a)–N(1) 1.371(6), C(4a)–C(7a) 1.393(4), and S(2)–Ph 1.801(3) Å.

unobserved. The structure was solved by direct methods and refined anisotropically to $R = 0.033$.[‡]

Similar thermal decomposition of the azide (3b) gave the yellow-brown sulphimide (4b) (85%), m.p. 72–73 °C. The sulphimides can also be prepared by photolysis of the azides (3), although this is less satisfactory since the sulphimides themselves are photo-labile. Thus photolysis of the azide (3a) in acetonitrile at 350 nm for 25 min gave the sulphimide (4a) (55%) together with the thieno[3,2-*b*]pyrrole (6a) (40%), m.p. 136–137 °C. Photolysis of the sulphimide (4a) under similar conditions (2 h) also gave (6a) (85%). The *S*-methyl compounds behaved similarly, the azide (3b) giving the sulphimide (4b) (40%) and the thienopyrrole (6b) (50%), m.p. 115–116 °C, on photolysis.

The structure of (6a) was confirmed by hydrolysis and decarboxylation to give 6-phenylthio-4*H*-thieno[3,2-*b*]-



pyrrole, m.p. 131–132 °C. Decoupling and nuclear Overhauser effect (n.O.e.) difference experiments showed clearly the presence of a proton at C-5 rather than C-6. This was inferred from its expected coupling to H-2 (J 1.5 Hz) and to the N–H (J 2.5 Hz), the absence of any coupling involving H-3, and the much greater (*ca.* 4:1) n.O.e. enhancement at H-5 than at H-3 resulting from pre-irradiation of the N–H. The structure of the methylthiothieno[3,2-*b*]pyrrole (6b) was also confirmed by the same degradation, and by n.m.r. spectroscopy.

The cyclic sulphimides (4) were expected to be photo-labile since the known photochemical reactions of sulphimides usually involve cleavage of the sulphur–nitrogen bond.⁵ Cleavage of this bond followed by electrocyclic ring closure of the resulting nitrene would give the intermediate (5). The thienopyrroles (6) then arise by [1,5] sigmatropic shifts of RS and of hydrogen. It is interesting that the product arises by exclusive migration of the sulphur substituent in (5) in preference to the ester, although ester groups normally migrate rapidly. Little is known about [1,*j*] sigmatropic shifts of alkyl- or aryl-thio-groups, though Pietra and co-workers have shown that alkylthio-groups migrate rapidly in what are formally [1,7] shifts.⁷

The sulphimides (4) are stable and can be stored indefinitely at room temperature, although they do rearrange at temperatures above 120 °C by a process which does not involve cleavage of the sulphur–nitrogen bond.⁸ It is likely that the ester substituent has a considerable influence on the stability of the cyclic ylide. This, and other aspects of the chemistry of these novel heterocyclic compounds, such as their reactions with electrophiles, are under investigation.

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[‡] 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.

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