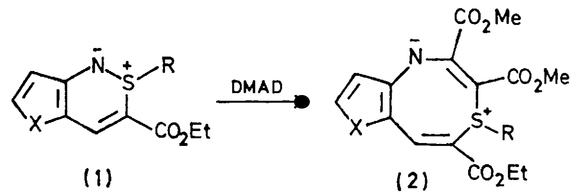
Reaction of 2-Azathiabenzenes with Dimethyl Acetylenedicarboxylate; *X*-Ray Structure of a $1\lambda^4$,4-Thiazocine

Richard D. Grant, Charles W. Rees, and David J. Williams

Department of Chemistry, Imperial College of Science & Technology, London SW7 2AY, U.K.

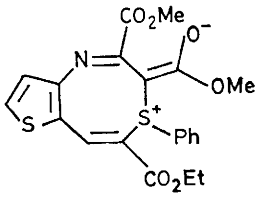
The azathiabenzene derivatives (**1**) react at room temperature with dimethyl acetylenedicarboxylate in aprotic solvents to give $1\lambda^4$,4-thiazocines (**2**) and in protic solvents to give the 2:1-adduct (**6**) in a new sulphimide reaction.

We have recently synthesised $1\lambda^4$,2-thiazines [*e.g.* (**1**)] and shown them to be stable sulphur–nitrogen ylides which can be considered as cyclic sulphimides or as 2-aza-derivatives of the highly reactive thiabenzenes.[1] We now describe the reac-



(1) (2)

a; X = CH=CH, R = Ph
b; X = S, R = Ph
c; X = O, R = Ph
d; X = O, R = Me



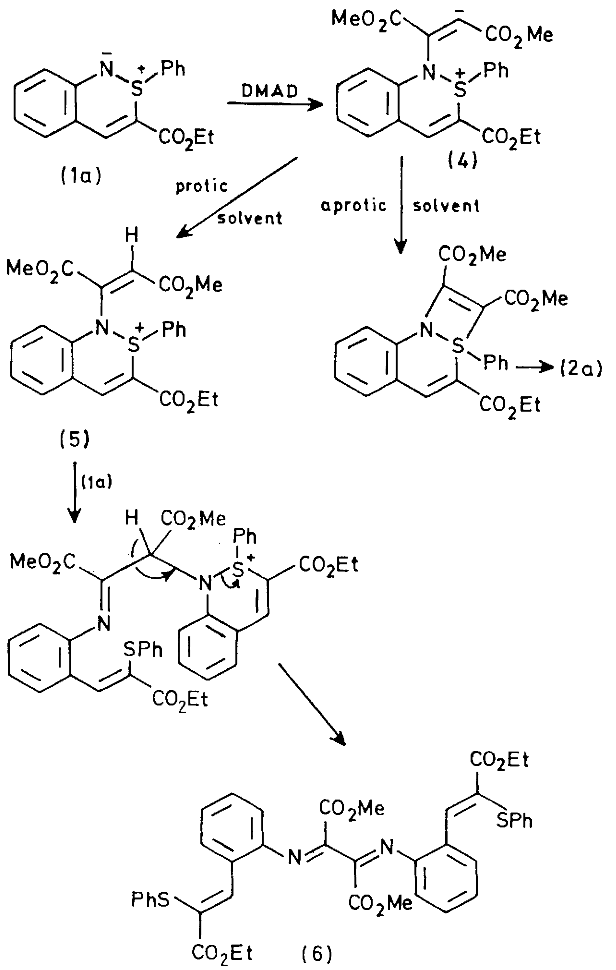
(3) ↔ (2b)

tions of these thiazines (**1**) with dimethyl acetylenedicarboxylate (DMAD) as a representative electrophilic and dienophilic substrate.

Acyclic sulphimides react readily with DMAD by formal [2 + 2] cycloaddition across the ylide bond, followed by opening of the four-membered ring to give sulphonium ylides.[2] In contrast, very little is known of the reactions of thiabenzenes with DMAD; in the only reports of this reaction, with 1-benzoyl-[3a] and 1-cyano-2-methyl-2-thianaphthalene,[3b] the initial step appears to be a [4 + 2] rather than [2 + 2] cycloaddition. It was thus of interest to see whether the azathiabenzene derivatives (**1**) would react with DMAD to parallel these thianaphthalenes or acyclic sulphimides. We now find that in aprotic solvents, the azathiabenzenes react exclusively as sulphimides by addition of DMAD directly across the ylide bond.

Treatment of the ylides (**1a**—**d**) with 1 equiv. of DMAD in benzene, toluene, or acetonitrile at room temperature for 1 to 3 days gives the fused 1λ^4,4-thiazocines (**2a**—**d**) as highly coloured (orange to violet), polar crystalline solids in the yields shown [(**2a**), 47%, m.p. 175—176 °C; (**2b**), 34%, m.p. 152—154 °C; (**2c**), 63%, m.p. 56—58 °C; (**2d**), 98%, 112—115 °C]. The structure of these 1 : 1-adducts which were all of the same type, was inferred from their analysis and spectral properties and confirmed by an *X*-ray structure determination (Figure 1) for the thienothiazocine (**2b**). The 1λ^4,4-thiazocine ring system has not previously been reported.† It is formally an 8 π-electron antiaromatic system but the *X*-ray structure shows the 8-membered ring to be tub shaped, thus precluding extensive cyclic conjugation. The thiazocines are apparently stabilized by substantial electron withdrawal by the ester group at C-3 since the bond lengths (Figure 1) indicate that the vinylogous sulphonium structure (**3**) is a major contributor.

Conversion of the thiazines (**1**) into the thiazocines (**2**) is thought to proceed by a mechanism, shown for (**1a**) in Scheme 1, similar to that proposed for the analogous reaction of acyclic sulphimides.[2] Since the first step is presumably



Scheme 1

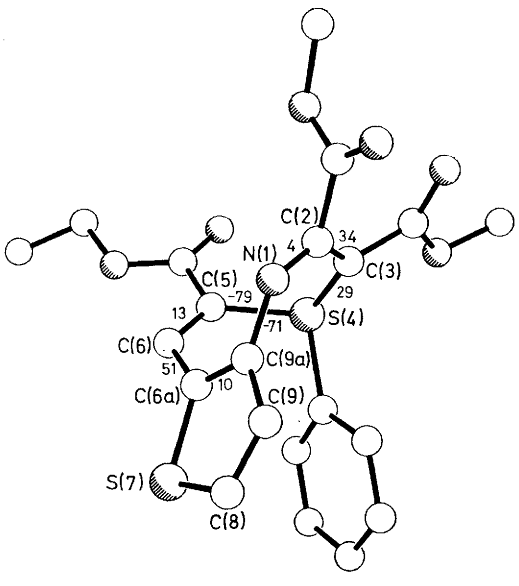


Figure 1. The crystal structure of (**2b**) with the torsion angles for the thiazocine ring (average torsion angle e.s.d. = 0.4°). Selected bond distances: N(1)–C(2) 1.286(4), C(2)–C(3) 1.432(4), C(3)–S(4) 1.707(3), S(4)–C(5) 1.791(3), C(5)–C(6) 1.335(4), C(6)–C(6a) 1.439(4), C(6a)–C(9a) 1.370(4), C(9a)–N(1) 1.405(4), C(6a)–S(7) 1.730(3), S(7)–C(8) 1.699(4), C(8)–C(9) 1.332(5), C(9)–C(9a) 1.416(5), S(4)–Ph 1.789(3), C(2)–CO 1.521(4), C(3)–CO 1.437(4), and C(5)–CO 1.482(4) Å.

---

† As far as we are aware, no λ^4-thiazocines nor indeed λ^4-thiocines have previously been reported.

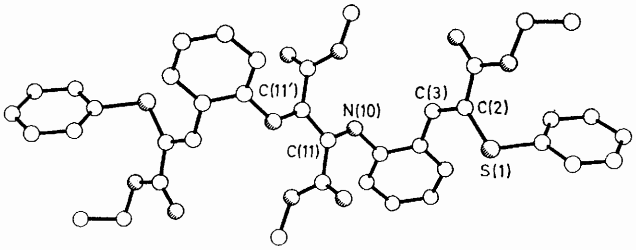


Figure 2. The crystal structure of (**6**). There is a crystallographic centre of symmetry at the centre of the DMAD unit. Selected bond distances: S(1)–Ph 1.767(3), S(1)–C(2) 1.747(3), C(2)–C(3) 1.341(4), N(10)–C(11) 1.278(3), and C(11)–C(11') 1.472(6) Å.

nucleophilic addition of the ylide to DMAD, it is possible that the resulting carbanion (**4**) could be intercepted by a proton source and the reaction diverted. This was observed when the solvent was changed to methanol or ethanol. Thus, when azathianaphthalene (**1a**) was treated with DMAD in ethanol at room temperature for 3 h, no thiazocine (**2a**) was observed but a 2:1-adduct (**6**), m.p. 144—146 °C, was isolated (65%) and its structure determined by *X*-ray crystallography (Figure 2). A possible mechanism for its formation,‡ involving attack by a second molecule of (**1a**) on the protonated, relatively stable species (**5**), is shown in Scheme 1. In agreement with this, the reaction of (**1a**) with DMAD in toluene containing a catalytic amount of trifluoroacetic acid gave the 2:1-adduct (**6**) as well as thiazocine (**2a**). In pure acetonitrile as solvent, (**2a**) was again the only product, suggesting that the course of the reaction is not markedly influenced by solvent polarity.

Thus, both reactions of the azathiabenzenes with DMAD appear to be initiated by nucleophilic addition of the ylide nitrogen to the acetylene, followed either by protonation of the carbanion or by its collapse onto sulphur (1,2-addition); no collapse onto carbon (1,4-addition) is observed in contrast with the reactions of the analogous sulphur–carbon ylides.[3] As far as we are aware, the formation of 2:1-adducts analogous to (**6**) has not previously been observed in the reactions of sulphimides with electrophilic substrates.

Crystal data: for (**2b**), $C_{21}H_{19}NO_6S_2$, $M = 445.50$, monoclinic, $a = 10.290(1)$, $b = 10.599(1)$, $c = 19.817(2)$ Å, $\beta = 101.25(1)^\circ$, $U = 2120$ Å^3, space-group $P2_1/n$, $Z = 4$. 2182 Independent reflections were measured on a diffractometer ($\theta \leqslant 50^\circ$) using Cu-$K_\alpha$ radiation, and of these 261 had $|F_o| < 3\sigma(|F_o|)$ and were classed as unobserved. The structure was solved by direct methods and refined anisotropically to $R = 0.038$.§ For (**6**), $C_{40}H_{36}N_2O_8S_2$, $M = 736.85$, monoclinic, $a = 9.090(2)$, $b = 12.388(2)$, $c = 17.153(4)$ Å, $\beta = 102.57(2)^\circ$, $U = 1885$ Å^3, space-group $P2_1/c$, $Z = 2$. Measurement conditions were as for (**2b**): 1925 independent reflections with 288 classed as unobserved. The structure was solved by direct methods and refined anisotropically to $R = 0.041$.§

We thank Dr. C. J. Moody for helpful discussions.

Received, 17th June 1982; Com. 694

References

1 C. J. Moody, C. W. Rees, S. C. Tsoi, and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1981, 927; R. D. Grant, C. J. Moody, C. W. Rees, and S. C. Tsoi, *ibid.*, 1982, 884.

2 T. L. Gilchrist and C. J. Moody, *Chem. Rev.*, 1977, **77**, 409; P. Barraclough, M. Edwards, T. L. Gilchrist, and C. J. Harris, *J. Chem. Soc., Perkin Trans.* 1, 1976, 716.

3 (a) M. Hori, T. Kataoka, H. Shimizu, S. Ohno, K. Narita, and H. Koyama, *J. Chem. Soc., Chem. Commun.*, 1981, 364; (b) M. Hori, T. Kataoka, H. Shimizu, K. Narita, S. Ohno, and H. Aoki, *Chem. Lett.*, 1974, 1101.

---

‡ The 2:1-adduct (**6**) was not formed from the 1:1-adduct (**2a**) with a second mole of starting material (**1a**) since an equimolar mixture of (**1a**) and (**2a**) in ethanol did not react.

§ 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.