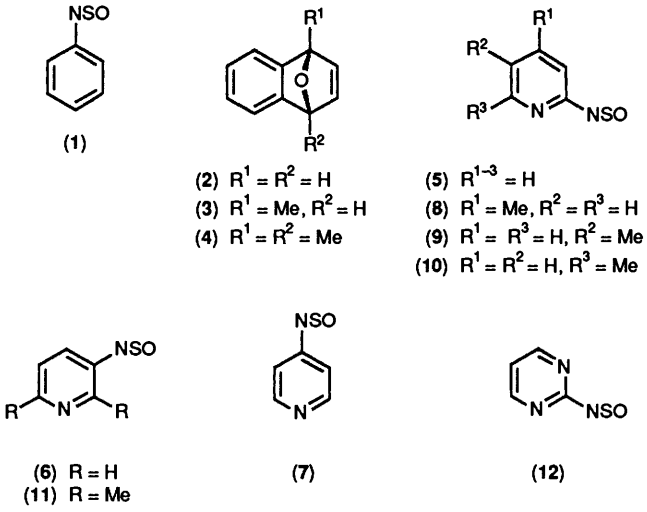
1,2-Thiazines and Related Heterocycles. Part 5.[1] Characterisation of some (*N*-Sulphinylamino)azines† and their Cycloadducts with 1,4-Epoxy-1,4-dihydronaphthalenes and other Dienophiles

Peter Hanson* and Stephen A. C. Wren
Department of Chemistry, University of York, Heslington, York YO1 5DD

A range of (*N*-sulphinylamino)azines has been synthesized and characterised, most for the first time. These heterocycles cycloadd as heterodienes to 1,4-epoxy-1,4-dihydronaphthalenes and similar electron-rich dienophiles through the sulphur atom of the sidechain and an *ortho* position of the azine ring. When the azine is unsymmetrically functionalised the cycloadditions are strongly periselective: 2-(*N*-sulphinylamino)pyridine reacts at the ring nitrogen, a preference that is not overturned by the introduction of steric hindrance; 3-(*N*-sulphinylamino)pyridine reacts at C-2 of the azine but addition may be diverted to C-4 by methylation at C-2. Regioselective additions to unsymmetrical dienophiles are also observed.

Several reactions of aryl sulphinylamines as heterodienes have been reported previously.[2–6] Collins[2] described the addition of *N*-sulphinylaniline (**1**) to bicyclo[2.2.1]hept-2-ene and to dicyclopentadiene, and Macaluso and Hamer[3] reported its addition to bicyclo[2.2.1]hepta-2,5-diene. Beecken[4] reported the cycloaddition of substituted sulphinylanilines to bicyclo[2.2.1]hept-2-ene. Hanson and Stone[5] described reactions of compound (**1**) and substituted derivatives with similar bridged alkenes, particularly with 1,4-epoxy-1,4-dihydronaphthalene (**2**) and its bridgehead-methylated derivatives (**3**) and (**4**); the cycloadditions were shown to be pericyclic.[6] The reactions of sulphinylamines as *dienophiles* have also been investigated in a parallel study in which it was shown that the regioselectivity of addition to unsymmetrical dienes may be accounted for by using Hückel orbitals in the frontier orbital approximation.[7] In order to explore selectivity of addition to aryl sulphinylamines as heterodienes it is necessary to work with unsymmetrical aryl systems. Earlier work[5] had indicated that 3-substituted *N*-sulphinylanilines might experience differential steric effects at the two positions *ortho* to the sulphinylamino function and so would be unsuitable for the investigation of electronically determined selectivity of addition. For this reason we chose to examine the reactivity of (*N*-sulphinylamino)azines. The mechanistic aspects of this work have already been reported.[1] In the present paper we characterise the (*N*-sulphinylamino)azines and their cycloadducts with the epoxy compound (**2**), its bridgehead-methylated derivatives, and similar dienophiles.



Results and Discussion

The 2- and 3-(*N*-sulphinylamino)pyridines (**5**) and (**6**) have been prepared previously by Beecken[8] who reacted metathetically the corresponding amines with *N*-sulphinylbenzenesulphonamide. The 3-isomer was characterised but the 2-isomer was not obtained pure and was handled in solution. Our preparations have involved sulphinylation of the initial aminoazines by reaction with $SOCl_2$ in refluxing benzene or toluene in the presence of two equivalents of triethylamine. The (*N*-sulphinylamino)azines were obtained after separation, by filtration, of triethylammonium chloride and removal of solvent. On vacuum distillation, the fresh sulphinylamines were bright yellow, orange, or red liquids or low-melting solids. They are very easily hydrolysed by atmospheric moisture which made elemental analysis impractical; they were therefore characterised spectroscopically.

(a) ^{13}C *NMR Spectra of the* (N-*Sulphinylamino*)*azines*.—^{13}C NMR spectra were obtained for solutions of freshly prepared sulphinylaminoazines in $CDCl_3$; they were assigned as follows. The differences in chemical shift between the carbon of benzene[9] and each of the four types of carbon in *N*-sulphinylaniline[10] were added to the chemical shifts of the carbons in pyridine and methylpyridines,[11] and pyrimidine[12] in the manner appropriate to the substitution pattern to generate 'predicted' ^{13}C NMR resonances for the various (*N*-sulphinylamino)azines. The shifts observed for the heterocycles were usually within 2 ppm of those predicted. The exceptions were the various 2-(*N*-sulphinylamino)pyridines where the substituted carbon resonated *ca.* 10 ppm to higher field than estimated; evidently, the heterocyclic N and the NSO sidechain, when adjacent, interact such that their combined deshielding effect is attenuated relative to the sum of their individual effects when exerted separately. The assignment of ^{13}C NMR spectra for the (*N*-sulphinylamino)azines investigated is given in Table 1 with that of PhNSO for comparison.

† Throughout this paper, azines refers to six-membered rings containing one or more N atoms, and *not* to the =N–N= entity.

Table 1. Assignments[a] of ^{13}C NMR spectral data for (*N*-sulphinylamino)azines.

(*N*-Sulphinylamino)azine	δ_C C-2	C-3	C-4	C-5	C-6	Other
4-(*N*-Sulphinylamino)pyridine (**7**)	150.7	118.2	146.2	118.2	150.7	
3-(*N*-Sulphinylamino)pyridine (**6**)	147.2	138.8	133.3	123.9	150.3	
2,6-Dimethyl-3-(*N*-sulphinylamino)pyridine (**11**)	153.2	134.4	133.4	120.2	158.5	20.3, 23.7
2-(*N*-Sulphinylamino)pyridine (**5**)	153.3	121.4	138.4	124.2	149.5	
4-Methyl-2-(*N*-sulphinylamino)pyridine (**8**)	149.9	121.8	149.2	125.0	149.2	20.8
5-Methyl-2-(*N*-sulphinylamino)pyridine (**9**)	150.8	120.9	138.0	134.1	149.1	17.8
2-Methyl-6-(*N*-sulphinylamino)pyridine (**10**)	159.0	124.0	138.5	119.1	152.5	24.3
2-(*N*-Sulphinylamino)pyrimidine (**12**)	158.1		158.3	118.9	158.3	
N-Sulphinylaniline (**1**)[b]	127.1	129.1	130.4	129.1	127.1	142.7 (C-1)

[a] Shifts are measured for solutions in $CDCl_3$, from $SiMe_4$ as internal standard. [b] See ref. 10.

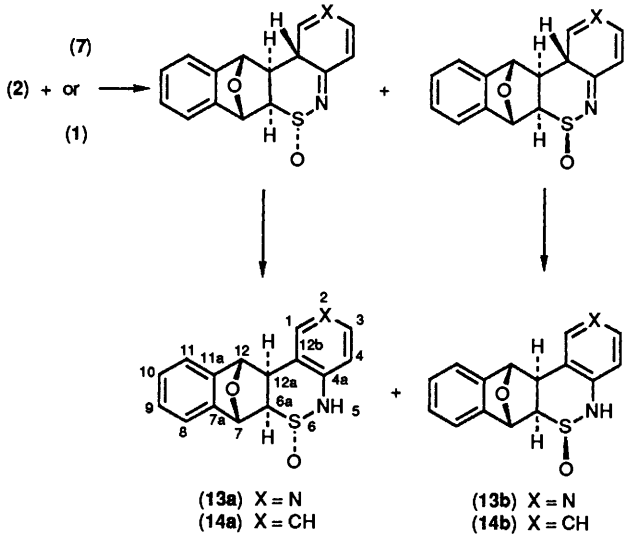
Table 2. Assignments[a] of ^{15}N NMR spectral data for (*N*-sulphinylamino)pyridines.

(*N*-Sulphinylamino)pyridine	δ_N N-1	NSO
4-(*N*-Sulphinylamino)pyridine (**7**)	−66.9	−56.7
3-(*N*-Sulphinylamino)pyridine (**6**)	−70.4	−59.1
2-(*N*-Sulphinylamino)pyridine (**5**)	−73.0	−56.8
N-Sulphinylaniline (**1**)[b]		−62.2
Pyridine[c]	−62.4	

[a] Shifts are measured for 50% solutions in deuteriobenzene from nitromethane as external standard. [b] See ref. 13. [c] See ref. 14.

(b) ^{15}N *NMR Spectra of the* (N-*Sulphinylamino*)*azines*.—The ^{15}N resonances of the NSO group in sulphinylaniline[13] (δ_N −62.2) and the heteroatom in pyridine[14] (δ_N −62.4) almost coincide for 50% solutions in C_6D_6, shifts being measured upfield from external neat $MeNO_2$. When the NSO group occurs as a substituent in the pyridine ring, the two signals diverge from this common value, the more so the closer are the two nitrogen atoms within the molecule (Table 2). We assign the more shielded (*i.e.*, more negative) signal to the pyridine heteroatom in each case; the shielding of the heterocyclic nitrogen then increases as it approaches the NSO function. This parallels the shielding of carbon in structure (**1**): $\delta_{C(4)} > \delta_{C(3)} > \delta_{C(2)}$ (see Table 1). The more deshielded signal in each case is assigned to the NSO resonance. Thus NSO groups that are conjugated with the heterocyclic nitrogen exhibit an essentially constant ^{15}N shift (δ_N −56.7 and −56.8) whereas the sidechain nitrogen which is not conjugated to the heteroatom is more shielded (δ_N −59.1). If the ^{15}N shifts of NSO groups reflect, in some degree, the shielding of the carbon of the pyridine ring to which the group is attached, they provide additional evidence that in 2-(*N*-sulphinylamino)pyridines the substituted carbon does not experience the extent of deshielding that the sum of the effects of the heterocyclic nitrogen and the substituent predicts.

(c) *Cycloadducts*.—(i) 4-(N-*Sulphinylamino*)*pyridine* (**7**). Reaction of 4-(*N*-sulphinylamino)pyridine (**7**) with 1,4-epoxy-1,4-dihydronaphthalene (**2**) in refluxing benzene resulted in a white precipitate, the NMR spectra of which indicated the presence of two products in a ratio ~5:1. These products were identified as the *trans*- and *cis-exo*-adducts (**13a** and **b**) differing in configuration at S, by analogy with the comparable adducts (**14a** and **b**) of compound (**1**) (Scheme 1). We have previously



Scheme 1.

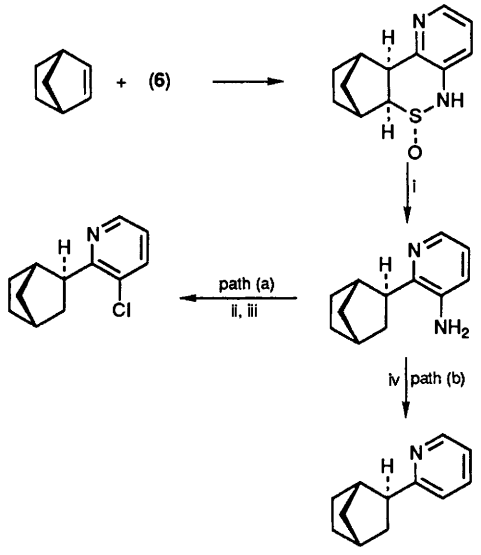
discussed in detail the assignment of the ^{13}C NMR spectrum of adduct (**14a**);[5] in Table 3 an assignment is now given of the spectrum of adduct (**14b**) and of the analogous azines (**13a** and **b**). In these adducts the change of stereochemistry at S scarcely affects the aromatic carbon resonances of the naphthalene moiety. The remaining resonances show greater changes of shift; however, their relative ordering is not changed between the two stereoisomers. The incorporation of the pyridine nitrogen also has little effect on the aromatic resonances of the naphthalene moiety; it affects the remaining resonances to similar extents in both stereoisomers and to the degrees expected from comparison of the ^{13}C NMR resonances of benzene and pyridine.

(ii) 3-(N-*Sulphinylamino*)*pyridines*. Beecken[8] deduced that the cycloaddition of compound (**6**) to bicyclo[2.2.1]hept-2-ene occurs periselectively at S and C-2 not C-4. This conclusion was reached following desulphurisation of the adduct: the resultant amine, on attempted reductive deamination, gave a product identified as a 3-chloro-2-(bicyclo[2.2.1]heptan-2-yl)pyridine, the chlorine being derived from the counterion of the diazonium intermediate (Scheme 2, path a). We have obtained unambiguous confirmation of Beecken's conclusion by effecting the deamination in non-aqueous medium[15] (Scheme 2, path b). That the product is a 2-substituted, not a 4-substituted, pyridine is clear from the observation of five, not three, ^{13}C resonances for the pyridine ring. Attempted reductive deamination in aqueous sulphuric acid led to the formation of a 3-hydroxy-2-(bicyclo[2.2.1]heptan-2-yl)pyridine.

Table 3. Assignments[a] of ^{13}C NMR spectral data for adducts[b] of 4- and 3-(*N*-sulphinylamino)pyridines (and PhNSO) with 1,4-epoxy-1,4-dihydronaphthalenes.

	δ_C													
Adduct	C-1	C-2	C-3	C-4	C-4a	C-6a	C-7	C-7a/11a[c]	C-8/11[c]	C-9/10[c]	C-12	C-12a	C-12b	C-Me
(14a)[d,e]	130.1	122.4	127.5	120.1	135.1	65.7	79.2	145.1, 145.3	119.3, 119.4	126.6, 126.6	88.1	40.5	127.0	
(14b)[e,f]	128.0	122.6	125.7	119.9	135.2	60.3	79.7	144.3, 146.	119.5, 119.6	126.5, 126.6	81.7	40.7	127.2	
(13a)	151.0		148.6	114.1	143.1	66.3	79.3	145.2, 145.3	119.6, 120.5	127.0, 127.3	88.5	37.7	122.9	
(13b)[f]	149.3		148.2	114.3	143.3	60.3	79.6	144.2, 146.3	119.6, 119.7	127.0, 127.2	81.6	38.6	121.6	
(15a)		143.2	123.0	127.2	132.1	67.0	79.4	145.3, 146.9	119.5, 120.0	126.7, 126.9	86.8	43.7	145.0	
(15b)[f]		143.1	122.6	126.7	131.9	62.0	79.9	145.8, 146.2	119.5, 119.7	126.7, 126.8	80.6	43.6	144.4	
(17)		142.4	122.8	127.0	132.0	71.4	84.5	146.0, 146.0	117.8, 118.0	127.0, 127.0	89.2	48.4	146.0	7-Me 14.9 12-Me 16.0
(18)		142.9	122.7	127.1	131.8	67.9	86.7	145.8, 146.9	117.9, 119.7	126.5, 126.6	85.6	45.4	148.1	7-Me 14.2
(19)[f]		142.6	122.9	126.9	132.3	70.2	77.5	144.7, 145.0	118.2, 119.3	126.9, 126.9	90.6	46.5	148.8	12-Me 15.7
(20a)[g]	121.8	149.8		146.8	127.3	66.0	79.4	145.3, 145.4	119.3, 119.5	126.8, 127.2	87.9	40.4	135.7	4-Me 20.3 2-Me 23.0
(20b)[f,g]	119.7	150.4		147.3	127.3	60.8	80.0	144.0, 146.0	119.5, 119.7	126.8, 127.2	81.2	40.4	135.1	4-Me 20.6 2-Me 23.4

[a] Shifts are measured for solutions in $(CD_3)_2SO$, from $SiMe_4$ as internal standard. [b] The nomenclature adopted preserves a numeration common to all tabulated adducts. See structure (**13a**). [c] Similar aromatic signals from the naphthalene moiety are not distinguished. [d] *Cf.* Ref. 5. [e] Measured for this work. [f] Minor isomers were not obtained pure; assignments were made by comparison of spectra of their mixtures with a major congener with the spectrum of the purified major product. [g] Assignment of Me resonances by comparison with the adduct from *N*-sulphinyl-2,4-xylidene (see ref. 5).



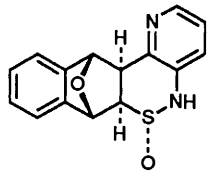
Scheme 2. *Reagents:* i, Raney nickel; ii, $NaNO_2$–HCl; iii, H_3PO_2; iv, $C_5H_{11}ONO$, THF.

Bicyclo[2.2.1]hepta-2,5-diene also added periselectively to compound (**6**) at S and C-2 as was evident from a comparison of the NMR spectra of the pyridine moiety of this adduct with those of the bicyclo[2.2.1]hept-2-ene adduct. Single products were obtained from the addition of compound (**6**) to both hydrocarbons. In each case the stereochemistry is taken to be *exo*, analogous to the addition of compound (**1**).[2–4] The configuration at S is presumed to be *trans*, as the *trans* stereoisomer predominates in the cycloaddition of compounds (**1**) and (**2**) and a bridging methano group is sterically more demanding than a bridging oxygen.

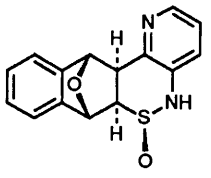
Reaction of compound (**2**) with the pyridine (**6**) in refluxing toluene gave two products in the ratio 5:1. These were identified as the *trans*- and *cis-exo*-adducts (**15a** and **b**). Prolonged reaction at room temperature gave adduct (**15a**) alone. The *exo*-ring junction is indicated by the lack of splitting of the bridgehead ^1H NMR signals by the protons at the ring junctions. That the two products (**15a** and **b**) differ only in stereochemistry at S was confirmed by the observation that their mixture was oxidised to a single product (**16**) by peracetic acid, the same product as obtained by oxidation of adduct (**15a**) alone. The ^{13}C NMR spectra of adducts (**15a** and **b**) (Table 3) when compared with the corresponding adducts of (**1**) indicated, if allowance be made for the presence of the ring heteroatom, that the cycloaddition of compounds (**2**) and (**6**) occurred with the same periselectivity as the addition of compound (**6**) to bicyclo[2.2.1]hept-2-ene, *i.e.* addition takes place at S and C-2 only; no addition at C-4 was detected. Methylation of the dienophile did not affect the periselectivity although the stereoselectivity was increased. Thus, 1,4-epoxy-1,4-dimethyl-1,4-dihydronaphthalene (**4**) was added to compound (**6**) in refluxing toluene to give a single adduct identified as (**17**). Similar addition of 1,4-epoxy-1-methyl-1,4-dihydronaphthalene (**3**) to compound (**6**) gave a mixture of two products in the ratio 4:1. The major product was purified chromatographically and was identified as compound (**18**); the minor isomer, which was not obtained pure, was identified as the regioisomer (**19**). These assignments of structure were made on the basis of comparisons of the ^{13}C and ^1H NMR spectra of the various adducts of compound (**6**) between themselves and with the adducts of compound (**1**) with the same dienophiles, previously reported.[5]

By contrast, methylation of the heterodiene at C-2 prevented cycloaddition at that position and diverted it to C-4. Thus 2,6-dimethyl-3-(*N*-sulphinylamino)pyridine (**11**) reacted with compound (**2**) in refluxing benzene to give the stereoisomers (**20a** and **b**) in the ratio ~5:1, estimated by integration of the ^1H NMR spectrum. Prolonged reaction at ambient temperature led to low yields of adduct (**20a**) alone.

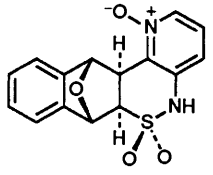
(iii) 2-(N-*Sulphinylamino*)-*pyridines and -pyrimidine*. The bright yellow colour of the product of the addition of compound (**5**) to epoxy compound (**2**) at room temperature in benzene was the first indication that the reaction differs significantly from those so far described. Addition at heterocyclic nitrogen was indicated by the lack of any N–H stretching frequency in the IR spectrum of the product and was confirmed by the observation



(15a)



(15b)



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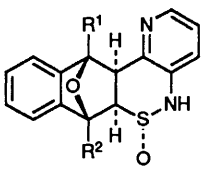
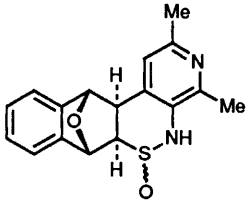
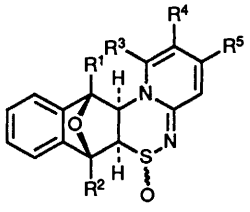


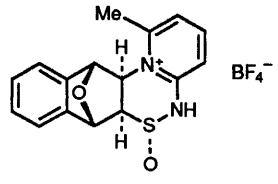
(17) $R^1 = R^2 = Me$
(18) $R^1 = H$, $R^2 = Me$
(19) $R^1 = Me$, $R^2 = H$



(20) a; *trans*
b; *cis*



(21) $R^{1-5} = H$: *trans*
(22) $R^3 = Me$, $R^1 = R^2 = R^4 = R^5 = H$: *trans*
(23) $R^5 = Me$, $R^{1-4} = H$ a: *trans*; b: *cis*
(24) $R^4 = Me$, $R^{1-3} = R^5 = H$ a: *trans*; b: *cis*
(26) $R^1 = R^2 = Me$, $R^{3-5} = H$: *trans*
(27) $R^{1-3} = Me$, $R^4 = R^5 = H$: *trans*
(28) $R^1 = Me$, $R^{2-5} = H$ a: *trans*; b: *cis*
(29) $R^2 = Me$, $R^1 = R^{3-5} = H$ a: *trans*; b: *cis*
(30) $R^1 = R^3 = Me$, $R^2 = R^4 = R^5 = H$: *trans*
(31) $R^2 = R^3 = Me$, $R^1 = R^4 = R^5 = H$: *trans*



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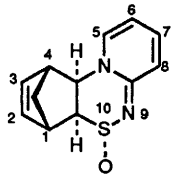

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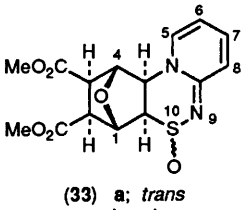
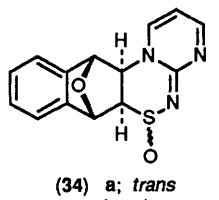


(33) a; *trans*
b; *cis*



(34) a; *trans*
b; *cis*

in the ^{13}C NMR spectrum (Table 4) of a number of protonated carbon signals equal to the sum of the numbers in the reactants; the ^1H and ^{13}C NMR spectra also showed that only a single product was formed. It was assigned the *trans* structure (**21**).

Similarly, 2-methyl-6-(*N*-sulphinylamino)pyridine (**10**) gave a single yellow adduct to which we assigned the *trans* structure (**22**). The latter two adducts were assigned a *trans* stereochemistry at S with confidence since 4- and 5-methyl-2-(*N*-sulphinylamino)pyridine (**8**) and (**9**) cycloadded similarly to compound (**2**) but each gave both a major and a minor product. The relative ^{13}C shifts of the aliphatic protons, in particular, of these compared with those of the *trans* and *cis* adducts of compounds (**1**), (**7**), and (**6**) previously described. The major and minor adducts were thus assigned structures (**23a** and **b**), respectively, for compound (**8**), and (**24a** and **b**), respectively, for compound (**9**). The ^{13}C shifts of the single adducts of compound (**3**) and its 6-methylated derivative were very similar to those of the *trans* isomers (Table 4). The colour of these adducts arises from the 2-iminopyridine chromophore. Protonation of adduct (**22**) by HBF_4 in aqueous methanol produced the colourless aromatic conjugate acid salt (**25**), treatment of which with alkali restored the colour.

Cycloaddition of compound (**5**) to 1,4-epoxy-1,4-dimethyl-1,4-dihydronaphthalene (**4**) produced a single yellow adduct taken to be compound (**26**). Remarkably, reaction of the same dienophile with compound (**10**) also gave addition to S and heterocyclic N despite both the proximity of methyl groups in the product (**27**), and the fact that the alternative *peri*-isomer, coupled at S and C-3, would be sterically less encumbered and probably stabler thermodynamically on account of fuller aromaticity. Clearly there is a strong electronic preference for the observed orientation of addition.

Nuclear Overhauser experiments were performed on adduct (**27**). Irradiation at the frequency of the aromatic methyl resonance at δ 2.34 produced an enhancement in the methyl signal at δ 1.20, thus identifying the latter signal as that due to 12-Me. Also enhanced were the doublets at δ 4.72 (confirming assignment to 12a-H) and δ 6.17 (confirming assignment to 2-H). Conversely, irradiation at the frequency of the methyl resonance at δ 1.20 enhanced the aromatic methyl signal and the doublet due to 12a-H; also enhanced was the doublet at δ 7.45, consistent with this arising from 11-H. Saturation of the methyl signal at δ 2.05 produced enhancements of the 6a-H doublet and of part of the aromatic multiplet at δ 7.25 which we therefore assign to 8-H.

Reaction of compound (**5**) with epoxy compound (**3**) produced a mixture of four adducts countable by their individual bridgehead and methyl proton resonances. The predominant isomer (*ca.* 50% of the total) was isolated by fractional crystallisation from chloroform and was identified, in the light of the foregoing NOE results, as the *trans* adduct (**28a**) by its characteristic methyl resonance. The second most abundant isomer was identified as the regioisomer (**29a**) and the minor products as their respective *cis* stereoisomers (**28b**) and (**29b**). Addition of compound (**10**) to the same dienophile gave only two products but in equal proportions; these were separated chromatographically and identified as the *trans* adducts (**30**) and (**31**). Again, therefore, the electronic preference of the cycloadditions counters the steric interactions that occur between a methyl group at position 12 and a methyl group or proton at position 1 and favours a regiochemistry of addition of 2-(*N*-sulphinylamino)pyridines to this dienophile which contrasts with that of compound (**1**).[5] The contrasting regioselectivities of addition of compound (**5**), on the one hand, and of compounds (**1**) and (**6**), on the other, to the epoxy compound (**3**) have been successfully modelled with Hückel orbitals for the heterodienes parameterised and used as discussed previously.[5,7] The dienophile was treated as a simple unsymmetrical electron-rich alkene (h_{C2} −0.3, h_{C3} −0.1, $k_{C=C}$ 1.1).

Cycloadducts (**32**) and (**33a** and **b**) have also been prepared. The former occurred as a single isomer of presumably *trans* stereochemistry. The stereoisomers (**33a** and **b**) were formed in

Table 4. Assignments[a] of ^{13}C NMR spectral data for adducts[b] of 2-(*N*-sulphinylamino)pyridines and 2-(*N*-sulphinylamino)pyrimidine with 1,4-epoxy-1,4-dihydronaphthalenes.

	δ_C												
Adduct	C-1	C-2	C-3	C-4	C-4a	C-6a	C-7	C-7a/11a[c]	C-8/11[c]	C-9/10[c]	C-12	C-12a	C-Me
(21)	135.9	108.4	137.6	123.3	150.3	65.6	75.3	143.6, 145.6	118.8, 121.4	126.6, 128.0	88.8	62.9	
(22)	145.3	109.8	135.4	120.7	151.5	67.0	75.7	143.8, 145.4	119.0, 121.6	126.7, 128.0	88.2	59.1	20.0
(23a)	137.0	111.1	147.2	121.5	150.2	64.7	75.1	143.8, 145.6	118.8, 121.0	126.5, 127.9	88.6	62.4	20.2
(23b)[d]	138.6	109.0	142.2	122.4	150.7	63.4	79.5	143.5, 145.5	119.2, 121.4	126.7, 127.9	87.4	60.3	20.4
(24a)	134.6	117.4	138.9	123.0	149.6	65.2	75.0	143.6, 145.6	118.9, 121.5	126.7, 128.0	88.8	62.7	16.7
(24b)[d]	136.8	120.6	141.4	123.0	154.2	63.7	79.6	142.3, 145.7	119.3, 121.5	126.8, 127.9	87.4	60.6	16.7
(26)	139.7	106.6	135.2	122.1	152.6	69.7	87.8	146.1, 149.8	117.2, 119.8	126.6, 128.0	90.8	68.4	12-Me 13.8 7-Me 15.4
(27)	149.8	108.9	134.9	120.5	154.3	71.2	87.8	146.1, 149.8	117.2, 119.8	126.6, 128.0	91.4	64.1	12-Me 12.7 7-Me 15.8 1-Me 20.0
(28a)	139.6	107.0	136.3	122.6	155.7	70.4	73.8	145.2, 147.0	119.0, 119.8	126.8, 127.8	93.1	65.0	12-Me 13.6
(29a)	137.7	108.7	135.5	122.8	151.9	66.0	88.6	149.6, 149.6	117.1, 121.8	126.4, 128.0	85.7	64.7	7-Me 14.5
(30)	147.3	109.0	135.4	121.0	152.1	72.7	74.0	145.2, 146.6	119.2, 121.0	126.8, 126.9	93.4	60.3	12-Me 12.5 1-Me 20.0
(31)	149.6	109.9	134.9	121.0	153.2	66.3	89.1	142.8, 145.8	117.3, 121.2	126.5, 128.2	85.5	62.8	7-Me 15.1 1-Me 20.0
(34a)	147.1	105.6	162.6		148.3	67.3	75.2	143.4, 145.4	119.0, 121.5	126.7, 128.0	88.3	63.2	
(34b)[d]	149.1	109.6	164.0		154.6	65.3	79.1	142.1, 145.4	119.6, 121.5	126.9, 129.2	86.8	62.8	

[a] Shifts are measured for solutions in $(CD_3)_2SO$, from $SiMe_4$ as internal standard. [b] The nomenclature adopted preserves a numeration common to all tabulated adducts. See structure (**13a**). [c] Similar aromatic signals from the naphthalene moiety are not distinguished. [d] Minor isomers were not obtained pure; assignments were made by comparison of spectra of their mixtures with a major congener with the spectrum of the purified major product.

the ratio 3:2 at ambient temperature as judged from NMR spectra in $(CD_3)_2SO$ which dissolved the mixture completely. However, in this solvent the proton signals from some *endo* protons were occluded by the moisture signal. The proton shifts quoted (see Experimental section) are for solution in $CDCl_3$ which dissolves adduct (**33b**) preferentially.

2-(*N*-Sulphinylamino)pyrimidine (**12**) reacted with compound (**2**) at ambient temperature in benzene to give yellow *trans* and *cis* cycloadducts (**34a** and **b**) in comparable amounts as judged from integrated ^1H NMR spectra. The less soluble adduct (**34a**) was fully characterised after separation either by precipitation from solution in dimethyl sulphoxide (DMSO) with water, followed by crystallisation from chloroform, or by Soxhlet extraction of the *cis* form from the mixed isomers with chloroform. The more soluble *cis*-adduct (**34b**) was not isolated pure but its ^1H and ^{13}C NMR spectra were assigned by comparison of the spectra of the mixed isomers with those of the purified *trans* form. The NMR spectra of *cis*-adduct (**34b**) exhibited a variability which depended on the history of its solutions. After recovery from solution in chloroform and redissolving in DMSO, the chemical shifts observed for the protons of the pyrimidine ring, and for 12a-H and 12-H, were different from those observed when the material had been precipitated in benzene and dissolved directly in DMSO. After exposure to chloroform, the doublets of doublets observed for 1-H, 2-H, and 3-H were shielded by *ca.* 0.1 ppm, the ring-junction proton 12a-H was also shielded by 0.1 ppm and the bridgehead proton 12-H by 0.05 ppm. The ^{13}C resonances for C-12a, C-1, C-2, and C-3 were shielded by 0.3, 0.6, 1.2, and 1.5 ppm, respectively; that for C-4a was deshielded by 0.6 ppm. The NMR spectra of DMSO solutions exhibited evidence of both increased moisture and traces of ethanol when the solute had been recovered from chloroform. The variation in shifts was therefore ascribed to a solvation of the *cis* isomer by adventitious hydroxylic solvents during manipulation in hot chloroform. Moisture in DMSO at room temperature does not affect the spectra, though on warming to 55 °C changes occurred. The chemical shifts of the *trans*-isomer (**34a**) were invariant but both its ^1H and ^{13}C NMR spectra indicated the formation of a chloroform solvate containing 0.5 mol $CHCl_3$ per mol of the adduct on exposure to this solvent.

Experimental

The ^1H, ^{13}C, and ^{15}N NMR spectra were measured variously on Varian A60A, JEOL FX90Q, and Brüker WP80 and MSL 300 spectrometers for solutions in $CDCl_3$, $(CD_3)_2SO$, or C_6D_6 as appropriate. Chemical shifts (δ) are quoted downfield from internal TMS for ^1H and ^{13}C spectra and upfield from external nitromethane for ^{15}N spectra. IR spectra were recorded on a Pye Unicam SP 1025 or a Perkin-Elmer 881 spectrometer, and mass-spectra were obtained at 70 eV on an AEI MS30 spectrometer linked to a DS55 data system. M.p.s were obtained using a Kofler hot-stage microscope and are uncorrected. Light petroleum refers to the fraction boiling over the range 40–60 °C.

(a) *Dienophiles.*—1,4-Epoxy-1,4-dihydronaphthalenes were prepared by trapping benzyne[16] with appropriate furans by the method of Stiles and Miller.[17] All are known compounds.[17,18]

exo,cis-*Dimethyl* 3,6-*epoxy*-1,2,3,6-*tetrahydrophthalate.* Cycloaddition of maleic anhydride (49 g, 0.5 mol) to furan (34 g, 0.5 mol) in diethyl ether (200 cm^3) occurred when the mixture was stirred for 6 h; on chilling of the product, *exo,cis*-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride (69 g, 83%) crystallised out, m.p. 122–123 °C (lit.,[19] 125–126 °C). The anhydride was dissolved in an excess of methanol containing conc. H_2SO_4 (1 mol equiv.) and was stirred overnight. After cold carbon treatment to remove the discolouring material and reduction of the volume of solution, the required diester crystallised out in 70% yield, m.p. 116–117 °C (lit.,[20] 119 °C). The bicyclo[2.2.1]-hept-2-ene and bicyclo[2.2.1]hepta-2,5-diene were commercial materials.

(b) *Aminoazines.*—All were commercial compounds which were used as supplied with the exception of 3-amino-2,6-dimethylpyridine which was prepared as follows.

2,6-Dimethylpyridine was nitrated by the method of Plazek[21] to give 2,6-dimethyl-3-nitropyridine, m.p. 36–37 °C (from cyclohexane) (lit.,[21] 37 °C) in 68% yield. To a solution of the nitropyridine (15.3 g, 0.1 mol) in methanol (400 cm^3) were added hydrazine hydrate (50 g, 1.0 mol) and 5% palladium on charcoal (300 mg) and the mixture was refluxed overnight. After filtration and removal of solvent, an oil was obtained which, on being chilled, solidified to the required 3-amino-2,6-dimethylpyridine (8.5 g, 70%), m.p. 120–122 °C (lit.,[22] 123 °C) (Found: M^+, 122.0843. Calc. for $C_7H_{10}N_2$: M, 122.0844); $\delta_H(CDCl_3)$ 2.36 (3 H, s, Me), 2.40 (3 H, s, Me), 3.55 (2 H, br, NH_2), and 6.81 (2 H, s, ArH); $\delta_C(CDCl_3)$ 19.8, 22.9, 121.0, 122.0, 137.7, 142.5, and 146.7.

(c) (N-*Sulphinylamino*)*azines*.—The general procedure was to dissolve the appropriate aminoazine (0.2 mol) in sodium-dried benzene or toluene (300 cm^3) with triethylamine (0.4 mol). To the refluxing, mechanically stirred mixture was added, dropwise, a solution of thionyl chloride (0.2 mol) in sodium-dried benzene or toluene (60 cm^3). After completion of addition the mixture was refluxed for a further 2 h; then the heavy precipitate of triethylammonium chloride was filtered off and washed with dry solvent. The combined filtrate and washings were evaporated to give a residual oil, which was immediately vacuum distilled under nitrogen. The mass spectra of the (*N*-sulphinylamino)pyridines showed loss of CO and SO as primary fragmentations directly comparable with those of PhNSO;[23,24] (*N*-sulphinylamino)pyrimidine, for which CO loss is not possible, showed loss of O, SO, and NSO. The IR spectra of all the sulphinylamines exhibited strong absorptions at 1 170–1 220 and 1 300–1 325 cm^{-1}, characteristic of S=O and N=S stretching modes, respectively.[25]

(i) 2-(N-*Sulphinylamino*)*pyridine* (**5**) (55%), b.p. 53–58 °C/0.05 mmHg, a bright orange oil which darkened to blood-red within 24 h (Found: M^+, 140.0040. $C_5H_4N_2OS$ requires M, 140.0044); m/z 140 (M^+, 55%), 112 (15), and 92 (33); $\nu_{max}(CCl_4)$ 1 186 (S=O) and 1 310 cm^{-1} (N=S); $\delta_H(CDCl_3)$ 7.2–7.4 (1 H, m), 7.7–7.9 (2 H, m), and 8.5–8.7 (1 H, m); $\delta_C(CDCl_3)$ see Table 1; $\delta_N(C_6D_6)$ see Table 2.

(ii) 3-(*N*-Sulphinylamino)pyridine (**6**) (74%), b.p. 42–46 °C/0.05 mmHg (lit.,[8] 73–73.5 °C/0.2 mmHg), a clear yellow oil darkening to dull orange over a period of several weeks (Found: M^+, 140.0041); m/z 140 (M^+, 100%), 112 (8), 107 (78), and 92 (49); $\nu_{max}(CCl_4)$ 1 170 (S=O) and 1 300 cm^{-1} (N=S); $\delta_H(CDCl_3)$ 7.08–7.47 (1 H, m), 7.83–8.32 (1 H, m), 8.37–8.64 (1 H, m), and 8.73–9.04 (1 H, m); $\delta_C(CDCl_3)$ see Table 1; $\delta_N(C_6D_6)$ see Table 2.

(iii) 4-(N-*Sulphinylamino*)*pyridine* (**7**) (46%), b.p. 84–86 °C/2 mmHg, a bright yellow oil which solidified, after distillation, to afford a yellow solid, m.p. 38–40 °C (Found: M^+, 140.0037. $C_5H_4N_2O_5$ requires M, 140.0044); m/z 140 (M^+, 100%), 112 (35), and 92 (5); $\nu_{max}(CCl_4)$ 1 175 (S=O) and 1 300 cm^{-1} (N=S); $\delta_H(CDCl_3)$ 7.50 (2 H, dd) and 8.80 (2 H, dd); $\delta_C(CDCl_3)$ see Table 1; $\delta_N(C_6D_6)$ see Table 2.

(iv) 2-*Methyl*-6-(N-*sulphinylamino*)*pyridine* (**10**) (60%), b.p. 72–74 °C/1.2 mmHg, orange-red oil which solidified to a low melting solid after distillation (Found: M^+, 154.0222. $C_5H_6N_2OS$ requires M, 154.0201); m/z 154 (M^+, 100%), 126 (8), 106 (11), and 105 (20); $\nu_{max}(CCl_4)$ 1 195 (S=O) and 1 310 cm^{-1} (N=S); $\delta_H(CDCl_3)$ 2.56 (3 H, s), 6.97–7.23 (1 H, m), and 7.48–7.68 (2 H, m); $\delta_C(CDCl_3)$ see Table 1.

(v) 5-*Methyl*-2-(N-*sulphinylamino*)*pyridine* (**9**) (32%), b.p. 94–96 °C/2.5 mmHg, a bright red oil which solidified to a low melting solid after distillation (Found: M^+, 154.0211); m/z 154 (M^+, 100%), 153 (6), 139 (5), 126 (5), 106 (11), and 105 (29); $\nu_{max}(CCl_4)$ 1 180 (S=O) and 1 315 cm^{-1} (N=S); $\delta_H(CDCl_3)$ 2.42 (3 H, s), 7.50–7.93 (2 H, m), and 8.46 (1 H, s); $\delta_C(CDCl_3)$ see Table 1.

(vi) 4-*Methyl*-2-(N-*sulphinylamino*)*pyridine* (**8**) (55%), b.p. 68–70 °C/0.2 mmHg, a bright red oil (Found: M^+, 154.0199); m/z 154 (M^+, 78%), 153 (2), 139 (4), 126 (9), 125 (7), 106 (10), and 105 (30); $\nu_{max}(CCl_4)$ 1 222 (S=O) and 1 310 cm^{-1} (N=S); $\delta_H(CDCl_3)$ 2.39 (3 H, s), 7.01 (1 H, d), 7.54 (1 H, s), and 8.41 (1 H, d); $\delta_C(CDCl_3)$ see Table 1.

(vii) 2,6-*Dimethyl*-3-(N-*sulphinylamino*)*pyridine* (**11**) (72%), b.p. 76–80 °C/1.0 mmHg, an orange oil which solidified on storage (Found: M^+, 168.0358. $C_7H_8N_2OS$ requires M, 168.0357); m/z 168 (M^+, 82%), 151 (100), 140 (10), 120 (20), and 119 (23); $\nu_{max}(CHCl_3)$ 1 160 (S=O) and 1 315 cm^{-1} (N=S); $\delta_H(CDCl_3)$ 2.48 (3 H, s), 2.51 (3 H, s), 6.93 (1 H, d, J 8 Hz), and 8.49 (1 H, d, J 8 Hz); $\delta_C(CDCl_3)$ see Table 1.

(viii) 2-(N-*Sulphinylamino*)*pyrimidine* (**12**) (28%), b.p. 88–90 °C/0.4 mmHg (bulb-to-bulb distillation), an orange oil which solidified (Found: M^+, 140.9991. $C_4H_3N_3OS$ requires: M, 140.9997); m/z 141 (M^+, 100%), 125 (5), 108 (5), 93 (12), 91 (18), and 79 (8); $\nu_{max}(CCl_4)$ 1 225 (S=O) and 1 325 cm^{-1} (N=S); $\delta_H(CDCl_3)$ 6.96 (1, H, t, J 6 Hz) and 8.45 (2 H, d, J 6 Hz); $\delta_C(CDCl_3)$ see Table 1.

(d) *Cycloadducts*.—(i) *Reaction of* 4-(N-*sulphinylamino*)*pyridine* (**7**) *and* 1,4-*epoxy*-1,4-*dihydronaphthalene* (**2**). 4-(*N*-Sulphinylamino)pyridine (2.8 g, 0.02 mol) and 1,4-epoxy-1,4-dihydronaphthalene (2.5 g, 0.02 mol) were refluxed for 18 h in benzene (50 cm^3). The mixed stereoisomers of the adduct (3.1 g, 55%) were isolated by filtration. Integration of the ^1H NMR spectrum indicated a *trans*/*cis* ratio of *ca.* 5:1. Recrystallisation from MeCN afforded trans,exo-7,12-*epoxy*-6a,7,12-12a-*tetrahydro*-5H-6-*thia*-2,5-*diazabenz*[a]*anthracene* 6-*oxide* (**13a**), m.p. 245–248 °C (decomp.) (Found: M^+, 284.0618. $C_{15}H_{12}N_2O_2S$ requires M, 284.0619); m/z 284 (M^+, 1%), 236 (20), 235 (10), 150 (24), 137 (23), 131 (12), and 118 (100); ν_{max}(Nujol) 1 053, 1 062, and 1 075 (SO), and 3 148 cm^{-1} (NH); $\delta_H[(CD_3)_2SO]$ 3.26 (1 H, d, $J_{6a.12a}$ 8.4 Hz, 6a-H), 3.47 (1 H, d, $J_{12a.6a}$ 8.4 Hz, 12a-H), 5.21 (1 H, s, 12-H), 5.60 (1 H, s, 7-H), 6.84 (1 H, d, $J_{3.4}$ 5.4 Hz, 4-H), 7.2–7.5 (4 H, m, 8-, 9-, 10-, 11-H), 8.27 (1 H, d, $J_{3.4}$ 5.4 Hz, 3-H), and 8.56 (1 H, s, 1-H), [N-H not observed]; $\delta_C[(CD_3)_2SO]$ see Table 3. The *cis*-isomer (**13b**) was not isolated pure but characteristic singlet proton resonances were discernible for 1-H (δ 8.88), 7-H (δ 6.05), and 12-H (δ 5.70); $\delta_C[(CD_3)_2SO]$ see Table 3.

(ii) *Reaction of* 3-(N-*sulphinylamino*)*pyridine* (**6**) *and bicyclo*-[2.2.1]*hept*-2-*ene*. 3-(*N*-Sulphinylamino)pyridine (8.6 g, 0.06 mol) and bicyclo[2.2.1]hept-2-ene (8.5 g, 0.09 mol) were refluxed for 24 h in benzene (45 cm^3). The cooled mixture was filtered to give trans,exo-1,2,3,4,4a,10a-*hexahydro*-9H-10-*thia*-5,9-*diaza*-1,4-*methanophenanthrene*-10-*oxide* (6.84 g, 48%), m.p. 247–249 °C [from EtOH] (lit.,[8] 261–262 °C) (Found: C, 61.5; H, 6.0; N, 12.0. $C_{12}H_{14}N_2OS$ requires C, 61.5; H, 6.2; N, 12.0%); m/z 234 (M^+, 19%), 218 (11), 217 (6), and 186 (100); ν_{max}(Nujol) 1 073 (SO) and 3 072 cm^{-1} (NH); $\delta_H[(CD_3)_2SO]$ 1.02 (1 H, br d, J_{gem} 10 Hz, 11-H_{anti}), 1.40–1.75 (5 H, br m, 2- and 3-H, and 11-H_{sym}), 2.33 (1 H, s, 4-H), 2.42 (1 H, s, 1-H), 3.08–3.28 (2 H, m, 4a-H and 10a-H), 7.05–7.25 (2 H, m, 7- and 8-H), 8.17 (1 H, dd, $J_{6,7}$ 3.7, $J_{6.8}$ 2.6 Hz, 6-H), and 9.06 (1 H, br s, N-H); $\delta_C[(CD_3)_2SO]$ 28.1, 30.1, 32.9, 38.3, 45.9, 46.6, 67.1, 122.3, 126.5, 131.3, 143.0, and 148.6.

Desulphurisation of the adduct. To a solution of the above *trans,exo*-adduct (3.0 g) in water (150 cm^3)–dioxane (40 cm^3) containing NAOH (18 g) was added Raney nickel (Ni:Al 1:1) (30 g) in small portions. The mixture was refluxed for 20 h and then steam distilled. The distillate was saturated with NaCl to precipitate *exo*-3-amino-2-(bicyclo[2.2.1]heptan-2-yl)pyridine (1.63 g, 68%), m.p. 103–104 °C (from cyclohexane) (lit.,[8] 104–105 °C).

Non-aqueous deamination. To a solution of *exo*-3-amino-2-(bicyclo[2.2.1]heptan-2-yl)pyridine (2.25 g) in refluxing THF

(20 cm^3) was added a solution of pentyl nitrite (3.0 g) in THF (40 cm^3); the mixture was refluxed for a further 5 h and was then kept overnight. After removal of solvent, the crude product was chromatographed (alumina/light petroleum, then diethyl ether) to give exo-2-(*bicyclo*[2.2.1]*heptan-2-yl*)*pyridine* (0.3 g, 15%) as an oil (Found: M^+, 173.1240. $C_{12}H_{15}N$ requires *M*, 173.1276); *m/z* 173 (M^+, 9%), 145 (9), 144 (48), 106 (100), and 79 (9); $\delta_H(CDCl_3)$ 0.8–2.5 (10 H, m), 2.80 (1 H, dd, ArC*H*), 6.7–7.1 (2 H, m, 3- and 5-H), 7.17–7.57 (1 H, m, 4-H), and 8.46 (1 H, br d, 6-H); $\delta_C(CDCl_3)$ 28.9, 30.1, 35.6, 36.5, 36.6, 42.8, 49.3, 120.2, 121.4, 135.6, 148.6, and 165.6. Unchanged amine (1.19 g) was also recovered.

Aqueous deamination. To a stirred solution of *exo*-3-amino-2-(bicyclo[2.2.1]heptan-2-yl)pyridine (1.2 g) in cold dil. H_2SO_4 was added a solution of an excess of $NaNO_2$ (1.5 g) in water (10 cm^3), followed by hypophosphorous acid (3.0 cm^3). Evolution of N_2 was immediate. After being stirred overnight, the mixture was filtered, and the insoluble product was washed with water, dried, and recrystallised from acetone to give exo-3-*hydroxy*-2-(*bicyclo*[2.2.1]*heptan-2-yl*)*pyridine* (0.71 g, 59%), m.p. 176–178 °C (vacuum sublimation) (Found: C, 76.2; H, 8.1; N, 7.6. $C_{12}H_{15}NO$ requires C, 76.2; H, 8.0; N, 7.4%); *m/z* 189 (M^+, 14%), 160 (34), and 122 (100); $\delta_H[(CD_3)_2SO]$ 0.8–1.8 (7 H, m), 2.0–2.5 (3 H, br s), 3.12 (1 H, dd, ArC*H*), 6.8–7.25 (2 H, m, 4- and 5-H), 7.95 (1 H, dd, 6-H), and 9.6 (1 H, br s, OH); $\delta_C[(CD_3)_2SO]$ 29.1, 29.9, 34.0, 35.0, 36.0, 41.8, 41.9, 120.7, 121.3, 138.4, 150.9, and 152.4.

(iii) *Reaction of* 3-(N-*sulphinylamino*)*pyridine* (**6**) *and bicyclo*-[2.2.1]*hepta*-2,5-*diene*. 3-(*N*-Sulphinylamino)pyridine (4.2 g, 0.03 mol) and bicyclo[2.2.1]hepta-2,5-diene (2.82 g, 0.03 mol) were refluxed together for 72 h in dry benzene. After having cooled, the adduct was filtered off, washed with benzene, and dried to give trans,exo-1,4,4a,10a-*tetrahydro*-9H-10-*thia*-5,9-*diaza*-1,4-*methanophenanthrene* (2.49 g, 35%), m.p. 244–248 °C (from EtOH) (Found: C, 62.0; H, 5.3; N, 12.1. $C_{12}H_{12}N_2OS$ requires C, 62.0; H, 5.2; N, 12.1%); *m/z* 232 (M^+, 16%), 184 (17), 183 (24), 167 (79), 150 (17), 149 (26), 137 (100), 119 (16), and 118 (42); ν_{max}(Nujol) 1 075 (SO) and 3 074 cm^{-1} (NH); $\delta_H[(CD_3)_2SO]$ 1.18 (1 H, d, J_{gem} 9 Hz, 11-H_{anti}), 1.73 (1 H, d, J_{gem} 9 Hz, 11-H_{syn}), 2.97 (2 H, br s, 1- and 4-H), 3.11 (2 H, br s, 4a- and 10a-H), 6.39 (2 H, s, 2- and 3-H), 7.1–7.3 (2 H, m, 7- and 8-H), 8.22 (1 H, dd, $J_{6,7}$ 3.9, $J_{6,8}$ 2.2 Hz, 6-H), and 9.25 (1 H, s, N-H); $\delta_C[(CD_3)_2SO]$ 41.6, 42.2, 44.0, 52.1, 65.4, 122.5, 126.8, 131.7, 138.1, 138.8, 143.3, and 148.7.

(iv) *Reaction of* 3-(N-*sulphinylamino*)*pyridine* (**6**) *and* 1,4-*epoxy*-1,4-*dihydronaphthalene* (**2**). 3-(*N*-Sulphinylamino)pyridine (6.5 g, 0.046 mol) was refluxed for 5.5 h with 1,4-epoxy-1,4-dihydronaphthalene (6.6 g, 0.046 mol) in dry toluene (50 cm^3). After the mixture had cooled, a first crop of a single adduct (8.56 g, 75%) was separated by filtration. This was recrystallised from acetone to give trans, exo-7,12-*epoxy*-6a,7,12,12a-*tetrahydro*-5H-6-*thia*-1,5-*diazabenz*[a]*anthracene* 6-*oxide* (**15a**), m.p. 246–248 °C (Found: C, 63.3; H, 4.3; N, 9.9. $C_{15}H_{12}N_2O_2S$ requires C, 63.4; H, 4.2; S, 9.9%); *m/z* 284 (M^+, 17%), 236 (31), 207 (26), and 118 (100); ν_{max}(Nujol) 1 060 (SO) and 3 210 cm^{-1} (NH); $\delta_H[(CD_3)_2SO]$ 3.28 (1 H, d, $J_{6a,12a}$ 8.5 Hz, 6a-H), 3.47 (1 H, d, $J_{12a,6a}$ 8.5 Hz, 12a-H), 5.24 (1 H, s, 12-H), 5.63 (1 H, s, 7-H), 7.0–7.6 (6 H, m, 3-, 4-, 8-, 9-, 10-, and 11-H), 8.25 (1 H, dd, $J_{2,3}$ 3.4, $J_{2,4}$ 2.7 Hz, 2-H), and 9.14 (1 H, s, N-H); $\delta_C[(CD_3)_2SO]$ see Table 3. The same material (34%) was obtained from extended reaction (24 days) of compounds (**2**) and (**6**) at ambient temperature.

On storage, the filtrate from the reaction at high temperature deposited a second crop of product (0.72 g, 5.5%) which contained both stereoisomers. Spectroscopic characteristics for *cis,exo*-7,12-epoxy-6a,7,12,12a-tetrahydro-5*H*-6-thia-1,5-diazabenz[*a*]anthracene 6-oxide (**15b**) are ν_{max}(Nujol) 1 046 and 1 061 (SO) and 3 160 cm^{-1} (NH); $\delta_H[(CD_3)_2SO]$ 3.07 (1 H, d, $J_{6a,12a}$ 9.2 Hz, 6a-H), 3.47 (1 H, d, $J_{12a,6a}$ 9.2 Hz, 12a-H), 5.69 (1 H, s, 12-H), 6.24 (1 H, s, 7-H), 7.1–7.6 (6 H, m, 3-, 4-, 8-, 9-, 10-, and 11-H), 8.31 (1 H, dd, $J_{2,3}$ 4.9, $J_{2,4}$ 2.4 Hz, 2-H), and 9.02 (1 H, s, N-H); $\delta_C[(CD_3)_2SO]$ see Table 3. Compound (**15b**) was not isolated pure.

Oxidation of trans,exo-7,12-*epoxy*-6a,7,12,12a-*tetrahydro*-5H-6-*thia*-1,5-*diazabenz*[a]*anthracene* 6-*oxide* (**15a**). A solution of compound (**15a**) (2.0 g) and hydrogen peroxide (100 vol; 3 cm^3) in glacial acetic acid (20 cm^3) was stirred at ambient temperature for 96 h. Filtration gave 7,12-*epoxy*-6a,7,12,12a-*tetrahydro*-5H-6-*thia*-1,5-*diazabenz*[a]*anthracene* 1,6,6-*trioxide* (**16**) (1.8 g, 81%), m.p. 269–272 °C (from $MeCO_2H$) (Found: C, 57.1; H, 3.8; N, 8.9. $C_{15}H_{12}N_2O_4S$ requires C, 56.9; H, 3.8; N, 8.9%); *m/z* 316 (M^+, 0.7%), 252 (0.5), 182 (7), and 118 (100); ν_{max}(Nujol) 1 140, 1 327 (SO_2), and 3 050 cm^{-1} (NH); $\delta_H[(CD_3)_2SO]$ 3.89 (1 H, d, $J_{6a,12a}$ 9.3 Hz, 6a-H), 4.01 (1 H, d, $J_{12a,6a}$ 9.3 Hz, 12a-H), 5.42 (1 H, s, 12-H), 5.89 (1 H, s, 7-H), 6.90 (1 H, d, $J_{3,4}$ 8.3 Hz, 4-H), 7.2–7.6 (5 H, m, 3-, 8-, 9-, 10-, and 11-H), 8.18 (1 H, d, $J_{2,3}$ 6.3 Hz, 2-H), (N-H not observed); $\delta_C[(CD_3)_2SO]$ 43.1, 62.2, 80.9, 84.9, 116.4, 119.9, 120.0, 124.8, 127.4, 127.5, 134.8, 137.9, 138.5, 143.7, and 143.9. An identical product resulted from the oxidation of compounds (**15a** and **b**) together.

(v) *Reaction of* 3-(N-*sulphinylamino*)*pyridine* (**6**) *and* 1,4-*epoxy*-1,4-*dimethyl*-1,4-*dihydronaphthalene* (**4**). 3-(*N*-Sulphinylamino)pyridine (1.5 g) and 1,4-epoxy-1,4-dimethyl-1,4-dihydronaphthalene (1.7 g) were refluxed for 7 days in dry toluene 25 cm^3). The cooled mixture was filtered to give trans,exo-7,12-*epoxy*-7,12-*dimethyl*-6a,7,12,12a-*tetrahydro*-5H-6-*thia*-1,5-*diazabenz*[a]*anthracene* 6-*oxide* (**17**) (1.65 g, 53%), m.p. 228–230 °C (from MeCN) (Found: M^+, 312.0931. $C_{17}H_{16}N_2O_2S$ requires *M*, 312.0933); *m/z* 312 (M^+, 50%), 264 (25), 249 (25), 149 (15), and 146 (100); ν_{max}(Nujol) 1 058 (SO) and 3 188 cm^{-1} (NH); $\delta_H[(CD_3)_2SO]$ 1.20 (3 H, s, 12-Me), 1.90 (3 H, s, 7-Me), 3.4 (2 H, s, 6a- and 12a-H), 7.35 (6 H, br s, 3-, 4-, 8-, 9-, 10-, and 11-H), 8.27 (1 H, t, $J_{2,3}$ and $J_{2,4}$ 3 Hz, 2-H), and 9.27 (1 H, s, N-H); $\delta_H[(CD_3)_2SO]$ see Table 3.

(vi) *Reaction of* 3-(N-*sulphinylamino*)*pyridine* (**6**) *and* 1,4-*epoxy*-1-*methyl*-1,4-*dihydronaphthalene* (**3**). A solution containing 3-(*N*-sulphinylamino)pyridine (1.6 g) and 1,4-epoxy-1-methyl-1,4-dihydronaphthalene (1.9 g) in dry toluene (15 cm^3) was refluxed for 36 h, cooled, and the precipitate was filtered off. It comprised two regioisomers in the ratio 4:1. The major isomer, separated by column chromatography ($Al_2O_3/CHCl_3$), was trans,exo-7,12-*epoxy*-7-*methyl*-6a,7,12,12a-*tetrahydro*-5H-6-*thia*-1,5-*diazabenz*[a]*anthracene* 6-*oxide* (**18**), m.p. 233–236 °C (Found: M^+, 298.0776. $C_{16}H_{14}N_2O_2S$ requires *M*, 298.0773); *m/z* 298 (M^+, 20%), 250 (17), 221 (10), 149 (23), and 132 (100); ν_{max}(Nujol) 1 055 and 1 064 (SO) and 3 198 cm^{-1} (NH); $\delta_H[(CD_3)_2SO]$ 1.90 (3 H, s, 7-Me), 3.21 (1 H, d, $J_{6a,12a}$ 9 Hz, 6a-H), 3.50 (1 H, d, $J_{12,6a}$ 9 Hz, 12a-H), 5.18 (1 H, s, 12-H), 7.1–7.6 (6 H, m, 3-, 4-, 8-, 9-, 10-, and 11-H), 8.25 (1 H, t, $J_{2,3}$, $J_{2,4}$ 4 Hz, 2-H), and 9.30 (1 H, s, N-H); $\delta_C[(CD_3)_2SO]$ see Table 3.

trans,exo-7,12-Epoxy-12-methyl-6a,7,12,12a-tetrahydro-5*H*-6-thia-1,5-diazabenz[*a*]anthracene 6-oxide (**19**) had $\delta_H[(CD_3)_2SO]$ 1.30 (3 H, s, 12-Me), 3.21 (1, H, d, $J_{6a,12a}$ 8 Hz, 6a-H), 3.50 (1 H, d, $J_{12a,6a}$ 8 Hz, 12a-H), 5.60 (1 H, s, 7-H), 7.1–7.6 (6 H, m, 3-, 4-, 8-, 9-, 10-, and 11-H), 8.25 (1 H, t, $J_{2,3}$, $J_{2,4}$ 4 Hz, 2-H), and 9.20 (1 H, s, N-H); $\delta_C[(CD_3)_2SO]$ see Table 3. Compound (**19**) was not isolated pure.

(vii) *Reaction of* 2,6-*dimethyl*-3-(N-*sulphinylamino*)*pyridine* (**11**) *and* 1,4-*epoxy*-1,4-*dihydronaphthalene* (**2**). 2,6-Dimethyl-3-(*N*-sulphinylamino)pyridine (1.7 g) and 1,4-epoxy-1,4-dihydronaphthalene (1.5 g) were refluxed for 24 h in benzene (10 cm^3). The resultant precipitate contained the two stereoisomers of the adduct in the ratio 5:1. Fractional crystallisation from MeOH afforded trans,exo-7,12-*epoxy*-2,4-*dimethyl*-6a,7,12,12a-*tetrahydro*-5H-6-*thia*-3,5-*diazabenz*[a]*anthracene* 6-*oxide* (**20a**) (1.25 g, 40%), m.p. 254–256 °C (decomp.) (Found: M^+, 312.0936. $C_{17}H_{16}N_2O_2S$ requires 312.0932; *m/z* 312 (M^+, 1.5%), 264 (45),

263 (13), 178 (25), 177 (19), and 118 (100); ν_{max}(Nujol) 1 040 (SO) and 3 180 cm^{-1} (NH); $\delta_H[(CD_3)_2SO]$ 2.39 (6 H, s, 2- and 4-Me), 3.17 (1 H, d, $J_{6a,12a}$ 8.6 Hz, 6a-H), 3.36 (1 H, d, $J_{12a,6a}$ 8.6 Hz, 12a-H), 5.21 (1 H, s, 12-H), 5.61 (1 H, s, 7-H), 7.1–7.6 (5 H, m, 1-, 8-, 9-, 10-, and 11-H), and 8.69 (1 H, s, N-H); $\delta_C[(CD_3)_2SO]$ see Table 3.

cis,exo-7,12-Epoxy-2,4-dimethyl-6a,7,12,12a-tetrahydro-5*H*-6-thia-3,5-diazabenz[*a*]anthracene 6-oxide (**20b**) had $\delta_H[(CD_3)_2SO]$ 2.42 (6 H, s, 2- and 4-Me), 3.00 (1 H, d, $J_{6a,12a}$ 8.6 Hz, 6a-H), 3.36 (1 H, d, $J_{12a,6a}$ 8.6 Hz, 12a-H), 5.66 (1 H, s, 12-H), 6.01 (1 H, s, 7-H), 7.1–7.6 (5 H, m, 1-, 8-, 9-, 10-, and 11-H), and 8.54 (1 H, s, N-H); $\delta_C[(CD_3)_2SO]$ see Table 3. Compound (**20b**) was not isolated pure.

2-(*N*-Sulphinylamino)pyridines are up to 50-fold more reactive than the heterodienes so far described;[1] they could consequently react at ambient temperature. In cases where a single adduct resulted, reaction at higher temperatures revealed no further products. Typically, the procedure was to stir stoicheiometric amounts of the reactants (0.02 mol) for hours or days in benzene or toluene solution (25 cm^3), then to isolate and characterise the precipitated product. Thus were prepared the following adducts; reaction times and yields, which were not optimised, are indicated parenthetically. NMR data for isomers which were not obtained pure are also given.

(viii) trans,exo-7,12-*Epoxy*-6a,7,12,12a-*tetrahydro*-6-*thia*-5,12b-*diazabenz*[a]*anthracene* 6-*oxide* (**21**) (20 h, 64%), m.p. 227–230 °C (from MeOH) (Found: C, 63.3; H, 4.3; N, 10.0. $C_{15}H_{12}N_2O_2S$ requires C, 63.4; H, 4.4; N, 9.8%); *m/z* 284 (M^+, 2%), 268 (2), 166 (7), 150 (41), 144 (17), 140 (17), and 118 (100); ν_{max}(Nujol) 1 060 and 1 070 cm^{-1} (SO); $\delta_H[(CD_3)_2SO]$ 3.75 (1 H, d, $J_{6a,12a}$ 8.5 Hz, 6a-H), 4.58 (1 H, d, $J_{12a,6a}$ 8.5 Hz, 12a-H), 5.29 (1 H, s, 12-H), 5.94 (1 H, s, 7-H), 6.25–6.55 (2 H, m, 2- and 4-H), 7.15–7.55 (5 H, m, 3-, 8-, 9-, 10-, and 11-H), and 7.78 (1 H, d, $J_{1,2}$ 7.0 Hz, 1-H); $\delta_C[(CD_3)_2SO]$ see Table 4.

(ix) trans,exo-7,12-*Epoxy*-1-*methyl*-6a,7,12,12a-*tetrahydro*-6-*thia*-5,12b-*diazabenz*[a]*anthracene* 6-*oxide* (**22**) (24 h, 93%), m.p. 213–214 °C (from $CHCl_3$) (Found: M^+, 298.0775. $C_{16}H_{14}N_2O_2S$ requires *M*, 298.0776); *m/z* 298 (M^+, 6%), 180 (11), 164 (15), 154 (55), 144 (30), 132 (70), 118 (75), 116 (70), and 115 (100); ν_{max}(Nujol) 1 078 cm^{-1} (SO); $\delta_H[(CD_3)_2SO]$ 2.41 (3 H, s, 1-Me), 3.74 (1 H, d, $J_{6a,12a}$ 8.5 Hz, 6a-H), 4.74 (1 H, d, $J_{12a,6a}$ 8.5 Hz, 12a-H), 5.21 (1 H, s, 12-H), 5.97 (1 H, s, 7-H), 6.25 (1 H, d, $J_{2,3}$ 7 Hz, 2-H), 6.38 (1 H, d, $J_{3,4}$ 9 Hz, 4-H), and 6.95–7.70 (5 H, m, 3-, 8-, 9-, 10-, and 11-H); $\delta_C[(CD_3)_2SO]$ see Table 4.

Conjugate acid (**25**) *of* trans,exo-7,12-*epoxy*-1-*methyl*-6a,7,12,12a-*tetrahydro*-6-*thia*-5,12b-*diazabenz*[a]*anthracene* 6-*oxide* (**22**). To a solution of compound (**22**) (0.5 g) in methanol (20 cm^3) was added, dropwise, 40% aq. HBF_4 (1.5 g). The mixture was stirred for 18 h then filtered to give the *salt* (**25**) (0.65 g, 88%), m.p. 257–261 °C (from MeOH) (Found: C, 50.5; H, 3.9; N, 7.5. $C_{16}H_{15}BF_4N_2O_2S$ requires C, 49.8; H, 3.9; N, 7.3%); ν_{max}(Nujol) 1 030–1 080 (SO and BF_4^-), and 3 290 cm^{-1} (NH); $\delta_H[(CD_3)_2SO]$ 2.75 (3 H, s), 4.20 (1 H, d, *J* 8.5 Hz), 5.20 (1 H, d, *J* 8.5 Hz), 5.80 (1 H, s), 6.26 (1 H, s), 7.0–7.75 (6 H, m), and 8.95 (1 H, t, *J* 8 Hz) (N-H not observed); $\delta_C[(CD_3)_2SO]$ 21.0, 64.1, 64.5, 76.0, 87.2, 116.3, 119.5, 120.3, 120.9, 127.6, 128.4, 143.2, 143.9 (2), 150.4, and 151.2.

(x) trans,exo-7,12-*Epoxy*-2-*methyl*-6a,7,12,12a-*tetrahydro*-6-*thia*-5,12b-*diazabenz*[a]*anthracene* 6-*oxide* (**24a**) (24 h, 52%), m.p. 244–247 °C (from $CHCl_3$) (Found: M^+, 298.0775. $C_{16}H_{14}N_2O_2S$ requires *M*, 298.0776); *m/z* 298 (M^+, 6%), 164 (27), 154 (54), 144 (19), 132 (65), 118 (82), 116 (72), and 115 (100); ν_{max}(Nujol) 1 055 cm^{-1} (SO); $\delta_H[(CD_3)_2SO]$ 2.06 (3 H, s, 2-Me), 3.69 (1 H, d, $J_{6a,12a}$ 8.5 Hz, 6a-H), 4.51 (1 H, d, $J_{12a,6a}$ 8.5 Hz, 12a-H), 5.29 (1 H, s, 12-H), 5.92 (1 H, s, 7-H), 6.45 (1 H, d, $J_{3,4}$ 9.2 Hz, 4-H), and 7.0–7.65 (6 H, m, 1-, 3-, 8-, 9-, 10-, and 11-H); $\delta_C[(CD_3)_2SO]$ see Table 4.

cis,exo-7,12-*Epoxy*-2-*methyl*-6a,7,12,12a-*tetrahydro*-6-*thia*-5,12b-*diazabenz*[a]*anthracene* 6-*oxide* (**24b**) (24 h, 34%), m.p. 217–220 °C (from $CHCl_3$) (Found: M^+, 298.0775); *m/z* 298 (M^+, 4%), 164 (33), 154 (39), 144 (19), 132 (43), 118 (83), 116 (70), and 115 (100); ν_{max}(Nujol) 1 020 cm^{-1} (SO); $\delta_H[(CD_3)_2SO]$ 2.18 (3 H, s, 2-Me), 3.21 (1 H, d, $J_{6a,12a}$ 9.2 Hz, 6a-H), 4.70 (1 H, s, $J_{12a,6a}$ 9.2 Hz, 12a-H), 5.44 (1 H, s, 12-H), 5.67 (1 H, s, 7-H), 6.70 (1 H, d, $J_{3,4}$ 9.2 Hz, 4-H), 7.05–7.65 (5 H, m, 3-, 8-, 9-, 10-, and 11-H), and 7.93 (1 H, s, 1-H); $\delta_C[(CD_3)_2SO]$ see Table 4.

(xi) trans,exo-7,12-*Epoxy*-3-*methyl*-6a,7,12,12a-*tetrahydro*-6-*thia*-5,12b-*diazabenz*[a]*anthracene* 6-*oxide* (**23a**) (24 h, 78%), m.p. 260–263 °C (decomp.) (from $CHCl_3$) (Found: M^+, 298.0781. $C_{16}H_{14}N_2O_2S$ requires *M*, 298.0776); *m/z* 298 (M^+, 13%), 180 (14), 164 (27), 154 (45), 144 (16), and 132 (100); ν_{max}(Nujol) 1 062 cm^{-1} (SO); $\delta_H[(CD_3)_2SO]$ 2.13 (3 H, s, 3-Me), 3.68 (1 H, d, $J_{6a,12a}$ 8.5 Hz, 6a-H), 4.55 (1 H, d, $J_{12a,6a}$ 8.5 Hz, 12a-H), 5.26 (1 H, s, 12-H), 5.93 (1 H, s, 7-H), 6.25 (1 H, d, $J_{1,2}$ 6. Hz, 2-H), 6.30 (1 H, s, 4-H), 7.2–7.6 (4 H, m, 8-, 9-, 10-, and 11-H), and 7.70 (1 H, d, $J_{1,2}$ 6. Hz, 1-H); $\delta_C[(CD_3)_2SO]$ see Table 4.

cis,exo-7,12-Epoxy-3-methyl-6a,7,12,12a-tetrahydro-6-thia-5,12b-diazabenz[*a*]anthracene 6-oxide (**23b**) had $\delta_H[(CD_3)_2SO]$ 2.22 (3 H, s, 3-Me), 3.16 (1 H, d, $J_{6a,12a}$ 8.5 Hz, 6a-H), 4.70 (1 H, d, $J_{12a,6a}$ 8.5 Hz, 12-H), 5.35 (1 H, s, 12-H), 5.65 (1 H, s, 7-H), 6.5 (2 H, br s, 2- and 4-H), 7.15–7.65 (4 H, m, 8-, 9-, 10-, and 11-H), and 7.95 (1 H, d, $J_{1,2}$ 6.0 Hz, 1-H); $\delta_C[(CD_3)_2SO]$ see Table 4.

(xii) trans,exo-7,12-*Epoxy*-7,12-*dimethyl*-6a,7,12,12a-*tetrahydro*-6-*thia*-5,12b-*diazabenz*[a]*anthracene* 6-*oxide* (**26**) (24 h, 71%), m.p. 227–229 °C (from acetone) (Found: C, 65.5; H, 5.4; N, 8.9. $C_{17}H_{16}N_2O_2S$ requires C, 65.4; H, 5.2; N, 9.0%); *m/z* 312 (M^+, 8%), 172 (16), 166 (32), 150 (21), 146 (100), and 140 (27); ν_{max}(Nujol) 1 085 cm^{-1} (SO); $\delta_H[(CD_3)_2SO]$ 1.29 (3 H, s, 12-Me), 2.09 (3 H, s, 7-Me), 3.74 (1 H, d, $J_{6a,12a}$ 8.6 Hz, 6a-H), 4.49 (1 H, d, $J_{12a,6a}$ 8.6 Hz, 12a-H), 6.36 (1 H, td, $J_{1,2} = J_{2,3}$ = 6.6, $J_{2,4}$ 1.3 Hz, 2-H), 6.60 (1 H, d, $J_{3,4}$ 9.2 Hz, 4-H), 7.15–7.35 (5 H, m, 3-, 8-, 9-, 10-, and 11-H), and 7.61 (1 H, d, $J_{1,2}$ 6.6 Hz, 1-H); $\delta_C[(CD_3)_2SO]$ see Table 4.

(xiii) trans,exo-7,12-*Epoxy*-1,7,12-*trimethyl*-6a,7,12,12a-*tetrahydro*-6-*thia*-5,12b-*diazabenz*[a]*anthracene* 6-*oxide* (**27**) (13 days, 50%), m.p. 172–174 °C (from $CHCl_3$) (Found: C, 66.0; H, 5.5; N, 8.4. $C_{18}H_{18}N_2O_2S$ requires C, 62.2; H, 5.6; N, 8.6%); *m/z* 326 (M^+, 2.5%), 278 (2), 172 (35), 154 (55), 146 (75), and 132 (45); ν_{max}(Nujol) 1 087 and 1 095 cm^{-1} (SO); $\delta_H[(CD_3)_2SO]$ 1.24 (3 H, s, 12-Me), 2.11 (3 H, s, 7-Me), 2.39 (3 H, s, 1-Me), 3.83 (1 H, d, $J_{6a,12a}$ 8 Hz, 6a-H), 4.75 (1 H, d, $J_{12a,6a}$ 8 Hz, 12a-H), 6.15 (1 H, d, $J_{2,3}$ 7 Hz, 2-H), 6.53 (1 H, d, $J_{3,4}$ 9 Hz, 4-H), and 6.9–7.6 (5 H, m, 3-, 8-, 9-, 10-, and 11-H); $\delta_C[(CD_3)_2SO]$ see Table 4.

(xiv) trans,exo-7,12-*Epoxy*-12-*methyl*-6a,7,12,12a-*tetrahydro*-6-*thia*-5,12b-*diazabenz*[a]*anthracene* 6-*oxide* (**28a**) (8 days, *ca.* 28%), m.p. 234–236 °C (from $CHCl_3$) (Found: M^+, 298.0766. $C_{16}H_{14}N_2O_2S$ requires *M*, 298.0776); *m/z* 298 (M^+, 4%), 166 (24), 158 (16), 150 (16), 140 (24), 132 (76), and 118 (100); ν_{max}(Nujol) 1 062 cm^{-1} (SO); $\delta_H[(CD_3)_2SO]$ 1.30 (3 H, s, 12-Me), 4.05 (1 H, d, $J_{6a,12a}$ 8.8 Hz, 6a-H), 4.39 (1 H, d, $J_{12a,6a}$ 8.8 Hz, 12a-H), 5.96 (1 H, s, 7-H), 6.28 (1 H, td, $J_{1,2} = J_{2,3}$ = 7.1, $J_{2,4}$ 1.3 Hz, 2-H), 6.52 (1 H, d, $J_{3,4}$ 9.0 Hz, 4-H), 7.1–7.5 (5 H, m, 3-, 8-, 9-, 10-, and 11-H), and 7.62 (1 H, d, $J_{1,2}$ 7.1 Hz, 1-H); $\delta_C[(CD_3)_2SO]$ see Table 4.

trans,exo-7,12-Epoxy-7-methyl-6a,7,12,12a-tetrahydro-6-thia-5,12b-diazabenz[*a*]anthracene 6-oxide (**29a**) was not obtained pure but the following NMR characteristics were measured for it on the mixture: $\delta_H[(CD_3)_2SO]$ 2.04 (1 H, s, 7-Me), 3.50 (1 H, d, $J_{6a,12a}$ 8.3 Hz, 6a-H), 4.71 (1 H, d, $J_{12a,6a}$ 8.3 Hz, 12a-H), 5.12 (1 H, s, 12-H), 6.41 (1 H, td, $J_{1,2} = J_{2,3}$ = 6.6, $J_{2,4}$ 1.4 Hz, 2-H), 6.58 (1 H, d, $J_{3,4}$ 9.0 Hz, 4-H), 7.15–7.55 (5 H, m, 3-, 8-, 9-, 10-, and 11-H), and 7.86 (1 H, d, $J_{1,2}$ 6.6 Hz, 1-H); $\delta_C[(CD_3)_2SO]$ see Table 4. The mixture also showed evidence

of the minor *cis*-isomers (**28b**) and (**29b**) but their spectra were not discernible in their entirety, nor assignable with confidence.

(xv) trans,exo-7,12-*Epoxy*-1,7-*dimethyl*-6a,7,12,12a-*tetrahydro*-6-*thia*-5,12b-*diazabenz*[a]*anthracene* 6-*oxide* (**31**) [5 days, 35%; separated from compound (**30**) by column chromatography (Al_2O_3/$CHCl_3$), title compound (**31**) eluting first], m.p. 196–198 °C (from acetone) (Found: C, 65.4; H, 5.1; N, 9.0. $C_{17}H_{16}N_2O_2S$ requires C, 65.4; H, 5.2; N, 9.0%); *m/z* 312 (M^+, 1%), 180 (2), 158 (32), 154 (62), and 132 (43); ν_{max}(Nujol) 1 089 cm^{-1} (SO); δ_H[$(CD_3)_2SO$] 2.10 (3 H, s, 7-Me), 2.48 (3 H, s, 1-Me), 3.51 (1 H, d, $J_{6a.12a}$ 8.5 Hz, 6a-H), 4.91 (1 H, d, $J_{12a.6a}$ 8.5 Hz, 12a-H), 4.98 (1 H, s, 12-H), 6.28 (1 H, d, $J_{2.3}$ 7 Hz, 2-H), 6.50 (1 H, d, $J_{3.4}$ 9 Hz, 4-H), and 7.0–7.7 (5 H, m, 3-, 8-, 9-, 10-, and 11-H); δ_C[$(CD_3)_2SO$] see Table 4.

trans,exo-7,12-*Epoxy*-1,12-*dimethyl*-6a,7,12,12a-*tetrahydro*-6-*thia*-5,12b-*diazabenz*[a]*anthracene* 6-*oxide* (**30**) (35%), m.p. 215–217 °C (from acetone) (Found: C, 65.5; H, 5.3; N, 8.8%); *m/z* 312 (M^+, 1%), 264 (1), 158 (24), 154 (59), and 132 (38); ν_{max} 1 071 and 1 092 cm^{-1} (SO); δ_H[$(CD_3)_2SO$] 1.30 (1 H, s, 12-Me), 2.35 (3 H, s, 1-Me), 4.10 (1 H, d, $J_{6a.12a}$ 9 Hz, 6a-H), 4.58 (1 H, d, $J_{12a.6a}$ 9 Hz, 12a-H), 6.00 (1 H, s, 7-H), 6.20 (1 H, d, $J_{2.3}$ 7 Hz, 2-H), 6.50 (1 H, d, $J_{3.4}$ 9 Hz, 4-H), and 7.0–7.7 (5 H, m, 3-, 8-, 9-, 10-, and 11-H); δ_C[$(CD_3)_2SO$] see Table 4.

(xvi) trans,exo-1,4,4a,10a-*Tetrahydro*-10-*thia*-4b,9-*diaza*-1,4-*methanophenanthrene* 6-*oxide* (**32**) (4 days, 85%), m.p. 192–196 °C (from $CHCl_3$) (Found: C, 62.1; H, 5.4; N, 11.9. $C_{12}H_{12}N_2OS$ requires C, 62.1; H, 5.2; N, 12.1%), *m/z* 232 (M^+, 7%), 216 (5), 184 (3), 150 (31), 140 (28), 118 (100), and 92 (37); ν_{max} 1 035 cm^{-1} (SO); δ_H[$(CD_3)_2SO$] 1.55 (1 H, d pseudo quin., J_{gem} 9.8, $J_{11anti.10a} = J_{11anti.4a} = J_{11anti.1} = J_{11anti.4}$ *ca.* 1.6 Hz, 11-H_{anti}), 2.07 (1 H, dt, J_{gem} 9.8, $J_{11syn.1} = J_{11syn.4}$ = 1.6 Hz, 11-H_{syn}), 3.05 (1 H, br s, 4-H), 3.13 (1 H, dd, $J_{4a.10a}$ 8.9, $J_{11anti.10a}$ 1.9 Hz, 10a-H), 3.37 (1 H, br s, 1-H), 4.2 (1 H, dd, $J_{10a.4a}$ 8.9, $J_{11anti.4a}$ 1.3 Hz, 4a-H), 6.26 (1 H, dd, $J_{2.3}$ 5.6, $J_{3.4}$ 3.1 Hz, 3-H), 6.48 (1 H, dd, $J_{2.3}$ 5.6, $J_{1.2}$ 2.8 Hz, 3-H), 6.49 (1 H, ddd, $J_{5.6} = J_{6.7}$ = 6.7, $J_{6.8}$ = 1.5 Hz, 6-H), 6.86 (1 H, dd, $J_{7.8}$ 9.7, $J_{6.8}$ 1.5 Hz, 8-H), and 7.31–7.36 (2 H, m, 5- and 7-H); assignments confirmed by decoupling experiments; δ_C[$(CD_3)_2SO$] 43.6, 45.6, 56.2, 62.5, 63.5, 114.5, 125.5, 137.6, 141.0, 141.4, 141.9, and 158.0.

(xvii) trans,exo,exo-*Dimethyl* 1,4-*epoxy*-1,2,3,4,4a,10a-*hexahydro*-10-*thia*-4b,9-*diazaphenanthrene*-2,3-*dicarboxylate* 10-*oxide* (**33a**) (36 h, 30%), m.p. 213–217 °C (from MeOH) (Found: M^+, 352.0731. $C_{15}H_{16}N_2O_6S$ requires *M*, 352.0729); *m/z* 352 (M^+, 0.3%), 336 (2), 140 (26), 113 (100), and 68 (48); ν_{max}(Nujol) 1 074 (SO) and 1 735 cm^{-1} (CO); δ_H($CDCl_3$) 3.09 (1 H, d, $J_{2.3}$ 9.1 Hz, 2- or 3-H), 3.24 (1 H, d, $J_{2.3}$ 9.1 Hz, 3- or 2-H), 3.67 (1 H, d, $J_{4a.10a}$ 8.3 Hz, 10a-H), 3.67 (3 H, s, Me), 3.69 (3 H, s, Me), 4.22 (1 H, d, $J_{4a.10a}$ 8.3 Hz, 4a-H), 4.94 (1 H, s, 4-H), 5.61 (1 H, s, 1-H), 6.27 (1 H, ddd, $J_{5.6} = J_{6.7}$ = 6.7, $J_{6.8}$ 1.5 Hz, 6-H), 6.68 (1 H, d, $J_{7.8}$ 9.3 Hz, 4-H), 7.03–7.15 (1 H, m, 7-H), and 7.34–7.41 (1 H, m, 5-H); δ_C[$(CD_3)_2SO$] 47.7, 50.9, 51.4, 51.6, 63.4, 63.9, 74.6, 87.6, 108.2, 123.1, 135.6, 136.8, 150.1, 169.8, and 170.2.

cis,exo,exo-Dimethyl 1,4-epoxy-1,2,3,4,4a,10a-hexahydro-10-thia-4b,9-diazaphenanthrene-1,4-dicarboxylate 10-oxide (**33b**) (36 h, 20%) was not isolated pure; δ_H($CDCl_3$) 3.09 (1 H, d, $J_{2.3}$ 9.1 Hz, 2- or 3-H), 3.34 (1 H, d, $J_{2.3}$ 9.1 Hz, 3- or 2-H), 3.56 (1 H, d, $J_{4a.10a}$ 8.3 Hz, 10a-H), 3.69 (3 H, s, Me), 3.70 (3 H, s, Me), 4.63 (1 H, d, $J_{4a.10a}$ 8.3 Hz, 4a-H), 4.92 (1 H, s, 4-H), 4.99 (1 H, s, 1-H), 6.56 (1 H, ddd, $J_{5.6} = J_{6.7}$ = 6.7, $J_{6.8}$ 1.5 Hz, 6-H), 6.89 (1 H, d, $J_{7.8}$ 9.0 Hz, 8-H), 7.03–7.15 (1 H, m, 7-H), and 7.34–7.41 (1 H, m, 5-H); δ_C[$(CD_3)_2SO$] 47.5, 51.3, 51.4, 51.5, 61.4, 63.0, 79.0, 86.2, 111.3, 124.1, 138.5, 138.8, 155.9, 169.6, and 170.2.

(xviii) trans,exo-7,12-*Epoxy*-6a,7,12,12a-*tetrahydro*-6-*thia*-4,5,12b-*triazabenz*[a]*anthracene* 6-*oxide* (**34a**) (24 h, 50%), m.p. 262 °C (decomp.) (from $CHCl_3$) (Found: M^+, 285.0587. $C_{14}H_{11}N_3O_2S$ requires *M*, 285.0602) *m/z* 285 (M^+, 2.5%), 167 (24), 151 (19), 144 (20), 141 (68), 118 (57), 116 (75), and 115 (100); ν_{max}(Nujol) 1 083 cm^{-1} (SO); δ_H[$(CD_3)_2SO$] 3.90 (1 H, d, $J_{6a.12a}$ 8.3 Hz, 6a-H), 4.61 (1 H, d, $J_{12a.6a}$ 8.3 Hz, 12a-H), 5.34 (1 H, s, 12-H), 5.99 (1 H, s, 7-H), 6.50 (1 H, dd, $J_{1.2}$ 6.8, $J_{2.3}$ 3.8 Hz, 2-H), 7.20–7.30 (2 H, m, 9- and 10-H), 7.39 (1 H, d, *J* 6.6 Hz, 8- or 11-H), 7.48 (1 H, d, *J* 6.9 Hz, 11- or 8-H), 8.22 (1 H, dd, $J_{1.2}$ 6.8, $J_{1.3}$ 2.3 Hz, 1-H), and 8.46 (1 H, dd, $J_{1.2}$ 3.8, $J_{2.3}$ 2.3 Hz, 3-H); δ_C[$(CD_3)_2SO$] see Table 4.

cis,exo-7,12-Epoxy-6a,7,12,12a-tetrahydro-6-thia-4,5,12b-triazabenz[*a*]anthracene 6-oxide (**34b**) was not isolated pure; its NMR characteristics measured on a mixture with (**34a**), as precipitated from benzene, were as follows: δ_H[$(CD_3)_2SO$] 3.43 (1 H, d, $J_{6a.12a}$ 8.2 Hz, 6a-H), 4.90 (1 H, d, $J_{12a.6a}$ 8.2 Hz, 12a-H), 5.53 (1 H, s, 12-H), 5.74 (1 H, s, 7-H), 7.01 (1 H, dd, $J_{1.2}$ 6.6, $J_{2.3}$ 4.0 Hz, 2-H), 7.24–7.32 (2 H, m, 9- and 10-H), 7.43 (1 H, d, *J* 5.9 Hz, 8- or 11-H), 7.49 (1 H, d, *J* 6.3 Hz, 11- or 8-H), 8.61 (1 H, dd, $J_{1.2}$ 6.6, $J_{1.3}$ 2.3 Hz, 1-H), and 8.70 (1 H, dd, $J_{2.3}$ 4.0 and $J_{1.3}$ 2.3 Hz, 3-H); δ_C[$(CD_3)_2SO$] see Table 4.

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