1,2-Thiazines and Related Heterocycles. Part 2.[1] Synthesis and Characterisation of the Cycloadducts of *N*-Sulphinylanilines and 1,4-Epoxy-1,4-dihydronaphthalenes, Derivatives of 5*H*-6-Thia-5-azabenz[*a*]anthracene 6-Oxide

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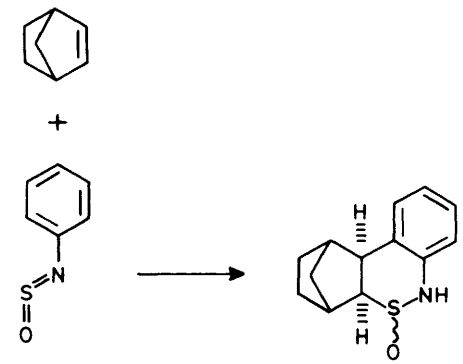
Cycloaddition of *N*-sulphinylanilines to 1,4-epoxy-1,4-dihydronaphthalenes yields 7,12-epoxy-6a,7,12,12a-tetrahydro-5*H*-6-thia-5-azabenz[*a*]anthracene 6-oxides. Positional isomerism may arise in the adducts from unsymmetrical substitution in the reactants; diastereoisomerism occurs owing to the chirality created at sulphur by the cycloaddition. The structures and isomeric preferences of the various adducts are elucidated and their reactions to give the title heterocycles and other products are described.

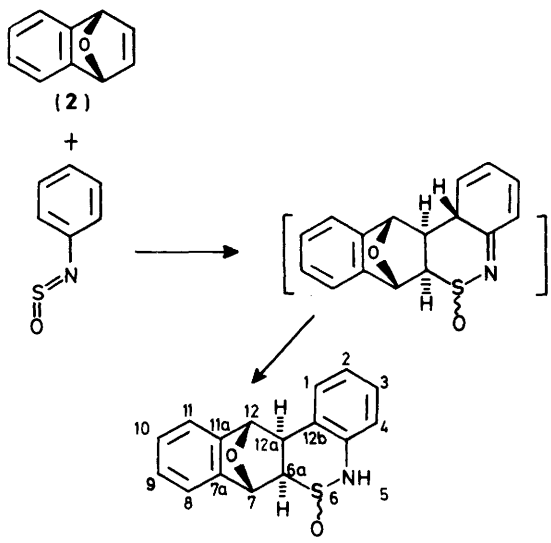
Several years ago the cycloaddition of *N*-sulphinylanilines, ArN=S=O, to norbornene derivatives (Scheme 1) to give 1,2-thiazine *S*-oxides, e.g. (**1**), was described.[2,3] Only bridged bicyclic alkenes were found to be reactive towards *N*-sulphinylanilines, although Beecken[4] described the cycloaddition of a few heterocyclic sulphinylamino compounds to ethoxyacetylene. In this early work the stereochemistry of the ring junction in compound (**1**) was inferred from the ^{1}H n.m.r. spectra, but little or no consideration has been given to the relative stereochemistry of the S–O bond. Also, since apparently so few alkenes undergo cycloaddition to *N*-sulphinylanilines, little has been done by way of development of this type of reactivity for the synthesis of 1,2-thiazine structures.

Previously, we have reported the cycloaddition of certain hetero-bridged bicyclic alkenes to *N*-sulphinylanilines and, in particular, have shown that the cycloadditions of *N*-sulphinylanilines to 1,4-epoxy-1,4-dihydronaphthalene (**2**) are pericyclic reactions of the Diels–Alder type with inverse electron demand.[1] Now we report the characterisation of the products of these reactions.



(**1**)

Scheme 1.



(**2**)

(**3**)

a ; S—O *trans* to bridging O
b ; S—O *cis* to bridging O

Scheme 2.

Results and Discussion

(*a*) *Structure of the Adducts.*—When 1,4-epoxy-1,4-dihydronaphthalene (**2**) is dissolved in a slight excess of *N*-sulphinylaniline and the solution set aside for several days, the mixture solidifies. Dilution with diethyl ether permits filtration and, on standing, the filtrate and washings yield a further crop of product; dilution of the reactants at the outset considerably slows the reaction at ambient temperature. This, however, is necessary in the case of solid substituted *N*-sulphinylanilines. Raising the temperature naturally increases the reaction rate, but it also increases the formation of the diastereoisomeric products (see below) which are not produced in significant quantities at ambient temperature in the cases of monosubstituted *N*-sulphinylanilines.

On the basis of our finding that the cycloaddition of *N*-sulphinylanilines to compound (**2**) is pericyclic and so probably involves a suprafacial–suprafacial approach of the reactants,[1] together with precedent for additions to bridged alkenes,[2–8] we expected an *exo*-ring junction to occur in the adduct as shown for compound (**3**) in Scheme 2.

Positional isomerism arises in the adducts from 3-substituted *N*-sulphinylanilines, a 1- or 3-substituent resulting in the product [*viz.* numerotation indicated for compound (**3**)]. On steric grounds the 3-substituted product is intuitively expected to predominate, as any interaction of the substituent with 12-H is thereby avoided. Positional isomerism may also arise in the cycloadducts if the dienophile is unsymmetrically substituted. We have examined the consequences of methylation of the bridgehead positions of compound (**2**) (*vide infra*).

Cycloaddition to *N*-sulphinylanilines, generally, creates a

chiral centre at S. Diastereoisomerism may therefore occur in the products which result from cycloaddition to 1,4-epoxy-1,4-dihydronaphthalenes, depending on whether the S–O bond is formed *cis* or *trans* to the bridging oxygen.*

Although the weight of evidence is that the *N*-sulphinylanilines exist with the (*Z*)-configuration about the N–S bond in the ground state,[9,10] if they were to enter the transition state for cycloaddition with this geometry, molecular models predict a large steric interaction between the sulphinyl oxygen, which has a bigger spatial requirement than the sulphur lone pair,[11] and the bridging oxygen. The expectation, therefore, is that the preferred configuration at sulphur for a kinetically controlled product is *trans*. A crystal structure determination has been carried out for the major adduct of 2-nitro-*N*-sulphinylaniline with compound (**2**) which confirms this reasoning.[12] It is unlikely that the nitro substituent would effect the stereochemistry of addition, and we infer that all the *N*-sulphinylanilines employed give a *trans*-cycloadduct as the kinetically preferred diastereoisomer. The preferred cycloadduct (**3a**) of *N*-sulphinylaniline and compound (**2**) is thus fully described as (6*RS*,6a*RS*,7*SR*,12*SR*,12a*RS*)-7,12-epoxy-6a,7,12,12a-tetrahydro-5*H*-6-thia-5-azabenz[*a*]anthracene 6-oxide. None of the substitutions in compound (**2**) considered in this paper affect the stereochemical prefix.

(*b*) *N.M.R. Spectra of the* trans-*Adducts.*— (i) ^{1}H *N.m.r. spectra.* The ^{1}H n.m.r. spectra of the *trans*-adduct (**3a**) consists of four groups of lines. At lowest field (δ 9.07) a broadened singlet occurs, due to 5_N-H. A complex resonance at δ 6.80—7.55, which we have not attempted to resolve, is assigned to the various aromatic protons. On the grounds of relative proximity to the electronegative SO function, the bridgehead protons 7- and 12-H are assigned the resonances observed at δ 5.59 and 5.14, respectively (the assignment is justified below). These signals show a small ill-resolved splitting of *ca.* 1 Hz arising from a long range coupling of 7- and 12-H as demonstrated by spin decoupling experiments. They show no coupling to 6a- and 12a-H of the ring junction, confirming the *endo*-configuration of the latter.[13] The *endo*-protons 6a- and 12a-H have coupled spins ($J_{6a,12a}$ 8 Hz) resulting in two doublet resonances, centred at δ 3.12 and 3.17 and having the appearance of a pseudo-quartet. The assignment of the upfield signal to 6a-H is confirmed by the disappearance of the four-bond coupling[14] of 2 Hz on irradiation of 5_N-H.

(ii) ^{13}C *N.m.r. spectra.* An examination of the ^{13}C n.m.r. spectra of compound (**3a**) and its derivative collectively has permitted the assignment of resonances to all the carbons. Although the symmetry of the dienophile is lost on cycloaddition to an *N*-sulphinylaniline, the carbon atoms of the benzo ring of compound (**2**) are remote from the perturbation and their paired, or still coincident, resonances are readily recognisable in all the spectra. The resonances of the carbon atoms in the sulphinylaniline moiety were assigned on the basis of the characteristic shifts induced by substituents together with multiplicities observed in off-resonance experiments. In general, the effects for *ipso*, *ortho*, *meta*, and *para* positions within the diene-derived moiety are in good agreement with those for simple benzene derivatives.[15] Assignments were possible even for 1- and 3-substituted adducts, congeners from the cycloaddition of compound (**2**) to 3-substituted *N*-sulphinylanilines which were not separated. The results are presented in Table 1. Unless indicated in the footnotes to the Table, resonances are not specifically assigned to paired atoms and, given the uncertainties, for any substance, other resonances which occur within 2 p.p.m. of each other and which exhibit like off-resonance multiplicities may be interchanged. For such closely similar cases the ordering has been made on the basis of expectation from the substituent shift.

Adduct (**3a**) manifests four aliphatic carbon resonances at δ 40.8, 66.0, 79.4, and 88.3 p.p.m. and, as expected, each gives a doublet in an off-resonance experiment. This splitting is lost from the downfield pair of resonances in the adduct from the 1,4-dimethylated derivative of compound (**2**) confirming their assignment to the bridgehead carbons. The resonance at δ 79.4 is assigned to C-7 and that δ 88.3 to C-12, also on the basis of substituent effects. Cycloaddition of *N*-sulphinylaniline to 1,4-epoxy-1-methyl-1,4-dihydronaphthalene leads to isomeric adducts which have a 7- or 12-methyl substituent; on steric grounds, the former isomer is expected to predominate. The major product from the cycloaddition has bridgehead resonances at δ 86.6 and 87.1 p.p.m. which is consistent with the assignment of the signal at δ 79.4 in the spectrum of compound (**3a**) to C-7, methylation deshielding it by 7—7.5 p.p.m. Complementary evidence is found from the effects of substituents at position 1 upon the other bridgehead signal. Reference to Table 1 shows that whenever the adduct bears a 1-substituent the bridgehead signal at δ 88.3 in compound (**3a**) is shifted upfield by 2—2.5 p.p.m. whilst the line at δ 79.4 is hardly perturbed. Assuming that the perturbing 1-substituent would cause a steric compression shift[16] of the adjacent bridgehead carbon, we assign the resonance at δ 88.3 to C-12. (Two of the sulphinylamines used, *N*-sulphinyl-3,5- and -2,5-xylidine give adducts which possess, necessarily, a substituent at C-1. The association of the perturbation of the C-12 bridgehead signal with a 1-substituent is unambiguously provided by the adducts derived from these two compounds.)

The ring junction resonances at δ 40.8 and 66.0 p.p.m. are assigned to C-12a and C-6a, respectively, on the grounds of their relative proximities to the electronegative sulphinyl group and the observation that the carbon attached to sulphur in *N*-phenylcyclohexylsulphinamide,[17] as a model compound, resonates at δ 62.4 p.p.m.

It is interesting to note that our argument so far has led to the conclusion that in compound (**3a**) the bridgehead carbon C-7 is shielded more than C-12, but for the corresponding protons the converse is true. A similar situation holds for the ring junction resonances. In confirmation of this, ^{13}C–^{1}H chemical shift cross-correlation experiments[18] were performed for the bridgehead and ring junction signals. By observation of the residual ^{13}C–^{1}H couplings in the off-resonance ^{13}C n.m.r. spectra of compound (**3a**) for eight different decoupler frequencies, the exact decoupling frequencies were interpolated. It was shown unambiguously that the more shielded bridgehead carbon is attached to the less shielded bridgehead proton and *vice versa*. The results for the ring junction resonances were less clear cut as the signal from C-12a is masked by those from $(CD_3)_2SO$, the only suitable solvent found, and location of the exact decoupling frequency for C-12a is therefore difficult. The results, however, strongly indicate again that the less shielded carbon bears the more shielded proton and *vice versa* at the ring junctions and consequently confirms the assignments that have been made.

(*c*) *Isomeric preferences.*—(i) *Alternative configuration at* S. When *N*-sulphinylaniline is treated with compound (**2**) in chlorobenzene at 80—110 °C, the adduct precipitates rapidly. A ^{1}H n.m.r. spectrum [$(CD_3)_2SO$] of the product shows extra lines when compared with the spectrum discussed above of compound (**3a**). In particular, a second NH resonance at δ 9.00 and a new pair of bridgehead protons at δ 5.67 and 5.98 are clearly observed; additional ring junction signals are less readily

* Throughout the rest of this paper, the terms *cis* and *trans* will refer to the stereochemical relationship of the S–O bond of the adduct and the bridging oxygen.

Table 1. Assignments[a] of ^{13}C n.m.r. spectra for compound (**3a**) and its derivatives

Sub-stituent	δ/p.p.m.													
	$C_{subst.}$	C-6a	C-12a	C-7	C-12	C-1	C-2	C-3	C-4	C-4a	C-12b	C-7a,-11a[b]	C-8,-11[b]	C-9,-10[b]
H		66.0	40.8	79.4	88.3	130.3	122.6	127.7	119.6	135.3	126.9	145.5	119.5	126.9
												145.5	119.6	126.9
1-NO_2		57.7	40.7	78.8	83.2	149.5	116.9	128.6	124.7	137.6	119.4	146.7	119.4	126.8
												146.7	119.1	126.8
2-NO_2		65.7	40.3	79.0	88.4	127.1	142.5	123.5	120.6	142.0	127.9	145.1	119.4	126.1
												145.1	119.9	126.9
3-NO_2		66.0	40.7	79.1	88.0	131.4	118.7	142.9	113.7	136.7	134.8	145.0	119.4	126.8
												145.0	120.3	127.2
4-NO_2		65.9	40.8	79.0	88.2	136.8	124.6	121.8	139.1	131.7	131.0	145.1	119.5	126.8
												145.1	120.3	127.2
1-MeO	55.8	64.9	39.9	79.0	86.6	156.8	104.6	128.2	112.1	135.7	114.1	145.0	119.4	126.6
												145.2	120.0	126.6
2-MeO	55.2	65.5	40.8	79.2	88.0	115.2	154.8	113.3	120.2	127.7	128.1	145.2	119.2	126.7
												145.4	120.2	127.0
3-MeO	54.9	65.6	39.9	79.0	88.1	130.8	108.3	158.5	104.6	136.1	118.7	145.0	119.4	126.6
												145.2	120.0	126.6
1-Cl		65.9	38.8	79.5	86.8	133.8	123.2	128.8	118.9	137.3	124.0	145.3	118.9	126.9
												145.3	119.5	127.2
2-Cl		65.5	40.2	79.1	88.0	129.6	128.9	127.3	121.0	134.2	125.9	145.1	119.2	126.7
												145.1	120.3	127.0
3-Cl		65.9	40.3	79.2	88.2	131.9	122.2	131.6	120.4	137.0	126.0	145.3	119.5	126.9
												145.3	119.7	127.2
4-Cl		66.1	42.2	79.1	88.3	129.1	123.0	128.0	123.1	132.1	129.5	145.1	119.4	126.7
												145.2	120.2	127.1
1-Me	19.1	65.9	37.9	79.3	86.6	136.6	120.4	124.7	117.8	129.2	128.0	145.2	119.6	127.4
												145.6	119.9	127.4
2-Me	20.3	65.7	40.7	79.1	88.0	130.4	131.3	128.0	119.3	132.5	126.4	145.2	119.3	126.4
												145.4	120.1	126.7
3-Me	20.6	65.8	40.4	79.2	88.2	130.0	123.2	136.8	120.1	135.0	123.7	145.2	119.3	126.7
												145.4	119.8	127.0
4-Me	17.4	65.7	40.9	79.2	88.3	129.0	121.9	127.9	126.9	133.0	126.9	145.1	119.3	126.7
												145.5	120.0	126.9
2-NH_2		65.5	42.1	79.2	87.8	115.3	143.5	113.8	120.1	124.4	126.9	145.0	119.2	126.6
												145.4	119.7	126.9
4-NH_2		65.8	41.1	79.2	88.1	118.0	122.6	113.6	138.5	120.1	127.1	145.0	119.2	126.5
												145.5	119.8	126.8
2-CO_2Me	51.9	65.9	40.9	79.2	88.4	131.6	123.6	129.0	120.5	140.4	127.1	145.3	119.4	126.8
	166.0											145.3	119.6	127.1
7-Me	14.4	66.6	42.2	86.6	87.1	129.8	122.2	127.3	119.2	134.9	126.9	145.0[c]	117.8[e]	126.6
												148.0[d]	119.9[f]	126.9
7,12-Me_2	15.1	69.9	45.7	88.5	84.7	131.5	121.4	127.5	119.8	135.0	124.5	148.2	117.8	126.7
	16.1											148.8	118.2	126.7
2,4-Me_2	17.2	65.7	41.0	79.2	88.1	128.1	130.5	129.6	126.7	130.5	126.9	145.0	119.1	126.5
	20.1											145.4	119.8	126.7
1,3-Me_2	17.2	65.6	38.2	79.4	86.8	133.8	123.9	132.7	123.9	128.5	124.8	145.0	119.5	126.8
	19.0											145.7	119.5	126.9
1,4-Me_2	18.8	65.8	37.7	79.2	86.6	136.0	118.1	125.2	120.8	134.6	126.7	145.0	119.3	126.7
	20.4											145.5	119.3	126.7

[a] Shifts are measured, for solutions in $(CD_3)_2SO$, from tetramethylsilane as internal standard. [b] Paired signals, where different, are not specifically assigned. [c] Signal from C-11a. [d] Signal from C-7a. [e] Signal from C-8. [f] Signal from C-11.

discernible, but two further lines at δ 2.98 and 3.24 suggest the presence of a second pseudo quartet, overlapping that of compound (**3a**), but centred *ca.* 0.2 p.p.m. to higher field. The aromatic multiplet remains essentially unchanged; however, it is evident from the integrated spectra of the mixture that aromatic resonances must occur in association with the new lines.

We ascribe structure (**3b**), *i.e.* the diastereoisomer with the alternative configuration at S, to this additional product obtained with (**3a**) at high temperature. The only likely alternative structures to (**3b**) would possess at least one *exo*-proton which would couple to the adjacent bridgehead with *J* *ca.* 4 Hz,[13] and no such splitting of any bridgehead resonance is observed.

For the reaction carried out at 90 °C, the ratio of compounds (**3a**):(**3b**) is *ca.* 4:1, as determined from the integrated ^1H n.m.r. spectra, but we have not isolated (**3b**), the more soluble isomer, uncontaminated by (**3a**). Similarly, the adducts obtained at 90 °C from 4-substituted *N*-sulphinylanilines all show (^1H n.m.r.) the presence of minor *cis* components. There appears to be no simple relationship between the proportions of the diastereoisomers observed and the electronic character of the substituents; this would be expected if they were mainly determined by the different steric interactions in the transition state of the *E* and *Z* configurations of the *N*-sulphinylaniline with the bridging oxygen of compound (**2**).

Although we have not investigated the reactions of 2-

Table 2. Assignments[a] of ^{13}C n.m.r. spectra for dimethylated derivatives of compound (**3a**) differing in the configuration at S

Sub-stituent	δ/p.p.m.													
	$C_{subst.}$	C-6a	C-12a	C-7	C-12	C-1	C-2	C-3	C-4	C-4a	C-12b	C-7a,-11a[b]	C-8,-11[b]	C-9,-10[b]
1,3-Me_2	17.2	65.6	38.2	79.4	86.8	133.8	123.9	132.7	123.9	128.5	124.8	145.0	119.3	126.8
trans	19.0											145.7	119.5	126.9
cis	17.4	59.2	42.3	77.1	85.0	134.8	125.3	134.1	124.4	128.5	124.8	143.6	118.7	126.7
	19.9											147.0	119.5	126.7
1,4-Me_2	18.8	65.8	37.7	79.2	86.6	136.0	118.1	125.2	120.8	134.6	126.7	145.0	119.3	126.7
trans	20.4											145.5	119.3	126.7
cis	18.8	59.8	41.9	77.0	84.7	137.0	119.3	126.7	121.6	136.5	126.7	143.7	117.4	126.7
	19.9											147.1	118.7	126.7

[a] Shifts were measured, for solutions in $(CD_3)_2SO$ from tetramethylsilane as internal standard. [b] Paired signals, where different, are not specifically assigned.

substituted *N*-sulphinylanilines with compound (**2**) at high temperatures, the spectra of the products precipitated at ambient temperature often show traces (*ca.* 5%) of the *cis*-isomer as judged from the characteristic bridgehead signals. (The behaviour of products from 3-substituted *N*-sulphinylanilines is discussed in the next section.)

For all the products the bridgehead proton signals of the *cis*-isomer occur 0.3—0.5 p.p.m. downfield from those of the corresponding *trans*-isomer. As for compound (**3a**), we assign the more deshielded bridgehead signal to 7-H and the relatively shielded bridgehead signal to 12-H. By comparison with compound (**3a**), for (**3b**) this represents a downfield shift of 0.3 p.p.m. for the 7-H signal and of 0.53 p.p.m. for the 12-H signal. The assignment implies the change in the configuration at S to have the greater effect on the more distant proton. The magnetic anisotropy of the S–O bond has been likened to that of both carbonyl and ethynyl bonds.[19,20] The present results imply that the anisotropic shielding effect on the bridgehead protons is greater when the S–O bond is oriented as in the *trans*-isomer (**3a**). If the conformations of the products in solution resemble that of the 4-nitro derivative of (**3a**) in the crystalline state, the structure of which has been determined, the greatest shielding effect is associated with a pseudoaxial orientation of the S–O bond, approximately parallel to the *endo* C–H bonds and perpendicular to the direction of the bridgehead C–H bonds.

We have not attempted to assign ^{13}C n.m.r. spectra for all the *cis*-diastereoisomers of the adducts reported in Table 1. However, we found that the products obtained from *N*-sulphinyl-2,5- and -3,5-xylidines contain significant proportions of the *cis*-diastereoisomers even when formed at ambient temperature (*ca.* 25 and 45%, respectively) and, moreover, in the latter case are easily separable by fractional crystallisation. We have examined the ^{13}C n.m.r. spectra of these materials to assess the effects of change in configuration at S on the pattern of carbon resonances.

The assignments of Table 2 were made in the same way as those of Table 1. In general, the change in configuration at S from *trans* to *cis* has the effect of deshielding the carbons in the diene moiety of the adduct plus C-12a, whilst the other atoms of the dienophile moiety which are close to S are shielded, and the rest are hardly affected. In contrast to the effects of the configuration change on the corresponding proton signals, the bridgehead carbon resonances manifest a lesser change of shift than the ring junction resonances; also, the bridgehead carbon resonances become relatively shielded, the proximal C-7 more so than the distal C-12.

(ii) *Positional isomers from 3-substituted* N-*sulphinylanilines.* The reactions of 3-substituted *N*-sulphinylanilines with compound (**2**) at ambient temperature yield two principal adducts in proportions of 2—3:1 as judged from the integrations of the ^1H n.m.r. signals. There are small variations in the observed chemical shifts according to the nature and position of the substituent.

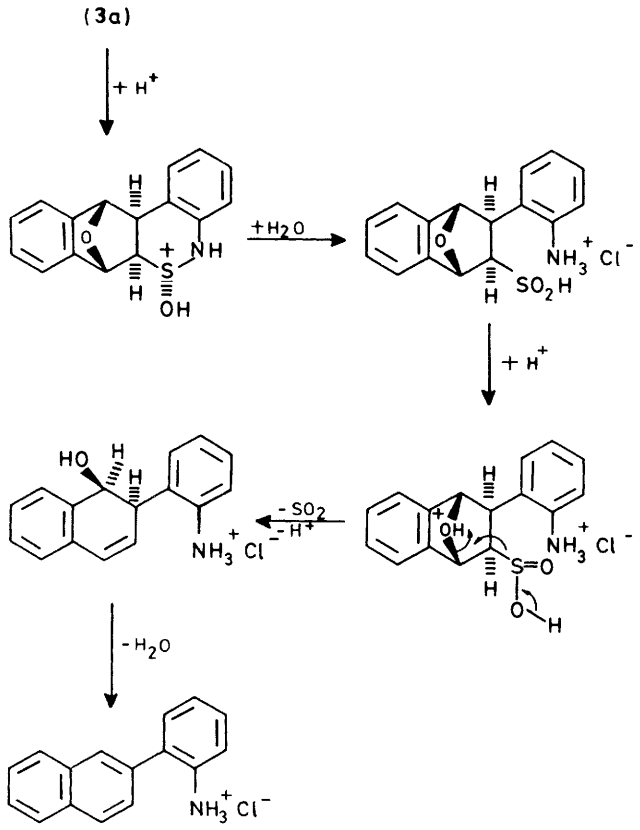
For any substituent we assign the minor resonances to a 1-substituted adduct and the major resonances to a 3-substituted isomer, which accords with expectation on steric grounds and with the perturbation noted previously of the C-12 resonance in the presence of a 1-substituent. Both isomers are ascribed a *trans*-stereochemistry as for the other adducts prepared at room temperature. This is confirmed by the appearance of additional signals from products obtained at elevated temperature (90 °C in chlorobenzene) indicating, again, that *cis*-adducts intervene significantly only at high temperature.

We note also that at high temperature the ratio of major products (*i.e.* 3-substituted, *trans*:1-substituted, *trans*) approaches 1:1, particularly for the more slowly reacting systems. This confirms our previous inference from kinetic results, also obtained at high temperature, of minimal steric effects on the cycloaddition reactions of 3-substituted *N*-sulphinylanilines.[1]

(iii) *Products from substituted dienophiles.* We have already mentioned adducts from *N*-sulphinylaniline and 1,4-epoxy-1,4-dihydronaphthalenes which bear either one or two bridgehead methyl groups [section (*b*, ii)]. At ambient temperature, the monomethylated dienophile yields two adducts in disparate proportions of *ca.* 11:1. Each manifests a single bridgehead proton resonance (δ 5.05 and 5.52), the minor showing the greater shift. Consistent with the foregoing, these are assigned to 12-H of the major isomer and 7-H of the minor isomer, respectively. Comparison of these shifts with those of the corresponding protons in compounds (**3a**) (δ 5.14 and 5.59) and (**3b**) (δ 5.67 and 5.98) indicates that both are *trans*-adducts. The major 7-methyl adduct is readily purified by fractional crystallisation.

The 1,4-dimethylated dienophile does not react with *N*-sulphinylaniline at an appreciable rate at room temperature. A single product resulted, however, on heating the reaction mixture for 16 h at 60 °C. Since the bridgehead positions of this material are substituted, the corresponding proton resonances are absent and the carbon resonances perturbed. The signals used in other adducts to diagnose the configuration at S are not therefore available; we assume that the adduct has a *trans*-stereochemistry.

(*d*) *Reactions of the Adducts.*—(i) *Substitution at* N. Treatment of compound (**3a**) at room temperature with NaH (1 equiv.) in dry Me_2SO removes 5_N-H. N-Substituted derivatives are then obtained by reactions of the resultant anion. Treatment

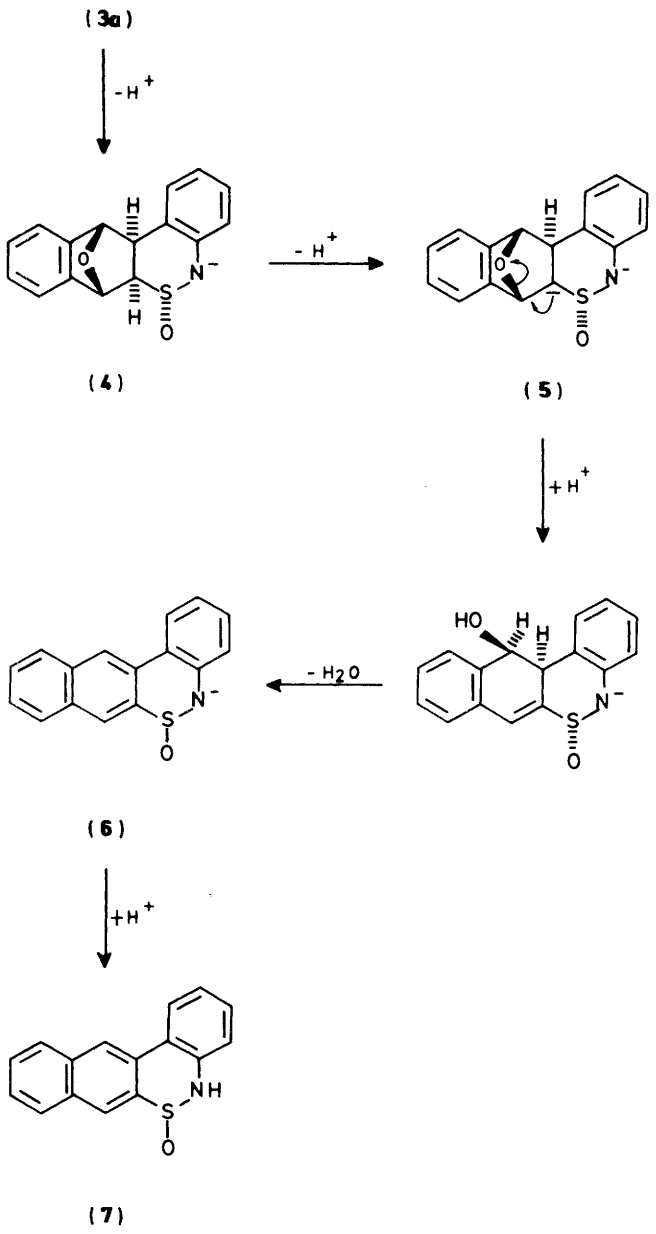


Scheme 3.

with alkylating agents gives the corresponding *N*-alkyl derivatives; attempts to acetylate compound (**3a**) by reaction of its conjugate base in Me_2SO with MeCOCl fail: a violent reaction between Me_2SO and MeCOCl intervenes leading to the formation of the intermediate electrophile $MeS^{+}{=}CH_2$ which effects a methylthiomethylation of compound (**3a**).[21,22] This was confirmed by comparison of the product with that from alkylation using $MeSCH_2Cl$. An acylation of compound (**3a**) was achieved in Me_2SO using $ClCO_2Et$.

(ii) *Aromatisation.* Although simple 1,4-epoxy-1,2,3,4-tetrahydrobenzene derivatives are readily dehydrated to benzenoid compounds by acid, this fails for compound (**3a**). Stirring with dilute aqueous acid leads to no change, whilst heating with concentrated hydrochloric acid results in a cleavage of the sulphinamide bond and the formation of 2-(2-naphthyl)aniline. We ascribe this behaviour to a preferred protonation of the sulphinyl oxygen rather than of the ether oxygen in compound (**3a**) (Scheme 3). A comparable cleavage of the heterocycle, but followed by a pericyclic desulphination, has been observed for monocyclic 1,2-thiazine oxides in acid conditions.[23]

Aromatisation of compound (**3a**) can, however, be achieved in basic conditions by stirring at 60 °C for several hours in Me_2SO with at least two equivalents of NaH. On subsequent pouring into water, 5*H*-6-thia-5-azabenz[*a*]anthracene 6-oxide (**7**) is precipitated (Scheme 4). The reaction has been monitored by ^1H n.m.r. spectroscopy: the first change in the spectrum of compound (**3a**) is the disappearance of the broadened signal from 5_N-H as the basic conditions facilitate its rapid exchange; subsequently, the spectrum of the conjugate base (**4**) appears. Here the various groups of resonances are shielded relative to their counterparts in the spectrum of compound (**3a**). Eventually, the spectrum of the aromatic conjugate base (**6**)

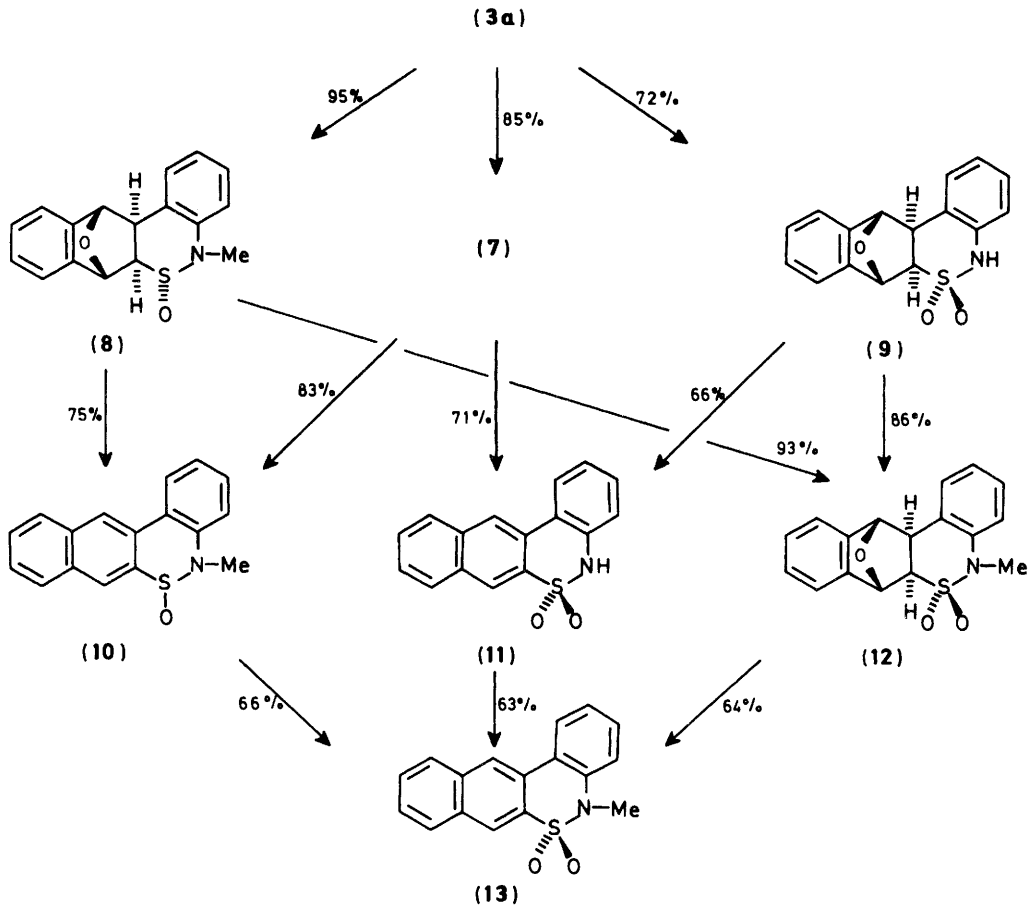


Scheme 4.

results. This anion makes the solution red, the colour disappearing on the precipitation of compound (**7**) by addition to acidified water. The mechanism of dehydration presumably involves the formation, from the first conjugate base (**4**), of a dianion (**5**) by the removal of 6a-H, activated by the adjacent sulphinyl group. The formation of the dianion is inferred to be rate determining and its destruction rapid as nothing observable on the n.m.r. time-scale, occurs between compounds (**4**) and (**6**).

(iii) *Oxidation.* The cyclic sulphinamide functions of compounds (**3a**) and (**3b**) and the substituted analogues are oxidised to the corresponding sultams by stirring at ambient temperature with peroxoacetic acid; increasing the temperature results in a degradation to intractable materials, however.

(iv) *Alternative reaction sequences.* Since the sulphinamide and sulphonamide functions are so similar, both structurally and electronically, it is possible to carry out the types of reaction described in sections in (i)—(iii) above in any order. Thus six



Scheme 5.

routes exist for converting compound (**3a**) into 5-methyl-5*H*-6-thia-5-azabenz[*a*]anthracene 6,6-dioxide (**13**) (Scheme 5). Each of these routes has been tried and the various intermediates characterised. In our hands the most efficient sequence for the synthesis of compound (**13**) from (**3a**) was methylation–oxidation–aromatisation which gave an overall yield of 56%.

(v) *Amino derivatives of compound* (**3a**). The amino derivatives of compound (**3a**) whose ^{13}C n.m.r. data are recorded in Table 1 were obtained by indirect routes. The 4-amino adduct was obtained by reduction of the corresponding nitro compound using palladium on charcoal (10%), and hydrazine hydrate, whilst the 2-substituted derivative was obtained from the reaction of excess of compound (**2**) with 1,4-bis(sulphinylamino)benzene. A single cycloaddition occurred and the 1:1 adduct precipitated. The unchanged NSO group was then solvolysed during work-up.

Experimental

M.p.s were obtained using a Kofler hot stage microscope and are uncorrected. I.r. spectra were recorded for Nujol mulls using Pye Unicam SP200 and SP1025 instruments; significant absorptions only are reported. Mass spectra were obtained at 70 eV using an A.E.I. MS30 spectrometer; major peaks only are recorded. ^1H N.m.r. spectra were obtained at 100 MHz using a JEOL MH100 spectrometer or at 60 MHz using a Varian A60A instrument, with tetramethylsilane as internal standard. ^{13}C N.m.r. spectra were recorded using JEOL FX60 and FX90Q spectrometers, also with tetramethylsilane as internal standard. The ^1H–^{13}C cross-correlation experiments were performed on the latter instrument. Eight decoupler frequencies spaced at intervals of 200 Hz were used to obtain off-resonance spectra. The residual couplings, taken from these spectra, were plotted as a function of decoupler frequency, then, using a least mean squares procedure, the exact decoupling frequencies of the attached protons were interpolated. From knowledge of the proton radio frequency used, the chemical shifts of the protons were calculated and compared with those obtained by direct observation. Ether refers to diethyl ether.

(*a*) N-*Sulphinylanilines*.—All the sulphinylanilines used are known compounds[9,10,24–28] and were prepared by the procedure described by Kresze *et al.*[29] They were purified by fractional distillation except for 3-and 4-nitro-*N*-sulphinylaniline which were recrystallised from light petroleum and 1,4-bis(*N*-sulphinylamino)benzene which was recrystallised from cyclohexane.

(*b*) 1,4-*Epoxy*-1,4-*dihydronaphthalenes*.—The dienophiles used were prepared by trapping benzyne[30] with furan, 2-methylfuran or 2,5-dimethylfuran after the manner of Stiles and Miller.[31] The resultant 1,4-epoxy-1,4-dihydronaphthalenes are all known compounds.[31,32]

(*c*) *Cycloadditions of* N-*Sulphinylaniline* (*Low Temperature*).—The general procedure was to dissolve the dienophile in slightly more than an equimolar proportion of *N*-sulphinylaniline and set the mixture aside, protected from moisture, at the lowest temperature consistent with convenient reaction times. For

compound (**2**) and its 1-methyl derivative the mixture solidified during several days at room temperature and the product was mobilised for filtration, and washed with ether; the 1,4-dimethyl derivative was made to react for 16 h at 60 °C, the product being precipitated on trituration with ether. The following were thus prepared.

(i) (6RS,6aRS,7SR,12SR,12aRS)-7,12-*Epoxy*-6a,7,12,12a-*tetrahydro*-5H-6-*thia*-5-*azabenz*[a]*anthracene* 6-*oxide* (**3a**) (85%), m.p. 269—270 °C (MeOH) (Found: C, 67.75; H, 4.8; N, 4.6. $C_{16}H_{13}NO_2S$ requires C, 67.82; H, 4.62; N, 4.94%); $\nu_{max.}$(Nujol) 1 065 (SO), 3 200 cm^{-1} (NH); *m/z* 283 (M^+, 1.5%), 235 (38), 234 (17), 218 (8), 217 (8), 206 (10), 204 (8), 149 (17), 136 (9), 130 (28), 119 (10), 118 (100), 117 (11), 90 (21), 89 (21), 77 (9), and 63 (9); δ_H[$(CD_3)_2SO$] 3.12 (1 H, dd, $J_{6a,12a}$ 8, $J_{6a,NH}$ 2 Hz, 6a-H), 3.37 (1 H, d, $J_{12a,6a}$ 8 Hz, 12a-H), 5.14 (1 H, s, 12-H), 5.59 (1 H, s, 7-H), 6.8—7.6 (8 H, m, ArH), and 9.07 (1 H, s, NH); δ_C[$(CD_3)_2SO$] see Table 1.

(ii) (6RS,6aRS,7SR,12SR,12aRS)-7,12-*Epoxy*-7-*methyl*-6a,7,12,12a-*tetrahydro*-5H-6-*thia*-5-*azabenz*[a]*anthracene* 6-*oxide* (53%), m.p. 252—254 °C (EtOH) (Found: C, 68.5; H, 5.4; N, 4.6. $C_{17}H_{15}NO_2S$ requires C, 68.66; H, 5.08; N, 4.71%); $\nu_{max.}$(Nujol) 1 050 (SO), 3 200 cm^{-1} (NH); *m/z* 297 (M^+, 3%), 279 (6), 249 (7), 234 (9), 232 (7), 231 (5), 230 (5), 204 (5), 149 (13), 148 (5), 136 (9), 133 (13), 132 (100), 131 (14), 117 (9), 104 (14), 103 (12), 90 (5), 89 (5), 78 (6), 77 (10), and 51 (5); δ_H[$(CD_3)_2SO$] 1.88 (3 H, s, Me), 3.05 (1 H, dd, $J_{6a,12a}$ 8, $J_{6a,NH}$ 2 Hz, 6a-H), 3.40 (1 H, d, $J_{12a,6a}$ 8 Hz, 12a-H), 5.07 (1 H, s, 12-H), 6.8—7.5 (8 H, m, ArH), and 9.08 (1 H, s, NH); δ_C[$(CD_3)_2SO$] see Table 1.

(iii) (6RS,6aRS,7SR,12SR,12aRS)-7,12-*Epoxy*-7,12-*dimethyl*-6a,7,12,12a-*tetrahydro*-5H-6-*thia*-5-*azabenz*[a]*anthracene* 6-*oxide* (23%), m.p. 198—199 °C (MeOH) (Found: C, 69.5; H, 5.5; N, 4.7; $C_{18}H_{17}NO_2S$ requires C, 69.49; H, 5.50; N, 4.50%); $\nu_{max.}$(Nujol) 1 055 (SO), 3 190 cm^{-1} (NH); *m/z* 311 (M^+, 10%), 248 (20), 149 (8), 148 (10), 147 (13), 146 (100), 145 (55), 144 (10), 136 (30), 131 (27), 130 (7), 117 (21), 116 (5), 115 (10), 103 (19), 102 (7), 91 (6), 90 (13), 89 (10), 77 (16), 76 (5), 63 (9), 51 (12), 50 (7), and 43 (20); δ_H[$(CD_3)_2SO$] 1.23 (3 H, s, 12-Me), 1.88 (3 H, s, 7-Me), 3.25 (2 H, s, 6a- and 12a-H), 6.85—7.40 (8 H, m, ArH), and 9.00 (1 H, s, NH); δ_C[$(CD_3)_2SO$] see Table 1.

(*d*) *Cycloadditions of Substituted* N-*Sulphinylanilines at Ambient Temperature*.—1,4-Epoxy-1,4-dihydronaphthalene was dissolved in a slight molar excess of the *N*-sulphinylaniline, or if the latter was solid, the mixture was made homogeneous with the minimum amount of benzene, and set aside, protected from moisture, for 2—10 days at ambient temperature. The precipitated cycloadducts were filtered off and washed with ether. N.m.r. spectra were recorded for solutions in $(CD_3)_2SO$ of solids so obtained. The 2- and 4-substituted *trans*-cycloadducts derived, respectively, from 4- and 2-substituted *N*-sulphinylanilines contained at most only trace amounts of diastereoisomeric material and were easily purified by recrystallisation. 4-Methoxycarbonyl- and 4-nitro-*N*-sulphinylanilines, the kinetics of whose reactions were found not to be comparable with those of other *N*-sulphinylanilines,[1] nevertheless gave appropriate cycloadducts. The following derivatives of compound (**3a**) were prepared in this manner.

(i) 2-*Methoxycarbonyl*- (75%), m.p. 258—259 °C (MeOH) (Found: C, 63.3; H, 4.55; N, 4.2. $C_{18}H_{15}NO_4S$ requires C, 63.33; H, 4.43; N, 4.10%); $\nu_{max.}$(Nujol) 1 030 (SO), 1 710 (CO), and 3 100 cm^{-1} (NH); *m/z* 341 (M^+, 0.4%), 294 (7), 293 (33), 292 (16), 264 (5), 233 (6), 207 (17), 206 (9), 204 (11), 194 (12), 188 (19), 176 (8), 147 (9), 144 (11), 119 (11), 118 (100), 116 (12), 90 (25), 89 (32), and 63 (18); δ_H[$(CD_3)_2SO$] 3.20 (1 H, d, $J_{6a,12a}$ 8 Hz, 6a-H), 3.54 (1 H, d, $J_{12a,6a}$ 8 Hz, 12a-H), 3.85 (3 H, s, Me), 5.18 (1 H, s, 12-H), 5.61 (1 H, s, 7-H), 6.89—8.12 (7 H, m, ArH), and 9.54 (1 H, s, NH); δ_C[$(CD_3)_2SO$] see Table 1.

(ii) 2-*Chloro*- (90%), m.p. 260—261 °C (EtOH) (Found: C, 60.8; H, 3.8; N, 4.4. $C_{16}H_{12}ClNO_2S$ requires C, 60.47; H, 3.81; N, 4.41%); $\nu_{max.}$(Nujol) 1 040 (SO), 3 160 cm^{-1} (NH); *m/z* 319 (M^+, 0.4%), (317 M^+, 0.8), 271 (11), 270 (11), 269 (33), 268 (14), 240 (7), 204 (8), 183 (8), 170 (7), 164 (23), 119 (10), 118 (100), 90 (17), 89 (21), and 63 (9); δ_H[$(CD_3)_2SO$] 3.12 (1 H, dd, $J_{6a,12a}$ 8, $J_{6a,NH}$ 2 Hz, 6a-H), 3.45 (1 H, d, $J_{12a,6a}$ 8 Hz, 12a-H), 5.22 (1 H, s, 12-H), 5.59 (1 H, s, 7-H), 6.80—7.60 (7 H, m, ArH), and 9.23 (1 H, br, NH); δ_C[$(CD_3)_2SO$] see Table 1.

(iii) 4-*Chloro*- (86%), m.p. 231—232 °C (EtOH) (Found: C, 60.4; H, 4.0; N, 4.3. $C_{16}H_{12}ClNO_2S$ requires C, 60.47; H, 3.81; N, 4.41%); $\nu_{max.}$(Nujol) 1 065 (SO), 3 180 cm^{-1} (NH); *m/z* 319 (M^+, 0.1%), 317 (M^+, 0.3), 271 (10), 270 (9), 269 (30), 268 (10), 240 (6), 204 (7), 182 (6), 170 (11), 166 (6), 164 (19), 151 (10), 119 (9), 118 (100), 115 (6), 102 (6), 90 (20), 89 (28), 88 (5), 77 (6), 76 (5), 75 (6), 64 (5), 63 (16), 62 (7), 51 (8), and 50 (6); δ_H[$(CD_3)_2SO$] 3.20 (1 H, d, $J_{6a,12a}$ 8 Hz, 6a-H), 3.47 (1 H, d, $J_{12a,6a}$ 8 Hz, 12a-H), 5.16 (1 H, s, 12-H), 5.60 (1 H, s, 7-H), 6.90—7.30 (7 H, m, ArH), and 8.88 (1 H, s, NH); δ_C[$(CD_3)_2SO$] see Table 1.

(iv) 2-*Nitro*- (88%), m.p. 294—296 °C (EtOH) (Found: C, 58.4; H, 3.8; N, 8.4. $C_{16}H_{12}N_2O_4S$ requires C, 58.53; H, 3.68; N, 8.53%); $\nu_{max.}$(Nujol) 1 050 (SO), 3 200 cm^{-1} (NH); *m/z* 328 (M^+, 0.5%), 281 (9), 280 (41), 279 (15), 263 (7), 251 (5), 233 (11), 205 (6), 204 (11), 194 (9), 181 (10), 176 (6), 175 (18), 135 (7), 129 (9), 119 (10), 118 (100), 116 (8), 115 (5), 102 (6), 91 (6), 90 (25), 89 (29), 77 (7), 76 (6), 54 (5), 63 (15), 62 (6), and 51 (8); δ_H[$(CD_3)_2SO$] 3.27 (1 H, d, $J_{6a,12a}$ 8 Hz, 6a-H), 3.65 (1 H, d, $J_{12a,6a}$ 8 Hz, 12a-H), 5.27 (1 H, s, 12-H), 5.64 (1 H, s, 7-H), 7.00—7.65 (5 H, m, ArH), 8.10 (1 H, dd, ArH), 8.50 (1 H, d, ArH), and 9.88 (1 H, br, NH); δ_C[$(CD_3)_2SO$] see Table 1.

(v) 4-*Nitro*- (57%), m.p. 229—231 °C (EtOH) (Found: C, 58.9; H, 3.8; N, 8.6. $C_{16}H_{12}N_2O_4S$ requires C, 58.53; H, 3.68; N, 8.53%); $\nu_{max.}$(Nujol) 1 075 (SO), 3 335 cm^{-1} (NH); *m/z* 328 (M^+, 0.1%), 263 (12), 262 (19), 247 (6), 234 (6), 233 (6), 232 (13), 219 (6), 218 (9), 205 (14), 204 (18), 203 (6), 181 (34), 177 (6), 165 (5), 164 (7), 147 (7), 135 (9), 134 (6), 119 (10), 118 (100), 116 (15), 105 (8), 104 (6), 103 (5), 102 (6), 91 (6), 90 (30), 89 (44), 88 (8), 77 (12), 76 (9), 75 (6), 65 (5), 64 (14), 63 (23), 62 (11), 52 (5), 51 (11), 50 (9), and 48 (7); δ_H[$(CD_3)_2SO$] 3.35 (1 H, d, $J_{6a,12a}$ 8 Hz, 6a-H), 3.63 (1 H, d, $J_{12a,6a}$ 8 Hz, 12a-H), 5.24 (1 H, s, 12-H), 5.69 (1 H, s, 7-H), 7.18—7.60 (5 H, m, ArH), 7.88—8.20 (2 H, m, ArH), and 9.95 (1 H, s, NH); δ_C[$(CD_3)_2SO$] see Table 1.

(vi) 2-*Methoxy*- (70%), m.p. 248—249 °C (EtOH) (Found: C, 64.9; H, 4.8; N, 4.6. $C_{17}H_{15}NO_3S$ requires C, 65.16; H, 4.82; N, 4.47%); $\nu_{max.}$(Nujol) 1 030 (SO), 3 120 cm^{-1} (NH); *m/z* 313 (M^+, 11%), 266 (11), 265 (55), 264 (26), 248, (7), 196 (7), 195 (54), 180 (7), 179 (45), 178 (20), 166 (36), 164 (12), 160 (40), 147 (37), 135 (7), 132 (20), 119 (11), 118 (100), 104 (10), 91 (7), 90 (16), 89 (23), and 63 (10); δ_H[$(CD_3)_2SO$] 3.05 (1 H, dd, $J_{6a,12a}$ 8, $J_{6a,NH}$ 2 Hz, 6a-H) 3.40, 1 H, d, $J_{12a,6a}$ 8 Hz, 12a-H), 3.76 (3 H, s, OMe), 5.20 (1 H, s, 12-H), 5.56 (1 H, s, 7-H), 6.77—7.55 (7 H, m ArH), and 8.87 (1 H, br, NH); δ_C[$(CD_3)_2SO$] see Table 1.

(vii) 2-*Methyl*- (82%), m.p. 309—311 °C (decomp.) (MeOH) (Found: C, 68.4; H, 5.1; N, 4.7. $C_{17}H_{15}NO_2S$ requires C, 68.65; H, 5.08; N, 4.73%); $\nu_{max.}$(Nujol) 1 030 (SO), 3 140 cm^{-1} (NH); *m/z* 297 (M^+, 4%), 249 (37), 248 (17), 220 (9), 163 (16), 150 (21), 144 (29), 131 (12), 130 (20), 119 (10), 118 (100), 90 (15), 89 (16), and 63 (8); δ_H[$(CD_3)_2SO$] 2.28 (3 H, s, Me), 3.07 (1 H, dd, $J_{6a,12a}$ 8, $J_{6a,NH}$ 2 Hz, 6a-H), 3.32 (1 H, d, $J_{12a,6a}$ 8 Hz, 12a-H), 5.15 (1 H, s, 12-H), 5.57 (1 H, s, 7-H), 6.66—7.55 (7 H, m, ArH), and 8.93 (1 H, br, NH); δ_C[$(CD_3)_2SO$] see Table 1.

(viii) 4-*Methyl*- (82%), m.p. 258—259 °C (EtOH) (Found: C, 68.6; H, 5.3; N, 4.35. $C_{17}H_{15}NO_2S$ requires C, 68.65; H, 5.08; N, 4.73%); $\nu_{max.}$(Nujol) 1 040 (SO), 3 200 cm^{-1} (NH); *m/z* 297 (M^+, 2%), 250 (6), 249 (28), 248 (10), 220 (6), 204 (4), 163 (12), 150 (19), 144 (21), 131 (19), 130 (32), 119 (10), 118 (100), 116 (5), 115 (11), 104 (5), 103 (8), 102 (7), 91 (11), 90 (27), 89 (31), 78 (7), 77 (17), 76 (6), 75 (5), 65 (8), 64 (6), 63 (21), 62 (7), 52 (8), 51 (16), and 50 (9); δ_H[$(CD_3)_2SO$] 2.19 (3 H, s, Me), 3.13 (1 H, d, $J_{6a,12a}$ 8

Hz, 6a-H), 3.39 (1 H, d, $J_{12a,6a}$ 8 Hz, 12a-H), 5.11 (1 H, s, 12-H, 5.60 (1 H, s, 7-H), 6.78—7.46 (7 H, m, ArH), and 8.50 (1 H, s, NH); δ_C[$(CD_3)_2SO$] see Table 1.

(ix) 2,4-*Dimethyl-* (60%), m.p. 275—278 °C (EtOH) (Found: C, 69.5; H, 5.6; N, 4.7. $C_{18}H_{17}NO_2S$ requires C, 69.41; H, 5.50; N, 4.52%); $\nu_{max.}$(Nujol) 1 040 (SO), 3 150 cm^{-1} (NH); *m/z* 311 (M^+, 5%), 264 (8), 263 (37), 262 (15), 234 (8), 193 (9), 177 (18), 164 (44), 158 (30), 145 (15), 144 (14), 130 (13), 119 (10), 118 (100), 90 (13), and 89 (14); δ_H[$(CD_3)_2SO$] 2.12 (3 H, s, 4-Me), 2.21 (3 H, s, 2-Me), 3.05 (1 H, d, $J_{6a,12a}$ 8 Hz, 6a-H), 3.27 (1 H, d, $J_{12a,6a}$ 8 Hz, 12a-H), 5.05 (1 H, s, 12-H), 5.52 (1 H, s, 7-H), 6.70—7.50 (6 H, m, ArH), and 8.30 (1 H, s, NH); δ_C[$(CD_3)_2SO$] see Table 1.

The mixed 1- and 3-substituted *trans*-adducts obtained from the reactions of 3-substituted *N*-sulphinylanilines were not, in general, readily separable; however, the predominant component of the product from *N*-sulphinyl-3-toluidine was separated by fractional crystallisation to give a further derivative of compound (**3a**).

(x) 3-*Methyl-* (50%), m.p. 266—269 °C (MeOH–$CHCl_3$, 2:1, then MeOH) (Found: C, 68.6; H, 5.1; N, 4.5. $C_{17}H_{15}NO_2S$ requires C, 68.85; H, 5.08; N, 4.73%); $\nu_{max.}$(Nujol) 1 040 (SO), 3 160 cm^{-1} (NH); *m/z* 297 (M^+, 2%), 250 (5), 249 (23), 248 (11), 220 (5), 204 (5), 163 (14), 162 (6), 150 (20), 144 (18), 131 (11), 130 (22), 119 (9), 118 (100), 115 (5), 91 (7), 90 (17), 89 (21), 77 (9), 63 (12), and 51 (7); δ_H[$(CD_3)_2SO$] 2.25 (3 H, s, Me), 3.08 (1 H, dd, $J_{6a,12a}$ 8, $J_{6a,NH}$ 2 Hz, 6a-H), 3.32 (1 H, d, $J_{12a,6a}$ 8 Hz, 12a-H), 5.10 (1 H, s, 12-H), 5.58 (1 H, s, 7-H), 6.67—7.60 (7 H, m, ArH), and 9.00 (1 H, br, NH); δ_C[$(CD_3)_2SO$] see Table 1.

Cycloaddition of *N*-sulphinyl-3,5-xylidine to (2) at ambient temperature led, in 60% yield, to a mixture of diastereoisomers differing in configuration at S, which were separated by fractional crystallisation. The less soluble *trans*-isomer is a derivative of compound (**3a**).

(xi) 1,3-*Dimethyl-*, m.p. 278—280 °C (decomp). ($CHCl_3$–MeOH, 10:1) (Found: C, 69.4; H, 5.4; N, 4.6. $C_{18}H_{17}NO_2S$ requires C, 69.41; H, 5.50; N, 4.52%); $\nu_{max.}$(Nujol) 1 032 and 1 048 (SO), 3 200 cm^{-1} (NH); *m/z* 311 (M^+, 1.5%), 264 (6), 263 (26), 262 (12), 234 (5), 177 (18), 176 (7), 165 (5), 164 (27), 158 (21), 145 (13), 144 (20), 143 (6), 130 (14), 119 (10), 118 (100), 115 (9), 91 (8), 90 (17), 89 (22), 77 (7), 63 (12), and 51 (7); δ_H[$(CD_3)_2SO$] 2.18 (3 H, s, 3-Me), 2.38 (3 H, s, 1-Me), 3.13 (1 H, d, $J_{6a,12a}$ 8 Hz, 6a-H), 3.40 (1 H, d, $J_{12a,6a}$ 8 Hz, 12a-H), 5.08 (1 H, s, 12-H), 5.62 (1 H, s, 7-H), 6.60—7.55 (6 H, m, ArH), and 8.28 (1 H, s, NH); δ_C[$(CD_3)_2SO$] see Table 1.

The more soluble isomer is a derivative of compound (**3b**), *viz.* (6SR,6aRS,7SR,12SR,12aRS)-7,12-*epoxy*-1,3-*dimethyl*-6a,7,12,12a-*tetrahydro*-5H-6-*thia*-5-*azabenz*[a]*anthracene* 6-*oxide*, m.p. 230—232°C ($CHCl_3$–MeOH, 5:1) (Found: C, 69.7; H, 5.3; N, 4.5. $C_{18}H_{17}NO_2S$ requires C, 69.41; H, 5.50; N, 4.52%); $\nu_{max.}$(Nujol) 1 083 (SO), 3 210 cm^{-1} (NH); *m/z* 311 (M^+, 0.2%), 264 (11), 263 (57), 262 (22), 246 (6), 245 (5), 234 (8), 218 (5), 177 (17), 176 (7), 165 (5), 164 (28), 159 (5), 158 (38), 145 (15), 144 (23), 143 (7), 131 (7), 130 (16), 119 (10), 118 (100), 117 (5), 115 (11), 91 (10), 90 (21), 89 (26), 77 (9), 65 (5), 63 (13), and 51 (8); δ_H[$(CD_3)_2SO$] 2.18 (3 H, s, 3-Me), 2.38 (3 H, s, 1-Me), 3.18 (1 H, d, $J_{6a,12a}$ 8 Hz, 6a-H), 3.35 (1 H, d, $J_{12a,6a}$ 8 Hz, 12a-H), 5.33 (1 H, s, 12-H), 5.87 (1 H, s, 7-H), 6.60—7.55 (6 H, m, ArH), and 8.30 (1 H, s, NH); δ_C[$(CD_3)_2SO$] see Table 2.

(*e*) *Cycloadditions at Elevated Temperatures.*—Conditions similar to those reported for kinetic measurements [1] were used: equal volumes of solutions of the reactants in chlorobenzene (1.5 mol dm^{-3}) were mixed and sealed, under vacuum, in tubes which were then heated at 90—120 °C for *ca.* 5 h. The tubes were cooled and then opened and the precipitated adducts were separated by filtration and washed with a small amount of ether. No attempts were made to separate isomers; n.m.r. spectra were obtained for solutions in $(CD_3)_2SO$ of solids so obtained.

(*f*) *Amino Derivatives of Compound* (**3a**).—(i) 4-*Amino Derivative.* The 4-nitro derivative of compound (**3a**) [see section (*d*, v) above] (0.8 g) was dissolved in EtOH (200 cm^3) and refluxed for 6 h with palladium on charcoal (10%; 0.2 g) and hydrazine hydrate (2 cm^3). After filtration to remove the catalyst, the filtrate was evaporated to dryness under reduced pressure and the residue purified by dry column chromatography on deactivated alumina, eluting with $CHCl_3$, to give (6RS,6aRS,7SR,12SR,12RS)-4-*amino*-7,12-*epoxy*-6a,7,12,12a-*tetrahydro*-5H-6-*thia*-5-*azabenz*[a]*anthracene* 6-*oxide* (0.5 g, 69%), m.p. 251—253 °C (Found: C, 64.2; H, 4.8; N, 9.5. $C_{16}H_{14}N_2O_2S$ requires C, 64.41; H, 4.73; N, 9.39%); $\nu_{max.}$(Nujol) 1 015 (SO), 3 190 (NH), 3 360, and 3 420 cm^{-1} (NH_2); *m/z* 298 (M^+, 7%), 281 (17), 251 (9), 250 (48), 249 (13), 233 (10), 232 (19), 217 (8), 216 (7), 180 (20), 165 (9), 164 (45), 163 (41), 151 (21), 145 (19), 132 (19), 131 (11), 119 (12), 118 (100), 104 (8), 90 (19), 89 (23), 77 (7), 64 (7), and 63 (11); δ_H[$(CD_3)_2SO$] 3.12 (1 H, d, $J_{6a,12a}$ 8 Hz, 6a-H), 3.35 (1 H, d, $J_{12a,6a}$ 8 Hz, 12a-H), 4.95 (2 H, s, NH_2), 5.19 (1 H, s, 12-H), 5.70 (1 H, s, 1-H), 6.60—7.00 (3 H, m, ArH), 7.20—7.70 (4 H, m, ArH), and 8.40 (1 H, s, NH); δ_C[$(CD_3)_2SO$] see Table 1.

(ii) 2-*Amino derivative.* 1,4-Bis(*N*-sulphinylamino)benzene was refluxed in dichloromethane for 12 h with compound (**2**) (2 mol equiv.). No tractable 2:1 adduct was formed but the yellow product, presumably a 1:1 adduct, upon recrystallisation from MeOH gave (6RS,6aRS,7SR,12SR,12aRS)-2-*amino*7,12-epoxy-6a,7,12,12a-*tetrahydro*-5H-6-*thia*-5-*azabenz*[a]*anthracene* 6-*oxide* (11%), m.p. 259—261 °C (Found: C, 64.1; H, 4.8; N, 9.0. $C_{16}H_{14}N_2O_2S$ requires C, 64.41; H, 4.73; N, 9.39%); $\nu_{max.}$(Nujol) 1 055 (SO), 3 200 (NH), 3 350, and 3 450 cm^{-1} (NH_2); *m/z* 298 (M^+, 5%), 282 (6), 250 (9), 249 (6), 245 (18), 216 (8), 199 (14), 198 (10), 180 (18), 178 (10), 176 (10), 175 (7), 174 (8), 173 (8), 172 (7), 164 (57), 163 (21), 149 (14), 146 (14), 135 (15), 132 (36), 131 (21), 119 (17), 118 (100), 108 (21), 105 (15), 90 (50), 89 (57), 83 (20), 77 (15), 69 (20), 64 (36), and 63 (36); δ_H[$(CD_3)_2SO$] 2.98 (1 H, d, $J_{6a,12a}$ 8 Hz, 6a-H), 3.18 (1 H, d, $J_{12a,6a}$ 8 Hz, 12a-H), 4.3 (2 H, br, NH_2), 5.10 (1 H, s, 12-H), 5.52 (1 H, s, 7-H), 6.35—6.70 (3 H, m, ArH), 7.10—7.50 (4 H, m, ArH), and 8.52 (1 H, s, NH); δ_C[$(CD_3)_2SO$] see Table 1.

(*g*) *Acid Hydrolysis of Compound* (**3a**).—The thiazine oxide (**3a**) (1.0 g) was dissolved in conc. HCl (60 cm^3) with warming and stirring. Heating to reflux caused effervescence and the formation of a tarry precipitate. After 4 h the precipitate was separated by filtration and recrystallised, with carbon treatment, from dil. HCl to give 2-(2-naphthyl)aniline hydrochloride (0.3 g, 33%), colourless needles, m.p. 175—180 °C [lit.,[33] 205 °C (decomp.)] Treatment of the hydrochloride (0.1 g) with dil. NaOH followed by extraction into ether, isolation and recrystallisation from aqueous ethanol afforded 2-(2-naphthyl)aniline (0.05 g, 62%), m.p. 93—95 °C (lit.,[34] 96.5—97.2 °C) (Found: M^+, 219.1045. Calc. for $C_{16}H_{13}N$; *M*, 219.1047); *m/z* 219 (M^+, 100%), 218 (78), 217 (43), 216 (11), 189 (6), 109.5 (9), 109 (7), 108.5 (20), 95.5 (5), and 94.5 (5); δ_C ($CDCl_3$) 115.7, 118.8, 126.0, 126.3, 127.4, 127.7, 127.9, 128.0, 128.5, 128.7, 129.6, 130.7, 132.6, 133.8, 137.2, and 143.8 p.p.m.

(*h*) S-*Oxidation of Compound* (**3a**).—Reaction of compound (**3a**) (2 g) with hydrogen peroxide (100 vol., 4 cm^3) in acetic acid (50 cm^3) at ambient temperature for 48 h resulted in a white precipitate which, on recrystallisation from EtOH, gave (6aRS,7SR,12SR,12aRS)-7,12-*epoxy*-6a,7,12,12a-*tetrahydro*-5H-6-*thia*-5-*azabenz*[a]*anthracene* 6,6-*dioxide* (**9**) (1.5 g, 72%), m.p. 267—269 °C (decomp.) (Found: C, 64.55; H, 4.45; N, 4.6.

$C_{16}H_{13}NO_3S$ requires C, 64.20; H, 4.38; N, 4.68%); $\nu_{max.}$(Nujol) 1 140 and 1 325 (SO_2), 3 250 cm^{-1} (NH); *m/z* 299 (M^+, 0.4%), 234 (1), 218 (1), 217 (2), 206 (2), 205 (1), 204 (3), 203 (1), 119 (9), 118 (100), 90 (11), and 89 (10); δ_H[$(CD_3)_2SO$] 3.62 (2 H, s, 6a-H and 12a-H), 5.32 (1 H, s, 12-H), 5.84 (1 H, s, 7-H), 6.80—7.60 (8 H, m, ArH), and 10.1 (1 H, br, NH); δ_C[$(CD_3)_2SO$] 46.9, 62.5, 80.9, 88.8, 119.2, 120.3, 120.5, 124.2, 127.2 (2C), 127.6 (2C), 130.0, 138.1, 143.7, and 144.6 p.p.m.

Identical material resulted from a similar oxidation of the mixture of diastereoisomers (**3a**) and (**3b**).

(*i*) N-*Substitutions of Compound* (**3a**).—(i) *Methylation.* Reaction of compound (**3a**) (2 g) with NaH (0.17 g) in dry Me_2SO (50 cm^3) for 2 h at ambient temperature, followed by addition of MeI (1 cm^3) and stirring for a further 1 h, gave a solution which, upon addition to water, produced a white precipitate. This, after filtration and drying, was recrystallised from EtOH to give (6RS,6aRS,7SR,12SR,12aRS)-7,12-*epoxy*-6a,7,12,12a-*tetrahydro*-5-*methyl*-5H-6-*thia*-5-*azabenz*[a]*anthracene* 6-*oxide* (**8**) (2 g, 95%), m.p. 243—244 °C (Found: C, 68.5; H, 4.9; N, 4.7. $C_{17}H_{15}NO_2S$ requires C, 68.66; H, 5.08; N, 4.71%); $\nu_{max.}$(Nujol) 1 060 cm^{-1} (SO); *m/z* 297 (M^+, 4%), 249 (22), 248 (7), 234 (19), 220 (5), 179 (5), 163 (13), 150 (28), 148 (8), 144 (18), 131 (24), 130 (17), 119 (10), 118 (100), 91 (5), 90 (13), 89 (16), 77 (8), and 63 (5); δ_H[$(CD_3)_2SO$] 3.25 (4 H, br, NMe and 6a-H), 3.43 (1 H, d, $J_{12a,6a}$ 8 Hz, 12a-H), 5.14 (1 H, s, 12-H), 5.66 (1 H, s, 7-H), and 6.90—7.50 (8 H, m, ArH); δ_C[$(CD_3)_2SO$] 37.7, 42.5, 68.2, 79.8, 88.8, 117.2, 119.1, 119.8, 123.5, 127.4, 127.6, 128.0, 128.4, 130.0, 137.1, 144.2, and 145.2 p.p.m.

(ii) *Methylthiomethylation.* A directly analogous reaction to the foregoing, but using $MeSCH_2Cl$ as the alkylating agent, gave (6RS,6aRS,7SR,12SR,12RS)-7,12-*epoxy*-6a,7,12,12a-*tetrahydro*-5-*methylthiomethyl*-5H-6-*thia*-5-*azabenz*[a]*anthracene* 6-*oxide* (25%), m.p. 226—228 °C (Found: C, 62.8; H, 5.0; N, 4.1. $C_{18}H_{17}NO_2S_2$ requires C, 62.95; H, 4.99; N, 4.08%); $\nu_{max.}$(Nujol) 1 075 cm^{-1} (SO); *m/z* 343 (M^+, 0.3%), 296 (9), 248 (19), 234 (16), 178 (13), 149 (11), 148 (35), 130 (35), 119 (11), 118 (100), 117 (15), 91 (12), 90 (22), 89 (31), 77 (17), 63 (19), 61 (24), 51 (12), and 45 (21); δ_H[$(CD_3)_2SO$] 2.17 (3 H, s, SMe), 3.27 (1 H, d, $J_{6a,12a}$ 8 Hz, 6a-H), 3.45 (1 H, d, $J_{12a,6a}$ 8 Hz, 12a-H), 4.80 (1 H, d, J_{gem} 14 Hz, CH_2), 5.03 (1 H, d, J_{gem} 14 Hz, CH_2), 5.16 (1 H, s, 12-H), 5.67 (1 H, s, 7-H), and 7.00—7.60 (8 H, m, ArH); δ_C[$(CD_3)_2SO$] 13.5, 41.4, 54.3, 68.1, 79.1, 87.8, 118.3, 119.4, 120.0, 122.8, 126.9 (2C), 127.4, 129.4, 130.3, 135.1, 144.6, and 145.3 p.p.m.

In a similar reaction at ambient temperature where MeCOCl, in lieu of an alkylating agent, was added *dropwise*, violent reaction with a considerable exotherm occurred. On work-up, an *N*-methylthiomethyl derivative of compound (**3a**), identical with that described above, was obtained in 23% yield. Effecting the reaction at 0 °C reduced the yield to zero and permitted only the recovery of compound (**3a**).

(iii) *Ethoxycarbonylation.* Acylation in the same conditions using ethyl chloroformate afforded (6RS,6aRS,7SR,12SR,-12aRS)-7,12-*epoxy*-5-*ethoxycarbonyl*-6a,7,12,12a-*tetrahydro*-5H-6-*thia*-5-*azabenz*[a]*anthracene* 6-*oxide* (40%), m.p. 155—158 °C (Found: C, 64.4; H, 4.75; N, 3.9. $C_{19}H_{17}NO_4S$ requires C, 64.21; H, 4.82; N, 3.94%); $\nu_{max.}$(Nujol) 1 050 (SO), 1 695 cm^{-1} (CO); *m/z* 355 (M^+, 4.5%), 307 (9), 235 (9), 234 (39), 233 (5), 218 (5), 217 (6), 206 (5), 204 (10), 176 (5), 149 (5), 148 (26), 136 (5), 131 (5), 130 (7), 119 (10), 118 (100), 117 (7), 90 (17), 89 (19), 77 (7), 63 (9), and 51 (5); δ_H[$(CD_3)_2SO$] 1.26 (3 H, t, J_{alk} 5 Hz, Me), 3.41 (1 H, d, $J_{6a,12a}$ 8 Hz, 6a-H), 3.56 (1 H, d, $J_{12a,6a}$ 8 Hz, 12a-H), 4.25 (2 H, q, J_{alk} 5 Hz, CH_2), 5.20 (1 H, s, 12-H), 5.68 (1 H, s, 7-H), and 7.16—7.50 (8 H, m, ArH); δ_C[$(CD_3)_2SO$] 14.0, 42.6, 62.5, 68.3, 78.6, 86.7, 119.8 (2C), 126.9 (2C), 127.3, 128.4, 129.7, 130.0, 130.7, 132.5, 143.7, 145.3, and 151.7 p.p.m.

(*j*) *Aromatisation* (*Dehydration*) *of Compound* (**3a**).—Reaction of compound (**3a**) (1.0 g) with NaH (0.17 g) in dry Me_2SO (50 cm^3) at 60 °C for 6 h resulted in a deep red solution which, on addition to ice–water (200 cm^3), gave a white precipitate. Recrystallisation from EtOH afforded 5H-6-*thia*-5-*azabenz*[a]*anthracene* 6-*oxide* (**7**) (0.8 g, 85%), m.p. 241—243 °C (Found: C, 72.55; H, 4.3; N, 5.5. $C_{16}H_{11}NOS$ requires C, 72.43; H, 4.18; N, 5.28%); $\nu_{max.}$(Nujol) 1 030 (SO), 3 150 cm^{-1} (NH); *m/z* 265 (M^+, 65%), 250 (7), 249 (33), 248 (47), 246 (5), 236 (7), 232 (9), 218 (18), 217 (100), 216 (31), 215 (8), 214 (9), 204 (16), 189 (10), 108 (14), 102 (7), and 94 (6); δ_H[$(CD_3)_2SO$] 7.13—7.45 (3 H, m, ArH), 7.50—8.55 (6 H, m, ArH), 8.86 (1 H, s, ArH), and 10.27 (1 H, s, NH); δ_C[$(CD_3)_2SO$] 119.9, 121.1, 122.9, 124.0, 124.6, 124.9, 126.8, 127.1, 128.4 (3C), 129.9, 131.4, 134.0, 134.1, and 135.6 p.p.m.

(*k*) 5-*Methyl*-5H-6-*thia*-5-*azabenz*[a]*anthracene* 6-*Oxide* (**10**).—(i) N-*Methylation of compound* (**7**). The preceding thiazine oxide (**7**) (1 g) was stirred with NaH (0.1 g) in Me_2SO for 2 h, then MeI (2 cm^3) was added and the mixture stirred for a further 0.5 h. The precipitate resulting from the addition to water was recrystallised from EtOH to give 5-*methyl*-5H-6-*thia*-5-*azabenz*[a]*anthracene* 6-*oxide* (**10**) (0.9 g, 83%), m.p. 156—158 °C (Found: C, 72.8; H, 4.5; N, 5.1. $C_{17}H_{13}NOS$ requires C, 73.09; H, 4.69; N, 5.01%); $\nu_{max.}$(Nujol) 1 075 cm^{-1} (SO); *m/z* 279 (M^+, 31%), 248 (5), 234 (6), 232 (19), 231 (100), 230 (24), 229 (7), 218 (7), 217 (8), 216 (20), 214 (6), 202 (10), 190 (5), 189 (7), 163 (5), 150 (6), 118 (10), 115 (6), 89 (5), 63 (7), and 51 (5); δ_H[$(CD_3)_2SO$] 3.60 (3 H, s, Me), 7.20—7.80 (5 H, m, ArH), 8.10—8.60 (4 H, m, ArH), and 8.85 (1 H, s, ArH); δ_C[$(CD_3)_2SO$] 38.2, 117.2, 123.0, 123.2, 124.1, 125.0, 125.2, 126.3, 126.9, 128.0, 128.2 (2C), 129.9, 131.4, 134.5, 135.8, and 136.2 p.p.m.

(ii) *Aromatisation of compound* (**8**). An identical product was obtained in 75% yield when compound (**8**) [see section (*i*, ii) above] was aromatised by the method described for (**3a**) [see section (*j*) above].

(*l*) 5H-6-*Thia*-5-*azabenz*[a]*anthracene* 6,6-*Dioxide* (**11**).—(i) S-*Oxidation of compound* (**7**). The thiazine oxide (**7**) (0.4 g) was stirred in acetic acid (20 cm^3) with H_2O_2 (100 vol., 2 cm^3) at room temperature for 48 h. A white precipitate resulted on pouring the solution into water (200 cm^3) which, on recrystallisation from EtOH, afforded 5H-6-*thia*-5-*azabenz*[a]*anthracene* 6,6-*dioxide* (**11**) (0.3 g, 71%), m.p. 250—252 °C (Found: C, 68.55; N, 4.1; N, 4.7. $C_{16}H_{11}NO_2S$ requires C, 68.31; H, 3.94; N, 4.72%); $\nu_{max.}$(Nujol) 1 150 and 1 315 (SO_2), 3 200 cm^{-1} (NH); *m/z* 281 (M^+, 100%), 230 (6), 218 (9), 217 (49), 216 (35), 215 (11), 214 (9), 190 (6), 189 (12), 108.5 (14), 107.5 (6), 95.5 (5), and 94.5 (10); δ_H[$(CD_3)_2SO$] 7.20—7.80 (5 H, m, ArH), 8.10—8.65 (3 H, m, ArH), 8.75 (1 H, s, ArH), 8.85 (1 H, s, ArH), and 11.45 (1 H, br, NH); δ_C[$(CD_3)_2SO$] 120.1, 121.4, 122.4, 124.2, 125.2, 125.4, 127.6, 128.2, 128.4, 128.8 (2C), 130.1, 131.0, 133.3, 134.0, and 136.5 p.p.m.

(ii) *Aromatisation of compound* (**9**). The sultam (**9**) [see section (*h*) above] was aromatised to compound (**11**) in 66% yield by the method described in (*j*) above for the aromatisation of compound (**3a**).

(*m*) (6RS,6aRS,7SR,12SR,12aRS)-7,12-*Epoxy*-6a,7,12,12a-*tetrahydro*-5-*methyl*-5H-6-*thia*-5-*azabenz*[a]*anthracene* 6,6-*Dioxide* (**12**).—(i) S-*Oxidation of compound* (**8**). Sulphoxidation of compound (**8**) by the method described above for (**7**) gave the methylated sultam (**12**) (93%), m.p. 204—206 °C (MeOH) (Found: C, 65.0; H, 4.8; N, 4.7. $C_{17}H_{15}NO_3S$ requires C, 65.16; H, 4.82; N, 4.47%); $\nu_{max.}$ 1 140 and 1 320 cm^{-1} (SO_2); *m/z* 313 (M^+, 1%), 195 (2), 163 (2), 144 (2), 131 (4), 130 (4), 119 (8), 118 (100), 90 (6), 89 (7), 77 (3), 64 (2), 63 (3), and 51 (2); δ_H[$(CD_3)_2SO$]

3.28 (3 H, s, Me), 3.59 (1 H, d, $J_{6a,12a}$ 8 Hz, 6a-H), 3.87 (1 H, d, $J_{12a,6a}$ 8 Hz, 12a-H), 5.32 (1 H, s, 12-H), 5.87 (1 H, s, 7-H), and 7.00—7.60 (8 H, m, ArH); δ_C[$(CD_3)_2SO$] 35.9, 47.8, 63.9, 81.5, 88.7, 119.7, 119.8, 121.9, 125.5, 127.8 (2C), 128.3, 129.0, 129.8, 141.5, 143.0, and 144.1 p.p.m.

(ii) N-*Methylation of compound* (**9**). Material identical with the product of the previous reaction was obtained (86%) by a methylation of the sultam (**9**) by the method given for compound (**3a**) in section (*i*, i) above.

(*n*) 5-*Methyl*-5H-6-*thia*-5-*azabenz*[a]*anthracene* 6,6-*Dioxide* (**13**).—(i) N-*Methylation of compound* (**11**). The aromatic sultam (**11**) was methylated by the procedure described for the methylation of compound (**3a**) in section (*i*, i) above to yield 5-*methyl*-5H-6-*thia*-5-*azabenz*[a]*anthracene* 6,6-*dioxide* (**13**) (63%), m.p. 196—197 °C (EtOH) (Found: C, 69.0; H, 4.5; N, 4.7. $C_{17}H_{13}NO_2S$ requires C, 69.13; H, 4.44; N, 4.74%); $\nu_{max.}$ 1 160 and 1 315 cm^{-1} (SO_2); *m/z* 295 (M^+, 100%), 279 (13), 264 (9), 263 (45), 249 (10), 248 (47), 232 (9), 231 (42), 230 (31), 229 (8), 217 (10), 216 (30), 214 (7), 202 (13), 189 (7), 147.5 (6), 131.5 (7), 124 (13), 115.5 (11), 115 (17), and 101 (9); δ_H[$(CD_3)_2SO$] 3.38 (3 H, s, Me), 7.40—7.90 (5 H, m, ArH), 8.10—8.50 (3 H, m, ArH), 8.68 (1 H, s, ArH), and 8.83 (1 H, s, ArH); δ_C[$(CD_3)_2SO$] 33.3, 120.7, 122.6, 122.9, 124.3, 125.3, 125.8, 127.8, 128.0, 128.4, 128.9, 130.4, 131.2, 131.3, 131.9, 134.6, and 139.4 p.p.m.

(ii) *Aromatisation of compound* (**12**). The aromatisation procedure described in section (*j*) gave compound (**13**) in 64% yield.

(iii) S-*Oxidation of compound* (**10**). Sulphoxidation of compound (**10**) by the previously described procedure [see section (*l*) above] gave compound (**13**) in 66% yield.

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