6π-Cycloadditions of Aryl and New Heteroaryl *N*-Sulphinylamines With 2,3-Dimethylbuta-1,3-diene: Synthesis, Kinetics, Substituent Effects, Theoretical Calculations, and Reaction Mechanism

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A range of new *N*-sulphinylamine derivatives of heteroaryl rings, including tetrazoles, oxadiazoles, thiadiazoles, thiazoles, and oxazoles is reported. The influence of the $-N=S^+-O^-$ group on the n.m.r. spectra of the ring to which it is bonded is discussed. The kinetics of the cycloaddition reactions of this group with 2,3-dimethylbuta-1,3-diene have been measured for a series of *para*-substituted phenyl-*N*-sulphinylamines and the rates correlated with MNDO calculated HOMO–LUMO separations and Hammett substituent constants.

The cycloaddition reactions of *N*-sulphinylamines have attracted major interest[1–4] since they were first reported[5] 35 years ago. The *N*-sulphinylamino group is an excellent reagent for [4 + 2]-cycloadditions with 1,3-dienes[1–5] and some derivatives also undergo [2 + 2]-cycloadditions with yneamines.[6] Synthetic interest in these reactions has been growing in recent years.[8–14] However there are some deficiencies of knowledge concerning these systems. For example only two heterocyclic *N*-sulphinylamine compounds, 3-sulphinylaminopyridine and 3-methylmercapto-5-sulphinylamino-1,2,4-thiadiazole have been isolated previously.[15] While carbon-13 n.m.r. spectra of *N*-sulphinyl compounds have been reported[16] the influence of the $-N=S^+-O^-$ group on n.m.r. shifts of bonded aryl rings is not to be found in n.m.r. reviews and books. Despite extensive study,[17–28] the possible *E*–*Z* isomerism of the $Ar-N=S^+-O^-$ group has not been elucidated but the weight of opinion, plus theoretical calculations,[26,27] favour a *Z*-structure.† Most importantly there is a major paucity of quantitative kinetic mechanistic data on the reaction. While this present work was in progress Hanson and Stockburn reported[12,13] the activation thermodynamic parameters for the cycloaddition of ethyl *N*-sulphinylcarbamate with some 1,3-dienes. Herein, we compare[29] our results for aryl-*N*-sulphinylamines with theirs and we report[29] the first kinetic substituent effect on the reaction and probe the relationship of rates to reactant HOMO–LUMO separations and Hammett substituent constants. The reaction is generally looked upon[1–17] as a Diels–Alder reaction but since C–N and C–S sigma bonds are being formed in the transition state it is unlikely to be a synchronous pericyclic reaction.‡

Results and Discussion

(a) *Heterocyclic* N-*Sulphinylamines and N.M.R. effects of the* –NSO *Groups.*—A wide range of heteroaryl-*N*-sulphinyl amines (**1**)§ was prepared by heating the amine with thionyl chloride in dry benzene (Scheme 1, Table 1). The heterocyclic *N*-sulphinylamines were more unstable and highly moisture-sensitive compared with *para*-substituted *N*-sulphinylanilines. Liquid compounds were purified by vacuum distillations but since a number of explosions were encountered with the high nitrogen derivatives we recommend temperatures not exceeding 60 °C and normal safety precautions. Microanalyses could not be obtained on them due to their instability but the soluble compounds were characterized by ^1H and ^{13}C n.m.r. spectroscopy and all were fully characterized as Diels–Alder adducts (**2**) with 2,3-dimethylbuta-1,3-diene (Scheme 1).

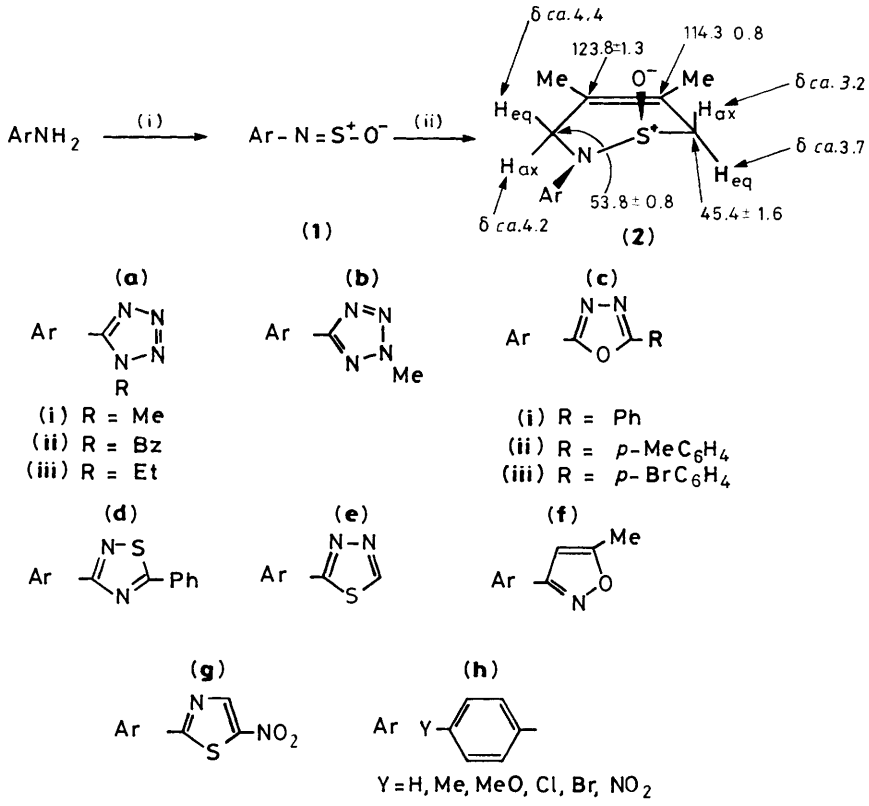
The influence of the $-N=S^+-O^-$ moiety on the proton and carbon n.m.r. spectra of the aryl ring to which it is bonded is not recorded in n.m.r. catalogues[30–32] despite the wide interest in these compounds. Throughout the series of compounds (**1**) a consistent upfield shift in the *ipso*-carbon signal was observed on changing $-NH_2$ to $-N=S^+-O^-$ (Table 1). A range of known *para*-substituted *N*-sulphinylanilines was prepared to check the generality of this. This trend was confirmed and in general the proton and carbon n.m.r. spectra of a series of substituted phenyl-*N*-sulphinylamines showed consistent additive effects for the substituent (Table 2). Changing the NH_2 group to $N=S^+-O^-$ caused large deshielding at the *ortho*-positions in proton spectra and also at C-2 and C-4 in the carbon spectra as well as significant shielding of the *ipso* carbon. The magnitude of these effects was comparable to those of carbonyl and sulphonyl substituents in agreement with the strong double-bond character in the N–S bond. Interestingly, with the strong resonance electron-donating substituent, *p*-MeO, the ^{13}C deshielding effects were reduced (Table 2, footnotes *c* and *d*), consistent with a reduced double-bond character in the N–S bond of this system (*cf.* MNDO calculations). In the new heterocyclic *N*-sulphinylamines (**1a–g**) the shielding of the *ipso* carbon (4–6 ppm) was particularly useful since these *N*-sulphinyl compounds were often unstable oils. Relative to benzene itself *N*-sulphinylbenzene showed a large deshielding at C-1 and a smaller deshielding at C-4 (Table 2).

(b) [4 + 2]-*Cycloaddition Reactions.*—*Synthesis.* The new heterocyclic *N*-sulphinylamines underwent particularly easy thermal cycloadditions with 2,3-dimethylbuta-1,3-diene to give the products (**2**) when stirred for periods of 10–60 min in benzene at <60 °C. Indeed, some of these reactions occurred within a few minutes at ambient temperatures. Similar cycloadditions with *para*-substituted phenyl-*N*-sulphinylamines (carried out for comparison purposes) required prolonged

† While this problem is addressed by further calculations in this paper, extensive attempts are ongoing to obtain a low-temperature *X*-ray crystal structure of one of these unstable compounds.

‡ A referee has required an explanation of the term 'synchronous'. This term is used as defined by M. J. S. Dewar, *J. Am. Chem. Soc.*, 1984, **106**, 209.

§ *Note added in proof:* The low-temperature *X*-ray crystal structure of compound (**1h**; Y=Br) has recently been determined: R. N. Butler, J. P. Duffy, P. McArdle, D. Cunningham, and G. A. O'Halloran, *J. Chem. Soc., Chem. Commun.*, 1989, 120.



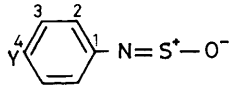
Scheme 1. *Reagents:* i, $SOCl_2$; ii, CH_2=C(Me)–C(Me)=CH_2. ^1H and ^{13}C n.m.r. shift ranges are as shown.

Table 1. Heterocyclic *N*-sulphinylamines and adducts.

Compound	M.p./°C	Yield (%)	δ[a](Δ)[b] (C-*ipso*)	Compound	M.p./°C	Yield (%)
(1ai)	42–44	78	150.3 (−5.5)	**(2ai)**	103–104	90
(1aii)	oil	90	149.8 (−5.4)	**(2aii)**	130–132	89
(1aiii)	oil	90	148.9 (−5.8)	**(2aiii)**	110–112	85
(1b)	oil	89	160.1 (−7.2)	**(2b)**	127–129	87
(1ci)	102–103	86	*c*	**(2ci)**	163–164	72
(1cii)	138–139	74	*c*	**(2cii)**	172–174	73
(1ciii)	177–179	84	*c*	**(2ciii)**	193–194	80
(1d)	oil	87	163.6 (−6.2)	**(2d)**	149–151	80
(1e)	105–107	89	*c*	**(2e)**	172–174	80
(1f)	oil	91	159.8 (−4.0)	**(2f)**	119–121	87
(1g)	84	83	*c*	**(2g)**	144–146	80

[a] ^{13}C Shift of C–N=S^+–O^- in $CDCl_3$. [b] Δ is the upfield shift relative to parent amine. [c] Insoluble.

Table 2. ^{13}C and ^1H n.m.r. data for compounds (**1**).



	Ring position			
	1	2	3	4
Δ^1Hδ relative to aniline[a]	—	1.30 ± 0.5	0.23 ± 0.1	0.62
Δ^1Hδ relative to benzene[b]	—	0.47	0.0	0.0
Δ^{13}Cδ relative to aniline[a]	−3.4 ± 0.5	12.6 ± 0.6	0.63[c] ± 0.2	13.6 ± 0.5[d]
Δ^{13}Cδ relative to benzene[b]	14.5	−1.1	1.0	2.25

[a] Δ is the mean chemical shift change when NH_2 is converted into N=S^+–O^- for Y = H, Cl, Br, Me (+ is downfield; − is upfield). [b] Δ is the shift difference between the parent compound (Y = H) and benzene (δ_H, 7.27; δ_C, 128.5). [c] For Y = MeO, this shift was −0.45 ppm. [d] For Y = MeO, this shift was 8.4 ppm.

heating for periods of 8–20 h in benzene under reflux. In general the withdrawing nature of the heterocyclic substituents probably facilitated the reaction. The adducts (**2**) were single pure products and the 270 MHz proton n.m.r. spectra resolved the axial and equatorial protons of the dihydro-1,2-thiazine oxide ring. The axial and equatorial protons appeared as four

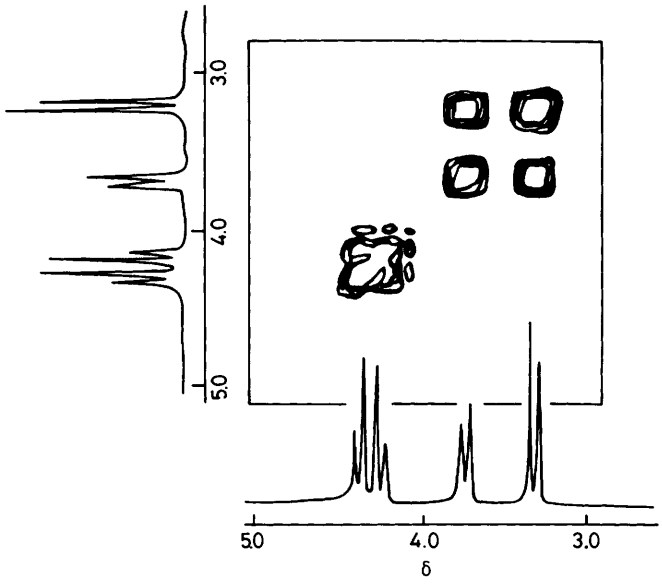
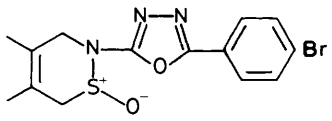


Figure 1. Methylene region of 2D n.m.r. spectrum (COSY) of compound (**2e**) at 270 MHz.



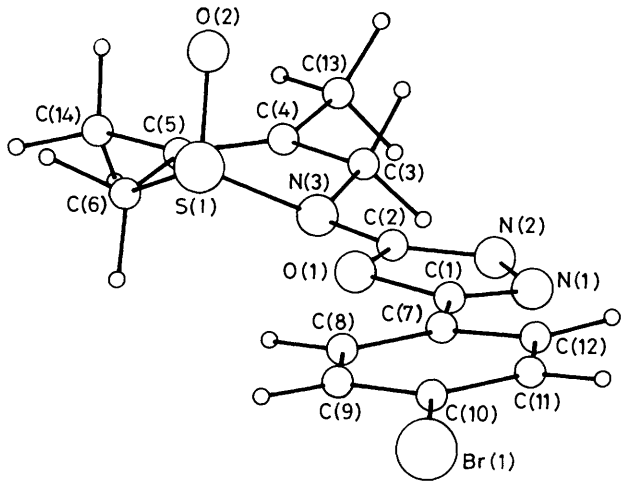


Figure 2. *X*-Ray crystal structure of compound (**2ciii**).

pairs of doublets and the coupled pairs were confirmed by decoupling and by a 2-dimensional COSY plot (Figure 1). The shifts shown for structure (**2**) in Scheme 1 were consistent over the range of compounds. The stereochemistry at sulphur is difficult to establish but it was shown to be axial in two related cases[7,11] and also confirmed as axial in the compounds (**2**) by an *X*-ray crystal structure of compound (**2ciii**) (Figure 2).

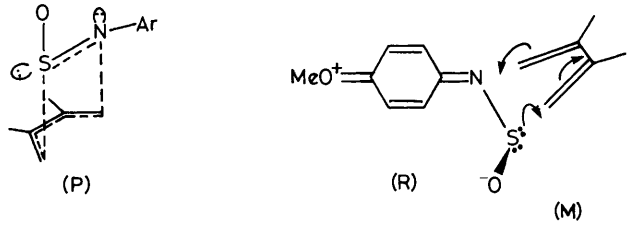
(c) *Kinetics, Mechanism, and MNDO Calculations.*—A kinetic study of the reaction of the series of compounds (**1h**) (Scheme 1) with 2,3-dimethylbuta-1,3-diene was carried out using equimolar concentrations in pure benzene in sealed glass ampoules at 350 K. Ampoules were withdrawn and quenched in ice at appropriate time intervals and the concentration of the remaining *N*-sulphinylaniline in the ampoule determined from the u.v. absorbance at $\lambda_{max.}$ for the *N*-sulphinyl derivative. The method was reliable and the rate constants were readily reproducible to ± 3% (Table 3).

Table 3. Kinetic data for the series (**1h**) at 350 K in benzene.

	Kinetics		MNDO Calculations[b]	
Y	$k/10^{-6}$ dm^3 mol^{-1} s^{-1}	$-\log k$	HOMO/eV	LUMO/eV
H[a]	3.35[a]	5.475	−8.9232	−1.7728
Me	1.84	5.735	−8.8447	−1.8056
MeO	0.96	6.018	−8.4843	−1.7599
Cl	6.18	5.210	−9.1522	−2.0223
Br	6.26	5.203	−9.1114	−1.9915

[a] Arrhenius data, 10^6k; *T*, 3.35, 350 K; 1.595, 340 K; 0.705, 330 K. [b] 2,3-Dimethylbuta-1,3-diene, HOMO, −9.0783 eV; LUMO, 0.3209 eV.

The reactions were slow and took many hours at 350 K (77 °C) in benzene. Arrhenius data were obtained at 330, 340, and 350 K for the parent compound (**1h**; Y = H) and they gave thermodynamic activation parameters: $\Delta H^{\ddagger}$, 72.0 kJ mol^{-1}, $\Delta S^{\ddagger}$, −145.5 J K^{-1} mol^{-1}, and $\Delta G^{\ddagger}$, 122.9 kJ mol^{-1}. These results are in good agreement with the results reported by Hanson and Stockburn[12] for the reaction of ethyl *N*-sulphinylcarbamate (EtO_2C–N=S$^+$–O) with 1,1′-bicyclohexenyl: $\Delta H^{\ddagger}$, 30.3 kJ mol^{-1}, $\Delta S^{\ddagger}$ −176.9 J K^{-1} mol^{-1}, and $\Delta G^{\ddagger}$ 83.0 kJ mol^{-1}. Of significance is the high negative entropy of the transition state in both cases. This is consistent with an ordered pericyclic reaction (P) (Scheme 2). The axial–equatorial arrangement of the S$^+$–O$^-$



Scheme 2.

and N–Ar groups in the products represents a *cis*-configuration for the *N*-sulphinyl moiety but this cannot confidently be extrapolated to the transition state because of the possibility of a nitrogen inversion. However if a *cis*-configuration in the starting state is carried directly through to the products a transition state of type (P) (Scheme 2) should be involved. The different $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ values for Ar–N=S$^+$–O$^-$ and EtO_2C–N=S$^+$–O$^-$ reflect the great reactivity of the latter which undergoes cycloadditions at ambient temperatures.

The substituent effects on the reaction, however, suggest a more complicated situation. *para*-Electron withdrawing groups in the phenyl-*N*-sulphinylamine enhanced the reaction rate while electron donating groups inhibited it. The rates showed a linear correlation with Hammett σ^+ values and gave a positive Hammett ρ value (ρ, 0.9 ± 0.1) (Figure 3). The rates showed no linear correlation with MNDO calculated values for Δ[HOMO(diene) − LUMO(ArN=S$^+$–O$^-$)] (Figure 3) but rather a curve which followed closely a plot of log *k* *versus* Hammett σ^n values. The refined MNDO calculations, allowing for deformation geometry on the benzene ring, suggested a significant resonance contribution from structures such as (R) (Scheme 2) when the *para* substituent is electron donating. Overall this results in a loss of double-bond character on the N–S bond of the *N*-sulphinyl group. The data in Table 3 for the HOMO − LUMO energy levels suggest that aryl *N*-sulphinylamines act as dienophiles of normal (direct) electron demand[33] with 2,3-dimethylbuta-1,3-diene. The correlation with σ^+ values and the positive Hammett ρ value for this reaction

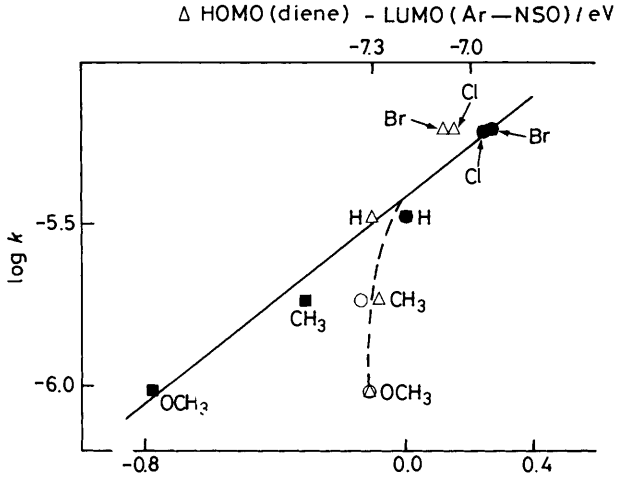


Figure 3. Plot of log *k* *versus* Hammett σ and σ$^+$ values and HOMO(diene)–LUMO(ArNSO) energy separations for the cycloaddition: ○, σ; ■, σ$^+$.

(Figure 3) compare with data obtained for the addition of arylidenepyrazol-5-ones to alkyl vinyl ethers [34] a reaction which has been described as a Diels–Alder reaction with normal (direct) electron demand.[34] As aryl *N*-sulphinylamines are dienophiles their cycloaddition behaviour might also be compared to those of substituent styrenes.[35] A similar correlation with σ$^+$ values and negative ρ values was found for the addition of styrenes to electron-deficient substituted cyclopentadienones. The negative ρ values were consistent with cycloaddition reactions of reverse electron demand [33] where the HOMO–LUMO gap is smaller for the HOMO(dienophile–LUMO-(diene) combination. The presence of the heteroatoms in –NSO lowers the LUMO energies (*ca.* −2 eV) relative to those for styrene (*ca.* 0 eV), thus shortening the HOMO(diene)–LUMO(dienophile) gap and giving an addition with normal electron demand.

The data in Figure 3 as well as the high negative entropy of activation suggest a mechanistic continuum between that of a concerted pericyclic reaction (transition state P, Scheme 2) and a Michael-type nucleophilic addition process (transition state M, Scheme 2), with the dominant mechanism depending upon the extent of the double-bond character of the N=S bond of the *N*-sulphinylamine.

Experimental and Calculations

M.p.s were measured with an Electrothermal apparatus. I.r. spectra were measured for KBr discs or neat (for oils) with a Perkin-Elmer 983G spectrophotometer. U.v. measurements for the kinetics were carried out on a Shimadzu U.V.-260 spectrophotometer. ^{1}H and ^{13}C n.m.r. spectra were measured in $CDCl_3$ with JEOL JNM-MH-100, FX60, and GX270FT spectrometers at probe temperatures using tetramethylsilane as reference. T.l.c. was carried out with aluminium-backed slides coated with silica gel 60 F_{254} and column chromatography was carried out on aluminium oxide 90 (70–230 mesh ASTM) and silica gel 60 (230–400 mesh ASTM). Thionyl chloride was purified by successive fractionations from quinoline in a glass apparatus fitted with an anhydrous calcium chloride drying tube. Benzene was dried over anhydrous calcium chloride, repeatedly distilled to b.p. 80 °C and stored over sodium wire. The amines used were prepared by procedures reported previously,[36–38] or purchased directly from Aldrich.

(a) *Synthesis of* N-*Sulphinylamines.*—The following are typical examples: (*a*) 5-Amino-1-methyltetrazole (4 g, 0.04 mol) in dry benzene (40 cm^3) was treated with thionyl chloride (8.75 cm^3, 0.12 mol), heated under reflux for 2 h and the resulting solution was evaporated under reduced pressure to give 1-methyl-5-sulphinylaminotetrazole (**1ai**), m.p. 42–44 °C (from benzene) (4.6 g, 78%); δ_C 33.3 (Me), and 150.3 (*ipso* C-5); δ_H 4.08 (s, 3 H, Me).

(*b*) 2-Amino-5-phenyl-1,3,4-oxadiazole (4 g, 0.019 mol) in dry benzene (40 cm^3) was treated with thionyl chloride (4.3 cm^3, 0.059 mol), heated under reflux for 2 h and the resulting solution was evaporated under reduced pressure to give 5-phenyl-2-sulphinylamino-1,3,4-oxadiazole (**1ci**), m.p. 102–103 °C (from benzene) (86%).

(*c*) Aniline (5.1 g, 5 cm^3; 0.055 mol) was dissolved in slightly warmed benzene (25 cm^3) and the mixture was cooled to ambient temperature and then treated dropwise, with stirring, with a solution of thionyl chloride (8.48 g, 5.2 cm^3; 0.071 mol) in dry benzene (17 cm^3). A yellow paste formed. The mixture was heated under reflux for 2 h to give a clear solution, which was evaporated under reduced pressure and the residue vacuum-distilled to give compound (**1h**; Y = H) as an oil, δ_C 142.97 (C-1, *ipso*), 127.4 (C-2), 129.5 (C-3), and 130.8 (C-4); δ_H 7.75 (m, 2 H, *ortho*), and 7.24 (m, 3 H, H *meta, para*). The following compounds were prepared similarly: compound (**1h**; Y = Me), oil; (**1h**; Y = MeO) m.p. 22–23 °C (Found: C, 49.9; H, 4.1; N, 8.12. $C_7H_7NO_2S$ requires C, 49.7; H, 4.15; N, 8.3%); (**1h**; Y = Cl), m.p. 33–35 °C (Found: C, 41.4; H, 2.4; N, 8.0. C_6H_4ClNOS requires C, 41.5; H, 2.3; N, 8.05%); (**1h**; Y = Br), m.p. 64–65 °C (Found: C, 32.95; H, 1.9; N, 6.6. C_6H_4BrNOS requires C, 33.0; H, 1.8; N, 6.65%); and (**1h**; Y = NO_2), m.p. 67–69 °C (Found: C, 39.5; H, 2.35; N, 15.2. $C_6H_4N_2O_3S$ requires C, 39.1; H, 2.2; N, 15.2%). All solid compounds were recrystallized from benzene or vacuum distilled from melts. **CAUTION:** Some **explosions** were encountered during vacuum distillation of the liquid heterocyclic derivatives (Table 1) and temperatures **not exceeding** 60 °C and caution are recommended.

(b) *Cycloadditions with* 2,3-*Dimethylbuta*-1,3-*diene.*—The following are typical examples: (*a*) A solution of freshly prepared 1-benzyl-5-sulphinylaminotetrazole (**1aii**) (2 g, 8.6 mmol) in dry benzene (3 cm^3) was treated with the diene (1.46 cm^3, 12.8 mmol) and stirred at ambient temperature for 1 min during which time the product, 2-(1-*benzyltetrazol*-5-*yl*)-3,6-*dihydro*-1,2-*thiazine* 1-*oxide* (**2aii**) separated, m.p. 130–132 °C (from benzene) (2.3 g, 89%) (Found: C, 42.0; H, 5.8; N, 23.4. $C_{14}H_{17}N_5OS$ requires C, 42.3; H, 5.6; N, 23.1%); δ_C 154.5 (tetrazole C-5′), 132.7 (Bz, C-1″) 129.0, 128.7, 127.4 (Bz, C-2″, C-3″, C-4″), 124.2 (C-4), 114.25 (C-5), 54.05 (C-3), 51.3 (1′-N–CH_2 of Bz), 46.1 (C-6), 19.45 (*Me*–C-4), and 16.85 (*Me*–C-5); δ_H 1.74 and 1.76 (2 s, 6 H, 2 Me–C), 3.15 (d, 1 H_{ax}, 6-CH), *J* 17 Hz), 3.35 (d, 1 H_{eq}, 6-CH), 3.70 (d, 1 H_{ax}, 3-CH, *J* 18.1 Hz), 4.25 (d, 1 H_{eq}, 3-CH), 5.48 (s, 2 H, 1′-N–C*H*$_2$– of Bz), and 7.19 and 7.37 (m, 5 H, Ph of Bz). The other compounds (**2**) (Table 1) were prepared similarly at temperatures <60 °C for reaction times ≤2 h. Crystallization of the product indicated the completion of the cycloaddition.

For the series of compounds (**2h**): A solution of *p*-chloro-*N*-sulphinylaniline (**1h**; Y = Cl) (1 g, 5.8 mmol) in dry cyclohexane (2 cm^3) was treated with the diene (0.98 cm^3, 8.7 mmol) and the mixture heated under reflux for 24 h and cooled at ambient temperature when 2-(p-*chlorophenyl*)-3,6-*dihydro*-1,2-*thiazine* 1-*oxide* (**2h**; Y = Cl), separated, m.p. 141–142 °C (from cyclohexane) (1.1 g; 75%) (Found: C, 56.6; H, 5.6; N, 5.6. $C_{12}H_{14}ClNOS$, requires C,56.4; H, 5.5; N, 5.5%); δ_C 144.6 (C-1′), 130.2 (C-4′), 129.2 (C-3′), 122.8 (C-2′), 124.2 (C-4), 114.9 (C-5), 54.6 (C-3), 46.45 (C-6), 19.45 (Me–C-4), and 17.2 (Me–C-5); δ_H 1.79 and 1.82 (2 s, 6 H, 2 Me), 3.17 (d, 1 H_{ax}, 6-CH, *J* 16.2 Hz), 3.5 (d, 1 H_{eq}, 6-CH), 3.65 (d, 1 H_{ax}, 3-CH, *J* 17 Hz), 4.15 (d, 1 H_{eq},

Table 4. Optimized bond distances/Å, bond angles/°, and relative energy values (ΔE_{rel}/kJ mol^{-1}).

Conformation-molecule	Method	d_{NS}	d_{SO}	d_{CN}	<CNS	<NSO	ΔE_{rel}
ZE CH_3NSO	exp[21]	1.525	1.466	1.421	126.0	117.0	—
	exp[28]	1.51	1.45	1.47	122.0	121.0	—
ZE CH_3NSO	MNDO	1.519	1.485	1.435	132.8	111.9	1.7
EE CH_3NSO		1.536	1.485	1.436	121.2	105.7	20.5
ZS CH_3NSO		1.521	1.485	1.436	131.1	111.5	0
ES CH_3NSO		1.538	1.484	1.438	122.7	105.6	22.6
ZE CH_3NSO	6-31G*	1.487	1.440	1.452	125.6	118.8	0
EE CH_3NSO		1.491	1.432	1.454	118.6	115.8	28.5
ZE CH_3NSO	3-21G*	1.482	1.445	1.479	128.1	118.7	0
EE CH_3NSO		1.486	1.438	1.481	123.1	116.4	38.1
ZS CH_3NSO		1.481	1.445	1.480	128.2	118.6	3.8
ES CH_3NSO		1.482	1.439	1.485	125.2	116.3	46.0
Z PhNSO	MNDO	1.526	1.485	1.391	134.6	112.9	0
E PhNSO		1.546	1.486	1.389	125.2	104.9	13.0

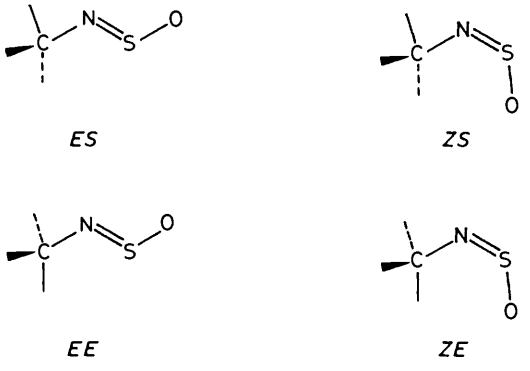


Figure 4. *N*-Sulphinyl configurations.

3-CH), 7.14 (d, 2 H, 2′-CH), and 7.30 (d, 2 H, 3-CH, AA′BB′, J_{AB} 9.0 Hz).

The other compounds (**2h**) were similarly prepared and recrystallized from cyclohexane; (**2h**; Y = H), m.p. 78–79 °C (60%); (**2h**; Y = Me), m.p. 99–100 °C (32%); (**2h**; Y = MeO), m.p. 105–106 °C (26%); (**2h**; Y = Br), m.p. 154–156 °C (80%); (**2h**; Y = NO_2), m.p. 178–180 °C (from benzene) (90%).

Full carbon-13 n.m.r. assignments on all of these compounds (**2**) as well as most of the compounds (**1**) and their corresponding parent amines are available as a Supplementary Publication No. SUP 56762 (9 pp).* Important features of these data are summarized in Scheme 1 and Tables 1 and 2.

(c) *Kinetic Measurements.*—Rate constants were measured under conditions similar to the synthetic reactions: typically, a stock solution (25 cm^3) containing equimolar quantities of the reactants in benzene (1 mol dm^{-3} in each reactant) was prepared at 25 °C, divided into six 2.5 cm^3 aliquots which were transferred to separate glass ampoules, each of which was frozen in an ice–methanol bath and sealed. The ampoules were immersed in a thermostatically controlled oil bath ($T \pm 0.1$ °C at $t = 0$). They were withdrawn at appropriate time intervals and quenched immediately in ice (time t), subsequently equilibrated at 25 °C, opened, and 0.1 cm^3 of the mixture was withdrawn and diluted 10^3-fold with benzene. The u.v. absorbance was measured at λ_{max} for the *N*-sulphinylaniline, giving the concentration ($a - x$) of the unchanged *N*-sulphinyl derivative. In accordance with the equation $kta = x/(a - x)$, a plot of t *versus* $x/(a - x)$ was linear through the origin with slope ka. All of the *N*-sulphinylanilines were shown to obey the Beer–Lambert relationship under these conditions and the $\lambda_{max.}$ values used were (**1h**; Y = H), 320 nm; (**1h**; Y = Me), 335 nm; (**1h**; Y = MeO), 362 nm; (**1h**; Y = Cl), 330 nm; and (**1h**; Y = Br), 330 nm. The method failed for compound (**1h**; Y = NO_2) due to insolubility and precipitation of products and starting materials. Each rate was measured three times and the mean k values (Table 3) are ±3%.

(d) *Theoretical Calculations.*—The hypervalence of the S atom in compounds can be measured in theoretical terms by the amount of d-orbital participation. The effect of d-orbitals on HOMO–LUMO energy gaps may not be important due to cancellation of errors, thus permitting studies using Hückel-like molecular orbital methods[12] for S atoms. However, subtle influences on the HOMO–LUMO gaps within a series of substituted phenyl *N*-sulphinylamines appear due to variations in geometry introduced by d-orbital participation.

The MNDO parameters used in this study are the latest published by Dewar's group and found in the GAUSSIAN-86 series of programmes.[39] These include an improved set of parameters for the S atom.[40] While d-orbitals are not included in these calculations, care was taken in the parametrization to reproduce experimental geometries of d-co-ordinate S-atom containing molecules. In non-empirical *ab initio* methods, neglect of d-orbitals in geometric optimization leads to the NS and SO bonds in HNSO being *ca.* 0.1 Å longer[26] than the experimental values.[41]

In order to have an idea of the reliability of the MNDO method for calculating the geometries of aryl *N*-sulphinylamines, a comparison of MNDO and *ab initio* optimized geometries of methyl *N*-sulphinylamine (CH_3NSO) was made with the experimental values.[21,28] The experiments[21,28] give a *Z*-configuration and a methyl group eclipsed to the S atom in CH_3NSO. Two basic sets were used for the *ab initio* LCAO–MO geometry optimizations,[39] the smaller 3-21G* and medium size 6-31G* sets which include d-orbitals on the S atom and on all non-H atoms, respectively.

Four combinations are possible for the *E*-*Z* configurations and eclipsed (*E*)-staggered (*S*) methyl conformations (Figure 4). The fully optimized geometries for these four positions of CH_3NSO were calculated with the MNDO and 3-21G*

* For details of the Supplementary Publication scheme see 'Instructions for Authors (1989),' *J. Chem. Soc., Perkin Trans. 2*, in the January issue.

methods. The *Z* and *E*, eclipsed geometries (*ZE* and *EE*) were also optimized with the 6-31G* basis set. The optimized bond distances and angles for the various positions are collected in Table 4 along with relative energies in kJ mol^{-1}.

The bond lengths obtained for CH_3NSO by the MNDO method are within 0.02 Å of experiment[21,28] but the bond angles vary by at least 5°. The *ab initio* results are close to experiment with the exception of the N=S bond which is calculated to be *ca.* 0.04 Å shorter than experiment.

Contrary to experiment the MNDO method predicts the *ZS* form to be more stable than the *ZE*. However, the energy difference is smaller (1.7 kJ mol^{-1}) and the MNDO method is known to give poor results for this type of conformational energy change.[42] The 3-21G* basis set results are in accord with the experimental conformation.

Both the MNDO and *ab initio* methods calculate the *Z* configuration to be more stable than the *E* form by a substantial amount. The MNDO results for CH_3NSO (*ca.* 20 kJ mol^{-1}) are closer to the large basis set 6-31G* results (28 kJ mol^{-1}).

Also included in Table 4 are results for the fully optimized geometries of aryl *N*-sulphinylamines. In the unsubstituted phenyl case, PhNSO, the *Z*-configuration is more stable by 13.0 kJ mol^{-1}. The longer NS and shorter CN bond lengths in PhNSO than in CH_3NSO reflect the various resonance forms which are more possible in the phenyl case.

(e) *Crystal Data.*—$C_{14}H_{14}N_3BrSO_2$. Monoclinic, $P2_1/c$, $a = 8.684(2)$, $b = 13.306(3)$, $c = 13.158(3)$ Å, $U = 1\,518.86$ $Å^3$, $Z = 4$, Mo-K_α radiation $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 27.62 cm^{-1}, $F(000) = 744$. A Hilger–Watts automatic four circle diffractometer was used to solve the structure, which was elucidated by direct methods and refined using SHELX76[43] from 1 106 reflections with $I > 3\sigma(I)$. Least-squares refinement with anisotropic thermal parameters for Br and hydrogen atoms in calculated positions converged to $R = 4.82\%$ and $R_w = 4.87\%$. The PLUTO program was used to obtain the drawings. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.†

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† For details of the CCDC deposition scheme, see 'Instructions for Authors (1989),' *J. Chem. Soc., Perkin Trans. 2*, 1989, issue 1.

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