1,2-Thiazines and Related Heterocycles. Part 4.[1] The Mechanism and Periselectivity of the Cycloadditions of *N*-Sulphinylaminoazines with 1,4-Epoxy-1,4-dihydronaphthalenes

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A kinetic investigation indicates that the cycloadditions of various *N*-sulphinylaminoazines, reacting as heterodienes, to 1,4-epoxy-1,4-dihydronaphthalene and its bridgehead methylated derivatives are pericyclic. The cycloadditions of the unsymmetrical 2- and 3-(*N*-sulphinylamino)pyridines are strongly periselective giving only the *peri*-isomers coupled *via* sulphur and ring positions 1 and 2, respectively. This selectivity can be accounted for in terms of Hückel orbitals if all π-interactions are considered; the frontier orbital approximation fails on account of the close spacing of orbital energies that occurs in extensively conjugated compounds.

When two reactants approach one another the nett repulsion is attenuated by the stabilisation which arises from the interactions of the filled orbitals of each reactant with the empty orbitals of the other. Perturbation theory premises that the energy of any transition state which is eventually formed from the reactants will be directly influenced by such stabilisation and, applied to second order, prescribes equation (1) for the

$$\Delta E = 2(\Sigma c_{ra} c_{sb} \beta_{ab})^2/(E_r - E_s) \qquad (1)$$

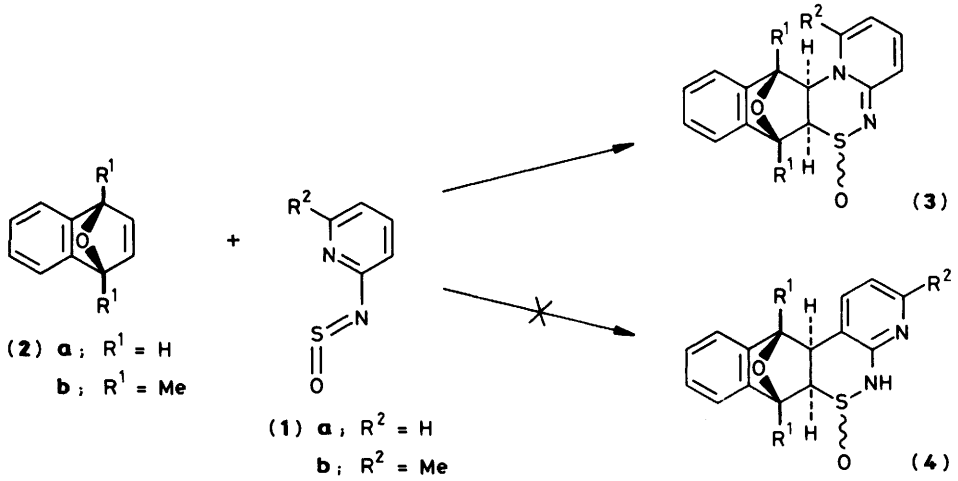
estimation of the contribution of each orbital pair where c_{ra} is the coefficient at atom a in molecular orbital r of one reactant, c_{sb} is the coefficient at atom b in molecular orbital s of the other reactant, and β_{ab} is the bond integral for the developing bond between atoms a and b.[2–7] An understanding of the outcome of kinetically competitive reactions therefore depends on how well relative stabilisations may be estimated. A degree of approximation in their estimation may be feasible without the loss of explanatory validity, but ultimately, there must be a limit to approximation beyond which the account of chemical behaviour either fails or is only fortuitously correct. The aim of the present work has been to define the limits of approximation permissible in accounting for pericyclic reactivities in sulphinylamines.

Table 1 details various stages of approximation that may be envisaged subsequent to that of applying equation (1); these restrict the orbital interactions to which the equation is applied. The orbital coefficients and energies that are used in equation (1) may be derived from MO calculations on the reactants at various levels of sophistication. When the literature contains appropriate data, obviously these may be used at any convenient level of approximation but when such data are lacking, it is wasteful of computational resources to execute high-level MO calculations in order merely to match frontier orbitals.[11] An organic chemist with an interest in rationalising the course of cycloadditions has need of easily and cheaply available MO data for use in the approximate treatments. Hückel MO, which are available within minutes using a microcomputer, are an obvious choice. The success of these, *via* their McLachlan variant,[13] in explaining the spin distribution in π-radicals[14,15] (itself a frontier orbital property) leads to the expectation that they should be suitable for use at a level of approximation comparable with the frontier orbital method. It is conceivable that the two approximations, the use of HMO *and* the FO method, might combine adversely to cause calculation not to accord with reality but, conversely, a cancelling of introduced errors can also occur: Minot and Anh[16] have suggested that the distortion of the electron distribution given by the Hückel method in part models the changes which occur when reactants begin to combine. If an initial calculation does not give a correct account, the nature of the changes in parameterisation needed to rectify the result can give insight into the mechanism. Cycloadditions involve the displacements of π-electrons in the reactants and decrease of the bond integrals of the corresponding π-bonds is an obvious first adjustment.

Equation (1) contains bond integrals β_{ab} for the σ bonds being formed in the reaction of interest. If these are ignored, it is equivalent to an assumption that the bonds being formed have a common value of bond integral which is factorised out of the

Table 1. Stages of approximation in calculation of perturbational stabilisation for cycloaddition

		Reference
Second-order perturbation	↓	8
	interaction of all occupied–unoccupied π-orbital pairs at all atomic centres	3
	↓	
	interaction of all occupied–unoccupied π-orbital pairs at atomic centres forming σ-bonds	9
	↓	
Frontier orbital approximation	HOMO–LUMO interactions at atomic centres forming σ-bonds	10, 11
	↓	
	major FO interaction only, at atoms forming σ-bonds; matching of FO coefficients (to predict selectivity); comparison of FO energy separation (to predict relative rates)	11, 12



Scheme 1.

terms found on application of the equation. A common value might be expected if the bonds being formed are of the same type but also, since bond integrals are taken to be proportional to overlap, dissimilar bonds may have values in common at different separations of the interacting atoms. Thus neglect of bond integrals when dissimilar bonds are forming implies an assumption about the geometry of the transition state or about the synchronicity of bond formation within it. We suggest that for present purposes it is reasonable first to ignore bond integrals and enquire whether Hückel orbital coefficients alone will account for an observed selectivity and, if so, then to consider the geometrical implications. It is to be expected that the importance of β_{ab} values will be greatest when the bonds forming in the transition state are very dissimilar; an example is the dimerisation of acrolein.[7]

We have previously shown that the regioselectivity of the pericyclic addition of *N*-sulphinylamines to unsymmetrical dienes may be comprehended in the frontier orbital approximation using Hückel orbitals.[1] A suitable parameterisation of the NSO function was found by matching the stabilisations, given by the calculations for different orientations of addition, to the transition-state energy differences implied by the observed ratios of regioisomers. An *N*-sulphinylamine is a dienophile of normal electron demand [12] and, consequently, the dominant term in the frontier orbital treatment is that arising from interaction of its LUMO with the HOMO of the diene. An unsaturated *N*-sulphinylamine such as PhNSO or EtO_2CNSO may also react as a heterodiene of inverse electron demand.[16–21] Again, therefore, the dominant frontier orbital in determining the reactivity should be the LUMO. It was thus of interest to ascertain whether the electronic description which serves to rationalise one mode of pericyclic reactivity in sulphinylamines would also serve for another, as it should if the description is not fortuitous in the first case.

In earlier work [20,21] we have studied in some detail the reactions of *N*-sulphinylanilines with 1,4-epoxy-1,4-dihydronaphthalenes. 3-Substituted sulphinylanilines are, in principle, capable of manifesting selectivity in cycloaddition: the dienophile can add at sulphur and at ring position 2 or 6. Addition at the 2 position, however, is subject to small but significant steric effects which obviate the use of 3-substituted sulphinylanilines as reliable probes of electronically determined periselectivity. In order to overcome this drawback we turned to sulphinylaminopyridines; as unsymmetrical arylsulphinylamines these should have steric requirements close to *N*-sulphinylaniline itself.

Results and Discussion

(a) *Materials.*—The reactants and products of the reactions studied in this paper will be described in detail elsewhere as several of the former and all of the latter are new. 3-(*N*-Sulphinylamino)pyridine is readily prepared and handled like *N*-sulphinylaniline;[22,23] 2-(*N*-sulphinylamino)pyridine has been handled only in solution previously.[22] We have obtained it pure but it is subject to deterioration within hours; ring methylation may give products which are easier to manage, however. 4-(*N*-Sulphinylamino)pyridine and 2-(*N*-sulphinylamino)pyrimidine proved difficult to manipulate, being prone to rapid hydrolysis and to deterioration, if neat, even when dry; nevertheless, the kinetic results obtained using these materials will be shown to be consistent with those from the other sulphinylaminoazines used.

The addition of 2-(*N*-sulphinylamino)pyridine (**1a**) to 1,4-epoxy-1,4-dihydronaphthalene (**2a**) results in the formation of a single product (**3a**) in which the dienophile is linked at S and the ring heteroatom (Scheme 1); a similar result is obtained when a 6-methyl substituent is introduced into the pyridine ring. When 4- or 5-methyl substituents are introduced into the heterocycle minor amounts of other adducts are formed but these are identified as stereoisomers not *peri*-isomers. Stereoisomers arise according to whether the S–O bond is *cis* or *trans* to the bridging oxygen. The comparable isomerism which occurs for analogous adducts of *N*-sulphinylanilines has been discussed in detail.[21] The transition states which lead to the various stereoisomers differ only slightly in energy. Such small energy differences could arise from variations in solvation, or in transition-state geometry, with the methylation pattern and we shall not consider them further here. The strong periselectivity for addition at N rather than the 3-position of the pyridine ring is demonstrated by the finding that 1,4-epoxy-1,4-dimethyl-1,4-dihydronaphthalene (**2b**) and 6-methyl-2-sulphinylaminopyridine (**1b**) cycloadd *via* N although to do so causes severe crowding of the methyl groups in the two reactants and the alternative unhindered addition at C(3) would lead both to a stronger bond and a better aromatised product (**4b**).

Strong periselectivity is also observed when (**2a**) reacts with 3-(*N*-sulphinylamino)pyridine (**5**): addition takes place at S and only C(2) of the heterodiene, not C(4), giving the stereoisomers of (**6**).

(b) *Kinetics.*—The rates of reaction of sulphinylaminoazines with 1,4-epoxy-1,4-dihydronaphthalenes were measured by

Table 2. Activation parameters for the cycloaddition of aryl sulphinylamines to (**2a**)

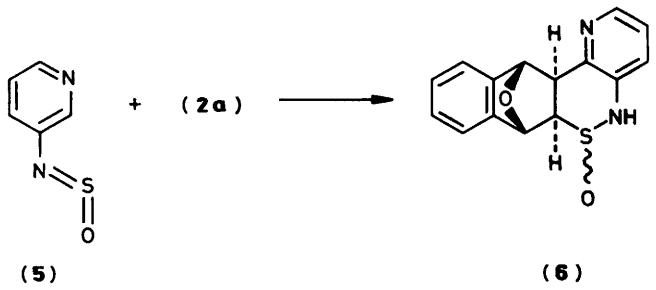
Heterodiene	T/°C	$10^5\ k$/ dm^3 mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J K^{-1} mol^{-1}	$\Delta G^{\ddagger}_{298}$/ kJ mol^{-1}
	40.2	3.43 ± 0.10			
	51.2	7.19 ± 0.25			
(**1b**)[a]	51.4	6.89 ± 0.48	49 ± 2	−173 ± 6	101 ± 2
	60.3	12.56 ± 0.54			
	70.0	19.30 ± 1.36			
	50.7_5	1.30 ± 0.04			
	60.5	2.77 ± 0.08			
(**5**)[a]	60.7_5	2.82 ± 0.09	64 ± 2	−140 ± 6	106 ± 2
	70.0	5.66 ± 0.12			
	74.5	6.96 ± 0.16			
PhNSO[b]			80	−104	111

[a] In benzene. [b] In chlorobenzene, see ref. 20.

Table 3. Solvent effects on rates of cycloaddition of sulphinylaminopyridines to (**2a**)

Heterodiene	T/°C	Solvent	Dielectric constant at 20 °C	$10^5\ k$/ dm^3 mol^{-1} s^{-1}
(**5**)	50.75	Benzene	2.284[a]	1.30 ± 0.04
	50.00	Chlorobenzene	5.708[a]	1.62 ± 0.02
	50.50	Acetonitrile	37.5[b]	1.80 ± 0.06
(**1b**)	51.40	Benzene	2.284[a]	6.89 ± 0.48
	51.40	Acetonitrile	37.5[b]	14.10 ± 0.54

[a] 'Handbook of Chemistry and Physics,' ed. R. C. Weast, Chemical Rubber Co., Ohio, 63rd edn., 1982. [b] 'American Institute of Physics Handbook,' ed. D. E. Bray, McGraw-Hill, New York, 2nd edn., 1963.



Scheme 2.

following the disappearance of (**2a**) from initially equimolar solutions of the reactants by g.l.c. Reactions were followed to >50% completion in most cases. Activation parameters were determined for (**1b**) and (**5**) from rate determinations at five different temperatures in the range 40—75 °C. They are given in Table 2 with those for *N*-sulphinylaniline[20] for comparison; all show the low activation enthalpy and the large negative activation entropy which characterise concerted reaction. In Table 3 are given rate constants determined for the same heterodienes in different solvents. It is clear that substantial change in solvent polarity, as measured by dielectric constant, causes but slight change in reaction rate, again indicative of concerted reaction in which little separation of charge occurs on passage to the transition state. Rate constants at 50 °C for (**1b**), (**5**) and other aryl *N*-sulphinylamines are given in Table 4; for the latter heterodienes no activation parameters have been obtained but there is no reason to suspect a change of mechanism from pericyclic. Indeed, we assert the contrary on the basis of a correlation which follows.

(c) *Calculations.*—Hückel calculations for arylsulphinylamine heterodienes and for an electron-rich dienophile were carried out, parameterised in various ways. Stabilisations were hence calculated for the heterodienes reacting in either possible orientation with the dienophile by using equation (1). Various occupied–unoccupied orbital-pair interactions were considered but the bond integrals, β_{ab}, for developing bonds were neglected, *i.e.* set to unity for purposes of calculation.

The various parameterisations used are given in Table 5. For the sulphinylaminopyridines, parameterisation 1 uses values derived previously for the NSO group[1] and literature recommendations for the pyridine ring.[24] It had been found previously that the regioselectivity predicted for sulphinylamine *dienophiles* was essentially independent of the value taken for k_{NS} in the range 0.5—1.0, the value 0.9 being arbitrarily selected from this range to reflect both a greater bond order of the N–S bond, relative to the S–O bond, in RN=S$^+$–O$^-$ and also a bond between first- and second-period elements.[1] Parameterisation 2 varies k_{NS} from the value taken in the first parameterisation to ascertain the effect of such change on the predicted behaviour of the sulphinylamines as *heterodienes*. In parameterisation 3, the bond integral for the endocyclic C–N bonds is reduced from the value in parameterisation 1. Two parameterisations were used for the electron-rich dienophile, one with more electropositive carbon atoms and less effective π-overlap than the other; the parameters chosen resulted in the two dienophile models having a LUMO energy in common (1.3β) but different HOMO energies (−0.7 and −0.9β, respectively).

The stabilisations calculated using the various parameter combinations are given in Table 6. As may be seen from Table 6, for 2-(*N*-sulphinylamino)pyridine, in all calculations the stabilisation derived from the major frontier orbital interaction, *i.e.* from interaction of the LUMO of the heterodiene with the HOMO of the dienophile, is greater for the observed *peri-*

Table 4. Rate constants[a] at 50 °C for the cycloadditions of aryl sulphinylamines to (**2a**)

	Heterodiene	10^5 k/ dm^3 mol^{-1} s^{-1}		Heterodiene	10^5 k/ dm^3 mol^{-1} s^{-1}
(i)	PhNSO	0.29[b]	(v)	2-NSO-6-MePyr	6.47 ± 0.38[c]
(ii)	3,5-$Me_2C_6H_3NSO$	0.417 ± 0.002	(vi)	2-NSO-5-MePyr	21.9 ± 0.6
(iii)	4-PyrNSO[d]	0.96 ± 0.06	(vii)	2-NSO-4-MePyr	29.3 ± 1.3
(iv)	3-PyrNSO	1.25 ± 0.04[c]	(viii)	2-PyrNSO	53.7 ± 1.6
			(ix)	2-Sulphinylaminopyrimidine	67.7 ± 3.4

[a] Quoted error is ± one standard deviation. [b] Extrapolated value, see ref. 20. [c] Interpolated from Table 2. [d] Pyr: pyridine.

Table 5. Hückel parameters utilised

(a) Arylsulphinylamines

Parameterisation	Coulomb integrals		Bond integrals	
	h_O	1.0	k_{SO}	0.83
	h_S	1.0	k_{NS}	0.90
1	h_N	0.5	$k_{CN(exo)}$	0.80
	h_C	0.0	k_{CC}	1.00
	$h_{C(Me)}$	−0.2	$k_{CN(endo)}$	1.00
	h_O	1.0	k_{SO}	0.83
	h_S	1.0	k_{NS}	0.50
2	h_N	0.5	$k_{CN(exo)}$	0.80
	h_C	0.0	k_{CC}	1.00
	$h_{C(Me)}$	−0.2	$k_{CN(endo)}$	1.00
	h_O	1.0	k_{SO}	0.83
	h_S	1.0	k_{NS}	0.90
3	h_N	0.5	$k_{CN(exo)}$	0.80
	h_C	0.0	k_{CC}	1.00
	$h_{C(Me)}$	−0.2	$k_{CN(endo)}$	0.80

(b) Dienophile

Parameterisation	Coulomb integrals		Bond integrals	
4	h_C	−0.3	k_{CC}	1.00
5	h_C	−0.2	k_{CC}	1.10

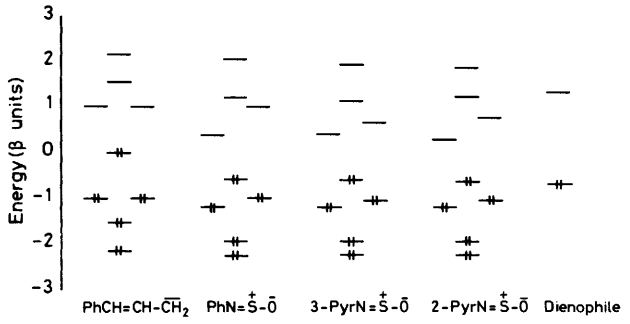


Figure 1. Comparison of the Hückel orbital energies for phenylallyl, arylsulphinylamines (parameterisation 3), and an electron-rich alkene dienophile (parameterisation 4)

isomer than for that which is not observed. The opposite is true for the minor frontier orbital interaction. When both frontier orbital terms are combined, only calculations 4 and 5, where the endocyclic k_{CN} value was 0.80, predict the observed periselectivity unambiguously. For calculations 1 and 2 where $k_{CN(endo)}$ was 1.00, the result depends on which parameterisation of the dienophile was used and then the difference between the stabilisations of the different *peri*-isomers is very small. Modification of the value of k_{NS} merely worsens the result (compare the predictions of calculations 2 and 3). When 'total' stabilisations are calculated by allowing interaction of all the occupied π-orbitals of each reactant with all the unoccupied π-orbitals of the other, the frontier orbital predictions of calculations 4 and 5 are confirmed but all other calculations fail.

For 3-(*N*-sulphinylamino)pyridine, all calculations make the wrong prediction of regioselectivity in the major frontier orbital term. The minor frontier orbital term does make the correct prediction but, when the FO terms are combined, only in calculation 3 is the compensation sufficient to ensure that the combined FO stabilisations predict correctly. When total stabilisations are examined it is evident that all the calculations predict the observed periselectivity for the 3-isomer but the difference in stabilisation of the two *peri*-isomers is most marked for calculations 4 and 5.

Taking the calculations together, therefore, only calculations 4 and 5 explain the observed periselectivities for both heterodienes but then only if total stabilisation energies are evaluated; the frontier orbital approximation works for (**1a**) but not for (**5**). The previously evolved parameterisation of the NSO group is effective for this mode of pericyclic reactivity, but we find it necessary to reduce the bond integral for the endocyclic CN bonds from the value recommended for pyridine. Since π-bonds to the heterocyclic nitrogen are disrupted in the cycloadditions of both sulphinylaminopyridines, this does not seem unreasonable.

There are two reasons for the limited success of the frontier orbital approximation. The first concerns orbital energies: 3-phenylallyl is the alternant hydrocarbon of which the matrix is modified to represent aryl sulphinylamines; Figure 1 shows the positions of the various Hückel orbitals of 3-phenylallyl and of the arylsulphinylamines of interest relative to one another and also relative to the two orbitals of the dienophile. It is apparent that although the incorporation of heteroatoms drastically affects the distribution of the energies of the orbitals of the hydrocarbon, there is a close similarity between the energies of the first six orbitals of the arylsulphinylamines which include their frontier orbitals; noticeable differences occur only at the level of the next-to-LUMO. Further, it is apparent that the energy differences between these next-to-LUMOs and the HOMO of the dienophile are less than those of the minor frontier orbital interactions and thus, depending on the orbital coefficients at the interacting atoms, have potential for a greater contribution to the total stabilisation. The second reason for the failure of the frontier orbital approximation, particularly for 3-(*N*-sulphinylamino)pyridine, is apparent from Figure 2 which shows the LUMOs of the three arylsulphinylamines. It is obvious that they have similar symmetries and that a node occurs close to the positions *meta* to the sidechain in each compound. This is, of course, close to the heteroatom in (**5**). The frontier orbital which contributes most to the stabilisation of the pericyclic transition state is thus insensitive to the substitution which characterises the 3-isomer.

Table 6. Stabilisations (β units) calculated for cycloadditions of sulphinylaminopyridines to an electron-rich alkene dienophile

Calculation 1 parameter combination 1 and 4[a]

Stabilisation	Major FO		Minor FO		Combined FO		Total	
peri-Isomer[b]	O	NO	O	NO	O	NO	O	NO
2-PyrNSO (**1a**)	−0.745	−0.675	−0.113	−0.173	−0.858	−0.848	−1.368	−1.397
3-PyrNSO (**5**)	−0.667	−0.708	−0.175	−0.141	−0.842	−0.849	−1.398	−1.388

Calculation 2 parameter combination 1 and 5[a]

Stabilisation	Major FO		Minor FO		Combined FO		Total	
peri-Isomer[b]	O	NO	O	NO	O	NO	O	NO
2-PyrNSO (**1a**)	−0.621	−0.563	−0.113	−0.173	−0.734	−0.735	−1.230	−1.261
3-PyrNSO (**5**)	−0.558	−0.594	−0.175	−0.141	−0.733	−0.735	−1.263	−1.252

Calculation 3: parameter combination 2 and 5[a]

Stabilisation	Major FO		Minor FO		Combined FO		Total	
peri-Isomer[b]	O	NO	O	NO	O	NO	O	NO
2-PyrNSO (**1a**)	−0.720	−0.712	−0.154	−0.207	−0.874	−0.919	−1.391	−1.438
3-PyrNSO (**5**)	−0.694	−0.700	−0.216	−0.188	−0.911	−0.889	−1.439	−1.420

Calculation 4: parameter combination 3 and 4[a]

Stabilisation	Major FO		Minor FO		Combined FO		Total	
peri-Isomer[b]	O	NO	O	NO	O	NO	O	NO
2-PyrNSO (**1a**)	−0.859	−0.628	−0.143	−0.167	−1.002	−0.795	−1.479	−1.406
3-PyrNSO (**5**)	−0.634	−0.729	−0.173	−0.142	−0.807	−0.871	−1.437	−1.397

Calculation 5: parameter combination 3 and 5[a]

Stabilisation	Major FO		Minor FO		Combined FO		Total	
peri-isomer[b]	O	NO	O	NO	O	NO	O	NO
2-PyrNSO (**1a**)	−0.712	−0.521	−0.143	−0.167	−0.855	−0.687	−1.323	−1.267
3-PyrNSO (**5**)	−0.530	−0.610	−0.173	−0.142	−0.703	−0.752	−1.296	−1.258

[a] See Table 5 for parameters used. [b] Columns labelled O correspond to calculations for *peri*-isomers which are observed and those labelled NO to *peri*-isomers which are not observed.

To summarise, we ascribe the limited success of the frontier orbital approximation in accounting for periselectivity of cycloaddition of sulphinylaminopyridines to the fact that these compounds have extensive conjugation which results in subjacent orbitals contributing significantly to the total stabilisation. This may not matter much if the amplitude of the LUMO is significant at the heteroatom as occurs for the 2-isomer, but if the amplitude is small, the LUMO is insensitive to the presence of the heteroatom and the significance of non-frontier orbitals in determining periselectivity is proportionately greater as happens for the 3-isomer.

This rationale is valid provided Hückel orbitals are sufficiently trustworthy for describing the electronic properties of the sulphinylamines. As evidence that this is so, in Figure 3 is presented the correlation of the total stabilisations calculated using such orbitals with the logarithms of the corresponding experimental rates of cycloaddition at 50 °C of aryl sulphinylamines; the data for Figure 3 are given in Table 7. Again, bond integrals for the bonds being formed have been taken as unity. We have not succeeded in improving the linearity of the plot in Figure 3 by assuming values other than 1 and there appears to be little purpose in doing so; even without further refinement the calculated stabilisation energies account for *ca.* 90% of the variance in the observed rates, which suggests that the Hückel results do adequately describe these systems. Previously, we have inferred that the bond integrals for S(3*p*)–C(2*p*) and

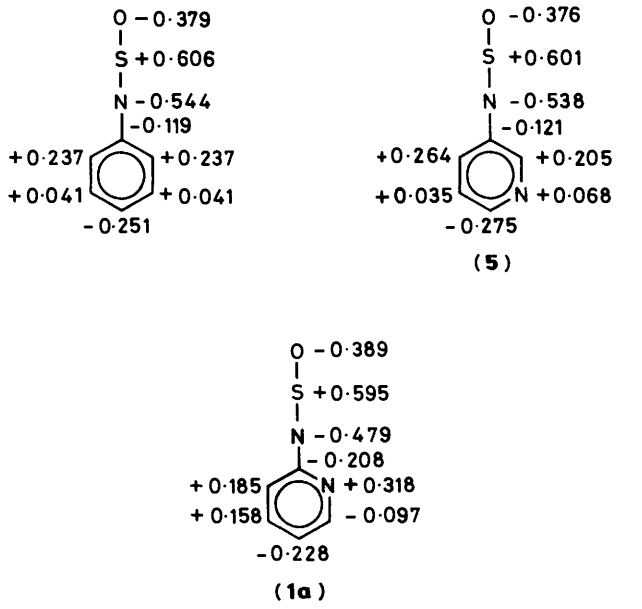


Figure 2. Comparison of LUMO coefficients for arylsulphinylamines (parameterisation 3)

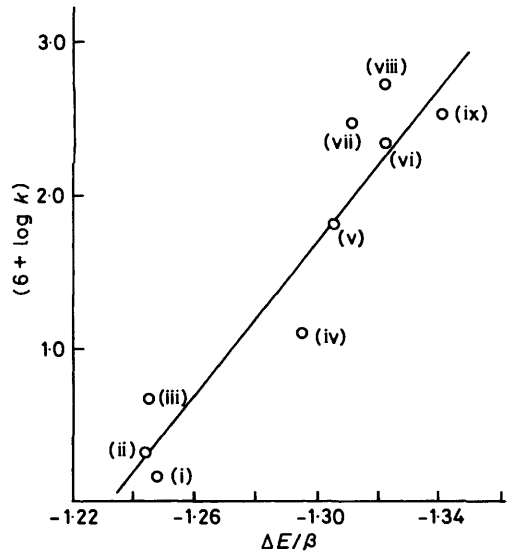


Figure 3. Variation of (6 + log$k$) with total stabilisation, ΔE; data from Table 7

Table 7. Correlation of logarithms of rate constants with calculated stabilisations

Heterodiene[a]	(6 + log$k$)[b]	Total stabilisation (β units) $-\Delta E(1)$[c]	$-\Delta E(2)$[d]
(i)	0.161	1.380	1.248
(ii)	0.319	1.376	1.244
(iii)	0.681	1.383	1.245
(iv) (**5**)	1.097	1.437	1.296
(v) (**1b**)	1.811	1.467	1.305
(vi)	2.340	1.478	1.322
(vii)	2.467	1.471	1.312
(viii) (**1a**)	2.730	1.479	1.323
(ix)	2.530	1.507	1.343

Regression of log rate constant upon calculated total stabilisation gives: log$k$ = −32.4 − 19.4ΔE(**1**); $100r^2$ = 91.4 and log$k$ = −37.2 − 25.3ΔE(2); $100r^2$ = 88.9.

[a] Heterodiene numbering and rates from Table 4. [b] Statistical correction applied for heterodienes with symmetrical aryl rings. [c] Parameters as in calculation 4 of Table 6. [d] Parameters as in calculation 5 of Table 6.

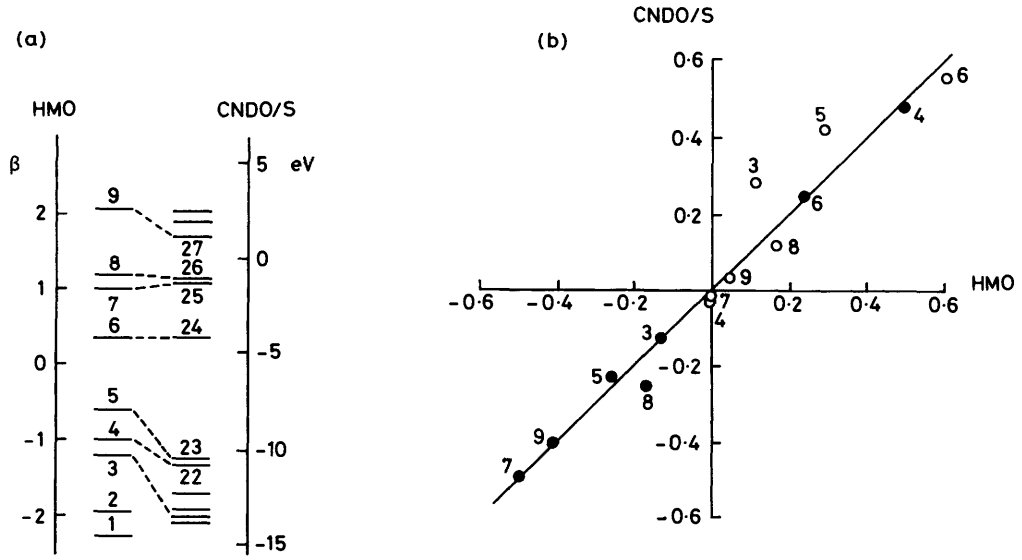


Figure 4. Comparison for HMO and 'modified' CNDO/S calculations of (a) orbital energy distributions and (b) orbital coefficients at S and C(2) in PhNSO; open circles: coefficients at S, full circles: coefficients at C(2); labels correspond to Hückel orbital numbering

N(2p)–C(2p) σ-bonds are equal for a 2 Å separation of the atoms.[1] The results for the various 2-(*N*-sulphinylamino)pyridines and the pyrimidine are therefore consistent with this separation of the planes of the reactants in the transition states for cycloaddition to electron-rich alkenes. For the remaining heterodienes where a C–C bond forms in place of a C–N bond the results are consistent with a transition state in which the C–C separation is *ca.* 2.1 Å if the C–S separation is 2 Å.[25,26]

Higher-level MO calculations have been reported only for sulphinylaniline and various derivatives:[27] these were 'modified' CNDO/S calculations made for all valence electrons and in which allowance was made for the participation of sulphur *d*-orbitals and for molecular geometry. In Figure 4a the comparison is made between the distributions of the energies of the Hückel orbitals and those 'modified' CNDO/S orbitals which are of predominantly π-character and corresponding symmetry; in Figure 4b the coefficients at S and C(2) of the Hückel MO are plotted against the out-of-plane components at the same atoms of the corresponding 'modified' CNDO/S MO.[28] The comparisons of Figure 4 indicate that Hückel calculation produces an account of the π-orbital properties of PhNSO which accords reasonably well with that obtained by a more sophisticated method, again lending weight to the suggestion that the success of the HMO method in explaining the cycloadditions of sulphinylamines is not fortuitous.

Experimental

(a) *Materials.*—The preparation of the sulphinylaminoazines and the characterisation of their adducts will be given elsewhere since most of the compounds are new.

(b) *Kinetics.*—Solutions containing equimolar proportions of the sulphinylaminoazine and 1,4-dihydro-1,4-epoxynaphthalene were made up in the selected solvent. Concentrations were in the range 0.1—1.0 mol dm^{-3}, the value chosen depending on the particular heterodiene and the need to have conveniently observable reaction rates. Portions of the solution (1 cm^3) were held in stoppered tubes in a bath thermostatted at the required temperature. At convenient intervals, one portion was removed, cooled, and diluted to 50 cm^3 with cyclohexane containing a known amount of 4-bromotoluene as an internal standard. The concentration of the unchanged dienophile in the diluted solution was determined relative to the internal standard by g.l.c.; the value taken was the average of five or six measurements made for each solution. The chromatographic conditions were: column, 10% Apiezon L on 60—80 mesh Celite; temperature, 150 °C; carrier gas, nitrogen, flow rate *ca.* 50 cm^3 min^{-1}; chromatogram quantitation by means of a Shimadzu C-R1B data processor. Errors in the reaction rates vary somewhat with the heterodiene and the temperature, the more reactive systems usually exhibiting greater scatter on their second-order kinetic plots. The errors quoted for the various rate constants given in the Tables are the standard deviations found by applying the least-mean-squares method to the second-order kinetic plots. Similarly, the errors on the activation parameters were determined stastically from the coefficients of the Eyring plots.

(c) *Hückel Calculations.*—Calculations were performed using either the University of York's DEC System 10 computer or an Acorn BBC B microcomputer. The Hückel program for the mainframe computer was originally written by Dr. D. R. Burnham and adapted by one of us (S. A. C. W.) for the calculation of stabilisation energies for cycloadditions; the microcomputer programs for executing the same tasks were written by A. Whitwood.

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