Chemistry of Sulphines. Part XXVIII.[1] Barriers to Rotation in Highly Substituted Arylthio, Alkyl- and Aryl-sulphinyl, and Arylsulphonyl *E*- and *Z*-Sulphines

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The barrier to rotation about the aryl–sulphine bond (α-barrier) in the *E*- and *Z*-sulphines (I) and (II) was determined by means of coalescence of the two diastereotopic *o*-methyl groups of the mesityl ring A. In the sulphinyl *E*-sulphine (III), in which the *ortho*-positions of ring A are unsubstituted, no barrier was observed. To determine the barrier about bond α in the arylthio and sulphonyl sulphines, a diastereotopic marker, the isopropyl group, was introduced in the *meta*-position of the ring A. Coalescence of the two methyl groups of Pr^i in arylthio sulphines (V) and (VI) and sulphonyl sulphines (IX) and (X) affords a method to measure the α-barrier in these sulphines. For comparison the α-barrier in the corresponding *S*-aryl thiocarboxylates (XI) and dithiocarboxylates (XII) were also determined. In the sulphinyl *E*- and *Z*-sulphines (VII) and (VIII), two rotational diastereoisomers are observed in the n.m.r. At higher temperatures there is a fast exchange between these diastereoisomers by rotation about α, resulting in coalescence of the two different sets of signals and thus providing an alternative method to determine the α-barrier in these sulphinyl sulphines. In the *E*-sulphines (VIIa—c) and in the *Z*-sulphine (VIIIc) the α-barrier is >23 kcal mol^{-1} and therefore the two rotational diastereoisomers could be isolated at room temperature. For these sulphines the direct equilibration method was also used to determine the α-barrier. The activation parameters of the α-barrier in these latter sulphines were calculated by means of an Arrhenius plot. In the sulphines with an *S*-mesityl group [(Ie), (IIe), (IV), (Vc)—(Xc)] in most cases a rotational barrier about the mesityl–sulphur bond was observed (β-barrier). This barrier was obtained by means of coalescence of the two *o*-methyl groups of the *S*-mesityl group. The α- and β-barriers are discussed in terms of steric interactions encountered in the preferred conformations for the different types of sulphines.

In recent years a series of sulphines derived from dithiocarboxylates by stepwise oxidation with peroxyacids [2–4] has received our attention. Since the CSO group is bent,[5,6] geometrical isomerism is possible, and hence six types of sulphines arise. The preferred conformations of the *E*- and *Z*-sulphines were determined [1] from their n.m.r. spectra and dipole moments. In this paper we present a study of the rotational barrier about the aryl-sulphine bond (α-barrier) in arylthio sulphines (V) and (VI), sulphinyl sulphines (I)—(III), (VII), and (VIII), and sulphonyl sulphines (IX) and (X). For comparison the rotational barriers about the aryl–carbonyl bond and the aryl–thiocarbonyl bond in the corresponding *S*-aryl thiocarboxylates (XI) and dithiocarboxylates (XII) were determined. Furthermore, in the compounds with an *S*-mesityl group [(Ie), (IIe), (IV), (Vc)—(XIIc)] the rotational barrier about the mesityl–sulphur bond β was determined.

N.m.r. spectroscopy offers an excellent method for determining energy barriers when two signals of equal intensity, the protons of which undergo no coupling with each other, coalesce to one signal. Free energy barriers may then be calculated from the coalescing signals by means of the Eyring equation (1) [7,8] in which

$$\Delta G^{\ddagger}_{c} = 4{\cdot}57T_c\,(10{\cdot}32 + \log T_c/k_c) \qquad (1)$$

T_c is the coalescence temperature and k_c the rate constant for rotation at the coalescence temperature. The value

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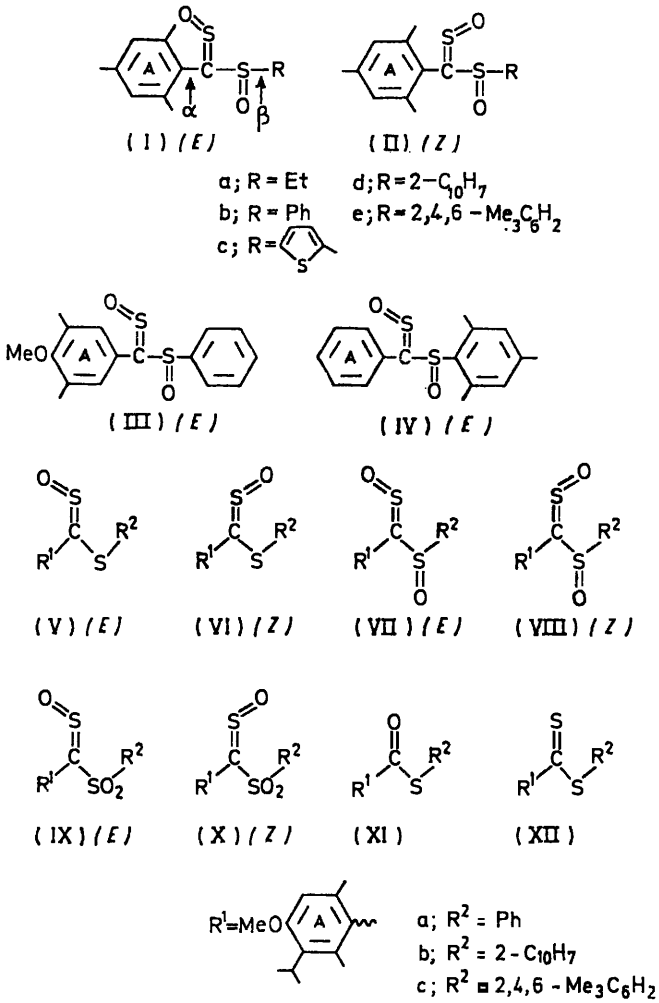
[4] B. Zwanenburg, L. Thijs, and J. Strating, *Rec. Trav. chim.*, 1971, **90**, 614.
[5] J. F. King and T. Durst, *J. Amer. Chem. Soc.*, 1963, **85**, 2676.
[6] B. Zwanenburg and J. Strating, *Quart. Rep. Sulfur Chem.*, 1970, **5**, 79.
[7] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' Wiley, New York, 1961.
[8] H. Kessler, *Angew. Chem.*, 1970, **82**, 237; *Angew. Chem. Internat. Edn.*, 1970, **9**, 219.

of k_c may be calculated from equation (2) [8,9] where $\Delta\nu$ is the chemical shift difference in Hz between the two coalescing signals obtained from the n.m.r. spectrum at a temperature taken well below T_c.

$$k_c = \pi\Delta\nu/\sqrt{2} \qquad (2)$$

It was found [4,10] that the *o*-methyl protons (and also the *m*-protons) of ring A in sulphines (I) and (II) appear



as different signals in the n.m.r. spectrum. This magnetic non-equivalence must be due to the presence of the pyramidal asymmetric sulphoxide function, which condition, however, is not sufficient. Application of Mislow's test [11] for diastereotopic groups implies that the *o*-methyl groups only become diastereotopic when interchange of the groups by rotation about the α bond, which is a two-fold axis of symmetry for these groups, is slow on the n.m.r. time scale.[12] When rotation about the α bond becomes fast, the basic requirement for the *o*-methyl groups being diastereotopic is no longer fulfilled, with the consequence that the methyl groups become equivalent, and therefore their signals coalesce to one. Hence, variable temperature n.m.r. analysis of these compounds provides a means of determining the rotational barrier about the α bond. During this analysis no *Z* to *E* (or *vice versa*) isomerization was observed.

Table 1 contains the coalescence data (T_c and k_c) and

TABLE 1

Coalescence data and $\Delta G^{\ddagger}_c$ values for the α bond in sulphines (I)—(III)

Compound	$\Delta\nu$/Hz (°C) [a]	T_c/°C	k_c/s^{-1}	$\Delta G^{\ddagger}$/kcal mol^{-1}
(Ia)	2·7 (32) *	130	6·0	22·4
(Ib)	31 (105) †	195	68·9	23·9
(Ic)	15 (32) *	180	33·3	23·7
(Id)	34 (105) †	197	75·5	23·9
(Ie)	25 (105) †	220	55·5	25·4
(IIa)	2·5 (32) *	74	5·6	19·2
(IIb)	98 (32) *	130	218	19·5
(IIc)	63·4 (32) *	115	141	19·1
(IId)	109 (32) *	139	242	19·9
(IIe)	40 (32) *	151	88·9	21·3
(III)	[b]	<-85		$<\sim 9$

[a] Chemical shift difference between the *o*-methyl groups of ring A, obtained at 100 MHz. [b] *m*-Methyl signals are still equivalent at −85° in CH_2Cl_2.

Solvent: * nitrobenzene; † *m*-dinitrobenzene.

$\Delta G^{\ddagger}_c$ for the α bond in sulphines (I)—(III). From the fact that for sulphine (III), in which the *ortho*-positions of ring A are unsubstituted, the *m*-methyl signals do not show up differently, not even at −85°, it can be concluded that there is only restricted rotation about the α bond when the *ortho*-positions of ring A are substituted, for example by methyl groups.

In order to determine also the rotational barrier about the α bond in the arylthio and sulphonyl sulphines, a diastereotopic marker was introduced into ring A, an isopropyl group. For reasons of synthetic accessibility a *p*-methoxy group had to be introduced into ring A. In contrast with the sulphines where A is mesityl [(I) and (II)], the *o*-methyls of ring A in sulphines (V)—(X) are chemically non-equivalent because A in these sulphines is asymmetrically substituted. Non-equivalence of the methyl groups within the isopropyl group is possible when rotation about the α bond is restricted. This non-equivalence holds for all conditions of rotation about the Ar–isopropyl bond and is an example of a well documented phenomenon [12-14] which produces non-equivalence of the X groups in any A–CX_2–B system where either A or B is asymmetric. Therefore, when the α bond is restricted two doublets of the methyl groups of Pr^i may be seen in the n.m.r. spectrum, and these coalesce to one doublet when the temperature is raised and rotation about the α bond becomes fast.

The coalescence data and $\Delta G^{\ddagger}_c$ for the α bond in the isomeric arylthio sulphines (Va—c) and (VIa—c), and sulphonyl sulphines (IXa—c) and (Xa—c) are compiled

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[10] A. Tangerman and B. Zwanenburg, *Tetrahedron Letters*, 1972, 5329.

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[12] M. van Gorkum, *Quart. Rev.*, 1968, **22**, 14.

[13] C. van der Vlies, *Rec. Trav. chim.*, 1965, **84**, 1289.

[14] J. J. Bergman and W. D. Chandler, *Canad. J. Chem.*, 1971, 353.

in Table 2. For comparison the rotational barriers about the α bond in the corresponding thiocarboxylates (XIa) and (XIc) and dithiocarboxylates (XIIa—c) were also determined.

TABLE 2

Coalescence data and $\Delta G^{\ddagger}_{c}$ values for the α bond in sulphines (V), (VI), (IX), and (X), thiocarboxylates (XI), and dithiocarboxylates (XII)

Compound	$\Delta\nu$/Hz (°C) [a]	T_c/°C	k_c/s^{-1}	$\Delta G^{\ddagger}$/kcal mol^{-1}
(Va)	5·7 (32) *	111	12·7	20·7
(Vb)	4·0 (32) *	98	8·9	20·2
(Vc)	6·7 (105) †	172	14·9	24·0
(VIa)	10·0 (32) *	137	22·2	21·7
(VIb)	27·5 (32) *	140	61·1	21·0
(VIc)	2·5 (32) *	92	5·6	20·2
(IXa)—(c) (Xa)—(c)	2·9—7·2 (105) †	>220		>~27
(XIa), (XIc)	*b*	<−90		<~9
(XIIa)	4·2 (32) *	69	9·3	18·6
(XIIb)	2·5 (32) *	52	5·6	18·0
(XIIc)	7·2 (32) *	102	16·0	20·0

[a] Chemical shift difference between the two isopropyl methyl groups, obtained at 100 MHz. [b] Isopropyl methyl groups are still equivalent at −90° in CS_2.

Solvent: * nitrobenzene; † *m*-dinitrobenzene.

In the sulphinyl sulphines (Ie), (IIe), and (IV) (R = mesityl), the *o*-methyl groups of R appear as two different signals [in (IIe) and (IV) at lower temperatures] which points to a rotational barrier about the β bond, which is a twofold axis of symmetry for those *o*-methyl groups. In these sulphines the sulphoxide function serves as the necessary asymmetric centre for the *o*-methyls of the R group to be diastereotopic. At higher temperatures the *o*-methyl singlets coalesce to one signal. For the same reason the *o*-methyl protons of R^2 in the sulphinyl sulphines (VIIc) and (VIIIc) become diastereotopic when the β bond is restricted in its rotation. In the arylthio (Vc) and (VIc) and sulphonyl sulphines (IXc) and (Xc) the aryl–CSO part of the molecules behaves as an asymmetric centre as long as rotation about the α bond is restricted. Therefore, this part of the molecule serves as the necessary asymmetric centre to produce diastereotopy of the *o*-methyl groups of R^2 provided that rotation about the β bond is also restricted. The β-barrier can only be measured when the condition α-barrier > β-barrier is fulfilled. The coalescence data and $\Delta G_c^{\ddagger}$ values for the β bond are compiled in Table 3. The β-barriers in the arylthio *E*-sulphine (Vc) and the corresponding thiocarboxylate (XIc) and dithiocarboxylate (XIIc) are too low to be measured by n.m.r.

Introduction of a *meta*-substituent into A gives a second asymmetric centre in the sulphinyl sulphines (VII) and (VIII) provided that rotation about the α bond is restricted. Therefore, coalescence of the isopropyl-methyl signals does not occur in these sulphines because even for fast rotation about the α bond the asymmetry in the molecule due to the sulphoxide function is still present. Other methods must be used to determine the α-barrier in these sulphines.

TABLE 3

Coalescence data and $\Delta G^{\ddagger}_{c}$ values for the β bond in sulphines (Vc), (VIc), (Ie), (IIe), (IV), and (VIIc)—(Xc), thiocarboxylate (XIc), and dithiocarboxylate (XIIc)

Compound	$\Delta\nu$/Hz (°C) [a]	T_c/°C	k_c/s^{-1}	$\Delta G^{\ddagger}$/kcal mol^{-1}
(Vc)	*b*	<−85		<~9
(VIc)	10 (−45) [c]	−5	22·2	14·0
(VIIc)	63 (32) [d]	103	140	18·5 [g]
(VIIIc)	16 (−10) [e]	9	35·5	14·5 [g]
(IXc)	20 (−15) [c]	33	44·4	15·6
(Xc)	16 (−55) [f]	−50	35·5	11·3
(XIc), (XIIc)	*b*	<−85		<~9
(Ie)	75 (32) [d]	94	167	17·9
(IIe)	60 (−10) [e]	23	133	14·4
(IV)	31 (−84) [c]	−58	68·9	10·6

[a] Chemical shift difference between the *o*-methyl groups of R or R^2, obtained at 100 MHz. [b] *o*-Methyl signals of R^2 are still equivalent at −85° in CH_2Cl_2. [c] In CH_2Cl_2. [d] In nitrobenzene. [e] In $CDCl_3$. [f] In chlorobenzene. [g] Determined from the signals of one rotational diastereoisomer [X for (VIIc) and Q for (VIIIc), see Figure 1]; the other diastereoisomer [Y for (VIIc) and P for (VIIIc)] gives similar $\Delta G_c^{\ddagger}$ values.

Because rotation about the α bond is slow on the n.m.r. time scale two rotational diastereoisomers are seen in the n.m.r. spectra, X and Y for the *E*-sulphines (VIIa—c) and P and Q for the *Z*-sulphines (VIIIa—c) (Figure 1). The preferred conformations of these sulphines as found previously [1] are incorporated in the Figure. The n.m.r. spectra of the respective isomers are listed in Table 4. The assignment of the different signals to the respective isomers was possible because at least one of the rotational diastereoisomers of (VIIa—c) and (VIIIc) could be isolated at room temperature ($\Delta G^{\ddagger}$ for the α bond > 23 kcal mol^{-1}). This is illustrated in Figure 2 for the *E*-sulphine (VIIa). In the equilibrium mixture of sulphines (VIIIa) and (VIIIb) ($\Delta G^{\ddagger}$ < 23 kcal mol^{-1}) one rotational isomer is present to a somewhat larger extent (57%) resulting in signals of different intensity for the two rotational diastereoisomers. Knowing the sets of signals, it remains to assign the structure which belongs to each of these sets. Accepting the preferred conformations as given in Figure 1 the *m*-proton of ring A in structures X and P should be intramolecularly shielded by the aryl ring R^2 and there-

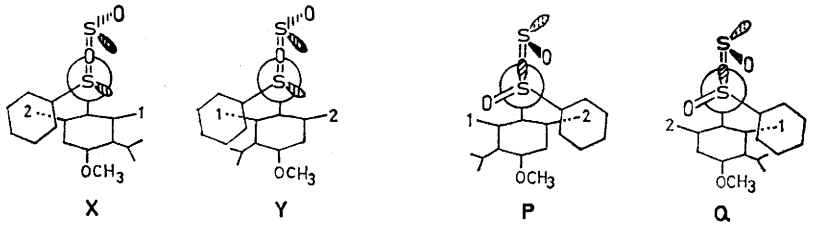


FIGURE 1

fore should absorb at higher field than the *m*-proton in isomers Y and Q. Furthermore, for the same reason, the

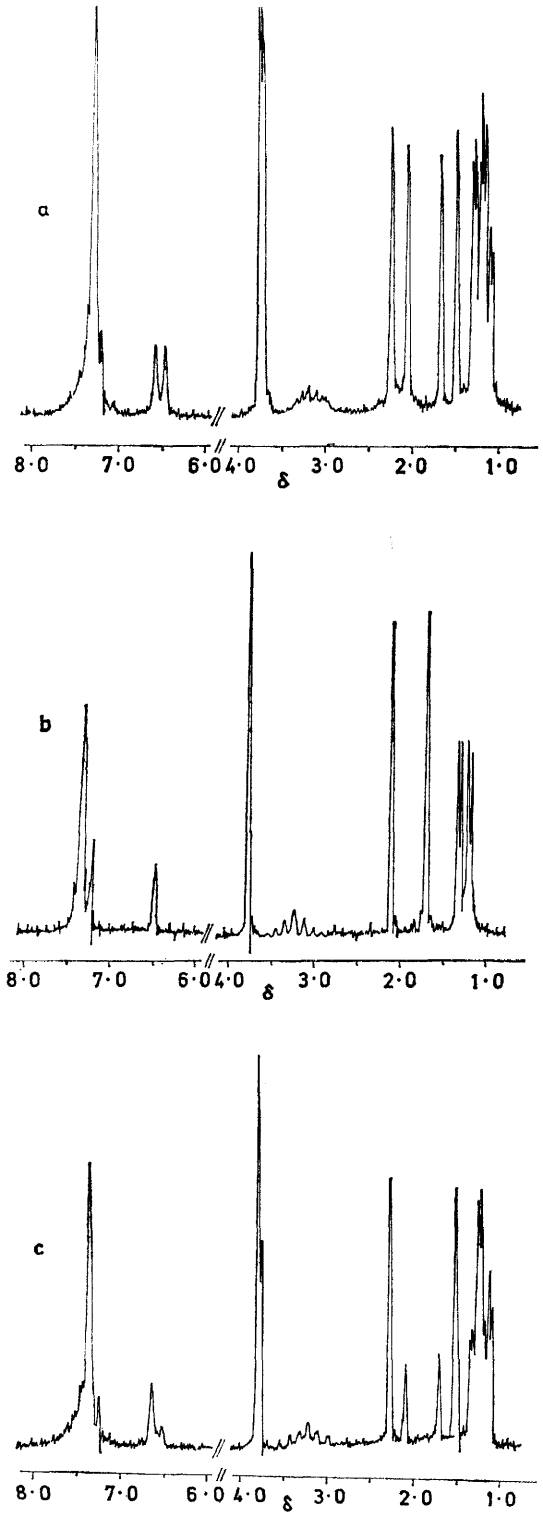
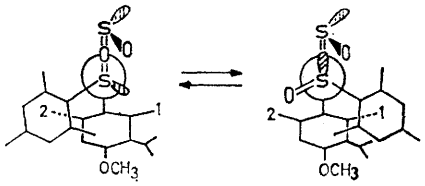


FIGURE 2 60 MHz N.m.r. of mesityl phenylsulphinyl (*E*)-sulphine (VIIa) in $CDCl_3$ at 32°: a, equilibrium mixture of diastereoisomers X and Y; b, pure X; c, mostly Y

isopropyl-methyl protons in isomers Y and Q are expected to appear at higher field than those in X and P. On this basis the assignment of the sets of signals to the respective isomers X and Y for the *E*-sulphines (VIIa—c) and P and Q for the *Z*-sulphines (VIIIa) and (VIIIb) as given in Table 4 was accomplished. This assignment was more complicated for sulphine (VIIIc). This behaves similarly to the mesityl mesitylsulphinyl *Z*-sulphine discussed in ref. 1. While the *Z*-sulphines (VIIIa) and (VIIIb) possess one remarkably rigid conformation in the temperature range −80 to 100° (the conformation given for the structures P and Q in Figure 1) the *Z*-sulphine (VIIIc) exists at room temperature as an equilibrium between the two half-folded conformations (1) and (2), given in Figure 3 for the rotational diastereoisomer Q.



(1) (2)

FIGURE 3

At lower temperatures conformation (1) is preferred, whereas for (VIIIa) and (VIIIb) conformations of type (2) are preferred. Therefore, the *m*-hydrogen of ring A becomes intramolecularly shielded in the diastereoisomeric structure Q for *Z*-sulphine (VIIIc) at lower temperatures, while for (VIIIa) and (VIIIb) this was the case for structure P.

When rotation about the α bond in sulphines (VII) and (VIII) becomes fast on the n.m.r. time scale equilibration between the rotational diastereoisomers will result in coalescence of the two sets of signals thus providing a means of determining the α-barrier. Coalescence of the *p*-methoxy-signals was in most cases used for measuring the α-barrier. The coalescence data are listed in Table 5.

For the sulphines (VIIa—c) and (VIIIc) for which at least one diastereoisomer could be isolated at room temperature (α-barrier > 23 kcal mol^{-1}) the α-barrier can also be obtained by using the direct equilibration method.[7,15,16] When for instance the isolated isomer X of sulphine (VIIa) is brought into solution, isomerisation takes place to an equilibrium composition with the equilibrium constant *K* [equation (3)]. $(k_1 + k_2)$ may be calculated by means of equation (4) [15,17] by plotting the left hand term against *t*. $[X]_t$ and $[Y]_t$ were obtained by

$$X \underset{k_1}{\overset{k_2}{\rightleftharpoons}} Y \quad (3a) \qquad K = [Y]/[X] = k_2/k_1 \quad (3b)$$

$$\log\left(\frac{[X]_t}{[X]_t + [Y]_t} - \frac{1}{K+1}\right) = -\frac{k_1 + k_2}{2{\cdot}303}\,t + C \quad (4)$$

integration of the *o*-methyl signals of ring A of isomers X and Y (see Figure 2). Combination of equations (3) and (4) gives the rate constants k_1 and k_2. Application of the Eyring equation [7] gives the free activation energies $\Delta G^{\ddagger}_{X}$

[15] A. Mannschreck, *Tetrahedron Letters*, 1965, 1341.
[16] W. Walter and E. Schaumann, *Chem. Ber.*, 1971, **104**, 3361.
[17] A. P. ter Borg and H. Kloosterziel, *Rec. Trav. chim.*, 1963, **82**, 741.

TABLE 4

N.m.r. data of the rotational diastereoisomers of the *E*- and *Z*-sulphines (VII) and (VIII)

Compound	Isomer	R¹ δ[*o*-CH_3(1)]	R¹ δ[*o*-CH_3(2)]	R¹ δ(*m*-H)	R¹ δ[$(CH_3)_2$CH]	R¹ δ(OCH_3)	R²
(VIIa)	X *	2·09	1·70	6·50	1·28; 1·25	3·75	
	Y	1·52	2·27	6·60	1·19; 1·17	3·78	
(VIIb)	X	2·10	1·75	6·46	1·31 [a]	3·76	
	Y *	1·48	2·35	6·64	1·20; 1·13	3·82	δ(*o*-CH_3)
(VIIc)	X *	2·22	1·83	6·48	1·26 [a]	3·73	2·61; 1·90
	Y	1·70	2·32	6·60	1·24; 1·19	3·77	2·67; 1·80
(VIIIa)	P	2·38	1·51	6·48	1·33; 1·27	3·78	
	Q	1·44	2·43	6·70	1·21 [a]	3·82	
(VIIIb)	P	2·40	1·41	6·42	1·25 [a]	3·74	
	Q	1·27	2·45	6·70	1·13 [a]	3·81	δ(*o*-CH_3) [b]
(VIIIc)	P } 32°	1·93	2·00	6·56	1·19; 1·18	3·76	2·23
	Q* } 32°	1·76	2·15	6·58	1·20; 1·18	3·76	2·19
	P } −45°	1·53	2·36	6·64		3·80	2·73; 1·62
	Q* } −45°	2·12	1·88	6·53		3·77	2·52; 1·90

Spectra recorded at 60 MHz in $CDCl_3$ at 32°, except for sulphine (VIIIc) whose spectra were recorded at 100 MHz in $CDCl_3$.

* Isolated in almost pure form.

[a] Although the isopropyl methyls are diastereotopic, they accidently absorb at the same δ value; with Eu(dpm)$_3$ these methyl groups are non-equivalent. [b] Coalescence of the *o*-methyls of R² occurred at 9° for isomer Q (Table 3) and at 16° for isomer P.

and $\Delta G^{\ddagger}_{Y}$ (Table 6). For sulphines (VIIa—c) $K = k_2/k_1 = 1$ and therefore $\Delta G^{\ddagger}_{X} = \Delta G^{\ddagger}_{Y}$. For sulphine (VIIIc)

TABLE 5

Coalescence data and $\Delta G^{\ddagger}_{c}$ values for the α bond in sulphines (VII) and (VIII)

Compound	Δν/Hz (°C)	T_c/°C	k_c/s^{-1}	$\Delta G^{\ddagger}$/kcal mol^{-1}
(VIIa) *	1·3 (105) [a]	154	2·9	24·4
(VIIb) *	2·9 (105) [a]	171	6·4	24·7
(VIIc)	*c*			
(VIIIa) †	83 (105) [b]	169	184	21·6
(VIIIb) †	3·5 (85) [a]	127	7·8	22·0
(VIIIc)	*c*			

Δν = chemical shift difference obtained at 100 MHz between [a] the signals of the *p*-methoxy group and [b] the signals of the *o*-methyl(1) in R¹ in the two rotational diastereoisomers. [c] Decomposition before coalescence.

Solvent: * *m*-dinitrobenzene; † nitrobenzene.

where $K = [P]/[Q] = 0{\cdot}75$, isomer Q is more stable than P by $\Delta G = RT\ln K = 0{\cdot}2$ kcal mol^{-1} (at 40°).

which are much more reliable than those obtained only by direct equilibration over a small temperature range.[16,18] The data in Tables 5 and 6 show that for sulphines (VIIa) and (VIIb) the $\Delta G^{\ddagger}$ values obtained at 40 and 50° agree well with those obtained at the coalescence temperature T_c.

DISCUSSION

In this section the differences in rotational barriers of the six types of sulphines will be discussed in terms of the differences in geometry and preferred conformation. A detailed analysis of the preferred conformations of these types of sulphines with A = mesityl has been described previously.[1] For sulphines with A = 2,6-dimethyl-3-isopropyl-4-methoxyphenyl the same preferred conformations are proposed because the spectral characteristics upon which the conformational analysis is based are the same. It should be mentioned that the preferred conformations do not change significantly when raising the

TABLE 6

Energy parameters of the hindered rotation about the α bond in sulphines (VIIa—c) and (VIIIc)

	T/°C	K	$10^{-4}k$/s^{-1} [b]	$\Delta G^{\ddagger}$/kcal mol^{-1}	E_a/kcal mol^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}
(VIIa) *	25	1	0·14	24·0			
	40	1	1·12	24·0	23·5	22·9	−3·5
	50	1	2·85	24·2			
(VIIb)*	25	1	0·15	24·0			
	40	1	0·97	24·1	23·3	22·7	−4·5
	50	1	2·80	24·2			
(VIIc)*	60	1	1·21	25·5			
	70	1	4·07	25·4			
(VIIIc) †	40	0·75 [a]	4·0 (k_1); 3·02 (k_2)	23·2(P); 23·4(Q)			
	50	0·75 [a]	1·35 (k_1); 1·02(k_2)	23·2(P); 23·4(Q)			

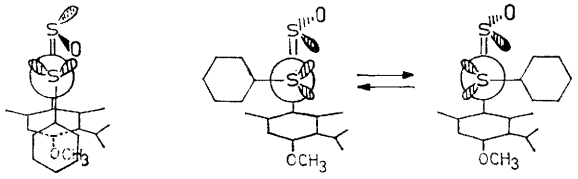
[a] $K = [P]/[Q] = k_2/k_1$. [b] For (VIIa—c) $k_1 = k_2$.

Solvent: * nitrobenzene; † $CDCl_3$

An Arrhenius plot [8,16] gives the Arrhenius activation energy E_a, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$. These parameters were only calculated for sulphines (VIIa) and (VIIb) (Table 6) because for these sulphines k_c and T_c were known (Table 5). Combination in the Arrhenius plot of k_c with the rate constants obtained by direct equilibration gives E_a values temperature as may be concluded from the spectra at a temperature close to coalescence. Hence, a discussion of the rotational barriers invoking preferred conformations is allowed.

[18] H. Shanan-Atidi and K. H. Bar-Eli, *J. Phys. Chem.*, 1970, **74**, 961.

Nakamura and Ōki [19] studied the barrier to rotation about the phenyl–carbonyl bond in aromatic ketones [ArC(O)R] with both *ortho*-positions in the phenyl ring substituted by either a methyl and a halogen or a methyl and a methoxy-group. They found barriers in the range of 9—15 kcal mol^{-1}. As shown in Table 2 for the thiocarboxylates (XIa and c) where the *ortho*-positions of ring A are both substituted by methyl groups, the α-barrier is <9·5 kcal mol^{-1}. Replacing the carbonyl group by the larger thiocarbonyl function results in a much higher α-barrier (18—20 kcal mol^{-1}). Attachment of an oxygen to the thiono-sulphur in the dithiocarboxylates in the *E*-conformation gives an expected increase in the α-barrier, because the sulphine oxygen in the *E*-sulphines (V) is situated between the *ortho*-methyl groups of ring A. When the sulphine oxygen points in the opposite direction [*Z*-sulphines (VI)] one would expect a smaller α-barrier than for the arylthio *E*-sulphines. However, the $\Delta G^{\ddagger}_{c}$ values for the *Z*-sulphines (VIa) and (VIb) are larger by *ca.* 1 kcal mol^{-1} than those of the corresponding *E*-isomers. Most likely, the steric interactions between the two aryl rings in the folded rigid conformation (3) in which these arylthio *Z*-sulphines exist (Figure 4), are responsible for the higher α-barrier. In the preferred gauche conformations (4) and (5) of the *E*-sulphines such interactions are much smaller.



(3) (4) (5)

FIGURE 4

The α-barrier in the sulphinyl *E*-sulphines (VIIa and b) (Table 5) is larger than that in the corresonding arylthio *E*-sulphines. The influence of the thiolo-oxygen on the α-barrier can be accounted for by its effect on the preferred conformations: that of the sulphinyl sulphines as given for X and Y in Figure 1 is more folded than those of the arylthio *E*-sulphines [conformations (4) and (5) in Figure 4]. The α-barrier in the sulphinyl *Z*-sulphines (VIIIa and b) is very close to that found for the arylthio *Z*-sulphines (VIa and b). A compromise between the following two opposing effects can explain this result: first, steric interactions of one *o*-methyl group of ring A with the sulphoxide oxygen in the preferred conformation of the sulphinyl *Z*-sulphines as given for structures P and Q in Figure 1, which interactions are absent in the arylthio *Z*-sulphines, will enlarge the α-barrier compared with the arylthio *Z*-sulphines; secondly, the interaction between the two aryl rings in the preferred half-folded conformation of the sulphinyl *Z*-sulphines will be smaller than that in the folded conformation (3) of the arylthio *Z*-sulphines and so reduce the α-barrier by comparison with that of the arylthio *Z*-sulphines.

[19] N. Nakamura and M. Oki, *Bull. Chem.Soc. Japan*, 1972, **45**, 2565.

The α-barriers in the sulphinyl *E*-sulphines (VII) are *ca.* 3 kcal mol^{-1} greater than those of the *Z*-isomers (VIII) (Table 5). The preferred conformations of the sulphinyl *E*- and *Z*-sulphines (see Figure 1) have the same degree of folding. However, there are two distinct differences, the orientation of the sulphine oxygen atom and the orientation of the sulphoxide oxygen atom. The difference in orientation of the sulphine oxygen atom will give a larger α-barrier for the sulphinyl *E*-sulphines while for the different position of the sulphoxide oxygen atom a larger α-barrier for the *Z*-sulphines is to be expected. The results indicate that of these opposing effects the former is dominating. The same argument holds for the differences in α-barrier between the sulphinyl *E*- and *Z*-sulphines (I) and (II) (Table 1). A comparison of the α-barriers in the *E*-sulphinyl sulphines (VII) and (I) and *Z*-sulphinyl sulphines (VII) and (II), respectively, shows that introduction of an isopropyl group in the *meta*-position of ring A in the sulphinyl sulphines raises the α-barrier in the case of the *E*-isomers by 0·5—0·8 kcal mol^{-1} and of the *Z*-isomers by *ca.* 2 kcal mol^{-1}. These higher α-barriers are most likely due to a buttressing effect [19,20] of the isopropyl group on the adjacent methyl group.

The α-barriers in the sulphonyl *E*- and *Z*-sulphines (IX) and (X) (Table 2) all exceed 27 kcal mol^{-1}. These much higher α-barriers for the sulphonyl sulphines by comparison with those of the corresponding sulphinyl sulphines are suggested to be due to strong steric interactions of the *o*-methyl groups of ring A with one of the sulphone oxygen atoms in the preferred conformations (6) and (7) for the *E*- and (8) and (9) for the *Z*-isomers (Figure 5).

Comparing the $\Delta G^{\ddagger}_{c}$ values of (Va), (VIa), and (XIIa) (R^2 = Ph) with those of (Vb), (VIb), and (XIIb) (R^2 = 2-$C_{10}H_7$), respectively (Table 2), it appears that the former are larger by *ca.* 0·6 kcal mol^{-1}. This can be explained by assuming that the ground state in the β-naphthyl compounds is destabilised compared with the ground state of the phenyl compounds by the larger steric hindrance of β-naphthyl while this destabilisation is less pronounced in the transition state, resulting in a lower activation energy for the β-naphthyl compounds (steric acceleration).

The α-barriers for the compounds in which R^2 is mesityl deserve special comment. The α-barrier in the dithiocarboxylate (XIIc) is 1·4 kcal mol^{-1} larger than that of (XIIa) where R^2 is phenyl (Table 2). This effect of the mesityl group is attributed to a buttressing effect of the *o*-methyl groups of R^2 on the thiocarbonyl group in the preferred stretched conformation (10) for the dithiocarboxylates [1,21] (Figure 6). The α-barrier in the arylthio *E*-sulphine (Vc) is 3·3 kcal mol^{-1} larger than in sulphine (Va), which can be explained adequately by invoking steric interactions of the *o*-methyl groups of the two rings in the preferred conformations (11) and (12) (Figure 6). In contrast, the α-barrier for the *Z*-sulphine (VIc) is lower by

[20] M. Rieger and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1950, **72**, 19.

[21] O. Exner, V. Jehlička, and J. Firl, *Coll. Czech. Chem. Comm.*, 1971, **36**, 2936.

1·5 kcal mol^{-1} than that of (VIa). Evidently, in the preferred conformations (13) and (14) (Figure 6) deduced for (VIc), the interaction between the *o*-methyl groups of both rings is smaller than the interaction between the aryl rings in the folded preferred conformation (3) (Figure 4) for the *Z*-sulphine (VIa). In the sulphinyl sulphines (Ie), (IIe), (VIIc), and (VIIIc), in the *E*- as well as in the *Z*-isomers, the α-barrier is 1·5—2·0 kcal mol^{-1} higher than in sulphines (Ia), (IIa), (VIIa), and (VIIIa) (see Tables 1, 5, and 6). This again is due to steric interactions between the *o*-methyl groups of the two rings in the mesityl β-barriers for the sulphinyl *Z*-sulphines (IIe) and (VIIIc) are smaller by *ca.* 4 kcal mol^{-1} by comparison with those of the corresponding *E*-sulphines (Ie) and (VIIc) although the same type of interactions between the *o*-methyl groups of the two rings will be present in the preferred conformations (1) and (2) as given for (VIIIc) in Figure 3. Molecular models suggest that in the preferred conformations of the sulphinyl *E*- and *Z*-sulphines, rotation about the β bond is coupled with rotation about the α bond by means of a cogwheel effect. Therefore, it is suggested that the β-barrier is larger in the sulphinyl

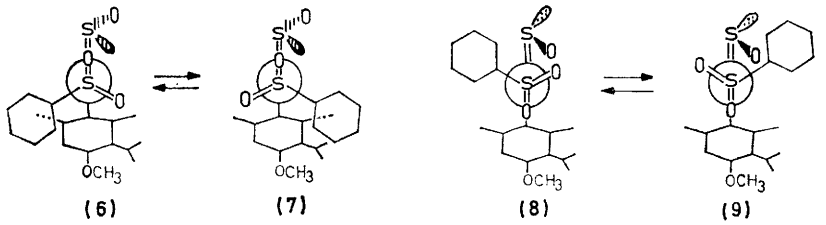


FIGURE 5

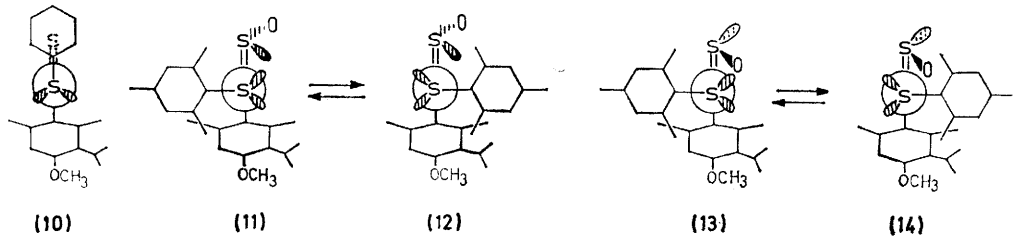


FIGURE 6

containing compounds. For sulphonyl sulphines with R^2 = mesityl the α-barrier is, as for R^2 = phenyl >27 kcal mol^{-1}.

It now remains to discuss the β-barrier as observed in sulphines when R or R^2 is a mesityl group. The data in Table 3 show that the β-barrier in the thiocarboxylate (XIc) and dithiocarboxylate (XIIc) which are both in the rigid *s-trans*-conformation [1,21] are <9 kcal mol^{-1}. The same holds for the arylthio *E*-sulphine (Vc) which is present in the gauche conformations (11) and (12). However, the β-barrier in the *Z*-isomer (VIc) which also is present in gauche conformations, *i.e.* (13) and (14) (Figure 6), is much larger (14 kcal mol^{-1}). Probably, steric interactions between the *o*-methyl groups of R^2 and the sulphine oxygen in the arylthio *Z*-sulphine, which will be larger than the interactions between the *o*-methyl groups of R^2 and the lone pair of the sulphine sulphur in the *E*-sulphine (Vc) account for this difference in β-barrier. The large β-barriers observed for the sulphinyl *E*-sulphines (Ie) and (VIIc) (17·9 and 18·5 kcal mol^{-1}, respectively) must be attributed to strong steric interactions between the *o*-methyl groups of both aromatic rings in the preferred conformations of types X and Y in Figure 1. Support for this explanation comes from the fact that the β-barrier for the sulphinyl *E* sulphine (IV), which does not have methyl groups in ring A, is considerably smaller (10·6 kcal mol^{-1}). The *E*-sulphines because the α-barrier is also larger by comparison with that of the *Z*-sulphines. In the preferred conformations of the sulphonyl *E*-sulphine (IXc) which are similar to those given in Figure 5 [conformations (6) and (7)] again steric interactions between the *o*-methyls of both rings are operating, resulting in a β-barrier of 15·6 kcal mol^{-1}. The β-barrier in the sulphonyl *Z*-sulphine (Xc) (11·3 kcal mol^{-1}) is mainly the result of steric interactions of the *o*-methyl groups of R^2 with the sulphine oxygen in the preferred conformations which are similar to those given in Figure 5 [conformations (8) and (9)], rather than by interactions between the *o*-methyl groups of both rings.

EXPERIMENTAL

The variable temperature n.m.r. spectra were recorded with Varian Associates A-60 or HA-100 spectrometers with Me_4Si as internal standard. Temperatures were measured by means of a copper–constantan thermocouple (±0·5°). The concentration of the substrates were 30 mg per 0·5 ml.

The dithiobenzoates (XIIa—c) and the dithiobenzoates which were used to synthesize the sulphines (I)—(IV) were

$$RSH \xrightarrow{Cl_2CS} RSC(=S)Cl \xrightarrow[AlCl_3]{ArH} RSC(=S)Ar \qquad (5)$$

prepared by reaction (5). The first step to the chlorodithioformates was performed according to ref. 22 and the second

[22] Houben-Weyl, 'Methoden der organischen Chemie,' Band 9, p. 808.

step to the dithiobenzoates according to Mayer *et al.*[23] For R = α-thienyl $SnCl_4$ was used as catalyst.

Chlorodithioformates.—Ethyl chlorodithioformate [24] and phenyl chlorodithioformate [22] were synthesized according to the literature. New compounds are: *α-thienyl chlorodithioformate*, b.p. 93° at 1 mmHg; 75% (Found: C, 30·55; H, 1·6; Cl, 18·45; S, 49·05. $C_5H_3ClS_3$ requires C, 30·85; H, 1·55; Cl, 18·2; S, 49·4%); *β-naphthyl chlorodithioformate* (61%), m.p. 86·5—87·5° [from light petroleum (b.p. 60—80°)] (Found: C, 55·5; H, 3·0; Cl, 14·85; S, 26·8. $C_{11}H_7ClS_2$ requires C, 55·35; H, 2·95; Cl, 14·85; S, 26·85%); *mesityl chlorodithioformate* (63%), m.p. 88—89° (from pentane) (Found: C, 52·35; H, 4·9; Cl, 15·35; S, 27·5. $C_{10}H_{11}ClS_2$ requires C, 52·05; H, 4·8; Cl, 15·35; S, 27·8%).

Dithiobenzoates.—For the preparation of the dithiobenzoates method B of Mayer *et al.*[23] was used with 1,2-dichloroethane as solvent, unless stated otherwise. The aromatic compounds in the Friedel-Crafts reaction were commercial except 2,4-dimethyl-6-methoxyisopropylbenzene, which was prepared as follows. 3,5-Dimethylanisole (20 g, 147 mmol) and propan-2-ol (8·8 g, 147 mmol) were heated overnight at 75° in 80% H_2SO_4 (90 g). The product was taken up in ether and the ether layer was washed with 4N-NaOH. After drying ($MgSO_4$), ether was removed and the product (23·4 g, 90%) distilled, b.p. 55° at 0·3 mmHg. New dithiobenzoates are: *ethyl 2,4,6-trimethyldithiobenzoate* (86%), m.p. 45·5—47·5° (from pentane) (Found: C, 64·35; H, 7·15; S, 28·25. $C_{12}H_{16}S_2$ requires C, 64·25; H, 7·2; S, 28·6%); *α-thienyl 2,4,6-trimethyldithiobenzoate* (47%), m.p. 70—70·5° (after chromatography on Al_2O_3 with benzene as eluant) (Found: C, 60·4; H, 5·0; S, 34·5. $C_{14}H_{14}S_3$ requires C, 60·4; H, 5·05; S, 34·55%); *β-naphthyl 2,4,6-trimethyldithiobenzoate* (86%), m.p. 137—139° [from light petroleum (b.p. 60—80°)] (Found: C, 74·45; H, 5·55; S, 19·85. $C_{20}H_{18}S_2$ requires C, 74·5; H, 5·65; S, 19·9%) (Solvent mesitylene); *mesityl 2,4,6-trimethyldithiobenzoate* (96%), m.p. 142—143° (Found: C, 72·35; H, 6·9; S, 20·4. $C_{19}H_{22}S_2$ requires C, 72·55; H, 7·05; S, 20·4%) (solvent mesitylene); *mesityl dithiobenzoate* (43%), m.p. 65—66° (from pentane) (Found: C, 70·65; H, 5·8; S, 23·4. $C_{16}H_{16}S_2$ requires C, 70·55; H, 5·9; S, 23·55%) (solvent benzene); *phenyl 3,5-dimethyl-4-methoxydithiobenzoate* (77%), red oil (after chromatography on Al_2O_3 with benzene as eluant); *phenyl 2,6-dimethyl-3-isopropyl-4-methoxydithiobenzoate* (XIIa) (52%), m.p. 119—120° [from light petroleum (b.p. 60—80°)] (Found: C, 69·2; H, 6·85; S, 19·35. $C_{19}H_{22}OS_2$ requires C, 69·05; H, 6·7; S, 19·4%); *β-naphthyl 2,6-dimethyl-3-isopropyl-4-methoxydithiobenzoate* (XIIb) (25%), m.p. 121—122° [after chromatography on Al_2O_3 with light petroleum (b.p. 60—80°) as eluant and crystallization from the same solvent] (Found: C, 72·55; H, 6·5; S, 16·7. $C_{23}H_{24}OS_2$ requires C, 72·6; H, 6·35; S, 16·85%); *mesityl 2,6-dimethyl-3-isopropyl-4-methoxydithiobenzoate* (XIIc) (45%), m.p. 161—163° [after chromatography on silica with benzene as eluant and crystallization from light petroleum (b.p. 60—80°)] (Found: C, 70·7; H, 7·7; S, 17·45. $C_{22}H_{28}OS_2$ requires C, 70·9; H, 7·6; S, 17·2%).

The *S*-arylthiobenzoates (XIa), m.p. 155—157°, and (XIc), m.p. 127—129°, were prepared by ozonization [25] of the corresponding *E*-sulphines (Va) and (Vc).

Sulphines.—Syntheses of the sulphines were performed as described in ref. 4 by stepwise oxidation of the corresponding dithiobenzoates. The oxidation was performed with *m*-chloroperbenzoic acid (MCPBA) (peracid content *ca.* 85%) in either ether or ether–dichloromethane. Oxidation of the dithiobenzoates with one equiv. of MCPBA gave a mixture of arylthio *E*- and *Z*-sulphines, which were separated by crystallization or chromatography. The arylthio sulphines were further oxidized with one equiv. of MCPBA to the corresponding sulphinyl *E*- and *Z*-sulphines and with two equiv. of MCPBA to the corresponding sulphonyl *E*- and *Z*-sulphines. In some cases (when mentioned) more than the stated amount of MCPBA was used to obtain the best yield. Oxidation to the arylthio and sulphinyl sulphines was carried out at 0° and oxidation to the sulphonyl sulphines at ambient temperature. The reaction was followed by t.l.c. Oxidation to the arylthio sulphines occurred almost instantaneously. The reaction time of the second and third oxidation steps varied from a few hours to a few days. All sulphines were crystallized from either ether–pentene (1 : 1) or from the same mixture with a little dichloromethane. Oxidation of the arylthio to the sulphinyl sulphines gave in most cases products contaminated with small amounts of starting substrate and sulphonyl sulphines which could not be removed by crystallization. Column chromatography on Florisil gave excellent purity (first elution with dichloromethane to remove contaminants, then with ether).

Sulphines (Ia—e) and (IIa—e) were described previously.[1]

3,5-Dimethyl-4-methoxyphenyl Phenylsulphinyl (E)-*Sulphine* (III).—Oxidation of the appropriate dithiobenzoate gave a mixture of phenylthio *E*- and *Z*-sulphines which were separated by chromatography on silica. Elution with CH_2Cl_2 gave the *E*-isomer (90%; yellow oil) and elution with CH_2Cl_2–ether (1 : 1) the *Z*-isomer (8%), m.p. 108—110°. The *E*-isomer was oxidized with 1·5 equiv. of MCPBA. After chromatography on Florisil, sulphinyl sulphine (III) (33%; yellow oil) was obtained.

Phenyl Mesitylsulphinyl (E)-*Sulphine* (IV).—Oxidation of the appropriate dithiobenzoate gave a mixture of mesitylthio *E*- and *Z*-sulphines which were separated by crystallization from ether–pentane (1 : 1) to give *E*-sulphine (70%), m.p. 62—63°, and *Z*-sulphine (19%), m.p. 101·5—103°. Oxidation of the *E*-isomer gave mostly the corresponding thiobenzoate and *sulphinyl sulphine* (IV) (14%), m.p. 77—79·5° (Found: C, 63·5; H, 5·45; S, 21·0. $C_{16}H_{16}O_2S_2$ requires C, 63·15; H, 5·3; S, 21·05%).

Sulphines (Va)—(Xa).—Oxidation of (XIIa) gave a mixture of 2,6-dimethyl-3-isopropyl-4-methoxyphenyl phenylthio sulphines (Va) and (VIa), which were separated by crystallization from ether–pentane (1 : 1) to give (Va) (55%), m.p. 115—116° (Found: C, 65·95; H, 6·5; S, 18·25. $C_{19}H_{22}O_2S_2$ requires C, 65·85; H, 6·4; S, 18·5%), and (VIa) (41%; yellow oil). Oxidation of (Va) gave *sulphinyl sulphine* (VIIa) 70%, which consisted of a 1 : 1 mixture of two diastereoisomers. Only diastereoisomer X (see text) could be obtained pure by fractional crystallization from CH_2Cl_2–ether–pentane, m.p. 108—110·5° (Found: C, 62·85; H, 6·22; S, 17·55. $C_{19}H_{22}O_3S_2$ requires C, 62·95; H, 6·1; S, 17·7%). Oxidation of (VIa) gave *sulphinyl sulphine* (VIIIa) 35%, m.p. 86—87° (Found: C, 62·75; H, 6·0; S, 17·65%). *Sulphonyl sulphine* (IXa) (65%) was obtained from (Va) by oxidation with two equiv. of MCPBA, m.p. 148—150° (Found: C, 60·45; H, 5·85; S, 17·0. $C_{19}H_{22}O_4S_2$ requires C, 60·3; H, 5·85; S, 16·95%). Oxidation of (VIa) with three equiv. of MCPBA gave a mixture of (IXa)

[23] H. Viola, S. Scheithauer, and R. Mayer, *Chem. Ber.*, 1968, **101**, 3517.

[24] L. C. F. Blackman and M. J. S. Dewar, *J. Chem. Soc.*, 1957, 162.

[25] B. Zwanenburg and W. A. J. Janssen, *Synthesis*, 1973, 617.

and (Xa), from which *sulphonyl sulphine* (Xa) was obtained by fractional crystallization from CH_2Cl_2–ether–pentane in 30% yield, m.p. 156—158° (Found: C, 60·5; H, 5·9; S, 17·1%).

Sulphines (Vb)—(Xb).—Oxidation of (XIIb) gave a mixture of 2,6-dimethyl-3-isopropyl-4-methoxyphenyl β-naphthylthio sulphines (Vb) and (VIb), which were separated by crystallization from ether–pentane (1 : 1) and chromatography on silica with benzene as eluant to give (Vb) (44%). m.p. 115—118° (Found: C, 69·3; H, 6·15; S, 16·15. $C_{23}H_{24}O_2S_2$ requires C, 69·65; H, 6·1; S, 16·15%) and (VIb) (30%), m.p. 127—129° (Found: C, 69·8; H, 6·1; S, 16·3%). Oxidation of (Vb) gave *sulphinyl sulphine* (VIIb) 46%, which consisted of a 1 : 1 mixture of two diastereoisomers. Only diastereoisomer Y (see text) could be obtained pure by fractional crystallization from ether–pentane (1 : 1), m.p. 136—137° (Found: C, 66·9; H, 5·9; S, 15·6. $C_{23}H_{24}O_3S_2$ requires C, 67·0; H, 5·85; S, 15·55%). Oxidation of (VIb) gave *sulphinyl sulphine* (VIIIb) 43%, m.p. 115—118° (Found: C, 66·95; H, 5·95; S, 15·6%). *Sulphonyl sulphines* (IXb) and (Xb) were obtained from (Vb) and (VIb), respectively, by oxidation with five equiv. of MCPBA giving (IXb) (59%), m.p. 126—129° (Found: C, 64·8; H, 5·8; S, 14·9. $C_{23}H_{24}O_4S_2$ requires C, 64·45; H, 5·65; S, 14·95%) and (Xb) (61%), m.p. 135·5—137° (Found: C, 64·3; H, 5·55; S, 14·95%).

Sulphines (Vc)—(Xc).—Oxidation of (XIIc) with one equiv. of MCPBA only gave the *2,6-dimethyl-3-isopropyl-4-methoxyphenylmesitylthio* (E)-*sulphine* (Vc) (80%), m.p. 173—175° (Found: C, 67·85; H, 7·4; S, 16·45. $C_{22}H_{28}O_2S_2$ requires C, 68·0; H, 7·25; S, 16·5%). The *Z*-isomer (VIc) was prepared by treating (XIIc) with one equiv. of chlorine in CCl_4 with a few ml of pyridine as catalyst. After hydrolysis a 1 : 1 mixture (80%) of (Vc) and (VIc) was obtained. Chromatography on silica with CH_2Cl_2 as eluant gave only partial separation. Oxidation of (Vc) with three equiv. of MCPBA at 0° for two days gave *sulphinyl sulphine* (VIIc) 41%, which consisted of a 1 : 1 mixture of two diastereoisomers. Only diastereoisomer X (see text) could be obtained pure by chromatography on Florisil and fractional crystallization from ether–pentane (1 : 1), m.p. 152—153·5° (Found: C, 65·5; H, 6·7; S, 16·0. $C_{22}H_{28}O_3S_2$ requires C, 65·3; H, 7·0; S, 15·85%). Oxidation of (VIc) contaminated with (Vc), with three equiv. of MCPBA at 0° for two days gave a mixture of (VIIc) and (VIIIc), which were separated by chromatography on Florisil [elution with CH_2Cl_2 gave (VIIc) and with ether gave (VIIIc)]. *Sulphinyl sulphine* (VIIIc) consisted of a 3 : 2 mixture of two diastereoisomers. Only diastereoisomer Q (8%) (see text) could be obtained pure by fractional crystallization from ether–pentane (1 : 1), m.p. 163—166° (Found: C, 65·5; H, 7·15; S, 15·65%). *Sulphonyl sulphine* (IXc) (50%) was obtained from (Vc) by oxidation with six equiv. of MCPBA, m.p. 178—180° (Found: C, 62·65; H, 6·75; S, 15·35. $C_{22}H_{28}O_4S_2$ requires C, 62·85; H, 6·7; S, 15·25%). Oxidation of a mixture of (Vc) and (VIc) with six equiv. of MCPBA gave a mixture of (IXc) and (Xc). Repeated fractional crystallization from ether–pentane (1 : 1) gave (Xc) 8%, m.p. 143—146°.

TABLE 7

N.m.r. data of R′ protons in sulphines (V), (VI), (IX), and (X) and dithiobenzoates (XII)

	δ[*o*-CH_3(1)] [a]	δ[*o*-CH_3(2)] [b]	δ(*m*-H)	δ[$(CH_3)_2$CH]	δ(OCH_3)
(Va)	2·17	2·21	6·58	1·26 [c]	3·77
(Vb)	2·20	2·24	6·57	1·24; 1·22	3·76
(Vc)	2·37	2·37	6·66	1·30 [c]	3·80
(VIa)	2·17	2·27	6·43	1·18 [c]	3·70
(VIb)	2·20	2·31	6·33	1·10; 0·81	3·57
(VIc)	2·28	2·40	6·56	1·25; 1·21	3·80
(IXa)	1·75	1·92	6·55	1·22 [c]	3·77
(IXb)	1·67	1·95	6·57	1·18 [c]	3·78
(IXc)	1·74	1·96	6·55	1·22; 1·20	3·74
(Xa)	2·21	2·21	6·60	1·28; 1·26	3·80
(Xb)	2·20	2·20	6·63	1·26; 1·25	3·81
(Xc)	2·02	2·23	6·60	1·23 [c]	3·80
(XIIa)	2·36	2·36	6·57	1·29 [c]	3·78
(XIIb)	2·36	2·36	6·54	1·28 [c]	3·75
(XIIc)	2·43	2·43	6·59	1·39; 1·36	3·81

Spectra recorded at 60 MHz in $CDCl_3$ at 32 °C.

[a] Methyl group, *ortho* to isopropyl group. [b] Methyl group, *para* to isopropyl group. [c] Although the isopropyl-methyls are diastereotopic, they absorb accidently at the same δ value; in nitrobenzene and *m*-dinitrobenzene the groups are non-equivalent.

The arylthio sulphines gave characteristic i.r. sulphine absorptions at 985—1015 and 1100—1130 cm^{-1}, the sulphinyl sulphines gave a strong sulphine band at 1090—1125 and a sulphoxide absorption at 1055—1080 cm^{-1}, and the sulphonyl sulphines gave a strong sulphine absorption at 1123—1137 cm^{-1} and strong sulphonyl bands at 1315—1330 and 1137—1152 cm^{-1}.

The n.m.r. data of the sulphinyl sulphines (I) and (II) have been reported in ref. 1 and those of the sulphinyl sulphines (VII) and (VIII) in Table 4. The most important n.m.r. data of sulphines (V), (VI), (IX), and (X) and the dithiobenzoates (XII) are compiled in Table 7.

We thank Mrs. L. C. J. van Herpen-de Cock for recording the 100 MHz spectra.

[4/2204 *Received, 25th October,* 1974]