11. Some Comments on the Conformations of Methyl Phenyl Sulfides, Sulfoxides and Sulfones

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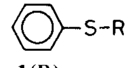
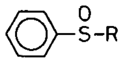
Summary

^{13}C-NMR. and He(Iα) photoelectron spectra of alkyl phenyl sulfides, sulfoxides and sulfones have been used to probe how their conformations depend on the size of the alkyl groups R. The results are interpreted to indicate that in the sulfides the S, R-bond is twisted out of the planar conformation with increasing size of the alkyl group, whereas in the sulfoxides and sulfones the preferred conformation with the S, R-bond perpendicular to the phenyl group plane seems to be independent of the size of R. These conclusions are in agreement with previous work on the alkyl phenyl sulfides and provide strong support for previous conjectures concerning the preferred conformations of alkyl phenyl sulfoxides and sulfones.

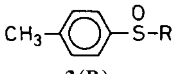
In this work we report the ^{13}C-NMR. spectra of the alkyl phenyl sulfides **1**(R), sulfoxides **2**(R) and **3**(R), sulfones **4**(R), as well as the He(Iα) photoelectron spectra of **2**(R), **3**(R) and **4**(R).



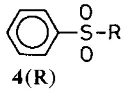
1(R)
R = Me, Et,
t-Bu



2(R)
R = Me, Et,
t-Bu



3(R)
R = Me, Et, *i*-Bu,
t-Bu, Benzyl



4(R)
R = Me, Et,
t-Bu

The aim of the investigation was to derive spectroscopic information concerning the dependence of the phenyl-sulfur C, S-bond twist angle φ on the size of the alkyl group R. In compounds such as **1**(R) to **4**(R) the angle φ is a function of mainly two effects:

a) the angular dependence of the conjugation of the functional group with the phenyl ring, and

b) the steric interference of R with the ortho positioned H-atoms and/or the electron cloud of the phenyl group π-system.

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The preferred conformation is one, in which both effects strike a minimum-energy compromise.

To focus attention on some of the problems underlying the attempted analysis, we describe the situation in simple *Hückel* language: Let $\pi_1 (=a_{2u}), \pi_2, \pi_3 (=e_{1g})$ be the three occupied π orbitals of the phenyl nucleus and χ_l those orbital(s) of the substituent $X(=SR, (SO)R, (SO_2)R)$ which have the proper local symmetry to interact with the π_k; if c_k is the coefficient of the orbital π_k at the substituent carrying position 1 and c_l the coefficient of the substituent orbital χ_l, then the matrix element τ_{kl} between these two orbitals is given in a first approximation by

$$\tau_{kl} \equiv \langle \pi_k | H | \chi_l \rangle = \beta c_k c_l \cos(\varphi + \theta_l) \tag{1}$$

In equ. 1, $\beta = \beta(X)$ is a resonance integral which can be calibrated for each type of group X. The angle φ describes the conformation, with the definition $\varphi = 0$ for the conformation in which the S,R-bond lies in the plane of the phenyl group. Finally θ_l is a phase angle, depending on the orientation of orbital χ_l relative to the C–S–R plane. Under the influence of the crossterms of equ. 1 the sets of basis orbitals π_k and χ_l mix to yield the molecular orbitals ψ_j of orbital energies ε_j.

Shifts and coupling constants derived from the ^{13}C-NMR. spectra depend, within our model, primarily on *all* electron indices (charge densities q_μ, bond orders $p_{\mu\nu}$ and/or the different types of polarizabilities) albeit, in general, in a not well understood fashion. If only doubly occupied orbitals π_k and χ_l are used as a basis for the model, then these indices are independent of the matrix elements τ_{kl}. Second order changes δq_μ(conj.) and $\delta p_{\mu\nu}$(conj.) in charge densities or bond orders occur only if we include antibonding orbitals π_k^* and/or χ_l^*. In particular inclusion of the π_k^* will allow polarization of the phenyl group π-system, *e.g.* under the influence of a purely inductive effect of a substituent, which shifts the *Coulomb* integral α_1 of the substituted C-atom by $\delta\alpha_1$. This shift, assumed to be independent of φ, will lead, for example, to a change $\delta q_\mu(\text{ind.}) = \pi_{1,\mu}\delta\alpha_1$ of the charge density in position μ, $\pi_{1,\mu}$ being the relevant atom-atom polarisability. On this, the conformation dependent charge change δq_μ(conj.) is superposed, so that the net change is $\delta q_\mu = \delta q_\mu(\text{ind.}) + \delta q_\mu(\text{conj.})$. Empirical correlations of the observed ^{13}C-shifts for the C-atom in position 4 of the phenyl group as a function of the type of substituent in position 1, shows that these shifts are a rather reliable measure of δq_4 [1] [2].

In contrast, the ionization energies I_j determined by photoelectron spectroscopy are essentially *one* electron properties if we accept *Koopmans*' approximation $-\varepsilon_j = I_j$. The conformation dependent changes of the ionization energy $I_j(\varphi)$ can be calculated from the matrix elements (1) and the basis orbital energies $A(\pi_k)$, $A(\chi_l)$ by diagonalizing the corresponding *Hückel* matrix for different values of φ.

Many examples are known where $I_j(\varphi)$ depends strongly on φ [3], but most of these refer to the particular case when only two high lying orbitals π_k, χ_l of equal, or almost equal orbital energy $(A(\pi_k) \approx A(\chi_l))$ mix under the influence of the coupling term τ_{kl} to yield a pair of molecular orbitals ψ_{j+}, ψ_{j-} above and/or well separated in energy from the rest of orbitals. (Typically $\psi_{j\pm}, \psi_j = \psi_{\text{HOMO}}$, $\psi_{\text{HOMO-(1 or 2)}}$.) Under these conditions the following approximation is adequate:

$$-I_{j\pm}(\varphi)=\varepsilon_{j\pm}(\varphi)\approx\frac{1}{2}\Big(A(\pi_k)+A(\chi_l)\Big)\pm\tau_{kl}(\varphi). \tag{2}$$

However, more often than not, $|A(\pi_k)-A(\chi_l)|>\tau_{kl}$ and the highest occupied orbitals are essentially perturbed π_k orbitals, *i.e.* $\psi_k\approx\pi_k$. In a first approximation, the corresponding ionization energy is then

$$-I_k(\varphi)=\varepsilon_k(\varphi)\approx A(\pi_k)+\sum_l\left(\frac{\tau_{kl}^2}{A(\pi_k)-A(\chi_l)}\right). \tag{3}$$

Consequently the dependence of I_k on φ is small and under these conditions photoelectron spectroscopy will be a rather poor tool for the investigation of conformational problems [4].

Combining ^{13}C-NMR. and photoelectron spectroscopy to study conformational problems can be of interest, because of the different time scales of the two methods. Whereas the former yields information about time averaged mean conformations, the latter can be used, under favorable conditions, to obtain insight into momentary conformations [5] [6].

Alkyl phenyl sulfides 1(R). - From the IR. [7], the UV. spectra [8] and from ab initio calculations [9] of **1**(Me) it has been deduced that the preferred conformation is the one with $\varphi=0$, *i.e.* with the S,Me-bond in the plane of the phenyl group, in contrast to **1**(R) with R = Et, *i*-Pr, *t*-Bu, where φ tends towards ~90° with increasing size of the alkyl groups R [5].

In the compounds **1**(R) one is presented with the very simple situation that only a single substituent group orbital χ_l, namely the sulfur-lone-pair orbital $n_S=3p(S)$ perpendicular to the C–S–R plane, can interact with the phenyl group π-orbitals. Of these, the HOMOs π_2, π_3 (of e_{1g} parentage) have almost the same basis energy $A(\pi)$ as the lone pair orbital n_S in thiophenol **1**(H) *i.e.* $A(\pi)\approx A(n_S)$ [5]. The π-orbital coefficients at the point of attachment are $c_3=1/\sqrt{3}$ for the orbital π_3, which is symmetric with respect to a reflection in the plane passing through centres 1 and 4, and $c_2=0$ for π_2, which is anti-symmetric. Accordingly, n_S can interact only with π_3, yielding ψ_1 and ψ_3, whereas π_2 remains essentially unaltered: $\psi_2\approx\pi_2$. By virtue of equ. 2 we have in a first, crude approximation:

$$\begin{aligned}I_1&=-(A(\pi)+A(n_S))/2+\beta/\sqrt{3}\\ I_2&=-A(\pi)\\ I_3&=-(A(\pi)+A(n_S))/2-\beta/\sqrt{3}\end{aligned} \tag{4}$$

Calibration yields $A(\pi)\approx-9.5$ eV and $\beta\approx-1.9$ eV if the experimental data for **1**(H) are used. These values are eminently reasonable, assuming that the twist angle in **1**(H) is $\varphi=0$.

Substitution of H in **1**(H) by alkyl groups R of increasing size has two effects:

a) The increase in inductive effect along the series R = Me → Et → *i*-Pr → *t*-Bu will shift $A(n_S)$ to higher values, as shown *e.g.* by the decrease in n_S^{-1} ionization energies of the dialkyl sulfides RSR [10] [11]:

R =	H	Me	Et	*i*-Pr	*t*-Bu
$I(n_S^{-1})$/eV =	10.48	8.68	8.48	8.26	8.07

(5)

This will lift the quasi degeneracy $A(\pi) \approx A(n_S)$ observed in **1**(H) and place n_S above π_2, π_3 in the compounds **1**(R);

b) Steric interference of R with the H-atoms in ortho-position to the RS-group will tend to increase φ and thus reduce the coupling τ_{kl} between π_2 and n_S according to (1).

Combining both effects, a simple and convincing rationalization of the observed photoelectron spectra is obtained as has been shown by *Mellor et al.* [5] and by *Schweig & Thon* [6] who studied the temperature dependence of the photoelectron spectrum of **1**(Me). Both groups of authors have analyzed their data under the simplifying assumption of a conformational equilibrium

$$\mathbf{1}(\mathrm{R};\ \varphi = 0) \rightleftharpoons \mathbf{1}(\mathrm{R};\ \varphi \approx 90°) \tag{6}$$

which is a crude approximation, perhaps acceptable for **1** (Me) (*cf.* [12]). In general one expects a continuum of conformations which can be described by a distribution function $f(\varphi)$, so that the probability of finding a conformation with twist angle φ is given by $dw = f(\varphi)\,d\varphi$. The function $f(\varphi)$ depends on the rotational potential $V(\varphi)$ which is not known for the general case **1**(R). *Schweig & Thon* have shown for the particular example **1**(Me) that it is a complicated function, depending critically, among other things, on the C—S—Me angle [6] (see also [9]). Therefore an analysis of the photoelectron spectra in terms of the strongly simplified two-conformation-model (see equ. 6) has to be taken with a grain of salt. Nevertheless, one can deduce with confidence from the photoelectron spectroscopic data [5] [13] that the mean twist-angle value $\bar{\varphi}$ increases monotonically along the series **1**(R) from R = Me to R = *t*-Bu, or, expressed with respect to equ. 6 that the equilibrium shifts towards the right-hand side [5].

The ^{13}C-NMR. results for the sulfides **1**(R) presented in *Table 1* indicate that in **1**(Me) the C-atom in position 4 is shielded relative to a benzene C-atom ($\delta_4 = -4.0$ ppm), whereas the same atom in **1**(*t*-Bu) is not ($\delta_4 \approx 0$). As mentioned above, in monosubstituted benzenes the chemical shift δ_4 of the C-atom in para-position correlates well with the charge changes δq_4 induced by substituents in position 1. However, in molecules of the type R—X-phenyl, such as those investigated in this paper (X=S), δ_4 does not vary in function of the size of the alkyl group R as long as the twist angle φ and thus the conjugation between the phenyl

Table 1. *^{13}C-NMR. chemical shifts δ_μ/ppm of the sulfides* **1**(R). The values in italics are the differences $\Delta\delta_\mu$/ppm relative to the shift value 128.7 ppm of benzene

R	Phenyl C-atoms in position				Alkyl group C-atoms	
	1	2	3	4		
Me[a])	138.4	126.5	128.6	124.7	15.6	
	+9.7	*−2.2*	*−0.1*	*−4.0*		
Et	136.9	(128.9)	(129.3)	125.9	27.8	14.5
	+8.2	*(+0.2*	*or* *+0.6)*	*−2.8*		
t-Bu	133.0	137.4	128.4	128.6	45.7	31.0
	+4.3	*+8.7*	*−0.3*	*−0.1*		

[a]) *Cf.* [14].

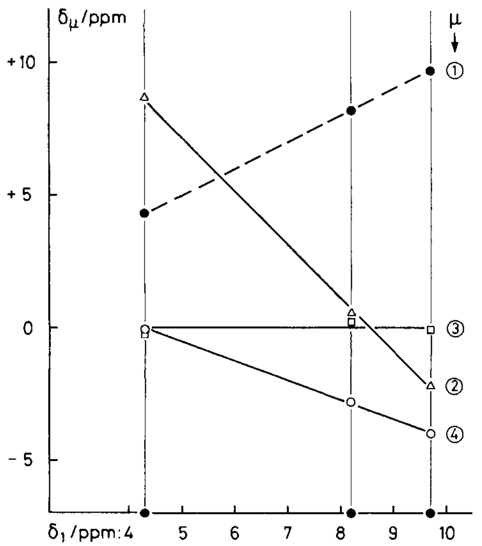


Fig. 1. *^{13}C-NMR. shifts of the sulfides* **1**(R). The shifts δ_μ ($\mu = 2,3,4$) are plotted in function of δ_1 *(cf. Table 1)*. The line $\mu = 1$ of unit slope is given as a reference.

group and the XR substituent remains the same, *e.g.* in the alkoxybenzenes R–O-phenyl where we find $\delta_4 = 120.7$, 120.6, 120.6 ppm for R = Me, Pr, Bu, respectively [15]. Further examples are provided by the molecules **2**(R), **3**(R) and **4**(R) discussed below. One is lead to the conclusion that the change δq_4(ind.) due to the inductive effect of a substituent XR in position 1 is independent of R for certain types of X, at least from a ^{13}C-NMR. point of view.

Figure 1 shows a plot of the chemical shifts δ_μ ($\mu = 2, 3, 4$) *vs.* δ_1 for **1**(R) with R = Me, Et and *t*-Bu. It is interesting to observe that there seems to be a good linear correlation between the different δ_μ values, and it should be noted that this type of linear interdependence is not limited to the title compounds. The reasons for this correlation are as yet not understood. However, for position 4 it is postulated that δ_4 is a linear function of the charge density q_4. In the absence of an inductive contribution one has $q_4 = q_0 + \delta q_4$ (conj.), with $q_0 = 1$ (as in benzene) and δq_4 (conj.) $= f(\varphi)$, *i.e.* depending on the twist angle around the phenyl-S bond.

To evaluate the order of magnitude of δq_4(conj.) we rely on a simple, calibrated *Hückel* model using the parameters $\alpha_C = -6.6$ eV, $\beta_{CC} = -2.7$ eV [16], $\alpha_S = -8.6$ eV, $\beta_{CS} = -1.7$ eV. The latter two values are calibrated on the photoelectron spectrum of **1**(Me) [6]. If $\beta_{CS} \cdot \cos\varphi$ is used for the dependence of the resonance integral between the sulfur n_S-orbital and the C-atom 2p AO in position 1, the following charge density changes δq_4(conj.) are obtained:

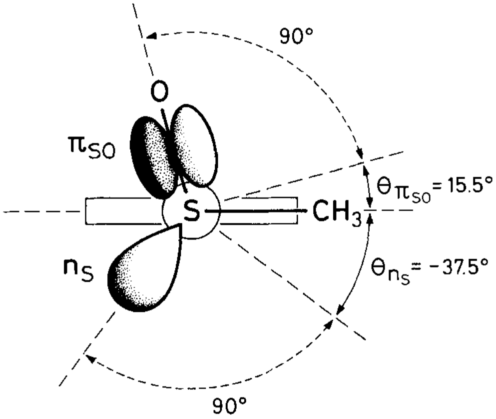
φ	0	15	30	45	60	75	90	
$\delta q_4(\text{conj.}) \cdot 10^2$	3.7	3.5	2.9	1.9	1.0	0.3	0.0	(7)

Assuming $\varphi = 90°$ in **1**(*t*-Bu) we find $\Delta\delta_4/\delta q_4(\text{conj.}) = -108$ ppm. This value is of the same order as the mean ratio -160 ppm deduced from the ^{13}C-chemical shifts of the cyclopentadienate anion $C_5H_5^-$ ($q_\mu = 1.200$; $\delta_\mu = 103.0$ ppm), benzene C_6H_6 ($q_\mu = 1.000$; $\delta_\mu = 128.7$ ppm) and tropylium cation $C_7H_7^+$ ($q_\mu = 0.857$;

$\delta_\mu = 156.3$ ppm) [17]. (It should be remembered that the *Hückel* model exaggerates the charge density changes δq_μ, which explains why a smaller ratio is deduced, using the values quoted in equ. 7.) This supports the assumption that the mean twist angle in this compound is somewhere around $\bar{\varphi} \approx 30°$, which is in agreement with the value suggested by molecular models.

Thus ^{13}C-NMR. and photoelectron spectroscopy yield a consistent description of the mean conformations of the sulfides **1**(R), within the limitations pointed out in [12].

Alkyl phenyl sulfoxides 2(R) and 3(R). - The structure of the sulfoxide group, as derived from the microwave spectrum of the parent compound dimethylsulfoxide [18], is characterized by the parameters R(S=O) = 148.5 pm, R(S–C) = 179.9 pm, $\sphericalangle$ (C–S–C) = 96.6° and $\sphericalangle$ (C–S–O) = 106.5°. If we assume that the sulfur-lone-pair lies in the plane that bisects the C–SO–C dihedral angle, then the orientations of the S–Me bond, of the S=O bond and of the sulfur-lone-pair are as follows for $\varphi = 0$ in the usual *Newman*-projection:



(8)

The phase angles $\theta_{n(S)} = -37.5°$ and $\theta_{\pi(SO)} = 15.5°$ are the ones to be used in expression (1) for the calculation of the matrix elements τ_{kl}.

If we want to perform the same *Hückel*-type calculations for the sulfoxides **2**(R) as for the sulfides, we need estimates for the basis energies of the n_S-lone-pair orbital and for the π_{SO} orbital. From the work of *Bock & Solouki* [19] [20], discussed in more detail below, we derive $A(n_S) = -9.0$ eV and $A(\pi_{SO}) = -10.2$ eV. Furthermore we estimate that $\beta_{CS} = -1.4$ eV and -1.7 eV for the interaction of the lone-pair orbital and the 3p-S orbital of π_{SO} respectively. Happily none of these parameters are very critical and changes within reasonable limits will not change our conclusions. With the above parameters the matrix elements which couple n_S and π_{SO} to the C-atom 2p orbital in position 1 are $\tau_{n_{S},1} = -0.8 \text{ eV} \cdot \cos(\varphi - 37.5°)$ and $\tau_{\pi_{SO},1} = -0.7 \cos(\varphi + 15.5°)$. Diagonalizing the corresponding matrix and calculating the charge densities q_4 in para-position to the SOR substituent in **2**(R) as a function of φ yields the following differences $\delta q_4(\text{conj.}) = q_4 - 1$:

φ	0° (180°)	30°	60°	90°	120°	150°	
$\delta q_4(\text{conj.}) \cdot 10^2$	0.9	1.0	0.7	0.3	0.3	0.5	(9)

It is immediately obvious that there is very little change in q_4 when we scan the conformations $0 \leqslant \varphi \leqslant 180$. In fact the range of δq_4(conj.) is only $0.7 \cdot 10^{-2}$ as compared to $3.7 \cdot 10^{-2}$ for the sulfides (see equ. 7). From this we predict that the range of ^{13}C-shifts δ_4 must be smaller than approximately 0.7 ppm but shielded with respect to benzene.

In *Table 2* are presented the observed ^{13}C-NMR. shifts for the sulfoxides **2**(R) and **3**(R). The shift range of δ_4 is found to be 0.5 ppm for **2**(R) and zero for **3**(R), which is in excellent agreement with the expectation. Needless to say, no valid conclusions can be drawn concerning the conformations of these compounds from the ^{13}C-NMR. shifts.

Table 2. *^{13}C-NMR. chemical shifts δ_μ/ppm of the sulfoxides* **2**(R) *and* **3**(R). The values in italics are for **2**(R) the differences $\Delta\delta_\mu$/ppm to the shift value $\delta = 128.7$ ppm of benzene, for **3**(R) the differences to the corresponding shifts of toluene, *i.e.* for $\mu = 1$, 125.5 ppm; $\mu = 2$, 128.3 ppm; $\mu = 3$, 129.1 ppm; $\mu = 4$, 137.7 ppm.

		Phenyl C-atoms in position				Alkyl group C-atoms		
		1	2	3	4			
2(R)	Me	146.4	123.4	129.1	130.6	43.6		
		+17.7	*−5.3*	*+0.4*	*+1.9*			
	Et	143.7	124.2	129.1	130.9	50.4	5.9	
		+15.0	*−4.5*	*+0.4*	*+2.2*			
	t-Bu	140.4	126.3	128.4	131.1	55.8	22.9	
		+11.7	*−2.4*	*−0.4*	*+2.4*			
3(R)	Me	142.9	123.6	130.0	141.5	21.3	44.1	
		+17.3	*−4.7*	*+0.9*	*+3.8*			
	Et	140.5	124.3	129.9	141.3	21.3	50.4	6.0
		+15.0	*−4.0*	*+0.8*	*+3.6*			
	t-Bu	137.1	126.3	129.1	141.5	21.3	56.6	22.8
		+11.6	*−2.0*	*0*	*+3.8*			

[a] *Cf.* [14].

Table 3. *Positions I_j^m in eV of the band maxima in the photoelectron spectra of the compounds* **2**(R), **3**(R) *and* **4**(R)

	Bands				
	①	②	③	④	⑤
2(Me)	8.8_5	9.7	9.7	10.0_0	
2(Et)	8.7_5	9.7	9.7	9.9	
2(*t*-Bu)	8.5_0	9.5	9.5	9.7	
3(Me)	8.7_0	9.5_5	9.5_5	10.0	
3(Et)	8.56	9.37	9.37	9.7	
3(*i*-Bu)	8.5_0	9.4_0	9.4_0	9.7_0	
3(*t*-Bu)	8.33	9.27	9.27	9.5_5	
3(Benzyl)[a]	8.4_5	(9.0_5)[a]	9.4_0	(10.0)[a]	
4(Me)	9.8_5	9.8_5	10.58	11.0_5	11.9
4(Et)	9.7_5	9.7_5	10.2_5	10.9	11.7_0
4(*t*-Bu)	9.7	9.7	9.9	10.8	11.5_5

[a] Because of the overlap of the four π-bands, this compound has a complicated, unresolved envelope. Thus the bands labeled ② and ④ are only shoulders, whereas ③ is a strong maximum containing the four π-bands.

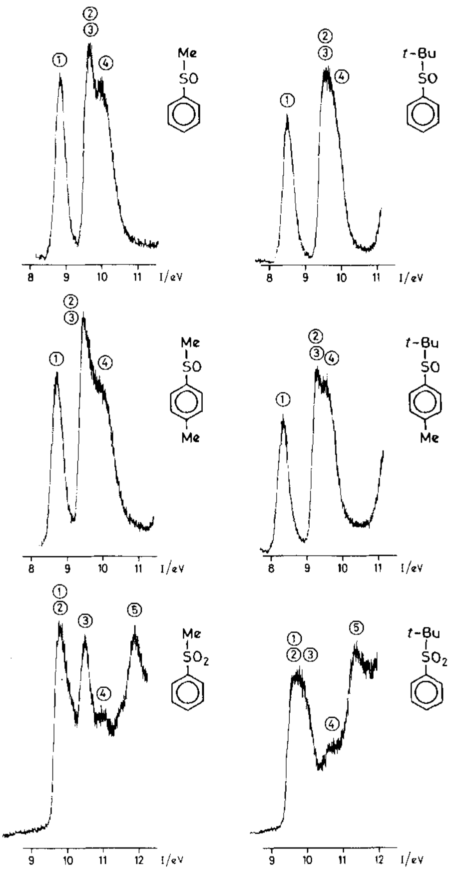


Fig. 2. *He(Ia) photoelectron spectra*

In *Figure 2* are shown the He(Iα) photoelectron spectra of **2**(R) and **3**(R) with R=Me and *t*-Bu. The observed positions I_j^m of the band maxima have been collected in *Table 3*. The spectrum of **2**(Me) has been recorded previously by *Bock et al.* [19] [20] whose results agreed with ours, within the usual limits of error. (The spectrum of **2**(Me) shown in [19] is indicative of a small amount of impurity, yielding a shoulder at $I < 9$ eV and an additional band in the region 11 eV $< I <$ 12 eV.)

From the work of *Bock & Solouki* [19] [20] it is clear that the first three bands in the photoelectron spectrum of the parent compound dimethylsulfoxide have to be associated with the following orbitals (*Koopmans*' approximation implied):

Band	Orbital	$CH_3-SO-CH_3$ Orbital-type	I_j^m/eV	
①	8a′	$n_S-(n_O)$	9.01	(10)
②	5a″	$\pi_{SO}-(\sigma_{CS}^-)$	10.17	
③	7a′	$n_O-(\sigma_{CS}^+)$	12.57	

This assignment is supported by their own CNDO/2 calculations, the *ab initio* calculations by *Rauk & Czizmadia* for H_2SO [21] and, above all, by extensive correlation with the photoelectron spectroscopic results for many other sulfoxides [21].

In the spectra of **2**(R) and **3**(R) the only potentially useful features for our purposes are the first bands ① which are due in all cases to a dominantly n_S^{-1}-ionization process, and the broad maximum containing three overlapping partial bands (② to ④), two of which are mainly of e_{1g} benzene-π-orbital parentage and one mainly due to electron ejection from π_{SO}. Obviously all these orbitals are rather mixed ones, as indicated for example by the simple *Hückel*-type calculation described above.

Apart from the twist angle φ, the first ionization energy $I_1^m(n_S)$ should also depend somewhat on the C–S–C and C–S–O angles [19]. However, it is safe to assume that these angles do not vary significantly in our compounds and that conformational strain, if any, would be relieved by rotation of the SO–R-group around the phenyl-S axis. This has been discussed by *Bock & Solouki* [19] [20] whose analysis of the photoelectron spectrum of **2**(Me) (and of related molecules) suggested that a conformation with $\varphi \approx 90°$ should be the favoured one.

Assuming that this is essentially correct, then the replacement of R = Me by a larger alkyl group should only have a marginal effect on the phenyl/SOR twist angle and thus on the conjugative interaction of the sulfur-lone-pair orbital n_S and of the double-bond π_{SO}-orbital with the phenyl-group-π-orbitals. Therefore the observed shifts of I_1^m should only be those which are due to the differences in

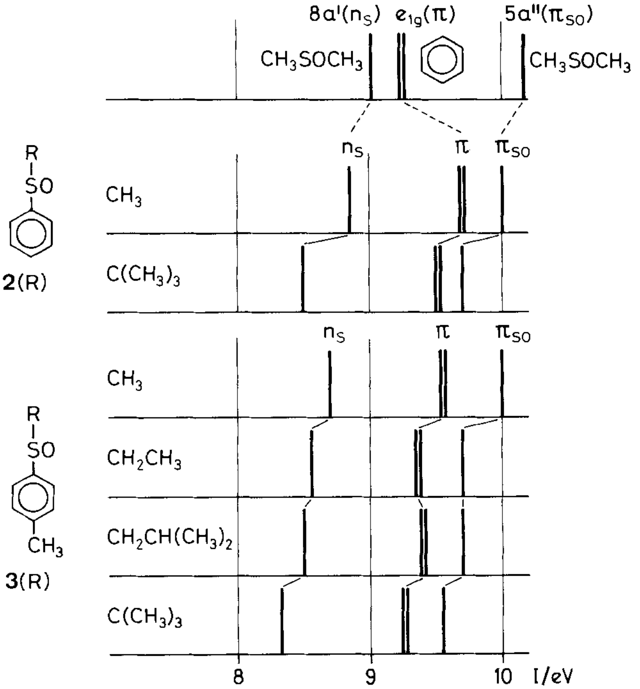


Fig. 3. *Correlation diagram for the band positions I_j^m of the sulfoxides* **2**(R) *and* **3**(R). On top of the diagram are shown band positions corresponding to the basis orbitals of the *Hückel*-type model described in the text. The labels n_S, π and π_{SO} indicate the basis orbital dominating the molecular orbital associated with the band.

the inductive and/or hyperconjugative effects of the various groups R. As these are also operative for the $e_{1g}(\pi)$ and π_{SO} orbitals, we expect that in the absence of conformational changes the ionization energies I_1^m to I_4^m should all shift monotonically and parallel to each other with increasing size of the alkyl groups R. Furthermore the size of the shifts should correspond to the ones observed in other systems XR where conformational effects are excluded [4]. As shown in the correlation diagram of *Figure 3* this is exactly what is observed.

We conclude this section with a few comments:

1) Assuming for the sake of an argument that the crude *Hückel*-type model for **2**(R) (with parameters for R = Me) can be used as a guide-line, it would follow that in the absence of steric effects, the preferred conformations of **2**(R) would be those with $\varphi \approx 20°$, *i.e.* the twist-angle range for which the total π-electron energy of the model reaches a minimum. In *Figure 4* is shown how the orbital energies ε_j of the highest four occupied orbitals of our model change with φ. Not too much importance should be attached to the absolute values in view of the crudeness of the model and its ad hoc calibration, but the relative spacings are presumably realistic. If this is so, then the best fit to the observed band pattern is obtained with $\varphi \approx 60° \pm 30°$. If these results are taken at face value one comes to the same conclusion as *Bock & Solouki* [19] [20], namely that the S–CH_3-bond of the $SOCH_3$ group in **2**(Me) is not coplanar with the phenyl ring, assuming a twist angle somewhere around $\varphi \approx 60°$. Consequently, replacing Me by a larger group R should only lead to a small change in φ;

2) An estimate of the shifts induced in the positions of the n_S- and π_{SO}-bands due to the replacement of a methyl by a *t*-butyl group can be derived from a comparison of the ionization energies of the corresponding bands in the photoelectron spectra of dimethylsulfoxide and di-*t*-butylsulfoxide [19] [20]:

	Me–SO–Me	*t*-Bu–SO–*t*-Bu	Δ	Δ_{corr}	
$I^m(n_S)$/eV	9.01	8.18	−0.83	−0.75	(11)
$I^m(\pi_{SO})$/eV	10.17	9.20	−0.97	−1.02	

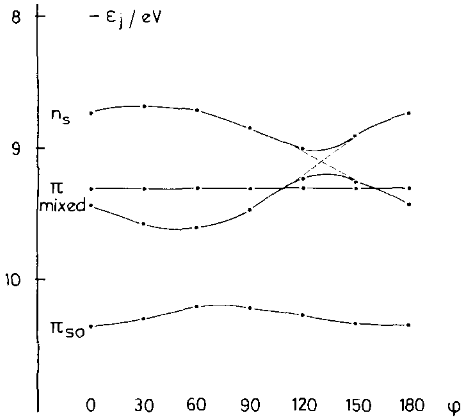


Fig. 4. *Dependence of the highest-orbital energies ε_j of the* Hückel-*type model for* **2**(R) *on the twist angle*

The uncorrected differences Δ (= shifts) incorporate the effects due to the changes in C–S–C and C–S–O angles. These effects have been subtracted [19] to yield the corrected values Δ_{corr} of equ. 11, which are the ones to be used in our analysis, because C–S–C and C–S–O angle changes are negligible when the methyl groups in **2**(Me) or **3**(Me) are replaced by *t*-butyl groups. The shifts observed in our photoelectron spectra are:

	$\Delta(n_S)$	$\Delta(\pi_{SO})$
2(Me)→**2**(*t*-Bu)	−0.35	−0.37 eV
3(Me)→**3**(*t*-Bu)	−0.30	−0.45 eV

(12)

It is seen that $\Delta(n_S)$ is exactly as expected, *i.e.* $\Delta_{\text{corr}}(n_S)/2 = -0.35$ to -0.40 eV, but that $\Delta(\pi_{SO})$ is a bit smaller than $\Delta_{\text{corr}}(\pi_{SO})/2 = -0.50$ eV. Assuming that this is significant, then a possible explanation would be that the π-orbital energies of π_{SO} and π (phenyl) are almost the same, so that even a small coupling between them leads to linear combinations $\sim(\pi_{SO} \pm \pi\,(\text{phenyl}))/\sqrt{2}$ and consequently to smaller shifts of the corresponding bands in the photoelectron spectra;

3) From the envelope of the maximum due to the overlapping bands ②, ③ and ④, one deduces that the gap between the ionization energies $I^m(\pi)$ and $I^m(\pi_{SO})$ is smaller in **2**(*t*-Bu) and **3**(*t*-Bu) than in **2**(Me) and **3**(Me), respectively. This is reasonable, because the basis orbital π_{SO} is more strongly affected than the orbitals π (phenyl) separated from R by one more C,S-bond. However, due to the orbital mixing described above, the shift difference is only small;

4) As expected, the para-positioned methyl group in **3**(R) induces small negative shifts in the n_S- and π-bands, relative to the positions of these bands in the photoelectron spectra of **2**(R). The size of these shifts (−0.15 eV for the $I^m(n_S)$ values, −0.15 to −0.2 eV for the $I^m(\pi)$ values) agrees with previous experience from substituted benzenes [4] [22];

5) The shifts of $I^m(n_S)$ in the photoelectron spectra of **3**(R), as a function of R correlate satisfactorily with the shifts of the lone-pair bands in the photoelectron spectra of the dialkylsulfides R–S–R [10] [11] and the dialkyldisulfides R–S–S–R [10] [11] [23], as well as with the characteristic substituent constants μ_R [4] [24]:

R	**2**(R) $\Delta I^m(n_S)$	R–S–R $\Delta I^m(n_S)/2$	R–S–S–R $\Delta \overline{I^m}(n_S)/2$	μ_R
Me	–	–	–	–
Et	−0.14 eV	−0.10 eV	−0.14 eV	−0.19
i-Bu	−0.20 eV			−0.38
t-Bu	−0.37 eV	−0.30 eV	−0.30 eV	−0.50

(13)

In the case of the disulfides R–S–S–R the value $\overline{I^m}(n_S)$ corresponds to the mean of the positions $I^m(n_S^+)$ and $I^m(n_S^-)$ of the in-phase and out-of-phase bands of the lone pairs;

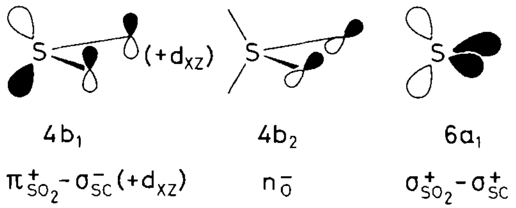
6) Our photoelectron spectroscopic and ^{13}C-NMR. results are thus compatible with the assumption that the conformation assumed by the SOR group is practically the same in all sulfoxides **2**(R) and **3**(R), a result also supported by IR. spectroscopy [25].

Alkyl phenyl sulfones 4(R). – The structure determination of the parent compound dimethyl sulfone shows that this group has local C_{2v}-symmetry and that its structural parameters are R(S=O)=143.5 pm, R(S–C)=177.1 pm, ∢ C–S–C =103° and ∢ O–S–O=121° [26]. The orbital structure of dimethyl sulfone is rather complicated. Combining photoelectron spectroscopic and theoretical results, *Solouki et al.* [27] have shown that the sequence of the five highest occupied orbitals is:

Band	Orbital	Orbital-type	I_j^m/eV
①	$4b_1$	$\pi^{+}_{SO_2} - (\sigma^{-}_{SC})$	10.65
②	$4b_2$	n^{-}_{O}	11.18
③	$6a_1$	$\sigma^{+}_{SO} - (\sigma^{+}_{SC})$	11.65
④	$2a_2$	$\pi^{-}_{SO_2}$	12.0
⑤	$3b_1$	σ^{-}_{SO}	~14

(14)

The first three orbitals, of the SO_2 group can be represented schematically as follows [27]:



(15)

In view of the complexity of the orbital picture it would be unrealistic to construct a *Hückel*-type model for **4**(R), along the same lines as in the two previous sections for **1**(R), **2**(R) and **3**(R). However, it can be deduced qualitatively, that the situation must be similar to the one encountered for the sulfoxides **2**(R) and **3**(R), *i.e.* that the change of q_4 (conj.) as a function of φ will be very small.

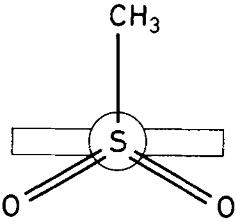
The ^{13}C-NMR. results for the sulfones **4**(R) presented in *Table 4* show, that the phenyl C-atoms in position 4 are deshielded relative to benzene, the SO_2R substituents behaving as electron-withdrawing groups. The corresponding change in charge density q_4 at position 4 must be mainly inductive (δq_4(ind.)). There is no change in deshielding when the size of the alkyl group is increased from R=Me to R=*t*-Bu ($\Delta\delta_4 = +4.8$ ppm in both cases) which suggests that either

Table 4. *^{13}C-NMR. chemical shifts δ_μ/ppm of the sulfones* **4**(R). The values in italics are the differences $\Delta\delta_\mu$/ppm relative to the shift value 128.7 ppm of benzene

R	Phenyl C-atoms in position				Alkyl group C-atoms	
	1	2	3	4		
Me[a])	140.6	127.1	129.2	133.5	44.2	
	+11.9	*−1.6*	*+0.5*	*+4.8*		
Et	138.8	128.2	129.3	133.6	50.6	7.4
	+10.1	*−0.5*	*+0.6*	*+4.9*		
t-Bu	135.7	130.7	128.7	133.5	59.8	23.7
	+7.0	*+1.8*	*0*	*+4.8*		

[a]) *Cf.* [14].

δq_4(conj.) is independent of φ, or that φ is almost independent of R. X-ray [28] and dipole-moment [29] studies suggest that **4**(Me) adopts a conformation with $\varphi \approx 90°$, as indicated in the following *Newman* projection:



(16)

Accordingly one would not expect any change in φ when Me is replaced by a larger alkyl group R.

The He(Iα) photoelectron spectra of **4**(R) with R = Me and *t*-Bu are shown in *Figure 2,* with R = Et in *Figure 5.* Observed band positions I_j^m have been collected in *Table 3.* The spectrum of **4**(Me) has been recorded previously by *Bock et al.* [27], whose results agree with ours, within the usual limits of error.

Replacement of one of the methyl groups in dimethyl sulfone by a phenyl group yields **4**(Me), for which the following assignment has been proposed by *Bock et al.* [27]:

Band	Orbital	Correlation with Phenyl-group- and $MeSO_2Me$-orbitals
① ②	$a'(\pi)$ $a''(\pi)$	e_{1g}
③	a'	$4b_1$
④	a''	$4b_2$
(⑤	?	? $6a_1$; $2a_2$)

(17)

In view of the complexity of the spectra, only the assignment of the first four bands is reasonably certain [27]. A remarkable fact is that the substitution of a H-atom by a SO_2Me group does not split the π-orbitals of e_{1g}-parentage significantly. This means that the differential, inductive stabilization of the symmetric and antisymmetric components of the degenerate pair e_{1g} (which would lead to an orbital sequence symmetric below antisymmetric) is compensated by the conjugative destabilizing interaction of the symmetric π-orbital with lower lying SO_2-orbitals of appropriate symmetry which closes the gap. The position of the double band ① ② is little affected by the size of the alkyl group R of **4**(R), this group being removed by two S–C σ-bonds from the benzene π-system.

Comparison of the photoelectron spectra of **4**(Me) and **4**(*t*-Bu) *(Fig. 2)* shows a considerable change in the envelope of the first three bands. To derive a meaningful assignment we have recorded the spectrum of **4**(Et) presented in *Figure 5.* It is obvious that band ③ is shifted closer to the double band ① ② than in the spectrum of **4**(Me). Extrapolation to the spectrum of **4**(*t*-Bu), as shown in the correlation diagram of *Figure 6,* makes it clear, that the broad feature between 9.5 and 10.5 eV in this spectrum is due to three overlapping bands ① ② ③.

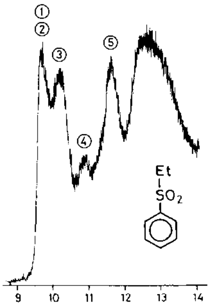


Fig. 5. *He(Ia) photoelectron spectrum of ethyl phenyl sulfone* **4**(Et)

With reference to the SO_2-group orbitals presented in equ. 14 and 15, it follows intuitively that $4b_1$ and $6a_1$ should be the two orbitals, the energies of which are strongly affected in **4**(R) by the type of substituting alkyl group R, because both are symmetric with respect to the xz-plane and therefore contain sizeable contributions from the S—C σ-bond orbitals. In contrast, the orbital energy of the antisymmetric orbital $4b_2$ is not expected to depend much on the size of R, because the C—S—C bonds lie on the node. This expectation is borne out by the correlation diagram of *Figure 6*, which provides additional support for the assignment proposed by *Bock et al.* [27].

From the correlation diagram of *Figure 6*, in particular from the constancy of the ionization energy associated with the removal of an electron from the orbitals $a'(\pi)$ and $a''(\pi)$, *i.e.* independent of the size of R, one has to conclude that there is no photoelectron-spectroscopic evidence for a change of conformation in the series **4**(Me) to **4**(*t*-Bu).

Conclusions. - For the series of the sulfides **1**(R) one observes significant changes in the ^{13}C-NMR. shifts δ_4 and in the splits between the bands in the photoelectron spectra [5] [6], when the size of the alkyl groups R is increased from R=Me to R=*t*-Bu. These changes yield straightforward information about the corresponding conformations of **1**(R), *i.e.* about the mean twist angle $\bar{\varphi}$.

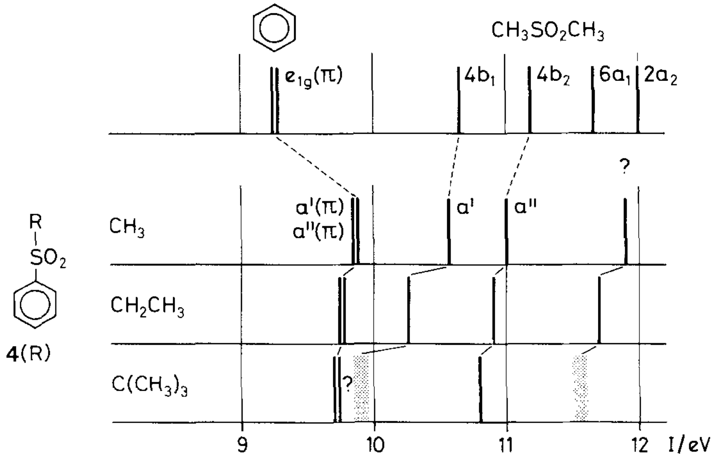


Fig. 6. *Correlation diagram for the band positions* I_j^m *of the sulfones* **4**(R) (see legend to *Fig. 3*)

In contrast, no change in the chemical shift δ_4 is observed in the ^{13}C-NMR. spectra of **2**(R), **3**(R) and **4**(R) for different alkyl groups R. This is an indication that the charge q_4 is practically independent of R within each series, which in turn suggests that the conjugative contribution δq_4(conj.) to q_4 is either very small and/or constant. Theory suggests that in **2**(R), **3**(R) and **4**(R) both conditions are fulfilled, so that very little, if anything, can be deduced about the conformations of the sulfoxides and sulfones from the ^{13}C-NMR. spectra.

From a photoelectron spectroscopic point of view the situation is only marginally better. The observed band shifts are due mainly to the changes in the inductive effect of the alkyl groups which tend to mask any conjugational contribution towards the ionization energies of **2**(R), **3**(R) and **4**(R). However, the correlations obtained are presumably best explained by assuming that φ is roughly constant within each series of compounds **2**(R), **3**(R) and **4**(R). Although the data presented are compatible with such a rationalization, they do by no means constitute a proof.

Experimental Part

^{13}C-NMR. spectra: Natural abundance spectra were recorded on a 250-CAMECA spectrometer operated in the pulsed *Fourier* Transform mode. Solutions were 0.5 to 0.6 molar in CDCl$_3$ at 20° with TMS as internal standard (CDCl$_3$: $\delta = 77.1 \pm 0.1$ ppm; $^1J_{CD} = 32 \pm 2\ s^{-1}$).

The signals of the C-atoms in position 4 are easily assigned on the basis of their relative intensity. For **1**(Me), **2**(Me) and **4**(Me) assignments have been derived by the gated decoupling technique, making use of $^3J_{CH}$ to differentiate between positions 2 and 3 *(cf. Table 5)*. All other assignments were obtained by comparison. In the case of the sulfoxides **3**(R) the known shift contributions of a methyl group in position 4 have been used to derive the assignment *(cf. Table 6)*.

Samples: The samples were either commercial ones (**1**(Me)) or synthesized according to literature procedures **1**(Et), **1**(*t*-Bu) [30]; **2**(Et) [31]; **2**(*t*-Bu) [32]; **3**(Me), **3**(Et), **3**(*t*-Bu) [33]; **4**(R) [32].

Table 5. *^{13}C-NMR. coupling constants in s^{-1} measured by the gated decoupling technique.* Error $\pm 2\ s^{-1}$. Abbreviations: *d* = doublet; *d* × *d* = doublet of doublets; *t* = triplet.

Compound		Position		
		1	2	3
1(Me)	^1J	160 (*d*)	160 (*d*)	164 (*d*)
	^3J	6 >4 (*d* × *d*)	6 (*d*)	5 (*t*)
2(Me)	^1J	162 (*d*)	162 (*d*)	162 (*d*)
	^3J	7 (*t*)	7 (*d*)	7 (*t*)
4(Me)	^1J	166 (*d*)	164 (*d*)	163 (*d*)
	^3J	7 ~5 (*d* × *d*)	7 (*d*)	7 (*t*)

Table 6. *^{13}C-NMR. chemical shifts in ppm due to the methyl group in position 4 in the sulfoxides* **3**(R)

R	Position			
	I	2	3	4
Me	−3.5	+0.2	+0.9	+10.9
Et	−3.2	+0.1	+0.8	+10.4
t-Bu	−3.3	0	+0.7	+10.4

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