NMR of Terminal Oxygen. Part 12.[1] SO_2 and Isoelectronic Compounds with a True π-Bond: ^{17}O NMR Spectra of Sulfinylamines R–N=S=O and Sulfines RR'C=S=O. The Conformation of *ortho*-Substituted Diaryl Sulfines

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The ^{17}O NMR shift values δ_O of 20 sulfinylamines R–N=S=O **2** and of 14 sulfines RR'C=S=O **3** (R and R' mostly arene groups) were compared with those of the isoelectronic SO_2 **1**. They show δ_O at much lower field than practically all other classes of S–O compounds; at the same time they exhibit the high substituent sensitivity which is typical for true π_p bond systems, and absent in S^+-O^- compounds. The difference is discussed in terms of bond order and electronic excitation energy. Comparison of the *E*- and *Z* isomers of *o*-methyldiaryl sulfines yields the conformation of these compounds: one arene ring is (nearly) coplanar with the CSO group and the other (nearly) perpendicular to it. This demonstration for the molecules in solution is supported by an X-ray structure determination.

^{17}O NMR is a valuable technique to characterize the bonding state of oxygen atoms in molecules.[2] The ^{17}O shift values of carbonyl oxygen are found in general at much lower field than those of bridging oxygen.[2] They are very sensitive to modifications of structure, varying over a range of >600 ppm. Electron donation from a geminal group X in –CO–X causes important upfield shifts (*e.g.* –CHO, δ_O = 562; $-CO_2Me$, 337; CO_2^-, 265),[3] whereas inductive electron withdrawal is rather ineffective (*e.g.* $-COCH_3$, 549 *vs.* $-COCF_3$ 544 ppm).[4] The sensitivity towards substituents in the *para*-position of arene rings in benzoyl compounds depends upon the degree of unsaturation of the carbonyl group; as usual the sensitivity can be measured by the Hammett-type ρ^+-values, which vary from 29 for $-COCF_3$ and 22 for –COMe to 8 for $-CO_2Me$ and 5 for $-CO_2^-$. Applying the 'tool of increasing electron demand',[5] the ρ^+ values of ^{17}O NMR shifts can be used to characterize the electrophilicity of carbonyl groups.[4]

N-Bound terminal oxygen seems to be in a similar situation, as judged from the great range of the δ_O values, between *ca.* 1500 and 200 ppm,[2] and the variable, sometimes very high substituent sensitivity, though the data are less abundant than for carbonyl. On the other hand P=O[2,6] and S=O[2,7] show quite different characteristics: the ^{17}O NMR signals appear at high field, close to P–O–R and S–O–R,[2] and are rather insensitive to geminal groups X (the δ_O values cover a narrow range of *ca.* 100 ppm; only Cl and Br, but not F cause a significant deviation), and quite insensitive towards substituents in an adjacent arene ring (ρ^+ values[6,7] typically 0–2). The difference between the second-row elements C and N and the third-row elements P and S is explained in terms of difference of hybridization (and geometry): in almost all compounds P and S can form π bonds only by invoking a d-orbital, which on theoretical grounds is energetically unfavourable, particularly in bonds to oxygen.[8]

P=O or S=O compounds forming a genuine π_p bond would furnish a test for this explanation. Whereas such compounds are not stable and/or easily accessible for P,[9] 2-coordinate S shows the right configuration: SO_2 (**1**) is a typical example; it can be formulated with one true double bond and one semipolar bond, of course in resonance. Its δ_O value (SO_2, 513 ppm[10]) has been found several hundred ppm downfield from typical S–O compounds: $RR'SO_2$ *ca.* 150, RR'SO *ca.* 0 ppm.[2] The isoelectronic sulfinylamines R–N=S=O (**2**) (R = Ph, δ_O = 410, and some of its aryl substituted derivatives), have been found in the same region,[11] as have the sulfinylimine anion $^-N=S=O$ ($\leftrightarrow N=SO^-$), δ_O = 449,[12] and bis(sulfinylamino)telluride, $Te(NSO)_2$, δ_O = 461.[13] We have now (a) applied the 'tool of increasing electron demand' to δ_O of a series of newly measured arylsulfinylamines (**2**) and (b) measured δ_O of a series of isoelectronic sulfines **3**.

O=S=O **1** RN=S=O **2** RR'C=S=O **3**

Results

Sulfinylamines (**2**).—[14] The ^{17}O NMR results obtained with 20 (known) sulfinylamines R–N=S=O (in MeCN solution) are presented in Table 1. For aromatic and an aliphatic R the δ_O values lie in a narrow range at *ca.* 400–420. An electron-attracting carbonyl group (PhCO in **2p** or EtOCO in **2q**) directly bound to N does not cause a great effect, only a shift of *ca.* 20 ppm downfield. An important upfield shift of *ca.* 150 ppm is effected by an amino group bound to N, as in the sulfinylhydrazine derivatives RR'N–NSO **2r** and **2s**. The same effect of electron donation resulting in an upfield shift of the sulfinyl signal is observed in the related *N*-sulfinylhydroxylamine derivative RO–NSO **2t**. In **2t** the lower-field signal at 323 ppm is attributed to the sulfinyl-*O*, shielded in comparison with PhNSO ($\Delta\delta_O$ = −94 ppm), the higher-field signal at 225 ppm to the bridge-O, deshielded in comparison with $RONR_2$ (in the case of an inversion of the assignments, the effects would be in the same direction, but too large; see below).

Substituents in the *para* position at the arene ring exert a significant effect, electron attractors diminishing the shielding of O. Compounds **2a–k** give a good correlation with the σ^+ constants: ρ^+ = 15.3 (r = 0.991; SD = 1.6; n = 11). A correlation with σ_p is much poorer (r = 0.94, SD = 4.1), confirming that –N=S=O is an unsaturated centre capable of through-conjugation;[15] its ρ^+ value for δ_O is close to that of the –COF group.[4] The electron attracting character of –N=S=O is also confirmed by the δ_O value of **2l**, which allows us to estimate

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Table 1 ^{17}O Chemical shift values of *N*-sulfinylamines R–N=S=O **2**[a]

No.	R	δ_O[b]
a	Ph	417.0; 410[c]
b	*p*-$Me_2NC_6H_4$	389.8
c	*p*-$MeOC_6H_4$	402.9[d]
d	*p*-MeC_6H_4	412.7
e	*p*-FC_6H_4	412.5; 412[c]
f	*p*-ClC_6H_4	417.2
g	*p*-BrC_6H_4	418.6
h	*p*-$CF_3C_6H_4$	424.3
i	*p*-CNC_6H_4	425.0
j	*p*-$NO_2C_6H_4$	426.7[e]
k	*p*-$COClC_6H_4$	428.5[f]
l	*p*-O=S=N–C_6H_4	422.5
m	2,4,6-$Me_3C_6H_4$	428.1
n	1-Naphthyl	415.4
o	Cyclohexyl	407.8
p	PhCO	436.2[g]
q	EtOCO	432.8[h]
r	PhNH	252.2
s	PhN(Me)	290.2
t	$PhCH_2O$	323.5[i]

[a] 0.5 mol dm^{-3} solution in CCl_4 at 35 °C. [b] Line-width at half height: 100–200 Hz; **2a**, **2e**, **2o**, **2p**: 70–100 Hz; **2b**, **2i**, **2r**: 200–300 Hz. [c] Ref. 11. [d] δ(MeO) = 59.3. [e] $\delta(NO_2)$ = 578.3. [f] δ(CO) = 497.6. [g] δ(CO) = 465.5. [h] δ(CO) = 320.0, δ(OEt) = 150.4. [i] δ(RO) = 224.7.

Table 2 ^{17}O Chemical shifts of sulfines RR'C=S=O **3**[a]

No.	R	R'	δ_O[b]
a	Ph	Ph	220.2[c]
b	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	206.5[d]
c	*m*-MeC_6H_4	*m*-MeC_6H_4	219.1
d	*p*-ClC_6H_4	*p*-ClC_6H_4	225.3
e	*m*-ClC_6H_4	*m*-ClC_6H_4	229.4
f	*p*-BrC_6H_4	*p*-BrC_6H_4	226.3
g	2-MeC_6H_4 (*E*)	Ph	227.5
h	2-MeC_6H_4 (*Z*)	Ph	218.8
i	2-Me-4-ClC_6H_3 (*E*)	4-ClC_6H_4	233.7
j	2-Me-4-ClC_6H_3 (*Z*)	4-ClC_6H_4	224.4
k	2-Me-4-$MeOC_6H_3$ (*E*)	4-$MeOC_6H_4$	218.1[e]
l	2-Me-4-$MeOC_6H_3$ (*Z*)	4-$MeOC_6H_4$	206.0[f]
m	2-Me-Fluorenyl (*E*)		229.9
n	1-Norcamphoryl	Cl	219.2[g]

[a] 0.3 mol dm^{-3} solutions in MeCN at 40 °C; **3m**: $CDCl_3$; **3f**: MeCN/CH_2Cl_2 1:1; **3j**: MeCN + 15% CH_2Cl_2. [b] Line-width at half height: 300–500 Hz; **3a**, **3k**, **3n**: *ca.* 200 Hz; **3l**: 560 Hz. [c] In CCl_4 solution: 234.3 ppm. [d] δ(MeO) = 58.4, 62. [e] δ(MeO) = 59.2 (broad). [f] δ(MeO) = 57.8 (broad). [g] δ(CO) = 524.7.

Table 3 Comparison of the ^{17}O chemical shifts of Me-free, *Z-ortho*-methyl- and *E-ortho*-methyl-diaryl sulfines, *p*-X–C_6H_3R–C(SO)–C_6H_4-*p*-X

X	*o*-H	*o*-Me (*Z*)	*o*-Me (*E*)
H	220.2 (**3a**)	218.8 (**3h**)	227.5 (**3g**)
MeO	206.5 (**3b**)	206.0 (**3l**)	218.1 (**3k**)
Cl	225.3 (**3d**)	224.3 (**3j**)	233.7 (**3i**)

for the group –NSO a σ^+ value of 0.46. A similar value, σ^+(NSO) = 0.37, is obtained evaluating the ^{17}O shift value of the –COCl group of *p*-sulfinylaminobenzoyl chloride **2k**, ClCO–C_6H_4NSO [δ_O(COCl) = 497.6] using ρ^+(COCl) = 20.5.[4] These values lie close to those of σ^+(NSO) = 0.3 obtained from ^{13}C NMR,[16] and σ_p(NSO) = 0.44 from UV spectra.[17] The downfield shift by the mesityl group in **2m** shows that steric or compressional effects[18] can also play a role.

Sulfines (**3**).—[19] The δ_O signals of the –C=S=O group are found at *ca.* 210–230 ppm (Table 2), *ca.* 200–300 ppm upfield from the isoelectronic compounds **1** and **2**, though still *ca.* 200 ppm downfield from the formally related sulfoxides R_2SO (δ_O *ca.* 0[2]). Substituents in the arene ring have a significant influence, evaluated as ρ^+ = 20.4 (r = 0.987, SD = 1.5, n = 6). Again, the σ_p constants, which do not apply to the resonance situation of unsaturated centres, give a less good correlation, in accord with the well-known unsaturated character of the sulfine group. The non-aromatic, chlorine-containing sulfine **3n** (the thermodynamically more stable isomer, probably *Z*) shows δ_O in the range of the aromatic compounds.

As the sulfine group is non-linear, with an angle of 114° at S,[19] unsymmetrically substituted diaryl sulfines exist as stable *syn–anti* isomers, separated by an interconversion barrier of 33 kcal mol^{-1}.[20] The structural assignment of the geometrical isomers has been made on the basis of several ^1H NMR criteria.[20b,21] It has now been confirmed, for the couple **3g**, **h**, by measurement of the lanthanide induced shift (LIS) effect: by complexing the O-atom of the sulfine group with the lanthanide reagent, protons *syn* to the CSO function experience a considerable induction, whereas *anti*-protons are less effected.[21] On adding increasing amount of $Eu(dpm)_3$ to the two isomeric *o*-tolylphenylsulfines, the methyl signal of the *syn*-isomer is much more effected than that of the *anti*-isomer: the slope of δ_H(Me) over [$Eu(dmp)_3$]/[sulfine] is 0.9 for the *E*-isomer and 2.0 for *Z*. At the same time the 2,6-H protons of the *E*-isomer (Ph *syn* to CSO) also experience a large LIS effect (slope 2.5). Finally it should be mentioned that the *Z* configuration of **3h** is now confirmed by an X-ray analysis (see below).

Table 2 includes three such *syn–anti* pairs, in which the symmetry has been destroyed by an *ortho*-methyl substituent in one of the arene rings. For comparison, the three parent compounds lacking the *o*-methyl group have also been measured (Table 3). In ^{17}O NMR the three series show coherent shift results: the *Z*-isomers show the same (±1 ppm) shift values as the Me-free compounds, whereas the *E*-isomers are found at *ca.* 10 ppm lower field. The stereochemical consequences of this result will be discussed below.

Discussion

Shift Values.—With shift values of 513, *ca.* 420, and *ca.* 220 ppm respectively, distinctly different from nearly all other S–O compounds, the isoelectronic π-systems **1**, **2** and **3** show also significant differences from one another. To explain them one can discuss their valence bond structures (excluding consideration of formulae with two double bonds, which would involve π_d orbitals).

$$O^-–S^+=O \leftrightarrow O=S^+–O^- \quad \mathbf{1}$$

$$RN^-–S^+=O \leftrightarrow RN=S^+–O^- \quad \mathbf{2}$$

$$R_2C^-–S^+=O \leftrightarrow R_2C=S^+–O^- \quad \mathbf{3}$$

In contrast to **1** the negative charge in **2** will not be distributed in a symmetrical way, but preferentially situated on oxygen, and even more so in **3**, for reasons of electronegativity. As in these resonance formulae the $S^+–O^-$ bond resembles the semipolar bond in sulfoxides, which show δ_O *ca.* 0, a higher weight of the $S^+–O^-$ formula will push the δ_O value upfield, in **3** more than in **2**. This argument is essentially one of (π-)bond order; it is supported by photoelectron spectroscopy and by *ab initio* calculations;[22] S–O bond length determinations confirm that sulfines have the weakest S=O bond, closest to that of sulfoxides: SO_2, 1.432; RNSO, 1.451; R_2CSO, 1.469; sulfoxides 1.497 Å.[22]

For carbonyl ^{17}O shifts it has been demonstrated that the arene substituent sensitivity ρ^+ yields a convenient measure of the unsaturation:[4] ρ^+ values vary from 29 ($-COCF_3$) to 5 ($-COO^-$). The values found for sulfinylamines, $\rho^+ = 15$, and sulfines, $\rho^+ = 20$, are in agreement with the unsaturated π-bond character of these functional groups, and contrast with the absence of substituent sensitivity ($\rho = 1$–3) in sulfinyl and sulfonyl groups presenting only semipolar S–O bonds, as in sulfones[23] and arenesulfinic and arenesulfonic derivatives.[7]

A more general argument is based upon the Karplus–Pople equation[24] (1) which allows, *via* the paramagnetic shielding σ_p,

$$\sigma_p = \text{const.} \times \Delta E^{-1} \times r^{-3} \times \Sigma Q \qquad (1)$$

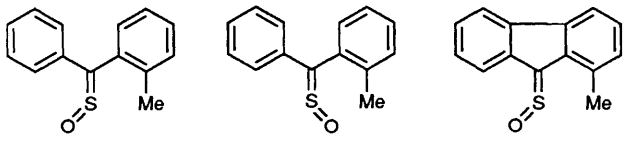
to approximate the shift values. The term ΣQ essentially represents the (π-)bond order, r the radius of the p-orbital of the measured atom; the excitation energy term ΔE is approximated by the lowest-energy electronic transition, with the restriction, however, that the transition, in order to be efficient in the direction of the magnetic vector of the light, has to be forbidden for the electric vector, *i.e.* for the UV–VIS spectrum; *e.g.* the n→π* bands of carbonyl groups fulfil this condition. Following eqn. (1), such transitions generate low-field shifts in the NMR spectrum. SO_2 has several low-intensity absorption bands between 300 and 400 nm,[25] of which at least that at 365 nm is symmetry-forbidden[26] and might cause a downfield shift in the NMR spectrum. Sulfinylamines **2** (in the absence of disturbing arene rings) show a low-intensity absorption at 300–310 nm (ε = 30–50);[14a] although we have no knowledge of a theoretical analysis, the low intensity suggests that this transiton is symmetry-forbidden, too, and can be NMR-active. Arene-free sulfines **3** show absorption at 270 nm, in the presence of aryl substituents (**3a**) the absorption lies at 329 nm,[27] but in both cases the high extinction (ε *ca.* 10^4) excludes that these transitions are symmetry-forbidden and could influence δ_O. As only **1** and **2**, but not **3** show UV absorptions to be connected with downfield shifts in the NMR spectrum,* the shift difference between these classes of compounds could, at least partially, be explained on the basis of the electronic excitation energy term ΔE. It has been discussed above on the basis of the bond-order term ΣQ, but it should be borne in mind that the two explanations do not necessarily exclude each other. In a more generaly way, it is not even clear how far the three terms of eqn. (1) are really independent from one another.

A magnetically active transition of the S=O bond electrons would be expected to influence not only the ^{17}O NMR of the terminal oxygen, but also the ^{33}S NMR of the central S atom. Actually the ^{33}S shift value of SO_2 appears at the extreme low-field end of S compounds, at δ_S = 374.9, several hundred ppm downfield from sulfoxides (δ_S *ca.* −20), sulfones (δ_S *ca.* −10) and sulfate ion (δ_S = 0).[29] Sulfinylamines RNSO, **2** resonate at somewhat higher field, but still in the low-field part of the spectral range, at δ_S *ca*, 269.[30] The parallelism with the ^{17}O resonance of these compounds is evident. Unfortunately, a δ_S value for a sulfine, difficult to measure, does not seem to be available.

On the other hand the ^{13}C signals of sulfines and the ^{14}N or ^{15}N signals of sulfinylamines are found in the normal region of doubly bonded systems, not influenced by the S=O part of these groups: sulfines δ_C *ca.* 190[20b] (*cf.* benzophenone 195 ppm); sulfinylamines δ_N *ca.* −65[31] (*cf.* imines *ca.* −50, oximes δ_N *ca.* −30[32]).

Resonance Effects with Sulfinylamino Groups.—By some of their electronic properties, particularly the presence of π-bonds and their polarization, the =S=O group can be compared with =O, *i.e.* $R_2C{=}S{=}O$ with R_2CO and R–N=S=O with R–N=O.[14a] Carbonyl and nitroso groups undergo strong resonance interaction with conjugated n-donors, as in amides and *N*-nitrosamines. ^{17}O NMR is a particularly sensitive tool to detect, *via* upfield shifts, a change in bond order caused by a conjugated n-donor:[4] amides and esters show upfield shifts (compared with aldehydes and ketones) of *ca.* 200 ppm,[2] nitrosamines[33] and nitrite esters[3] (compared with *C*-nitroso compounds[34]) even *ca.* > 500 ppm. We have applied the test to sulfinylamines by measuring δ_O of the *N*-substituted Ph(R)N–NSO (**2r**, R = H; **2s**, R = Me), which we found *ca.* 150 ppm upfield from aryl- and alkyl-sulfinylamines **2a**–**o**. The O analogue RO–NSO **2t** shows a similar upfield effect of *ca.* 90 ppm, whereas the S-atom, a weak donor in RS–NSO,[11b] shows no clear effect on δ_O.† The result agrees with that expected for resonance interaction between the n-donors N and O and the unsaturated system: (RR'N=S=O↔)RR'N–N=S^+–O^- ↔$RR'N^+$=N–S–O^-. It contrasts with the values found for sulfinic and sulfonic amides and esters, where, in the absence of true π-systems and of resonance, the effects upon replacing C by O or N are negligible or even in the opposite, *i.e.* downfield direction.[7] A quantitative comparison of –NSO with NO is, of course, not possible. For sulfines, the corresponding comparison is still lacking.

Conformation of o-*Methyldiaryl Sulfines.*—Whereas the configuration of the *syn–anti* isomers of diarylsulfines is well established on the basis of different NMR experiments (^1H and ^{13}C), and now confirmed by LIS (see above) and by an X-ray analysis (see below), the conformation of the arene rings with respect to the plane of the sulfine group has not been made explicit. One might expect to find it similar to that of the related benzophenones, in which each aryl ring is turned by 28° out of the plane of the carbonyl group,[36] and in which rapid rotation makes the molecule symmetric ('pseudo-planar') on the NMR time scale. Actually, for reasons of convenience, the formulae of diarylsulfines are normally drawn coplanar (Scheme 1); the ^1H



3g (*E*) **3h** (*Z*) **3m**

Scheme 1

and ^{13}C NMR arguments mentioned above do not contradict this conformation. However, the ^{17}O shift values, particularly of the compounds characterized by the presence of an *o*-Me group in one of the aromatic rings, allow us to abandon the pseudo-coplanar conformation in favour of a different one.

For pseudo-coplanar conformations, the *E*-isomers (**3g**, **k**, **i**, SO *anti* to the *o*-tolyl ring) should give shift values δ_O close to the Me-free compounds (**3a**, **b**, **d**), and probably different from

* A symmetry-forbidden absorption band might be obscured by the strong allowed band, or combined with it, without being accessible to UV spectrometry. One can imagine, however, that such a transition manifests itself in other magneto-optical spectroscopies, notably in circular dichroism. This approach has occasionally been used for the analysis of UV spectra,[28] but, to our knowledge, not yet in NMR spectroscopy (H.D.).

† Me_3Si, an electron attractor, shows a downfield shift effect in Me_3Si–NSO ($\Delta\delta_O$ *ca.* 50 ppm),[11b] comparable but smaller than the downfield effect which Me_3Si exerts on the carbonyl oxygen in RCO–$SiMe_3$.[35]

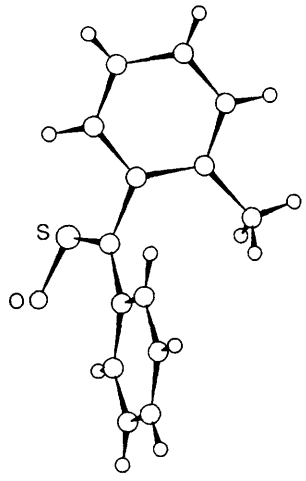
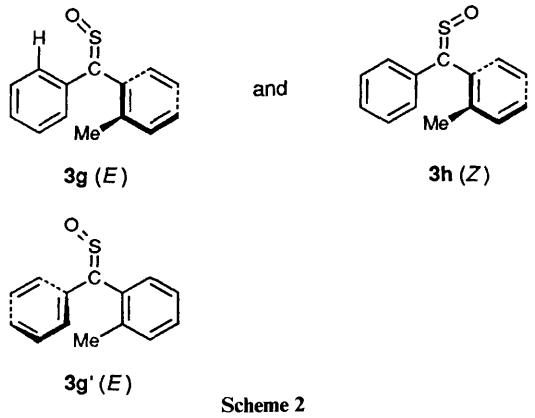


Fig. 1 X-ray structure of diarylsulfine **3g**

the *Z*-forms (**3h**, **l**, **j**). The same prediction, $\delta(anti) \sim \delta$(Me-free) $\neq \delta(syn)$, could be made for a conformation in which both arene rings are on average (nearly) perpendicular to the plane of the carbonyl group. However, the experiments (Table 3) clearly show the contrary for each of the three groups of compounds (X = H, Cl, MeO): the shift values δ_O of the *Z*-isomers are close to those of the Me-free compounds ($\pm$ 1–2 ppm), whereas the *E*-isomers are found *ca.* 10 ppm downfield.

This result can be explained on the basis of specific non-coplanar conformations: conjugational effects would tend to make one of the arene rings (nearly) coplanar with the sulfine group; in the *Z*-isomer this is the Me-free benzene ring. The *o*-tolyl ring is (nearly) perpendicular to that plane. In the *E*-isomer the mutual position of the two arene rings and of the plane of the CSO group remain the same as in *Z*, but the sulfine-O is turned towards the coplanar benzene ring. In this configuration the *Z* isomers are expected to show the same shift values as the corresponding Me-free compounds: their O atoms are in similar positions. The *E*-isomers differ, as the O atoms are subject to slight steric compression from a coplanar aromatic hydrogen atom. It is well known that in ^{17}O NMR compressional effects (as well as steric hindrance of resonance) induce downfield shifts;[18] this explains the *ca.* 10 ppm lower-field shift of the *E*-isomers. It is confirmed by the shift value of the coplanar 2-methylfluorenylsulfine **3m**, which has an *anti* configuration analogous to the non-cyclized *E*-compound **3g**, and in which the (near) coplanarity of the oxygen with the aromatic hydrogen atom is enforced: δ_O of **3m** is quite close to that of **3g**, 229.9 and 227.5 ppm respectively.



Scheme 2

It should be mentioned that none of the ^1H and ^{13}C arguments cited above is in contradiction with the conformations developed here. Even more so, the new conformations for **3g** and **3h** allow us to understand an older, unexplained observation[21] (confirmed by us): in the LIS experiment the protons in the 2,6-position of the phenyl group of the *E*-isomer **3g** (SO/Ph *syn*) are 2.1 times more sensitive to the lanthanide shift reagent than the 6-proton of the tolyl ring of the *Z*-isomer (SO/Tol *syn*). The reason is that in the *E*-isomer the complexing SO group comes very close to the (nearly) coplanar phenyl-H, whereas in the *Z*-isomer SO is (nearly) perpendicular to the tolyl ring.

At first sight one might have hesitated to assign the *E*-isomer to the conformation **3g** and not to the alternative **3g'**, in which the *o*-tolyl ring is (nearly) coplanar with the sulfinyl group and the phenyl group perpendicular to it; this would avoid the compression of O with the coplanar aryl-H. However, this conformation has to be excluded because it is not in agreement with the ^{17}O results of Table 3, nor with the LIS result cited above. The explanation is that in **3g'** there would be interaction of the methyl group with the π-electron cloud of the benzene ring forced into its proximity. It means that, for the stability of the *E*-isomer, crowding between O and the coplanar aryl-H is less unfavourable than crowding between Me and the perpendicular arene ring. Actually, the long bond length C–S in the sulfinyl group and the bond angle C–S–O = 115°[19] make the interaction of O with the coplanar aromatic H thermodynamically sustainable (though spectroscopically observable).

The conclusions given above concerning the conformations in solution have been fully supported by an X-ray analysis of the *E*-isomer **3g** (Fig. 1).[37] It confirms the *anti* configuration, and shows the (nearly) coplanar conformation of the phenyl ring with the C–C(=S=O)–C group [the S–O bond presents a torsion angle of 15° with respect to C(CSO)–C(ipso)]. The tolyl ring forms an angle of 66° with that plane. The distance of the O atom to the interfering coplanar aromatic *ortho*-H is 2.30 Å. In the model **3g'**, in which the tolyl ring is coplanar with the sulfinyl group and the phenyl ring perpendicular (created by computer manipulation of the crystallographic data) the hindrance between the methyl group and the phenyl ring is clearly visible: the distance between the *ipso*-carbon of the phenyl ring and the closest Me-H of the tolyl group is only 1.84 Å, too small, particularly in view of the 'thickness' of the aromatic ring.

Conclusions

^{17}O NMR shift values and substituent sensitivities have been found useful (a) to distinguish the π-bound S=O compounds SO_2 **1**, sulfinylamines **2** and sulfines **3** from $S^+–O^-$ containing sulfoxides, sulfones, sulfonates *etc.*; (b) to differentiate **1**, **2** and **3** from one another, discussing bond order and UV energy terms; (c) to observe resonance type interactions of the electron attracting sulfinylamino group –N=S=O with n-donors; (d) to elucidate the conformations of *ortho*-substituted *E*- and *Z*-diarylsulfines.

Experimental

^{17}O NMR spectra were recorded on a Bruker WH-360 spectrometer equipped with a 10 mm probe at 48.8 MHz in the Fourier transform (FT) mode without lock. System control, data acquisitions and data managements were performed by an Aspect-2000 microcomputer. The instrumental settings were as follows: spectral width 50 000 Hz (1025 ppm); 2 K data points; pulse width 33 μs; acquisition time 20 ms; preacquisition delay 5 μs; 1.4–2.3 M scans; measurements were made with sample spinning (27 Hz). An even number (28–32) left-shifts (LS) were applied to the FID signal; the latter was zero-filled to 8 K words, and exponentially multiplied with a 100 Hz line-broadening

factor (LB) before being subjected to the FT. The chemical shifts are reported relative to $\delta_O(H_2O) = 0.0$; dioxane ($\delta_O = 0$) was used as an external standard; downfield shifts are positive. The general reproducibility of chemical shift values is *ca.* ± 1 ppm (± 0.2 ppm within the same series). ^{1}H NMR spectra were measured at 200 MHz.

Compounds.—O-*Benzyl*-N-*sulfinylhydroxylamine*[38] **2t** was prepared from *O*-benzylhydroxylamine and $SOCl_2$ in the presence of pyridine,[39] and distilled in a Kugelrohr at 153–154 °C/50 Torr: ν_{max}(film)/cm^{-1} 1490, 1450, 1360, 1195 and 1015; δ_C($CDCl_3$, 62.8 MHz) 81.16 (CH_2).

Di-p-bromophenyl sulfine **3f**.[40] M.p. 106–108 °C (Found: 41.90; H, 2.16; S, 8.49. $C_{13}H_8Br_2OS$ requires C, 41.96; H, 2.17; S, 8.62%); ν_{max}(CS_2)/cm^{-1} 1117 and 1005 (CSO); δ_H(200 MHz; $CDCl_3$) 7.23 (2 H), 7.57 (2 H), 7.61 (2 H) and 7.72 (2 H); δ_C(50.3 MHz; $CDCl_3$) 131.1, 131.4, 132.6, 133.0 (arom.) and 186.6 (CSO).

LIS Experiments.—[21] To solutions of **3g** respectively **3h** in $CDCl_3$ were added increasing amounts of Eu(dpm)$_3$ (0.1 to 0.3 mol per mol of sulfine), and the ^{1}H spectrum recorded.

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