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Note

^{17}O NMR of a Thiirene-1-oxide and Related Sulfoxides†

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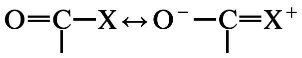
ABSTRACT: In contrast to carbonyl compounds, the ^{17}O chemical shifts of aryl sulfoxides are deshielded by electron donor substituents and show only slight sensitivity. In a thiirene-1-oxide the effect of interaction between the C=C and S—O groups is also small. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{17}O NMR; sulfoxides; substituent effects; thiirene-1-oxide

The difference in bonding between carbonyl groups, which show true π bonds subject to resonance **A** ↔ **B**, and sulfinyl groups with semipolar bonds **C**:[2]

$$\begin{array}{ccc} >\!C{=}O \leftrightarrow\, >\!C^{+}{-}O^{-} & & >\!S^{+}{-}O^{-} \\ \mathbf{A} \qquad\quad \mathbf{B} & & \mathbf{C} \end{array}$$

manifests itself very clearly in the ^{17}O NMR spectra. In simple aldehydes and ketones the oxygen is strongly deshielded [$\delta(^{17}\text{O}) \approx 550$ ppm], this being attributed[3] to the simultaneous presence, in the C=O π bond, of a relatively high-energy n orbital and a low-lying π* orbital, which are mixed under the influence of the external magnetic field. By contrast, in the absence of a π bond and its corresponding n–π* excitation, the sulfoxide oxygen is shielded, similarly to that of an S—O single bond [$\delta(^{17}\text{O}) \approx 0$ ppm, Table 1]. Furthermore, by resonance



$$O{=}\underset{|}{C}{-}X \leftrightarrow O^{-}{-}\underset{|}{C}{=}X^{+}$$

electron-donating groups bound to the carbonyl group strongly increase the shielding of the oxygen; for instance, in acetyl compounds MeCOX (compared with MeCOMe), X = Cl makes an upfield shift of $\Delta\delta = -67$ ppm, X = OMe $\Delta\delta = -214$ ppm and X = NMe$_2$ $\Delta\delta = -228$ ppm.[1,4a] On the other hand, in methane sulfinyl compounds MeSOX, where resonance is absent, the effect of these substituents (compared with MeSOMe) is in the opposite direction: for X = Cl one

Table 1. ^{17}O chemical shifts of substituted diaryl sulfoxides Ar–SO–Ar′ (1)[a]

Compound	Ar	Ar′	$\delta(^{17}\text{O})$(ppm)[b]
1a	Ph	Ph	3.4 (3.7,[c] 2[d])
1b	Ph	p-MeC$_6$H$_4$	4.3 (2.4[e])
1c	Ph	p-ClC$_6$H$_4$	3.5
1d	Ph	p-MeOC$_6$H$_4$	6.7[f]
1e	Ph	p-Me$_2$NC$_6$H$_4$	10.2[c]
1f	Ph	Mesityl	−1.6
1g	p-ClC$_6$H$_4$	p-ClC$_6$H$_4$	4.5
1h	p-MeOC$_6$H$_4$	p-MeOC$_6$H$_4$	10.4[g]
1i	p-Me$_2$NC$_6$H$_4$	p-Me$_2$NC$_6$H$_4$	12.2[c]
1j	Mesityl	Mesityl	10.4
1k	p-ClC$_6$H$_4$	p-Me$_2$NC$_6$H$_4$	11.4[c]
1l	Ph	1-Naphthyl	2.5
1m	Ph	2-Naphthyl	4.1
1n	1-Naphthyl	1-Naphthyl	7.6[c]
1o	Ph	PhCH$_2$	5.9 (5.8,[c] −14[h])

[a] 0.5 M solution in CCl$_4$ at 50 °C, unless stated otherwise. δ(H$_2$O) = 0.0 ppm.
[b] Linewidth: 200–400 Hz for **1a**–**e**, **g**–**i**, **k**, **o**, **p**; 400–600 Hz for **1f**, **l**–**n**; 1000 Hz for **1j**.
[c] 0.5 M solution in toluene at 60 °C.
[d] Ref. 7: solvent CH$_2$Cl$_2$.
[e] Ref. 7: solvent CDCl$_3$.
[f] δ(OMe) = 61.2 ppm.
[g] δ(OMe) = 53.5 ppm.
[h] Ref. 7: neat.

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† NMR of Terminal Oxygen, Part 21. For Part 20, see Ref. 1.

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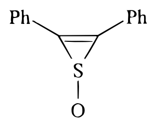
finds $\Delta\delta = +177$ ppm, for OMe $\Delta\delta = +127$ ppm and for NMe_2 $\Delta\delta = +57$ ppm.[5] It is the purpose of this paper to extend the difference in ^{17}O shifts between carbonyl and sulfinyl groups by further comparisons.

The carbonyl oxygen in benzaldehydes and acetophenones is sensitive to the effect of electron-donating and -attracting substituents in the aryl ring. For instance, in acetophenone the shielding effect of a methoxy group in the *para* position is $\Delta\delta(^{17}O) = -18$ ppm,[4a,6] and even in benzamide, a compound in which the sensitivity of $\delta(^{17}O)$ towards substituent effects is strongly diminished, $\Delta\delta(^{17}O)$ is still -4 ppm;[1] in both cases, the effect on $\delta(^{17}O)$ follows the donor–acceptor properties of the substituent.[1] By contrast, in the corresponding methyl aryl sulfoxides the substituent effect of the *p*-methoxy group is zero[7] or, in other cases, even in the opposite sense. We found that in diaryl sulfoxides one *p*-methoxy group makes $\Delta\delta(^{17}O) = +3$ ppm deshielding (**1d**, Table 1), two *p*-MeO groups in the *p,p'*-disubstituted compound $\Delta\delta(^{17}O) = +7$ ppm (**1h**, Table 1). Other electron donors in *para* positions also show small and deshielding effects (Table 1). The same behavior of small deshielding effects by electron-donor (and also by electron-attractor) substituents in the *para* position had been reported before for derivatives of arenesulfinic acids ArSOX (X = OMe, O—, NH_2);[8] it can also be found in sulfonyl derivatives such as methyl aryl sulfones[9] and arenesulfonic acid derivatives.[8,10]

In aryl groups in carbonyl systems, which impose torsion angles between the ring and the C=O group, conjugation is diminished and thus the chemical shift value of O is increased; e.g. in acetophenones ArCOMe with Ar = mesityl one finds shift differences $\Delta\delta(^{17}O) = +49$ ppm and with Ar = α-naphthyl $\Delta\delta(^{17}O) = +33$ ppm.[4b] Sulfoxides, lacking coplanarity, are not expected to show this effect; accordingly, we found that mesityl and α-naphthyl groups produce only very small changes in $\delta(^{17}O)$ in diaryl sulfoxides (**1f**, **j**, **l**–**n**, Table 1).

A particular situation had been found in cyclopropenones. In general, conjugation with a CC double bond hardly affects ($< \pm 10$ ppm) the ^{17}O shift values of ketones (including, e.g., cyclic ketones);[4a] however, there is a very strong shielding effect on going from acetone [$\delta(^{17}O) = 571$ ppm] or from a cyclopropanone [$\delta(^{17}O) = 524$ ppm for R = *t*-Bu] to a cyclopropenone [$\delta(^{17}O) = 246$ ppm for R = Ph; $\delta(^{17}O) = 234$ ppm for R = Me].[11] This effect is attributed to particularly strong polarization (towards **B**) of the carbonyl group, due to partial aromaticity of the cyclopropenone ring.[12] It expresses itself also in high shielding of the carbonyl carbon, $\delta(^{13}C)(CO) = 155$ ppm, instead of $\delta(^{13}C)(CO) = 215$ ppm in a cyclopropanone and 207 ppm in acetone.[13] These ^{17}O and ^{13}C effects, specific to the three-membered ring system, are absent in five- and six-membered ring enones.



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ArSOCH=CHPh

3a Ar = Ph
b Ar = *p*-Tol

Table 2. ^{17}O chemical shifts of unsaturated sulfoxides[a]

Compound	$\delta(^{17}O)$ (ppm)[b]
2	18.0
3a	4.1
3b	5.0

[a] 0.5 M solution in toluene at 60 °C (**2a**, **b**) or 25 °C (**3**).
[b] Linewidth 200–300 Hz.

The corresponding thiirene-1-oxides have been the subject of considerable theoretical interest because of their possible antiaromaticity.[14] They show shorter S—O bonds and higher IR frequencies than normal, open-chain sulfoxides.[15] Recent calculations have demonstrated the absence of antiaromaticity;[16] actually, the diphenyl derivative **2** has proved to be remarkably stable.[17] We found that its ^{17}O signal, at + 18 ppm, is close to the general region of open-chain sulfoxides, both saturated [$\delta(^{17}O) \approx 0$ to $+15$ ppm[18]] and unsaturated [$\delta(^{17}O) \approx 5$ ppm; **3a**, **b**, Table 2]. A small deshielding effect upon cyclization contrasts with the strong shielding in the case of cyclopropenones; whether it can be seen in relation to the increased bond strength of the S—O bond cannot be decided.

A deshielding effect introduced by the double bond would appear even more pronounced if one compares the $\delta(^{17}O)$ value of **2**, $\delta(^{17}O) = 18$ ppm, with that of the saturated thiirane-1-oxide, $\delta(^{17}O) = -71$ ppm.[19] This might be due, however, to particularly high shielding in the latter, which distinguishes it from all measured saturated or unsaturated sulfoxides, and has so far not found a satisfactory explanation.

EXPERIMENTAL

Spectra

Natural abundance ^{17}O NMR spectra were recorded on a Bruker WH-360 instrument equipped with a 10 mm probe at 48.8 MHz in the Fourier transform (FT) mode without lock. System control, data acquisition and data management were performed by an Aspect-2000 microcomputer. The instrumental settings were as follows: spectral width, 50 000 Hz (1025 ppm), 2K data points, pulse width 33 μs, acquisition time 20 ms, pre-acquisition delay 5 μs and 1.5K–2.3M scans; measurements were made with sample spinning (27 Hz). An even number (8–28) of left shifts (LS) were applied to the FID signal; the latter was zero-filled to 8K words, exponentially multiplied with a 100 Hz line-broadening factor (LB) before being subjected to FT. Chemical shifts are reported relative to $\delta(H_2O) = 0.00$ ppm; dioxane ($\delta = 0$ ppm) was used as an external standard; downfield shifts δ and increased shielding σ are positive.

The reproducibility of chemical shift values is $< \pm 1$ ppm.

Compounds

Sulfoxides **1a–h**, **j–m**, **o** and **p** and **3a** and **b** were prepared by the reaction of the corresponding methyl arylsulfinate with an arylmagnesium reagent[20] and **1i** and **n** from *N*,*N*′-thionyldiimidazole with the corresponding arylmagnesium reagent.[21] Compounds **1a**,[7] **g–j**,[21] **o**[7] and **p**,[7] **2**[17] and **3b**[22] were known. All compounds were characterized by ^{1}H NMR and IR spectra [ν(S–O): 1030–1040 cm^{-1}]. The new compounds showed correct combustion analysis data, with the exception of the oily products **1f** and **3a**, which were used in crude form.

p-Methylphenyl phenyl sulfoxide (**1b**), m.p. 69–73 °C (recrystallized from diethyl ether–light petroleum); *p*-chlorophenyl phenyl sulfoxide (**1c**), m.p. 48–49 °C (from diethyl ether–light petroleum); *p*-methoxyphenyl phenyl sulfoxide (**1d**), m.p. 63–64 °C (from diethyl ether); *p*-*N*,*N*-dimethylaminophenyl phenyl sulfoxide (**1e**), m.p. 134–138 °C (from CH_2Cl_2–diethyl ether); mesityl phenyl sulfoxide (**1f**), oil; *p*-*N*,*N*-dimethylaminophenyl *p*-chlorophenyl sulfoxide (**1k**), m.p. 123–127 °C (from CH_2Cl_2–diethyl ether); 1-naphthyl phenyl sulfoxide (**1l**), m.p. 89–94 °C (from diethyl ether); 2-naphthyl phenyl sulfoxide (**1m**), m.p. 57–60 °C; bis(1-naphthyl) sulfoxide (**1n**), m.p. 168–170 °C (from CH_2Cl_2–diethyl ether); 2,3-diphenylthiirene-1-oxide (**2**),[17] m.p. 95–96 °C (from ligroin), ^{13}C NMR ($CDCl_3$) 137.6 ppm (s, CSO), IR (S–O) 1065 cm^{-1}; (*E*)-2-phenylethenyl phenyl sulfoxide (**3a**), oil.

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