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NMR of Terminal Oxygen 6*— ^{17}O NMR of the S—O 'Double Bond': Derivatives of Arylsulphinic and Arylsulphonic Acids

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The ^{17}O NMR spectra of terminal oxygen atoms in esters, anions and amides of substituted arenesulphinic acids and in esters and amides of substituted arenesulphonic acids were measured. The signals of the terminal O appear close to those of the bridge O. Compared with carbonyl O, terminal S—O shows (a) a lower sensitivity to the electronic influences of geminal groups, (b) only a low sensitivity to arene ring substituents and (c) small solvent effects. The difference between C- and S-bound O is discussed in terms of π-bond character. Dy^{3+} complexation occurs with the terminal O in methyl arenesulphinates.

KEY WORDS ^{17}O NMR Arenesulphinyl esters Arenesulphinylamides Arenesulphinates Methyl arenesulphonates Arenesulphonamides SCS effects Lanthanide shifts

INTRODUCTION

To characterize the 'double' bond between sulphur (or other second-row main group elements) and oxygen,[2] the classical picture of a 'semipolar' $S^+—O^-$ bond has been replaced for some time by that of a σ-bond strengthened by a π-bond using a d-orbital of the S atom (π_d-bond).[3] The participation of d-orbitals has been contested for theoretical reasons,[4] but is still often discussed.[5] New experimental results would be welcome. ^{17}O NMR is a technique, which, owing to its large spectral window (>1000 ppm for organic compounds) combined with good precision and reproducibility, and high sensitivity to structural effects, is a valuable tool in characterizing the bonding situation of oxygen atoms.[6]

For oxygen atoms bound to carbon we have demonstrated[7] a fundamental difference between a bridge O, which gives signals at high field (typically 0–100 ppm), and a terminal O, which is found at much lower field (e.g. *ca.* 550 ppm for aldehydes). Further, —O— is much less sensitive to structural influences than =O; the resonance effects of electron donating geminal groups X in —CO—X are particularly important; they increase the shielding of O: PhCO—Me 549, PhCO—Cl 484, PhCO–OCOPh 386, PhCO—F 353, PhCO—OMe 337, PhCO—NH_2 326, PhCO—O^- 265 ppm.[8] The shift values of the carbonyl oxygen are also influenced by the electronic effects of substituents in neighbouring aryl groups (Y in *p*-YC_6H_4CO—).[9] The shielding of carbonyl O atoms is sensitive to solvent effects,[10] to complexation with lanthanide shift reagents (in particular Dy^{3+} complexes)[11] and, as Boykin and Baumstark[12] have shown, to steric hindrance.

It has already been pointed out[6,13] that the spectral range of S-bound oxygen (*ca.* 200 ppm in organic compounds) is much narrower than that of C-bound oxygen (>700 ppm). Further, the difference between a bridge and terminal O can be small or negligible: MeO—S—S—OMe δ = 14 ppm, Me_2S=O 13 ppm.[7] The same is true when the two types of O are simultaneously linked to the same S, as for instance in arylsulphonates, $ArSO_2OR$. We present here the results of a systematic study of the ^{17}O NMR spectra of derivatives of arylsulphinic acids, ArSO—X, and arylsulphonic acids, $ArSO_2$—X. ArSOOH is the simplest S compound containing simultaneously terminal and bridge O and it presents a superficial similarity with ArCOOH.[14] Derivatives of $ArSO_3H$ were chosen for comparison; some compounds have already been measured by Barbarella[15] and Häkkinen and Ruostesuo.[16] As shift values are subject to too many, often unknown, influences we applied two chemically more significant criteria: the effect of geminal groups X bound to sulphur and the sensitivity to substituents in Ar (including steric hindrance).

RESULTS AND DISCUSSION

The following groups of compounds have been measured: esters (methyl **1** and ethyl **2**) of arenesulphinic acids ArSO—OR, anions $ArSOO^-$ **3** and amides ArSO—NH_2 **4**; electron-donating or -attracting substit-

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uents were introduced in to the *para* positions of the aryl group. Some compounds in which resonance, if it exists, would be sterically hindered by torsional effects are included (Table 1). In the arenesulphonic series methyl esters $ArSO_2$—OMe **5** and a few amides $ArSO_2NH_2$ **6** (see also Ref. 16) were measured (Table 2). Most compounds were obtained by standard procedures or were commercially available.

		Ar		Ar	
ArSOOMe	1	Ph	a	p-$O_2NC_6H_4$	g
ArSOOEt	2	p-$MeOC_6H_4$	b	m-$O_2NC_6H_4$	h
$ArSO_2^-Na^+$	3	p-MeC_6H_4	c	2,4,6-$Me_3C_6H_2$	i
$ArSONH_2$	4	p-FC_6H_4	d	1-Naphthyl	k
$ArSO_2OMe$	5	p-ClC_6H_4	e	2-Naphthyl	l
$ArSO_2NH_2$	6	p-NCC_6H_4	f		

Assignment of signals in esters

The identification of neighbouring signals in arylsulphinic esters, ArSOOR, was achieved by a variation of R: on replacing Me by Et the signal at *ca.* 115 ppm changed only by 2 ppm, whereas the other, more sensitive signal ($\Delta\delta \approx 30$ ppm), must correspond to the —OR bridge. The shift difference of *ca.* 30 ppm downfield is similar to that between methyl and ethyl acetate ($\Delta\delta = 29$ ppm).[7] We have used the same method to confirm the tentative assignment of the signals in dimethyl sulphite, $(MeO)_2SO$ ($\delta = 176$ and 115 ppm),[7] by measuring diethyl sulphite ($\delta = 178$ and 149 ppm, in MeCN solution), and in dimethyl sulphate, $(MeO)_2SO_2$ ($\delta = 150$ and 102 ppm),[7] by measuring diethyl sulphate ($\delta = 148$ and 131 ppm, MeCN); in both cases the terminal O resonates at slightly lower field than the bridge O.

In methyl *p*-toluenesulphonate the peak assignment was made by specific labelling: p-$MeC_6H_4S^{17}O_2OMe$ was prepared from the labelled sulphochloride (obtained via hydrolysis of unlabelled tosyl chloride with enriched $H_2{}^{17}O$); the label appeared in the low-field peak (156 ppm). In the other arenusulphonate esters the peaks were assigned by analogy.

As a first general result one can state (Table 1 and 2) that the shift difference between S=O and S—O—R is small, and not always unidirectional, in contrast to the large shift difference (*ca.* 200 ppm upfield) between C=O and C—O—R in carboxylic esters.[7]

Effect of geminal bound atoms

On going from —SO— to the analogous —SO_2— compound the additional oxygen atom has a significant, although not very large, effect on the shift value of the terminal O: *ca.* 40 ppm downfield on going from sulphinic to sulphonic esters, and *ca.* 60 ppm downfield for the corresponding amides (Tables 1 and 2). A larger downfield effect had been found for the difference between sulphoxides (*ca.* 0 ppm) and sulphones (*ca.* 150 ppm)[17] or sulphinates (*ca.* 115 ppm).[15] The deshielding

Table 1. ^{17}O NMR shift values[a] of derivatives (1–4) of arenesulphinic acids, ArSOX

		ArSO—OMe[b] (1)		ArSO—OEt[b] (2)		$ArSO_2Na$[c] (3)	$ArSONH_2$[d] (4)
No.	Ar	δ(=O)[e]	δ(—O—)[f]	δ(=O)[g]	δ(—O—)[h]	δ(O)[i]	δ(O)[j]
b	p-$MeOC_6H_4$	114.9	100.1[k]	116.7	133.5[l]		100.2[m]
c	p-MeC_6H_4	113.3	97.4	116.8	130.3	145.7	99.3
a	Ph	114.9	97.8[n]	117.6	129.9	145.6	99.2
e	p-ClC_6H_4	116.0	98.0	118.5	131.6	146.5	100.2
f	p-NCC_6H_4	116.3	100.3	119.1	132.0	146.0	
g	p-$O_2NC_6H_4$	118.7	100.3	121.7	132.0	147.0	101.0[o]
h	m-$O_2NC_6H_4$			120.9	130.0		
i	Mesityl	131.0	106.1	133.2	133.2		105.1
k	1-Naphthyl	106.7	92.7	117.3	130.5		
l	2-Naphthyl			109.0	130.7		
		$\rho = 3.4$		$\rho = 3.8$		$\rho \approx 1$	$\rho \approx 1$
		$r = 0.85$		$r = 0.92$			
		S.D. = 1.0		S.D. = 0.80			

[a] From external tap water.
[b] 0.5 M in CCl_4 at 48 °C.
[c] 0.5 M in ^{17}O-depleted water at 40 °C.
[d] 0.5 M in MeCN at 60 °C.
[e] Line width 50–200 Hz.
[f] Line width 200–400 Hz.
[g] Line width 100–300 Hz.
[h] Line width 300–700 Hz.
[i] Line width 150–180 Hz.
[j] Line width 60–120 Hz.
[k] δ(OMe) = 59.7.
[l] δ(OMe) = 58.5.
[m] δ(OMe) = 53.8.
[n] δ(=O) = 115.7; δ(—O—) = 99.0 (1.1 M in MeCN at 40 °C; measured by Dr P. Péchy). δ(=O) = 109.5; δ(—O—) = 96.9 (1.0 M in MeOH at 40 °C).
[o] $\delta(NO_2)$ = 577.6.

Table 2. ^{17}O NMR shift values[a] of methyl arenesulphonates (5) and arenesulphonamides (6)

No.	Ar	$ArSO_2OMe$[b] (5) $\delta(=O)$[d]	$\delta(-O-)$[e]	$ArSO_2NH_2$[c] (6) $\delta(O)$[f]
b	p-$MeOC_6H_4$	156.8	122.7	
c	p-MeC_6H_4	157.2	121.9	164
a	C_6H_5	157.6[g]	121.2	163
d	p-FC_6H_4	158.3	121.6	
e	p-ClC_6H_4	158.3	122.7	165
g	p-$NO_2C_6H_4$	159.5	123.1	166
		$\rho = 2.43$		$\rho \approx 2.6$
		$r = 0.96$		
		S.D. = 0.28		

[a] From external tap water.
[b] 4.5 M in $CHCl_3$ at 60 °C.
[c] 4 M in DMSO at 85 °C.
[d] Line width 50–100 Hz.
[e] Line width 150–200 Hz.
[f] Line width 300–500 Hz (for **6g** > 1000 Hz).
[g] The same value was found for **5c**[$S=^{17}O$].

effect has been attributed to increased π-bond character,[13] but other factors cannot be excluded (see below).

In acyl derivatives, RCOX, changes in X influence the shift values greatly and increasing their electron donating power enhances the shielding of O: between X = Me (acetophenone) and $X = O^-$ (benzoate anion) the shift difference is −283 ppm (upfield).[8] In the PhSOX series the effects are smaller and in the opposite direction: $\Delta\delta = +138$ ppm between X = Me[18] and $X = O^-$. They do not behave as a function of the p donating power of X, a fact which demonstrates that resonance interactions are not a determining factor here. The series of $PhSO_2X$ compounds shows an even lower influence from X and $\Delta\delta = +22$ ppm (between X = Me[18–20] and $X = O^-$ [21]); electron-attracting atoms are deshielding. In both series, as in that of sulphate derivatives, only X = Cl has a larger deshielding effect which is, however, not yet understood.[22]

Effects of *para* substituents in the aromatic ring

As mentioned above, some carbonyl oxygen shifts are very sensitive to electronic influences exerted by aryl ring substituents. Chemical shift values are determined by electronic excitation energy, atomic orbital dimension and a bond order–charge density term.[23] For benzoyl derivatives the latter term is prevalent; this we have shown[8] by applying the 'tool of increasing electron demand,' a method originally developed for the characterization of carbenium ions:[24] the greater the electron deficiency of an unsaturated centre, the more will its properties (spectroscopic or other) be sensitive to electronic influences of substituents in the arene ring (the sensitivity being expressed by a Hammett type ρ coefficient). The 'tool' can be used to give a measure of the π-bond character (electrophilicity) of a carbonyl group in YC_6H_4COX: the arene substituent sensitivity ρ depends on the electron demand of C=O, and is therefore modified by electron-donor groups X attached to CO. For instance in *para*-substituted benzaldehydes the shift difference between an Me_2N and an O_2N group is 67 ppm downfield (Hammett type sensitivity: $\rho^+ = 26.3$), whereas in benzoate ions it is only 14 ppm ($\rho^+ = 5.1$).[8] For most COX groups it emerged that the substituent sensitivity, ρ^+, is paralleled by the shift value δ of PhCOX: PHCHO 574 *vs.* $PhCOO^-$ 265 ppm; this demonstrates the prevalence of the π-order term for the determination of δ(O) in this class of compounds.

Comparison with SO and SO_2 systems shows (Tables 1 and 2) that in none of the four series of sulphinic acid derivatives **1–4** does the substituent shift range exceed a few ppm. If one attempts to correlate the δ values with Hammett substituent constants σ (better than σ^+), the sensitivity values, ρ, obtained are small, 3.4 for **1** and 3.8 for **2** and *ca.* 1 for **3** and **4**; they show poor correlation coefficients. The same is true for the sulphonic acid derivatives: $\rho = 2.4$ for **5** and *ca.* 2.6 for **6** (in agreement with published data[16]). For the anions $ArSO_3^-$ Bugner[21] has found $\rho = 1.8$, which fits well with our results. In these series, electron-attracting substituents diminish the shielding. *M* donors, such as MeO increase it slightly; whether this occurs via a small contribution by electron attraction of the $S^+—O^-$ group, or by a different effect, cannot be distinguished. At any rate it has to be concluded that, in contrast to —COX, resonance effects and π-bond order to not play a significant role in determining the shift values in —SOX and $—SO_2X$ compounds.

The substituent sensitivities of the bridge O in the sulphinic and sulphonic ester series is still smaller than that of the terminal O, i.e. close to zero.

Steric effects. The largest deviation from the mean shift value for the terminal O in the sulphinic esters **1** and **2** is found for the mesityl derivatives **1i** and **2i**, which show $\Delta\delta = 16$ ppm (downfield) for the terminal O, but almost no effect for the bridge O. This is, of course, not a purely electronic effect, but must have a steric component. Steric disturbance of resonance by torsional interactions, resulting in downfield shifts (*ca.* 30 ppm), has been found in many aromatic carbonyl compounds,[12] but cannot be the origin of the shift difference in arylsulphinic esters. The effect might be attributed either to molecular distortion, as in pyridine *N*-oxides,[25] or to van der Waals compression,[26] which have both been shown to cause downfield shifts.

Comparison with ^{33}S NMR. It should be mentioned that, in contrast to the O atoms, the central sulphur of the arenesulphonates shows an inverse ('reverse') aryl substituent effect in ^{33}S NMR: electron-attracting substituents in Ar enhance the shielding (for $ArSO_3^-$ $\rho = -4.3$);[27] the same can be deduced from 3 data on ^{33}S of arylsulphones[28] (which also show a normal substituent effect on ^{17}O). Inverse aryl substituent effects are generally found in the NMR spectra of the central Z atom of compounds of the type Ar—Z—X (with X = N, O, F or $=CR_2$ in a π-system). The inverse effect has been found, for instance, for Z = C in several benzoyl derivatives[29] and in benzonitriles,[29,30] and for Z = N in nitrobenzenes.[31] In these cases, as in all others, the terminal X (e.g. O) shows a normal aryl substituent effect, i.e. electron-attracting substituents diminish the shielding.

The inverse effect on the central Z atom has been explained[29] by π-polarization, a particular electronic transmission mechanism involving through-space polarization of the side-chain π-system by the substituent dipole. This explanation, however, leaves unexplained the fact that the inverse aryl substituent effect also exists with side-chains devoid of π-systems, as with Z = C in benzotrifluorides.[32] and with second-row Z elements such as Si in arenetrifluorosilanes[33] and related compounds, Z = P in arenephosphonates and arenedifluorophosphonates,[34] and Z = S as mentioned above. As one can hardly believe that an aryl substituent exerts a considerable change on the polarization of, for example, a highly polarized $S^+—O^-$ bond in arenesulphonates, one has to admit that a comprehensive theory of the inverse substituent effect still seems to be lacking.

Solvent effects

In the system acetonitrile–water, the terminal O of **1a** is shifted upfield with increasing amounts of water, more so than the bridge O. In both, however, the effect is only a few ppm (see also Ref. 35), which is small compared with that for acetone[10] or for pyridine *N*-oxide.[24] It seems that hydrogen bonding in protic solvents plays a lesser role in sulphinates.

Effects of Dy^{3+}

As lanthanide shift reagents form complexes directly with oxygen atoms of the substrate, their shift effects upon ^{17}O signals are one to two orders of magnitude larger than those on ^{13}C or ^{1}H. $Dy(dpm)_3$ has been shown to be the most effective reagent in ^{17}O NMR;[11] the mechanism is essentially that of a contact shift. With a carbonyl O the shift effect, extrapolated to $[Dy(dpm)_3]:[substrate] = 1$, is several thousand ppm upfield. Bridge O atoms normally show lower $\Delta\delta$ values:[11] for methyl *p*-methylbenzoate we found $\Delta\delta(=O) = -3200$ ppm, $\Delta\delta(—O—) = -110$ ppm. For sulphones, lanthanide shifts, $\Delta\delta$, of *ca.* -1000 ppm have been reported.[36] We have chosen **1a** to compare the shift effects upon =O and —O—.

On applying increasing amounts of $Dy(dpm)_3$ to a solution of **1a** in CCl_4, we found a significant upfield shift effect on the terminal O, which finally appeared at $\delta = 26$ ppm (at [Ln] = 0.021 M, [substrate] = 0.57 M); extrapolated to 1:1, one obtains $\Delta\delta(=O) = -2500 \pm 500$ ppm. On the other hand, the bridge O was very little influenced: $\delta = 93$ ppm [$\Delta\delta(—O—) = -100 \pm 100$ ppm]. It is clear that the complexation takes place at the terminal and not at the bridge oxygen, nor at the nucleophilic S, where both O signals would be expected to be influenced in a similar way.

CONCLUSION

In nearly all S—O compounds the terminal O is not bound by a true π-bond (except in SO_2). The stereochemistry at S, pyramidal or tetrahedral, is so different from the planar configuration of a carbonyl group that similarity cannot be expected. In ^{17}O NMR the difference is borne out not only by the shift values of S=O, which are at considerably higher field than C=O (except in SO_2[13]), but also, more significantly, by a much lower sensitivity towards geminal atoms and towards arene substituents. All values are hardly differentiated between terminal and bridge O, in contrast to vibrational spectra[37] and bond lengths.[38] The difference in sensitivity properties between C=O and S=O is interpreted as a difference in π-bond character: the results are in agreement with a polarized formulation $S^+—O^-$, with π-bond character (by back-donation; assuming that π_d has characteristics similar to π_p) either absent or of little importance.

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, 50000 Hz (1025 ppm); 2K data points; pulse width 33 μs; acquisition time, 20 ms; preacquisition delay, 5 μs; 1400–2300 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 8K 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 $\delta(H_2O) = 0.00$ ppm; dioxane ($\delta = 0.0$ ppm) 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). For solvents, sample concentrations and temperature conditions, see Tables 1 and 2.

^{1}H NMR spectra were recorded on a Bruker AC-250 or a Bruker WP-80 spectrometer; the peaks corresponding to aryl-H are not listed for the spectral characterization. Infrared (IR) spectra were recorded on a Perkin-Elmer 1420 spectrophotometer. Melting points were measured on a Büchi 510 capillary apparatus and are uncorrected.

Liquid compounds were purified by distillation in a Kugelrohr at 1 Torr. Microanalyses were performed by Mrs I. Beetz (Kronach, Germany).

Materials

Compounds **5b** and **g** and **6** were commercially available, as were sodium benzene- and *p*-toluenesulphinate; the other starting sodium arenesulphinates were prepared by standard procedures.

Methyl and ethyl arenesulphinates (1, 2). *Procedure A (adapted after a method[39] of preparation of arenephosphinic esters).* Methyl *p*-cyanobenzenesulphinate (**1f**). To

a solution of *p*-cyanobenzenesulphinic acid (1.90 g, 11.5 mmol) in CH_2Cl_2 (50 ml) was added at 0 °C methyl chloroformate (1.10 g, 11.5 mmol) followed by pyridine (0.91 g, 11.5 mmol). After 1 h at 0 °C (evolution of gas), the homogeneous solution was washed with water and $NaHCO_3$ solution and dried ($MgSO_4$). After solvent removal the crude product was distilled in a Kugelrohr (1 Torr, *ca.* 125 °C): 1.90 g (92% yield), colourless oil, IR (film): 2230 (CN), 1480, 1450, 1390, 1130 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): 3.65 ppm (s, 3 H). $C_8H_7NO_2S$: calculated, C 53.03, H 3.89, N 7.73, S 17.69; found, C 52.87, H 3.83, N 7.77, S 17.71%.

Procedure B.[40] Methyl *p*-chlorobenzenesulphinate (**1e**).[41] Sodium *p*-chlorobenzenesulphinate (2.0 g, 10 mmol, Aldrich) and methyl chloroformate (1.1 g, 11 mmol) in methanol (15 ml) were stirred for 1 h at room temperature. The solvent was evaporated and the residue was taken up in CH_2Cl_2 and washed with water. After drying ($MgSO_4$) and solvent evaporation, Kugelrohr distillation gave 1.0 g (47%) of **1e**. IR (film): 1570, 1470, 1390, 1130, 1080 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): 3.50 ppm (s, 3 H).

Methyl benzenesulphinate (**1a**)[42] (procedure B). IR (film): 1440, 1130 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): 3.50 ppm (s, 3 H). Ethyl benzenesulphinate (**2a**)[40] (procedure B). IR (film): 1590, 1490, 1440, 1380, 1130, 1005 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): 1.27 (t, $J = 7$ Hz, 3 H), 3.50–4.40 ppm (m, 2 H). Methyl *p*-methoxybenzenesulphinate (**1b**)[43] (procedure B). IR (film): 1590, 1490, 1455, 1300, 1250, 1170, 1125, 1080, 1020 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): 3.46 (s, 3 H); 3.90 (s, 3 H). Ethyl *p*-methoxybenzenesulphinate (**2b**) (procedure A). IR (film): 1590, 1490, 1460, 1440, 1300, 1250, 1130, 1020 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): 1.31 (t, $J = 7$ Hz, 3 H); 3.52–4.41 ppm (m, 2 H); 3.90 (s, 3 H). $C_9H_{12}O_3S$: calculated, C 53.98, H 6.04, S 16.01; found, C 54.00, H 6.00, S 15.92%. Methyl *p*-methylbenzenesulphinate (**1c**)[40] (procedure B). IR (film): 1590, 1490, 1450, 1130 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): 2.50 (s, 3 H); 3.50 ppm (s, 3 H). Ethyl *p*-methylbenzenesulphinate (**2c**)[40] (procedure B). IR (film): 1470, 1440, 1380, 1130, 1000 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): 1.30 (t, $J = 7$ Hz, 3 H); 3.55–4.42 ppm (m, 2 H). Ethyl *p*-chlorobenzenesulphinate (**2e**) (procedure A). IR (film): 1570, 1470, 1385, 1260, 1130 1080, 1010 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): 1.30 (t, $J = 7$ Hz, 3 H); 3.54–4.40 ppm (m, 2 H). $C_8H_9ClO_2S$: calculated, 46.95, H 4.43, Cl 17.32, S 15.67; found, C 47.01, H 4.37, Cl 17.30, S 15.78%. Ethyl *p*-cyanobenzenesulphinate (**2f**) (procedure A). IR (film): 2230 (CN), 1480, 1390, 1135, 1000 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): 1.35 (t, $J = 8$ Hz, 3 H); 3.61–4.25 ppm (m, 2 H). $C_9H_9NO_2S$: calculated, C 55.37, H 4.65, N 7.17, S 16.42; found, C 55.34, H 4.55, N 7.30, S 16.41%. Methyl *p*-nitrobenzenesulphinate (**1g**)[44] (procedure A). IR (film): 1600, 1520, 1340, 1130, 1100 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): 3.59 ppm (s, 3 H). Ethyl *p*-nitrobenzenesulphinate (**2g**)[44] (procedure A). IR (film): 1600, 1525, 1340, 1130, 1000 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): 1.38 (t, $J = 7$ Hz, 3 H); 3.60–4.52 ppm (m, 2 H). Ethyl *m*-nitrobenzenesulphinate (**2h**) (procedure A). IR (film): 1600, 1525, 1345, 1260, 1135, 1000 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): 1.35 (t, $J = 7$ Hz, 3 H); 3.50–4.50 ppm (m, 2 H), $C_8H_9NO_4S$: calculated, C 44.65, H 4.21, N 6.51, S 14.90; found, C 44.56, H 4.14, N 6.54, S 14.83%. Methyl 2,4,6-trimethylbenzenesulphinate (**1i**) (procedure A). IR (film): 1600, 1450, 1130 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): 2.28 (s, 3 H); 2.57 (s, 6 H); 3.77 (s, 3 H); 6.90 ppm (s, 2 H). $C_{10}H_{14}O_2S$: calculated, C 60.57, H 7.12, S 16.17; found, C 60.68, H 7.08, S 16.19%. Ethyl 2,4,6-trimethylbenzenesulphinate (**2i**) (procedure A). IR (film): 1600, 1440, 1380, 1130, 1010 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): 1.37 (t, $J = 7$ Hz, 3 H); 2.28 (s, 3 H); 2.60 (s, 6 H); 4.20 (q, $J = 7$ Hz, 2 H); 6.93 ppm (s, 2 H). $C_{11}H_{16}O_2S$: calculated, C 62.23, H 7.60, S 15.10; found, C 62.24, H 7.62, S 15.03%. Methyl 1-naphthylsulphinate (**1k**)[40,45] (procedure A). IR (film): 1590, 1500, 1450, 1120 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): 3.40 ppm (s, 3 H). Ethyl 1-naphthylsulphinate (**2k**) (procedure A). IR (film): 1590, 1500, 1380, 1125, 1000 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): 1.20 (t, $J = 7$ Hz, 3 H); 3.37–4.43 ppm (m, 2 H). $C_{12}H_{12}O_2S$: calculated, C 65.43, H 5.49, S 14.56; found, C 65.23, H 5.38, S 14.57%. Methyl 2-naphthylsulphinate (**1l**)[40,45] (procedure A). IR (film): 1620, 1570, 1500, 1450, 1340, 1265, 1120 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): 3.51 ppm (s, 3 H). Ethyl 2-naphthylsulphinate (21)[40] (procedure B). IR (film): 1580, 1500, 1380, 1340, 1120, 1010 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): 1.25 (t, $J = 7$ Hz, 3 H); 3.52–4.45 ppm (m, 2 H).

Arenesulphinamides (4)[46]. Benzenesulphinamide (**4a**).[47] IR (KBr): 1555, 1470, 1435, 1080, 1010 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): 4.55 ppm (s, 2 H). 4-Methoxybenzenesulphinamide (**4b**) was prepared from the corresponding acid[48] by a standard method.[47] M.p. 135–136 °C [recrystallized from diethyl ether–methanol (2:1)]. IR (KBr): 1600, 1560, 1450, 1060, 1040 cm^{-1}. ^1H NMR ($CDCL_3$, 250 MHz): 3.85 (s, 3 H); 4.47 ppm (s, 2 H). $C_7H_9NO_2S$: calculated, C 49.10, H 5.30, N 8.18, S 18.73; found, C 49.19, H 5.36, N 8.22, S 18.77%. *p*-Methylbenzenesulphinamide (**4c**).[47] IR (KBr): 1560, 1490, 1080, 1040, 1020, 1010 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): 2.42 (s, 3 H); 4.46 ppm (s, 2 H). *p*-Chlorobenzenesulphinamide (**4e**).[49] IR (KBr): 1565, 1470, 1095, 1080, 1020, 1000 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): 4.53 ppm (s, 2 H). *p*-Nitrobenzenesulphinamide (**4g**).[50] IR (KBr): 1600, 1520, 1350, 1310, 1080, 1040 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): 4.54 ppm (s, 2 H). 2,4,6-Trimethylbenzenesulphinamide (**4i**) was prepared from the corresponding acid[51] by a standard method.[47] M.p. 115–118 °C [from ethyl acetate–diethyl ether (1:1)]. IR (KBr): 1600, 1560, 1450, 1060, 1040 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): 2.30 (s, 3 H); 2.62 (s, 6 H); 4.45 ppm (s, 2 H). $C_9H_{13}NOS$: calculated, C 58.98, H 7.15, N 7.64, S 17.50; found, C 59.06, H 7.05, N 7.53, S 17.48%.

Methyl arenesulphonates (5). The compounds were prepared following a phase-transfer procedure;[52] their purity was controlled by gas chromatography. Compounds **5c** and **5g** are commercially available; for **5a** see Ref. 52. Methyl *p*-methoxybenzenesulphonate (**5b**).[53] IR (CCl_4): 1600, 1375, 1265, 1190, 1170, 1000 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): 3.75 (s, 3 H); 3.91 ppm (s, 3 H). MS: *m/z* 202 (64) (M^+), 171 (100), 123 (42), 107 (33), 77 (31). Methyl *p*-fluorobenzenesulphonate (**5d**).[54] IR

(CCl_4): 1600, 1375, 1190, 1005 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz): 3.81 ppm (s, 3 H). MS: *m/z* 190 (93) (M^+), 159 (100), 95 (61), 75 (26). Methyl *p*-chlorobenzenesulphonate (**5e**).[55] IR (CCl_4): 1485, 1380, 1195, 1090, 1000 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz); 3.78 ppm (s, 3 H).

Methyl *p*-[S=^{17}O]toluenesulphonate (**5c**[S=^{17}O]). *p*-Toluenesulphochloride (19 g, 0.1 mol), $H_2{}^{17}O$ (2.0 ml, 0.12 mol), 21.3% ^{17}O), concentrated H_2SO_4 (20 µl) and dioxane (30 ml) were heated for 5 days at 90 °C. Unchanged starting material was precipitated by addition of (isotopically normal) water and filtered off, the filtrate neutralized with NaOH and the resulting sodium *p*-[^{17}O]toluenesulphonate isolated and converted into *p*-[^{17}O]toluenesulphonyl chloride following Ref. 56. After two recrystallizations from benzene–light petroleum, m.p. 68 °C. Compound **5c**[S=^{17}O] was prepared as above[52] and distilled at 80 °C/0.04 Torr; yield 69%. Purity was controlled by gas chromatography. ^1H NMR ($CDCl_3$, 80 MHz): 2.46 (s, 3 H); 3.75 ppm (s, 3 H). MS: enriched sample, *m/z* 187 (16.1) ($M^+ + 1$), 186 (100); non-enriched, *m/z* 187 (3.4), 186 (100); enrichment 12.7%; 60% tracer incorporation.

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