hydrofuran (300 mL). The reaction mixture was heated to reflux for 1 h to assure transmetalation and then cooled to 5 °C, followed by the addition of a solution of compound **5** in tetrahydrofuran (200 mL) over a 10-min period. The reaction mixture was refluxed an additional 48 h, cooled (10 °C), and hydrolyzed by adding 150 g of ice followed by the slow addition of 1 L of 5 N HCl. The tetrahydrofuran was distilled off, and the resulting aqueous solution was refluxed for 4 h, cooled, and extracted with toluene (500 mL). The aqueous layer was basified to pH 8 with 50% sodium hydroxide solution and the product extracted into toluene (1 L). The toluene layer was treated with carbon, dried, and concentrated under vacuum to yield a residue which was dissolved in heptane (500 mL) and cooled to yield 164.5 g (89.5%) of product **7**: mp 95–96 °C; NMR ($CDCl_3$) δ 7.7–6.7 (m, 11 H), 3.2 (s, 2 H), 2.1 (s, 6 H); IR (Nujol) 1662, 1651, 1601 cm^{-1}. Anal. Calcd for $C_{22}H_{19}ClFNO$: C, 71.83; H, 5.21; N, 3.81. Found: C, 72.13; H, 5.19; N, 3.71.

Methanesulfonate of 9-Chloro-7-(*o*-fluorophenyl)-5*H*-dibenz[*c*,*e*]azepine (1). To a cold (−5 °C) solution of compound **7** (36.7 g, 0.1 mol) in methylene chloride (200 mL) was added dropwise a solution of cyanogen bromide (13 g, 0.12 mol) in methylene chloride (50 mL). When the addition was complete, the reaction mixture was stirred for 2 h (0–5 °C) and then concentrated in vacuo. The white solid residue was dissolved in tetrahydrofuran (400 mL) and added slowly (30 min) to a cold (−5 °C) solution of anhydrous ammonia (~50 g) in anhydrous ethanol (600 mL). The reaction mixture was stirred at room temperature overnight and then concentrated in vacuo to a residue which was dissolved in toluene (200 mL). The toluene solution was washed with saturated sodium carbonate solution (50 mL) and water (150 mL) and concentrated to an oil which was then dissolved in ethanol (60 mL). To the ethanol solution was added slowly with cooling methanesulfonic acid (10.7 g, 0.11 mol), and after continued cooling (−10 °C) the product crystallized to yield 35 g (~85% yield) of compound **1** as its methanesulfonate salt: mp 186.6–187.6 °C; NMR ($CDCl_3$) δ 8.1–7.0 (m, 11 H), 5.6 (d, J = 12.6 Hz, 1 H), 4.2 (d, J = 12.6 Hz, 1 H), 2.78 (s, 3 H). Anal. Calcd for $C_{20}H_{13}ClFN{\cdot}CH_3SO_3H$: C, 60.31; H, 4.10; N, 3.35. Found: C, 60.35; H, 4.39; N, 3.22.

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Registry No. **1**, 81537-93-1; **1** $MeSO_3H$, 82374-05-8; **2**, 82374-06-9; **4**, 82374-07-0; **5** (isomer 1), 82374-08-1; **5** (isomer 2), 82374-09-2; **7**, 81537-96-4; *p*-chloroanisole, 623-12-1; *o*-fluorobenzoyl chloride, 393-52-2; isopropylamine, 75-31-0; *o*-fluoro-*N*-isopropylbenzamide, 64141-89-5; *N*,*N*-dimethylbenzylamine, 103-83-3; *o*-lithium-*N*,*N*-dimethylbenzylamine, 27171-81-9.

Oxygen-17 Nuclear Magnetic Resonance Spectroscopy of Sulfoxides and Sulfones. Alkyl Substituent Induced Chemical Shift Effects

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Oxygen-17 NMR chemical shifts have been determined for a number of cyclic and acyclic as well as aliphatic, olefinic, and aryl sulfoxides and sulfones. The ^{17}O NMR chemical shifts for the acyclic, aliphatic, and aromatic sulfoxides reported here absorb in the narrow range between δ −20 and +20, while the cyclic, aliphatic sulfoxides absorb between δ −13 and +66 relative to external (but naturally abundant) $H_2{}^{17}O$. The sulfonyl oxygens are deshielded relative to the sulfinyl oxygens, exhibiting chemical shifts for acyclic and cyclic sulfonyl oxygens between δ 120 and 183 for the sulfones reported here. Diastereotopic sulfonyl oxygens exhibit chemical shift nonequivalence. Substituent-induced chemical shift effects by a methyl or methylene group on the sulfinyl and sulfonyl oxygens are discussed.

Introduction

Oxygen-17 NMR spectroscopy is rapidly becoming a useful and potentially powerful tool for the elucidation of bonding and structural features of oxygen-containing organic molecules in spite of the extremely low natural abundance (0.037%) and sensitivity (2.91×10^{-2} times that for ^1H at constant field) as well as the quadrupole moment of the ^{17}O nucleus.[1] Oxygen-17 nuclear shieldings in sulfoxides and sulfones may be best understood from the results of semiempirical calculations which indicate that while "local" diamagnetic[2] and paramagnetic contributions are important, ^{17}O NMR shifts are largely dominated by the paramagnetic term[1,3] (eq 1). In this equation, ΔE is

$$\sigma_P{}^O = -\frac{e^2\hbar^2}{2m^2c^2\Delta E}\langle r^{-3}\rangle_{2p_O}\sum Q_{SO} \qquad (1)$$

referred to as the "average energy" approximation and can be expressed as $\sum_i \Delta E_i^{-1}$ where ΔE_i is the excitation energy from the ground electronic state to the various excited states of increasing higher energy. However, the first state (lowest energy) is often approximated to ΔE (i.e., $\Delta E_1 \approx \Delta E$).[1d] The expectation value of the inverse cube of the mean radius of the atomic 2p orbital of oxygen is symbolized by $\langle r^{-3}\rangle_{2p_O}$. Q_{SO} describes the elements of charge density on oxygen and the extent of multiple bond contributions between sulfinyl/sulfonyl sulfur and oxygen. While all of these terms appear to be mutually dependent, some contribute to the paramagnetic shielding term more heavily than others.

Our interest in the ^{17}O NMR spectral properties of simple sulfoxides and sulfones was prompted by (i) the fact that few systematic investigations have been performed

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Table I. ^{17}O NMR Chemical Shifts of Cyclic and Acyclic Sulfoxides

compd	$\delta(^{17}O)$, ppm
dimethylsulfoxide (**1**)[a-c]	12, 19[j]
diethyl sulfoxide (**2**)[d]	−6
diisopropyl sulfoxide (**3**)[e]	−20
di-*tert*-butyl sulfoxide (**4**)[a]	−2
di-*n*-propyl sulfoxide (**5**)[a]	−6
di-*n* butyl sulfoxide (**6**)[f]	−7
di-3-butenyl sulfoxide (**9**)[f]	−9
diphenyl sulfoxide (**10**)[a]	2
benzyl phenyl sulfoxide (**11**)[d]	−14
phenyl methyl sulfoxide (**12**)[a]	−1
p-methoxyphenyl methyl sulfoxide (**13**)[a]	−1
thiane 1-oxide (**14**)[f,g]	1
thiolane 1-oxide (**15**)[e,h]	16
thietane 1-oxide (**16**)[a,i]	66

[a] Dichloromethane solvent. [b] δ 13 (neat) (ref 30). [c] δ 20 (ref 4a). [d] Chloroform solvent. [e] Neat. [f] Acetonitrile solvent. [g] δ −3 in chloroform; δ −2 in acetone (ref 4a). [h] δ 15 in $CHCl_3$; δ 12 in acetone (ref 4a). [i] δ 61 in $CHCl_3$; δ 68 in acetone (ref 4a). [j] 100 °C.

Table II. ^{17}O NMR Chemical Shifts of Cyclic and Acyclic Sulfones

compd	$\delta(^{17}O)$, ppm
dimethyl sulfone (**17**)[a,b]	164
diethyl sulfone (**18**)[c]	140
diisopropylsulfone (**19**)[d]	120
di-*tert*-butyl sulfone (**20**)[c]	122
di-*n*-propyl sulfone (**21**)[e]	147
di-*n*-butyl sulfone (**22**)[e,f]	148
divinyl sulfone (**23**)[d]	141
diphenyl sulfone (**25**)[a,g]	138
thiane 1,1-dioxide (**26**)[e,h]	146
thiolane 1,1-dioxide (**27**)[e]	164
thietane 1,1-dioxide (**28**)[c,j]	183

[a] Chloroform solvent. [b] δ 163 in chloroform; δ 165 in acetone (ref 4a). [c] Dichloromethane solvent. [d] Neat. [e] Acetonitrile solvent. [f] δ 145 in both chloroform and acetone solvents (ref 4a). [g] δ 139 in chloroform; δ 137 in acetone (ref 4a). [h] δ 142 in chloroform; δ 149 in acetone (ref 4a). [i] δ 165 in chloroform; δ 164 in acetone (ref 4a). [j] δ 182 in both chloroform and acetone solvents (ref 4a).

on sulfinyl and sulfonyl compounds,[4] (ii) the unique opportunity to gather new information which might lead to a better understanding of the multiple bonding characteristics between the oxygen and sulfur heteroatoms,[5a] and (iii) the opportunity to explore and perhaps define the origins of substituent-induced chemical shift (SCS) effects[6] in ^{17}O NMR.

Results and Discussion

The ^{17}O NMR chemical shifts of aliphatic, acyclic sulfoxides occur between δ 20 and −20 ppm (Table I), while the corresponding sulfones exhibit chemical shifts between δ 120 and 183 ppm (Table II) relative to external, naturally abundant $H_2{}^{17}O$. It is, perhaps, initially surprising that the ^{17}O chemical shifts of the aliphatic sulfoxides with monocoordinated oxygen are so near the chemical shift of water having a dicoordinated oxygen. This is particularly striking when ^{17}O NMR shift comparisons are made between dialkyl ketones (δ 530–580)[1a,c] and sulfoxides while noting the relative similarities in the Allred "average" electronegativities of sulfur (2.58) and carbon (2.55).[7] If the difference in the range of ^{17}O NMR shifts for ketones and sulfoxides is controlled largely by the magnitude of the ΔE term (eq 1), the observed low-energy UV transitions involving the nonbonding electrons on oxygen (e.g., n → π*)[8] in both sulfoxides and ketones would predict that sulfoxides would be more shielded than the analogous ketones. Furthermore, assuming the dipolar description of the sulfinyl linkage is of major importance,[12] multiple bond contributions should diminish and the increase in electron density at the sulfinyl oxygen would cause expansion of the oxygen 2p orbital radius, affording a subsequent reduction in the magnitude of the $\langle r^{-3}\rangle_{2p_O}$ term when compared to ketones. The result of these effects would also lead to a reduction in the paramagnetic shielding contribution in sulfoxides.

Table III. ^{17}O NMR γ-Methyl Substituent Induced Chemical Shift (SCS) Effects in Sulfoxides and Sulfones

compd	γ-Me,[a] ppm	γ-Me/Me,[b] ppm
diethyl sulfoxide (**2**)	−18 (−25)[c]	−9 (−12.5)[c]
diisopropyl sulfoxide (**3**)	−32 (−39)	−8 (−9.8)
di-*tert*-butyl sulfoxide (**4**)	−14 (−21)	−2.3 (−3.5)
diethyl sulfone (**18**)	−24	−12
diisopropyl sulfone (**19**)	−44	−11
di-*tert*-butyl sulfone (**20**)	−42	−7

[a] The γ-Me effect is the difference between in ^{17}O NMR chemical shift of the reference compound (either **1** or **17**) and the object compound [e.g., γ-Me = $\delta_{SO}(2) - \delta_{SO}(1)$]. [b] The γ-Me/Me value is the net γ-Me effect divided by the number of methyl groups added to the reference compound to give the object compound. [c] The γ-Me and γ-Me/Me values in parentheses were calculated by using the ^{17}O shift of **1** (δ 18.7, neat, 100 °C) as reference.

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(8) In dialkyl sulfoxides, the wavelength region between 203 and 230 nm (near UV) characterizes transitions due to the nonbonding electrons on sulfur to the C–S antibonding orbital or to a sulfur 3d orbital [i.e., $n_S \rightarrow \sigma^*$ (C–S) or $n_S \rightarrow 3d_S$] as well as transitions for the nonbonding electrons on oxygen: $n_O \rightarrow \pi^*$. However, the specific assignments of $n_S \rightarrow 3d_S$[9] and $n_O \rightarrow \pi^*$ transitions have not been convincingly made. For example, Mislow et al.[10] report a Cotton effect for (+)-methyl *n*-butyl sulfoxide centered at a λ_{max} below 210 nm and based on its solvent dependency assigned it as an $n_O \rightarrow \pi^*$ transition. The shoulder at 215 nm is relatively solvent insensitive. On the other hand, Mangini et al.[11] point out that the 203-nm absorption of **1** (methylcyclohexane) undergoes a bathochromic shift, while the 216-nm band undergoes a hypsochromic displacement to afford a net inflection at 207 nm in ethanol solvent. The greater hydrogen bonding capability of oxygen vs. sulfur tends to support the assignment of the 216-nm band as an $n_O \rightarrow \pi^*$ transition since a blue shift would be expected in going from a nonpolar to a hydrogen bonding solvent.

(9) The preference for the $n_S \rightarrow 3d_S$ transition over the $n_S \rightarrow \sigma^*$ (C–S) transition is considered reasonable largely because of the insensitivity of the absorption to the groups attached to the sulfur atom. See Leandri, G.; Mangini, A.; Passerini, R. *J. Chem. Soc.* **1957**, 1386–1395.

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The rather large downfield shifts for the aliphatic, acyclic sulfones appear consistent with expectations from other physical data which indicate that the sulfonyl S=O bonds possess more multiple bond character than the sulfinyl bond.[14] The increase in the double bond character in sulfones probably stems from the effect of the "contracted" 3d orbitals of the sulfonyl sulfur which allow for a more efficient overlap with the smaller oxygen 2p orbitals.[15] Accordingly, the lower field shifts of the sulfone oxygens are in agreement with expectations based on the apparent increase in both the (d–p)π bond order (i.e., greater Q_{SO} contribution) and $\langle r^{-3}\rangle_{2p_O}$ terms caused by the inductive effect of the sulfonyl sulfur. Possible deshielding effects arising from geminal oxygen–oxygen (through-space) interactions[16] may also be important. Dialkyl sulfones are transparent in the near UV[17] and one might reasonably conclude that the range of sulfonyl ^{17}O NMR shifts is not critically associated with contributions from ΔE when compared to the ^{17}O shifts of the sulfoxides.

Substituent-Induced Chemical Shift (SCS) Effects. In acyclic organosulfur compounds both sulfinyl and sulfonyl oxygen nuclei experience *upfield* shifts when a hydrogen atom attached to Cβ is replaced by a methyl or methylene group (i.e., γ-Me effect, see Table III). NMR

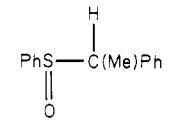
$$C\delta\text{–}C\gamma\text{–}C\beta\text{–}\underset{X = S(=O) \text{ and } S(=O)_2}{X}\text{–}C\beta\text{–}C\gamma\text{–}C\delta$$

chemical shifts of dimethyl sulfoxide (**1**), diethyl sulfoxide (**2**), and diisopropyl sulfoxide (**3**) reflect Me effects of –18 ppm for **2** and –34 ppm for **3** (or –8 to –9 ppm/methyl). By contrast, the ^{17}O shift for di-*tert*-butyl sulfoxide (**4**) is –2 ppm and only 14 ppm to higher field than the shift for **1**.[18]

Similar, yet slightly larger, *shielding* γ-Me effects are operative when the Cβ hydrogens in sulfones are replaced by methyl groups (Table III). Comparisons of the ^{17}O chemical shift differences between dimethyl sulfone (**17**), diethyl sulfone (**18**), and diisopropyl sulfone (**19**) reveal γ-Me effects of –24 ppm for **18** and –44 ppm for **19** (γ-Me/Me for **18** and **19** = –12 and –11 ppm, respectively), while the ^{17}O shift of di-*tert*-butyl sulfone (**20**; δ 122) compared with that of **17** (δ 164) translates into a γ-Me effect/Me of –7 ppm.

The *diminution* in the γ-Me effects within the sulfoxide and sulfone series with increasing methyl substitution parallels ^{17}O NMR shifts trends reported for dialkyl ketones[16a] and aldehydes.[16a] As steric crowding increases about alkyl methyl ketones, dialkyl ketones, and in the present case, dialkyl sulfoxides and sulfones, the γ-Me shielding effect at the monocoordinated oxygen is systematically reduced. The attenuation in the γ-methyl effect is much less remarkable in the aldehydes[16a] where one of the substituents is a hydrogen atom.[19]

The γ-Me effect at the ^{17}O nucleus appears to be qualitatively analogous to the familar γ shift effect[20] which is well-documented in the ^{13}C NMR literature and describes the shielding effects arising from the interactions between second and/or third row atoms occupying the γ gauche conformation.[21] This rationale has been used to distinguish the diastereoisomeric phenyl 1-phenylethyl [^{17}O]sulfoxides, (*RR*/*SS*)-**8** and (*RS*/*SR*)-**8**.[4b] The higher



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shielding in the (*RR*/*SS*)-**8** isomer was rationalized in terms of a substantial time-average increase in the γ-Me effect. Eliel et al.[22] have also demonstrated with the use of "conformationally homogeneous" 2-isopropyl-5-methyl-1,3-dioxanes[23] that the dicoordinated oxygens γ gauche to the axial C5 methyl group are shielded by 11.8 ppm, while the γ anti methyl group exerts a negligible deshielding effect (0.3 ppm).[24]

Two interrelated aspects of the γ-Me effects require comment. The γ-Me effects in the sulfones are slightly larger than those calculated for the sulfoxides; however, the diminishing γ-Me effects *within* the homologous series are common to both series of organosulfur compounds. The C–S–C bond angles in dialkyl sulfoxides and sulfones are considerably smaller (i.e., the CSC bond angle varies from 96.6° in **1** to 111.9° in **4**)[25] than those in the analogous ketones and steric interactions between two alkyl substituents should become increasingly more severe as their size increases. While steric interactions between the proximal alkyl groups serve to increase the number and perhaps magnitude of γ gauche Me interactions in both sulfoxide and sulfone, it is clear that the impact will be largest in the sulfones since the equivalent sulfonyl oxygens experience more γ gauche Me interactions. In a similar way, increased γ-Me interactions within a series of aliphatic alcohols cause an increase in the shielding of the hydroxyl oxygen nucleus.[26]

For sulfones and sulfoxides with large alkyl groups (e.g., *tert*-butyl), the "gear effect"[27] does not provide an efficient mechanism for energy minimization between the interacting alkyl groups because of their close proximity. Therefore, the repulsive interactions between the large

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(18) This rather consistent upfield shift of the ^{17}O nuclei with increased alkyl substitution in both sulfoxide and sulfone series appears to parallel the bathochromic shift of the long-wavelength transition in the near UV (for sulfoxides, see ref 8) which is contrary to expectations if contributions from ΔE terms are important in rationalizing the ^{17}O shift trends *within* the dialkyl sulfoxide series. The UV data for simple dialkyl sulfoxides (cyclohexane solvent) are as follows [λ_{max} (log ϵ): **1** [203 nm (3.47), *216* (3.12)] (methylcyclohexane solvent), **2** [208 nm (3.56), *221* (3.20)], **3** [208 nm (3.47), *227* (3.00)], **6** [*200* nm (3.20)], where italic λ_{max} values represent inflections or shoulders.[11]
(19) In a series of alkyl acetates, the ^{17}O carbonyl resonances show a trend toward *lower field* as alkylation at C_α increases. Presumably, this trend reversal is due to (a) deshielding δ-Me effects coupled with (b) a diminished (2p–2p)π interaction between the ethereal oxygen and the carbonyl group. See Sugawara, T.; Kawada, Y.; Iwamura, H. *Chem. Lett.* **1978**, 1371–4.
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alkyl groups contribute to an expansion of the C–S–C angle[5a] and a *deshielding effect* at the sulfinyl and sulfonyl oxygens might be expected by analogy with the ^{17}O shift trends within a series of dialkyl ketones.[16a] In this latter case an increase in the C–C(O)–C bond angle appears to lead to a deshielding of the oxygen nucleus.[16a]

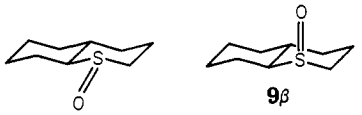
The diminution in the γ-Me effect with increased C–S–C bond angles may be best understood from the results of CNDO/2 calculations for a series of aliphatic sulfoxides.[3a] As the C–S–C bond angle increases from 90° to 120°, the π_{SO} orbital achieves increased stability. While this implies better overlap between the $2p_O$–$3d_S$ orbitals, it also suggests an increase in both the Q_{SO} and $\langle r^{-3}\rangle_{2p_O}$ terms which combine to enhance the deshielding of the ^{17}O nucleus. Presumably, a similar effect is operative in the dialkyl sulfones as well.

As probably expected, sulfoxide **2**, di-*n*-propyl sulfoxide (**5**; δ −6), di-*n*-butyl sulfoxide (**6**; δ −7), and di-3-butenyl sulfoxide (**7**; δ −9) have essentially identical ^{17}O chemical shifts. Similarly, ethyl sulfone **18**, di-*n*-propyl sulfone (**21**), and di-*n*-butyl sulfone (**22**) exhibit ^{17}O shifts in the relatively narrow range of δ 140–148 ppm, implying that carbons farther removed than C_γ in the acyclic systems have either no influence or exhibit a slight deshielding effect on the ^{17}O chemical shifts of the sulfinyl or sulfonyl oxygen(s).[28] These findings are consonant with the observations of Kintzinger[1c] where the effect of alkyl substitution on the ^{17}O shifts of aldehydes and ketones has been summarized in terms of β^π and γ^π *shielding* effects and δ^π *deshielding effects*.[29] The earlier findings of Christ et al.[30] and the more recent results of Sugawara et al.[19] and Crandall and Centeno[26] demonstrate that similar trends in ^{17}O shifts exist for dicoordinate oxygen within a series of alcohols.

The chemical shifts of sulfone **18** and divinyl sulfone (**19**) are virtually identical (δ 140 and 141, respectively). We must conclude that if there is a substantial $(2p–3d)\pi$ interaction between C=C and SO_2 in sulfone **19**,[31] the ^{17}O shift is not a sensitive probe for its detection.[32,33]

Aryl Sulfoxides. Oxygen-17 NMR shifts for diphenyl sulfoxide (**10**), phenyl methyl sulfoxide (**12**), and *p*-methoxyphenyl methyl sulfoxide (**13**) vary only slightly from δ 2 to −1. The fact that all of the shifts reflect shielding relative to sulfoxide **1** only indicates that the phenyl ring exerts a shielding influence on the sulfinyl oxygen, but it is not possible with the limited quantity of ^{17}O data currently available to partition resonance, steric, inductive effects, and other contributions. It is, however, interesting that benzyl phenyl sulfoxide (**11**) exhibits an ^{17}O chemical shift of δ −14, apparently reflecting a substantial *shielding* contribution from the benzyl group which may be largely steric in origin.

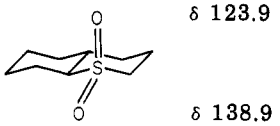
Cyclic Sulfoxides and Sulfones. The ^{17}O chemical shift of thiane 1-oxide (**14**) results from time-averaged contributions from the axial and equatorial sulfinyl oxygens.[36] If it can be assumed that the γ-Me effect arising from comparison of the ^{17}O shifts of **1** and **2** (−18 ppm) is due entirely to γ gauche interactions between the methyls and oxygen-17, then the ^{17}O shift for **14** (δ 1) may be entirely reasonable. Conclusive support for γ gauche methyl or methylene SCS shielding effect in a six-membered ring comes from a comparison of the ^{17}O shifts for the diastereoisomeric sulfoxides of *trans*-1-thiadecalin.[37] The ^{17}O shift for **9β** (δ −11.4) with the axial sulfinyl oxygen is 17.0 ppm to higher field than that of **9α** (δ 5.6) with the equatorial sulfinyl oxygen.



9α **9β**

Because of the possibility for conformational mobility (pseudorotation)[38] of thiolane 1-oxide (**15**) and the absence of distinct γ gauche methylene interactions, the ^{17}O chemical shift of δ 16 may not be unreasonable. However, the ^{17}O chemical shift of thietane 1-oxide (**16**) is 50 ppm downfield from **15**. Although sulfoxide **16** exists in solution with the sulfinyl oxygen predominantly in the pseudoequatorial array,[39] it is not immediately apparent what factor(s) contribute to this relatively large deshielding effect.[4a] In all of the sulfoxides studied here, the extent to which a γ *anti* methyl (methylene) group *shields*[40] or *deshields* monocoordinated oxygen through a third-row heteroatom (sulfur) is not currently known. Overall, the trend in the ^{17}O shifts for **14** → **15** → **16** is not paralleled by the cyclic ketones where a slight shielding effect is observed as the ring size decreases.[16]

trans-Thiadecalin 1,1-dioxide (**24**),[37] possessing both axial and equatorial monocoordinated oxygens, exhibits ^{17}O chemical shifts for the diastereotopic sulfonyl oxygens at δ 123.9 and 138.9, reflecting a shift difference of 15 ppm.



24

By analogy with the ^{17}O shifts of the diastereoisomeric sulfoxides **9α** and **9β**, we have tentatively assigned the absorption at δ 123.9 to the axial sulfonyl oxygen. Other diastereotopic SO_2 oxygens have been reported for an appropriately substituted thietane *S,S*-dioxide[2a] and a thiosulfonate[2a] as well as an acyclic sulfone.[2b]

The sulfonyl oxygens in the cyclic sulfones are deshielded in increments of ca. 19 ppm as the ring size decreases from 6 → 5 → 4. The magnitude of the deshielding

(28) Mason makes the point that the σ_p term is little affected by the increase in an alkyl substituent beyond Cβ and Cλ within a series of N=O compounds; see ref 2a.
(29) See also, Brouwer, H.; Stothers, J. B. *Can. J. Chem.* **1972**, *50*, 1361–70.
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(32) It has been previously pointed out that increased $(2p–2p)\pi$ interactions generally lead to upfield shifts of the carbonyl oxygen.[33,34]
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(35) It is interesting that the bond lengths in **23**, determined by electron diffraction methods, are relatively normal and do not support $(2p–3d)\pi$ interactions with sulfonyl sulfur. See Hagarattai, I. "Sulfone Molecular Structures"; Springer-Verlag: Berlin, Germany, 1978; pp 56–62.
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(40) It is, of course, known in ^{13}C NMR that the γ-SO *anti* effect in six-membered rings is *shielding*.[37] However, this may be related more to the orientation of the sulfinyl sulfur lone pair than to the conjugate transfer of charge from oxygen to carbon.[41]

effect in the cyclic sulfoxides differs from the cyclic sulfones, but the trend is similar. Block et al.[2a] have previously noted the extensive deshielding of the ^{17}O nuclei in sulfoxide **16** and sulfone **28** compared to that of the homologues. The term "four-membered ring sulfone effect" was coined to characterize the unusual ^{17}O and ^{13}C chemical shifts in sulfone **28** and presumably sulfoxide **16**.

Solvent Effects on the Oxygen-17 Shift of Dimethyl Sulfoxide. For carbonyl compounds, the solvent effects on the position of ^{17}O resonances can be quite large. In fact, Reuben[42a] and Jeu[42b] have shown that the ^{17}O absorption in acetone is shielded by 52–57 ppm in aqueous media.[42c] We have examined the solvent dependence of the ^{17}O chemical shift of dimethyl sulfoxide [δ 18.7 (neat, 100 °C); δ 17.6 (25 v/v % toluene, 100 °C); δ 12.1 (35 v/v % CH_2Cl_2, 25 °C); δ 9.8 (30 v/v %, $CHCl_3$, 25 °C); δ 8 (30, 50 v/v % CH_3CH_2OH, CH_3OH, respectively, 25 °C)]. The data indicate that the sulfinyl oxygen in **1** is only slightly sensitive to aprotic solvents and is shifted upfield 10–11 ppm in CH_3OH or CH_3CH_2OH solvents in comparison to neat **1**. This lack of a substantial solvent dependent ^{17}O chemical shift in aprotic media for sulfoxide **1** limits speculation on whether **1** is monomeric or forms "association polymers"[43] or "dimers"[44] in solution.

Experimental Section

Melting points were obtained in a Mel-Temp melting point apparatus with an open capillary tube and are uncorrected.

Structural assignments of all sulfides, sulfoxides, and sulfones were supported by detailed ^1H and ^{13}C NMR analyses and will be the subject of a future publication. ^1H NMR spectra were recorded on the Perkin-Elmer Model R24B, Varian Model XL-100-12, and Bruker WM-250 NMR spectrometers. All Fourier-transform spectra were obtained at ambient temperatures (ca. 30 °C) with off-resonance and noise decoupling. The ^1H and ^{13}C NMR chemical shifts of samples as deuteriochloroform ($CDCl_3$) solutions are presented in parts per million (δ) downfield from internal tetramethylsilane (Me_4Si).

Gas–liquid chromatographic (GLC) analyses were performed on a Hewlett-Packard Model 5754B research gas chromatograph using a 12 ft × 0.025 in. (i.d.) stainless-steel column packed with a 1% with 10% DC-550 on chromosorb W and a 6 ft × 0.025 in. stainless-steel column packed with a 1% DC-550 on Chromosorb W. Cyclohexane was used as internal reference standard for GLC analyses. Oxygen-17 NMR spectra were obtained on the Varian Model XL-100-12 NMR spectrometer using an in-house multinuclear module and an external fluorine lock referenced to distilled water with 40 transients s^{-1}. The Bruker WM-250 NMR spectrometer was also used to obtain ^{17}O NMR data. The ^{17}O shifts are reproducible to ±1 ppm and were obtained at 25 °C unless otherwise indicated.

General Procedure for Oxidation of Sulfides to Sulfoxides. The sulfoxides were prepared by oxidation of the corresponding sulfides with *m*-chloroperoxybenzoic acid (*m*-CPBA) in dichloromethane solvent at 0–5 °C (ice bath). Neutralization with saturated aqueous sodium bicarbonate solution and removal of dichloromethane gave the crude sulfoxides in acceptable yields. Homogeneous samples could be obtained by distillation under reduced pressure or recrystallization.[45]

General Procedure for Oxidation of Sulfides to Sulfones. The sulfones were prepared by treating the sulfides with 2 equiv of *m*-CPBA in dichloromethane or alternatively dissolving the sulfides in glacial acetic acid followed by treatment with 2.2 equiv of hydrogen peroxide (except for sulfides containing labile olefinic bonds). With *m*-CPBA, the reaction mixture was washed with a saturated solution of sodium bicarbonate. With hydrogen peroxide, the reaction mixture was extracted with dichloromethane and then treated with aqueous $NaHCO_3$. In both cases the dichloromethane solutions were dried ($MgSO_4$) and concentrated to dryness (rotary evaporator) to give the crude sulfones. Purification by recrystallization or distillation under reduced pressure gave homogeneous material.

Dimethyl sulfoxide was obtained from Fisher Scientific. Divinyl sulfone was obtained from Union Carbide Co. and distilled before use. Thiolane 1-oxide and dimethyl sulfone were purchased from Aldrich Chemical Co. and used without further purification. The diastereoisomeric sulfoxides of *trans*-thiadecalin and *trans*-thiadecalin 1,1-dioxide were prepared previously[37] and di-3-butenyl sulfoxide was obtained from Dr. Robert P. Rooney.

Diethyl sulfoxide [bp 77–79 °C (2.4 torr); 70% yield (lit.[46] bp 45–47 °C (0.15 torr))]; di-*n*-propyl sulfoxide [bp 45–53 °C (0.08 torr); 45% yield (lit.[47] bp 72 °C (0.1 torr))]; di-*n*-butyl sulfoxide [mp 31–34 °C; 87% yield (lit.[48] mp 34 °C)]; diphenyl sulfoxide [mp 70–71 °C; 70% yield (lit.[49] mp 71 °C)]; dibenzyl sulfoxide [mp 133–134 °C; 68% yield (lit.[50] mp 133 °C)]; thietane 1-oxide [bp 23–24 °C (0.08 torr); 37% yield (lit.[51] bp 91.2 °C (14 torr))]; diisopropyl sulfoxide [bp 35–36 °C (0.10 torr); 66% yield (lit.[47] bp 59 °C (0.9 torr))]; di-*tert*-butyl sulfoxide [mp 62–64.5 °C; 50% yield (lit.[52] mp 63.5–65.0 °C)]; benzyl phenyl sulfoxide [mp 119–120 °C; 82% yield (lit.[53] mp 121 °C)]; phenyl methyl sulfoxide [bp 80–82 °C (0.05 torr); 77% yield (lit.[54] bp 70 °C (0.025 torr))]; *p*-methoxyphenylmethyl sulfoxide [mp 43–45 °C; 60% yield (lit.[55] mp 45–46 °C)].

Diethyl sulfone [mp 72 °C; 64% yield (lit.[56] mp 74 °C)]; di-*n*-butyl sulfone [mp 44–45 °C; 83% yield (lit.[47] mp 46 °C)]; diphenyl sulfone [mp 126–128 °C; 79% yield (lit.[47] mp 128–129 °C)]; dibenzyl sulfone [mp 150–151 °C; 73% yield (lit.[47] mp 151 °C)]; thietane 1,1-dioxide [mp 74.075.5 °C; 69% yield (lit.[51] mp 77–78 °C)]; diisopropyl sulfone [bp 45–50 °C (0.09 torr); 69% yield (lit.[47] bp 78 °C (0.05 torr))]; di-*tert*-butyl sulfone [mp 129–130 °C; 63% yield (lit.[57] mp 129–130 °C)].

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