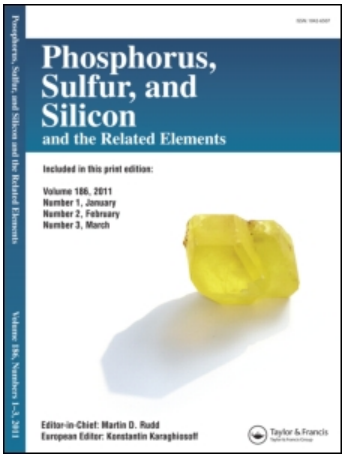

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INTRAMOLECULAR HYDROGEN BONDING IN 2-HYDROXYDIARYL SULFOXIDES

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INTRAMOLECULAR HYDROGEN BONDING IN 2-HYDROXYDIARYL SULFOXIDES

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A number of 2-hydroxydiaryl sulfoxides were examined for intramolecular hydrogen bonding by IR spectroscopy. It was shown that the sulfoxide absorption occurred in the 1005–1010 cm^{-1} range while the hydroxyl absorption was shifted into the C—H absorption region in carbon disulfide solution. In addition, the sulfoxide absorption of bis(2-hydroxy-3-*t*-butyl-5-methylphenyl) sulfoxide was shown to be at 955 cm^{-1}, a $\Delta\nu_{S-O}$ of 95 cm^{-1}, resulting from intramolecular H-bonding.

INTRODUCTION

Recently, we reported[2] the direct synthesis of a variety of 2- and 4-hydroxydiaryl sulfoxides. The 2-hydroxy compounds are interesting in that intramolecular H-bonding between the sulfoxide oxygen and the hydroxyl proton is possible. Several reports have discussed the possibility of intramolecular hydrogen bonding in substituted 2,2′-thiobisphenols[3,4] and substituted 2-hydroxydiphenyl sulfones.[5,6] On the other hand, Meyers and co-workers[7–9] and Oae and co-workers[10,11] have investigated in some detail the relative acidities of bis(2-hydroxyphenyl) and bis(4-hydroxyphenyl) sulfides, sulfoxides, and sulfones as well as of 2- and 4-hydroxyphenyl phenyl sulfur compounds. In the above investigations, the authors have alluded to the possibility of hydrogen bonding in these types of compounds, particularly as to how intramolecular hydrogen bonding might affect the acidities of the 2-hydroxy and bis(2-hydroxy) compounds. Where infrared spectral data were presented, the compounds were examined as KBr pellets (S=O, 950–980 cm^{-1}; OH, 3060–3160 cm^{-1}). Under these conditions (solid phase), strong intermolecular interactions could give misleading interpretations as to the presence of intramolecular hydrogen bonding.

Amstutz *et al.*[6] earlier concluded that intramolecular H-bonding was responsible for the displacement of the sulfoxide stretching frequency to 994 cm^{-1} and the absence of a hydroxyl absorption in the 3000–3600 cm^{-1} range in the IR of 2-hydroxydiphenyl sulfoxide (**1a**). However, the spectrum was obtained in the solid phase in Nujol. Therefore, it would be tentative to attribute these IR characteristics to intramolecular H-bonding.

In the characterization of the 2-hydroxydiaryl sulfoxides in our earlier work, we found the sulfoxide stretching frequencies to be in the 1025–985 cm^{-1} range as obtained in KBr pellets.[2] In addition, 4-hydroxythioxanthene sulfoxides exhibit sulfoxide stretching frequencies in the 960–970 cm^{-1} (KBr) range.[12] In these examples, intramolecular hydrogen bonding is structurally possible. On the other hand, substi-

tuted 4-hydroxyphenyl phenyl sulfoxides[2] and substituted bis(4-hydroxyphenyl) sulfoxides,[10,11] compounds in which intramolecular hydrogen bonding is structurally impossible, also exhibit the sulfoxide stretching frequency (KBr) in the 950–1015 cm^{-1} range.

Thus, it appears that an IR examination of 2-hydroxyphenyl phenyl sulfoxides **1** in dilute solution of non-polar solvents would be appropriate if intramolecular H-bonding is to be invoked. In addition, the presence of only one hydroxyl group per molecule in **1** (vs. two in the bis compounds) reduces the number of possible intramolecular interactions, e.g., HO—HO interactions.

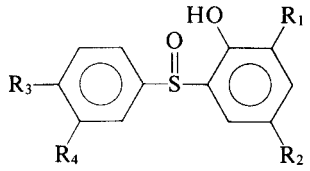
RESULTS AND DISCUSSION

Initially, we intended to examine the shift of the hydroxyl group in the infrared spectrum. However, we found, as Amstutz *et al.*[5,6] did, that the group was shifted into the 2900–3000 cm^{-1} region,[13] overlapping the aliphatic and aromatic C—H absorptions, and was so broadened that it was useless as a diagnostic tool, especially at the lower concentration where we were working. Thus, our report at this time centers around the shift of the sulfoxide in the infrared spectrum.

Sulfoxide absorption data for some representatively substituted 2-hydroxydiaryl sulfoxides (**1**) are shown in Table I and for some comparative diaryl sulfoxides and 4-hydroxydiaryl sulfoxides in Table II. These data were obtained on carbon disulfide solutions at 1×10^{-4} M. All **1** compounds exhibited the sulfoxide frequency in the 1005–1010 cm^{-1} range while the comparative compounds in Table II exhibited the absorption in the 1045–1050 cm^{-1} range. Even while the 4-hydroxy compounds ex-

TABLE I

Sulfoxide stretching frequencies for substituted 2-hydroxydiphenyl sulfoxides (**1**)

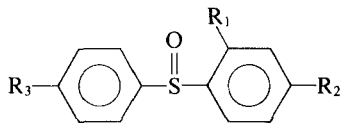


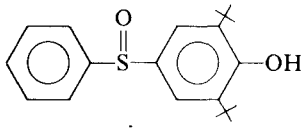
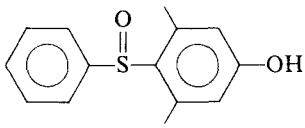
	R_1	R_2	R_3	R_4	S=O frequency (cm^{-1})[a]
1a	H	H	H	H	1010
b	H	CH_3	H	H	1010
c	H	t-C_4H_9	H	H	1010
d	CH_3	t-C_4H_9	H	H	1010
e	t-C_4H_9	CH_3	H	H	1010
f	t-C_4H_9	t-C_4H_9	H	H	1010
g	H	CH_3	CH_3	H	1005
h	H	t-C_4H_9	CH_3	H	1005
i	CH_3	CH_3	CH_3	H	1005
j	CH_3	t-C_4H_9	CH_3	H	1005
k	CH_3	t-C_4H_9	t-C_4H_9	H	1005
l	t-C_4H_9	CH_3	t-C_4H_9	H	1005
m	t-C_4H_9	CH_3	CH_3	H	1005
n	H	CH_3	Cl	H	1005
o	H	CH_3	OCH_3	Cl	1005

[a] 1×10^{-4} M solutions in carbon disulfide.

TABLE II

Sulfoxide stretching frequencies for some model diaryl sulfoxides (**2**)



	R_1	R_2	R_3	S=O frequency (cm^{-1})[a]
2a	H	H	H	1050
b	H	CH_3	CH_3	1050
c	H	OCH_3	H	1050
d	OCH_3	OCH_3	H	1048
e	OCH_3	OCH_3	$t\text{-}C_4H_9$	1048
				1045
				1048

[a] Solutions in carbon disulfide.

hibit the sulfoxide absorption at 990–1015 cm^{-1} in KBr, the absorption is in the normal range for non-hydrogen bonded sulfoxides in carbon disulfide solution. These latter data suggest that electronic effects from the hydroxyl groups are not responsible for the shift of the sulfoxide in the 2-hydroxy compounds. In addition, it appears that even in somewhat hindered 4-hydroxydiaryl sulfoxides, there are intermolecular interactions in the solid phase which cause a shift in the sulfoxide frequency to longer wavelengths.

Hindrance or inductive effects of substituents near the hydroxyl group did not have any influence on the observed sulfoxide stretching frequency. In fact, the only distinctive structural feature which had an effect on the position of the sulfoxide frequency was the presence or absence of a substituent in the *para* position of the ring not possessing the hydroxyl group (Table I, see R_3). Those compounds (**1**g–o) having a *para* substituent exhibited a sulfoxide frequency at 1005 cm^{-1} while those (**1**a–f) without exhibited the frequency at 1010 cm^{-1}. Without the appropriate model compunds to make a fair comparison, we cannot speculate at this time as to the reason for this behavior.

TABLE III

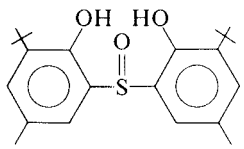
Cryoscopic molecular weight data for representative 2-hydroxydiaryl sulfoxides.

Compounds	Formula Weight	Exp'tal Weight
1d	288	268
1h	288	283
1k	344	323

To be more certain that we were not dealing with an intermolecularly H-bonded complex of two or more molecules of **1**, the cryoscopic molecular weights in benzene of three representative compounds were determined. The data in Table III reveal that all three exist as monomeric species in non-polar solution, as was similarly observed[5] earlier for **1**a.

Meyers[9] has already discussed alternative interactions which might account for the shift of the sulfoxide frequency to longer wavelengths in diaryl sulfoxides. The oxygen of an o-OH group could interact with the partially positive sulfur of the sulfoxide, through a highly strained 4-membered ring, thus decreasing the S=O force constant. This was demonstrated through the use of *o*- and p-methoxy groups and accounted for a 5–10 cm^{-1} shift of the sulfoxide absorption for the ortho compared to the para compound. We would like to propose that intramolecular hydrogen bonding through a 6-membered cyclic species is primarily responsible for the shifts (~40 cm^{-1}) we observed in **1**. Consistent with this interpretation is the fact that the hydroxyl absorptions in **1** were strongly shifted into the 2900–3000 cm^{-1} range, as was previously mentioned. It would be tenuous to invoke a O=S----OH interaction similar to the O=S----OCH_3 interaction proposed by Meyers when a sterically and thermodynamically favorable intramolecular H-bonding interaction would be available to the molecule. Myers has used this O=S----OH interaction to support the observation[7] that 2-hydroxy diphenyl sulfoxides are more acidic than 4-hydroxy ones, since H-bonding would tend to decrease the acidity of the 2-hydroxy compounds over the 4-hydroxy ones. We tend to agree more with the alternative argument that the stability of the anion from the 2-hydroxy isomer is more stable than that from the 4-hydroxy isomer and thus determines the observed acidity.

We also examined compound **3** for intramolecular H-bonding. Interestingly, under similar conditions, the sulfoxide absorption appeared at 955 cm^{-1} while the hydroxyl



3

absorption appeared at 3200 cm^{-1}. These data can be interpreted to suggest that both hydroxyl protons are bound to the sulfoxide oxygen, shifting the sulfoxide absorption to a much lower frequency. However, neither hydroxyl group is bound as strongly to the sulfoxide oxygen as those in compounds **1**. Thus, the hydroxyl frequency is shifted out of the 3000 cm^{-1} region to 3200 cm^{-1}. This nearly 100 cm^{-1} shift of the sulfoxide frequency is, to our knowledge, the largest observed shift of a sulfoxide absorption resulting from hydrogen bonding. In fact, this shift rivals those that result upon complexation of I_2 or ICl/CCl_4 with the oxygen of other diaryl sulfoxides.[14] An alternative explanation for the observed shifts in **3** would be that one hydroxyl group is intramolecularly bound to the sulfoxide oxygen while the oxygen of the other interacts with the sulfur as Meyers[9] proposed. Thus, the hydrogen bonded hydroxyl group could then absorb at 2900–3000 cm^{-1} while the other non-H-bonded one could absorb at 3200 cm^{-1}. The combination of these two interactions would tend to weaken the S=O force constant, exhibiting a highly shifted absorption. We intend to lend credence to one of these explanations through an examination of **3** by X-ray crystallography.

EXPERIMENTAL

With the exceptions of **1**n and **2**e, all the compounds used in this study were either commercially available (**2**a, b) or were previously reported.[2,15,16]

Melting points were determined on a Mel-Temp apparatus and are uncorrected. ^{1}H NMR spectra were determined on a Varian Model A60 and ^{13}C NMR spectra on a Bruker Model HX-90E. Elemental analyses were determined by Huffman Labs, Wheatridge, Colorado. The solution molecular weights of **1**d, h and k were determined using a Beckman cryoscopic apparatus. Benzene was employed as the solvent and concentrations of 0.06, 0.07 and 0.08 molar were examined. Cooling curves were obtained at each concentration and the molecular weights were calculated by means of the freezing point depression equation.

The infrared spectra were determined on a Perkin Elmer Model 567 grating double beam spectrophotometer using 10 ± .005 mm KBr solution cells. All spectra were obtained on carbon disulfide solutions, due to its better solubility characteristics (vs. CCl_4), at concentrations of 5×10^{-2} to 1×10^{-4} M, at 23°C.

*2,4-Dimethoxy-4'-*t*-butyldiphenyl Sulfoxide* (**2**e)

This compound was prepared according to the general procedure[2] using p-t-butylbenzenesulfinyl chloride and 1,3-dimethoxybenzene with anhydrous aluminum chloride in methylene chloride. Recrystallization from ethyl acetate afforded a white solid, mp 138.5–140°C; NMR ($CDCl_3$) δ 1.28 (s, 9H), 3.76 (s, 3H), 3.77 (s, 3H), 6.40 (d, 1H, J = 2.1 Hz), 6.62 (dd, 1H, J = 8.5, 2.1 Hz), 7.75 (d, 1H, J = 8.5 Hz), 7.39 (d, 2H, J = 8.7), 7.61 (d, 2H, J = 8.7). Anal. Calcd. for $C_{18}H_{22}O_3S$: C, 67.89; H, 6.96; S, 10.07. Found: C, 68.20; H, 7.09; S, 10.36.

2-Hydroxy-5-methyl-3'-chloro-4'-methoxydiphenyl Sulfoxide (**1**n)

This compound was prepared according to the general procedure[2] using 3-chloro-4-methoxybenzenesulfinyl chloride[17] and p-cresol with anhydrous aluminum chloride in methylene chloride. There was obtained a white crystalline solid (acetone), mp 165–167°C; ^{1}H NMR ($CDCl_3$) δ 2.27 (s, 3H), 3.90 (s, 3H), 6.7–7.8 (m, 6H), OH undetected. The proton decoupled ^{13}C NMR spectrum exhibited 12 different aromatic carbons. Anal. Calcd. for $C_{14}H_{13}O_3ClS$: C, 56.66; H, 4.42; Cl, 11.95; S, 10.80. Found: C, 56.54; H, 4.53; Cl, 11.68; S, 10.75.

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