Conformational consequences of intramolecular hydrogen bonding by OH to the directional lone-pair of sulfur in derivatives of methyl phenyl sulfide, diphenyl sulfide, and diphenyl disulfide

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Complete spectral parameters for the ^{1}H nmr spectra of 2-hydroxyphenyl methyl sulfide, **2**, 2-hydroxyphenyl phenyl sulfide, **3**, bis(2-hydroxy-3-*tert*-butyl-5-methylphenyl) sulfide, **4**, and bis(2-hydroxyphenyl) disulfide, **5**, are reported for CCl_4 solutions at 305 K. For **2** the parameters are consistent only with a conformation in which the C—S—C plane is roughly perpendicular to the aromatic plane. The conformational determinant is the OH···3*p* hydrogen bond which forces the mainly 3*p* orbital on sulfur into the benzene plane. In **3** a similar arrangement is found about the sulfur atom, with the phenyl group lying in the C—S—C plane and therefore perpendicular to the hydroxyphenyl plane (skew conformation). In **4** two OH···3*p* hydrogen bonds exist, yielding a gable (twist) conformation. Compound **5** exists in the axial conformation with probable C_2 symmetry, the CSSC dihedral angle and the CCSS torsion angles all being near 90°. For none of the compounds is there any evidence for OH···π interactions.

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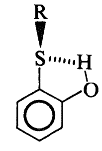
On rapporte les paramètres spectraux complets des spectres de rmn du ^{1}H des composés suivants en solution, dans le CCl_4, à 305 K: sulfure de l'hydroxy-2 phényle et de méthyle, **2**, sulfure de hydroxy-2 phényle et de phényle, **3**, sulfure du bis(hydroxy-2 *tert*-butyl-3 méthyl-5 phényle), **4** et du disulfure de bis(hydroxy-2 phényle), **5**. Les paramètres du composé **2** sont uniquement en accord avec une conformation dans laquelle le plan C—S—C est approximativement perpendiculaire au plan du noyau aromatique. Le déterminant conformationnel est la liaison hydrogène OH···3*p* qui oblige l'orbitale principale 3*p* du soufre à passer dans le plan du benzène. Dans le cas du composé **3**, on trouve un arrangement semblable autour de l'atome de soufre avec le groupe phényle oriente dans le plan C—S—C et par conséquent perpendiculaire au plan de l'hydroxyphényle (conformation *gauche*). Deux liaisons hydrogènes OH···3*p* existent dans le composé **4**, donnant une conformation gable (twist). Le composé **5** existe dans une conformation axiale avec une symétrie probable C_2, l'angle dièdre CSSC et les angles de torsion CCSS étant tous deux pratiquement à 90°. On n'a pas pu établir l'existence d'interactions OH···π dans aucun de ces composés.

[Traduit par le journal]

Introduction

The existence of intramolecular OH···π hydrogen bonds in 2-phenylphenol and in derivatives of 2-benzylphenol is attested by infrared spectroscopy (1) and by X-ray crystallography (2). Furthermore, infrared, ultraviolet, and nmr data in CCl_4 solution are interpreted in terms of predominant intramolecular OH···π bonding in *ortho* hydroxy derivatives of diphenyl sulfide and diphenyl disulfide (3). Apparently, the ^{1}H nmr data are not useful in the deduction of the conformations adopted as a consequence of the OH···π bonds (3). A ^{13}C nmr study concludes that ^{13}C shifts are insensitive to the intramolecular hydrogen bonding but assumes the OH···π intramolecular interaction as proven (4).

It is interesting, therefore, that a detailed ^{1}H nmr investigation of 2-hydroxythiophenol, **1**, in CCl_4 shows its conformation as one in which the SH bond prefers to lie perpendicular to the benzene plane (5). In the absence of the hydroxyl group the SH bond prefers the molecular plane by 3.2 kJ/mol (6), the mainly 3*p* orbital conjugating with the π system. Also, the hydroxyl group in phenol shows a preference of 14.6 kJ/mol for the benzene plane (7, 8*a*). The most favorable conformation, **1** (R=H), is therefore a consequence of a stereospecific electrostatic attraction between the directional 3*p* lone pair on the polarizable sulfur atom and the O—H dipole (5).



1 R = H
2 R = CH_3
3 R = C_6H_5

When R=CH_3, the preferred conformation may still be determined by the OH···3*p* attraction. Furthermore, the latter may well play an important role in the conformations adopted for R = C_6H_5 and perhaps also for R = SC_6H_5.

In this paper, chemical shifts and spin–spin coupling constants are used in arguments about the conformations of **2**, **3**, bis(2-hydroxy-3-*tert*-butyl-

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TABLE 1. The ^1H nmr spectral parameters for 2-hydroxyphenyl methyl sulfide, **2**, 2-hydroxyphenyl phenyl sulfide, **3**, and bis(2-hydroxyphenyl) disulfide, **5**

	Value				Value		
Parameter	**2**[a]	**3**[b]	**5**[c]	Parameter	**2**	**3**	**5**
νOH	649.518(2)	635.674(2)[e]	613.062	$^4J_o^{H,OH}$	−0.114(3)	−0.09(2)	−0.08(2)
νCH_3	226.974(2)[d]	—	—	$J_m^{OH,H}$	0.449(3)	0.473(3)	0.481(5)
ν_3	689.093(2)	698.486(2)	692.452(3)	$J_p^{H,OH}$	≤ 0.02	≤ 0.02	≤ 0.02
ν_4	714.983(2)	727.193(2)	726.416(3)	$J^{H,CH}$	±0.04±0.01	—	—
ν_5	676.643(2)	684.438(2)	674.701(3)	Root-mean square deviation	0.009	0.007	0.011
ν_6	738.529(2)	744.625(2)	716.157(3)				
$^3J_{34}$	8.184(2)	8.215(3)	8.236(4)				
$^3J_{45}$	7.373(2)	7.364(3)	7.348(5)	Peaks observed	44[f]	42	39
$^3J_{56}$	7.718(3)	7.743(3)	7.774(4)	Transitions calculated	80[g]	80	80
$^4J_{35}$	1.340(2)	1.333(3)	1.328(4)				
$^4J_{46}$	1.675(2)	1.694(3)	1.694(5)	Transitions assigned	80	77	79
$^5J_{36}$	0.391(3)	0.389(3)	0.384(4)				

[a] 5 mol% in CCl_4.
[b] 1.8 mol% in CCl_4.
[c] 3 mol% in CCl_4.
[d] In Hz at 100.001_2 MHz and 305 K to low field of internal TMS. For the C_6H_5 group of **3**, ν_o, ν_m, and ν_p are 699.602(5), 713.310(4), and 703.901 (7) Hz.
[e] Numbers in parentheses are standard deviations in the last significant figure.
[f] Excluding CH_3 peaks.
[g] Above an intensity of 0.05.

5-methyl) sulfide, **4**, and of bis(2-hydroxyphenyl) disulfide, **5**. No evidence for OH···π bonding is found.

Experimental

Compounds

The 2-hydroxyphenyl methyl sulfide, **2**, was prepared from the 2-amino derivative (Parish) via diazotization (8*b*) and **3** was prepared as follows. A mixture of 2-bromophenol (5g, 0.029 mol), benzenethiol (3.2g, 0.029 mol), and sodium ethoxide (4.8g, 0.06 mol) in dry dimethylformamide (100 mL) was heated under reflux for 8h in a nitrogen atmosphere. The reaction mixture was cooled, poured into 2 *M* HCl solution (200 mL), and the resultant milky solution was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extract (diphenyldisulfide, 3.2g, 50%, was isolated from these extracts after basic extraction) was washed with water (6 × 100 mL) and then was extracted with 2 *M* NaOH (3 × 30 mL). These basic extracts were acidified with 2 *M* HCl and the mixture was extracted with CH_2Cl_2 (3 × 30 mL). Evaporation of the washed (H_2O) and dried ($MgSO_4$) organic extracts left an oil which was distilled to give **3** (1.4g, 20%) as a clear oil, bp 95–103°C at 0.5 Torr. No attempt was made to maximize the yield. $C_{12}H_{10}OS$ requires M 202, found M^+202. Compound **4** came from Aldrich and **5** was formed in the presence of air in a CCl_4 solution of **1**.

^1H nuclear magnetic resonance measurements

Samples were prepared as dilute solutions in CCl_4 and contained about 4 mol% of tetramethylsilane (TMS). The solutions were degassed by the freeze–pump–thaw method and were then flame-sealed into 5 mm od nmr sample tubes. Care (9) was taken to retard intermolecular hydroxyl proton exchange.

The ^1H nmr spectra were recorded on an HA 100 spectrometer in the frequency sweep mode at a probe temperature of 305 K. Calibrations of peak positions were performed by the reading of sweep and manual oscillator frequencies for markers placed at ca. 5 Hz intervals with a dispersion of 1 Hz/cm and sweep rates of 0.02 and 0.01 Hz/s. Repetition of this procedure and interpolation yielded peak frequencies with a typical rms deviation of ≤ 0.02 Hz.

Results and discussion

Spectral analyses

These used the computer program LAME (10, 11). The derived ^1H nmr spectral parameters for **2**, **3**, and **5** are presented in Table 1. The C_6H_5 spectrum of **3** also yields to analysis; all but a few of its peaks could be unequivocally identified. Figure 1 provides evidence for the high spectral quality obtained in this work.

The conformation of 2-hydroxyphenyl methyl sulfide, 2

In **2**, $^5J_m^{H_4,OH}$ is 0.45 ± 0.01 Hz (assuming an accuracy of three times the standard deviation in Table 1), whereas in 2-hydroxythiophenol it is 0.42 ± 0.01 Hz (5). As discussed in detail for the latter compound (5), this stereospecific coupling and the absence of significant coupling to H-5 and H-6 means that at least 95% of **2** exists in a conformation containing an OH···S hydrogen bond (compare **1**); and this interaction involves a negligible out-of-plane twist about the C—O bond.

The conformation about the C—S bond in **2** can be reasonably deduced as follows. Temperature-dependent photoelectron spectra imply that the

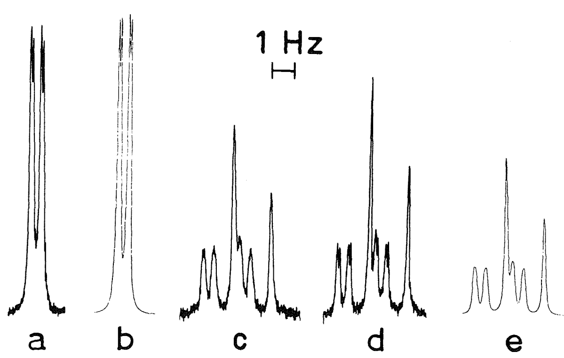
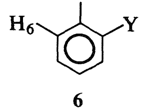


FIG. 1. In (a) is shown the hydroxyl proton spectrum of a 5 mol% solution of **2** in CCl_4 at 305 K and 100.001 MHz (centerband). In (b) the calculated spectrum assumes the parameters in Table 1 and a linewidth at half height of 0.10 Hz. *Parts* of the multiplets from H-3 *and* H-5 are displayed in (c), whereas (d) has the same region under conditions of methyl proton decoupling. The small coupling (0.11 Hz) of H-3 to the hydroxyl proton is apparent. In (e) the calculated spectrum assumes that H-3 and H-5 are also coupled to the methyl protons by 0.04 Hz (compare (c)). Altering this coupling by 0.02 Hz produced disagreement. It should be noted that the linewidths of all peaks from H-4 and H-6 were 0.10 ± 0.01 Hz ("spectrometer" or "sample" linewidth) and these protons are coupled to the methyl protons by ≤ 0.02 Hz.

planar ($C_2C_1SC = 0°$) form of thioanisole is favored by 3.5 kJ/mol over the (probably) perpendicular conformer (12). This number is close to the twofold barrier in thiophenol, suggesting $3p \cdots \pi$ conjugation as a major contributor to the stability of the planar forms. MO calculations are also available (13, 14). Therefore it is reasonable that in both **1** and **2** the polar O—H bond seeks the directional lone pair on sulfur, twisting it into the molecular plane and causing the S—H and S—CH_3 bonds to move into the perpendicular plane. This conformation of **2** should have three consequences: (*i*) the chemical shift of the methyl protons should show evidence for a perpendicular form, (*ii*) as should the ring proton shifts, and (*iii*) no proximate coupling of CH_3 and H-6 protons should exist.

Taking the coupling evidence first, a comparison with *ortho* substituted anisoles, **6** (X = O), is in



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order. Because of the relatively strong conjugation when X = O, the anisoles usually favor a conformation with a zero angle of twist (15, 16) about the C—O bond (planar). As a consequence (17, 18) a proximate coupling of −0.30 ± 0.02 Hz between the methyl protons and H-6 exists. INDO MO FPT calculations (19) reproduce this phenomenon (20), which has its origin in the close approach of the coupled nuclei and/or the relevant bond orbitals. The coupling is observed also for 2-hydroxyanisole, in which an intramolecular hydrogen bond exists (18).

Now, in *ortho* substituted thioanisoles, such a coupling also occurs (21). Contrary to ref. 21, there is a ${}^5J_o^{H_6,CH_3}$ of (−) 0.24 Hz in 2-methoxythioanisole and of −0.36 Hz in 2,5-dichlorothioanisole.[3] These numbers and their signs are again consistent with a proximate (through-space) coupling mechanism for a preferred **6** (X = S). However, in **2**, ${}^5J_o^{H,CH_3}$ is not larger than 0.02 Hz in magnitude (see Fig. 1) indicating that **2**, in which the hydrogen atoms containing the coupled protons are separated by more than their Van der Waals radii, and not **6** (X = S) is the stable conformation.

Furthermore, in **2** the methyl protons resonate at $\delta_{CH_3} = 2.27$ ppm (Table 1). In 4-hydroxythioanisole, δ_{CH_3} is 2.41 ppm and is 2.44 ppm in thioanisole (22*a*). The upfield shift in **2** is analogous to that observed for the SH proton in the corresponding hydroxythiophenol (5) and can be attributed to the magnetic anisotropy of the benzene nucleus. Similar calculations to those in refs. 5 and 22*b*, taking reasonable geometries (5, 12) for **2** and **6** (X = S), predict an upfield shift of ca. 0.3 ppm for the methyl protons in **2** relative to **6** (X = S). This is an extreme value because in 4-hydroxythioanisole the relatively low barrier to rotation about the C—S bond implies that the methyl protons sample conformations other than **6**. Therefore an upfield shift of less than 0.3 ppm is anticipated. Accordingly, the observed shift of 0.14 ppm for the methyl protons is consistent with a perpendicular conformation of **2**.

Turning to the ring proton shifts, their equality in **2** and **1** is striking (Table 2). Because the latter exists as the perpendicular **1**, the equalities suggest the same conformation for **2**. A comparison with 2-hydroxyanisole is also useful. In Table 2, two sets of predicted shifts are given, based on the shifts observed for the corresponding phenyl derivatives. One set assumes that the SCH_3 and OCH_3 substituents do not contribute to the shifts in the two disubstituted compounds. The other set assumes additive contributions from both substituents in a compound. A comparison of the mean deviations between observed and calculated shifts, $\langle \Delta\delta \rangle$, implies that the SCH_3 group in **2** is no longer conjugated with the π system of the benzene nucleus.

Of course, it is known (25, 26) that a simple

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[3] Unpublished work in this laboratory.

TABLE 2. ^1H chemical shifts[a] of 1-X-2-Y benzene derivatives in CCl_4 solution

X, Y	δ_2	δ_3	δ_4	δ_5	δ_6	$\delta_{CH3(SH)}$	$\langle\Delta\delta\rangle$[d]	Ref.
SH,H	7.19	7.13	7.05	7.13	7.19	(3.23)	—	23
SCH_3,H	7.16	7.14	7.04	7.14	7.16	2.44	—	24
SH,OH	—	6.88	7.16	6.76	7.38	(2.81)	—	5
SCH_3,OH	—	6.89	7.15	6.77	7.39	2.27	—	—
	—	(6.64)[b]	(6.89)	(6.71)	(7.01)	—	0.24	—
	—	((6.73))[c]	((7.10))	((6.82))	((7.10))	—	0.13	—
OH,H	6.73	7.10	6.82	7.10	6.73	—	—	9
OCH_3,H	6.75	7.15	6.81	7.15	6.75	3.76	—	24
OCH_3,OH	—	6.81	6.76	6.70	6.72	3.81	—	18
	—	(6.63)[b]	(6.67)	(6.72)	(6.60)	—	0.10	—
	—	((6.73))[c]	((7.10))	((6.82))	((7.10))	—	0.23	—

[a] In ppm relative to internal TMS; different concentrations will cause variations of ca. 0.02 ppm for various measurements.
[b] On an additive basis, $\delta_{C_6H_6} = 7.25$ in CCl_4.
[c] Assuming only OH contributes to the shifts.
[d] The mean deviation between observed and calculated shifts for all four protons.

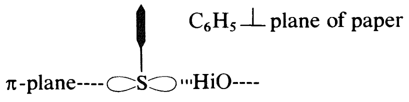
additivity scheme for the ring proton shifts in *ortho* disubstituted benzenes somewhat lacks predictive power, particularly for protons next to the substituents. Therefore, centering attention on δ_4, i.e., for the proton placed *para* to SCH_3 or OCH_3, note that a shift to low field occurs in going from methyl phenyl sulfide to **2** whereas a high field shift occurs for the corresponding anisoles (OH causes a high field shift at a *meta* position). Accordingly, conjugation between the 3*p* orbital of the sulfur atom and the π system has been decreased in **2**, but not between the corresponding oxygen orbitals and the π system in 2-hydroxyanisole. In fact, a detailed comparison of δ_4 in the various compounds suggests almost no conjugative electron donation by SCH_3 in **2**.

Note also the marked shift to low field of H-6, the proton *ortho* to the SCH_3 group in **2**. The so-called "heavy-atom" perturbation (27, 28) is accentuated in **2**. We attribute this shift to the proximity of the directional, mainly 3*p*, lone-pair in **2**. It should also be noted that H-6 in thiophenol or thioanisole resonates farther to low field than expected for a π donor (compare phenol), also a "heavy-atom" effect, observable because the barrier to internal rotation in these two compounds is not large compared to thermal energies.

It seems clear that the ring proton shifts in **2** are compatible with a perpendicular conformation and not with a "planar" conformation as found for 2-hydroxyanisole. Taken together, the present ^1H nmr data are consistent only with a relatively strong OH···3*p* hydrogen bond in **2**. Because no coupling between the hydroxyl proton and H-6 is observed, the perpendicular conformer **2** must exist to the extent of at least 95% in CCl_4 at 305 K. The photoelectron spectrum and a crystal structure of **2** should confirm the ^1H nmr work. The photoelectron spectrum of thioanisole (29) is describable in terms of a 3*p* model for the delocalization of the sulfur lone pair.

2-Hydroxyphenyl phenyl sulfide, 3

The chemical shift of the hydroxyl proton, 6.36 ppm, and its coupling to H-4, 0.47 Hz (Table 1), imply the same conformation at sulfur and oxygen as in **2**, as does the large δ value for H-6. The four ring protons are all deshielded relative to the corresponding protons in **2**. The largest deshielding occurs for H-4, the proton most distant from the phenyl ring. If the deshielding for **3** relative to **2** arises from the magnetic anisotropy of the phenyl ring, the *only* conformation consistent with the observed $\Delta\delta_3 \sim \Delta\delta_5 < \Delta\delta_4$ is one in which the phenyl group lies roughly perpendicular to the substituted benzene plane, i.e., with a conformation **7**. For this conformation, the anisotropy model



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and reasonable CSC angles and C—S bond lengths (30, 31) predicts $\Delta\delta_4 > \Delta\delta_3 = \Delta\delta_5$, with $\Delta\delta_4 \sim 0.07$ ppm. $\Delta\delta_{OH}$ is calculated as 0.04 ppm. Any other conformation, reached by twisting about the C_1—S bond in **7**, involves striking contradictions between model and observation.

In **7** the 3*p* orbital can conjugate most effectively with the second phenyl π system and may be favored (by about 3 kJ/mol) for this reason. Because of partial delocalization into the second phenyl, the OH···3*p* bond may also be somewhat weaker than in **2** and could account for the observed shift to high field of 0.14 ppm in **3**. An empirical relationship (32) suggests this weakening as only 0.4 to 0.8 kJ/mol. The partial delocalization might also help to account for the $\Delta\delta_6$ of 0.06 ppm (calculated as 0.10 ppm). Of course, **7** is an idealized structure. The real conformation undergoes torsional motions, among others. Nevertheless, no other conformation is expected to display the low field shifts given in Table 1.

A further test involves δ_o, δ_m, and δ_p in the C_6H_5 group. These are 6.996, 7.133, and 7.039 ppm, respectively, from a full analysis (rms error of 0.014 Hz). Diphenyl sulfide itself may have C_s or C_2 symmetry (30) or a twisted (33) conformation. The experimental uncertainties imply marked freedom of motion about the C—S bonds. In CS_2 solution, δ_o, δ_m, δ_p are 7.264, 7.235, 7.170 ppm (33). The striking shift in **3** is δ_o, which now lies at highest field. Indeed, structure **7** places an *ortho* proton into the shielding region of the other benzene ring, so that, on average, the anisotropy model predicts an upfield shift of ca. 0.5 ppm. The observed value relative to diphenyl sulfide is 0.27 ppm. The C_6H_5 group is constrained to **7** by only 3 kJ/mol. Therefore it will sample other conformations as well and these have lower anisotropy shifts for the *ortho* protons. Considering the approximate nature of the anisotropy model and the CS_2 solvent for diphenyl sulfide, the agreement is satisfactory. Further, $\Delta\delta_m$ is calculated as 0.12 ppm (observed 0.10 ppm) and $\Delta\delta_p$ as 0.05 ppm (observed 0.13 ppm). $\Delta\delta_p$ is independent of the orientation about the C_1—S bond. Therefore the additional shift to high field is very likely due to the enhanced $3p,\pi$ conjugation relative to diphenyl sulfide. In fact, in benzenethiol δ_p is 7.05 ppm (Table 2).

Taken together, the shift and coupling data for **3** firmly imply **7** as the low energy conformation in solution, with the provision that the C_6H_5 group is relatively weakly constrained in its motion about the C—S bond. Conformation **7** is usually called a skew conformation (34).

*Bis(2-hydroxy-3-*tert*-butyl-5-methyl) sulfide,* 4

This compound was examined for two reasons. First, its infrared spectrum has been interpreted in terms of two different intramolecular OH···π bonds, together with simultaneous OH···π and OH···O interactions for one hydroxyl group and out-of-plane twisting of both hydroxyl groups (3). Second, these interpretations have been used in ^{1}H and ^{13}C nmr studies of related compounds (4).

The most interesting spectral parameters are $\delta_{OH} = 6.42_0$ ppm (3 mol% in CCl_4) and $^5J_m^{\mathrm{OH,H_4}} = 0.59 \pm 0.04$ Hz (three times the standard deviation). The magnitude of ^5J_m is that expected for a trisubstituted phenol (35) and indicates a conformation in which the OH···S bond predominates. No coupling between the hydroxyl and methyl protons was observed. A finite coupling is expected if **4** takes on conformations in which the hydroxyl groups are rotated away from the planes of their respective benzene rings. Again, the hydroxyl proton shift agrees with an OH···S hydrogen bond (compare numbers in Table 1) but not with extensive OH···π interaction. In comparison, the analogous parameters (36) for 2-benzyl-4-chlorophenol imply an intramolecular OH···π interaction of about 1 kJ/mol in free energy, but note that there δ_{OH} is 4.43 ppm (3 mol% in CCl_4 and 305 K).

Characteristic broadening of the H-4 peaks (6.94_5 ppm) by small couplings with the *tert*-butyl protons gave an unequivocal assignment of the ring proton shifts with H-6 at 6.90_3 ppm. In a 2 mol% solution in CCl_4 of 2-*tert*-butylphenol, δ_3 is 7.16 ppm and δ_5 is 6.94 ppm. A methyl group causes an upfield shift of 0.18 ppm at an *ortho* position (25). In the absence of sulfur, additivity of shifts predicts δ_4 as 6.98 and δ_6 as 6.76 ppm in **4**. In the gable (butterfly) conformation, in which two OH···3*p* interactions exist (on either end of the 3*p* orbital), the anisotropy of the phenyl groups should cause $\delta_6 = 6.89$ and $\delta_4 = 6.93$ ppm, effectively identical to the observed shifts.[4]

In other words, the present model implies that the low-field shift caused by a coplanar 3*p* orbital at an *ortho* proton, as discussed above for **1** to **3**, is *absent* if the 3*p* orbital is involved in two OH···3*p* hydrogen bonds. This implication is intriguing in terms of chemical shift theory (note that the electronegativity of a C_6H_5S group is thought to be 2.0, i.e., probably the same as that of hydrogen (30)). A first test demands a structure determination of **4** or of 2,2′-dihydroxydiphenyl sulfide.

The detailed ^{1}H nmr data provide no evidence for other than OH···S preferences in **4**.

Bis(2-hydroxyphenyl) disulfide, 5

The conformations of diphenyldisulfides have received much experimental (37–39) and theoretical (40–43) attention. Here we take a simple view designed to rationalize the observed chemical shifts in terms of one conformation.

The dihedral angle in H_2S_2 is ca. 90° and the HSS angle is also near 90° (44). The filled 3*p* lone pair electrons minimize their mutal repulsion by a twist of 90° to give the observed conformation. If hydrogen atoms are replaced by phenyl groups, the CSSC dihedral angle remains near 90° (38, 45, 46). Furthermore if $3p,\pi$ conjugation is to be maintained, then the CCSS torsion angles are favored at 0°, yielding the observed *equatorial* (47) conformation. In the latter, an *ortho* proton again lies near a

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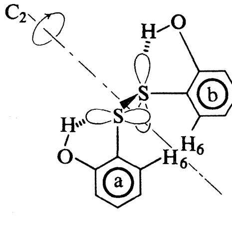
[4] If $\delta_{OH} = 6.03$ ppm from **1** is taken as a reference, the anisotropy model predicts δ_{OH} as 6.35 ppm (6.42 observed).

$3p$ orbital of the *other* SC_6H_5 fragment. The closest H···S distance of about 2.3 Å is much smaller than that of 3.0 Å in **2**. In terms of the discussion in previous sections, this proximity accounts for the large δ_o of 7.44 ppm in equatorial diphenyl disulfide (the phenyl rings reorient rapidly about the C—S bonds and S—S bonds on this shift scale).

Now, for **5**, δ_{OH} is 6.13 ppm (similar to the 6.04 ppm in 2-hydroxythiophenol) and $^5J_m{}^{OH,H_4}$ is 0.48 Hz. Intramolecular hydrogen bonds exist, therefore. The equatorial form of **5** would imply hydrogen bonding to the diffuse $3s$ lone pair on the *ortho* sulfur atom. However, a further twist of 90° about each C—S bond produces the *axial* form in which OH···$3p$ bonds can exist. In this form **8**, the hydroxyl groups lie on one side of the molecule, which brings the H-6 protons close to the neighbouring rings but outside each other's contact distance. $3p,\pi$ conjugation is largely lost and there is a C_2 axis perpendicular to the S—S bond.



Ring b is ca. 2 Å below ring a
C_2 axis ⊥ S—S and bisecting ∢CSSC

8

The anisotropy model for the benzene ring and reasonable geometry about sulfur (37) predicts that for **8**, O—H, H-3, and H-4 should shift (downfield) by 0.09, 0.04, and 0.02 ppm, respectively; whereas H-5 and H-6 should shift (upfield) by −0.03 and −0.36 ppm, respectively. In the above order, the observed shifts relative to **1** are 0.10, 0.04, 0.10, −0.03, and −0.22 ppm. Considering that **8** is not rigid and that the reference compound is not ideal, the agreement is satisfactory. A number of other possible conformers produced much larger discrepancies between observed and calculated shifts. Anisotropy models are semiquantitative at best, of course. The present results provide *no* evidence for OH···π interactions (3). It is of interest that the corresponding diamino compound has this conformation in the crystal, i.e., axial with the amino groups on the same side of the molecule (38, 45). From our viewpoint, this conformation is expected. Again, the corresponding dinitro compound has an equatorial form (48), as anticipated because of the absence of a stereospecific hydrogen bond and probably also because the nitro groups enhance the $3p,\pi$ conjugation (37, 49).

3,3′-Dihydroxy-2-pyridyl disulfide adopts the equatorial conformation (37) in the crystal. There is one *inter*molecular OH···N hydrogen bond and the other hydroxyl group in the molecule is not involved in hydrogen bonding. Conformation **8** would bring the (negatively charged) nitrogen atoms to within about 3 Å (they replace the C—H_6 bonds in **5**). It is quite possible that the N,N electrostatic repulsion, together with the lack of $3p,\pi$ conjugation, in a conformation **8** is higher in energy than the observed conformation in which $3p,\pi$ conjugation is retained and one OH···N intermolecular hydrogen bond occurs.

The model used for all the molecules in this paper distinguishes between mainly s and mainly p type lone-pair orbitals on sulfur. The model rationalizes the approximately perpendicular conformation deduced for **1** (5). The pressure to keep $3s$ orbitals fully occupied (50) supports the simple viewpoint taken in the present discussion. Furthermore, equilibrium bond electron densities can be bent away from the corresponding internuclear axes in a variety of molecules (51). There is also considerable evidence for a nonspherical shape of sulfur in crystals, giving rise to directional preferences in interactions with divalent sulfur (52). In particular, electrophiles approach sulfur in a plane roughly perpendicular to the X—S—Y plane.

The present model is similar to one which would be based on canonical molecular orbitals obtained from, say, single-determinant molecular orbital calculations. An alternative approach would invoke localized molecular orbitals giving equivalent, roughly sp^3, lone-pairs on sulfur. This approach could not account in a straightforward way for the observed conformation of **1**, for example, simply because of the equivalency of the lone-pairs (see ref. 53 for a nice discussion of canonical and localized molecular orbitals). An X-ray investigation of **2** would decide the quality of the model used in this paper.

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