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The Perpendicular Conformation of 2-Hydroxythiophenol. Intramolecular Hydrogen Bonding to a Specific Lone Pair

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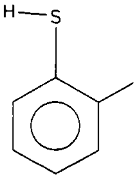
Abstract: The long-range coupling constants between ring protons and the side-chain protons in the ^{1}H NMR spectrum of 2-hydroxythiophenol in CCl_4 solution demonstrate that more than 95% of the molecules exist as a conformer in which the sulfhydryl group prefers a plane approximately perpendicular to the benzene plane. Molecular-orbital calculations can be interpreted as favoring this conformation over the possible planar forms. A simple interpretation holds that electrostatic forces from the polar hydroxyl group twist the mainly 3p orbital of the sulfur atom into the benzene plane, causing a concomitant rotation of the sulfhydryl bond into a perpendicular conformation. The chemical shift of the sulfhydryl proton is consistent with this conformer. The hydroxyl and sulfhydryl protons are spin-spin coupled via the intramolecular hydrogen bond.

Introduction

The infrared spectrum of 2-hydroxythiophenol in CCl_4 solution at ambient temperatures is assigned to roughly equal concentrations of **2** and **3**, a small amount of **1**, and, at concentrations greater than about 1 M, to the additional presence of hydrogen-bonded dimers.[3] On the other hand, Schroeder-Lippencott potential functions are used[4] to derive a potential energy of −1.6 kJ/mol for the S-H···O hydrogen bond in **3** and one of −10.0 kJ/mol for the O-H···S bond in **2**.



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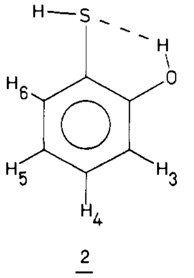

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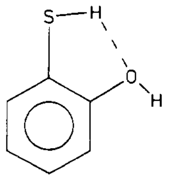

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MO calculations[5] at the CNDO/2 level find **1** and **2** as 4.1 and 0.29 kJ/mol less stable than **3**, respectively, whereas the STO-3G minimal basis set computations yield **1** and **2** as 5.0 and 9.0 kJ/mol less stable than **3**. The CNDO/2 results are apparently in rough agreement with the infrared assignments.

Intuitively, **2** is the most stable in nonpolar solvents, for the O-H bond is much more polar than the S-H bond[6] and the sulfur atom is relatively polarizable, so that **2** appears as a

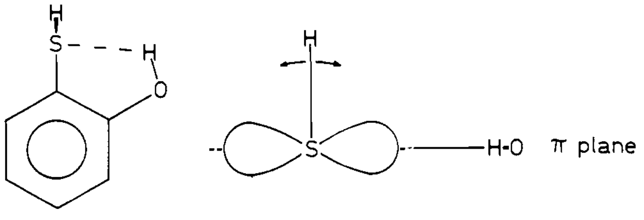

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Table I. Proton Chemical Shifts and Spin-Spin Coupling Constants in 2-Hydroxythiophenol

	value			value	
parameter	sample 1[a]	sample 2[b]	parameter	sample 1	sample 2
ν_{OH}	606.393(3)[c]	603.326(2)	${}^4J_o{}^{H3,OH}$	−0.108(4)	−0.108
ν_{SH}	283.430(2)	281.333(3)	${}^6J_p{}^{H5,OH}$	−0.002(3)	0.0
ν_3	687.239(3)	688.129(2)	${}^5J_m{}^{H4,OH}$	0.423(3)	0.421(3)
ν_4	714.127(2)	715.560(2)	${}^5J_m{}^{H6,OH}$	0.001(3)	0.0
ν_5	675.179(2)	675.825(2)	${}^5J_m{}^{H3,SH}$	0.358(3)	0.362(4)
ν_6	736.639(2)	738.208(2)	${}^5J_m{}^{H5,SH}$	0.382(3)	0.404(4)
${}^3J_{34}$	8.167(3)	8.174(2)	${}^4J_o{}^{H6,SH}$	−1.054(3)	−1.089(3)
${}^3J_{45}$	7.392(3)	7.384(3)	${}^6J_p{}^{H4,SH}$	−0.946(3)	−0.973(3)
${}^3J_{56}$	7.729(3)	7.744(3)	rms deviation	0.010	0.009
${}^4J_{35}$	1.354(3)	1.354(3)	transitions calcd	192	192
${}^4J_{46}$	1.668(3)	1.669(2)	peaks obsd	92	98
${}^5J_{36}$	0.372(3)	0.374(2)	transitions assigned	151	114[d]
${}^5J_o{}^{OH,SH}$	−0.142(4)	−0.142			

[a] Containing some disulfide but is ca. 3.3 mol % in CCl_4. [b] 1.9 mol % in CCl_4. [c] Numbers in parentheses are standard deviations in the last significant figure. [d] Excluding the sulfhydryl and hydroxyl peaks in the iterations.

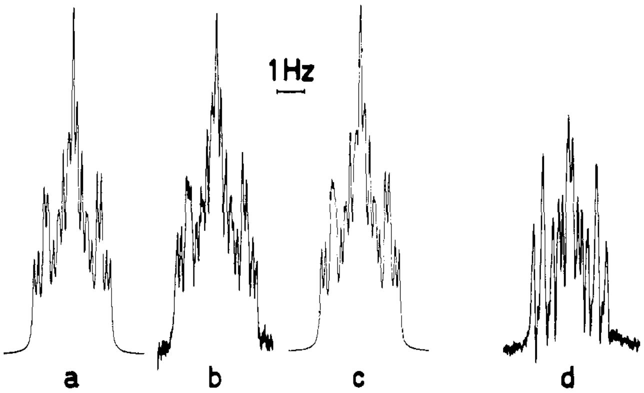

Figure 1. In (a) the calculated spectrum of the sulfhydryl proton is shown for the parameters given for sample 1 in Table I. In (b) the observed spectrum is displayed and is the same for all samples. In (c) the calculated spectrum is shown for the spectral parameters for sample 2 in Table I. In (d) the observed spectrum is displayed under conditions in which the hydroxyl peaks are irradiated. The splitting of 0.14 Hz disappears.

sensible low-energy conformation in the absence of extensive intermolecular hydrogen bonding. In this paper, strong evidence for the predominance of **4**, to the relative exclusion of **1**–**3**, is presented.

Experimental Section

A 5 mol % solution of 2-hydroxythiophenol (Parish Chemical Co.) in CCl_4 was degassed by the freeze-pump-thaw technique. The solution contained a small amount of tetramethylsilane (Me_4Si) and was flame-sealed into a 5-mm o.d. NMR sample tube, containing molecular sieve. The solution was previously dried as described for phenol solutions.[7-10] Intermolecular hydroxyl and sulfhydryl proton exchange was sufficiently slow to allow the observation of spin-spin coupling constants involving these protons. The ${}^1H$ NMR spectrum was calibrated in the frequency-sweep mode on an HA100 spectrometer at a probe temperature of 305 K. Calibrations involved the repeated reading of sweep and manual oscillator frequencies of marker lines placed at ca. 5 Hz intervals. Decoupling experiments and weak irradiations of selected peaks[11,12] were performed in the usual manner.

The sample preparation procedure resulted in the formation of some disulfide, whose resonance peaks could be distinguished from those of the 2-hydroxythiophenol. The actual concentration of the latter was therefore known only approximately, but is estimated to be 3.3 ± 0.2 mol %. The spectral analysis was satisfactory. However, in the interests of accuracy, another sample was also calibrated. It contained negligible amounts of the disulfide.

Molecular orbital calculations were performed on an IBM/370 system. The calculations at the CNDO/2 level of approximation[13] were done for standard geometries,[14] for the most part, with bond parameters for the CSH linkage, as given in Table II of a later section. Partial optimization of the geometry of the side chains was carried out at the STO-3G level of ab initio MO theory.[15] See Table II.

Results and Discussion

Spectral Analysis. Table I contains the spectral parameters as obtained from a six-spin analysis based on the computer program LAME.[16,17] For sample 2, the hydroxyl and sulfhydryl resonances were indistinguishable experimentally from sample 1 (as well as for a 2.3 mol % solution in CCl_4). The plethora of nearly coincident transitions for the side-chain protons suggested that an iteration on the ring proton peaks only would yield an independent set of long-range couplings between the side chain and ring protons. The results of such a procedure are given in Table I (sample 2).

In Figure 1 the observed and calculated sulfhydryl proton spectra are compared. Appearances would indicate that the sulfhydryl coupling parameters listed under sample 2 in Table I are slightly to be preferred over those under sample 1. However, if an error of four times the standard deviations (precision) is assumed, the actual differences in these parameters may not be of great significance (see Table I).

Conformational Deductions from ${}^5J_m{}^{H,OH}$. ${}^5J_m{}^{H4,OH}$ is 0.42 Hz and ${}^4J_o{}^{H3,OH}$ is −0.11 Hz (Table I). Decoupling experiments indicated negligible narrowing of resonance peaks arising from H-6 and H-4. The observed couplings are entirely similar to those in 2-hydroxyanisole[18] for which the intramolecularly hydrogen-bonded conformer is stabilized by 8.4 kJ/mol.[19] The $J^{H,OH}$ values for 2-hydroxythiophenol therefore imply an at least 95% abundance of the conformer in which the hydroxyl group lies cis to the sulfhydryl group. If conformers **1** and **3** were at all abundant, an observable ${}^5J_m{}^{H6,OH}$ would occur, both **1** and **3** yielding a maximum in this coupling and a minimum in ${}^5J_m{}^{H4,OH}$. In fact, a large data set exists[7-10] consistent with a vanishing ${}^5J_m{}^{H4,OH}$ in **1** and **3** and a negligible ${}^5J_m{}^{H6,OH}$ in **2**.

Consequently, the cis orientation of the hydroxyl group is assured and **1** and **3** will be ignored in the ensuing discussion, which concludes that the sulfhydryl group must lie approximtely perpendicular to the benzene plane.

Angle Dependence of ${}^6J_p{}^{H,SH}$ and ${}^6J_p{}^{H,OH}$. The twofold barrier to internal rotation in phenol is 14.6 kJ/mol and very likely arises from conjugation between the oxygen lone pair and the π electrons.[20-22] At ambient temperatures the molecule is essentially planar, the amplitude of out-of-plane torsions being small in a classical sense. It follows that any long-range spin-spin coupling constants between the hydroxyl proton and the ring protons, which arise from out-of-plane conformations of the hydroxyl group, will be small. Thus, if it is assumed[23] that the coupling to the para proton, $^6J_p^{H,OH}$, obeys the equation

$$^6J_p^{H,XH} = {}^6J_{90}\langle \sin^2\theta \rangle \tag{1}$$

in which θ is the angle by which the O–H bond twists out of the benzene plane and $\langle \sin^2\theta \rangle$ is the expectation value of $\sin^2\theta$, $^6J_p^{H,OH}$ in phenol should be near zero. Indeed, it is less than 0.03 Hz in magnitude.[9] The analogous coupling in benzaldehyde is similarly small[24,25] in agreement with an internal rotation barrier of ca. 30 kJ/mol.[26–28] On the other hand, in some toluene derivatives the six-bond couplings between para protons and α protons on the side chain have sizable magnitudes, in line with rather smaller internal barriers.[29] Equation 1 can be understood in terms of a σ–π coupling mechanism in which the σ electrons of the O–H bond, polarized by the proton magnetic moment, in turn polarize the π electrons of the ring. This spin polarization is most effective when the O–H (or X–H$_\alpha$ bond in general) lies in a plane perpendicular to the benzene plane.

In benzenethiol, the barrier to internal rotation is only 3.2 kJ/mol in the gas phase.[30,31] In that event $\langle \sin^2\theta \rangle$, as calculated by a hindered rotor model[33] for an assumed twofold barrier, is significantly large at ambient temperatures. Therefore, an observed $^6J_p^{H,SH}$ of −0.33 Hz is reasonable in terms of eq 1.[34] A V_2 of 3.2 kJ/mol implies a $^6J_{90}$ of −0.97 Hz if the barrier is unchanged in solution (it had been assumed to be −1.06 Hz in solution[34]). Further work[35] assumed a ratio of 1.15 for $^4J_o^{H,SH}/^6J_p^{H,SH}$. This assumption led to a substituent dependence of V_2 in para-substituted benzenethiol derivatives.[35] V_2 ranges from ca. 10 kJ/mol in the *p*-nitro derivative to essentially zero for the *p*-amino compound. The variation in V_2 could be understood in terms of the double-bond character of the C–S bond, decreasing as strong π-electron donors appeared at the para position.[35]

Conformational Deductions from $^2J_p^{H,OH}$ and $^6J_p^{H,SH}$. The unobservably small value (<0.03 Hz) of $^6J_p^{H_5,OH}$ in 2-hydroxythiophenol demonstrates the essential coplanarity of the O–H bond and the benzene framework, a demonstration entirely in keeping with a conformer of type **2**.

Now, the large magnitude of 0.96 Hz for $^6J_p^{H,SH}$ implies an out-of-plane orientation of the S–H bond. Indeed, if $^6J_{90}$ is −0.97 Hz in this molecule, then the S–H bond lies in a plane essentially perpendicular to the benzene plane.[36] On the other hand, if $^6J_{90}$ is −1.06 Hz (implying a somewhat larger barrier to internal rotation in benzenethiol in solution than in the vapor phase), then the S–H bond is twisted about 75° out of the benzene plane. Of course, while the intramolecular hydrogen bond stabilizes this conformation, it is still true that torsion will occur about the C–S bond. Therefore, a number for a (classical) angle θ is somewhat misleading. Nevertheless, it is reasonable to state that the S–H bond prefers a plane approximately orthogonal to the molecular plane.

Confirmation of 4 from $^4J_o^{H,SH}$ and $^5J_m^{H,SH}$. The ratio of ^4J_o to ^6J_p is 1.12 ± 0.03, in fair agreement with the assumption of 1.15 used previously.[31] The quoted range assumes an error in the coupling constants of four times their standard deviations. The four-bond coupling may well contain a σ-electron component, possibly more sensitive to substituent perturbation than the σ–π dominated $^6J_p^{H,SH}$. In any event, the large magnitude of $^4J_o^{H,SH}$ is consistent with the deduction based on $^6J_p^{H,SH}$.

The two $^5J_m^{H,SH}$ values differ by $0.02_9 \pm 0.02_4$ Hz (4 × 0.003 × 2). $^5J_m^{H,SH}$ is stereospecific[6] for conformations in which the S–H bond lies in the plane of the ring (see the discussion above for $^5J_m^{H,OH}$). Clearly, the essential equality of the two $^5J_m^{H,SH}$ values is again consistent with the proposed conformation.

S–H and O–H Chemical Shifts. The chemical shift, δ_{SH}, of thiophenol in a 5 mol % solution in CCl_4 is 3.23 ppm[34] and is 3.26 ppm at infinite dilution,[38] in accord with a very small association between solute molecules at the higher concentration. For 2-hydroxythiophenol, δ_{SH} is 2.83 ppm (Table I). To a first approximation, the shift of 0.4 ppm to high field in the latter may be attributed to (1) a decrease in the low-field shift arising from the magnetic anisotropy of the benzene ring as the S–H bond twists out of plane; (2) electron donation from the O–H moiety. In terms of the approximate anisotropy models of Abraham[39] and of Johnson and Bovey,[40] and of a simple geometry of thiophenol (see MO calculations below), the S–H proton resonance peak shifts to high field by 0.24 ppm when the S–H twists into a plane perpendicular to the benzene plane. In *p*-methoxythiophenol, δ_{SH} is 3.15 ppm. If this shift is taken as a measure of electron-density changes at S–H, the anisotropy shift in 2-hydroxythiophenol is estimated at 0.32 ppm to high field. Ordinarily, a π-electron donor causes larger high-field shifts at ortho than para positions, so that the 0.32 ppm may be an overestimate. On the other hand, in **4** the sulfur 3p orbital is not available for π acceptance. In addition, other perturbations may be present. It seems clear, however, that δ_{SH} is consistent with **4**.

In 2-methoxythiophenol, δ_{SH} is 3.66 ppm, interpretable as caused mainly by hydrogen bonding in a roughly 50% abundant conformer analogous to **3**.[18]

In 2-methoxyphenol, δ_{OH} is 5.41 ppm in CCl_4 solution.[18] In 2-hydroxythiophenol, δ_{OH} is 6.07 ppm. If, as is often supposed, the extent of the shift to low field is proportional to the strength of the hydrogen bond, the O–H···S hydrogen bond in the latter compound is stronger than in the former. In any

Table II. Computed Relative Energies (kJ/mol) of Various Conformers of 2-Hydroxythiophenol

	geometry^{a-c}				energy	
conformer	O–H	S–H	∠COH	∠CSH	STO-3G	CNDO/2
1	0.987	1.330	105.2	95.1	4.47	
		standard			4.69	9.73
2	0.987	1.328	105.2	95.1	8.96	
		standard			7.63	0.00
3	0.987	1.330	105.4	95.4	0.00	
		standard			0.00	8.11
4	0.986	1.334	105.0	95.5	4.54	
		standard			4.23	4.95
5^d	0.988	1.334	105	95.3	~16.	
		standard			13.74	15.26

^{a} All partially optimized geometries had C–O and C–S lengths of 1.390 and 1.783 Å, respectively, as found for **4** by STO-3G optimization. ^{b} Standard geometries from ref 14, together[5] with ∠CSH = 98°, C–S and S–H lengths of 1.814 and 1.328_5 Å, respectively. ^{c} The C_2C_1SH dihedral angle for **4** minimized at 13–15° from 90°, i.e., S–H twisted away from O–H. ^{d} **5** is obtained from **4** by rotating the hydroxyl group by 180°, i.e., O–H is now trans to the sulfhydryl group.

case, δ_{OH} and δ_{SH} in 2-hydroxythiophenol are consistent with conformer **4** and certainly not with **1** or **3**.

Coupling through the Hydrogen Bond. $^5J_o^{OH,SH}$ is -0.14 Hz. Proton-proton couplings over five formal bonds are normally positive. In particular, **1** is expected to display a positive coupling. The small, negative value can be understood as coupling via a "direct" mechanism[41] via a predominantly electrostatic hydrogen bond.[42-44] A large covalent contribution[44] to the hydrogen bond should yield a larger magnitude of $^5J_o^{OH,SH}$.

Molecular Orbital Calculations. The results of the CNDO/2 and STO-3G computations are given in Table II, where the geometries are also defined. Clearly, the data on the isolated molecules do not agree with the experiment in solution (at least at first sight), although our CNDO/2 energies support intuition and the potential functions[4] that, of all the planar forms, **2** is the most stable by at least 8 kJ/mol. Furthermore, both CNDO/2 and STO-3G agree that **4** is preferred over **5** (related to **4** by switching the hydroxyl group to a position trans to the sulfhydryl group) by about 10 kJ/mol. This value might be taken as an indication of the strength of the O-H· · ·S hydrogen bond, consistent with $^5J_m^{H,OH}$.

In our opinion, the MO results are faulty in that they overestimate the energy necessary to twist the S-H bond into a perpendicular orientation. Thus, for thiophenol, our previous STO-3G calculations gave this energy as[34] 13.6 kJ/mol, in obvious disagreement with the known twofold barrier of 3.2 kJ/mol in the gas phase. A similar overestimate occurs for phenol.[45] A CNDO/2 calculation on the optimized geometry[34] of thiophenol gave 8.6 kJ/mol for V_2.

Thus, if $13.6 - 3.2 = 10.4$ kJ/mol is subtracted from the STO-3G energies of the perpendicular **4**, this conformer becomes 6 kJ/mol more stable than any of the planar conformers. Again, if an adjustment of $8.6 - 3.2 = 5.4$ kJ/mol is applied to the CNDO/2 data in Table II, conformer **4** also becomes the most stable, but clearly not in as good agreement with the experiment as the adjusted STO-3G data.

No dipole-moment data are available for 2-hydroxythiophenol. The STO-3G values are 1.49, 1.82, 1.78, and 1.44 D for **1–4**, respectively.

A Pictorial Description of the Stability of 4. The MO calculations are complex and contain various approximations. A simple interpretation of the stability of **4** goes as follows.

If the barrier to internal rotation in thiophenol of 3.2 kJ/mol is attributed to conjugation, it is sensible that an O-H· · ·S hydrogen bond energy of ca. 10 kJ/mol can lead to the stability of **4**. In addition, **4** is favored by an entropy of R ln 2 over **1–3**. A C-S-H angle of 95° means that the 3s orbital is only weakly involved in the bonding,[46] indicating in turn that a good description of the lone pair on the sulfur atom in planar thiophenol places one pair into the mainly 3s orbital and locates the other pair in the 3p orbital perpendicular to the benzene plane. The lone pair in the mainly 3s orbital is diffuse but the directional lone pair in the mainly 3p orbital is twisted into the benzene plane by electrostatic forces from the polar O-H bond. Consequently, the S-H bond now occupies the plane previously preferred by the 3p electron pair. The pressure to keep the 3s orbital totally occupied[47] accounts for the hybridization preference.

Conclusions

The perpendicular conformation of 2-hydroxythiophenol exists to the extent of at least 95% in CCl_4 solution at 305 K. Part of this stability relative to the planar conformations is due to R ln 2 in the entropy. In structural terms, the stability arises from stereospecific intramolecular hydrogen bonding of the hydroxyl group to the mainly 3p lone pair on the sulfur atom. A microwave determination of the structure would be useful. The compound is a liquid at room temperature, unlike phenol.

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