

## THE SULFHYDRYL GROUPS IN 4-AMINO- AND 4-METHOXY-THIOPHENOL PREFER THE PLANE NORMAL TO THE MOLECULAR FRAME

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In 4-aminothiophenol and 4-methoxythiophenol the conformations of lowest energy are those in which the S—H bond lies in a plane perpendicular to the benzene plane.  $V_2$  is  $2.9 \pm 0.4$  and  $1.9 \pm 0.4$  kJ/mol, respectively. By way of contrast,  $V_2$  in 4-nitrothiophenol is  $9.0 \pm 0.8$  kJ/mol and the S—H bond prefers the molecular plane.

### 1. Introduction

The two-fold barrier,  $V_2$ , to out-of-plane motion of the hydroxyl group in phenol is 14.5 kJ/mol [1–3]. It increases (decreases) by 4 kJ/mol in the presence of a 4-nitro (4-hydroxyl) substituent [4], reflecting the changes in conjugation between the lone pair on oxygen and the  $\pi$  system (change in double-bond character of the C—O bond).

The  $J$  method [5] indicates a similar dependence of  $V_2$  in thiophenol and its 4-substituted (4-X) derivatives [6,7]. The method depends on the relationship

$${}^6J_{\text{p}}^{\text{H,SH}} = {}^6J_{90} \langle \sin^2 \theta \rangle, \quad (1)$$

in which  ${}^6J_{\text{p}}(\text{Hz})$  is the spin—spin coupling constant over six bonds between the sulfhydryl proton and the *para* ring proton.  ${}^6J_{90}$  is the magnitude of  ${}^6J_{\text{p}}$  when the angle of twist,  $\theta$ , about the C—S bond is  $90^\circ$ ; and  $\langle \sin^2 \theta \rangle$  is the expectation value of  $\sin^2 \theta$ , obtainable from a hindered rotor treatment [5,8] in terms of  $V_2$  and other parameters.

A crucial parameter is  ${}^6J_{90}$ , originally [6,7] estimated as  $-1.06$  Hz; representing the maximum magnitude of the  $\sigma$ — $\pi$  interaction between the S—H bond and the  $\pi$  orbitals of the benzene ring. For the 4-X-thiophenols,  ${}^4J_{\text{o}}^{\text{H,SH}}$  was approximated as  $1.16 {}^6J_{\text{p}}$ , so that it could be used in (1) to find  $\langle \sin^2 \theta \rangle$ . It was then found that  $V_2$  ranged between  $\approx 10$  kJ/mol for

X =  $\text{NO}_2$  and  $\approx -1$  kJ/mol for X =  $\text{NH}_2$ . Because of the uncertainty in  ${}^6J_{90}$  and  ${}^4J_{90}$ , further discussion was unwarranted.

It was then pointed out by Larsen [9], that combined microwave and far infrared data (MW/IR) yield  $V_2$  as 3.2 kJ/mol in thiophenol [3] and as 0.72 kJ/mol in 4-fluorothiophenol [9]. Furthermore, subsequent work on 2-hydroxythiophenol [10] demonstrated that the stereospecific intramolecular hydrogen bond,  $\text{OH} \cdots \text{S}$ , constrained the S—H bond to a plane approximately perpendicular to the molecular frame. The values of  ${}^4J_{\text{o}}^{\text{H,SH}}$  and  ${}^6J_{\text{p}}^{\text{H,SH}}$  were  $-1.09$  and  $-0.97$  Hz, respectively, approximating to  $\theta = 90^\circ$ .

### 2. $V_2$ for seven thiophenols

Taking all these data together, firmer estimates of  $V_2$  can now be made. These are collected in table 1 and are obtained as follows. If  $V_2$  in thiophenol is 3.2 kJ/mol (MW/IR), then  ${}^4J_{90}$  must be  $-1.07$  Hz because  $\langle \sin^2 \theta \rangle$  is then  $0.380/1.07$  or 0.355. This number corresponds to the  $\langle \sin^2 \theta \rangle$  calculated for  $V_2 = 3.2$  kJ/mol from the hindered rotor model at 305 K (temperature of measurement of  ${}^4J_{\text{o}}$  in thiophenol),  $I_{\text{r}} = 2.74 \times 10^{-47}$  kg m<sup>2</sup>, and using 25 basis functions (15 give the same result). A similar calibration of  ${}^4J_{90}$  with a  $V_2$  of 0.72 kJ/mol (MW/IR) yields  $-1.14$  Hz. The numbers are close to that found for  ${}^4J_{90}$  in 2-

Table 1  
Two-fold barriers to rotation about the C-S bond in some 4-X-thiophenols

Substituent	$-^4J_{\text{O}}^{\text{H,SH}}$ (Hz)	$V_2$ (kJ/mol)		
		1 a)	2 a)	3 a)
NO <sub>2</sub>	0.20 <sub>3</sub>	8.9	9.0 ± 0.8	9.1
Br	0.33 <sub>3</sub>	3.9	4.8	4.8
H	0.38 <sub>0</sub>	3.2	3.4	3.7
CH <sub>3</sub>	0.43 <sub>9</sub>	1.9	2.2	2.5
F	0.53 <sub>1</sub>	0.2	0.4	0.7
OCH <sub>3</sub>	0.64 <sub>9</sub>	-2.3	-1.9	-1.5
NH <sub>2</sub>	0.69 <sub>7</sub>	-3.3	-2.9 ± 0.4	-2.4

a) Column 1 has  $^4J_{90}$  as  $-1.07$  Hz, designed to produce agreement with  $V_2$  in thiophenol determined from microwave/infrared data [3]; column 3 has  $^4J_{90}$  as  $-1.14$  Hz in order to produce agreement with the microwave/infrared data on 4-fluorothiophenol [9]. The value of  $^4J_{\text{H,SH}}$  ( $\approx 90^\circ$ ) in 2-hydroxythiophenol is  $-1.09 \pm 0.02$  Hz [10]. Column 2 has  $^4J_{90}$  as  $-1.10$  Hz. See text for discussion

hydroxythiophenol, suggesting that consistent  $V_2$  values are obtainable in this way.

The three columns of  $V_2$  numbers in table 1 assume  $^4J_{90}$  values of  $-1.07$ ,  $-1.10$ , and  $-1.14$  Hz. The error indications assume that the uncertainty in the measured coupling constants is 0.02 Hz (the standard deviations in the least-squares analyses were all less than 0.01 Hz). In any event, it is unlikely that the error in  $V_2$  is greater than 1 kJ/mol and the middle column is probably the best set of estimates obtainable in this way.

### 3. Other couplings as a check on $V_2$

In thiophenol,  $^6J_{\text{p}}^{\text{H,SH}}$  is  $-0.33_4$  Hz [6]. A  $V_2$  of 3.2 kJ/mol entails a  $^6J_{90}$  of  $-0.94$  Hz [via the hindered rotor treatment and (1)], whereas a  $V_2$  of 3.7 kJ/mol (other limit in table 1) implies a  $^6J_{90}$  of  $-1.00$  Hz. The mean agrees with  $^6J_{90}$  approximated in 2-hydroxythiophenol.

Again,  $^7J_{\text{p}}^{\text{SH,CH}_3}$  ( $X = \text{CH}_3$ ) should be  $^6J_{90} \langle \sin^2 \theta \rangle$ , i.e.  $0.97$  ( $0.399_5$ ) or  $0.39$  Hz. Here  $0.97$  is the mean magnitude of  $^6J_{90}$  above and  $\langle \sin^2 \theta \rangle$  is the value for S-H group corresponding to  $V_2 = 2.2$  kJ/mol (table 1). The relationship follows because, in toluene derivatives,  $^6J_{\text{p}}^{\text{H,CH}_3} = -^7J_{\text{p}}^{\text{CH,CH}_3}$ . In other words, replace-

ment of a C-H bond in benzene by a  $\text{CH}_3$  group leaves the magnitude of the  $\sigma-\pi$  interaction unchanged. The observed  $^7J_{\text{p}}^{\text{SH,CH}_3}$  is  $0.40 \pm 0.02$  Hz [7].

Finally,  $^6J_{\text{p}}^{\text{SH,F}}$  ( $X = \text{F}$ ) is calculated as  $\langle \sin^2 \theta \rangle$  ( $1.12/0.62$ ) or  $0.88$  Hz.  $^6J_{\text{p}}^{\text{F,CH}_3}$  in 4-fluorotoluene is  $1.12 \pm 0.02$  Hz [11] and  $^6J_{\text{p}}^{\text{H,CH}_3}$  in toluene is  $-0.62 \pm 0.02$  Hz [12]; giving the ratio of the  $\sigma-\pi$  parameters for these two couplings, transmitted by a  $\pi$ -electron mechanism [13]. The observed  $^6J_{\text{p}}^{\text{SH,F}}$  is  $1.01 \pm 0.02$  Hz [7]. It should be noted that  $^6J_{\text{p}}^{\text{H,F}}$  in aromatic systems may well contain an angle-independent component of  $\approx 0.1$  Hz [14,15].

### 4. Perpendicular conformations for $X = \text{NH}_2$ , $\text{OCH}_3$

For these compounds,  $\langle \sin^2 \theta \rangle$  is greater than 0.5 and  $V_2$  is indicated as negative in table 1. This means that the conformation of minimum energy has  $\theta = 90^\circ$ . The conjugation of the mainly 3p lone pair on the sulfur atom (the C-S-H angle in the planar conformation of thiophenol is  $\approx 96^\circ$  [16]) with the  $\pi$  system is weak and is reduced further by the  $\pi$  donors,  $\text{NH}_2$  or  $\text{OCH}_3$ . Therefore it is reasonable that repulsion between the S-H and *ortho* C-H protons (alternatively, between S-H and *ortho* C-H bonds) leads to a preferred perpendicular conformation.

Of course, a statement concerning a definite conformational angle is not implied here [17]. The experiments measure  $\langle \sin^2 \theta \rangle$ , from which follow  $V_2$  and a preferred conformation. Nevertheless, it is interesting that the substituted phenyl group in the crystal of 4-dimethylaminophenyl phenyl sulfide lies perpendicular to the C-S-C plane [18], but that in the corresponding nitro derivative the substituted phenyl group lies parallel to the C-S-C plane [19]. If packing forces do not determine these geometries, a comparison with the  $V_2$  values and conformations in table 1 suggests the reason for the contrasting geometries in the two diphenyl sulfides.

### 5. Solvent effects on barriers

The coupling constant data are for solutions at 305 K (mainly  $\text{CCl}_4$ ). It is our belief that (except in extreme cases) collisions with solvent molecules may well alter the rate at which the S-H group reorients,

but that this does not reflect on the intrinsic barrier measured by the slow (time scale of seconds)  $J$  method.

The  $^4J_{\text{H,SH}}$  values vary little in different solvents. For example,  $^5J_{\text{O}}$  ( $\text{X} = \text{NH}_2$ ) is  $-0.69_7$  in  $\text{CCl}_4$ ,  $-0.71_3$  in benzene- $d_6$ , and is  $-0.68_2$  Hz in  $\text{CDCl}_3$  [7].

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