in the solid state, it may therefore be anticipated that the effect of the naphthalene ring on the chemical shifts of the three diastereotopic methyl groups in **4** and **5** at the slow exchange limit will differ markedly from those of the peri *tert*-butyl methyls in **1** (three singlets in the ^{1}H NMR spectrum at δ 0.61, 1.40, and 1.78 ppm).[4]

Empirical Force Field Calculations on 1,8-Bis(trimethylelement)naphthalenes. The EFF approach[12] has recently been used to study the dynamic stereochemistry of **2**, **3**, and **5**.[13,14] It therefore seemed of interest to compare calculated structures with those determined by X-ray analysis.

The ground states of **2–5** were each calculated[12,15] using the approximations previously described.[13,16] Salient features of the calculated structures are presented in Table IV. Comparison with the appropriate entries in Tables I-III reveals satisfactory overall agreement between calculated and X-ray structures. In particular, the structural deformations, as reflected in the values of Z1-C1-C8-Z2, C1/8-C9-C10-C4/5, and Z1/2-C1/8-C4/5, are well reproduced. Most notably, the $(CH_3)_3Z$ groups exhibit the conformations found in the crystal, i.e., conformation A for **4** and **5** and conformation B for **1** (**2**) (Figure 3).

The Z-C bond lengths in **1** (**2**) are reasonably well reproduced. However, the expected reversal of the Z-C_{sp^3} and Z-C_{sp^2} bond lengths is not reproduced for **4** and **5**; the approximations used in calculations on the higher homologues may be responsible for this discrepancy.

Since the bonding parameters for Si are closer to those of Ge[16] than to those of C, it may be predicted that the structure of **3** more closely resembles that of **4** than that of **2** (**1**). This prediction is supported by the EFF calculations (Table IV). While those parameters which reflect the pyramidality at C1/8 and the twist of the C1-C9-C8 and C4-C10-C5 planes (see above) are very similar for **3**, **4**, and **5**, there is a significant gap between the values for **2** (**1**) and those found in the higher homologues. Furthermore, the $(CH_3)_3Si$ groups adopt conformation A (Figure 3), which is also preferred by **4** and **5**, in contrast to conformation B, which is adopted by **2** (**1**).

Thus it appears that molecular deformations in the homologous series of 1,8-bis(trimethylelement)naphthalenes follow the order $\mathbf{2} \gg \mathbf{3} > \mathbf{4} > \mathbf{5}$. A test of this prediction awaits the synthesis of **3**.

Acknowledgments. We thank the National Science Foundation (CHE77-07665) for support of this work and the Swedish Natural Science Research Council for a postdoctoral fellowship to one of us (U.S.).

Supplementary Material Available: Final positional and thermal parameters, with standard deviations, and structure factor tables for **4** and **5** (19 pages). Ordering information is given on any current masthead page.

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(15) A corrected value of −25.92 kcal/mol was used for the C_{ar}–C_{ar}–C_{ar}–C_{ar} torsional potential.
(16) The naphthalene ring was simulated by two fused benzene rings.[13] Parameters for silicon, germanium, and tin were those of carbon with the following longer preferred bond lengths for the stretching functions: Z–C_{sp^3}, 1.87, 1.98, and 2.15 Å; Z–C_{sp^2}, 1.85, 1.955, and 2.12 Å, for Z = Si, Ge, and Sn, respectively.

Conditions Favoring Retention of Configuration in S_N2 Reactions. A Perturbational Study

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Abstract: Salem's frontier orbital treatment of the Walden inversion may be extended to show that retention of configuration is favored by (a) a reaction center Z of low electronegativity, (b) a leaving group X of high electronegativity and/or with contracted valence orbitals, (c) a high percentage of s character in the hybrid atomic orbital of Z in the ZX bond, (d) a "hard" nucleophile. Condition (b) applies rigorously to homologous series, i.e., to comparisons of X's belonging to the same column of the periodic table. At least for the case of silicon compounds, it is *not* necessary in order to reproduce the experimental trends to introduce in the calculations either d orbitals for the reaction center or pseudorotations for the transition state.

Although many theoretical studies have been devoted to the S_N2 reaction over the last few years,[2] its stereochemistry remains an intriguing problem. To the best of our knowledge, there is still no proven example of an S_N2 reaction with retention of configuration[3] if the reaction center is a saturated carbon atom.[4] However, if the reaction center is a silicon atom, it is possible, depending on the nature of the substrate and of the nucleophilic reagent, to obtain highly stereoselective reactions with either predominant retention or inversion of configuration.[5,6] It is interesting to note that all these various stereochemistries may be rationalized with the help of one single perturbational scheme.

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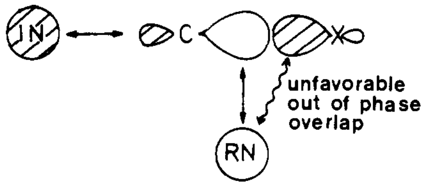


Figure 1. Interaction between the nucleophile's HOMO and the substrate σ^*_{CX} (RN = frontside attack leading to retention of configuration, IN = rearside attack leading to inversion of configuration).

Let us start by recalling Salem's treatment of the Walden inversion.[7] Frontier orbital approximation is assumed, i.e., the major interaction during the reaction will occur between the nucleophile's HOMO and the substrate's LUMO. The structure of the latter is shown in Figure 1, with the big lobes of the hybrid AOs pointing toward each other. A frontside attack (RN) of the nucleophile, leading to retention of configuration, corresponds therefore to an attack on the big lobe of C, but this favorable factor is more than compensated by the unfavorable out-of-phase overlap between the reagent and the leaving group (Figure 1, wavy arrow), so that rear-side attack with inversion of configuration (IN) finally prevails. This qualitative reasoning has been confirmed by numerical calculations (vide infra).

Clearly, if Salem's treatment is correct, it should be possible to *increase the probability of getting retention of configuration by increasing the favorable interaction between the nucleophile and the reaction center and/or by decreasing the unfavorable interaction between the nucleophile and the leaving group.* This can be done by increasing the contribution of the reaction center Z in the substrate's LUMO, by decreasing that of the leaving group X in the same MO, by lengthening the ZX bond, and by use of "hard" nucleophiles.

I. Influence of the Reaction Center Z

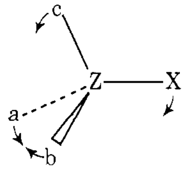
Consider two atoms Z and X of different electronegativities. When a bond is created between Z and X, their atomic orbitals ϕ_Z and ϕ_X combine together to give two bond orbitals, σ_{ZX} and σ^*_{ZX} (Figure 2). The antibonding combination may be written in the first approximation

$$\sigma^*_{ZX} \simeq \phi_Z + \frac{\langle \phi_Z | P | \phi_X \rangle}{E_Z - E_X} \phi_X \qquad (1)$$

In other words, σ^*_{ZX} is essentially ϕ_Z, mixed out of phase with a smaller quantity of ϕ_X. As shown in eq 1, the mixing coefficient is inversely proportional to the energy gap $E_Z - E_X$ (where E_i is the energy, before interaction, of the orbital ϕ_i). Provided that the integral $\langle \phi_Z | P | \phi_X \rangle$ remains substantially the same, increasing this gap will enhance the contribution of ϕ_Z and diminish that of ϕ_X in σ^*_{ZX}. This can be done by raising ϕ_Z and/or lowering ϕ_X.

Physically, raising ϕ_Z corresponds to a decrease of the electronegativity of the reaction center Z. The simplest way to reach this objective is by *going down the same column in the periodic table,* i.e., by replacing Z = C by Z = Si.[8] In fact, this replacement introduces also other changes which, fortunately, have the same stereochemical consequences. Thus given a leaving group X, the Si-X bond will be longer than the C-X bond and this bond lengthening will diminish the unfavorable interaction between X and the nucleophile for the frontside RN attack. The valence orbitals have also changed from 2s and 2p for C to 3s and 3p for Si. They become more diffuse and overlap better at large distances with the nucleophile; again the probability of the RN attack is enhanced.

Consider now a tetracoordinated Z atom: ZabcX. If the aZb angle is decreased (by including atoms a, Z, and b in a strained cycle, for example), the cZX angle becomes more opened. This means that in the ZX bond the ϕ_Z hybrid atomic orbital now contains more s character and is more dissymmetric. It follows that the favorable overlap between the reaction center Z and the incoming nucleophile is increased (decreased) for a RN (IN) attack. It is a well-known experimental fact that *cyclic silicon compounds give more retention of configuration than their open-chain homologues, if the leaving group X is extracyclic.*[9] Notice that, owing to the different CC and CSi bond lengths, a six-membered ring containing one Si atom is already strained. Conversely, it may be predicted that, if Si and X are both included in a strained cycle, the probability of getting retention of configuration is reduced. Again, this is in good agreement with experimental results.[10]



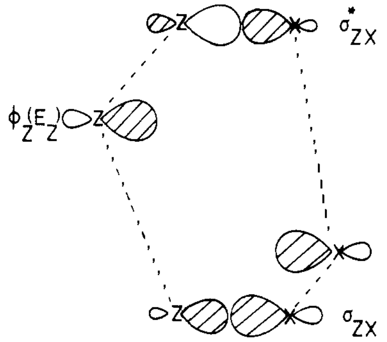


Figure 2. Bonding σ_{ZX} and antibonding σ^*_{ZX} combinations of two nondegenerate atomic orbitals ϕ_Z and ϕ_X.

II. Influence of the Leaving Group X

Equation 1 shows that, to reduce the contribution of ϕ_X in the σ^*_{ZX} orbital, ϕ_X should be lowered. It is tempting to conclude, by analogy with the preceding section, that increasing the electronegativity of the leaving group will automatically favor retention of configuration. In fact, the situation is more complex.

When one replaces, say, X = Cl by X = F, besides the favorable electronegativity change, two other modifications occur as well. The valence orbitals of X become more contracted, thus decreasing the unfavorable overlap between X and the nucleophile Nu. But at the same time, the ZX bond shortens, increasing the X-Nu overlap in a RN attack.

Thus, of the three simultaneous changes, two (increased electronegativity and contracted valence orbitals) will favor retention of configuration, while the third (ZX bond shortening) will favor inversion of configuration. It is very difficult to decide a priori which factor will predominate. Numerical calculations (vide infra) indicate that, in the previous example (Cl → F), the ZX bond shortening does not fully compensate the two former effects. Therefore, *replacing X by some higher element in the same column of the periodic table (i.e., changing X = Cl to X = F or X = SR to X = OR) will generally increase the percentage of retention of configuration.*[11]

However, the bond-shortening effect may become competitive with the two others if X is replaced by an element of another column of the periodic table: experimentally, X = SR and X = F give analogous results.[11] The importance of the size of the valence orbitals comes to the fore when X = H. Although the SiH bond is quite short and the electronegativity of hydrogen quite low, retention of configuration is commonly observed with H as a leaving group. This is not really surprising.

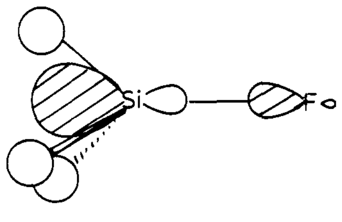


Figure 3. Structure of the superjacent MO of SiH_3F.

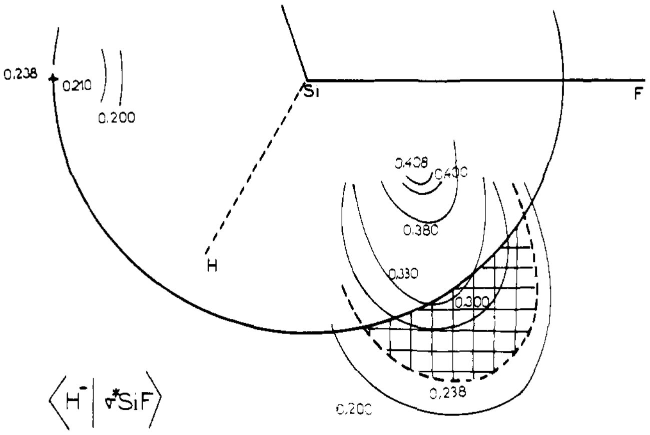


Figure 4. HOMO-LUMO overlap map for H^- approaching SiH_3F.

Let us recall that the main requirement for retention of configuration is a feeble repulsion between the leaving group X and the nucleophile Nu. Now the hydrogen 1s orbital is small and overlaps little with the nucleophile's orbitals. Furthermore, hydrogen is the only leaving group with no lone pair and no core electrons: the H-Nu repulsion is therefore drastically reduced.

The stereochemical influence of the leaving group has been studied by Sommer,[12] who suggested that "a good (poor) leaving group favors inversion (retention) of configuration". Classification of leaving groups may be made using the pK_a of the conjugate acid XH. If the pK_a is smaller than 6 (BrH, ClH, RCO_2H), X is considered to be a good leaving group. If the pK_a is larger than 10 (ROH, H_2), X is considered to be a poor leaving group. Sommer's rule is generally well obeyed, especially if the comparison is between atoms of the same column. Exception may occur if one compares elements of two different columns. For example, on the basis of the pK_a values, F should be considered a good leaving group (LG) (pK_a of FH = 3.17)[13] and MeS a poor LG (pK_a of MeSH $\simeq$ 10).[13] As mentioned earlier, both LG give very similar stereochemical results.[11] Our treatment provides a rationalization for both Sommer's rule and its exceptions.

III. Influence of the Nucleophile Nu

The influence of the nucleophile on the stereochemistry of substitution on silicon compounds is well known.[14,15] The experimental trends were initially rationalized by the intervention of the countercation which is more or less able to assist the departure of the LG and thus to induce a S_Ni-Si mechanism.[14] However, this interpretation is not in agreement with solvent effects: an increase in the solvating power of the solvent promotes retention of configuration[15h] and accelerates the reaction.[11] Analogous results are obtained in the presence of complexing agents (TMDA, cryptand).[15i] Corriu and his coworkers then suggested an empirical rule according to which "the harder (softer) the nucleophile, the more retention (inversion) of configuration".[15]

Now a hard reagent is usually a small one, with contracted valence orbitals.[16] Its long-range overlap with the LG will be negligible and frontside attack leading to retention of configuration is therefore possible. On the other hand, a soft nucleophile usually has diffuse valence orbitals.[16] It has therefore a sizable overlap with the LG and the stereochemistry is shifted toward inversion of configuration.

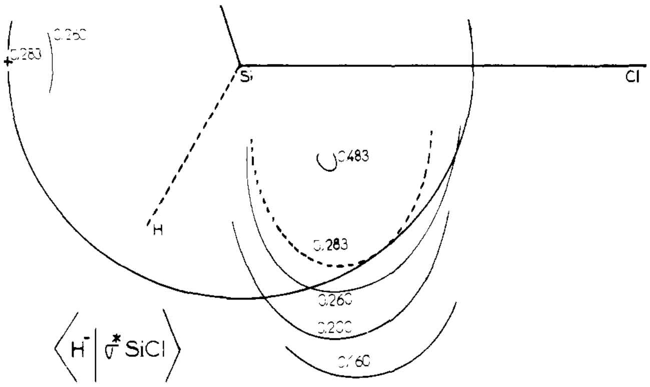


Figure 5. HOMO-LUMO overlap map for H^- approaching SiH_3Cl.

But the size of the reagent is not the only controlling factor. A change in the nucleophile's hardness implies also a modification of its HOMO level. When this level is high, frontier orbitals interaction is predominant. When this level is low, the relative importance of the HOMO-LUMO interaction is decreased and that of the (nucleophile's HOMO-substrate's superjacent MO or higher MOs) interaction(s) is increased. As shown in Figure 3, the big lobe of the Si hybrid orbital points to the rear in the superjacent MO, which therefore favors inversion of configuration. We are then led to the conclusion that, all things being equal, a nucleophile with a high-lying HOMO will give more retention of configuration than a nucleophile with a low-lying HOMO. It has been shown that in aprotic solutions the HOMO of a hard anion lies at higher energy than that of a soft anion, but the HOMO level ordering is reversed in protic solutions.[17] Therefore the foregoing rule reduces to Corriu's rule in aprotic solutions but gives opposite predictions in protic solutions. Notice also that in protic solutions hard anions are highly solvated and thus possess a large effective bulk. A more detailed discussion of solvent and cation effects is presented at the end of this paper.

IV. Numerical Calculations

The foregoing qualitative treatment has been checked by STO-3G calculations, using the GAUSSIAN 70 programs.[18] We first considered the SiH_3F molecule. When a hydride ion, simulating a nucleophile, is approached from the rear, the overlap between the hydride 1s orbital and the substrate's LUMO increases, reaches a maximum, and then decreases. A circle is drawn, centered on the silicon atom and passing by the point with the maximum overlap. The HOMO-LUMO overlap is then calculated for various frontside approaches. The curves of equal overlap are shown in Figure 4. When the nucleophile is in the hachured region, the HOMO-LUMO interaction is stronger than in the backside attack, despite the fact that the distance separating the two reagents is larger. Retention of configuration is then possible.

The same overlap mapping is done with SiH_3Cl as the substrate. Figure 5 shows that to get, in a frontside attack, the same overlap as in a rearside attack the nucleophile must come inside the circle. The electronic and steric repulsions are then higher for the frontside attack and the stereochemistry is shifted toward inversion of configuration. A similar conclusion is reached for the case of CH_3F (Figure 6).

In Figures 4-6, only the attractive (nucleophile's HOMO-substrate's LUMO) interaction is considered. In an attempt to take into account both the attractive and the re-

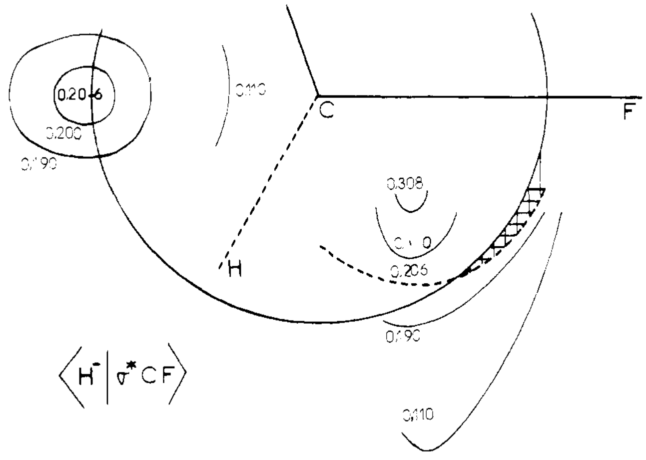


Figure 6. HOMO-LUMO overlap map for H^- approaching CH_3F.

pulsive terms, the energy of the supermolecule (nucleophile + substrate) has been minimized. The substrate may be CH_3F, CH_3Cl, SiH_3F, or SiH_3Cl and the nucleophile is simulated by H^-. Standard geometries are used for the substrate (CH = 1.09, CF = 1.36, CCl = 1.77, SiH = 1.423, SiF = 1.613, SiCl = 2.09 Å, and all angles are taken equal to 109.4712°) and no relaxation is allowed during the hydride approach. Furthermore, the hydride is compelled to stay in the plane defined by the three atoms H*, Z, and X (Figure 7). Admittedly, this model is quite crude and the resulting figures are not to be taken at their face values. However, these calculations may be considered as a perturbation treatment where all orbital interactions are taken into account and it is therefore expected that the trends they reveal may have some physical significance.

The results are shown in Figure 7. For CH_3F and CH_3Cl, there is only one minimum corresponding to a backside approach of the nucleophile (**1** and **2**). Silicon compounds give rise to two local minima corresponding to a backside and a frontside approach. The energy difference between **3** and **4** is smaller than that between **5** and **6**, suggesting that S_N2 with retention of configuration is easier with SiH_3F than with SiH_3Cl. Notice that in **4** and **6** the hydride is located on the side opposite to H*. As a matter of fact, it has not been possible to simulate an approach on the side of H*, the basic character of H^- coming then to the fore, and abstraction of H* is preferred to a substitution reaction.

V. Cation and Solvent Effects

The influences of the solvent and the countercation deserve some comments. Sommer[12] pointed out that substitution of a methoxy group occurs with retention of configuration in nonpolar solvents and with inversion of configuration in protic solvents. Corriu found that in polar solvents the percentage of retention of configuration[15h] and the rate of reaction[11] increase with the basicity of the solvent. In other words, electrophilic assistance to the departure of the LG slows down the reaction and favors inversion of configuration.

It has been already mentioned in section III that protic solvents, which increase the bulk of the nucleophile and lower its HOMO level, tend to promote inversion of configuration. On the other hand, solvation of the LG lengthens the ZX bond and augments the LG's effective electronegativity; these changes favor retention of configuration. However, these two effects are partly canceled by a hybridization change at the silicon atom. As shown by STO-3G calculations, protonation of silyl fluoride lengthens the SiF bond (1.74 Å in protonated SiH_3F vs. 1.613 Å in free SiH_3F) and lowers the LUMO (0.0165 vs. 0.5065 au), but at the same time it decreases the s character in the hybrid Si atomic orbital. The coefficients of Si in the LUMO are respectively 0.72 (3s) + 0.87 (3p) for SiH_3F and 0.53 (3s) + 0.73 (3p) for $SiH_3F + H^+$. According to the discussion of section I, this hybridization change should disfavor retention of configuration. Anyhow, it seems reasonable to suppose that solvation of the nucleophile (a charged species) is more important than solvation of the substrate (a neutral species). A shift toward inversion of configuration may therefore be expected.

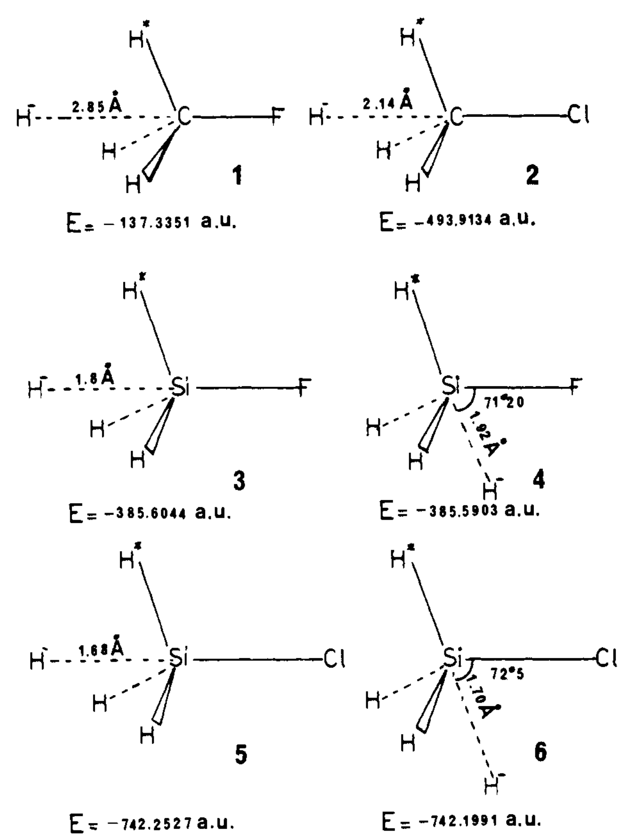


Figure 7. Some favorable directions of approach of a nucleophile.

Similar arguments may be used to rationalize the influence of dipolar aprotic solvents. When the solvent becomes more basic, the substrate's LUMO is raised but the nucleophile's HOMO is raised even more. The HOMO-LUMO energy gap is diminished, leading to a rate increase as well as a shift toward retention of configuration.

VI. Conclusion

At least for the case of silicon compounds, it is thus possible to reproduce the experimental trends using a simple perturbation argument which does not require the introduction of either silicon d orbitals or pseudorotations in the transition state. Whether these factors play a role in the reaction is still an open question. It is clear, however, that the stereochemistry of substitution reactions on silicon compounds cannot be taken as a proof of their intervention.

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

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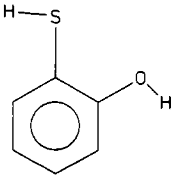
Abstract: The long-range coupling constants between ring protons and the side-chain protons in the ^{1}H NMR spectrum of 2-hydroxythiophenol in CCl_4 solution demonstrate that more than 95% of the molecules exist as a conformer in which the sulfhydryl group prefers a plane approximately perpendicular 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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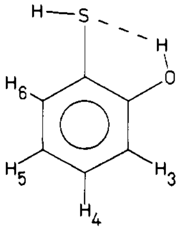

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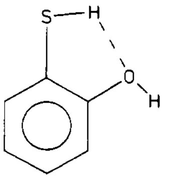

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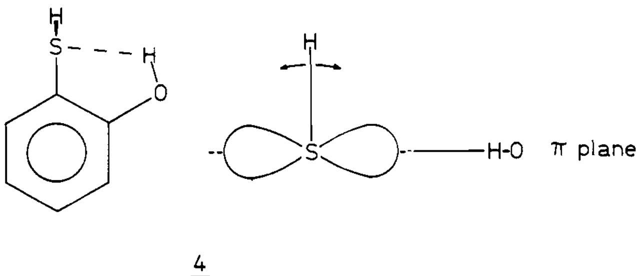
MO calculations[5] at the CNDO/2 level find **1** and **2** as 4.1 and 0.29 kJ/mol less stable than **3**, respectively, whereas the STO-3G minimal basis set computations yield **1** and **2** as 5.0 and 9.0 kJ/mol less stable than **3**. The CNDO/2 results are apparently in rough agreement with the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