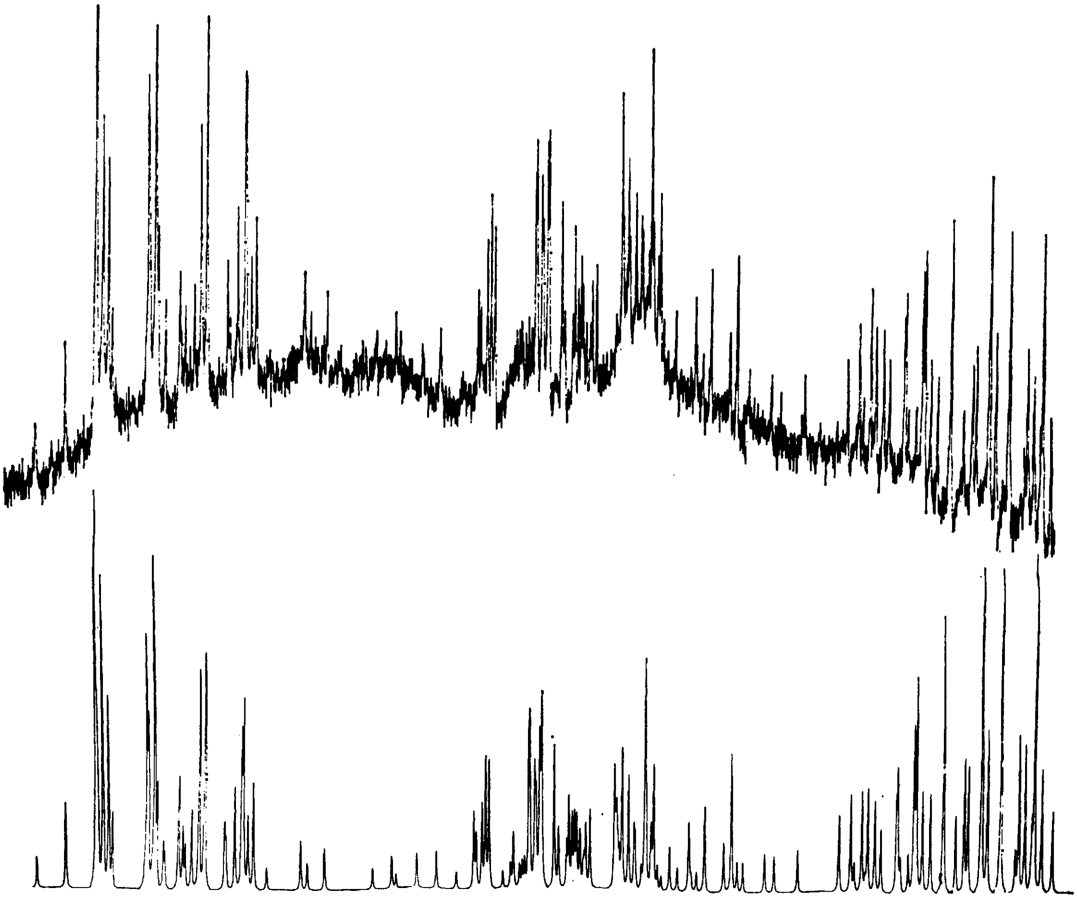
Nematic Phase Nuclear Magnetic Resonance Investigation of Rotational Isomerism. Part 6.† The Conformation of Thiophenol in Solution

By **Lodovico Lunazzi** * and **Piero Bellomo**, Istituto di Chimica Organica, Universitá, Risorgimento 4, Bologna, Italy

C. Alberto Veracini * and **Anna Amanzi**, Istituto di Chimica Fisica and Laboratorio CNR di Chimica Quantistica, Universitá, Risorgimento 35, Pisa, Italy

The 100 MHz n.m.r. spectra of thiophenol and 4-chlorothiophenol oriented in a liquid crystalline solvent were obtained and interpreted. Analysis of the direct dipolar couplings shows that in both molecules a planar conformation would require a $\widehat{CSH}$ angle distorted by 7—10° with respect to the known values of thiols. On the other hand a non-planar conformation with the CSH plane twisted by 26 ± 3° with respect to the phenyl ring agrees with the structural parameters of thiols and with the experimental dipolar couplings. It has been also observed that the off-diagonal element of the ordering matrix S_{xy} is negligible, thus suggesting that rotation of the SH group occurs faster than molecular reorientation.

N.M.R. spectroscopy of molecules dissolved in liquid crystalline solvents can give quite accurate structural information.[1-3] For conformational studies in solution the method is more reliable than most other techniques. For the substituted aromatic derivatives so far investigated by this method, it has usually been found that the substituents (OH,[4] CHO,[5-10] COF,[11] $COCH_3$,[12,13] OCH_3 [13]) are coplanar with the aromatic ring. In the few cases where twisting angles were observed (3,3-bithienyl,[14] biphenyls,[15,16] 4,4′-bipyridyl [17]) the substituent was a second aromatic ring which, with its larger steric repulsion, forced the molecule out of planarity. A recent report [18] indicates however that thioanisole might exist in a non-planar conformation: we thus undertook an investigation of the simpler parent compound, thiophenol, to verify the possible existence of non-planar conformers in a non-hindered aromatic derivative.



Experimental (upper) and computed 100 MHz n.m.r. spectrum of thiophenol partially oriented in a liquid crystalline solvent. The line width used in the spectral simulation is 4.0 Hz

RESULTS AND DISCUSSION

The 100 MHz n.m.r. spectrum of thiophenol partially oriented in a liquid crystal is reported in the Figure. The Hamiltonian which describes the n.m.r. spectrum of a

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† Part 5, ref. 19.

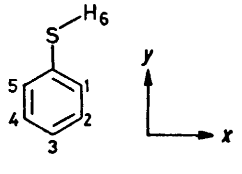
partially oriented molecule depends[1-3] on chemical shifts (ν_i), spin–spin coupling constants (J_{ij}), and direct dipolar couplings (D_{ij}): other terms,[1-3] not being relevant in the present case, were disregarded. The values of ν_i, J_{ij}, and D_{ij} employed to obtain the computer simulated spectrum in the Figure are given in Table 1. The spin–spin couplings were taken from the isotropic spectrum and the chemical shifts and dipolar couplings are the result of iterative fitting of the spectral lines. The direct dipolar couplings (D_{ij}) depend on the molecular orientation and interproton distances, according to the general relationship (1) (see refs. 1—3). They

$$D_{ij} = -\frac{\hbar}{2\pi}\gamma_i\gamma_j\left\langle\frac{3\cos^2\theta_{ij} - 1}{r^3_{ij}}\right\rangle \qquad (1)$$

can thus be employed to obtain simultaneously the shape and orientation of thiophenol.

TABLE 1

Experimental values of the dipolar couplings (Hz) of oriented thiophenol compared with those of three possible conformations (see text). The experimental 100 MHz chemical shifts (Hz) referred to an arbitrary mid-point of the spectrum are: ν_1 −200.8 ± 0.3, ν_2 −199.0 ± 0.3, ν_3 −206.0 ± 0.3, ν_6 +114.5 ± 0.4. The spin–spin couplings (Hz) were assumed from the is otropic spectrum (J_{12} 7.8, J_{15} 2.0, J_{23} 7.5, J_{24} 1.6 Hz)



	Experimental	Twisted by 22.75° ($\widehat{CSH}$ 96.5°)	Planar ($\widehat{CSH}$ 96.5°)	Planar ($\widehat{CSH}$ 104°)
D_{12}	−889.2 ± 0.3	−889.2	−886.9	−889.3
D_{13}	−116.1 ± 0.5	−116.5	−116.2	−116.5
D_{14}	−9.5 ± 0.4	−9.1	−9.0	−9.1
D_{15}	-36.8_5 ± 0.7	+36.4	+36.4	+36.4
D_{16}	−365.8 ± 0.6	−365.7	−367.5	−365.7
D_{23}	-79.8_5 ± 0.5	−79.8	−79.2	−79.8
D_{24}	+33.8 ± 0.7	+33.9	+33.9	+33.9
D_{26}	−76.1 ± 0.7	−75.5	−84.0	−74.3
D_{36}	−55.2 ± 0.5	−54.7	−67.1	−55.1
R.m.s. deviation (Hz)		0.3_5	4.9	0.6_5
S_{zz}		−0.0804	−0.0801	−0.0804
S_{xx}		−0.0217	−0.0218	−0.0218
S_{xy}		+0.0008	+0.0491	+0.0190

Of the nine experimental D_{ij} values, six depend on the orientation and on the geometry of the phenyl ring, the other three on the position of SH with respect to phenyl. Using these six D_{ij} values, we defined the co-ordinates of the ring protons assuming an r_{23} distance of 2.468 Å. The co-ordinates of H(1)–(5) and the orientational parameters S_{xx} and S_{zz} (Table 2) are the output of a best fitting procedure.

We then looked for a conformation of the SH group that would match all nine experimental D_{ij} values. Whereas in the case of the rigid part of the molecule only two orientational parameters (*i.e.* S_{zz} and S_{xx}) are required owing to the C_{2v} symmetry of the five ring protons, in the whole molecule a third (off-diagonal) element is in principle required (here S_{xy}) in that the symmetry of the six protons is C_s. However, if rotation about the C–S bond is faster than reorientation of the molecule in the liquid crystal, the S_{xy} term would vanish since dynamic C_{2v} symmetry would be recreated.[10,19]

In order therefore to complete the conformational study, the same co-ordinates previously determined for the rigid part were employed, whereas those of H(6) (*i.e.* SH) were obtained from S–H and C–S bond lengths of 1.33 and 1.78 Å, respectively, and a $\widehat{CSH}$ angle of 96.5°. Although accurate experimental data on the geometry of thiophenol are not available, the S–H length and $\widehat{CSH}$ angle are well established from other thiols (*e.g.* CH_3SH).[20,21] On the other hand the C–S bond length of aliphatic thiols (1.82 Å) [20,21] is expected to be shorter in the aromatic series, owing to conjugation:

TABLE 2

Co-ordinates (Å) of the protons of thiophenol employed in the present investigation. The values of H(1)—(5) result from the optimisation of the rigid part with r_{23} 2.468 Å. The two orientational parameters were S_{zz} −0.080 4 ± 0.002 0 and S_{xx} −0.021 7 ± 0.000 5 and the r.m.s. deviation for the six D_{ij} values was 0.28 Hz. For the meaning of the values of SH [*i.e.* H(6)] see text

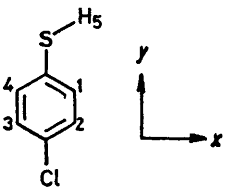
	x	*y*	*z*
H(1)	2.078 ± 0.025	2.567 ± 0.014	
H(2)	2.128 ± 0.005	0.170 ± 0.008	
H(3)	0.0 (assumed)	−1.08 (assumed)	
H(4)	−2.128 ± 0.005	0.170 ± 0.008	
H(5)	−2.078 ± 0.025	2.567 ± 0.014	
H(6) (planar, $\widehat{CSH}$ 96.5°)	1.368	4.714	
H(6) (planar, $\widehat{CSH}$ 104°)	1.338	4.873	
H(6) (22.75° twisted $\widehat{CSH}$ 96.5°)	1.236	4.714	0.509_5

a value of 1.78 Å has been thus taken from aromatic sulphides.[22,23] Support for the choice of these parameters comes from an *ab initio* theoretical study of thiophenol [24] where optimisation of the geometrical parameters yielded $\widehat{CSH}$ 95—96° and C–S 1.76—1.78 Å, depending on the conformation.

The co-ordinates of SH obtained with these assumptions are given in Table 2. The dipolar couplings computed with these values, assuming that thiophenol is planar, do not match the experimental data. To obtain a planar conformation in agreement with experiment, the $\widehat{CSH}$ angle should be 104°, a geometrical distortion (>7°) too large to be realistic. Even worse results are obtained assuming a free rotational model or a perpendicular conformation (*i.e.* the CSH plane orthogonal to the phenyl ring). The failure of these models to describe the conformation of thiophenol indicates that the molecule is not planar but twisted by an angle >0 and <90°. A complete description of this model would require the use of five orientational parameters and also of a potential function with two unequal barriers at 0 and 90°. Owing to the paucity of experimental D_{ij} values this complete model cannot be tested since the unknowns exceed the available equations. A number of reasonable approximations have thus to be introduced.

TABLE 3

Experimental values of the dipolar couplings (Hz) of oriented 4-chlorothiophenol compared with those of three possible conformations. The experimental 100 MHz chemical shifts (Hz), referred to an arbitrary point of the spectrum are: ν_1 −284.6 ± 1.3, ν_2 −384.5 ± 1.4, ν_5 −86.4 ± 1.1



	Experimental	Twisted by 29.3° ($\widehat{CSH}$ 96.5°)	Planar ($\widehat{CSH}$ 96.5°)	Planar ($\widehat{CSH}$ 107°)
D_{12}	−1 393.0 ± 0.6	−1 393.3	−1 390.8	−1 393.1
D_{13}	+2.9 ± 0.6	+2.9$_5$	+3.5	+2.9
D_{14}	+94.2 ± 1.3	+94.2	+95.1	+94.2
D_{15}	−501.5 ± 0.9	−501.5	−502.3	−501.5
D_{23}	+94.2 ± 1.3	+94.2	+95.1	+94.2
D_{25}	−117.8 ± 1.0	−118.2	−136.2	−117.4
R.m.s. deviation (Hz)		0.1$_5$	7.6	0.1$_5$
S_{zz}		−0.1106	−0.1097	−0.1106
S_{xx}		−0.0606	−0.0613	−0.0606
S_{xy}		−0.0003	+0.0985	+0.0492

As in many other cases [1-4] the potential function was neglected which means that a single conformation was considered to be appreciably populated. Furthermore we consider the barrier at 0° to be much lower than that at 90°. This assumption seems reasonable in that many analogous molecules are planar: [6-13] in addition the root mean square (r.m.s.) deviation for the planar conformation of thiophenol (4.9 Hz, Table 1) is much smaller than for the perpendicular conformation (r.m.s. error 18.7 Hz).

In consequence the motion of SH above and below the plane of the phenyl ring was assumed to be faster than reorientation of the molecule in the liquid crystal. A dynamic plane is thus created and the C_s symmetry of the planar structure maintained: accordingly three orientational parameters are again required for describing the orientation.

This model gives good agreement with the experimental data for a twisting angle of 22.75° without any distortion of the $\widehat{CSH}$ angle from 96.5° (Table 1). It is also worth mentioning that the off-diagonal element S_{xy} decreases with increasing the twisting angle and eventually becomes negative, crossing a null. It happens that the zero value for S_{xy} is reached in correspondence with the minimum r.m.s., deviation between computed and experimental D_{ij} values, thus yielding a negligible value for S_{xy} (Table 1) in the twisted conformation.

In order to check these results the experiment was repeated with a molecule (4-chlorothiophenol) which is expected to have an analogous conformation but a different orientation. Furthermore the results for thiophenol were based on the assumption of a given distance (r_{23} 2.468 Å): in the 4-chloro derivative a different interproton distance has to be assumed. In this way the conclusions should be as independent as possible from accidental coincidence. The spectrum of 4-chlorothiophenol has been interpreted and the corresponding parameters are given in Table 3. The co-ordinates of the ring protons, based on a distance between the *meta*-protons of 4.260 Å, are reported in Table 4, together with the co-ordinates of SH, obtained as for thiophenol. Again a planar structure with a normal $\widehat{CSH}$ angle (96.5°) turns out to be incorrect: to match the experimental data an even larger distortion of $\widehat{CSH}$ (107°) than for thiophenol would be required.

TABLE 4

Co-ordinates (Å) of the protons of 4-chlorothiophenol employed in the present investigation. The values of H(1)—(4) result from the optimisation of the rigid part with r_{23} 4.260 Å. The orientational parameters were S_{zz} $-0.110\,6 \pm 0.002\,0$ and S_{xx} $-0.060\,6 \pm 0.000\,4$. For the meaning of co-ordinates of SH [*i.e.* H(5)] see text

	x	y	z
H(1)	2.130 ± 0.005	2.586 ± 0.010	
H(2)	2.130 ± 0.005	0.133 ± 0.010	
H(3)	-2.130	-0.133	
H(4)	-2.130	2.586	
H(5) (planar, $\widehat{\mathrm{CSH}}$ 96.5°)	1.368	4.715	
H(5) (planar, $\widehat{\mathrm{CSH}}$ 107°)	1.320	4.940	
H(5) (29.3° twisted $\widehat{\mathrm{CSH}}$ 96.5°)	1.197	4.715	0.646

The model for a twisted conformation, on the other hand, gives good results for a twisting angle of 29.3°; the S_{xy} value once more becomes negligible corresponding to the minimum r.m.s. deviation between experimental and computed D_{ij} couplings.

It thus seems that thiophenol and its *para*-derivatives are not planar in solution, for planar conformation would require $\widehat{\mathrm{CSH}}$ angles almost as large as COH in phenol,[25] whereas it is well known that the angles at a sulphur atom are much smaller than the corresponding angles at oxygen. In connection with this observation it is worth mentioning that the assumption of the planarity of OH in phenol could explain the poor agreement observed in ref. 4 for the co-ordinates of the hydroxy proton and, possibly, the quite anomalous[4] value of S_{xy}.

A model for a twisted conformation seems to overcome these difficulties in thiophenol: the different value of the twisting angle in the 4-chloro derivative (29 *versus* 23°) is probably due to experimental errors in the D_{ij} values and also to the fact that, purposely, slightly different geometries of the benzene ring were used. We believe that a value 26 ± 3° is quite realistic.

Finally, this investigation seems to indicate that not only is the motion of SH above and below the plane of phenyl ring faster than reorientation, as we assumed when allowing for the existence of S_{xy}, but also the motion through the perpendicular transition state is faster than reorientation. In other words, the two potential barriers expected for thiophenol seem to be low enough to allow motion of SH without coupling with reorientation. This means that not only thiophenol can be considered as having C_s dynamic symmetry (*i.e.* one symmetry plane) but can be described by C_{2v} dynamic symmetry (*i.e.* two symmetry planes).

This result is opposite to that reported for a variety of aromatic ketones.[8-13] To understand this fact it has to be considered that their rotational barriers between the ground (planar) and the transition state (perpendicular) have $\Delta G^{\ddagger}$ values ranging from 7.7^{-1} for benzaldehyde[26] to 5.4 kcal mol^{-1} for acetophenone,[27] corresponding to rotation rates, at +30 °C, of $10^{7.2}$ and 10^{9} s^{-1}, respectively. The rotational barrier of thiophenol between the ground state (planar in the calculations or slightly twisted from planarity in our study) and the perpendicular transition state has been estimated[24] to lie in the range 1.3—3.3 kcal mol^{-1}, with a rotation rate (10^{12}—$10^{10.5}$ s^{-1}) larger than that for ketones by a few orders of magnitude. It is not unlikely therefore that the rotation of SH is fast enough to exceed that of reorientation in the liquid crystal, thus creating effective C_{2v} symmetry. We cannot exclude unambiguously, however, that the null value of S_{xy} might be due to the impossibility of appreciating the small effect of the moment of the SH bond. Nevertheless, whatever the interpretation of the orientational data, the conformation of thiophenol in solution is certainly not planar.

EXPERIMENTAL

Thiophenol and 4-chlorothiophenol were dissolved (*ca.* 20% molar) in Merck Nematic Phase IV[2] and some acid alumina was added to the samples to eliminate traces of water which would favour the exchange of SH. The spectra were run on a JEOL PS 100 spectrometer in the continuous wave mode at the probe temperature. Of the 105 observable lines of the spectrum of thiophenol, 84 among the most intense were used in iteration, which yielded an r.m.s. error of 2.7 Hz. The spectrum of 4-chlorothiophenol displayed 43 lines which were all used in the iteration with an r.m.s. error of 3.8 Hz.

LAOCOONOR and LEQUOR programs were employed to carry out the spectral analysis, and the SHAPE program (courtesy of Professor P. Diehl) in the interpretation of the rigid part of the molecule.

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