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INTRAMOLECULAR NH···O AND NH···S HYDROGEN BONDS IN *o*-AMINOPHENOLS AND *o*-AMINOTHIOPHENOLS

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Abstract—IR absorption spectra in dilute CCl_4 solution in the fundamental NH stretching region show that the intramolecular NH···S H-bond interaction in *o*-aminothiophenol and *o*-thioanisidine is stronger than the corresponding NH···O interaction in *o*-aminophenol and *o*-anisidine. This conclusion is based on HNH angle estimates, integrated band intensities, and the *cis-trans* isomerism of the —NHD group in these compounds relative to similar measurements on the corresponding *p*-substituted aromatic amines. These observations can be explained by the larger size of S relative to O, the substituent effects on the NH_2 group, and the rigidity of the molecule holding the proton-donor and proton-acceptor groups. While there is no evidence for intramolecular OH···N interaction in *o*-aminophenol, intramolecular SH···N interaction is noted in *o*-aminothiophenol.

INTRODUCTION

ALTHOUGH the classical concept of a "hydrogen bond" involved a relatively acidic proton-donor group and a proton-acceptor group with a highly electronegative atom like O or N, modern instrumental refinements are providing numerous examples of H-bonds with SH groups as proton donors and/or S atoms as proton acceptors.[1–3] Of particular interest are intramolecular H-bonds, where the proton-donor and proton-acceptor groups cannot separate.

This paper describes a comparative study of intramolecular hydrogen bonds in *o*-aminophenol and *o*-aminothiophenol, and in the methylated derivatives *o*-anisidine and *o*-thioanisidine.

The method employed involves frequency and integrated intensity measurements on the fundamental symmetric and asymmetric NH_2 bands, supplemented by an examination of the NHD bands in partially deuterated samples. The *o*-substituted compounds referred to are compared with the corresponding *p*-substituted analogues to observe the effect of removing the adjacent OH, SH, OCH_3 or SCH_3 group. In this way the electronic effect transmitted through the ring to the NH_2 group is not altered significantly. Further, model compounds in which strong intramolecular NH···X H-bonding is expected, and others in which *o*-substituents exert steric effects only (or none), are examined in a similar way.

Intramolecular H-bond formation involving an NH_2 group on an aromatic ring as a proton donor has been recognized in the following ways in the IR spectrum in the 3μ region:

(1) a decrease in band width for both the antisymmetric (ν_{as}) and symmetric (ν_s) NH stretching vibrations,[4]

(2) an increase in the antisymmetric NH integrated band intensity (A_{as}), with an accompanying increase in the intensity ratio (A_{as}/A_s),[4]

(3) a change in the NH frequencies ν_{as} and ν_s such that the calculated "apparent HNH angle" increases,[4]

(4) reduced solvent sensitivity of the NH stretching vibrations,[5] although caution in interpretation is required,[6]

(5) a positive deviation of ν_{as} from the linear correlation $(\nu_{as} - \nu_s) = 0{\cdot}4219\,\nu_s - 1348{\cdot}2\ \mathrm{cm}^{-1}$, which holds generally for the fundamental NH bands of anilines,[7] and

(6) *cis-trans* isomerism of the —NHD group in partially deuterated samples.[8, 9, 10, 11]

RESULTS AND DISCUSSION

The NH_2, NHD, and ND_2 frequency data are tabulated in Table 1. Table 2 gives the NH(D) and ND(H) frequency separations observed in partially deuterated compounds, the integrated intensity data, and the calculated HNH angles. Some relevant data on reference compounds drawn from other publications on *o*-substituted anilines are included.

Apparent HNH angle calculations. The <HNH can be calculated directly from the fundamental NH stretching frequencies, assuming that only the N and H atoms move in the symmetric and antisymmetric NH_2 stretching vibrations, that the NH_2

TABLE 1. FUNDAMENTAL NH_2, NHD AND ND_2 STRETCHING FREQUENCIES IN RING-SUBSTITUTED ANILINES (dil CCl_4 soln)

	$\nu_{NH}(\mathrm{cm}^{-1})$				$\nu_{ND}(\mathrm{cm}^{-1})$			
Substituent	NH_2 asym.	—NHD free	—NHD bonded	NH_2 sym.	ND_2 asym.	—NDH free	—NDH bonded	ND_2[b] sym.
p-OH	3459	*a*		3380		*a*		
o-OH	3489	*a*		3397.$_5$		*a*		
p-OCH_3	3460	—		3382	—	—		—
o-OCH_3	3488	3441.$_5$		3396	2610	2543.$_5$		2487
p-SH	3488	3444		3400.$_5$	2607.$_5$	2544.$_5$		2495 2451.$_5$
o-SH	3476.$_5$	3449.$_5$	3413	3378.$_5$	2599.$_5$	2546	2521	2490.$_5$ 2455
p-SCH_3	3485.$_5$	3441		3399	2605	2543		2495 2487 2450
o-SCH_3	3476	3450	3399.$_5$	3371	2597.$_5$	2546	2514	2486.$_5$ 2477 2450.$_5$
o-CH_3	3480.$_5$	3438.$_5$		3398	2604	2540.$_5$		2491 2460
o-$CH(CH_3)_2$	3478	3432.$_5$		3394	2690	2597		2537.$_5$ 2487.$_5$

[a] Deuteration not attempted because of the insolubility of these compounds in CCl_4.

[b] The origin of a second absorption band in this region has been ascribed to Fermi resonance of $\nu_s(ND_2)$ with a combination band of the aromatic system,[11] and to the combination band $(\nu_{C-N} + \delta_{ND_2})$.[12]

deformation force constant is much smaller than the NH stretching force constant, and that the two NH bonds are equivalent.[4, 18] Previous work has shown that the <HNH in *m*- and *p*-substituted anilines increases with the electron-withdrawing character of the substituents, and that the "apparent <HNH" is enhanced in *o*-substituted anilines in which intramolecular NH···X H-bonding is expected.[4] Thus for ethyl *p*-aminobenzoate and ethyl anthranilate values of 113·4° and 123·6° were obtained, respectively (see Table 2 for other examples).

The calculations of Wolff and Staschewski[19] show that for a primary NH_2 group in which only one NH bond is involved in H-bonding, the separation between ν_{as} and ν_s can be accounted for by a reduction in one NH stretching force constant. In this model a constant <HNH is assumed. In spite of the implicit assumption that the two NH bonds must be equivalent, the application of the valency force field equations to acetamide leads to a completely acceptable angle (in dil CCl_4 solution, $\nu_s = 3420{\cdot}5\ cm^{-1}$, $\nu_{as} = 3540{\cdot}5\ cm^{-1}$, calc. $<HNH = 120{\cdot}9°$).[20] The two NH bonds in acetamide are definitely not equivalent, since partial deuteration leads to *cis-trans* isomerism of the —NHD group.[20] Similar angle calculations for *o*-substituted anilines have been criticized on the grounds that the equations become insoluble when the hydrogen bond becomes very strong.[21] However, these results must have at least relative significance for angles below 120° in view of the excellent agreement with the known planar structure of acetamide in the example cited above.

Table 2 shows that in *o*-aminophenol, *o*-anisidine, *o*-aminothiophenol, and *o*-thioanisidine the <HNH values are 3–5° larger than in the corresponding *p*-substituted compounds. For *o*-alkyl substituents these differences are 1° or less, except for *o*-t-butyl where it is 2·5°, and where the steric effect of the substituent has been recognized.[16, 17] The t-Bu group may introduce asymmetry in the environment of the NH_2 group by shielding it from the solvent on one side. Furthermore, the <HNH increases in the

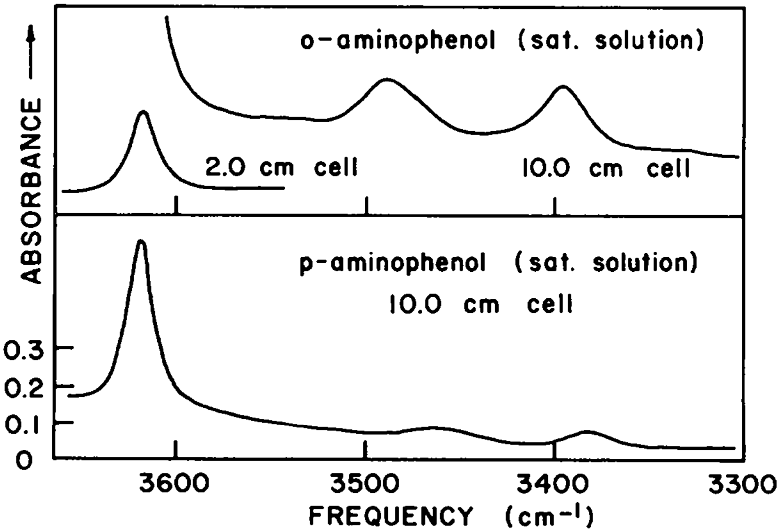


FIG 1. Fundamental OH and NH_2 stretching vibrations of *o*- and *p*-aminophenol in dil CCl_4 solution.

TABLE 2. INTEGRATED NH_2 BAND INTENSITIES, NHD FREQUENCY SEPARATIONS AND ESTIMATED APPARENT HNH ANGLES IN RING-SUBSTITUTED ANILINES (dilute CCl_4 solution)

Substitutent	$\Delta(NHD)_{trans-cis}$ (cm^{-1})[a]		NH_2 Band Intensities[b,c]			$<HNH$[c]
	NH	ND	A_{as}	A_s	(A_{as}/A_s)	(°)
A. *Phenols and thiophenols*						
p-OH			d	d	1·25	109·3
o-OH			d	d	1·40	113·4
p-OMe	0	0	2·67	1·97	1·35	109·9
o-OMe	0 (0)[11]	0 (0)[11]	4·16	3·13	1·33	113·2
p-SH	0	0	2·96	3·54	0·84	112·2
o-SH	36·5 (34)[7]	25	3·70	2·79	1·33	115·2
p-SMe	0	0	2·81	3·43	0·82	112·0
o-SMe	50·5 (31)[7]	32	4·21	3·05	1·38	117·2
B. *Examples of other intramolecular* NH···X *bonds*						
p-COOEt	(0)[9,15]	(0)[9,15]	4·06	6·29	0·64	113·4
o-COOEt			9·02	9·36	0·96	123·6
o-COOMe	(66)[9] (65)[16]	(45)[9] (42)[16]				
p-NO_2	(0)[12]	(0)[12]	4·62	10·62	0·43	113·6
o-NO_2	(31)[9] (34)[7]	(15)[9] (16)[7]	9·48	9·02	1·05	121·7
p-COMe			4·56	6·75	0·68	113·4
o-COMe	(106)[16]	(63)[16]	7·57	8·35	0·91	133·4
C. *Reference Compounds*						
p-Me	0	0	2·66	2·15	1·24	110·7
o-Me	0 (0)[11]	0 (0)[11]	2·44	2·00	1·22	111·5
o-Et	(0)[17]	(0)[17]				
p-i-Pr			2·57	2·26	1·14	110·2
o-i-Pr	0	0	2·37	1·86	1·28	111·2
p-t-Bu	(0)[16,17]	(0)[16,17]	2·64	2·25	1·17	111·0
o-t-Bu	(45)[16,17]	(31)[16,17]	2·54	1·48	1·72	113·5

[a] These values are ("free" NH–"bonded" NH) and ("free" ND–"bonded" ND) arising from the *cis–trans* isomerism of the --NHD group. A reported value of zero indicates that the band(s) could not be resolved into two components, but does not preclude the existence of two closely spaced components.[13]

[b] The units of *A* are 1 × 10^6 cm $mole^{-1}$ ($\log_e$). Except for the exponential factor, these are the A_{RJ} units of Jones and Seshadri,[14] where conversion factors to other integrated band intensity scales are also given.

[c] Except for *o*- and *p*-aminophenol and the sulphur compounds these values have been reported previously in ref. 4.

order o-OH ≈ o-Me < o-SH < o-SMe ≪ o-COOEt, etc, which is interpreted to be the order of increasing intramolecular NH···X interaction.

Intensities. Previous work[4] on a large number of o-substituted anilines has indicated that the ν_{as} NH_2 stretching band intensity (A_{as}) is enhanced by intramolecular H-bonding. This has been rationalized in terms of the direction of the transition moment in this vibrational mode. The ν_s NH_2 stretching band intensity (A_s) is affected less, in general, so that an increase in (A_{as}/A_s) may also serve as a guide to intramolecular H-bonding in o-substituted anilines. These features are illustrated in Table 2 (B) with selected examples of relatively strong intramolecular H-bonds.

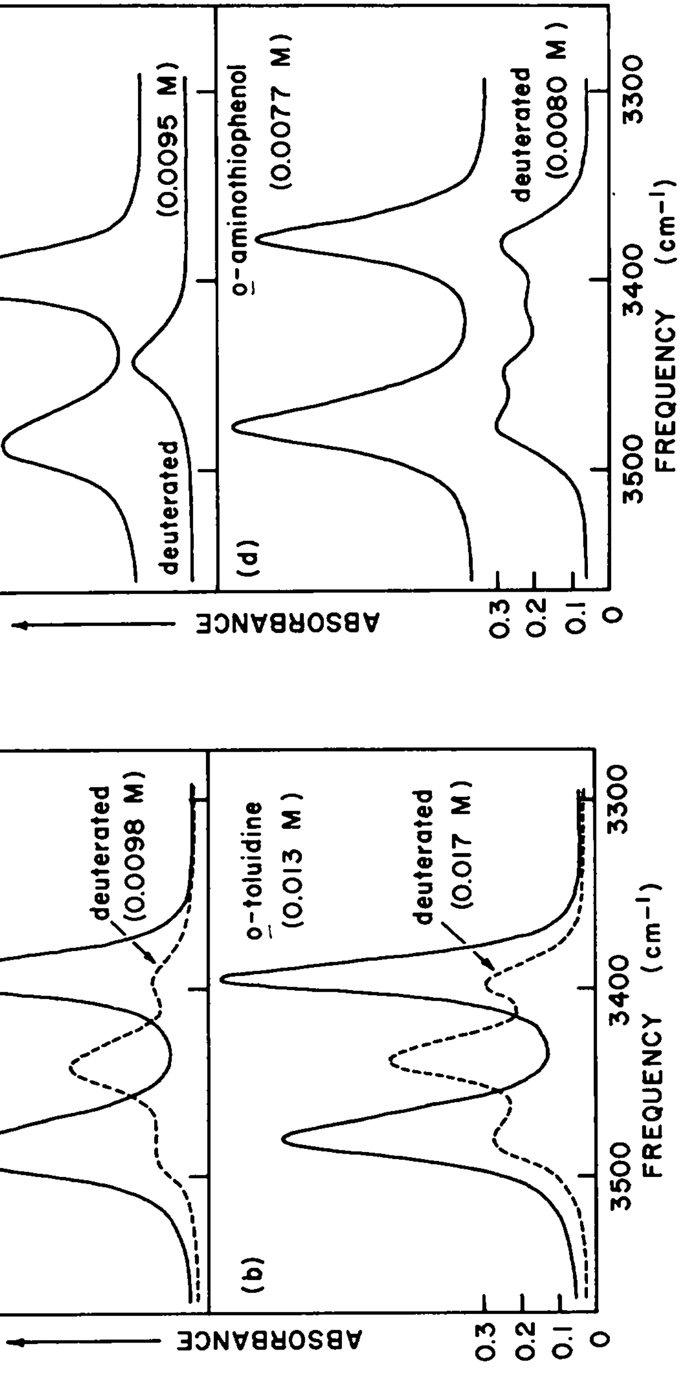
Although o- and p-aminophenol are relatively insoluble in CCl_4, the intensity ratio (A_{as}/A_s) can still be determined accurately (Fig 1). Only a small increase in this ratio is noted for o-aminophenol (Table 2(A)). For o- and p-anisidine the intensity ratios are identical, but both A_{as} and A_s are larger in the former compound. The conclusion drawn is that only very weak intramolecular NH···O H-bonds exist in o-aminophenol and o-anisidine.

In both o-aminothiophenol and o-thioanisidine A_{as} and the ratio (A_{as}/A_s) are considerably larger than in the corresponding p-substituted compounds, but A_s values are lower. This may be taken as evidence that the intramolecular NH···S interaction exceeds the NH···O interaction. The conjugative interaction of the highly polarizable S atom with the aromatic ring is decreased since some of its charge density is now involved directly in the NH···S bond, and the orientation of the SH bond may not be strictly co-planar with the aromatic ring. This reduces A_s, which arises largely from changes in the N lone pair dipole, plus an interaction term with the π-electrons. A reduction in A_s is also observed in o-nitroaniline, relative to p-nitroaniline (Table 2 (B)).

Deuteration studies. In partially deuterated anilines intramolecular H-bonds lead to *cis-trans* isomerism of the NHD group:

In p-substituted anilines the NH stretching vibration of NHD falls almost exactly in the centre between ν_s and ν_{as} of NH_2, and the ND stretching vibration of NHD bears the same relationship to ν_s and ν_{as} of ND_2. In o-substituted anilines where intramolecular H-bonding occurs, both the NH and ND bands of the NHD group are split into two components because of the partial free rotation about the C--N bond. The band separations ("free" ν_{NH}-"bonded" ν_{NH}, and "free" ν_{ND}-"bonded" ν_{ND}) may be used as a measure of the NH···X interaction.

Figs 2 and 3 show the results of partial deuteration experiments. The numerical data appear in Table 2. No NH or ND band splitting is observed for o-anisidine, and the spectrum in fact resembles that of o-toluidine (Fig 2b). Intramolecular NH···O interaction in o-anisidine (and by inference, in o-aminophenol) therefore must be weak. In o-aminothiophenol (Fig 2d and 3f) the NH and ND separations are


(a)
o-anisidine
(0.0084 M)
deuterated
(0.0098 M)
(b)
o-toluidine
(0.013 M)
deuterated
(0.017 M)
ABSORBANCE
0.3
0.2
0.1
0
3500
3400
3300
FREQUENCY (cm⁻¹)
(c)
p-aminothiophenol
(0.0061 M)
deuterated
(0.0095 M)
(d)
o-aminothiophenol
(0.0077 M)
deuterated
(0.0080 M)
ABSORBANCE
0.3
0.2
0.1
0
3500
3400
3300
FREQUENCY (cm⁻¹)

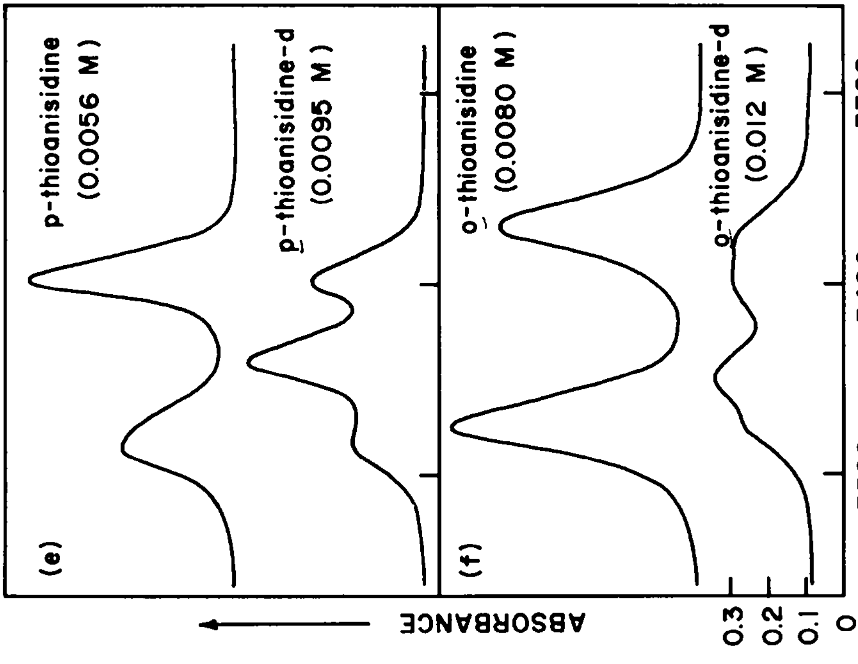


FIG 2. Fundamental NH_2 stretching vibrations in *o*-substituted anilines, and NH(D) stretching vibrations in partially deuterated samples, in dil CCl_4 solution.

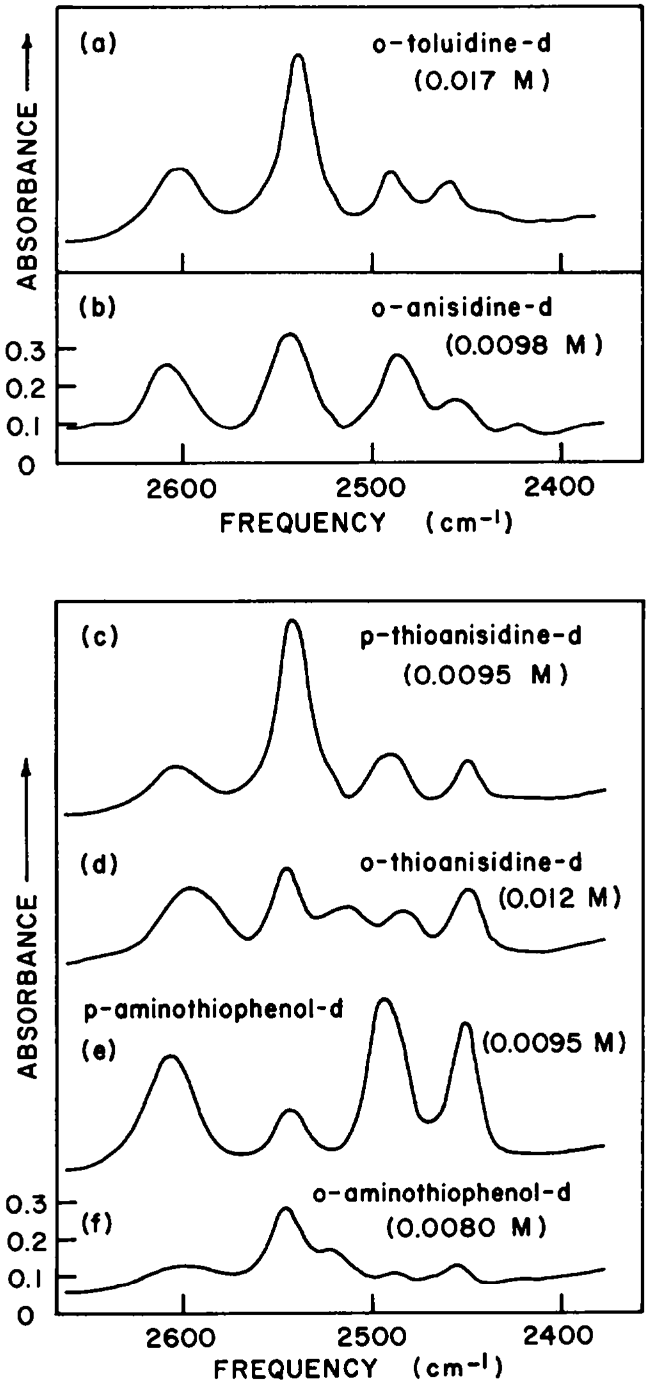


FIG 3. Fundamental ND_2 and ND(H) stretching vibrations in partially deuterated *o*-substituted anilines, in dil CCl_4 solution.

36·5 and 25 cm^{-1} respectively, and in *o*-thioanisidine (Figs 2f and 3d) they are 50·5 and 32 cm^{-1} respectively. This shows that strong intramolecular NH···S interaction exists, which is augmented as the electron density on S is increased on methylation.[22]

Steric effects. Since NH and ND band splitting of 45 and 31 cm^{-1} respectively is observed for *o*-t-butylaniline it was previously concluded[16,17] that *cis-trans* isomerism of the NHD group can also arise on steric grounds. This is an important consideration in comparing intramolecular NH···O and NH···S bonds in *o*-aminophenol and *o*-aminothiophenol, since the van der Waals radius of O is only 1·4 A° whereas that of S is 1·85 A°.

The present investigation showed that no NH or ND band splitting occurs in *o*-toluidine, *o*-ethylaniline, or *o*-isopropyl aniline. Furthermore, in *o*-alkyl anilines, including *o*-t-butylaniline, both A_{as} and A_s are significantly smaller than in the corresponding *p*-alkyl anilines. The marked opposite change in A_{as} for *o*-anisidine, *o*-aminothiophenol, and *o*-thioanisidine relative to the corresponding *p*-substituted anilines substantiates the view that intramolecular NH···X bonds are involved.

Intramolecular OH···N *and* SH···N *bonds.* The fact that ν_{OH} in *p*- and *o*-aminophenol occur at exactly the same frequency, plus the absence of any secondary bands or shoulders in the spectrum of the latter, indicates that intramolecular OH···N H-bonds are absent, i.e. only the *trans* conformation exists. The weak nature of the NH···O interaction is also confirmed, since the OH bond experiences no perturbation. From dipole moment measurements in dioxan, Lumbroso and Bertin[23] concluded that *o*-aminophenol was 25% *cis*; the IR data do not support this view. The maximum resonance interaction of the O atom with the ring arises when the OH group is in the plane of the aromatic ring, and similarly the maximum resonance interaction of the NH_2 group with the ring arises when the plane bisecting the < HNH and passing through the lone pair orbital is perpendicular to the plane of the aromatic ring. It is hard to see how a *cis* OH group could be accommodated without severe steric interference. In the more mobile system ethanolamine[24] both intramolecular NH···O and OH···N H-bonds have been observed.

In N,N-dimethyl-*o*-aminophenol a strong intramolecular OH···N bond exists, and only this conformation appears to be present, with ν_{OH} reduced by 244 cm^{-1}.[25] Here the increased basicity of the tertiary N atom is sufficient to favour the bonded form, although it may not be strictly *cis*. The gain in stability because of the strong OH···N bond may more than offset the loss of resonance energy arising from re-orientation of the OH and/or $N(CH_3)_2$ groups to favour the H-bond.

In *o*-aminothiophenol the ν_{SH} band appears at 2548 with a shoulder at ~2559 cm^{-1}, the latter corresponding to the "free" ν_{SH} frequency of *p*-aminothiophenol at 2563 cm^{-1} (Fig 4),* in reasonable agreement with the known substituent dependence of ν_{SH}.[28] David and Hallam[26] assign the main band at 2548 cm^{-1} in *o*-aminothiophenol to "bonded" SH(*cis*).

From dipole moment measurements in dioxan Lumbroso and Bertin[23] concluded that *o*-aminothiophenol was 60% *cis*, and Puranik and Kumar[29] earlier also favoured this form (albeit with the assignment of the 2610 cm^{-1} band to ν_{SH} in one conformation). The sharp ν_{as} and ν_s NH_2 stretching bands in *o*-aminothiophenol require that

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* David and Hallam[26,27] report ν_{SH} in monomeric *p*-aminothiophenol in dilute CCl_4 solution at 2559 cm^{-1}, but note that decomposition problems were encountered.

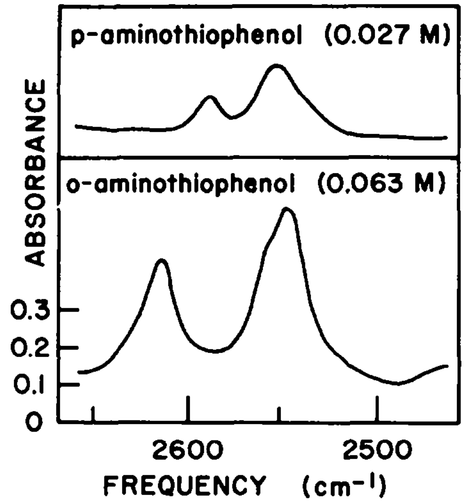
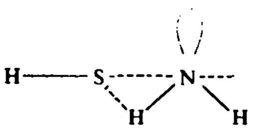


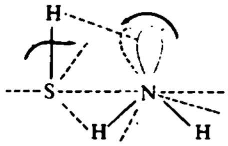
Fig. 4. Fundamental SH stretching vibrations in *p*- and *o*-aminothiophenol, in dil CCl_4 solution.

one NH always remain H-bonded to S; thus conformations in which the intramolecular NH···S bond is replaced by an SH···N bond as suggested by David and Hallam[26] are probably ruled out. Bearing in mind that the barrier to internal rotation of the SH group in thiophenol is less than 0·3 kcal/mole[30] while the barrier to internal rotation of the OH group in phenol is more than 3·0 kcal/mole,[31] conformations like II may have to be considered in addition to I. The equivalence of the two NH_2 groups in *o*-phenylenediamine and evidence for double intramolecular NH···N bonding[7,32] requires that a conformation like II also be considered here.



I

Plane of benzene ring



II

From Dreiding models:
$d_{S\cdots H} = 2{\cdot}6$ A°
(sum of van der Waals radii = 3·05 A°)

Approx. 45° rotation of SH from perpendicular brings $d_{N\cdots H}$ 2·7 A°
(sum of van der Waals radii)

The σ_R^0 substituent constants of Taft *et al.*[33] for *p*-OH and *p*-SH are −0·43 and −0·15 respectively, supporting the view that the loss of 3*p*-π resonance for an out-of-plane SH group might be off-set by the stabilization gained through H-bond formation.

Recent knowledge that S participates in both electron-releasing (3p) and electron-attracting (3d) conjugation[34] is also consistent with an out-of-plane SH group. Blocking experiments have established that the S *d*-orbitals play an important part in π-bonding,[35] and as one *d*-orbital is lost from the conjugation scheme on rotation of the SH group out of the plane of the ring another *d*-orbital takes its place. The presence of the very strong donor NH_2 group in the π-system may make non-planarity of the SH group easier. UV spectra indicate that the lone pair of a primary amino group is in conjugation with the aromàtic π-electrons even in heavily *o*-substituted anilines.[36]

CONCLUSIONS

All the IR measurements indicate that intramolecular NH···S interaction is stronger than intramolecular NH···O interaction in these molecules. Notwithstanding the lower electronegativity of S, the answer must lie in the larger size of S. Dreiding models using an sp^3 N atom show the (N)H···S distance to be 2·6 A° in *o*-aminothiophenol, relative to the sum of 3·05 A° for the van der Waals radii of H and S. In *o*-aminophenol the (N)H···O distance is 2·5 A° in comparison with the O and H van der Waals radii sum of 2·60 A°. Furthermore, the polarity of the NH bonds in *o*-aminothiophenol will exceed that in *o*-aminophenol, since the Hammet σ value for *p*-SCH_3 is 0·0 while that for the *p*-OCH_3 group is $-0{\cdot}27$, with corresponding values for *p*-SH and *p*-OH being $+0{\cdot}15$ and $-0{\cdot}37$ respectively.[38]

The fundamental ν_{OH} frequencies of 2-methoxyphenol and 2-methylthiophenol in dilute CCl_4 solution are 3560 and 3415 cm^{-1} respectively, while the out-of-plane OH deformation modes lie at 428 and 537 cm^{-1} respectively. Here, too, intramolecular OH···S bonding is thus held to be stronger than intramolecular OH···O bonding.[37]

EXPERIMENTAL

All the compounds employed were commercial materials purified by recrystallization, fractional distillation, or vacuum sublimation until satisfactory agreement with physical constants in the literature was obtained. CCl_4 (reagent grade) was dried over P_2O_5 and fractionally distilled through a spinning band column. Deuteration was achieved by equilibration of the amine with three successive portions of MeOD (Fluka AG, 99%). All traces of MeOH were removed under high vacuum.

Experimental measurements were made with a Beckman IR-7 prism-grating spectrophotometer, operating in the fourth grating order with a spectral slit width of about 1·5 cm^{-1}. The frequency calibration of this instrument has been described.[39] Matched 2·0 and 10·0 cm quartz ("Infrasil") cells were used.

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