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The Hydrogen Bond in Sulphur-containing Compounds

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The contemporary state of the problem of the proton-donating ability of the mercapto-group and the proton-accepting ability of a sulphur atom in sulphur-containing compounds in the formation of a hydrogen bond is described. The effect of the hydrogen bond on various physicochemical properties of sulphur-containing compounds is examined. A comparison is also made of the ability of sulphur-containing compounds and their oxygen-containing analogues to form a hydrogen bond. 306 references.

CONTENTS

I. Introduction 22
II. Proton-donating ability of the mercapto-group in organic compounds in the formation of hydrogen bonds (S-H←S, S-H←O, S-H←N, S-H←Hal) 22
III. Proton-withdrawing ability of a sulphur atom in organic and inorganic compounds in the formation of hydrogen bonds (O-H←S, N-H←S, C-H←S). 25
IV. Comparison of the abilities of sulphur- and oxygen-containing compounds to form hydrogen bonds 29

I. INTRODUCTION

Several reviews have already appeared[1-9] which deal with the general problems of the hydrogen bond (HB) X–H←Y, its properties in various classes of compounds, and methods of investigation. The bulk of the information relates to HB of the types O–H←O, O–H←N, and N–H←O. The ability of the mercapto-group and a sulphur atom to form HB, that is, HB of the types S–H←Y, or X–H←S (where Y = O, N, S, F, Cl, or Br; X = O or N) has not been reviewed and all the information on this problem that has accumulated is scattered in individual papers.

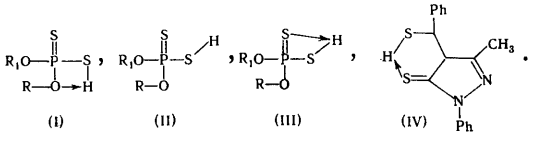
The present article reviews the available (including 1970) information on the HB S–H←Y and X–H←S (X and Y = O, N, or S) in various classes of organic compounds.

II. PROTON-DONATING ABILITY OF THE MERCAPTO-GROUP IN ORGANIC COMPOUNDS IN THE FORMATION OF HYDROGEN BONDS (S–H←S, S–H←O, S–H←N, S–H←Hal)

1. The S–H←S Hydrogen Bond

The ability of aliphatic and aromatic mercaptans to form S–H←S HB was questionable for a long time. Despite extensive investigations of various physicochemical properties of thiols[10-33] the opinion persisted until the 'fifties' that autoassociation in such systems did not exist.

In 1956, on the basis of the splitting of the ν_{SH} band in the infrared spectra of solutions of *o,o'*-diethyl and *o,o'*-dimethyldithiophosphoric acids [presumably *OO*-diethyl and *OO*-dimethyl *S*-hydrogen phosphorothiolothionates (Ed. of Translation)] in CCl_4, Menefee and coworkers[34] postulated the autoassociation of the molecules of these compounds by means of an S–H←S HB. The same type of association is assumed in dithiophosphoric[35,36], diphenyldithiophosphinic[37] [diphenylphosphinodithioic? (Ed. of Translation)], and dithiobenzoic[35] acids. However, recent cryoscopic studies showed that the dithiophosphoric acids [*S*-hydrogen phosphorothiolothionates (Ed. of Translation)] exist as monomers in benzene solution[38]. The observed splitting of the ν_{SH} bands in the vibrational spectra of the dialkyl *S*-hydrogen phosphorothiolothionates (~ 2550 and 2590 cm^{-1})[38-43] is explained by the existence of rotational isomers with an S–H←O intramolecular hydrogen bond (IHB) (I) between the SH group and an ester oxygen[38,42,43]. The band in the higher frequency region (~ 2590 cm^{-1}) evidently corresponds to the rotational isomer with a free SH group (II) and not the isomer with the S–H←S IHB (III)[42]:



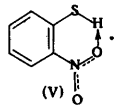
In the dithiobenzoic acid molecule (dilute solutions in cyclohexane) Issleib and Grundler[44] postulate chelation by a direct S–H←S IHB, which is responsible for the appearance of two energetically non-equivalent $n \rightarrow \pi^*$ transitions in the CSS group. The presence of an S–H←S IHB is also responsible for the absence of a concentration dependence of the ν_{SH} frequency of the ν_{SH} vibrations (2400 cm^{-1}) in the infrared spectra of solutions of 4-mercapto-3-methyl-1-phenylbenzylidene-5-thiopyrazole (IV) in CCl_4.[45] The association of ethylene trithiocarbonate [1,3-dithiolan-2-thione (Ed. of Translation)] and of thiofenchone with thiophenol, *p*-thiocresol, *p*-chlorothiophenol, *p*-bromothiophenol, and butane-1-thiol by means of an S–H←S HB is accompanied by a blue shift of the $n-\pi^*$ absorption band of the thiocarbonyl group.[46,47]

On the basis of the splitting of the ν_{SH} band in the infrared spectra (2580 and 2560 cm^{-1}), Spurr and Byers[48] established the ability of aliphatic thiols and thiophenol to undergo autoassociation by means of an S–H←S HB. Splitting of the ν_{SH} absorption band due to an S–H←S HB was also observed in the infrared spectra of solutions of *p*-chlorothiophenol (2583 and 2569 cm^{-1}) and *p*-methylthiophenol (2584 and 2571 cm^{-1}) in CCl_4.[49] Other results obtained as a result of investigations of the infrared and NMR spectra of thiophenol[49-54], the infrared spectra of the halogen derivatives of thiophenol[52], the NMR spectra of *o*- and *m*-methylthiophenols[55], the infrared and NMR spectra of aliphatic thiols[53,54,56-62], the infrared spectra of dithiocarbamic acid[63], and the NMR spectra of sulphanes

H_2S_x ($x = 1-9$),[64] also confirm the ability of thiols to undergo autoassociation by means of an S–H←S HB. The NMR spectra suggest that an S–H←S IHB exists in the H_2S_3 molecule[64]. Crystallographic results show the existence of an S–H←S HB in hydrogen sulphide[65]. The formation of dimers and trimers of hydrogen sulphide (matrix-isolated in solid nitrogen) was also proved recently by infrared spectroscopy[60].

2. S–H←O and S–H←N Hydrogen Bonds

According to results obtained in studying physicochemical properties in solutions of thiols in proton-withdrawing solvents associates are formed by means of S–H←O and S–H←N intermolecular HB[15,67-72], and this is also confirmed, despite various objections[29,33,73,74], by the results of spectroscopic investigations. Cleveland and coworkers[75] observed splitting of the ν_{SH} band (2536 and 2569 cm^{-1}) in the Raman spectra of solutions of thiophenol in dioxan, and this is attributable to an S–H←O HB. This is confirmed by the results of investigations of the association of thiophenol with dioxan and acetone by infrared spectroscopy[51]. Gragerov and Pogorelyi[76] determined the energies of the S–H←O HB of the associates of thiophenol, its derivatives, and thio-2-naphthol with acetone. A similar splitting of the ν_{SH} band is observed in the infrared spectra of solutions of thiophenol in diethyl, ethyl phenyl, and diphenyl sulphoxide[77] and of *p*-nitrophenol and *o*-nitrophenol in CCl_4.[78] Chelation by an S–H←O_2N IHB is presumed for *o*-nitrophenol (V). The S–H←O_2N HB leads to splitting of both $\nu_S(NO_2)$ and $\nu_{AS}(NO_2)$ absorption bands[78]. As was noted in Section II.1, an S–H←O IHB also exists in alkyl dithiophosphoric acids:



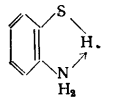
(V)

The association of thiophenol, *p*-nitrothiophenol, and *o*-nitrothiophenol with dioxan by an S–H←O HB is also accompanied by some increase in the dipole moment of these thiols in comparison with the dipole moment measured in benzene (Table 1).

It has been shown that the rate of proton exchange is increased in proportion to the strength of the S–H←O HB of the associates of thiophenol or its derivatives with acetone[79].

The ability of thiophenol to associate with proton-withdrawing solvents by an HB was shown in several NMR studies[46,80-82], and by infrared[83,84], and ultraviolet[46] spectroscopy. A similar type of interaction with proton-withdrawing solvents is also effected for methanethiol, propane-1-thiol, and hydrogen sulphide[56,85-87]. Table 2 gives the equilibrium constant (K_{26}) at 26°C and the energy ($-\Delta H$) of the S–H←Y HB (Y = O or N) for some 1 : 1 associates of thiophenol with proton-withdrawing solvents.

A thorough investigation of the ability of *o*-amino- and *o*-hydroxy-thiophenol to form an HB was made by David and Hallam[49]. Evidently, in *o*-aminothiophenol in CCl_4 there is an S–H←N IHB (VI)[49,88], although the dipole moment in benzene does not agree with the *cis*-configuration[89]:



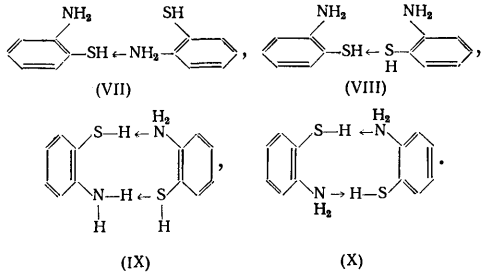
(VI)

However, it must be borne in mind that the S–H←N IHB may be destroyed with the formation of associates of benzene-*o*-aminothiophenol.

Table 1. Dipole moments of thiophenol and of its derivatives in benzene (B) and dioxan (D).[78]

Compound	μ_B, D	μ_D, D	$\Delta\mu_i=\mu_D-\mu_B$
C_6H_5SH	1.19—1.23	1.28	0.10—0.06
o-$NO_2C_6H_4SH$	4.69	4.81	0.12
p-$NO_2C_6H_4SH$	3.77	4.07	0.30

In concentrated solutions in CCl_4 *o*-aminothiophenol exists as dimers of open (VII or VIII) or cyclic (IX or X) structure[49]:



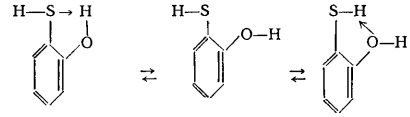
(VII) (VIII)

(IX) (X)

Table 2. Equilibrium constants and energies of the HB of thiophenol–proton-withdrawing solvent associates.

Solvent	K_{26}, litre $mole^{-1}$	$-\Delta H$, kcal $mole^{-1}$	Reference
Acetone	0.29	3.2	76
Pyridine	0.22	2.4	81
N-Methylpyrazole	0.14	2.1	81
Tributyl phosphate	0.43	2.0	81
Dimethylformamide	0.24	1.8	81
Benzene	0.04	0.5	81
N-Methylacetamide	—	0.9	80

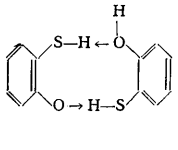
The complex relation between concentration and the frequencies and intensities of the ν_{OH} and ν_{SH} bands in the infrared spectra of solutions of *o*-hydroxythiophenol in CCl_4 is due to the formation of a different type of HB between the OH and SH groups. As the concentration is raised the IHB of (XIa) and (XIb) are broken and dimers of *o*-hydroxythiophenol are formed (XIc) and (XId).



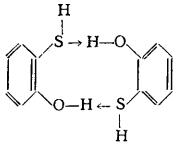
(XIa) (XI) (XIb)

$\nu_{(S-H)}$ 2595 cm^{-1} 2595 cm^{-1} 2547 cm^{-1}

$\nu_{(O-H)}$ 3463 cm^{-1} 3606 cm^{-1} 3606 cm^{-1}



(XIc)
ν(S—H) 2535 cm^{-1}
ν(O—H) 3606 cm^{-1}



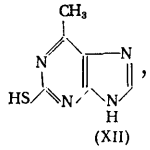
(XId)
2595 cm^{-1}
3463 cm^{-1}

The ability of 5-mercaptoquinoline to form associates by means of an S–H←Y HB is seen from the decrease in the frequency of the ν_{SH} band in benzene compared with that in carbon tetrachloride ($\Delta\nu$ = 21 cm^{-1}) and the increase in the dipole moment on going from benzene to dioxan as solvent ($\Delta\mu_1$ = 0.28D).[90-92]

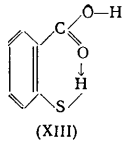
The previously expressed hypothesis of the absence of association in aliphatic aminothiols[33] was disproved by an investigation of the infrared spectra of solutions of aminothiols of the general formula $R_{3-n}N(CH_2CH_2SH)_n$ in CCl_4.[93] The splitting of the ν_{SH} band (2620 and 2560 cm^{-1}) in these systems is due to an S–H←N hydrogen HB. The autoassociation energy for various aminothiols $R_{3-n}N(CH_2CH_2SH)_n$ varies from 1.9 to 2.5 kcal mole^{-1} (calculated from $\Delta\nu$).

On the basis of spectroscopic results, the absence of association in thiocarboxylic acids RCOSH by means of a HB has been noted repeatedly[32,35,94,95]. However, thioacetic acid can evidently undergo this type of interaction in the liquid phase[96]. Recently published results confirm this opinion: as a result of autoassociation by an S–H←O HB both the $\nu_{C=O}$ and ν_{SH} absorption bands of thioacetic and thiobenzoic acids are split[97].

X-ray diffraction and neutron diffraction results show the possibility of the existence of an S–H←O HB in crystalline 2-mercapto-6-methylpurine (XII)[98]:



(XII)

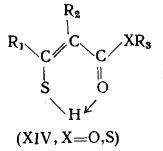


(XIII)

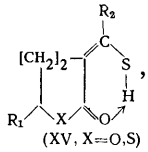
Chelation in the thiosalicylic acid molecule is effected by an S–H←O IHB (XIII), as a result of which the $\nu_{C=O}$ absorption band in the infrared spectra is split (1718 and 1730 cm^{-1}).[99]

The energy of the IHB in thiosalicylic acid is 0.9 kcal mole^{-1}. The presence of S–H←O IHB has been established in β-thioketoesters (XIV; X = O)[100-103], β-thioketothiol esters (XIV; X = S)[104-107], α-thioacyl-lactones (XV, XVI, XVII; X = O) and α-thioacylthiol-lactones (XV, XVIII; X = S)[108], monothio-β-diketones (XIX)[100,109-113], and the β-mercaptoamide of cinnamic acid (XXI)[106,114] by NMR methods and by infrared and ultraviolet spectroscopy.

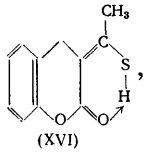
Chelation of the S→H–O type (XX) in monothio-β-diketones has been suggested[115,116-119], but has not yet been proved satisfactorily[100]. Chelation by an S–H←O IHB was also found in 1-mercaptoanthraquinone (XXII)[120], thioglycollic acid (XXIIIa) and (XXIIIb)[121], and dimercaptopropenones (XXIV)[122]:



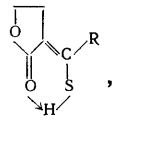
(XIV, X=O,S)



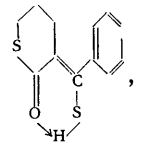
(XV, X=O,S)



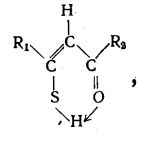
(XVI)



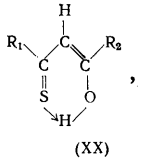
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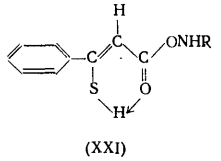
(XVIII)



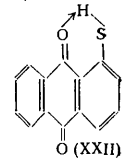
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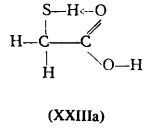
(XX)



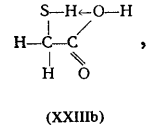
(XXI)



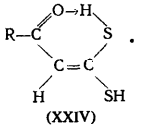
(XXII)



(XXIIIa)



(XXIIIb)

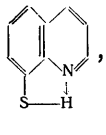


(XXIV)

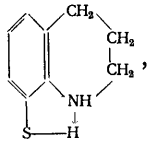
The anomalously low frequency of the $\nu_{C=O}$ vibrations (1560 cm^{-1}) in dimercaptopropenones is due to the formation of a six-membered quasiaromatic ring (XXIV), which according to Shigorin[123] leads to the strongest IHB in oxygen-containing compounds.

Use of infrared spectroscopy and dipole moments enables us[91,92,124-126] to establish the existence of 8-mercaptoquinoline, its methyl and halogeno-derivatives in solutions and in the liquid phase in the *cis*-configuration with an S–H←N IHB (XXV), which confirmed the earlier assumption of chelation in the molecules of 8-mercaptoquinoline[127,128] and its 2-methyl derivative[129]. $-\Delta H$ of the S–H←N IHB is 2.4–3.2 kcal mole^{-1} for various 8-mercaptoquinoline derivatives. In polar organic solvents the S–H←N IHB in these compounds is not destroyed with the formation of associates having a direct intermolecular HB S–H←Y.

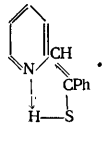
The 1,2,3,4-tetrahydro-8-mercaptoquinoline molecule also contains a ring with an S–H←N IHB (XXVI), the energy of which is 1.5 kcal mole^{-1}.[130] However, unlike 8-mercaptoquinoline, in this instance autoassociates are formed by means of S–H←S or S–H←N HB and also associates with proton-withdrawing solvents by means of S–H←Y HB. The strength of the S–H←N IHB being higher in 8-mercaptoquinoline than in 1,2,3,4-tetrahydro-8-mercaptoquinoline is due to the different hybridisations of the nitrogen atoms in these compounds[125]. According to the infrared spectra, there is an S–H←N IHB in phenyl 2-picolyl thioketone (XXVII)[131]:



(XXV)



(XXVI)



(XXVII)

3. The S–H←Hal Hydrogen Bond

Little information about the S–H←Hal HB is available. The assumption, based on measurements of the dipole moment, of the existence of *o*-chlorothiophenol and *o*-bromothiophenol in the *cis*-configuration with an S–H←Hal IHB[78] agrees well with the wavenumbers of the ν_{SH} vibrations (2552 and 2545 cm^{-1}, respectively), being appreciably lower than that for thiophenol (2587 cm^{-1})[52].

The infrared spectra and dipole moments suggest that chelation by an S–H←Hal IHB is also achieved in 6-fluoro-, 6-chloro-, and 6-bromo-5-mercaptoquinoline, and in 7-fluoro-, 7-chloro-, and 7-bromo-8-mercaptoquinoline[90,92,125]. The strength of the S–H←Hal IHB in these compounds increases from the bromo- to the fluoro-derivative.

III. PROTON-WITHDRAWING ABILITY OF A SULPHUR ATOM IN ORGANIC AND INORGANIC COMPOUNDS IN THE FORMATION OF HYDROGEN BONDS (O–H←S, N–H←S, C–H←S)

1. O–H←S and N–H←S Hydrogen Bonds

Owing to the presence of unshared electron pairs, sulphur atoms in organic compounds can participate in the formation of HB also as an acceptor of a proton (that is, a donor of electrons), and in particular this is confirmed by the existence of S–H←S HB in aliphatic and aromatic thiols (see Section II).

Table 3. Blue shift of the n-π^* band of the C=S group, association constant, and energy of the S→H–O HB of ETTC–proton-donating solvent associates.

Solvent	pK_{OH} (Refs.46, 135 & 136)	σ^*(Ref.137)	ETTC		
			K_{26}, litre mole^{-1} (Ref.132)	$-\Delta H$, kcal mole^{-1} (Ref.133)	$\Delta\nu(n\rightarrow\pi^*)$, cm^{-1} (Ref.46)
H_2O	7.05	—	—	6.5	—
CH_3OH	15.50	0.000	—	2.4	825
C_2H_5OH	15.93	−0.100	0.286	2.0	705
n-C_3H_7OH	16.10	−0.115	0.245	—	—
n-C_4H_9OH	16.10	−0.130	0.198	—	—
iso-C_3H_7OH	17.10	−0.190	0.137	1.9	585
t-C_4H_9OH	19.20	−0.300	0.038	1.7	585
$C_6H_5CH_2OH$	15.40	+0.215	0.620	—	—
$CF_3HCF_2CH_2OH$	12.74	+0.600	—	—	2404
CF_3CH_2OH	12.40	+0.920	—	—	2275
$CHCl_3$	—	—	—	1.9	—

A reliable criterion of the formation of associates by compounds which contain a thiocarbonyl group, by means of a C=S→H–X HB is thought to be the blue shift of the absorption band of this group. The assumption of the formation of a C=S→H–O HB on the basis of this effect between ethylene trithiocarbonate [1,3-dithiolan-2-thione (Ed. of Translation)] (ETTC, XXVIII) and alcohols[46,132,133] agrees completely with the infrared spectra for the ETTC-(proton-donating solvent) systems[134]. The blue shift of the $n\rightarrow\pi^*$ band of the thiocarbonyl group, the association constant at 26°C,[132] and $-\Delta H$ of the C=S→H–O HB of the ETTC–(proton-donating solvent) associates[133] are given in Table 3. This shows a distinct correlation between K_{26} and the acidic properties (pK_{OH}), that is, with the proton-donating properties of the alcohols, which is characterised by the inductive constant of the hydrocarbon radical of the alcohol (σ^*).

A tendency is also noted for an increase in the blue shift of the n-π^* band of the C=S group with increase in the proton-donating ability of the molecule in various alcohols (Tables 3 and 4) and phenols (Table 5). However, a similar correlation between the proton-donating ability (pK_a or σ^*) of the compounds of various classes (alcohols, phenols) and the blue shift of the band of the C=S group (ETTC) is not observed.

Table 4. Blue shift of the n-π^* band of the C=S group in alcohols[46].

Compound	$\Delta\nu(n\rightarrow\pi^*)$, cm^{-1}			
	CH_3OH	C_2H_5OH	iso-C_3H_7OH	t-C_4H_9OH
Thiazolidinethione	2100	1770	1600	1600
ETTC	825	705	585	585
Thiofenchone	430	440	300	270

Recently, the absence of a correlation between $-\Delta H$ of the C=S→H–O HB of ETTC–(phenols or acid derivatives of phenols) associates was also reported[138]. However, the reliability of the results and the conclusions of this work[138] are doubtful—for example, $\Delta\nu(n$-$\pi^*)$ is the same for solutions of ETTC in phenol, p-chlorophenol, and m-cresol. There are many published examples which show that for compounds of a single type RX–H (where X = O or S) there is a distinct correlation between their acidic properties and spectral ones and also the thermodynamic characteristics of the RX–H–Y HB with the same proton acceptor Y (Tables 3–6 and Section IV).

Table 5. Blue shift of the n-π^* band of the C=S group of ETTC in the phenols (R = C_6H_4OH).[46]

R	σ	pK_{OH}	$\Delta\nu(n\rightarrow\pi^*)$, cm^{-1}
p-Cl	0.23	9.38	1020
H	0.00	9.95	390
p-CH_3	−0.17	10.19	380
p-OCH_3	−0.27	10.20	235

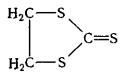
We have observed a clear correlation between the proton-donating ability of normal aliphatic alcohols and $-\Delta H$ of the S^-→H–O HB of the associates of zwitter-ion form (8-mercaptoquinoline, 5-mercaptoquinoline, and their derivatives)—alcohol (Table 6)[139-142].

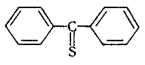
The decrease in $-\Delta H$ for the S^-→H–O HB for 8-mercaptoquinoline as compared with that of 5-mercaptoquinoline is due to the presence of an S^-→H–N IHB in the molecule of the former[141,142].

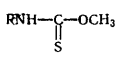
The blue shift of the n-π^* band of the C=S group for solutions of thiobenzophenone (XXIX) in ethanol[143,144], methyl (XXX; R = CH_3) and isopropyl thiocarbamates (XXX; R = Pr^i), thiocamphor (XXXI), ETTC (XXVIII) in phenol[145], alkylthioureas (XXXII) in phenol and ethanol[146], and 2-mercaptobenzothiazole (LIX) in acetic acid[147] are also due to C=S→H–O HB.

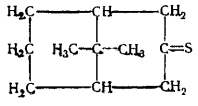
The association of alkylthioureas and thiocamphor with phenol by S→H–O HB[146,148,149] is also confirmed by the shift of the ν_{OH} band of phenol to lower frequencies. A similar type of interaction is also observed for the association of phenol with N≡CSN$(CH_3)_2$.[150] $-\Delta H$ of the

S→H–O HB for some of these systems are given in Table 7.


(XXVIII)


(XXIX)


(XXX)


(XXXI)

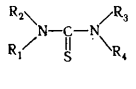

(XXXII)

Table 6. Energy of the S⁻→H–O HB of associates of the zwitter-ion form of 8-mercaptoquinoline (R), of its methyl derivatives (CH_3–R), and of 5-mercaptoquinoline (R_1) with aliphatic alcohols.

Solvent	σ*	$-\Delta H$, kcal mole^{-1}					
		R	$2CH_3$–R	$4CH_3$–R	$6CH_3$–R	$7CH_3$–R	R_1
CH_3OH	0.000	1.40	1.45	2.17	1.56	1.52	2.00
C_6H_5OH	0.100	0.80	0.85	1.56	0.90	0.86	1.60
n-C_3H_7OH	0.115	0.76	0.70	1.45	0.82	0.75	1.54
n-C_4H_9OH	0.130	0.73	0.65	1.26	0.71	0.65	1.50

The energies of the S→H–O HB of the associates of thiocamphor with propanol and tetrafluoropropanol are 1.8 kcal mole^{-1} ($\Delta\nu_{OH}$ = 120 cm^{-1}) and 3.6 kcal mole^{-1} ($\Delta\nu_{OH}$ = 170 cm^{-1}) respectively[46].

X-ray diffraction studies show a strong S→H–O HB exists in the crystalline 6-thiopurine riboside hydrate[151] and sodium *NN*-diethyldithiocarbamate trihydrate[152]. There is also a similar interaction in crystalline monohydrates of bis(isoquinoline-1-carboxaldehyde thiosemicarbasonato)nickel[153], 6-mercaptopurine[154,155], potassium[156] and caesium[157] trithiocarbonates, and barium thiosulphate[158].

Table 7. Energy of the HB ($-\Delta H$) between compounds containing a thiocarbonyl group and phenol.

Compound	$-\Delta H$, kcal mole^{-1}	Reference	Compound	$-\Delta H$, kcal mole^{-1}	Reference
Alkylthiourea	4—4.8	146	Thiocamphor	5.0	145
Thiocarbamates	4.0	145	Ethylenetrithiocarbonate (ETTC)	3.2	145

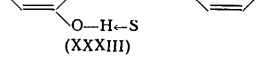
Spectroscopic investigation of the interaction of sulphides with proton-withdrawing solvents shows that in these systems association is also effected by means of S→H–O HB. The splitting of the ν_{OH} band in the infrared spectra of the *p*-chlorophenol–sulphide[159,160], phenol–sulphide[160,166], and phenol–aryl sulphide[167] systems is due to excitation of the OH group of the S→H–O HB with sulphide sulphur (Table 8).

The values[162,164] of $-\Delta H$ of the S–H→O HB of dibutyl sulphide–phenol and diethyl sulphide–phenol associates (Table 8) are evidently somewhat too high. According to Table 8, $-\Delta H$ of the S→H–O HB is greater in these instances than for associates of the corresponding sulphides with *p*-chlorophenol. However, bearing in mind the higher acidic properties of *p*-chlorophenol (pK_{OH} = 9.38[168]) compared with those for phenol (pK_{OH} = 9.98[169]) a strengthening of the S→H–O HB on going from phenol to *p*-chlorophenol can be postulated. The higher stability of the *p*-chlorophenol–sulphide associates compared with that of the sulphide–phenol associates is also shown by the greater shift of the ν_{OH} band to lower frequencies in the first instance. $\Delta\nu$ and $-\Delta H$ vary symbathically for monotypical compounds[1], which is observed, for example, for the tetrahydrothiopyran–phenol and tetrahydrothiopyran–*p*-chlorophenol systems (Table 8). Consequently, the value of $-\Delta H$ = 3.40 kcal mole^{-1} [163] for associates diethyl sulphide–phenol is more probable than $-\Delta H$ = 4.60 kcal mole^{-1}.[164]

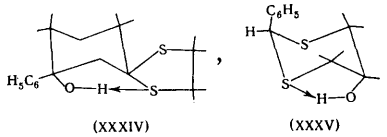
Table 8. Displacement of the ν_{OH} band and energy of the S→H–O HB of phenol and *p*-chlorophenol with the sulphides.

Compound	Phenol				*p*-Chlorophenol			
	$\Delta\nu$, cm^{-1}	reference	$-\Delta H$, kcal mole^{-1}	reference	$\Delta\nu$, cm^{-1}	reference	$-\Delta H$, kcal mole^{-1}	reference
Dibutyl sulphide	254	162	4.26	162	280	159	3.7	159
Diethyl sulphide	250	161	4.60	164	274	159	3.5	159
Ditto	210	163	3.40	163	—		—	
Methyl phenyl sulphide	170	161	3.40	161	—		—	
Ethyl propyl sulphide	—		—		276	159	3.7	159
Ethylene sulphide	210	160	2.38	160	—		—	
Propylene sulphide	222	160	2.42	160	—		—	
Trimethylene sulphide	248	160	2.91	160	—		—	
Tetrahydrothiopyran	244	160	2.99	160	282	159	3.9	159
Tetrahydrothiophen	262	160	3.39	160	—		—	

On the basis of the spatial position of the functional groups in 2-hydroxythiobenzophenone the formation of an S→H–O HB can be postulated (XXXIII), which evidently explains the absence of a blue shift for the n–π^* absorption band in proton-donating solvents (ethanol)[170]:


(XXXIII)

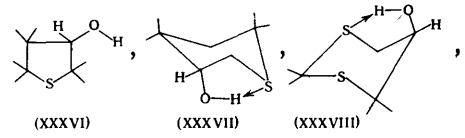
Finding the presence of an S→H–X IHB is often used in conformational analysis. Mertes[171,172] attributes the absorption at 3446 cm^{-1} (according to Szmant and Rigau[173], at 3500 cm^{-1}) and 3478 cm^{-1} in the infrared spectra of phenylmercaptoindanol (XXXIV) and 5-hydroxy-2-phenyl-1,3-dithione (XXXV) to the ν_{OH} vibrations of the *cis*-configuration, with an excited S→H–O IHB:


(XXXIV) (XXXV)

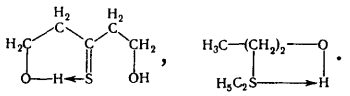
According to Szmant and Rigau, $-\Delta H$ of the S→H–O IHB in (XXXIV) is 2.5 kcal mole^{-1}.[173]

The shift of the ν_{OH} band to lower frequencies owing to the formation of an S→H–O type of IHB was also observed in the infrared spectra of thiocyclopentan-3-ol (XXXVI)[174] some of its derivatives[175], thiocyclohexanol (XXXVII),[174]

1,3-dithiocyclohexan-5-ol (XXXVIII),[174] its 2-phenyl derivative[176], 3-thiopentane-1,5-diol (XXXIX),[177] ω-ethylmercaptoalkanols (XL)[165,178], 2,2'-thiodiphenol[179], its derivatives[180], 2,2'-thiobis-(3,4,6-trichlorophenol), and 2,2'-thiobis-(4,6-dichlorophenol)[179]:

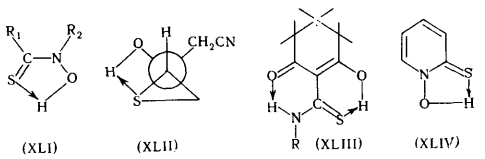


(XXXVI) (XXXVII) (XXXVIII)

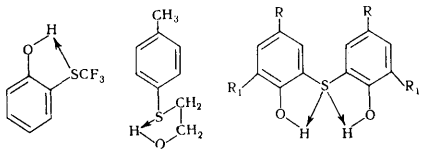


(XXXIX) (XL)

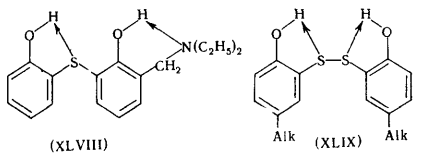
Chelation by S→H–O HB was also found in *o*-methylthiophenol, 2-methyl-6-methylthiophenol, *o*-isopropylthiophenol[181,182,183], thioacetylhydroxamic acid (XLI)[184], 1-cyano-3,4-epithio-2-hydroxybutane (XLII)[185] by NMR and infrared spectroscopy, in 4,4-dimethyl-2,6-dioxothiocyclohexanecarboxanilide (XLIII)[186], in monothio-β-diketones (XX)[115] by the NMR method, in 1-hydroxy-2-thiopyridone (XLIV)[188], and *o*-trifluoromethylphenol (XLV)[183] by infrared spectroscopy and in compounds of the (XLVI)–(L) type by dipole moments and infrared spectroscopy[180,188,189] and NMR[190,191].



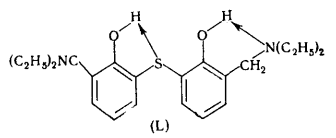
(XLI) (XLII) (XLIII) (XLIV)



(XLV) (XLVI) (XLVII)



(XLVIII) (XLIX)

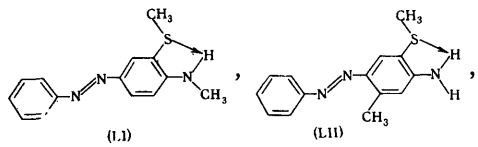


(L)

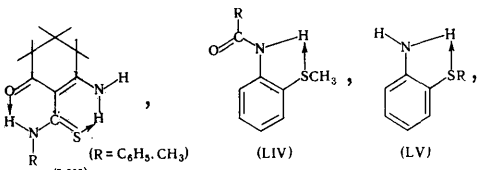
However, the problem of the presence of an S→H–O IHB in (XLVII) (when R_1 = H, CH_3), and also in XLVIII and XLIX) evidently cannot be regarded as settled. According to the results of recent investigations it seems that an S→H–O IHB can be formed only in the compounds (XLVII) with a sufficiently bulky substituent R_1 (t-butyl etc.).[190]

It is also noteworthy that the assumption of the presence of an S→H–O IHB in compounds (XX) based on the appearance in the NMR spectra of the signal of an OH group does not agree with the results of various other investigations[100,109-113] (section II.2).

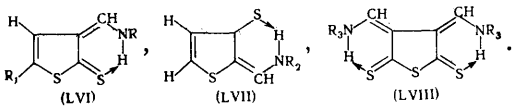
Chelation by means of an S→H–N type IHB has been established on the basis of the ν_{NH} band in the infrared spectra in dimetoate [sic. the compounds referred to in Ref. 192 are *o*-methylthio-derivatives of *N*-methylaniline and *N*-methyl-4-aminoazobenzene (Ed. of Translation)][192] and in compounds (LI) and (LII)[193], and by NMR spectroscopy in compounds (LIII)[186] and (LIV)[194]. NMR and infrared spectroscopy show that an S→H–N IHB exists in *o*-aminothiophenols (LV)[195] and mercaptoaldimines of the thiophene series (LVI)–(LVIII)[196,197]:



(LI) (LII)

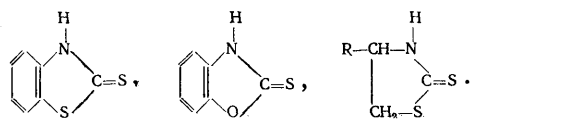


(LIII) (R = C_6H_5, CH_3) (LIV) (LV)



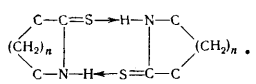
(LVI) (LVII) (LVIII)

Association by an HB of S→H–N type was first proved by Hopkins and Hunter[71] on the basis of cryoscopic measurements of the molecular weights of thioamides. This was later confirmed spectroscopically[198-204]. The broad band in the infrared spectra of 2-mercaptobenzothiazole (LIX), 2-mercaptobenzoxazole (LX), 2-mercaptothiazoline (LXI; R = H), and 2-mercapto-4-methylthiazole (R = CH_3) at 3050 cm^{-1} is due to the ν_{NH} vibrations of the associated molecules by the S→H–N HB[198]:



(LIX) (LX) (LXI) (R = H, CH_3)

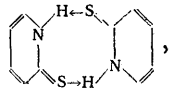
The proton-withdrawing ability of the thiocarbonyl group of these compounds in the formation of HB is confirmed by the blue shift of the n–π^* band of the C=S group for solutions of 2-mercaptobenzothiazole in proton-donating solvents[147]. According to Kulevsky and Froehlich[205], the splitting of the ν_{NH} band in the infrared spectra of solutions of thiolactams in benzene is due to the formation of dimers of structure (LXII):



(LXII)

The value of $-\Delta H$ of the S→H–N HB of thiobutyrolactam is 5.8 kcal $mole^{-1}$, that of thiovalerolactam 3.1 kcal $mole^{-1}$, and that of thiocaprolactam 3.3 kcal $mole^{-1}$. A similar conclusion was reached[206] concerning the autoassociation of thiocaprolactam in benzene from the infrared spectra and dipole moments. The dimerisation of (LXII) leads to a considerable decrease in μ (2.78 D) in comparison with μ of the monomer (4.59 D). It is necessary to note the considerable discrepancy in the values of the dimerisation constants for thiocaprolactam

(K_D = 370 litre mole^{-1} [205] and K_D = 93 litre mole^{-1} [206]) is noteworthy. K_D = 370 litre mole^{-1} is evidently too high if it is taken into account that for caprolactam K_D = 270 litre mole^{-1} and $-\Delta H$ for the O→H–N HB of the caprolactam dimers is 5.5 kcal mole^{-1}. [206] Cryoscopic [207,208] and dielectric [209] measurements and also investigation of the infrared spectra [187] showed that 2-thiopyridone in benzene and chloroform is dimerised like thiocaprolactams by the S→H–N HB (LXIII):



(LXIII)

The dimerisation of 2-thiopyridone in benzene leads, as for thiocaprolactam, to a considerable decrease in μ (2.78 D) in comparison with μ of the monomer (5.26 D for the *N*-methyl derivative). The dimers of thiocaprolactam and 2-thiopyridone are destroyed in dioxan [207, 208].

The infrared spectra show the association of *N*-methylaniline with thiocamphor by an S→H–N HB, the energy of which is 5.7 kcal mole^{-1}. [46]

Intermolecular association by means of an S→H–N HB is also effected in the sulphide–thiocyanic acid system (Table 9). [209]

Table 9. Displacement of the ν_{NH} band and $-\Delta H$ for the S→H–N HB of thiocyanic acid with sulphides [209].

Solvent	$\Delta\nu$, cm^{-1}	$-\Delta H$, kcal mole^{-1}	Solvent	$\Delta\nu$, cm^{-1}	$-\Delta H$, kcal mole^{-1}
Dimethyl sulphide	380	3.48	Di-t-butyl sulphide	440	4.48
Ethyl methyl sulphide	390	3.47	Tetrahydrothiapyran	400	3.69
Diethyl sulphide	400	3.49	Tetrahydrothiophen	420	3.62
Di-n-butyl sulphide	400	3.59	Trimethylene sulphide	383	3.28

It is suggested that the anti-swelling action of 6-thioguanine [210] is due to the formation of an S→H–N HB between the sulphur atom in this analogue of guanine and the amino-group of cytosine, which is situated opposite the sulphur atom in DNA [211]. An analogous interaction is also assumed between the thiocarbonyl group of thionicotinamide and the amino-group of adenine in the sulphur-containing analogue of dihydrophosphopyridine nucleotide [212].

The formation of an S→H–N HB in crystals has been discussed [213–215]. In crystalline 2-mercaptobenzothiazole there is a considerable decrease in the N...S distance (2.48 Å) in comparison with the N...S distance due to the van der Waals interaction associated with the S→H–N HB [216]. Penfold [217] assumes the presence of an S→H–N HB in crystalline 2-thiopyridone, the strength of which is considerably less than in crystalline 2-mercaptobenzothiazole (the N...S distance in 2-thiopyridone is 3.26 Å). On the basis of crystallographic results (Table 10) an analogous type of intermolecular interaction can be assumed in crystalline ammonium diamidothiophosphate [218], diammonium amidothiophosphate [219], thiosemicarbazide [220–222], pyridazo-3-thione [213,223], 3-hydroxy-5-thio-1,2,4-thiazole [224], thioacetamide [225], 1-thiocarbamylimidazoline-2-thione [226], 2,5-diamino-4-mercapto-6-methylpyrimidine [227], xanthene hydride [228], triethylenediaminecadmium(II) thiosulphate [229], 3-ethoxy-2-ketobutyraldehyde bis(thiosemicarbazone) [230], 2,4-dithiouranyl [231], the thiourea–parabanic acid (oxalylurea) complex [232], 2-propyl-4-thiocarbamoylpyridine [233], 4-thiocarbamoylpyridine [234], 4-formylpyridine thiosemicarbazone [235], 2-formylthiophen thiosemicarbazone [236], thiocytosine [237], copper ammonium thiomolybdate [238], 2,2′-diaminodiphenyl disulphide [239], thiocarbohydrazide [240], dithio-oxamide [241], 2-mercapto-6-methylpurine [98], 1,2,4-trithiolane-3,5-dione [242], 6-thioguanine [243], thiourea [244,245], trimethylenethiourea [246], allylthiourea [247], and also (despite certain objections [248]) in ethylenethiourea [1].

Table 10. N...S intermolecular distance.

Distance, A	Compound	Reference
3.366	pyridaz-3-thione	213,223
2.48	2-mercaptobenzothiazole	216
3.26	2-thiopyridone	217
3.400—3.484	ammonium diamidothiophosphate	218
3.312—3.478	diammonium amidothiophosphate	219
3.34; 3.39, 3.359; 3.409	thiosemicarbazide	220 221,222
3.24	3-hydroxy-5-thiol-1,2,4-triazole	224
3.396—3.504	thioacetamide	225
3.40	1-thiocarbamoylimidazolidine-2-thione	226
3.40	2,5-diamino-4-mercapto-6-methylpyrimidine	227
3.35	xanthene hydride	228
2.75; 2.93	triethylenediaminecadmothiosulphate	229
3.32—3.54	bis(thiosemicarbazone)-3-ethoxy-2-keto-butyraldehyde	230
3.315; 3.335	2,4-dithiouracyl	231
3.312	thiourea–parabanic acid	232
3.39	2-propyl-4-thiocarbamoylpyridine	233
3.44	4-thiocarbamoylpyridine	234
3.496	4-formylpyridine thiosemicarbazone	235
3.348; 3.360	2-formylthiophen thiosemicarbazone	236
3.34	thiocytosine	237
3.48	copper–ammonium thiomolybdate	238
3.48; 2.29; 2.67	2,2′-diaminodiphenyl disulphide	239
3.406	thiocarbohydrazide	240
3.43; 3.46	dithio-oxamide	241
3.37	2-mercapto-6-methylpyrin	98
3.60	1,2,4-trithiolan-3,5-dione	242
3.327; 3.303	6-thioguanine	243
3.35—3.43	thiourea	244,245
3.31	trimethylenethiourea	246
3.36	allylthiourea	247
3.44	ethylenethiourea	1

The existence of an S→H–N HB in crystalline thiourea and its tertiary derivatives was also shown by infrared spectroscopy [249,250].

2. The S→H–C Hydrogen Bond

The possibility of the formation of an HB of S→H–C type has also been noted. Engberts [251] recently suggested, on the basis of NMR results, such interaction between α-diazosulphones (RSO_2CHN_2) and thiophen. According to Bellamy and Rogasch [134], the association of chloroform with ETTC is assumed to be by an S→H–C HB. The ability of chloroform to form S→H–C HB with 8-mercaptoquinoline, its derivatives, their zwitter-ion forms, and aliphatic thiols has been postulated [56,125,141,252]. An analogous interaction, judging by interatomic distances, can evidently be presumed in crystalline 2,4-dithiouracyl [231], thiocarbamoyl-4-pyridine [234] and ethionamide [ethyl-2-thiocarbamoyl-4-pyridine] [253].

However, owing to the lack of experimental results the problem of an S→H–C type of HB still remains open.

IV. COMPARISON OF THE ABILITIES OF SULPHUR- AND OXYGEN-CONTAINING COMPOUNDS TO FORM HYDROGEN BONDS

The proton-donating ability of the X–H group in the formation of X–H···Y HB is usually linked with the acidic properties of the compounds RX–H (where X, Y = O or S)[254-262]. As the acidic properties of X–H increase there is an increase in the strength of the X–H···Y HB with the same acceptor of a proton. This correlation is also observed in the series of thiophenol derivatives[263] (Table 11). From this point of view a tendency (greater than for the hydroxyl group) for the mercapto-group to undergo association with the same proton-withdrawing molecule is to be expected. However, in reality on comparing proton-donating molecules with which the atom X (X–H) is situated in different Periods of the Mendeleev system, there is not a proportionality between the ability of the X–H group to act as a proton donor in the formation of an HB and its strength as an acid. For example, for the hydrohalogen acids the acidic properties of which decrease in the order HI > HBr > HCl > HF, the energy of the HB with the same proton-withdrawing molecule changes in the reverse order[264,265].

Table 11. Frequency characteristics of the ν_{SH} band of thiophenol and of its *p*-substituted derivatives in proton-withdrawing solvents.

Substituent	pK_a	CCl_4		Benzene		Acetonitrile		Acetone	
		ν_{SH}	$\Delta\nu$	ν_{SH}	$\Delta\nu$	ν_{SH}	$\Delta\nu$	ν_{SH}	$\Delta\nu$
NH_2	9.7	2559	0	2551	3.1	2547	4.7	2541	7.0
OCH_3	8.8	2572	0	2565	2.7	2561	4.3	2548	9.3
H	8.3	2590	0	2574	6.2	2565	9.7	2558	12.4
Cl	7.3	2588	0	2567	8.1	2557	12.0	2544	17.0
NO_2	5.8	2589	0	2562	10.4	2547	16.2	2519	27.0

An analogous effect is also observed for compounds which contain SH and OH groups. Compounds which contain an SH group always exhibit more acidic properties than their hydroxyl-containing analogues. However, under strictly equal conditions compounds of the RSH type form a less stable HB than compounds of the ROH type. For example, thiophenol (pK_{SH} = 6.5 [266]) forms less stable HB than phenol (pK_{OH} = 9.98 [169]) with proton-withdrawing solvents (Table 12).

An analogous effect is also observed for autoassociation of phenol and thiophenol, for which $10^2\Delta\nu/\nu$ (the relative displacement of the maximum of the ν_{XH} band in the formation of an HB) is 3.4 [273] and 0.73 [49] respectively. The effect of the S–H···O_2N IHB in *o*-nitrothiophenol on the displacement of the $\nu_s(NO_2)$ and $\nu_{as}(NO_2)$ bands ($10^2\Delta\nu/\nu$ = 1.54) is also considerably less than for the O–H···O_2N IHB of *o*-nitrophenol ($10^2\Delta\nu/\nu$ = 9.6 [78]). Several studies have shown that the rate of exchange of the protons in SH groups is several orders of magnitude less than in OH groups, which is the result of the strength of the S–H···S HB being less than that of the O–H···O HB.[76,274,275] The lesser ability of the mercapto-group to form HB is also confirmed by the lower association constants of aliphatic thiols compared with those of aliphatic alcohols (Table 13).

This agrees well with the investigation of chelation in thiosalicylic acid[99] and 8-mercaptoquinoline[125]. The energy of the S–H···O IHB in thiosalicylic acid ($-\Delta H$ = 0.9 kcal mole^{-1}) is considerably less than the O–H···O IHB in salicylic acid ($-\Delta H$ = 5 kcal mole^{-1} [278,279]) despite the lower acidity of the latter.

Table 12. Spectroscopic and thermodynamic characteristics of hydrogen bonds formed by thiophenol and phenol with proton-withdrawing solvents.

Proton acceptor	Thiophenol					Phenol				
	$10^{-2}\frac{\Delta\nu}{\nu}$	A, litre cm^{-2} mole^{-1}	K_{26}, litre mole^{-1}	$-\Delta H$, kcal mole^{-1}	reference	$10^{-2}\frac{\Delta\nu}{\nu}$	A, litre cm^{-2} mole^{-1}	K_{26}, litre mole^{-1}	$-\Delta H$, kcal mole^{-1}	reference
Pyridine	4.45	—	0.22	2.4	44,81	12.9	—	77	6.0	263,267
								42	6.5	45
Dimethylformamide	—	—	0.24	1.8	44,81	6.3	—	70	6.1	268
	—	—	—	—	—	—	—	64	—	46
Dioxan	1.43	—	—	—	44	6.85	3.34	4.1	5.5	269,270
Acetone	0.97	—	—	—	44,76	6.5	—	—	—	263
Tetrahydrofuran	2.5	0.68	—	—	78	8.3	3.49	—	5.7	269
Benzene	0.81	0.35	0.039	0.5	78,81	1.32	0.97	0.37	1.56	269,271
	—	—	—	—	—	—	—	0.20	1.60	46
Diethyl sulphoxide	3.75	—	—	—	77	10.0	—	—	—	77
Ethyl phenyl sulphoxide	2.70	—	—	—	77	9.5	—	—	—	77
Diphenyl sulphoxide	1.85	—	—	—	77	8.3	—	—	—	77
Dibutyl ether	0.73	—	—	—	32	7.5	—	—	—	269,272

The strength of the S–H···N IHB in 8-mercaptoquinoline ($-\Delta H$ = ~ 3 kcal mole^{-1}) is much less than that of the O–H···N IHB in 8-hydroxyquinoline ($-\Delta H$ = ~ 6 kcal mole^{-1}).[125] The acidic properties of 8-mercaptoquinoline (pK_{SH} = 8.48 [280]) greatly exceed those of 8-hydroxyquinoline (pK_{OH} = 9.89 [281]).

Table 13. Association constants (K) of aliphatic alcohols and thiols.

Substance	K, litre mole^{-1}	Reference	Substance	K, litre mole^{-1}	Reference
Ethanol	0.64	276	Ethanethiol	0.021	48
n-Propanol	0.89	277	Propane-1-thiol	0.052	48
n-Butanol	0.78	277	Butane-1-thiol	0.016	48

The experimentally observed inverse relationship between the ability of the mercapto- and hydroxyl groups to form HB and their acidic properties is due to the difference in the nature of the S–H and O–H chemical bonds.

From the point of view of the covalent nature of the X–H···Y HB[282,283], the existence of a definite relation between the proton-donating ability of the X–H group and the tendency of the H atom of this group to receive electrons of atom Y is postulated[284]. Evidently two mechanisms of the transfer of electrons to the H atom are possible: to the vacant (antibonding[250,260-285]) orbital X–H or to the 1*s* orbital of the bonded H atom[283,286] with use therein of its residual overlap capability. The latter should increase with decrease in the *S*-integral for the overlap of the X–H bond[287]. The value of the *S*-integral

depends on the nature of the remaining part of the molecule (R) and the electronegativity (EN) of the atom X. With increase in the inductive nature of R and in the EN of atom X there is a decrease in the probability of the residence of the electrons in the overlap region which reduces S and increases the proton-donating ability of X–H. Consequently, the strength of the X–H···Y HB for a given donor of electrons Y depends on the degree of "protonisation" of the hydrogen atom[288]. For the same atom X the degree of "protonisation" and the acidic properties of the molecule due to the influence of the radical R on the X–H bond are symbatic to one another.

Table 14. Dipole moments of 2-thiopyridone, 2-pyridone, and their *N*-methyl derivatives in dioxan (μ_D).[208]

Compound	μ_D, D
2-Pyridone	2.94
N-Methylpyrid-2-one	4.07
2-Thiopyridone;	5.29
N-Methyl-2-thiopyridone	5.49

In comparing proton-donating molecules which contain different atoms X it is also necessary to take into account differences in the value of the *S* overlap integral[289]. For many compounds the proton-donating ability of the X–H group correlates well with the EN of atom X[289] and also with the size of the electron cloud (with the principal quantum number of the valence electrons of atom X[99,288,290]). These correlations are evidently a reflection of relation between the proton-donating ability and *S* already mentioned[289], since *S* is a function of both the difference in EN and the dimensions of the atoms being bonded[291,292]. Correlation of the proton-donating ability of the X–H groups with the EN of the atoms X is observed when there is a considerable difference in EN or when the sizes of atoms X are similar. When the atoms X have similar EN the sizes of the electron clouds must be considered (for example, N–H and Cl–H or C–H and I–H)[289].

In compounds with an S–H group, as compared with their oxygen analogues, the valence orbitals of the sulphur atom are much more delocalised in space than those of the oxygen atom. This is connected with the greater principal quantum number of the valence electrons of the sulphur atom. Because of this the *S* overlap integral of the S–H bond is considerably greater than that of the O–H bond. In accordance with this, an increase in the *S* integral leads to a decrease in the "protonisation" of the H atom, that is, to a decrease in the proton-donating ability of the S–H group and consequently to a decrease in the strength of the S–H···Y HB in comparison with the strength of the O–H···Y HB. However, the S–H bond is considerably weaker than the O–H bond, owing to the greater delocalisation in space of the valence orbitals of the sulphur atom, compared with those of the oxygen atom. The lower energy of the bonding of the hydrogen atom in the S–H group is a reason for the higher acidity of the compounds with an S–H group compared with those of their oxygen analogues. Consequently, replacement of an oxygen atom by a sulphur atom in the X–H group (X = O or S) brings about, on the one hand, a decrease in the degree of "protonisation" of the hydrogen atom, leading to a weakening of the HB with the proton-withdrawing molecule, and, on the other, to the loosening of the X–H bond, increasing its ability for ionisation.

A comparison of the proton-withdrawing capability of sulphur and oxygen atoms in the formation of HB is also of interest.

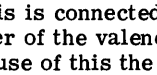
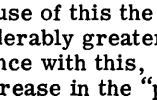
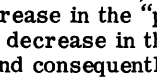
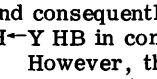
2-Thiopyridone (Section III) is dimerised[208] in solutions in benzene, as also is 2-pyridone[208]. According to measurements of the dipole moments of 2-thiopyridone, 2-pyridone, and their *N*-methyl derivatives, the dimers of 2-thiopyridone (unlike 2-pyridone) are broken down in solutions (Table 14).

Table 15. $\Delta\nu_{OH}$ and $-\Delta H$ of the O–H···Y HB of $(C_4H_9)_2Y$–C_6H_5OH associates[162].

Y	$\Delta\nu_{OH}$, cm^{-1}	$-\Delta H$, kcal mole^{-1}
O	278	5.98
S	254	4.26
Se	210	3.72

According to results obtained in an investigation of $(C_4H_9)_2Y$–C_6H_5OH associates (Y = O, S, Se) the energy of the O–H···Y HB and the displacement of the ν_{OH} band to lower frequencies decreases in the order O > S > Se (Table 15).

Table 16. Displacement of the ν_{OH} band, association constant (K_{20}), and energy of formation of the associates ($-\Delta H$) of ethers and thioethers with phenol and its derivatives.

Compound	Y	Phenol (Refs.160 & 163)			*p*-Chlorophenol (Ref.159)		
		$\Delta\nu$, cm^{-1}	K_{20}, litre mole^{-1}	$-\Delta H$, kcal mole^{-1}	$\Delta\nu$, cm^{-1}	K_{20}, litre mole^{-1}	$-\Delta H$, kcal mole^{-1}
$(C_4H_9)_2Y$	O	—	—	5.71	305	13.6	5.4
	S	—	—	4.19	280	3.2	3.7
$C_2H_5YC_9H_7$	O	—	—	—	300	16.2	5.3
	S	—	—	—	276	3.4	3.7
$(C_2H_5)_2Y$	O	270	9.6	4.6	300	12.1	5.0
	S	165	4.7	3.4	274	3.0	3.5
	O	290	9.36	4.32	—	—	—
	S	244	1.38	2.99	—	—	—
	O	295	9.83	4.25	316	34.5	5.8
	S	262	2.49	3.39	282	8.3	3.9
	O	299	13.3	4.97	—	—	—
	S	248	1.37	2.91	—	—	—
	O	220	5.95	3.75	—	—	—
	S	222	1.08	2.42	—	—	—

Investigations of the interaction of the esters and thioesters triethyl phosphate and triethyl phosphorothioate with proton-donating solvents (phenol and its derivatives) also showed that the strength of the O–H···Y HB formed by sulphur-containing compounds (Y = S) is much less than that for their oxygen-containing analogues (Y = O) (Tables 16 and 17).

For IHB an analogous relation between the strengths of the O–H⋯S and O–H⋯O HB was shown by examples of ω-ethylmercaptoalkanol and ω-methoxyalkanol[178]. The high strength of the O–H⋯S IHB compared with that of the O–H⋯O IHB in five-membered rings[181,183,184] is an exception. It seems that in five-membered rings the N–H⋯S IHB is also much stronger than the N–H⋯O.[195] This is explained by the sulphur atom being larger than the oxygen atom, which leads to a greater overlap of the orbitals having a lone pair with the 1*s* orbital of the hydrogen atom being greater for sulphur.

Table 17. Displacement of the ν_{OH} band, association constant (K_{20}), and energy of formation of the associates ($-\Delta H$) of triethyl phosphate and triethylthiophosphorothionate with phenol and pentachlorophenol[163].

Compound	Y	Phenol			Pentachlorophenol		
		Δν, cm^{-1}	K_{20}, litre $mole^{-1}$	$-\Delta H$, kcal $mole^{-1}$	Δν, cm^{-1}	K_{20}, litre $mole^{-1}$	$-\Delta H$, kcal $mole^{-1}$
$(C_2H_5O)_3P=Y$	O	345	350,5	6.7	481.1	153.1	5.2
	S	172	4.5	3.2	202	2.9	3.3

In the literature the proton-withdrawing ability of a molecule in the formation of an X–H⋯Y HB is usually correlated with the first ionisation potential of this compound[159,285,293–295]. Here however, it must be borne in mind that such a correlation is well achieved in a series of monotypical compounds, for example, in a series of ketones or esters[296–299].

From this point of view, taking into account that the bonding of the valence electrons of the sulphur atom is weaker than that for the oxygen atom, a higher electron-donating ability is to be expected for the sulphur-containing compounds. For typical donor–acceptor complexes with charge transfer the ability for complex formation is usually, with certain exceptions[300], higher for sulphur-containing compounds[145,163,301–304]. However, such a relation is not observed between the electron-donating ability of SR_2 and OR_2 and the strength of the HB formed by them with the same RX–H.

The experimentally observable higher ability of oxygen-containing compounds to form HB compared with that of their sulphur-containing analogues must be regarded from the viewpoint of the difference in the electronic structure of the sulphur and oxygen atoms.

Schneider[290] explains the difference in the proton-withdrawing abilities of sulphur and oxygen in the formation of HB by the degree of *s*-character of the orbitals of their non-generalised electrons. The unshared pairs of electrons of the sulphur and oxygen occupy hybrid *sp*-orbitals. According to published data the strength of the HB depends on the magnitude of the *s*-character of the hybrid *sp*-orbitals of the lone pair. For example, ethers (sp^3 hybridisation, 25% *s*-character) form stronger HB than ketones (sp^2 hybridisation, 33% *s*-character).[159,305] However, the strength of the HB formed by the lone pair increases with decrease in the *s*-character of its orbitals only up to a certain limit. For example, ethylene oxide, the lone pairs of which occupy pure *s*- and *p*-orbitals (hybridisation is absent) form less stable HB than ethers[159].

Hence the strength of the HB depends on the magnitude of the atomic dipole and the degree of spatial localisation of the lone pair: an increase in the *s*-character in the *sp*-hybrid orbital leads to a decrease in the asymmetry of the cloud of the unshared pair relative to the nucleus and to its spreading in space, which reduces the energy of interaction with the hydrogen atom. In ethers (esters) (Table 10) the C–O–C valence angle is close to 109°, but in the corresponding thioethers the C–S–C angle is always 7–12° less[306], that is, the orbitals of the lone pairs in the thioethers exhibit a considerably greater *s*-character than in ethers, in consequence of which the thioethers form less stable HB[159,160]. In triethyl phosphate the oxygen has sp^2 hybridisation and in triethyl phosphorothioate the unshared pairs of the sulphur occupy almost pure *s*- and *p*-orbitals (this also occurs in the C=O group as compared with the C=S group), which also leads to the P=S⋯H–O (C=S⋯H–O) HB being weaker than the P=O⋯H–O (C=O⋯H–O) HB.

Ginzburg[159] considers that the low energy of formation of HB involving a sulphur atom as the proton acceptor may also be partly due to the greater *s*-character of the lone pair orbitals. He thinks the main reason is that on going from an oxygen atom to a sulphur atom there is an increase in the principal quantum number of the electrons of the outer clouds which is accompanied by an increase in the symmetry of the lone pair orbitals and a decrease in their spatial localisation. For example, sulphur is known to form less stable covalent bonds than oxygen with the same atom. Consequently, the degree of overlap of the electron clouds in a C–S bond is less than in the C–O bond, that is, there is weakening of the bond owing to the orbitals of the sulphur atom being less localised in space. The greater "spreadability" of the orbitals of the sulphur atom with lone pairs than the corresponding orbitals of the oxygen atom is also mainly responsible for the lower ability of the sulphur atom to form HB in sulphur-containing compounds in comparison with the oxygen atom in their oxygen-containing analogues.

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