Hydrogen-bond basicity of thioamides and thioureas

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The thermodynamic hydrogen-bond basicity scale pK_{HB} (logarithm of the formation constant of 4-fluorophenol–base complexes in CCl_4) has been determined for 18 thiocarbonyl bases, mainly thioamides and thioureas, and correlated to a spectroscopic basicity scale, the ν(OH) frequency shifts of methanol hydrogen bonded to the same bases. We confirm that the major site for hydrogen bonding is the sulfur atom and that the thiocarbonyl bases are always weaker than the corresponding carbonyl bases on the pK_{HB} scale. Iminology strongly increases hydrogen-bond basicity and the thiourea iminologue $Me_2NC(Me)=NCSNMe_2$ is the most basic thiocarbonyl base presently known. The apparently high basicity of secondary cyclic thioamides and thioureas is discussed.

Following the pioneering work of Gurka and Taft,[1] we are currently[2-6] building a thermodynamic hydrogen-bond basicity scale based on pK_{HB}, the logarithm of the formation constant K_{HB} of the 1:1 4-fluorophenol–base complex in CCl_4 at 298 K [eqns. (1) and (2)]. In the hydrogen bond-formation equilibrium

$$B + 4\text{-F-}C_6H_4\text{-OH} \rightleftharpoons 4\text{-F-}C_6H_4\text{-OH}\cdots B \quad (1)$$

$$K_{HB} = [\text{Hydrogen-bonded complex}]/[B]\,[4\text{-F-}C_6H_4\text{-OH}]; \quad pK_{HB} = \log_{10} K_{HB} \quad (2)$$

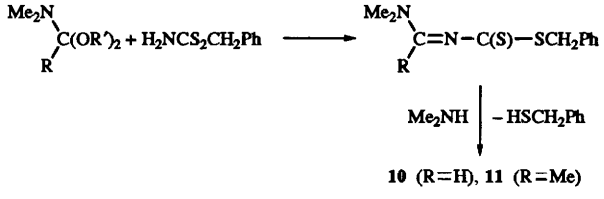
(1), 4-fluorophenol is a reference hydrogen-bond donor chosen for technical reasons. In particular it gives, in the whole range of the scale, numerical values of K_{HB} measurable by various methods, of which IR spectroscopy appears the easiest and the most accurate.

Compared with oxygen bases, little attention has been paid to the hydrogen-bond basicity of their sulfur counterparts. There are no measured pK_{HB} values for thiocarbonyl compounds in Gurka and Taft's work.[1] The hydrogen-bond formation constants of phenols with tetramethylthiourea,[7-11] dimethylthioacetamide,[7,10] dimethylthioformamide,[9,11] $NCCSNMe_2$,[7] $MeSCSNMe_2$,[7] $MeOCSNMe_2$,[7] dimethylthiobenzamide[7] and heterocyclic thioamides and thioureas[11,12] have been measured in a number of studies. Unfortunately they refer to various phenols (phenol,[7] 4-chlorophenol,[11,12] 4-nitrophenol,[10] 3,4-dinitrophenol[11] and other substituted phenols[8,9]) and different solvents (CCl_4, CCl_3CH_3[10] and cyclohexane[11]). These data are not entirely satisfactory in so far as we have chosen to build a scale defined from a reference process [eqn. (1)] rather than to gather inhomogeneous data into a statistical scale, and, in any case, the data set needs to be enlarged.

In this work, we have measured the pK_{HB} scale for 11 thioamides, 5 thioureas and, for comparison, thiocamphor and ethylenetrithiocarbonate. We present also a spectroscopic scale of hydrogen-bond basicity, the lowering $\Delta\nu$(OH) of the OH stretching of the hydrogen-bond donor methanol on going from the free to the hydrogen-bonded OH group. From these data, we discuss here (*i*) the hydrogen-bonding site, (*ii*) the comparison of sulfur bases with their oxygen analogues, (*iii*) the super-basicity of two thiourea iminologues and (*iv*) the anomalous behaviour of compounds with the s-*cis* C(S)NH moiety, with specific consideration of methimazole, a very potent synthetic anti-thyroid agent.

Experimental

In Table 1, chemicals **1**, **3**, **7**, **9**, **14**, **16**, **17** and **18** are commercial compounds (Aldrich). The sulfuration, *via* P_2S_5 or Lawesson's reagent,[13] of the oxygen analogues gives compounds **2**, **4**, **5**, **6**, **8**, **12**, **13** and **15**. Compounds **10** and **11** are obtained according to Scheme 1.[14]



Scheme 1

IR measurements were carried out with a Fourier-transform Bruker IFS 45 spectrometer by selecting 1 cm^{-1} resolution. A 1 cm quartz cell was thermostatted at 25 ± 0.1 °C.

The FTIR spectroscopic method for measuring formation constants [eqn. (2)] of hydrogen-bonded complexes of 4-fluorophenol has previously been described.[2-6] The maximum error in pK_{HB} is estimated to be ±0.04 for tertiary thioamides and thioureas. However the self-association of secondary thioamides and thioureas brings additional errors (*vide infra*).

The dimerization constants of the thioamide **9** and thioureas **15** and **16** have been obtained by the IR Allen method[16] measuring both the intensity fall of the monomer ν(NH) band and the intensity rise of the dimer ν(NH) band with increasing concentrations.

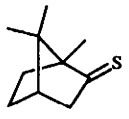
The IR shifts $\Delta\nu$(OH) are known to ±3 cm^{-1} if the ν(OH···S) band is symmetrical, but asymmetry causes larger errors.

Results

The primary pK_{HB} values and IR shifts $\Delta\nu$(OH) are reported in Table 1. The last column contains the Abraham's hydrogen-bond basicity parameter[17] β_2^H, which is a linear transform of pK_{HB} *via* eqn. (3). This parameter permits a quantitative

$$\beta_2^H = (pK_{HB} + 1.1)/4.636 \quad (3)$$

Table 1 Hydrogen-bond basicity of thiocarbonyl bases: IR shifts $\Delta\nu$(OH)/cm^{-1}, primary pK_{HB} values and β_2^H values

No.	Compound	Formula	$\Delta\nu_1$(OH)[a]/cm^{-1}	$\Delta\nu_2$(OH)[b]/cm^{-1}	pK_{HB}	β_2^H
	Thioamides					
1	*N,N*-Dimethylthiocarbamoyl chloride	$ClCSNMe_2$	111	207	0.50	0.35
2	*N,N*-Dimethylthiobenzamide	$PhCSNMe_2$	157	279	1.02	0.46
3	*N,N*-Dimethylthioformamide	$HCSNMe_2$	162	321	1.05[d]	0.46
4	*N*-Methylthioacetamide	MeCSNHMe	[c]	305	1.14	0.48
5	4,*N,N*-Trimethylthiobenzamide	$4\text{-}MeC_6H_4CSNMe_2$	167	288	1.15	0.49
6	*N,N*-Dimethyl-4-methoxythiobenzamide	$4\text{-}MeOC_6H_4CSNMe_2$	172	294	1.16	0.49
7	*N,N*-Dimethylthioacetamide	$MeCSNMe_2$	184	324	1.32	0.52
8	*N,N*-Dimethyl-4-aminothiobenzamide	$4\text{-}H_2NC_6H_4CSNMe_2$	[c]	[c]	1.33	0.52
9	ε-Thiocaprolactam	$HNCH_2CH_2CH_2CH_2CH_2CS$	[c]	[c]	1.60[f]	0.58
10	*N,N*-Dimethyl(*N,N*-dimethylamino)methyl-ideneaminothioamide	$Me_2NCH{=}NCSNMe_2$	225	386	1.79	0.62
11	*N,N*-Dimethyl-1-(*N,N*-dimethylamino)-ethylideneaminothioamide	$Me_2NC(Me){=}NCSNMe_2$	254		2.06[g]	0.68
	Thioureas					
12	*N,N*-Dimethyl-*N',N'*-diethylthiourea	$Et_2NCSNMe_2$	190	340	1.29	0.52
13	*N,N'*-Dimethyl-*N,N'*-ethylenethiourea	$MeNCH_2CH_2N(Me)CS$	180	316	1.32	0.52
14	*N,N,N',N'*-Tetramethylthiourea	$Me_2NCSNMe_2$	194	338	1.35[e]	0.53
15	*N*-Methyl-*N,N'*-propylenethiourea	$HNCH_2CH_2CH_2N(Me)CS$	[c]	[c]	2.00[f]	0.67
16	Methimazole	$HNCH{=}CHN(Me)CS$	[c]	[c]	2.29[f] 2.11[h]	0.73 0.69
	For comparison					
17	Ethylenetrithiocarbonate	SCH_2CH_2SCS	105	198	0.30	0.30
18	Thiocamphor		130	260	0.34	0.31

[a] IR shift of methanol = 3644 − ν(OH · · · S). [b] IR shift of 4-fluorophenol = 3614 − ν(OH · · · S). [c] The ν(NH) band prevents measurements of the ν(OH · · · S) band. [d] Ref. 9 quotes the value of 0.98 at 30 °C. [e] Ref. 9 quotes the value of 1.27 at 30 °C. [f] Calculated by eqn. (8). [g] Calculated by eqn. (4). [h] From measurements in CH_2Cl_2 converted into CCl_4.

estimate of the formation constant for many hydrogen-bonded complexes.[18]

Gentric and co-workers[11,12,19] have measured the hydrogen-bond basicity of numerous heterocyclic thioamides and thioureas towards 4-chlorophenol in CCl_4 at 25 °C. From the linear free energy relationship found by Abraham *et al.*[17] between log K_B (formation constant of 4-chlorophenol complexes) and pK_{HB}, we can calculate secondary pK_{HB} values (Table 2). The last column of Table 2 contains the pK_{HB} difference between the N(H)CS and N(Me)CS compounds, which will be discussed further.

Secondary pK_{HB} values are also reported in Table 2 for $MeOCSNMe_2$ and $MeSCSNMe_2$ from the formation constants of their complexes with phenol[7] and the linear free energy relationship[17] log K(phenol) = 0.946pK_{HB} − 0.057.

The spectroscopic data and the cyclic dimerization constants of compounds **9**, **15** and **16**, obtained by the Allen method,[16] are reported in Table 3.

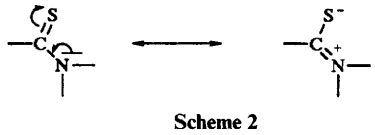
Discussion

Hydrogen-bonding site and the relation between spectroscopic and thermodynamic scales

The compounds studied have several potential acceptor sites for hydrogen-bond formation. The main ones seem to be the sulfur and one (thioamides), two (thioureas and **8**) or three (**10** and **11**) nitrogens. The blue shift of the n→π* transition of the thiocarbonyl group in hydrogen-bond donor solvents,[7] the shift to lower wavenumbers by complex formation with phenol of IR bands containing some character of the ν(C=S) vibration[20] and the shift to higher wavenumbers by complexation with phenol of IR bands containing some character of ν(C–N) vibration[20] strongly suggest that the donor site for hydrogen bonding is the sulfur atom of the thiocarbonyl group.

In this work we find (Fig. 1) that a very satisfactory correlation exists between the thermodynamic scale pK_{HB} and the spectroscopic scale $\Delta\nu_1$(OH) [eqn. (4)] for those thioamides and thioureas for which $\Delta\nu_1$(OH) could be measured. In eqn. (4), n, is the number of data points, r, the correlation coefficient and s, the standard deviation. We have previously found pK_{HB}/$\Delta\nu$(OH) relationships for other families (nitriles,[3] alcohols,[4] amides,[5] nitro bases[2] and amidines[6]), but (*i*) they obey different equations and (*ii*) they are not followed by polyfunctional bases. Both this family-dependence and this monofunctionality condition require the existence of one common major site of hydrogen bonding in thioamides and thioureas in order that eqn. (4) be obeyed. Since the push-pull mechanism (Scheme 2) is supported by the high

$$pK_{HB} = 0.0109\Delta\nu_1(OH) - 0.71 \quad (4)$$
$$n = 10 \quad r = 0.991 \quad s = 0.05$$

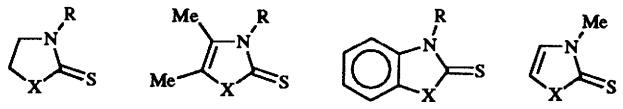


Scheme 2

C–N rotation barrier[21,22] and high mesomeric moment[23] of thioamides and increases the sulfur electron density at the expense of nitrogen(s), sulfur must be preferred to nitrogen(s) as the common major site for hydrogen bonding.

A last piece of evidence for S-fixation is found in the

Table 2 pK_{HB} and β_2^H secondary values for heterocyclic thioamides **19**–**22'**, $MeOCSNMe_2$ and $MeSCSNMe_2$



19 R = H **19'** R = Me; **20** R = H **20'** R = Me; **21** R = H **21'** R = Me; **22'**

No.	R	X	pK_{HB} [a]	β_2^H	No.	R	X	pK_{HB} [a]	Δ [b]	β_2^H
19a	H	O	1.38	0.53	**22'c**	Me	NMe	1.55	0.74	0.57
19b	H	S	1.32	0.52	**19'b**	Me	S	0.91	0.41	0.43
19c	H	NMe	1.88	0.64	**19'c** [c]	Me	NMe	1.34 [d]	0.54	0.53
20a	H	O	1.81	0.63	**20'a**	Me	O	1.23	0.58	0.50
20b	H	S	1.81	0.63	**20'b**	Me	S	1.13	0.68	0.48
20c	H	NMe	2.17	0.70	**20'c**	Me	NMe	1.79	0.38	0.62
21a	H	O	1.24	0.50	**21'a**	Me	O	0.78	0.46	0.40
21b	H	S	1.15	0.48	**21'b**	Me	S	0.66	0.49	0.38
21c	H	NMe	1.53	0.57	**21'c**	Me	NMe	1.19	0.34	0.49
22'b	Me	S	0.83	0.42						
					23	$MeOCSNMe_2$		0.81 [e]	—	0.41
					24	$MeSCSNMe_2$		0.66 [e]	—	0.38

[a] $pK_{HB} = (\log K_B - 0.074)/1.065$. Log K_B is from ref. 19. [b] $\Delta = pK_{HB}$(**19**, **20**, **21**) − pK_{HB}(**19'**, **20'**, **21'**). For compound **22'c**: $\Delta = pK_{HB}$ (**16**) − pK_{HB} (**22'c**). [c] Numbered **13** in Table 1. [d] The primary (Table 1) and secondary values agree within experimental errors. [e] $pK_{HB} = [\log K(\text{phenol}) + 0.057]/0.946$. Log K(phenol) is from ref. 7.

Table 3 Wavenumbers and extinction coefficients of the stretching NH vibration of the monomeric and dimeric forms of secondary thioamide and thioureas and cyclic dimerization constants K_D

No.	Compound	Solvent	ν_1(NH)/cm^{-1} (monomer)	ν_2(NH)/cm^{-1} (dimer)	ε_1/$dm^3\ mol^{-1}\ cm^{-1}$ (monomer)	ε_2/$dm^3\ mol^{-1}\ cm^{-1}$ (dimer)	K_D/$dm^3\ mol^{-1}$
9	ε-Thiocaprolactam	CCl_4	3400	3189	206	148	69
15	*N*-Methyl-*N*,*N'*-propylenethiourea	CCl_4	3450	3225	254	172	35
16	Methimazole	CCl_4	3474	3145	282	153	3375
16	Methimazole	CH_2Cl_2			222	210	60

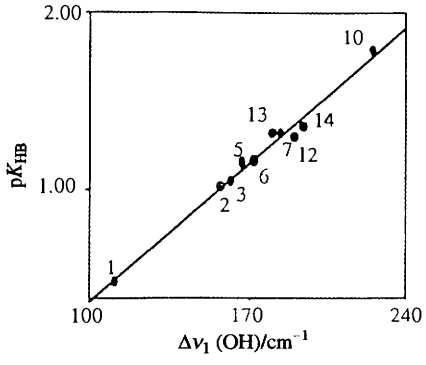


Fig. 1 Relationship between the thermodynamic hydrogen-bond basicity scale pK_{HB} and the spectroscopic basicity scale $\Delta\nu_1$(OH) for the family of thioamides and thioureas. Numbers refer to Table 1.

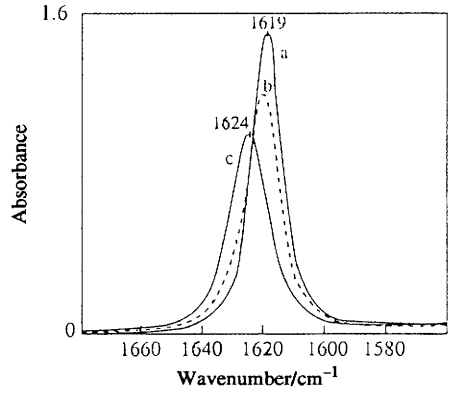


Fig. 2 The ν(C=N) band of $Me_2NCH{=}NCSNMe_2$ at 1619 cm^{-1} in C_2Cl_4 (0.1 cm cell, 5 × 10^{-3} mol dm^{-3}) is shifted to higher wavenumber in its complex with 4-fluorophenol. Concentrations of 4-fluorophenol are (a) 0, (b) 0.01 and (c) 0.1 mol dm^{-3}.

thioamidoformamidine **10**, where the ν(C=N) frequency *increases* from 1619 cm^{-1} in the free molecule to 1624 cm^{-1} in its complexation with 4-fluorophenol (Fig. 2). The fixation of 4-fluorophenol on the imino nitrogen of **10** would have decreased the ν(C=N) frequency.[6]

Comparison of thioamides and thioureas to their oxygen analogues

The pK_{HB} of thioamides and thioureas are always lower than the pK_{HB} of the corresponding amides and ureas. This weaker hydrogen-bond basicity of sulfur bases compared with oxygen bases is well established also for ethers and thioethers[1] and phosphine oxides and phosphine sulfides.[24] In the language of the Hard and Soft Acid and Base Theory,[25] it reflects the preferred hard phenol–hard oxygen base interaction to the hard phenol–soft sulfur base interaction.

We observe similar structural effects on the hydrogen-bond basicity of amides and ureas and thioamides and thioureas. Firstly, the sequence of the X-substituent effect which is the same in the series $XCSNMe_2$ and $XCONMe_2$: Cl < OR < H ~ Ph < Me ~ NMe_2 < $Me_2NCH{=}N$. Secondly, Fig. 3 shows that for both the carbonyl and the thiocarbonyl groups the first substitution of a methyl by a dimethylamino group greatly increases pK_{HB}, whereas pK_{HB} remains unchanged by

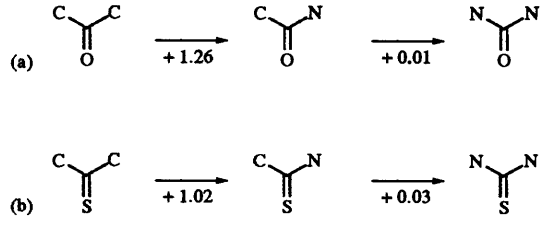


Fig. 3 pK_{HB} increments in going from (a) ketone to amide and urea (taken from ref. 16) and (b) thioketone to thioamide and thiourea

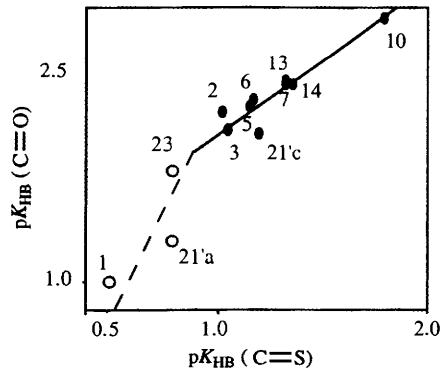


Fig. 4 Comparison of structural effects on the pK_{HB} of amides and ureas (taken from ref. 5) *vs.* pK_{HB} of thioamides and thioureas. Numbers refer to Tables 1 and 2. The line for electron-donating substituents (●) has, approximately, a slope 1. The line for electron-withdrawing substituents (○) is still higher. This does not confirm the slope 0.607 of eqn. (5) and ref. 11.

the second substitution of a methyl by a dimethylamino group. This non-additivity of the electron-donating effect of the NMe_2 group has been first observed in the series ketone/amide/urea [5,24] and attributed to saturation electronic effects [26] and/or steric effects.[27]

In spite of these similarities, we do not confirm the previously proposed [11] general proportionality of structural effects on the hydrogen-bond basicity of carbonyl and thiocarbonyl compounds [eqn. (5)]. Fig. 4 shows rather that the sensibility of

$$\beta_2^H(C{=}S) = -0.04 + 0.607\beta_2^H(C{=}O) \quad (5)$$

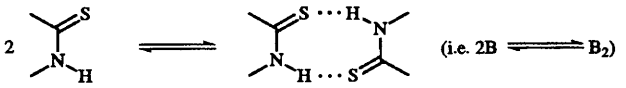
pK_{HB} to structural effects is much greater for carbonyl than for thiocarbonyl bases when the substituent is electron-withdrawing (Cl, OR) and tends to become equal in the two series for electron-donating substituents (Me, Me_2N, $Me_2NCH{=}N$).

Super hydrogen-bond basicity of the thiourea iminologues 10 and 11

If we exclude compounds **15** and **16** for which the high pK_{HB} values might be partly artefacts (*vide infra*), the most basic compound is $Me_2NCH{=}N{-}CSNMe_2$, which can be regarded as an iminologue [28] of tetramethylthiourea. This thiourea iminologue reaches a pK_{HB} value of 1.79, greater than the values of tributylamine (1.57) [1] or benzylamine (1.75).[1] Thus we confirm previous findings [28,29] that iminology constitutes a powerful structural effect for increasing very significantly hydrogen bonding basicity. Preliminary results on a second thiourea iminologue, **11**, shows that a H/Me substitution in the imino transmitter group still increases the spectroscopic basicity from 225 to 254 cm^{-1}. From eqn. (4) and $\Delta\nu_1 = 254$ cm^{-1}, we calculate $pK_{HB} = 2.06$ for $Me_2NC(Me){=}NCSNMe_2$.

The case of secondary thioureas and thiolactams

Compounds **9** (ε-thiocaprolactam), **15** (*N*-methyl-*N*,*N*′-propylenethiourea) and **16** (methimazole) possess an NH hydrogen-bond donor group *cis* to the thiocarbonyl hydrogen-bond acceptor group and can self-associate in stable cyclic dimers [12] [eqns. (6) and (7)]. If we take into account the equilibrium (6),



(6)

$$K_D = [B_2]/[B]^2 \quad (7)$$

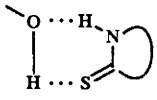
K_{HB} depends on the dimerization constant, K_D, according to eqn. (8). We have measured K_D by the Allen method [16] and

$$K_{HB} = 4K_D\,[\text{HB complex}]/[4F{-}C_6H_4{-}OH]\,[\sqrt{1 + 8K_D([B]_0 - [\text{HB complex}])} - 1] \quad (8)$$

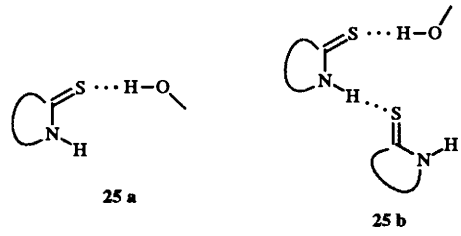
found K_D (**9**) = 69, K_D (**15**) = 35 and K_D (**16**) = 3375 dm^3 mol^{-1}. The values of pK_{HB} for **9**, **15** and **16** in Table 1 are those calculated using eqn. (8), which takes into account equilibria (1) and (6).

We were quite surprised to find much higher pK_{HB} values for secondary cyclic (*s-cis*) thioamides and thioureas than for their tertiary analogues. The differences in pK_{HB}between the N(H)CS and N(Me)CS compounds range from 0.34 to 0.74 (Table 2). The weaker electron-release of NHMe,[30] compared with NMe_2, should give lower pK_{HB} values, as found for the *s-trans* [31] secondary thioamide MeCSNHMe (pK_{HB} = 1.14) compared with the tertiary analogue $MeCSNMe_2$ (pK_{HB} = 1.32).

One or several of the following hypotheses could explain the high pK_{HB} values found for cyclic secondary thioamides and thioureas. (*i*) A lower steric effect of the NH group, compared to NMe. (*ii*) A cyclic stable structure [11] of the 4-fluorophenol/cyclic thioamides complexes. (*iii*) An artefact. The extent of



hydrogen-bonded complexation in eqn. (8) is measured, by our IR method, by the intensity decrease of the ν(OH) vibrator of 4-fluorophenol and could be due not only to species **25a** but also to species **25b**, already postulated by Gentric.[19] Since we have



25 a **25 b**

not taken into account the equilibria of formation of **25b** in eqn. (8), artificially high [19] pK_{HB} values should be obtained for the formation of **25a** (the 1:1 complex of interest for comparison with tertiary thioamide), if significant quantities of **25b** exist in CCl_4 solutions.

In order to test the hypothesis (*iii*), we decided to decrease the dimerization by using CH_2Cl_2 as solvent, a medium less favourable to associations than CCl_4. We carried out the experiments on methimazole **16**, not only because **16** gives the apparently highest pK_{HB} value in Table 1, but also because it is the thiourea with the greatest anti-thyroid activity known. The study of equilibria (1) and (6) in CH_2Cl_2 gives K'_D (**16**) = 60

$dm^3\ mol^{-1}$ and $pK'_{HB} = 1.19$ [from eqn. (8)]. This last value can be converted into $pK_{HB} = 2.11$, from the linear free energy relationship $pK'_{HB} = 0.82\ pK_{HB} - 0.54$ that relates[32] the hydrogen-bond basicities measured in CH_2Cl_2 and CCl_4. This value is 0.18 lower than the value calculated when large quantities of dimers are present in CCl_4 solution (remember that $K_D = 3375\ dm^3\ mol^{-1}$ in CCl_4), and is consistent with hypothesis (*iii*). However, it remains significantly higher than that (1.55) found for the NMe compounds **22'c** and it appears, in this example, that the high pK_{HB} values found for the cyclic s-*cis* secondary thioamides and thioureas are also the consequence of smaller steric interactions and/or of a cyclic structure[11] of the hydrogen-bonded complex.

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