

# Hydrogen-bond basicity of the sulfonyl group. The case of strongly basic sulfonamidates $\text{RSO}_2\text{N}^-\text{N}^+\text{Me}_3$

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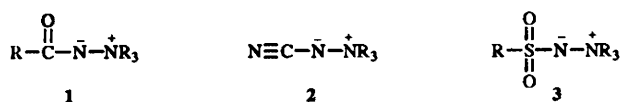
The hydrogen-bond basicity scale  $\text{p}K_{\text{HB}}$  (logarithm of the formation constant of 4-fluorophenol–base complexes in  $\text{CCl}_4$ ) has been determined for 13 sulfonyl bases, and correlated to the infrared shifts, on complexation, of the  $\nu(\text{OH})$  vibrations of 4-fluorophenol and methanol. In 1:1 complexes, oxygen complexation is observed, even for sulfonamides, sulfamides and sulfonamidates. Substitution on the sulfonyl group by  $\text{N}=\text{CHNMe}_2$ ,  $\text{N}=\text{SMe}_2$  or  $\text{N}^-\text{N}^+\text{Me}_3$  gives the strongest sulfonyl bases known. Since sulfonamides are less basic than sulfones, the electron-donating mechanism of  $\text{N}^-\text{N}^+\text{Me}_3$  to  $\text{SO}_2$  in sulfonamidates is probably mainly inductive.

It is well known that amides are much stronger Lewis bases than ketones,<sup>1,2</sup> this is explained as a result of delocalization of the nitrogen lone pair electrons, giving a higher electron density on the carbonyl oxygen. In the same vein, cyanamides give considerably stronger complexes with Lewis bases than do nitriles.<sup>1,3–5</sup> On the contrary, the Lewis basicity of sulfonamides (and sulfinamides) is slightly lower than for sulfones (and sulfoxides).<sup>6–12</sup> This shows that the analogue of the classical carboxamide resonance is insignificant.<sup>7,9,11,12</sup>

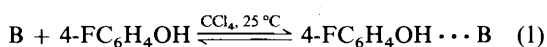


A reason might be<sup>6</sup> that the d-orbitals on the sulfur act as a ‘sink’ for the  $\text{p}\pi$  electrons donated from the nitrogen.

Amidates **1**, cyanamidates **2** and sulfonamidates **3** are dipolar



ions containing a cationic nitrogen bonded to an anion derived respectively from an amide, a cyanamide and a sulfonamide. We have recently shown<sup>13,14</sup> that amidates **1** and cyanamidates **2** are still much stronger bases than amides and cyanamides respectively, on the hydrogen-bond basicity scale  $\text{p}K_{\text{HB}}$ . This scale is based on the formation of 1:1 hydrogen-bonded complexes of a base **B** with a reference hydrogen-bond donor under standard conditions of solvent and temperature. For technical reasons, the  $\text{p}K_{\text{HB}}$  scale is constructed from 4-fluorophenol in carbon tetrachloride at 298 K [eqns. (1)–(3)].



$$K_{\text{HB}}/\text{dm}^3 \text{ mol}^{-1} = \frac{[4\text{-FC}_6\text{H}_4\text{OH} \cdots \text{B}]}{[\text{B}][4\text{-FC}_6\text{H}_4\text{OH}]} \quad (2)$$

$$\text{p}K_{\text{HB}} = \log_{10} K_{\text{HB}} \quad (3)$$

The exceptionally high basicity of amidates **1** and cyanamidates **2** does not originate in the fixation of 4-

fluorophenol to the anionic nitrogen, since we have shown<sup>13,14</sup> that the fixation site remains the oxygen atom in amidates and the  $\text{sp} \text{N}=\text{C}$  nitrogen in cyanamidates, but in a much more efficient electron-donating effect of the  $\text{N}^-\text{N}^+\text{Me}_3$  substituent rather than its  $\text{NR}_2$  counterpart.

In this work, we determine for the first time the hydrogen-bonding site and basicity of the sulfonamidates **3** with the hope of discovering sulfonyl bases that are stronger than sulfonamides and sulfones. We chose to study *N*-trimethylammoniooctanesulfonamidate ( $\text{OctSO}_2\text{N}^-\text{N}^+\text{Me}_3$ ) in the aliphatic series, *N*-trimethylammoniotoluene-*p*-sulfonamidate ( $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{N}^-\text{N}^+\text{Me}_3$ ) in the aromatic one, and *N*-(*p*-tolylsulfonylimino)dimethyl- $\lambda^4$ -sulfane ( $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{N}=\text{SMe}_2$ ) which is related to sulfonamidates in so far as the  $\text{N}=\text{S}$   $\pi$  bonding appears to be highly ionic in character.<sup>15</sup>

Equilibrium constants have previously been measured for the complexation of sulfates,<sup>16</sup> sulfonates,<sup>16</sup> sulfones<sup>8–10,12,16–18</sup> and sulfonamides<sup>6–12,18</sup> with alcohols and phenols, but not with 4-fluorophenol. For the sake of comparison, we therefore decided to measure  $\text{p}K_{\text{HB}}$  for these sulfonyl bases. In particular the sulfonamide iminologue  $\text{PhSO}_2\text{N}=\text{CHNMe}_2$ , which was previously found<sup>19</sup> to be more basic than the sulfonamide  $\text{PhSO}_2\text{NMe}_2$ , was re-studied.

In addition to the thermodynamic scale  $\text{p}K_{\text{HB}}$ , we also measured the complexation induced shifts of the OH stretching vibration of methanol and 4-fluorophenol. These  $\Delta\nu(\text{OH})$  are generally considered as spectroscopic scales of hydrogen-bond basicity. Within a family of bases, the thermodynamic  $\text{p}K_{\text{HB}}$  and spectroscopic  $\Delta\nu(\text{OH})$  scales are often well correlated,<sup>20</sup> provided the site of hydrogen-bond fixation is not sterically hindered, and remains unchanged within the series.<sup>2,4,21–23</sup>

The measurements were performed both in  $\text{CCl}_4$  and  $\text{CH}_2\text{Cl}_2 \cdot \text{CCl}_4$  is the standard solvent for establishing the  $\text{p}K_{\text{HB}}$  scale, but the three sulfonamidates and dimethyl sulfone are not sufficiently soluble in this solvent. Consequently the hydrogen-bonded complexes of 4-fluorophenol [eqn. (1)] and methanol were also studied in  $\text{CH}_2\text{Cl}_2$ . Correlations between data in  $\text{CH}_2\text{Cl}_2$  and  $\text{CCl}_4$  were established in order to calculate the  $\text{p}K_{\text{HB}}$  values of these four sulfonyl bases.

## Experimental

Sulfonyl bases **4–12** in Table 1 were Aldrich compounds carefully purified and dried by standard procedures. Methanol,

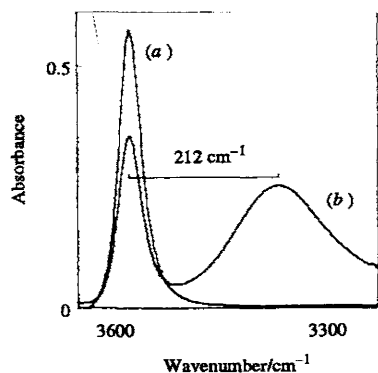


Fig. 1 IR bands of (a) the free OH group of 4-fluorophenol ( $3 \times 10^{-3}$  mol dm $^{-3}$  in CH $_2$ Cl $_2$ ) and (b) the hydrogen-bonded OH group of 4-fluorophenol-*p*-MePhSO $_2$ N=SMe $_2$  complex ( $6 \times 10^{-2}$  mol dm $^{-3}$  of *p*-MePhSO $_2$ N=SMe $_2$  is added to the 4-fluorophenol solution).  $\Delta\nu'_2(\text{OH}) = 212$  cm $^{-1}$ . The absorbance decrease of the free OH band allows a Beer-Lambert determination of the complex concentration at equilibrium, and the  $K'_{\text{HB}}$  calculation.

CCl $_4$  and CH $_2$ Cl $_2$  were spectroscopic grade compounds dried on molecular sieves.† 4-Fluorophenol was purified by sublimation. The preparation of solutions and the filling of cells were carried out in a dry glove-box.

Compound **13** was synthesized as described previously<sup>24</sup> from dimethylformamide dimethyl acetal and benzenesulfonamide and recrystallized from methanol. Compound **14** was synthesized out by the method B of King.<sup>25</sup> The method of Wawzonek and Meyer<sup>26</sup> was followed for the synthesis of compounds **15** and **16**.

Infrared measurements were carried out with a Fourier transform spectrometer Bruker IFS 48 by selecting 1 or 2 cm $^{-1}$  resolution. Measurements of overlapping bands were performed by a mathematical decomposition and/or deconvolution programmes included in the Opus™ Bruker software. A 1 cm Infrasil cell was thermostatted at  $25 \pm 0.1$  °C for thermodynamic measurements in CCl $_4$  and CH $_2$ Cl $_2$ . A 4 cm cell was necessary for the  $\Delta\nu(\text{OH})$  measurements of compounds slightly soluble in CCl $_4$ . The study of the SO $_2$  stretching was performed in CaF $_2$  cells of various pathlengths according to solubility and solvent transparency.

The FT-IR spectroscopic method for measuring the formation constants  $K_{\text{HB}}$  has been described previously.<sup>4,23</sup> The very low concentration of 4-fluorophenol (*ca.*  $10^{-3}$  mol dm $^{-3}$ ) and high concentration of sulfonyl bases (in a molar ratio ranging from 1:10 to 1:30) make negligible the probability of two OH bonded to one SO $_2$ , and generally of complexes of higher stoichiometry than 1:1. Values of  $\text{p}K_{\text{HB}}$  are probably accurate to better than  $\pm 0.03$ .

The complexation induced shifts of the OH stretching vibration of methanol and 4-fluorophenol are defined as:  $\Delta\nu_1 = 3644 - \nu_1(\text{OH} \cdots)$  for methanol-base complexes in CCl $_4$ ;  $\Delta\nu_2 = 3614 - \nu_2(\text{OH} \cdots)$  for 4-fluorophenol-base complexes in CCl $_4$ ;  $\Delta\nu'_1 = 3625 - \nu'_1(\text{OH} \cdots)$  for methanol-base complexes in CH $_2$ Cl $_2$  and  $\Delta\nu'_2 = 3585 - \nu'_2(\text{OH} \cdots)$  for 4-fluorophenol-base complexes in CH $_2$ Cl $_2$ .

## Results

The  $\text{p}K_{\text{HB}}$  (in CCl $_4$ ),  $\log K'_{\text{HB}}$  (in CH $_2$ Cl $_2$ ), and  $\Delta\nu(\text{OH})$  basicity scales are reported in Table 1. The fifth column of this table is a linear transform of  $\text{p}K_{\text{HB}}$ , calculated by eqn. (4), which is used in

$$\beta_2^{\text{H}} = (\text{p}K_{\text{HB}} + 1.1)/4.636 \quad (4)$$

† In CH $_2$ Cl $_2$ , no attempt was made to remove the ethylenic stabilizer which cannot influence eqn. (1), due to its low concentration (100 ppm) and very low basicity ( $K_{\text{HB}}$  *ca.*  $0.2$  dm $^3$  mol $^{-1}$ ).

linear solvation energy relationships and for the prediction of the stability of many hydrogen-bonded complexes.<sup>27</sup> A correlation analysis of these scales leads to the following results. We first observe that the  $\Delta\nu(\text{OH})$  of methanol is highly correlated to the  $\Delta\nu(\text{OH})$  of 4-fluorophenol, both in CCl $_4$  [eqn. (5)] and in CH $_2$ Cl $_2$  [eqn. (6)]. This shows that the basicity

$$\Delta\nu_1 = 0.594 \Delta\nu_2 - 18.2 \quad n = 11 \quad r = 0.998 \quad s = 2 \text{ cm}^{-1} \quad (5)$$

$$\Delta\nu'_1 = 0.540 \Delta\nu'_2 - 12.1 \quad n = 8 \quad r = 0.999 \quad s = 1.5 \text{ cm}^{-1} \quad (6)$$

sequence of the sulfonyl group is the same towards MeOH and 4-FC $_6$ H $_4$ OH. In these equations,  $n$  is the number of data points,  $r$  the correlation coefficient and  $s$  the standard deviation of the estimate.

Moreover eqns. (7)–(9) show that the basicity sequence does

$$\Delta\nu_1 = 1.274 \Delta\nu'_1 - 13.0 \quad n = 6 \quad r = 0.995 \quad s = 4 \text{ cm}^{-1} \quad (7)$$

$$\Delta\nu_2 = 1.106 \Delta\nu'_2 - 7.4 \quad n = 7 \quad r = 0.994 \quad s = 8 \text{ cm}^{-1} \quad (8)$$

$$\text{p}K_{\text{HB}} = 1.029 \log K'_{\text{HB}} + 0.97 \quad n = 4 \quad r = 0.966 \quad s = 0.09 \quad (9)$$

not change when CCl $_4$  is replaced by CH $_2$ Cl $_2$  either for the spectroscopic [eqns. (7) and (8)] or for the thermodynamic [eqn. (9)] scale. Eqn. (9) is for a limited number of points since  $K'_{\text{HB}}$  could be measured neither for the too weakly basic sulfate and sulfonate, nor for the insoluble sulfonamides and Me $_2$ SO $_2$ . However, we believe that it is significant since a similar linear free energy relationship between  $\text{p}K_{\text{HB}}$  and  $\log K'_{\text{HB}}$  has already been found valid for seven oxygen bases.<sup>28</sup>

The correlations of eqns. (10)–(13) between spectroscopic

$$\log K'_{\text{HB}} = 0.017 16 \Delta\nu'_1 - 0.73 \quad n = 8 \quad r = 0.996 \quad s = 0.05 \quad (10)$$

$$\log K'_{\text{HB}} = 0.009 28 \Delta\nu'_2 - 0.94 \quad n = 8 \quad r = 0.996 \quad s = 0.05 \quad (11)$$

$$\text{p}K_{\text{HB}} = 0.016 72 \Delta\nu_1 + 0.175 \quad n = 9 \quad r = 0.985 \quad s = 0.05 \quad (12)$$

$$\text{p}K_{\text{HB}} = 0.009 95 \Delta\nu_2 - 0.136 \quad n = 9 \quad r = 0.988 \quad s = 0.05 \quad (13)$$

and thermodynamic basicity scales are the most useful. This allows us to confirm that the oxygen atoms of SO $_2$  are the common hydrogen-bonding site for the sulfonyl bases **4–16** (*vide infra*) and also to calculate  $\text{p}K_{\text{HB}}$  for insoluble compounds **7** and **14–16**. The  $\text{p}K_{\text{HB}}$  calculations will be illustrated for the sulfonamides **15** and **16**. The sulfonamide **16** is sufficiently soluble in CCl $_4$  to measure  $\Delta\nu_1 = 163$  and  $\Delta\nu_2 = 305$  cm $^{-1}$ . The introduction of these values in eqns. (12) and (13) give  $\text{p}K_{\text{HB}} = 2.90$ . The sulfonamide **15** is soluble only in CH $_2$ Cl $_2$ . We get  $\Delta\nu'_1 = 125$  and  $\Delta\nu'_2 = 255$  cm $^{-1}$  and calculate  $\Delta\nu_1 = 146$  cm $^{-1}$  from eqn. (7) then  $\text{p}K_{\text{HB}} = 2.62$  from eqn. (12), and  $\Delta\nu_2 = 275$  cm $^{-1}$  from eqn. (8) then  $\text{p}K_{\text{HB}} = 2.60$  from eqn. (13). Table 1 reports the mean of these two values.

## Discussion

### Hydrogen-bonding site

In addition to the oxygens of the SO $_2$  group, the ether oxygen(s) of the sulfate **4** and sulfonate **5**, the nitrogen(s) of sulfonamides,

**Table 1** Thermodynamic and spectroscopic scales of hydrogen-bond basicity for sulfonyl bases

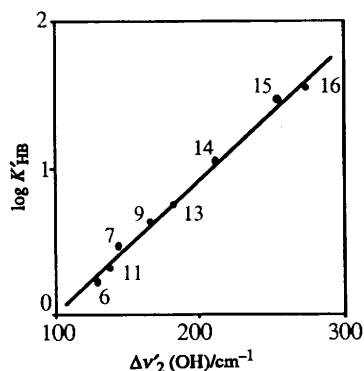
| No. | Compound  | Formula  | $pK_{HB}$         | $\beta_{HB}^{\#}$ | $\Delta v_1(OH)^a$<br>MeOH<br>CCl <sub>4</sub> | $\Delta v_2(OH)^a$<br>4-FC <sub>6</sub> H <sub>4</sub> OH<br>CCl <sub>4</sub> | $\log K'_{HB}$<br>CH <sub>2</sub> Cl <sub>2</sub> | $\Delta v'_1(OH)^a$<br>MeOH<br>CH <sub>2</sub> Cl <sub>2</sub> | $\Delta v'_2(OH)^a$<br>4-FC <sub>6</sub> H <sub>4</sub> OH<br>CH <sub>2</sub> Cl <sub>2</sub> |
|-----|---|--|-------------------|-------------------|--|---|---|--|---|
| 4   | Diethyl sulfate   | EtOSO <sub>2</sub> OEt   | 0.80              | 0.41              | 35   | 91  | <i>e</i>  | <i>e</i>   | 79  |
| 5   | Ethyl methanesulfonate  | MeSO <sub>2</sub> OEt  | 1.02              | 0.46              | 52   | 119   | <i>e</i>  | <i>e</i>   | <i>f</i>  |
| 6   | Diphenyl sulfone  | PhSO <sub>2</sub> Ph   | 1.21              | 0.50              | 63   | 137   | 0.22  | 59   | 131   |
| 7   | Dimethyl sulfone  | MeSO <sub>2</sub> Me   | 1.40 <sup>b</sup> | 0.54              | 74   | 152   | 0.47  | 66.5   | 145   |
| 8   | Tetramethylene sulfone  | CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SO <sub>2</sub>          | 1.47              | 0.55              | 77   | 157   | <i>f</i>  | <i>f</i>   | <i>f</i>  |
| 9   | Dibutyl sulfone   | BuSO <sub>2</sub> Bu   | 1.52              | 0.57              | 86   | 172   | 0.63  | 80   | 167   |
| 10  | <i>N,N</i> -Dimethylbenzenesulfonamide                                    | PhSO <sub>2</sub> NMe <sub>2</sub>   | 1.19              | 0.49              | 61   | 134   | <i>f</i>  | <i>f</i>   | <i>f</i>  |
| 11  | <i>N,N</i> -Dimethylmethanesulfonamide                                    | MeSO <sub>2</sub> NMe <sub>2</sub>   | 1.30              | 0.52              | 68   | 142   | 0.32  | 61   | 140   |
| 12  | <i>N,N,N',N'</i> -Tetraethylsulfamide                                     | Et <sub>4</sub> NSO <sub>2</sub> NEt <sub>2</sub>  | 1.47              | 0.55              | 77   | 168   | <i>f</i>  | <i>f</i>   | <i>f</i>  |
| 13  | <i>N,N</i> -Dimethyl- <i>N'</i> -phenylsulfonylformamidine                | PhSO <sub>2</sub> N=CHNMe <sub>2</sub>   | 1.81 <sup>a</sup> | 0.63              | 92   | 188   | 0.75  | 87   | 183   |
| 14  | <i>N</i> -( <i>p</i> -Tolylsulfonylimino(dimethyl)- $\lambda^4$ -sulfane) | <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> N=SMe <sub>2</sub>             | 2.14 <sup>b</sup> | 0.70              | 120 <sup>c</sup>                               | 227 <sup>d</sup>  | 1.05  | 104  | 212   |
| 15  | <i>N</i> -Trimethylammoniotoluene- <i>p</i> -sulfonamidate                | <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> N <sup>+</sup> Me <sub>3</sub> | 2.61 <sup>b</sup> | 0.80              | 146 <sup>c</sup>                               | 275 <sup>d</sup>  | 1.47  | 125  | 255   |
| 16  | <i>N</i> -Trimethylammoniooctanesulfonamidate                             | OctSO <sub>2</sub> N <sup>+</sup> Me <sub>3</sub>  | 2.90 <sup>b</sup> | 0.85              | 163  | 305   | 1.55  | 136  | 275   |

<sup>a</sup> cm<sup>-1</sup>. <sup>b</sup> Calculated from eqns. (12) and (13). <sup>c</sup> Calculated from eqn. (7). <sup>d</sup> Calculated from eqn. (8). <sup>e</sup> Too weakly basic. <sup>f</sup> Not studied. <sup>g</sup> This value is considered more reliable than the previously published one (1.89).<sup>19</sup>

**Table 2** Stretching  $\text{SO}_2$  wavenumbers and their shifts  $\Delta\nu$  on complexation<sup>a,b</sup>

| No. | Compound  | $\nu_{\text{as}}$ | $\nu_{\text{s}}$ | $\Delta\nu_{\text{as}}$ | $\Delta\nu_{\text{s}}$ | Solvent   | HBD <sup>c</sup>                                  |
|-----|---|-------------------|------------------|-------------------------|------------------------|---|---|
| 7   | MeSO <sub>2</sub> Me  | 1312.6            | <i>d</i>         | 9                       |                        | CH <sub>2</sub> Cl <sub>2</sub>                   | 4-FC <sub>6</sub> H <sub>4</sub> OH               |
|     |   | 1325.5            | <i>d</i>         | 9                       |                        | CCl <sub>4</sub>                                  | (CF <sub>3</sub> ) <sub>2</sub> CHOH <sup>e</sup> |
| 11  | MeSO <sub>2</sub> NMe <sub>2</sub>  | <i>d</i>          | 1147.2           |                         | 5                      | CH <sub>2</sub> Cl <sub>2</sub>                   | 4-FC <sub>6</sub> H <sub>4</sub> OH               |
|     |   | 1350.0            | <i>d</i>         | 10                      |                        | CCl <sub>4</sub>                                  | 4-FC <sub>6</sub> H <sub>4</sub> OH               |
| 13  | PhSO <sub>2</sub> N=CHNMe <sub>2</sub>  | <i>d</i>          | 1159.8           |                         | 7                      | CCl <sub>4</sub>                                  | (CF <sub>3</sub> ) <sub>2</sub> CHOH <sup>e</sup> |
|     |   | 1350.3            | 1155.3           | 2                       | 4                      | CCl <sub>4</sub>                                  | (CF <sub>3</sub> ) <sub>2</sub> CHOH <sup>e</sup> |
| 15  | <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> N <sup>+</sup> N <sup>-</sup> Me <sub>3</sub> | 1255.0            | 1132.9           | 5                       | 6                      | ClCH <sub>2</sub> CH <sub>2</sub> Cl <sup>e</sup> | 4-FC <sub>6</sub> H <sub>4</sub> OH               |
| 16  | OctSO <sub>2</sub> N <sup>+</sup> N <sup>-</sup> Me <sub>3</sub>  | <i>d</i>          | 1112.5           |                         | 4                      | ClCH <sub>2</sub> CH <sub>2</sub> Cl <sup>e</sup> | 4-FC <sub>6</sub> H <sub>4</sub> OH               |

<sup>a</sup> cm<sup>-1</sup>. <sup>b</sup>  $\Delta\nu = \nu(\text{free SO}_2) - \nu(\text{hydrogen-bonded SO}_2)$ . Approximate values because of band overlapping. <sup>c</sup> Hydrogen-bond donor. <sup>d</sup> Not studied because of solvent and/or HBD transparency. <sup>e</sup> Chosen for solubility and/or transparency reason(s).



**Fig. 2** Comparison of the thermodynamic and spectroscopic hydrogen-bond basicity scales for the family of sulfonyl bases. Numbers refer to Table 1. The bases with the SO<sub>2</sub>N moiety and the sulfones occur on the same line of eqn. (11).

sulfamide and, more likely, the anionic nitrogen of sulfonamides, are potential acceptor sites for hydrogen-bond formation. However, it appears that the oxygens of the sulfonyl group are the only major site for compounds 4–16 since we observe: (i) *one* symmetrical band (Fig. 1) for the stretching of the hydrogen-bonded OH group of methanol and 4-fluorophenol. This indicates *one* kind of complex; (ii) excellent relationships for eqns. (10)–(13) between the thermodynamic scales,  $\text{p}K_{\text{HB}}$  or  $\log K'_{\text{HB}}$ , and the spectroscopic scales,  $\Delta\nu(\text{OH})$  or  $\Delta\nu'(\text{OH})$ , as illustrated in Fig. 2. Such relationships can exist only if compounds 4–16 have the same acceptor site in common.<sup>2,4,20–23</sup> This common acceptor site is necessarily the SO<sub>2</sub> group since it is the only site of sulfones 6–9 that obeys eqns (10)–(13); (iii) lowering of the SO<sub>2</sub> stretching wavenumber on complexation (Table 2). The lowering of the XO stretching wavenumber is a well defined and robust criterion for confirming oxygen complexation in the hydrogen-bonded complexes of XO bases, and especially SO bases,<sup>6,20,29</sup> and (iv) in the case of 13, raising of the C=N stretching wavenumber from 1623 cm<sup>-1</sup> in the free molecule to 1628 cm<sup>-1</sup> in its complex with hexafluoropropan-2-ol. The fixation of this hydrogen-bond donor on the imino nitrogen would have decreased the  $\nu(\text{C}=\text{N})$  wavenumber.<sup>30</sup> Similarly the  $\nu(\text{C}=\text{N})$  of Me<sub>2</sub>NCH=NC-SPh increases by 5 cm<sup>-1</sup> on sulfur complexation with 4-fluorophenol.<sup>31</sup>

We do not know if the hydrogen bond that has been created on the sulfonyl group is (a) two- or (b) three-centred. Species (b) has been speculated for the complex of tetramethylene sulfone with phenol.<sup>17</sup> However, a species similar to (a) has been demonstrated for the sulfur dioxide–hydrogen fluoride



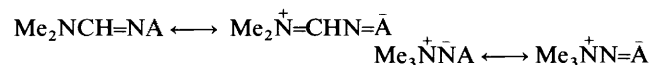
hydrogen-bonded complex.<sup>32</sup> Curiously, when extending the  $\text{p}K_{\text{HB}} - \Delta\nu$  correlations of eqns. (12) and (13) to SO bases,

it is found<sup>33</sup> that sulfoxides, sulfites and sulfinamides stand approximately 0.3  $\text{p}K$  unit below the lines of eqns. (12) and (13), which is the log 2 statistical correction to be applied to the formation of SO<sub>2</sub> complexes with structure (a) for a correct comparison with SO bases.

#### Influence of molecular structure on the hydrogen-bond basicity of the SO<sub>2</sub> group

Consider first the compounds 4–12 bearing the ‘well behaved’ substituents Me, Bu, Ph, NMe<sub>2</sub> and OEt on the sulfonyl group. These substituents have well known<sup>34</sup> field-inductive and resonance substituent constants,  $\sigma_{\text{F}}$  and  $\sigma_{\text{R}}^+$ . We observe that sulfonamides 10 and 11 are slightly less basic than sulfones 6–9. In terms of the classical inductive and resonance effects on basicity, this means that the NMe<sub>2</sub> substituent does not donate electrons to the oxygens of the sulfonyl group by its strong resonance effect ( $\sigma_{\text{R}}^+ = -0.64$ ), but withdraws electrons by its weak inductive effect ( $\sigma_{\text{F}} = +0.10$ ). This sulfonamide behaviour brings to light the importance of inductive effects in this series of compounds, and, indeed, we find a modest but statistically significant correlation between  $\text{p}K_{\text{HB}}$  and  $\Sigma\sigma_{\text{F}}$  ( $n = 8$ ,  $r = 0.85$ ;  $r = 0.92$  if we exclude the sulfamide 12).

In compounds 13–16, there are no  $\sigma$  constants known for the substituents N=CHNMe<sub>2</sub>, N=SMe<sub>2</sub> and N<sup>+</sup>N<sup>-</sup>Me<sub>3</sub>.<sup>‡</sup> However, our results show that these substituents are strong electron-donors to a SO<sub>2</sub> group, since they produce ‘super-basic’ sulfonyl bases. In fact alkyl sulfonamides are the strongest sulfonyl bases presently known, and exceed dimethyl sulfoxide, on the  $\text{p}K_{\text{HB}}$  scale. This extends to the SO<sub>2</sub> function our previous findings that N=CHNMe<sub>2</sub> is a stronger electron-donor than NMe<sub>2</sub>,<sup>5</sup> and that N<sup>+</sup>N<sup>-</sup>Me<sub>3</sub> is the strongest neutral electron-donor substituent presently known.<sup>13,14</sup> However we previously had in mind that resonance was the main electron-donating mechanism (see the resonant forms below, where A is a  $\pi$  electron-attracting function).



In the present results the sulfonamide behaviour and its corollary, the  $\text{p}K_{\text{HB}}$  vs.  $\Sigma\sigma_{\text{F}}$  correlation, indicate that the electron-donating mechanism of the N=CHMe<sub>2</sub>, N=SMe<sub>2</sub> and N<sup>+</sup>N<sup>-</sup>Me<sub>3</sub> substituents to the SO<sub>2</sub> function is mainly inductive. As far as the nitrile and carbonyl functions are concerned, the question of percentage of induction and resonance in the overall electron-donating effect of N=CHNMe<sub>2</sub>, N=SMe<sub>2</sub> and N<sup>+</sup>N<sup>-</sup>Me<sub>3</sub> remains open. The lone pair–lone pair repulsion effect also

<sup>‡</sup> We thank a referee for the following comment: ‘while  $\sigma$ -values for N=CHNMe<sub>2</sub> may not be known, one might note that values of  $\sigma_{\text{F}} = -0.01$  and  $\sigma_{\text{R}} = -0.37$  have been reported for N=C(NH<sub>2</sub>)<sub>2</sub> (A. Heising and W. Schmalt, *Chem. Ber.*, 1978, **111**, 320). A negative  $\sigma_{\text{F}}$  is particularly remarkable and of some relevance in this context.’

plays a great role on basicity.<sup>18</sup> It is not yet understood how this effect is shared in the inductive–resonance separation.

Finally we note the position of the newly studied substituent N=SMe<sub>2</sub> near  $\bar{N}^+NMe_3$  in the electron-donating sequence (towards a SO<sub>2</sub> function):  $\bar{N}^+NMe_3 > N=SMe_2 > N=CHNMe_2 > NMe_2$ . This similarity of  $\bar{N}^+NMe_3$  and N=SMe<sub>2</sub> in enhancing the basicity of the SO<sub>2</sub> function, indicates a significant contribution of the resonant form  $\bar{N}^+SMe_2$ , and confirms dipole moment results<sup>15</sup> on PhC(O)N=SMe<sub>2</sub>, suggesting the S=N π bonding to be highly ionic in character, ca. 40%.

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