CARBONYL OXYGEN AS A HYDROGEN-BOND SUPER-BASE: THE AMIDATES

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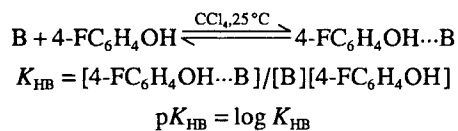
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An infrared spectroscopic study of the 1 : 1 hydrogen-bond association of amidates with both methanol and 4-fluorophenol showed that the site of complexation is the oxygen of the amidate function. However the formamidate $HCON_2Me_3$ forms a second 1 : 1 complex on the nitrogen of the amidate. The formation constants of the hydrogen-bond complexes of the amidates with the reference hydrogen-bond donor $4\text{-}FC_6H_4OH$ indicate that the amidates are stronger hydrogen-bond bases than are amides and amide vinylogues. As such, the amidates constitute the strongest carbonyl bases hitherto investigated on the hydrogen-bond basicity scale.

INTRODUCTION

Since the pioneering work of Taft's group,[1,2] the scale of hydrogen-bond basicity pK_{HB} has been found especially useful in solution chemistry. This scale is based on the formation of hydrogen-bonded complexes of a base B with a hydrogen-bond reference donor; for technical reasons this is 4-fluorophenol in carbon tetrachloride at 25 °C:
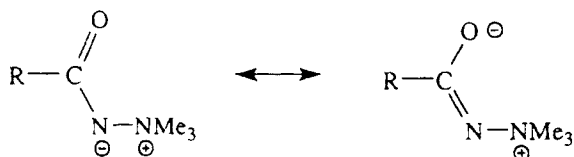
$$B + 4\text{-}FC_6H_4OH \underset{\longleftarrow}{\overset{CCl_4, 25°C}{\longrightarrow}} 4\text{-}FC_6H_4OH\cdots B$$

$$K_{HB} = [4\text{-}FC_6H_4OH\cdots B]/[B][4\text{-}FC_6H_4OH]$$

$$pK_{HB} = \log K_{HB}$$

The scale embraced by pK_{HB} ranges from *ca* −1·1 for bases with little inclination to form hydrogen bonds to *ca* +4 for those that form the most stable hydrogen-bonded complexes. Values of pK_{HB} can be transformed to give a parameter $\beta_2^H = (pK_{HB} + 1\cdot1)/4\cdot636$, which now ranges from 0 (no basicity) to 1 (basicity of HMPA), and which is capable of further extension.[3] This parameter is useful in linear solvation energy relationships[4] and for the prediction of the stability of many hydrogen-bonded complexes.[5]

Currently we are developing and extending the pK_{HB} scale and are studying structure–hydrogen-bonding basicity relationships for a wide variety of organic functionalities including amidines,[6] alcohols,[7]

nitriles[8] and amides.[9] In the case of nitriles we have demonstrated how the synergy of various structural factors enables nitriles that are super-basic (with regard to hydrogen bonding) to be realized.[10]

Within the family of carbonyl compounds, amides and ureas are among the most basic.[9] This is exemplified by the pK_{HB} values of methyl acetate, 1·00, acetone, 1·18, and dimethylacetamide, 2·44; the corresponding values of β_2^H are 0·45, 0·49 and 0·76. Taft *et al.*[11] have shown that amide vinylogues are still more basic than dimethylacetamide on the GB scale of Brønsted basicity in the gas phase and on the $-\Delta H_{BF_3}$ Lewis basicity scale. They also proposed values of β_2^H that were equal to, or even greater than, that of HMPA for these compounds. These values, however, are only based on relationships between the β_2^H and some other basicity scales; until they receive experimental confirmation these derived values must be regarded as tentative. Abraham's group[12] has also emphasized the importance of vinylogy as a strategy to increase hydrogen-bonding basicity.

Since Gal and Morris[13] have shown that the Lewis basicity of *N*-ammoniobenzamidates $XC_6H_4CON^-N^+Me_3$ is higher than that of the corresponding *N*,*N*-dimethylbenzamides, we felt it relevant to determine for the first time the hydrogen-bonding basicity of a series of amidates **2–11** with the aim of discovering carbonyl hydrogen-bonding bases that are stronger than amides and ureas (the highest pK_{HB} and

$$
\begin{array}{cc}
\underset{\ominus\ \oplus}{\overset{\overset{O}{\parallel}}{\underset{N-NMe_3}{R-C}}} & \longleftrightarrow \quad \underset{\oplus}{\overset{\overset{O}{\underset{\diagup}{}}\ominus}{\underset{N-NMe_3}{R-C}}} \\
\text{(1a)} & \text{(1b)}
\end{array}
$$

(2) R = H   (8) R = 1-Adamantyl
(3) R = Me   (9) R = p-MeOC$_6$H$_4$
(4) R = Et   (10) R = p-MeC$_6$H$_4$
(5) R = Nonyl   (11) R = p-F$_3$CC$_6$H$_4$
(6) R = Pr^i
(7) R = Bu^t

β_2^H hitherto *measured* are 2·79 and 0·84 for N,N'-dimethyl-N,N'-trimethylenurea[9]).

To achieve our aim we require (i) an important contribution of resonance form **1b** and (ii) an oxygen rather than the amidate nitrogen being the donor site for hydrogen bonding. The first condition seems well established since the carbonyl frequency v(C=O) is particularly low,[14,15] the bonds C=O and C−N$^-$ (the designation of bonds here and elsewhere is taken from structure **1a**) are respectively longer and shorter than those of similar compounds without charge delocalization[16] and the mesomeric moment of the group $^-$N−C=O is enhanced.[17] The second has not, to our knowledge, been investigated, and studies of the site of bonding of other acids to amidates does not allow the prediction of the site of hydrogen bonding in the present series. Liler and Morris[18] showed that in aqueous solution the initial protonation took place on nitrogen for compounds **3** and **9**, and the second protonation occurred on the carbonyl oxygen in the case of methoxyformamidate. Additionally, BF$_3$ bonds to carbonyl oxygen of the benzamidates **9–11** according to Gal and Morris[13] and PdCl$_2$ and PtCl$_2$ bond to the nitrogen of N-trimethylammoniopicolinamidate.[19] It therefore appeared necessary at the outset to ascertain the site of fixation of the hydrogen bond.

EXPERIMENTAL

Materials. Alkyl and substituted benzamidates were synthesized by a modification of the method of Smith *et al.*[20] Yields were consistently higher with the aromatic series. Whereas the substituted benzamidates and larger alkylamidates were well defined solids, the lower alkylamidates were hygroscopic.

Most of the compounds have been reported previously: **3**,[18] **4**,[21] **5**,[22] **6**,[23] **7**,[23] **8**,[24] and **9–11**.[15]

Formamidate **2** was synthesized by the above method[20] to give a hygroscopic solid for which accurate microanalytical data were difficult to obtain. Sublimed material obtained from a dry sample of **2** was analysed

by accurate mass determination with an upgraded Kratos MS 902S spectrometer linked to a Kratos DS 90 data system. Found, m/z 102·0806; C$_4$H$_{10}$N$_2$O requires M 102·0793.

The other amidates were carefully dried and purified by sublimation under reduced pressure. Carbon tetrachloride, dichloromethane and methanol were of spectroscopic grade from Merck and were dried over molecular sieves. 4-Fluorophenol was purified by sublimation. All solutions were prepared in a dry glove-box.

Spectra. IR spectra were determined on a Bruker IFS 48 Fourier transform IR spectrometer with a resolution of 1 or 2 cm^{-1} in 1 or 4 cm Infrasil quartz cells for the study of the v(OH) region, and in 1 mm KBr cells for study of the v(C=O) and v(C−N$^-$) regions. The spectra were treated with Opus software, which enables complex bands to be broken down mathematically into their gausso-lorenzian components.

UV spectra were determined on a Perkin-Elmer Model 554 spectrometer at a resolution of 2 nm in Suprasil quartz cells of 1 cm length.

Equilibrium constants. In CH$_2$Cl$_2$ the equilibrium constants were determined by IR spectroscopy on the v(OH) vibration of 4-fluorophenol according to known methods.[7] In CCl$_4$ the equilibrium constants are higher and it was necessary to lower the concentrations of both 4-fluorophenol and the amidate in order not to displace the equilibrium too significantly. Accordingly, we used UV spectrometry because the molar extinction coefficient of the first $\pi \rightarrow \pi^*$ transition of the 4-fluorophenol is *ca* ten times higher than that of the v(OH) infrared band. As a consequence of hydrogen bonding, this transition undergoes a bathochromic shift of *ca* 6 nm. The UV absorptions were treated by the method of Rose and Drago.[25] Only compounds **6–8** are sufficiently soluble in CCl$_4$ for their equilibrium constants to be determined in this solvent. The other equilibrium constants were determined in CH$_2$Cl$_2$. Lack of solubility of formamidate **2** in CCl$_4$ and CH$_2$Cl$_2$ prevented the determination of the equilibrium constant for this compound. On account of the low solubility, and their hygroscopic nature, reproductibilities of pK_{HB} varied between ±0·05 and ±0·10. The temperature of the cells was maintained constant at 25 °C by a Peltier effect.

RESULTS AND DISCUSSION

Site(s) of fixation of hydrogen-bond donors

These were studied by vibrational spectroscopy. When a hydrogen-bond donor, such as methanol or 4-fluorophenol, bonds to an amidate of the present series in CCl$_4$ or CH$_2$Cl$_2$, the vibrators that are most sensitive

to complexation are ν(OH), ν(C=O) and ν(C−N⁻). The number of O−H stretching bands created by association reflects the number of sites of fixation of the OH group, whereas the displacement $\Delta\nu$(OH) gives an indication of the strength of the hydrogen bond. The direction of the displacement of the ν(C=O) bands around 1600 cm⁻¹ and those of ν(C−N⁻) around 1350 cm⁻¹ enables a distinction to be made between O- and N-fixation on the following basis.

(i) An O-complexation indicates a preponderant contribution of resonance form **1b** and is associated with a diminution of the ν(C=O) value, in keeping with an enhanced single-bond character for this bond; in accord with this, the ν(C−N⁻) value increases as the C−N⁻ bond assumes more double-bond character. Comparable behaviour is exhibited by amides.[26] Thus, for *N,N*-dimethylacetamide ν(C=O) diminishes by 25 cm⁻¹ and the band at 1409 cm⁻¹, which presents the greatest ν(C−N) character, increases by 6 cm⁻¹ as a consequence of hydrogen-bond formation between carbonyl oxygen and 4-fluorophenol.[9] Still greater enhancements of ν(C−N⁻) are brought about by coordination of BF₃ at carbonyl oxygen.[13]

(ii) N-complexation would inhibit delocalization of nitrogen lone pairs toward carbonyl oxygen; this would favour enhancement of the ν(C=O) and diminution of the ν(C−N⁻) values.[26] These are the observations brought about by N-coordination of PdCl₂ and PtCl₂ with both urea[26] and *N*-trimethylammoniopico-linamidate.[19]

Alkylamidates 3–8

The ν(OH) vibration of methanol is lowered by *ca* 300 cm⁻¹; a single ν(OH) band of the complex is observed, probably due to a single complexation site. The evolution of the form of this band, illustrated in Figure 1 along the series R = Me, Et, Prⁱ, Buᵗ and 1-adamantyl, is characteristic of an association that involves carbonyl oxygen[27] via a mainly angular complex[27] **13a** for the sterically undemanding methyl, to a predominantly linear counterpart **13b** for the bulky *tert*-butyl (shown) and 1-adamantyl.[27]

Formation of the hydrogen bond at carbonyl oxygen is confirmed by diminution of the ν(C=O) frequency by 12–21 cm⁻¹, and a corresponding increase of the ν(C−N⁻) band by 4–10 cm⁻¹ after the addition of 4-fluorophenol to solutions of amidates **3–8** in CH₂Cl₂.

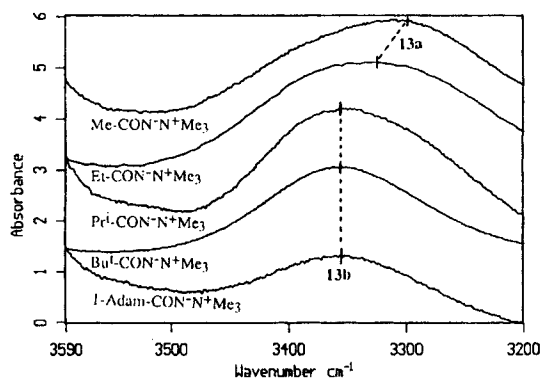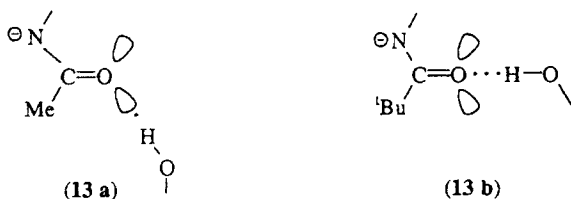
Figure 1. ν(OH) region of methanol–alkylamidates complexes in CCl₄. A unique band appears whose shape evolves regularly from the least hindered (methyl) to the most hindered (1-adamantyl). The apparent maximum is determined either by the low-frequency component band of the angular complex **13a** (Me) or by high-frequency component band of the linear complex **13b** (1-adamantyl, Bu', Pr'), as for the methanol–alkylamides complexes[27]

The equilibrium of O-complexation,

$$\text{C=O (free)} \rightleftharpoons \text{C=O}$$
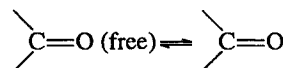
(hydrogen-bonded to 4-FC₆H₄OH), is demonstrated in Figure 2, which shows disappearance of the free carbonyl band, at 1582 cm⁻¹ for EtCON⁻N⁺Me₃, and concomitant increase in the carbonyl band of the complex at 1564 cm⁻¹ on progressive addition of 4-fluorophenol.

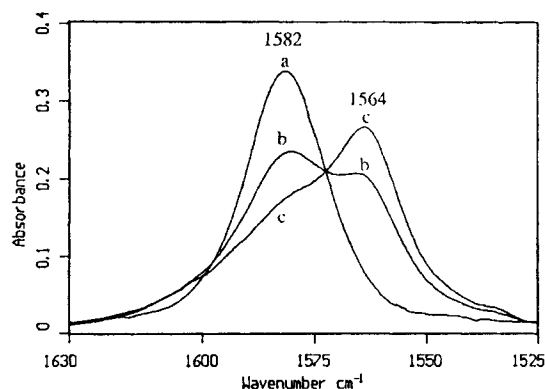Alkylamidates **3–8** are thus seen to behave like carbonyl bases toward hydrogen-bond donors,

(13 a)   (13 b)

Figure 2. ν(C=O) region of the 4-FC₆H₄OH–EtCON⁻N⁺Me₃ complex in CH₂Cl₂: (a) 6×10⁻³ M EtCON⁻N⁺Me₃; (b) 6×10⁻³ M EtCON⁻N⁺Me₃ + 6×10⁻³ M 4-FC₆H₄OH (53% complex); (c) 6×10⁻³ M EtCON⁻N⁺Me₃ + 13×10⁻³ M 4-FC₆H₄OH (77% complex)

irrespective of the steric or electronic effects of the alkyl group.

Benzamidates 9–11

In the presence of methanol these compounds show a single band ν(OH) of the complex; this again signifies a single site of complexation. Observed complexation-induced displacements of ν(OH) range from 239 cm^{-1} for the electron-attractive p-CF$_3$ substituent to 278 cm^{-1} for the conjugative electron-donor p-OMe. The smaller values observed for the benzamidates indicate a lower basicity than for the alkylamidates; in similar vein benzamides are less basic than alkylamides.[9]

In the presence of 4-fluorophenol, the ν(C=O) bands near 1560 cm^{-1} are shifted only slightly, from 5 cm^{-1} for p-CF$_3$ to 8 cm^{-1} for p-OMe. These smaller $\Delta\nu$(C=O) values, compared with the alkylamidates, are explained by a combination of (i) a lower basicity of the aromatic amidates and (ii) a coupling with the ν_{8b} vibration at *ca* 1600 cm^{-1} of the aromatic ring. This band moves towards the low frequencies jointly with the ν(C=O) band, which indicates that the perturbation introduced by complexation is shared by the vibration modes at 1560 and 1600 cm^{-1}; in other words, the modes must be coupled. This coupling has already been proposed in a previous study.[15]

In contrast, the ν(C–N$^-$) bands of benzamidates increase by 10 cm^{-1} on complexation with 4-fluorophenol. The equilibrium of O-complexation,

$$\text{$^-$N—C}{=}\text{O (free)} \rightleftharpoons \text{$^-$N–C}{=}\text{O}$$
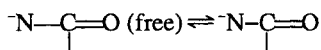
(hydrogen-bonded to 4-FC$_6$H$_4$OH) is demonstrated in Figure 3 by the disappearance of the free ν(C–N$^-$)

band at 1338 cm^{-1} of *N*-trimethylammonio-p-methyl-benzamidate and the corresponding appearance of a band ν(C–N$^-$) of the complex at 1348 cm^{-1} on progressive addition of 4-fluorophenol.

Whatever the electronic effect of the substituent, the benzamidates investigated here are hydrogen-bonding bases via oxygen.

Formamidate 2

On account of the low solubility of compound 2 in CCl$_4$, the ν(OH) region of the methanol–formamidate complex was not studied.

Figure 4 shows that in the presence of increasing quantities of 4-fluorophenol the ν(C=O) band of the formamidate 2 at 1607 cm^{-1} diminishes and is progressively replaced by two new bands, one at 1593 cm^{-1} ($\Delta\nu = -14$ cm^{-1}) attributable to O-fixation of the hydrogen bond and the other at 1617 cm^{-1} ($\Delta\nu \approx +10$ cm^{-1}) on account of a second complex, this time on amidate nitrogen. The appearance of two complexes simultaneously while formamidate 2 is in molar excess over 4-fluorophenol suggests strongly that there exist two 1:1 complexes, rather than a 1:1 complex plus a 1:2 complex.

The ν(C–N$^-$) band at 1360 cm^{-1} confirms the presence of two complexes, one on oxygen which leads to a new band at a higher frequency (1366 cm^{-1}) and the other on amidate nitrogen which gives a second new band at a lower frequency (1354 cm^{-1}).

Formamidate 2 therefore behaves as both a carbonyl base and a nitrogen base. From a mathematical break-down of the spectra in Figure 4, the complex to oxygen is estimated to have an absorbance about twice that of

Figure 3. ν(C–N$^-$) region of the 4-FC$_6$H$_4$OH–p-MeC$_6$H$_4$CON$^-$N$^+$Me$_3$ complex in CH$_2$Cl$_2$: (a) 10^{-2} M benzamidate; (b) 10^{-2} M benzamidate + 10^{-2} M 4-FC$_6$H$_4$OH (38% complex); (c) 10^{-2} M benzamidate + 2 × 10^{-2} M 4-FC$_6$H$_4$OH (59% complex)
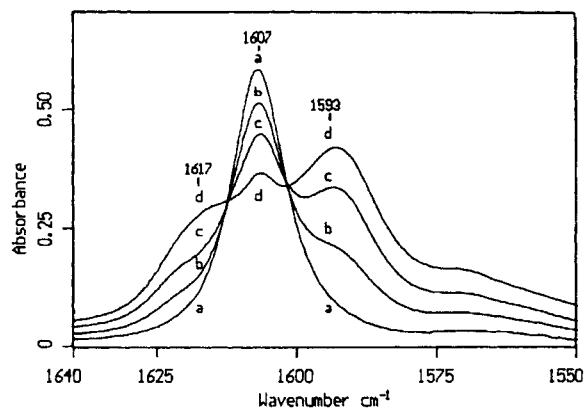
Figure 4. ν(C=O) region of the 4-FC$_6$H$_4$OH–HCON$^-$N$^+$Me$_3$ complex in CH$_2$Cl$_2$: ~6 × 10^{-3} M HCON$^-$N$^+$Me$_3$ + 4-FC$_6$H$_4$OH at (a) 0, (b) 6 × 10^{-3}, (c) 15 × 10^{-3} and (d) 56 × 10^{-3} M. The free peak in the centre of the band is surrounded by the oxygenated complex peak at low frequency and by that of nitrogen complex at high frequency

Table 1. Spectroscopic data[a] on the complexes between amidates $RCON^-N^+Me_3$ with methanol and 4-fluorophenol

R	$\nu(C=O)$[b]	$\Delta\nu(C=O)$[c,d]	$\nu(C-N^-)$	$\Delta\nu(C-N^-)$[c,d]	$\Delta\nu(OH)$[c,e]
H	1607[f]	−10, +14	1360[f]	−6, +6	[i]
Me	1583[f]	+17	1363[f]	−10	335[j]
Et	1582 (560)	+18	1355 (105)	−7	311[k]
Nonyl	1580 (511)	+18	1360(100)	−7	[l]
Pr^i	1588 (522)	+21	1358 (110)	−5	291[m]
Bu^t	1569 (628)	+17	1357 (117)	−4	285
1-Adamantyl	1563 (517)	+12	[g]	[g]	289
p-MeOC$_6$H$_4$	1559 (293)	+8	1339 (446)	−10	278
p-MeC$_6$H$_4$	1555 (321)	+6	1338 (507)	−10	269
p-F$_3$CC$_6$H$_4$	1565 (555)	+5	1340[h]	[h]	239

[a] cm^{-1}.
[b] In CH_2Cl_2; molar extinction coefficients in $l\ mol\ cm^{-1}$ are given in parentheses.
[c] $\Delta\nu = \nu_{free} - \nu_{complex}$.
[d] Complexes of 4-fluorophenol for solutions in CH_2Cl_2.
[e] Complexes of 4-fluorophenol for solutions in CCl_4.
[f] Saturated solutions.
[g] Several intense bands in the region $1360\ cm^{-1}$ make assignment uncertain.
[h] Overlap with an intense band at $1322\ cm^{-1}$ due to the CF_3 substituent.
[i] Insoluble in CCl_4.
[j] Dissymmetric band, apparent maximum determined principally by the angular complex 13a.
[k] Apparent flattened maximum.
[l] Not studied.
[m] Dissymmetric band, apparent maximum determined principally by the linear complex 13b.

the complex to nitrogen. With the proviso that the molar extinction coefficient of the $\nu(C=O)$ bands of the complexes to oxygen and to nitrogen are not too different, it can be concluded that the formation constant of the complex to oxygen is about twice that of its counterpart to nitrogen.

Summary of spectroscopic data of the hydrogen-bonded complexes of amidates 2–11 with methanol and 4-fluorophenol

Displacements of the $\nu(OH)$ bands of the methanol–amidate complexes in CCl_4 and of the $\nu(C=O)$ and $\nu(C-N^-)$ bands of the 4-fluorophenol–amidate complexes in CH_2Cl_2 are presented in Table 1. The band at *ca* $1600\ cm^{-1}$ of the amidates evolves in a similar manner to that of the $\nu(C=O)$ band of the corresponding amides, which confirms its $\nu(C=O)$ character in the former. The correlation between the carbonyl frequencies in the two series is given by

$$\nu(C=O)XCON^-N^+Me_3$$
$$= 1\cdot01[\nu(C=O)XCONMe_2] - 90\cdot2$$

$n = 8$ (X = p-MeOC$_6$H$_4$, C$_6$H$_5$, H, Me, Et, Pr$_i$, 1-adamantyl, OMe*), $r = 0\cdot962$, $s = 8\ cm^{-1}$ ($n =$ number

of data points; $r =$ correlation coefficient; $s =$ standard deviation)

Hydrogen-bond super-basicity of amidates

Table 2 presents the log K_{HB} values of the amidates in CH_2Cl_2 in the main, and also pK_{HB} in CCl_4 when solubility permits. It also gives for comparison values of log K_{HB} and pK_{HB} for amides, a lactam, a vinylogous amide and HMPA.

Figure 5(A) shows the hydrogen-bonding basicity scale log K_{HB} in CH_2Cl_2 for the amidates, dimethylformamide and HMPA. It is apparent that the alkylamidates are *ca* $0\cdot5$ pK unit more basic than the benzamidates, which is in accord with the greater electron-donor character of alkyl groups. Further, the amidates are considerably more basic than tertiary amides (more than one pK unit for the alkylamidates). Alkylamidates appear to be even slightly more basic in CH_2Cl_2 than HMPA, which hitherto had been one of the strongest known hydrogen-bonding bases.

These results are essentially reproduced in CCl_4. The pK_{HB} scale in this solvent is shown in Figure 5(B) for the three alkylamidates whose complexation constant with 4-fluorophenol was capable of determination in CCl_4, and is compared with other carbonyl bases and with HMPA. Not only do the amidates have pK_{HB} values higher than the most basic amide, lactam and urea presently known, but their pK_{HB} exceeds by *ca* $0\cdot5$ pK (*ca* $0\cdot1\beta_2^H$ unit) that of the vinylogous amide described

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* The frequencies of the $\nu(C=O)$ bands of $MeOCON^-N^+Me_3$ and $MeOCONMe_2$ are $1643\ cm^{-1}$ (in CH_2Cl_2) and $1711\cdot5\ cm^{-1}$ (in CCl_4), respectively.

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Table 2. Hydrogen-bonding basicity of amidates $RCON^-N^+Me_3$ and, for comparison, other compounds in CH_2Cl_2 and/or CCl_4

| Compound	Log K_{HB}	Compound	pK_{HB}	β_2^H
Amidates in CH_2Cl_2		*Amidates in CCl_4*		
R = Me	2·45[a]	R = Pr^i	3·32[a]	0·95
Et	2·59[a]	Bu^t	3·25[a]	0·94
Nonyl	2·39[a]	1-Adamantyl	3·56[a]	1·01
Pr^i	2·51[a]			
Bu^t	2·39[a]	*Other compounds in CCl_4*		
1-Adamantyl	2·43[a]	N,N-Dimethylformamide	2·10[b]	0·69
p-MeOC$_6$H$_4$	2·09[a]	N,N-Diethylacetamide	2·47[b]	0·77
p-F$_3$CC$_6$H$_4$	1·78[a]	1-Methyl-2-piperidone	2·60[b]	0·80
		N,N'-Dimethyl-N,N'-trimethyleneurea	2·79[b]	0·84
Other compounds in CH_2Cl_2		3-Dimethylamino-5,5-dimethylcyclohexenone	2·92[a]	0·87
N,N-Dimethylformamide	1·18[a]	HMPA	3·56[c]	1·00
Bu^{t}CON(C$_6$H$_{11}$)$_2$	1·31[a]			
HMPA	2·37[d]			

[a] This work.
[b] Ref. 9.
[c] Ref. 1.
[d] Ref. 28.
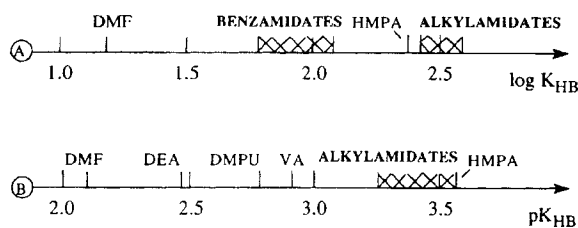
Figure 5. Climbing the hydrogen-bond basicity ladder from amides (DMF, DEA) to amidates via a urea (DMPU) and a vinylogous amide (VA), in (A) CH_2Cl_2 and (B) CCl_4. Alkylamidates appear of comparable basicity to HMPA

in the literature as the strongest hydrogen-bonding base. Actually the value $\beta_2^H = 1·04$ calculated by Taft *et al.* for this compound is only 0·87, a value experimentally determined by us here in order to compare vinylogous amides with amidates.

In summary, this work leads to the order of hydrogen-bonding basicity alkylamidates $\approx$ HMPA > vinylogous amide $\approx$ benzamidates > amides, and alkylamidates are currently both the strongest known hydrogen-bonding carbonyl bases and, in attaining comparable basicity to HMPA, the strongest known oxygenated hydrogen-bonding bases.

ACKNOWLEDGEMENTS

REFERENCES

1. D. Gurka and R. W. Taft, *J. Am. Chem. Soc.* **91**, 4794 (1969).
2. R. W. Taft, D. Gurka, L. Joris, P. von R. Schleyer and J. W. Rakskys, *J. Am. Chem. Soc.* **91**, 4801 (1969).
3. M. H. Abraham, P. L. Grellier, D. V. Prior, J. J. Morris and P. J. Taylor, *J. Chem. Soc.,Perkin Trans. 2* 521 (1990).
4. R. W. Taft, J. L. Abboud, M. J. Kamlet and M. H. Abraham, *J. Solut. Chem.* **14**, 153 (1985).
5. M. H. Abraham, P. L. Grellier, D. V. Prior, R. W. Taft, J. J. Morris, P. J. Taylor, C. Laurence, M. Berthelot, R. M. Doherty, M. J. Kamlet, J. L. Abboud, K. Sraïdi and G. Guihéneuf, *J. Am. Chem. Soc.* **110**, 8534 (1988).
6. E. D. Raczynska, C. Laurence and M. Berthelot, *Can. J. Chem.* **70**, 2203 (1992).
7. C. Laurence, M. Berthelot, M. Helbert and K. Sraïdi, *J. Phys. Chem.* **93**, 3799 (1989).
8. M. Berthelot, M. Helbert, C. Laurence and J. Y. Le Questel, *J. Phys. Org. Chem.* **6**, 302 (1993).
9. J. Y. Le Questel, C. Laurence, A. Lachkar, M. Helbert and M. Berthelot, *J. Chem. Soc., Perkin Trans. 2* 2091 (1992).
10. M. Berthelot, M. Helbert, C. Laurence, J. Y. Le Questel, F. Anvia and R. W. Taft, *J. Chem. Soc., Perkin Trans. 2* 625 (1993).
11. R. W. Taft, J. F. Gal, S. Geribaldi and P. C. Maria, *J. Am. Chem. Soc.* **108**, 861 (1986).
12. M. H. Abraham, P. P. Duce, D. V. Prior, D. G. Barratt, J. J. Morris and P. J. Taylor, *J. Chem. Soc., Perkin Trans. 2* 1355 (1989).
13. J. F. Gal and D. G. Morris, *J. Chem. Soc., Perkin Trans. 2* 431 (1978).
14. W. J. McKillip, E. A. Sedor, B. M. Culbertson and S. Wawzonek, *Chem. Rev.* **73**, 255 (1973).
15. C. Laurence, M. Berthelot, M. Luçon, D. G. Morris and A. G. Shepherd, *J. Chem. Soc., Perkin Trans. 2* 1206 (1981).

16. A. F. Cameron, N. J. Hair, D. G. Morris and D. M. Hawley, *Chem. Commun.* 725 (1971).
17. H. Lumbroso, Ch. Liégeois, D. G. Morris and J. D. Stephen, *Tetrahedron* **34**, 557 (1978).
18. M. Liler and D. G. Morris, *J. Chem. Soc., Perkin Trans. 2* 909 (1977).
19. H. Kise, H. Endo and M. Seno, *Bull. Chem. Soc. Jpn.* **50**, 3245 (1977).
20. R. F. Smith, A. C. Bates, A. J. Battisti, P. G. Byrnes, C. T. Mroz, T. J. Smearing and F. X. Allricht, *J. Org. Chem.* **33**, 851 (1968).
21. J. E. Kresta, R. J. Chang, S. Kathiriya and K. C. Frisch, *Makromol. Chem.* **180**, 1081 (1979).
22. Y. Matsuda, K. Takada, I. Ikeda and S. Komori, *Kinzoku Hyomen Gijutsu* **26**, 91 (1975); *Chem. Abstr.* **82**, 146989 u.
23. H. P. Benecke, *Tetrahedron Lett.* 997 (1977).
24. W. J. McKillip and R. C. Seagel, *Can. J. Chem.* **45**, 2619 (1967).
25. N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.* **81**, 6138 (1959).
26. R. S. Drago, *Physical Methods in Chemistry.* Saunders, Philadelphia (1977).
27. C. Laurence, M. Berthelot and M. Helbert, *Spectrochim. Acta, Part A* **41**, 883 (1985).
28. L. Joris, J. Mitsky and R. W. Taft, *J. Am. Chem. Soc.* **94**, 3438 (1972).