Hydrogen-bond Basicity of Esters, Lactones and Carbonates

François Besseau, Christian Laurence and Michel Berthelot
Laboratoire de Spectrochimie, Faculté des Sciences et des Techniques, 44072 Nantes Cedex, France

The thermodynamic hydrogen bond basicity scale $\mathrm{p}K_{\mathrm{HB}}$ (logarithm of the formation constant of 4-fluorophenol–base complexes in CCl_4) has been determined for esters, lactones and carbonates, and correlated to a spectroscopic basicity scale. In the esters $R^1CO_2R^2$ the hydrogen bond basicity is decreased by bulky alkyl R^1 substituents (steric effect) but increased by branched and lengthened alkyl R^2 substituents (electronic effects). Quantitative structure–basicity relationships have been established in the XCO_2Et (X varying from CF_3 to NMe_2) and $XC_6H_4CO_2Et$ (X varying from 4-NO_2 to 4-NMe_2) series. Vinylology strongly increases hydrogen bond basicity—$Me_2NCH{=}CHCO_2Et$ is the most basic ester presently known. Cyclisation increases the hydrogen bond basicity of esters and carbonates.

There is limited available data on esters and lactones and none on carbonates, for the hydrogen bond basicity scales $\log K_B^H$ (ref. 1) and $\log K_\beta$.[2] In order to determine the influence of structure on the hydrogen bond basicity of the $-CO_2-$group, we present here our $\mathrm{p}K_{\mathrm{HB}}$ hydrogen bond basicity scale, previously studied for several families of bases,[3-6] for esters, lactones and carbonates. This scale is based on the logarithm of the formation constant K_{HB} of the 4-fluorophenol–base 1:1 complex in CCl_4 at 298 K [reaction (*a*) and eqn. (1)]. In the equilibrium (*a*),

$$B + 4\text{-}FC_6H_4OH \rightleftharpoons 4\text{-}FC_6H_4OH \cdots B \qquad (a)$$

$$K_{\mathrm{HB}} = [\mathrm{Complex}]/[4\text{-}FC_6H_4OH]\,[\mathrm{Base}];\ \mathrm{p}K_{\mathrm{HB}} = \log_{10} K_{\mathrm{HB}} \qquad (1)$$

4-fluorophenol is a reference hydrogen bond donor chosen for technical reasons.[7]

We have measured 41 primary $\mathrm{p}K_{\mathrm{HB}}$ values by FTIR spectroscopy and also calculated 15 secondary $\mathrm{p}K_{\mathrm{HB}}$ values, from linear free energy relationships and a linear correlation between $\mathrm{p}K_{\mathrm{HB}}$ and $\Delta\nu(\mathrm{OH})$—the lowering of the $\nu(\mathrm{OH})$ frequency of methanol on going from the free to the hydrogen-bonded OH group. Both primary and secondary values can be transformed into the parameter β_2^H by eqn. (2).[1]

$$\beta_2^H = (\mathrm{p}K_{\mathrm{HB}} + 1.1)/4.636 \qquad (2)$$

The β_2^H parameter permits a quantitative estimate of the value of the formation constant for the hydrogen-bonded complex with many hydrogen bond donors of known hydrogen bond acidity.[8] However, only primary values have sufficient accuracy to enable reliable quantitative structure–basicity relationships to be established.

Our sample of compounds is numerous and diverse enough for studying the influence on hydrogen bond basicity of: (i) electronic and steric effects of alkyl R^1 and R^2 groups in the $R^1CO_2R^2$ series; (ii) electronic effects in the XCO_2Et and $XC_6H_4CO_2Et$ series; (iii) vinylology; and (iv) cyclisation.

Experimental

Chemicals were commercial and after purification were generally 99.5% pure according to GLC. Ethyl 1-adamantanecarboxylate ($\nu_{CO} = 1727\ \mathrm{cm}^{-1}$) was synthesized from the acid chloride and ethanol.

The FTIR spectroscopic method for measuring hydrogen bond formation constants has been described previously.[3] Values of $\mathrm{p}K_{\mathrm{HB}}$ are probably accurate to better than ± 0.03 (± 0.06 for CF_3CO_2Et, CCl_3CO_2Me and CCl_3CO_2Et). IR measurements were carried out with Fourier-Transform spectrometers (Bruker IFS 45 or Nicolet 510 M) by selecting 1 cm^{-1} resolution; a 1 cm quartz Infrasil cell was thermostatted at 25 ± 0.2 °C. All measurements were performed in CCl_4.

Results

The $\mathrm{p}K_{\mathrm{HB}}$, IR frequency shifts [$\Delta\nu(\mathrm{OH})$] of the methanol complexes, and β_2^H values are reported for the primary set in Table 1. A nice relationship [eqn. (3)] between the frequency

$$\Delta\nu(\mathrm{OH})XCO_2Et = 1.012\,[\Delta\nu(\mathrm{OH})XCO_2Me] + 3.8 \qquad (3)$$
$$n = 8(\mathrm{X{:}NMe_2, NPh_2, c\text{-}Pr, Me, Ph, EtO, H, CCl_3})$$
$$r = 0.9995 \quad s = 1\ \mathrm{cm}^{-1}$$

shifts of methyl and ethyl esters' complexes gives coherence to our spectroscopic data.

A satisfactory correlation [eqn. (4)] also exists between the thermodynamic basicity scale ($\mathrm{p}K_{\mathrm{HB}}$) and the spectroscopic basicity scale [$\Delta\nu(\mathrm{OH})$] for acyclic non-aromatic esters, carbonates and carbamates (data for carbamates are from ref. 5).

$$\mathrm{p}K_{\mathrm{HB}} = 1.51\,[\Delta\nu(\mathrm{OH})/100] - 0.16 \qquad (4)$$
$$n = 24 \quad r = 0.985 \quad s = 0.08$$

The relative imprecision of this relationship stems from the difficulty in estimating accurately the position of the maximum of the $\nu(\mathrm{OH}\cdots\mathrm{O{=}C})$ absorption for those compounds where overlapping bands occur corresponding to the presence of two stereoisomeric complexes.[9] Other significant deviations might result from lone pair–lone pair repulsions which are highly significant in diethyl oxalate, the most deviating point.

A slightly different line [eqn. (5)] is found for aromatic

$$\mathrm{p}K_{\mathrm{HB}} = 1.92\,[\Delta\nu(\mathrm{OH})/100] - 0.58 \qquad (5)$$
$$n = 7 \quad r = 0.996 \quad s = 0.02$$

esters (Fig. 1). Ethyl 4-nitrobenzoate and ethyl 4-cyanobenzoate are excluded from this correlation because their $\mathrm{p}K_{\mathrm{HB}}$ correspond to two simultaneous 1:1 complexes: $\mathrm{OH}\cdots\mathrm{O{=}C}$ and

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

No.	Compound	Formula	$\Delta\nu(OH)$	pK_{HB}	β_2^H
	Aliphatic esters				
1	Methyl trichloroacetate	CCl_3CO_2Me	25[a]	0.11	0.26
2	Ethyl trifluoroacetate	CF_3CO_2Et	13[a]	~0.08	0.25
3	Ethyl trichloroacetate	CCl_3CO_2Et	28[a]	0.15	0.27
4	Ethyl propiolate	$HC{\equiv}CCO_2Et$	50	0.63	0.37
5	Ethyl formate	HCO_2Et	58	0.66	0.38
6	Ethyl chloroacetate	$ClCH_2CO_2Et$	52	0.67	0.38
7	Ethyl fluoroacetate	FCH_2CO_2Et	54	0.74	0.40
8	Diethyl oxalate	EtO_2CCO_2Et	43	0.95 (0.65)[b]	f
9	Methyl acetate	$MeCO_2Me$	77	1.00	0.45
10	Ethyl 2,2-dimethylpropanoate	Bu^tCO_2Et	83	1.04	0.46
11	Ethyl phenylacetate	$PhCH_2CO_2Et$	71	1.05	0.46
12	Ethyl 1-adamantanecarboxylate	$C_{10}H_{15}CO_2Et$	85	1.06	0.47
13	Ethyl acetate	$MeCO_2Et$	83	1.07	0.47
14	Ethyl propionate	$EtCO_2Et$	81	1.08	0.47
15	Ethyl isobutyrate	Pr^iCO_2Et	83	1.09	0.47
16	*tert*-Butyl acetate	$MeCO_2Bu^t$	~73, ~124	1.10	0.47
17	Ethyl cyclopropanecarboxylate	$c\text{-}PrCO_2Et$	90	1.12	0.48
18	(*E*)-Ethyl cinnamate	$PhCH{=}CHCO_2Et$	83	1.14	0.48
19	Isopropyl acetate	$MeCO_2Pr^i$	85	1.15	0.49
20	Triacetin	$(MeCO_2CH_2)_2CH(O_2CMe)$	65	1.31 (0.84)[b]	f
21	Ethyl 3-dimethylaminoacrylate	$Me_2NCH{=}CHCO_2Et$	148	2.09	0.69
	Aromatic esters				
22	Ethyl 4-nitrobenzoate	$4\text{-}NO_2C_6H_4CO_2Et$	57	0.63[c]	f
23	Ethyl 4-bromobenzoate	$4\text{-}BrC_6H_4CO_2Et$	72	0.78	0.41
24	Methyl benzoate	$PhCO_2Me$	76	0.89	0.43
25	Ethyl 4-cyanobenzoate	$4\text{-}NCC_6H_4CO_2Et$	60[e]	0.90[d]	f
26	Ethyl benzoate	$PhCO_2Et$	81	0.94	0.44
27	Ethyl 4-methylbenzoate	$4\text{-}MeC_6H_4CO_2Et$	85	1.05	0.46
28	Diethyl terephthalate	$4\text{-}EtO_2CC_6H_4CO_2Et$	69	1.06 (0.76)[b]	f
29	Ethyl 4-methoxybenzoate	$4\text{-}MeOC_6H_4CO_2Et$	88	1.13	0.48
30	Ethyl 4-dimethylaminobenzoate	$4\text{-}Me_2NC_6H_4CO_2Et$	106	1.45	0.55
	Carbonates				
31	Dimethyl carbonate	$MeOCO_2Me$	68	0.82	0.41
32	Ethyl methyl carbonate	$MeOCO_2Et$	71	0.84	0.42
33	Diethyl carbonate	$EtOCO_2Et$	76	0.88	0.43
34	Vinylene carbonate	$OCHCHOCO$	42	0.69	0.39
35	Propylene carbonate	$OCHMeCH_2OCO$	73	1.22	0.50
	Lactones				
36	β-Propiolactone	$O[CH_2]_2CO$	49	0.86	0.42
37	β-Butyrolactone	$OCHMeCH_2CO$	54	0.97	0.45
38	Coumarin	$CH[CH]_3CC[CH]_2C(O)O$	88	1.30	0.52
39	γ-Butyrolactone	$O[CH_2]_3CO$	93	1.32	0.52
40	γ-Valerolactone	$OCHMe[CH_2]_2CO$	92	1.43	0.55
41	δ-Valerolactone	$O[CH_2]_4CO$	107	1.57	0.58
42	ε-Caprolactone	$O[CH_2]_5CO$	98	1.63	0.59

[a] Inaccurate data owing to the overlap of the free and complexed methanol $\nu(OH)$ bands. [b] Statistically corrected value for use in $pK_{HB}/\Delta\nu(OH)$ or pK_{HB}/σ relationships. [c] Logarithm of the sum of the formation constants of the ester and nitro complexes. [d] Logarithm of the sum of the formation constants of the ester and nitrile complexes. [e] Apparent frequency shift from a band composed of the $\nu(OH\cdots O{=}C)$ and $\nu(OH\cdots NC)$ bands. [f] Meaningless and/or not useful.

$OH\cdots O_2N$ for $4\text{-}NO_2C_6H_4CO_2Et$ and $OH\cdots O{=}C$ and $OH\cdots N{\equiv}C$ for $4\text{-}NCC_6H_4CO_2Et$ (*vide infra*).

Cyclic esters (lactones) and carbonates stand significantly above the line of eqn. (4) because their *E* configuration, compared to the *Z* configuration of acyclic esters and carbonates,[10,11] makes easier the access to oxygen carbonyl lone pairs, and increases the repulsion between lone pairs on the oxygens.

Eqns. (4) and (5) are used for calculating secondary pK_{HB} and β_2^H values for those esters for which only $\Delta\nu(OH)$ has been measured. The experimental $\Delta\nu(OH)$ and calculated pK_{HB} and β_2^H values are reported in Table 2.

Secondary pK_{HB} values can also be calculated from the formation constants K_X for the complexes of aliphatic esters with *p*-chlorophenol or 2-naphthol measured by Senechal and Bellon[12] in cyclohexane or heptane.Very good linear free energy relationships (6)–(9) are obtained between pK_{HB} and

$$pK_{HB} = 0.955 \log K_X\,(\text{4-chlorophenol, } C_6H_{12}) - 1.322 \quad (6)$$
$$n = 7 \quad r = 0.993 \quad s = 0.02$$

$$pK_{HB} = 0.966 \log K_X\,(\text{2-naphtol, } C_6H_{12}) - 1.129 \quad (7)$$
$$n = 7 \quad r = 0.993 \quad s = 0.02$$

Table 2 Hydrogen bond basicity of esters: experimental frequency shifts $\Delta\nu(OH)/cm^{-1}$ of methanol and secondary calculated pK_{HB} and β_2^H values

No.	Compound	Formula	$\Delta\nu$(OH)	pK_{HB}	β_2^H
43	4-Nitrophenyl acetate	$MeCO_2C_6H_4NO_2$	32	0.32[a]	0.31
44	Phenyl formate	HCO_2Ph	34	0.35[a]	0.31
45	Methyl formate	HCO_2Me	54	0.65[a]	0.38
46	*S*-Ethyl methylcarbonate	$EtSCO_2Me$	59	0.73[a]	0.39
47	*tert*-Butyl benzoate	$PhCO_2Bu^t$	75	0.97[a]	0.45
48	Ethyl 4-fluorobenzoate	$4\text{-}FC_6H_4CO_2Et$	76	0.88[b]	0.43
49	Methyl cyclohexanecarboxylate	$C_6H_{11}CO_2Me$	81	1.06[a]	0.47
50	Ethyl 3-methylbenzoate	$3\text{-}MeC_6H_4CO_2Et$	83	1.01[b]	0.46
51	Methyl cyclopropanecarboxylate	$c\text{-}C_3H_5CO_2Me$	85	1.12[a]	0.48

[a] Calculated from eqn. (4). [b] Calculated from eqn. (5).

Table 3 Secondary pK_{HB} and β_2^H values of aliphatic esters, from data of Senechal and Bellon[12] and the linear free energy relationships (6)–(9)

No.	Compound	Formula	pK_{HB}	β_2^H
52	Propyl acetate	$MeCO_2Pr$	1.15	0.49
53	Butyl acetate	$MeCO_2Bu$	1.13	0.48
54	Isobutyl acetate	$MeCO_2Bu^i$	1.14	0.48
55	*sec*-Butyl acetate	$MeCO_2Bu^s$	1.16	0.49
56	Ethyl butyrate	$PrCO_2Et$	1.11	0.48
57	Ethyl isovalerate	Bu^iCO_2Et	1.11	0.48

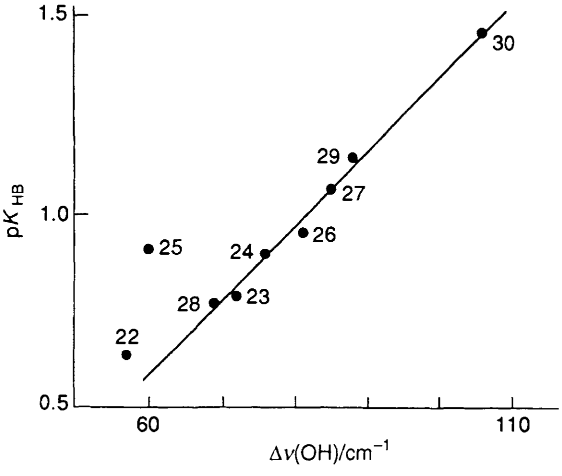

Fig. 1 Comparison of the thermodynamic and spectroscopic hydrogen bond basicity scales for aromatic esters. Numbers refer to Table 1. Ethyl 4-nitrobenzoate **22** and ethyl 4-cyanobenzoate **25** stand above the line of eqn. (5).

$$pK_{HB} = 0.936 \log K_X\,(\text{4-chlorophenol},\ C_7H_{16}) - 1.140 \quad (8)$$
$$n = 7 \quad r = 0.987 \quad s = 0.03$$

$$pK_{HB} = 1.013 \log K_X\,(\text{2-naphtol},\ C_7H_{16}) - 1.094 \quad (9)$$
$$n = 7 \quad r = 0.985 \quad s = 0.03$$

log K_X for seven esters common to the two data sets. They allow the calculation of six new secondary pK_{HB} values reported in Table 3.

Discussion

Hydrogen Bonding Site(s).—Although both alkoxy and carbonyl oxygens of the ester function may be hydrogen-bonded, the frequency lowering of the ν(C=O) vibration[13–15] and the concomitant frequency increase of the ν(C–O) band[15] indicate that interaction is predominantly with the carbonyl group. Nitrogen is also a potential hydrogen bond acceptor atom in $Me_2NCH{=}CHCO_2Et$ and $4\text{-}Me_2NC_6H_4CO_2Et$, but the observation of one $\nu(OH\cdots)$ band suggests that only one complex is formed, and the magnitude of the shift of ν(C=O) to lower frequencies indicates an ester complex. Another piece of evidence is that these two compounds obey the relationship between pK_{HB} and $\Delta\nu$(OH) [eqns. (4) and (5)]. It shows that there is no difference between $Me_2NCH{=}CHCO_2Et$ or $4\text{-}Me_2NC_6H_4CO_2Et$ and the other esters, and particularly that the preferred hydrogen-bonding site is the carbonyl group in all cases.

However, ethyl 4-nitrobenzoate and ethyl 4-cyanobenzoate stand significantly above the line of eqn. (5) for aromatic esters (Fig. 1). This might mean that a second formation constant is added to the ester formation constant. In the case of $4\text{-}N{\equiv}CC_6H_4CO_2Et$ this is easily verified by vibrational spectroscopy since addition of 4-fluorophenol to a solution of the cyanoester in C_2Cl_4 not only brings about a lowering of the ν(C=O) band from 1731 to 1708 cm^{-1}, which signifies an ester complex, but also effects a corresponding increase of the ν(C≡N) band from 2232 to 2241 cm^{-1}, which, in turn, signifies a nitrile complex.[6] For ethyl 4-nitrobenzoate the decrease of the ν(C=O) band from 1725 to 1707 cm^{-1} (in CH_2Cl_2) also shows the existence of the ester complex, and the formation constant indicates a nitro complex from the following analysis. The existence of two 1:1 complexes should mean that the total constant, 4.3 $dm^3\ mol^{-1}$, is the sum of an ester (K_{CO_2Et}) constant and a nitro K_{NO_2} constant; K_{CO_2Et} can be calculated from $\Delta\nu(OH) = 57\ cm^{-1}$ and eqn. (5) for aromatic esters to be 3.2 $dm^3\ mol^{-1}$. The difference, 1.1 $dm^3\ mol^{-1}$, is significant. It compares well with a value calculated from the correlation between pK_{HB} and the Hammett–Taft substituent constants[16] in the substituted nitrobenzene series,[17] and is attributed to K_{NO_2}.

Ethyl oxalate and ethyl terephthalate give also two 1:1 complexes but they are equivalent and the log 2 statistical correction to pK_{HB} gives the hydrogen bond basicity of one CO_2Et group. The situation seems more difficult for the three 1:1 complexes of triacetin. However we observe only one ν(C=O) band at 1753 cm^{-1} for free triacetin and one $\nu(OH\cdots)$ band for its hydrogen bond complex. This indicates that both the free and hydrogen-bonded carbonyl groups are nearly equivalent. Indeed a log 3 statistical correction gives $pK_{HB} = 0.84$ for the mean hydrogen bond basicity of one carbonyl group, which agrees fairly well with the calculated pK_{HB} 0.82 from eqn. (3) and $\Delta\nu(OH) = 65\ cm^{-1}$.

Steric and Electrical Effects of Alkyl Groups in the $R^1CO_2R^2$ *Series.*—The lengthening and branching of alkyl groups influence pK_{HB}, but not regularly, and we observe differences when the alkyls are located in either the acyl or alkoxy moieties of the ester. In the ethyl ester series R^1CO_2Et, Fig. 2 shows a slight pK_{HB} increase (+0.04) when we lengthen or branch R^1, then a decrease below the starting value for the bulky adamantyl and Bu^t substituents. In the acetate series $MeCO_2R^2$, the basicity increase (+0.15) is more important, and

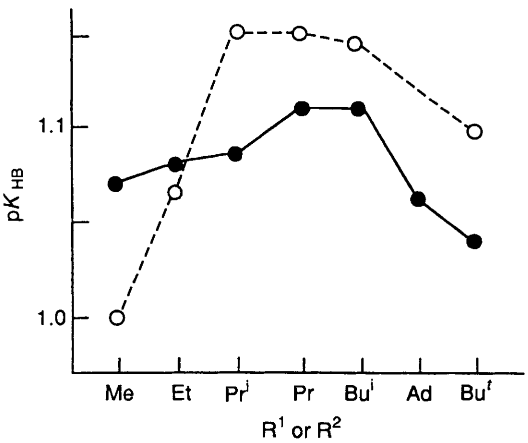

Fig. 2 Variation of pK_{HB} for aliphatic esters $R^1CO_2R^2$ by lengthening and branching alkyl substituents in the R^1CO_2Et (●) and $MeCO_2R^2$ (○) series

the bulky groups still give higher basicity than the original Me compound. It is well known that the basicity decrease comes from steric effects of bulky groups. The basicity increase could be attributed to increasing electron-donating (or electron-repelling) effects of alkyls by lengthening and/or branching. Thus the irregular variation of pK_{HB} could result from opposite electrical and steric effects of alkyl groups, and the different alkyl behaviour in the acyl and alkoxy moieties could be due to a greater sensitivity to steric effects of alkyl substitution on the acyl than on the alkoxy.

Electrical Effects of Substituents in XCO_2Et *and* p-$XC_6H_4CO_2Et$.—In the XCO_2Et series, the electronic effects of the X substituents CF_3, CCl_3, CO_2Et, HC≡C, H, $ClCH_2$, FCH_2, $PhCH_2$, c-Pr, Ph, OEt, OMe and NMe_2 on the hydrogen bond basicity can be analysed by means of eqn. (10)[16] where pK°_{HB}

$$pK_{HB}\ (\text{or }\Delta\nu) = pK^{\circ}_{HB}\ (\text{or }\Delta\nu^{\circ}) + \rho_\alpha\sigma_\alpha + \rho_F\sigma_F + \rho_R\sigma_R^{+} \quad (10)$$

(or $\Delta\nu^{\circ}$) refers to HCO_2Et, σ_α, σ_F and σ_R^+ measure the polarizability, field and resonance effects of X substituents, and the regression coefficients ρ_α, ρ_F and ρ_R measure the sensitivity of hydrogen bond basicity to these effects.

Eqns. (11) and (12) show that frequency shifts, $\Delta\nu$, are better

$$pK_{HB} = 0.80 - 0.32\,\sigma_\alpha - 1.79\,\sigma_F - 1.31\,\sigma_R^{+} \quad (11)$$
$$n = 14 \quad r = 0.949 \quad s = 0.15$$

$$\Delta\nu(OH) = 61.1 - 22.3\,\sigma_\alpha - 118.7\,\sigma_F - 102.8\,\sigma_R^{+} \quad (12)$$
$$n = 14 \quad r = 0.978 \quad s = 7\ cm^{-1}$$

correlated than formation constants pK_{HB}.

This could occur from a smaller sensitivity of $\Delta\nu(OH)$ than pK_{HB} to steric effects which are not included in eqn. (10). Possible non-additive effects of X and OEt groups on the carbonyl, lone pair–lone pair repulsions and rotational isomerism (for example for the FCH_2 and $ClCH_2$ substituents) are also not taken into account in eqns. (10)–(12).

The sensitivity coefficients ρ_α, ρ_F and ρ_R of equations (11) and (12) show that field effects play the leading part and that polarizability effects are not important. The confidence levels on ρ_α are 97% in eqn. (12) and 90% in eqn. (11). These low values raise the question of whether polarizability effects are physically significant for solution hydrogen bond basicity. In the XCO_2Et series we can only notice that if we do not keep the σ_α term, the intercepts $\Delta\nu^{\circ}$ and pK°_{HB} rise to 72 cm^{-1} and 0.95, respectively, which are less satisfactory values than 61 cm^{-1} and 0.80 compared to the HCO_2Et experimental values (58 cm^{-1} and 0.66).

In ring-substituted ethyl benzoates *p*-$XC_6H_4CO_2Et$, the larger distances between the substituents and the hydrogen bonding centre indicate that polarizability effects are not significant. The dual substituent parameter equation gives excellent correlations [eqns. (13) and (14)].

$$\Delta\nu(OH) = 80.7 - 38.3\,\sigma_F - 44.5\,\sigma_R^{+} \quad (13)$$
$$n = 6 \quad r = 0.994 \quad s = 1.9\ cm^{-1}$$

$$pK_{HB} = 0.96 - 0.714\,\sigma_F - 0.877\,\sigma_R^{+} \quad (14)$$
$$n = 6 \quad r = 0.998 \quad s = 0.02$$

Eqn. (14) permits the calculation of the ester contribution to the total hydrogen bond basicity of ethyl 4-nitrobenzoate and ethyl 4-cyanobenzoate (*vide supra*). For the 4-$NO_2C_6H_4CO_2Et$/4-FC_6H_4OH complex, we have measured $K_t = K_{CO_2Et} + K_{NO_2} = 4.3$ dm^3 mol^{-1}; from $\sigma_F = 0.65$ and $\sigma_R^+ = 0$ for 4-NO_2,[16] we calculate $K_{CO_2Et} = 3.1$ dm^3 mol^{-1} and, by difference, $K_{NO_2} = 1.2$ dm^3 mol^{-1}, in excellent agreement with the value found *supra*. For the 4-$NCC_6H_4CO_2Et$/4-FC_6H_4OH complex, $K_t = K_{CO_2Et} + K_{CN} = 8$ dm^3 mol^{-1}; from $\sigma_F = 0.60$ and $\sigma_R^+ = 0$ for 4-CN,[16] we calculate $K_{CO_2Et} = 3.4$ dm^3 mol^{-1} and, by difference, $K_{CN} = 4.6$ dm^3 mol^{-1}, which is exactly the value found from $\sigma_F = 0.24$ and $\sigma_R^+ = 0$ for 4-CO_2Et[16] and the correlation equation similar to (14) established in a previous work[6] for 4-substituted benzonitriles.

Vinylology.—We have previously given evidence[18] that vinylology, but not benzology, increases the hydrogen bond basicity of push–pull nitriles. Thus the basicity order for nitriles is $Me_2NCH=CHCN$ (170) > Me_2NCN (1.56) > 4-$Me_2NC_6H_4CN$ (1.23). The same situation is found * for the carbamate Me_2NCO_2Et, the carbamate vinylogue $Me_2NCH=CHCO_2Et$ and the carbamate benzologue 4-$Me_2NC_6H_4CO_2Et$: $Me_2NCH=CHCO_2Et$ (2.09) > Me_2NCO_2Et (1.83) > 4-$Me_2NC_6H_4CO_2Et$ (1.45). Thus vinylology emerges as an important structural tool in the hands of chemists wishing to increase hydrogen bond basicity.† In the ester family, vinolology produces a 'super-basic' ester, a justified qualification if we realize that $Me_2NCH=CHCO_2Et$ is more basic than Et_3N (pK_{HB} = 1.93)[7] and 4-picoline (pK_{HB} = 2.03).[7]

In the same vein, it is noteworthy that ethyl cinnamate $PhCH=CHCO_2Et$, the vinylogue of ethyl benzoate $PhCO_2Et$, is more basic by 0.10 pK_{HB} unit than its parent.

Cyclisation.—Inside the lactone series, we observe (Fig. 3) that hydrogen-bond basicity increases with ring size, from the four-membered β-propiolactone to the seven-membered ε-caprolactone. The basicity sequence with ring size, 4 < 5 < 6 < 7, for lactones is thus different from the sequence, 5 < 6 > 7, previously found[5] for lactams, and may indicate different mechanisms of interaction with the carbonyl group of the nitrogen lone pair (in lactams) and of the ether oxygen lone

---

* We thank a referee for drawing to our attention that the base-enhancing effect of vinylology has already been anticipated for esters in ref. 2.

† We thank a referee for drawing to our attention a very similar sentence in ref. 2. 'The principle of vinylology can probably be used to construct some exceedingly powerful proton acceptors as and when the need arises.'

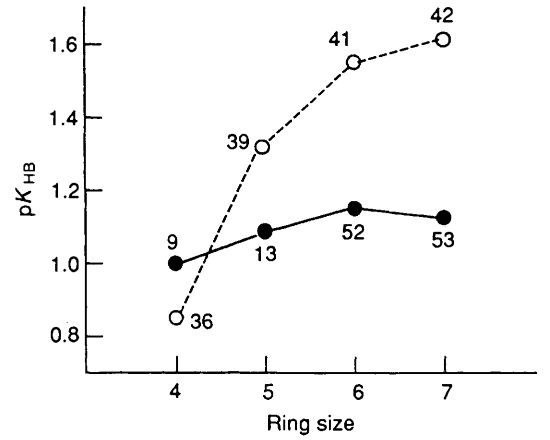

Fig. 3 Variation of pK_{HB} with the ring size of lactones (○) and comparison with the acyclic esters $MeCO_2R$ (●). Numbers refer to Tables 1 and 3.

pairs (in lactones). We also notice that $\overline{\text{OCHMeCH}_2\text{CO}}$ and $\overline{\text{OCHMe[CH}_2]_2\text{CO}}$ are more basic by 0.11 pK_{HB} unit respectively than $\overline{\text{O[CH}_2]_2\text{CO}}$ and $\overline{\text{O[CH}_2]_3\text{CO}}$, which agrees with the previous finding in acyclic esters that branching increases the electron-donating (or -repelling) effect of alkyl groups ($MeCO_2Pr^i$ is more basic by 0.08 pK_{HB} unit than $MeCO_2Et$).

If we exclude the very strained four-membered lactones, lactones are significantly more basic than the corresponding acyclic esters by 0.25 to 0.50 pK_{HB} unit (Fig. 3). This increase of basicity probably arises from two factors. First, the access of 4-fluorophenol to the carbonyl lone pairs becomes easier because cyclisation pulls back the alkyl substituents. Secondly, whereas the preferred *Z* configuration of acyclic esters minimises the repulsions of lone pairs on the two oxygen atoms, the necessarily *E* configuration of lactones maximises these repulsions. Consequently the carbonyl oxygen electrons are more readily available for (or more easily polarized towards) the electron acceptor 4-fluorophenol.

The same reasons explain why propylene carbonate is more basic than acyclic carbonates. As expected, the basicity difference is greater between corresponding acyclic and cyclic carbonates (+0.38) than between lactones and corresponding acyclic esters (+0.25).

References

1 M. H. Abraham, P. L. Grellier, D. V. Prior, J. J. Morris and P. J. Taylor, *J. Chem. Soc., Perkin Trans 2*, 1990, 521.
2 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*, 1989, 1355.
3 C. Laurence, M. Berthelot, M. Helbert and K. Sraïdi, *J. Phys. Chem.*, 1989, **93**, 3799.
4 E. D. Raczynska, C. Laurence and M. Berthelot, *Can. J. Chem.*, 1992, **70**, 2203.
5 J. Y. Le Questel, C. Laurence, A. Lachkar, M. Helbert and M. Berthelot, *J. Chem. Soc., Perkin Trans. 2*, 1992, 2091.
6 M. Berthelot, M. Helbert, C. Laurence and J. Y. Le Questel, *J. Phys. Org. Chem.*, 1993, **6**, 302.
7 D. Gurka and R. W. Taft, *J. Am. Chem. Soc.*, 1969, **91**, 4794.
8 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. M. Abboud, K. Sraïdi and G. Guihéneuf, *J. Am. Chem. Soc.*, 1988, **110**, 8534.
9 C. Laurence, M. Berthelot and M. Helbert, *Spectrochim. Acta, Part A*, 1985, **41**, 883.
10 N. L. Owen, *J. Mol. Struct.*, 1973, **18**, 1.
11 K. Wiberg and R. F. Waldron, *J. Am. Chem. Soc.*, 1991, **113**, 7705.
12 D. Sénéchal and L. Bellon, *C. R. Hebd. Seances Acad. Sci., Ser. C.*, 1975, **281**, 635.
13 L. Vanderheyden and Th. Zeegers-Huyskens, *J. Mol. Liq.*, 1983, **25**, 1.
14 T. Gramstad, *Spectrochim. Acta*, 1963, **19**, 497.
15 K. B. Patel, G. Eaton and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 275.
16 C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165.
17 M. Berthelot and C. Laurence, unpublished work.
18 M. Berthelot, M. Helbert, C. Laurence, J. Y. Le Questel, F. Anvia and R. W. Taft, *J. Chem. Soc., Perkin Trans. 2*, 1993, 625.

Paper 3/06173F
Received 15*th October* 1993
Accepted 27*th October* 1993