

TRIBUTYLAMMONIUM CYANAMIDATE $\text{Bu}_3\text{N}^+-\text{N}^--\text{C}\equiv\text{N}$: A 'SUPER-BASIC' NITRILE GROUP MORE BASIC, ON THE HYDROGEN-BOND BASICITY SCALE, THAN ANY AMINE OR PYRIDINE

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An IR spectroscopic study of the hydrogen bonding of $\text{Bu}_3\text{N}^+\text{N}^-\text{C}\equiv\text{N}$ with 4-fluorophenol showed that the site of complexation is the nitrogen of the nitrile function. The formation constant of the 1:1 complex in CCl_4 indicates that this cyanamidate is a stronger hydrogen-bond base than is any nitrile, amine or pyridine. The $\text{Bu}_3\text{N}^+\text{N}^-$ group increases the basicity of the nitrile group very efficiently because of the conjugation of two lone pairs on the anionic nitrogen with the π systems of the cyano group. This conjugation is also exemplified by the very low $\nu(\text{C}\equiv\text{N})$ wavenumber (2104 cm^{-1}).

INTRODUCTION

It is well known that amines and pyridines are more basic than nitriles on all scales of basicity. In particular on the $\text{p}K_{\text{HB}}$ scale of hydrogen-bond basicity, defined by Taft *et al.*¹ and recently studied by our groups,² acetonitrile has $\text{p}K_{\text{HB}}=0.91$, pyridine 1.88 and quinuclidine 2.63.

Cyanamides $\text{R}_2\text{N}-\text{C}\equiv\text{N}$ are, of course, stronger bases than alkyl cyanides $\text{RC}\equiv\text{N}$ because of the resonance form $\text{R}_2\text{N}^+=\text{C}=\text{N}^-$, and dimethylcyanamide has $\text{p}K_{\text{HB}}=1.56$.³ We have recently discovered 'super-basic' nitriles,⁴ the cyanamide vinylogue $\text{Me}_2\text{NCH}=\text{CHC}\equiv\text{N}$ ($\text{p}K_{\text{HB}}=1.70$) and the cyanamide iminologues $\text{Me}_2\text{NCH}=\text{NC}\equiv\text{N}$ ($\text{p}K_{\text{HB}}=2.09$) and $\text{Me}_2\text{NC}(\text{Me})=\text{NC}\equiv\text{N}$ ($\text{p}K_{\text{HB}}=2.24$). In the same vein, cyanoguanidines are also super-basic nitrile;⁵ a $\text{p}K_{\text{HB}}$ of 2.20 was calculated for *N*¹-methyl-*N*²-propylcyanoguanidine. Accordingly, the last three compounds have the nitrile function more basic than triethylamine ($\text{p}K_{\text{HB}}=1.93$) and 4-picoline ($\text{p}K_{\text{HB}}=2.03$). However, they remain below unhindered amines (quinuclidine,

$\text{p}K_{\text{HB}}=2.63$) and push-pull pyridines (4-dimethylaminopyridine, $\text{p}K_{\text{HB}}=2.81$).

The effects of R_2N and $\text{R}_2\text{NCH}=\text{CH}$ on the hydrogen-bond basicity of the nitrile group are qualitatively reproduced on the acetyl group, and in the family of carbonyl bases the order of hydrogen-bond basicity is⁶ amide vinylogue > amide > ketone. We have recently shown⁶ that the $\text{R}_3\text{N}^+\text{N}^-$ group, in which anionic and cationic nitrogens are bonded together, donates more to the carbonyl than R_2N and $\text{R}_2\text{NCH}=\text{CH}$, and so amidates $\text{R}_3\text{N}^+\text{N}^-\text{C}(\text{O})\text{R}$ constitute the strongest carbonyl bases on the $\text{p}K_{\text{HB}}$ scale hitherto investigated.

This strong electron release of $\text{R}_3\text{N}^+\text{N}^-$ led us to attach it to the strongly electron-attracting cyano group with the aim of reaching the highest rung yet on the hydrogen-bond basicity ladder. To our knowledge, there do not appear to be any basicity data on trialkylammonium cyanamidates. In this work, we chose to study tributylammonium cyanamidate; the three butyl groups were deemed necessary in order to achieve sufficient solubility in CCl_4 , the solvent of choice to perform

infrared determinations not only of the formation constant of a hydrogen-bonding complex but also of the donor site for hydrogen bonding.

EXPERIMENTAL

Synthesis of tributylammonium cyanamidate was carried out by the method of Hutchins and Swern⁷ using tri-*n*-butylamine instead of trimethylamine. The crude product was obtained in 52% yield and was recrystallized from *n*-butyl chloride, m.p. 74–75°C. Mass spectrometry (electron impact, 70 eV) did not give a parent ion at $M^+ = 225$, but did show a strong ion at m/z 185 ($M - 40$), as noted previously⁷ for trimethylammonium cyanamidate. Chemical ionization mass spectrometry, using isobutane, gave $M + 1 = 226$. Microanalysis: found, C 69.37, H 12.35; $C_{13}H_{27}N_3$ requires C 69.26, H, 12.08%.

The purification of chemicals, the Fourier transform measurements and the equilibrium constant determination method have been described in previous papers.^{3,4,6}

RESULTS AND DISCUSSION

Site of fixation of 4-fluorophenol and methanol

This was studied by vibrational spectroscopy in CCl_4 solution. Both the anionic and the nitrile nitrogens are potential sites. When adding the hydrogen-bond donors

methanol and 4-fluorophenol to $Bu_3N^+N^-C\equiv N$, the vibrators that are more sensitive to complexation are $\nu(OH)$ and $\nu(C\equiv N)$. The very intense ($\epsilon = 930 \text{ l mol}^{-1} \text{ cm}^{-1}$) and sharp ($\Delta\nu_{1/2} = 12 \text{ cm}^{-1}$) $\nu(C\equiv N)$ band at 2104 cm^{-1} is shifted towards higher frequencies on hydrogen-bond formation. This shift, 14 cm^{-1} with 4-fluorophenol, indicates nitrile nitrogen coordination, since an increase in the frequency of the nitrile absorption on Lewis acid addition^{8,9} or hydrogen bond formation^{3,10} appears to be quite general. In Figure 1 we do not observe any absorption at lower frequencies which would have indicated anionic nitrogen coordination. In fact, a single $\nu(OH)$ band of the complex is observed at 3400 cm^{-1} with methanol and 3189 cm^{-1} with 4-fluorophenol, indicating one site of fixation of the OH group (in the dilute concentration range used in this work). The displacements $\Delta\nu(OH) = \nu(OH)_{\text{free}} - \nu(OH)_{\text{complex}}$ are 244 cm^{-1} for methanol and 425 cm^{-1} for 4-fluorophenol. Compared with the $\Delta\nu(OH)$ values for nitriles, cyanamides, cyanamide vinylogue and cyanamide iminilogues,^{3,4} these values indicate that the cyanamidate possesses the strongest known hydrogen-bond basicity for a nitrile function in a neutral species.

Hydrogen-bond super-basicity of the cyanamidate

As a thermodynamic basicity scale, we use pK_{HB} , the logarithm of the formation constant of the 1:1

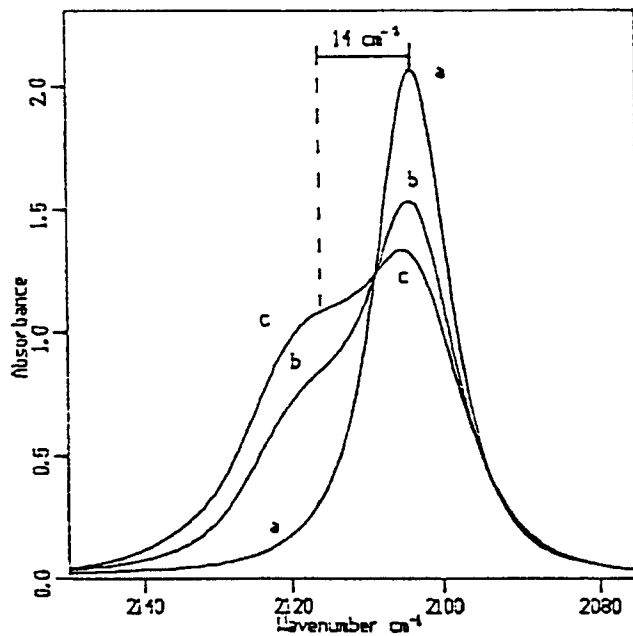


Figure 1. $\nu(C\equiv N)$ region of 4- FC_6H_4OH -cyanamidate solutions in CCl_4 . Concentrations: cyanamidate, $2 \times 10^{-3} \text{ mol l}^{-1}$; 4- FC_6H_4OH , (a) 0, (b) 2×10^{-3} and (c) $4 \times 10^{-3} \text{ mol l}^{-1}$. Cell thickness: 1 cm

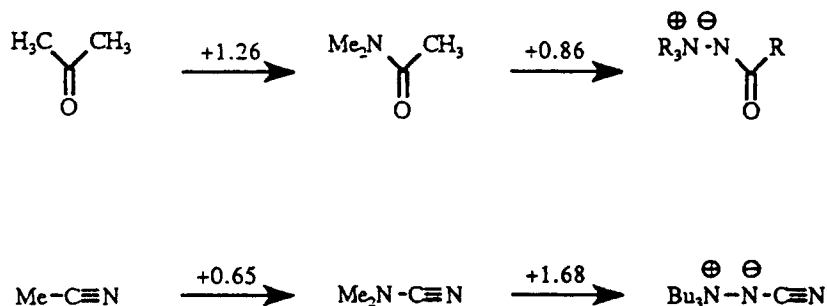
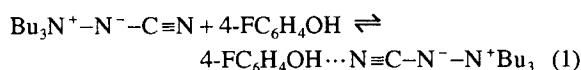


Figure 2. Increments in the values of pK_{HB} with successive substitution of Me by $\text{N}(\text{Me})_2$ and $\text{R}_3\text{N}^+\text{N}^-$ in the carbonyl and nitrile bases

hydrogen-bond complex of cyanamidate with 4-fluorophenol in CCl_4 at 25°C :



$$K_{\text{HB}} = [\text{complex}]/[\text{cyanamidate}][4\text{-fluorophenol}];$$

$$pK_{\text{HB}} = \log K_{\text{HB}} \quad (2)$$

We find $pK_{\text{HB}} = 3.24$, a value higher than those for the most basic nitrile,⁴ $\text{Me}_2\text{NC}(\text{Me})=\text{NC}\equiv\text{N}$, the most basic amine,¹ quinuclidine, and the most basic pyridine, 4-dimethylaminopyridine.

Comparison of amidate and cyanamidate basicities

Figure 2 compares how much the hydrogen-bond basicity increases on going successively from nitrile to cyanamide and cyanamidate and from ketone to amide and amidate. It appears that Me_2N conjugates more efficiently with the carbonyl than with the cyano group, at least from the point of view of hydrogen-bond basicity. In contrast, replacement of the Me_2N group by $\text{R}_3\text{N}^+\text{N}^-$ increases pK_{HB} twice as much in the nitrile as in the carbonyl family. Probably the two lone pairs on the anionic nitrogen conjugate better with the two π systems of the cyano group than with the single π system of the carbonyl group. The highly conjugated system of the cyanamidate is also indicated by the very

low wavenumber (i.e. low bond order, i.e. significant weight of the mesomeric structure $\text{N}=\text{C}=\text{N}^-$), 2104 cm^{-1} , of the $\text{C}\equiv\text{N}$ stretching, which is lowered by 152 cm^{-1} compared with acetonitrile.

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