How Do the Nucleophilicity and Size of an Isocyano Carbon Atom Differ from those of a Cyano Nitrogen Atom?

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Hydrogen-bond stretching force constants k_σ and distances $r(\mathrm{B}\cdots\mathrm{X})$ from the rotational spectra of the C_{3v} dimers B ••• HX, where B = CH_3NC or CH_3CN and X = F, Cl, CN or CCH, have been used to establish the difference in magnitude of the gas-phase nucleophilicity and of the van der Waals radius between the isocyano carbon atom in CH_3NC and the cyano nitrogen atom in CH_3CN.

The relative nucleophilicities of alkyl cyanides and the isomeric isocyanides are quantities of interest in physical organic chemistry. Various physical properties of methyl isocyanide have been interpreted[1] as indicating that the predominant contribution to the valence-bond description of the molecule is made by the polar structure $CH_3N^+{\equiv}C^-$ first proposed by Lindemann and Wiegrebe.[2] The isocyano carbon atom then carries a non-bonding (n) electron pair with a formal negative charge. A nucleophilic character is therefore not unexpected. Although the N atom in the isomeric CH_3CN also carries an n-pair, it is formally neutral. The negative charge on C, the lower electronegativity of C than N, and the observation of a greater molar bond refraction for the isocyano group than for the cyano group led to the suggestion[3] that the n-pair in RNC molecules is more loosely bound than in RCN. Consequently, RNC might[1] be a stronger Lewis base and a better nucleophile than RCN. Some evidence for such an order is available.

First, the shifts $\Delta\nu$ in the wavenumbers of OH and CH stretching vibrations are greater when these groups form hydrogen bonds to NC[4–6] than when the bonds are to CN. Secondly, the gas-phase proton affinity[7] of CH_3NC (844 kJ mol^{-1}) is greater than that of CH_3CN (788 kJ mol^{-1}). Thirdly, but less directly, the reactivity of CH_3NC with anhydrous hydrogen halides or aqueous acids or halogens is significantly greater.[8,9] However, all of this evidence should be interpreted cautiously. For example, the order of IR shifts might not parallel the order of proton acceptor ability of B in hydrogen bond formation.[4] Moreover, proton affinities are defined as ΔH°_m for $BH^+ \longrightarrow H^+ + B$ and there is some evidence that the ions CH_3NCH^+ and CH_3CNH^+ are not isostructural.[9] The difference in gas-phase proton affinity might therefore measure more than just the difference in nucleophilicity of the n-pair on C in CH_3NC and on N in CH_3CN. A more appropriate gauge of relative nucleophilicity might be one that measures the propensity of the n-pair to interact with a non-perturbing positive charge.

A convenient scale of nucleophilicity based on such a non-perturbing interaction has been proposed recently.[10] The nucleophilicity of the acceptor region of a molecule B is derived from the hydrogen-bond stretching force constant k_σ of the weakly bound dimer B ••• HX, k_σ being one measure of the strength of the hydrogen bond, *i.e.* through the energy $\frac{1}{2}k_6\,\mathrm{d}r^2$ required to produce a unit infinitesimal displacement along the dissociation coordinate. The success of a set of empirical rules[11] and a simple electrostatic model[12] in rationalizing a wide range of angular geometries of dimers B ••• HF, for example, is consistent with the view[13] that the electrophilic end $H^{\delta+}$ of HF acts as a non-perturbing probe of an n-pair carried by B. The experimental angular geometries were all determined for the isolated dimer B ••• HF in the gas phase by rotational spectroscopy, from which technique k_σ is also available. When a sufficiently large number of k_σ values had been determined, it was realized[10] that a nucleophilicity N could be assigned to each B and an electrophilicity E to each HX so that the whole set of k_σ could be reproduced by the expression in eqn. (1) where

Table 1 Gas-phase nucleophiicities N and electrophilicities E of some molecules B and HX[a]

B	N	HX	E
CO	3.4	HF	10.0
PH_3	4.4	HCl	5.0
H_2S	4.8	HCN	4.25
$(CH_3)_3P$	6.9	HCCH	2.4
HCN	7.3		
$(CH_3)_3CCN$	9.0		
H_2O	10.0		
NH_3	11.5		

[a] Values from ref. 10.

$$k_\sigma = cNE \qquad (1)$$

$c = 0.25$ N m^{-1}. A selection of these gas-phase N and E values is displayed in Table 1.

Until recently, the k_σ values important for the determination of $N(CH_3NC)$, namely those for CH_3NC ••• HF and CH_3NC ••• HCl, were not available because of the reactivity of CH_3NC and HX alluded to above. The development of a fast-mixing and freezing technique[14] has now allowed the rotational spectra of these dimers to be observed, however. In this technique two mixtures, one of CH_3NC diluted in argon and the other of HF similarly diluted, for example, are kept separate until the point at which they expand into a vacuum through a nozzle. The dimers CH_3NC ••• HF formed on mixing achieve collisionless expansion within a few microseconds, are thereby frozen and no reaction is possible thereafter. The expanded gas can then be probed with microwave radiation and the rotational spectrum of CH_3NC ••• HF recorded.[15]

The force constants k_σ determined from centrifugal distortion constants D_J made available by analysis of the rotational spectra of CH_3NC ••• HX (X = F, Cl, CN and CCH)[15–18] are summarized in Table 2. The necessary relationship between D_J and k_σ for these isostructural C_{3v} molecules is set out elsewhere.[19] The k_σ for the corresponding series of isomers CH_3CN ••• HX, similarly determined,[20–23] are also given in Table 2. By taking the E value of the appropriate HX from Table 1, each k_σ in Table 2 generates an N value. As seen in Table 2, the N values for the CH_3NC ••• HX series closely parallel those of the CH_3CN ••• HX series. Moreover, it is clear that N is indeed a property of the acceptor molecule B in each series and that the mean value of N is identical for CH_3NC and

Table 2 Hydrogen-bond stretching force constants k_σ for dimers $CH_3NC\cdots HX$ and $CH_3CN\cdots HX$

	B = CH_3NC		B = CH_3CN	
$B\cdots HX$	k_σ/N m^{-1}	N(B)[a]	k_σ/N m^{-1}	N(B)[a]
$B\cdots HF$	19.9(3)[b]	8.0	20.1(5)[c]	8.0
$B\cdots HCl$	11.4(1)[d]	9.1	10.70(3)[e]	8.6
$B\cdots HCN$	8.7(2)[f]	8.2	9.51(2)[g]	8.2
$B\cdots HCCH$	4.78(1)[h]	8.0	4.75(1)[i]	7.9
	mean	8.3(4)	mean	8.3(5)

[a] Calculated from eqn. (1) and the appropriate E value from Table 1. [b] Ref. 15. [c] Ref. 20. [d] Ref. 16. [e] Ref. 21. [f] Ref. 17. [g] Ref. 22. [h] Ref. 18. [i] Ref. 23.

Table 3 Distances $r(B\cdots X)$ in $CH_3NC\cdots HX$ and $CH_3CN\cdots HX$

Dimer	B = CH_3NC	B = CH_3CN	
$B\cdots HX$	$r(C\cdots X)$/Å[a]	$r(N\cdots X)$/Å[a]	Δr/Å[b]
$B\cdots HF$	2.840[c]	2.752[d]	0.088
$B\cdots HCl$	3.400[e]	3.292[f]	0.108
$B\cdots HCN$	3.423[g]	3.272[h]	0.151
$B\cdots HCCH$	3.596[i]	3.426[j]	0.170
		mean	0.13(3)

[a] All $r(B\cdots X)$ calculated using the model discussed in ref. 23. [b] $\Delta r = r(C\cdots X) - r(N\cdots X)$. [c] Ref. 15. [d] Ref. 20. [e] Ref. 16. [f] Ref. 21. [g] Ref. 17. [h] Ref. 22. [i] Ref. 18. [j] Ref. 23.

CH_3CN, even though imperfections in the model lead to small variations of N within a given series. On this basis, the gas-phase nucleophilicities of CH_3NC and CH_3CN must be considered indistinguishable and to lie in magnitude between those of HCN and $(CH_3)_3CCN$ (see Table 1).

Another quantity of some physico-chemical interest available *via* the rotational spectra of $CH_3NC\cdots HX$ and $CH_3CN\cdots HX$ dimers is the van der Waals radius of the isocyano carbon atom. The distances $r(C\cdots X)$ and $r(N\cdots X)$ have been determined for the isostructural series $CH_3NC\cdots HX$ and $CH_3CN\cdots HX$, respectively, by an internally consistent method that allows for the contributions of the intermolecular bending modes to the zero-point motion and is described in detail elsewhere.[23] The results are displayed in Table 3, also included in which are the quantities $\Delta r = r(C\cdots X) - r(N\cdots X)$. The main conclusion of interest is that Δr is positive and close to 0.1 Å for each X. In addition, there is a small systematic increase in Δr as the interaction becomes weaker. As discussed previously,[12] distances $r(B\cdots X)$ in hydrogen-bonded dimers $B\cdots HX$ are a reasonable approximation to the sum of the van der Waals radii of the acceptor atom on B and the atom X. The implication of the present work is therefore that the van der Waals radius of isocyano C exceeds that of cyano N by approximately 0.1 Å, *i.e.* by the mean value of Δr (Table 3). Given the accepted van der Waals radius of N as 1.4 Å, the above discussion suggests a value of 1.5 Å for isocyano C.

Acknowledgements

A research grant from the SERC in support of this work is gratefully acknowledged.

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Paper 1/06441J
Received 24*th December* 1991
Accepted 9*th January* 1992