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Ion Chemistry of Cyanides and Isocyanides. 1. The Carbon Lone Pair as Proton Acceptor: Proton Affinities of Isocyanides. Alkyl Cation Affinities of N, O, and C Lone-Pair Donors

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Abstract: The proton affinities (PAs) of the isocyanides RNC, R = CH_3, C_2H_5, i-C_3H_7, t-C_4H_9, and C_6H_5, range from 199 to 207 kcal/mol. The PAs of all the isocyanides are higher than those of the corresponding cyanides, RCN, by a constant 11.5 ± 1 kcal/mol, regardless of the identity of R. The isomerization energies of the $RNCH^+$ ions to $RCNH^+$ are 5–11 kcal/mol and are smaller by 11–15 kcal/mol than the isomerization energies of the respective neutral cyanides. The bond dissociation energies $D°$ for R^+–NCH, R^+–CNH, R^+–OH_2, and R^+–NH_3 show unexpectedly good linear correlations with the stabilities of the R^+ ions as measured by the hydride affinity, i.e., $D°(R^+–H^-)$. Ab initio calculations are used to analyze the trends in proton affinities. The results show that the main structural effects of protonation on RNC are the shortening of the N–C and the lengthening of the R–N bonds. The calculations also suggest that the larger PAs of RNC vs. RCN arise primarily from larger charge transfer and electrostatic interactions in the isocyanides. However, the parallel increase of the PAs of both RCN and RNC as R gets bigger is due primarily to the increasing polarizabilities of the substituents.

Compounds containing the nitrile group are ubiquitous constituents of planetary atmospheres and interstellar clouds. Ion chemistry is important in these environments which are subject to cosmic rays and ionizing UV radiation. The present series of papers, therefore, examines the ion chemistry of protonated cyanides and isocyanides.

Isocyanides are also interesting because they belong to a unique class of proton acceptors where the protonation site is a carbon lone pair. In this sense, proton affinity data on isocyanides complement proton affinity data on conventional lone-pair electron donors such as oxygen, nitrogen, sulfur, and phosphorus.

The present paper consists of three parts. The first part presents the experimental results and a qualitative discussion of some aspects of the results. The second part deals with alkyl ion affinities. For this purpose we note that protonated isocyanides may be considered alkylated hydrogen cyanides, i.e., HCN–R^+. We, therefore, use the present data to derive the alkyl cation affinities of HCN, i.e., the bond-dissociation energies $D°(R–NCH^+)$. These results are compared with the alkyl cation affinities of other lone-pair donors, specifically, H_2O, NH_3, and HNC. The point of interest here is whether the alkyl cation affinities correlate with the stabilities of the ions as measured by the hydride affinities of R^+.

The last part presents a theoretical examination of the trends observed in the experimental data. Specifically, we look into the following questions: (1) Why is the proton affinity of RNC higher than that of the corresponding RCN isomer and why are these differences independent of R? (2) What bond length changes occur in RNC upon protonation and what are the origins of these changes? (3) What is the source of the alkyl substituent effect on the observed proton affinities?

Experimental and Computational Methods

A. Experimental. The proton affinities of CH_3NC, C_2H_5NC, and t-C_4H_9NC were determined by using the NBS pulsed ion cyclotron resonance (ICR) instrument and conventional ICR equilibrium techniques.[1,2] The proton affinities of i-C_3H_7NC and C_6H_5NC were determined by bracketing measurements. The ions were generated in reaction systems consisting of HCN and the corresponding halides, either RCl or RI. In these systems, the $RNCH^+$ ions are produced by one or more of ion–molecule reactions 1–4, i.e., direct association between the fragment ions and HCN (reaction 1), alkylation by R_2X^+ (reaction 2), and alkylation with elimination of X or HX (reactions 3 and 4).

$$R^+ + NCH \rightarrow RNCH^+ \quad (1)$$

$$RXR^+ + NCH \rightarrow RNCH^+ + RX \quad (2)$$

$$RX^+ + NCH \rightarrow RNCH^+ + X \quad (3)$$

$$HCNH^+ + RX \rightarrow RNCH^+ + HX \quad (4)$$

The occurrence of one or more of reactions 1–4 in these systems was established by double resonance. The isomeric identities of the product ions were implied by the results of the proton transfer measurements themselves, since the proton affinities of the RCN isomers are substantially lower than the measured values.

As usual, in the bracketing experiments we attribute the occurrence of proton transfer from $RNCH^+$ to reference bases B to the exoergic ($\Delta G < 0$) nature of the reactions and the nonoccurrence of such reactions to the endoergic ($\Delta G > 0$) nature of the reaction. Double resonance examination of reaction 5 consists of observing a decrease in the BH^+ signal when $RNCH^+$ is ejected. In the case of $C_6H_5NCH^+$ this was not conclusive, however, since, typically, $RNCH^+$ is built up slowly by reactions 1–4 and constitutes only a few percent of the total ion concentration.

$$RNCH^+ + B \rightarrow BH^+ + RNC \quad (5)$$

Hence, most of the BH^+ results from other processes, and the ejection of $RNCH^+$ does not necessarily lead to a perceptible decrease of the BH^+ signal. Therefore, the bracketing of $C_6H_5NCH^+$ was done by determining whether the addition of various reference bases B affected the time profile of the $C_6H_5NCH^+$ ion.

We should also note that for the isocyanides the equilibrium measurements were complicated by the occurrence of reaction 6. Fortunately, this reaction is slower than the proton-transfer reactions. Therefore, equilibrium could be attained in reaction systems containing isocyanides, even though reaction 6 took place. The kinetic aspects of reactions 1–6 will be reported elsewhere.

$$RNCH^+ + RNC \rightarrow RNCR^+ + HCN \quad (6)$$

The samples of CH_3NC and C_2H_5NC were prepared by the method of Casanova et al.[3] The other reagents were from commercial sources and were used as purchased.

B. Theoretical. The calculations were carried out ab initio on a VAX 11/780 computer utilizing the Gaussian 82 system of programs.[4] It has

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(1) Lias, S. G.; Euler, J. R.; Ausloos, P. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *19*, 219.

(2) Lias, S. G.; Ausloos, P.; Horvath, Z. *Int. J. Chem. Kinet.* **1976**, *8*, 719.

(3) Casanova, J.; Shuster, R. E.; Werner, N. D. *J. Chem. Soc.* **1963**, 4280.

been shown that it is necessary to include polarization functions in the basis set in order to obtain numerically accurate proton affinities.[5,6] However, trends in proton affinities are reproduced reasonably well by the 4-31G basis.[7-10] Since relative proton affinities were of interest here, the 4-31G basis set was employed in this work. The relative values were checked by comparing the 4-31G results with the 6-31G*//4-31G results obtained from this work and ref 11 and 12. The notation 6-31G*//4-31G designates that the energy was obtained at the 6-31G* basis set level with use of the 4-31G optimum geometry.

No zero-point vibrational energy or electron correlation effects were taken into account. Zero-point energy corrections will lower the computed proton affinities by up to 10 kcal mol^{-1}.[5] In general, electron correlation corrections appear to be unimportant in these protonation reactions.[5]

The geometries of the neutral and protonated systems were optimized completely (within the given point group) assuming that the hydrogens of the alkyl groups are staggered. The 4-31G optimum geometries of HCN,[7] HNC,[7] $HCNH^+$,[7] CH_3CN,[11] CH_3NC,[11] CH_3CNH^+,[12] and CH_3NCH^+[12] have been published previously. The equilibrium structures were determined to 0.001 Å and 0.1° by the force relaxation method.[13]

Experimental Results and Discussion

The results of the equilibrium and bracketing measurements are presented in Table I. For comparison, the proton affinities (PAs) of the cyanides are also shown. The proton affinities of the isocyanides are always higher than those of the cyanide isomers. The difference may reflect primarily the fact that protonation of the isocyanides yields a C–H bond, while that of the isocyanides yields an N–H bond. Interestingly, ΔPA (columns 6 and 7, Table I) is constant at 11.5 ± 1 kcal/mol, regardless of the identity of the alkyl group. In other words, the effect of a given alkyl substituent on the PA of CH_3CN and CH_3NC is identical, despite their dissimilar electron-donor atoms. This suggests that the alkyl substituent effect is due primarily to the increased polarizability of the base as R enlarges, which would be identical in both classes of compounds.

Given the proton affinities, the heats of formation $\Delta H_f°$ of the $RNCH^+$ ions can be calculated if $\Delta H_f°$ of RNC is known. We used the experimental heats of isomerization of CH_3CN and C_2H_5CN to calculate the $\Delta H_f°$ of the corresponding isocyanides.[14] For the other compounds we assumed a constant value for $\Delta H°_{\text{isomerization}}$ of 20 kcal/mol, as indicated by theoretical results.[15]

The calculated $\Delta H_f°$ values can be used to derive several other thermochemical quantities. We note that the heats of isomerization ($RCNH^+ \rightarrow RNCH^+$) of the ions (Table I) range from 5 to 11 kcal/mol and are thus smaller by 11–15 kcal/mol than the heats of isomerization of the respective neutrals. Of course, while in the neutrals isomerization exchanges a C–C bond for a N–C bond, in the ions isomerization exchanges a C–C and a N–H bond for a H–C and a N–C bond, respectively. Therefore, unlike in the neutrals, in the ions compensating effects are possible.

Alkyl Cation Affinities of HCN, HNC, and Other Lone-Pair Donors. Correlations with Hydride Affinities

By using the thermochemical data it is possible to calculate the bond-dissociation energies $D°(R^+\text{–NCH})$, i.e., the alkyl cation affinities of HCN (Table I). Once again, these are substantially

Table I. Thermochemistry of Proton-Transfer Reactions $BH^+ + RNC \rightarrow RNCH^+ + B$ and Thermochemical Properties of Isocyanides and C_4H_9CN

BH^+	RNC	$\Delta G°_{335}$	GB(RNC)	$GB(RNC)_{av}$	PA(RNC)^b	PA(RCN)^c	$\Delta H°_f(R^+)^c$	$\Delta H°_f(RNCH^+)^d$	$\Delta H°_{isom}{}^e$	$D°(R^+\text{–NCH})^f$	$D°(R^+\text{–CNH})^f$
	HNC			182.4^c	190.2^c	171.4	365	225.1		171.2	190.0
$c\text{-}(CH_2)_4OH^+$	CH_3NC	0.1	191.3	191.5	199.3	188.4	262	206.9	11.9	87.1	118.0
$(C_2H_5)_2COH^+$		1.8	191.6								
$(n\text{-}C_3H_7)_2OH^+$	C_2H_5NC	$<0^g$	>194.5	195.9	203.7	192.6	216	194.8	9.8	53.2	
$(n\text{-}C_4H_9)_2OH^+$		0.0	195.9								
$(i\text{-}C_3H_7)_2COH^+$		$>0^g$	<197.0								
$(i\text{-}C_3H_7)_2COH^+$	$i\text{-}C_3H_7NC$	$<0^g$	197.0	197.7	205.5	194.3	191	184.5	7.5	38.5	
$(i\text{-}C_3H_7)_2OH^+$		$>0^g$	<198.4								
$(i\text{-}C_3H_7)_2OH^+$	$t\text{-}C_4H_9NC$	−1.1	199.4	199.7	207.5	195.5	166	175.1	5.2	22.9	
(pyrrole)H^+		0.9	199.4								
$C_6H_5NH_3^+$		2.2	200.3								
$(i\text{-}C_3H_7)_2OH^+$	C_6H_5NC	$<0^h$	>198.4	199.4	207.2	195.9	271	229.8	7.8	73.2	
(pyrrole)H^+		$>0^h$	<200.3								
$(CH_3)_2COH^+$	$t\text{-}C_4H_9CN$	1.0	189.9	187.7		195.5					
$1,3\text{-}(CH_3)_2C_6H_4H^+$		0.7	187.7								

^{a}All values in kcal/mol. ^{b}Derived from PA(RNC) = GB(RNC) + 7.8 kcal/mol (ref 19), where GB is the gas basicity. Proton affinities referred to $PA(NH_3)$ = 204 kcal/mol. ^{c}Reference 19. $^d\Delta H°_f(RNCH^+) = \Delta H°_f(RNC) + \Delta H°_f(H^+) - PA(RNC)$. $\Delta H°_f$ values as follows: CH_3NC 41.7 and C_2H_5NC 33.5 with use of $\Delta H°_f(RNC) = \Delta H°_f(RCN) + \Delta H°_f(RCN \rightarrow RNC)$, and taking the latter values from ref 14. For the other isocyanides, $\Delta H°_f(RCN \rightarrow RNC)$ = 20 kcal/mol is used (ref 15). $^e\Delta H°_{isom} = \Delta H°_f(RCNH^+ \rightarrow RNCH^+)$. $^fD°(R^+\text{–NCH}) = \Delta H°_f(R^+) + \Delta H°_f(HCN) - \Delta H°_f(RNCH^+)$, thermochemical values used as indicated. For analogous calculations of $D°(R^+\text{–CNH}^+)$, $\Delta H°_f(RCNH^+)$ values are taken from ref 19. ^{g}Bracketing experiments based on double resonance ion ejection. ^{h}Bracketing experiments based on reactivity.

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(4) Gaussian 82, release H, J. S. Binkley, M. Frisch, R. Krishnan, D. J. DeFrees, H. B. Schlegel, R. A. Whiteside, E. M. Fluder, R. Seeger, and J. A. Pople, 1982, Carnegie-Mellon University.

(5) Del Bene, J. E.; Frisch, M. J.; Raghavachari, K.; Pople, J. A. *J. Phys. Chem.* **1982**, *86*, 1529.

(6) Woodin, R. L.; Houle, F. A.; Goddard, W. A., III *Chem. Phys.* **1976**, *14*, 461.

(7) Latham, W. A.; Hehre, W. J.; Curtiss, L. A.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 6377.

(8) Kollman, P.; Rothenberg, S. *J. Am. Chem. Soc.* **1977**, *99*, 1333.

(9) Umeyama, H.; Morokuma, K. *J. Am. Chem. Soc.* **1976**, *98*, 4400.

(10) Del Bene, J. E.; Vaccaro, A. *J. Am. Chem. Soc.* **1976**, *98*, 7256.

(11) Lohr, L. L., Jr.; Hanamura, M.; Morokuma, K. *J. Am. Chem. Soc.* **1983**, *105*, 5541.

(12) Würthwein, E.-U. *J. Org. Chem.* **1984**, *49*, 2971.

(13) (a) Pulay, P. *Mol. Phys.* **1969**, *17*, 197. (b) Schlegel, H. B.; Wolfe, S.; Bernardi, F. *J. Chem. Phys.* **1975**, *63*, 3632.

(14) Bhagal-Vayjooee, M. H.; Collister, J.; Pritchard, H. O. *Can. J. Chem.* **1977**, *55*, 2634.

(15) Beach, D. B.; Eyermann, C. J.; Smit, S. P.; Xiang, S. F.; Jolly, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 536.

Table II. Correlations[a] of R^+–XH vs. R^+–H^- Bond Dissociation Energies, for R = CH_3^+, $C_2H_5^+$, *i*-$C_3H_7^+$, and *t*-$C_4H_9^+$, and Deviations for $C_6H_5^+$

XH	slope	intercept	corr coef	σ	dev($C_6H_5^+$)[b]	dev(H^+)[c]	$D°(CH_3^+\text{–XH})$	$D°(t\text{-}C_4H_9^+\text{–XH})$	PA(XH)
H_2O	0.69	–150.0	0.9998	0.4	18.7	38	68.5	11.0	166.5
CH_3OH	0.74	–149.6	0.9997	0.7	12.0	35	84.0	23.0	181.9
NH_3	0.80	–148.4	0.9996	0.8	1.7	31	105.2	39.0	204.0
CH_3NH_2[d]	0.85	–150.4			6.2	25	116.5		214.1
HNC	0.86	–149.5	0.9992	1.2	6.1	1	118.0	47.1	190.2
HCN	0.78	–156.0	0.9997	0.7	8.3	18	87.1	22.9	171.4
H_2S[e]	0.80	–166.0	0.9994	0.9		19	84.0	18.5	170.2

[a] Correlation for $D°(R^+\text{–X}) = bD°(R^+\text{–}H^-) + a$. All values are in kcal/mol and are based on thermochemical data from the present work and ref 19. [b] $\text{Dev}(C_6H_5^+) = D°(C_6H_5^+\text{–X})_{\text{exp}} - D°(C_6H_5^+\text{–X})_{\text{calcd}}$, where the experimental values are based on experimental proton affinities, regardless of the site of protonation, and the calculated values are based on correlation parameters. [c] $\text{Dev}(H^+) = D°(H^+\text{–X})_{\text{exp}} - D°(H^+\text{–X})_{\text{calcd}}$, where the experimental values are from experimental proton affinities (ref 19) and the calculated values are from the correlations, using $D°(H^+\text{–H}) = 398.2$ kcal/mol. [d] Based only on $D°(CH_3^+\text{–}NH_2CH_3)$ and $D°(C_2H_5^+\text{–}NH_2CH_3)$. Data for *i*-$C_3H_7^+$ and *t*-$C_4H_9^+$ are not available. [e] Based on three points. Data for *i*-$C_3H_7^+$ are not available.

smaller than the respective R^+–CNH bond-dissociation energies.

The $D°$ values should decrease with increasing stability of the carbonium ions, R^+, as is indeed seen in Table I. A general measure of the stability of a carbonium ion is the affinity of the ion for the electron-pair donor H^-, i.e., the hydride affinity or $D°(R^+\text{–}H^-)$. Therefore, one may expect a relationship between $D°(R^+\text{–}H^-)$ and $D°(R^+\text{–X})$. Figure 1 plots the attachment energies of the R^+ ions to the four electron-pair donors HCN, HNC, H_2O, and NH_3 vs. the hydride affinity. In fact, remarkably good linear relations, expressed as eq 7, are obtained for all of the alkyl ions and n-donors.

$$D°(R^+\text{–X}) = a + bD°(R^+\text{–}H^-) \qquad (7)$$

The statistics of the correlations are shown in Table II. Noteworthily, all of the correlation coefficients are above 0.999. In other words, the relative affinities of the aliphatic carbonium ions with respect to all of the n-donors are linearly related to each other, as well as to the hydride ion affinities. It is interesting that these correlations also apply to $D°(R^+\text{–CNH})$ which involves C–C bond dissociation.

Table II shows that the intercepts of all of the correlation lines, except those relating to the two weakest type of bonds, i.e., R^+–NCH and R^+–SH_2, are identical at –150 ± 1 kcal/mol. While the interpretation of this finding is not obvious, we note that the main difference between $D°(R^+\text{–X})$ and $D°(R^+\text{–}H^-)$ is that while both involve the dissociation of a σ bond, the latter also involves charge separation. In addition, notice that the extrapolation along the abscissa toward the origin of Figure 1 is in the direction of increasingly stabilized carbonium ions. Correspondingly, the ionization potentials (IPs) of the respective radicals in the sequence CH_3, C_2H_5, *i*-C_3H_7, and *t*-C_4H_9 decrease from 226 to 192, 173, and 159 kcal/mol, approaching asymptotically about 150 kcal/mol, which is the same as the value of the common intercept. In other words, in the limit of an "ideally stabilized carbonium ion" the σ bond-dissociation component in both $D°(R^+\text{–X})$ and $D°(R^+\text{–}H^-)$ vanishes. For this hypothetical ion, $D°(R^+\text{–}H^-)$ consists purely of the $R\cdot \rightarrow R^+ + e^-$ charge separation or ionization energy, and this term extrapolates, both from the IPs and from the correlations of Table II, to 150 kcal/mol.

$C_6H_5^+$ deviates from the linear correlations of the aliphatic carbonium ions (Figure 1 and Table II). Of course, with the phenyl compounds special resonance effects may be possible. However, the deviation is small in $C_6H_5^+\text{–}NH_3$, where ring or substituent protonation are energetically similar.[16] On the other hand, a very large divergence is observed for phenol when the experimental PA is used. For phenol, McIver et al.[17] suggest that the proton affinity of the oxygen function is lower by about 15 kcal/mol than that of the ring. Of course, when $C_6H_5^+\text{–}OH_2$ bond dissociation occurs, the oxygen-protonated form of $C_6H_5OH_2^+$ is pertinent. Using the proton affinity for oxygen protonation, we obtain a point close to the R^+–OH_2 correlation line. This implies that this correlation may be used as a quantitative test of the relative stabilities of ring protonated vs. substituent protonated aromatic species.

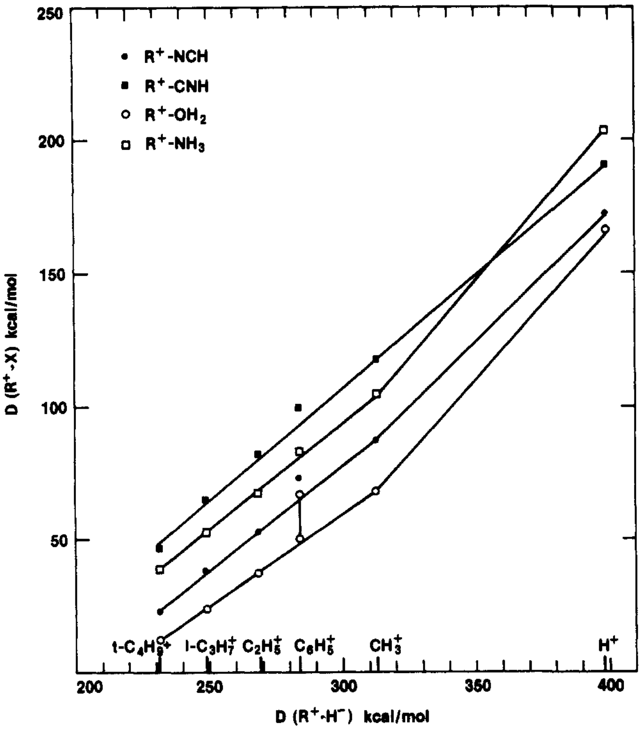

Figure 1. R^+–X bond-dissociation energies vs. hydride affinities (i.e., R^+–H^- bond-dissociation energies). Dissociation energies calculated by using data from the present work and ref 19 and 33. For $C_6H_5^+\text{–}OH_2$, lower point from estimated PA for oxygen protonation (ref 17), upper point from experimental PA. See correlation parameters in Table II.

With use of such reasoning, Figure 1 and Table II indicate that for both C_6H_5CN and C_6H_5NC ring protonation is more exothermic by about 8 kcal/mol than substituent protonation. This is inconsistent with the arguments of Lau and Kebarle, who suggest that the CN group of C_6H_5CN is protonated based on σ^+-substituent coefficients.[18] Collisional dissociation studies would be useful to resolve the question of the protonation site in aromatic cyanides and isocyanides.

The extrapolation of the correlation lines from R^+ = carbonium ions to H^+ is shown also in Figure 1 and Table II. In general, the proton affinity is higher by 18–38 kcal/mol than the correlations would predict. The deviation roughly decreases with increasing proton affinity of the electron pair donor. Therefore, carbonium ion affinities and proton affinities are not good quantitative predictors of each other, although qualitatively the relative ordering of the carbonium ion affinities of various n-donors follows the ordering of the proton affinities (Table II). However, the $D°(R^+\text{–CNH})$ values are higher than expected from the proton

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(16) Wood, K. V.; Burinsky, D. J.; Cameron, D.; Cooks, R. G. *J. Org. Chem.* **1983**, *48*, 5236 and references cited therein.

(17) DeFrees, D. J.; McIver, R. T.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 3853.

(18) Lau, Y. K.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 7452.

(19) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

Table III. Properties of the Bases Related to the EL, CT, and PL Components of the Proton Affinity

base	ΔE^a	$\epsilon_{1s}(B)^b$	μ^c	Δq_{CT}	ϵ_σ	% B[d] (σ-HOMO)	Δq_H(tot)	$\Delta q_\pi(C_1N)$
HNC	191.7	−11.278 45	2.65	0.513	−0.477 64	81	0.109	0.000
CH_3NC	207.6	−11.258 20	3.44	0.532	−0.457 86	82	0.255	0.042
C_2H_5NC	210.7	−11.255 54	3.50	0.538	−0.454 71	81	0.303	0.041
i-C_3H_7NC	211.9	−11.254 72	3.51	0.540	−0.453 02, −0.454 14[e]	82[f,g]	0.333	0.049
HCN	182.2	−15.586 42	3.21	0.456	−0.572 13	63	0.162	0.000
CH_3CN	198.4	−15.558 81	4.09	0.482	−0.547 89	58	0.261	0.055
C_2H_5CN	201.7	−15.556 22	4.19	0.486	−0.535 51	38	0.306	0.055
i-C_3H_7CN	203.9	−15.554 30	4.25	0.489	−0.524 41	18[g]	0.343	0.061

[a] Energy in kcal. [b] Energy in hartrees. [c] Calculated dipole moments in Debyes. The experimental dipole moments are 2.98, 3.92, 3.85, and 4.02 D for HCN, CH_3CN, CH_3NC, and C_2H_5CN, respectively.[32] [d] This parameter was calculated by summing the squares of the 2s and $2p_x$ coefficients. [e] Energies of the two nearly degenerate σ-HOMOs. [f] The combined percent electron density on the terminal carbon atom in the two nearly degenerate σ-HOMOs. The individual percentages are 57 ($\epsilon = -0.45302$ au) and 33 ($\epsilon = -0.45414$ au). [g] The $2p_y$ AOs (i.e., the other p orbital in the plane of the base) contribute to these MOs but have the wrong symmetry to overlap with the proton. The % B (σ-HOMO) is 90% and 20% for i-C_3H_7NC and i-C_3H_7CN, respectively, if these AOs are included in the calculations.

affinity of HNC, probably because this involves a C–C bond.

The $D°$ values for the above correlations are calculated from eq 8. The procedure can be reversed and the correlations in Table

$$D°(R^+–XH) = \Delta H°_f(R^+) + \Delta H°_f(XH) - \Delta H°_f(RXH^+) = \Delta H°_f(R^+) + \Delta H°_f(XH) - \Delta H°_f(RX) - \Delta H°_f(H^+) + PA(RX) \quad (8)$$

II used to predict, for example, proton affinities or $\Delta H_f°(R^+)$ provided the other entities in eq 8 are known.

The common intercepts of the plots (Figure 1) should be of help in predicting carbonium ion affinities of n-donors Y if the value of $D°(R^+–Y)$ for one R^+, e.g., CH_3^+, is known. For such cases correlation lines can be constructed by using the common intercept and the known CH_3^+–X dissociation energy.

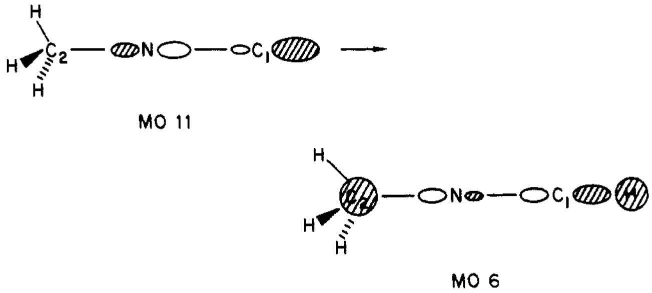
Ab initio Results and Analysis

In this section we apply ab initio calculations to examine some of the trends in the experimental data. We consider the protonation of HNC, CH_3NC, C_2H_5NC, i-C_3H_7NC, and their cyano counterparts.

A number of calculations have been reported in the literature on neutral and protonated HCN, HNC, CH_3CN, and CH_3NC. Several of the articles have been concerned with the rearrangement of HCN to HNC[20,21] and of CH_3CN to CH_3NC.[11,22,23] The latter was one of the reactions studied by Lohr et al.[11] in their work on thermal rearrangements on the C_2H_3N potential energy hypersurface. Some of the other calculations include the following. Würthwein[12] has investigated the structures and stabilities of seventeen isomers of $C_2H_4N^+$, including CH_3CNH^+ and CH_3NCH^+. Moffat[23] has compared the STO-3G structures and isomerization energies of CH_3CN, CH_3NC, C_2H_5CN, C_2H_5NC, i-C_3H_7CN, i-C_3H_7NC, and their protonated analogues formed by hydride abstraction. He has determined the stabilization energies of the carbonium ions, also.[23] Howell et al.[24] have probed the changes in σ-donating and π-accepting ability of CH_3NC and CH_3CN as a function of molecular geometry.

The proton affinities of HCN,[7,8] HNC,[7] CH_3CN,[8,11,12] and CH_3NC[11,12] have been computed earlier at the 4-31G//4-31G level (and other basis set levels[5,11,12,25]); however, to our knowledge, the proton affinities of the ethyl and isopropyl cyanides and isocyanides have not. In addition, no detailed analysis of the questions raised in the introduction has been made.

Scheme I



A. Geometries. The 4-31G optimum geometries of the neutral and protonated bases are presented in Figure 2. The data show that for both sets of neutral and both sets of protonated systems varying R changes corresponding bond lengths by 0.01 Å or less. Similar results were obtained from the STO-3G calculations on the neutral bases.[23] Furthermore, when the RCN systems are protonated, the C_1N bond length decreases by approximately 0.01 Å, the C_2C_3 bond length increases by approximately 0.01 Å, and the remaining bond lengths are affected very little for each R. The C_1N bond length shortening has been observed at other basis set levels, also.[5,24] When the RNC systems are protonated, the C_1N bond length decreases by approximately 0.04 Å, the C_2N bond length increases by approximately 0.04 Å, and the remaining bond lengths are affected very little for each R. Protonating RCN or RNC produces changes in the bond angles of no more than 3° for each R.

The origins of the variations in the C_1N and C_2N bond lengths brought about by protonation of RNC can be rationalized by comparing the orbital composition of the highest occupied σ molecular orbital (σ-HOMO) in the neutral base with the orbital composition of the molecular orbital (MO) with which it correlates in the protonated base. The modifications of the C_1N and C_2C_3 bond distances produced by protonating RCN are too small for their origins to be elucidated by this method; thus, they will not be discussed further here. The pair of orbitals (MO 11 and MO 6) is shown schematically below for CH_3NC (Scheme I), since it is the simplest system and is representative of the other two isocyanides. The analyses for C_2H_5NC and i-C_3H_7NC are complicated by their lower symmetry and by the near degeneracy of the two highest energy σ-MOs. Nevertheless, the H^+-induced charge redistributions are similar for all three molecules.

Scheme I shows that protonation of CH_3NC generates charge density changes in MO 11 that (1) greatly diminish the electron density in the C_1 (2s) atomic orbital (AO), (2) significantly diminish the electron density in the nitrogen 2s and $2p_x$ AOs (i.e., the p orbital along the C–N–C internuclear axis), and (3) increase the electron density in the C_2 (2s) AO. Furthermore, protonation causes the sign of the N ($2p_x$) AO to reverse. These changes reduce the C_1 (2s)–N (2s) antibonding overlap substantially, convert the C_1 (2s)–N ($2p_x$) overlap from antibonding to bonding,

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(20) Pearson, P. K.; Schaefer, H. F., III; Wahlgren, U. *J. Chem. Phys.* **1975**, *62*, 350.

(21) Komornicki, R.; Ishida, K.; Morokuma, K.; Ditchfield, R.; Conrad, M. *Chem. Phys. Lett.* **1977**, *45*, 595.

(22) Saxe, P.; Yamaguchi, Y.; Pulay, P.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1980**, *102*, 3718.

(23) Moffat, J. B. *Int. J. Quantum Chem.* **1981**, *19*, 771.

(24) Howell, J. A. S.; Saillard, J.-Y.; LeBeuze, A.; Jaouen, G. *J. Chem. Soc., Dalton Trans.* **1982**, 2533.

(25) Smith, S. F.; Chandrasekhar, J.; Jorgensen, W. L. *J. Phys. Chem.* **1982**, *86*, 3308.

(26) Pau, C.-F.; Hehre, W. J. *J. Phys. Chem.* **1982**, *86*, 321.

(27) Umeyama, H.; Morokuma, K. *J. Am. Chem. Soc.* **1977**, *99*, 1316.

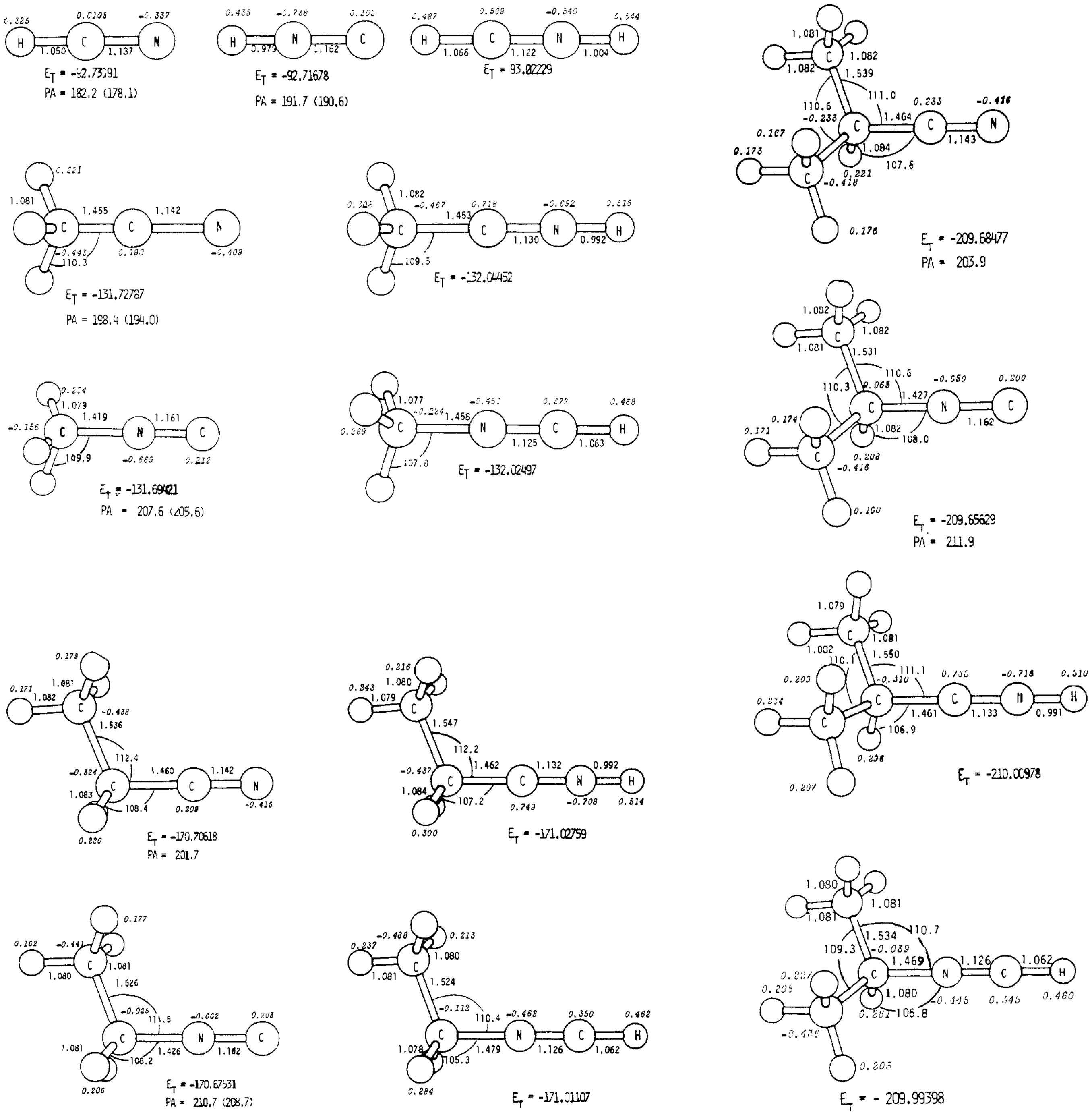

Figure 2. 4-31G optimum geometries, total energies, proton affinities, and atomic charges from population analysis (in italics) for the neutral and protonated cyanides and isocyanides. The 6-31G*//4-31G proton affinities (in kcal mol^{-1}) are in parentheses. The 4-31G total energies (in hartrees) and proton affinities for HCN, HNC, and $HNCH^+$ are from ref 7. The E_T's for CH_3CN and CH_3NC are from ref 11; the E_T's for CH_3CNH^+ and CH_3NCH^+ are from ref 12. Bond lengths in Å; bond angles in deg.

convert the C_1 ($2p_x$)–N ($2p_x$) overlap from bonding to antibonding, and convert the C_2 (2s)–N (2s, $2p_x$) overlap from nonbonding to antibonding. Since 63% of the electron density in MO 11 is localized in the C_1 (2s) AO (see Table III), the first two modifications are dominant for the C_1N bond. Thus, the overall result is a shortening of the C_1N bond and a lengthening of the C_2N bond. The C_1–N bond length change is not as great as might be expected from the large electron density shifts observed since competing effects are involved.

A similar comparison of the π-HOMO(s) shows that the electron density shifts in the π-HOMO(s) produced by protonation do not completely account for the observed bond length changes. These shifts would cause both the C_1N and the C_2N bonds to lengthen. Furthermore, when all of the π-orbitals are taken into account, the charge redistributions lead to bond length changes that essentially add out.

B. Energetics. The 4-31G total energies and the 4-31G and 6-31G*//4-31G proton affinities of the molecules considered are given in Figure 2. The computed proton affinities are universally too high compared to the experimental ones (Figure 2 and Table I), although the disparity is slightly worse for the RCN than for the RNC bases. This indicates that the ion–dipole component is larger than the polarization component of the proton affinities of RCN and RNC.[24] The overestimation of the calculated proton affinities can be primarily attributed to not correcting the values for the zero-point vibrational energy differences. However, the exaggerated bond polarities and dipole moments obtained at the 4-31G basis set level, particularly for the RCN molecules, contribute as well (see Table III).

The trends in the experimental proton affinities are quite well reproduced by both the 4-31G and 6-31G* computations (Figures 2 and 3). In fact, though the magnitudes of the 6-31G* inter-

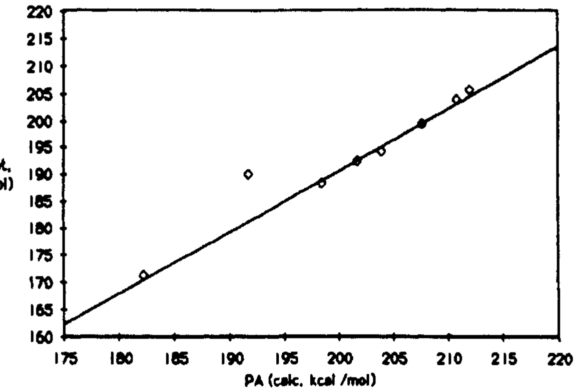

Figure 3. Experimental vs. 4-31G calculated proton affinities of the cyanides and isocyanides. The slope of the line is 1.14.

action energies are closer to the experimental ones than the 4-31G values are, there is very little difference in the relative energies obtained from the two basis sets. The only point that deviates significantly from the line in Figure 3 is the point for HNC. In view of the difficulty in measuring the experimental proton affinity of HNC[26] this disagreement is not unexpected, and we propose that the PA of HNC should be ~5 kcal mol^{-1} lower than the reported experimental value.[26]

C. Trends in the Proton Affinity. The proton affinity can be decomposed into three main terms, namely, the charge transfer (CT), electrostatic (EL), and polarization (PL) terms.[8,27] The electrostatic energy is due to the ion-molecular multipole interaction, and the polarization energy is due to the ion-induced molecular multipole interaction. The polarization and charge transfer components are often combined and called the delocalization (DL) component. Kollman and Orthenberg[8] have shown that for molecules with polarizable bonds, i.e., unsaturated bases such as carbonyls and nitriles, the magnitudes of the three constituents are comparable. Presumably, the same will be true of the isonitrile bases as well.

Changes in the molecular dipole moment along the bond axis μ and in the orbital energies of the proton-accepting atom (i.e., the terminal C or N) ϵ_{1s} (B) have been shown to parallel changes in the electrostatic contribution to the proton affinity.[8-10,28,29] The charge transfer term for these bases is dependent on the energy of the highest occupied σ molecular orbital ϵ_σ and on the degree of localization of the electron density in the σ-HOMO on the terminal atom B, % B (σ-HOMO). The CT is directly related to % B (σ-HOMO) and indirectly related to ϵ_σ. Information can be obtained about the charge transfer contribution from Mulliken population analysis Δq_{CT},[30] also, especially for a series of related molecules.

Alkyl substituents are known to increase the polarizability of a base, since they supply more electron density to the proton-accepting atom than a hydrogen does, i.e., alkyl substitution yields a larger delocalization of the positive charge transferred to the base.[8,9] The polarizability is, therefore, linked directly to the total amount of charge transferred from the alkyl hydrogens to the rest of the base Δq_H(tot) and to the net amount of π-electron density gained in the C_1N bond $\Delta q_\pi(C_1N)$. The latter correlation holds since the σ-electron density lost by the C_1N bond upon protonation is partially replaced by the π-electron density gained by this bond. The mechanism by which electron density is redistributed through the π-orbitals is readily described in terms of a simple PMO treatment of the interaction between the R group and the CN, HCN^+, or HNC^+ moiety. This type of charge redistribution will contribute to the stabilization of the cations if (1) a filled π-orbital on the R fragment interacts with an empty π-orbital on the CN or $HCN^+(HNC^+)$ fragment, i.e., a hyperconjugative interaction occurs, and (2) the R-$NCH^+(CNH^+)$ interaction is stronger than the R–NC(CN) interaction.

Table IV. Differences δ(RNC–RCN) in the Parameters Related to the Proton Affinity

parameter	R = H	R = CH_3	R = C_2H_5	R = *i*-C_3H_7
$\delta\Delta E^a$	9.5	9.2	9.0	8.0
$\delta\epsilon_{1s}(B)^b$	4.30797	4.30061	4.30068	4.29958
$\delta\mu^c$	−0.56	−0.65	−0.69	−0.74
$\delta\Delta q_{CT}$	0.053	0.050	0.052	0.051
$\delta\epsilon_\sigma{}^b$	0.09449	0.09003	0.08080	0.07139
δ % B (σ-HOMO)	18	24	43	64
$\delta\Delta q_H$(tot)	−0.053	−0.006	−0.003	−0.010
$\delta\Delta q_\pi(C_1N)$	0.000	−0.013	−0.014	−0.012

[a] Energy in kcals. [b] Energy in hartrees. [c] Dipole moments in Debyes.

Table III lists μ, ϵ_{1s}(B), ϵ_σ, % B (σ-HOMO), Δq_{CT}, Δq_H(tot), and $\Delta q_\pi(C_1N)$. The 4-31G data are given in the table. The 4-31G atomic charges obtained by Mulliken population analysis[30] are presented in Figure 2.

The Proton Affinity of RCN vs. RNC. The results in Tables I and III demonstrate that the calculated and experimental proton affinities of RNC are larger than those of RCN for every R. Of course, for R = H, the proton affinity of the isocyanide is larger than the proton affinity of the cyanide since HNC is less stable than HCN. For the other R's, the situation is more complicated because the cation is not identical for the two bases. The disparity in the proton affinities of the isonitriles and nitriles for R = CH_3, C_2H_5, and *i*-C_3H_7 can be accounted for primarily by the fact that the isonitriles are stronger σ-donors. Consider the charge transfer parameters for the two types of bases (Table III). Howell et al.[24] have reported that the energy of the σ-lone-pair orbital is higher for CH_3NC than for CH_3CN and that the percent electron density in this orbital on the terminal atom is larger for the former than the latter molecule. (The data in Table III for these parameters are from this work rather than from Howell et al.'s[24] since they used a different basis set and a different geometry in their calculations.) The larger charge transfer for the isocyanide is reinforced by its larger Δq_{CT} (Table III) and by the slightly greater mixing of the H^+ atom into the cation orbital that correlates with the σ-HOMO of the isocyanide (the % H^+ is 8.6 for CH_3NC and 7.7 for CH_3CN). As expected, the same trends hold for the other R groups as well (Table III). Consequently, the charge transfer term in the interaction energy is bigger for the isocyanides than it is for the cyanides.

The 1s orbital energies ϵ_{1s}(B) (Table III) predict that the electrostatic component of the proton affinity is also greater for RNC than for RCN. On the other hand, the calculated dipole moments μ are larger for RCN than for RNC. However, the experimental values of μ for CH_3CN (3.92 D)[32] and CH_3NC (3.85 D)[32] suggest that the calculated dipole moments are overestimated for the nitriles and underestimated for the isonitriles and that their dipole moments are actually similar in magnitude for a given R.

The magnitude of the polarization term is essentially equivalent for the cyanides and isocyanides with the same R. There is very little difference in the amount of charge transferred from the alkyl hydrogens to the rest of the base and in the net amount of π-charge transferred to the C_1N bond (Table III) for a specific pair of bases. Thus, the lower proton affinity of RCN compared to that of RNC for a given R is due to weaker charge transfer and electrostatic interactions for RCN. This agrees with the observations of others on the causes of the relative proton affinities of bases of similar structure, such as NH_3 vs. H_2O.[8,9]

Not only are the RNC proton affinities larger for each R but they are larger by approximately equal amounts, i.e., 11.5 ± 1 kcal mol^{-1}, for R = CH_3, C_2H_5, and *i*-C_3H_7 (Table I). In order to understand the reason for the consistency in the ΔPA(RNC–RCN)'s, consider the differences δ(RNC–RCN) for R = CH_3,

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(28) (a) Martin, R. L.; Shirley, D. A. *J. Am. Chem. Soc.* **1974**, *96*, 5299. (b) Mills, B. E.; Martin, R. L.; Shirley, D. A. *Ibid.* **1976**, *98*, 2380.

(29) Catalán, J.; Mó, O.; Pérez, P.; Yáñez, M. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1409.

(30) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833, 1841, 2338, 2343.

(31) Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1978**, *100*, 6572.

(32) *Handbook of Chemistry and Physics*, 59th ed.; Weast, R. C., Ed.; 1978; p E-63.

(33) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Supplement 1.

C_2H_5, and i-C_3H_7 in the parameters μ, Δq_{CT}, $\epsilon_{1s}(B)$, $\Delta q_{\pi}(C_1N)$, and Δq_H(tot) (Table IV). All of these differences have very similar magnitudes regardless of R. Any dissimilarities in them can be accounted for by the fact that the $\delta\Delta E$(RNC–RCN) values are not exactly equal, particularly for R = i-C_3H_7, at 9.2, 9.0, and 8.0 kcal mol^{-1}, respectively. The only parameters for which the δ(RNC–RCN) values are not nearly equivalent for each R are ϵ_σ and % B (σ-HOMO) (Table IV). The $\delta\epsilon_\sigma$ values decrease as R gets bigger, suggesting that the RCN molecules are becoming proportionally better bases than the RNC molecules as R gets bigger. In contrast, the inequalities in % B (σ-HOMO) increase as R gets bigger, suggesting that the RCN molecules are becoming proportionally poorer bases as R gets bigger. Thus, the two effects add out and $\delta\Delta q_{CT}$ is identical for all three alkyl groups (Table IV). The net result is that, rather than having compensatory effects among the three components involved, the ΔPAs are equivalent for R = CH_3, C_2H_5, and i-C_3H_7 because the ΔET and the ΔDL terms have essentially the same magnitudes for all of the R's.

With the exception of $\delta\Delta q_H$(tot) the above analysis holds for R = H as well, which is not unexpected since the calculated $\delta\Delta E$ is 9.5 kcal mol^{-1} for R = H. The value of $\delta\Delta q_H$(tot) deviates from the others because N–H and C–H hydrogens are being compared when R = H.

The Alkyl Effect. Other researchers[8,9] have shown that for many bases the increase in the proton affinity that occurs when a hydrogen is replaced with an alkyl group is primarily due to the increase in the polarizability of the base. In fact, in some cases, the electrostatic interaction energy is actually decreased by the substitution.[8,9] In contrast, Kollman and Rothenberg[8] have found that the PL, EL, and CT contributions all become larger upon methyl substitution of HCN, although ΔCT is small. Comparing the data in Table III for CH_3CN vs. HCN and for CH_3NC vs. HNC one sees that μ, q_H(tot), and $\Delta q_\pi(C_1N)$ are bigger and that $\epsilon_{1s}(B)$ and ϵ_σ are less stable for both methyl-substituted bases. (Some of the values reported in both this paper and ref 8 differ since they used experimental geometries.) The above is also true for R = C_2H_5 and i-C_3H_7 compared to R = H. This suggests that the origins of the alkyl substituent effect are similar for the cyanides and isocyanides.

Although there is a correlation between $\Delta q_\pi(C_1N)$ and the PA, notice that all of the magnitudes of $\Delta q_\pi(C_1N)$ are quite small. This indicates that the redistribution of electron density through the π-orbitals makes only a minor contribution to the alkyl effect. The reason for this is that for both sets of neutral and protonated bases, the filled π-orbitals on the R group interact with only the *filled* π-orbitals on the CN, HNC^+, or HCN^+ moiety.

The enlargement of the proton affinity associated with replacing a hydrogen on a carbon α to the C_1N group is considerably smaller than it is for replacing a hydrogen on the C_1N group itself (Table I and Figure 2). The much reduced changes in all of the parameters in Table III for the former substitution are consistent with this observation. In fact, the only parameters that show significant variations as the size of the alkyl group increases from CH_3 to i-C_3H_7 are Δq_H(tot) for both sets of bases and ϵ_σ and % B (σ-HOMO) for the isocyanide bases. The latter modifications compensate each other. Thus, the data indicate that the increase in the polarizability of the nitrile or isonitrile base resulting from this type of exchange is the primary cause of the increase in the proton affinity. Since the magnitudes of the proton affinity changes are essentially equivalent for the two sets of bases, the magnitudes of the polarizability changes must be essentially equal, also, in agreement with the analysis presented in an earlier section. Umeyama and Morokuma[9] obtained similar results when they compared ethylamine with methylamine.

Acknowledgment. The support of the Air Force Geophysics Laboratory Information Resources Center is gratefully acknowledged.

Note Added in Proof. Preliminary data obtained with use of larger basis sets and including correlation corrections support the conclusions presented in this article. These data will be reported in a subsequent paper.[34]

Registry No. CH_3NC, 593-75-9; C_2H_5NC, 624-79-3; i-C_3H_7NC, 598-45-8; t-C_4H_9NC, 7188-38-7; C_6H_5NC, 931-54-4; $CH_3NC{\cdot}H^+$, 84756-51-4; $C_2H_5NC{\cdot}H^+$, 102397-33-1; i-$C_3H_7NC{\cdot}H^+$, 102397-34-2; t-$C_4H_9NC{\cdot}H^+$, 102397-35-3; $C_6H_5NC{\cdot}H^+$, 102397-36-4; CH_3CN, 75-05-8; C_2H_5CN, 107-12-0; i-C_3H_7CN, 78-82-0; t-C_4H_9CN, 630-18-2; C_6H_5CN, 100-47-0; $CH_3CN{\cdot}H^+$, 20813-12-1; $C_2H_5CN{\cdot}H^+$, 19003-56-6; i-$C_3H_7CN{\cdot}H^+$, 70019-67-9; t-$C_4H_9CN{\cdot}H^+$, 98720-83-3; $C_6H_5CN{\cdot}H^+$, 56683-68-2.

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(34) Deakyne, C. A.; Meot-Ner (Mautner), M., manuscript in preparation.