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The Carbon Lone Pair as Electron Donor. Ionic Hydrogen Bonds in Isocyanides

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Abstract: Hydrogen bond dissociation energies ($\Delta H°_D$) in protonated dimer ions containing isocyanides were measured by pulsed high-pressure mass spectrometry, and the interactions were analyzed by ab initio calculations. Strong bonding (80−105 kJ/mol (19−25 kcal/mol)) is observed when the carbon lone pair is the electron donor, i.e. in the complexes of isocyanides with protonated amines and protonated isocyanides ($R_3NH^+\cdots CNR$ and $RNCH^+\cdots CNR$ complexes). The bonding is weaker (60−90 kJ/mol (14−21 kcal/mol)) in the complexes of oxygen bases with protonated isocyanides, i.e. in $RNCH^+\cdots O$-type complexes. Inverse linear correlations between $\Delta H°_D$ and the proton affinity difference of the components show slopes of −0.22 for $R_3NH^+\cdots CNR$- and −0.25 for $RNCH^+\cdots O$-type complexes. The intercepts yield intrinsic bond strengths ($\Delta PA = 0$) of 107.7 (25.7 kcal/mol) and 100.0 kJ/mol (23.9 kcal/mol), respectively. Geometry optimizations were carried out at four calculational levels, the largest of which is MP2/6-31+G(d,p). Single-point energies were obtained with increasingly flexible basis sets up to cc-pVTZ+. Trends in dissociation energies within the cyanide and isocyanide series of complexes and between the two series of complexes hold for every basis set considered. Calculated and experimental $\Delta H°_D$ values agree within the standard uncertainty of ±6 kJ/mol (1.5 kcal/mol) for only four of the nine complexes for which experimental data are available. The hydrogen bonding properties of sp-type carbon vs nitrogen lone pairs are illustrated by comparing analogous isocyanide and cyanide complexes. The relative importance of the electrostatic and delocalization components of the dissociation energy is different for the two sets of complexes, with delocalization effects being more important for the isocyanides.

Introduction

Strong ionic hydrogen bonds have been observed in complexes of oxygen and nitrogen bases. The bond strengths in such dimers, bonded by $NH^+\cdots N$, $NH^+\cdots O$, and $OH^+\cdots O$ interactions, range up to 145 kJ/mol (35 kcal/mol).[1−3] In contrast, unconventional $(CH_3)_4N^+(B)$ and $(CH_3)_3O^+(B)$ complexes with $CH^+\cdots N$ or $CH^+\cdots O$ hydrogen bonds have binding energies of 38−75 kJ/mol (9−18 kcal/mol).[4] Unconventional ionic hydrogen-bonded complexes with NH^+ groups bonded to π-bonds or to aromatic rings have similar binding energies.[5]

An additional type of unconventional ionic hydrogen bond occurs when carbon lone pairs are available as electron donors, such as in isocyanides and carbenes. One question of interest is whether the carbon lone pair functions as efficiently as an electron donor as the more common oxygen and nitrogen lone pairs do.

We have found that carbon lone pairs are strong electron donors when isocyanides bind to carbonium ions[6] or to a proton,[7] where the reactions form covalent C−C and C−H bonds. However, the interactions can be different for protonated hydrogen-bonded systems, e.g. $NH^+\cdots N$, $NH^+\cdots O$, and $OH^+\cdots O$

interactions are predominantly electrostatic.[8,9] Although recent experimental[10−14] and computational[15] studies have been carried out on neutral complexes for which an isocyano carbon is the electron-donating atom, the behavior of carbon lone pairs in ionic hydrogen bonds is unexplored. In this work we investigate this behavior in complexes of isocyanides both experimentally and theoretically.

We also examine complexes for which protonated isocyanides are the proton donors. These complexes contain unconventional $CH^+\cdots O$ hydrogen bonds, such as those found in the complexes of quaternary ammonium ions with oxygen compounds.[4] The sp-bonded CH^+ proton in isocyanides may be more positively charged than the sp^3-bonded methyl proton in quaternary ions. This would make the isocyanide CH^+ a stronger proton donor, but the question is whether it is comparable in strength to the usual NH^+ and OH^+ donors.

Experimental and Computational Details

The experimental measurements were done on the NIST pulsed high-pressure mass spectrometer with standard methods.[16] Reaction mixtures were prepared in a 3-L bulb heated to 150 °C and were allowed to

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(1) Keesee, R. G.; Castleman, A. W. *J. Phys. Chem. Ref. Data* **1986,** *15,* 1011.

(2) Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1973,** *95,* 3504.

(3) Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1984,** *106,* 1265.

(4) Meot-Ner (Mautner), M.; Deakyne, C. A. *J. Am. Chem. Soc.* **1985,** *107,* 469.

(5) Deakyne, C. A.; Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1985,** *107,* 474.

(6) Deakyne, C. A.; Meot-Ner (Mautner), M. *J. Phys. Chem.* **1990,** *94,* 232.

(7) Meot-Ner (Mautner), M.; Karpas, Z.; Deakyne, C. A. *J. Am. Chem. Soc.* **1986,** *108,* 3913.

(8) Kollman, P.; McKelvey, J.; Johansson, A.; Rothenberg, S. *J. Am. Chem. Soc.* **1975,** *97,* 955.

(9) Deakyne, C. A.; Meot-Ner (Mautner), M.; Campbell, C. L.; Hughes, M. G.; Murphy, S. P. *J. Chem. Phys.* **1986,** *84,* 4958.

(10) Legon, A. C.; Lister, D. G.; Warner, H. E. *J. Am. Chem. Soc.* **1992,** *114,* 8177.

(11) Legon, A. C. *J. Chem. Soc., Perkin Trans.* **1992,** *2,* 329.

(12) Legon, A. C.; Lister, D. G.; Rego, C. A. *Chem. Phys. Lett.* **1992,** *189,* 221.

(13) Legon, A. C.; Thorn, J. C. *J. Mol. Struct.* **1992,** *270,* 449.

(14) Legon, A. C.; Lister, D. G.; Warner, H. E. *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 202.

(15) Del Bene, J. E. *J. Am. Chem. Soc.* **1993,** *115,* 1610.

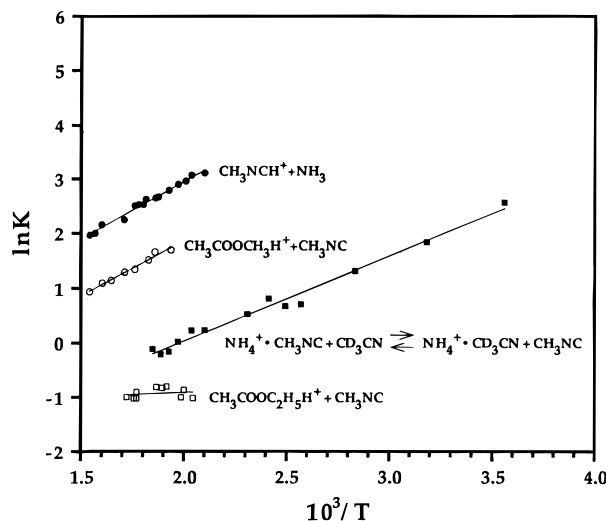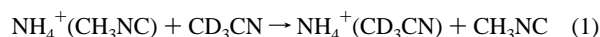(16) Meot-Ner (Mautner), M.; Sieck, L. W. *J. Am. Chem. Soc.* **1991,** *113,* 4448.

Figure 1. Van't Hoff plots for proton transfer reactions $AH^+ + B \leftrightarrow BH^+ + A$ for the reactants as shown and for the ligand exchange reaction as shown.
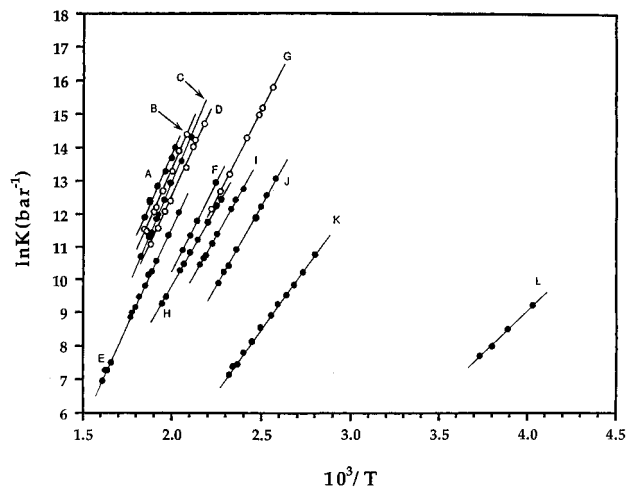

Figure 2. Van't Hoff plots for the association reactions, $AH^+ + B \rightarrow AH^+(B)$. The resulting complex ions were as follows: (A) $NH_4^+(CH_3NC)$; (B) $C_2H_5NCH^+(C_2H_5NC)$; (C) $CH_3NCH^+(CH_3NC)$; (D) $CH_3NH_3^+(CH_3NC)$; (E) $CH_3NH_3^+(C_2H_5NC)$; (F) $CH_3NCH^+(CH_3OCH_3)$; (G) $(CH_3)_2NH_2^+(CH_3NC)$; (H) $CH_3NCH^+(CD_3CN)$; (I) $(CH_3)_3NH^+(CH_3NC)$; (J) $CH_3NCH^+(CH_3OH)$; (K) $CH_3NCH^+(H_2O)$; and (L) $CH_3CNCH_3^+(H_2O)$.

flow to the ion source through glass and stainless steel lines also heated to 150 °C. The reaction mixtures contained $5 \times 10^{-3} - 1\%$ of the reactants or ligands of interest in N_2 or CH_4 carrier gas (total pressures, 4−6 mbar). Trace amounts of $CHCl_3$ were added as an electron capture agent to increase ion residence times. The $CH_3CNCH_3^+$ ion was prepared by methylation of CH_3CN in carrier gas containing CH_3Cl. The mixtures were ionized by 1-ms pulses of 1000 eV electrons, and the ion intensities were observed to further reaction times of 2−5 ms.

Samples of CH_3NC and C_2H_5NC were prepared by the methods of Casanova et al.[17] The other samples were from commerical sources and were used as purchased. We note that isocyanides can isomerize to the respective cyanides and that for CH_3NC the homogeneous kinetics are known.[18] From the kinetic data we calculate that even with the most efficient bath gas, the half-life of the CH_3NC isomerization is $>2.5 \times 10^2$ s at our highest experimental temperature of 550 K at a total pressure of 7 mbars. This is at least three orders of magnitude slower than the total exchange time of the sample in the ion source, which is <0.1 s. Furthermore, homogeneous or heterogeneous isomerization can cause substantial deviation from linearity in van't Hoff plots,[19] but the van't Hoff plots in Figures 1 and 2 show no such deviation up to the highest experimental temperatures. In addition, as a specific check for isomerization, we measured exchange reaction 1 from 280 to 540 K. If the CH_3NC isomerized to CH_3CN, the two

$$NH_4^+(CH_3NC) + CD_3CN \rightarrow NH_4^+(CD_3CN) + CH_3NC \quad (1)$$

ligands would be identical, except for small isotope effects, and $\Delta H°$ and $\Delta S°$ would be approximately zero. However, the results give non-zero values consistent with the respective clustering values[1] (Table 3 below), and the van't Hoff plot is linear over a wide temperature range (Figure 1). Thus, the isomerization rate parameters, the linear van't Hoff plots, and the internal consistency of the data all suggest that isomerization is not significant.

For the thermochemical data obtained from the van't Hoff plots, the standard uncertainty for the component arising from random effects is derived from the standard deviations of the slopes (for $\Delta H°$) and intercepts (for $\Delta S°$) in the least-squares fit to a linear regression analysis. The indicated uncertainties are these values multiplied by a coverage factor. The coverage factor was obtained from the temperature distribution for a confidence interval of 0.95 with $n - 2$ degrees of freedom, where n is the number of points on each plot. An independent estimate of the uncertainty arising from both random and systematic

effects is given by Meot-Ner and Sieck,[16] by Hunter and Lias,[20] and by replicate data sets for association reactions from various sources in ref 1. The results suggest a standard uncertainty of ±6 kJ/mol for $\Delta H°$ and of ±8 J/(mol·K) for $\Delta S°$.

The dimers investigated computationally are $NH_4^+(HCN)$, $NH_4^+(HNC)$, $NH_4^+(CH_3CN)$, $NH_4^+(CH_3NC)$, $CH_3NH_3^+(HCN)$, $CH_3NH_3^+(HNC)$, $CH_3NH_3^+(CH_3CN)$, $CH_3NH_3^+(CH_3NC)$, $CH_3CNH^+(CH_3CN)$, $CH_3CNH^+(CH_3NC)$, $CH_3NCH^+(CH_3CN)$, and $CH_3NCH^+(CH_3NC)$. Fully optimized geometries of these protonated dimers were computed with the ab initio Gaussian 90[21] and 92[22,23] series of programs, at the Hartree−Fock level with the 3-21G and 6-31G(d) basis sets and at the correlated MP2 level with the 6-31+G(d) and 6-31+G(d,p) basis sets. The cores of the non-hydrogen atoms were kept frozen for the latter calculations.[24,25] Reported bond lengths represent convergence to 0.001 Å and bond angles to 0.1°. Normal-mode vibrational frequencies were obtained at all four levels for which optimized structures were computed to confirm that the optimized structures are equilibrium structures and to determine zero-point energies (ZPEs) and heat capacity corrections.[26,27] The HF/3-21G and HF/6-31G(d) vibrational frequencies have been adjusted by the usual factor of 0.89.[28] Recently Grev et al.[29] recommended that calculated zero-point energies (ZPEs) be scaled

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

(18) Schneider, F. W.; Rabinovitch, B. S. *J. Am. Chem. Soc.* **1962**, *84*, 4215.

(19) Meot-Ner (Mautner), M.; Sieck, L. W. *Int. J. Mass Spectrom. Ion Proc.* **1991**, *109*, 187.

(20) Hunter, E. P.; Lias, S. G. *J. Phys. Chem. Ref. Data* Submitted for publication.

(21) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzalez, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian 90, Revision F, 1990; Gaussian, Inc.: Pittsburgh, PA.

(22) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian 92, Revision C, 1992; Gaussian Inc.: Pittsburgh, PA.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian 92/DFT, Revision G.1, 1993; Gaussian, Inc.: Pittsburgh, PA.

(24) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(25) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.

(26) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem. Symp.* **1979**, *13*, 325.

(27) Pitzer, K. S. *Quantum Chemistry*; Prentice Hall: Englewood Cliffs, NJ, 1961.

(28) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, NY, 1986.

differently from vibrational frequencies. Therefore, the HF/3-21G and HF/6-31G(d) ZPEs have been adjusted by their suggested factor of 0.91. The MP2/6-31+G(d) and MP2/6-31+G(d,p) vibrational modes and zero-point energies are unscaled. The electronic energies, ZPEs, thermal vibrational, rotational, and translational terms, and pressure−volume work term were utilized to compute enthalpies of reaction.[30] Torsional vibrational modes characterized by scaled frequencies of <500 cm^{-1} were treated as pure rotations.[28]

The protocol recommended for hydrogen-bonded systems calls for optimizing geometries with the MP2/6-31+G(d,p) model.[15,31,32] Unfortunately, this model is still impractical (and possibly infeasible) for larger clusters. In fact, the MP2/6-31+G(d,p) harmonic vibrational frequencies for $CH_3CNH^+(CH_3CN)$, $CH_3NCH^+(CH_3CN)$, and CH_3-$NCH^+(CH_3NC)$ had to be determined numerically, since insufficient disk space was available (>3 Gbytes was needed) to determine them analytically. Thus, we have included the three other models in this study. Although only the MP2/6-31+G(d,p) results will be discussed in detail, we will briefly compare the geometries, ZPEs, and thermal vibrational energies obtained with the four models. Additional information is supplied as Supporting Information.

Single-point calculations with several more flexible basis sets were carried out with HF/6-31G(d) and MP2/6-31+G(d,p) geometries. The 6-31+G(d), 6-31+G(2d,2p), and 6-311++G(2d,2p) basis sets were used with the HF/6-31G(d) geometries; the 6-31+G(2d,2p), 6-311++G-(2d,2p), and four augmented Dunning[33,34] correlation consistent basis sets were used with the MP2/6-31+G(d,p) geometries. The cc-pVXZ+ basis sets, X = D and T, contain diffuse sp functions on the non-hydrogen atoms.[31] The aug-cc-pVDZ basis contains s, p, and d diffuse functions on the heavy atoms and s and p diffuse functions on the hydrogens,[34] whereas the aug′-cc-pVDZ basis is aug-cc-pVDZ minus the diffuse functions on the hydrogens. Electron correlation was included via Møller−Plesset perturbation theory (MPn)[24,25] and via infinite-order quadratic configuration interaction theory with noniterative incorporation of triple excitations (QCISD(T)).[35] The latter calculations were performed since MP hydrogen bond energies are sometimes slowly convergent. Thus, the theoretical models recommended by Del Bene (MP4/cc-pVTZ+//MP2/6-31+G(d,p))[15,31,32] and by Pudzianowski (MP2/6-311++G(2d,2p)//MP2/6-31+G(d,p))[36] for the reliable treatment of hydrogen bonding in neutral and cationic complexes have been considered in this work. Although the discussion will focus on the effective QCISD(T)/cc-pVTZ+//MP2/6-31+G(d,p) binding energies, we will briefly compare the results obtained with all of the computational procedures. The remaining calculated binding energies are supplied as Supporting Information.

The dissociation energies have not been corrected for basis set superposition error (BSSE). Cook et al.[37] have pointed out that the use of ghost functions with correlation treatments leads to special problems that do not occur with self-consistent-field (SCF) treatments. Counterpoise calculations create a set of spurious virtual orbitals that are not important at the SCF level but cause an overcorrection at the correlated level. The computations on neutral and ionic clusters carried out by Pudzianowski[36] and Del Bene[31] support Cook et al.'s observation.

Experimental and Computational Results and Analysis

A. The Proton Affinity of CH₃NC. The proton affinity (PA) of CH_3NC was measured by ion cyclotron resonance in this laboratory[7] and by SIFT by Knight et al.[38] Both experi-

(29) Grev, R. S.; Janssen, C. L.; Schaefer, H. F., III. *J. Chem. Phys.* **1991**, *95*, 5128.

(30) Del Bene, J. E. *Mol. Struct. Energetics* **1986**, *1*, 319.

(31) Del Bene, J. E. *Int. J. Quantum Chem. Quantum Chem. Symp.* **1992**, *26*, 527.

(32) Del Bene, J. E.; Shavitt, I. *J. Mol. Struct. (THEOCHEM)* **1994**, *307*, 27.

(33) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(34) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(35) Wiese, W. L.; Weiss, A. W. *Phys. Rev.* **1968**, *175*, 50.

(36) Pudzianowski, A. T. *J. Chem. Phys.* **1995**, *102*, 8029.

(37) Cook, D. B.; Sordo, J. A.; Sordo, T. L. *Int. J. Quantum Chem.* **1993**, *48*, 375.

(38) Knight, J. S.; Freeman, C. G.; McEwan, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1404.

Table 1. Thermochemistry^a of Proton Transfer Reactions BH^+ + $CH_3NC \leftrightarrow CH_3NCH^+$ + B and the Proton Affinity of CH_3NC

B	$\Delta H°$	$\Delta S°$	PA(B)^b	PA(CH₃NC)
CH_3COOCH_3	−16.5(1.9)	−17.5(4.2)	823.0	839.5
$CH_3COOC_2H_5$	−1.4(4.8)	−10.3(9.7)	835.7	837.1
NH_3	17.5(1.1)	10.4(3.6)	854.0	836.5
			av	837.7 ± 2.6^c

^{a} $\Delta H°$ and PA in kJ/mol, $\Delta S°$ in J/(mol·K). Uncertainty estimates in parentheses, see text. ^{b} From ref 20. ^{c} Weighted average of the three values, with the indicated standard uncertainty calculated from the standard deviation of the slopes of the van't Hoff plots multiplied by a standard coverage factor of 2.[71]

ments were single-temperature determinations of the $\Delta G°$ of proton transfer reactions with the $\Delta H°$ and PA calculated by using assumed $\Delta S°$ values. The results from the two sources differed by 8.8 kJ/mol (2.1 kcal/mol). We therefore redetermined this PA value via temperature studies vs three reference compounds. Van't Hoff plots are given in Figure 1 and the results are summarized in Table 1. Individual PA values for the reference compounds are taken from the recent updated database by Hunter and Lias.[20] Referenced to the recommended scale, the present experimental measurements give PA(CH₃NC) = 837.7 kJ/mol (200.2 kcal/mol).

Since the relative hydrogen bond strengths of many complexes have been found to correlate with the relative proton affinities of the electron donors,[39] it is important to check whether the experimental ordering of the proton affinities of CH₃CN, CH₃NC, HCN, and HNC is reproduced by our calculations. Table 2 compares the experimental and calculated proton affinities of these four molecules. The values reported in the table as our best estimates for the proton affinities correspond effectively to calculations at the QCISD(T)/cc-pVTZ+ level on MP2/6-31+G(d,p) geometries. QCISD(T) total energies were obtained with three different basis sets, namely, cc-pVDZ+, aug′-cc-pVDZ, and aug-cc-pVDZ. For any given protonation reaction, the difference in the QCISD(T) and MP2 contributions to the electron correlation energy is nearly independent of the basis set utilized, varying by no more than 1 kJ/mol. Since the difference in these two contributions appears to be additive, we have adjusted each MP2/cc-pVTZ+ proton affinity by an amount equal to the average of the three differences (for that particular reaction) rounded off to the nearest 0.5 kJ/mol (0.1 kcal/mol), eq 2. The change in the zero-point vibrational energy (ΔZPE) and the change in the thermal vibrational energy ($\Delta\Delta E^v_{298}$) are also listed in Table 2. These data are combined with the change in the thermal translational energy ($\Delta\Delta E^t_{298}$), the change in the thermal rotational energy ($\Delta\Delta E^r_{298}$), and the change in the pressure−volume work term (ΔPV) to give $\Delta\Delta E_{298} + \Delta PV$.

$$\Delta E(\text{eff}) = \Delta E(\text{MP2/cc-pVTZ+}) + (\Delta E(\text{QCISD(T)}) - \Delta E(\text{MP2}))$$

$$= \Delta E(\text{MP2/cc-pVTZ+}) + \Delta\text{QCI} \qquad (2)$$

The effective QCISD(T)/cc-pVTZ+//MP2/6-31+G(d,p) calculated proton affinities are in excellent agreement with the experimental values.[20] Our calculated proton affinities are also in good accord with those obtained with G2 theory.[40]

Experimentally, CH₃CN is more stable than CH₃NC by 99 kJ/mol (24 kcal/mol).[41] The effective QCISD(T)/cc-pVTZ+//MP2/6-31+G(d,p) calculated difference is 100 kJ/mol (24 kcal/

(39) Desmeules, P. J.; Allen, L. C. *J. Chem. Phys.* **1980**, *72*, 4731.

(40) Smith, B. J.; Radom, L. *J. Am. Chem. Soc.* **1993**, *115*, 4885.

(41) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data, Suppl. 1* **1988**, *17*, 1.

Table 2. Calculated Proton Affinities of CH$_3$NC, CH$_3$CN, HNC, and HCN[a]

base	ΔE[b]	ΔE(eff)[c]	ΔZPE[d]	$\Delta\Delta E^v_{298}$[d]	$\Delta\Delta E_{298} + \Delta PV$[d]	PA(calc)	PA(expt)[e]
CH$_3$CN	797.2	806.2	−28.7	−0.9	−23.4	782.8	779.2
CH$_3$NC	865.7	860.7	−29.6	−0.3	−23.7	837.0	837.7[f]
HCN	730.4	739.4	−30.6	−0.6	−25.0	714.4	712.9
HNC	804.3	799.3	−31.1	0.0	−24.9	774.4	772.3

[a] Energies in kJ/mol. [b] MP2/cc-pVTZ+//MP2/6-31+G(d,p) calculation. [c] Effective QCISD(T)/cc-pVTZ+//MP2/6-31+G(d,p) calculation. ΔE has been corrected by the difference in the MP2 and QCISD(T) energies. [d] See text for definition. [e] Reference 20. [f] This work.
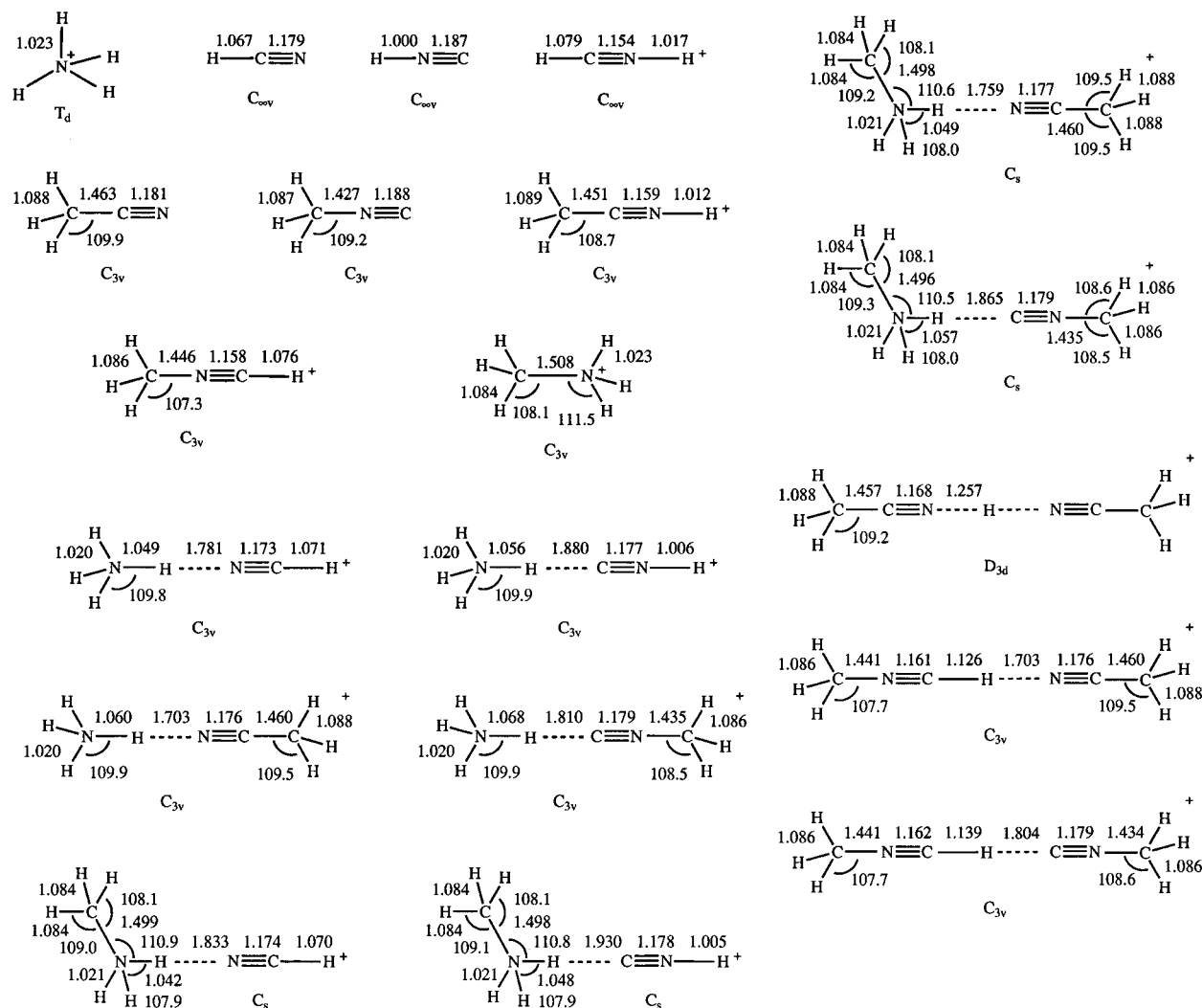

Figure 3. MP2/6-31+G(d,p) optimum geometries. Bond lengths are in Å; bond angles are in deg. Intermolecular N−H···B and H···B≡X bond angles that are not 180° are respectively as follows: CH$_3$NH$_3$$^+$(HCN) 176.6°, 178.3°; CH$_3NH_3$$^+$(HNC) 176.5°, 178.3°; CH$_3NH_3$$^+$(CH$_3$CN) 176.4°, 177.8°; and CH$_3$NH$_3$$^+$(CH$_3$CN) 176.2°, 177.9°.

mol). (The relative stabilities of CH$_3$CN and CH$_3$NC are 99, 100, and 100 kJ/mol at the QCISD(T)/cc-pVDZ+//MP2/6-31+G(d,p), QCISD(T)/aug′-cc-pVDZ//MP2/6-31+G(d,p), and QCISD(T)/aug-cc-pVDZ//MP2/6-31+G(d,p) levels of theory, respectively.) The calculated proton affinity of CH$_3$NC is 4.5 kJ/mol (1 kcal/mol) too low with respect to that of CH$_3$CN compared to the experimental values.[20] These results suggest that the correlated hydrogen bond strengths of the isocyano bases may be slightly underestimated relative to those of the cyano bases.

B. Geometries of the Complexes. MP2/6-31+G(d,p) equilibrium structures are depicted in Figure 3. The hydrogen bond angle ∠A−H···B is 180° for every complex except those for which CH$_3$NH$_3$$^+$ is the proton donor. In the latter complexes the deviation from linearity is at most 4°. The H···C≡N and H···N≡C bond angles in the CH$_3$NH$_3$$^+$ complexes are also

nonlinear by at most 2°. The most stable CH$_3$···CH$_3$ and CH$_3$···NH$_3$ orientations are staggered.

The changes in the geometrical parameters within the subunits upon hydrogen bond formation are small as expected. Only those asymmetric complexes involving CH$_3$NH$_3$$^+$, CH$_3$NC, and HNC show differences in bond lengths ≥0.01 Å and in bond angles ≥0.5° compared to the values in the isolated monomers. For a given electron donor, the directions and magnitudes of all of the changes are insensitive to the proton donor despite the wide range in r_2 values (distance between the hydrogen-bonded proton and the electron-donating atom) and in the strengths of the interactions (see below). The same observation holds for a given proton donor. The intramolecular bond lengths and bond angles in symmetric CH$_3$CNH$^+$(CH$_3$CN) are about midway between the values in the isolated neutral and protonated subunits.

Table 3. Thermochemistry[a] of Dissociation Reactions $AH^+(B) \rightarrow$ $AH^+ + B$ Involving Isocyanides and Cyanides

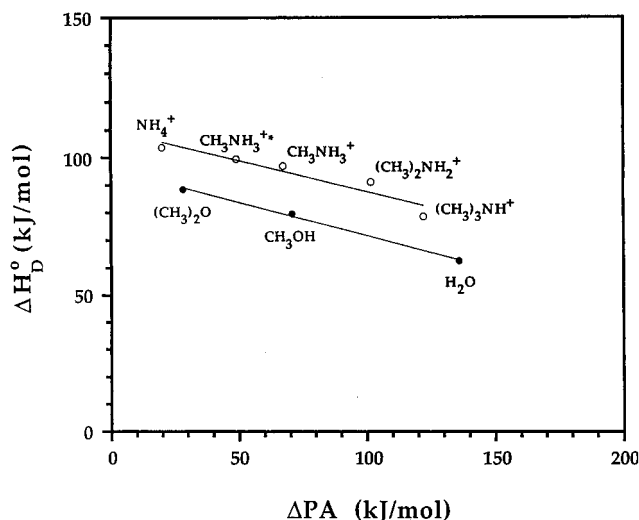| AH^+	B	$\Delta H^\circ_D(RNC)$	$\Delta H^\circ_D(RCN)^b$	$\Delta S^\circ_D(RNC)$
Complexes with Isocyanide Ligands				
NH_4^+	CH_3NC	100.4(7.0)	115.5	84.5(12.7)
$CH_3NH_3^+$	CH_3NC	99.7(3.2)	102.5	95.0(6.6)
$CH_3NH_3^+$	C_2H_5NC	99.5(2.7)	102.4	101.6(4.4)
$(CH_3)_2NH_2^+$	CH_3NC	86.2(1.4)		90.1(3.4)
$(CH_3)_3NH^+$	CH_3NC	81.6(3.2)		86.6(8.7)
Complexes of Protonated Isocyanides				
CH_3NCH^+	CD_3CN	80.1(1.9)	126.4	78.3(4.0)
CH_3NCH^+	H_2O	61.9(2.9)	103.8	82.4(7.4)
CH_3NCH^+	CH_3OH	79.5(3.4)		96.9(10.7)
CH_3NCH^+	CH_3OCH_3	88.7(4.6)		91.7(11.1)
Protonated Isocyanide Dimers				
CH_3NCH^+	CH_3NC	105.6(4.0)	126.4^c	103.4(7.9)
$C_2H_5NCH^+$	C_2H_5NC	105.4(3.4)		99.5(13.2)
Complex of Alkylated Isocyanide				
$CH_3CNCH_3^+$	H_2O	41.8(3.4)		92.1(18.2)
Ligand Exchange Reaction				
$NH_4^+(CH_3NC)$	CD_3CN	−13.0(5.5)		−26.4(11.1)

^{a} ΔH°_D in kJ/mol, ΔS°_D in J/(mol·K). Uncertainty estimates in parentheses, see text. ^{b} ΔH°_D for analogous reaction involving cyanides, i.e. where RNC and/or RNCH$^+$ are replaced by RCN and/or RCNH$^+$, respectively. Values from ref 1. ^{c} ΔH°_D for $CH_3CNH^+(CH_3CN)$.

The r_2 bond distances are all shorter when B is RCN than when B is RNC (Figure 3). The MP2/6-31+G(d,p) optimum structures of ClH···CNCH$_3$ and ClH···NCCH$_3$ obtained by Del Bene[15] also have a shorter r_2 for the cyano complex. For a given proton donor Δr_1, the difference between the A−H$^+$ bond length in the complex and in the isolated proton donor, is larger when complexation occurs through the carbon. In fact, for a given proton donor the ordering of Δr_1 follows the ordering of the proton affinities of the bases B, i.e. $CH_3NC > CH_3CN > HNC > HCN$.[16] This relationship has also been observed for other systems.[39] For a given electron donor, the ordering for Δr_1 follows the reverse ordering of the proton affinities of the proton donors, i.e. $CH_3CN > CH_3NC > NH_3 > CH_3NH_2$.[16] Similar correlations are not observed for R, the distance between the proton-donating and electron-donating atoms.

The observations discussed above for the MP2/6-31+G(d,p) calculational level hold for the HF/3-21G, HF/6-31G(d), and MP2/6-31+G(d) calculational levels as well. However, optimizing the geometries at a less extensive level than MP2/6-31+G(d,p) is not without some risk. First, $CH_3CNH^+(CH_3CN)$ is a symmetric complex with the MP2/6-31+G(d,p) model, whereas the other three models yield an asymmetric complex. Second, $CH_3CNH^+(CH_3NC)$ is a stable cluster at the HF level but not at the MP2 level. Thus, this work has produced two more examples of hydrogen-bonded complexes for which the proton-transfer potential changes from a double-well to a single-well type when larger basis sets are employed and when electron correlation is taken into account.

For those clusters for which comparisons can be made, the best guesses overall for the MP2/6-31+G(d,p) intermolecular bond lengths are provided by the HF/3-21G parameters. The optimum geometrical parameters found with the four levels of calculation can be compared more explicitly by using the data in Tables S1 and S2 in the Supporting Information. Table S1 lists the optimum monomer geometrical parameters, and Table S2 lists selected intermolecular parameters for the complexes.

C. Thermochemistry of the Complexes: Experimental. Van't Hoff plots for the complexes containing isocyanides are shown in Figure 2. The thermochemical results are summarized in Table 3, which also gives values for the analogous cyanide complexes.[1]

Figure 4. Correlation lines between ΔH°_D and ΔPA. ΔPA values are from ref 20. Open circles: Complexes of the ions shown with CH_3NC (an asterisk indicates with C_2H_5NC). Filled circles: Complexes of CH_3NCH^+ with the molecules shown.

Table 4. Correlation between ΔH°_D and PA for Bonds Involving Cyanides[a] and Isocyanides; Parameters for the Least-Squares Lines $\Delta H^\circ_D = a - b\Delta PA$

bond	a^b	b	N^c	coeff^d
NH^+···CNR	107.7 ± 4	−0.22 ± 0.05	5	0.914
NH^+···NCR	147.7 ± 2	−0.34 ± 0.01	4	0.984
$RNCH^+$···O	100.0 ± 1	−0.25 ± 0.01	3	0.998
$RCNH^+$···O	118.4 ± 3	−0.31 ± 0.03	5	0.977

^{a} From ref 42. ^{b} kJ/mol. ^{c} Number of points in correlation. ^{d} Correlation coefficient. The standard deviations of the slopes and intercepts from a least-squares fit to a linear correlation line are indicated.

In ionic hydrogen-bonded complexes, the proton is shared less efficiently as the proton affinity difference of the components increases. As a result, inverse correlations of the form of eq 3 are observed. The intercept a is the bond strength in the absence of proton affinity differences, and this can be viewed as the "intrinsic strength" of the AH^+···B-type hydrogen bond. ΔPA is the proton affinity of A minus the proton affinity of B.

$$\Delta H^\circ_D = a - b\Delta PA \qquad (3)$$

Correlations of this kind are observed in Figure 4 for the NH^+···CNR- and $RNCH^+$···O-type complexes studied in this work. Table 4 presents the values of a and b and the correlation statistics obtained for several AH^+···B-type interactions involving cyanides and isocyanides.[42] The slopes of the present correlation lines are −0.22 and −0.25, respectively. These slopes are somewhat smaller than those for analogous NH^+···NCR- and $RCNH^+$···O-type complexes containing cyanides[42] and those for conventional NH^+···N, NH^+···O, and OH^+···O complexes.[43] The intercept is 107.7 kJ/mol (25.7 kcal/mol) for the NH^+···CNR complexes, which is significantly smaller than the intercept of 147.7 kJ/mol (35.3 kcal/mol) for the NH^+··· NCR complexes.

In the previous study[42] we noted that cyanide ligands are bonded to NH^+-protonated species primarily by electrostatic interactions. The charge transfer in these complexes is smaller than that, for example, in NH^+···N-type complexes in amines. From the present data we note that the *intrinsic* strength of NH^+···CNR complexes, 107.7 kJ/mol (25.7 kcal/mol), is

(42) Speller, C. V.; Meot-Ner (Mautner), M. *J. Phys. Chem.* **1985**, *89*, 5217.

(43) Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1984**, *106*, 1257.

comparable to that of NH$^+$···N complexes in amines. *In this sense* therefore the sp carbon lone pair is a comparable electron donor to amine nitrogen lone pairs, which suggests that electrostatic effects are weaker in NH$^+$···CNR complexes than in NH$^+$···NCR complexes and that delocalization effects are stronger.

For the RNCH$^+$···O-type complexes, the intrinsic bond strength as given by the intercept is 100.0 kJ/mol (23.9 kcal/mol), which is somewhat smaller than that for the analogous RCNH$^+$···O-type complexes, 118.4 kJ/mol (28.3 kcal/mol).[42] If the interaction in these complexes is also chiefly electrostatic, the difference in intrinsic bond strength may be due primarily to the smaller positive charge on the proton of the protonated isocyanides (0.317 vs 0.529 for CH$_3$NCH$^+$ vs CH$_3$CNH$^+$ from CHELPG[44,45] analysis). The charge on the carbon of the C≡N group in both the protonated cyanide (0.582) and isocyanide (0.160) is also positive, which is indicative of the importance of the resonance structures R−C$^+$=N−H and R−N=C$^+$−H.

In the RNCH$^+$(R$_2$O) complexes, R$_2$O can bond to either the methyl group or the isocyanide proton. The latter interaction is more likely since the positive charge on the isocyanide proton is larger than that on a methyl proton, 0.317 vs 0.180 (CHELPG charges). To gain insight into this question, we examined the CH$_3$CNCH$_3$$^+$(H$_2$O) complex, for which the H$_2$O molecule can bond only to methyl protons. The measured complexation energy of 41.8 kJ/mol (10.0 kcal/mol) is significantly smaller than the value of 61.9 kJ/mol (14.8 kcal/mol) found for CH$_3$-NCH$^+$(H$_2$O). The stronger bonding in the latter complex supports an isocyanide proton−water interaction.

Comparing the cyanide vs isocyanide complexes in Table 4 shows that larger slopes of the correlation lines are associated with larger intercepts, i.e. stronger hydrogen bonds are more sensitive to PA differences. In earlier work we showed that this can be rationalized by the electrostatic nature of the bonding, in that a larger partial positive charge on the hydrogen-bonded proton leads to both larger slopes and larger intercepts.[42,46] The interactions in these complexes will be analyzed in more detail in the computational section below.

(i) CH$^+$···C Hydrogen Bonds. Finally, we observed the dimers CH$_3$NCH$^+$(CH$_3$NC) and C$_2$H$_5$NCH$^+$(C$_2$H$_5$NC). In these complexes a CH$^+$···C hydrogen bond is formed where carbon functions as both the proton- and electron-donating atom. The hydrogen bond strengths of 105.6 (25.2 kcal/mol) and 105.4 kJ/mol (25.2 kcal/mol), respectively, are substantial and not much lower than the NH$^+$···N hydrogen bond strength of 126.4 kJ/mol (30.2 kcal/mol) in CH$_3$CNH$^+$(CH$_3$CN) (Table 3). In fact, the bonding energy of CH$_3$NCH$^+$ to the carbon lone pair donor CH$_3$NC is significantly stronger than that to the nitrogen lone pair donor CH$_3$CN (80.1 kJ/mol (19.1 kcal/mol)).

D. Thermochemistry of the Complexes: Computational. MP2/cc-pVTZ+//MP2/6-31+G(d,p) dissociation energies (ΔE_D) for the reactions AH$^+$(B) → AH$^+$ + B are collected in Table 5. The estimated QCISD(T) correction (ΔQCI), the change in the ZPE (ΔZPE), the change in the thermal vibrational energy ($\Delta\Delta E^v_{298}$), and the change in the enthalpy correction ($\Delta\Delta E_{298}$ + ΔPV) for the reactions are also given in the table. Three related tables have also been provided as Supporting Information. Table S3 presents computed dissociation energies as a function of level of calculation. The energies are arranged in order of increasing basis set size. The effect of extending the electron correlation correction from MP2 to QCISD(T) is shown in Table S4. Table S5 lists ΔZPE, $\Delta\Delta E^v_{298}$, and $\Delta\Delta E_{298}$ +

Table 5. Dissociation Energy (ΔE_D) and Corrections to the Dissociation Energy for the Reactions AH$^+$(B) → AH$^+$ + B[a]

complex	ΔE_D[b]	ΔQCI[c]	ΔZPE[c]	$\Delta\Delta E^v_{298}$[c]	$\Delta\Delta E_{298}$ + ΔPV[c]
NH$_4$$^+$(HCN)	91.8	−1.5	−5.8	−6.7	−3.8
NH$_4$$^+$(HNC)	96.4	−5.0	−5.5	−6.3	−3.1
NH$_4$$^+$(CH$_3$CN)	116.0	−1.5	−4.1	−7.1	−2.5
NH$_4$$^+$(CH$_3$NC)	119.1	−5.5	−3.3	−6.9	−1.5
CH$_3$NH$_3$$^+$(HCN)	83.8	−1.5	−4.8	−7.7	−3.8
CH$_3$NH$_3$$^+$(HNC)	88.0	−4.5	−4.8	−7.3	−3.4
CH$_3$NH$_3$$^+$(CH$_3$CN)	106.1	−1.5	−3.3	−8.1	−2.7
CH$_3$NH$_3$$^+$(CH$_3$NC)	108.9	−5.5	−3.0	−7.8	−2.1
CH$_3$CNH$^+$(CH$_3$CN)	139.5	−6.0	−3.5	−8.6	3.6
CH$_3$NCH$^+$(CH$_3$CN)	101.2	0.0	−3.6	−9.0	−3.9
CH$_3$NCH$^+$(CH$_3$NC)	103.8	−4.5	−1.0	−9.2	−1.5

[a] Energies in kJ/mol. [b] MP2/cc-pVTZ+//MP2/6-31+G(d,p) calculation. [c] See text for definition.

ΔPV for each of the calculational models considered in this work.

ΔQCI was estimated separately for each AH$^+$(B) → AH$^+$ + B reaction by finding the average of the ΔE_D(QCISD(T)) − ΔE_D(MP2) differences for that reaction (Table S4) and rounding it off to the nearest 0.5 kJ/mol (0.1 kcal/mol). It is important to note that for any given complex the QCISD(T) correction appears to be additive, i.e. for any given complex the correction is essentially independent of the basis set employed. For example, ΔE_D(QCISD(T)) − ΔE_D(MP2) was determined with three basis sets, namely cc-pVDZ+, aug′-cc-pVDZ, and aug-cc-pVDZ. For NH$_4$$^+$(CH$_3$NC) the differences are 6.0, 5.7, and 5.5 kJ/mol, respectively. Similar results were cited for the computed proton affinities of CH$_3$CN, CH$_3$NC, HCN, and HNC.

(i) MP2 vs QCISD(T) Hydrogen Bond Energies. Earlier work indicates that the majority of the electron correlation contribution to hydrogen bond energies is present at the MP2 level. Higher level contributions are often small and of opposite sign.[47−51] For the cyano and isocyano complexes the majority of the electron correlation contribution is present at the MP2 level, and in fact, the contribution is overestimated at that level (Table 5). The overestimation is larger for the isocyanides (4−7 kJ/mol (1−2 kcal/mol)) than it is for the cyanides (1−2 kJ/mol (0.2−0.5 kcal/mol)). The only exception is CH$_3$CNH$^+$(CH$_3$-CN); the results for this cluster follow the trend for the isocyano rather than the cyano clusters.

(ii) CN vs NC Hydrogen Bond Energies. Analogous cyanide and isocyanide complexes are nearly equal in stability (Table 5). In fact, the deviation in hydrogen bond strengths is reduced from ≤4.5 kJ/mol (1 kcal/mol) to ≤2.5 kJ/mol (0.5 kcal/mol) when ΔQCI is taken into account. Other researchers have obtained similar results for related neutral complexes. Studies of HCOOH···CO vs HCOOH···OC,[52] FH···CO vs FH···OC,[53] and HOH···CO vs HOH···OC[53] indicate that analogous hydrogen-bonded complexes have essentially equal energies at the SCF level. The AH···CO dimers are preferentially stabilized at the MP2 level. ClH···CNCH$_3$ and ClH···NCCH$_3$ also have essentially equal hydrogen bond strengths.[15]

(iii) Trends in the Calculated Hydrogen Bond Energies. Both electrostatic and delocalization (charge transfer) effects can be important in hydrogen bonding.[53−58] Table 6 lists

(44) Chirlian, L. E.; Francl, M. M. *J. Comput. Chem.* **1987**, *8*, 894.
(45) Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem.* **1990**, *11*, 361.
(46) Meot-Ner (Mautner), M.; Sieck, L. W. *J. Phys. Chem.* **1985**, *89*, 5222.

(47) Frisch, M. J.; Pople, J. A.; Bel Bene, J. E. *J. Phys. Chem.* **1985**, *89*, 3664.
(48) Deakyne, C. A. *J. Phys. Chem.* **1986**, *90*, 6625.
(49) Deakyne, C. A. *Mol. Struct. Energetics* **1987**, *4*, 105.
(50) Del Bene, J. E. *J. Comput. Chem.* **1987**, *8*, 810.
(51) Del Bene, J. E. *J. Comput. Chem.* **1989**, *10*, 603.
(52) Lundell, J.; Räsänen, M.; Latajka, Z. *J. Phys. Chem.* **1993**, *97*, 1152.
(53) Reed, A. E.; Weinhold, F.; Curtiss, L. A.; Pochatko, D. J. *J. Chem. Phys.* **1986**, *84*, 5687.

Table 6.   Parameters Related to the Dissociation Energy (ΔE_D) for the Reactions $AH^+(B) \rightarrow AH^+ + B^a$

complex	$\Delta E_D{}^b$	R^c	$r_2{}^c$	$\Delta r_1{}^c$	$\Delta q_{CT}{}^c$	$(q_H q_B/r_2)^d$	$\nu_{AHB}{}^c$
$CH_3CNH^+(CH_3CN)$	136.6	2.514	1.257	0.114	0.273	−0.205	362
$NH_4^+(CH_3CN)$	110.5	2.763	1.703	0.037	0.0930	−0.128	240
$CH_3NH_3^+(CH_3CN)$	101.9	2.807	1.759	0.026	0.0778	−0.0910	228
$CH_3NCH^+(CH_3CN)$	96.4	2.830	1.704	0.050	0.0979	−0.0908	170
$NH_4^+(HCN)$	88.1	2.830	1.781	0.026	0.0700	−0.0924	235
$CH_3NH_3^+(HCN)$	81.2	2.873	1.833	0.019	0.0610	−0.0662	225
$NH_4^+(CH_3NC)$	113.1	2.878	1.810	0.045	0.142	−0.107	232
$CH_3NH_3^+(CH_3NC)$	104.4	2.920	1.865	0.034	0.123	−0.0765	225
$CH_3NCH^+(CH_3NC)$	98.4	2.943	1.804	0.063	0.151	−0.0764	161
$NH_4^+(HNC)$	91.8	2.936	1.880	0.033	0.114	−0.0670	232
$CH_3NH_3^+(HNC)$	84.6	2.977	1.930	0.025	0.0996	−0.0481	226

[a] MP2/6-31+G(d,p) data, MP2 density. [b] Energy in kJ/mol. [c] See text for definition. [d] q_H is the CHELPG charge on the hydrogen-bonded proton prior to hydrogen bond formation. q_H is 0.529, 0.445, 0.328, and 0.317 for CH_3CNH^+, NH_4^+, $CH_3NH_3^+$, and CH_3NCH^+, respectively. q_B is the CHELPG charge on the electron-donating atom prior to hydrogen bond formation. q_B is −0.488, −0.370, −0.435, and −0.283 for CH_3CN, HCN, CH_3NC, HNC, respectively.

parameters that provide information on these two components of the hydrogen bond energy. In $q_H q_B/r_2$, q_H is the charge on the hydrogen-bonded proton in the isolated proton donor and q_B is the charge on the electron-donating atom in the isolated electron donor. For the discussion below, the magnitude of the electrostatic contribution will be monitored by the magnitude of $q_H q_B/r_2$.[59] Δq_{CT} is the total electron density transferred from the electron donor to the proton donor when the hydrogen bond is formed. Reed, Weinhold, and co-workers[53,58] have found that the total charge transferred, as determined by the NPA (natural population analysis) method,[60,61] is a useful measure of ΔE_{CT} provided there is not significant charge transfer in both directions. ν_{AHB} is the vibrational frequency of the hydrogen bond stretch/compression normal mode. R is the distance between the proton-donating and electron-donating atoms.

Population analyses were carried out with HF/6-31G(d) and MP2/6-31+G(d,p) wave functions with HF and MP2 electron densities, respectively. The MP2/6-31+G(d,p) data are reported in Table 6, but the trends are the same for the two methods. Both CHELPG (charges derived from fitting the electrostatic potential)[44,45] and NPA[60,61] analyses were performed. Recently Wiberg and Rablen[62] compared atomic charges derived from several different methods, including CHELPG and NPA. They concluded that CHELPG charges are perhaps the most useful in estimating intermolecular Coulombic interactions, but charge redistributions brought about by substituents or other structural changes are different for the CHELPG analysis than for the other analyses. Thus, CHELPG charges were used to determine q_H and q_B in the table, but NPA charges were used to determine Δq_{CT}. Nevertheless, most of the trends observed in the table are independent of the procedure employed to derive the charges.

The data in Table 6 can be used to rationalize the observed trends in the MP2 (and SCF) hydrogen bond energies. Although the MP2/6-31+G(d,p)//MP2/6-31+G(d,p) data are reported in the table, the trends in hydrogen bond energies are independent of the basis set employed (Table S3, Supporting Information). The table is arranged in order of decreasing ΔE_D for the two sets of bases.

(54) Liu, S.-Y.; Dykstra, C. E. *Chem. Phys.* **1986**, *107*, 343.
(55) Kollman, P. *J. Am. Chem. Soc.* **1977**, *99*, 4875.
(56) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.
(57) Røeggen, I.; Ahmadi, G. R. *J. Mol. Struct. (THEOCHEM)* **1994**, *307*, 9.
(58) King, B. F.; Weinhold, F. *J. Chem. Phys.* **1995**, *103*, 333.
(59) Umeyama, H.; Morokuma, K. *J. Am. Chem. Soc.* **1977**, *99*, 1316.
(60) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.
(61) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899 and papers cited therein.
(62) Wiberg, K. B.; Rablen, P. R. *J. Comput. Chem.* **1993**, *14*, 1504.

Consider the entire set of $AH^+\cdots NCR$ or $AH^+\cdots CNR$ dimers, where R = H and Me. For the five or six complexes in each set, the correlation between ΔE_D and Δq_{CT}, r_2, and Δr_1 is broken by the complexes for which CH_3NCH^+ is the proton donor. The magnitudes of these parameters would place the CH_3NCH^+ complexes immediately above the NH_4^+ complexes in relative energy, which is the position they would occupy based on the inverse order of the proton affinity differences PA(A) − PA(B), B = CH_3CN or CH_3NC.[7,16] From the values of $q_H q_B/r_2$ in Table 6 the decrease in the electrostatic term is not sufficient to account for the position of the CH_3NCH^+ complexes in the group. The exchange repulsion must also weaken the $CH_3NCH^+\cdots CH_3CN$ or CH_3NC interactions relative to the other $AH^+\cdots CH_3CN$ or CH_3NC interactions. The anomalously small values of r_2 for the CH_3NCH^+ dimers indicate that this is the case.

The frequencies of the hydrogen bond stretching mode ν_{AHB} fall in the range 160−365 cm^{-1}, which is very close to the range of roughly 200−350 cm^{-1} observed by Pudzianowski[36] in his investigation of ten ionic hydrogen-bonded dimers. For a given electron donor B, there is a direct (albeit sometimes weak) correlation between the interaction energy and the frequency. The trend reported by Pudzianowski of decreasing frequency with increasing proton affinity of A is not repeated in this work; again it is broken by the CH_3NCH^+ complexes. In complexes with the same proton donor, ν_{AHB} is at best weakly dependent on the electron donor. In fact, ν_{AHB} ranges from only 225 to 240 cm^{-1} for all of the asymmetric $NH^+\cdots B$ systems.

Irrespective of the electron donor, methyl substitution of the proton donor A leads to a weakening of the hydrogen bond (Tables 5 and 6). In this case, the trends in $q_H q_B/r_2$, q_H, Δq_{CT}, and Δr_1 parallel the trends in ΔE_D. The proton affinity of the proton-donating base A, r_2, and R are inversely related to ΔE_D. Thus, the interaction energy is smaller for the systems involving a methyl-substituted proton donor, since both the electrostatic and delocalization terms are smaller for those systems.

For any given proton donor, methyl substitution of the electron donor B strengthens the hydrogen bond (Tables 5 and 6). For this substitution ΔE_D varies directly with $q_H q_B/r_2$, q_B, Δq_{CT}, PA(B), and Δr_1 and indirectly with r_2 and R. Smaller electrostatic and delocalization components lead to a weaker hydrogen bond for the unsubstituted complex.

Now compare the cyano and isocyano complexes of a single proton donor. When the base is a cyanide $q_H q_B/r_2$ is larger, q_B is more negative, and r_2 and R are shorter (Table 6). When the base is an isocyanide Δq_{CT} and Δr_1 are larger, consistent with the greater σ-donating ability[63] and lower ionization potential[64] of the isocyano bases. These data suggest that despite the

Table 7. Dissociation Enthalpies ($\Delta H°_D$) for the Reactions
$AH^+(B) \rightarrow AH^+ + B^a$

complex	$\Delta E_D(eff)^b$	$\Delta H°_D(calc)$	$\Delta H°_D(expt)$
$NH_4^+(HCN)$	90.3	86.5	91.6[c]
$NH_4^+(HNC)$	91.4	88.3	
$NH_4^+(CH_3CN)$	114.5	112.0	115.5[c]
$NH_4^+(CH_3NC)$	113.6	112.1	100.4
$CH_3NH_3^+(HCN)$	82.3	78.5	87.0[c]
$CH_3NH_3^+(HNC)$	83.5	80.1	
$CH_3NH_3^+(CH_3CN)$	104.6	101.9	102.5[c]
$CH_3NH_3^+(CH_3NC)$	103.4	101.3	99.7
$CH_3CNH^+(CH_3CN)$	133.5	137.1	126.4[c]
$CH_3NCH^+(CH_3CN)$	101.2	97.3	80.1
$CH_3NCH^+(CH_3NC)$	99.3	97.8	105.6

^{a} ΔE and ΔH in kJ/mol. ^{b} MP2/cc-pVTZ+//MP2/6-31+G(d,p) ΔE_D adjusted for the estimated QCISD(T) correction. See text. ^{c} Reference 1.

similar hydrogen bond strengths of analogous cyanide and isocyanide complexes (Tables 5 and 6), the relative importance of the electrostatic and delocalization components differs in the two sets of complexes.

Lundell et al.[52] have carried out an energy decomposition analysis[65,66] of HCOOH⋯CO and HCOOH⋯OC. Their results indicate that the delocalization contribution to the SCF interaction energy is larger for the HCOOH⋯CO complex, as are the electrostatic and exchange-repulsion contributions. In fact, the sum of the electrostatic and exchange-repulsion terms (the Heitler−London term) is repulsive when complexation occurs through the carbon but is attractive when complexation occurs through the oxygen. In their study of FH⋯CO, FH⋯OC, HOH⋯CO, and HOH⋯OC Reed et al.[53] also found that ΔE_{CT} is greater for the AH⋯CO systems.

The size of an isocyano carbon atom versus a cyano nitrogen atom has been explored by Legon and co-workers.[10−13] They have utilized rotational spectroscopy to determine the distance R between the electron-donating atom and the proton-donating atom in eight neutral AH⋯B complexes, where B = CH_3CN or CH_3NC and A = F, Cl, CN, or CCH. The R values for corresponding cyano and isocyano complexes all differ by about 0.1 Å, and the differences increase slightly as the interaction energy decreases. Similar results are found for the positively-charged complexes examined in this work (Table 6). Since R is a reasonable approximation to the sum of the van der Waals radii of the electron-donating and proton-donating atoms[67] and the accepted van der Waals radius of N is 1.4 Å, the data suggest a value of 1.5 Å for the van der Waals radius of isocyano C.

E. Experimental vs Calculated Dissociation Enthalpies. Effective QCISD(T)/cc-pVTZ+//MP2/6-31+G(d,p) dissociation energies ($\Delta E_D(eff)$) and dissociation enthalpies ($\Delta H°_D$) are given in Table 7. $\Delta E_D(eff)$ was obtained by using the additivity approximation in eq 2.

The experimental and calculated dissociation enthalpies agree within the standard uncertainty of ±6 kJ/mol (1.5 kcal/mol) for only four of the nine complexes for which experimental data are available. Two other complexes have $\Delta H°_D(calc)$ and $\Delta H°_D(exp)$ values that lie within ±8 kJ/mol (2 kcal/mol) of each other. The calculated binding enthalpy of $CH_3CNH^+(CH_3CN)$ is overestimated by 11 kJ/mol (2.6 kcal/mol) compared to the experimental binding enthalpy. The experimental value of $\Delta H°_D$ for $CH_3CNH^+(CH_3CN)$ is a solid number and the

convergence in binding energies is poorest for this system (Tables S3 and S4, Supporting Information). Thus, it appears that higher level calculations are required to properly characterize this symmetric dimer.

For each analogous pair of isocyanide and cyanide complexes, the calculated hydrogen bond enthalpies are essentially equal (to within 2 kJ/mol (0.5 kcal/mol)). This similarity in stability is not uniformly observed for the experimental hydrogen bond enthalpies, which accounts for some of the discrepancy in the two sets of data (Table 7). Arguments can be made that lend support to the calculated data. First, the relative dissociation enthalpies within each series of complexes and between the two series of complexes hold for every basis set and calculational level considered in this work. Second, it has been shown that neutral and cationic complexes exhibit similar bonding patterns,[39,68,69] and Legon and co-workers'[10−14] spectroscopic studies (see above) find identical hydrogen bond strengths for analogous CH_3CN and CH_3NC complexes, within experimental error. (The hydrogen bond strengths were measured by the intermolecular stretching force constant k_σ.) Third, according to the calculations, for any given electron donor, methyl substitution of the proton-donating atom reduces the binding enthalpy by some 10 kJ/mol (2.4 kcal/mol). There is experimental support for this trend,[1] including the relative binding enthalpies given in Table 3 for $CH_3NH_3^+(CH_3NC)$, $(CH_3)_2$-$NH_2^+(CH_3NC)$, and $(CH_3)_3NH^+(CH_3NC)$ and for $NH_4^+(CH_3CN)$ and $CH_3NH_3^+(CH_3CN)$. $NH_4^+(CH_3NC)$ breaks the pattern since its $\Delta H°_D(exp)$ is essentially identical with that of $CH_3NH_3^+(CH_3NC)$, which suggests that $\Delta H°_D(exp)$ for $NH_4^+(CH_3NC)$ is too low. (It is also possible, of course, that $\Delta H°_D(exp)$ for $CH_3NH_3^+(CH_3CN)$ is too high. However, this possibility seems less likely since lowering this value would break other patterns in Table 3). Fourth, the experimental results rank the two series of dimers in different orders, whereas the theoretical results rank both series in the same order. This disagreement is caused primarily by the discrepancies in the calculated and experimental hydrogen bond strengths of $NH_4^+(CH_3NC)$ and $CH_3NCH^+(CH_3CN)$. Note, however, that for both the computations and experiment, $CH_3CNH^+(CH_3CN)$ is substantially more strongly bound than either CH_3NCH^+ complex (Table 7).

F. Overview of the Supporting Information. A brief overview of the Supporting Information follows. First, adding diffuse functions to the basis set decreases the dissociation energy, but as the basis set is made still more flexible the hydrogen bond strengths increase and then level off. The complexation energies computed with the smaller correlation consistent basis sets are always larger than those computed with basis sets of comparable size derived from the 6-31G(d) basis. More importantly, the data obtained with the smaller correlation consistent basis sets are closer in magnitude to the data obtained with the two largest basis sets (MP2/6-311++G(2d,2p) and MP2/cc-pVTZ+). Second, SCF binding energies are larger when complexation occurs through the nitrogen, but only by ≈11 kJ/mol (2.6 kcal/mol). Complexation through the carbon is preferentially stabilized when electron correlation is taken into account, making the calculated ΔE_Ds essentially equal for analogous cyanide and isocyanide dimers. Third, for the many complexes for which the shape of the proton-transfer potential energy curve is unaffected by the level of calculation, if (1) performing MP2/6-31+G(d,p) calculations is not computationally feasible and (2) only trends are desired, then the results

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

(64) Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. *Molecular Photoelectron Spectroscopy*; Interscience: London, 1976.

(65) Latajka, Z. *J. Mol. Struct. (THEOCHEM)* **1991**, *251*, 245.

(66) Latajka, Z. *J. Mol. Struct. (THEOCHEM)* **1992**, *253*, 225.

(67) Buckingham, A. D.; Fowler, P. W. *Can. J. Chem.* **1985**, *63*, 2018.

(68) Carroll, M. T.; Bader, R. F. W. *Mol. Phys.* **1988**, *65*, 695.

(69) Platts, J. A.; Laidig, K. E. *J. Phys. Chem.* **1995**, *99*, 6487.

(70) Frisch, M. J.; Del Bene, J. E.; Binkley, J. S.; Schaefer, H. F., III. *J. Chem. Phys.* **1986**, *84*, 2279.

(71) Taylor, B. N.; Kuyatt, C. NIST Technical Note No. 1297.

from this work indicate that the HF/6-31G(d) or MP2/6-31+G-(d) geometries and vibrational frequencies could be used. Fourth, despite significant dissimilarities in the equilibrium structures found with the three largest models, the correlated interaction energies appear to be remarkably insensitive to the geometry utilized to calculate them (this work and refs 47 and 70). Fifth, the same agreement between the experimental and calculated data would be obtained if (1) an MP4 rather than a QCISD(T) correction was employed in eq 2 and (2) ΔE_D was calculated by using the MP2 data for the aug'-cc-pVDZ, aug-cc-pVDZ, 6-31+G(2d,2p), or 6-311++G(2d,2p) basis set rather than for the cc-pVTZ+ basis set. Thus, this work provides additional examples of binary systems for which the MP4/aug'-cc-pVDZ and, for the cyano complexes, the MP2/6-311++G(2d,2p) models reproduce the results of larger models.

Summary

In summary, the following points were made.

(1) The proton affinity of CH_3NC has been remeasured and is found to be 837.7 ± 2.6 kJ/mol (200.2 ± 0.6 kcal/mol).

(2) The ΔH°_D values for the $NH^+\cdots CNR$- and $RCNH^+\cdots O$-type interactions obey the relationship $\Delta H^\circ_D = a - b\Delta PA$.

(3) Intrinsic hydrogen bond dissociation energies for the $R_3NH^+(RNC)$ and $RNCH^+(R_2O)$ complexes are comparable in strength to those for the $R_3NH^+(NR_2)$ complexes but weaker than those for the $RCNH^+(RCN)$ and $R_2OH^+(R_2O)$ complexes.

(4) Geometries were optimized fully at the HF/3-21G, HF/6-31G(d), MP2/6-31+G(d), and MP2/6-31+G(d,p) calculational levels. There are two significant differences in the results obtained with these four levels. First, $CH_3CNH^+(CH_3NC)$ is a minimum on the SCF potential energy surfaces but not on the MP2 potential energy surfaces. Second, $CH_3CNH^+(CH_3CN)$ changes symmetry from C_{3v} to D_{3d} at the MP2/6-31+G(d,p) level. For the ten complexes for which the shape of the proton-transfer potential energy curve remains unchanged, single-point energies and trends in stabilization enthalpies are remarkably unaffected by the choice of calculational level when the three largest levels are used.

(5) The $H^+\cdots B$ distance r_2 is shorter for the cyanides, consistent with their greater stability at the SCF level. The change in the $A-H^+$ distance Δr_1 is greater for the isocyanides, consistent with their larger proton affinity. The distance R

between the heavy atoms differs by about 0.1 Å for all corresponding cyano and isocyano complexes, consistent with the larger van der Waals radius of isocyano C compared to cyano N.[11]

(6) The frequencies of the hydrogen bond stretching mode ν_{AHB} range from 160 to 365 cm^{-1}, which is very close to the range of roughly 200−350 cm^{-1} observed by Pudzianowski[36] in his investigation of ten ionic hydrogen-bonded dimers.

(7) Calculated ΔH_{DS} are essentially equal for analogous cyanide and isocyanide dimers. The MP2 correlation correction is significantly overestimated (by 4−7 kJ/mol (1−2 kcal/mol)) compared to the QCISD(T) correction for the isocyanides.

(8) Effective QCISD(T)/cc-pVTZ+//MP2/6-31+G(d,p) hydrogen bond energies were obtained via an additivity approximation based on MP2/cc-pVTZ+//MP2/6-31+G(d,p) energies. Hydrogen bond enthalpies at this level were compared with experiment; the values agree within the standard uncertainty of ± 6 kJ/mol (1.5 kcal/mol) for only four of the nine complexes for which experimental data are available. Two other complexes have $\Delta H^\circ_D(calc)$ and $\Delta H^\circ_D(exp)$ values that agree to ± 8 kJ/mol (2 kcal/mol).

(9) The relative importance of the electrostatic and delocalization components of the dissociation energy is different for the two sets of complexes, with delocalization effects being more important for the isocyanides.

Supporting Information Available: Tables of monomer geometries, intermolecular geometrical parameters, and calculated ΔE_D, MPn and QCISD(T) ΔE_D and corrections to ΔE_D for the reactions $AH^+(B) \rightarrow AH^+ + B$ (12 pages). See any current masthead page for ordering and Internet access instructions.

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