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Structures and Binding Energies of Proton-Bound Pairs of HCN and CH_3CN with NH_3, H_2O, HF, CH_3NH_2, CH_3OH, and CH_3F

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In this study, 12 nitrile-containing proton-bound dimers were investigated with ab initio molecular orbital calculations: $(HCN)(NH_3)H^+$, $(HCN)(H_2O)H^+$, $(HCN)(HF)H^+$, $(HCN)(CH_3NH_2)H^+$, $(HCN)(CH_3OH)H^+$, $(HCN)(CH_3F)H^+$, $(CH_3CN)(NH_3)H^+$, $(CH_3CN)(H_2O)H^+$, $(CH_3CN)(HF)H^+$, $(CH_3CN)(CH_3NH_2)H^+$, $(CH_3CN)(CH_3OH)H^+$, and $(CH_3CN)(CH_3F)H^+$. The geometries of these dimers were optimized at the MP2/6-31+G(d) level of theory, and their binding energies (relative to the lowest energy dissociation products) were calculated with the G2, G2(ZPE=MP2), G2(MP2), and G2(MP2,SVP) methods. The trends in the binding energies follow the absolute value of the difference in proton affinity of the constituent monomers; the larger the PA difference, the smaller the binding energy. An empirical relationship has been derived that may prove useful in predicting the binding energies of other nitrile-containing cluster ions. The results are compared to experimental values where available.

1. Introduction

Clusters of molecules can be viewed as an intermediate state of matter between the dilute gas phase and solution, and studying them allows the effects of solvation on the chemistry of gas-phase molecules and ions to be explored.[1−5] A family of cluster ions that has received considerable attention is proton-bound clusters. One of the reasons for this is their role in atmospheric chemistry.[6,7] As altitude decreases, the ion chemistry of the atmosphere goes from being dominated by the atomic and diatomic ionization products of N_2 and O_2 (above ∼90 km)[8] to a complex ensemble of water hydrate clusters $(H_2O)_nH^+$.[9,10] Other cluster ion series have been observed though, and in addition to the first-row hydrides, species such as CH_3CN have been postulated to be involved in atmospheric cluster ions.[6] Laboratory results have confirmed that nitriles can play a significant role in cluster ion chemistry.[11,12]

The solvation enthalpies of the proton-bound clusters $(HCN)_nH^+$ and $(CH_3CN)_nH^+$ have been experimentally measured by Deakyne et al.[11] using high-pressure mass spectrometry, while those of the acetonitrile−methanol series of clusters have been probed by El-Shall et al.[13] The kinetics of the reactions of protonated methanol clusters with acetonitrile have been investigated by Zhang et al.[14] A recent report from this laboratory examined the unimolecular reactions of the methanol−acetonitrile proton-bound dimer and found that the cluster undergoes an isomerization reaction to form the ion−molecule complex $(CH_3CNCH_3)(H_2O)^+$ prior to water loss.[15] Central to the interpretation of these experimental results is the theoretically calculated structures and relative thermochemistry of the clusters in question.

There has been widespread interest in calculating the properties of proton-bound complexes, especially the dimers of water and other first-row hydrides.[16−25] This study presents the results of ab initio calculations of the structures and binding energies of 12 proton-bound dimers involving nitriles and first-row hydrides: $(HCN)(NH_3)H^+$, $(HCN)(H_2O)H^+$, $(HCN)(HF)H^+$, $(HCN)(CH_3NH_2)H^+$, $(HCN)(CH_3OH)H^+$, $(HCN)(CH_3F)H^+$, $(CH_3CN)(NH_3)H^+$, $(CH_3CN)(H_2O)H^+$, $(CH_3CN)(HF)H^+$, $(CH_3CN)(CH_3NH_2)H^+$, $(CH_3CN)(CH_3OH)H^+$, and $(CH_3CN)(CH_3F)H^+$. By examining such a set of dimers, trends in binding energies can be derived that may be extended to the larger members of this cluster family. In addition, many experimental studies of cluster ion solvation can only determine the relative enthalpies; the current theoretical results allow us to fix the relative experimental enthalpies, giving absolute values for cluster ion heats of formation.

2. Computational Procedures

Standard ab initio molecular orbital calculations[26] were performed using the GAUSSIAN 94[27] suite of programs. Geometries were optimized at the HF/6-31G(d), MP2/6-31G(d), and MP2/6-31+G(d) levels of theory employing the “opt=tight” keyword in Gaussian 94. This makes the convergence criteria more stringent and usually results in a geometry closer to the true local minimum-energy structure at a particular level of theory. For $(CH_3CN)(HF)H^+$ and $(CH_3CN)(CH_3NH_2)H^+$, it was necessary to calculate the second-derivative matrix at each point along the geometry optimization in order to obtain equilibrium structures. An earlier assessment of theoretical treatments for nitrile-containing proton-bound pairs showed that geometries obtained at the MP2/6-31+G(d) level provide an adequate foundation for further single-point energy calculations.[28] In that study, four H^+-bonded dimers were taken as prototypes for nitrile-containing proton-bound dimers: $(HCN)_2H^+$, $(HCN)(NH_3)H^+$, $(HCN)(H_2O)H^+$, and $(HCN)(HF)H^+$. Convergence of the geometric parameters of these four cluster ions was found to require extended basis sets with diffuse and polarization functions. In general, however, the MP2/6-31+G(d) level of theory was found to provide geometries that were in good qualitative agreement with those obtained at very high levels of theory such as MP2/6-311+G(2df,p), and QCISD/6-311+G(d,p). The main effect of polarization on hydrogen was to change the long H-bond in each dimer, and in this respect, the present results are only approximate. Changes in that long bond were found to be less than 0.23 Å in all cases.[28]

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Vibrational frequencies were calculated for all geometries optimized at the HF/6-31G(d) and MP2/6-31G(d) levels of theory and for many of the dimers at the MP2/6-31+G(d) level of theory. Many of the clusters in this study exhibit very small vibrational modes corresponding to the hindered internal rotation about the proton bridge.

Single-point energies were obtained at the G2,[29] G2-(ZPE=MP2),[30] G2(MP2),[31] and G2(MP2,SVP)[32] levels of theory. Scaling factors for zero-point energies (ZPEs) used in these high-level treatments were those recommended for the individual procedures (i.e., HF/6-31(d) frequencies scaled by 0.8929 for G2, G2(MP2), and G2(MP2,SVP) and MP2/6-31G-(d) frequencies scaled by 0.9646 for G2(ZPE=MP2)). In the previous assessment from this laboratory,[28] the ZPE values of the previously mentioned four prototype dimers were studied as a function of the level of theory. Using recommended scaling factors,[33] the ZPE values for $(HCN)(NH_3)H^+$, $(HCN)(H_2O)H^+$, and $(HCN)(HF)H^+$ calculated at the HF, MP2, and B3-LYP levels of theory (with the 6-31G(d) basis set) were all within 2−3 kJ mol^{-1} of one another. Changes in the ZPE upon inclusion of diffuse and polarization functions were found to be minor (<3 kJ mol^{-1}). The only exception was for $(HCN)_2H^+$, for which the ZPE changed by approximately 10 kJ mol^{-1} in going from HF to MP2 and B3-LYP. Using the ZPE scaling factors recommended by the individual G2 procedures did not result in large changes, the maximum being 4 kJ mol^{-1} for $(HCN)(NH_3)H^+$.

The heats of formation at 0 K were derived by the atomization method,[34] using experimental $\Delta_f H°_0$ of the constituent atoms.[35] The binding energies of the clusters were derived from the difference in energy between the lowest dissociation products and the intact dimers. The basis set superposition error (BSSE)[36] was not corrected for in these systems. The magnitude of the BSSE is small relative to the binding energy of proton-bound clusters (<10 kJ mol^{-1}),[28,37] and it is unclear whether methods such as the counterpoise correction[36] provide realistic approximations of BSSE in these systems.[22] In addition, comparison with experiment in our earlier assessment suggested that the omission of BSSE corrections does not greatly affect the overall reliability of the calculated binding energies.[28]

Del Bene[17] has done considerable work on the structures and energies of proton-bound dimers of the first-row hydrides. A preferred method for geometry optimization used in this work is the MP2/6-31+G(d,p) level of theory. The inclusion of polarization functions on hydrogen is most significant for anionic clusters, and as mentioned above, their inclusion in the proton-bound dimers in this study does not result in large changes in geometry, except for the long hydrogen bond in each dimer. For comparison purposes, the $(CH_3CN)(NH_3)H^+$ dimer was optimized at the MP2/6-31+G(d,p) level of theory. The major difference between this structure and that obtained at the MP2/6-31+G(d) level of theory (shown in Figure 1) is a 0.062 Å shortening of the hydrogen bond to CH_3CN. The G2 heat of formation of this structure was found to be only 1 kJ mol^{-1} lower than that obtained for the MP2/6-31+G(d) structure.

3. Results and Discussion

Cluster Geometries and Energies. MP2/6-31+G(d) optimized geometric parameters for the clusters discussed below are shown in Figure 1. In all cases, the bridging proton is denoted as H_b. The 0 K heats of formation calculated with G2, G2(ZPE=MP2), G2(MP2), and G2(MP2,SVP) are listed in Table 1, the 0 K binding energies are listed in Table 2, and the fragmentation product energies can be found in Table 3.

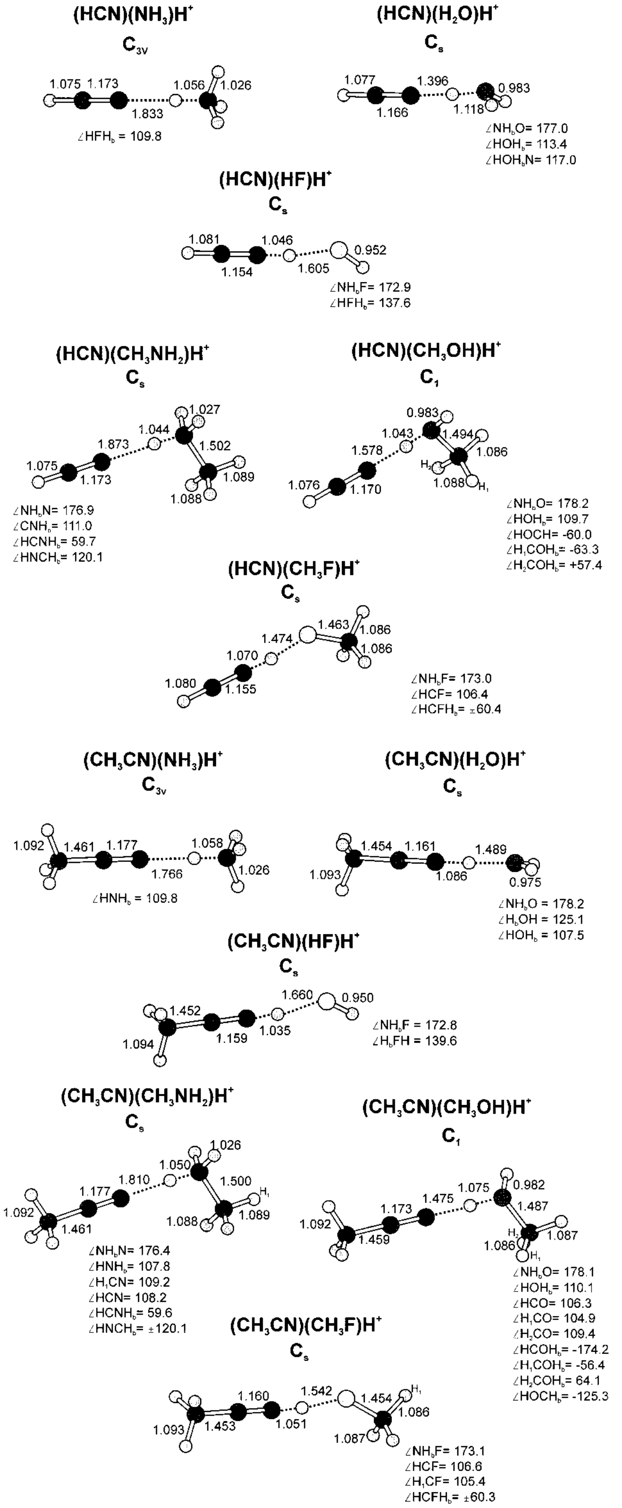

Figure 1. Optimized geometric parameters for the 12 proton-bound dimers in this study. All geometries were obtained at the MP2/6-31+G-(d) level of theory using the "opt=tight" keyword in Gaussian 94. Bond lengths are reported in angstroms and angles in degrees.

$(HCN)(NH_3)H^+$. The HCN−ammonia proton-bound dimer has C_{3v} symmetry at the MP2/6-31+G(d) level of theory and at higher levels of theory.[28] The asymmetric hydrogen bonds in the dimer (1.833 and 1.056 Å) indicate that the complex may be thought of as an NH_4^+ ion solvated by HCN. The charge distribution bears this out, the HCN moiety being essentially neutral. The G2 $\Delta_f H°_0$ of the dimer is 690 kJ mol^{-1} and the 0 K binding energy is 85 kJ mol^{-1}, the lowest energy dissociation products being HCN + NH_4^+.

TABLE 1: Summary of Cluster $\Delta_f H°_0$ Values Obtained in This Study[a]

	$\Delta_f H°_0$			
cluster	G2	G2 (ZPE=MP2)	G2 (MP2)	G2 (MP2,SVP)
$(HCN)(NH_3)H^+$	690	687	691	691
$(HCN)(H_2O)H^+$	595	590	591	594
$(HCN)(HF)H^+$	618	614	615	614
$(HCN)(CH_3NH_2)H^+$	680	678	681	681
$(HCN)(CH_3OH)H^+$	601	597	599	601
$(HCN)(CH_3F)H^+$	634	630	633	632
$(CH_3CN)(NH_3)H^+$	617	626	619	617
$(CH_3CN)(H_2O)H^+$	501	507	499	499
$(CH_3CN)(HF)H^+$	509	517	508	504
$(CH_3CN)(CH_3NH_2)H^+$				609
$(CH_3CN)(CH_3OH)H^+$				519
$(CH_3CN)(CH_3F)H^+$				527

[a] Values in kJ mol^{-1}. MP2/6-31+G(d) geometry used in all cases. G2, G2(MP2), and G2(MP2,SVP) values use standard HF/6-31G(d) ZPE (scaled by 0.8929 according to the G2 scheme). G2(ZPE=MP2) employs a scaled (by 0.9646) MP2/6-31G(d) ZPE.

$(HCN)(H_2O)H^+$. The HCN−water proton-bound dimer has C_s symmetry at MP2/6-31+G(d).[28] The proton in this dimer is more equally shared between the two monomers than was predicted for $(HCN)(NH_3)H^+$, which is consistent with the proton affinities of HCN and H_2O being closer together than in the latter cluster (the PA of difference between HCN and NH_3 is 141 kJ mol^{-1}, while that between HCN and H_2O is 24 kJ mol^{-1}, Table 2).[28] The $O-H_b$ bond (1.118 Å) is actually shorter than the $N-H_b$ bond (1.396 Å), which is seemingly in contradiction to the lowest energy products being $HCNH^+ + H_2O$. However, these bond lengths are longer and shorter, respectively, than the corresponding bonds in dimers in which the proton is more formally associated with the oxygen atom (for example, in $(HCN)(CH_3OH)H^+$, the $O-H_b$ bond length is very close to a typical hydroxy bond length, 1.043 Å, while the $N-H_b$ bond is much longer, 1.578 Å, Figure 1). The binding energy is greater than for the ammonia cluster, 119 kJ mol^{-1}, corresponding to a $\Delta_f H°_0$ value of 595 kJ mol^{-1}.

$(HCN)(HF)H^+$. The proton-bound dimer of HCN and HF has C_s symmetry,[28] and now the proton is decidedly on the HCN moiety, producing an $HCNH^+$ ion solvated by HF. The PA of HF is considerably lower than that of HCN (479 vs 707 kJ mol^{-1}), which is consistent with the long hydrogen bond to HF (1.605 Å). The G2 binding energy of the dimer is one of the smallest in this study, 60 kJ mol^{-1}, and is only slightly larger than that for the cluster between CH_3CN and HF (Table 2). Accordingly, the PA difference between HCN and HF is one of the largest of the dimers studied here, 227 kJ mol^{-1}. The G2 $\Delta_f H°_0$ is 618 kJ mol^{-1}.

$(HCN)(CH_3NH_2)H^+$. Methyl substitution of NH_3 to form the proton-bound dimer of HCN and methylamine decreases the G2 binding energy of the cluster from 85 to 77 kJ mol^{-1}. The dimer has C_s symmetry with hydrogen bonds that are similar to those in $(HCN)(NH_3)H^+$ (1.873 and 1.044 Å). The decrease in binding energy is consistent with an increase in the difference in PA of the monomers in going from the simple dimer to the methyl-substituted dimer. The PA difference for $(HCN)(NH_3)H^+$ is 141 kJ mol^{-1}, while that for $(HCN)(CH_3NH_2)H^+$ is 188 kJ mol^{-1} (Table 2).

$(HCN)(CH_3OH)H^+$. The methanol−HCN proton-bound dimer has C_1 symmetry at the MP2/6-31+G(d) level of theory. Like $(HCN)(H_2O)H^+$, the proton is bound primarily to the oxygen atom, forming a complex between HCN and $CH_3OH_2^+$. In this case, the PA of methanol is significantly higher than that of HCN (749 as opposed to 707 kJ mol^{-1}). The G2 0 K binding energy of the dimer is 115 kJ mol^{-1}, very close to that of $(HCN)(H_2O)H^+$. The PA difference between the monomers is similar in both cases, 24 kJ mol^{-1} for the water complex and 43 kJ mol^{-1} for the methanol complex, which is consistent with the similarity of their respective binding energies. The G2 0 K $\Delta_f H°_0$ of this dimer is 601 kJ mol^{-1}.

$(HCN)(CH_3F)H^+$. The $HCN-CH_3F$ proton-bound dimer has C_s symmetry and structural characteristics similar to $(HCN)(HF)H^+$. The proton is now bound to the HCN group, forming an $HCNH^+$ ion solvated by methyl fluoride. As with $(HCN)(HF)H^+$, the hydrogen bond to F is long, 1.474 Å. The geometry is consistent with the relative PA values of the two monomers, the G2 0 K PA of HCN being 113 kJ mol^{-1} greater than that of CH_3F (Table 2). The binding energy of 84 kJ mol^{-1} is larger than that of $(HCN)(HF)H^+$ as the PA difference between the monomers is smaller in the methyl fluoride cluster (113 as compared to 227 kJ mol^{-1} for the HF cluster).

$(CH_3CN)(NH_3)H^+$. Like the HCN−ammonia dimer, the acetonitrile−ammonia dimer has C_{3v} symmetry at the MP2/6-31+G(d) level of theory. The dimer can be considered to be an NH_4^+ ion solvated by an acetonitrile molecule, the hydrogen bond to ammonia, 1.058 Å, being close to a covalent N−H bond. The binding energy of this dimer, 110 kJ mol^{-1}, is greater than that of $(HCN)(NH_3)H^+$ (85 kJ mol^{-1}) because the PA difference between CH_3CN and NH_3 is almost 70 kJ mol^{-1} less than in the smaller cluster. The G2 $\Delta_f H°_0$ for this dimer is calculated to be 617 kJ mol^{-1}.

TABLE 2: Summary of Cluster Binding Energies Obtained in This Study and the Absolute Proton Affinity Difference between the Constituent Monomers, |ΔPA|[a]

	binding energy					
cluster	G2	G2(ZPE=MP2)	G2(MP2)	G2(MP2,SVP)	expt	|ΔPA|[b]
$(HCN)(NH_3)H^+$	85	92	85	92		141
$(HCN)(H_2O)H^+$	119	122	119	121		24
$(HCN)(HF)H^+$	60	67	59	66		227
$(HCN)(CH_3NH_2)H^+$	77	87	78	87		188
$(HCN)(CH_3OH)H^+$	115	126	115	123		43
$(HCN)(CH_3F)H^+$	84	95	84	93		113
$(CH_3CN)(NH_3)H^+$	110	110	110	119		72
$(CH_3CN)(H_2O)H^+$	97	87	95	94	104 ± 4[c]	93
$(CH_3CN)(HF)H^+$	53	44	51	54		296
$(CH_3CN)(CH_3NH_2)H^+$				112		119
$(CH_3CN)(CH_3OH)H^+$				119[d]		27
$(CH_3CN)(CH_3F)H^+$				76		182

[a] Values reported at 0 K in kJ mol^{-1}. [b] G2 values based on MP2/6-31+G(d) geometries, obtained in the present study. [c] Deakyne et al.[11] [d] See also Mayer.[15]

TABLE 3: Lowest Energy Fragmentation Product $\Delta_f H°_0$ Values[a]

	$\sum\Delta_f H°_0$				
products	G2	G2-(ZPE=MP2)	G2-(MP2)	G2-(MP2,SVP)	expt[b]
$HCN + NH_4^+$	775	779	775	783	777
$HCNH^+ + H_2O$	714	713	710	715	712
$HCNH^+ + HF$	678	680	674	680	679
$HCN + CH_3NH_3^+$	757	765	759	768	766
$HCN + CH_3OH_2^+$	716	723	714	724	717
$HCNH^+ + CH_3F$	718	725	717	725	712
$CH_3CN + NH_4^+$	727	735	728	736	722
$CH_3CNH^+ + H_2O$	598	593	594	593	597[c]
$CH_3CNH^+ + HF$	561	561	559	558	563[c]
$CH_3CN + CH_3NH_3^+$	709	721	712	721	711
$CH_3CNH^+ + CH_3OH$	643	639	640	639	646.1[c]
$CH_3CNH^+ + CH_3F$	602	605	601	603	596.6[c]

[a] In kJ mol^{-1}. MP2/6-31+G(d) optimized geometries and scaled HF/6-31G(d) ZPEs, except for G2(ZPE=MP2), see text. [b] Employing $\Delta_f H°_0$ values from the compendium of Lias et al.[35] unless otherwise stated. Values in this compendium quoted only at 298 K were corrected to 0 K with theoretical thermal correction factors. [c] Based on the PA of CH_3CN quoted by Hunter and Lias (779.2 kJ mol^{-1}).[38]

$(CH_3CN)(H_2O)H^+$. The proton-bound dimer of CH_3CN and H_2O has C_s symmetry (Figure 1).[11] Unlike $(HCN)(H_2O)H^+$, the proton now resides formally on the nitrile, the hydrogen bond to water being 1.489 Å. The G2 0 K binding energy of this cluster is 97 kJ mol^{-1}, some 20 kJ mol^{-1} lower than that predicted for $(HCN)(H_2O)H^+$. This is a consequence of the increased PA difference between the two monomers (93 as opposed to 24 kJ mol^{-1} for the cluster between HCN and H_2O), Table 2. The $\Delta_f H°_0$ calculated with G2 theory is 501 kJ mol^{-1}.

$(CH_3CN)(HF)H^+$. The acetonitrile−HF proton-bound dimer has C_s symmetry and an asymmetric hydrogen bond. Indeed, the cluster can be described as a protonated acetonitrile molecule solvated by HF, the $F-H_b$ bond (1.660 Å) being longer than that in $(HCN)(HF)H^+$ (1.605 Å). The binding energy of this cluster is predicted to be only 53 kJ mol^{-1}, the lowest value for the clusters in this study. Accordingly, the PA difference between CH_3CN and HF is the largest of any other dimer, 296 kJ mol^{-1}. The G2 0 K heat of formation of this dimer is 509 kJ mol^{-1}.

$(CH_3CN)(CH_3NH_2)H^+$. The geometry of $(CH_3CN)(CH_3NH_2)H^+$ is analogous to $(HCN)(CH_3NH_2)H^+$, having C_s symmetry and similar hydrogen bond lengths. The bond to acetonitrile is 1.810 Å (1.873 Å for the HCN containing cluster), while the bond to methylamine is 1.050 Å (as compared to 1.044 Å in the smaller analogue). It was impractical to obtain G2 energies for a system this large with our resources, so only the G2(MP2,SVP) level of theory was employed, a level of theory that we previously found to yield reliable thermochemical values for nitrile-containing cluster ions.[28] A comparison of the performance of G2 variants for the present series of 12 clusters can be found below. The G2(MP2,SVP) 0 K binding energy for this dimer is 112 kJ mol^{-1}. This is greater than that calculated for $(HCN)(CH_3NH_2)H^+$ (87 kJ mol^{-1} at the G2(MP2,SVP) level of theory, Table 2) but less than the acetonitrile−ammonia complex (119 kJ mol^{-1}). Accordingly, the PA difference between CH_3CN and CH_3NH_2 lies between those of the other two dimers (119 as opposed to 188 kJ mol^{-1} for $(HCN)(CH_3NH_2)H^+$ and 72 kJ mol^{-1} for $(CH_3CN)(NH_3)H^+$). The $\Delta_f H°_0$ calculated at the G2(MP2,SVP) level of theory is 609 kJ mol^{-1}.

$(CH_3CN)(CH_3OH)H^+$. The methanol−acetonitrile proton-bound dimer has C_1 symmetry at the MP2/6-31+G(d) level of theory. Like $(HCN)(CH_3OH)H^+$, the geometry of the cluster can be described as protonated methanol solvated by CH_3CN (Figure 1). However, the lowest energy simple-bond dissociation products are $CH_3CNH^+ + CH_3OH$ since the PA of acetonitrile is over 25 kJ mol^{-1} higher than that of methanol. This cluster has been experimentally studied by El-Shall and co-workers,[13] Zhang and Castleman,[14] and Mayer.[15] The first two experimental studies focused on the relative thermochemistry of acetonitrile−methanol clusters but were unable to derive experimental values for the binding energy of the mixed dimer, only the higher homologues. Work from this laboratory[15] on the unimolecular chemistry of this dimer ion showed that a second reaction competes with dissociation to $CH_3CNH^+ + CH_3OH$, yielding $CH_3CNCH_3^+ + H_2O$. The water loss products come about by the isomerization of the proton-bound dimer to an ion−molecule complex $(CH_3CNCH_3)(H_2O)^+$, which is lower in energy than the proton-bound dimer. The G2(MP2,SVP) binding energy reported here, 119 kJ mol^{-1}, is 4 kJ mol^{-1} lower than that of $(HCN)(CH_3OH)H^+$ and 25 kJ mol^{-1} greater than that of $(CH_3CN)(H_2O)H^+$. The PA difference between acetonitrile and methanol (25 kJ mol^{-1}) lies between the PA difference for these other two clusters (Table 2). The G2(MP2,SVP) $\Delta_f H°_0$ for this dimer is 519 kJ mol^{-1}, which is similar to the G2 value (522 kJ mol^{-1}) reported in earlier work from this laboratory.[15]

$(CH_3CN)(CH_3F)H^+$. The proton-bound acetonitrile−methyl fluoride dimer has C_s symmetry and can be regarded as a protonated acetonitrile molecule solvated by CH_3F (Figure 1). The structure is analogous to the HCN dimer with CH_3F in that there is a long H−F hydrogen bond of 1.542 Å. The binding energy of this cluster calculated at the G2(MP2,SVP) level of theory is 76 kJ mol^{-1}, which is greater than the cluster between acetonitrile and HF but less than $(HCN)(CH_3F)H^+$. The PA difference between CH_3CN and CH_3F, 182 kJ mol^{-1}, lies intermediate to those of the aforementioned dimers (Table 2).

Comparison of G2 Variants. The 0 K heats of formation and binding energies for this series of 12 cluster ions have been obtained at the G2, G2(ZPE=MP2), G2(MP2), and G2(MP2,SVP) levels of theory (Tables 1 and 2). There is generally good agreement between the four methods, as found in a recent assessment from this laboratory.[28] The heats of formation are all within 8 kJ mol^{-1} of one another, with the majority being within 5 kJ mol^{-1}. The largest discrepancies occur for G2(ZPE=MP2). This was seen previously in our assessment[28] and can be attributed to the change in zero-point vibrational energy in going from HF/6-31G(d) to MP2/6-31G(d) values. There is a slightly larger spread in the values for the binding energies, arising from the increased error in the calculation of total energies for the dissociation products using the less demanding G2 variants (Table 3). Still, the total spread in binding energies among the four methods averages around only 10 kJ mol^{-1}. So it appears that all of the G2 variants tested here give reasonable binding energies for these 12 proton-bound dimers.

Binding Energies. The binding energies of the above proton-bound dimers follow the general trend predicted by Kebarle[39] and Larson and McMahon[40] for oxygen-substituted heterodimers; an increase in the difference between the PA of the two constituent monomers results in a decrease in the binding energy of the unsymmetric dimer (Figure 2). A linear regression through the data in Figure 2 produces a line with slope −0.26 ± 0.03 and intercept of 125 ± 9 kJ mol^{-1}. This relationship may be useful for predicting the binding energies of other nitrile-containing proton-bound dimers. The regression predicts that for two monomers of equal PA, the binding energy should be approximately 125 ± 9 kJ mol^{-1}. The G2 binding energy of the $(HCN)_2H^+$ dimer has been calculated to be close to this,

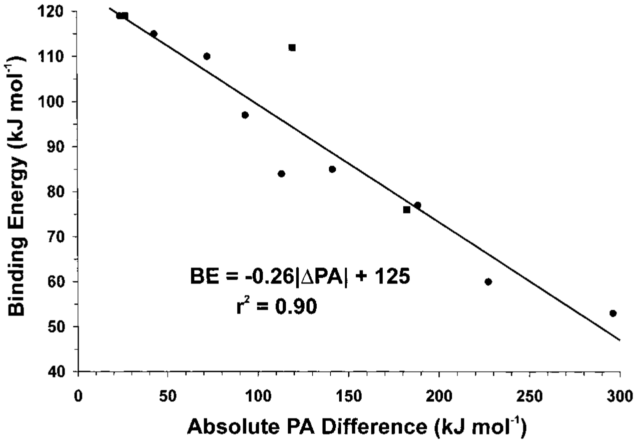

Figure 2. Plot of the G2 dimer binding energy vs the absolute value of the proton affinity difference of the constituent monomers. For the three largest dimers, $(CH_3CN)(CH_3NH_2)H^+$, $(CH_3CN)(CH_3OH)H^+$, and $(CH_3CN)(CH_3F)H^+$, G2(MP2,SVP) values were used (■).

118 kJ mol^{-1},[28] while the experimental values for the two symmetric dimers $(HCN)_2H^+$ and $(CH_3CN)_2H^+$ are also close to this value, 126 kJ mol^{-1}.[41]

4. Summary

The structures and heats of formation of the proton-bound dimers between first-row hydrides (NH_3, H_2O, HF, CH_3NH_2, CH_3OH, and CH_3F) and HCN and CH_3CN have been obtained from theoretical calculations. The binding energies calculated for these 12 cluster ions follow the trend first described by Kebarle for unsymmetrical proton-bound alcohol dimers; that is, the binding energy decreases as the proton affinities of the two constituent monomers become more dissimilar. An empirical relationship between the absolute PA difference of the two monomers (|ΔPA|) and the binding energy of the dimer (BE), BE (kJ mol^{-1}) $= -0.26|\Delta PA| + 125$ kJ mol^{-1}, may be useful for predicting the binding energies of other dimers involving nitriles.

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