Does Ammonia Hydrogen Bond?

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Spectroscopic characterizations of the stereochemistry of complexes of ammonia (NH_3) have strongly confirmed some long-held ideas about the weak interactions of NH_3 while casting doubt on others. As expected, NH_3 is observed to be a nearly universal proton acceptor, accepting hydrogen bonds from even some of the weakest proton donors. Surprisingly, no evidence has been found to support the view that NH_3 acts as a proton donor through hydrogen bonding. A critical evaluation of the work that has been done to gather such evidence, as well as of earlier work involving condensed-phase observations, suggests that NH_3 might well be best described as a powerful hydrogen-bond acceptor with little propensity to donate hydrogen bonds.

THE CONCEPT OF HYDROGEN BONDING HAS BEEN A POWERFUL one in the study of intermolecular interactions, primarily because it allows successful predictions of molecular structures. The prevalence of hydrogen bonding in biological and aqueous systems together with the simplicity of the theory have led to extensive study of this particular intermolecular interaction (*1*). This concept has played a major role in the understanding of the structure of ice and of liquid water as well as other condensed media, has been an essential part of theories of solvation in aqueous systems, and has had important impact in biochemistry, especially in theories about the structures and functions of proteins (*2*).

An effective definition of hydrogen bonding has been provided by Pimentel and McClellan (*1*). A hydrogen bond is said to exist when (i) there is evidence of a bond, and (ii) there is evidence that this bond specifically involves a hydrogen atom already covalently or ionically bonded to another atom. This definition is flexible enough to include the nonlinear hydrogen bonds observed in cyclic $(HF)_3$ (*3, 4*), yet restrictive enough to resist the acceptance of every hydrogen-containing molecule as a hydrogen bonder. The fundamental examples of hydrogen-bonding molecules have been H_2O, HF, and NH_3. Although it is not difficult to obtain evidence demonstrating that a complex satisfies the first part of the above definition, rigorously proving that it satisfies the second part is much more difficult, as it essentially requires locating the positions of the protons in the system. This difficult task has been most directly approached in the past through neutron diffraction studies of crystals. A more recent approach has been to study the structures of gas-phase dimers through rotational and vibrational spectroscopy. With this approach the fundamental interaction that is needed for input into condensed-phase theories, that is, the intermolecular pair potential, can be studied. An important aspect of such a study of pair interactions is that a separate and independent evaluation of the propensity of a species to donate and to accept hydrogen bonds can be carried out.

Gas-Phase Hydrogen Bonding

Abundant data, most of which has been obtained by either high-resolution microwave (*5–7*) or infrared spectroscopy (*8*), confirms that hydrogen bonding can occur in the gas phase. As expected, both H_2O and HF readily form hydrogen bonds, both as donors and as acceptors of the hydrogen bond. Although NH_3 vigorously accepts hydrogen bonds in the gas phase, there is yet no example in which NH_3 acts as a hydrogen-bond donor. The stereochemistry of the weak interactions of ammonia is dominated by its lone-pair orbital, which leads to the characterization of NH_3 as a strong Lewis base. NH_3 accepts hydrogen bonds in the complexes H_3N–HCN (*9*), H_3N–HF (*10*), H_3N–HOH (*11*), H_3N–HCl (*12*), H_3N–HBr (*13*), H_3N–HCCH (*14*), H_3N–HCF_3 (*15*), and H_3N–HSH (*16*). Because NH_3 can serve as a hydrogen-bond acceptor with even the weakest donors, it serves as an ideal calibrant of gas-phase acidities. Even in interactions that do not involve hydrogen bonding, NH_3 acts more like a Lewis base that interacts through its lone-pair electrons, as in the T-shaped H_3N–CO_2 (*17*) and H_3N–N_2O (*18*) complexes, with the nitrogen of NH_3 essentially directed toward the central atom of each triatomic molecule. A summary of the structural data of NH_3 van der Waals complexes is given in Table 1. The binding energies (D_0) of several NH_3 complexes have been established through CO_2-laser photodissociation experiments to be less than 2.8 kcal/mol (*19*).

The above points are illustrated by the van der Waals stereochemistry of the first-row hydrides. Consider the six dimeric species that may be formed from the HF, H_2O, and NH_3 monomers. If it is assumed that the dimers bond through linear hydrogen bonds with the basic monomer oriented with a lone pair of electrons pointing toward the donated hydrogen atom, and if it is also assumed that the ability to donate hydrogen bonds increases from NH_3 to H_2O to HF, the structures of five of these dimers can be correctly deduced. The predicted structures are shown in Fig. 1. All are in essential agreement with experimental data (*10, 11, 20–22*), except for the NH_3 dimer. In that case alone NH_3 is required to donate a hydrogen bond, and in that case alone this simple hydrogen-bonding model fails to predict the experimental structure. In Fig. 1 the observed hydrogen-bonding lengths are also displayed; the HF hydrogen bonds are shortest (and presumably strongest) and range from 1.78 to 1.83 Å, whereas the H_2O hydrogen bonds vary from 2.02 to 2.05 Å.

It is reasonable to ask what other basic substances (besides NH_3 itself) may reveal NH_3 as a hydrogen-bond donor if it possesses this capacity. Reasonable candidates for this task are CO and Ar. Those

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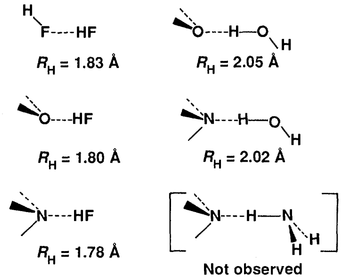


Fig. 1. Linearly hydrogen-bonded structures of the dimeric complexes of the first-row hydrides, HF, H_2O, and NH_3. High-resolution spectroscopy has established these structures to be correct except in the case of NH_3 dimer.

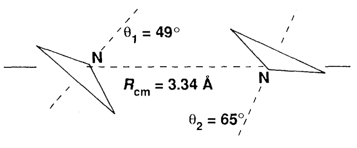


Fig. 2. Least biased representation of the experimentally observed structure of NH_3 dimer. Each NH_3 monomer is drawn as the projection of a cone, since the locations of the hydrogen atoms along the base of the cones are not known. The dihedral angle between the planes formed by R_{cm} and the C_3 symmetry axes of the two ammonia units is not known.

complexes of NH_3, CO, and Ar that have been studied with HF, H_2O, and even HCN are all characterized by linear hydrogen bonds [the structure of Ar–(H_2O) is not known]. If NH_3 effectively hydrogen bonds, one might expect linear hydrogen-bonded complexes of NH_3 with NH_3, CO, and Ar. These three hypothetical structures, in which NH_3 donates a hydrogen bond, have been observed to be incorrect by high-resolution microwave spectroscopy. The experimentally determined structures of these species will be discussed in the next section. These results were quite unexpected and required that the pair interactions of NH_3 are not dominated by hydrogen-bond donation, as was previously supposed.

Microwave Spectroscopy of van der Waals Complexes of NH_3

The (NH_3)–(NH_3) (*23–25*), (NH_3)–(CO) (*26*), and (NH_3)–Ar (*27*) complexes were each studied by high-resolution microwave spectroscopy with the use of molecular-beam electric resonance (*28*) and Fourier transform (*29*) techniques. The complexes are formed in an adiabatic expansion in a supersonic jet that cools them to very low rotational temperatures (1 to 10 K). From the rotational spectra, three structurally important quantities are generally obtained: the average rotational constant for rotation of the complex with its angular momentum oriented perpendicular to R_{cm} (the line connecting the centers of mass of the two subunits); μ_a, the projection of the dipole moment of the complex on the **a** inertial axis (the **a** axis is essentially along R_{cm}); and eqQ_{aa}, the diagonal component of the quadrupole coupling constant of the complex along the **a** axis.

The rotational constant of the complex provides a sensitive measure of R_{cm}. The dipole moment and quadrupole coupling constant each provide information about the orientation of the subunits of the complex. The quadrupole coupling constant in particular provides a precise measure of the polar angle of a subunit that possesses an atom with a nuclear electric quadrupole moment. By polar angle, we mean the angle between the symmetry axis of the subunit and the **a** inertial axis of the complex (essentially R_{cm}). For the three complexes discussed here, only the orientations of the NH_3 subunits are measured by this technique.

We have studied in the NH_3 dimer complex five isotopomers of the complex to assure ourselves that large-amplitude zero point oscillations do not produce structural artifacts (*25*): $^{14}NH_3$–$^{14}NH_3$, $^{14}NH_3$–$^{15}NH_3$, $^{15}NH_3$–$^{14}NH_3$, $^{14}ND_3$–$^{14}ND_2H$, and $^{14}ND_3$–$^{14}ND_3$. For the primary isotopomer, the value of R_{cm} is 3.337 Å. From the quadrupole coupling constant of each NH_3 subunit we obtain its polar angle. The result is $\theta_1 = 49°$ and $\theta_2 = 65°$. This experimental structure is not at all like the expected "classical" linear hydrogen-bonded structure (Fig. 1). The measured value of μ_a (0.74 D) is consistent with this structure ($\theta_1 = 49°$ and $\theta_2 = 65°$) and is much smaller than the value expected for the classical structure (~2 D). These results are somewhat surprising, and it is natural to ask whether some dynamical effect might be clouding our view of the structure. Large-amplitude tunneling motions between symmetrically equivalent configurations of the complex are an important concern because of the high symmetry of this system. It must be shown that the tunneling dynamics and normal vibrational averaging effects do not produce a vibrationally averaged structure that is grossly different from the equilibrium structure of the complex. The evidence concerning this point is drawn from the isotopic substitution experiments and is quite convincing. The variation of the polar angles of the complex with isotopic substitution is only 3° or 4°, and shows that these measurements provide a good estimate of the equilibrium structure of the complex and that dynamical effects do not severely complicate the experimental structure determination.

This result is a bit surprising, since interchange tunneling dynamics play such an important role in the spectroscopy of the analogous HF dimer system (*20*). By interchange tunneling, we mean a motion that interchanges the structural roles of the two subunits and thereby reverses the direction of μ_a. A classification of the tunneling-rotational eigenstates of the NH_3 dimer in the molecular symmetry group (*24*) provides a clear explanation for this phenomenon. This analysis predicts that the dynamics of the NH_3 dimer will depend strongly on the internal angular momentum of the two NH_3 tops. In particular, states of the NH_3 dimer that have no angular momentum in either top or a single unit of angular momentum in each top will behave similar to the HF dimer. These states will undergo interchange tunneling. States of the dimer with one unit of angular momentum in one top and zero units of angular momentum in the second top will behave quite differently. These states have no interchange tunneling to first order and can only interchange tunnel through a second-order effect. The asymmetric excitation of internal rotation in the two subunits breaks the symmetry of the problem and quenches the interchange tunneling for these particular quantum states (*30*). The experimentally observed electric-dipole selection rules indicate that it is these noninterchanging states of the dimer that have been studied thus far.

The structure of the NH_3 dimer is shown in Fig. 2. Each NH_3 subunit is drawn as a cone to indicate that we have no experimental evidence concerning the positions of the six hydrogen atoms except that they lie along the bases of the cones. The symmetry axes of the two NH_3 monomers are drawn coplanar for convenience; there is yet no experimental evidence concerning that aspect of the structure as well. The structure is far removed from the "classical" linear hydrogen-bonded structure; the polar angles differ from those of the classical structure by more than 45°. Although the exact position of the potential minimum with respect to the orientation of the hydrogen atoms is not known, none of the allowed structures can be easily described as hydrogen bonded. Perhaps the best hydrogen bond would result if the NH_3 subunit that is tilted at 65° donated a hydrogen bond with the hydrogen atom in the plane defined by the symmetry axes of the two subunits. Even then the hydrogen bond formed would be quite peculiar. The N–H $\cdots$ N bond angle would be only 120° (compared to the ideal value of 180°), and the hydrogen-bond length would be 2.64 Å. Even then the weakly hydrogen bonded systems H_3N–HCCH (*14*), H_3N–HCF_3 (*15*), and H_3N–HSH (*16*) have much shorter bond lengths (2.33 Å,

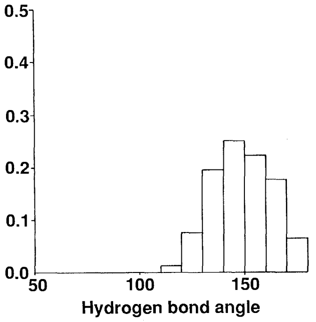


Fig. 3. Histogram showing the distribution of hydrogen-bond angles for a randomly oriented NH_3 molecule in an octahedral crystal site (the model is explained in the text). Even for this random distribution, structures that appear to be nearly linearly hydrogen bonded have significant probability.

2.31Å, and 2.32 Å, respectively). Thus the NH_3 dimer is not properly described as a hydrogen-bond complex.

Modern electronic structure theory is an increasingly powerful guide to the geometries of small molecules. Several good theoretical calculations have been performed to investigate the intermolecular potential of the NH_3 dimer. The conclusions drawn from these calculations have been surprisingly divergent. Three electronic structure calculations (each correcting for electron correlation) and two electrostatic calculations have obtained essentially three distinct structures. Structures near the classical linear hydrogen-bonded structure were obtained by Frisch *et al.* ($\theta_1 = 8^\circ$, $\theta_2 \simeq 110^\circ$) (*31*); by Liu *et al.* ($\theta_1 = 12^\circ$, $\theta_2 = 101^\circ$) (*32*); and by Stone ($\theta_1 \simeq 15^\circ$, $\theta_2 \simeq 105^\circ$) (*33*). Latajka and Scheiner found a centrosymmetric structure (*34*) ($\theta_1 = \theta_2 = 68^\circ$) with no dipole moment. Sagarik *et al.* found a compact structure (*35*) with $\theta_1 = 61^\circ$ and $\theta_2 = 75^\circ$; this last calculation shows the best agreement with experiment in terms of both polar angles and the electric dipole moment.

Although the ammonia dimer is the most dramatic example of the lack of proton-donor behavior of NH_3, the NH_3-CO system is a further demonstration. Carbon monoxide accepts hydrogen bonds from the hydrogen halides, water, and hydrogen cyanide. The complex (NH_3)–(CO) is a reasonable candidate to be hydrogen bonded. The spectroscopy of this system is quite complicated (*26*); three $\Delta J = 1, K = 0$ progressions, and two $\Delta J = 1, K = 1$ progressions have been observed, where J and K are the quantum number labels of the rotational states. This implies that nonrigidity plays an important role in this species. Internal rotation about the NH_3 symmetry axis is undoubtedly one dynamical effect. Furthermore, at least two factors indicate that this system is particularly weakly interacting. The value of R_{cm} is fairly large at 3.6 Å. In H_3N-CO_2 the corresponding value is only 3.05 Å (*17*). Furthermore, a stretching frequency for the weak bond may be estimated from the spectroscopically measured centrifugal distortion constant. Its value is only 41 cm^{-1}. This value is only slightly larger than that of Ar_2 (26 cm^{-1}) (*36*) and much smaller than that of H_3N-CO_2 (98 cm^{-1}) (*17*). Extensive isotopic substitution in this complex has shown that the orientation of the NH_3 symmetry axis is well defined. The NH_3 polar angle falls between 35.4° and 37.0° for (ND_3)–(CO), (ND_2H)–(CO), (NDH_2)–(CO), (NH_3)–(CO), and (NH_3)–(^{13}CO). The same consistency is seen in the component of the dipole moment along the **a** inertial axis. It varies between 1.28 D and 1.25 D, which is perfectly consistent with the ~36° polar angle and with its isotopic variation. Furthermore, the effect of isotopic substitution on the rotational constant shows that the hydrogen atoms are directed away from the CO subunit in a distinctly non–hydrogen-bonded arrangement. Although the orientation of the CO subunit in this system has not been measured, the NH_3 subunit is not properly oriented to participate in hydrogen bonding.

The (NH_3)–(CO) complex has not been studied theoretically to the extent that the NH_3 dimer has. A recent electronic structure calculation (accounting for electron correlation through second-order Møller-Plesset perturbation theory) by Reed *et al.* (*37*) found two minima of nearly identical binding energy in the intermolecular potential. One minimum was at the linear hydrogen-bonded configuration, and the other was at a non–hydrogen-bonded structure similar to that reported here, with a polar angle of ~21°. Several NH_3 complexes were studied, and these researchers concluded that the weak σ^* electron-pair-acceptor strength of NH_3 is responsible for its difficulty in donating a proton in hydrogen-bond formation.

Although the complexes of argon with the hydrogen halides are characterized by linear hydrogen bonds, and Ar–(HCN) is probably best viewed as linearly hydrogen bonded (*38*), Ar–(NH_3) does not possess a well-defined hydrogen-bonded structure (*27*). It is an inherently dynamical complex in which the usual structural concepts lose their value. There is a well-defined separation distance (R_{cm} = 3.84 Å), but the NH_3 subunit is not rigidly oriented even by van der Waals' standards. In this regard, the intermolecular potential for Ar–(NH_3) seems similar to what we expect for Ar–(CH_4). The NH_3 monomer undergoes three-dimensional internal rotation and also probably inverts through its umbrella coordinate. The evidence for the internal rotation is provided by the quadrupole coupling constant and by the dipole moment of the complex. An attempt to infer a rigid orientation for the NH_3 subunit through these quantities fails, since the two constants yield markedly different estimates of the polar angle. From each quantity the NH_3 subunit appears to be oriented at its respective magic angle, that is, the angle for which the corresponding monomer property has no projection along the **a** axis of the dimer. From the quadrupole coupling constant we obtain $\theta = 58.3(1)^\circ$ (the number in parentheses is the error in the last digit), whereas the dipole moments produces $\theta = 85(5)^\circ$. In the limit of totally free internal rotation, the quadrupole coupling constant in this state should approach zero and the dipole moment should become quite small. In fact, each of these quantities is small, the magnitude of the quadrupole coupling constant of the complex is less than 10% of that of NH_3, and the **a** component of the dipole moment is less than 20% of the NH_3 dipole moment. Although the orientation of the complex at the minimum of the intermolecular potential is not yet known, the energy well is not very deep or restrictive in the angular coordinates. In this sense, at least, the Ar–(NH_3) van der Waals complex is not well described by a hydrogen-bonding model.

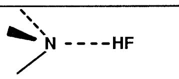
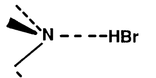
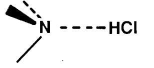
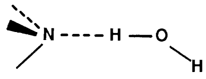
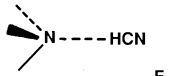
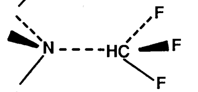
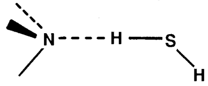
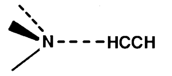
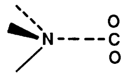
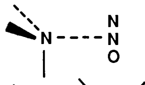
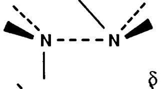
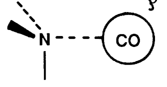
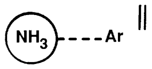
NH_3 in the Condensed Phase

The structures of the complexes of NH_3 suggest that NH_3 is an active hydrogen-bond acceptor but is quite reluctant to donate hydrogen bonds. This gas-phase view of NH_3 interactions is in sharp contrast with the traditional view of NH_3 interactions described in most freshman chemistry textbooks (*39*). In the traditional view, NH_3 is a facile donor and acceptor and readily forms hydrogen bonds to itself. This amphoteric view of NH_3 interactions is mainly supported by condensed-phase observations that do not structurally characterize the pair interactions. It is, of course, possible that NH_3 simply behaves differently in the condensed phase, where many-body interactions may be important. Then the resulting description of NH_3 interactions would be environment dependent. This would be very different from the situation with HF and H_2O. In crystalline HF (*40*) and H_2O (*41*), the structures of the nearest neighbors in the crystal closely mimic the structures of the analogous gas-phase dimers, the obvious difference being a 0.1- to 0.2-Å contraction of the hydrogen-bonding distance in the condensed phase. The condensed-phase evidence for NH_3 hydrogen bonding is actually much less convincing than that available for HF and H_2O. The two most often cited pieces of evidence for NH_3

hydrogen bonding are its anomalously high boiling point and its crystal structure (*42*). This evidence does not fare well under careful analysis.

The crystal structure of NH_3 has been interpreted as hydrogen bonded, yet the N–H···N bond angle is not 180°, but only 164(2)°. This is a serious problem, since with three hydrogen atoms on each subunit it is difficult to conceive of any reasonable crystal structure without some hydrogen atoms pointed in the general direction of a nitrogen atom. We have modeled this problem computationally by placing one NH_3 molecule in an octahedral site that is surrounded by six nitrogen atoms. The NH_3 molecule is rotated over a fine grid of all possible orientations. At each orientation the most favorable N–H···N bond angle is recorded. The distribution of hydrogen-bond angles that results from this random distribution of orientations is shown in Fig. 3. The most probable hydrogen-bond angle for a randomly oriented NH_3 crystal would be 149°. Furthermore, the distribution of angles has a full width at half maximum of ~40°. The actual angle measured in the NH_3 crystal is well within this distribution of random angles and is as close to the peak of this distribution as it is to the idealized hydrogen-bond angle of 180°. The peak of distribution might be even closer to the measured angle if one included non–hydrogen-bonding orientational effects such as the repulsion between two NH_3 molecules that directs their lone-pair electrons toward each other. Thus it is not obvious that the crystal structure of NH_3 indicates that NH_3 is an effective hydrogen-bond donor.

Table 1. Observed structures of NH_3 complexes.

Bonding partner	R (Å)*	μ_a (D)	Structure
HF	1.78	(4.4)†	
HBr	1.83		
HCl	1.85		
H_2O	2.02	2.97	
HCN	2.16	5.26	
CF_3H	2.31		
H_2S	2.32	2.67	
HCCH	2.33	1.99	
CO_2	2.99	1.77	
N_2O	3.09	1.51	
NH_3	3.27	0.74	
CO	(3.59)‡	1.25	
Ar	(3.84)‡	0.28	

*This is the distance separating the atoms connected by the dashed line in the figure. For the hydrogen-bonded complexes, this is the hydrogen-bond length. †The dipole moment of $H_3N–HF$ has not yet been measured. Given value is an estimate that includes the induced dipole-moment effects. ‡This distance is a center-of-mass separation. §The orientation of the CO subunit in $(NH_3)–(CO)$ has not yet been determined. ‖The NH_3 subunit in $Ar–(NH_3)$ is not rigidly oriented.

There are other features of the crystal structure of NH_3 that resist interpretation as hydrogen bonding. The length of the hydrogen bond is large compared to those of the hydrogen-bonded crystals of HF and H_2O. For HF (*40*) and H_2O (*41*) these distances are ~1.57 Å and ~1.74 Å, respectively. In the NH_3 crystal (*42*) the distance of 2.37 Å is nearly 50% larger. This does not suggest a strong directional interaction as in the other two systems. Pimentel and McClellan (*1*) reviewed condensed-phase N–H···N hydrogen bonds and reported an average heavy-atom separation of 3.10 Å with a standard deviation of 0.13 Å. The corresponding value for the NH_3 crystal is 3.38 Å. This distance is more than two standard deviations larger than the average value. Pimentel and McClellan cited the large bond length in this system as "the limiting distance at which hydrogen bonding vanishes." Similar evidence is present in the $NH_3 \cdot H_2O$ crystal (*43*). The bond lengths for H_2O hydrogen bonding to H_2O or NH_3 are much shorter (~0.5 Å) than the distance that might be interpreted as NH_3 hydrogen bonding to H_2O.

The anomalously high boiling points of the first-row hydrides have been presented as evidence for hydrogen bonding. This conclusion may only be reached through extremely indirect reasoning. Although strong hydrogen bonding will undoubtedly lead to elevated boiling points, the converse of this statement is not necessarily true. The anomalous boiling points probably indicate a larger association energy in these systems for some reason. A calculation of the NH_3 boiling point, however, is a difficult many-body problem. To bypass this complicated dynamical problem and extract detailed structural information seems at best an optimistic procedure. The danger of this procedure can be seen by examining trends in other macroscopic properties that are equally difficult to interpret but suggests that NH_3 differs from HF and H_2O in the condensed phase. Trends in liquid dielectric constant, in entropy of vaporization, and in the effect of methylation on boiling point all distinguish NH_3 from hydrogen-bonding substances like HF and H_2O. These trends are not presented as a convincing argument against NH_3 hydrogen bonding but rather as an indication of the ambiguity involved in interpreting these macroscopic observations. The boiling point of NH_3 may be anomalous for reasons other than hydrogen bonding.

Conclusions

For many years the traditional view has been that the condensed-phase interactions of NH_3 are dominated by hydrogen bonding. NH_3 has been viewed as an amphoteric substance that can donate as well as receive a proton in hydrogen bonding. Surprisingly, gas-phase structural studies of NH_3 complexes challenge this view of the weak interactions of NH_3. The picture of NH_3 interactions that emerges is only in partial agreement with the traditional view. In its pair interactions, NH_3 is an excellent hydrogen-bond acceptor. With even the feeblest Lewis acids, NH_3 consistently donates its lone-pair electrons and forms readily predictable structures. Thus the structures of $H_3N–HCN$, $H_3N–HF$, $H_3N–HOH$, $H_3N–HCl$, $H_3N–HBr$, $H_3N–HCCH$, $H_3N–HCF_3$, and $H_3N–HSH$ are all characterized by linear hydrogen bonds. It is also the lone-pair electrons of NH_3 that are active in its interaction with the weak Lewis acids CO_2 and N_2O. However, NH_3 shows no evidence for hydrogen-bond donation in its gas-phase interactions with Lewis bases.

The hydrogen-bonding behavior of HCl seems to be just the opposite of that of NH_3, though perhaps less extreme. That is, HCl is an excellent hydrogen-bond donor but a poor acceptor. Although there is evidence that HCl forms hydrogen bonds with itself (unlike NH_3), it is clear that it does not play the role of the acceptor well. For example, HF is a better hydrogen-bond donor than HCl (HF has shorter bond lengths in its complexes with H_2O and CO). In the HF–HCl complex (*44*), however, it is HCl that hydrogen bonds to HF. The obvious explanation for this is that HCl donates the hydrogen because it is a poor acceptor. Another indication of this inability is the nonrigidity and the small binding energy observed in (HCl)–(HCl) (*45, 46*).

If NH_3 itself is a poor hydrogen bond donor, we may ask, "What is required to activate an N–H group so that it will hydrogen bond?" This sort of question was originally asked about the C–H group, and considerable condensed-phase and gas-phase work have shown that HCN, HCCH, and various halogenated alkanes form C–H hydrogen bonds. HCN, HCCH, and CF_3H each form hydrogen-bonded complexes with NH_3 in the gas phase. Not surprisingly, activated N–H hydrogen bonds have also been observed. Double hydrogen bonds, in which one of the bonds is the result of proton donation by an amide have been seen in amide–trifluoroacetic acid complexes (*47*) and in water–formamide (*48*). The N–H $\cdots$ O hydrogen bonds in these systems are quite short at $\sim$1.6 Å and 1.99 Å, respectively. Intramolecular-amine hydrogen-bond donation has been observed in ethylenediamine and similar species (*49*). Much condensed-phase evidence relates to N–H hydrogen bonds in amines, amides, and ammonium ions. Hydrogen-bond lengths for these systems are typically only 0.1 to 0.2 Å longer than those observed in O–H hydrogen bonds. These observations are important elements in current theories of the structure and dynamics of proteins and nucleic acids, and thus it will be important to perform more gas-phase studies of N–H hydrogen-bonding trends, particularly those involving systems with single hydrogen bonds.

Definite conclusions concerning hydrogen bonding can be elusive, since it is difficult to rigorously define a hydrogen bond. The classic examples of hydrogen bonds are nearly linear, span short distance, and exhibit strong interactions. Although the definition of hydrogen bonding can be expanded to allow exceptions to these guidelines, without care one might classify methane as a hydrogen-bonding substance. The hydrogen-bonding concept is useful since it allows predictions to be made and observations of the hydrogen bond as a dominant effect to be explained. Given that HF and H_2O hydrogen bond, their crystal structures as well as their gas-phase dimer structures can be predicted; hence the hydrogen-bonding concept is valuable in these systems. In contrast, the concept is misleading as a predictor of the NH_3 dimer orientation and separation distance and not very illuminating as a rationalization of the NH_3 crystal structure. For these reasons it does not seem useful to view NH_3 as a hydrogen-bond donor, particularly in its gas phase or pair interactions. If NH_3 is to be classified as a hydrogen-bond donor, it must be considered a very poor donor, forming weaker, longer, and less linear hydrogen bonds than even HCCH (*14*), CF_3H (*15*), and H_2S (*16*).

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