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The Pnicogen Bond: Its Relation to Hydrogen, Halogen, and Other Noncovalent Bonds

STEVE SCHEINER*
Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300, United States

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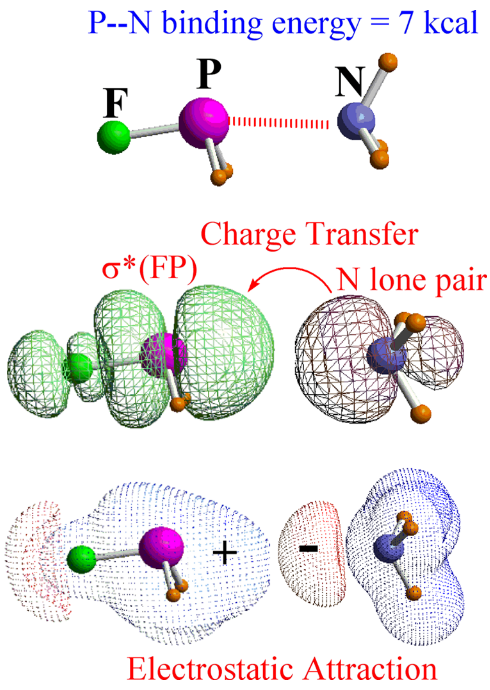

Among a wide range of noncovalent interactions, hydrogen (H) bonds are well known for their specific roles in various chemical and biological phenomena. When describing conventional hydrogen bonding, researchers use the notation AH···D (where A refers to the electron acceptor and D to the donor). However, the AH molecule engaged in a AH···D H-bond can also be pivoted around by roughly 180°, resulting in a HA···D arrangement. Even without the H atom in a bridging position, this arrangement can be attractive, as explained in this Account. The electron density donated by D transfers into a AH σ^* antibonding orbital in either case: the lobe of the σ^* orbital near the H atom in the H-bonding AH···D geometry, or the lobe proximate to the A atom in the HA···D case. A favorable electrostatic interaction energy between the two molecules supplements this charge transfer. When A belongs to the pnictide family of elements, which include phosphorus, arsenic, antimony, and bismuth, this type of interaction is called a pnicogen bond. This bonding interaction is somewhat analogous to the chalcogen and halogen bonds that arise when A is an element in group 16 or 17, respectively, of the periodic table.

Electronegative substitutions, such as a F for a H atom opposite the electron donor atom, strengthen the pnicogen bond. For example, the binding energy in $FH_2P\cdots NH_3$ greatly exceeds that of the paradigmatic H-bonding water dimer. Surprisingly, di- or tri-halogenation does not produce any additional stabilization, in marked contrast to H-bonds. Chalcogen and halogen bonds show similar strength to the pnicogen bond for a given electron-withdrawing substituent. This insensitivity to the electron-acceptor atom distinguishes these interactions from H-bonds, in which energy depends strongly upon the identity of the proton-donor atom.

As with H-bonds, pnicogen bonds can extract electron density from the lone pairs of atoms on the partner molecule, such as N, O, and S. The π systems of carbon chains can donate electron density in pnicogen bonds. Indeed, the strength of $A\cdots\pi$ pnicogen bonds exceeds that of H-bonds even when using strong proton donors such as water with the same π system.

H-bonds typically have a high propensity for a linear AH···D arrangement, but pnicogen bonds show an even greater degree of anisotropy. Distortions of pnicogen bonds away from their preferred geometry cause a more rapid loss of stability than in H-bonds. Although often observed in dimers in the gas phase, pnicogen bonds also serve as the glue in larger aggregates, and researchers have found them in a number of diffraction studies of crystals.

Introduction

Because of their importance to a multitude of chemical and biological phenomena, noncovalent bonds have been the subject of inquiry for many years. These interactions span a wide range of strength, from weak van der Waals forces between nonpolar entities, to ion–ion attractions that can be very strong indeed. One such noncovalent interaction which has been carefully analyzed is the hydrogen (H) bond, AH···D (A refers to the electron acceptor and D to the donor). But even with its long record of study,[1−3]

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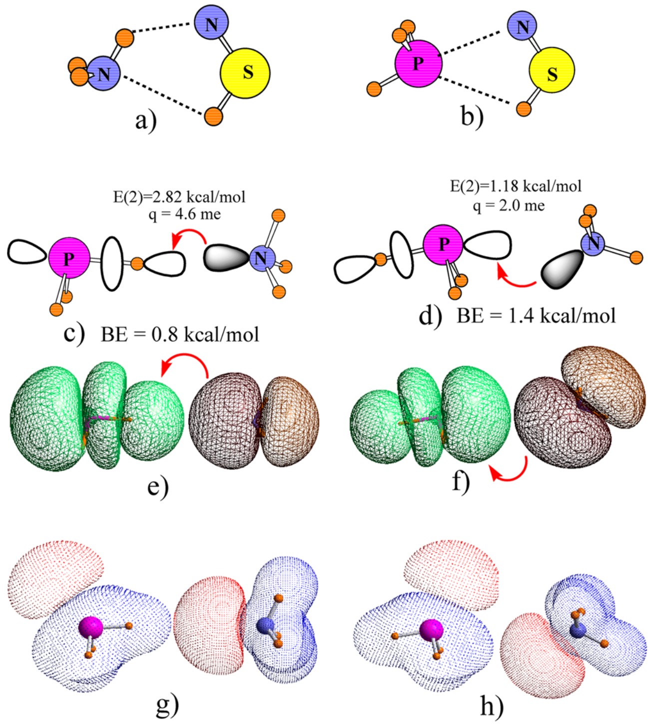

FIGURE 1. Optimized geometries of the complexes pairing HSN with (a) NH_3 and (b) PH_3. Minima on the PH_3/NH_3 heterodimer surface are shown as (c) H-bonded and (d) P···N bonded. The occupied lone pair of NH_3 is indicated schematically by the filled lobe, and the empty lobes represent the vacant antibonding σ^* P–H orbital. Red arrows represent charge transfer q with $E(2)$ as its energetic consequence. The NBO N lone pair is brown and vacant σ^*PH green in (e) and (f). Positive/negative electrostatic potentials in (g) and (h) are blue/red.

ongoing investigations have led to some surprises. For example, AH···D H-bonds wherein the interaction shifts the A-H stretching mode to higher frequencies, rather than the red shifts more commonly observed, may not be the usual occurrence, but are no longer considered anomalous.

During a quantum chemical investigation of blue-shifting SH···N H-bonds,[4] it was found that when HSN was paired with any of a series of amines, a SH···N H-bond occurs and is supplemented by a NH···N H-bond in a cyclic structure, as illustrated in Figure 1a. When the amine was replaced by a phosphine, however, rather than simply substitute the latter NH···N H-bond by an analogous PH···N, the H atoms attached to the P rotated out of the way, leaving the P to face the N atom of HSN directly, as in Figure 1b. This avoidance of a bridging position by the phosphine H atoms was not due to steric repulsions, but was the product of a true attraction between the P and N atoms.

It is this attraction between a pnicogen atom such as P and an electron donor molecule, dubbed a pnicogen bond, that serves as the subject of this Account. (These atoms are alternately referred to as pnictogen or pnigogen.[5]) This noncovalent bond is thoroughly analyzed as to its source, and the effects of various substituents. It is compared with other noncovalent interactions, such as H and halogen bonds, to identify common as well as unique features. It is demonstrated that pnicogen bonds can be more attractive than even some strong H-bonds, dominating the geometries of dimers as well as larger aggregates. (This Account excludes other intermolecular forces that are dominated by dispersion, e.g., between a pair of alkanes or aromatic rings.)

Simple Hydrides

By replacing the earlier complexes[4] with the PH_3/NH_3 heterodimer, it was possible to focus attention on the P···N interaction in isolation from the perturbing influence of a second H-bond in the cyclic structures in Figure 1a and b. Calculations revealed[6] a PH···N H-bonded structure shown in Figure 1c as a minimum in the potential energy surface, with a binding energy of 0.8 kcal/mol. Nearly twice as stable is the geometry depicted in Figure 1d which contains a direct P···N confrontation, with all H atoms rotated away from the P···N axis. Dipole–dipole forces between the PH_3 and NH_3 monomers are repulsive. Moreover, there was no apparent σ-hole of positive charge around either molecule[7] that might simply account for this attraction. On the other hand, a more complete treatment of the electrostatic component of the interaction which takes into account multipoles higher than dipole does indicate a certain amount of attraction (see below).

Dissection of the binding energies by two different energy partitioning schemes[6] revealed that contributions arising from the mutual polarizing effects of each molecule upon the electronic structure of its partner were a prime contributor. These forces, sometimes termed induction, or charge transfer and polarization, revealed a big advantage of the P···N bonded **1d** structure over the H-bonded geometry **1c**. Natural bond orbital (NBO) analysis of the wave function quantified the transfer of small amounts of charge from one localized orbital to another, along with an estimate of the energetic contribution made by each such transfer. The curved red arrow in Figure 1c symbolizes the charge transfer from the lone pair of the proton acceptor to the σ^* antibonding orbital of the donor that is a common occurrence in H-bonds. In the case of the PH···N H-bond of **1c**, the transfer of 4.6 millielectrons (*me*) is associated with an energetic stabilization of 2.82 kcal/mol. When the P–H bond is turned away from the N atom as in **1d**, the same sort of transfer is still possible, the difference being that the N lone pair overlaps with the lobe of the PH σ^* orbital that is proximate to the P, rather than to the H as in **1c**. The schematic diagrams of these molecular orbitals (MOs) are replaced in Figure 1e and f by the actual NBO MOs which indicate that the P lobe of the σ^*PH MO is larger than the H lobe which aids its overlap with the N lone pair in **1d**, and hence the amount of transfer remains quite significant, 2.0 m*e*. Charge transfer into a σ^* orbital ought to weaken, and hence lengthen, the related P–H bond. This effect is confirmed in either case, by 0.7 mÅ in **1c** and by the even larger amount of 2.8 mÅ in **1d**. Figure 1g and h displays the full electrostatic potentials around each monomer, which aid in understanding the electrostatic attraction in both configurations, and why the NH_3 molecule is turned away by a certain amount from the P···N axis in **1d**, as this reorientation helps to reduce repulsion between the red negative electrostatic regions.

Having observed that P could be attracted to a N atom, it was natural to wonder if such a phenomenon is restricted to P or is characteristic of other atoms as well. S and Cl lie in the same row of the periodic table, so S···N and Cl···N attractions might be viable as well, as would an As···N bond for third-row As. Indeed, calculations[8] revealed that all three of these bonds are present, using SH_2, HCl, and AsH_3 as substitutes for PH_3 in complexes with NH_3. The occurrence of a Cl···N or S···N attraction was not shocking as they can be categorized as a halogen bond or chalcogen bond, respectively, both of which have received some attention in the literature.[9–12] What was striking, though, was the near interchangeability of these atoms, in the sense that the strengths of the S···N, Cl···N, and As···N bonds are all quite similar, not only to one another but to P···N as well. This similarity offered a striking contrast with H-bonds wherein the energetics are very sensitive indeed to the nature of the proton donor atom, varying from less than 1 kcal/mol for PH···N to more than 8 kcal/mol for ClH···N.[8] Yet the A···N stabilization energies are all within 1 kcal/mol of one another for all four A atoms.

A second contrast with H-bonds arises in the context of the contributions of various components to the binding. Whereas electrostatics nearly dominate the H-bonds, twice as large as any other component, this term is matched and sometimes overshadowed by induction and dispersion in the A···N interactions. And as in the P···N bond, the other A···N bonds also are dependent upon charge transfer from the N lone pair into the antibonding σ^* A–H orbital. The near interchangeability of the P and As atoms is supported by calculations[13] that find the stabilization energy of the NO_2PH_2···NCH complex is virtually unchanged when the P atom is replaced by As.

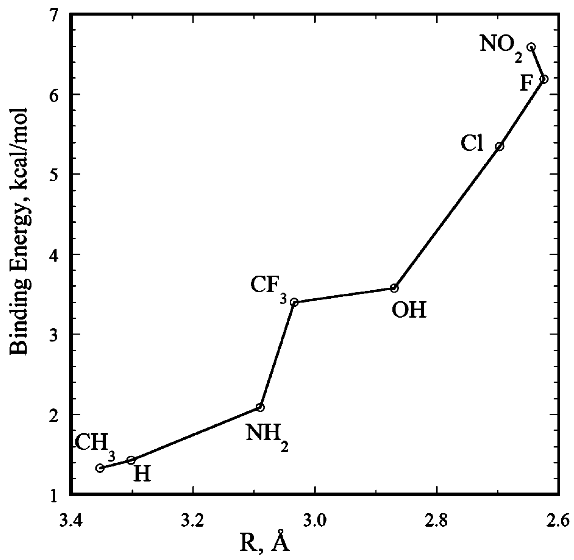

FIGURE 2. Growth of binding energy of BH_2P···NH_3 complexes as B is varied, as labeled on each point, concomitant with a contraction of the intermolecular *R*(P···N) separation.

Of course, dissection of a total interaction energy into its constituent components can be subject to a certain degree of arbitrariness.[14] While some have argued that halogen, chalcogen, and pnicogen bonds derive their stability primarily from electrostatics,[7,15,16] inductive and dispersive forces have been held responsible by others.[17–19] Our calculations have suggested roughly equal contributions from electrostatics and induction, with a smaller dispersion component.

Effects of Substituents

It is well-known that BAH···D H-bonds are strengthened considerably as the electronegativity of the substituent B on the electron acceptor A atom is enhanced, commonly attributed to the drawing of electron density away from the H atom, which polarizes the AH bond. It was natural to inquire as to whether a similar bond strengthening might occur when the bridging H atom was turned away from electron donor D to leave the BHA···D interaction. This issue was examined using the H_3P···NH_3 system as a starting point, replacing one H atom of PH_3 by a number of different atoms and groups.[20] Substituent B positions itself nearly 180° from the N, again consistent with the transfer of charge from the N lone pair into the P lobe of the B–P σ^* antibonding orbital. Figure 2 displays the growth of the binding energy, along with a contracting intermolecular equilibrium distance, for B

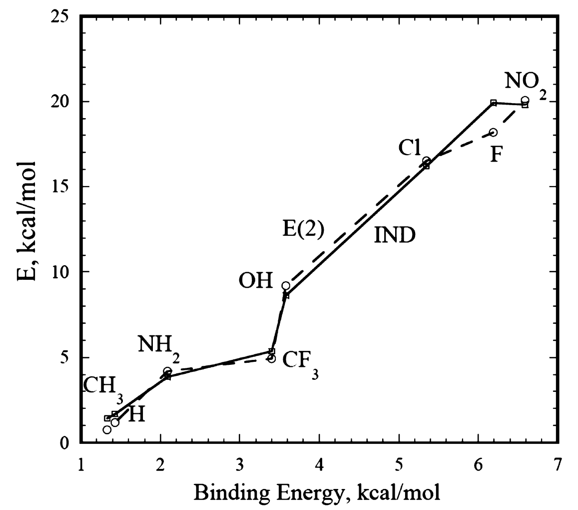

FIGURE 3. Comparison of total induction energy (IND) with that arising only from the transfer of charge from the N lone pair to the σ^* antibonding PB orbital *E*(2) in $BH_2P\cdots NH_3$ complexes.

substituents:

$$B = CH_3 < H < NH_2 < CF_3 < OH < Cl < F < NO_2$$

(There is one "hiccup" in the sense that the NO_2 derivative is slightly more strongly bound than F, although the distance *R* is somewhat longer.) This pattern is consistent with the idea that, just as in H-bonds, binding energy grows with increasing electronegativity of the substituent. The net result is that a $P\cdots N$ bond can be quite strong indeed, amounting to nearly 7 kcal/mol for the F and NO_2 substituents.

As in the case of the simple hydrides, the interaction arises from approximately equal parts electrostatics and charge transfer/induction, both growing proportionately along with the full binding energy. The dispersion energy makes up a significant part of the interaction for the weaker complexes, but grows less quickly with electronegativity of B, so that it is dwarfed by electrostatics and induction for the more strongly bound complexes. In principle, the induction energy includes a range of different components in addition to the $N_{lp}\rightarrow\sigma^*PB$ transfer. Nonetheless, the dominance of the latter contribution is clearly evident in Figure 3 which reveals that the full induction energy (IND) is nearly identical in magnitude to the NBO *E*(2) term which is associated with $N_{lp}\rightarrow\sigma^*PB$.

The ability of an electron-withdrawing substituent to strengthen a pnicogen bond was also apparent in an examination of the NH_3 dimer which does not engage in a $N\cdots N$ type bond. When one NH_3 is replaced by FNH_2, the $FN\cdots N$ configuration becomes a true minimum on the surface, bound by 4 kcal/mol.[21] It is perhaps remarkable that the direct internitrogen attraction is very nearly as strong as the $FNH\cdots N$ H-bond, especially given the ability of the F substituent to enhance the latter via electron withdrawal from the bridging proton.

Perhaps even more impressive is the case wherein the P is replaced by S. SH_2 is considered a decent proton donor, and thus, FSH is anticipated to form quite strong H-bonds. And so it does, engaging in a $FSH\cdots NH_3$ H-bond with a binding energy of 4.8 kcal/mol.[22] The global minimum, however, bound by nearly twice that amount, swings the proton donor molecule around so that the S and N interact directly, with the F atom pivoted nearly 180° from the $S\cdots N$ axis. It is striking that this $XS\cdots N$ bond is preferred also over the halogen-bonded arrangements $HSX\cdots NH_3$ in all cases, whether X is F, Cl, or Br.

Within the context of H-bonds, it is known that the potency of a proton donor is progressively enhanced with each successive halogen substitution. Taking the family of CH donors as an example, CF_3H is a stronger proton donor than is CF_2H_2, which is in turn more potent than CFH_3.[23,24] One might therefore expect a similar trend with respect to $B_nA\cdots D$ interactions. However, this was found not to be the case for the $X_nH_{3-n}P\cdots NH_3$ complexes;[25] indeed any halogenation (whether F, Cl, or Br) beyond the first such substituent acted to *weaken* the $XP\cdots N$ bond. Why was this the case? After all, more electron-withdrawing halogen substituents increase the partial positive charge on the P atom, which ought to enhance its attraction for N. But again, focusing on an atomic charge is misleading as is the molecular dipole moment; the *full* electrostatic attraction is relatively insensitive to the number of halogen atoms.

In many chemical situations, the P electron-acceptor atom will be bonded to carbon chains of one sort or another. How might the length and type of each such chain affect the P atom's ability to engage in a $P\cdots N$ bond? Simple alkyl chains were compared to those containing double and triple bonds,[26] as well as conjugated and aromatic systems. The saturated chains weakened the $RP\cdots N$ interaction slightly, whereas unsaturated chains of any sort produced a small strengthening, particularly triple bonds; chain length has a minimal effect. The interaction is further strengthened by F substitution on the chain, and this effect is attenuated as the F atom moves further from the P along the chain.

It should be added here that the presence of substituents on the electron *donor* atom, in this case N, can play a role as well. As an example, adding alkyl groups amplifies the strength of the interaction. Pairing $N(CH_3)_3$ with the potent electron acceptor FH_2P yields a $FP\cdots N$ bond with a stabilization energy[20] of 11 kcal/mol, more than twice that of the H-bond in the water dimer. This amplification is likely due to the ability of the methyl groups to release electrons to the N, which can in turn be donated across the noncovalent bond to FH_2P.

Very recent studies of related pnicogen bonds[27,28] confirm the idea that placement of an electronegative substituent on the electron acceptor strengthens the interaction. As an extension of this idea, when both molecules serve as simultaneous electron donor and acceptor, as in a symmetric $FH_2P\cdots PH_2F$ system,[29] the most favorable geometry places both F atoms opposite the P of the partner molecule. The ability of the F substituent to facilitate a pnicogen bond extends to a pair of As atoms as in the $FH_2As\cdots AsH_2F$ homodimer.[30] In asymmetric systems, with a clear donor and acceptor, an electronegative substituent on the electron donor will tend to weaken the interaction,[31a] although the effect is smaller than when it is located on the acceptor. Finally, the ability of three electronegative substituents to enable the formation of a pnicogen bond is consistent with calculations[16] wherein three F or CN substituents were added to N, P, and As, and these molecules then permitted to interact with NCH as electron donor, and other calculations[31b] where three halogens were situated symmetrically on both donor and acceptor molecule. However, this work did not consider mono- or disubstitution so was silent on the subject of how degree of substitution affects the interaction.

Electron Acceptors and Donors Other than P and N

As indicated above, P is not the only atom that can engage in these interactions, as S, Cl, and As can as well, and with very similar stabilization energies. Having noted this for the simple hydrides, the next question arises as to whether substituents will have the same strengthening effects on these other atoms as they do on P. The appropriate calculations in which BSH and BCl were paired with NH_3 were carried out,[32] and the binding energies of the complexes are compared with those for BH_2P electron acceptors in Figure 4. The patterns have some strong similarities. All show a growing binding energy in the order

$$B = CH_3 < H < NH_2 < CF_3 < OH < Cl < F$$

and the values are fairly similar from P to S to Cl, harkening back to the similarities noted earlier in the simple hydrides. With regard to the weaker bonds on the left side of the figure, BHS and BH_2P engage in bonds of nearly equal strength, with the halogen bonds involving BCl somewhat weaker. The pattern changes for B=F where FCl proves to form a much stronger complex than does FSH which is in turn superior to FH_2P. The FCl molecule forms the strongest interaction with NH_3, with a stabilization energy in excess of 10 kcal/mol. However, NO_2 reverses the trend for F, with P > S > Cl. (This behavior was attributed[32] to internal charge redistributions that occur within the NO_2 group.) Regardless of the identity of the electron acceptor atom, the $N_{lp}\rightarrow\sigma^*(AB)$ charge transfer plays a major role in the binding, as does the electrostatic energy.

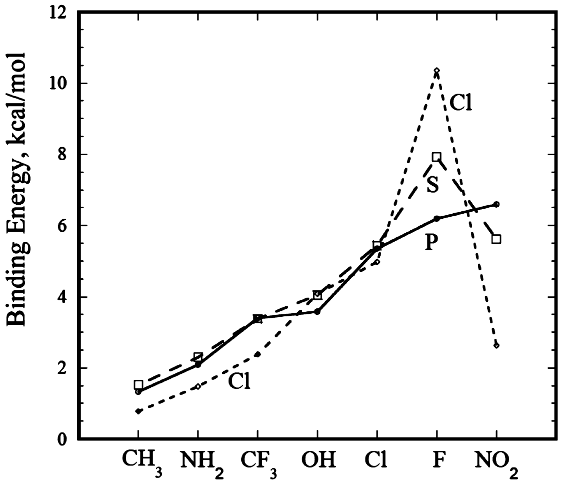

FIGURE 4. Effects of substituents B (horizontal axis) upon the binding energy of $BA\cdots NH_3$ complexes, with A = P, S, Cl as indicated on each curve.

The above has taken NH_3 and its lone pair as a sort of universal electron donor. But what other donors can participate in this type of interaction? In the first place, one can easily imagine that the lone pairs of S and O atoms could also serve this function. And indeed calculations[33] have shown this to be the case. In contrast to the identity of the electron-acceptor atom which has a small effect upon the strength of the bond, the interaction is quite sensitive to the donor. The O lone pairs of H_2O are considerably less potent than NH_3, but more effective than the S analogues in H_2S. When these atoms are engaged in a double bond, as in H_2CO and H_2CS, they are more effective. Although weaker than complexes with NH_3 as electron donor, these structures are nonetheless quite strongly bound. For example, HOH engages in a $P\cdots O$ bond with FH_2P with binding energy comparable to the H-bond it forms with another water molecule.

As in the case of H-bonds, the π bonds in which C atoms engage may also serve as a source of electron density. The complexes of FH_2P with the π systems of $HC{\equiv}CH$, $H_2C{=}CH_2$,

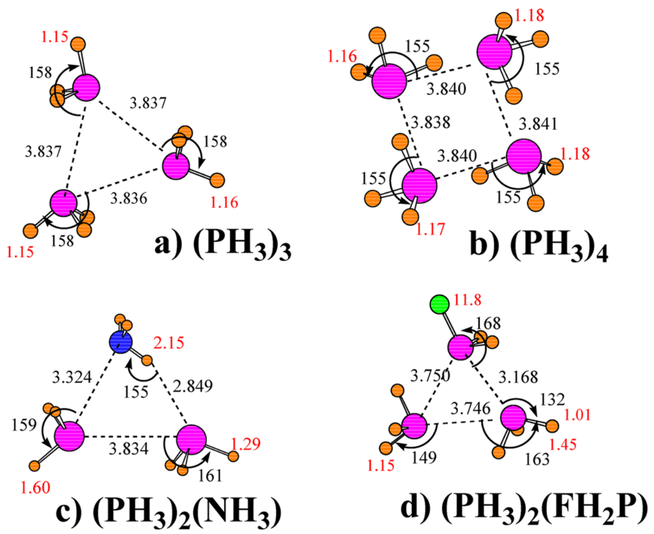

FIGURE 5. Structures of the global minima of trimers and tetramers. Interatomic distances and angles are shown in units of Å and degrees, respectively. Red numbers refer to the value of *E*(2) in kcal/mol for the indicated electron transfer into the σ^* antibonding orbital.

butadiene, and benzene all fall within the 3–4 kcal/mol range,[33] with double bonds somewhat more effective than triple bonds. These π donors add a new ingredient to the binding. In addition to the $\pi \rightarrow \sigma^*$(PF) transfer, there is also a back transfer in the reverse direction. A certain amount of electron density originating in the P lone pair makes its way into the vacant π^* orbital. This additional stabilizing factor helps account for the extraordinary stability of these complexes. For example, the binding energies of these $FH_2P\cdots\pi$ complexes are greater even than the $H\cdots\pi$ bonds formed by strong proton donors like HOH or HF with the same π systems, bonds that have been touted[34,35] as contributing factors to protein structure.

Persistence of Pnicogen Bonds in Larger Systems

It is fair to ask whether the presence of pnicogen bonds such as those which are documented here persist in systems that are larger and more complex than dimers in vacuo. In order to address the question of larger complexes, a number of trimers and tetramers were considered[36] which contain PH_3, NH_3, and FH_2P. There were numerous minima identified on the surface of each complex, but in each case the global minimum contained pnicogen bonds of the sort analyzed here. These structures are illustrated in Figure 5 where the intermolecular separations and relevant angles are included. The PH_3 homotrimer in Figure 5a is symmetrical, containing three $HP\cdots P$ bonds, each of length 3.84 Å. Each relevant H atom is turned some 158° from the $P\cdots P$ axis, allowing the PH σ^* antibond to accept density from the facing P atom lone pair. The amount of *E*(2) energy arising from each such transfer is indicated by the red number near the pertinent H atom, amounting to some 1.15 kcal/mol. A 4-fold symmetry is evident in the tetramer of Figure 5b, containing very similar values of $R(P\cdots P)$, $\theta(HP\cdots P)$, and *E*(2). The total binding energies of the trimer and tetramer are 2.9 and 4.8 kcal/mol, respectively, similar to the quantity obtained by simply multiplying the number of $HP\cdots P$ bonds by the 1.1 kcal/mol stabilization energy of the pure PH_3 dimer. Note that the global minima both eschew a $PH\cdots P$ H-bond, in favor of $P\cdots P$.

In contrast, a H-bond is part of the global minimum when one of the PH_3 molecules of the trimer is replaced by NH_3. This $NH\cdots P$ interaction in Figure 5c is supplemented by a pair of pnicogen bonds, one of the $HP\cdots P$ sort as in the homotrimer, but also a stronger $HP\cdots N$ bond, as occurs as the dominant feature of the simple PH_3/NH_3 dimer. By far the largest degree of electron donation is seen in the complex of Figure 5d which contains a FH_2P molecule. *E*(2) for the $FP\cdots P$ bond amounts to 11.8 kcal/mol. Also consistent with its strength is the very short $R(P\cdots P)$ distance of 3.168 Å, 0.6 Å shorter than the $HP\cdots P$ bonds in this structure.

Experimental verification of these sorts of noncovalent bonds are derived primarily from analysis of crystal structures where any such bonds are part of larger molecules, and are surrounded by other molecules as well. $P\cdots N$ bonds have been noted in several systems.[37,38] As one example, the pairing of 1,4-dimethylpiperazine[39] with PBr_3 yields an intermolecular $R(P\cdots N)$ distance of 2.802 Å, very close to its computed value.[25] Pnicogen bonds of the $P\cdots P$[40−45] and $N\cdots N$ varieties[46] have also been observed, as has an $As\cdots As$ bond.[47] And finally, diffraction studies[48] support the idea of the charge transfer to a π^* orbital that calculations infer is a contributing factor to the stability of the pnicogen bonds involving unsaturated systems.

Sensitivity to Angular Distortion

H-bonds are thought to be highly directional, preferring a $AH\cdots D$ angle of close to 180°. How might pnicogen bonds compare? This issue was studied[49] by comparing the energies required to distort various $BA\cdots NH_3$ complexes from their equilibrium geometries with the same quantity for H-bonds. Some of the results are displayed in Figure 6 where it is evident that the solid curves representing $FA\cdots NH_3$ complexes are considerably sharper than the broken curves that indicate the H-bonds. This greater anisotropy is all the more notable in that the $FA\cdots N$ bonds are not necessarily

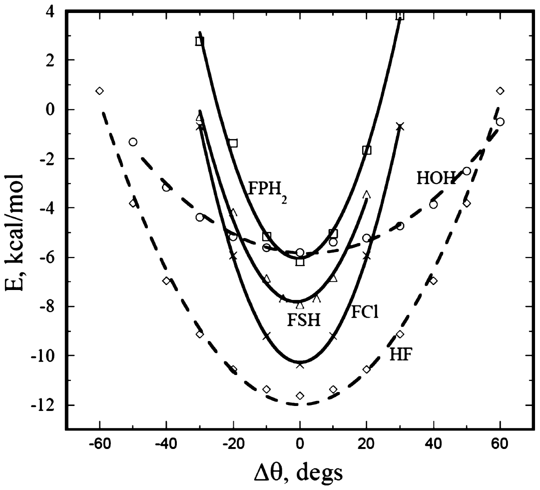

FIGURE 6. Rise in energy that accompanies angular distortion in the complex of each indicated electron acceptor with NH_3. Curves represent parabola that are fit to the data points shown. H-bonding systems are denoted by broken curves.

stronger than the H-bonds; for example, H-bonded $FH\cdots NH_3$ forms the strongest complex of all yet clearly has a shallower bending curve than the $FA\cdots N$ bonds.

The linearity of H-bonds is often attributed to electrostatics, and this term undoubtedly plays a role. However, a careful analysis of the various components[49] showed that it is not electrostatics, but rather exchange, that is, steric repulsion, which accounts for the differential bending potentials. The electron density of the proton donor molecules falls away more quickly as one moves off of the A−H line. This diminished density allows the displacement of the partner molecule to occur with a lesser degree of steric repulsion in the H-bonded dimers.

Summary

There are a number of similarities between H-bonds and the noncovalent interactions discussed here, which include pnicogen as well as halogen and chalcogen bonds. The stability of all types is based in part upon charge transfer from the electron-donor atom (usually its lone pair) to a σ^* antibonding orbital of the acceptor. The acquisition of density in the latter orbital weakens and lengthens the bond in question, whether A−H or A−B. In addition to this charge transfer/induction component, electrostatic attraction makes a major contribution as well. This component is obvious in the case of H-bonding where the H is usually positively charged, or in halogen bonds where a region of positive density (sometimes termed a σ-hole) is located on the halogen atom. The electrostatic attraction in the pnicogen bonds is more subtle, as it does not require any such σ-hole.[6] Instead one must consider the full three-dimensional electrostatic potential, which also helps guide the two molecules into place in the equilibrium geometry of the complex. However, it is emphasized that electrostatic considerations alone are not sufficient to predict or explain the equilibrium geometry; it is vital to also include factors that maximize the charge transfer, that is, the propensity for a near linear $BA\cdots D$ arrangement.[8,20−22,25,32,33] And of course, dispersion/London forces play a role in all noncovalent bonds, although usually smaller than electrostatics or induction. All of the interactions are strengthened upon substitution of electron-withdrawing substituents upon the electron accepting atom.

Perhaps more interesting than the similarities are the differences. Whereas electrostatics is dominant in most H-bonds,[8] it must share that role with induction in the pnicogen bonds which is found to surpass electrostatics in a number of cases. The strength of $AH\cdots D$ H-bonds is highly dependent upon the identity of the A atom, just as the halogen bond is sensitive to the specific halogen atom. In marked contrast, the pnicogen bond shows little dependence upon the identity of the A atom. Further, a H-bond strengthens considerably as multiple electronegative groups are added to the electron acceptor atom, whereas the addition of more than one such group has a much smaller, and weakening, effect upon the pnicogen bond.

Although all sorts of interactions include an increase of density in the pertinent σ^* antibonding orbital, there are differences in the effect upon the A−B bond length. Halogen bonds typically show a smaller lengthening of the X−C bond than the relevant quantities in H and pnicogen bonds.[8] With respect to the electron donor, $P\cdots\pi$ interactions with unsaturated carbon chains are quite strong, competing effectively even with the powerful proton donors FH and HOH.[33] The electron-acceptor atoms P and Cl, which might be considered representative of pnicogen and halogen bonds, respectively, react quite differently to two particular substituents. While FCl forms a very much stronger halogen bond than does NO_2Cl, the opposite is true for the pnicogen bonds containing FH_2P and $(NO_2)H_2P$. And finally, the $BA\cdots D$ bonds are substantially more sensitive to angular distortion than are H-bonds.

It is hoped that this Account will generate an awareness of pnicogen bonds and their potential strength, as well as stimulate researchers to consider their presence in various systems, in the same manner as the growing appreciation of weak $CH\cdots O$ H-bonds catalyzed an avalanche of observations in all sorts of systems including protein structures.

There remain further questions to be answered about the specific nature of the pnicogen bond, but it is clear that it represents a potentially strong force which can take its place in the pantheon of other better recognized noncovalent bonds.

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BIOGRAPHICAL INFORMATION

Steve Scheiner earned his B.S. at City College of New York in 1972, and his Ph.D. in 1976 from Harvard University applying quantum chemical methods to enzyme activity, under the tutelage of William Lipscomb. After two years as a Weizmann Postdoctoral Fellow at Ohio State University, he took a faculty position at Southern Illinois University—Carbondale and then moved to Utah State University in 2000. His research has centered generally around molecular interactions of relevance to biological systems, with a particular focus on H-bonds and proton transfers, and more recently on weak noncovalent interactions.

FOOTNOTES

*E-mail: steve.scheiner@usu.edu.
The author declares no competing financial interest.

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