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Lower Limits on Hydrogen Bond Strength. Charge of Bridging H Atom

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Abstract

While it is usually agreed that a major component in the composition of a H-bond is the electrostatic attraction associated with a positive charge on the bridging H, there has recently arisen some question as to whether a true H-bond can exist when this atom bears a negative charge. Quantum chemical calculations address this question for a variety of potential proton donor molecules where the H atom is bonded to atoms covering a wide range of electronegativity, including the halogen, chalcogen, pnicogen and tetrel families, as well as metal atoms. These molecules are bound to Lewis bases by a variety of noncovalent bonds, including tetrel and halogen bonds, but H-bonds are rare, and exceedingly weak when the H atom does not carry a substantial positive charge.

Keywords: H-bond; tetrel bond; σ-hole; π-lump; dispersion

INTRODUCTION

The original inception of the hydrogen bond (HB) placed a proton between two very electronegative elements [1-4]. The A and B atoms within this AH··B configuration were thought to represent N, O, or F atoms from the first row of the periodic table. The high polarity of the AH bond endowed the bridging H with a substantial positive charge, which was able to attract the B nucleophile with an opposite charge. As the same time, a certain amount of charge is transferred from a lone electron pair of B to the antibonding σ*(AH) orbital of the proton donor unit, adding another layer of stabilization. The ensuing weakening of the A-H covalent bond is signaled in a number of ways, most prominent of which is its stretch and the red shift of its vibrational frequency in the IR spectrum, along with a downfield shift of the proton's NMR signal [5-9].

This original rigid set of restrictions began to fray when it was observed that the source of the electron density being transferred from the nucleophile was not limited to a lone pair, but could be replaced by the π-cloud of an unsaturated alkene or alkyne, or the more extended π-cloud of an aromatic ring, either homo or heteroaromatic [10-17]. The less flexible and mobile electrons within σ-bonds are also capable of participating as proton acceptors on occasion [18-22].

The earlier limits also began to erode when it was learned that the CH group can serve as proton donor, despite the very similar electronegativity of C and H, which retards the buildup of positive charge on the H. Indeed, a sizable literature has built up in recent years that documents such CH··X HBs, and their implications for chemistry and biology [23-32]. Although these bonds tend to be rather weak, they can be strengthened a bit by changing the hybridization of the C or appropriate substituents on either of the two participating subunits [33]. And as a second factor, the introduction of a charge into one of the H-bond participating molecules provides a boost in what may be termed charge assistance or amplification [34-36]. Likewise, the replacement of first-row atoms by their heavier counterparts also reduces the electronegativity, again lessening any positive charge that might accrue to the H atom to which they are bonded. As one moves down Group 16 for example, the positive charge on the hydroxyl H diminishes for SH, and smaller still for SeH [37-41].

The dihydrogen bond presents an interesting combination of several of these concepts [42-47]. When attached to an electropositive atom such as a metal, the H acquires a significant negative charge. As such, it would be hard pressed to participate as electron acceptor in a HB with a nucleophile. However, when confronted with a positively charged H of a typical proton donor such as a hydroxyl group, the two H atoms of opposite charge can attract one another. But it is important to stress that the negatively charged H acts as electron donor in such a dihydrogen bond.

So in summary, as the atom to which the H is attached becomes less electronegative, whether by moving to the left or downward in the periodic table, the charge on the H becomes less positive, and then switches sign entirely when bonded to many of the metal atoms. During this transition, the HB with a nucleophile becomes progressively weaker, and can vanish entirely. As

the negative charge on the H continues to rise, it reverses its role from electron acceptor to donor, in the aforementioned dihydrogen bonds.

A recent paper [48] had challenged the idea that a H atom with a substantial negative charge is incapable of acting as electron acceptor in a HB. The authors advanced the intriguing proposition that HBs of significant strength might ensue when the negatively charged H attached to a Si center is approached by a nucleophile such as ICF_3 or BrCN. Their experimental measurements and quantum chemical calculations did find a stabilizing interaction, and certain symptoms within the complexes that might lead in that direction. However, later detailed calculations [49,50] clarified that these interactions were not HBs at all but rather I··HSi and Br··HSi halogen bonds where the σ(SiH) bonding orbital serves as the source of charge that is transferred to the halogen center.

But even if these particular SiH bonds are not capable of acting as proton donor within a HB, due in large part to a very appreciable negative charge on the H, the question remains in a broader sense. As the positive charge on the proton of an AH group becomes smaller and smaller, at what point does a HB cease to be possible. That is, how small a charge is too small? To carry this issue just a bit further, is it possible for a H center with a negative charge, even if a small one, to act as proton donor in a bona fide HB? It is the goal of the present work to answer these questions in a direct fashion. An H atom is attached to a wide range of atoms, varying all the way across the periodic table from halogen to metal, and down each column, from first to fourth row. For each AH_n molecule, the charge on the H center is measured by several different protocols, since there is no one means of unambiguously quantifying the charge on an atom. Then, the possibility of this H atom to participate in a HB is assessed when paired with different sorts of bases.

METHODS

The Gaussian 16 [51] suite of programs was employed to carry out the quantum chemical calculations, applying the DFT M06-2X functional [52] in conjunction with the triple-ζ def2-TZVP basis set. The pseudopotential placed on fourth-row atoms by this basis takes into consideration certain relativistic effects. M06-2X has been repeatedly assessed to be one of the most accurate functionals for H-bonding and related noncovalent interactions [53-61]. Geometries were fully optimized, and characterized as true minima by harmonic vibrational analysis which yielded all positive frequencies. The interaction energy E_{int} is equal to the difference between the energy of the dyad and the sum of the energies of the two monomers in the geometry they adopt within the complex; E_{int} was corrected for basis set superposition error by the standard counterpoise prescription [62].

The Multiwfn program [63] located and quantified the maxima of the molecular electrostatic potential (MEP) on the ρ=0.001 au isodensity surface of each isolated monomer. A variety of schemes were used to assess the charge on the bridging H. In addition to the Mulliken and natural charges [64], this charge was measured by the Hirshfeld technique [65] as well as Voronoi deformation density [66] quantities. CHELPG charges fit to the electrostatic potential [67] as well

as restrained electrostatic potential (RESP) [68] were considered as alternates as well. The AIMAll program [69] provided QTAIM topological analysis [70,71] of the electron density as represented by bond paths and their bond critical points. NBO analysis [72] identified and quantified the interorbital interactions within complexes. NMR calculations employed the gauge-invariant atomic orbital approximation [73,74].

RESULTS

In the first section below, a number of simple hydrides of the type AH_n are paired with NH_3 as a moderately strong proton acceptor, in order to test for the possibility of an AH··N HB. The A atoms span the entire range of the periodic table from the most electronegative halogens in Group 17, through the lower numbered groups encompassing chalcogen, pnicogen, tetrel, and triel atoms, and extending further to the left into the transition and alkaline earth metals. This wide range of electronegativity is expected to provide a similarly wide range of charge on the putative bridging H atom. The first base which is paired with each of these potential proton donors is NH_3. This particular molecule has been considered widely as the nucleophile in multiple papers in the past which facilitates comparisons to the literature. Another benefit is its small size which minimizes any secondary interaction which might obfuscate the possible HB that is the focus of this work. The second molecule which is paired with these potential proton donors is HX, where X refers to any of the halogen atoms. As explained below, HX has dual functionality. On one hand, the basicity of the X atom is quite variable, so spans a range from very weak to quite strong. Secondly, the presence of the H atom tests the proton-donating ability of the AH_n unit to maintain a AH··X HB, as compared to the alternate XH··A arrangement.

Complexes with NH_3

It must first be understood that the notion of an atomic charge is a nebulous one. There is no quantum mechanical operator that represents such a property, which is not in itself a physical observable. Evaluation of an atomic charge rests on the drawing of a boundary around that nucleus which separates the electron density assigned to it from that assigned to a neighboring center. Any such boundary is by its definition an arbitrary one, which has led to a host of different protocols in the literature.

Rather than base the assessment of the charge on the H atom on a single scheme, several such protocols were considered here so as to determine if there is any agreement between them, and what is the range that they encompass. In this way, it is hoped to supply some reasonable idea of the charge on this bridging atom. The first two columns of Table 1 list the natural and Mulliken charges assigned to the H center of each AH_n molecule. The Hirshfeld scheme is applied in the next column, followed by Voronoi density difference values (VDD). One can also consider atomic charges that provide a best fit to the electrostatic potential: This idea is utilized to extract CHELPG charges, as well as a variant that includes certain restraints, the RESP approach. The values obtained via each of these schemes are listed in Table 1 to provide first a range that these

different charges cover. Their mean value is displayed in the next column which might be taken as the best estimate of these charges.

An entirely different approach rests on the molecular electrostatic potential (MEP), which is less arbitrary, with a rigorous definition and derivation, based on nuclear charges and the distribution of the electron density. As a means of quantifying the MEP near the proton of interest, the maximum of the MEP was computed on a surface of constant density. Specifically, V_{max} in the next column of Table 1 refers to the maximum of the MEP on the 0.001 au isodensity surface surrounding the molecule, and lying in the vicinity of the H atom. This particular prescription is commonly used as a means to quantify the depth of the σ or π-hole in Lewis acid units.

As the most electronegative group, it is unlikely that a H atom bound to one of the halogen atoms would be negatively charged. Indeed, the H connected to Br contains a positive charge. Although there is some variation in its precise value, there is no argument that it is positive. As evident in the first row of Table 1, all protocols offer a positive charge, with a mean of +0.17. V_{max} is quite positive as well, with a value of +38.7 kcal/mol. A NH_3 molecule placed in the vicinity of this H forms a rather strong BrH··N HB, with an interaction energy of -11.7 kcal/mol, as reported in the last column of Table 1. Although the charge on the proton bonded to the chalcogens S and Te are not quite as large as for BrH, all the methods assess it as positive, with only minute negative values for several schemes. The HB energies are -3.5 and -2.0 kcal/mol, respectively. These smaller quantities reflect the smaller charge on the proton. The linearity of the HB is evident in Fig 1a for the TeH_2 acid, adding to the evidence of it being a true HB, despite its energy of only 2.0 kcal/mol. There is an AIM bond path connecting H with N, with a bond critical point density of 0.0145 au, as listed in Table 2, even larger for BrH and SH_2. NBO finds a charge transfer from the N lone pair to the σ*(TeH) antibonding orbital, with a second-order perturbation energy of 6.48 kcal/mol. Electron density shifts in the correct direction, from NH_3 to TeH_2, in the amount of 0.019 e, as reported by the CT quantity. And as another hallmark of a HB, the central proton suffers a NMR deshielding, shifting downfield by 3.2 ppm. Yet another typical characteristic of HBs is the red shift of the A-H stretching frequency within the acid. These quantities are clearly large and negative for all of these acids: BrH, SH_2, and TeH_2.

The lesser electronegativity of the pnicogen family permits the attached H atoms to be less positive, an effect which is amplified as the size of the pnicogen atom rises from P to As to Sb. V_{max} is positive throughout this series, but only marginally so, less than 10 kcal/mol. The H charge diminishes along this series, with an average that is quite small, changing from +0.017 for PH_3 down to -0.065 for SbH_3. One might summarize the charge on H is quite small in this series, even if its sign is not entirely clear. The HBs formed by these acids are very weak, 1 kcal/mol, for PH_3 and AsH_3. The weakness of these HBs are reflected in the smallness of the quantities in Table 2, but they all confirm a HB, albeit a very weak one. The switch in sign of the H charge on going to SbH_3 causes the disappearance of a HB, as there is no corresponding minimum when it is combined with NH_3. It would appear then that crossing the boundary from positive to negatively charged H seems to preclude a HB.

Atoms of the tetrel group tend to lesser electronegativity, which ought to lend a more negative charge to H atoms bonded to them. This pattern is confirmed by the data in Table 1, where the H charges span a wider range from positive for C to negative for the heavier tetrels. These signs are largely consistent regardless of the atomic charge scheme applied. While Vmax is clearly positive for CH_4, it borders on zero for the other tetrels. The positively charged H of CH_4 can indeed sustain a HB to NH_3, although quite a weak one, with interaction energy of only 0.7 kcal/mol. Despite its weakness, all of the parameters in Table 2 confirm its identity as a HB, and the geometries in Fig 1 are all quite linear. Although V_{max} for the H atom of SiH_4 and GeH_4, is slightly positive, the charge scheme analyses suggest slight negative values. The reversal in charge leads to exceedingly weak HBs, both less than 0.2 kcal/mol, with a HB length of some 3.0 Å, and with the other indicators similarly small. But this possibility vanishes for SnH_4, where all measures suggest a negative H which is unable to engage in a HB.

Shifting further to the left in the periodic table continues to reduce the electronegativity of the central atom, thereby providing an increasingly negative H on each. The hydrogens bound to the triel atoms Al and In in AlH_3 and InH_3 are consistently and substantially negative, and do not even contain a V_{max} in their vicinity. The same is true for transition atom Ti, whether in the context of TiH_2 or TiH_4. And the hydrogens attached to alkaline earth Be in BeH_2 are similarly negatively charged. For all of these systems, the unambiguously negative H atoms are unable to form a HB. Note that these negative charges are not necessarily very large in magnitude, in the ranges between -0.2 and -0.3, so even a small negative charge, or absence of V_{max}, precludes H-bond formation.

In order to think about the level of consistency of the various measures of H atomic charge, along with their mean, Table 1 presents the root mean square deviation (RMSD) for each monomer. Comparison with the mean values in the preceding column indicate that those atoms with a significant negative charge, which thereby forgo a substantive HB with NH_3, are clearly negative. That is, even extending to the very outer range of charge encompassed by this RMSD would not lead to a positive H.

The penultimate column of Table 1 contains the natural charge of the bridging H within each complex. Comparison with the values in the first Nat column of the table verifies the known shift of electron density away from the proton when it engages in a HB. The charge on this H center becomes more positive/less negative by some 0.03 - 0.04 e. And as a secondary feature, the charge on the H within the complex, like that in the unassociated monomer, needs to be positive in order to form a HB of any substance at all.

Another indicator of the presence of a HB is a shift in the vibrational frequency of the pertinent A-H stretching mode. Although most common is a shift to the red, there are a significant and growing number of examples where this shift is toward higher frequency. The last column of Table 2 finds these weak HBs are no exception to this diversity. While red shifts are observed toward the top of the table, the particularly weak (and questionable) SiH··N and Ge··H HBs are characterized by a small blue shift.

As mentioned above, there are numerous and varied indicators that verify the systems labeled as HBs do in fact fit that description, arising not only from geometrical disposition, but also from AIM and NBO, direction of charge transfer, and NMR chemical shift data. Still another litmus test as to the identity of the interaction arises from a three-dimensional mapping of the electron density rearrangement that accompanies the formation of the dimer. The green regions in Fig 2 indicate areas where this dimerization of SiH_4 with NH_3 depletes the density, while increases are signaled by purple colors. The large green area surrounding the bridging proton represents the shift of density away from H that is largely responsible for the NMR shielding reduction characteristic of H-bonding. Some of this density shifts into the Si-H region, while the peripheral H centers are the beneficiaries of additional density as well.

As a brief aside, it might be noted that there are several systems where E2 is larger in magnitude than the full interaction energy. This disparity is not an anomaly since the NBO measure of the second-order perturbation energy for any particular intermolecular orbital charge transfer differs in formulation from the induction energy. Taking $BrH\cdot\cdot NH_3$ as an example, a symmetry-adapted perturbation theory (SAPT) partitioning of the interaction energy yields an induction component of -24.2 kcal/mol, much smaller than the NBO E2 for the $N_{lp}\rightarrow\sigma^*(BrH)$ transfer of 73.0 kcal/mol.

Complexes with HX

Another means to examine the propensity of a potential proton donor toward HB formation is by pairing it with a molecule like HX, where X refers to a halogen, with dual functionality. The negative X atom with its lone pairs can effectively bind with a generic proton donor, but rotation of the HX presents instead its positive H terminus which can interact with any negative regions of AH_n. By examining the full range of HF, HCl, HBr, and HI, one can cover a full spectrum of atomic charge and nucleophilicity of the halogen atom, as well as the acidity of the molecule.

GeH_4 was taken as the central molecule for this detailed analysis as its H atoms bear a charge that is typical of several of the others. While its natural charge is somewhat negative, the Mulliken charge is essentially neutral, and there is only a very shallow positive maximum in the potential surrounding this hydrogen nucleus. Each of the various HX molecules was paired with GeH_4 and the potential energy surface searched for any minima. The resulting optimized geometries are displayed in Fig 3.

The dyad with HF yields only a single minimum which is cyclic of a sort. The H atoms on the two units are separated by 2.026 Å while the F approaches within 3.267 Å of Ge. The AIM diagram presents a bond path between the two H atoms, whose bond critical point has a density of 0.0110 as reported in the first line of Table 3. NBO analysis confirms the presence of this dihydrogen bond, with an E2 value of 0.63 kcal/mol. It might be stressed here that the H atom bound to Ge serves as the electron donor, as the much more positively charged HF proton serves as acceptor within this dihydrogen bond linkage. But NBO presents evidence of another, stronger bond. The tetrel bond between Ge and F is characterized by E2=1.09 kcal/mol, even though AIM suggests no such bond. Altogether, the interaction energy of this complex is 1.41

kcal/mol. Replacement of HF by HCl yields a very similar geometry, and a slightly diminished interaction energy of 1.09 kcal/mol. The longer H··H contact distance of 2.688 Å removes the dihydrogen bond from the picture, leaving only the tetrel bond, in both the AIM and NBO perspectives.

Further reduction of the electronegativity of the X atom brings about other options. Structure A in Fig 3 for HBr is much like the preceding geometries for HF and HCl. As for HF, AIM presents only a H··H dihydrogen bond, while the NBO analysis makes this bond quite weak, secondary to the tetrel bond between Ge and Br. The HBr surface also contains a second minimum B which rotates the HBr molecule around so as to approach the GeH_4 with its Br atom. This complex, with a slightly smaller interaction energy than A, is stabilized primarily by a tetrel bond. The weaker halogen bond involving transfer from the GeH bond to the σ*(BrH) antibond has a much smaller E2 but is the only bond that shows up in the AIM diagram. Another confirmation of the greater strength of the former TB is the direction of overall charge transfer, from HBr to GeH_4, in the amount of 0.006 e. The transition from HBr to HI provides the same pair of minimum geometries. HI A in Fig 3 looks much like HBr A, although the AIM picture has switched from the H··H bond path to Ge··I. This result is consistent with the Ge··I tetrel bond found with NBO. HI B again mimics HBr B in most respects including the dominance of the TB over the XB.

In summary, the various GeH_4/HX dyads are stabilized by several sorts of bonds, including tetrel and halogen bonds, as well as a dihydrogen bond in two cases. But in no case do any of the HX molecules engage in a HB to the H atoms of GeH_4, over the entire range of the proton-accepting power of the X atom of HX.

The results for the GeH_4/HCl dyad are largely repeated when the central Ge is transformed to the lighter Si tetrel. Even the very strong NMe_3 nucleophile is incapable of inducing a SiH··N HB, preferring instead a HSi··N tetrel bond. Replacing one H of GeH_4 by F raises the charge on the remaining H centers, with V_{max}=+23.4 kcal/mol. The H natural charge is -0.204 and the Mulliken charge is +0.003. But even so, a HF molecule is drawn to the Ge center over the H atoms, yielding FGe··F tetrel bonded structure, rather than a GeH··F HB.

With respect to other central atom types, HCl does not bind to BeH_2 in the framework of a BeH··Cl HB, preferring instead a strong Be··Cl noncovalent bond. A similar finding applies to AlH_3, where the two molecules simply dissociate from one another. Pnicogen atoms also forsake a HB to the Cl of HCl. The most stable structure in the AsH_3/HCl dyad contains what would appear at first sight to be a sort of trifurcated As··Cl HB to the AsH_3 protons, as illustrated in Fig 4. However, the accompanying AIM diagram forgoes any such connection of the H atoms, presenting a direct As··Cl bond path instead. NBO agrees with this interpretation, identifying the major interorbital transfer as a halogen bond from the As lone pair to the σ*(HCl) orbital.

CONCLUSIONS

There are multiple ways by which to assign a charge to individual atoms within a molecule, all of them arbitrary to some degree, so the unambiguous evaluation of the charge on a H which

might act as a bridge in a HB is a nettlesome problem. Nevertheless, it is possible to arrive at some general consensus as to whether a H atom bears a positive or negative charge, at least in cases where this charge is substantial. There are also numerous cases where the actual sign of the charge on H is questionable, but what is not debatable is that the charge is quite small in magnitude. Less questionable or arbitrary is the sign of the electrostatic potential in the vicinity of the proton in question. What emerges from the calculations is the conclusion that H atoms that bear a significant negative charge are very reluctant to form a HB to even a fairly strong base. Indeed, such HBs are forbidden when the electrostatic potential surrounding the bridging H does not bear a positive maximum. Any HB formed to a H with a very small charge, on the border between positive and negative, is exceedingly weak, on the order of 1 kcal/mol or less. There are cases where a peremptory glance at the geometry of a dyad can lead to the mischaracterization of an interaction as a HB, but a deeper dive will reveal its true nature as some alternative type of bonding.

Supporting Information

The Supporting Information contains the cartesian coordinates of complexes.

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Conflicts of interest

There are no conflicts to declare.

REFERENCES

[1] L. Pauling. The Nature of the Chemical Bond; Cornell University Press: Ithaca, NY, 1940.
[2] G. C. Pimentel, A. L. McClellan. The Hydrogen Bond; Freeman: San Francisco, 1960.
[3] W. C. Hamilton, J. A. Ibers. Hydrogen Bonding in Solids; W. A. Benjamin: New York, 1968.
[4] S. N. Vinogradov, R. H. Linnell. Hydrogen Bonding; Van Nostrand-Reinhold: New York, 1971.
[5] R. M. Badger, S. H. Bauer, *J. Chem. Phys.* **1939**, *5*, 839-851.
[6] W. F. Forbes, *Can. J. Chem.* **1962**, *40*, 1891-1898.
[7] M. D. Joesten, L. J. Schaad. Hydrogen Bonding; Marcel Dekker: New York, 1974.
[8] P. Schuster, G. Zundel, C. Sandorfy. The Hydrogen Bond. Recent Developments in Theory and Experiments; North-Holland Publishing Co.: Amsterdam, 1976.
[9] P. Schuster. Hydrogen Bonds; Springer-Verlag: Berlin, 1984.
[10] S. K. Burley, G. A. Petsko, *FEBS Lett.* **1986**, *203*, 139-143.
[11] B. V. Cheney, M. W. Schulz, J. Cheney, *Biochim. Biophys. Acta* **1989**, *996*, 116-124.
[12] P. Mastrorilli, V. Gallo, S. Todisco, M. Latronico, G. Saielli, *Chem. Eur. J.* **2016**, *22*, 7964-7969.

[13] F. Zapata, L. Gonzalez, A. Caballero, I. Alkorta, J. Elguero, P. Molina, *Chem. Eur. J.* **2015**, *21*, 9797-9808.
[14] A. E. Aliev, J. R. T. Arendorf, I. Pavlakos, R. B. Moreno, M. J. Porter, H. S. Rzepa, W. B. Motherwell, *Angew. Chem. Int. Ed.* **2015**, *54*, 551-555.
[15] M. Saggu, N. M. Levinson, S. G. Boxer, *J. Am. Chem. Soc.* **2012**, *134*, 18986-18997.
[16] J. W. G. Bloom, R. K. Raju, S. E. Wheeler, *J. Chem. Theory Comput.* **2012**, *8*, 3167-3174.
[17] M. A. Muñoz, M. Galán, L. Gómez, C. Carmona, P. Guardado, M. Balón, *Chem. Phys.* **2003**, *290*, 69-77.
[18] S. J. Grabowski, *J. Phys. Org. Chem.* **2013**, *26*, 452-459.
[19] S. J. Grabowski. Understanding Hydrogen Bonds: Theoretical and Experimental Views; Royal Society of Chemistry: Cambridge, 2021.
[20] S. J. Grabowski, *ChemPhysChem.* **2019**, *20*, 565-574.
[21] I. Alkorta, C. Martín-Fernández, M. M. Montero-Campillo, J. Elguero, *J. Phys. Chem. A* **2018**, *122*, 1472-1478.
[22] J. Echeverría, *CrystEngComm* **2017**, *19*, 6289-6296.
[23] D. J. Sutor, *Nature* **1962**, *195*, 68-69.
[24] R. D. Green. Hydrogen Bonding by C-H Groups; Wiley Interscience: New York, 1974.
[25] K. L. Hudson, G. J. Bartlett, R. C. Diehl, J. Agirre, T. Gallagher, L. L. Kiessling, D. N. Woolfson, *J. Am. Chem. Soc.* **2015**, *137*, 15152-15160.
[26] E. Y. Tupikina, G. S. Denisov, A. S. Antonov, P. M. Tolstoy, *Phys. Chem. Chem. Phys.* **2020**, *22*, 1994-2000.
[27] S. A. C. McDowell, K. E. K. Edwards, *Mol. Phys.* **2017**, *115*, 3199-3205.
[28] H. I. Rivera-Arrieta, J. M. Turney, H. F. Schaefer, *J. Chem. Theory Comput.* **2017**, *13*, 1478-1485.
[29] Y. Liu, W. Zhao, C.-H. Chen, A. H. Flood, *Science* **2019**, *365*, 159-161.
[30] S. Scheiner, T. Kar, *J. Phys. Chem. B* **2005**, *109*, 3681-3689.
[31] J. G. Wasserman, K. J. Murphy, J. J. Newby, *J. Phys. Chem. A* **2019**, *123*, 10406-10417.
[32] A. Bhattacherjee, S. Wategaonkar, *J. Phys. Chem. A* **2017**, *121*, 8815-8824.
[33] S. Scheiner, S. J. Grabowski, T. Kar, *J. Phys. Chem. A* **2001**, *105*, 10607-10612.
[34] S. M. Cybulski, S. Scheiner, *J. Am. Chem. Soc.* **1989**, *111*, 23-31.
[35] E. A. Hillenbrand, S. Scheiner, *J. Am. Chem. Soc.* **1984**, *106*, 6266-6273.
[36] S. M. Cybulski, S. Scheiner, *Chem. Phys. Lett.* **1990**, *166*, 57-64.
[37] S. Gholami, M. Aarabi, S. J. Grabowski, *J. Phys. Chem. A* **2021**, *125*, 1526-1539.
[38] K. K. Mishra, K. Borish, G. Singh, P. Panwaria, S. Metya, M. S. Madhusudhan, A. Das, *J. Phys. Chem. Lett.* **2021**, *12*, 1228-1235.
[39] A. Chand, D. K. Sahoo, A. Rana, S. Jena, H. S. Biswal, *Acc. Chem. Res.* **2020**, *53*, 1580-1592.
[40] A. Chand, H. S. Biswal, *J. Indian Inst. Sci.* **2020**, *100*, 77-100.
[41] E. Arunan, G. R. Desiraju, R. A. Klein, J. Sadlej, S. Scheiner, I. Alkorta, D. C. Clary, R. H. Crabtree, J. J. Dannenberg, P. Hobza, H. G. Kjaergaard, A. C. Legon, B. Mennucci, D. J. Nesbitt, *Pure Appl. Chem.* **2011**, *83*, 1637-1641.
[42] R. Custelcean, J. E. Jackson, *Chem. Rev.* **2001**, *101*, 1963-1980.
[43] V. I. Bakhmutov. Dihydrogen Bond: Principles, Experiments, and Applications; John Wiley and Sons: Hoboken, NJ, 2008.
[44] H. Ishikawa, T. Kawasaki, R. Inomata, *J. Phys. Chem. A* **2015**, *119*, 601-609.
[45] S. J. Grabowski, F. Ruiperez, *Phys. Chem. Chem. Phys.* **2016**, *18*, 12810-12818.

[46] G. Orlova, S. Scheiner, *J. Phys. Chem. A* **1998**, *102*, 4813-4818.
[47] G. Orlova, S. Scheiner, *J. Phys. Chem. A* **1998**, *102*, 260-269.
[48] S. Civiš, M. Lamanec, V. Špirko, J. Kubišta, M. Špet'ko, P. Hobza, *J. Am. Chem. Soc.* **2023**, *145*, 8550-8559.
[49] L. de Azevedo Santos, P. Vermeeren, F. M. Bickelhaupt, C. Fonseca Guerra, *J. Am. Chem. Soc.* **2024**, *146*, 25701-25709.
[50] E. Arunan, P. Metrangolo, G. Resnati, S. Scheiner, *Cryst. Growth Des.* **2024**, *24*, 8153-8158.
[51] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox. Wallingford, CT, 2016.
[52] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215-241.
[53] G. Paytakov, T. Dinadayalane, J. Leszczynski, *J. Phys. Chem. A* **2015**, *119*, 1190-1200.
[54] B. S. D. R. Vamhindi, A. Karton, *Chem. Phys.* **2017**, *493*, 12-19.
[55] R. Podeszwa, K. Szalewicz, *J. Chem. Phys.* **2012**, *136*, 161102.
[56] S. Karthikeyan, V. Ramanathan, B. K. Mishra, *J. Phys. Chem. A* **2013**, *117*, 6687-6694.
[57] M. Majumder, B. K. Mishra, N. Sathyamurthy, *Chem. Phys.* **2013**, *557*, 59-65.
[58] M. A. Vincent, I. H. Hillier, *Phys. Chem. Chem. Phys.* **2011**, *13*, 4388-4392.
[59] A. D. Boese, *ChemPhysChem.* **2015**, *16*, 978-985.
[60] M. Walker, A. J. A. Harvey, A. Sen, C. E. H. Dessent, *J. Phys. Chem. A* **2013**, *117*, 12590-12600.
[61] L. F. Molnar, X. He, B. Wang, K. M. Merz, *J. Chem. Phys.* **2009**, *131*, 065102.
[62] S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553-566.
[63] T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580-592.
[64] A. E. Reed, L. A. Curtiss, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735-746.
[65] F. L. Hirshfeld, *Theor. Chim. Acta* **1977**, *44*, 129-138.
[66] C. Fonseca Guerra, J.-W. Handgraaf, E. J. Baerends, F. M. Bickelhaupt, *J. Comput. Chem.* **2004**, *25*, 189-210.
[67] J. Zhang, *J. Chem. Theory Comput.* **2018**, *14*, 572-587.
[68] C. I. Bayly, P. Cieplak, W. Cornell, P. A. Kollman, *J. Phys. Chem.* **1993**, *97*, 10269-10280.
[69] T. A. Keith. TK Gristmill Software: Overland Park KS, 2013.
[70] R. F. W. Bader, *J. Phys. Chem. A* **1998**, *102*, 7314-7323.
[71] P. L. A. Popelier. Atoms in Molecules. An Introduction; Prentice Hall: Harlow, UK, 2000.
[72] F. Weinhold, C. R. Landis, E. D. Glendening, *Int. Rev. Phys. Chem.* **2016**, *35*, 399-440.
[73] R. Ditchfield, *Chem. Phys. Lett.* **1976**, *40*, 53-56.
[74] R. Ditchfield, R. E. McKinney, *Chem. Phys.* **1976**, *13*, 187-194.

Table 1. Measures of charge on the H atom of AH_n monomer and interaction energy for HB complex with NH_3. Charge on H in e, V_{max} and E_{int} in kcal/mol.

	q_H								V_{max}	q_{comp}	E_{int}
	Nat	Mull	Hirschfeld	VDD	CHELPG	RESP	mean	RMSD			
BrH	0.201	0.315	0.092	0.080	0.140	0.179	0.168	0.079	38.7	0.265	-11.68
SH_2	0.138	0.166	0.054	0.039	0.141	0.145	0.114	0.049	25.3	0.184	-3.54
TeH_2	-0.003	0.081	-0.003	-0.005	0.011	0.044	0.016	0.032	14.2	0.044	-2.01
PH_3	-0.005	+0.080	-0.014	-0.027	0.049	0.052	0.017	0.040	9.7	0.032	-1.03
AsH_3	-0.032	+0.076	-0.035	-0.054	0.007	0.023	-0.008	0.044	7.2	0.006	-0.83
SbH_3	-0.135	-0.007	-0.069	-0.060	-0.053	-0.028	-0.065	0.040	1.7	X[a]	X[a]
CH_4	0.209	0.139	0.033	0.014	0.097	0.122	0.098	0.066	8.8	0.238	-0.70
SiH_4	-0.156	-0.026	-0.070	-0.067	-0.126	-0.090	-0.089	0.042	1.5	-0.129	-0.13
GeH_4	-0.149	+0.002	-0.077	-0.084	-0.159	-0.092	-0.093	0.053	1.2	-0.119	-0.17
SnH_4	-0.211	-0.055	-0.097	-0.083	-0.229	-0.150	-0.135	0.065	-1.4	X	X
AlH_3	-0.573	-0.113	-0.157	-0.155	-0.338	-0.325	-0.267	0.158	X[a]	X	X
InH_3	-0.360	-0.102	-0.149	-0.154	-0.343	-0.286	-0.222	0.101	X	X	X
TiH_2	-0.383	-0.150	-0.206	-0.186	-0.482	-0.405	-0.281	0.126	X	X	X
TiH_4	-0.219	-0.097	-0.169	-0.131	-0.398	-0.342	-0.203	0.110	X	X	X
BeH_2	-0.573	-0.052	-0.166	-0.197	-0.340	-0.307	-0.266	0.164	X	X	X

[a] X indicates absence of H-bonding configuration or V_{max} where indicated.
[b] Minimum in potential along H··N axis

Table 2. Measures of HB strength in complexes with NH_3.

	R Å	ρ_{BCP} 10^{-4} au	E2 kcal/mol	CT e	$\Delta\sigma_H$ ppm	$\Delta\nu_{AH}$[a] cm^{-1}
BrH	1.569	782	73.04	0.150	-15.42	-1216.5
SH_2	2.236	177	7.24	0.018	-3.71	-127.2
TeH_2	2.379	145	6.48	0.019	-3.25	-68.4
PH_3	2.643	89	2.05	0.005	-1.66	-3.2
AsH_3	2.663	89	2.37	0.006	-1.69	-6.1
SbH_3	X	X	X	X	X	X
CH_4	2.681	77	1.24	0.003	-1.46	-3.3
SiH_4	3.082	43	0.60	0.002	-0.74	3.7
GeH_4	2.954	55	0.96	0.003	-1.00	7.4
SnH_4	X	X	X	X	X	X

[a]relative to asymmetric stretching mode of monomer

Table 3. Bonding parameters in complexes with GeH_4

	$-E_{int}$	type	AIM	ρ_{BCP}	type	NBO	E2
HF	1.41	diH	H··H	0.0110	TB	HGe··F	1.09
					diH	H··H	0.63
HCl	1.09	TB	HGe··Cl	0.0055	TB	HGe··Cl	2.00
HBr A	1.06	diH	H··H	0.0052	TB	HGe··Br	1.57
					diH	H··H	0.17
HBr B	0.87	XB	HBr··H	0.0057	TB	HGe··Br	2.05
					XB	HBr··H	0.26
HI A	1.11	TB	HGe··I	0.0050	TB	HGe··I	1.96
HI B	1.00	XB	HI··H	0.0061	TB	HGe··I	1.90
					XB	HI··H	0.53

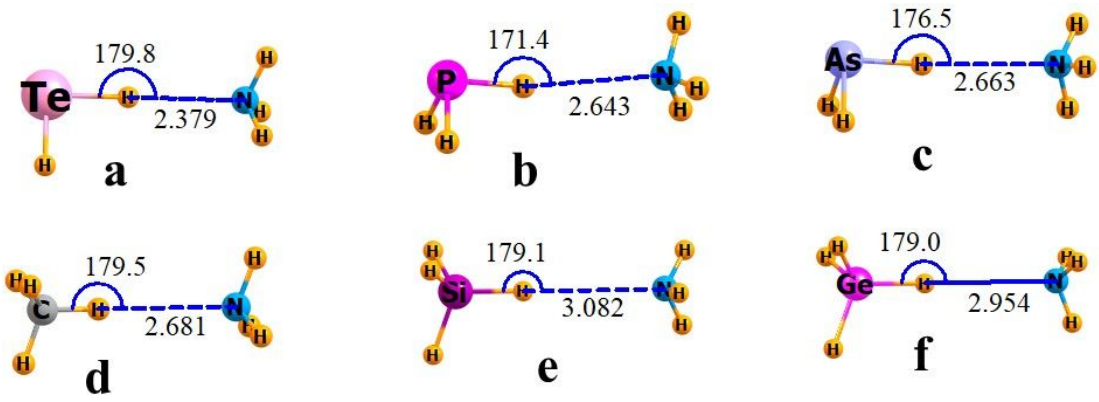

Fig 1. Optimized HB geometries of a) TeH_2, b) PH_3, c) AsH_3, d) CH_4, e) SiH_4, and d) GeH_4 with NH_3. Distances in Å, angles in degs.

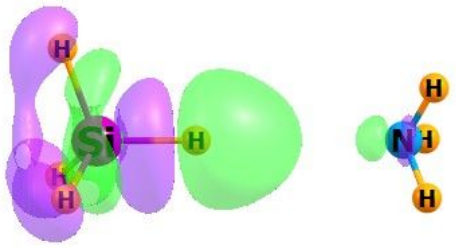

Fig 2. Shift of electron density caused by complexation of SiH_4 with NH_3. Purple and green areas respectively correspond to gains and losses of density, of magnitude ±0.0002 au.

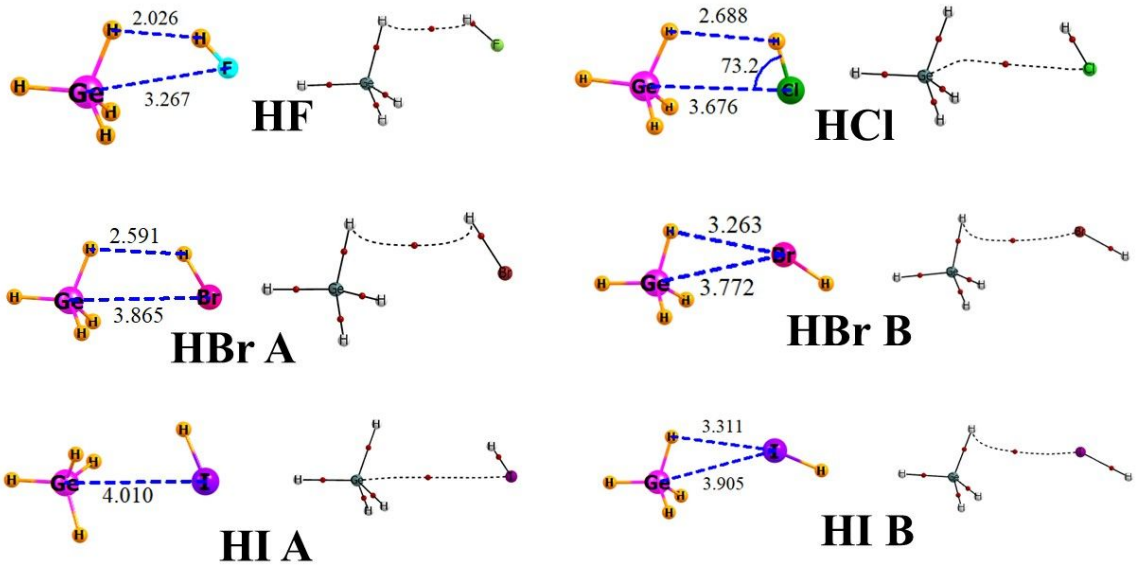

Fig 3. Geometric structures and AIM diagrams of complexes pairing GeH_4 with HX molecules. Small red sphere indicates bond critical point. Distances in Å, angles in degs.

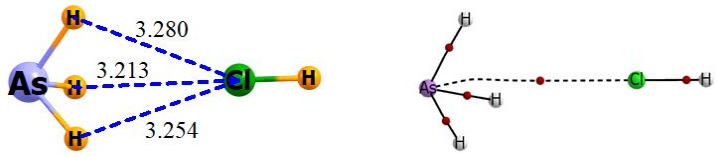

Fig 4. Geometric structure and AIM diagram of complex pairing AsH_3 with HCl. Small red sphere indicates bond critical point. Distances in Å.

Data Availability

Data are available upon request from the author.