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IUPAC Recommendations

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Definition of the pnictogen bond (IUPAC Recommendations 2023)

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Abstract: This recommendation proposes a definition for the term "pnictogen bond"; the term pnictogen bond designates a subset of the attractive interactions between an *electrophilic* region on a *pnictogen* atom in a *molecular entity* and a *nucleophilic* region in another, or the same, molecular entity.

Keywords: IUPAC organic and biomolecular chemistry division; IUPAC physical and biophysical chemistry division; nomenclature; noncovalent interactions; pnictogen bond; self-assembly; supramolecular chemistry.

CONTENTS

1 Preface ..... **xxx**
2 Definition ..... **xxx**
2.1 On common PnB donors and acceptors xxx
2.2 List of features of PnB xxx
3 Issues associated with the PnB ..... **xxx**
4 Terms ..... **xxx**
Membership of sponsoring bodies ..... **xxx**
References ..... **xxx**

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1 Preface

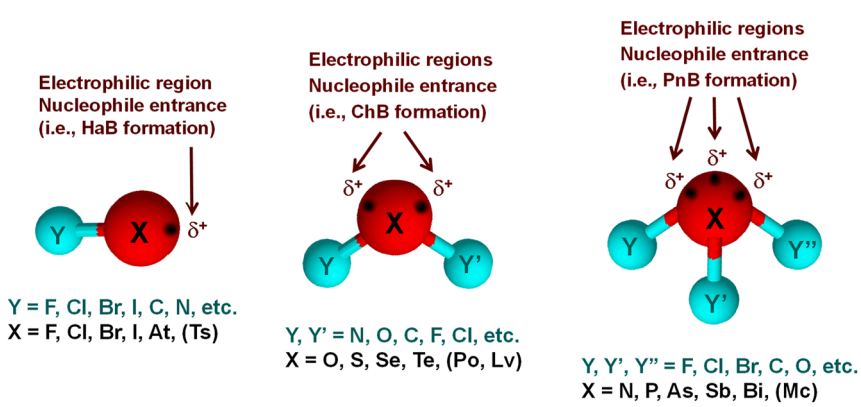
This recommendation proposes a definition for the term “pnictogen bond” (PnB) and suggests it to be used to designate a subset of the intermolecular and intramolecular interactions formed by pnictogen atoms (i.e., atoms of the Group 15 elements) bonded in a molecular entity [1]. The alternative spelling “pnicogen bond” can also be used to designate these bonds; the latest IUPAC Recommendations on Inorganic Chemistry states that pnictogen is IUPAC approved and the alternative spelling pnicogen is also used [2].

In this recommendation, the use of the terms donor and acceptor, and of the derived expressions is consistent with the use of the same terms for the hydrogen bond (HB) [3, 4], the halogen bond (HaB) [5], and the chalcogen bond (ChB) [6], three interactions that exhibit similarities with the PnB. The respective IUPAC recommendations specify that the HB donor, the HaB donor, and the ChB donor are the molecular entities containing the electrophilic [1] hydrogen, halogen, and chalcogen atoms, respectively. Hereinafter, the PnB donor is the molecular entity containing the electrophilic pnictogen atom, the PnB donor atom is the electrophilic pnictogen atom, and the PnB donor region is the electrophilic region on the PnB donor atom. The PnB acceptor is the molecular entity functioning as the nucleophile [1], similar to the terminology used for the HB, HaB, and ChB. In other words, for HB, HaB, ChB, and PnB, the interaction donor and the interaction acceptor are the acceptor of electron density and the donor of electron density, respectively. The terms PnB acceptor atom and PnB acceptor region (as well as the terms HB donor atom/region, HaB donor atom/region, and ChB donor atom/region) are used in this recommendation according to consistent meanings.

Covalently bonded atoms have an anisotropic distribution of the electron density and present regions of higher and lower electron density at their outer zones and at these regions, the molecular surface electrostatic potential is frequently negative and positive, respectively [7–9], and attractive interactions with regions of opposite electrostatic potential can be formed.

Hydrogen atoms bonded to atoms, or groups, more electronegative than themselves are partially positive and this is at the origin of the HB [3, 4]. The surface electrostatic potential at hydrogen outer regions is nonuniform [10], and this is related to HB directionality at the hydrogen atoms (the HB donor atoms).

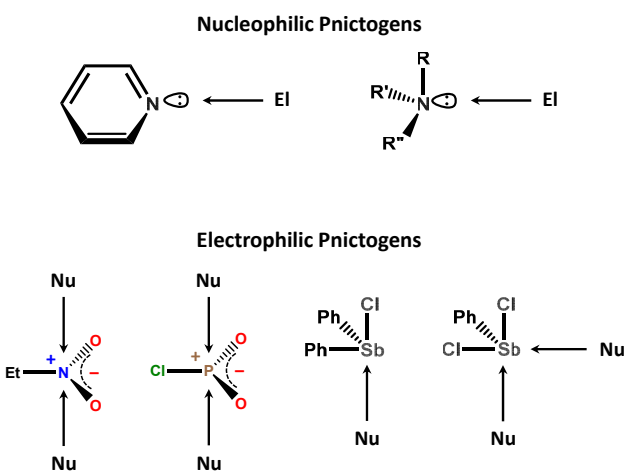
Halogen atoms forming one covalent bond can function as electron-rich atoms (i.e., nucleophiles, Lewis bases [1]). This is the case, for instance, when halogen atoms donate electron density to, and attractively interact with, hydrogen atoms or metal cations [11–14] approaching the halogen preferentially at its lone pairs. Halogen atoms can also function as electron-poor atoms (i.e., electrophiles, Lewis acids [1]). This is the case, for instance, when they accept electron density from, and attractively interact with, lone-pair possessing atoms and anions [15] approaching the halogen approximately on the extension of, and opposite to, the covalent bond formed by the halogen (Scheme 1, left). The halogen lone pairs and the region opposite to the covalent bond at the halogen (σ-hole) are the positions of preferred formation of short contacts with Lewis acids and bases, respectively, as they



Scheme 1: Schematic evidencing the preferred location of electrophilic regions in monovalent halogens (left), divalent chalcogens (mid), and trivalent pnictogens (right). These electrophilic regions (σ-holes) are on the extension of the covalent bonds formed by the respective atoms.

correspond to the regions of higher and lower electron density where the electrostatic potential is typically negative and positive, respectively. The IUPAC recommendation defining the halogen bond [5] acknowledges that an electrophilic behavior can be shown by halogen atoms in quite different moieties [1], including molecular entities wherein halogen atoms form more than one covalent bond [16, 17]. This recommendation establishes that a halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity.

Similarly, chalcogen atoms can behave as both nucleophiles and electrophiles (Lewis bases and acids, respectively). The nucleophilic behavior of chalcogen atoms is most common for oxygen, the most electronegative [1, 18] and least polarizable [1, 19] chalcogen, e.g., oxygen can frequently function as a hydrogen bond acceptor atom. Other elements of the Group 16 can behave as nucleophiles, e.g., when donating electron density to a halogen or hydrogen atom [20, 21]. The electrophilic behavior of chalcogen atoms is common for the less-electronegative and more polarizable elements. These elements frequently form attractive interactions with neutral or negatively charged nucleophiles (typically amine or pyridine nitrogen atoms or halide anions) [22]. The two classes of interactions described above differ in their electronic features and their directionalities relative to the covalent bonds formed by the chalcogen atom. Chalcogen atoms that form two single covalent bonds are approached by electrophiles after a trajectory roughly 20° from the perpendicular to the plane through the two covalent bonds as in these positions there are the lone pairs of the chalcogen atoms, namely, there is excess electron density and negative electrostatic potential. Differently, the approach of nucleophiles to the chalcogen atoms is preferentially on the extensions of the two covalent bonds, the regions named σ-holes where the electron density is depleted and the electrostatic potential is frequently positive (Scheme 1, mid). An IUPAC recommendation [6] recently recognizes the general ability of chalcogen atoms, hypervalent [23] chalcogen atoms included [24], to interact with nucleophiles and proposes to name as chalcogen bonds (ChBs) only those attractive interactions wherein the chalcogen atom is the electrophile.



Scheme 2: Typical cases where nitrogen functions as nucleophile and forms HBs [25] or HaBs [26] on interacting with an atom (El) with electrophilic regions (top); nitrogen [27], phosphorus [28], or antimony [29, 30] function as atoms with electrophilic regions and form PnBs on interaction with nucleophiles (Nu) (bottom). Arrows indicate the approach direction of El/Nu. In the two left cases of electrophilic pnictogens, the regions with positive electrostatic potential and electrophilic character (typically named π-holes [7, 28, 31]) are approximately above and below the plane of the reported moiety [1]; Nu approaches N and P atoms at right angle to the plane of the moiety. In the two right cases of electrophilic pnictogens, the regions with positive electrostatic potential and electrophilic character (typically named σ-holes [7–9, 28, 31]) are approximately on the extension of, and opposite to, a covalent bond at Sb; Nu approaches this atom after directions approximately coaxial with this bond.

Elements of Group 15 can behave as electron-rich (nucleophilic) atoms and form attractive interactions with electron-poor (electrophilic) partners. This is the case, for instance, when pnictogen atoms act as HB [3, 4] or HaB [5, 15] acceptors (Scheme 2, top). This nucleophilic behavior is most common for nitrogen, the element with the highest electronegativity and the lowest polarizability in the Group, in analogy with what is described above for chalcogen atoms. It has long been known that the Group 15 atoms can additionally function as electron-poor (electrophilic) atoms, i.e., they can attractively interact with electron-rich (nucleophilic) atoms (Scheme 1, right and Scheme 2, bottom). Antimony, thanks to its low electronegativity and high polarizability, can function as a particularly strong Lewis acid. For example, antimony pentachloride is the standard Lewis acid in the time-honored Gutmann scale [32] of Lewis basicity, and antimony pentafluoride is a reference compound to identify Lewis superacids [33]. Interactions formed by the Group 15 elements in the two classes of interactions described above differ in their electronic features and also differ in their directionality relative to the covalent bonds formed by the pnictogen atom as the regions of preferential approach of electrophiles or nucleophiles are those with negative or positive surface electrostatic potential, respectively.

Acknowledging an established usage in the chemical literature [34], this recommendation proposes that the term "pnictogen bond" (PnB) is used to designate uniquely the specific subset of the intermolecular and intramolecular interactions, wherein the Group 15 elements act as electrophile [35] and wherein separations, energies, and/or other experimental/theoretical parameters differ from those of corresponding covalent/ionic bonds. A short definition of the term is given at the beginning of the next section, followed by explanatory examples in the form of an inexhaustive list of some common PnB donors and acceptors. A list of experimental and/or theoretical features follows; although not comprehensive, these features can be used as an evidence for the presence of a PnB. This recommendation is concluded by a discussion of some important issues on the PnB, to provide the reader with qualitative information for a correct use of the term. This recommendation runs purposefully side by side with the recommendations for the terms halogen bond and chalcogen bond [5, 6]. Similarities in the overall logical flow and verbiage of these three recommendations are pursued to develop a consistent set affording a systematic terminology for the different interactions that are formed by different elements but possess similarities in geometric and electronic features.

To better outline and contextualize the PnB defined in this recommendation, it might be useful to mention and briefly discuss some other terms that are used in the literature. The term secondary bond [36] is used to indicate a set of different interactions formed by p-block elements and sharing the common feature that the interaction is collinear with a covalent bond at the p-block element. The terms σ-hole bond and π-hole bond [7–9, 28] are employed as umbrella terms for interaction sets, wherein the shared feature is that the nucleophile approaches the electrophile collinear with a covalent bond formed by the electrophile or orthogonal to a planar portion of the electrophile, respectively.

2 Definition

pnictogen bond (PnB)

weak attractive interaction between an *electrophilic* region on a *pnictogen* atom in a *molecular entity* (wherein the *pnictogen* is involved in other stronger bonds) and a *nucleophilic* region in another, or the same, *molecular entity*.

Note 1: A typical PnB is denoted by the three dots in R–Pn•••A, wherein R is collectively representing the groups covalently bonded to the pnictogen atom Pn, Pn (the PnB donor atom) is any atom (possibly hypervalent [37]) of Group 15 having at least one electrophilic (electron poor) region (the PnB donor region) involved in a bond with A, R–Pn (the PnB donor) is a molecular entity containing the electrophilic pnictogen atom, and A (the PnB acceptor) is a molecular entity having at least one nucleophilic (electron rich) region (the PnB acceptor region).

Note 2: An electrophilic region (typically associated with a σ- or π-hole) on a pnictogen atom in a molecular entity and a nucleophilic region in another or the same molecular entity can form bonds spanning a range of separations, energies, and other experimental or theoretical parameters; the use of the term PnB has to be limited to cases where separations, energies, and/or other experimental/theoretical parameters differ from those of corresponding covalent/ionic bonds (see onward).

Note 3: The polar character of the pnictogen atom in the interaction (i.e., the electrophilic role in pnictogen bonded systems or its nucleophilic role in the other systems) is established by considering the physical and chemical properties of the starting molecular entities before the interaction formation and/or of the system assembled by the interaction (see onward).

Note 4. *Bonds wherein a pnictogen atom acts as the nucleophile and those wherein its electrophilic role cannot be identified must not be named PnBs*.

Note 5: Pnictogen atoms can concurrently form one or more than one PnB [38]; the PnB donor and/or PnB acceptor can be charged molecular entities, thus forming charge-assisted PnBs.

2.1 On common PnB donors and acceptors

The elements of Group 15 form bonds with many other elements so that pnictogens can produce a very wide diversity of functional groups characterized by quite different properties. A list of common PnB donors containing functional groups [1] whose pnictogen atoms are particularly prone to form PnBs would thus be either very long or highly incomplete. To provide a quick but fairly comprehensive identification of such functional groups, we report below some selected atoms and groups that effectively promote the PnB donor ability of a pnictogen atom when covalently bonded to it.

A noncomprehensive list of atoms and groups promoting the PnB formation includes

- fluorine, chlorine, and bromine atoms (as in homocrystals of dichloro-1,1-dimethylethylstibane [39], dichloro(phenyl)stibane [40], and dibromo(4-methylphenyl)stibane [41] wherein halogen atoms are the nucleophile);
- oxygen groups, namely alkoxy, aryloxy, acyloxy, or oxo groups (as in nitroalkyl and nitroaryl derivatives [27, 42], di(quinoline-7-yl)cyclohexylphosphonite [43], (−)-(1*S*,5*S*,7*S*)-2,4,10-trioxa-1,3,5,7-tetraarsaadamantane ((−)-arsenicin A) [44], 2,4,6,8-tetramethyl-1,3,5,7,2,4,6,8-tetraoxatetraarsocane [45], tris(2,2-dimethylpropanoato)arsenic [46] wherein oxygen atoms are the nucleophile);
- cyano and perfluoroalkyl groups (as in dimethylarsanecarbonitrile [47], tris(pentafluoroethyl)bismuthane [48] wherein nitrogen and fluorine atoms are the nucleophile, respectively);
- positively charged heteroaromatic group (as in (diphenylbismuthanyl)trimethylphosphanium chloride [49], 2,2′-(chlorophosphanediyl)bis(1,3-diisopropyl-4,5-dimethyl-1*H*-imidazol-3-ium) trifluoromethanesulfonate [50], 2-(dichlorostibanyl)-1,3-diisopropyl-4,5-dimethyl-1*H*-imidazol-3-ium trifluoromethanesulfonate [51], 2-(dibromostibanyl)-1,3-bis(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium tetrabromoaluminate [52] wherein the respective anions are the nucleophile).

A noncomprehensive list of PnB acceptors A includes

- lone-pair possessing atoms (e.g., N atom of pyridines or amines, O atom of ethers or carbonyl groups);
- π systems (e.g., double or triple bonds between carbon atoms, arene moieties);
- anions (e.g., when halide anions or polyatomic oxyanions interact with the neutral phosphorus of 1-(4-carboxymethyl-benzyl)-1,3,5-triaza-7-phosphaadamantan-1-ium bromide [53] or the neutral antimony of 5-ethyl-2,3,7,8,14,15-hexamethyl-5*H*-5,10-[1,2]benzenodibenzo[*b*,*e*][1,4]phosphastibinin-5-ium iodide and its bromide analogue [54]).

2.2 List of features of PnB

The evidence for the occurrence of a PnB may be experimental or theoretical, or better, a combination of both. A nonexhaustive list of features that are useful as indications for the PnB presence is reported below. The greater is the number of satisfied features, the more reliable the characterization of an interaction as a PnB.

In a typical pnictogen-bonded adduct R–Pn···A:

- in neutral adducts, the interatomic distance between the PnB donor atom Pn and the PnB acceptor atom A is marginally smaller than the sum of the respective van der Waals radii [55] and substantially longer than the sum of covalent radii [56];
- the PnB acceptor A tends to approach the donor-atom Pn either along the extension of one of the σ covalent bonds at Pn and opposite to the bond (forming the so-named σ-holes bonds [7–9, 28, 31]) or perpendicular to the plane formed by three coplanar covalent bonds at Pn (forming the so-named π-holes bonds [7, 28, 31]); if the former geometry is observed, deviation from the linear extension is frequently more pronounced in PnBs than in ChBs and HaBs [8];
- the pnictogen atom interacts with a lone-pair orbital approximately along the orbital axis and with a π region perpendicular to the π bond plane [28];
- the R–Pn covalent bond opposite to the PnB tends to be longer in the pnictogen bonded adduct than in the unbonded R–Pn moiety [57];
- with a given acceptor A, the PnB strength typically decreases when the electronegativity of Pn increases and the electron withdrawing ability of R in R–Pn decreases [31, 34, 35, 58–60];
- the analysis of the electron density topology usually shows a bond path and a bond critical point [23] between Pn and A;
- the infrared absorption and Raman scattering observables of both R–Pn and A are affected by PnB formation [57, 61–63];
- the UV–vis absorption bands of the PnB donor chromophore change upon PnB formation [64];
- the Pn···A PnB formation typically affects the nuclear magnetic resonance observables (e.g., chemical shift values, quadrupolar and spin–spin coupling constants) of nuclei in both R–Pn and A [57, 65–67].

3 Issues associated with the PnB

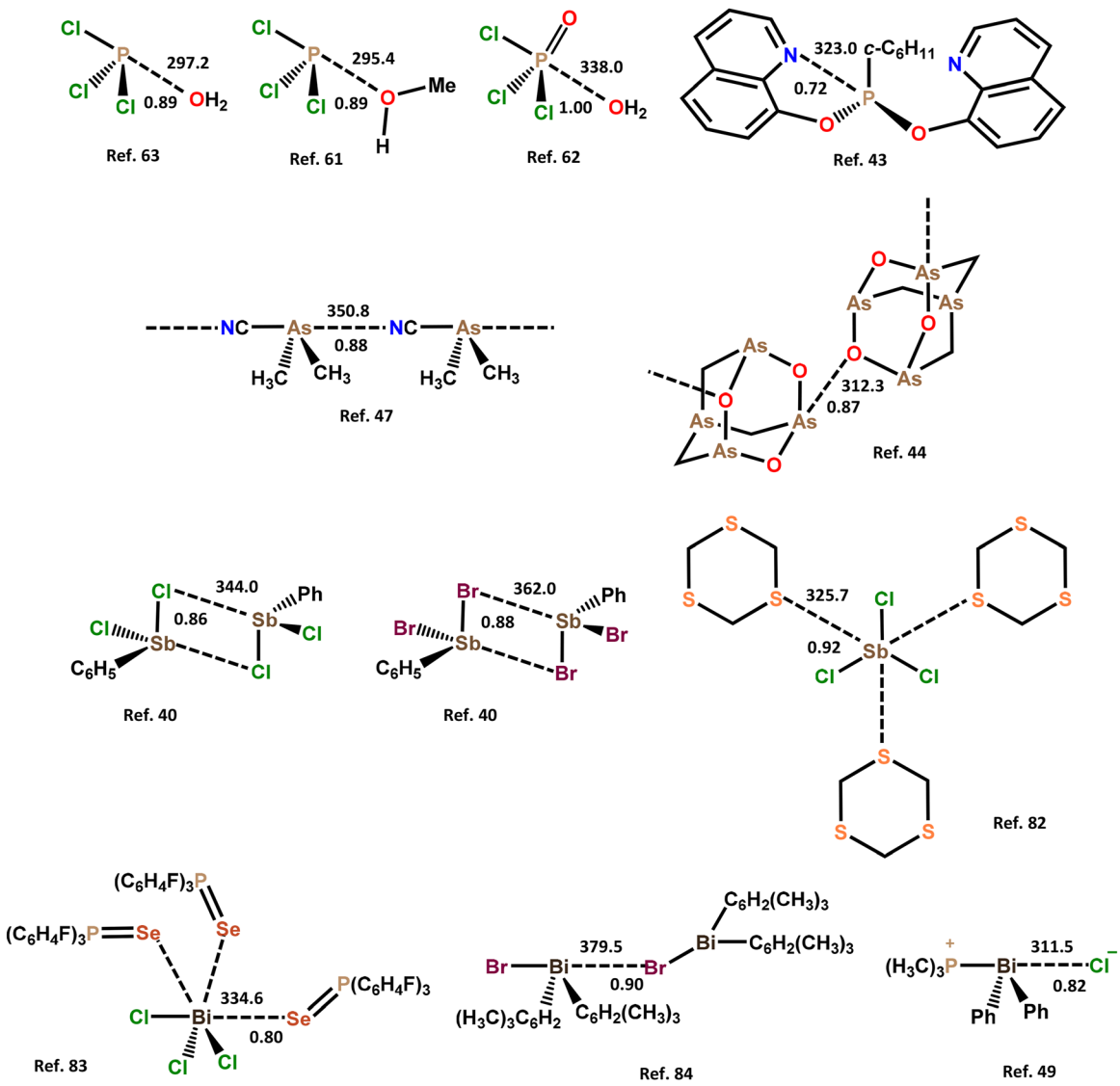
The Group 15 elements include elements with quite different characteristics spanning from nonmetals to metals, and the bond landscape of derivatives of the lightest pnictogens can differ substantially from that of the heaviest ones. Nitrogen, the most electronegative pnictogen [18], is the least prone to function as electrophile. This element typically affords the weakest and longest PnBs [7, 8], the separation of involved atoms being usually close to or slightly smaller than the sum of van der Waals radii of involved atoms. Electrophilicity and PnB donor ability increase moving from phosphorus to arsenic and antimony, namely when electronegativity decreases [35, 64, 66–68]. Bismuth, the least electronegative pnictogen, is the most disposed to act as electrophile and to expectedly form strong and short PnBs. Indeed, when bismuth derivatives interact with donors of electron density, the interaction energy and separation are frequently close to or slightly longer than those of the corresponding covalent bonds. These contacts are typically understood as coordinative interactions [68] and should not be named PnBs, this latter term applying only to longer and weaker contacts. Also, some contacts between nucleophiles and trivalent or pentavalent derivatives of antimony, or less frequently of arsenic, are characterized by energies and separations similar to those of corresponding covalent bonds. This is the case, for instance, for some bonds formed by Cl^- or Br^- with $BiCl_3$, $SbCl_5$, $AsCl_5$, or their fluorinated analogues, which can be as short as Bi/Sb/As–Cl/F covalent bonds in the starting molecular entities; when so, these bonds must not be named PnBs.

The bonds' geometry at the pnictogen atom in the isolated PnB donor may undergo a change on PnB formations and deformation tends to increase with the PnB strength. In an adduct wherein a Group 15 atom functions as the electrophile, the short contact formed with the nucleophile is a PnB limited to cases where the geometry of the PnB donor undergoes a minor rearrangement on bond formation.

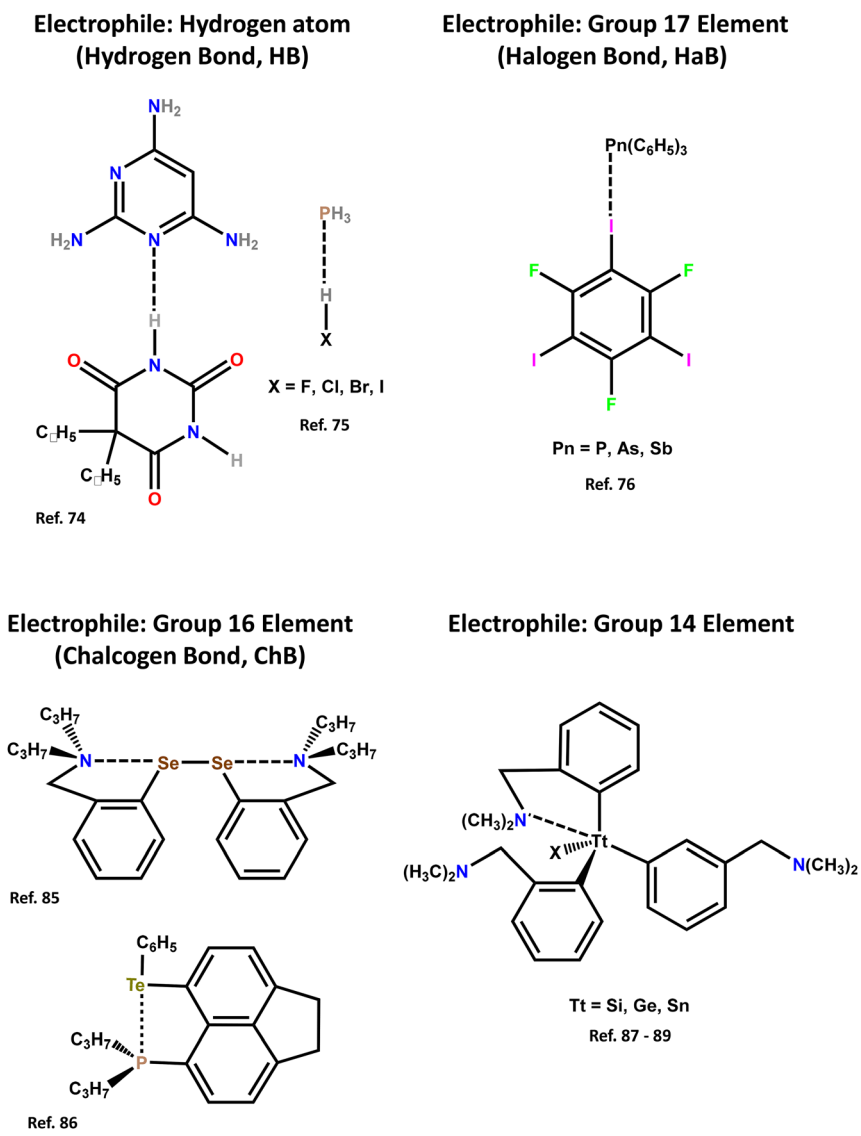
In the Preface of this recommendation, the PnB was introduced by adopting a viewpoint based on electrostatics, but calculations indicate that, similar to HaB and ChB, additional effects also contribute to the PnB formation. The seminal statement on the HaB "The *attractive nature* of the interaction is mainly due to electrostatic effects, but polarization, charge-transfer, and dispersion contributions all play an important role in causing interpenetration of van der Waals volumes" [69], holds also for the PnB [70–73]. The relative relevance of

these and other components (the covalent component included) depends, among others, on the nature of the involved atoms and of the residues covalently bonded to them.

A list is reported below (Scheme 3) of exemplary cases where the use of the term PnB is consistent with the definition given above as the pnictogen atom forms an attractive interaction, via an electrophilic region, with a nucleophilic region in another, or the same, molecular entity. Another list follows of exemplary cases wherein the pnictogen atom functions as the nucleophile (Lewis base) and the use of the term PnB is inappropriate (Scheme 4). The naming of interactions sketched in Schemes 3 and 4 is consistent with the relevant IUPAC definitions [3–6], with the established ability of pnictogen atoms to act as both nucleophiles [15, 74–76] and electrophiles [32–35], and with the different terms traditionally employed to indicate the variety of bonds formed by pnictogen atoms [36]. Importantly, the use of the term PnB for interactions in Scheme 3 is consistent with the whole history of the term, from the very initial employments [77, 78] to the most recent systematizations [79], going through its position in a taxonomy of chemical interactions [80].



Scheme 3: Structural formulas of systems wherein the Group 15 element forms PnBs (dotted line). PnB separations (pm) and the normalized contacts (Nc) are reported close to the interactions. Normalized contacts for an interaction between atoms *i* and *j* are the ratio $D_{ij}/(rvdW_i + rvdW_j)$, where D_{ij} is the experimental or computed distance between *i* and *j* and $rvdW_i$ and $rvdW_j$ are the van der Waals radii [55] of *i* and *j*; if the electron donor *j* is an anionic atom, $rvdW_j$ is substituted by rP_j, the Pauling ionic radius of anion atom *j* [81]. Normalized contacts are useful indicators because they allow for a more informative comparison of distances between different interacting atoms than do the absolute values of such separations.



Scheme 4: Structural formulas of systems wherein the bond between interacting moieties (dashed line) must not be named PnB.

Cases wherein the group 15 element forms a PnB (Scheme 3):

- the P•••O interaction in the PCl_3/H_2O, PCl_3/CH_3OH, $POCl_3/H_2O$ dimers [61–63] and the P•••N interaction in di(quinolin-7-yl)cyclohexylphosphonite [43];
- the As•••N interaction in dimethylarsanecarbonitrile [47] and the As•••O interaction in (–)-2,4,10-trioxa-1,3,5,7-tetraarsaadamantane [44];
- the Sb•••Cl, Sb•••Br, and Sb•••S interactions in dichloro(phenyl)stibane [40] and its dibromo analogue [41] and in the adduct formed by $SbCl_3$ with 1,3,5-trithiane [82], respectively;
- the Bi•••Se, Bi•••Br, and Bi•••Cl interactions in the cocrystal between $BiCl_3$ and triphenyl-λ^5-phosphaneselenone [83], in crystalline di(2,4,6-trimethylphenyl)bromobismuthane [84] and (diphenylbismuthanyl)trimethylphosphanium chloride [49].

Cases wherein the interaction formed by the Group 15 element is not a PnB (Scheme 4):

- the contacts observed in the solid between the NH group of 5,5-diethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione and a pyrimidine nitrogen [74] or in the gas between HX (X = F, Cl, Br, and I) and the phosphorus of phosphane [4, 75]; these interactions are hydrogen bonds (HBs);

– the attractive intermolecular interaction between the pnictogen atom in triphenylphosphane, triphenylarsane, and triphenylstibane and an iodine atom of 1,3,5-trifluoro-2,4,6-triiodobenzene in the corresponding co-crystals; these interactions are halogen bonds (HaBs) [76];
– the phosphorus–chalcogen contacts present in crystals of *N,N'*-{[diselanediylbis(2,1-phenylene)]bis(methylene)}bis(*N*-propylpropan-1-amine) [85] and diisopropyl[6-(phenyltellanyl)-1,2-dihydroacenaphthylen-5-yl]phosphane [86]; these interactions are chalcogen bonds (ChBs);
– the contacts between nitrogen and tin in crystalline tris[2-(dimethylaminomethyl)phenyl]stannane derivatives [87] and the analogous short contacts between nitrogen and germanium, or silicon, in crystalline tris[2-(aminomethyl)phenyl]germane [88], or silane [89], derivatives; in these interactions, the electrophile is the Group 14 element.

4 Terms

Topical chemical terms used in this recommendation but missing till now an IUPAC definition are listed below. For these terms, citations are given to papers where the meaning of the term is the same as in this recommendation:
– π-hole bond [7, 28, 31];
– σ-hole bonds [7–9, 28, 31].

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