The Nitrogen Bond, or the Nitrogen-Centered Pnictogen Bond: The Covalently Bound Nitrogen Atom in Molecular Entities and Crystals as a Pnictogen Bond Donor

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Abstract: The nitrogen bond in chemical systems occurs when there is evidence of a net attractive interaction between the electrophilic region associated with a covalently or coordinately bound nitrogen atom in a molecular entity and a nucleophile in another, or the same molecular entity. It is the first member of the family of pnictogen bonds formed by the first atom of the pnictogen family, Group 15, of the periodic table, and is an inter- or intra-molecular non-covalent interaction. In this featured review, we present several illustrative crystal structures deposited in the Cambridge Structure Database (CSD) and the Inorganic Crystal Structure Databases (ICSD) to demonstrate that imide nitrogen is not the only instance where nitrogen can act as an electrophilic agent. Analysis of a set of carefully chosen illustrative crystal systems shows that a covalently bound nitrogen atom in a variety of molecular entities features a $\sigma$-hole or even a $\pi$-hole, and these have the ability to sustain attractive engagements with negative sites to form inter- and/or intramolecular interactions that drive, or assist, the formation of a crystalline phase.

Keywords: pnictogen bonding; nitrogen as pnictogen bond donor; geometries; crystal structure analysis; ICSD and CSD database analyses; MESP characterizations; sum of the van der Waals radii concept

1. Introduction

IUPAC definitions, features and characteristic properties that can be used to identify non-covalent interactions, such as hydrogen bonding, chalcogen bonding and halogen bonding in chemical systems have been promulgated in 2011 [1], 2013 [2] and 2019 [3], respectively. A task group has been charged with categorizing tetrel bonding, pnictogen bonding, and other non-covalent interactions, involving the elements of Groups 14–16 of the periodic table [4]. The proposed characteristics of these bonding interactions have emerged from observations of a variety of engineered chemical systems in the crystalline, liquid and gas phases, and examining signatures arising from IR [5,6], Raman [7,8], UV/vis [9,10], and NMR [10,11] methods, and from ab initio and density functional theory calculations [12–14]. The characteristic features vary from system to system because they are dependent on the nature of the electron density distribution associated with the electron donor and electron acceptor fragments driving the non-covalent interactions.

In this featured review, we show that nitrogen in molecular entities can act as an electrophile when covalently bonded with appropriate electron-withdrawing atomic domain(s). This electrophilic feature of N can form nitrogen-centered pnictogen bonding interactions (or simply nitrogen bonding interactions) when in close proximity with a negative site on the same or a neighboring molecule, and hence is responsible in part for the stability of the resulting supermolecular or intramolecular entity.
The nitrogen bond in chemical systems occurs when there is evidence of a net attractive interaction between the electrophilic region associated with a covalently or coordinately bound nitrogen atom in a molecular entity and a nucleophile in another, or the same molecular entity. It is the first member of the family of pnictogen bonds formed by the first atom of the pnictogen family, Group 15, of the periodic table, and is an inter- or intra-molecular non-covalent interaction.

A nitrogen bond in a molecular entity may be regarded as a $\sigma$-hole centered pnictogen bond, especially when the covalently bound nitrogen features a positive $\sigma$-hole along the R–N bond extension, where R is the remainder of the molecular entity and is in attractive engagement with a negative site in the same or a neighboring molecule. A $\sigma$-hole is defined as a charge density deficient region on an atom A that appears along the outer extension of the R–A covalent bond [15,16]. By contrast, a nitrogen bond may be regarded as a $\pi$-hole centered pnictogen bond when the nitrogen in molecular entities features a $\pi$-hole [17] on its electrostatic surface and has the ability to engage attractively with a negative site in a neighboring molecule, or a site that has an electron density different to that of the $\pi$-hole, thus providing stability to the geometry of the resulting structure. A $\sigma$-hole interaction in a chemical system is generally observed to be directional, whereas a $\pi$-hole is non-directional. There are many studies on $\sigma$-hole and $\pi$-hole [17] interactions in chemical systems, including similarities, differences, controversies and misconceptions [18–25].

Nevertheless, nitrogen is a crucial constituent in the development of high-density materials, and, of course, is crucial for ammonia synthesis [26–29]. Apart from its well-known use as a feedstock for the production of fertilizers [30], we may be on the brink of a viable ammonia economy [31]. “Green ammonia” is a carbon-free hydrogen-containing compound with immense interest due to its high density and high hydrogen storage capability [29,32–34].

We considered nitrogen because a fundamental understanding of its modes of interaction in forming complex chemical systems would surely elevate our current knowledge of nitrogen-centered pnictogen bonding (i.e., nitrogen as a pnictogen bond donor). The role of pnictogen bonding containing heavier members of the pnictogen family (viz. P, As, Sb and Bi) in catalysis has also been demonstrated on several occasions [35–38], and in other areas, such as anion transport and recognition chemistry [39], solution and gas-phase chemistry [40–42], computational chemistry [13], supramolecular chemistry [43], coordination chemistry [44,45], medicinal chemistry [46], crystallography [47,48] and crystal engineering [49,50], among other research fields.

Nitrogen is the lightest member of the pnictogen family (Group 15), and the third most electronegative element after fluorine and oxygen. When it is present in a molecular entity, it is well known to be a site for interaction with electrophiles [51]. HCN, N$_2$, NO, HCCCN, CH$_3$CN, and NO$_3$ are a few examples where nitrogen is entirely negative, and hence, serves as a site to interact with electrophiles to form molecular complexes in the gas phase or adducts in the solid state. Nitrogen in molecules, such as NH$_3$ and in amines, is often found, both experimentally and theoretically [52,53], to be negative. This is a consequence of its strong electronegative character. It is also less polarizable than the other members of the pnictogen family. Its lone-pair electrons, if visualized from a Lewis structure viewpoint, dominate along the extension of the R–N covalent bonds in compounds in which it is covalently bonded and is an electron density donor towards electrophiles, forming hydrogen bonds, halogen bonds or chalcogen bonds, and acts as a Lewis base to metal ions [54]. This is the probable reason why fluorine, oxygen and nitrogen—being highly electronegative but with low polarizability—often have a negative $\sigma$-hole [21]. However, under certain circumstances, nitrogen can act as an acceptor of electron density, for example, in hypervalent non-covalent interactions, as demonstrated by Chandra and coworkers [35]. They observed an intermolecular interaction between nitromethane, CH$_3$NO$_2$ and NH$_3$ at low temperature within an inert gas matrix, which was characterized by IR spectroscopy and supported by first-principles calculations. The nitrogen in CH$_3$NO$_2$ acts as an electron density acceptor from the nitrogen in NH$_3$, forming a CH$_3$O$_2$N···NH$_3$ dimer and is stabilized by an N···N pnictogen bond. The directional...
prevalence of this interaction over the C–H···N and N–H···O hydrogen bonding interactions was shown by ab initio calculations, demonstrating that σ-hole/π-hole driven interactions lead to the formation of the dimer, despite nitrogen’s low polarizability.

Presented in this review are a set of illustrative crystal systems, demonstrating that nitrogen in the molecular entities that comprise these crystal systems serves as a nitrogen bond donor (electrophilic), and hence is responsible (at least in part) for their geometric stability and functionality. It should be noted that the definition and characteristic features of pnictogen bonding are yet to be formalized, and the term “pnictogen bonding” has come into use only relatively recently [56–59]. The origin and etymology of the terms pnictogen (also sometimes referred to as pnigogen or pnicogen) and pnictide can be traced back to a suggestion by the Dutch chemist Anton Eduard van Arkel (1893–1976) in the early 1950s [60]. Unsurprisingly, therefore, the characteristic (geometric) features of pnictogen bonding in several crystal structures re-examined in this work were not formally identified and characterized by the original workers who had reported the crystals. Our search of the Cambridge Structure Database (CSD) [61] and the Inorganic Chemistry Structure Database (ICSD) [62] produced hundreds—if not thousands—of structures in which nitrogen could conceivably feature a positive site. This was speculated upon based on the directional feature, together with the intermolecular distance of separation. It is worth mentioning that pnictogen bonds have been known since the middle of last century—if not formally identified and named as such—as have halogen and hydrogen bonds, and were certainly not first described only in 2011, as has been asserted [63].

The characterization of non-covalent interactions in many crystal structures has been undertaken based on the “less than the sum of the van der Waals (vdW) radii” concept [64], a widespread concept that has been invoked, for example, in structural and supramolecular chemistry [64–66], biological and medicinal chemistry [67,68], and crystallography [69–74]. According to this concept, when the inter- or intramolecular distance of separation is associated with a structural motif, for example, Pn···D (Pn = the pnictogen atom; D = an electron donor, such as O, N, a halogen anion, etc.), is less than the sum of the vdW radii of Pn and D, then it possible that Pn and D atomic basins are bonded to each other by an attractive engagement. This bonding has been referred to as a “close contact”, or simply “a non-covalent interaction” [75]. The criterion, however, rejects those interactions that have intermolecular bond distances slightly larger than the sum of vdW radii of Pn and D. This could be misleading because the proposed vdW radii [76,77] are not necessarily accurate [78] (within an uncertainty of ±0.2 Å) because a spherical symmetry of atoms in molecules was generally assumed for their determination [75], and that there have been many systems reported theoretically and experimentally that fail to strictly obey the criterion [79–83]. Since the charge density profile of atoms in molecules is anisotropic, the vdW “radius” of an atom in a molecular entity is likely to vary between molecular entities. As several have suggested previously [66,75,77,84], we recognize a potential non-covalent interaction between interacting atomic basin even when the distance interaction is greater by several tenths of an Ångstrom than the sum of the respective vdW radii of bonded atomic basins. While doing so, directional features, together with chemical intuition and interpretations provided by the original authors, were considered. In addition, the underlying concepts of molecular electrostatic surface potentials (MESP) [79–83] were utilized in several instances to verify the putative interactions that emerged from the “less than the sum of the vdW radii” concept.

Given the sheer number of candidate structures available in the CSD and ICSD, we decided not to attempt a statistical analysis to delineate the possible occurrence and range of bond distances and angles of approach featuring intermolecular contracts formed between a nitrogen atom and other interacting atomic domains. To do so, one would have to carefully inspect each and every structure to observe whether nitrogen in those crystals does indeed have a positive site; chemical intuition alone does not suffice, and the results could be misleading without extensive computational work. Our search of, for example, the CSD, resulted in thousands of crystals, especially when the intermolecular distance and
the angle associated with the motif R–N···X (R = any atom of the periodic table; X = O, N, C, F, Cl, Br, and I, etc.) were constrained to the range of 2.5–3.9 Å and 150°–180°. When we inspected the structures, it was found that (1) a large body of them comprises primary, secondary and tertiary interactions, and (2) many of them also comprise N that feature a negative site and is engaged in hydrogen bonding, (3) and many of them contain structures with missing H atoms or overlapping molecular fragments, such that it was very difficult to draw any conclusion about whether N could be a pnictogen bond donor in the crystals above. However, when the distance and angle criteria associated with the motif were restricted to the ranges, 2.8–3.9 Å and 170°–180° (or 3.0–3.5 Å and 170°–180°) (or 3.3–3.7 Å and 175°–180°), the number of hits in the CSD search was greatly reduced to a few hundred. This enabled us to visually scan most of the crystal structures and to select those where nitrogen-centered pnictogen bonding was likely to occur. We, therefore, emphasize that the examples given below are not exhaustive, but illustrative, since our ultimate aim is to inform the reader of the potential significance of nitrogen-centered pnictogen bonding in crystals so that this can be borne in mind when new materials are designed in silico.

2. Computational Details

We energy-minimized several monomeric entities responsible for the illustrative crystal systems chosen for this review, using density functional theory at the ωB97X-D [85] and second-order Møller–Plesset (MP2) levels of theory [86]. For reasons described below, basis sets, such as Jorge-ATZP (where ATZP is the augmented triple-ζ plus polarization basis set), Aug-CC-pVTZ and def2-TZVPD were chosen.

The MESP calculations were performed on the fully relaxed geometries of the monomeric entities in the gas phase. This was done to provide insight into the possible ability of these entities—when in close proximity to another similar (or different) entity—to interact attractively with the partner species, causing or assisting in the formation of a supermolecular assembly. Specifically, we computed the local most minimum and maximum of potential, \( V_{S,\text{min}} \) and \( V_{S,\text{max}} \), respectively, on their electrostatic surfaces. The 0.001 a.u. (electrons bohr\(^{-3}\)) isoelectron density envelope that arbitrarily defines the van der Waals surface of a molecular entity was used on which to compute the electrostatic potential [87–89]. We used the sign and magnitude of these potentials to infer whether specific regions on the surfaces of these molecular entities are electrophilic or nucleophilic [51,89–91].

Accordingly, we utilized the following concepts to provide insight into the way a specific site in a molecular entity makes an attractive engagement with another site in another similar, or different, molecular entity, contributing to the formation of the crystal lattice. A specific region on an atom in a molecular entity was considered to be electrophilic when the sign of either \( V_{S,\text{min}} \) or \( V_{S,\text{max}} \) was positive, i.e., \( V_{S,\text{min}} > 0 \) or \( V_{S,\text{max}} > 0 \). When they are negative, \( V_{S,\text{min}} < 0 \) or \( V_{S,\text{max}} < 0 \), then the region was considered to be nucleophilic [92–94].

An intermolecular, or intramolecular interaction, generally occurs (but not always) when a region of an atom or fragment with a positive \( V_{S,\text{min}} \) (or \( V_{S,\text{max}} \)) is in close proximity to that with a negative \( V_{S,\text{min}} \) (or \( V_{S,\text{max}} \)). For instance, σ-holes on an atom A in a molecular entity along an extension of the bond R–A are generally associated with \( V_{S,\text{min}} \) and lone-pair, and π-holes with \( V_{S,\text{min}} \). Clearly, the nucleophilic portions of a given entity interact attractively with the regions of the most positive electrostatic potential on a neighboring (or the same) entity, leading to σ···lone-pair, σ···π, σ···σ and π···π interactions. This is the case for interactions that are coulombic in origin (a positive site attracting a negative one [54,80,95]). However, there are examples known in which anti-electrostatic interactions have been shown to occur [96,97], as well as instances where a positive site attracts a positive site [98], and a negative site attracts a negative site [51] when they are in close proximity. Although this has been suggested to be a consequence of electrostatic polarization [99–103], dispersion plays a significant role in stabilizing such interactions [25,89,98]. Other researchers also used a similar methodology for theoretical studies of non-covalent interactions in other chemical systems [104–108].
We employed the concepts of Type-I, Type-II and Type-III geometric topologies of bonding (Scheme 1) to characterize nitrogen-centered pnictogen bonds in the crystals illustrated in this overview [24,94].

Scheme 1. Geometric topology of chemical bonding interactions formed by the pnictogen atom in molecular complexes and crystals, where Pn, D, R and R’ refer to the covalently bound pnictogen atom, the interacting atomic domain (generally nucleophilic), and the remaining part of the molecular entities associated with Pn and D atomic basins, respectively. $\delta^{\pm}$ signifies the local polarity (positive or negative), and the small region on atom Pn along R–Pn bond extension colored in green indicates a $\sigma$-hole.

The electronic structure calculations were performed using the Gaussian 16 program package [109]. The Mercury 4.0 [110], Gaussview 5.0 [111], AIMAll [112], Multiwfn [113], and VMD [114] suite of programs were utilized for the analysis and drawing.

3. Illustrative Chemical Systems in the Crystalline Phase

3.1. The Solid-State Structure of Dinitrogen, $N_2$

We begin by looking at dinitrogen itself. Solid $N_2$ displays exceptional polymorphism under extreme conditions. Some of its known phases include $\alpha$, $\beta$, $\gamma$, $\delta$, $\epsilon$, $\iota$ and $\theta$ [115–117]. Because the phases of the crystal depend on an external agency (temperature and pressure), the packing is different in each phase. Consequently, the intermolecular interactions between the $N_2$ molecules in these crystals are different.
The α-phase (third allotrope) of solid N\(_2\), with \(Z = 4\), space group \(Pa-3\), Figure 1a, determined using electron diffraction measurements \([118]\), is mainly stabilized by \(\pi\cdots\text{N}\) (lone-pair) interactions between the N\(_2\) molecules. The centers of the N\(_2\) molecules are on an f.c.c. lattice with each molecule pointing in a different direction. The intermolecular distance between N in one molecule and the midpoint of the \(\pi\) bond in a neighboring molecule is 3.565 Å. We attribute this interaction to \(\pi\)-centered pnictogen/nitrogen bonding.

The β-phase of hexagonal N\(_2\) (\(Z = 2\), Figure 1b \([119]\), comprises two types of intermolecular bonding modes, including N\(\cdots\text{N}\) and \(\pi\cdots\pi\). The first of these contacts occur between the N\(_2\) molecules along the crystallographic \(c\)-axis, as shown in Figure 1b, with \(r(\text{N}\cdots\text{N}) = 3.015\ \text{Å}\) and \(\angle\text{N}\equiv\text{N}\cdots\text{N} = 132.3^\circ\). It is perhaps a Type-Ib topology of pnictogen bonding. The second type of contact is the result of a slip parallel arrangement between the N\(_2\) molecules in the crystal along the crystallographic \(a\) and \(b\) axes, with an intermolecular distance of 3.861 Å between the centroids of a pair of triple bonds on two neighboring N\(_2\) molecules (\(r(\pi\cdots\pi) = 3.861\ \text{Å}\)).

The γ-phase of tetragonal N\(_2\) (\(Z = 2\), Figure 1c \([119]\), consists of N\(\cdots\text{N}\) and \(\pi\cdots\text{N}(\text{lone-pair})\) interactions. The former ones are longer than the latter. Similar to the β-phase, the N\(\cdots\text{N}\) contacts follow a Type-Ia topology of bonding, with \(r(\text{N}\cdots\text{N}) = 3.292\ \text{Å}\) and \(\angle\text{N}\equiv\text{N}\cdots\text{N} = 121.8^\circ\), but are weaker. The \(\pi\cdots\text{N}\) (lone-pair) pnictogen bonded interactions have \(r(\pi\cdots\pi) = 3.415\ \text{Å}\) and are stronger than the \(\pi\cdots\pi\) interactions in β-N\(_2\). Regardless of the nature of the intermolecular interactions, they are all marginally shorter or somewhat longer than twice the vdW radius of N, 3.32 Å (\(r_{\text{vdW}}(\text{N}) = 1.66\ \text{Å}\) \([77]\)).

The ε-phase of rhombohedral N\(_2\) (\(Z = 24\), Figure 1d \([120]\), has two types of N\(\equiv\text{N}\cdots\text{N}\) bond distances, \(r(\text{N}\equiv\text{N}\cdots\text{N}) = 2.727\ \text{Å}\) and 2.801 Å, corresponding to \(\angle\text{N}\equiv\text{N}\cdots\text{N} = 133.1^\circ\) and 120.9°, respectively, and are less than twice the vdW radius of N, 3.32 Å. Additionally, N(lone-pair)\(\cdots\pi\) interactions may be present between the N\(_2\) molecules in the crystal, with \(r(\text{N}(\text{lone-pair})\cdots\pi) = 2.958\ \text{Å}\).

The crystal structures of the high-pressure \(\delta\) and \(\delta^*\) phases of nitrogen were also investigated using single-crystal X-ray diffraction (not shown) \([121]\). The structure of the \(\delta\) phase is isostructurally similar to that of \(\gamma\)-O\(_2\). Thus, it comprises spherically disordered molecules, with a preference for avoiding pointing along the cubic \(\langle 100\rangle\) directions, and disk-like molecules with a uniform distribution of orientations. The structure of the \(\delta^*\) phase is tetragonal, and the space group was identified unambiguously as \(P4_2/ncm\) at 14.5 GPa.

We did not observe any potentially directional interactions in either of the pressure-induced phases of N\(_2\). In all cases, the N\(\cdots\text{N}\) interactions follow a Type-Ia/Type-Ib topology of bonding and occur between interacting sites of dissimilar electron density. The possibility of the N\(\cdots\text{N}\) and \(\pi\cdots\text{N}\) (lone-pair) interaction can be inferred from the MESP model of an isolated molecule, Figure 1e. The delocalized bonding region in N≡N is equipped with a belt of positive potential characterized by near equivalent local most maxima (tiny red spheres). In contrast to what might be expected on the surface of a covalent bound halogen in a molecular entity, such as, for example, in HBr and HCl, we observed that each N along the N≡N bond extension is accompanied by a local most minima of potential (tiny blue spheres in Figure 1e) and is very negative. This signifies that there is a buildup on charge density on the surface of N along the outer N≡N and the buildup is significant compared to the lateral sites on the same atoms.
Figure 1. The nature of bonding interactions between the N\textsubscript{2} molecules in the crystals of (a) α-N\textsubscript{2}, (b) β-N\textsubscript{2}, (c) γ-N\textsubscript{2}, and (d) ε-N\textsubscript{2}. (e) The 0.001 a.u. isodensity mapped MESP plot of an isolated N\textsubscript{2} molecule, obtained at the MP2(full)/aug-cc-pVTZ level of theory. The local minima and maxima of potential are marked by tiny circles in blue and red, respectively. Selected bond lengths and bond angles are in Å and degree, respectively. Crystallographic axes are not shown in (a, c) for clarity. The crystal symmetry is shown for each case, together with ICSD references.
3.2. The Nitrogen Trihalides, \( \text{NX}_3 \) and Their Crystal Structures

We now discuss a set of other examples in which covalently bound nitrogen acts as an electrophile, as observed in crystalline systems reported over many years. In these systems, covalently bound nitrogen, as in \( \text{NX}_3 \) \((X = F, \text{Cl}, \text{Br}, \text{I})\), has a positive region on the R–N bond extension that is capable of attracting a negative site on an identical, or in a different molecule. This can be appreciated by looking at the MESPs shown in Figure 2, obtained using \( \omega \text{B97XD}/\text{Jorge-ATZP} \). The top view of Figure 2 shows nitrogen having a positive electrostatic potential along the X–N bond extensions, regardless of the nature of the halogen derivative attached to it. It is largest \((16.6 \text{ kcal} \cdot \text{mol}^{-1})\) along the F–N bond extensions in \( \text{NF}_3 \). As one passes from \( \text{NF}_3 \) through \( \text{NCl}_3 \) to \( \text{NBr}_3 \), there is a decrease in \( V_{\text{S,max}} \) from \( 16.6 \text{ kcal} \cdot \text{mol}^{-1} \) to \( 5.4 \text{ kcal} \cdot \text{mol}^{-1} \) to \( 2.7 \text{ kcal} \cdot \text{mol}^{-1} \), and the stability of the \( \sigma \)-hole on N in \( \text{NX}_3 \) occurs in the order X = F > Cl > Br. By contrast, the lone-pair dominated region on N is negative, and the negativity increases in the order \( \text{NF}_3 \) \((-4.1 \text{ kcal} \cdot \text{mol}^{-1}) \) > \( \text{NCl}_3 \) \((-11.8 \text{ kcal} \cdot \text{mol}^{-1}) \) > \( \text{NBr}_3 \) \((-14.2 \text{ kcal} \cdot \text{mol}^{-1}) \). These results demonstrate the amphoteric character of N in \( \text{NX}_3 \).

**Figure 2.** Comparison of the \( \omega \text{B97XD}/\text{Jorge-ATZP} \) calculated 0.001 a.u. isodensity envelope mapped potential on the electrostatic surfaces of \( \text{NX}_3 \) \( (X = F, \text{Cl}, \text{Br}, \text{I}) \) molecules. Selected \( V_{\text{S,max}} \) and \( V_{\text{S,min}} \) values in kcal mol\(^{-1}\) are shown, which are the local most maximum and minimum of potential (red and blue circles), respectively. Two views of each MESP graph are shown. In the top view, bonded N faces the reader, whereas, in the bottom view, it is the three halogens that face the reader. The Quantum Theory of Atoms in Molecules (QTAIM \([122]\))-based molecular graph is shown for each entity, with the circles in green representing bond critical points and bonds in atom color.

The MESP results for \( \text{NI}_3 \) are also included in Figure 2, but clearly do not follow the same trend noted above. This may be an artifact of the basis set we used for these calculations, and we clarify this further below. Whilst the numerical values of potential may be out of line, the reactive nature of the N site along and around the I–N bond extensions in \( \text{NI}_3 \) behaves qualitatively similar to that found for the other three \( \text{NX}_3 \) entities.
As shown in the bottom view of Figure 2, $V_{S,max}$ in NX3 increases monotonically from X = F through I along the N–X bond extension, indicating that the magnitude of the $\sigma$-holes associated with these potentials increases in the same order and the $\sigma$-holes are surrounded by belt-like negative potentials. In other words, the least polarizable F has the smallest $\sigma$-hole on N–F bond extensions and the most polarizable I has the largest $\sigma$-hole on the N–I bond extensions. The difference in $V_{S,max}$ between NB3 and NI3 is not large and, as we commented above, the MESP values for NI3 with the chosen basis set used may not be very reliable.

In all cases, the central region of the triangular face formed by the three X atoms in each NX3 is found to be positive. The positive and negative nature of $V_{S,max}$ and $V_{S,min}$ on the surface of each constituent atomic domain in NX3 suggest that each of them not only has the ability to form complexes with another identical (or different) molecule but also has the ability to act both as an acid and a base.

In order to determine whether or not the inconsistency in the nature of the negative and positive regions on the surface of specific atoms in the series of four molecules NX3 is a basis set artifact, we examined the same properties using another basis set, def2-TZVPD, available in the basis set exchange library [123]. We have also adopted a higher level of theory, MP2, for the same calculation as it is one of the simplest and most useful levels of theory beyond Hartree–Fock that accounts for effects arising from electron–electron correlation. The results are summarized in Table 1.

Table 1. $\omega$B97XD/def2-TZVPD and MP2(full)/def2-TZVPD computed 0.001 a.u. isodensity envelope mapped the local most minima and maxima of potential on the electrostatic surfaces of NX3 (X = F, Cl, Br, I) molecules. $V_{S,max}$ and $V_{S,min}$ values in kcal mol$^{-1}$.

| Species | NF3 | NCl3 | NB3 | NI3 |
|---------|-----|------|-----|-----|
| Method | $\omega$B97XD | MP2 (Full) | $\omega$B97XD | MP2 (Full) | $\omega$B97XD | MP2 (Full) | $\omega$B97XD | MP2 (Full) |
| Extrema of potential $V_{S,max}$ | | | | | | | | |
| N–X (one on each X) | 4.7 | 5.2 | 25.0 | 29.7 | 28.2 | 36.3 | 32.1 |
| X–N (one on each extension) | 16.5 | 16.5 | 5.2 | 4.6 | 3.5 | 3.5 | 2.1 | 2.3 |
| Center of the triangular X3 face | 8.8 | 7.5 | 5.6 | 4.9 | 5.4 | 4.3 | 6.4 | 4.9 |
| $V_{S,min}$ | | | | | | | | |
| On lone-pair region on N | −4.1 | −3.7 | −11.9 | −12.6 | −14.1 | −13.8 | −17.2 | −15.2 |
| On F (within the X3 face) | −1.8 | −1.9 | −3.7 | −3.4 | −4.3 | −3.9 | −4.9 | −4.0 |
| On X (opposite of the X3 face) | −1.3 | −1.3 | −4.0 | −4.1 | −4.8 | −4.6 | −5.3 | −4.8 |

As can be seen from the data in Table 1, and regardless of the correlated method used in conjunction with the def2-TZVPD basis set, the N has a positive $\sigma$-hole along the X–N bond extensions. These $\sigma$-holes become less positive as the size of the halogen in NX3 increases from F down to I, and there are three equivalent holes on N in each NX3. By contrast, the halogen derivative has a single $\sigma$-hole on its surface along the N–X bond extension, so there are also three positive $\sigma$-holes on the surfaces of the three X atoms that are also equivalent (only one is listed in Table 1). They systematically increase with the increasing size of the halogen in NX3, in agreement with what might be expected from their polarizabilities.

3.2.1. Nitrogen Trifluoride, NF3

The crystal structure of NF3 was reported only recently, and corresponds to the low-temperature $\alpha$-phase [124]. Since powder neutron diffraction measurements were performed, it is expected that the intermolecular geometry is more accurate than might have been obtained from X-ray diffraction measurements.

The $\alpha$-phase of NF3 crystallizes in the orthorhombic space group $Pnma$, with lattice parameters $a = 6.71457(13)$ Å, $b = 7.30913(14)$ Å, $c = 4.55189(8)$ Å, cell volume ($V$) = 223.396(7) Å$^3$, and $Z = 4$ at $T = 6$ K. The $\beta$-phase of NF3 corresponds to a high-temperature phase.
and was observed to be a plastic crystal (space group $P4/mnm$) with lattice parameters $a = 15.334(6) \, \text{Å}$, $c = 7.820(3) \, \text{Å}$, $V = 1838.6(12) \, \text{Å}^3$, and $Z = 30$ at $T = 60 \, \text{K}$. It was suggested that the crystal structure of this latter phase is closely related to that of the Frank–Kasper sigma phase, but the one deposited in the ICSD (ref. code 1891641) does not contain the geometry of $\beta$-NF$_3$ (the fluorine atoms are missing).

The unit-cell of the $\alpha$-phase comprises four units of NF$_3$, as shown in Figure 3a. It shows the intermolecular bonding modes between the building blocks responsible for the unit-cell of the NF$_3$ crystal; these are consistent with the attraction between the positive and negative sites of electrostatic potential localized on different atomic domains (Figure 3b). In particular, Type-IIa N–F···F and F–N···F non-covalent interactions are observed and are inferred from the intermolecular distances and angles of interaction. The former is less directional but shorter than the latter (Figure 3a).

The real nature of the intermolecular interactions between the molecular units in the crystal may not be apparent in inspecting the unit-cell alone; a periodic extension of the unit-cell is necessary. The $2 \times 2$ supercell structure of $\alpha$-NF$_3$ is shown in Figure 3c. Although there are many more interactions between the molecules of NF$_3$ in the crystal, we have highlighted in Figure 3c only the prominent bonding modes formed by the N site. As revealed by the MESP model (Figure 2a), the three positive sites along the F–N bond extensions do indeed donate pnictogen-centered $\sigma$-hole bonds to the lateral portions of the F sites in the nearest NF$_3$ units (Figure 3a). Of the three, two are equivalent and the other is longer ($3.169 \, \text{Å}$ vs. $3.368 \, \text{Å}$). They are all directional since $\angle F$–N···F for each of the two equivalent interactions is $172.3^\circ$ and that for the longer bond is $174.5^\circ$ (Figure 3a).

In crystalline $\alpha$-NF$_3$, the nitrogen in the NF$_3$ molecule acts as a hexa-furcated center in donating $\sigma$-hole bonds. It donates three highly directional $\sigma$-hole bonds (vide supra) and two relatively less directional equivalent $\sigma$-hole bonds ($r(N···F) = 3.301 \, \text{Å}$ and $\angle F$–N···F = $143.4^\circ$) that are caused by the attraction between the positive site on the central region of the surface formed by the three fluorine atoms in one molecule and the negative region dominated by the lone-pair of a neighboring molecule, thereby forming five pnictogen bonds (Figure 4a,b). Because nitrogen has a negative site (readily appreciated in its Lewis structure) evidenced by the $V_{S,\text{min}} = -3.6 \, \text{kcal} \cdot \text{mol}^{-1}$ shown in Figure 2a, it shows a tendency to accept a $\sigma$-hole bond from the covalently bound fluorine of another interacting NF$_3$ molecule, responsible for the formation of an F···N halogen bond (Figure 4b). The back-to-back arrangement between the NF$_3$ molecules, Figure 4a, causing the additional intermolecular interactions noted above, is a result of a $\pi(N)$···$\pi(N)$ interaction. The behavior of N in forming so many non-covalent interactions appears to be unique to this system.

Our investigation shows that fluorine has the ability to act both as a hexa- and tetra-furcated center, as shown in Figure 4c,d, respectively. It is evident from Figure 4c that fluorine is an acceptor of three $\sigma$-hole bonds, thus forming one F–N···F and two N–F···F halogen bonds; it is a donor of a single $\sigma$-hole bond, forming an N–F···N halogen bond; and it shows capacity to form two or more N–F···F–N halogen-bonded Type-Ia and/or Type-Ib interactions—all within a distance of 2.90–3.20 Å. The Type-Ia N–F···F–N halogen-bonded contacts, such as those marked in Figure 4d, are commonly observed in fully fluorinated compounds, for example, the crystal of C$_6$F$_6$ [125], and in similar compounds [126–128]. Clearly, the complex topology of bonding between the NF$_3$ molecules in the crystal structure requires a variety of theoretical studies to detail the nature and the strength of the interactions involved.
Figure 3. (a) The unit-cell of $\alpha$-NF$_3$ (CSD ref. code 1891640), showing selected N···F and F···F $\sigma$-hole-centered intermolecular interactions and the intermolecular angles for the approach of the electrophile. (b) Illustration of selected local maximum and minimum of electrostatic potential (red and blue spheres, respectively) mapped on the 0.001 a.u. isoelectron density surface of NF$_3$ obtained at the $\omega$B97XD/aug-cc-pVTZ level of theory. (c) The network of N···F and F···F $\sigma$-hole centered pnictogen and halogen bonding interactions in $2 \times 2$ supercell geometry of $\alpha$-NF$_3$. Bond lengths and bond angles in Å and degrees, respectively. Dotted lines represent intermolecular interactions.
3.2.2. Nitrogen Trichloride, NCl₃

The crystal structure of NCl₃ was reported in 1975 [129]. It crystalizes in the orthorhombic space group Pnma. There are 12 molecules in the unit-cell, as shown in Figure 5a. The mean N–Cl bond distance is 1.75(1) Å and the mean bond angle is 107(2)°. The insights gained from the values of $V_{S,max}$ and $V_{S,min}$ on the surface of an isolated NCl₃ molecule above (Figure 2b) can now be used to understand its chemical reactivity.
Figure 5. (a) The unit-cell of the NCl₃ crystal (ICSD ref. code: 4034). (b) Illustration of the nature of Cl···Cl intermolecular interactions between the molecular building blocks. (c) Illustration of the nature of the N···Cl interactions. (d) Nature of the local topology of bonding around N in NCl₃, showing N is a penta-furcated center. (e) Nature of the reactive sites on the electrostatic surface of the NCl₃ molecule responsible for the N···Cl, Cl···N and Cl···Cl interactions, computed with ωB97X-D/aug-cc-pVTZ. (f) The nature of various N···Cl and Cl···N interactions in the crystal. (g) The nature of Cl···Cl and Cl···N halogen-bonded interactions in the crystal. Values of bond lengths and bond angles in Å and degrees, respectively.

The N–Cl···N and N–Cl···Cl intermolecular interactions holding the NCl₃ molecules together in the crystal can be rationalized by referring to Figure 5b,c, respectively. The extent to which covalently bound N in the NCl₃ molecule is engaged with the negative sites on
neighboring NCl$_3$ molecules, and producing the observed solid-state structure, is illustrated in Figure 5d. The bonding features are as expected when positive and negative sites on molecular surfaces are in close proximity, inferred from the MESP of NCl$_3$ (Figure 5e).

The pattern of intermolecular interactions between bonded N and Cl in the NCl$_3$ crystal is illustrated in Figure 5f. It is evident that each N donates three σ-holes. Two of these, the attraction between a covalently bonded N in an NCl$_3$ molecule and chlorines on neighboring molecules, generate a zig-zag chain-like pattern. They are inequivalent, in contrast to the analogous interactions observed in the NF$_3$ crystal described above. The $r$(N···Cl) ($\angle$Cl–N···Cl) for these two contacts are 3.960 Å (160.8°) and 3.894 Å (171.6°), respectively, suggesting a Type-IIa nitrogen bonding topology. The remaining σ-hole bond formed by N, Figure 5d,f, is longer and quasi-linear ($r$(N···Cl) = 4.358 Å and $\angle$Cl–N···Cl = 173.2°), and is a result of the packing of molecules in the crystal. As shown in Figure 5d, each N site serves as a penta-furcated center in accepting and donating σ-hole bonds.

The three pnictogen bonds are augmented by σ-centered N–Cl···N and N–Cl···Cl halogen bonds in stabilizing the crystal. These Type-IIa N–Cl···N bonds are highly directional ($r$(Cl···N) = 3.190 Å and $\angle$N–Cl···N = 177.1°), and are formed between the σ-hole on the N–Cl bond extension in one molecule and the lone-pair dominated negative site on N in another interacting molecule (Figure 5g).

The three N···Cl contacts highlighted in yellow in Figure 5f are repeated throughout the crystal. Two of them are equivalent ($r$(N···Cl) = 3.298 Å) and the other slightly longer ($r$(N···Cl) = 3.360 Å). They are significantly bent, with $\angle$Cl–N···Cl of 140.3° and 140.1°, respectively. We assign them to be Type-IIb based on the classification of bonding topology provided in Scheme 1. They are enforced by the attraction between the positive site in the central region of the triangular face formed by three Cl atoms in the NCl$_3$ molecule and the lone-pair dominated negative site on the N of a neighboring molecule. One might characterize this as an N(π)···N(π) pnictogen bond, consistent with the surface extrema revealed by the MESP model (Figure 5e).

Figure 5g shows the pattern of occurrence of Type-IIa N–Cl···Cl halogen bonds. Those having a Cl···Cl bond distance (and $\angle$N–Cl···Cl) of 3.580 Å (168.4°) are more directional than those with the corresponding values of 3.548 Å (157.6°). Indeed, they are shorter and less directional than Cl···N halogen bonds with bond distances (angles) of 4.305 Å (173.8°), Figure 5g. There are numerous Cl···Cl contacts present in the crystal (not shown).

3.3. Halogen Azides, XN$_3$

Halogen azides XN$_3$ (X = F, Cl, Br, I), crystallographically known for some time [130–134], have also been studied more recently [135,136]. ClN$_3$ forms a chain-like polymer in the solid state, and BrN$_3$ a helical structure, due to the formation of intermolecular Br···N$\sigma$ and N$_\beta$···N$\gamma$ interactions. The unit-cells of IN$_3$ yield structures of polymeric (–I–N$_3$–)$_n$ chains that are interlocked into layers, yet two modifications were reported for IN$_3$. Its crystal structure, first determined by X-ray diffraction in 1993 [134], corresponds to the α-phase of the crystal. The second modification of the crystal is called the β-phase [135,137]. Although most of the past studies, including the recent one published in 2021 [137], have determined the lattice constants and important covalent bonding features, which have enhanced our knowledge of covalent p-block azide chemistry, the intermolecular bonding interactions between the XN$_3$ molecules responsible for the crystals are yet to be explored computationally. The study of Schulz and coworkers [135] demonstrates that ClN$_3$ adopts a polymeric structure in the solid state with short intermolecular Cl···Cl distances, as was observed for the elemental halogen. The crystal structures of ClN$_3$ [135], and BrN$_3$ [136], are illustrated in Figure 6a,b and Figure 7a, respectively.
Figure 6. (a,b) Two different views of the crystal structure of chlorine azide (ICSD ref code: 424502). The nature of (c) π(N)···(N) contacts, and (c,d) a pattern of the π(N)···(N), N···Cl, and Cl···Cl contacts in the crystal. (e) Illustration of Cl···Cl and π···N intermolecular halogen bonding and pnictogen bonding interactions in the crystal. (f) The nature of non-linear Cl···N halogens in the same crystal. Selected bond distances and bond angles are in Å and degree, respectively.

From the resonance structure, the central N atom of $N_2^-$ in $XN_3$ is expected to be positive; this is indeed what we find with our MESP calculations (vide infra). The calculated $V_{S_{\text{max}}}$ and $V_{S_{\text{min}}}$ are both positive on the surface of this atom, and carry opposite signs for the terminal and covalently bonded N. This explains why the σ-hole on the X atoms in a given $XN_3$ ($X = \text{Cl}, \text{Br}$) is directed towards the negative N/X of a neighboring molecule, and why the negative tip on the terminal N atom in a given $XN_3$ is directed towards the positive region on the central N atom of the $N_2^-$ in another $XN_3$ (see, for example, Figure 6c–f). Both the interaction types are short and significantly linear, with $r(\pi(N)···N)$ and $\angle N=N···N$ values of 3.677 Å and 177.7° in $\text{NCl}_3$ (Figure 6e), respectively, and of 3.093 Å and 163.3° in $\text{NBr}_3$ (Figure 7b), respectively. The nature of the intermolecular links between bonded atomic basins can be deduced from Figure 6c–f, including the potential involvement of Type-I and Type-II π(N)···N (Figure 6c–e), and Cl···N and Cl···Cl (Figure 6e,f) nitrogen and halogen bonding interactions. In some cases, a secondary interaction may arise as
a consequence of the primary interaction. For instance, the primary Cl···Cl Type-IIa interaction \(r(\pi(N)\cdots N) = 3.372 \text{ Å}\) shown in Figure 6e is likely to be responsible for the development of the Cl···N secondary interactions \(r(\text{Cl} \cdots N) = 4.154 \text{ Å}\) that are probably very weak.

The packing between the molecular units in ClN\(_3\), or BrN\(_3\) (Figure 7a), is not very different, and the pattern of intermolecular interactions found in ClN\(_3\) is also evident in BrN\(_3\). In addition to the observed \(\pi(N)\cdots(N)\) and Br···N pnictogen- and halogen-bonded interactions between the BrN\(_3\) units (Figure 7b,c), the slip parallel arrangement between the NBr\(_3\) units (Figure 7d), which is also seen in the crystal of ClN\(_3\), and which is caused by the attraction between \(\pi\) electron densities, is seen in Figure 7d. Clearly, N···X···N halogen bonding and N=N···N pnictogen bonding interactions play a vital role in the assembly of the molecular units, and hence, in the stability of these azido-based crystals.

The conclusions reached about the reactivity of the surfaces of XN\(_3\) molecules above are consistent with the positive and negative signs of the local most minima and maxima of potential, summarized in Table 2. As can be seen from the data, the most positive region is identified on the surface of the central N atom of N\(_3^-\) in XN\(_3\) in XN\(_3\) compared to that of the terminal and halogen-bonded nitrogen atoms. The largest values of \(V_\text{L,max}\) are 30.2 and 30.8 kcal·mol\(^{-1}\) in FN\(_3\) with \(\omega B97XD\) and MP2 (full), respectively. This becomes less positive as the size of the halogen increases from F down to I in XN\(_3\), a trend that is independent of the correlated method employed. On the other hand, the axial portion of the covalently bonded halogen atom is negative in FN\(_3\) but positive in XN\(_3\) (X = Cl, Br, I). This is consistent with F in FN\(_3\) being significantly less polarizable than the heavier halogens in XN\(_3\) (X = Cl, Br, I), as expected from their polarizabilities (F < Cl < Br < I), and explains why covalently bound Cl and Br atoms make \(\sigma\)-hole centered halogen bonding.
interactions with the negative site centered on the covalently bonded N in a neighboring molecule (see Figures 6e,f and 7b,c for the ClN$_3$ and BrN$_3$ systems, respectively).

Table 2. ωB97XD/def2-TZVPD and MP2(full)/def2-TZVPD computed 0.001 a.u. isodensity envelope mapped local most minima and maxima of potential on the electrostatic surfaces of XN$_3$ (X = F, Cl, Br, I) molecules. $V_{S,max}$ and $V_{S,min}$ values are in kcal mol$^{-1}$. Atom numbering of the N$_3^{-}$ moiety in all members of the series is as in FN$_3$.

| Species | Method | FN$_3$ | ClN$_3$ | BrN$_3$ | IN$_3$ |
|---------|--------|--------|--------|--------|--------|
| Extrema | $V_{S,min}$ | ωB97XD | MP2 (Full) | ωB97XD | MP2 (Full) | ωB97XD | MP2 (Full) |
| On N3 of N2=N3 | −4.5 | −4.3 | −8.4 | −9.1 | −10.3 | −11.2 | −13.8 | −13.8 |
| On N1 of N2=N1 | −12.5 | −11.6 | −14.6 | −13.4 | −15.0 | −13.4 | −15.9 | −14.5 |
| On X of N1–X | −14.5 | −13.4 | −5.6 | −4.1 | −3.7 | −2.1 | −1.1 | 0.02 |
| $V_{S,max}$ | | On X of N–X | −3.4 | −1.7 | 23.5 | 25.3 | 31.7 | 33.1 | 42.8 | 41.2 |
| | | On N1 of N2=N1 | −6.4 | −5.3 | −2.2 | −0.8 | −0.5 | 1.0 | 2.5 | 3.4 |
| | | On N2 | 25.8 | 24.6 | 23.7 | 21.5 | 22.4 | 20.1 | 21.0 | 18.3 |
| | | On N2 | 30.2 | 30.8 | 24.6 | 23.4 | 22.3 | 20.7 | 17.8 | 16.4 |

The MP2(full) and ωB97XD predicted electrostatic potentials are consistent with the conclusions reached above for most regions on the surfaces of XN$_3$, although MP2(full) produces lower values for most sites. A regular trend in a minimum or maximum on the surface of a given molecule is maintained across the series. For instance, the $V_{S,min}$ on the surface of the terminal N along the N=N bond extension in FN$_3$ is calculated with MP2(full) to be negative (−4.3 kcal mol$^{-1}$) and is increasingly larger on the same atom in the other three systems of the family as one passes from FN$_3$ to ClN$_3$ to BrN$_3$ to IN$_3$. An anomaly is found on the nature of the lateral portion of the covalently bonded iodine in IN$_3$, for which MP2(full) and ωB97XD have predicted the $V_{S,min}$ associated with it to be slightly positive or close to neutral (0.02 kcal mol$^{-1}$) and fully negative (−1.1 kcal mol$^{-1}$), respectively. Which one of these is more reliable can only be cross-checked with a computational exploration of the interactions of this site with the negative site on other molecules. Nevertheless, this result unequivocally suggests that the magnitude of electrostatic potential (and sometimes its sign) is dependent on the nature of electron correlation [23,25,89], and hence care should be taken when computing potentials on the electrostatic surfaces of chemical systems. Another way to overcome this is to use a slightly larger isodensity envelope, such as 0.0015 a.u. or 0.0020 a.u., on which to compute the potential. We have discussed the usefulness of these envelopes elsewhere [22,25,87,89].

3.4. Other Azides

Our conclusions about the nature of intermolecular bonding in the halogen azides are consistent with the views of Bursch and coworkers [138] for analogous systems. Specifically, these authors have reported the properties of non-covalent interactions between azides
and oxygen-containing moieties in some chemical systems. Representative examples of molecules reported in that study are shown in Figure 8. Each shows close azide–oxygen contacts in the solid state. It was observed that the intramolecular N···O nitrogen bonded contacts are much shorter than the sum of the van der Waals radii of the respective atomic basins. For the Nterminal−Ncentral···X angle (where X is a pnictogen, chalcogen or halogen) in the systems examined, there was a strong accumulation of data points between 85° and 130°. As stated by the authors, caution needs to be exercised in interpreting the angular nature of these interactions because every structure was not individually examined. In the representative structures shown in Figure 8, the Nterminal−Ncentral···O angles are 105.4°, 103.7°, 88.4° and 93.9° for Figure 8a–d, respectively. Although the intramolecular interactions in the representative structures were observed to be unusually bent (perhaps not unexpectedly as they are developed intramolecularly), they are characteristic of pnictogen bonding since the central N atom of the azide moiety in the molecular entities is positive, and is involved in an attractive interaction with the negative sites on covalently bonded O. One may attribute the N···O interaction to a π···lone-pair type pnictogen bond since a p-type orbital on N is responsible for driving this interaction. This may also explain why the directionality of the π-centered pnictogen bond does not follow any specific (linear) topology of bonding. The theoretically calculated association energies for the systems above were reported to be ranged from $-1.0$ to $-5.5$ kcal·mol$^{-1}$.

The final azide we consider is phosphorus azide, P$_3$N$_2$ [139]. The unit-cell contains two molecules of P$_3$N$_2$. They are bonded to each other through π(N$_3$)···N and N···N non-covalent interactions, as shown in Figure 9a,b. The N···N intermolecular distances range between 2.90 and 3.30 Å, and are all less than twice the van der Waals radius of N, 3.32 Å. Clearly, intermolecular pnictogen bonding is one of the principal features responsible for the formation of the crystalline phase of the P$_3$N$_2$.

3.5. Miscellaneous Examples

We end this section by looking at a number of other examples to illustrate the importance of the involvement of N-centered pnictogen bonding in crystalline materials.

The first is the crystal structure of nitrosonium nitrate (NO$^+$NO$_3^-$), Figure 10a, reported only recently [140], but it is a system that has been studied many times, dating back to 1948 [141–146]. The crystalline state, as determined by XRD measurements at high pressure, consists of N≡O$^+$ cations and sp$^2$-trigonal planar NO$_3^-$ anions stabilized via charge-assisted N···π and N···O nitrogen bonding interactions. Our analysis suggests that both N and O in NO$^+$ in the crystal are involved in several intermolecular interactions with the surrounding NO$_3^-$ units. The N of each nitrosonium group has five nearest neighbor O sites from three surrounding NO$_3^-$ units within its inner coordination sphere, with r(N···O) between 2.15 and 2.30 Å (some are shown in Figure 10b,c). Similarly, the O atom of NO$^+$ has five oxygen atoms from four closest NO$_3^-$ units, as its first intermolecular neighbors. The O···O distances vary between 2.27 and 2.36 Å, slightly longer than the N···O bond distances (not shown), as expected since O is slightly larger than N (r$_{vdW}$(O) = 1.50 Å and r$_{vdW}$(N) = 1.66 Å) [77]. This analysis is consistent with that of the authors of the study [140]. However, we identified that π-hole(N)···N interactions occur in the crystal at an intermolecular distance of 2.539 Å (see Figure 10b), and are undoubtedly π-hole-centered pnictogen bonds.
Representative examples of compounds with close intramolecular oxygen–azide contacts were observed in some structures reported in the solid state [138]; (a) 6-azido-5-[1,2-bis(benzyloxy)ethyl]-2,2-dimethyltetrahydro-2H-furo[2,3-d][1,3]dioxole; (b) 2-[(benzenesulfonyl)methyl]phenyl][methyl]azidoacetate; (c) 1-(azidomethyl)-2-[(benzenesulfonyl)methyl]benzene; (d) dimethyl (2-azidoethyl)[(4-nitrophenyl)methyl]propanedioate. Nitrogen is depicted in blue, oxygen in red, sulfur in yellow, and carbon in gray. The interatomic distances between the central N of the azide and the closest oxygen atom are given in Å, and bond angles in degrees. Thermal ellipsoids are shown at the 50% probability level. The names of the molecular entities and CSD ref. codes are shown. The space-filling model is depicted in each case.
Figure 9. (a) The crystal structure of 2,2,4,4,6,6-hexa-azido-2,4,6-triphospha-1,3,5-triazine (P₃N₂₁) showing π(N₃)···N pnictogen bonded interactions. (b) Illustration of N···N and π(N₃)···N non-covalent interactions between four molecular units of P₃N₂₁. Selected bond lengths and bond angles are in Å and degree, respectively. Nitrogen is depicted in blue, and phosphorous in orange.

Figure 10. (a) The crystal structure of monoclinic (P2₁/m) nitrosium nitrate NO⁺NO₃⁻, CSD ref. code IMABAC. (b,c) Illustration of the nature of π-hole(N)···N and N···O bonding interactions in the crystal, respectively. Selected bond distances and bond angles are in Å and degree, respectively. Atom type is given in (b).

In crystalline tetramethylpyrazinium pentaiodide monohydrate [147], Figure 11, the feasibility of N···I interactions is evident. They are charge-assisted pnictogen bonds, with bond distances in the range 3.7–4.1 Å, and are close to, or longer than, the sum of the vdW radii of N and I, 3.70 Å. They are π-centered since the π-hole on N accepts electron density from the iodine atom in I₅⁻. In addition, there are numerous H···I and (C)π···I
type intermolecular interactions that are also responsible for the overall structure of the crystalline material.

Figure 11. Illustration of N···I pnictogen bonds in the unit-cell of the crystal of tetramethylpyrazinium pentaiodide (CSD ref. code ZEPBIF). Nitrogen is depicted in blue, oxygen in red, iodine in purple, and carbon in gray. H atoms are not shown for clarity. Selected bond distances are in Å.

Many structures of compounds containing Group 15 elements deposited in the CSD owe their stability to a variety of intermolecular interactions, including pnictogen bonding. Group 15 elements in molecules are often trivalent or tetravalent and hence they may contain more than one σ-hole along the R–Pn bond extensions (viz. as in NX3 shown above). Recently, for instance, Kumar and coworkers [148] suggested that tetrel and pnictogen bonds complement hydrogen and halogen bonds in framing the interactional landscape of barbituric acids. In particular, and by means of a CSD search, these workers have argued that the imide nitrogen atoms in some fluoro-, chloro- and bromo-substituted derivatives of barbituric acid and indandione can act as effective pnictogen bond donors, thereby featuring N···O nitrogen bonds. These contacts appear simultaneously with C···O tetrel bonds, and other interactions, and hence provide stability to the backbone of the overall crystal lattice.

As observed in the crystal structure of NO+NO3‒ (vide supra), one might speculate that N···O nitrogen bonding interactions occur in the crystal structures of ammonium 1,3,4,6-tetranitro-2,5-diazapentalene, (NH4)2C6N6O8 [149], Figure 12a, and 1,3,4-trinitro-7,8-diazapentalene, C6H3N3O6 [150], Figure 12b, and that N···F pnictogen bonding occurs in the crystal of 3,3-bis(difluoroaminomethyl)oxetane, C5H8F4N2O [151], Figure 12c. In the first two, the N···O interactions are π-centered; the π electron density delocalized on the surface of N of the NO2 fragment in [C6N6O8]2‒ is in an attractive engagement with the O’s lone-pair in another unit of [C6N6O8]2‒. The occurrence of the pnictogen bonded interaction in the crystal is facilitated by charge-assisted H···N hydrogen bonds between NH4+ and the dianion. The N(π)···O interactions are equivalent, with r(N(π)···O) = 2.945 Å, and are less than vdW radii of N and O, 3.16 Å. In the case of the crystal structure of 1,3,4-trinitro-7,8-diazapentalene, C6H3N3O6, there is no ion pair, yet the N(π)···O pnictogen bonded interactions still occur between the C6H3N3O6 units. However, in this case, primary/secondary interactions (viz. H···O hydrogen bonds, and C(π)···O interactions) are expected to play a crucial role in the overall stability of the crystal.
Figure 12. The nature of nitrogen-centered pnictogen bonding in the crystals of (a) \( (\text{NH}_4)_2\text{C}_6\text{N}_6\text{O}_8 \) [149], (b) \( \text{C}_6\text{H}_3\text{N}_5\text{O}_6 \) [150], and (c) \( \text{C}_5\text{H}_8\text{F}_4\text{N}_2\text{O} \) [151]. Selected bond distances are shown in Å and degree, respectively. Selected atom types are shown in (a,c) that are involved in making non-covalent interactions. The CSD ref. code is given in each case.

In the crystal of \( \text{C}_2\text{H}_6\text{F}_4\text{N}_2\text{O} \) [151] the interacting molecules are bonded to each other through F–N···F nitrogen bonds, Figure 12c (left). They appear to show up in two different flavors: one with an intermolecular bond distance of 3.076 Å and the other with an intermolecular bond distance of 3.205 Å. The second is directional \( \angle \text{F–N} \cdots \text{F} = 165.8^\circ \) and follows the Type-IIa topology of bonding and appears along the extension of the F–N covalent bonds. The first is non-linear and is taken to be a \( \pi \)-hole centered interaction \( r(\text{N(\pi)} \cdots \text{O}) = 3.076 \) Å. In addition, each monomer unit in the crystal has an N(\( \pi \))···N(\( \pi \)) pnictogen bonding interaction, with \( r(\text{N(\( \pi \))} \cdots \text{N(\( \pi \))}) = 3.140 \) Å. There is a distinct possibility of intermolecular pnictogen bonding in the crystal being driven by H···F hydrogen bonds (Figure 12c, right) that are shorter than the pnictogen bonds. Therefore, the hydrogen bonds are probably the primary intermolecular interaction, leading to the formation of secondary pnictogen interactions in this crystalline material.
The crystal structure of a perhydropyrazolopyrazole is shown in Figure 13a [152]. The N atom in the N–N covalent bond of pyrazole seems to be positive along its outer extension, and the lateral site is negative. This explains why the electropositive H site of the hydroxyl group in an included methanol solvent molecule is able to form a hydrogen bond, leading to the formation of a reasonably strong O–H⋯N hydrogen bond (r(H⋯N) = 2.043 Å and \( \angle O-H\cdots N = 170.9^\circ \); Figure 13b). We also observed Type-IIa quasi-linear N⋯Cl nitrogen bonds in the crystal with \( r(N\cdots Cl) = 3.958 \) Å and \( \angle N-N\cdots Cl = 176.4^\circ \), Figure 13b. This emerges from the fact that the lateral site in the covalently bound Cl, which is nucleophilic, interacts with the axial site of N along the N–N bond extensions, and that the interaction is directional. Apart from these interactions, there are numerous \( \pi\cdots\pi \) stacking interactions, Cl⋯Cl halogen bonds, and H⋯Cl hydrogen bonds in the crystal (not explicitly shown).

Figure 13. (a) The nature of N⋯Cl pnictogen bonding in the unit-cell of the crystal of a perhydropyrazolopyrazole, [1,3-bis(4-chlorophenyl)tetrahydro-1H,5H-pyrazolo[1,2-a]pyrazol-2-yl](4-methylphenyl)methanone [152]. There is a methanol solvate in the structure. (b) The local nature of intermolecular interactions between the monomeric units in the same crystal. Selected bond lengths and bond angles are in Å and degrees, respectively. The dotted lines represent intermolecular interactions, and those in red represent hanging contacts.

Olejniczak and coworkers [153] recently reported crystalline materials formed as a consequence of CH⋯N and N⋯N interactions in the high-pressure structures of some pyridazines, viz. 6-azido-1,2,4-triazolo[4,3-b]pyridazine (C\(_5\)H\(_3\)N\(_7\)) (as an anhydrate) and its 3-methyl derivative (C\(_6\)H\(_5\)N\(_7\)) (as a hydrated clathrate). Short C–H⋯N and N⋯N intermolecular contacts could be observed in the structures; the latter involves attraction exclusively between the azide groups. Figure 14a shows the unit-cell of the crystal of C\(_5\)H\(_3\)N\(_7\), and Figure 14b shows the binary arrangement between the C\(_5\)H\(_3\)N\(_7\) molecular units in the crystal. As shown in the latter, there is a pair each of N⋯N and H⋯N close contacts between the two interacting units. The first is more directional than the second and follows a Type-IIa pattern of nitrogen bonding. In addition to these interactions, nitrogen-centered \( \pi\cdots\pi \) stacking interactions appear to play a very important role in the stability of the crystal, as may be inferred from Figure 14a. The intermolecular distances of the N⋯N contacts are different, 3.369 and 3.165 Å. The latter is shorter, and the former is longer than twice the vdW radius of N, 3.32 Å, and both are directional.
Figure 14. (a) The unit-cell of the crystal structure of 6-azido[1,2,4]triazolo[4,3-b]pyridazine (C₅H₃N₇), showing possible N···N close contacts between the interacting monomer units. (b) Illustration of N···N and H···N pnictogen and hydrogen bonds between the pair of two units of C₅H₃N₇. Bond lengths and bond angles in Å and degrees, respectively. The CSD ref. code of the crystal is NETJUR01.

Allcock coworkers [154] have reported the crystal structure of a series of short-chain and cyclic phosphazenes bearing o-dichloro- and o-dimethyl-phenoxy groups. Figure 15a shows one of them, (O)PCl₂N=P(o-OC₆H₃Cl₂)₃. Within the skeletal framework of the molecular entity, the lateral sites of the ortho-Cl atoms are negative. There is an overlap between the Cl and N atomic basins corresponding to an intermolecular distance of 3.264 Å (Figure 15b), which is less than the sum of the vdW radii of Cl and N atoms, 3.48 Å ($r_{vdW}(Cl) = 1.82$ Å and $r_{vdW}(N) = 1.66$ Å). This intramolecular N···Cl close contact is a π-hole centered nitrogen bond. The nitrogen site is also in an attractive engagement with the two nearest C and Cl atoms. The N···C close contact ($r(N···C) = 2.901$ Å) appears to be a π···π interaction, and the N(π)···Cl close contact with an intramolecular distance of 3.695 Å is a force consequence of the Cl–P···Cl pnictogen bond. The overall stability of the crystal is, however, a result of significant H···Cl and H···O, π···π stacking interactions (between arene moieties), and Cl···Cl halogen-bonded intermolecular interactions that may be deduced from the unit-cell of the crystal itself (Figure 15a).

Figure 15. (a) The unit-cell of crystalline tris(2,6-dichlorophenoxy)phosphazeno-dichloro-oxo-phosphorus, (O)PCl₂N=P(o-OC₆H₃Cl₂)₃, (CSD ref. code PADJUZ). (b) Illustration of possible intramolecular pnictogen bonding within the framework of the molecular building block. Selected bond distances and bond angles in (b) are in Å and degree, respectively. The selected atom type is depicted.
4. Conclusions

In this featured review, we highlighted the importance and nature of the modes of nitrogen-centered pnictogen bonding (or, simply, the nitrogen bond) observed in many crystals deposited in the CSD and ICSD. Several of them have been known since the last century, even though the term “pnictogen bond”, or even “nitrogen bond” was not coined during that time. They turn out to occur in four different flavors: N(σ)···lone-pair, N(π)···lone-pair, N(σ)···π and N(π)···π(N). The rationalization of these interacting modes was made possible by exploring the MESP of isolated monomers constituting the crystals in several instances, together with chemical intuition. We have shown that the singular occurrence of pnictogen bonding in crystals is very rare, and hence is accompanied or reinforced by other primary/secondary interactions in a great majority of crystals, such as halogen bonds, hydrogen bonds, and/or π···π stacking interactions. Whereas there have been few previous studies reported of pnictogen bonding with covalently bonded nitrogen as an electrophilic agent (viz. imide nitrogen [148]), as the nitrogen in the molecular entity is often observed to be negative, this overview highlighted the local modes of intra- and intermolecular bonding interactions in several examples containing nitrogen that has a positive site. This is expected to guide researchers on future studies of nitrogen-centered pnictogen bonding and the design in silico of novel materials. We did not carry out a statistical analysis of structures deposited in the CSD and ICSD of pnictogen bonding to reveal possible ranges of intermolecular distances and angles of the approach of the electrophile on N in molecular entities, since pnictogen bonding is heavily affected by other primary and secondary interactions. As pointed out by a reviewer, even though a single example would be sufficient proof of existence, stronger arguments can be made if such cases are definitely shown not to be outliers. Since no rigorous theoretical first-principles calculations have been performed on most of the systems highlighted in this study, it is expected that the illustrative crystal systems may be used as model systems to investigate the energy stability and other physio-chemical properties (viz. vibrational frequency shift and NMR chemical shifts) to reveal the characteristic features of pnictogen bonds. The attempt will no doubt help provide a reasonable description of the strength of nitrogen bonds in supermolecular entities.

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