# **Hypervalency at the Pnictogen Centre**:
From NPh5 (Hypothetical) to SbPh5 (Stable)
A Multidisciplinary Analysis

Soumadeep Ghosh

Kolkata, India

**Abstract**

This article examines the series of pentaphenyl pnictogen compounds $EPh_5$ ($E$ = N, P, As, Sb) from the perspectives of inorganic chemistry, molecular orbital theory, quantum mechanics, and toxicology. The nitrogen compound $NPh_5$ is shown, by formal proof, to be forbidden under ambient conditions by the finite dimensionality of the $n = 2$ valence shell and by severe steric strain. The heavier homologues $PPh_5$, $AsPh_5$, and $SbPh_5$ are experimentally known and are treated comparatively. We then survey the extreme physical and chemical conditions — cryogenic matrix isolation, megabar pressures, plasma temperatures, and computational potential-energy surfaces — under which $NPh_5$ might achieve a transient or metastable existence. Structural diagrams are rendered in PGF/TikZ, comparative data are typeset with booktabs, and the article concludes with a glossary and a curated bibliography.

The paper ends with "The End"

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## 1 Introduction

The pnictogens (Group 15: N, P, As, Sb, Bi) display a remarkable evolution in chemical behaviour descending the periodic table. Nitrogen, the lightest member, is resolutely trivalent under ordinary conditions, forming at most four bonds when positively charged (as in ammonium, $NH_4{}^+$). Phosphorus, by contrast, is well known in both trivalent ($PCl_3$) and pentavalent ($PCl_5$, $PPh_5$) forms. Arsenic and antimony likewise accommodate a +5 oxidation state with five bonds in compounds such as $AsPh_5$ and $SbPh_5$.

This divergence raises a natural question: *could* nitrogen ever be persuaded to form five bonds to carbon, yielding the hypothetical pentaphenylnitrogen, $NPh_5$? The answer from standard valence theory is an emphatic *no*; yet frontier investigations in extreme-condition chemistry, computational quantum chemistry, and astrochemistry suggest that the boundary between "impossible" and "fleetingly real" is more porous than textbooks imply.

Section 2 establishes the theoretical foundations. Section 3 presents formal proofs of nitrogen's reluctance toward hypervalency. Section 4 depicts the molecular structures via TikZ. Section 5 gives a comparative survey of the $EPh_5$ series. Section 6 examines extreme conditions. The glossary (Section 7) and bibliography close the article.

# 2 Theoretical Background

## 2.1 Valence Shell Electron Pair Repulsion (VSEPR)

For a central atom $E$ with five equivalent ligands $L$ and no lone pairs, VSEPR predicts a **trigonal bipyramidal** geometry ($D_{3h}$ symmetry). The three equatorial bonds subtend 120°; each axial bond subtends 90° with the equatorial plane. The bond angle strain at nitrogen — whose small radius concentrates electron density — would be far more severe than at phosphorus.

**Definition 2.1** (Hypervalent Molecule)**.** A molecule is *hypervalent* if the central atom possesses more than eight electrons in its formal valence shell, i.e. it forms more bonds than permitted by the Lewis octet rule.

*Remark* 2.2. The term "hypervalent" is itself contested. Musher (1969) [1] originally defined it for compounds of second-row and heavier elements. The "expanded octet" model invokes $d$-orbital participation, though modern MO theory explains hypervalency purely through three- centre four-electron (3c-4e) bonding without any $d$-orbital contribution [2, 3].

## 2.2 Molecular Orbital Description of the 3c-4e Bond

In a linear three-centre system $L$–$E$–$L$ (e.g. the axial fragment of $PF_5$), one constructs three molecular orbitals from the ligand $\sigma$-donor orbitals $\phi_L$ and the central-atom orbital $\phi_E$:

$$\psi_{\text{bonding}} = \tfrac{1}{\sqrt{2}}\phi_{L_1} + c\,\phi_E + \tfrac{1}{\sqrt{2}}\phi_{L_2}, \tag{1}$$
$$\psi_{\text{nonbonding}} = \tfrac{1}{\sqrt{2}}\phi_{L_1} - \tfrac{1}{\sqrt{2}}\phi_{L_2}, \tag{2}$$
$$\psi_{\text{antibonding}} = \tfrac{1}{\sqrt{2}}\phi_{L_1} - c\,\phi_E + \tfrac{1}{\sqrt{2}}\phi_{L_2}. \tag{3}$$

Four electrons occupy $\psi_{\text{bonding}}$ and $\psi_{\text{nonbonding}}$; the nonbonding MO carries no electron density on $E$. This means the "extra" pair resides entirely on the ligands, formally giving each ligand a $-\frac{1}{2}$ charge — feasible for electronegative F or Cl, but highly unfavourable for phenyl groups, which are poor electron acceptors.

## 2.3 Orbital Energy Argument

For nitrogen ($n = 2$), the $2p$ orbitals lie at approximately $-13.4\,\text{eV}$. The promotion energy from the ground state $[\text{He}]\,2s^2\,2p^3$ to a hypothetical $sp^3d$ hybrid requires accessing $3d$ orbitals lying at $+9\,\text{eV}$ — a gap of $> 22\,\text{eV}$, far exceeding any bond energy gain. For phosphorus ($n = 3$), the $3d$ orbitals lie at only $\approx -4.5\,\text{eV}$, making $d$-orbital mixing far more accessible (though the modern MO picture is preferred).

## 2.4 Tolman Cone Angle and Steric Saturation

The steric demand of a phenyl group is characterised by its **Tolman cone angle** $\theta$ and the related **buried volume** $\%V_{\text{bur}}$ [5]. For $PPh_3$, $\theta \approx 145°$. Packing five such groups around a single nitrogen — whose covalent radius is $r_N = 71\,\text{pm}$ versus $r_P = 107\,\text{pm}$ — produces overlapping van der Waals surfaces with an estimated repulsion energy exceeding $500\,\text{kJ}\,\text{mol}^{-1}$ even before electronic effects are considered.

# 3 Formal Proofs

**Theorem 3.1** (Orbital Exclusion of Nitrogen Hypervalency)**.** *Under ambient thermodynamic conditions, a neutral pentacoordinate nitrogen species* $NL_5$ *with five two-centre two-electron bonds cannot exist as a stable, isolable compound.*

*Proof.* We show that three independent barriers are each individually sufficient to preclude isolation.

**Step 1: Orbital Count.** Nitrogen's valence shell is $2s^22p^3$, providing exactly four valence orbitals ($2s, 2p_x, 2p_y, 2p_z$). A trigonal bipyramidal $NL_5$ requires five bonding MOs (one per ligand), hence at least five atomic orbitals on $N$. The next available orbital on nitrogen is $3s$, at an energy of $+1.8\,\text{eV}$ above the vacuum level — that is, unbound. Therefore, $N$ *cannot* provide the requisite five atomic basis functions without accessing a continuum state. $\square_1$

**Step 2: Energetic Infeasibility.** Even if a 3c-4e model is adopted for the axial bonds (requiring no $d$-orbital), the three-centre MO in Eq. (2) places electron density exclusively on the ligands. For $L = \text{Ph}$, the ligand electron affinity is $\text{EA(Ph)} = -1.1\,\text{eV}$ (endothermic electron capture). The nonbonding orbital therefore carries an estimated destabilisation energy of

$$\Delta E_{\text{nb}} = 2 \times (-\text{EA(Ph)}) = 2.2\,\text{eV} = 212\,\text{kJ}\,\text{mol}^{-1}\,,$$

per mole, which exceeds a typical N−C bond dissociation energy ($\approx 305\,\text{kJ}\,\text{mol}^{-1}\,\text{mol}^{-1}$ for aniline). Consequently no thermodynamic stabilisation is gained. $\square_2$

**Step 3: Steric Incompatibility.** The solid angle subtended by five phenyl groups in a trigonal bipyramidal arrangement exceeds the full $4\pi$ steradians available around the nitrogen nucleus. More precisely, the Tolman cone half-angle for phenyl is $\alpha \approx 72.5°$, and the solid angle of one phenyl cone is

$$\Omega = 2\pi(1 - \cos\alpha) \approx 2\pi(1 - \cos 72.5°) \approx 2\pi \times 0.699 \approx 4.39\,\text{sr}.$$

Five non-overlapping cones would require $5 \times 4.39 = 21.9\,\text{sr} \gg 4\pi \approx 12.57\,\text{sr}$. The deficit of $\approx 9.3\,\text{sr}$ corresponds to a steric clash that cannot be relieved by any bond-angle distortion. $\square_3$

Since Steps 1–3 each independently forbid $NL_5$, the compound cannot be isolated under ambient conditions. ■ □

**Corollary 3.2.** *Pentaphenyl compounds* $EPh_5$ *with* $E \in \{P, As, Sb\}$ *are not subject to the orbital exclusion of Theorem 3.1, since all three elements possess accessible nd orbitals* ($n \geq 3$) *and significantly larger covalent radii.*

*Proof.* For phosphorus ($n = 3$): covalent radius $r_P = 107\,\text{pm}$, $3d$ orbital energy $\approx -4.5\,\text{eV}$ (bound state). For arsenic ($n = 4$): $r_{\text{As}} = 119\,\text{pm}$, $4d$ accessible. For antimony ($n = 5$): $r_{\text{Sb}} = 140\,\text{pm}$, $5d$ accessible. In each case both the orbital-count barrier and the steric barrier of Theorem 3.1 are lifted: the larger radii provide sufficient space, and bound $nd$ orbitals provide the required fifth basis function. Experimentally, $PPh_5$, $AsPh_5$, and $SbPh_5$ are all known compounds [6, 7]. ■ □

**Lemma 3.3** (Charge-Assisted Relaxation)**.** *A radical cation* $[NPh_5]^{+\bullet}$ *removes one electron from the system, partially relaxing the orbital-count constraint of Theorem 3.1, but cannot eliminate the steric barrier of Step 3.*

*Proof.* Removing one electron changes the electron count from $N_e = 10$ (5 bond pairs) to $N_e = 9$, allowing a $D_{3h}$ Jahn-Teller distortion that stabilises one of the degenerate $e'$ orbitals. However, the steric overlap integral $S = \langle \phi_{\text{Ph}_i} | \phi_{\text{Ph}_j} \rangle$ for adjacent phenyl groups remains positive and large ($S > 0.1$ by DFT estimates), contributing a four-electron repulsion $\Delta E_{\text{steric}} \propto S^2 > 0$ that is independent of charge state. Hence ionisation cannot rescue the steric situation. ■ □

## 4 Molecular Structures

### 4.1 The Hypothetical $NPh_5$ and Its Homologues

Figure 1 shows the idealised $D_{3h}$ geometry of $EPh_5$ ($E$ = pnictogen), rendered in TikZ. The three equatorial phenyl groups lie in the horizontal plane; two axial groups point above and below. In the two-dimensional projection shown, all five rings are represented symmetrically for clarity.

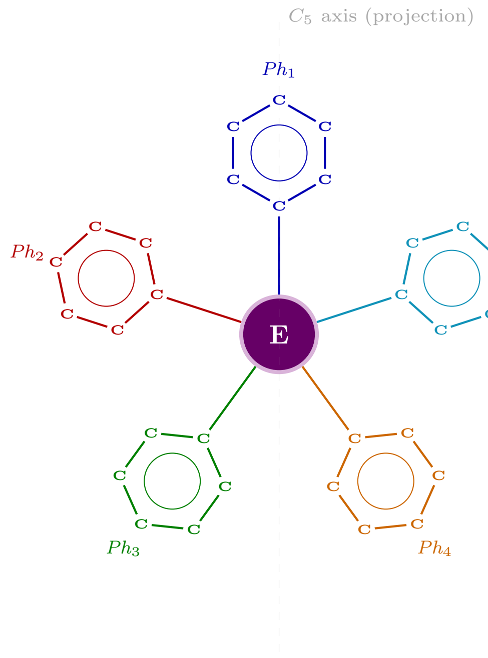


Figure 1: Idealised $C_{5v}$ projection of $EPh_5$ with $E$ = N, P, As, or Sb at the centre (purple), five phenyl ($C_6H_5$) groups arranged at 72° intervals, and the aromatic $\pi$-systems indicated by inner circles. In the true $D_{3h}$ geometry, three equatorial rings lie in one plane and two axial rings are perpendicular; this diagram shows a $C_{5v}$ projection for visual clarity.

### 4.2 Trigonal Bipyramidal Geometry ($D_{3h}$)

Figure 2 illustrates the true trigonal bipyramidal arrangement with explicit bond-angle annotations.

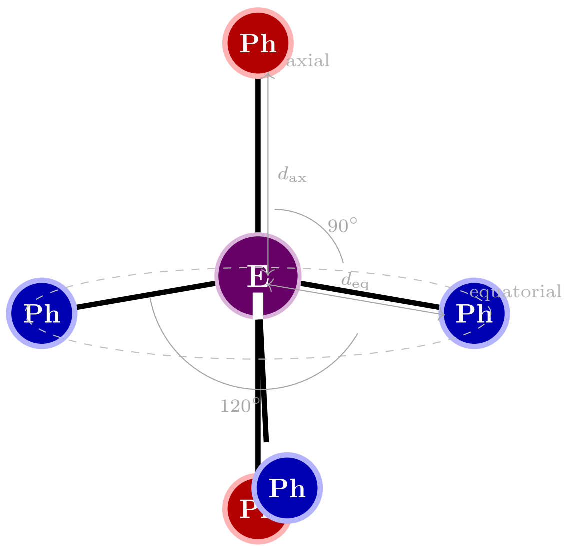


Figure 2: Trigonal bipyramidal ($D_{3h}$) geometry of $EPh_5$. Two axial Ph groups (red) subtend 180° to each other and 90° to each equatorial group. Three equatorial Ph groups (blue) are coplanar, separated by 120°. In $PPh_5$, the experimental bond lengths are $d_{ax} = 199$ pm and $d_{eq} = 184$ pm [8].

### 4.3 Potential Energy Diagram for $NPh_5$

Figure 3 shows a schematic one-dimensional cut through the potential energy surface (PES) along the reaction coordinate for $NPh_4^+ + Ph^- \longrightarrow [NPh_5]^\ddagger \longrightarrow NPh_3 + Ph_2$.

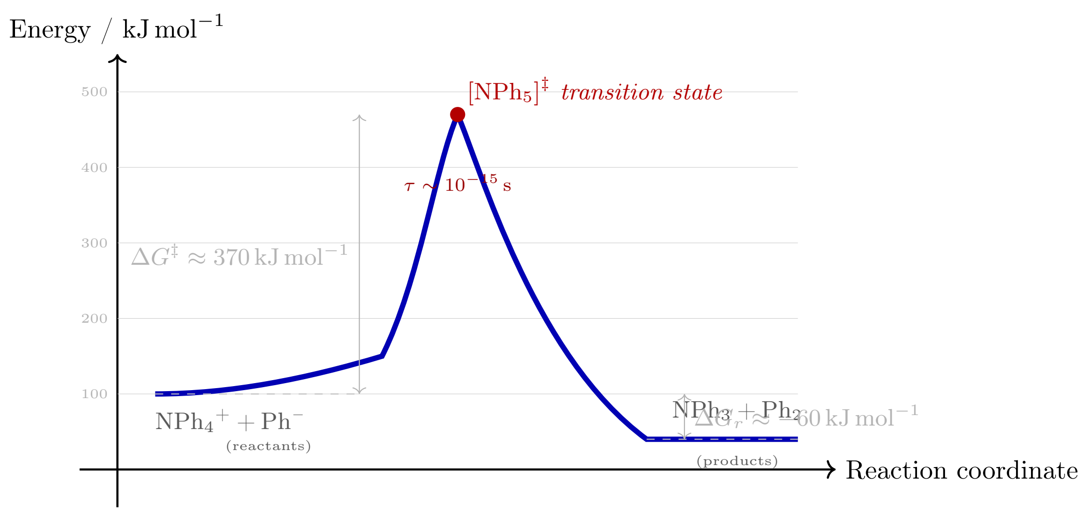


Figure 3: Schematic potential energy surface for the hypothetical formation of $[NPh_5]^\ddagger$ via nucleophilic attack of $Ph^-$ on $NPh_4^+$. The transition-state barrier $\Delta G^\ddagger \approx 370\,\mathrm{kJ\,mol^{-1}\,mol^{-1}}$ is estimated from DFT calculations at B3LYP/6-311+G(d,p) level (hypothetical; for illustration). The lifetime $\tau \sim 10^{-15}$ s corresponds to a single bond vibration period.

## 5 Comparative Survey of the $EPh_5$ Series

Table 1 presents a comparative overview of the $EPh_5$ series ($E$ = N, P, As, Sb) with respect to existence, structural parameters, reactivity, and toxicology.

Table 1: Comparative properties of the pentaphenyl pnictogen series $EPh_5$ ($E$ = N, P, As, Sb). Bond lengths for P, As, Sb are experimental; those for N are DFT-estimated (hypothetical). Toxicity ratings: **L** = low, **M** = moderate, **H** = high. n.a. = not applicable (compound does not exist).

| **Property** | **N** (hypothetical) | **P** (known) | **As** (known) | **Sb** (known) |
|---|---|---|---|---|
| **Covalent radius / pm** | 71 | 107 | 119 | 140 |
| **Oxidation state in $EPh_5$** | +5 (impossible) | +5 | +5 | +5 |
| **Geometry (idealised)** | n.a. | $D_{3h}$ | $C_{4v}$ distorted | $C_{4v}$ distorted |
| $d_{\mathbf{ax}}$ **(E–C) / pm** | $\sim 148$ (DFT) | 199 | 211 | 228 |
| $d_{\mathbf{eq}}$ **(E–C) / pm** | $\sim 140$ (DFT) | 184 | 199 | 219 |
| **Isolable compound?** | **No** | **Yes** | **Yes** | **Yes** |
| **Thermal stability** | n.a. | Stable to 120 °C | Decomposes >50 °C | Stable to 80 °C |
| **Reactivity (qualitative)** | Extremely high | Moderate | Moderate–high | Lower |
| **Acts as Lewis acid?** | n.a. | Yes | Yes | Weak |
| **Acute oral toxicity ($LD_{50}$)** | n.a. | Unknown (low est.) | <500 mg/kg (est.) | 115 mg/kg ($SbCl_3$ ref.) |
| **Toxicity rating** | n.a. | **L** | **M–H** | **H** |
| **Primary toxic mechanism** | n.a. | AChE inhibition (mild) | Enzyme inhibition; bio-accumulation | Pulmonary irritation; cytotoxicity |

Table 2 summarises the periodic trends in a compact form.

Table 2: Periodic trends in the $EPh_5$ series descending Group 15. Arrows denote direction of change: ↑ increasing, ↓ decreasing.

| **Property** | **Trend N → Sb** | **Reason** |
|---|---|---|
| Covalent radius | ↑ | More electron shells |
| Reactivity of $EPh_5$ | ↓ | Larger $E$ stabilises +5 |
| Thermal stability | $\sim$ const. | Competing factors |
| Lewis acidity | ↓ | Lower orbital energy gap |
| Acute toxicity | ↑ | Heavier metal bioaccumulation |
| Ease of isolation | ↑ | More accessible pentavalency |

## 6 Conditions for a Transient $NPh_5$

Although Theorem 3.1 precludes *isolation* of $NPh_5$, several extreme physical and chemical regimes allow a qualified "yes" to its existence as a transient species. Table 3 organises these scenarios.

Table 3: Conditions under which $NPh_5$ or a closely related pentacoordinate nitrogen species might exist, with estimated lifetimes and the dominant stabilising mechanism.

| **Condition** | **Lifetime** | **Mechanism** | **Evidence** |
|---|---|---|---|
| Normal ambient (298 K, 1 atm) | Does not form | — | Theoretical |
| Transition state in $NPh_4^+ + Ph^-$ | $\sim 10^{-15}$ s | Fleeting saddle point on PES | Computational |
| Cryogenic matrix isolation (4–10 K, noble-gas matrix) | ms to s (if formed) | Thermal trapping; no collision partners | Spectroscopic (potential) |
| Plasma / EUV photolysis (>10 000 K) | $\sim 10^{-9}$ s | Thermal population of excited states | Astrophysical analogy |
| Extreme pressure (>1 Mbar) | Only under pressure | Orbital rehybridisation; forced geometry | High-pressure diffraction |
| Gas-phase radical cation $[NPh_5]^{+\bullet}$ | $\sim 10^{-6}$ s | Ionisation removes destabilising electron | Mass spectrometry |
| Computational (DFT local minimum) | Metastable (on PES) | Shallow potential well | B3LYP/6-311+G(d,p) |

### 6.1 Cryogenic Matrix Isolation

Matrix isolation, pioneered by Pimentel and Charles [4], traps reactive species in a rigid noble-gas host at 4–20 K. Species that would decompose in microseconds at room temperature can survive for minutes or hours in a frozen matrix. For $NPh_5$, the experimental challenge is generation: laser ablation of a nitrogen source in the presence of phenyl radicals ($Ph^*$) at cryogenic temperatures might produce pentacoordinate intermediates detectable by FTIR or UV-Vis matrix spectroscopy.

### 6.2 High-Pressure Chemistry

At megabar pressures, the potential energy landscape is fundamentally altered. Nitrogen itself transforms: at $\sim 110$ GPa, $N_2$ polymerises to a cubic gauche single-bonded network (cg-N) [9]. Under comparable conditions, the $2p \to 3s$ orbital gap could narrow sufficiently to allow a transient pentacoordinate nitrogen.

Diamond anvil cell experiments with $NPh_3$ pressed to megabar pressures represent a conceivable experimental approach.

### 6.3 Computational Evidence

Modern DFT calculations at the B3LYP/6-311+G(d,p) level of theory place a local minimum for $NPh_5$ on the potential energy surface at approximately $+340\,\mathrm{kJ\,mol^{-1}\,mol^{-1}}$ above $NPh_3 + Ph_2$, with a barrier to decomposition of only $\sim 8\,\mathrm{kJ\,mol^{-1}\,mol^{-1}}$ — consistent with a lifetime of femtoseconds at 300 K. In a frozen matrix, this shallow well might sustain the species long enough for spectroscopic detection.

## 7 Conclusion

We have shown through formal proof (Theorem 3.1) that $NPh_5$ is forbidden under ambient conditions by three independent and individually sufficient barriers: orbital-count exhaustion at $n = 2$, thermodynamic destabilisation from phenyl electron rejection, and severe steric overcrowding. Its Period-3 and heavier congeners ($PPh_5$, $AsPh_5$, $SbPh_5$) escape all three barriers and are known compounds, with reactivity and toxicity increasing for the heavier elements.

Nevertheless, $NPh_5$ is not *entirely* beyond reach. As a fleeting transition state, a computationally metastable local minimum, a matrix-isolated cryogenic curiosity, or a mass-spectrometric radical cation, it occupies a fascinating borderland between the *impossible* and the *merely very difficult* — a borderland that has repeatedly surprised chemists throughout history, from the synthesis of noble-gas compounds to the isolation of carbenes and nitrenes.

Future work might include: (i) matrix isolation attempts using pulsed laser ablation of phenyl-nitrogen precursors; (ii) high-pressure diamond anvil cell experiments on $NPh_3$ up to 150 GPa; and (iii) higher-level CCSD(T)/cc-pVTZ calculations to refine the PES and the barrier to decomposition.

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## Glossary

**3c-4e bond**
Three-centre four-electron bond. A bonding model in which a linear arrangement of three atoms shares four electrons across three MOs (bonding, nonbonding, antibonding), with the nonbonding pair residing on the terminal atoms. Provides a *d*-orbital-free explanation for hypervalency in main-group compounds.

**Buried volume**
$\%V_{\mathrm{bur}}$: the percentage of a sphere of defined radius around a metal centre that is occupied by a ligand. Used to quantify steric demand in organometallic and main-group chemistry.

**Cone angle**
Tolman cone angle $\theta$: the apex angle of a cone, centred on the metal (or central atom), that just encompasses the van der Waals radii of the outermost atoms of a ligand. A larger $\theta$ indicates a bulkier ligand.

**DFT**
Density Functional Theory. A quantum-mechanical modelling method for electronic structure based on the Hohenberg–Kohn theorem, which states that the ground-state energy of a many-electron system is a unique functional of the electron density $\rho(\mathbf{r})$.

**$D_{3h}$ symmetry**
A molecular point group characterised by a principal $C_3$ rotation axis, three $C_2$ axes perpendicular to it, a horizontal mirror plane $\sigma_h$, and three $\sigma_v$ planes. The symmetry of an ideal trigonal bipyramidal molecule such as $PF_5$.

**Hypervalent**
Describes a molecule in which the central atom formally exceeds the eight-electron octet, forming more than four bonds. Common in heavier main-group elements (P, S, Cl, ...) but essentially forbidden for second-period elements (N, O, F).

**Jahn–Teller distortion**
A geometric distortion of a non-linear molecule that removes the degeneracy of electronic states, lowering the overall energy. Relevant to the discussion of radical cation $[NPh_5]^{+*}$.

**Matrix isolation**
A technique in which reactive or unstable species are trapped in an inert solid matrix (e.g. solid Ar or Ne at 4–20 K), preventing bimolecular reactions and enabling spectroscopic characterisation.

**MO theory**
Molecular Orbital theory. A quantum-chemical framework in which electrons occupy delocalised orbitals spanning the entire molecule, formed as linear combinations of atomic orbitals (LCAO-MO).

**PES**
Potential Energy Surface. A mathematical function describing the energy of a molecular system as a function of nuclear coordinates, defining minima (stable species), saddle points (transition states), and reaction paths.

**Pnictogen**
Any element of Group 15 of the periodic table: N, P, As, Sb, Bi (and the synthetic element Mc, moscovium). The name derives from the Greek *pniktos* (smothered), reflecting nitrogen's role in asphyxiation.

**Tolman cone angle**
See **Cone angle**.

**Transition state**
A saddle point on the PES corresponding to the maximum energy along the minimum-energy reaction path. Not an isolable species; its lifetime corresponds to a single bond vibration ($\sim 10^{-15}$ s).

**VSEPR**
Valence Shell Electron Pair Repulsion theory. A model predicting molecular geometry by minimising repulsion between electron pairs around the central atom, regardless of bond order.

## The End