Life and death with nitrogen

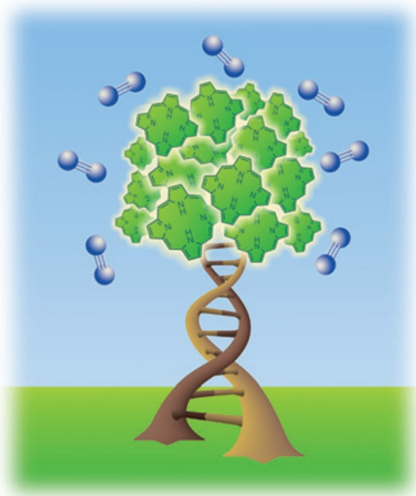
Although first known among chemists for its noxious or lifeless character, nitrogen was later revealed to be involved in many life, and death, processes. **Michael Tarselli** ponders on this unforeseen characteristic.

Noticing that nitrogen gas (N_2) supported neither combustion nor life, many scientific luminaries of the eighteenth century — Scheele, Priestley, Lavoisier... — referred to nitrogen as 'noxious air', or even 'lifeless'. Yet element 7 has boasted an unparalleled career in the ensuing 300 years, participating in organic catalysis, bombs, power generation, food contamination, and the elucidation of DNA's structure.

Nitrogen heads up Group 15, the appropriately named pnictides (from the Greek *pnigein*, 'to choke'), which includes other life-and-death players: arsenic, a poison also found in drugs, and phosphorus, toxic yet present in the backbone of DNA. These elements have three unpaired electrons in their *p* valence shell, and may also bond through their *s* electrons, so they ideally want 3 to 5 bonds. In its elemental state, nitrogen forms the diatomic gas N_2 that makes up more than 70% of the air we breathe.

Nitrogen's penchant for forming three covalent bonds while keeping a lone pair 'open for business' leads to numerous catalytic and biochemical applications. Much of the burgeoning field of organocatalysis[1] relies on small species derived from two nitrogenous precursors: proline, an amino acid, and urea, the first organic molecule prepared synthetically (Friedrich Wöhler, 1828). In nature, porphyrins — polypyrrole macrocycles present in haem enzymes and chlorophyll — host transition metals to perform basic life functions: photosynthesis, oxygen transport and destruction of toxins in the blood. Several heavy metals (molybdenum, vanadium, iron), allow soil bacteria in the roots of legumes to fix N_2 into usable plant metabolites.

Life is intricately linked to nitrogen, found in every DNA nucleobase. Isotopic labelling with heavy isotope ^{15}N allowed Meselson and Stahl to verify that a single strand of DNA could template its own replication. Chemists interested in tinkering with life's codes have designed 'extended' nucleobases[2], which can replicate and pair up much like normal DNA.



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Newborn babies owe a lot to another nitrogenated compound, folic acid (vitamin B_9), critical to proper foetal development during pregnancy. Melamine ($C_3H_6N_6$), however, recently made darker headlines. In food, nitrogen normally comes from proteins, and nitrogen analysis thus serves to measure protein content. Used to dope infant formula and pet food to artificially inflate their apparent protein content, melamine made both people and pets ill.

Nitrogen plays a pivotal role in the development of renewable energies. Nocera's 'hangman' assemblies[3], which generate oxygen and hydrogen gas from water splitting to power fuel cells, feature an octafluoro–corrole backbone, which binds cobalt through coordination to four nitrogen atoms. One possible way to safely transport hydrogen fuel is through ammonia borane ($H_2N–BH_3$) complexes. New solar cells[4] also rely on dyes containing metal–nitrogen bonds to catch ambient light, making for flexible, highly efficient, cost-effective devices.

Entire wars have turned on nitrogen compounds: the Haber–Bosch process (ammonia production by catalytic reaction of N_2 with H_2) was developed around the First World War; before then, explosives were produced from concentrated nitrates found in guano (bird droppings). Nitrogen's penchant for explosion extends to TNT, ammonium nitrate, nitroglycerin and nitrogen triiodide — which decomposes at a feather's touch, making for a thrilling demonstration tool. Despite knowing that compounds with high nitrogen-to-carbon ratios, like azides and tetrazoles, are potentially explosive, chemists cannot resist. Recently, Klapötke and co-workers synthesized a compound with a 10-nitrogen-atom chain, which was barely stable enough to allow analysis and shattered several pieces of lab glassware[5].

The life-or-death duality is observed throughout medical and pharmaceutical history. Nitrogen is often associated with stench and death: we can smell putrescine and cadaverine, two volatile amines emitted from dead tissues, in vanishingly small amounts. Cyanide, a poison known since antiquity, contains a C≡N moiety. Feeling faint? 'Smelling salts' that bring a person back to consciousness often consist of ammonium carbonate. Aniline dyes, originally thought useless waste from coal tars, exhibited potent biological activity, giving rise to the modern pharmaceutical industry[6].

Given its tendency to corrupt, catalyse, nurture, or destroy, nitrogen has proved its lifeless reputation dead wrong. ❐

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