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Polynitrogen compounds
1. Structure and stability of N_4 and N_5 systems

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A contribution to celebrate the 65th birthday of Professor Luc G. Vanquickenborne who spent much time building up quantum chemistry and coordination chemistry in Leuven

Contents

Abstract

This review, presented in three parts, summarizes the results concerning the molecular and electronic structure and the thermodynamic stability of polynitrogen compounds N_n, with n ranging from 4 to 60, as revealed by quantum chemical calculations published in the past 30 years, and where available, by experimental observations. In the present Part 1, attention is paid to the tetranitrogen (N_4) and pentanitrogen (N_5) systems whose existence and stability have been demonstrated by recent experimental studies. The two following parts will be devoted to the properties of larger clusters, N_n with $n \geq 6$. The potential use of the nitrogen clusters as efficient, safe and environment-friendly high energy high-density materials (HEDM) will be discussed. The interactions between these polynitrogen compounds with metals, metal cations and metal complexes, and the factors influencing the ligand stability, will also be examined.

Keywords: Polynitrogen compounds; Tetranitrogen; Pentanitrogen; High energy density materials; Structures; Stability; Ab initio quantum chemical calculations

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1. Prologue

Nitrogen is a dominant chemical element thanks to its massive presence in air (by about 78% in volume) and living organisms as an essential constituent of proteins and nucleic acids (involved in the 'nitrogen cycle' in nature). The name *Nitrogen* came from the Latin term *Nitrum*, and the Greek term *Nitron genes* (meaning 'nitre forming') [1]. In French, the corresponding name, *l'azote*, which was inspired by Lavoisier from its inert nature, effectively means 'sans vie' (the term *zote* also came from the Greek *zôê*, meaning *life*). Both the German '*Stickstoff*' and Dutch '*stikstof*' terms refer to a matter improper for the respiration.

In 1772, two simple but remarkable N-containing compounds were isolated by some great chemists: molecular nitrogen (N_2) and nitrous oxide (N_2O). Ever since, the fate and applications of these two natural and long-lived gases have closely been associated with the tremendous progresses in chemical sciences and well-being of human society. Nitrous oxide was discovered by Priestley upon reduction of NO by Fe or Fe/S mixtures [2] and later known as the 'laughing gas' thanks to its many beneficial applications in, among others, medicine and food industry. Recently, N_2O has however been listed as one of the six strong greenhouse gases in the 'Kyoto Protocol' whose production should be significantly reduced and strictly controlled [3].

In the same year 1772, dinitrogen was first isolated in pure form from air, independently by Rutherford and Scheele and Cavendish [1,4]. More than a century later, Curtius [5] prepared in 1890 for the first time hydrazoic acid and its metallic derivatives containing the stable and isolable azide anion. Coincidently, metal azides could be prepared when passing N_2O into the corresponding molten amide at high temperatures [4] (nowadays, azide anion is generated in high pressure NH_3/N_2O discharge). Thus, for the whole 20th century, only dinitrogen N_2 and azide anion N_3^- were known to be stable homoatomic polynitrogen compounds. The instability of higher members of this family seemingly arises from the peculiarly strong nitrogen–nitrogen triple bond of N_2. Other N_n clusters containing significantly weaker double and single bonds become thermodynamically much less stable and thus tend to decompose into multiple N_2 fragments with very large exothermicity. The inert nature of N_2 could better be illustrated by the Haber–Bosch process, which is a well known industrial procedure for producing ammonia by reaction of N_2 with H_2, and of immense importance for the nitrogen fixation by fertilizers. In this process, even in the presence of catalysts, severe experimental conditions such as high temperature (450 °C) and high pressure (250 atm) are commonly employed [6]. In view of such inert character of N_2, numerous experimental attempts to produce stable N_n compounds involving N_2 and N_3 radical and their ions, were indeed not successful. The N_6^- radical detected in 1995 using the IR laser-flash photolytic technique on a nanosecond time frame turned out to be a weak complex between both azidyl groups [7,8].

In 1999, Christe and coworkers [9] described the surprising synthesis of the pentanitrogen cation N_5^+, which was trapped as a salt with AsF_6^-. The salt containing the novel cation is a white powder, sparingly soluble in anhydrous HF, and only marginally stable at room temperature, but could be stored for weeks at lower temperature (−78 °C) without noticeable decomposition. The N_5^+ ion has proven to be a powerful oxidizer and reacts explosively with water or organic materials. It was told [10] that explosion of a few milligrams of the N_5^+ salt actually destroyed a sample chamber!

Subsequently, the same group [11] reported that the (N_5^+ SbF_6^-) and (N_5^+ $Sb_2F_{11}^-$) salts are stable up to 70 °C. Thus, the N_5^+ cation became the third stable member of the polynitrogen family. Its high stability strikes the imagination of chemists, stimulates their chemical creativity and raises high hope for the possibility of building large (neutral and ionic) allotropes of nitrogen. It was recently reported that the neutral tetranitrogen was generated the from the N_4^+ cation and detected by neutralisation-reionization mass spectrometry [12]. More recently, the long-sound pentazole anion N_5^- was finally identified in the gas phase, also by mass spectrometry [13], and its existence was evaluated to be much longer with a half-time of $t_{1/2} = 2.2$ days in methanol solution at 0 °C [14]. A phenomenon of history acceleration seems to actually occur in this area!

In this context, it is understandable that pertinent and successful experimental studies are far outnumbered by theoretical investigations making use of quantum chemical methods. We now attempt to summarize the results obtained on N_n compounds using both experimental and theoretical approaches published in the past 30 years or so. Concerning the theoretical results, we do not provide in what follows, details of computational methods, as these can be found in numerous textbooks and/or reviews. In addition, Bartlett and coworkers [15] have recently prepared a useful theoretical compilation on polynitrogen compounds which contains, for each N_n system with n ranging from 4 to 10, the optimised geometries, vibrational frequencies, heats of formation, as well as vertical excitation and ionisation energies of several energetically lower-lying isomers. The properties were computed using various quantum chemical methods. It is not our intent to reproduce here these efforts with a comprehensive review on all the isomeric structures, but rather to focus principally on the most stable and/or most interesting forms, in considering their possible ways of formation, molecular structures and electronic properties. We do not compare the numerous and scattered values obtained by different theoretical methods for a certain property, but rather select the most reliable value to date for the discussion. In doing so, we hope to provide the readers with a more focused vision on this novel and intriguing class of compounds.

2. Some basic properties of lower homologues

Atomic nitrogen has the valence orbital configuration $(2s)^2(2p)^3$ and thereby a quartet ground electronic state (^4S). Although the reactivity of atomic nitrogen is of fundamental importance in combustion and atmospheric chemistry, most of its reactions occur in its lowest-lying doublet states rather than in its ground state, which is not very reactive. The electronic transitions $^2D \leftarrow {}^4S$ and $^2P \leftarrow {}^2D$ of atomic nitrogen were experimentally determined at 19 142 (2.38 eV) and 9586 cm^{-1} (1.19 eV), respectively [16]. The nitrogen atom possesses large ionisation energies, with the first value $IE_1(N) = 14.54$ eV arising from removal of 2p-electrons and the second $IE_2(N) = 29.60$ eV coming from ejection of 2s-electrons. In contrast, the atom has a small but negative electron affinity $EA(N) = -0.07$ eV [17,18]. The nitrogen cation exhibits a triplet ground state (^3P) followed by a singlet excited state (^1D). The energy gap $^1D \leftarrow {}^3P$ in N^+ amounts to 1.89 eV [18b].

Combination of the six unpaired 2p-electrons in two nitrogen atoms leads to formation of an extremely strong triple bond in the ground state $^1\Sigma_g^+$ of N_2, which is characterized by a short bond length of 1.10 Å, a high stretching frequency of 2359 cm^{-1} and a large bond dissociation energy of $D_o(N_2) = 945$ kJ mol^{-1} (Eq. (1)). Such bond energy is by far larger than that of three corresponding single N–N bonds (being $3 \times 158 = 474$ kJ mol^{-1}) or a single N–N bond plus a double N=N bond (being $158 + 418 = 576$ kJ mol^{-1}) or 1.5 times a double N=N bond (being $1.5 \times 418 = 627$ kJ mol^{-1}) [17,19].

The ground state orbital configuration of molecular nitrogen was determined experimentally to be $(1\sigma_g)^2(1\sigma_u)^2(1\pi_u)^4(2\sigma_g)^2$, which is consistent with its observed diamagnetism. The N_2 molecule is characterized by high excitation energies, with the lowest (singlet) electronic transition $1\pi_g \leftarrow 2\sigma_g$ occurred at around 8.6 eV. However, the triplet $A^3\Sigma_u^+$ state is actually the lowest excited state of N_2 being 6.22 eV above the ground state. Following quenching of triplet N_2 by atomic nitrogen (^4S), electronically excited N atoms (^2D, ^2P) could be generated. The ionisation energies of N_2 are even larger than those of atomic nitrogen, with the first $IE_1(N_2) = 15.58$ eV [17]. The resulting N_2^+ radical cation has a X $^2\Sigma_g^+$ ground state followed by the excited states A $^2\prod$\2Plu$_u$ (IE_2 at around 17.1 eV) and $B^2\Sigma_u^+$ (IE_3 at around 18.7 eV). Following ionisation, the nitrogen–nitrogen bond become slightly weaker. In fact, the bond length, vibrational frequency and bond dissociation energy of $N_2^+(^2\Sigma_g^+)$ amount to $r(N–N) = 1.116$ Å, $\nu = 2207$ cm^{-1} and $D_o = 845$ kJ mol^{-1}, respectively [17].

Fig. 1 schematically illustrates the relative energies of the trinitrogen system in different states. The N_3 free radical turns out to have a linear geometry and X $^2\prod_g$ electronic ground state. Combination of the gas phase heats of formation $\Delta H^\circ_{f,298}(N) = 473$ and $\Delta H^\circ_{f,298}(N_3) = 454$ kJ mol^{-1} leads to an atomisation energy of N_3 of 965 kJ mol^{-1} (Eq. (2)), which is only marginally larger, by 20 kJ mol^{-1}, than the N_2 dissociation energy (cf. above). Similarly, an experimental study [20] demonstrated that the azidyl radical N_3 is also unstable with respect to the spin-forbidden dissociation limit (Eq. (3a)). Of the three dissociation limits given in Eqs. (3a), (3b) and (3c), only the process Eq. (3b) is spin-allowed for the N_3 ground state [21]. In other words, the atomic N should first be excited into its ^2D state to be able to form a new chemical bond with N_2. The energy cost for such process is 230 kJ mol^{-1} (2.38 eV). On the one hand, a preliminary excitation $^2D \leftarrow {}^4S$ is necessary to create an empty $2p_z$ orbital on N, which is going to interact with the lone pair 2s orbital of N_2 forming a new bond. On the other hand, interaction of the doubly-occupied $2p_y$ orbital of N with the vacant π* orbital of N_2 making another new bond. Overall, two of the components of the ^2D state of N (with $M = \pm 1$ and ± 2) are appropriate for the formation of N_3, which is in fact stable with respect to this asymptotic limit Eq. (3b).

$$\begin{gathered} N_2(^1\Sigma_g^+) \rightarrow 2N(^4S) \\ D_o = 945 \text{ kJ mol}^{-1} \ (9.79 \text{ eV}) \end{gathered} \tag{1}$$

$$\begin{gathered} N_3(^2\Pi_g) \rightarrow 3N(^4S) \\ D_o = 965 \text{ kJ mol}^{-1} \ (10.00 \text{ eV}) \end{gathered} \tag{2}$$

$$\begin{gathered} N_3(^2\Pi_g) \rightarrow N(^4S) + N_2(^1\Sigma_g^+), \\ D_o = -5 \text{ kJ mol}^{-1} \ (-0.05 \text{ eV}) \end{gathered} \tag{3a}$$

$$\begin{gathered} N_3(^2\Pi_g) \rightarrow N(^2D) + N_2(^1\Sigma_g^+), \\ D_o = 230 \text{ kJ mol}^{-1} \ (2.38 \text{ eV}) \end{gathered} \tag{3b}$$

$$\begin{gathered} N_3(^2\Pi_g) \rightarrow N(^2P) + N_2(^1\Sigma_g^+), \\ D_o = 341 \text{ kJ mol}^{-1} \ (3.53 \text{ eV}) \end{gathered} \tag{3c}$$

$$\begin{gathered} N_3(^2\Sigma_u^+) \rightarrow N(^2P) + N_2(^1\Sigma_g^+), \\ D_o = 436 \text{ kJ mol}^{-1} \ (4.52 \text{ eV}) \end{gathered} \tag{4a}$$

$$\begin{gathered} N_3^-(^1\Sigma_g^+) \rightarrow N^-(^3P) + N_2(^1\Sigma_g^+) \\ D_o = 268 \text{ kJ mol}^{-1} \ (2.78 \text{ eV}) \end{gathered} \tag{4}$$

$$\begin{gathered} N_3^+(^3\Sigma_g^-) \rightarrow N^+(^3P) + N_2(^1\Sigma_g^+) \\ D_o = 336 \text{ kJ mol}^{-1} \ (3.48 \text{ eV}) \end{gathered} \tag{5}$$

$$\begin{gathered} N_3^+(^1\Delta_g) \rightarrow N^+(^1D) + N_2(^1\Sigma_g^+) \\ D_o = 411 \text{ kJ mol}^{-1} \ (4.26 \text{ eV}) \end{gathered} \tag{6}$$

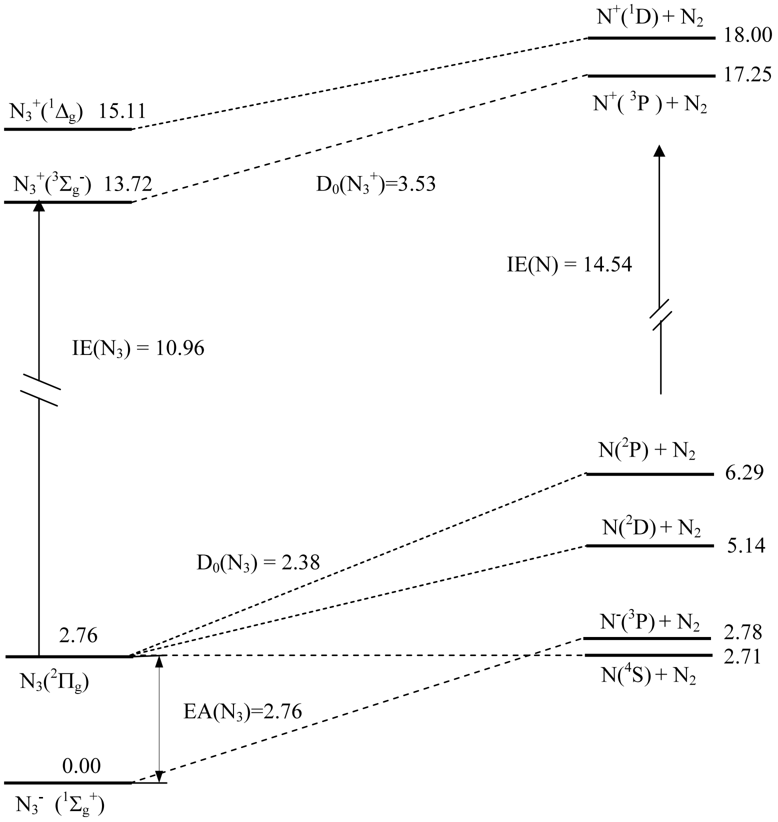


Fig. 1. Schematic representation of relative energies of the trinitrogen system. Values given in eV, were tabulated from experimental results. The scale is arbitrary.

In the linear framework, both N_3 lower-lying excited states $^2\Sigma_u^+$ and $^2\prod_u$ lie 4.52 and 5.02 eV, respectively, above the ground state. On the ground state potential energy surface, the cyclic $^2B_1$ form was calculated to be 125 kJ mol^{-1} less stable than the linear one [22]. The cyclic isomer also dissociates into the $N(^2D) + N_2(^1\Sigma_g^+)$ asymptote via an energy barrier of 138 kJ mol^{-1} and could thus be involved in the formation of tetranitrogen species (this point will be discussed in a following section).

The azidyl N_3 radical possesses a substantial positive electron affinity $EA(N_3) = 2.76$ eV [23] (2.69 eV in Ref. [24]). With a heat of formation of $\Delta H^\circ_{f,298}(N_3^-) = 188 \pm 10$ kJ mol^{-1}, the resulting anion N_3^- is stable with respect to electron detachment. Thanks to the negative electron affinity of atomic nitrogen $EA(N) = -0.07$ eV pointing toward the instability of atomic anion N^- with respect to electron detachment, the azide anion becomes also stable by 268 kJ mol^{-1}, relative to a bond fission Eq. (4). Two UV absorption bands originated from azide anion and centred at 230 and 180 nm were assigned to the $^1\Delta_u \leftarrow ^1\Sigma_g^+$ and $^1\Sigma_u^+ \leftarrow ^1\Sigma_g^+$ excitations, respectively [25]. The triplet cyclic N_3^- was found to be a metastable isomer of ordinary linear singlet and to involve in the formation of isotopically scrambled in N_2 matrix experiment [26].

The vertical ionisation energies of azidyl radical were determined as $IE_1(N_3) = 11.06$, $IE_2(N_3) = 12.19$ and $IE_3(N_3) = 12.86$ eV [27]. The absorption bands in the He(I) photoelectron spectrum of $N_3(^2\prod_g)$ correspond to its ionisation to the $^3\Sigma_g^-$, $^1\Delta_g$ and $^1\Sigma_g^+$ electronic states of the cation generated, respectively. Otherwise put, in its triplet ground state, the N_3^+ cation is characterized by a centro-symmetric linear form and a heat of formation of $\Delta H^\circ_{f,298}(N_3^+) = 1521 \pm 10$ kJ mol^{-1}. Combination of this value and that of $N^+(^3P)$ allows a dissociation energy $D_o(N_3^+) = 336 \pm 10$ kJ mol^{-1} to be evaluated Eq. (6). A lower limit for the latter quantity was established at 328 ± 20 kJ mol^{-1} (3.4 ± 0.2 eV) using electron impact mass spectrometry [28]. In its singlet electronic state, a cyclic N_3^+ isomer (C_{2v}), the triazirinyl cation, which has two π electrons and is thus an aromatic species, turns out to be about 110 kJ mol^{-1} above the linear triplet form [29].

Starting from the N_3 radical, addition or removal of a non-bonding electron does not significantly affect the N–N bond lengths, namely 1.181 Å in N_3, 1.185 Å in N_3^+ and 1.188 Å in N_3^- (values in their ground states). On the contrary, the electron contributes significantly to the force constants of the three species inducing appreciable changes in the vibrational motions. Indeed, the fundamental frequencies ν_1 (symmetric stretch), ν_2 (bending) and ν_3 (asymmetric stretch) range from 1287, 473 and 1658 $\mathrm{cm^{-1}}$ in N_3 radical, respectively, to 1344, 642 and 2004 $\mathrm{cm^{-1}}$ in N_3^- anion, and finally to 1170, 426 and 929 $\mathrm{cm^{-1}}$ in N_3^+ cation [26,30,31]. In the cation, the asymmetric stretch wavenumber becomes even smaller than the symmetric stretch and is subjected to strong anharmonic resonances.

Due to the fact that first ionisation energy of N_2 (15.58 eV) is larger than that of N (14.53 eV), the asymptotic energy fragments of $N_3^+(^3\Sigma_g^-)$ are $N^+(^3P)+N_2(^1\Sigma_g^+)$ as seen in 5 rather than $N(^4D)+N_2^+(^2\Sigma_g^+)$. Proceeding in the direction of trinitrogen formation, similar to the case of $N(^2D)$, the $2p_z$ orbital in $N^+(^3P)$ is effectively empty and thus allows a stabilising interaction with the N_2 lone pair 2s-orbital yielding a new chemical bond in N_3^+ [32].

In the radiolysis of nitrogen, N_3^+, along with N_4^+, were found to be the major ions generated by ionising radiations. Recombination of these ions with electrons usually occur, and the relevant rate constant of the $N_3^+ + e$ process in atmospheric pressure nitrogen at ambient temperature was determined to be $k_{\mathrm{recomb}} = (3.7 \pm 0.7) \times 10^{-6}\ \mathrm{cm^{-3}\ s^{-1}}$. The rates are decreased with the increase of pressure [33].

3. The N_4 system

3.1. Neutral singlet: tetranitrogen tetrahedrane

In a cluster of nitrogen, the lowest-energy N_4 entity is a van der Waals complex between two molecular nitrogens $(N_2)_2$. The earlier infrared spectroscopic study [34] suggested that the dimer has a T-shaped equilibrium conformation, with a distance of 3.7–4.2 Å separating the centers-of-mass of both monomers. From experimental data, the binding energy was evaluated to be 66 $\mathrm{cm^{-1}}$ (0.8 kJ $\mathrm{mol^{-1}}$). Most ab initio quantum chemical studies were concerned with the construction of accurate intermolecular potentials and thereby the dimer structure and spectroscopic properties [35–41]. Accordingly, the $(N_2)_2$ dimer was confirmed to have a T-shape of C_2 symmetry, with a complexation energy of at most 80 $\mathrm{cm^{-1}}$, a frequency of the stretching van der Waals mode of 22 $\mathrm{cm^{-1}}$ and a maximum internal rotation barrier of 30 $\mathrm{cm^{-1}}$, in fair agreement with experimental results. However, the other linear or rectangular forms also exist with tiny energy differences [41]. It is known that in the Earth's atmosphere, even a relatively small dimerization constant could still be compensated by a high partial pressure of the related monomers. Populations of the various clusters vary considerably with altitude.

Quantum chemical studies on N_4 molecules published in the 1970's and 1980's [42–49] mainly considered the geometry and vibrational frequencies of the tetrahedral form N_4-T_d (Fig. 2), which was believed to be the most stable bound isomer, other than the weak Van der Waals complexes. Subsequent studies in the 1990's were devoted not only to an accurate determination of the geometry, vibrational frequencies and stability of the T_d form with respect to decomposition to two N_2 molecules, but also to other possible isomers in various electronic states [50–76].

Upon successive replacements of CH units in tetrahedrane by N atoms, the corresponding strain energy is actually decreased; the more nitrogen atoms there are, the less strained is the compound [50,51]. The strain energy, estimated by isodesmic reaction energies, in the tetrahedral tetranitrogen was evaluated to be about 234 kJ $\mathrm{mol^{-1}}$ which is less than half of the value of 540 kJ $\mathrm{mol^{-1}}$ found in the isostructural $(CH)_4$ [57]. This is in part due to the inherently smaller ring strain energy of nitrogen three-membered cluster compared with that of hydrocarbons. The presence of electron lone pairs on nitrogens, but not on carbons, also contributes to the differences. The 'aza-stabilization' could in fact be attributed to a delocalisation of the nitrogen lone pair ($n \rightarrow \sigma^*$ interaction), which is actually enhanced in cyclic species. In hydrocarbons, the '*ring strain additivity rule*' [58], which notes that the strain energy of a polycyclic system is ca. equal to the sum of the strain energies of the individual component rings, is well applied. This additivity apparently holds true for nitrogen clusters.

In 1991, wavefunctions including large amounts of electron correlation at the fourth-order perturbation and coupled-cluster theory levels for N_4 became available [52–54], and large-scale CCSD(T) computations showed that N_4-T_d is about 778 kJ $\mathrm{mol^{-1}}$ above two N_2 molecules [53]. A summary of the relative energies of singlet N_4 stationary points is given in Fig. 2. The decomposition pathway and the energy barrier separating both isomeric species were investigated in several papers [52–56]. It is of interest to consider in some detail the corresponding transition structure N_4-TS1. The orbital configurations of the tetrahedral form and the two separated monomers $2N_2$, in D_{2d} symmetry, are depicted as follows:

$$N_4\text{-}T_d\text{: } (1a_1)^2(1b_2)^2(1e)^4(2a_1)^2(2b_2)^2(2e)^4(3a_1)^2(3b_2)^2 \times (3e)^4(4a_1)^2(1b_1)^2$$

$$2N_2\text{: } (1a_1)^2(1b_2)^2(1e)^4(2a_1)^2(2b_2)^2(2e)^4(3a_1)^2(3b_2)^2(3e)^4 \times (4a_1)^2(1b_2)^2$$

Both stationary points differ from each other by the last pair of electrons (b_1 and b_2) meaning that the N_4 configuration corresponds to a doubly-excited configuration of $2N_2$, or vice-versa. As a consequence, N_4-TS1 arises from an avoided crossing of two distinct electronic states; each being dominated by one of these orbital configurations in different regions of the potential energy surface. In the transition structure region, a mixture of both states is expected. According to the

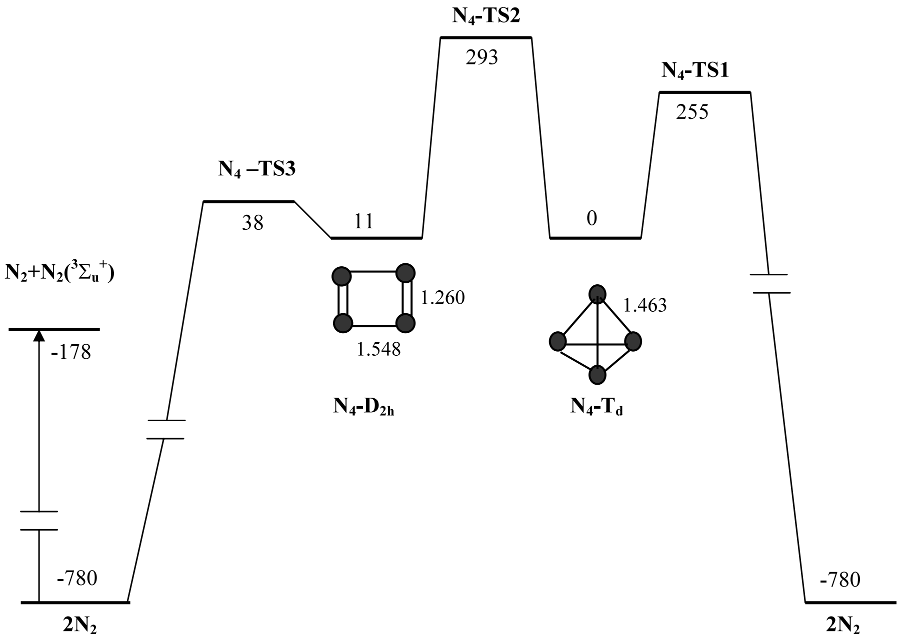


Fig. 2. Schematic representation of relative energies of some singlet N_4 stationary points. Values given in kJ mol^{-1}, were tabulated from G2 calculations. The scale is arbitrary.

Woodward–Hoffmann rules, the cycloaddition path is formally forbidden by orbital symmetry. It was argued that [43,52] the TS should adopt a D_{2d} symmetry. Subsequent computations [53–55] using multi-configurational wavefunctions either with CPF or CASSCF(12,12) methods, demonstrated however that N$_4$-TS1 features a lower C_s symmetry in which both reactants and products belong to the $^1A'$ representation but still have different orbital occupancy (by a double excitation), namely:

N_4-T_d: $\ldots(10a')^2(4a'')^2(11a')^0$

and

N_4-TS1: $\ldots(11a')^2(3a'')^2(4a'')^0$

In other words, a lowering of the transition structure symmetry does not make the reaction path a symmetry allowed reaction. Recent CASSCF(12,12) computations with full vibrational characterisation showed that N$_4$-TS1 is slightly distorted from C_s and thus does not bear any symmetry [76]. The barrier height for the N$_4$-T_d decomposition via N$_4$-TS1 was computed to be internally consistent varying from 255 [53,63] to 263 kJ mol^{-1} [55].

The tetrahedral N$_4$-T_d exhibits high-lying singlet excited states. Its first vertical excited state ($^1T_1$) is about 9.35 eV [68] above the ground state. Five lowest-lying states are of valence character whereas the remaining ones are of Rydberg character. There are two optically accessible singlet states of T_2-symmetry being at about 10.4 and 10.8 eV, but they are associated with relatively weak transitions [70]. The transition to the third T_2 state at 10.9 eV has larger oscillator strength.

Before examining the triplet species, it is important to have a look at other singlet N_4 isomeric forms [40,54,57,59,60] in which the planar rectangular tetra-aza-cyclobutadiene (tetrazete) N$_4$-D_{2h} deserves a special attention (Fig. 2). This has alternate single and double bonds rather than a system with four equivalent aromatic N–N bonds (D_{4h}), which is characterized as a second-order saddle point [40]. Unlike the all-carbon analogues where cyclobutadiene is more stable by 109 kJ mol^{-1} than tetrahedrane, the tetrazete N$_4$-D_{2h} was found to be 11 kJ mol^{-1} higher in energy than N$_4$-T_d (G2 value [62]) even though the anti-aromatic character is rather similar in both C and N systems. The lone pairs repulsion is the likely reason for a destabilised rectangular form.

Again, the interconversion between both T_d and D_{2h} isomers is prohibited by symmetry due to the fact the ground state electronic configurations of both isomers (within a D_2 pathway) differ from each other by an exchange in the occupation of the boundary orbitals, $\ldots(5a)^2(4b_2)^0$ in N$_4$-T_d and $\ldots(4b_2)^2(5a)^0$ in N$_4$-D_{2h}. The crossing point for the two configurations resulting in the transition structure N$_4$-TS2 (C_{2v}) is about 293 kJ mol^{-1} above the T_d form (Fig. 2) [63].

Similar to tetrahedrane, the minimum energy D_{2h} pathway for fragmentation of the rectangular is symmetry-forbidden [64]. Both ground state orbital configurations are similar except for a change of occupancy of the higher-lying orbitals $3b_{2u}$ (doubly occupied in N$_4$-D_{2h}) and $4b_{1u}$ (doubly occupied in 2N$_2$). In other words, the one configuration is formed by a double excitation of the other. Due to the high exothermicity, the cycloreversion of N_4-D_{2h} is however a relatively easy process. The most elaborated quantum chemical computations to date (using a multi-reference coupled-cluster method MR-AQCC, based on the geometry optimized at CASSCF(12,12)) pointed out that the decomposition pathway passes through the transition structure N_4-TS3 (C_{2v}) and is associated with a small but significant effective energy barrier of 27 kJ mol^{-1} [65] (Fig. 2). Owing to the fact that in the ground state ^1A_g of the rectangular form, the most populated rotational level at room temperature is being only a few kJ mol^{-1} above the ground vibrational level, N_4-D_{2h} may be 'observable' at low temperatures, in spite of its short-lived life. The lowest excited state of tetrazete is identified as a $^1B_{3u}$ state, which is characterized by excitation energy of about 1.5 eV and a geometry similar to that of the ground state. On this basis, of low excitation energy and large Frank–Condon factor, it was suggested that this excited state could be useful for detection of the rectangular form by means of laser-induced fluorescence (LIF) spectroscopy [66].

It appears that in its singlet electronic state, a N_4 molecule could best be searched in its tetrahedral geometry N_4-T_d. Accurate predictions of its IR and Raman spectra have abundantly been available and analysed [69–71]. The fundamental harmonic vibrational frequencies are predicted as 1296 (A_1), 936 (T_2) and 724 cm^{-1} (E).

Protonation of N_4-T_d results in a vertex protonated equilibrium structure whereas the bond protonated form corresponds to a saddle point between two vertex forms [75] (cf. Chart 2). The proton affinity was found to be rather low, PA(N_4, T_d) = 590 ± 15 kJ mol^{-1}.

3.2. Neutral triplet: azido-nitrene

As seen in Fig. 2, the triplet asymptote $N_2(^1\Sigma_g^+) + N_2(^3\Sigma_u^-)$ actually lies about 178 kJ mol^{-1} below N_4-T_d. In addition, the latter has a low-lying triplet state being only about 50 kJ mol^{-1} [53] above its singlet ground state. As a consequence, both energy surfaces are expected to cross each other at different places. The mechanism of such singlet–triplet intersystem crossing was examined [56] providing some insights into the feasibility of radiationless decay of a bound electronic state. Accordingly, for N_4-T_d, the spin-forbidden decay channel (resulting from crossing between two states of different spin multiplicity) has a reduced barrier of about 118 kJ mol^{-1}, which is ca. half of the barrier for the spin-allowed decay channel of 255 kJ mol^{-1} mentioned above. Thus, when starting from the tetrahedral N_4-T_d, a spin–orbit coupling might lead the singlet tetranitrogen supersystem to its triplet electronic state. Although the lowest-lying vibrational levels of this system are not pre-dissociated significantly by the resulting radiationless decay mechanism, it tends to reduce substantially the energy barrier and thereby, the lifetime of N_4-T_d.

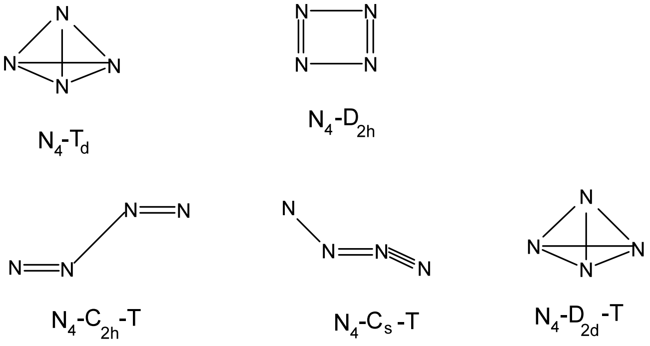


Chart 1.

In 1993, an open-chain structure N_4-C_{2h}, having a ^3B_u triplet state was found to be lower in energy than both singlet tetrahedral N_4-T_d and rectangular N_4-D_{2h} isomers [60] (Chart 1). Energies obtained at the G2 level placed triplet N_4-C_{2h}-T by at least 46 kJ mol^{-1} below N_4-T_d [61,62]. This triplet structure has four π electrons, creating two π bonds between internal and terminal nitrogens. While the central N–N distance is about 1.46 Å, both terminal N=N bonds have a double character. The two unpaired electrons are localized mainly in in-plane 2p-orbitals of both terminal atoms. A characteristic of N_4-C_{2h}-T is that it exhibits a negative vertical singlet–triplet energy gap (the vertical singlet being 170 kJ mol^{-1} lower than the optimal triplet) and could thus be considered as an exciplex having a very short lifetime.

Subsequent studies [62,63] on the triplet potential energy surface demonstrated that the reduced symmetry N_4-C_s-T form, having shorter nitrogen–nitrogen distances and a $^3A''$ state, also exists as an equilibrium structure. Both unpaired electrons are now localized on one terminal nitrogen pointing toward a highly reactive species. The latter form is situated however at higher in energy than the $N_2(^1\Sigma_g^+) + N_2(^3\Sigma_u^-)$ limit, but has a positive singlet–triplet gap of 66 kJ mol^{-1}. A suggestion was made that the triplet N_4-C_s-T 'might be observed experimentally as a long-lived intermediate, under certain conditions' [63].

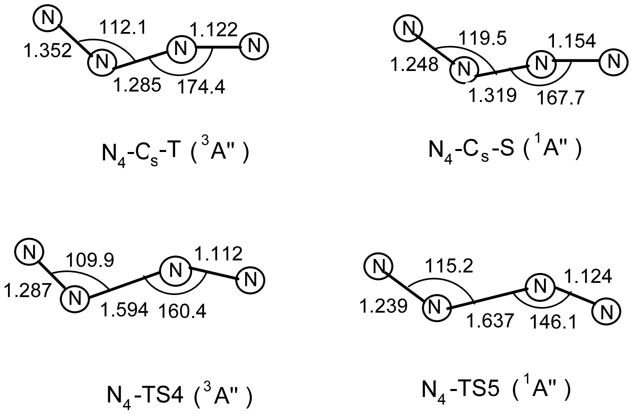
A more recent study [73] using the coupled-cluster method at the CCSD(T)/cc-pvTZ level, confirmed that even though there are several triplet cyclic equilibrium structures, only the two forms N_4-C_{2h}-T and N_4-C_s-T are thermodynamically more stable than N_4-T_d by 88 and 56 kJ mol^{-1}, respectively. Nevertheless, when using multi-configurational wavefunctions at the CASSCF(12,12)/cc-pVTZ level, N_4-C_{2h}-T could no longer be located as a local energy minimum on the triplet potential energy surface; all its geometry optimizations invariably led to dissociation. In contrast, the

N_4-C_s-T is confirmed to be a true energy minimum. Although no transition structures for various fragmentation processes have been located for N_4-C_s-T, it has been stated, on the basis of electronic distribution alone, that N_4-C_s-T should ‘have a very short lifetime under normal conditions’ [73].

Among other triplet equilibrium structures located, the form N_4-D_{2d}-T displayed in Chart 1, having a $^3A_1$ electronic state, was found to be about 84 kJ mol^{-1} above N_4-T_d, but protected by a rather shallow potential well of 31 kJ mol^{-1} against a fragmentation giving $N_2(^1\Sigma_g^+) + N_2(^3\Sigma_u^-)$. Such a stability appeared sufficient to allow an inspiring suggestion to be made that the triplet N_4-D_{2d}-T ($^3A_1$) is ‘the most likely candidate to be observed experimentally’ [73].

In view of an apparent discrepancy in available literature concerning the identity of an ‘observable’ triplet N_4 species, Nguyen and coworkers [76] carried out appropriate quantum chemical computations on the relevant triplet potential energy surface and the results will be discussed in a following section. Here, let us mention that the low symmetry N_4-C_s-T ($^3A''$) isomer effectively features an open-chain skeleton, short bond distances and slight bending of an azide moiety, $-N{=}N{\equiv}N$ (Fig. 3). Analysis of the spin density indicates that all the excess spin is indeed concentrated on its terminal fourth atom; this fact confers to the isomer a nitrene character. It is obvious that formal replacement of H in the parent HN nitrene by an azido group (N_3) leads to N_4-C_s-T. In other words, N_4-C_s-T is nothing else than *azido-nitrene.* Its dissociation giving a nitrogen atom is endothermic Eq. (7) by simple bond fission without energy barrier.

$$N_4\text{-}C_s(^3A'') \rightarrow N_3(^2\Sigma_u^+) + N(^4S) \quad D_o = 203 \text{ kJ mol}^{-1} \ (2.10 \text{ eV}) \tag{7}$$



N_4-C_s-T ($^3A''$) N_4-C_s-S ($^1A''$)

N_4-TS4 ($^3A''$) N_4-TS5 ($^1A''$)

Fig. 3. Selected geometrical parameters of some triplet N_4 stationary points. Bond lengths are given in angstrom and bond angles in degrees. Values were obtained from CASSCF(12,12) computations.

$$N_4\text{-}C_s(^3A'') \rightarrow N_2(^1\Sigma_g^+) + N_2(^3\Sigma_u^-) \quad D_o = -95 \text{ kJ mol}^{-1} \ (-0.98 \text{ eV}) \tag{8}$$

$$N_4\text{-}C_s(^1A'') \rightarrow N_2(^1\Sigma_g^+) + N_2(^1\Sigma_u^-) \quad D_o = 51 \text{ kJ mol}^{-1} \ (0.53 \text{ eV}) \tag{9}$$

In contrast, the cleavage of the central bond is exothermic Eq. (8) and characterized by a transition structure N_4-TS4 ($^3A''$) which also bears a trans-bent conformation with a central bond of about 1.6 Å (Fig. 3, values from CASSCF(12,12) calculations). The energy barrier associated with the decomposition process of N_4-C_s-T through N_4-TS4 amounts to about 60 kJ mol^{-1}, evaluated using MR-CISDQ-CASSCF(12,12)/6-311+G(3df) computations [76]. The fact that N_4-C_s-T lies lower in energy than the singlet N_4-T_d and is fairly resistant with respect to N_2 loss makes it the most stable bound N_4 isomer.

Azido-nitrene also exhibits a singlet excited state N_4-C_s-S which has an electronic open-shell $^1A''$ and the same orbital configuration as the triplet N_4-C_s-T state (Fig. 3). The singlet–triplet separation of azido-nitrene, being the energy difference between N_4-C_s-S and N_4-C_s-T amounts to 69 kJ mol^{-1}. Decomposition of this singlet state giving the fragments $N_2(^1\Sigma_g^+) + N_2(^1\Sigma_u^-)$ occurs through the transition structure N_4-TS5 ($^1A''$) with an energy barrier of 55 kJ mol^{-1} and the corresponding reaction Eq. (9) is endothermic by 51 kJ mol^{-1}. This process is of interest in such a way that when operating in the opposite direction, reactive interaction of molecular nitrogen with its lower-lying excited state $N_2(^1\Sigma_u^-)$ is exothermic and could be achieved producing an excited singlet N_4 entity.

In summary, extensive theoretical studies clearly suggested the existence of at least two distinct N_4 entities: the first has a closed-shell singlet electronic state, whereas the second belongs to the triplet manifold. While the singlet tetrahedrane N_4-T_d is compellingly predicted to have a comfortable kinetic stability with respect to dissociation (by a barrier height of at least 118 kJ mol^{-1} including a less-favoured singlet–triplet crossing), the triplet azido-nitrene N_4-C_s-T is thermodynamically more stable, kinetically less stable, but still protected with a sizable energy barrier of about 60 kJ mol^{-1}.

The harmonic vibrational frequencies of azido-nitrene are predicted as 2246 (A′), 1065 (A′), 824 (A′), 614 (A′), 350 (A″) and 169 (A′) cm^{-1} (CASSCF(12,12) values) [76].

The heats of formation of the tetranitrogen species have been evaluated as follows: $\Delta H_f^\circ(N_4,\ T_d) = 770 \pm 15$ KJ mol^{-1}, $\Delta H_f^\circ(N_4,\ D_{2h}) = 781 \pm 15$ kJ mol^{-1}, ΔH_f°(azidonitrene,triplet) $= 714 \pm 15$ kJ mol^{-1}, and ΔH_f°(azidonitrene, singlet) $= 783 \pm 15$ kJ mol^{-1} (values at 0 K) [76].

3.3. $N_4^{+\bullet}$ radical cations

Various nitrogen cations $N_n^{\bullet+}$ have usually been generated following ionization of the nitrogen clusters. Starting from a $(N_2)_2$ dimer, a $N_4^{\bullet+}$ radical cation could be formed upon ionisation using different techniques such as photoelectron spectroscopy, photoionization, electron impact or bombardment, microwave discharge, X-ray irradiation or other mass spectrometric techniques... and then undergo different ion–molecule reactions ([77–91] and references quoted therein). It should be stressed that there have been a large number of experimental studies on the production and reactions of the $N_4^{\bullet+}$ generated in either gas phase or plasmas, but examination of these subjects goes beyond the scope of the present review. Let us note that the low pressure limiting rate constant of the $N_2+N_2^+$ association reaction amounts to $k^\circ=(2.0)\times10^{-29}$ cm^6 s^{-1} (with helium bath gas) and varies slightly when using other bath gases [90]. The recombination rate constant of $N_4^{\bullet+}$ with electron in atmospheric nitrogen pressure was measured to be $(4.6\pm0.9)\times10^{-6}$ cm^3 s^{-1}, at ambient temperature, which is comparable to that of $N_3^+ + e$ [33]. Neutralization of nitrogen cluster cations usually leads to their decay.

The $^{14}N_4^{\bullet+}$ and $^{15}N_4^{\bullet+}$ cations were also generated by the ion-neutral reaction $N_2+N_2^+$ using various isotopes and isolated in solid neon matrix at 4K for ESR spectroscopy study [82]. The ESR parameters are compatible with a linear centro-symmetric radical N_4^+-$D_{\infty h}$ with a $^2\Sigma_{u+}$ ground electronic state (Fig. 4).

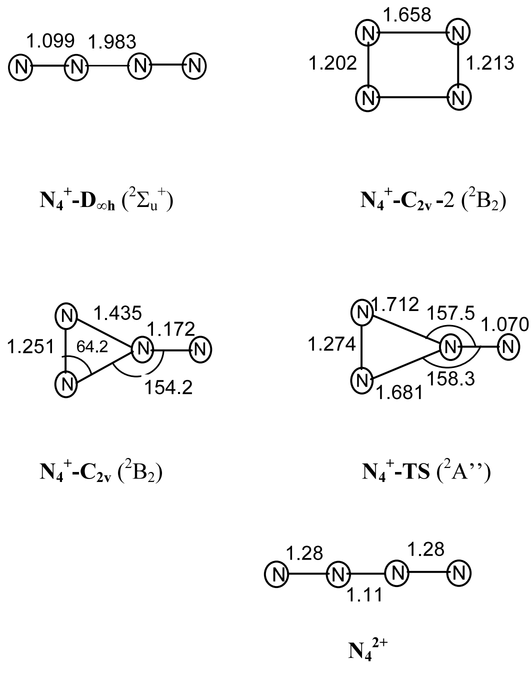


Fig. 4. Selected geometrical parameters of some N_4^+ radical cation stationary points. Bond lengths are given in angstrom and bond angles in degrees. Values were obtained from CASSCF(12,12) computations.

The magnetic parameters derived from ESR spectra are: $g_\parallel=2.0016$ and $g_\perp=1.9998$, $A_\parallel(^{14}N)=311$ MHz and $A_\perp(^{14}N)=264$ MHz for the two central atoms and $A_\parallel(^{14}N)=10.4$ MHz and $A_\perp(^{14}N)=20.4$ MHz for the two outer nitrogens.

The isotropic and dipolar components of the nuclear hyperfine A tensor can be obtained from the measured parameters: $A_{iso}=(A_\parallel+2A_\perp)/3$ and $A_{dipolar}=(A_\parallel-A_\perp)/3$. The values of $A_{iso}=-10.1$ MHz and $A_{dipolar}=10.3$ MHz were derived for the two outer atoms and $A_{iso}=280$ MHz and $A_{dipolar}=15.7$ MHz for the two inner N atoms.

This assignment is consistent with earlier extensive Hartree–Fock computations [92] that pointed out a linear structure to be the most stable cation. The positive charge is indeed delocalized over both subunits, but at large separations, the charge location is actually $N_2+N_2^+$, and the resulting bonding is dominated by charge-quadrupole interaction. The unpaired electron resides mainly on the inner N atoms with significant 2s and $2p_\sigma$ character and associated with the largest A values [82]. Intensive MO calculations of hyperfine splitting constants [82,93] provided further support for the experimentally-derived ESR parameters of the tetranitrogen radical cation.

Vibrational spectra of $^{14}N_4^{\bullet+}$ and $^{15}N_4^{\bullet+}$ cations were also recorded in neon matrix [84]. A weak to moderately intense IR absorption at 2238 cm^{-1} was assigned to $^{14}N_4^{\bullet+}$ cation. This frequency is intermediate between the ground state fundamental of N_2^+, 2175 cm^{-1}, and that of N_2, 2330 cm^{-1}. Normal mode analysis of IR absorption pattern of isotopically substituted $N_4^{\bullet+}$ also support a centro-symmetric linear ground state. Both symmetric vibrations of σ_g^+ symmetry (ν_1 and ν_2) are IR-inactive, but could be derived to be 2283 and 430 cm^{-1}, respectively, from isotopomers. The antisymmetric ν_3 vibration of σ_u^+ symmetry is active and corresponds to the 2238 cm^{-1} band. High level MO computations [94–96] suggested the following values for the lower frequency stretching, $\nu_4=91$ and $\nu_5=133$ cm^{-1} [95]. The bending frequencies were not accurately measured, but combined experimental [87–89] and theoretical [94,95] results suggested that these modes have frequencies near 100 and 200 cm^{-1}. It appears that all vibrational frequencies related to the intermolecular motions range from 400 to 100 cm^{-1}. Measurements of the low frequencies are rather a difficult task because the trans-bending modes are rigorously IR-inactive and the cis-bending mode was predicted to be more than 200 times weaker than the asymmetric stretch in the IR region.

The linear geometry of the energetically lowest-lying N_4^+-$D_{\infty h}$ cation was clearly established by a determination of its rotational constants from a rotational resolution of the IR band of the asymmetric stretching ν_3 recorded using tunable diode laser spectroscopy

[88,89]. The band origin was observed at 2234.5 cm^{-1} and the rotational constants were determined to be $B_0 = 0.11205$ and $B_1 = 0.11176\ \mathrm{cm}^{-1}$. The best theoretical value derived from CCSD-T computations amounts to $B_0 = 0.1117\ \mathrm{cm}^{-1}$ [95]. Note that the quadrupole moment and dipole polarizabilities of the cation were also computed [95] and they could be of use in accounting for the long-range parts of the ion-neutral interaction potentials in large nitrogen clusters $N_4^+(N_2)_n$.

Overall, in its ground state, the linear N_4^+-$D_{\infty h}$ form has a rather long central distance of 1.98–2.00 Å (Fig. 4). The central N–N bond energy, which measures the N_2–N_2^+ bond strength, ranges from 88 to 105 kJ mol^{-1} [80–87]. High level ab initio computations [76,99] provided a value of about 110 kJ mol^{-1} for the bond energy relative to the asymptote $N_2(^1\Sigma_g^+) + N_2^+(^2\Sigma_g^+)$ Eq. (10), thus supporting the upper limit value of 105 ± 6 kJ mol^{-1} (1.09 ± 0.06 eV) obtained using mass spectrometry techniques [87].

$$N_4^+(^2\Sigma_u^+) \rightarrow N_2(^1\Sigma_g^+) + N_2^+(^2\Sigma_g^+) \qquad D_o = 105\ \mathrm{kJ\ mol^{-1}}\ (1.09\ \mathrm{eV}) \tag{10}$$

$$N_2(^1\Sigma_g^+) + N_2^+(^2\Sigma_g^+) \rightarrow N_3^+(^3\Sigma_g^-) + N(^4S) \qquad D_o = 480\ \mathrm{kJ\ mol^{-1}}\ (4.97\ \mathrm{eV}) \tag{11}$$

The photoelectron spectrum of gas phase dimer $(N_2)_2$ was recorded from a pulsed molecular beam [83]. The first PES band which is broad and centered at 15.2 ± 0.1 eV, could be assigned to the ground state equilibrium structure N_4^+-$D_{\infty h}$. More interesting is perhaps the experimental result in which the second PES band is even broader and has a maximum at 16.7 eV. It was proposed that the second band is originated from a stable dimer ion formed from the excited $^2\Pi$ state of the N_2^+ cation. Earlier study [81] on the photodissociation of $N_4^{\bullet +}$ at 270 nm also showed formation of the excited ion $N_2^+(B\ ^2\Sigma_u^+)$, which presumably came from the decay of an excited state of $N_4^{\bullet +}$.

The collision between molecular nitrogen and its cation was extensively investigated [97]. The reaction (11) generating the nitrogen atom is quite endothermic, by 480 kJ mol^{-1} (4.97 eV), and therefore only occurred at thermal energy following excitation of N_2^+. The cross sections of reaction (11) reach a maximum value at collision energy of about 11.3 eV after which they decline rapidly [91]. The latter value is consistent with the sum of 9.80 eV including the dissociation energies of N_4^+-$D_{\infty h}$ ($D_o = 1.09$ eV) and $N_3^+(^3\Sigma_g^-)$ ($D_o = 3.74$ eV). This suggests that the linear N_4^+-$D_{\infty h}$ actually involves as an intermediate in this reaction. Due to the high thermal energy required, the first quartet excited state of N_4^+-$D_{\infty h}$ was suggested to be responsible for the production of N_3^+ at thermal collision energies. The lowest-lying quartet state $^4A'$ of $N_4^{\bullet +}$ has a planar trans-bent shape of azido-nitrene and lies about 5 eV above the ground state. The bond fission in the quartet state is barrier-free in C_s symmetry but associated with an energy barrier of about 1 eV in a constrained linear framework [91].

The linear form N_4^+-$D_{\infty h}$ corresponds to the adiabatic radical cation of the neutral van der Waals dimer $(N_2)_2$. Let us now consider the ionization of the singlet tetrahedral N_4-T_d, singlet rectangular N_4^+-D_{2h} and triplet N_4-C_s-T. Removal of an electron from azido-nitrene N_4-C_s-T gives rise to the vertical ion (N_4^+-C_s) which, in its $^2A'$ state, corresponds to a vertical ionization energy of 9.17 eV (value from MR-CISDQ computations [76]). Geometry relaxation from the bent vertical ion invariably leads to the equilibrium linear N_4^+-$D_{\infty h}$, implying large gain in stabilisation energy of 200 kJ mol^{-1}. Thus the adiabatic ionization energy of azido-nitrene, evaluated as the energy difference between N_4^+-$D_{\infty h}$ and N_4-C_s-T, amounts to $\mathrm{IE_a}$(azidonitrene) $= 7.3 \pm 0.2$ eV.

Regarding N_4-T_d, its vertical ionization energy derived from a ^2E cation, is quite high, being 14.2 eV. Because the vertical SOMO is doubly degenerate, a Jahn–Teller effect takes place lowering the molecular symmetry. Geometry relaxation was proved to be substantial: the bonds break and the rings open finally giving the ion N_4^+-C_{2v}. The energy gain associated with such structural change is enormous, up to 4 eV. The adiabatic ionization energy, evaluated as the energy difference between N_4^+-C_{2v} and N_4-T_d, amounts to $\mathrm{IE_a}$(N_4-tetrahedrane) $= 10.4 \pm 0.2$ eV [76]. The ring at three centres N_4^+-C_{2v} which has a $^2B_2$ electronic state and could be regarded as a $^2\Pi$ ion, undergoes a mild N_2-loss via the transition structure N_4^+-TS (Fig. 4).

Similarly, ionisation of the rectangular form N_4-D_{2h} also gives rise to a $^2B_2$ ion, N_4^+-C_{2v}-2, but with a smaller geometry relaxation (Fig. 4). The minimum N_4^+-C_{2v}-2 is being 4.25 eV above N_4^+-$D_{\infty h}$. The adiabatic ionization energy amounts to $\mathrm{IE_a}$(N_4-rectangle) $= 10.8 \pm 0.2$ eV. Regarding the $N_2 + N_2^+$ system, the barrier for cycloaddition forming N_4^+-C_{2v}-2 is substantially reduced, which makes the pericyclic pathway less forbidden with respect to the neutral counterpart [64].

The ionisation process certainly constitutes a remarkable difference between the behavior of triplet azidonitrene and singlet tetrahedrane: while ionization of the former yields the linear $^2\Sigma$ ground state, ionization of the latter leads to a $^2\Pi$ ion. Both structures thus belong to two distinct energy surfaces, where the $^2\Pi$ is a $N_4^{\bullet +}$ excited state. In each case, the large difference between neutral and ionized geometries results in a very weak Frank–Condon overlap, irrespective of the forward direction.

If the ion N_4^+-C_{2v} could be considered as an excited state of the ion N_4^+-$D_{\infty h}$, then the corresponding transition energy amounts to 3.7 eV (358 kJ mol^{-1}). This computed value is not in line with that of 1.7 eV derived from the PES study mentioned above [83]. In other words, the identity of the second band in the PE spectrum of Ref. [83] remains to be resolved [98]. This is probably due to another ionization of molecular nitrogen.

Structure, energy and ^{15}N-NMR chemical shift of the dication N_4^{2+} were also calculated [105]. In its linear equilibrium, the dication has a short terminal (1.11 A) and central (1.28 A) distances, representing a bis-diazonium $N_2^+–N_2^+$ character (Fig. 4). Interest in the dication comes from the fact that its successive combination with the available azide anion N_3^- might yield N_7^+ cation and N_{10} molecule. The combinations are extremely exothermic thanks to large electrostatic attraction, and indeed, the reaction energies proved substantial, −1769 kJ mol^{-1} (N_7^+) and −2445 kJ mol^{-1} (N_{10}).

The heat of formation of the linear radical cation has been estimated to be $\Delta H_f^\circ(N_4^+$, linear$) = 1398 \pm 15$ kJ mol^{-1} [76], whereas that of the dication amounts to $\Delta H_f^\circ(N_4^{2+}$, linear$) = 3192 \pm 15$ kJ mol^{-1} [105].

3.4. En route to a bound N_4 species

3.4.1. A successful route

In view of the relative stability and availability of the $N_4^{\bullet +}$ radical cation, a plausible way of generating a neutral N_4 is actually to start from that cation. An appropriate and convenient experimental technique used for such route is obviously the neutralization–reionisation mass spectrometry (NRMS). Cacace et al. [12] recently carried out such NRMS experiment and reported a positive identification of a neutral N_4 species. An inherent shortcoming is that the technique is not able to reveal the structure and/or electronic state of the neutral species it generated and identified.

On the basis of the linear geometry of the starting cation N_4^+-$D_{\infty h}$ and the observed fragment pattern of the $^{14}N_2^{15}N_2$ neutrals, the authors concluded that '*the neutral N_4 is characterized by an open-chain geometry with two distinct, closely bound N_2 unit joined by a longer weaker bond.*' [12]. Note that the lifetime of neutrals and cations involved in a NRMS experiment is in the order of microsecond [102]. It appears that none of the neutral structures described in Chart 1 fully corresponds to this description. Only azido-nitrene N_4-C_s-T in part satisfies the suggested geometry. Nevertheless, the results summarized above allow us to understand the results of the NRMS experiment. Let us now examine the different processes summarized in Fig. 5, which displays the relative energies of different neutral and ionized N_4 structures, computed using a multi-reference configuration interaction method, MRCISD-Q/CASSCF(12,12) [76,104].

As stated above, the starting radical cation produced in electron bombardment on N_2 gas is no doubt the linear ion N_4^+-$D_{\infty h}$. In the first cell of a tandem mass spectrometer, a fraction of the ions was neutralized by electron transfer from a target gas, such as Xe or NH_3. Because the ionization energy of the target gas employed (< 12 eV) is far smaller than the neutralization energy needed to reach the $(N_2)_2$, the vertical neutralized entity could not reach a closed-shell singlet state. On the contrary, a vertical open-shell singlet state at the point $(N_4\text{-S})_{vert}$ being 431 kJ mol^{-1} above N_4-C_s-T, could be reached due to its high energy content. Although the vertical neutral $(N_4\text{-S})_{vert}$ is expected to attain azido-nitrene N_4-C_s-S following geometry relaxation, it lies well above the transition structure for fragmentation N_4-TS5. Therefore, the singlet nitrene is not likely to survive and subsequently be subjected to a reionization.

The vertical triplet point $(N_4\text{-T})_{vert}$ could be produced upon neutralisation of N_4^+-$D_{\infty h}$ by an energy transfer of about 6.2 eV, and actually lies 88 kJ mol^{-1} (0.91 eV) above its adiabatic structure N_4-C_s-T and 33 kJ mol^{-1} (0.34 eV) above the ground vibrational state of the relevant transition structure for fragmentation N_4-TS4. Bearing such small but sufficient excess internal energy, the vertical $(N_4\text{-T})_{vert}$ could undergo a bond breaking producing $N_2(^1\Sigma_g^+) + N_2(^3\Sigma_u^+)$. Under these energetic conditions, the lifetime of the neutralized triplet azido-nitrene is estimated in the order of picosecond magnitude, which turns out to be too short to involve in a subsequent reionization step.

In this context, the observation of a neutral N_4 entity during the NRMS experiment as reported in Ref. [12], could come from two factors. The first factor is that, owing to the smaller geometric difference between $(N_4\text{-T})_{vert}$ and N_4-C_s-T, a stronger Franck–Condon factor could favor formation of a small portion of the neutralized azido-nitrene, which was then stabilized upon collision into its equilibrium form. After collision giving a cation neutralization, a fraction of internal energy of the forming neutral might be dissipated into translational energy. As a result, the internal energy of this neutral could become smaller than the energy barrier for fragmentation, and it could survive at the end of the neutralization step.

A second possible factor is that a neutral N_4 could be formed and reionized in a high energy excited state, for example a Rydberg state. Formation of metastable excited states is often invoked to explain the observation of unstable neutrals in NRMS experiments [103]. In such a state, the electron is bound to the cation at rather long distance, but the neutral has a radiative lifetime compatible with the observed metastability, and a low probability for radiative transition to a dissociative ground state. Nevertheless, in the absence of detailed information on the properties of the N_4 excited states, these are rather speculative interpretations. In addition, appropriate kinetic RRKM-type treatments of the neutral species formation in various energy conditions

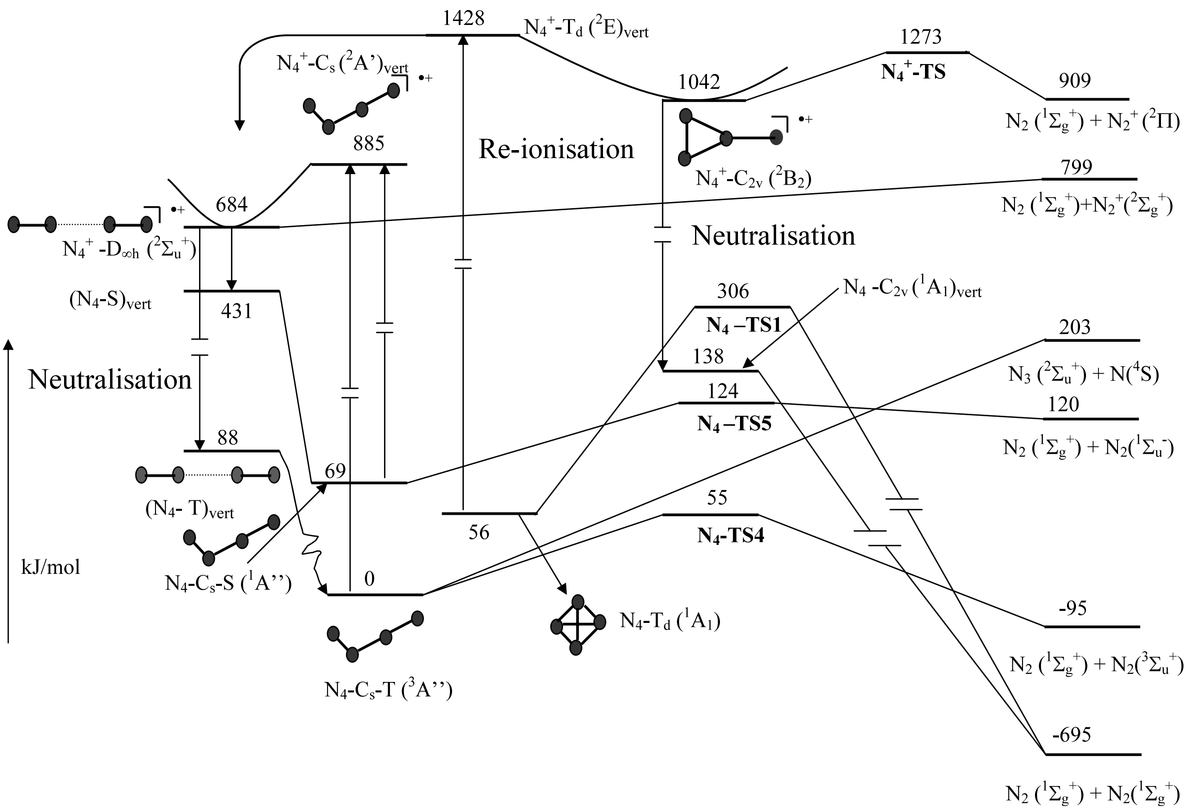


Fig. 5. Schematic profiles of potential energies showing the neutralisation and reionisation processes starting from the linear N_4^+ radical cation. Values given in kJ mol^{-1}, were tabulated from MR-CISD-Q/CASSCF(12,12) computations. The scale is arbitrary.

appear to be necessary to understand some of the subtleties of experimental observations.

On the other hand, Flammang and coworkers [104] recently attempted, but were not fully successful, to reproduce the NRMS results of Ref. [12] using a different tandem mass spectrometer (having a longer time of flight) and under different experimental conditions (using another collision target gas). The most remarkable difference in both NR systems was that a recovery signal corresponding to survivor ions was not observed under the latter conditions [104]. Note that the collisional activation (CA) spectra of the tetranitrogen ion survivors, that usually give more affirmative information on the neutrals structure, were not available yet.

Regarding the tetrahedral form N_4-T_d, its neutralisation and reionisation processes, as depicted in Fig. 5, make a relevant NRMS experiment an almost impossible target to achieve. In this context, further effort needs to be invested in both experimental and theoretical sides to help designing ways of generating bound N_4 molecules and understanding their formation mechanism.

3.4.2. Hypothetical routes

Another detectable bound tetranitrogen species is obviously the tetrahedrane N_4-T_d. Considering the substantial energy barrier on the singlet state (Fig. 5), it was tempting to suggest that tetrahedral N_4 could be trapped by, for example, matrix isolation techniques in conjunction with characterisation by infrared and/or mass spectrometries, following a prolonged irradiation of liquid nitrogen with radiation of wavelength less than 140 nm [52,54]. Indeed, a brutal but simple approach to make this metastable molecule is to create a high energy plasma and then to quench any possible N_4 that might be formed.

It was reported [67] that a N_4 species was observed during an experiment in which the nitrogen plasma generated by microwave or electrical discharge in gaseous N_2 was quenched on a cold window at low temperatures (6–35 K). The IR spectrum taken from the resulting matrix showed a weak t_2 peak at 936.7 cm^{-1}, which shifts to 900.0 cm^{-1} when isotopomer $^{15}N_2$ was used. Both peaks do not correlate with any other features in the obtained IR spectra and were therefore interpreted as originated from N_4-T_d. Nevertheless, it is noticeable that no bands attributable to the latter were observed in Raman spectra, and mixed ^{14}N and ^{15}N isotopomers were not seen in IR spectra. Reliable quantum chemical calculations [68–71] on the IR and Raman spectra of the tetrahedral form showed that the experimental interpretation in Ref. [67] is, at least, questionable for the isotopic shift. The reported isotopic shift was in fact not consistent with that derived from calculations. Therefore, the identity of both observed IR peaks mentioned above and a conclusive assignment of other spectral features remain to be determined by further experimental investigations.

Similar concept is that direct or indirect excitation of electronic states in liquid or solid nitrogen followed by collision-induced addition of a ground state and an excited state N_2, hereby forming N_4. The excited N_2 species should have energy of at least 11 eV above the ground state. The excitation could be carried out by laser irradiation, ion bombardment, r.f. excitation or in a hollow-cathode discharge [70]. A disadvantage is that such a route requires substantial internal energy whose dissipation usually occurs. For the purpose of detection, Raman spectroscopy has been shown to be superior to IR spectroscopy, owing to the detection limits for tetrahedral N_4 in liquid and solid nitrogen are 34 and 90 ppm, respectively, by Raman techniques [70].

It was argued that N_4 could better be generated from N_2 in some excited states containing single N–N bond rather than multiple N≡N bond [68]. Because the singlet and triplet states of N_2 featuring this property are susceptible to radiative decay to lower states having triple bonds, the most likely path of this type needs to involve bound quintet states of N_2, namely the $A'\ {}^5\Sigma_g^+$ and $C''\ {}^5\Pi_u$ states. The latter are bound states relative to the $({}^4S+{}^4S)$ and $({}^4S+{}^2D)$ dissociation limits of atomic nitrogens, respectively, with small but sufficient binding energies (from 0.5 to 1.0 eV).

A conceivable synthetic route to N_4-T_d was proposed starting from a cyclic N_3 radical. Indeed, MO calculations [22] demonstrated that although the energy of the cyclic N_3 $(C_{2v}, {}^2B_1)$ is about 129 kJ mol^{-1} higher than that of the linear $N_3({}^2\Pi_g)$, the former is lying in a relatively deep potential well, protected by an energy barrier of 132 kJ mol^{-1} for rearrangement to the linear form and a barrier height of 138 kJ mol^{-1} against dissociation to an excited state of nitrogen atom, $N_2({}^1\Sigma_g^+)+N({}^2D)$. Proceeding in the $N+N_2$ addition channel, the excited $N({}^2D)$ nitrogen atom could be generated by quenching of triplet N_2 with previously deposited ground state nitrogen atom, $N({}^4S)$. A cyclization leading to the cyclic $N_3({}^2B_1)$ is characterized by an energy barrier of about 29 kJ mol^{-1}, implying that the reagents must possess a certain threshold energy (Eq. (12)). Addition of another nitrogen atom $N({}^2D)$ to the cyclic $N_3({}^2B_1)$ giving tetrahedral N_4, is a barrierless exothermic process with a reaction energy of -567 kJ mol^{-1} (Eq. (13)).

$$N_2({}^1\Sigma_g^+) + N({}^2D) \rightarrow N_3(C_{2v},\ {}^2B_1) \quad \Delta H_r = -108\ \text{kJ mol}^{-1} \tag{12}$$

$$N_3(C_{2v},\ {}^2B_1) + N({}^2D) \rightarrow N_4(T_d,\ {}^1A_1) \quad \Delta H_r = -567\ \text{kJ mol}^{-1} \tag{13}$$

The feasibility of this route relies in the fact that the excited $N({}^2D)$ nitrogen atom has a lifetime of 37 s. The inherent disadvantages are on the one hand, a competition with a linear N_3 formation (occurred in the first step, Eq. (12)) and on the other hand, a nitrogen abstraction yielding $2N_2$ (more favoured by a large exothermicity in the second step, Eq. (13)).

An extreme approach which deserves some attention, is to use the experimental conditions of very high pressures and/or very high densities. Suggestions have recently been made to compress six bi-pentazole N_{10} to form N_{60} under high pressures [100]. It has also been shown that a phase transition from molecular oxygen O_2 to cyclic O_4 occurs at pressure of 0.1 Mbar [101]. The concept lying behind is that under extreme conditions, a change in relative stability might be realized making formation of metastable species such as tetranitrogen possible. This point will be examined in some more detail in a next paragraph when discussing the larger N-clusters.

The proton affinity of the tetrahedral form is rather low, PA(N_4, T_d) = 590 kJ mol^{-1}. Many standard deprotonation agents have PA's greater than 820 kJ mol^{-1}. Therefore, if a certain technique could first generate the protonated N_4H^+ form, subsequent deprotonation could be peformed to produce the elusive N_4 neutral molecule (Chart 2) [75].

Hydrogenation of N_4 leads to several stable tetrazanes (N_4H_6) and tetrazenes (N_4H_4). Tetrazane exhibits an even larger proton affinity PA(N_4H_6) = 1090 kJ mol^{-1}, and a heat of formation of $\Delta H_f^\circ(N_4H_6) = 293 \pm 15$ kJ mol^{-1} [111]. The latter quantity is similar to the heat of formation of HN_3 (294 kJ mol^{-1}). In this regard, hydrogenated H_mN_n compounds might be used as starting materials to produce N_n species. However, information about their kinetic stabilities and their condensed-phase density are not available yet.

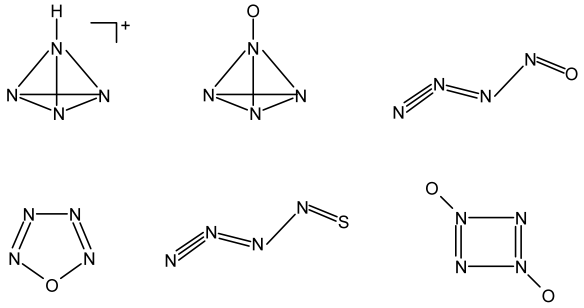


Chart 2.

In light of the high stability of N_2O, an imaginable way of trapping N_4 is by oxidation. The resulting (N_4O) system possesses various isomers [106–109] including the open-chain nitrosyl-azide (N≡N=N–N=O which exits in both s-cis and s-trans isomers), a five-membered ring, and a C_{3v} form in which the oxygen atom is attached to one nitrogen of the tetrahedral N_4 (Chart 2) [109]. While the five-membered ring is not stable relative to cycloreversion [106–108], nitrosyl-azide was experimentally observed [110] even though its dissociation into N_2+N_2O requires a small activation energy of 28 kJ mol^{-1} [106,107]. Elimination of NO from the C_{3v} form is also prohibited by a small energy barrier of about 20 kJ mol^{-1} due to the high exothermicity [109]. Replacement of oxygen by sulfur tends to reinforce the stability of the thionitrosyl azide, N≡N=N–N=S which seems to be the most likely candidate for experimental observation from, for example, a reaction of a NS^+ salt with azide anion [107].

Addition of a second oxygen atom to the N_4 ring lead to a planar four-membered ring which could best be seen as a dimer of N_2O (Chart 2). The (N_4O_2) ring is quite stable with respect to cycloreversion [109].

Finally, a commonly assumed possibility of trapping unstable species is to use metals and/or metals ions. In this direction, aluminum atoms were probed and various stable AlN_4 and Al_2N_4 have been established [112]. The interaction of polynitrogen species with metals and metal clusters will be discussed in a subsequent section of this review.

4. The N_5 system

4.1. N_5^+ cations

The gas phase equilibria of solvation reactions of N_3^+ with N_2 clusters were measured using a pulsed electron-beam high pressure mass spectrometry [113]. The complexes $N_3^+\cdot(N_2)_n$ observed resulted mainly from electrostatic interactions of the cation with N_2 bound ligands. The first enthalpy and entropy of complexation ($n=1$) were determined at -19 kJ mol^{-1} and -20.0 eu, respectively. The spectrum of the N_5^+ complex was also recorded by detecting N_3^+ photofragments using UV absorption (near 282 nm) [114]. Narrow absorptions were observed due to the N_3^+ $A^3\Pi \leftarrow X^3\Sigma_g^-$ transition. Photofragmentation involved non-radiative relaxation followed by N_2 loss, indicating the weak nature of triplet N_3^+ complexes.

As mentioned in the Prologue, Christe and coworkers [9,11] were able to produce the salts containing a bound and stable N_5^+ cation. These authors recorded the ($^{14,15}N$)-NMR and IR-Raman spectra of the salts and have greatly benefited from having accurate ab initio results at their disposal when characterizing the novel entity. This point illustrated again the symbiotic relationship and fruitful interplay between theory and experiment in the detection of novel and non-conventional molecules.

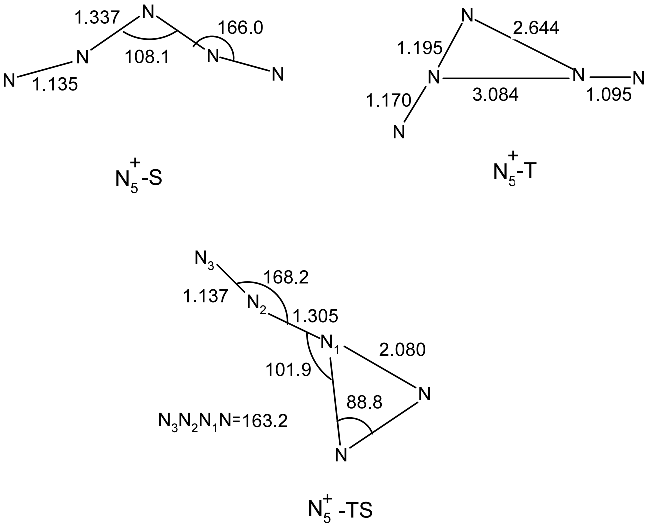


Fig. 6. Geometrical parameters of some N_5^+ cation stationary points. Bond lengths are given in angstrom and bond angles in degrees. Values were obtained from B3LYP computations.

The N_5^+ system can be regarded as a combination of N_3^+ and N_2. Because the trinitrogen cation has a triplet ground state, both multiplicities could be expected in the pentaatomic species. The calculated geometries for the equilibrium structures of both lowest-lying singlet and triplet states are shown in Fig. 6 [117].

Geometry optimizations in the closed-shell singlet electronic state of N_5^+ done using different levels of theory [115–123] invariably led to a symmetrical structure having a C_{2v} symmetry N_5^+-S. The orbital (electronic) configuration of N_5^+-S is depicted as follows: $[\ldots(1a_2)^2(6b_2)^2(8a_1)^2(2b_1)^2]$. The two highest occupied orbitals thus correspond to the out-of-plane (b_1) and in-plane(a_1) combinations of the nitrogen lone pairs. The N_5^+-S ion has two short and two long N–N bonds. While the short bond in this case (around 1.12–1.15 Å, depending on the method employed) is slightly longer than that of molecular nitrogen but somewhat shorter than that found in azide anion (around 1.18–1.20 Å), the long bond of 1.31–1.35 Å turns out to be longer than the typical N=N double bond. Due to the fact that the rotational constant A is inherently dependent on the central NNN bond angle, there is actually a large fluctuation on the computed values of A, amounting to up to 15% of a computed value in going from one level to another. In view of the flatness of potential energy surface along this angle coordinate, it would be a difficult task to definitively predict the rotational constant A with a high degree of accuracy. For both the B and C constants, the calculated values are more consistent with one another suggesting that the former is about 220–230 MHz larger than the latter. The rotational constant B is predicted to be $B_e(N_5^+\text{-S}) = 3150 \pm 100$ MHz [117].

Because the N_3^+ ion possesses a linear geometry and a triplet ground state, it seems reasonable to conceive an interaction between the triatomic triplet ion with molecular nitrogen to obtain a pentanitrogen triplet ion. Nevertheless, the linear triplet structure has a small degenerate negative vibrational frequency (a Π mode, distortion being possible in two directions). A perpendicular structure in which the N_3 moiety bisects the N_2, or vice versa, could not be located. Relaxation of the geometry within the C_s symmetry led finally to the optimised structure N_5^+-T shown in Fig. 6. It is clear that the latter ion results from an asymmetrical interaction of a lone pair of molecular nitrogen with one N=N bond of N_3^+. The latter is slightly stretched (+0.015 Å) relative to the non-interacting N=N bond. The inter-fragment distances are relatively long, being larger than 2.6 Å.

Of particular interest is the energy difference between both N_5^+-S and N_5^+-T isomers. It turns out that the singlet N_5^+-S constitutes the ground electronic state of the pentanitrogen cation, whose energy is consistently lower than that of N_5^+-T. The triplet-singlet separation is however small equal to about 26 ± 10 kJ mol^{-1} as derived from CCSD(T) computations [117]. Note that in the all-carbon isoelectronic cyclopentadienyl cation ($C_5H_5^+$), both singlet and triplet states remain cyclic with a singlet–triplet separation gap of about 27 kJ mol^{-1}, in favour of the triplet form [124]. There are several high-symmetry N_5^+ isomeric forms, but they are all highly energetic being about 500–1000 kJ mol^{-1} less stable than N_5^+-S [118].

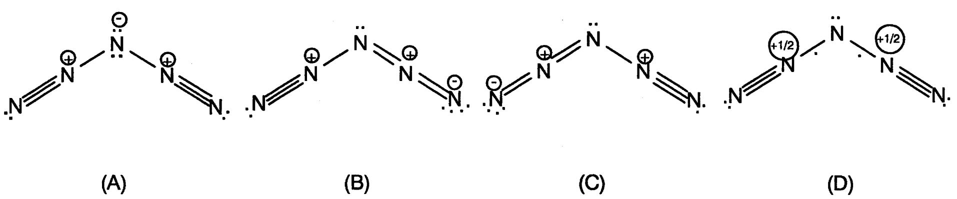
The heat of formation of free gaseous pentanitrogen cation has been evaluated as $\Delta H_{f,0}$ (N_5^+-S, $^1A_1$) = 1470 ± 10 kJ mol^{-1} and $\Delta H_{f,298}$ (N_5^+-S, $^1A_1$) = 1461 ± 10 kJ mol^{-1} [9,117,118,120].

The complexation energy of N_5^+-T, with respect to the N_2 plus N_3^+ fragment, is evaluated at −18 kJ mol^{-1} [117], which compares well with the experimental formation enthalpy of −19 kJ mol^{-1} derived by pulsed electron-beam high-pressure mass spectrometry (MS) experiments [113]. In the latter, the authors mixed molecular nitrogen and N_3^+ cation initially produced in its triplet ground state. The good agreement lends a further support for the formation of the triplet complex N_5^+-T in the MS experiment. It is equally apparent that there is no change in spin property when the triplet N_3^+ interacts with molecular nitrogen within a nanosecond time frame. The triplet complex was detected even though the singlet bound counterpart is more stable.

Without the effect of counteranions, the formation mechanism of N_5^+-S from addition of N_2F^+ to HN_3, involves a weak pre-association complex from which a concerted elimination of HF via a four-membered transition structure, could occur yielding N_5^+-S. The corresponding energy barrier is about 50 kJ mol^{-1} relative to the complex [116]. Nevertheless, the energies of all the intermediate steps are much lower than that of the starting reagents.

There have been different views on the electronic structure of the singlet N_5^+-S. From geometrical parameters, N_5^+-S can be regarded, in a way, as a substituted azide (R-N_3) in which the R substituent is replaced by the N_2^+ group [117]. Another view [9,11] described the two bond lengths in terms of the balance between two *valence structures*, one with single bonds from the central atom and one where all the bonds are double. Natural bond orbital (NBO) analysis suggested that the two terminal bonds have triple character [118]. There are apparently strong donor-acceptor interactions between on the one hand, the central N^+ lone pair and the vacant π* orbital of the two N≡N bonds, and on the other hand, the empty 2p(N^+) orbital and the π(NN) orbitals, resulting in a stabilising hyperconjugation. The central atom is negatively charged whereas the positive charge is mainly located at middle atoms.

Another view consisted in considering the cation as a system of two partially perturbed three-center four-electron bonds localized in the corresponding terminal NNN fragments, corresponding thus to structure of an azidyl diazonium cation (N_3–N^+≡N) [121]. In the same vein, the existence of five-center six-electron bond extended over the whole molecular skeleton was also proposed to elucidate the ion structure [122a]. Using a



valence-bond approach which quantifies the various increased-valence structures [122], the most important resonance forms of N_5^+ are given in the structures (**A**–**D**), along with the expected structure having the positive charge on the central atom.

It was also argued [32] against such resonance bonding approach (as redundant), and proposed instead that the bonding in N_5^+ could naturally be explained by considering the in situ central nitrogen N^+ cation to find itself in the first excited state ^1D, forming two equivalent dative (harpoon-like) bonds with molecular nitrogen, $N{\equiv}N \rightarrow N^+ \leftarrow N{\equiv}N$. The $N^+(R)_2$ cations with $R = CO$, NH_3 or rare gases, are also stable species with respect to bond fission. According to this view, interaction of the first N_2 molecule with $N^+(^1D)$ leads to the singlet $N_3^+(^1\Delta_g)$ state, described as the reverse of Eq. (6) given above, with an exothermicity of -411 kJ mol^{-1}. Addition of the second N_2 entity to the singlet N_3^+ gives rise to N_5^+-S with an additional energy gain of 194 kJ mol^{-1}. In total, the addition of $2(N_2)$ to $N^+(^1D)$ results in an exothermicity of about 605 kJ mol^{-1} [32].

It appears to us that the various views summarised above on N_5^+ electronic structure are not contradictory but rather complementary: the ones are based on geometry or electronic distribution of the already formed cation, whereas the others describe a formation mechanism beginning with a (preliminary) excitation of nitrogen atom cation.

Decomposition of N_5^+-S is endothermic by about 44 kJ mol^{-1} relative to N_3^+ (triplet)$+N_2$, but by at least 150 kJ mol^{-1} if the N_3^+(singlet)$+N_2$ fragments could be the products [117,119,123]. In addition, the N_2 loss is prohibited by a marked energy barrier of at least 170 kJ mol^{-1} through the transition structure N_5^+-TS (Fig. 6). Proceeding in the opposite direction, addition of N_3^+ (singlet) to N_2 via the same N_5^+-TS is associated with an energy barrier of about 20 kJ mol^{-1} [123]. This points out that the pentanitrogen cation is a fairly stable gas phase species. Under experimental conditions, its stability is no doubt reinforced by the presence of counter anions in the salts.

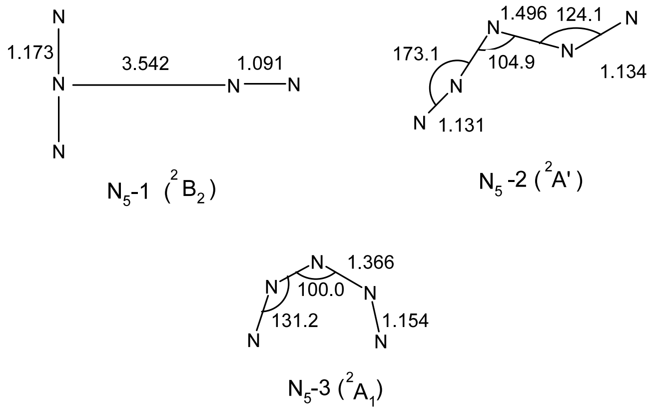


Fig. 7. Geometrical parameters of some N_5 radical stationary points. Bond lengths are given in angstrom and bond angles in degrees. Values were obtained from UB3LYP computations for N_5-1 and N_5-3 and UHF for N_5-2.

Formation of the singlet structure in the salt $[N_5^+][AsF_6^-]$ [9,11] is further substantiated by the vibrational analysis. In fact, there is a fair agreement between experimental IR–Raman wavenumbers obtained for $N_5^+AsF_6$ crystals and computed gas phase values for N_5^+-S, and the complete set of nine fundamental frequencies of the singlet cation could be established as follows: 2271 (A_1, stretch), 871 (A_1, stretch), 680 (A_1, bend), 209 (A_1, bend), 480 (A_2, torsion), 420 (B_1, torsion), 2211 (B_2, stretch), 1088 (B_2, stretch) and 400 (B_2, bend). The computed counterparts for the triplet complex differ very much from the observed ones where vibrational frequencies resulting from molecular interaction are rather small.

4.2. N_5 radicals

The most stable N_5 isomer is a weak complex N_5-1 ($^2B_2$) between N_3 and N_2 with a quite long intermolecular distance (Fig. 7) whose complexation energy amounts to about -5 kJ mol^{-1} [118].

The existence of a N_5-2 ($^2A'$) isomer, which is formally an open-chain pentazene radical, or azidodiazenyl radical $N_3{-}N{=}N$, being about 170 kJ mol^{-1} above N_5-1 is not confirmed by higher levels calculations [118].

The radical N_5-3 has a C_{2v} open and distorted pentagonal structure in which both terminal atoms point inward rather than outward as in the cation N_5^+-S. Its electronic state $^2A_1$ corresponds to a σ-radical centered on the central atom in-plane orbital and lies at least 235 kJ mol^{-1} above the dissociation limit N_3+N_2 [118,123].

The heats of formation were evaluated as $\Delta H_{f,0}(N_5, {}^2A_1) = 749 \pm 10$ kJ mol^{-1} and $\Delta H_{f,298}(N_5, {}^2A_1) = 741 \pm 10$ kJ mol^{-1} [118]. Upon ionisation, all three radical forms give rise to the most stable cation N_5^+-S. The ionization energy and electron affinity of the N_5-3 radical were calculated to be $IE_a(N_5) = 7.47 \pm 0.3$ eV and $EA(N_5) = 5.06 \pm 0.3$ eV, respectively [123].

All theoretical studies [117–119,123] were consistent with each other demonstrating that the N_5 radical is staying on an extremely shallow potential energy and readily undergoing decay into separate fragments. In N_5-3, the relevant energy barrier for bond fission producing the more stable fragments amounts merely to a few kJ mol^{-1}, rendering the radical kinetically unstable.

Applying the argument presented above on N_5^+ formation [32] to that of N_5 from N and $2N_2$, it could be noted that the nitrogen atom needs to be first excited into its $N(^2D)$ state before combining with N_2. The excited N atom is appropriate (in $M = \pm 1$ and ± 2

components) for forming N_3 (Eq. (3b)), but then, there is no space left for combining with a second N_2 molecule. As a consequence, the N_5 radical is not a stable species [123].

4.3. N_5^- anions

To obtain the electron affinity of the N_5 radical, ab initio calculations have referred to the N_5^+ anion, which is in fact the long-sound pentazole anion. The history of pentazoles (RN_5), the all-nitrogen analogues of cyclopentadienes and the last members of the azoles series began a century ago when Hantzsch tried in 1903, but failed, to prepare phenylpentazole (Ph-N_5) from benzenediazonium azide [125]. The following half of a century was characterized by failure [126], misunderstanding [127] and dispute [128]. It was not until 1956 that this 'classical problem' was solved by Huisgen and Ugi [129] when they were able to demonstrate the effective formation of phenylpentazole. Spectroscopic evidence for pentazole existence was reported much later including NMR chemical shifts [130,131], X-ray crystal structure [132] and some other data [133]. At the present time, only arylpentazoles are available whereas the parent HN_5 and alkyl derivatives remain elusive [134–137,136]. As a consequence, alternative information on molecular properties and stability of this class of compounds was gathered from quantum chemical computations [139–144].

Sana et al. [142] investigated in 1979 the detailed (HN_5) potential energy surface exploring the pathways related to both open-chain pentazene and cyclic pentazole isomers. In spite of the limited accuracy inherent to the levels of theory employed at that time (HF and limited CI wavefunctions with minimal basis sets), the reported energy surface proved to be qualitatively helpful. The suggestion made in that work [142] that the pentazene isomer could be detectable, has stimulated a successful experimental search for this isomer [136]. The kinetic stability of various pentazoles with respect to 1,3-dipolar cycloreversion yielding RN_3+N_2, has subsequently been evaluated using higher levels of quantum chemical methods [14,138,143].

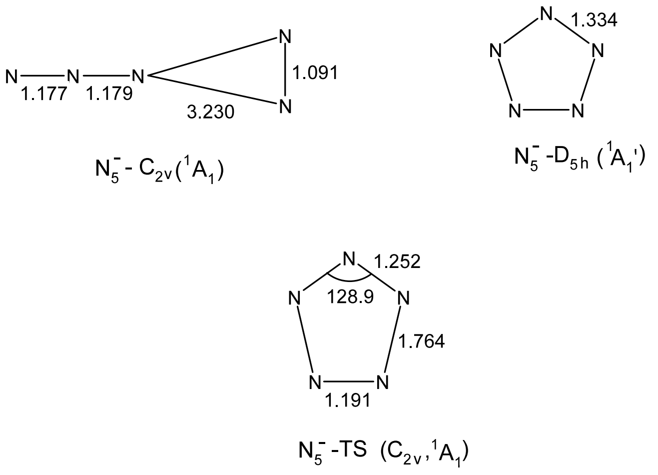


Fig. 8. Geometrical parameters of some N_5^- anion stationary points. Bond lengths are given in angstrom and bond angles in degrees. Values were obtained from B3LYP computations.

Similarly, the pentazole anion N_5^- was for a long time an experimentally elusive species. Attempts to generate the anion from neutral pentazoles were not successful. It was probable that the anion involved as an intermediate in the isotopic exchange $^{14}N_3^- + ^{15}N_2$ reaction [145], but its presence was not invoked to explain the observation nor further explored. Earlier theoretical studies [146,147], however, suggested a reasonable kinetic stability of the pentanitrogen anion, at least in the gas phase. Extended Hückel theory computations [147] indicated the possibility of trapping it as ligand in transition metal complexes. More recent studies [148–150] emphasized similar behaviours.

The N_5^- anion was shown to have a highly symmetrical cyclic structure N_5^--D_{5h} ($^1A_1'$) [61,118,146,147,151] (Fig. 8), whereas the open-chain pentazene anion isomer is not stable with respect to either fragmentation giving $N_5^- + N_2$, or cyclization yielding pentazole anion. The distance of the regular pentagon amounts to about 1.33–1.34 A, which is in between the single and double nitrogen–nitrogen bond lengths. The aromatic character of the anion π-electron system is particularly strong which is characterized by a value of NICS(1) = −16.5. Note that the corresponding NICS value in benzene is −10.0, and the more negative the NICS value, the more aromatic the system.

The harmonic vibrational wavenumbers of the N_5^- anion were evaluated as follows (values in cm^{-1} obtained from CCSD(T) method): 783 (E_2''), 1060 (E_2'), 1124 (E_2'), 1222 (A_1') and 1286 (E_1'), with a probable error of ± 20 cm^{-1}. Only the modes E_1' are IR active whereas the modes E_2' and A_1' are Raman active [69,151].

The N_5^- anion is about 65 and 70 kJ mol^{-1} less stable than the $N_3^- + N_2$ fragments and the weak complex N_5^--C_{2v} ($^1A_1$), respectively (Fig. 8). The latter is formed by electrostatic interaction with rather long intermolecular distance (> 3 Å) and a small binding energy of about −5 kJ mol^{-1}.

The heats of formation of azide radical $\Delta H^\circ_{f,0}(N_3) =$ 459 kJ mol^{-1} and $\Delta H^\circ_{f,298}(N_3) = 454$ kJ mol^{-1}, and azide anion, $\Delta H^\circ_{f,0}(N_3^-) = 193$ kJ mol^{-1} and $\Delta H^\circ_{f,298}(N_3^-) = 188$ kJ mol^{-1} allow the corresponding values for N_5^- to be evaluated, $\Delta H^\circ_{f,0}$(pentazole anion) $= 260 \pm 10$ kJ mol^{-1} and $\Delta H^\circ_{f,298}$(pentazole anion) $= 253 \pm 10$ kJ mol^{-1}.

The ionisation and double ionisation of pentazole anion are estimate to be $IE_a(N_5^-) = EA(N_5) = 5.06$ eV, and $DIE_a(N_5^-) = 12.52$ eV, respectively. The former value is by far larger than the ionisation energy of azide anion, $IE_a(N_3^-) = EA(N_3) = 2.76$ eV. As a consequence, with an excess energy of larger than 2.3 eV upon ionisation, the vertical N_5 system has enough internal energy to undergo dissociation into N_3+N_2, irrespective of the existence or non-existence of the N_5 radical. Similarly, the vertical doubly-ionised structure of cyclic pentazole anion lies about 7.5 eV above the equilibrium open cation N_5^+-S. Such a huge amount of energy gained upon ionisation is likely to allow the cationic system to undergo fragmentation following geometry relaxation.

The first vertical excited state of pentazole anion corresponds to an $^1E_1''$ state with a transition energy of 6.62 eV (CASPT2 values). This state is unstable relative to Jahn–Teller distortions. Relaxation of geometry results in a $^1B_2$ (C_{2v}) state with an energy of around 6 eV above the ground $^1A_1'$ state. Other vertical states have similar energy locations, such as the $^1E_2'$ (6.65 eV), $^1E_1'$ (6.70 eV)... and are also forbidden for symmetry reason [76].

The proton affinity is predicted to be substantial, PA(pentazole anion) = 1318 ± 10 kJ mol^{-1}.

The anion can also undergo 1,3-dipolar cyclo-reversion which occurs via transition structure N_5^--TS generating $N_3^-+N_2$ and is associated with an energy barrier of 110 kJ mol^{-1} [123] (Fig. 8). The latter is markedly larger than the barrier of 84 kJ mol^{-1} derived for cycloreversion of neutral parent HN_5 [143]. The calculated energy barrier is consistent with the fact that pentazole anion is relatively stable in the gas phase.

Benin et al. [14] used 4-hydroxyphenylpentazoles and their salts as precursors in their kinetic measurements of the degradation of pentazoles in solution and obtained a set of activation parameters. These authors were not able to directly identify pentazole anion using controlled ozonolysis. However, along with previously reported data [133,134], they evaluated the stability of pentazole anion in solution. The latter was predicted to have a half-lifetime of $t_{1/2}=2.2$ days, whereas the half-lifetime of the neutral HN_5 was suggested at about 10 min in methanol at 0 °C. Note that activation free energies for N_2-eliminarion from arylpentazoles amount to 82–86 kJ mol^{-1} [14], values comparable to theoretical estimates on simpler five-membered rings [138,143].

According to a referee, a report on the detection of the pentazole anion was presented at a conference some years ago, but so far we have not been able to locate it yet.

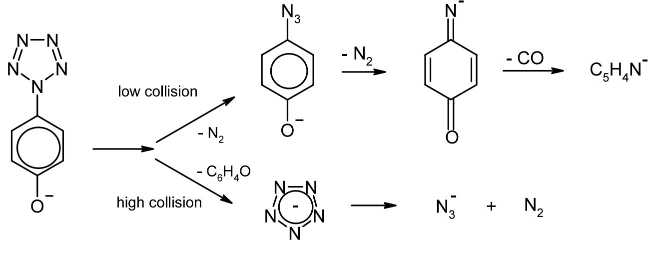


Chart 3.

Recently, a pentanitrogen anion has been detected using mass spectrometry (MS) techniques. Vij et al. [13] demonstrated the N_5^- existence following infusion of a neutral pentazole into a tandem mass spectrometer. As in Ref. [14], the new approach here was actually the use of 4-hydroxyphenyl-pentazole to generate a phenolate anion whose decomposition appears a quite successful route to pentazole anion. Similarly, 4-aminophenylpentazole derivatives seem also to be good precursors from which the C–N bond could be cleaved while leaving the five-membered ring unperturbed [13]. Using various MS techniques such as negative-ion electrospray ionization (ESI-MS) and collision-induced dissociation (CID), it was found that when accelerated and collided with target gas, the phenolate anion followed different fragmentation pathways depending on the collision voltage. At low energy collision, only N_2 elimination was observed. But at high energy collision, it was possible to assign the peaks arising from a (N_5^-) entity. It is apparent that the use of high voltage allowed the C–N bond to be cleanly cleaved (cf. Chart 3). The pentanitrogen anion subsequently lost N_2 generating N_3^-. Experiments using isotopic ^{15}N-precursors provided additional evidence for N_5^- formation. It seems thus plausible that pentazole anion could be trapped and stabilized in salts in the presence of cations, in a similar way as its N_5^+ counterpart.

4.4. Synthetic use of N_5 species

The successful preparation of stable pentanitrogen cation and detection of pentazole anion are beyond any doubt stimulating developments in such a way that they could be used as building-blocks for preparation of larger nitrogen clusters.

It was suggested that the azido-pentazole, the most stable N_8 species, might be prepared from both N_5 and N_3 moieties [151]. Condensation of N_5^+ cation with azide anion N_3^+ could lead first an open-chain form, namely a diazidyl diimide (N_3–N=N–N_3), which subsequently could undergo a 1,5-electrocyclization giving finally azidopentazole. The bi-cyclic analogue was shown to be less stable than azidopentazole [61,151]. Nevertheless, it turned out that this route was not suitable which yielded ‘nothing but explosions’! [152].

Other possible routes have been suggested, including a $HN_3+N_5^+$ reaction to generate a protonated N_8 [153], and a $N_5^-+N_5^+$ combination [154,155] to produce N_{10}. Nevertheless, the most plausible, feasible and perhaps most promising way of using pentazole anion is to trap it in transition metal complexes. The behaviour of N_5^- is predicted to be similar to that of cyclopentadienyl anion ($C_5H_5^-$) in interacting with metal fragments [147–150]. This aspect will be discussed in a following part. Recent successful synthesis of a carbon-free sandwich complex containing the pentaphosphorus anion, $[(P_5)_2Ti]^{2-}$ [156] would raise hope for a preparation of all-nitrogen analogues of metallocenes in a near future!

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