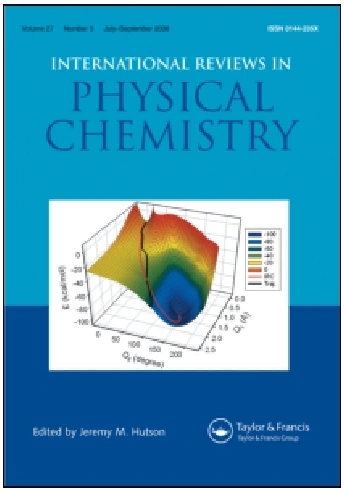

International Reviews in Physical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

All-nitrogen chemistry: how far are we from N_{60}?

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To cite this Article Samartzis, Peter C. and Wodtke, Alec M.(2006) 'All-nitrogen chemistry: how far are we from N_{60}?', International Reviews in Physical Chemistry, 25: 4, 527 — 552
To link to this Article: DOI: 10.1080/01442350600879319
URL: http://dx.doi.org/10.1080/01442350600879319

International Reviews in Physical Chemistry,
Vol. 25, No. 4, October–December 2006, 527–552

Taylor & Francis
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All-nitrogen chemistry: how far are we from N_{60}?

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(*Received 12 May 2006; in final form 7 August 2006*)

Two hundred years of research have produced only a handful of synthesized all-nitrogen molecules and ions but a lot of stable N_n candidates are waiting to be detected. Experimentally, besides the long-known neutrals N_2 and linear-N_3 there are recent reports of N_4 and cyclic-N_3 production. In the ions, N_5^+ and N_5^- have been reported. Ongoing theoretical work has predicted species like N_4, N_6, N_8, N_{10} and even N_{60} to be stable. We review the work that has been done recently in this area in both experiment and theory.

Contents

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International Reviews in Physical Chemistry
ISSN 0144–235X print/ISSN 1366–591X online © 2006 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/01442350600879319

1. Introduction

The first member of the polynitrogen (N_n) compound family, nitrogen (N_2), first reported by Daniel Rutherford in his thesis in 1772 [1] but at the same time independently investigated by Scheele, Cavendish and Priestley, is an extremely stable molecule. Its $^1\Sigma_g^+$ ground state has a bond length of 1.10 Å, a vibrational stretching frequency of 2359 cm^{-1} and a bond energy of 226 $\mathrm{kcal\,mol}^{-1}$ [2]. It is not difficult to detect it in nature, as it makes up about 79% of the Earth's atmosphere. However, if one looks at larger polynitrogen species (N_n with $n > 2$), none exists naturally in our planet and very few have been detected in the laboratory. The reason is that the triple bond in N_2 is much stronger (226 $\mathrm{kcal\,mol}^{-1}$) than the sum of three single ($3 \times 38.2 = 114.6\,\mathrm{kcal\,mol}^{-1}$) or 3/2 times the strength of the double ($1.5 \times 99.9 = 149.85\,\mathrm{kcal\,mol}^{-1}$) N–N bonds, so a polynitrogen molecule has a tendency to decompose into N_2 molecules. That also explains why in more than 200 years of research since the discovery of N_2, only a handful of nitrogen allotropes have been experimentally observed.

Seen in a more optimistic light, the large energetic release from N_n molecule decomposition is strong motivation for research into polynitrogen molecules as *clean high-energy density materials* (HEDMs). These materials decompose to environmentally clean N_2, and produce enormous amounts of energy per unit mass without harmful waste. Theoretical calculations in the past 30 years have evaluated the structure and stability of numerous isomers of possible N_n molecules with n ranging from 3 to 60. Although all calculations show high potential energies with respect to molecular nitrogen, only select isomers [3] exhibit a unique property that makes them good HEDM candidates: significant energetic barriers to dissociation, enough to allow a relatively long lifetime and therefore experimental detection and possible use.

Unfortunately, there is still no easy and general way to make these molecules. Despite that, in the last seven years there have been experimental reports that have doubled the number of detected polynitrogen species. In 1999 Christe and coworkers [4] reported a stable N_5^+ cation in $N_5^+SbAs_6^-$ salts. Two years later, Cacace *et al.* [5] detected an N_4 isomer with a lifetime of more that 1 μs. At about the same time, again Christe's group produced N_5^- following collision-induced dissociation of para-pentazolylphenolate anion [6]. One year later, Hansen and Wodtke [7] reported the first evidence for the production of a ring isomer of N_3, strengthened by later experimental [8–13] and theoretical [14–16] work.

In light of the apparent experimental revolution in the field, a review by Nguyen [17] discussed theoretical and experimental results for the structures and energetic stabilities of polynitrogen species focusing mainly on N_4 and N_5 neutral and ionic species. In the present review, we discuss the structure and energetics of ground and excited states of all known and predicted polynitrogen species focusing mainly on the neutrals. We have made every effort to include all work reported in the literature, however we apologize in advance for any omissions or errors.

We divide the material by mass. The extensive old and new work on N_3 is presented first, followed by a quick overview of N_4 and N_5 research. Then theoretical predictions for nitrogen allotropes with six, seven and eight nitrogen atoms are discussed. We close with reporting the best possible candidates for formation of bigger molecules up to N_{60}.

2. Trinitrogen (N_3)

Interestingly, the first discussion of N_3 chemistry stems from the HN_3 synthesis of Curtius in 1890 [18], which marks also the first detection ever of a stable N_3 species, the N_3^- anion, produced in aqueous solutions of HN_3. It is a curious historical note that, in the pre-quantum-chemistry era, Curtius was drawn to the cyclic-N_3 structure and repeatedly draws N_3 as cyclic in his discussion of its chemistry, even in his discussion of the possible structures of HN_3 [18]. We now know that the lowest energy conformer of three N atoms is the *linear-N_3* radical. This issue of linear vs. cyclic ground state was settled when Thrush [19] first recorded its 270 nm absorption in a flash photolysis experiment of HN_3. Thrush assigned the 270 nm bands to $^2\Sigma \leftarrow {}^2\Pi$ transitions. Douglas and Jones [20] examined the same bands at high resolution and confirmed Thrush's assignment, further determining the transitions as $^2\Sigma_u^+ \leftarrow {}^2\Pi_g$. In addition they determined that the ground $^2\Pi_g$ state has a linear geometry with terminal-to-terminal nitrogen length of 2.363 Å consisting of two equal bonds of 1.1815 Å length each (in comparison, N_2 has a bond length of 1.09768_5 Å). From the resolved rotational structure, they extracted rotational constants for the ground and excited state ($B(^2\Sigma_u^+) = 0.43238 \pm 0.0001\ \mathrm{cm}^{-1}$ and $B(^2\Pi_g) = 0.43117 \pm 0.0001\ \mathrm{cm}^{-1}$) and the energy of the A state ($T_0 = 4.56$ eV). It is interesting to note that Winewisser [21] finds two different N–N bond lengths from measurements of the microwave spectrum of HN_3, 1.243 Å for N1–N2 and 1.134 Å for N2–N3, N1 being the nitrogen bound to H. The end-to-end N_3 size in HN_3 is thus 2.377 Å, slightly longer than the N_3 radical. Later FTIR work [22] confirmed that the ground state of the N_3 radical has a linear $D_{\infty h}$ symmetry with a bond length of 1.18115 Å.

Early SCF calculations [23–26] on N_3 did not predict the radical size accurately. Archibald and Sabin [24] calculated an asymmetric but linear (NNN angle = 180°) radical with bond lengths of 1.24 and 1.14 Å. Dyke and coworkers [25] performed geometry optimization calculations of the neutral N_3 in order to calculate vertical ionization potentials. Their value for the molecule's size is 2.317 Å (1.204 + 1.113 Å), substantially smaller than experimental results in both N_3 and HN_3. The first agreement of experiment and theory comes with configuration interaction (CI) level calculations [27] where the predicted bond length (1.1815 Å) agrees with Douglas and Jones's experimental value. The ground state, calculated at the CI level, has a $D_{\infty h}$ symmetry, although at the SCF level they too find $C_{\infty v}$ symmetry and $1.204 + 1.113 = 2.317$ Å bond length, in agreement with Dyke *et al.* Later HF/6-31G* work [28] predicts a symmetric geometry and a 1.159 Å bond length, MP2/6-31G* calculations [29] predict a 1.184 Å bond length, CASCI calculations [30] give 1.17 Å and B3LYP calculations [30] 1.2 Å. Other DFT calculations give similar results [31, 32]. More recently, MRCISD(T) work [14] predicted a bond length of 1.1854 Å. It is clear that agreement between theory and experiment gets better with increasing levels of theory.

The vibrational frequencies of the linear-N_3 ground state are known [20, 33–35]. LIF experiments [33] on neutral N_3 identified weak emission bands from the 000 level of the $A^2\Sigma_u^+$ state to the 000 and 020 levels of the $^2\Pi_g$ ground state. From that they obtained $\nu_1 = 1320\,\text{cm}^{-1}$ and $\nu_2 = 457\,\text{cm}^{-1}$ for the ground state. Matrix isolation experiments [35] measured a weak $\nu_2 = 472.7\,\text{cm}^{-1}$ and a weak $\nu_1 + \nu_3$ combination band at $2944.9\,\text{cm}^{-1}$ in addition to a strong ν_3 antisymmetric stretch at $1657.5\,\text{cm}^{-1}$. FTIR gas phase measurements [22] determined $\nu_3 = 1644.68\,\text{cm}^{-1}$ and provided accurate molecular constants for the $A^2\Sigma_u^+$ state ($T_0 = 36738.7497(18)\,\text{cm}^{-1}$, $B_0 = 0.4326453(64)\,\text{cm}^{-1}$). Theoretical calculations by Biterrerova *et al.* [36], Prasad [37], and Zhang *et al.* [14] agree with the above values.

The heat of formation of N_3 was reported [38] to be $112 \pm 5\,\text{kcal}\,\text{mol}^{-1}$, which compares well with the Martin *et al.* [39] calculation of $109.25\,\text{kcal}\,\text{mol}^{-1}$. This value agrees with the experimental result of $113.69\,\text{kcal}\,\text{mol}^{-1}$ obtained by Continetti *et al.* [40] by high-resolution translational energy measurements of N_3 dissociation products. Linear-N_3 is metastable [38, 40] ($D_0 = -0.05 \pm 0.1$eV) with respect to spin-forbidden dissociation to $N(^4S) + N_2(^1\Sigma_g^+)$. Although the spin-forbidden photodissociation process has been observed [40], the dominant dissociation pathway is to spin-allowed products $N(^2D) + N_2(^1\Sigma_g^+)$ [35, 41, 42] which is enhanced when the excited state ($A^2\Sigma_u^+$) is excited in the bending mode [40].

Higher excited states of N_3 have been explored [20, 40, 41]. The position of $A^2\Sigma_u^+$ was determined [20] to be 4.56 eV. LIF experiments [33] estimated its lifetime to be less than 20 ns. Recent work narrowed that number to 132 ± 21 ps for the 000 and 64 ± 10 ps for the 010 excited state vibrational levels using an intracavity doubled ring laser operating at 272 nm [43]. CI calculations [27] predicted four valence excited states of N_3: $^4\Pi_u$ (4.52 eV), $^2\Sigma_u^+$ (4.62 eV), 1 $^2\Pi_u$ (5.13 eV) and 2 $^2\Pi_u$ (6.39 eV) and five Rydberg states: $^4\Sigma_g^-$ (6.53 eV), $^2\Sigma_g^-$ (6.94 eV), 1 $^2\Delta_g$ (8.09 eV), $^4\Sigma_u^-$ (8.32 eV), $^2\Sigma_u^-$ (8.47 eV). These calculations suggested that the N_3 absorption at 270 nm leads to the $^4\Pi_u$ as well as the $^2\Sigma_u^+$ state. Zhang *et al.* [14] in high-level *ab initio* MRCISD(T) calculations of N_3 provide optimized geometries and energies of the ground ($^2\Pi_g$, 1.81 Å) and three excited states of N_3 ($A^2\Sigma_u^+$, $B^2\Pi_u$ and $a^4\Pi_u$). The three excited states are very close to each other in energy (112, 111 and $102\,\text{kcal}\,\text{mol}^{-1}$, respectively).

Martin, Francois and Gijbels, in a calculation of boron, nitrogen and boron–nitrogen clusters [39], predict several minima involving cyclic-N_3 isomers on the doublet N_3 surface. Calculations [30] of the doublet and quartet N_3 hypersurface at the CAS/CI and DFT levels of theory, also show bend minima and predict the existence of a $^2B_1$ ring correlating to $N(^2D) + N_2(^1\Sigma_g^+)$ with high barriers to dissociation and linearization. Bittererova *et al.* [36] calculated energies, geometries and harmonic frequencies of low-lying N_3 doublet states at the CASSCF, MRCI and CCSD(T) levels of theory and they found (along with additional N_3 (C_{2v}) stationary points on the hypersurface) a linear ($^2\Pi_g$) electronic ground state, a stable ($^2B_1$) cyclic structure and a C_s transition state ($^2A''$) connecting the two. Based on these calculations they proposed a barrierless exothermic reaction mechanism of *cyclic*-$N_3(^2B_1)$ ring with $N(^2D)$ atoms as an alternative route to form singlet tetrahedral-N_4 (T_dN_4, tetraazatetrahedrane).

More recently, Zhang *et al.* [14] used high-level *ab initio* calculations to study the ground and lower doublet and quartet excited states of N_3. In the MRCISD(T) level, they identified the $^2B_1$ cyclic minimum 30.3 kcal mol^{-1} above the linear-N_3 ground state (figure 1). At the energy minimum, cyclic-N_3 is an isosceles triangle with two bonds at 1.4659 Å and 49.8° apex angle. The cyclic-to-linear isomerization barrier is predicted to be 32.1 kcal mol^{-1} and the cyclic dissociation barrier (to $N(^2D) + N_2$) to be 33.1 kcal mol^{-1} above the cyclic minimum. This work also predicted the lowest seam of crossing for possible spin-forbidden dissociation to be 28.28 kcal (again with respect to the cyclic minimum). Thus, it is reasonable to suggest that cyclic-N_3 is predicted to be a

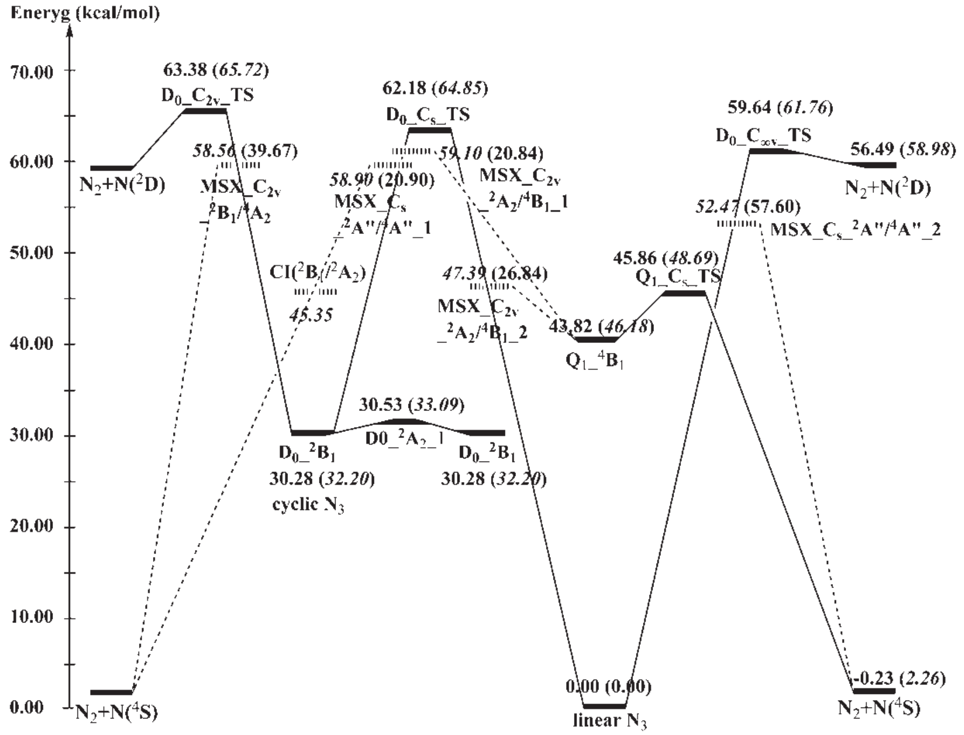

Figure 1. High-level *ab initio* calculated energies for the ground electronic states of linear and cyclic-N_3 and transition states for isomerization and dissociation to spin-allowed and spin-forbidden products. First number is ZPE-corrected energy and the number in parentheses is the energy without ZPE correction. These calculations predict that cyclic-N_3 should be stable. (*Reprinted with permission from ref. [14]. Copyright 2005, American Institute of Physics.*)

stable azide isomer. The barrier for the formation of N_3 from $N(^2D) + N_2$ was found to be 3.1 kcal mol^{-1} higher for the cyclic than for the linear isomer. Adiabatic and non-adiabatic N_3 dissociation was also explored in this work. At the MRCISD(T) level of theory, they find a 2.0 kcal mol^{-1} barrier for dissociation on the lowest quartet surface minimum $^4B_1$. On the ground doublet surface, the linear-N_3 has a 59.6 kcal mol^{-1} barrier to dissociation and the cyclic-N_3 a 33.1 kcal mol^{-1} barrier. In non-adiabatic dissociation of doublet linear and cyclic-N_3 states through avoided crossings with the quartet surface the authors located six MSXs (minima on the seam of crossing) on various dissociation and reaction coordinates (figure 1). Spin–orbit interaction and one-dimensional Landau–Zener model calculations showed that the non-adiabatic transition probability becomes appreciable only when the kinetic energy of the nuclei approaches zero.

Babikov *et al.* [16] explored the 3D potential energy hypersurface of cyclic-N_3 locating three pseudorotation minima where N_3 is an acute triangle with 49.8° apex angle and two equal (1.4659 Å) sides connected by three transition states (0.0386 eV above the minima) where it becomes an obtuse triangle with 71.93° apex angle and two (1.3058 Å) equal sides. They also discuss a conical intersection predicted 0.57 eV above the surface minima that gives rise to geometric phase effects (GPE), predicted [15] to shift the vibrational level energies by anywhere from 100 to 600 cm^{-1} with respect to values predicted with standard theoretical methods that neglect GPE. Perhaps of greater importance, the GPE calculations show the vibrational symmetry of the ground state is E whereas non-GPE calculations identify an A_1 symmetry. Indeed the shapes of the vibrational wavefunctions are dramatically different for GPE calculations, in comparison to non-GPE predictions. Thus an accurate accounting of the GPE is essential to the accurate theoretical prediction of, for example, the IR absorption spectrum of the cyclic-N_3 molecule especially for transition probabilities. The same statement would apply to any other prediction of cyclic-N_3 properties that is sensitive to the vibrational wavefunctions, for example the photoelectron spectrum. In the final stages of publication of this review, two reports were brought to our attention, one recently published and another currently in preparation, that present high-level *ab initio* calculations of the ionization threshold and the photoelectron spectrum of N_3 as well as the potential energy surface of cyclic-N_3^+ that take into account GPE [44, 45].

There is accumulating experimental evidence concerning the detection of the cyclic isomer of N_3 by photolysis of a suitable precursor. In 2003, Hansen and Wodtke [7] were the first to report a bimodal translational energy distribution for Cl resulting from photolysis of ClN_3 at 235 nm, using velocity map imaging (VMI). Based on the kinetic energy of the fragments, they assigned the fast component to production of Cl along with linear-N_3 and they suggested that the slow component energetics make it very likely to originate from Cl + cyclic-N_3. In support of this suggestion the anisotropy they recorded for the slow and fast channel is significantly different ($\beta = 0.4$ vs. 1.7), indicating different dissociation dynamics. Besides cyclic-N_3, and in the absence of other energetically accessible N_3 electronic states at 235 nm, other possible explanations for the slow Cl could be highly vibrationally excited linear-N_3 or an alternative three-body dissociation mechanism for ClN_3 producing Cl, N and N_2.

The second explanation was excluded when photofragmentation translational spectroscopy experiments [9, 10] of ClN_3 photolysis at 248 nm detected slow and fast N_3 fragments directly. The detected N_3 is momentum-matched by Cl fragments, however a portion of slow Cl does not have a slow N_3 counterfragment. That was attributed to dissociation of N_3 into $N(^2D) + N_2$ [9]. The slow N_3 was termed the 'High Energy Form' of N_3 or HEF-N_3.

HEF-N_3 was also observed in a recent H-tagging experiment studying photolysis of HN_3 [11]. A slow H (corresponding to HEF-N_3) production threshold was observed at 5.6 eV HN_3 photolysis energy, coincident with predictions of a high-level *ab initio* calculation for the ring-closing threshold of HN_3 on the S_1 potential energy surface. Velocity map imaging experiments [12] show that HEF-N_3 production exhibits a similar production threshold at 4.83 ± 0.17 eV ClN_3 photolysis energy. However, high-level *ab initio* calculations on the much larger ClN_3, similar to those carried out for HN_3, are difficult to perform, time-consuming and have as yet not been reported. It is worth noting however in passing that the accessible internal energy of HEF-N_3 produced in the 4.83 eV photolysis of ClN_3 is close to the calculated [14] isomerization threshold of cyclic to linear-N_3.

In addition to neutral N_3, both azide anion and cation have been studied extensively. Initial conflicting estimates [38, 46, 47] of the N_3 ionization energy were resolved by photoelectron spectroscopy (PES) experiments [25] that determined the ionization potential to be 11.06 ± 0.01 eV. This value was confirmed by later CID experiments [48] on N_3^+ and more recently by synchrotron ionization photofragment translational spectroscopy measurements on ClN_3 248 nm photolysis products [8]. These latter experiments also determined a photoionization threshold for HEF-N_3 which is 0.4–0.5 eV lower than that of linear-N_3. This observation is in good agreement with an estimate (10.58 eV) of the cyclic-N_3 ionization threshold one obtains by combining calculated [49] energetics of cyclic-N_3^+ cation with the linear-N_3 ionization threshold. High-level *ab initio* work on the photoelectron spectrum of cyclic-N_3 [45] calculated a value of 10.595 eV for the ionization threshold of cyclic-N_3 which also agrees well with the experimental threshold obtained for HEF-N_3.

Ionization of linear-N_3 leads to the $N_3^+(X^3\Sigma_g^-)$ ground state which was calculated by Dyke and coworkers to have $C_{\infty v}$ symmetry. Cai [50] calculated low-lying $C_{\infty v}$ states of N_3^+ ($X^3\Sigma_g^-$(0 eV), $a^1\Delta$ (1.45 eV), $A^3\Pi_u$ (5.2 eV), $1^1\Pi_u$ (6.8 eV) at the MRSDCI level of theory. Discrete $A^3\Pi_u \leftarrow X^3\Sigma_g^-$ absorption of N_3^+ has been observed [51] between 245 and 283 nm by detecting N^+ photofragments and confirmed that $N_3^+X^3\Sigma_g^-$ has a linear centrosymmetric geometry. Cyclic minima of the N_3^+ potential energy surface have been proposed before [52, 53]. Byun *et al.* [23] calculated (using RHF) a cyclic D_{3h} global minimum on the singlet surface of N_3^+ with energy 11 kcal lower than the linear symmetrical open chain structure. More recently, CASSCF and MRCI *ab initio* calculations of N_3^+ show linear ($X^3\Sigma_g^-$, $A^3\Pi_u$, $a^1\Delta_g$, $b^1\Sigma_g^+$), bent ($B^3\Sigma_u^-, c^1\Sigma_u^-$) and cyclic($a'^1A_1$) electronic states [49].

In conclusion, halogen azide photolysis appears, at present, to be the most promising pathway for the formation of cyclic-N_3. However, although the structures and properties of all halogen azides have been studied [54–57], there is much to be done before we understand the ring-closing mechanism that can lead to the cyclic azide isomer.

3. Tetranitrogen

Although weakly bound, the $(N_2)_2$ van der Waals complex has been reported and studied previously [58–61]. The most widely studied, both theoretically [62–69] and experimentally [64, 65, 69–73], is N_4^+, a linear centrosymmetric ion with ${}^2\Sigma_u^+$ ground state, known to form in nitrogen discharges [74, 75]. The dissociation dynamics of N_4^+ have also been investigated [76–79].

For neutral N_4, there have been numerous theoretical studies and very few experimental reports with different synthetic approaches. In order to produce N_4, Zheng *et al.* [80] tried the approach of N_2 discharge quenched on a He-cooled window. They actually observed an IR active frequency at $936\,cm^{-1}$ (shifted to $900\,cm^{-1}$ for ${}^{15}N$ substitution), and attributed this to T_dN_4; however, the isotopic shift was far from what was later predicted by high-level theoretical studies [81–85].

Cacace *et al.* [5, 86], using another approach, observed neutral N_4 starting from the known N_4^+ cation and using neutralization–reionization mass spectrometry (NRMS) to go from the cation to the neutral and back to the cation for spectrometric detection. By observing only ${}^{14}N_2$ and ${}^{15}N_2$ mass peaks when using ${}^{14}N_2/{}^{15}N_2$ mixes to do the experiment, they established that what they observe cannot be T_dN_4 (which would also produce ${}^{15}N{}^{14}N$). Instead they assigned their observations to the presence of a weakly bound open-chain N_4 complex with lifetime exceeding 1 µs. Nguyen *et al.* [87], also using NRMS but under slightly different conditions, could not reproduce Cacace's N_4 neutral results although they observed N_4^+. Based on their theoretical calculations, they postulated that what Cacace *et al.* had observed was azidonitrene (N_3–N), coming from neutralization of the N_4^+ *doublet* state, however its small re-ionization efficiency made its detection difficult and sensitive to experimental conditions. Recently, Rennie and Mayer [88] were able to reproduce Cacace's results, again using NRMS, and aided by high-level *ab initio* calculations they claim that the observed N_4 originates from a *quartet* N_4^+ excited state. They also examine the neutralization energetics and conclude that the observed neutral cannot be the weakly bound $(N_2)_2$. In another approach, Barber *et al.* [89] reported their results from Xe UV irradiation in the presence of ${}^{14}N_2$ and ${}^{15}N_2$ molecules. They observe the formation of ${}^{14}N{}^{15}N$ which they attribute to the formation of tetrahedral or rectangular N_4 intermediates.

Despite growing experimental results, the vast majority of work on N_4 is still theoretical and concerns the tetrahedral form (figure 2a), already examined with low-level methods in the 1970s and 1980s [52, 90–96]. More recently Francl and Chesick reported *ab initio* calculations [97] at the MP4SDQ/DPZ level of theory and determined T_dN_4 as a potential surface minimum with a bond length of 1.419 Å and energy $195\,kcal\,mol^{-1}$ above the energy of two N_2 molecules, with a $75\,kcal\,mol^{-1}$ barrier to dissociation over a D_{2d} transition state. Lee and Rice [98] at the CCSD(T)/DZP level of theory report T_dN_4 to be $186\,kcal\,mol^{-1}$ above two N_2 molecules with a bond length of 1.472 Å. They calculated a transition state of C_s symmetry, $61\,kcal\,mol^{-1}$ (at MRCI + Q level of theory) above T_dN_4. Lauderdale, Stanton and Bartlett [99] at the SCF level of theory calculated geometries and vibrational frequencies and also found a similar C_s transition state that leads to a C_{2v} minimum on the N_4 surface and not to two N_2 molecules. However, at the MBPT2 level of theory, the C_s transition state becomes a saddle point (two imaginary frequencies), and the C_{2v} minimum becomes the transition

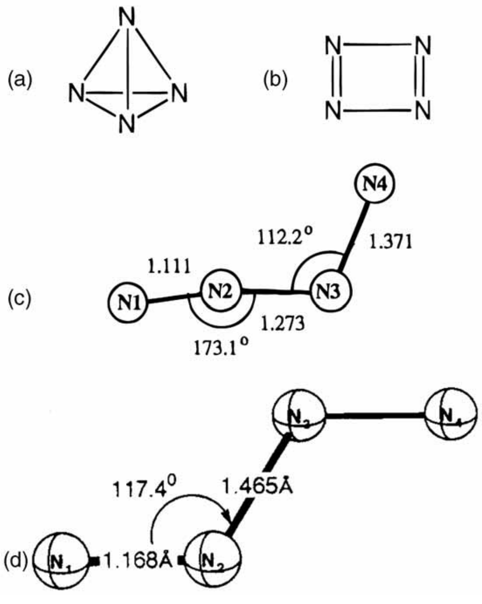

Figure 2. N_4 isomer structures, predicted to be minima on the N_4 singlet and triplet surfaces: (a) tetraazahedrane (T_dN_4); (b) tetrazete; (c) $C_{2h}N_4$; (d) C_sN_4. (*Structures (a), (b) and (d) were obtained from Ref. [101] with permission from the American Chemical Society and (c) from Ref. [103] with permission from Wiley-VCH Verlag.*)

state (one imaginary frequency). In face of that, they proceeded with geometry optimization of the C_{2v} structure and located a different C_s minimum. Dunn and Morokuma [100] resolved the issue at the CASSCF/MRCI level of theory and determined that dissociation of T_dN_4 to two N_2 proceeds over a transition state of C_s symmetry with a barrier of 63 kcal mol^{-1}. One year later, Korkin *et al.* [101] re-examined the issue and calculated a C_s transition state located 78.9 kcal mol^{-1} (at the MBPT2 level of theory) or 58.6 kcal mol^{-1} (at the QCI theory level) above tetrahedral N_4. They proposed a dissociation mechanism in which this transition state does not dissociate directly to two N_2 molecules but leads to a C_{2v} (at the HF level) or a C_s intermediate (at the MBPT2 level) which has a low barrier to two N_2 molecule production. In addition to the singlet T_dN_4, Lee and Rice find (at the SCF, MP2 and CPF levels of theory) a $^3A''$ state which lies 13 ± 4kcal mol^{-1} above the singlet T_dN_4 and has C_s symmetry. Yarkony [102] investigated the spin-forbidden decay of tetrahedral-N_4 via the crossing between $^1A'$ and $^3A''$ and found a barrier of 28 kcal mol^{-1} for this process.

A D_{2h} tetrazete isomer of N_4 (figure 2b) is found to lie 12 kcal mol^{-1} higher than T_dN_4 at the MBPT(2) levels of theory [99], while Glukovtsev and Schleyer's QCISD(T)/6-311+G* calculations [103] find it to be lower by 3 kcal mol^{-1}. Korkin *et al.* [101] find a crossing point at 14 kcal mol^{-1} between the tetrazete and two N_2 surfaces at the QCISD(T) theory level. Also, they estimate an interconversion barrier between the T_d to D_{2h} forms of 70 kcal mol^{-1} above the T_dN_4 minimum.

High-level calculations find that the most stable N_4 isomer is an open chain, however there is disagreement with respect to its structure [101, 103–105]. At the QCISD(T) level of theory [103] the open chain is a triplet (^3B_u) structure of C_{2h} symmetry (figure 2c) and is 157.5 kcal mol^{-1} above two N_2 molecules and 24.1 and 21.2 kcal mol^{-1} below T_dN_4 and $D_{2h}N_4$, respectively. At the G2 level of theory [104], the open chain structure is 14.8 kcal mol^{-1} lower than tetrazete (D_{2h}) and 12.1 kcal lower than T_dN_4. Also at the QCISD(T) level of theory, Korkin *et al.* [101] have shown that the C_{2h} triplet (^3B_u) minimum of N_4 is 41.5 kcal mol^{-1} higher in energy than a (unstable) singlet with the same geometry. They found another triplet state, of C_s symmetry (figure 2d), 8.6 kcal mol^{-1} higher than ^3B_u, to be the minimum. Bittererova and coworkers [105] used DFT(B3LYP), CCSD(T) and CASS(12,12) to investigate the triplet potential energy surface of N_4 and agree with Korkin *et al.* that the C_{2h} structure is not a minimum while they find the C_s structure to be a minimum and to lie 13.4 kcal mol^{-1} below T_dN_4. They also determined that a D_{2d} structure, 20.2 kcal mol^{-1} above T_dN_4, is the lowest closed structure triplet of N_4. In agreement with Bittererova *et al.*, Nguyen *et al.* [87] calculated a stable azidonitrene C_s structure with a $^3A''$ ground state, and a barrier of 13.2 kcal mol^{-1} leading to two N_2. Their CCSD(T) and MRCISD+Q level calculations find also a C_s $^1A''$ state 16.5 kcal mol^{-1} above the $^3A''$ state. As mentioned above they use this state to explain the experimental observation of N_4 through NRMS experiments.

In higher excited states, Bittererova *et al.* investigated 11 low-lying excited singlet states [83] of N_4 at the TD-DFT and EOM-CCSD levels of theory and used CASSCF, CASPT2, CASPT3 and MRCI+Q methods to calculate vertical excitation energies for the lowest five. They determined that all five states are of valence character and predicted two weak T_2 symmetry optical transitions at 10.44 and 10.82 eV and a third one at 10.89 eV with an oscillator strength one order of magnitude higher. They also looked into the rectangular (D_{2h}) excited states of N_4 [106]. This study involved EOM-CCSD calculations of vertical excitation energies and oscillator strengths for the lowest 20 singlet states of D_{2h} N_4. Special attention was paid to the geometry of the first excited state, $^1B_{3u}$, in the hope that those calculations would be helpful in LIF detection of rectangular N_4. In addition, N_4 (D_{2h}) dissociation was investigated at the CASSCF level of theory revealing a new C_{2v} transition state and an effective dissociation barrier of 6.5 kcal mol^{-1}.

Recently, Evangelisti [107] carried out a CAS-SCF energy study of an N_4 cluster for a fixed value of the system volume (constrained to a D_{2d} symmetry) and showed that for small system volume (high density) the energy of the T_dN_4 minimum lies lower than the separated two N_2 molecules minimum. This suggests that, at high densities, tetrahedral-N_4 might be more stable than two N_2 molecules, with a pressure-driven phase transition between the two forms occurring at a very high pressure.

4. Pentanitrogen

Although pentanitrogen ions were detected only recently, pentazole aromatic derivatives were first synthesized by Huisgen and Ugi [108] at low temperatures and are reasonably well characterized today [109–114].

N_5^+ was synthesized by Christe and coworkers [4, 115], in the form of $N_5^+AsF_6^-$ salt and characterized by low-temperature Raman and ^{14}N and ^{15}N NMR and crystallography [116]. The white powder salt is marginally stable at room temperatures but can be stored for weeks at −78°C. More N_5^+ salts were synthesized recently [117]. Geometry optimizations [118–127] on N_5^+ differ slightly in the reported numbers depending on the method employed, but in general they agree that N_5^+ is an open symmetric V-shaped chain with shorter terminal nitrogen bonds and longer inner nitrogen bonds (figure 3a). Experimentally measured [4, 128] vibrational frequencies of N_5^+ cation are shown in table 1, along with the vibrational frequencies measured for other N_n species.

Shortly after the discovery of the N_5^+ cation, Nguyen and Ha [120] published CCSD(T) and B3LYP calculations showing that the ground state of N_5^+ is the closed shell singlet, with the triplet N_5^+ being $6.2\,\mathrm{kcal\,mol^{-1}}$ higher (at the CCSD(T) level of theory). The 0 K heat of formation for singlet N_5^+ was calculated at $351.3 \pm 3.6\,\mathrm{kcal\,mol^{-1}}$ and the ionization energy of N_5 at $7.4 \pm 0.2\,\mathrm{eV}$. The ground state N_5^+ is $10.5\,\mathrm{kcal\,mol^{-1}}$ lower in energy than the triplet $N_3^+ + N_2$ dissociation products and $43.3\,\mathrm{kcal\,mol^{-1}}$ lower than the singlet $N_3^+ + N_2$ products. The triplet N_5^+ is a weakly bound (4.3 kcal binding energy) complex of triplet N_5^+ and N_2 [4, 120, 121].

Predicted neutral N_5 structures are shown in figure 3b. The most stable form (N_5–1) is predicted to be a weak N_3–N_2 complex with 1.2 kcal binding energy [121]. An open chain pentazene radical (figure 3b, 2) [121] (40.6 kcal above the N_5 complex) and a C_{2v} open structure (figure 3b, 3) [121, 127] ($56.16\,\mathrm{kcal\,mol^{-1}}$ above $N_2 + N_3$ limit) were also predicted. Heats of formation were also evaluated for 0 K at $179 \pm 2.4\,\mathrm{kcal\,mol^{-1}}$ [121]. All studies agree that the radical's potential well is very shallow rendering it rather unstable. Manaa [129] optimized the closed ring geometry of N_5 at the MP2, B3LYP and QCISD levels of theory. MP2 optimization tended to open the ring, and second derivative calculations at all levels proved that the optimized structure is in fact a first-order saddle point leading through further decomposition to N_2.

As mentioned above, pentazole derivatives have existed for half a century. However, only recently was N_5^- anion detected, by Vij *et al.* [6] in a mass spectrometry study of a pentazole derivative: 4-hydroxy-phenylpentazole. Through negative ion ESI and CID at low collision energies, they observed only N_2 and N_3^- production and decomposition of the azole ring. However, at high collision energies they observed the mass corresponding to N_5^-. Shortly after this report, the N_5^- anion was also detected in a laser desorption ionization study of solid p-dimethylaminophenylpentazole [130]. In addition, the synthesis of HN_5 and ZnN_5 salt was reported [131] as evidence for the existence of N_5^- in solutions; however those results could not be reproduced [132].

N_5^- covalently bound anion has been shown by theory to possess a highly symmetric D_{5h} cyclic structure (figure 3c, 13) with 1.33–1.34 Å bonds and strong aromatic character [3, 121, 133–135]. Although it is $15.5\,\mathrm{kcal\,mol^{-1}}$ less stable than $N_3^- + N_2$, dissociation must go over a $26.3\,\mathrm{kcal\,mol^{-1}}$ barrier [127] which makes N_5^- a stable anion. However, G3 level energy calculations [121] show that the covalently bound anion is $16.7\,\mathrm{kcal\,mol^{-1}}$ less stable than a weakly bound $N_3^- - N_2$ complex (figure 3c, 12). In the same work [121], structures 14 and 15 of figure 3c are less stable than structure 2. The heat of formation of N_5^- (at 0 K) is calculated to be $\Delta H_{f,0} = 62.3\,\mathrm{kcal\,mol^{-1}}$ [128]. Its electron affinity is calculated to be 5.06 eV,

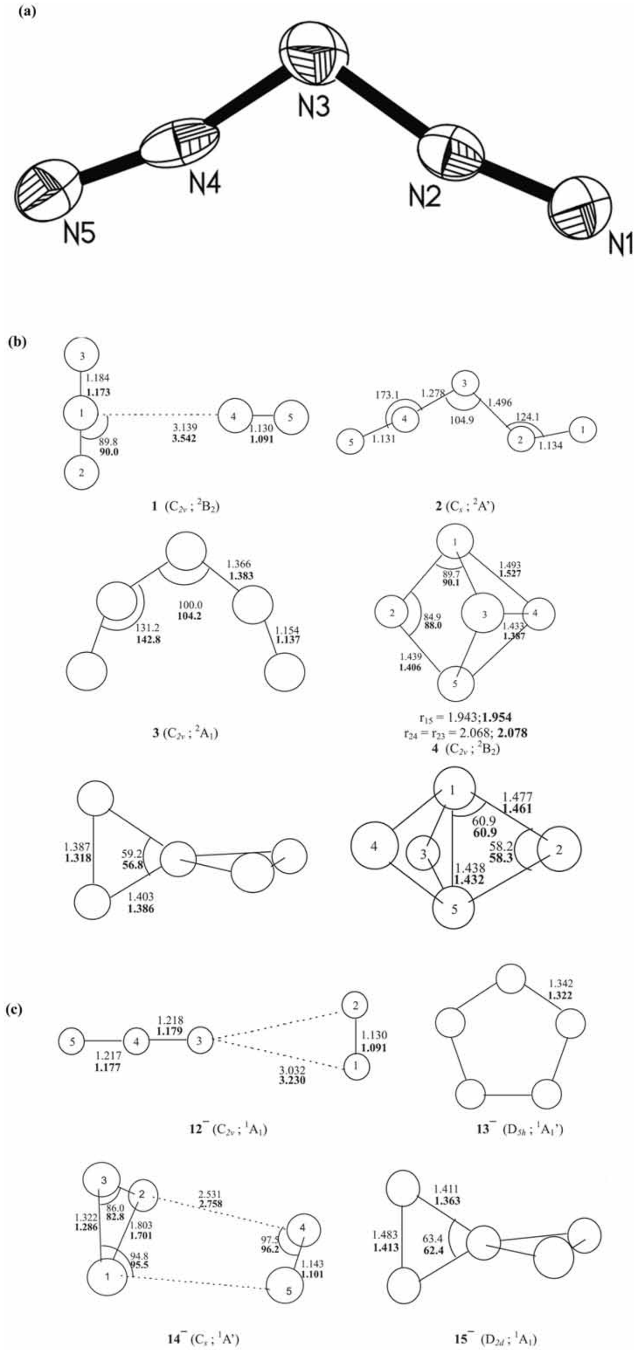

Figure 3. Structures for pentanitrogen species: (a) crystallographic structure of experimentally detected N_5^+ cation; (b) predicted structures of the N_5 neutral; (c) predicted structures of the N_5^- anion. Geometry optimization for the structures in (b) and (c) was done with MP2 (top number) and B3LYP (bottom number). (*Structure (a) is reprinted from Ref. [116] with permission from the American Chemical Society. Structures (b) and (c) are reprinted from Ref. [121] with permission from Elsevier*).

Table 1. Experimentally measured [4, 127] vibrational frequencies of N_2, linear-N_3, N_3^- and N_5^+ species.

Mode number	Symmetry	Description	Frequency (cm^{-1})
N_2			
1	σ_g	Stretch	2359
Linear-N_3			
1	σ_g	Symm. stretch	1320
2	σ_u	Assym. stretch	1645
3	π	Bend	457
N_3^-			
1	σ_g	Symm. stretch	1335
2	σ_u	Assym. stretch	1986
3	π	Bend	626
N_5^+			
1	b_2	NN str	2267
2	a_1	NN str	2206
3	b_2	NN str	1064
4	a_1	NN str	870
5	a_1	Bend	671
6	b_2	Bend	414
7	a_2	Out of plane bend	474
8	b_1	Bend	421
9	a_1	Bend	204

much higher than the electron affinity of N_3^- [17]. Nguyen [17] has calculated excited states of N_5^- at the CASPT2 level. The first excited state they found is a $^1E_1''$ at 6.62 eV, which is unstable with respect to Jahn–Teller distortions.

5. Hexanitrogen

There have been experimental reports in the literature that could be explained by N_6 formation. Hayon and Simic [136] suggested that N_2 generation through a second-order decay of N_3 radicals in a pulsed radiolysis study of the $N_3^- + OH \rightarrow N_3 + OH^-$ reaction could be due to the formation of N_6. Vogler *et al.* [137] reported an absorption peak at 380 nm after flash photolysis of cis-[Pt$(N_3)_2(PPh_3)_2$] in ethanol at 77 K which disappeared at higher temperatures and was attributed to the formation of the N_6 radical. Workentin *et al.* [138, 139] reported N_6^-anion radical formation from N_3 radical and N_3^- reaction in acetonitrile, based on a broad featureless absorption around 700 nm and an IR peak at 1842 cm^{-1} combined with *ab initio* calculations. The observed N_6^- was in fact a weakly bound complex of N_3 and N_3^-.

A lot of theoretical work [99, 140–146] on N_6 has pointed out that the shape of the potential energy surface depends strongly on the calculation method applied. Ha and Nguyen [147] have shown that the benzene analogue (hexa-azabenzene) is not an energy minimum for N_6, whereas they have also calculated vibrational frequencies for prismane (figure 4, structure 2) and a number of other isomers that have been identified as stable minima. From the reported isomers only prismane, dewarbenzene (figure 4, structure 3), benzvalene (figure 4, structure 4) and D_2 twisted boat (figure 4, structure 5)

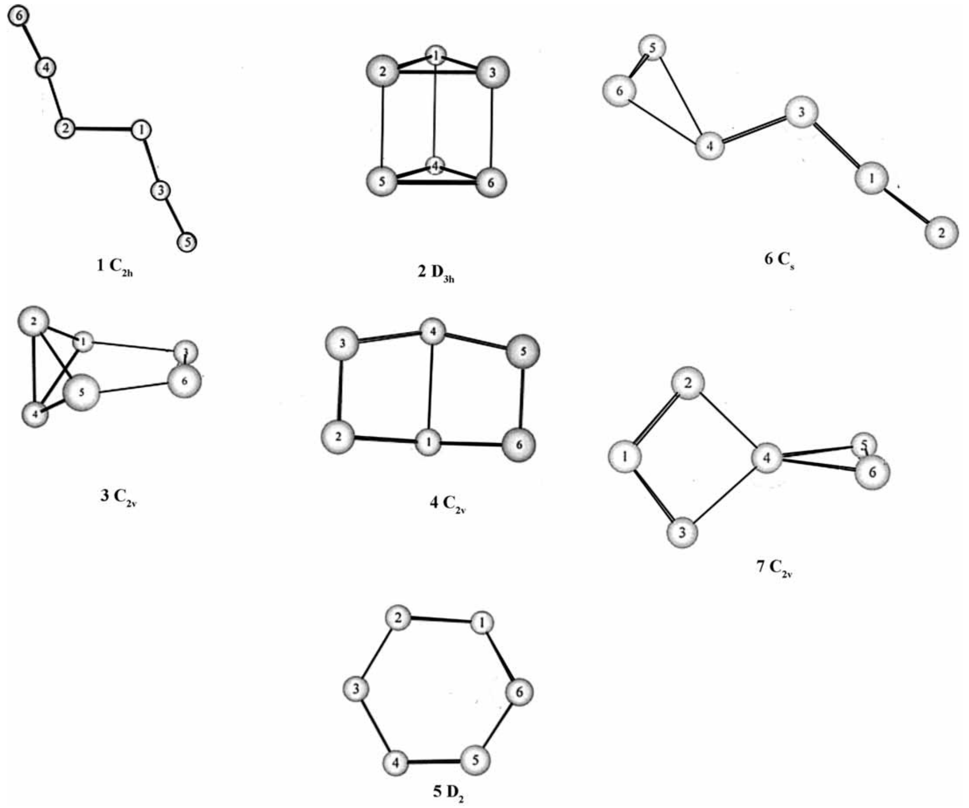

Figure 4. Some of the predicted isomers of N_6. (*Reprinted from ref. [154] with permission from the American Chemical Society*.)

are undoubtedly predicted to be minima in all of HF [148, 149], MP2 [148, 149] and DFT [150] levels of theory.

The open chain diazide (figure 4, structure 1) is considered to be the most stable N_6 isomer [3, 151], despite being an unstable state in the MP2/6-31G(d) level of theory [148] because at this level the imaginary vibrational frequency observed is so small ($40i\,\mathrm{cm}^{-1}$) that this geometry can be regarded as very close to a minimum. Klapotke [152] reinvestigated the issue at the HF, MP2 and CCD levels of theory and found the diazide chain to be a minimum at all levels of theory (all real vibrational frequencies). The isomer's decomposition and synthesis pathway has been well established [127, 153, 154]. It is known that the cleavage to N_2 goes over a 18 kcal barrier [127, 153, 155].

Li and Liu [155], in calculations at the B3LYP/6-311G(d) and CCSD/6-311G(d)//B3LYP/6-311G(d) levels of theory, explored transition states for isomerization and dissociation of the stable N_6 isomers. They concluded that all isomers except prismane have relatively low isomerization and dissociation barriers, so prismane was suggested as the most likely candidate for detection.

6. Heptanitrogen

For heptanitrogen, most calculations have been done on ions; however, it appears that for all charged states, the stable isomer is a W-shaped structure. Michels *et al.* [156] reported N_7^- W-shaped geometry in a study of azidamines. Law *et al.* [157] examined four N_7^+ cations and seven N_7^- anions at the G3 level of theory and report heats of formation and structures. The most stable cation they find has a W shape, while the most stable anion is a weak $N_2 \cdots N_5^-$complex. Liu *et al.* [158] studied nine N_7 isomers at the HF, MP2 and B3LYP theory level. They calculated geometries, energies and harmonic frequencies and found that the most stable isomer of N_7^+ has a C_{2v} symmetry and for N_7^- also C_2 or C_{2v} symmetry similar to the W-shaped structure of the ions. Finally, Zhao and Li [159] studied structures of two new and three known N_7 isomers with MP2 and B3LYP and concluded that the most stable isomer has a W shape.

In neutral N_7, Li *et al.* [160] studied seven N_7 isomers at the UHF, MP2 and B3LYP levels of theory and found five of them to be minima, with a linear chain being the most stable. Wang *et al.* [161] reported calculations at the UHF, MP2 and B3LYP levels of theory on five more isomers finding a linear, W-shaped isomer to be the most stable. The same group [162] however performed Gaussian-3 calculations on N_7 isomers and identified a structure with pentazole ring and N_2 side chain as the most stable. This suggests that further theoretical investigation into N_7 structures is necessary and might reveal even more stable geometries.

7. Octanitrogen

There is no experimental evidence yet for the production of any N_8 isomer. Trinquier, Malrieu and Dudley [91] showed that octaazacubane (cubic N_8, figure 5a) is higher in energy than two N_4 molecules with a pseudopotential SCF method. Engelke and Stine [163] optimized the N_8 geometry at the SCF/STO-3G,4-31G,4-31G* level and found a minimum for each basis set, based on vibrational frequency calculations. No electron correlations were taken into account. Lauderdale *et al.* [99] computed the N_8 geometry at the SCF and MBPT(2) level and while their SCF results compare well with Engelke and Stine, they find that including electron correlation has large effects on the geometry and vibrational frequencies. Symmetry arguments suggest that cubic N_8 should have a significant barrier to decomposition.

Evangelisti [164] published an *ab initio* study of the charged systems N_5^+, N_3^- and N_5^-, and investigated the stability of the ionic clusters $N_5^+N_3^-$, $N_5^+N_5^-$ and $(N_5^+N_5^-)_2$. The ionic cluster $N_5^+N_5^-$ has a local minimum in a C_{2v} geometry, and is stable with respect to charge transfer. Similar results are obtained for $(N_5^+N_5^-)_2$ in C_{2h} symmetry, while no true minimum was found for the $N_5^+N_3^-$ form.

Leininger *et al.* [165], again with *ab initio* molecular electronic structure methods, examined three isomers of N_8: octaazacubane (O_h symmetry, figure 5a), a D_{2d} structure analogous to cyclooctatetraene (octaazacyclooctatetraene, figure 5c), and a D_{2h} planar bicyclic form, aza-pentalene (figure 5b). They optimized geometries using DZP basis sets and SCF, MP2, CISD and CCSD methods. Harmonic vibrational frequencies and infrared intensities were obtained at the SCF and MP2 levels of theory.

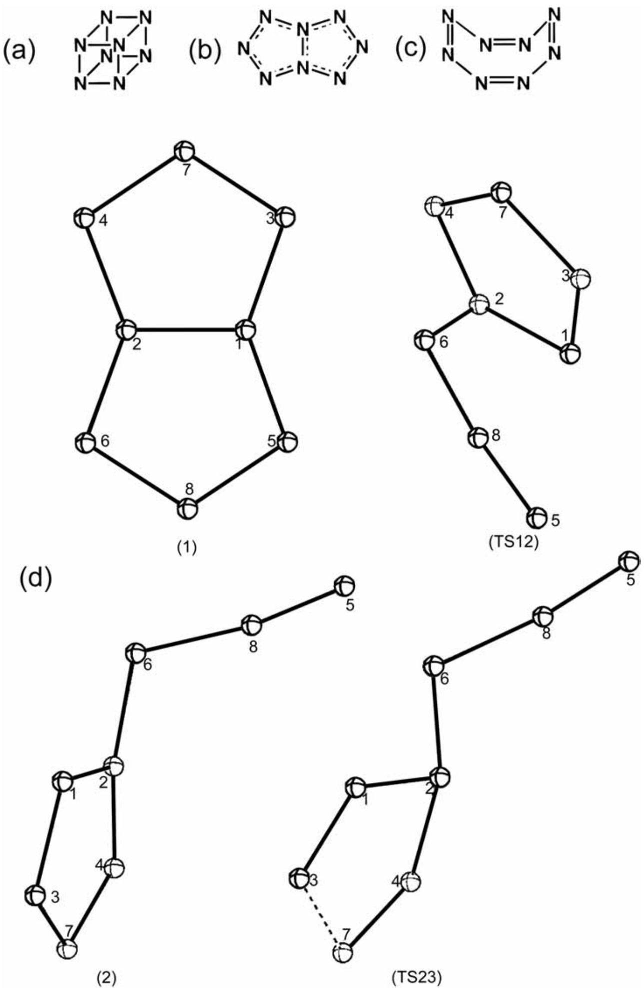

Figure 5. Some stable N_8 isomers: (a) octaazacubane; (b) azapentalene; (c) cyclooctatetraene; (d) azapentalene(1) decomposition, first to azopentazole(2) through TS12 and from azopentazole to N_2 through TS23. (*Structures (a)–(c) are reprinted from ref. [3] with permission from the American Chemical Society. Figure (d) is reprinted from ref. [169] with permission from Wiley.*)

Their vibrational analysis indicates that all three structures represent potential energy minima with the aza-pentalene bicyclic structure (figure 5b) being the absolute minimum, 225 kcal mol^{-1} above four N_2 molecules. Cubic N_8 is 198 kcal mol^{-1}, while octaazacyclooctatetraene (figure 5c) is only 35 kcal mol^{-1} higher than azapentalene. The same results are confirmed by Gorini and coworkers [166]. Gagliardi *et al.* [167] investigated 10 N_8 isomers at the HF and MP2 levels of theory and confirmed that the bicyclic azapentalene form is the most stable.

Tian *et al.* [168] found minima for another two structures with single N–N bonds, one of D_{2h} and one of C_{2v} symmetry. Although these structures are more stable than octaazacubane by 47 and 72 kcal mol^{-1} respectively, they are still less stable than bicyclic-N_8. Dixon *et al.* [128] used *ab initio* methods at the CCSD(T) level of theory to calculate accurate heats of formation for N_3, N_3^-, N_5^+ and N_5^- and proposed that $N_3^-N_5^+$ and $N_5^-N_5^+$ salts will be unstable, which for the latter case is consistent with

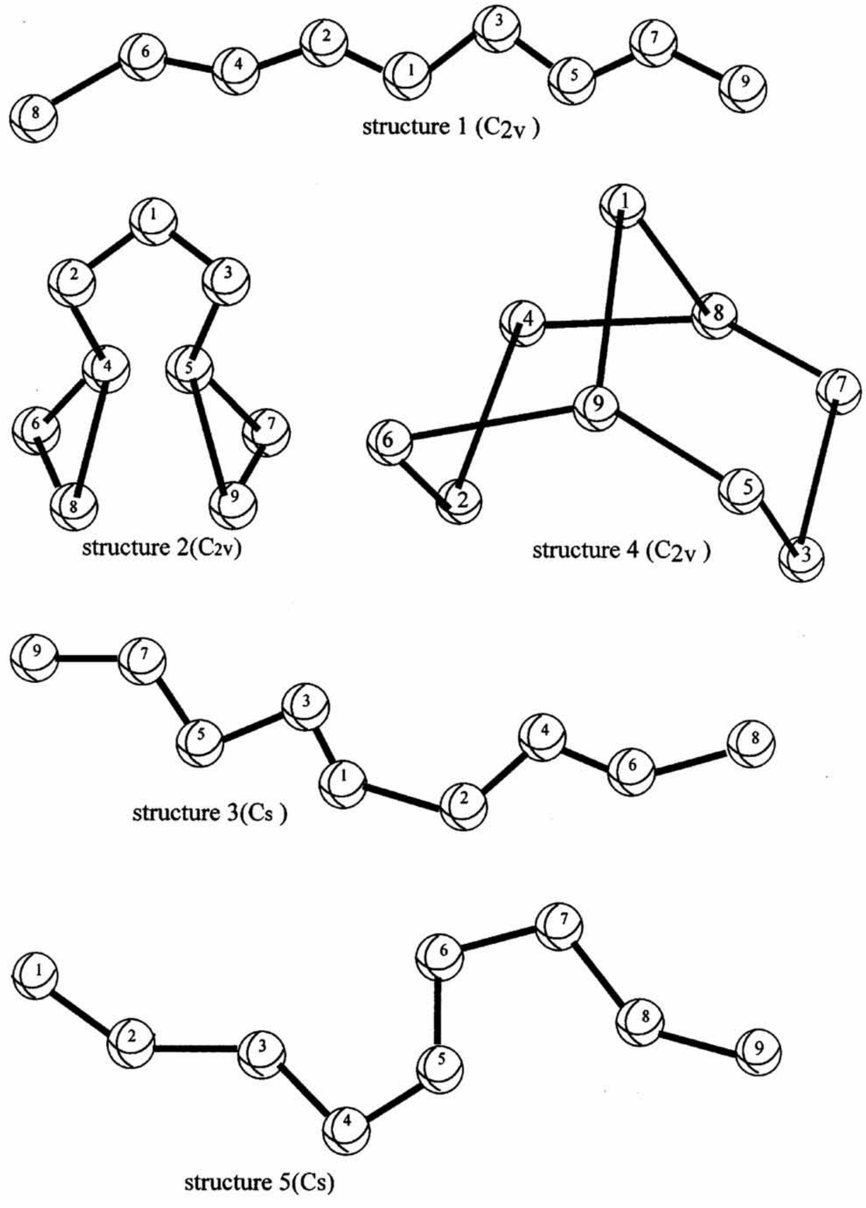

Figure 6. Some structures of N_9 explored by theoretical calculations. Structure 1 proved to be the most stable structure for N_9 and N_9^+, while structure 3 is the most stable for N_9^-. (*Reprinted from ref. [171] with permission from Springer.*)

experimental observation. Gagliardi *et al.* [122] explored the formation of N_8 as a salt of N_5^+ and N_3^- at the CASPT2 level of theory and concluded that it is not possible.

Evangelisti and coworkers [169] explored the dissociation of the stable azapentalene bicyclic-N_8 isomer to four N_2 molecules at the CASSCF and CASPT2 levels of theory. They find that it proceeds through opening one of the rings to form azidopentazole over a $15\,\text{kcal mol}^{-1}$ barrier and then azidopentazole dissociates to four N_2 over a $20\,\text{kcal mol}^{-1}$ barrier (figure 5d). Azidopentazole (figure 5d, 2) is found to be $3\,\text{kcal mol}^{-1}$ more stable than azapentalene (figure 5d, 1). Based on the small barriers observed, they conclude N_8 is not suitable as a HEDM, however it could be observed experimentally. Later work by Nguyen [135] and Glukhovtsev [3] established azidopentazole (figure 5d, 2) as the most stable N_8 isomer. Schmidt *et al.* [170], in a study of 'cubic' fuels investigated the dissociation of cubic N_8 at the HF and MP2 levels and proposed a mechanism involving a small dissociation barrier ($15\,\text{kcal mol}^{-1}$).

8. Polynitrogen compounds with more than eight nitrogens

8.1 *N_9*

Li, Wang and Xu [171] used HF, MP2 and DFT methods to calculate stable structures for N_9, N_9^+ and N_9^-. They determined four neutral N_9 minima, four N_9^- minima and one N_9^+ minimum (figure 6) and calculated structures, energies and vibrational frequencies. The most stable N_9 is of C_{2v} symmetry (figure 6, structure 1) and the most stable N_9^- is shown in figure 6, structure 3 (C_s symmetry). Only the C_{2v} form of N_9^+ (figure 6 structure 1), is stable. Thompson and Strout [172] calculated the barriers for dissociation of N_9 and N_{11} at the HF, MP2 and CCSD(T) levels of theory. They conclude that the barriers are too low to characterize them as HEDMs. However the dissociation barrier heights (roughly 10–30 kcal mol^{-1}) are probably large enough to recommend attempts at observing those molecules.

8.2 *N_{10}*

In a search for minima on the N_{10} surface, Ren *et al.* [173] investigated nine structures without double bonds and found all nine to be minima at RHF, eight to be minima at B3LYP and seven to be minima at the MP2 level of theory. Wang [174] used DFT(B3LYP) and MP2 methods to find 11 minima, with barriers on the order of $10\,\text{kcal mol}^{-1}$ for dissociation or isomerization and they predict that these species will be kinetically unstable. Similarly [152], MP2 level of theory predicts an activation barrier of 9.3 kcal and CCSD(T) level of theory a barrier of $5.2\,\text{kcal mol}^{-1}$ for the dissociation of N_{10} to $N_8 + N_2$. The products lie 53.6 kcal and 45.2 kcal lower at the MP2 and CCSD(T) levels, respectively [152]. Manaa [129] studied the two N_5 ring structure of N_{10} at the HF, MP2, B3LYP and QCISD levels of theory, finding a saddle point for the planar form (rings on the same plane) and a local minimum for the perpendicular (the two rings on two planes perpendicular to each other) form, separated by 3–6 kcal mol^{-1} (depending on the computational method used). He calculated the

N_5–N_5 bond energy at 93 (QCISD) and 84 (B3LYP) kcal mol^{-1}, indicating a strong bond and proposed that N_{10} could be a good building block for N_{60}. However, as the N_5 ring is unstable, dissociation to two N_5 radicals proceeds further to N_2 production, giving out 286(QCISD), 270(MP2) or 224(B3LYP) kcal mol^{-1} in total. More recently, Zhou *et al.* [175] examined the stabilities of nine N_{10} structures at the G3 level of theory, and found a bowl-like structure with three five-membered rings to be most stable. Given the multitude of structures still to be investigated, one can expect that another geometry will be found to be even more stable than this bowl structure in future work.

8.3 *N₁₁*

Liu *et al.* [176] calculated stable structures for N_{11}^{+} and N_{11}^{-} at the HF, MP2, CCSD(T), B3LYP and B3PW91 levels of theory. A pleasant surprise is that a C_{2v} structure (figure 7a) of a N_5 ring with two N_3 chains is the minimum in N_{11}^{+} instead of an open chain structure. However, an open chain is the minimum for N_{11}^{-} (figure 7b).

8.4 *N₁₂*

Bruney *et al.* [177] examined a variety of N_{12} cage configurations to find the thermodynamically most stable, using the HF, DFT, MP2 and MP4 level of theory.

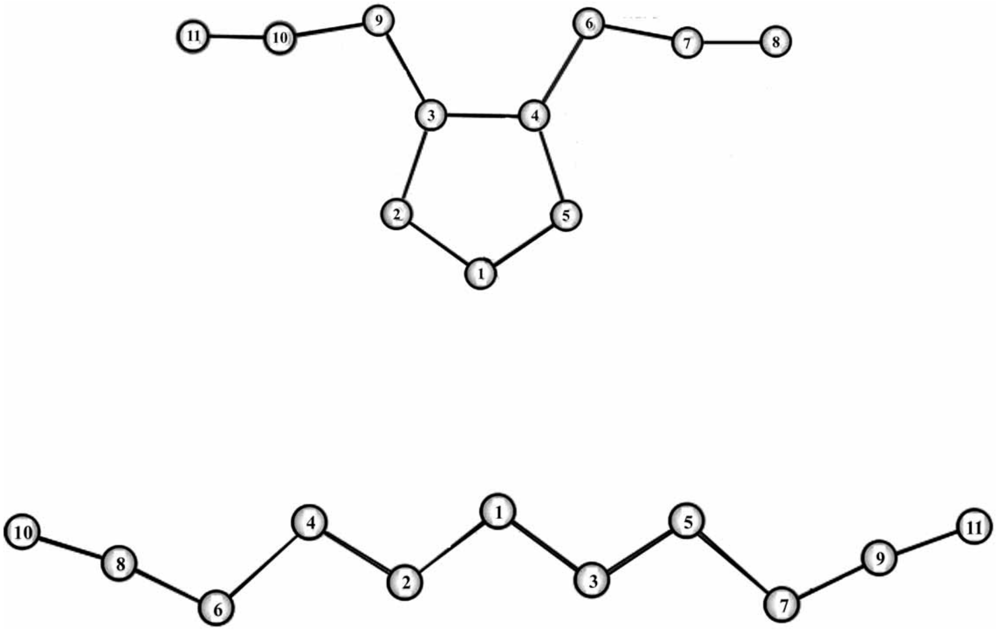

Figure 7. Stable structures for N_{11}^{+} (top) and N_{11}^{-} (bottom). (*Structures reprinted from ref. [176] with permission from Elsevier.*)

They find that N_5 rings have a stabilization effect on the total energy. N_3 triangles also stabilize the cage but to a lesser extent. Strout [178] has similar results for N_{14} and N_{16} cages. Li *et al.* [179] find, in a DFT study of N_{12} isomers, that the most stable isomer consists of two N_5 rings connected by two N atoms, closely followed in energy (4.0 kcal higher) by one N_5 ring with an N_7 chain. Dissociation of all isomers is studied and they find that dissociation barriers are less than 10 kcal mol^{-1}.

8.5 N_{13}–N_{15}

Li and Yin [180] at the HF, B3LYP and MP2 levels of theory, find that the most stable N_{13} isomer consists of two N_5 rings connected with three N atoms. Also, in other structures, those containing an N_5 ring are more stable. One can suggest that for N_5^- and for N_n with $n > 10$ the N_5 rings play an important stabilization role.

Ab initio work by Guan *et al.* [181, 182] on N_{14} structures shows that the structure with two N_5 rings connected with an N_4 chain is most stable. In addition, other isomers with N_5 rings are stabilized with respect to isomers without N_5 rings.

Cheng *et al.* [183] calculated (using DFT, RHF and MP2 methods) six isomers of the N_{15}^- cluster. The most stable conformation is a complex of N_{10} with N_5^-. However, a C_s structure (two N_5 rings connected with an N_5 chain) was found which has 18.2 and 14.2 kcal mol^{-1} barriers for dissociation to N_2 and N_5^- (D_{5h}), respectively, at the B3LYP theory level. The alkane-like N_{15}^- conformation has a barrier to dissociation to $N_3^- + 6N_2$ of 11.2 kcal mol^{-1}. The same group [184] investigated the stability of three ring-containing N_{15}^+ clusters using DFT. They find all three to be minima of the potential energy surface. For all of them, they find low (around 10 kcal mol^{-1}) decomposition barriers. Sturdivant, Nelson and Strout [185] studied N_{18} cages. They observe that pyramidalization of nitrogen leads to N_{18} more than N_5 or N_3 ring formation.

8.6 N_{20}–N_{36}

Bliznyuk, Shen, and Schaefer have shown that N_{20} has a dodecahedral geometry with energy about 50 kcal mol^{-1} above 10 N_2 molecules [186]. Ha *et al.* [187] also studied N_{20} isomers at the MP2 and B3LYP levels of theory and find three minima: an icosahedral cage (figure 8a), a D_{5v} bowl (figure 8b) and a D_5 ring (figure 8c). The cage is calculated to have about 200 kcal mol^{-1} more energy than both the bowl and the ring with the ring being the most stable of the three. Strout's group showed [188] that the icosahedral cage is not the most stable cage using MP4 and DFT calculations. They find a more cylindrical cage (figure 8d, bottom) to have lower energy and they postulate that probably more configurations will be even more stable.

The same group [189] studied various N_{24}, N_{30} and N_{36} cages at the HF, B3LYP and MP4 levels of theory. They find that N_5 ring stabilization, observed for N_{12}, N_{14} and N_{16} cages, now plays the same role as N_3 triangles. The main stabilization comes from the formation of cylindrical structures with hexagonal rings.

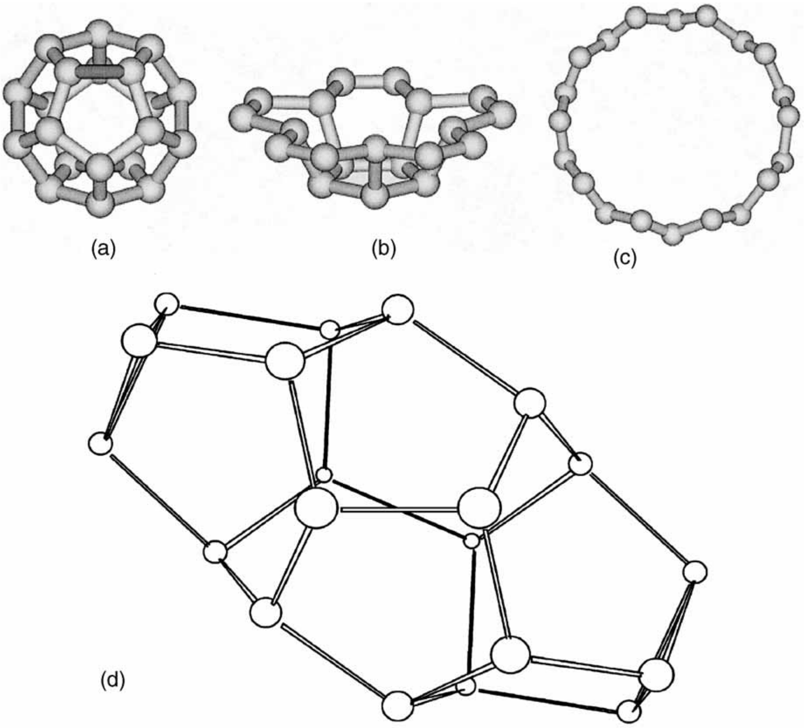

Figure 8. (a)–(c): Stable N_{20} structures The most stable is the 20-membered ring. (d) A cage structure of N_{20}, shown to be more stable than the icosahedral structure (a). (*Structures (a)–(c) are reprinted from ref. [187] with permission from Elsevier. Structure (d) is reprinted from ref. [188] with permission from the American Chemical Society.*)

8.7 N_{60}

Li *et al.* [190] carried out calculations at the HF/STO-3G and HF/6-31G levels reporting I_h and S_6 structures of N_{60} and concluded that S_6 structure, a cage structure with 12 concave N atoms, is more stable based on total energy comparison. Manaa [129] optimized the geometry and calculated IR active vibrational frequencies of N_{60} formation from N_{10} building blocks at the SCF/cc-PVDZ, SCF/6-31G* and AM1 levels of theory. The predicted bond lengths for pentagonal bonds and bonds connecting the pentagons are 1.43(1.441) Å and 1.437(1.482) Å, respectively, at the SCF/cc-PVDZ (AM1) level of theory. The SCF, IR active, low modes are at 251, 483 and 1298 cm^{-1} (608, 701 and 1153 for AM1) and the energy for the reaction $N_{60} \rightarrow 6\ N_{10}$ was calculated at 2430 $\mathrm{kcal\,mol}^{-1}$ at the HF/cc-pVDZ level. He suggests that the molecule could be formed experimentally under extreme pressure conditions. Wang and Zgierski [191] optimized geometry and calculated vibrational frequencies at the HF/6-31G* and B3LYP levels for I_h and S_6 structures. They found that the I_h symmetry structure (figure 9a) is not a minimum (four imaginary frequencies at the HF/6-31G* level and 12 imaginary frequencies at the B3LYP level). Two S_6 structures are minima at the HF

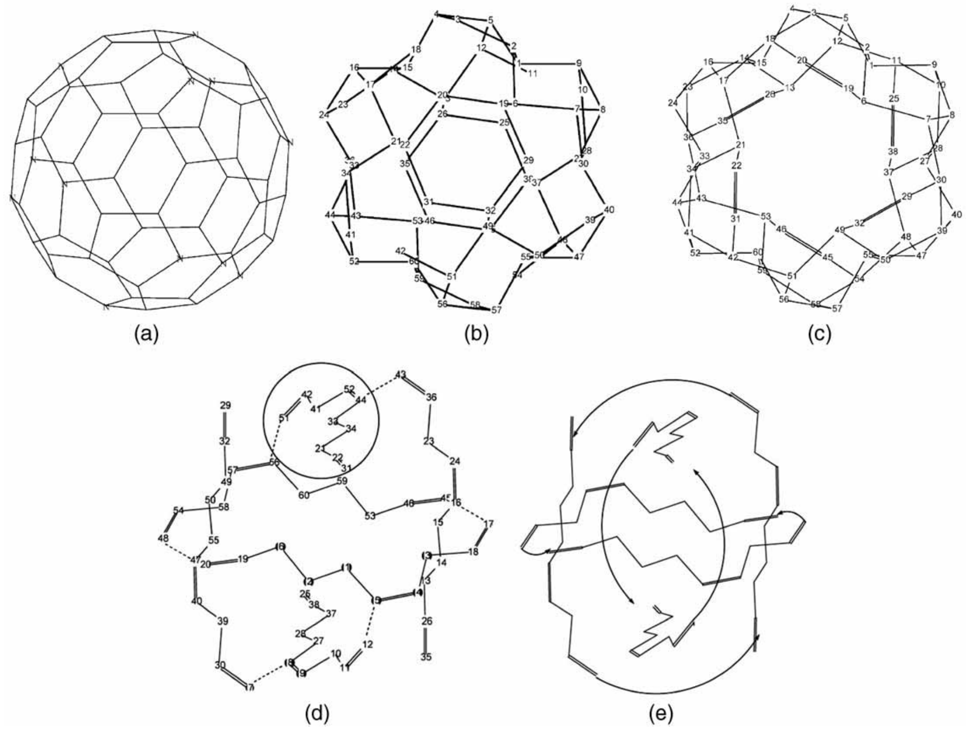

Figure 9. Structures of N_{60} explored for stability at: (a)–(c) the HF/6-31G∗ and (d) the B3LYP levels of theory Vibrational frequency analysis showed that structure (a) is not a minimum in either level. Structures (b) and (c) are minima at the HF level but the B3LYP method converges to structure (d), which can be pictured to be composed of N_{10} chains as shown in (e). (*Structures reprinted from ref. [191] with permission from Elsevier*.)

level, one (figure 9b) 876.5 kcal mol^{-1} and the other (figure 9c) 1220.5 kcal mol^{-1} lower than the I_h structure. They both have 12 concave N atoms and a wide range of bond lengths and angles. At the B3LYP/6-31G* level, they identified one minimum of S_6 symmetry (figure 9d), comprising six open chain N_{10} molecules (figure 9e). This S_6 structure is 96.5 kcal mol^{-1} higher than six N_{10} (open chain) molecules and 1622.9 kcal mol^{-1} higher than 30 N_2 molecules. The difference between HF and B3LYP predictions has been explained in terms of missing dynamic electron correlations in the HF method. More recently Zhou *et al.* [192] reported a stable cage structure of N_{60} in a study of N_{2n} cages and also a stable nanotube-like N_{72} cage, the largest reported so far [193]. It is possible that higher level calculations will give rise to additional large stable N_n structures.

9. Conclusions

We have attempted to describe the progress in theoretical predictions and experimental evidence for the formation of all-nitrogen molecules. For small numbers of N atoms

(≤ 5), available experimental results agree reasonably well with high-level theoretical calculations. However, as the number of N atoms (and the number of possible structures) increases, different theoretical methods give different, often conflicting, results. As more and more powerful computer systems become available and theoretical tools become more and more sophisticated, we expect to see more high-level calculations converging to specific structures for large polynitrogen compounds. In the experimental field, the evidence for new N_3, N_4 and N_5 species in the last few years increases expectations for detection of higher nitrogen allotropes. To answer the question of the title: we are still far from detecting N_{60}, but we are considerably closer than we were a few years ago.

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