

## Searching for Ways to Create Energetic Materials Based on Polynitrogen Compounds (Review)

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Polynitrogen compounds (containing only nitrogen atoms) are promising candidates as energetic materials for rocket engineering. The high energy content of these compounds is due to the significant difference in bond energy between nitrogen atoms. In particular, molecular nitrogen ( $N_2$ ) is characterized by a uniquely strong triple bond — 229 kcal/mole, whereas the single-bond energy is only 38.4 kcal/mole. From theoretical estimates, use of polynitrogen compounds can provide a specific impulse of 350–500 sec with material density in a range of 2.0–3.9 g/cm<sup>3</sup>. This paper gives a brief review of the current status of experimental and theoretical studies in the chemistry of polynitrogen compounds.

**Key words:** polynitrogen compounds, bond energy, specific impulse, polymeric nitrogen.

### INTRODUCTION

Progress in rocket engineering depends largely on advances in the creation of new energetic materials which have high enthalpy of formation (to meet the demand for increasing rocket velocity and range) and high density of the initial substance (to meet the demand for increasing useful load with the total rocket mass being unchanged). The specificity of the second demand is reflected in current terminology: in the 21st century, the term high energy density material (HEDM) has become widely used in the foreign literature to refer to the new generation of energetic materials [1].

Polynitrogen compounds (PNC), which are also referred to as allotropic modifications of nitrogen, i.e., compounds consisting only of nitrogen atoms (of the form  $N_2$ ,  $N_3$ ,  $N_4$ , etc.) are promising candidates as HEDM. According to theoretical and (still scarce) experimental data, they are characterized by uniquely high enthalpy of formation (2–5 kcal/g) and sufficiently high density in the condensed phase (2–4 g/cm<sup>3</sup>) [2]. It is believed that their use will allow solid rocket propellants to compete in energetic efficiency with liquid propellants. A further advantage of using PNC as rocket

propellants is that their decomposition results in pure (molecular) nitrogen, which does no harm to the environment.

A distinctive feature of PNC is that their thermal decomposition is accompanied by release of a large amount of heat. This is due to the fact that the nitrogen atoms in these compounds are linked by single or double bonds, which are much weaker than the triple bond in molecular nitrogen  $N_2$ . Indeed, the  $N\equiv N$  triple-bond energy is characterized by a record-breaking high value of 229 kcal/mole, whereas the  $N=N$  double-bond energy is 100 kcal/mole, and the  $N-N$  single-bond energy is only 38.4 kcal/mole [3]. Accordingly, the sum of the energies of three single bonds or one-and-a-half double bonds is lower than the triple-bond energy. We note that, for carbon atoms, the inverse ratio between the bond energies is observed, i.e., the triple-bond energy is lower than the sum of the energies of three single bonds or one-and-a-half double bonds: 194.9 kcal/mole for  $C\equiv C$ , 143.7 kcal/mole for  $C=C$ , and 87.6 kcal/mole for  $C-C$ . In practice, this implies that carbon compounds are characterized by the presence of stable polymers, whereas nitrogen compounds by stable monomers. Natural allotropic modifications of nitrogen have not been found, except for molecular nitrogen.

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TABLE 1

Calculated Vacuum Specific Impulse ( $I_{\text{vsp}}$ ) and Temperatures in the Combustion Chamber ( $T_c$ ) for Various Mass Contents of Propellant Components ( $p = 70$  atm)

CH <sub>1.7</sub> , %	N <sub>4</sub> , %	AP, %	Al, %	$I_{\text{vsp}}$ , sec	$T_c$ , K
10	—	70	20	289.8	3667
10	20	56	14	320.4	3934
10	40	42	8	349.1	4136
10	60	30	—	379.9	4680
10	90	—	—	419.3	6338
—	100	—	—	458.6	7793

PNC are typical representatives of the class of endothermic compounds characterized by a positive enthalpy of formation. Because of high enthalpy, PNC generally have a high degree of thermodynamic instability and, hence, do not exist in the free state. Nevertheless, if the problem of stabilizing such compounds is successfully solved, their subsequent use, in particular, in rocket motors would provide substantial energetic benefits. This changes the principle whereby the working medium — high-enthalpy gas — is produced. Unlike in the classical hydrocarbon oxidation scheme traditionally used in rocket motors to heat the reaction products, the exothermic decomposition of polynitrogens leads by itself to the formation of hot molecular nitrogen which produces a thrust when exhausted from the nozzle. A calculation of the vacuum specific impulse  $I_{\text{vsp}}$  (thrust produced by 1 kg of propellant) for hypothetical compositions containing polynitrogen compounds shows prospects of their application in rocket engineering. Table 1 gives calculated ballistic parameters for model compositions based on PNC and standard components: ammonium perchlorate (AP; NH<sub>4</sub>ClO<sub>4</sub>), and aluminum. An inert hydrocarbon polymer with conditional formula CH<sub>1.7</sub> and an enthalpy of formation of  $-64$  cal/g [4] was used as the binder fuel.

The estimation was performed for N<sub>4</sub> polynitrogen compound (tetrahedral structure). According to quantum-chemical calculations, the heat of formation for its various isomers  $\Delta_f H_{\text{gas}}^{0\text{ K}}$  varies in the range of 174–211 kcal/mole [3]. For simplicity, the calculations were made with an average heat of formation of 200 kcal/mole (3570 cal/g). As noted above, experimental data on the characteristics of PNC are extremely scarce; therefore, for estimations, one has to use the results of quantum-chemical calculations. We note that high-accuracy quantum-chemical calculations of the heat of formation are possible only for the gas

phase. Accordingly, computational papers usually give heats of formation of substances in the gaseous state (most often, at a temperature of 0 K —  $\Delta_f H_{\text{gas}}^{0\text{ K}}$ ). Since the enthalpy of formation of a substance in the condensed state differs from that in the gaseous phase by the unknown enthalpy of sublimation, calculated data for such compounds will be considered approximate.

From the table, it is evident that the calculated characteristics of the specific impulse for the PNC based propellant are comparable and even superior to the characteristics of known liquid propellants:  $I_{\text{vsp}} = 300$  sec for the pair RP-1 fuel (of the type of kerosene) + liquid oxygen and  $I_{\text{vsp}} = 390$  sec for the pair liquid hydrogen + liquid oxygen [5]. The specific mass of the PNC based composition is substantially higher than that in the case of liquid propellants. Record-breaking values of the specific impulse can be obtained by using single-bonded polymeric nitrogen in a unique crystalline form (the so-called cubic gauche structure which will be considered below). This solid nitrogen has a calculated density of 3.9 g/cm<sup>3</sup> and a heat of formation equal to 290 kcal/mole (4970 cal/g) [6], which provides a theoretical value of the specific impulse  $I_{\text{vsp}} = 510$ –513 sec at a chamber temperature of  $\approx 8540$  K.

The estimates show that, during combustion of propellants with a high content of N<sub>4</sub>, the gas temperature in the combustion chamber can exceed  $(6$ – $7) \cdot 10^3$  K, and this is a critical issue for the use of propellants containing PNC. In addition, an analysis of literature data shows that, at present, there are no the stable polynitrogen compounds accessible to practical use. Thus, the prospects of using PNC can be considered only in the distant future.

The present review is arranged as follows: information is first given on the history of discoveries in the area of polynitrogen compounds, after which the results of theoretical and experimental studies of the synthesis of new materials are considered, and at the end, a brief review of current advances in the research on PNC is given.

## HISTORICAL INFORMATION

Molecular nitrogen N<sub>2</sub> was first isolated from air by English chemists in 1772 [7]. The discoverer of nitrogen D. Rutherford called it dead gas. 118 years later, in 1890, the azide anion N<sub>3</sub><sup>-</sup> [8] was discovered; its salts are metastable and decompose to release a large amount of heat. Another 109 years later, in 1999, a compound containing the N<sub>5</sub><sup>+</sup> cation was synthesized for the first time [5]. It should be noted that, this synthesis was preceded by comprehensive theoretical studies, which

predicted the existence of many metastable polynitrogen compounds, from  $N_3$  to  $N_{60}$  [3]. Practical implementation of these predictions involved great technical difficulties due to instability of the synthesis products standard conditions. Nevertheless, in the subsequent years, the  $N_3^+$  cation, the  $N_5^-$  anion, and the  $N_3$  and  $N_4$  neutral molecules [3] were obtained experimentally. In addition, in 2001–2004, solid nitrogen was synthesized in amorphous and polymeric crystalline forms, and in 2007, it was reported on the creation of a composite material containing a small amount of  $N_8$  compound on carbon nanotubes (for more details, see the section Experimental Studies). More detailed information on advances in the theory and practice of research on new polynitrogen compounds is presented below.

## THEORETICAL STUDIES

Quantum-chemical calculations of polynitrogen compounds have been actively performed from the second half of the past century. In 1976, Scott [9] reported the results of theoretical and experimental studies of the properties of PNC, including the synthesis of solid nitrogen. In 2006–2007, solid reviews [3, 6] were published, providing a detailed picture of the status of theoretical studies in this area. An analysis of reviews and original papers shows that obtaining objective and reliable theoretical data requires the use of advanced computational methods. As is noted in a review [6], theoretical studies should pursue the following objectives: 1) to determine the minima on the curve of the potential energy surface responsible for various conformers and isomers of compounds with a specified structural formula; 2) to establish the degree of stability of the examined structure to monomolecular decomposition; 3) to determine the properties of the structure that stabilize the compound studied. In practice, geometry optimization and calculation of the relative enthalpy of various isomers at 0 K are performed using simple computational methods, as a rule, the density functional methods. For each structural formula, there are numerous isomers which differ in thermodynamic stability. The further challenge of theory is to estimate the stability of concrete isomers and give recommendation for their synthesis. Qualitative estimates of the stability of compounds are obtained by calculating the activation barriers of primary reactions of decomposition or (for barrier-free reactions) bond dissociation energies. The barriers of primary reactions should be high enough (about 20 kcal/mole) to provide compounds with long lifetimes sufficient for their experimental detection and subsequent practical use.

Theoretical studies of polynitrogen compounds started with investigation of allotropic modifications of trinitrogen  $N_3$ . In the first paper [8] reporting on the discovery of the  $N_3^-$  anion in aqueous solutions of  $HN_3$  made in the pre-quantum chemistry era, the hypothesis of a cyclic structure of  $N_3^-$  was proposed. Much later, investigation of intense photolysis of hydrogen azide revealed a stable  $N_3$  molecule, which turned out to be a linear radical [10]. In theoretical studies [11, 12], the geometry and normal vibration frequencies of the  $N_3$  linear radical were calculated with increasing accuracy. This molecule is characterized by a high energy content. Thus, according to calculations [13], the heat of formation of  $N_3$  is equal to  $112 \pm 5$  kcal/mole, which is close to the value of 109.3 kcal/mole found in [14].

In continuing theoretical studies, a number of researchers returned to the idea of a cyclic structure of the  $N_3$  molecule. Relatively recently, detailed calculations [15] of the energies of the ground electronic states for  $N_3$  compounds have been performed, showing that, along with the stable linear structure, a metastable cyclic  $N_3$  isomer exists (in the form of an isosceles triangle with a bond length of 1.4659 Å and an angle between them of 49.8°). The energy barrier for the transition from the cyclic to linear isomer is equal to 32.1 kcal/mole, and that for the decomposition into atomic and molecular nitrogen,  $N(^2D) + N_2$ , is equal to 33.1 kcal/mole. This provides prospect for attempts at experimental detection of this isomer. The bond length in the linear isomer equal to 1.1854 Å was obtained using the MRCISD method (T) [15].

In the last two decades, along with the neutral isomer, the  $N_3^+$  cation has also been studied theoretically [16–18].

Theoretical investigations of the structure of tetranitrogen  $N_4$  began in the early 1990s. The first theoretical studies were devoted to the properties of the van der Waals complex  $(N_2)_2$  [19, 20]. In addition, much effort has been devoted to studying the  $N_4^+$  cation [21, 22], which was earlier detected experimentally in an electric discharge [23]. It is assumed that  $N_4^+$  can be a precursor of the  $N_4$  neutral compound, which is of great practical interest.

The most detailed computation data have been obtained for the  $T_d N_4$  tetrahedral molecule: high-level (MP4SDQ/DPZ) methods have been used to optimize the geometry (the bond length was found to be equal to 1.419 Å) and calculate the enthalpy of formation  $\Delta_f H_{\text{gas}}^0 = 195$  kcal/mole [24]. Subsequently, these data have been repeatedly refined, and calculations using advanced methods [DFT (B3LYP), CCS D(T) and CASS (12, 12)] have shown that isomers of  $N_4$  with structure in the form of an open chain are more stable. In par-

ticular, it was found [25] that the isomer with the  $C_s$  structure has a minimum on the potential energy surface which is 13.4 kcal/mole below the level for  $T_dN_4$ . On the other hand, calculations [26] performed for high pressures indicate the presence of a relatively stable high-density form of  $T_dN_4$ .

Theoretical investigation of pentanitrogen was pioneered in 1991 [27]. After some pause in research, an experimental paper [28] appeared which reported on the discovery of the  $N_5^+$  cation. The structure of  $N_5^+$  was calculated in [29] with a predicted heat of formation of 351 kcal/mole. Subsequently, a close value (353 kcal/mole) was obtained in [30]. In the same study, the heat of formation for the  $N_5^-$  anion at  $T = 0$  K was calculated to be equal 62.3 kcal/mole. Interesting data on the structure of potentially stable forms of the neutral  $N_5$  molecule were presented in [31]. The heat of formation of this molecule at  $T = 0$  K was estimated at 179 kcal/mole. In the paper cited, a calculation was made of the structure of the  $N_5^-$  anion, which was earlier discussed in [32].

A detailed analysis of the stability of compounds involving the  $N_5^+$  cation showed [30] that the complex  $N_5^+N_5^-$  is characterized by strong instability. At the same time, according to this analysis, the heat of formation of  $N_5^+N_5^-$  (decomposition into 5 molecules of  $N_2$ ) is  $\approx 297$  kcal/mole and the expected density in the condensed phase is  $\approx 1.5$  g/cm<sup>3</sup>. Such parameters of the substance make it a candidate as an energetic monopropellant provided that the problem of thermodynamic stability of the compound is solved.

Theoretical studies of the structure of six-cycle polynitrogen — the  $N_6$  neutral molecule — revealed a large number of isomers. Therefore, a comparison of calculations results using various theories was required to carry out a selection of potentially stable compounds. As a result, the prismatic structure ( $D_{3h}$ -symmetry) was found to have a high dissociation energy, exceeding 34 kcal/mole [33], and was recommended for experimental research.

Less optimistic predictions about experimental detection follow from calculations of the structure of  $N_8$ . Theoretical calculations [34–37] performed since 1990 have shown that almost all  $N_8$  isomers studied have low dissociation barriers. This does not offer a hope for the production of a stable compound but does not prohibit attempts to detect it in experiments. Potentially, azapentalene (225 kcal/mole, a planar form with two cycles,  $D_{2h}$ ) has the greatest heat of formation, exceeding the heat of formation of octaazacubane ( $O_h$ -symmetry, 198 kcal/mole) [35], which is widely represented in popular articles on polynitrogen compounds.

Reliable data on polynitrogen compounds containing more than eight nitrogen atoms are difficult to obtain because of the great length and complexity of such calculations, but the development of computer facilities gives hope for the solution of these problems in the near future. We note the studies devoted to huge molecules containing 60 or more nitrogen atoms. Calculations of the  $N_{60}$  molecule were first published in 1997 [38], where it was concluded that the  $S_6$  structure consisting of blocks of 12 nitrogen atoms had the greatest stability. Later, the calculations performed at the USA Livermore National Laboratory [39] showed the possibility of formation of a  $N_{60}$  molecule consisting of six links, each of 10 nitrogen atoms. It was hypothesized that the “nitrogen fullerene” molecule could be obtained experimentally at extremely high pressures. Subsequent detailed investigation [40] of the structure and stability of the  $N_{60}$  molecule found that higher-level theory (B3LYP in comparison with HF) providing dynamic electronic corrections gave a lower enthalpy of formation for  $N_{60}$  (decomposition of  $N_{60}$  into 30  $N_2$ ), namely 1623 kcal/mole against 2430 kcal/mole [39].

Recently, calculations of potentially stable compounds, such as nitrogen nanotubes,  $N_{78}$ , [41] and carcass cylindrical forms of  $N_{84}$  [42] have been reported.

A substantial part of the theoretical studies has been devoted to the effect of extremely high pressures on nitrogen molecules. It is generally agreed that such pressures should break covalent bond in molecules. It is expected that nitrogen molecules subjected to pressure will form first chain structures, then layered structures and, finally, solid-state structures. Numerous examples of calculations of such structures are contained in early studies [43, 44], but subsequent studies [45, 6] revealed a unique feature of the behavior of nitrogen molecules: transition at high pressures directly to a solid-state structure of high density (3.9 g/cm<sup>3</sup>) — the cubic gauche structure (Cg-structure). The Cg-structure is a completely coordinated three-dimensional structure similar to the diamond structure for carbon atoms but having left- and right-hand forms [6]. It is suggested that both forms can exist simultaneously in the sample after compression. Along with the above-mentioned Cg-structure, calculations have given numerous chain structures far inferior to it in energy. A structure comparable in energy, which was called hexagonally packed chains (HPC), is described in [6]. At pressures above 400 GPa, it transforms to a completely bonded structure in which each nitrogen atom is bonded to three neighbors. Interest in the structure of HPC is also due to the fact that it can have a metallic nature, which holds promise for creating a superconducting material with a high phase-transition temperature. The main

problem that remains to be solved is the structural instability of the compound.

In a detailed review [46] devoted to an analysis of the theoretical information available in the literature on the structure of polynitrogen compounds at high pressures, it is emphasized that, in view of the results of the calculations performed in recent years, the phase diagram of nitrogen seems much more interesting and complex than it was considered several years ago. In particular, the review cited describes the structure of dense nitrogen ( $2.76 \text{ g/cm}^3$  at  $p = 35 \text{ GPa}$ ) with Immm-symmetry which is promising in terms of thermodynamic stability. This structure is considered intermediate between the structures of molecular nitrogen at low pressure and single-atomic nitrogen at high pressure. It has been suggested that such a metastable material may find application under conditions of atmospheric pressure at cryogenic temperatures.

A systematic approach to search for new phases of single-bonded polymeric nitrogen at high pressure is outlined in [47]. It is reported that, along with the already known forms (Cg, BP, A7, and LB — the gauche structure, black phosphorus, arsenic, and layered boat structures) of polymeric nitrogen, this approach makes it possible to calculate the structures of eight more new metastable forms of single-bonded nitrogen. According to the calculation data, the new forms can remain stable at low pressure, whereas the BP and A7 forms, widely discussed in the literature, are unstable at low pressure.

In conclusion of this section, it is necessary to mention attempts to theoretically calculate stable polynitrogen compounds with inclusion of foreign atoms. One of the possible solutions of the problem is proposed in [6]. It has been shown that inclusion of hydrogen atoms leads to passivation of the structure of amorphous single-bonded nitrogen. Another approach was proposed by Canadian researchers who proposed to dope or encapsulate carbon nanotubes with  $\text{N}_4$  and  $\text{N}_8$  polynitrogen compounds. It was originally suggested that  $\text{N}_4$  compound could be included in a nanotube wall (doping), and  $\text{N}_8$  compound encapsulated inside a tube [48].

In this case, the maximum theoretical content of  $\text{N}_4$  in the nanotube can reach 10% and the maximum content of  $\text{N}_8$  should be 1.5–2 times lower. A subsequent paper [49] presented a more detailed calculation of the structured system  $\text{N}_8$ -carbon nanotube and a physical validation of the existence and stability of this system. It is argued that charge transfer would lead to hybridization of the conduction states for a chain of nitrogen atoms and carbon nanotube. Molecular-dynamics calculations show that the system remains stable under normal conditions ( $p = 1 \text{ atm}$  and  $T = 300 \text{ K}$ ) and, hence, it is promising for application.

## EXPERIMENTAL STUDIES

### Synthesis of $\text{N}_3$

The azide anion,  $\text{N}_3^-$ , was discovered experimentally at the end of the XIX century [8], but its detailed investigation began a half century later. It is known from theory that the so-called linear radical  $\text{N}_3$ , being a linear structure, has the lowest potential energy. Experimental evidence of its existence was obtained in experiments with flash-photolysis of  $\text{HN}_3$  [10, 50]. The bond length between the neighboring nitrogen atoms in the  $\text{N}_3$  radical, which was measured in [50] to be equal to  $1.1815 \text{ \AA}$ , was calculated theoretically [15] only 40 years later, in 2005. At approximately the same time, an analysis [51, 52] of experimental data on the photolysis of  $\text{ClN}_3$  exposed to ultraviolet radiation ( $\lambda = 235 \text{ nm}$ ) led to the hypothesis about the existence of a cyclic isomer of  $\text{N}_3$ . The energy spectrum of the decomposition products of  $\text{ClN}_3$  contained a contribution from slow  $\text{N}_3$ , called HEF- $\text{N}_3$  (a high-energy form of  $\text{N}_3$ ). Subsequently, the existence of neutral HEF- $\text{N}_3$  was confirmed in experiments [53] with photolysis of  $\text{HN}_3$  containing labeled hydrogen atoms. A very recent experimental study [54] reported on detection of relatively long-living cyclic  $\text{N}_3$  species (microsecond lifetime) produced by photochemical decomposition of methyl azide,  $\text{CH}_3\text{N}_3$ , irradiated at a wavelength of  $196 \text{ nm}$ .

In addition to studies of  $\text{N}_3^-$  and neutral  $\text{N}_3$ , experimental efforts have been made to study the  $\text{N}_3^+$  azide cation. In 1982, the ionization energy of  $\text{N}_3^+$  was determined to be equal to  $11.06 \pm 0.01 \text{ eV}$  [55], which was further confirmed in [56, 57].

### Synthesis of $\text{N}_4$

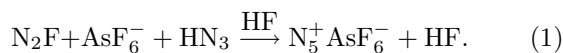
The first experimental observations of tetranitrogen were concerned with the formation of the  $\text{N}_4^+$  radical cation in an electric discharge in nitrogen [58, 59]. It was much more difficult to detect the  $\text{N}_4$  neutral molecule predicted and described in numerous theoretical studies (see [3]). Attempts to detect  $\text{N}_4$  by means of an electric discharge in nitrogen and deposition of the products on glass cooled by liquid helium were not successful [60]. The first success came in 2002, a sophisticated mass-spectrometric technique (neutralization-reionization mass spectrometry, NRMS) made it possible to record a signal from the  $\text{N}_4$  molecule [61, 62]. Two years later, this observation was supported by the same method in a comprehensive study [63], in which detailed quantum-chemical calculations were performed and mass spectra of both the  $\text{N}_3^+$  and  $\text{N}_4^+$  ions and  $\text{N}_4$  molecule were measured experimentally. The essence of

the technique is as follows. A flow of  $N_4^+$  ions is let in a primary cell and is subjected to electron bombardment, resulting in the formation of  $N_4$  neutral molecules and charged fragments. At the entrance into the second cell there is a deflecting electrode at a voltage of +500 V, which removes all charged particles from the gas flow. The resultant gas has a mass spectrum with zero intensity of ions. The gas particles are then subjected to additional ionization, and mass spectra containing signals at  $m/z = 14, 28,$  and  $56$  ( $N^+, N_2^+$  and  $N_4^+$ , respectively) are recorded. Thus, the experimental procedure includes the production of an intense flow of initial  $N_4^+$  ions, accumulation of the signal from twice ionized  $N_4$  neutral molecules, and variation in the ionization and neutralization energies. It was found that the neutralization energy for  $N_4$  was equal to  $10.3 \pm 0.5$  eV. This value differs significantly from the neutralization energy of the  $N_2 \cdot N_2$  dimer molecule (14.5–14.7 eV) corresponding to van der Waals clusters. According to data [61–63], the NRMS technique makes it possible to record signals from  $N_4$  neutral molecules with a lifetime of  $\approx 1$   $\mu$ sec. It should be noted, however, that complete agreement between experimental and theoretical results for the  $N_4$  molecule has not yet been obtained.

### Synthesis of $N_5^+$ and $N_5^-$

An important advance in the chemistry of polynitrogen compounds was the report of American researchers on the synthesis of the  $N_5^+$  cation in early 1999 [64]. The  $N_5^+$  cation was a third allotropic nitrogen compound, after  $N_2$  and  $N_3^+$ , that has become accessible to human practice. Its discovery has made our hopes for the creation of high energy density materials more realistic. The calculated enthalpy of formation for  $N_5^+$  is 350 kcal/mole (or 5000 cal/g).

The first synthesis of the  $N_5^+$  cation was performed at a temperature of  $-78^\circ\text{C}$  by the reaction



The resulting salt was characterized in detail by means of Raman and nuclear-magnetic resonance spectroscopy. It was found that this compound could be stored at room temperature but was capable of reacting explosively with water and organic substances. Soon, as a result of extensive studies, the  $N_5^+ SbF_6^-$  salt was synthesized, which was stable to a temperature of  $60^\circ\text{C}$  and insensitive to impact [65]. This was followed by the synthesis of other salts which were thermally stable at temperatures up to  $50$ – $60^\circ\text{C}$ :  $N_5^+ SnF_5^-$  and  $N_5^+ B(CF_3)_4^-$ . A brief description of these studies is given in [66]. It is concluded that the low thermal stability of salts con-

taining the  $N_5^+$  cation is due to the instability of the cation itself.

Unfortunately, the salts listed above have a low energy potential, which was a reason for searching a suitable high-energy anion. Numerous attempts resulted in the synthesis [66] of salts with a record-breaking nitrogen content:  $N_5^+ [P(N_3)_6]^-$  and  $N_5^+ [P(N_3)_4]^-$ . A disadvantage of these compounds is high mechanical and thermal sensitivity, and this has prompted search for ways to make the high energy potential of the  $N_5^+$  cation realizable.

One of the possible solutions of the problem consisted of the synthesis of  $N_5^+ N_5^-$  compound, which required the development of a method for producing  $N_5^-$ . The theoretically predicted  $N_5^-$  cyclic anion was first produced experimentally and characterized by a group of American researchers in 2002 [67]. The best results were obtained with pyridinium parapentaazolyphenolate in an acetonitrile solution using the starting reactant with a labeled  $^{15}\text{N}$  atom. Attempts of other researchers to produce  $N_5^-$  by reactions involving rupture of the C—N bond or by oxidation of para-methoxyphenyl groups have been unsuccessful. Attempts of experimenters to synthesize stable  $N_5^+ N_5^-$  compound by using salts containing  $N_5^+$  cations and anions and to synthesize  $N_5^+ N_3^-$  compound have also failed. Subsequent theoretical calculations and experiments [30] have shown that compounds of the  $N_5^+$  cation with the  $N_5^-$  and  $N_3^-$  anions are thermodynamically unstable and their decomposition has low activation energy.

### Polymeric Nitrogen

According to general physical concepts, at ultra-high pressure, molecular motion of nitrogen is complicated and the two-atomic gas dissociates and transforms to the solid state (similarly to the production of metallic hydrogen). Solid amorphous nitrogen, predicted theoretically in 1980, was first produced in 2001 [68] by compression of nitrogen in a diamond anvil. The black solid substance proved stable at pressures of 100–240 GPa and temperatures of 100–300 K. By decreasing the temperature below 100 K and gradually reducing the pressure, it was possible to store amorphous nitrogen at atmospheric pressure. This substance has the properties of a semiconductor with a narrow conduction band and does not exhibit signs of crystal structure in x-ray diffraction studies (amorphous body). According to theory, the product substance consists of clusters of nonmolecular nitrogen. Another predicted form of solid nitrogen was produced experimentally in 2004 [69] by

compression of molecular nitrogen in a diamond anvil up to a pressure of 140 GPa at a cell temperature (laser heating) higher than 2000 K. This form has the cubic gauche structure (Cg-N) and exists in the form of polymeric nitrogen with single covalent bonds between three neighboring atoms. Because of similarity to the structure of diamond (which, however, has four carbon atoms in the cell), the Cg-N structure can be called nitric diamond. Interest in this crystal structure is due to its unique energy characteristics: the theoretically calculated heat of formation is 290 kcal/mole [66]. The substance obtained by overcompression is transparent in visible light. It is characterized by a high bulk compression modulus  $B_0 \approx 300\text{--}340$  GPa and an atomic volume  $V_0 = 6.6 \text{ \AA}^3$ , close to that calculated theoretically. Measured x-ray diffraction and Raman dispersion spectra are in good agreement with those predicted theoretically.

We note that the results [69] on the synthesis of Cg-N crystalline compound were subjected to criticism [70]. The critical remarks were about the necessity of investigating the products of the possible interaction of the heater material (boron plate) with nitrogen at temperature above 1800 K and pressure above 10 GPa. Subsequent papers of the authors of [69] proved the validity of the pioneering results obtained in 2004.

A detailed study [71] of x-ray phase diagrams showed that increasing the pressure at room temperature to 50–60 GPa led to transition from the  $\epsilon\text{-N}_2$  form of solid molecular nitrogen (rhombohedral structure,  $R\bar{3} \text{ sec}$ ) to the  $\xi\text{-N}_2$  form of molecular nitrogen (rectangular structure with a screw axis). A further increase in pressure to 150–180 GPa caused destruction of the molecular state of nitrogen. To produce the Cg-N crystalline gauche structure with identical distances between nitrogen atoms in the three-link structure, it is necessary to raise the cell temperature to  $\approx 2000$  K. At a pressure of 110 GPa, the temperature required for the synthesis is equal to 1900 K, but at lower pressures, synthesis does not occur even at 3000 K. However, by increasing the pressure to 140 GPa, the cell temperature can be reduced to 1400 K. High temperature was attained [71] by laser heating (1.064  $\mu\text{m}$  wavelength radiation) of a plate of pressed boron 1  $\mu\text{m}$  thick. At the center of the plate, a transparent substance was detected, whose x-ray spectrum corresponded to Cg-N crystalline compound. At the edges of the plate, where the temperature is lower, a solid opaque deposit of amorphous nitrogen was observed.

A later paper [72] gives a detailed analysis of experimental conditions and possible errors in the synthesis of Cg-N crystalline nitrogen. It is noted that the heating time influences the sizes of the resulting crystals. Dur-

ing fast pulse heating (tens of seconds), small crystals are formed. To produce large crystals (above 10  $\mu\text{m}$ ), one should increase the heating time to several minutes. X-ray and Raman spectra of the solid substance formed in the region subjected to high temperature show no signals corresponding to molecular nitrogen. This implies that in this region there was complete transformation of nitrogen to the Cg-N crystalline state. It is suggested that such process proceeds in the form of a wave of self-propagating synthesis, which decays on the cold surface of the diamond cell.

Interesting results have been recently reported in a paper [73] devoted to studying the direct laser heating of nitrogen at ultrahigh pressure. In these experiments, a 1053-nm wavelength laser radiation was absorbed directly by nitrogen in a diamond cell without using additional absorbing elements. A cell 50  $\mu\text{m}$  in diameter and 25  $\mu\text{m}$  high was filled with liquid nitrogen and subjected to high pressures. At a pressure of 70 GPa and room temperature, molecular nitrogen transformed to the  $\xi\text{-N}_2$  state, and then at 125–130 GPa, to the  $\eta\text{-N}_2$  state, a brown solid substance. Subsequent heating to 1400 and 2000 K led to the formation of amorphous (polymer) nitrogen and transparent crystalline Cg-N nitrogen, respectively. The change in the color of the solid substance correlated with Raman spectra and x-ray diffraction patterns obtained on a synchrotron source. In addition to the experimental verification of the results of [69], the purpose of the work was to obtain information on the influence of electron ionization due to temperature effect ( $T\Delta S$ ) on the crystal structure and phase diagram of solid nitrogen. As a result, a detailed state diagram in the temperature–pressure coordinates was constructed, showing the formation of various states of nitrogen due to the effects of both pressure and temperature. An important role of kinetic factors in phase changes of nitrogen was emphasized. This, in particular, may restrict the formation of the Cg-N state at room temperature. At high temperatures, these restrictions become insignificant because an increase in entropy favors the formation of dissociated states (less saturated valence bonds). Thus, the formation of a reddish amorphous phase and then transparent Cg-N crystals can be attributed to transition from the triple bonds in the  $\xi\text{-N}_2$  molecular state to double bond and then single bond in Cg-N. This implies a need for detailed studies of transition states of amorphous nitrogen, which may be of significant scientific and practical importance.

Important experimental information on the phase state of nitrogen at high pressure near the melting point was obtained in [74]. Contactless measurements of nitrogen temperature in a diamond anvil were carried out

by spectroscopic methods: by Raman spectra at pressures up to 50 GPa and using the Stokes to anti-Stokes peak intensity ratio at pressures above 50 GPa. This provided more reliable data on the melting points of solid nitrogen (from the molecular nitrogen in the liquid state) than those obtained by measuring the temperature of the substrate heated by laser radiation. Simultaneously, unequivocal data on the phase state of polymeric nitrogen were obtained and compared with previously recorded changes in the color of solid nitrogen. The melting curve of solid molecular nitrogen ( $\delta\text{-N}_2$ ) at a pressure of 65–75 GPa was found to have a wide maximum with a subsequent reduction in the melting point to 1550 K at a pressure of 87 GPa. At these values of temperature and pressure, a triple point occurs at which molecular nitrogen exists simultaneously in the liquid phase and in two solid phases,  $\delta\text{-N}_2$  and  $\varepsilon\text{-N}_2$ . The existence of a maximum on the melting curve indicates that at pressures of 70–88 GPa, the density of liquid nitrogen exceeds the density of  $\delta\text{-N}_2$  solid molecular nitrogen. At relatively high pressures (110–150 GPa), nitrogen exists in the solid single-bonded state in an amorphous phase,  $\eta\text{-N}$ . This state is metastable at temperatures of 300–500 K and transforms to the thermodynamically stable Cg–N state at temperatures above 1700–2000 K. An analysis of the state diagrams of nitrogen in the  $p$ ,  $T$  coordinates shows that it has numerous polymorphic states with close enthalpy values. Therefore, kinetic factors play a determining role in experimentally observed phase transitions.

### Doping of Carbon Nanotubes

An original method of synthesis and preservation of polynitrogen compounds has been developed by Canadian researchers [48]. The method is based on using chemical vapor deposition (CVD) to produce nitrogen-doped carbon nanotubes. It was expected that this method would one to deposit  $\text{N}_4$  or  $\text{N}_8$  compounds on the tube surface or inside the tube. It was implemented under laboratory conditions as follows. A ceramic boat with a small sample of a melanin powder (0.20 g) as the upper layer and a microsample (0.01 g) of a ferrocene powder as the lower layer was placed at the inlet of a tubular furnace and heated to 850°C. In the furnace there was a ceramic boat with silicon substrate. Ferrocene vapor (dicyclopentadiene iron,  $\text{C}_2\text{H}_5)_2\text{Fe}$ ) and melanin ( $\text{C}_3\text{H}_6\text{N}_6$ -1,3,5-triazino-2,4,6-triamine) entered the furnace with an argon flow containing a 1% additive (by volume) of ethylene to increase the amount of carbon accessible to the synthesis of nanotubes. During the first 5 min, the furnace temperature was maintained

at 850°C, and within the subsequent 5 min, it was increased to 950°C, after which the heating was turned off, followed by cooling to room temperature at a constant argon flow. Ferrocene evaporated at an early stage of heating (its evaporation temperature is  $\approx 200^\circ\text{C}$ , which is lower than the evaporation temperature of melamine,  $\approx 300^\circ\text{C}$ ). The carbon nanotubes formed were 50 nm in diameter and about 25  $\mu\text{m}$  long.

Transmission electron photomicrographs of nitrogen-doped carbon nanotubes show a bamboo-like structure characterized by the presence of structural defects on the inner graphitized layers. The outer surface of the tubes did not contain impurities of catalyst particles, unlike in usual carbon nanotubes. The size of the longitudinal segments of the bamboo-like structures is 20–40 nm, and it is approximately constant along the tube length. Energy dispersion x-ray spectroscopy confirmed the presence of nitrogen atoms uniformly distributed among carbon atoms in the nanotubes. Iron atoms were not found on the outer surface of the nanotubes. The content of nitrogen atoms inside the doped nanotubes was determined by photoelectron x-ray spectroscopy to be 2% by weight.

The growth mechanism of doped carbon nanotubes is little understood. It can only be hypothesized that nitrogen and carbon atoms are deposited on the surface of iron-containing catalytic particles from the oversaturated reactant vapor. However, the structure of the doped sites and their arrangement have been studied insufficiently. It is necessary to note that, in a theoretical paper [49], only the encapsulation of  $\text{N}_8$  inside carbon nanotubes was discussed and no attention was given to the question of the introduction of  $\text{N}_4$  into their surface.

### CONCLUSIONS

Polynitrogen compounds have received increased theoretical and empirical attention in the last 10–15 years. The synthesis of such compounds involves great technical difficulties because this new class of chemical substances has no analogs under terrestrial conditions and the thermodynamic stability of the currently produced polynitrogen compounds is rather insignificant. Despite the difficulties, real advances have been made in the synthesis of some neutral and charged compounds:  $\text{N}_3$ ,  $\text{N}_3^+$ ,  $\text{N}_3^-$ ,  $\text{N}_4$ ,  $\text{N}_5^+$ , and  $\text{N}_5^-$ . There are also preliminary data on the synthesis of  $\text{N}_8$  encapsulated in carbon nanotubes. Unfortunately, at present, the above-listed compounds cannot be used in practice because they have a very short lifetime ( $\approx 1 \mu\text{sec}$  for  $\text{N}_4$ ) or low energy as part of thermodynamically stable salts. In this connection, the synthesis and determination of the



properties of crystalline single-bonded Cg–N nitrogen has a special significance. This solid substance, which was first produced at the end of the last century, has currently been synthesized at several laboratories of the world and can be stored at room temperature up to a pressure of  $\approx 40$  GPa and under high cooling up to atmospheric pressure. Theoretical studies of the properties of Cg–N are in progress. It has been shown [75] that in the Cg–N structure, three of the five valence electrons form single covalent bonds linking three nitrogen atoms, and the remaining lone electron pair forms an orbital which stabilizes the structure. Mechanical destruction of the Cg–N structure occurs mainly by shear stress, resulting in transition from the orthorhombic structure to the monoclinic structure.

Progress in the synthesis of new polynitrogen compounds depends largely on the development of theoretical methods for studying their properties, and this area has been the focus of extensive research efforts of many groups of researchers all over the world. Their results have provided a reliable basis for the purposeful search for ways to synthesize new polynitrogen compounds. The search is motivated by the prospects of producing new energetic materials with uniquely high enthalpy of formation and density.

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