Single-bonded cubic form of nitrogen

cubic gauche nitrogen and other polynitrogen compounds as novel high energy density materials:

a brief theoretical study and characterization based on research by Mikhail I. Eremets, Alexander G. Gavriliuk, Ivan A. Trojan, Dymitro A. Dzivenko and Reinhard Boehler.

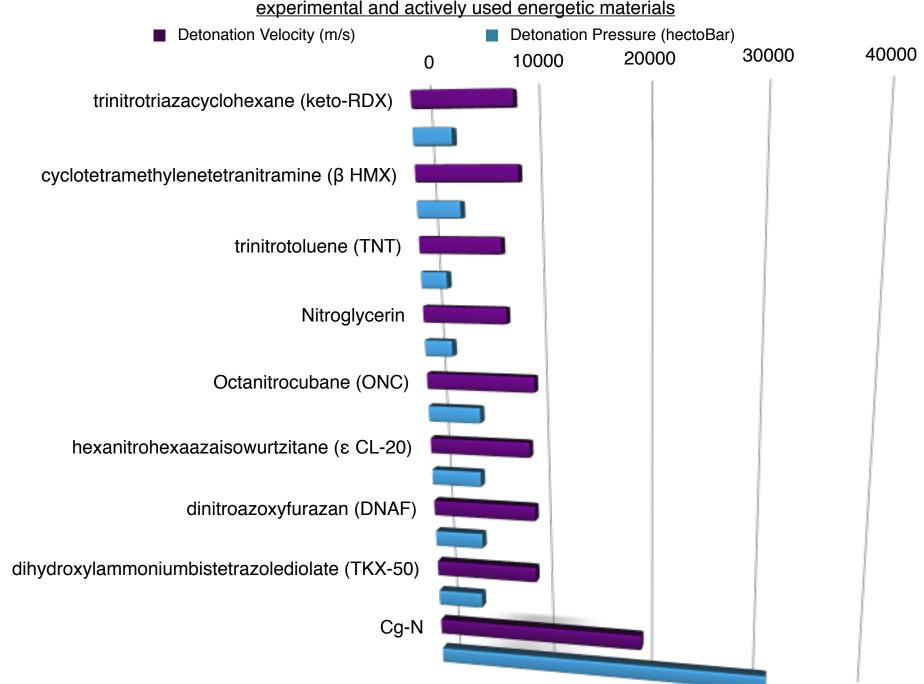
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Introduction

High energy density materials derive their energy from the oxidation of the carbon backbone, as the rockery and military industries increase their demands for higher energy density materials which are more stable and environmentally friendly while maintaining a very high energy density, new methods must be developed to meet these demands. The following report will cover the properties of a new compound with never before seen energy density, and no environmental toxicity. In order to give the reader an adequate perspective of the monumental importance of this new compound and the impact it will have on life as we know it, the power of current energetic materials will be given as a reference point. Cubic gauche nitrogen was believed by many to be impossible but recently, this novel compound of unseen amounts of energy has been synthesized in very small amounts by researchers at the max plank institute of chemistry in mainz Germany. The current state of energetic materials, characterization of cubic gauche nitrogen, synthesis of cubic gauche nitrogen, possible methods of stabilization, and other nitrogen based energetic materials will be reported.

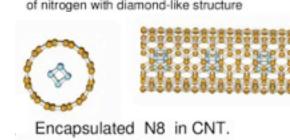
The current state of energetic materials

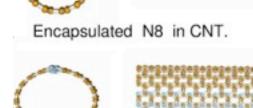
The most powerful modern energetic materials including CL-20, ammonium dinitramide, octanitrocubane, are all too expensive too synthesize and demonstrate only relatively small improvements of about 10 - 30% over their modern counterparts like RDX (the main ingredient in C-4) and HMX. Octanitrocubane has 8 nitrogen groups making the most highly nitrated compound practical for use, but it costs more than gold due to the enormous length of the synthesis procedure and offers only 30% performance increase over RDX. Because it is likely that it will be a long time before an affordable high yield procedure is developed for the synthesis of octanitrocubane, alternatives must be found, and that has led to the development of nitrogen doped carbon nanotubes. I will provide several brief charts showing the the characterization of several popular high energy density materials to compare to nitrogen doped carbon nanotubes.



Characterization of Cq Nitrogen It should be noted that although Cq-N has held the primary focus of research due to it being one of the few synthesized and possessing great energetic properties, it is not the only form of polymeric nitrogen and as such, other forms of polymeric nitrogen may be referenced. For the sake of clarity. I will say that the definition of polymeric nitrogen simply means nitrogen singly bonded to other nitrogen atoms rather than the typical triple bonding found in atmospheric nitrogen. Cg-N demonstrates superior characteristics in every possible way, as it is both more environmentally friendly and far more energetic than any previous material

making it an ideal candidate for advancements in space exploration and military technology as Single-bonded polymeric phase (cubic gauche) of nitrogen with diamond-like structure

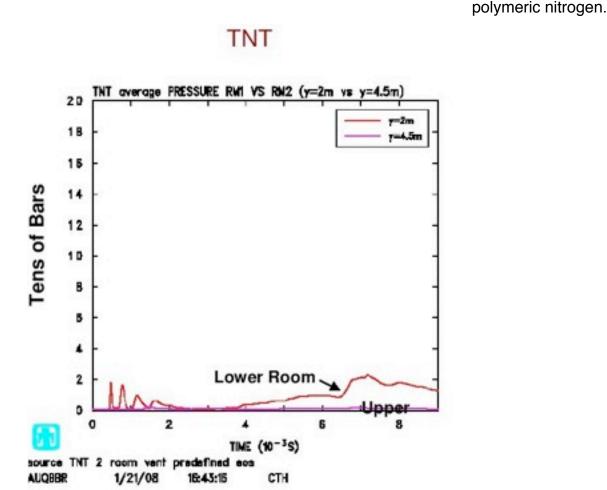


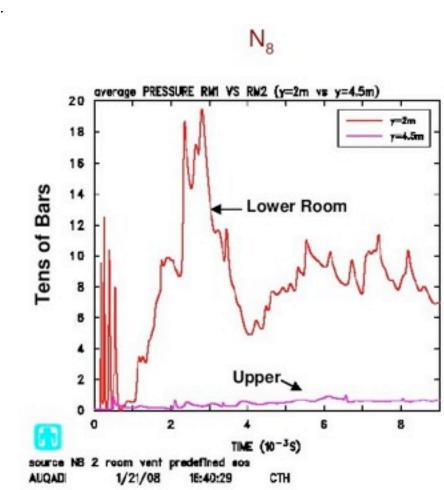


well as countless possible domestic uses. Cg-N is a molecule composed of eight atoms of nitrogen bonded to each other with single bonds. Cg-N was prepared in very minute quantities at the max planck institute for chemistry in mainz, Germany via the compression of atmospheric nitrogen under 115.4 GPa pressures in a diamond anvil cell at 2000K. As seen in the chart above, The power of Cg-N is 5 times greater than anything before it with a detonation velocity of 19,740 m/s, a density of 3.1 g/cm³, a detonation pressure of 3,140,000 times atmospheric pressure, a bulk modulus of 300 GPa, a heat of formation of 6673 cal/g and no environmental toxicity as it decomposes into atmospheric nitrogen, Cg-N is so energetic that 1cm³ contains 34kJ of energy. Part of the reason why polymeric nitrogen has such a large energy content is due to the amount of atoms per unit volume. Conventional high energy materials like diesel oil, gasoline, HMX, and liquid H2/O2 mixtures contain alternating covalent bonds with very weak van der Waals interactions between the molecules. Polymeric nitrogen is not held back by this as it connects to it's neighboring atoms to form a continuous chain of extremely high energy.

Because of it's enormous bulk modulus, Cg-N has been referred to as the nitrogen diamond and thus poses a promising future as a new type of ultra-hard material. curiously, the other elementary solids in the nitrogen group (phosphorus, arsenic, antimony, and bismuth) did not display the cubic gauche phase. Cg-N has been calculated to be non-conductive at ambient conditions. The modern workhorse of the military and primary cyclic nitramine used in modern solid rocket propellants (RDX) has a detonation velocity of about 8,900 m/s, a density of about 1.89 g/cm³, and a detonation pressure of 341 kBars (341,000 times atmospheric pressure). The problem is that Cg-N will become unstable when pressures drop below 43 GPa, a theoretical solution has been proposed, and that is to insert polymeric nitrogen into carbon nanotubes. There have been two suggested methods for

the insertion of nitrogen into carbon nanotubes including encapsulation and doping. encapsulation is placing Cg-N in the center of carbon nanotubes, and doping is inserting N4 groups into the walls of carbon nanotubes. Why is Cg-N stable when encapsulated in carbon nanotubes? This can be answered with a fascinating phenomena of physics. This phenomena is the following: When a polymeric nitrogen molecule enters a carbon nanotube, it is held stable in it's position by a charge transfer from the nanotube to a hybridized orbital that is created by conduction states of the nanotube and the nitrogen. The charge transfer is however sensitive to the radius of the carbon nanotube and thus by using temperature control, we can cause the diameter of carbon nanotubes to increase or decrease. have doped carbon nanotubes with nitrogen in minute quantities. In the structure of Cg-N, three of it's electrons form single covalent bonds linking three nitrogen atoms while the remaining lone electron pair serves to stabilize the structure by forming an orbital. The bond length of Cg-N was observed at 1.346 Å. The extremely high energy yield of cubic gauche nitrogen is due to the single bonding that occurs between the nitrogen atoms. The energy content of single bonded nitrogen is 160 kJ/mol while triple bonded nitrogen (atmospheric nitrogen) has virtually inseparable atoms of nitrogen with a bond energy of 954 kJ/mol. The decomposition of Cg-N into atmospheric nitrogen is a highly exothermic reaction resulting in a energy release of 6673 cal/g compared to a meager 1100 cal/g for TNT. It has been calculated that if used as rocket fuel, the specific impulse of polymeric nitrogen would exceed 510 sec making it more powerful than any propellant used by nasa currently. This new form of nitrogen may become the gateway allowing for humanity's long sought after goal of galactic colonization to become reality. If we were to initiate the decomposition of Cg-N in a bunker, the pressure produced would be immense. The graph below compares the calculated pressure in a bunker over time with TNT vs the pressure over time in the same environment using





Synthesis of Cq Nitroger

The existence of polymeric nitrogen was first theoretically predicted by the scientists C. Mailhiot, L. H. Yang, A. K. McMahan from Lawrence Livermore National Laboratory in 1992 by using density functional theory in their research paper entitled Polymeric Nitrogen. The first successful synthesis of nitrogen in the cubic gauche phase was carried out in 2004 via a novel setup for a high temperature and

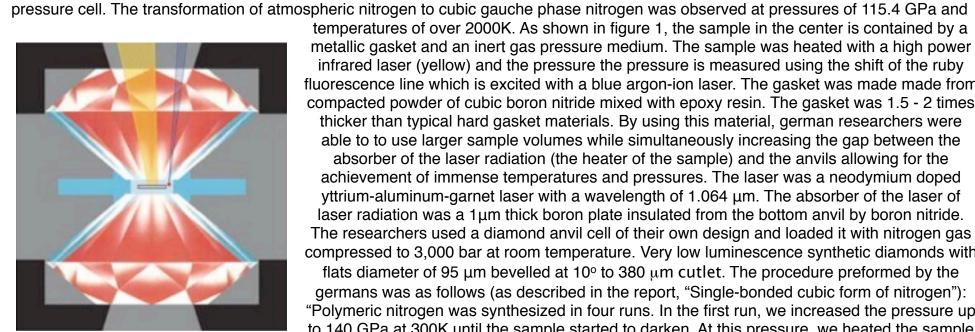


Fig. 1

temperatures of over 2000K. As shown in figure 1, the sample in the center is contained by a metallic gasket and an inert gas pressure medium. The sample was heated with a high power infrared laser (yellow) and the pressure the pressure is measured using the shift of the ruby fluorescence line which is excited with a blue argon-ion laser. The gasket was made made from compacted powder of cubic boron nitride mixed with epoxy resin. The gasket was 1.5 - 2 times thicker than typical hard gasket materials. By using this material, german researchers were able to to use larger sample volumes while simultaneously increasing the gap between the absorber of the laser radiation (the heater of the sample) and the anvils allowing for the achievement of immense temperatures and pressures. The laser was a neodymium doped yttrium-aluminum-garnet laser with a wavelength of 1.064 µm. The absorber of the laser of laser radiation was a 1µm thick boron plate insulated from the bottom anvil by boron nitride. The researchers used a diamond anvil cell of their own design and loaded it with nitrogen gas compressed to 3,000 bar at room temperature. Very low luminescence synthetic diamonds with flats diameter of 95 µm bevelled at 10° to 380 µm cutlet. The procedure preformed by the germans was as follows (as described in the report, "Single-bonded cubic form of nitrogen"): Polymeric nitrogen was synthesized in four runs. In the first run, we increased the pressure up to 140 GPa at 300K until the sample started to darken. At this pressure, we heated the sample

in steps with intermediate recordings of Raman spectra at room temperature. After the first

heating to 980K, the transformation accelerated. The sample darkened further, but remained in the molecular state— the vibron in the Raman spectra of nitrogen did not change. The high-frequency edge from the diamond anvils sharpened, indicating uniform pressure distribution, which dropped to 120 GPa. No further changes were observed after heating up to 1,400 K. After heating to 1,700 K, the sample further darkened and the intensity of the vibron of nitrogen significantly decreased. At 1,980 K, the vibron peaks became indistinguishable from the background, all wide bands in the low-frequency part of spectrum disappeared, and luminescence measured from the nitrogen sample significantly increased. A ring around the absorber appeared, probably due to melting of

Untransformed

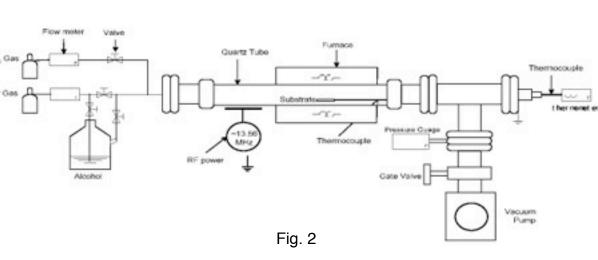
the sample. Instead of further darkening, unexpectedly, the sample became transparent (the absorber plate became clearly visible in reflected light). After successive heatings up to 2,500 K and 2,600 K, the transparent colorless part spread out over a larger area and could be seen in transmitted light (a white strip at the upper part in Fig. 1b, indicated by the yellow arrow). The nitrogen at the edge of the gasket hole was not heated to the high temperatures and remained dark. The pressure in the centre of the sample reduced to 115 GPa. The sample luminescence decreased, the vibron peaks disappeared, and a new Raman peak appeared at 840 cm-1. Thus, an apparent transition happened at 115 GPa at temperatures above 2,000 K." Figure 2

shows a picture of one of the nitrogen phases observed in the reaction chamber as well as an x ray diffraction spectrum. The Germans were the first to synthesize polymeric nitrogen, however, it was synthesized by others as well. Cg-N was synthesized by M. J. Lipp and his team from Lawrence Livermore National

Laboratory by direct laser heating of N2 to over 2000K at 120 - 130GPa by a 1053 nm laser. In the procedure used by M. J. Lipp, a high pressure cell 50 µm in diameter with a height of 25 µm was filled with liquid nitrogen

-15 µm and subjected to high pressures. At a pressure of 70 GPa and room temperature, molecular nitrogen transformed to the ξ-N2 state, as the pressure was elevated to 125 - 130 GPa, the nitrogen transformed into the η-N2 state, a brown solid substance. Heating was then preformed via a laser to 1400 and 2000K which led to the formation of amorphous nitrogen and transparent crystalline Cg-N phase. several other laboratories have preformed similar procedures and obtained Cg-N.

Possible methods of stabilization There have been many suggested methods of stabilizing polymeric nitrogen, a few of them include the use of carbon nanotubes, graphene, and boron nanotubes. First off, there have been many approaches proposed to synthesizing polymeric N8 in carbon nanotubes, most of these approaches consist of first forming the nitrogen into a chain of n8 molecules interconnected to each other. Among many of these approaches, researchers have suggested the formation of encapsulated Cg-N via the synthesis of N₈ from N₂ inside carbon nanotubes. It was calculated by using density



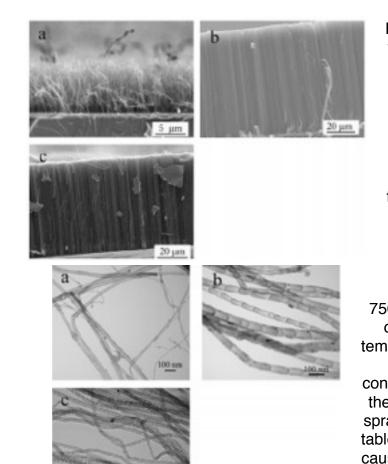
functional theory that the barrier of 4N₂ encapsulated in carbon nanotubes to N₈ encapsulated in carbon nanotubes is 1.07 eV per N₂, that is 0.2 eV larger than the energy difference between these two structures which should be a sufficient energy barrier to prevent the spontaneous decomposition of N₈ into N₂. It has been proposed that the formation of N₆ and N₂ in carbon nanotubes is the first step to carbon nanotube encapsulated N₈. Although encapsulated N8 has not yet been synthesized, nitrogen doped carbon nanotubes have been synthesized by Hao Liu and his team from Canada. The synthesis of N8 encapsulated in

P = 115 GPa

T = 300 K

 $2\Theta (\text{deg}, \lambda = 0.416861 \text{ Å})$

carbon nanotubes will probably require a similar synthesis procedure to the one used by Hao Liu. The synthesis of nitrogen doped carbon nanotubes was accomplished via aerosol assisted chemical vapor deposition using the apparatus in figure 2. The synthesis of nitrogen doped carbon nanotubes was carried out in the following manner: The substrate used was a silicon wafer with a 600 µm oxidation layer. The substrate was sputtered with a 30 nm thick aluminum buffer layer in order to obtain uniform and high density nitrogen doped carbon nanotubes. The sputtering was carried out under a pressure of 4.0 mTorr and a power of 300 W. The synthesis was carried out with a homemade system consisting of three parts: an aerosol generator, a modified quarts chamber placed in a furnace and a gas trap for the exhausting gases. The method used was based on the decomposition of an aerosol spray consisting of a liquid hydrocarbon source and an evaporable catalyst for the CNTs' formation. There were three argon inlets and one hydrogen inlet used. One inlet with carrier gases flowed through the aerosol solution and then carried aerosol into the reaction chamber. AN additional argon inlet enables dilution of the obtained aerosol mixture. The Hydrogen was



between multiple graphene layers as nitrogen chains.

Like with carbon nanotubes, the stabilization is

caused by a charge transfer (of 0.4 electrons) from

the graphene matrix to the nitrogen chain however,

unlike with carbon nanotubes, a hybridized orbital is

not created in the case of graphene stabilized

rockets and jets to robots and batteries. The

graphene stabilization method is a much more

the use of vapor deposition or highly complex

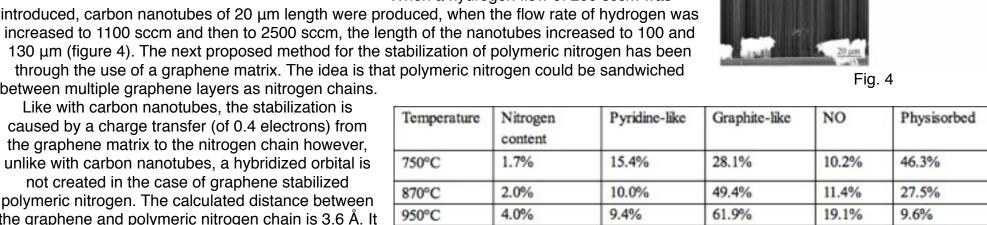
engineering of pressure chambers with highly

specific applications, the synthesis of graphene

encased polymeric nitrogen will much easier to

also introduced into the reaction chamber from it's inlet. The metal catalyst precursor Fe⁺³ (acetylacetonate) was dissolved in acetonitrile (CH₃CN) which serves as a solvent for the aerosols and as a source of carbon and nitrogen. The concentration of Fe-ions in acetonitrile was 1.1 mM. The solution was placed inside a sonication generator and kept at constant room temperature during the synthesis at this temperature via cooling water. The pretreated silicon substrate was then placed in a ceramic boat, inside the chamber. The furnace was then heated to a temperature between 700C and 1000C after a 20-minute purge of air in the chamber by 400 cm³/minute (sccm) of argon gas. As soon as the target temperature was reached, the aerosol droplets were produced by ultrasonication at a frequency of 850 KHz and transported by argon gas introduced from one inlet with a flow rate between 550 and 2,500 sccm. Simultaneously, hydrogen was introduced with a flow rate between between 200 and 2,500 sccm as the reaction gas which reduced the catalyst precursor to form the active Fe⁰ catalyst during the continuous injection. An additional argon inlet was employed to keep the total gas flow rate of 4000 sccm in the reaction chamber. The growth time used was 30 minutes. Figure 3 shows pictures of carbon nanotubes synthesized by the above process at 750°C, 870°C and 950°C. Using X-ray photoelectron spectroscopy, the properties of the carbon nanotubes grown with conditions were analyzed. It was apparent that as the temperature increased, so did the nitrogen content. It was also observed that the length of

nitrogen doped carbon nanotubes decreases from 80 μm to 60 μm as the nitrogen contents increase from 2.0% to 4.0%. The length of the carbon nanotubes was also influenced by the spray rate of the aerosol this correlation is given in table 3. The compartments visible in the nanotubes causes the bamboo-like structure, this is due to the presence of nitrogen in the graphitic network, which induces curvature of the graphitic layer. The flow rate of hydrogen was observed to be a critical factor in the length of carbon nanotube growth. When a hydrogen flow of 200 sccm was introduced, carbon nanotubes of 20 µm length were produced, when the flow rate of hydrogen was



| polymeric nitrogen. The calculated distance between | 870°C | 2.0% | 10.0% | 49.4% | 11.4% | 27.5% | |
|---|-------------|----------|---------------|---------------|-------|-------------|--|
| the graphene and polymeric nitrogen chain is 3.6 Å. It | 950°C | 4.0% | 9.4% | 61.9% | 19.1% | 9.6% | |
| is believed that the use of great pressure on layered graphene with N2 sandwiched between each layer | Table 1 | | | | | | |
| plus the use of other elements as catalysts should be | Hydrogen | Nitrogen | Pyridine-like | Graphite-like | NO | Physisorbed | |
| a viable route to the synthesis of N ₈ between | flow rate | content | - Co. | 20 | | 2 | |
| graphene sheets. The N ₂ phase in graphene is separated from the N ₈ phase by a gap of 2.2 eV per | 200 secm | 1.3% | 11.9% | 63.4% | 12.1% | 12.6% | |
| N ₂ molecule. The proposed synthesis procedure is | 1100 sccm | 2.0% | 10.0% | 49.4% | 11.4% | 27.5% | |
| believed to provide enough energy to bridge this gap. | 2500 sccm | 1.7% | 15.4% | 28.2% | 10.1% | 46.3% | |
| If we can sandwich polymeric nitrogen between two graphene sheets as shown if figure 5, many new | Table 2 | | | | | | |
| developments would emerge in every field from | Aerosol gas | Nitrogen | Pyridine-like | Graphite-like | NO | Physisorbed | |

content 550 sccm 1.7% 17.6% 33.2% 18.1% 31.0% attractive method to test experimentally, as unlike the 1500 sccm 2.0% 10.0% 49.4% 11.4% 27.5% method of encapsulation, this method will not rely on 2500 sccm 1.9% 10.7% 47.4% 13.9% 28.1% Table 3

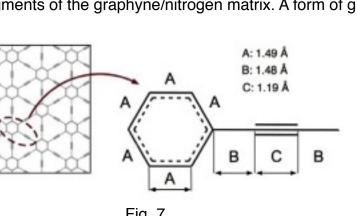
Fig. 5

accomplish as the synthesis will rely on pressure on layers of graphene with polymeric nitrogen between each layer. An interesting subject of study may be the use of graphyne instead of graphene. Graphyne is a sister of graphene that like graphene posses a single layer thick of carbon atoms but has a different structure which induces different properties. The structure of graphyne (figure 6) demonstrates different properties unique to it's particular configuration. Graphyne can adopt many structural configurations. Graphyne is characterized by it's different bond states. Graphene is a curious state of matter because it's bonds are halfway between single and double bonds, graphyne however contains both double and triple bonds and it's atoms do not need to be in a hexagonal configuration. The particular configuration demonstrated in figure 6 is the configuration of 6,6,12graphyne and has been theorized but never synthesized. The 6,6,12 form of

graphyne is predicted by density functional theory to act as a semiconductor. The semiconducting properties of 6,6,12 graphyne (c) are due to the fact that although dirac cones should still exist, they are predicted to exist in a distorted, squashed form. The structures of graphene and three forms of graphyne are presented in figure 6. Whether graphyne can be used in the stabilization of polymeric nitrogen is baed on my own speculation, however I believe that it is worth a hard look. As I have previously stated, the stabilization of polymeric nitrogen in a graphene matrix is due to a charge transfer. The bonding and therefore energetic properties are different in graphyne and thus the correct conditions to facilitate a charge transfer may not be present. A further analysis using more accurate calculations such as density

functional theory would be required in order to get a better understanding of the potential of such a compound. In addition to the conditions for a correct charge transfer being absent, the atomic structure of graphyne may not align with polymeric nitrogen the way that graphene has been predicted to, this dilemma may be solved by reconfiguring either the graphyne or using a different form of polymeric nitrogen. I have not preformed in depth calculations, I am only presenting this idea in hopes that it may be considered and perhaps present a new avenue for the future of novel energetic

materials. The ability to destabilize polymeric nitrogen in segments at will with controlled energy release parameters would provide the possibility for the use of polymeric nitrogen as a new form of fuel for cars with zero environmentally toxic emissions. This is a very difficult goal that may be possible if my hypothesis for the modification of polymeric nitrogen via stabilization in a graphyne matrix is possible. Some of the many barriers to the achievement of this goal include the fact that the stabilization would need to be very strong in order to prevent nearby decompositions of polymeric nitrogen from inducing a chain reaction and causing all polymeric nitrogen near it to detonate The controlled release of energy from high energy compounds would allow for much better rocket technology. By inducing high resistance in a certain section of the nitrogen/graphyne and a high flow of electrons simultaneously, it would be possible to destabilize desired segments of the graphyne/nitrogen matrix. A form of graphyne with a hexagonal structure like graphene may serve for better confinement.



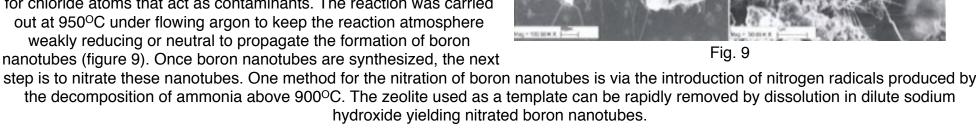
and triple bonds. Finally, I will address the subject of polymeric nitrogen stabilized via boron nanotubes. Recently, it has been observed that boron nanotubes are remarkably similar to their more popular cousin carbon. The process used for the synthesis of nitrogenated boron nanotubes will be described Nitrated boron nanotubes were grown via chemical vapor deposition in a

The bond lengths of one form of graphyne (figure 7) showing the aromatic, single

Fig. 7 process similar to that used for nitrated carbon nanotubes. First, boron nanotubes are grown by thermal chemical vapor deposition of MgB₂ which decomposes into it's elements because of the heat (900 - 950°C). The magnesium ions then intercalate between the initially formed boron sheets to catalyze the formation of boron nanotubes without being heavily incorporated into the final product. One of the properties unique to boron nanotubes is that unlike carbon nanotubes in which each carbon can only be bound to one other carbon, in boron nanotubes, a boron atom can bond to six other boron atoms. The

drawback to that procedure is that the boron nanotubes possess a highly irregular diameter, and the main reaction product is actually boron nanowires. In order to synthesize boron nanotubes of a consistent diameter, a template must be used to guide the growth of the nanotubes and thus minimize the formation of defects. Zeolites (figure 8), have arrays of consistent pore size and are thus ideal for use a templates for boron nanotubes. The best known method for the chemical vapor deposition of boron nanotubes relies on intimate out at 950°C under flowing argon to keep the reaction atmosphere

mixing of MgB₂ alone or mixed with Ni2B in different atomic ratios with MCM-41 alters the zeolite to contain the Mg catalyst without the need for chloride atoms that act as contaminants. The reaction was carried weakly reducing or neutral to propagate the formation of boron nanotubes (figure 9). Once boron nanotubes are synthesized, the next



Other Nitrogen Based Energetic Materials

There have been many energetic materials proposed for the future, my topic is nitrogen in the cubic gauche phase so I will only reference research in the nitrogen based energetic materials. Nitrogen fullerene, $N_5^+N_5^-$, N_4 , $N_5^+P(N_3)_6^-$, $N_5^+SbF_6^-$, $[N_5^+]_2[SnF_6]_2^-$, $[N_5^+][P(N_3)_6]^-$, $[N_5^+]_2[SnF_6]_2^-$ [B(N₃)₄], etc... are all compounds that are causing a great deal of curiosity in the scientific community as a result of high energy capacities. The nature of matter changes drastically under pressure, the ultimate of all high pressure chemistry is the synthesis of metallic hydrogen... the highest energy theoretical material of all. It was first theorized by Riad Manna that nitrogen fullerenes would form under high enough temperatures and pressures. Nitrogen fullerenes are not expected to exceed Cg-N in energy, however, they do pose interesting possibilities to the energetics industry. Nitrogen fullerene may be stable at ambient conditions, and it possesses enormous amounts of energy including a predicted detonation velocity over 17.31 km/s, a detonation pressure of 196 GPa, and a density of 2.67 g/ cm3. Currently, only one fullerene has been synthesized, and that is the carbon fullerene. There have however been several all nitrogen

calculation for N₅+ was carried out in 1991 that stated that the synthesis of N₅+ should be possible but little attention was given to it. The electron affinity of N_5^+ is $N_2F^+AsF_6^- + HN_3 \xrightarrow{HF} N_5^+AsF_6^- + HF$ calculated at 10.55 eV. It was not until 1998 that the synthesis of N₅+AsF₆- would be accomplished. The synthesis of this novel compound gained world fame ver

compositions synthesized besides Cg-N. One of the most important fields in modern high energy density materials is A theoretical

+AsF₆- was accomplished via the

Engineering News This was the first highly energetic salt based on N₅⁺. The synthesis of N₅⁺AsF₆⁻ was accomplished in the reaction equation in figure 10. The energy contained in the salt has been observed to be immense. It is widely known that energetic materials should have a high heat of formation, the heat of formation of N5+AsF6- is very high at 351 kcal/mol. Table 4 shows the heat of formation for many common energetic materials for comparison, to find the heat of combustion subtract the heats of formation of the decomposition products from the heat of formation of the energetic compound. The Raman apparatus was unfortunate

such it was named as named as one of chemistry's top five achievements in 1999 by Chemical and

quickly as it was the second stable polynitrogen compound in history and as

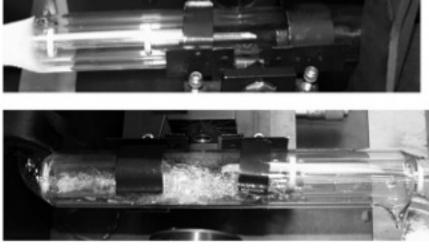


Fig. 11 Reduction of N₂F₄ to N₂F₂ Graphite $+ AsF_5 \rightarrow C_{12}AsF_5$

 $C_{12}^+AsF_5 + N_2F_4 \rightarrow 2C_{12}^+AsF_6^- + trans-N_2F_2$ trans – cis isomerization of N₂F₅; $trans - N_2F_2 + AsF_5 \xrightarrow{T/P} N_2F^+AsF_6^-$

 $N_2F^+AsF_6^- + NaF \xrightarrow{HF} NaAsF_6 + cis - N_2F_2$ Formation of N₂F⁺SbF₆⁻: $cis-N_2F_2 + SbF_5 \xrightarrow{HF} N_2F^+SbF_6$

 If N₂F₄ is not available, add: $H_2NCONH_2 \rightarrow F_2NCONH_2 \rightarrow NHF_2 \rightarrow N_2F_4$

 $N_5^+SbF_6^- + Na^+[P(N_3)_6^-] \xrightarrow{SO_2} N_5^+[P(N_3)_6^-] + NaSbF_6 \downarrow (15)$ $N_5^+SbF_6^- + Na^+[B(N_3)_4^-] \xrightarrow{SO_2 \atop -64 \text{ °C}} N_5^+[B(N_3)_4^-] + NaSbF_6 \downarrow (16)$ $N_2F^+SbF_6^- + HN_3 \xrightarrow{HF} N_5^+SbF_6^- + HF$

Compound formation (kJ/mol) -333.66 Nitroglycerin RDX 83.82 HMX 104.77 in facing a spontaneous release of the PETN -514 energy of a few milligrams of this salt, a before and after picture of this incident is TNT -54.89 given in figure 11. The preparation of the **TETRYL** 38.91 N₂F+AsF₆ was described by karl O. Christe to be a "time-consuming, multi-CI-20 step synthesis". The preparation of N_2F 172.6 Octanitrocubane reactions presented in figure 12. AsF₅ in the trans-cis isomerization was replaced 12 Hydrazine with AIF3 eliminating the need for the displacement step between N₂F+AsF₆--295.77 Ammonium and NaF. These modifications greatly Perchlorate reduced the cost and time required for the synthesis of N₂F+SbF₆- There have -150.6 Ammonium Dinitramide Table 4

Heat of

been other highly energetic salts prepared by Karl. Among these energetic salts, the most promising of these were $N_5^+[P(N_3)_6]^-$, and $N_5^+[B(N_3)_4]^-$. These highly energetic salts were synthesized via the reactions in figure 13. These salts though highly energetic also posses a high sensitivity to the extent that they undergo energetic energetic decomposition at the slightest provocation from shock or temperature. The $N_5+[B(N_3)_4]$ - salt has a remarkable energy content as 95.7 % of this salt is composed of energetic nitrogen. In total, 13 novel N₅+ salts were isolated and characterized. Many of these salts were highly unstable and would thus decompose very quickly. Another stable polynitrogen salt was N₅+SbF₆- which was synthesized via the reaction in figure 14 and was prepared by the following procedure: by first condensing HN₃ at -196°C into a pre-passivated and pre-weighed Teflon ampoule containing a known amount of BF. The resulting mixture was homogenized at ambient temperature. The ampoule was taken into the glove box, where a stoichiometric amount of N₂F

vacuum line and evacuated. Subsequent slow warming of the reaction mixture to room temperature for about 30 min, followed by removal of all volatile material resulted in the isolation of N₅+SbF₆- in >99% yield. Because SbF₅ is a stronger Lewis acid than AsF₅ N₅+SbF₆ is considerably more stable than N₅+AsF₆. N₅+SbF₆ is stable up to 70°C and is insensitive to mechanical shock. N₅+SbF₆- has the appearance of a white solid. Only 5 grams of N₅+SbF₆- have been synthesized to avoid the accidental

+SbF₆- was added at -196°C. The cold ampoule was attached to the metal

decomposition of large quantities. N₅+B(CF₃)₄-. Due to the unique molecular structures of these novel nitrogen salts, I am unable to reliably calculate the energetic parameters of said compounds and their energetic properties were referenced very little by Karl or any member of his team. As only the heats of formation of a few N5+ have been characterized, it may desired to find more detailed information regarding the energetic parameters of the compound which can be done by preparing the compound and testing it experimentally, finding a formula for calculating the

detonation velocity, and detonation pressure for non-conventional

energetic materials (any energetic materials which are not C-H-N-O)

or contacting Karl O. Christe for further information at

kchriste@usc.edu. The primary focus of the synthesis of these

polynitrogen salts is to develop starting materials for the synthesis of

nitrogen allotropes like N₅+N₅-. Another theoretical polynitrogen

compound is N₁₈H₆ with a calculated detonation velocity of 17,653 m/s, a detonation pressure of 133.07 GPa, a density of 2.191 g/cm³, and a heat of formation of 669.121 kcal/mol. Several polynitrogen compounds are theoretically characterized in the chart below as you can see, Cg nitrogen is among these polynitrogen compounds, and it's detonation velocity was underestimated by about 6,000 m/s

| No of Nitrogen Atoms | Electronic Energy (Hartrees) | Geometry | Heat of Formation (kcal/mol) | Density (g/cc) | Velocity of Det. (km/s) | C-J Pressure (GPa) | Polarizability |
|--------------------------------|------------------------------------|----------|------------------------------------|-------------------|-------------------------------|--------------------------|----------------|
| 4 | -218.781 | 2 | 268.77 | 1.752 | 13.24 | 77.02 | 23.464 |
| 6 | -328.102 | 43 | 345.58 | 1.974 | 14.04 | 93.32 | 36.426 |
| 8 | -438.440 | 1 | 406.69 | 2.151 | 14.86 | 108.39 | 45.987 |
| 10 | -546.875 | 1 | 473.42 | 2.211 | 12.08 | 58.05 | 59.45 |
| 12 | -656.170 | (1) | 579.82 | 2.283 | 12.53 | 64.07 | 76.891 |
| N ₁₈ H ₆ | -988.349 | ASH | 669.121 | 2.191 | 17.653 | 133.07 | 110.834 |

Cubic Gauche Nitrogen has been synthesized and thoroughly characterized and demonstrates superior characteristics for energy content and environmental friendliness. The characteristics of polynitrogen compounds have been examined and polynitrogen compounds and their salts have been shown to demonstrate superior characteristics in all respects except stability. By these calculations, it is apparent that the future of the rocketry, military, and possibly automotive divisions can not rely on C-H-N-O energetic materials due to the limits of the amount of energy that they can store, and eventually, all high energy density materials must be replaced by polynitrogen compounds ace, military, and automotive divisions. in order to meet the increasing demands

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15.

23

25.

28

(Si Al) grey

Oxygen- red

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