More than a Handful...N$_5^+$

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Synthetic molecules having very high energy content are in great demand. They are eagerly sought after as fuels or explosives. These molecules have been pushed thermodynamically uphill by chemical or light energy and placed in a well at the top. Due to the large energy of activation required for climbing out of the well before rolling downhill they stay at the top. Designing such kinetically stable molecules with very high energy contents can be a frustrating task for the chemist. Molecules that are readily drawn on the drawing board (or on the computer screen) can play 'hard to get' in the laboratory. Sometimes they just have an easy path downhill which may not have been intuitively obvious (a hole in the well!). Furthermore, the increasing awareness of environmental concerns has placed severe restrictions on the type of molecules one may design. Given this scenario, it is easy to see why the claim of K O Christe [1] and others to have made a high energy density molecule composed of nitrogen, is so attractive. The molecule's interesting structure adds to the excitement.

The energy content of a fuel is related to the energies of the bonds in its molecule relative to the energy content of the product molecules. This would be related to the heat of formation ΔH_f, which should be large and positive for a high-energy molecule. We can identify the following two conditions for such molecules. It should have (a) very weak bonds and (b) made up of elements, which in their standard state have very strong bonds and great thermodynamic stability. The variation of bond energies across the period makes an interesting study (see *Table* 1). Among the second row elements, Li to Ne, the stability of elements as diatomics increases with electron count and peaks at nitrogen where the formation of a N-N triple bond leads to a gain of 942 kJ mol^{-1} of energy. (The only other comparable molecule is a heteronuclear diatomic CO, which has a bond energy of 1072 kJ mol^{-1}). After nitrogen we have weaker diatomics due to the filling up of antibonding orbitals. Another useful comparison is given by the single bond energies of these elements. A progressive decrease is observed and the bond energy of F_2 is the least.

For designing an excellent fuel or explosive, the compounds formed after the energy releasing reaction also needs to be considered.

Table 1. Homonuclear bond energies in kJ mol^{-1} for 2nd row elements

Element	Bond		
	Single	Double	Triple
Li	105		
B	293		
C	345	602	835
N	167	418	956
O	142	493	
F	155		

Products should have a large and negative heat of formation. Since carbon forms very strong bonds with oxygen, oxidation of carbon rich molecules to CO and CO_2 releases a lot of energy and is the basis of most fuels available. Based on the bond energy criteria discussed above it should also be possible to convert nitrogen rich compounds to N_2 and gain energy.

Utilizing this information, K O Christe and co workers arrived at the conclusion that a polynitrogen compound would be an ideal candidate for a high energy density molecule (HEDM). It would be one with as many N-N single bonds as possible and one that would not be readily transformed to nitrogen. The latter condition is essential for the molecule to be kinetically stable and isolable. Having searched the chemical literature for references to polynitrogen compounds they made the startling discovery that until now, only two polynitrogen compounds N_3^- and N_2 are available in significant quantities. The rest – a host of them – have been the subject of numerous computational studies but have never seen the light of day. A few of the interesting structures of polynitrogen compounds are shown in *Figure* 1. The stable compounds among these would be those for which resonance structures do not convert to N_2. Others would be unstable (like the N_6 isomers given in *Figure* 1) and decompose to nitrogen readily. Klapotke [2] has pointed out that some of these compounds could have alternatively more stable structures, thus in comparison with the open chain N_{10} the
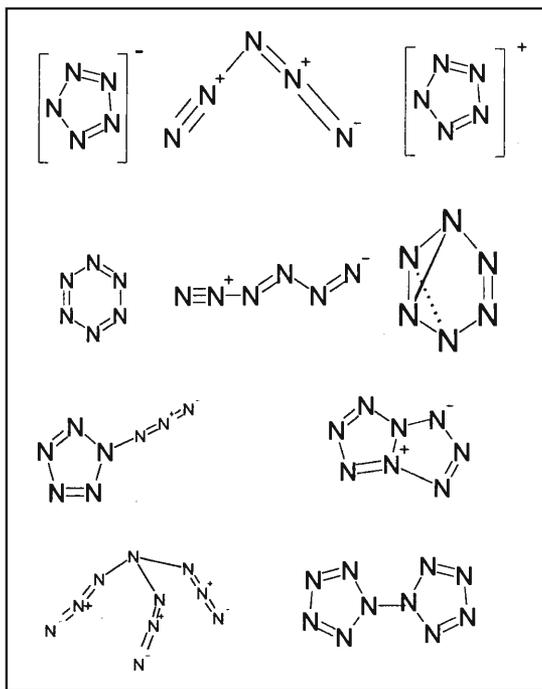
Figure 1. Structures of polynitrogen compounds.

cyclic structure for N_{10} is favorable because it is aromatic.

Guided by the computational studies that were available, Christe and others arrived at the simplest target compound N_5^+. Using suitable reagents they devised the elegant route shown below. Notice that the double decomposition yields only the target molecule for the other product is the solvent. This ingenious route to the target compound allowed them to synthesize N_5^+ in high yield without having to separate the product from impurities. Given the rather high energy of decomposition, they could not have resorted to purification if side products were present.
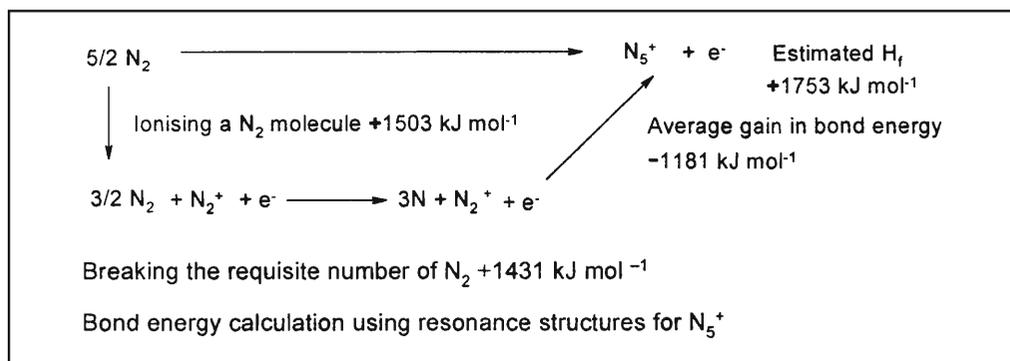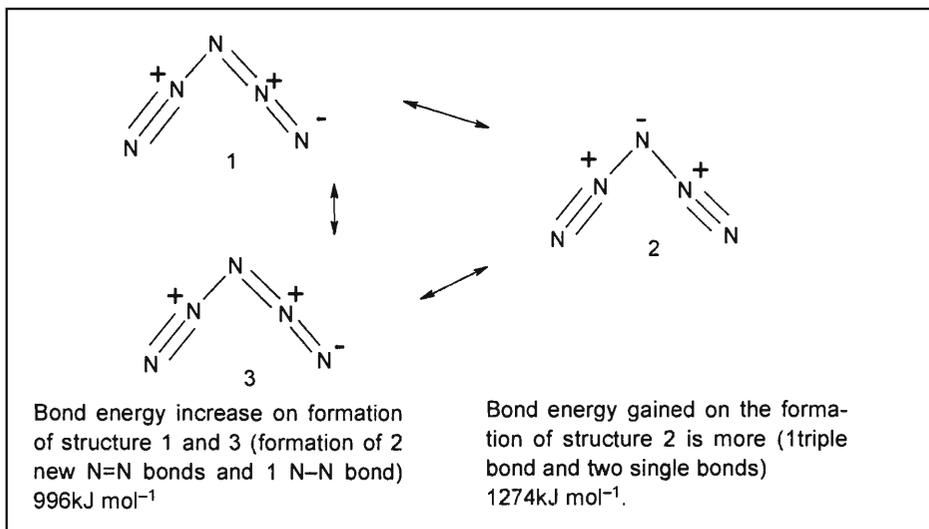
$$N_2F^+AsF_6^- + HN_3 \xrightarrow[\text{HF (Solvent)}]{} N_5^+AsF_6^- + HF$$
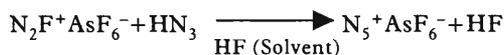
Although this compound is only 'reasonably stable' at room temperature, it is quite stable at $-78°C$ and can be safely stored for weeks and studied. They unambiguously determined the structure of the species using a combination of vibrational spectroscopy and magnetic resonance spectroscopy and also synthesized two different isotopically labelled (^{15}N) N_5^+ molecules using labelled HN_3. Based on the resonances of the labelled nitrogen, they confirmed the symmetrical bent structure of the molecule and also computed the chemical shifts in the NMR spectra for this molecular structure and found it to be comparable. Then the infrared and Raman spectra of the molecule were measured. The vibrational spectrum of the molecule was calculated for the proposed structure as well. The computed vibrational spectrum matched perfectly the observed spectrum not only for the unlabelled N_5^+ but also for the ^{15}N labelled N_5^+ One to one correspondence of vibrational frequencies would be virtually impossible if the observed structure did not match the proposed structure.

Based on the structure of the molecule, a large positive heat of formation for the cation of about 1469 $kJmol^{-1}$ was calculated. Their confirmation of this very large energy content was however unintended. During one of their attempts to measure the Raman spectrum of the molecule, much to their dismay, an expensive accessory for the Raman spectrometer was blown up! Mind you, they were using just 5 mg of the compound. What is the real source of this high energy content? One could make a rough estimate of the heat of formation of this molecule based on the known bond energies of N_2, N-N, $N=N$ and the energy required to remove an electron.

Two major sources of error in this simple calculation based on Hess's heat law are the bond energy and ionisation energy we have used. Resonance energy has not been accounted for and this would stabilize the molecule further and reduce the heat of formation we have calculated. The energy required to pull an electron off a large molecule is always less than that required to pull it off a small molecule. So ionization of N_5 to N_5^+ should require less energy. Both factors would lead to a smaller value for the heat of

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5/2 N_2 ————————————————→ N_5^+ + e^- Estimated H_f
                                                    +1753 kJ mol^{-1}

| Ionising a N_2 molecule +1503 kJ mol^{-1} Average gain in bond energy
                                                    -1181 kJ mol^{-1}

3/2 N_2 + N_2^+ + e^- ———→ $3N + N_2^+ + e^-$

Breaking the requisite number of N_2 +1431 kJ mol^{-1}

Bond energy calculation using resonance structures for N_5^+

Bond energy increase on formation
of structure 1 and 3 (formation of 2
new N=N bonds and 1 N–N bond)
996kJ mol^{-1}

Bond energy gained on the forma-
tion of structure 2 is more (1triple
bond and two single bonds)
1274kJ mol^{-1}.

formation. It is surprising that in spite of these omissions, the value we have calculated is close to the sophisticated calculation they have made. The energy cycle makes it clear that the primary reason for the large and positive heat of formation in the molecule is the energy required for stripping off one of the electrons from nitrogen. So the high energy density of N_5^+ is partly due to the conversion of weaker $N=N$ bonds to $N{\cong}N$ and largely due to the energy released when it is neutralized.

Synthesis of this molecular ion sets the stage for the synthesis of higher polyatomic species. Other species with increased stability at room temperature might be needed in order to make these polynitrogen compounds useful as fuels. Christe and others have demonstrated the value of a carefully planned synthetic strategy. They have shown that chemistry is not for the faint hearted nor is it for the unimaginative. Only innovative synthetic chemistry can lead to futuristic materials.

Suggested Reading

[1] K O Christe, W W Wilson, J A Sheehy, and J A Boatz, *Angew. Chem. Int. Ed.* (Engl), Vol 38, 2004, 1999.
[2] T M Klapotke, *Angew. Chem. Int. Ed.* (Engl), Vol 38, 2536, 1999.

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In 1827, Fourier compared this fortunate influence of Earth's atmosphere to a hothouse. He said Earth's gases are like the greenhouse's glass walls. In other words, air has a greenhouse effect.

Next Hundred Years, J Weiner, 1990