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Received: December 23, 1998 [Z 12821 IE]
German version: *Angew. Chem.* **1999**, *111*, 2180 – 2184

Keywords: molecular recognition · peptides · peptide – peptide interactions

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N_5^+: A Novel Homoleptic Polynitrogen Ion as a High Energy Density Material**

Karl O. Christe,* William W. Wilson, Jeffrey A. Sheehy, and Jerry A. Boatz

Dedicated to Professor George Olah

Polynitrogen compounds are of significant interest as high energy density materials (HEDM) for propulsion or explosive applications.[1–3] In spite of numerous theoretical studies predicting that certain all-nitrogen compounds might be stable, only a few unsuccessful experimental studies aimed at their actual synthesis have been undertaken.[4] Presently, only two homoleptic polynitrogen species are known that can be prepared on a macroscopic scale: dinitrogen, N_2, which was independently isolated in pure form from air in 1772 by Rutherford, Scheele, and Cavendish, and the azide anion, N_3^-, discovered in 1890 by Curtius.[5] Other species such as $N_3^{\bullet}$, N_3^+, and N_4^+ have been observed only as free gaseous or matrix-isolated ions or radicals.[6–8] In view of the extensive theoretical studies indicating that molecules such as N_4, N_8, $N(N_3)_2^-$, $N(N_3)_3$, and $N(N_3)_4^+$ are vibrationally stable,[4] the lack of a single successful synthesis of a new species on a macroscopic scale is surprising and may be a testament to the great experimental difficulties resulting from their high endothermicities, which give rise to instability and unpredictable explosiveness.

The high energy content of polynitrogen candidates stems from the N–N single and double bonds they possess. The average bond energies of 160 and 418 kJ mol^{-1}, respectively, are much less than one-third or two-thirds the N_2 triple bond energy of 954 kJ mol^{-1}.[9] Therefore, any transformation of a polynitrogen compound to N_2 molecules is accompanied by a very large energy release, and any new metastable polynitrogen compound will be isolable and manageable only if it possesses a sufficiently large energy barrier to decomposition.

In view of the dearth of potential synthetic pathways for the construction of homoleptic polynitrogen rings or polycycles, and because many chain- or branch-type polynitrogen compounds are calculated to be lower in energy than their cyclic or polycyclic isomers,[3] our efforts are focused on the synthesis of catenated polynitrogen species, which may be more readily accessible. The weakest link in a chain always

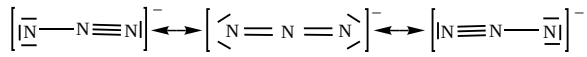
[*] Dr. K. O. Christe, Dr. W. W. Wilson, Dr. J. A. Sheehy, Dr. J. A. Boatz
Propulsion Sciences and Advanced Concepts Division
Air Force Research Laboratory (AFRL/PRS)
Edwards Air Force Base, CA 93524 (USA)
Fax: (+1) 661-275-5471
E-mail: karl.christe@ple.af.mil
and
Loker Hydrocarbon Research Institute
University of Southern California
Los Angeles, CA 90089 (USA)

[**] This work was funded predominantly by the Defense Advanced Research Projects Agency, with additional support from the Air Force Office of Scientific Research and the National Science Foundation. We thank A. Kershaw for recording the NMR spectra, Dr. M. Fajardo for the mass spectra, Prof. J. Stanton for calculating the nitrogen NMR shifts, and Dr. P. Carrick, Dr. S. Rodgers, Dr. M. Berman, and Dr. A. Morrish for continuing encouragement and support.

  1433-7851/99/3813-2004 $ 17.50+.50/0

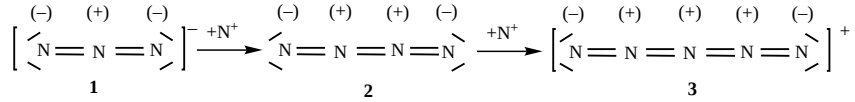
determines the overall strength, so it is imperative to search for target compounds devoid of any isolated N–N single bonds that cannot gain partial multiple bond character through resonance with neighboring bonds.

The building principle and unique resonance stabilization of the well-known and exceptionally stable azide anion (**1**, Scheme 1), in which each N–N bond has full double bond



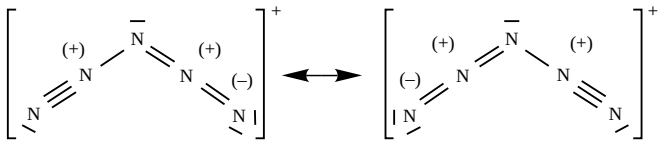
Scheme 1. Resonance structures of N_3^- (**1**).

character, might be further extended by the addition of nitrogen atoms containing only four valence electrons, that is, N^+ ions. This leads first to neutral N_4 (**2**) and then to the N_5^+ cation (**3**, Scheme 2).



Scheme 2. Addition of N^+ to N_3^- (**1**) to form N_4 (**2**) and N_5^+ (**3**) as well as the electronic charge distrubutions in **1**–**3**.

Although **2** and **3** contain, like azide, only cumulated linear N=N bonds, the electronic charge distributions shown in Scheme 1 are only favorable for N_3^-, whereas the neighboring positive charges render structures **2** and **3** energetically unfavorable. However, the problem of neighboring equal-sign charges can be remedied for N_5^+ with the resonance structures shown in Scheme 3, which result in a bent structure of C_{2v} symmetry with a bond order of 1.5 for the central N–N bonds. For linear N_4, analogous structures cannot be written, and therefore N_5^+ was chosen as the prime target of our synthesis program.



Scheme 3. Resonance structures of N_5^+ (**3**).

Only one previous report on N_5^+ was found in the literature, a theoretical study of a series of ABCBA-type compounds by Pyykkö and Runeberg.[10] Based on MP2/6-31G* calculations, they predicted a planar C_{2v}-symmetric structure with a B-C-B angle of 110.7°. The possible synthesis of N_5^+ was considered in 1992 by G. Rasul in his Ph.D. proposal at the University of Southern California, but it was not pursued.[11] Theoretical calculations were used to predict whether the candidate is vibrationally stable, and IR, Raman, and NMR spectra were calculated to aid in the identification and characterization. For N_5^+, these calculations predict the stable C_{2v} structure depicted in Figure 1. We report now the synthesis and characterization of $N_5^+AsF_6^-$, which constitutes only the third known compound containing a homoleptic polynitrogen moiety that is preparable on a macroscopic scale.

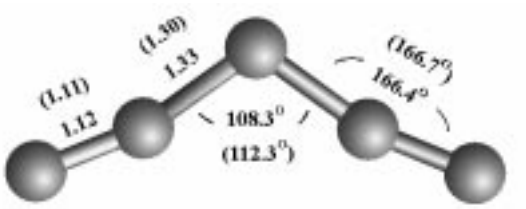
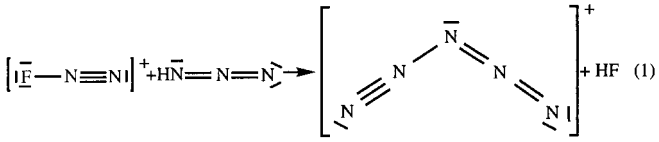


Figure 1. Optimized structures of N_5^+ calculated at the B3LYP (values given in parentheses) and CCSD(T)/6–311 + G(2d) levels of theory.

In designing a synthesis, it is useful to find energetic starting materials that already possess the energy-enhancing weakened bonds, the required formal charges, and suitable ligands that allow for an exothermic and facile coupling reaction. If the target molecule is a cation such as N_5^+, the presence of a formal positive charge in one of the starting materials is very important in view of the high first ionization potential of N_2 (1503 kJ mol^{-1}). Equation (1) shows that the N_2F^+ cation and HN_3 are ideal starting materials for the synthesis of N_5^+ because they already possess the desired types of bonds, N_2F^+ provides the formal positive charge, and, in view of the weak N–F and strong H–F bond, the HF elimination reaction is expected to be exothermic.



(1)

A final important point is the need for a reaction medium that offers good solubility at low temperatures, can act as a heat sink for the exothermic reaction, and can stabilize a product that is potentially very shock sensitive. For N_5^+, anhydrous HF was chosen because of its high dipole moment, low melting point (−80 °C), and high volatility.

Application of these principles led to a surprisingly straighforward synthesis of N_5^+ according to Equation (2). A

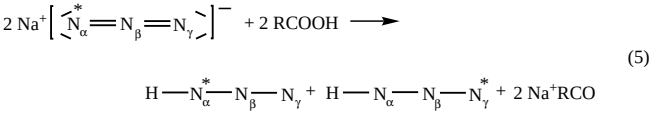
$$N_2F^+AsF_6^- + HN_3 \xrightarrow[-78\,^\circ C]{HF} N_5^+AsF_6^- + HF \quad (2)$$

$$HN_3 + HF + AsF_5 \xrightarrow{HF} H_2N_3^+AsF_6^- \quad (3)$$

$$4\,N_5^+AsF_6^- + 2\,H_2O \longrightarrow 4\,HF + 4\,AsF_5 + 10\,N_2 + O_2 \quad (4)$$

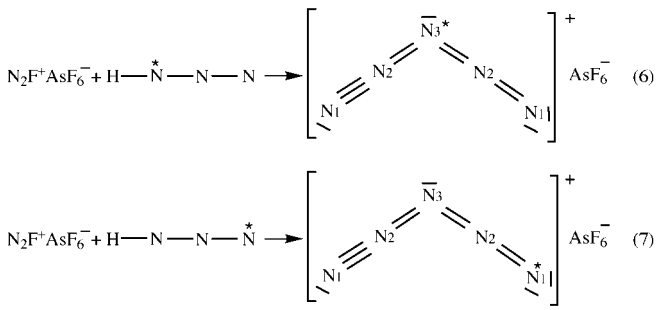
small excess of HN_3 was used to ensure complete conversion of the $N_2F^+AsF_6^-$. The only detectable by-product was less than 20 mol% of protonated HN_3,[12] formed according to Equation (3). The AsF_5 required for the protonation of HN_3 to proceed could have formed by decomposition of some $N_5^+AsF_6^-$, or less likely by hydrolysis of $N_5^+AsF_6^-$ with traces of water in the system [Eq. (4)].

For the synthesis of ^{15}N-labeled N_5^+, ^{15}N-labeled HN_3 was prepared from stearic acid and ^{15}N-labeled $Na^+N_3^-$ [Eq. (5)].



(5)

The reaction of labeled HN_3 with $N_2F^+AsF_6^-$ produced a roughly equimolar mixture of N_5^+ with ^{15}N in either the 1- or 3-position [Eqs. (6), (7)].



The $N_5^+AsF_6^-$ salt is a white solid that is sparingly soluble in anhydrous HF. It is marginally stable at 22 °C and can be stored for weeks at −78 °C without noticeable decomposition. It can be handled both in HF solution or as a solid and, in our experience, has not exploded during careful normal handling or when squashed with a stainless steel spatula at −196 °C. It has survived numerous exposures to a focused 488-nm Ar-ion laser beam (1.5 watt) at −130 °C, although a 5-mg sample did explode on one occasion with sufficient force to destroy our low-temperature Raman device. It is a powerful oxidizer, capable of igniting organic substances such as foam rubber even at low temperatures. The reaction of $N_5^+AsF_6^-$ with water is violently explosive and should be avoided. This is not surprising in view of the facts that O_2^+ is a powerful oxidizer and the first ionization potential of N_2 (1503 kJ mol^{-1}) is significantly higher than that of O_2 (1206 kJ mol^{-1}); the electron affinity of N_5^+ is the subject of a further computational study. The high energy density of N_5^+ was also confirmed by a calculation using the G2 method[13] that gave formation enthalpies of $\Delta H_f^0 = 1478$ and $\Delta H_f^{298} = 1469$ kJ mol^{-1} for free gaseous N_5^+.

Solid ^{15}N-labeled $N_5^+AsF_6^-$ in a quartz tube (3 mm outer diameter) was warmed in a stepwise manner from −78 to +22 °C under a vacuum of 10^{-7} Torr while monitoring the volatile products with a mass spectrometer; the principal decomposition product detected was N_2. After pumping at 22 °C for 20 min, however, most of the solid remained and was identified by low-temperature Raman spectroscopy as $N_5^+AsF_6^-$, thus demonstrating that the compound has reasonable stability at room temperature. In samples prepared from an excess of HN_3 and containing some $H_2N_3^+AsF_6^-$[12] as a by-product, HN_3 and its fragments, HF, and AsF_5 were also observed in the mass spectra.

The ^{14}N and ^{15}N NMR spectra of N_5^+ labeled in either the 1- or 3-position and the ^{14}N NMR spectrum of unlabeled N_5^+ were recorded at −63 °C in anhydrous HF solution that was acidified with about 2 mol % of AsF_5 to slow down a potential exchange between the cation and the solvent.[14] The spectra of the ^{15}N-labeled mixture are shown in Figure 2, and the observed and calculated chemical shifts are compared in Table 1.

The signals due to N1 and N3 were observable in the ^{15}N spectra at $\delta = -237.3$ and −100.4, respectively, in excellent agreement with the calculated values of $\delta = -235$ and −95. The signal-to-noise ratio of the ^{15}N spectrum was low due to the poor solubility of $N_5^+AsF_6^-$ in HF at −63 °C, and a long delay time (60 s) was needed because of the slow relaxation rates. The area ratio of the two signals was about 1:1, indicating that the synthesis of HN_3 from end-labeled N_3^- and stearic acid had resulted in about equimolar quantities of N_α- and N_γ-labeled HN_3. In addition to the two N_5^+ signals, two weaker signals at $\delta = -312.0$ (t, $^1J(^1H,^{15}N) = 100.7$ Hz) and −111.4 (s) were observed in the ^1H-coupled ^{15}N NMR spectrum that are attributable to N_α and N_γ, respectively, of $[H_2N_\alpha N_\beta N_\gamma]^+$.[12] This was verified by recording the spectrum of a known sample of $H_2N_3^+AsF_6^-$ in HF solution.

In the ^{14}N spectrum of labeled and unlabeled $N_5^+AsF_6^-$ a single resonance at $\delta = -165.3$ was observed and assigned to

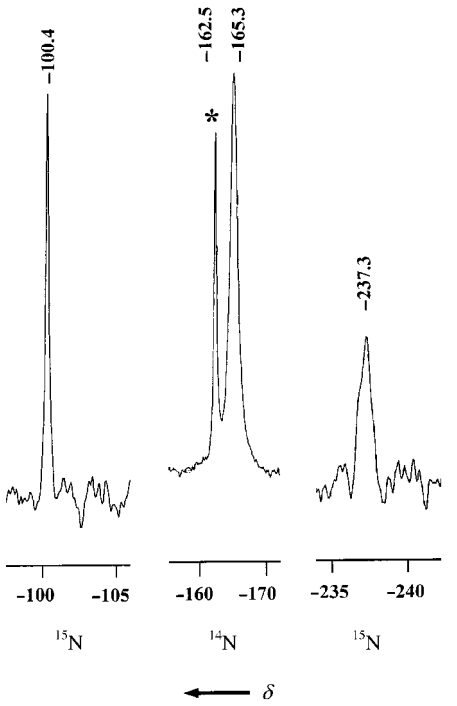


Figure 2. Sections of ^{14}N and ^{15}N NMR spectra for an equimolar mixture of singly ^{15}N-labeled $[^{15}N^{14}N^{14}N^{14}N^{14}N]^+$ and $[^{14}N^{14}N^{15}N^{14}N^{14}N]^+AsF_6^-$ recorded at −63 °C in anhydrous HF solution that was acidified with 2 mol % AsF_5. The resonance marked by an asterisk is due to $H_2N_3^+$ (see text for details).

Table 1. Observed and calculated ^{15}N and ^{14}N NMR data for N_5^+.

	δ[a] observed[b]		calculated[c]		
	^{15}N	^{14}N	N1	N2	N3
$[^{15}N1\text{-}^{14}N2\text{-}^{14}N3\text{-}^{14}N2'\text{-}^{14}N1']^+$	−237.3				
		−165.3[d]	−235	−166	−95
$[^{14}N1\text{-}^{14}N2\text{-}^{15}N3\text{-}^{14}N2'\text{-}^{14}N1']^+$	−100.4				

[a] Chemical shifts are given relative to that of neat CH_3NO_2 as external standard. [b] The spectra were recorded ^1H-coupled at −63 °C in anhydrous HF solution which was acidified with AsF_5. [c] Calculated at the CCSD(T)/QZP level of theory. An empirical correction of −20 ppm was applied to all calculated values, based on a comparison between the calculated and observed shifts of a number of closely related molecules and ions. [d] The other two resonances are badly broadened owing to exchange and were not detected in the ^{14}N spectrum.

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N2 of N_5^+ based on the calculated value of $\delta = -166$. The signals due to N1 and N3 could not be observed in the ^{14}N spectra under these conditions due to excessive quadrupole broadening. The N_β signal of $[H_2N_\alpha N_\beta N_\gamma]^+$ was also observable in the ^{14}N spectra of the labeled and unlabeled cations as a sharp resonance at $\delta = -162.5$, while signals for N_α and N_γ were strongly quadrupole broadened. It is fortunate that N2 of N_5^+ gives rise to a sharp ^{14}N signal and that the single ^{15}N substitution provided us with an equal mixture of ^{15}N labels on N1 and N3, thus allowing the unambiguous observation of all three signals of N_5^+. Their excellent agreement with the calculated values provides positive proof for the presence of a C_{2v}-symmetric N_5^+ cation.

Additional unambiguous proof for the presence of C_{2v}-N_5^+ was provided by the vibrational spectra of $N_5^+AsF_6^-$ and the $^{14}N-{}^{15}N$ isotopic shifts observed for the mixture of $^{15}N1$- and $^{15}N3$-labeled $N_5^+AsF_6^-$. The low-temperature Raman spectra of unlabeled and a mixture of labeled $N_5^+AsF_6^-$ are shown in Figures 3 and 4, respectively, and the observed frequencies are summarized in Tables 2 and 3. The vibrational assignments for octahedral AsF_6^- in Table 2 are well established[15] and do not require any further discussion; those for N_5^+ are based on our calculations. As can be seen, the four N–N stretching modes were observed with the predicted frequencies and intensities.

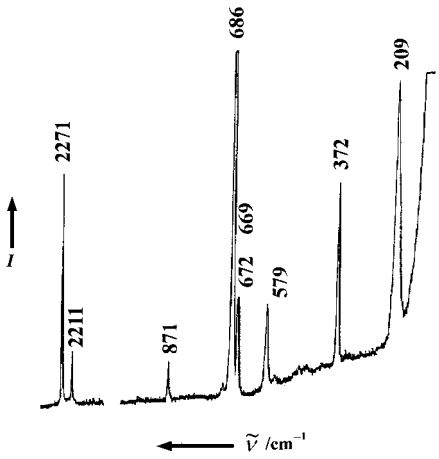

Figure 3. Low-temperature Raman spectrum of unlabeled solid $N_5^+AsF_6^-$.

The spectra of $^{15}N1$- and $^{15}N3$-labeled N_5^+ allowed accurate measurements of the isotopic shifts for modes $\nu_2(A_1)$, $\nu_7(B_2)$, and $\nu_1(A_1)$. Again, the agreement between experiment and theory is very good and confirms the validity of the predicted structure given in Figure 1. Since the observed frequencies of N_5^+ are intermediate between those predicted at the CCSD(T) and the B3LYP levels of calculation, the actual geometry of N_5^+ is probably also intermediate between the CCSD(T) and B3LYP values of Figure 1. Therefore, the following geometry is interpolated for $[N1\text{-}N2\text{-}N3\text{-}N2\text{-}N1]^+$: $r(N1{-}N2) = 1.11$ Å, $r(N2{-}N3) = 1.315$ Å, $\sphericalangle(N1\text{-}N2\text{-}N3) = 166.6°$, and $\sphericalangle(N2\text{-}N3\text{-}N2) = 110.3°$.

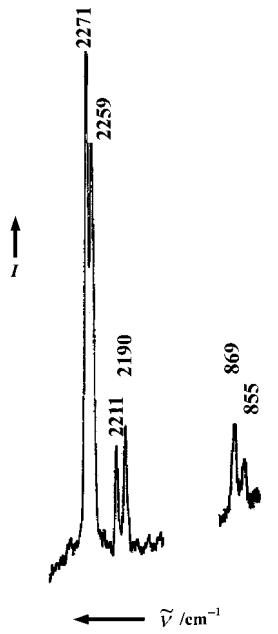

Figure 4. Low-temperature Raman spectrum of an equimolar mixture of solid $[^{15}N^{14}N^{14}N^{14}N^{14}N]^+AsF_6^-$ and $[^{14}N^{14}N^{15}N^{14}N^{14}N]^+AsF_6^-$.

The results from a normal coordinate analysis of N_5^+ are summarized in Table 4. They show that the A_2, B_1, and B_2 vibrations and $\nu_1(A_1)$ are all highly characteristic, but that $\nu_2(A_1)$ is a mixture of stretches and bends.

The internal force constants of greatest interest are the stretching force constants f_r and f_R of the terminal and the central N–N bonds, respectively. Interpolation of the data in Table 4 and adjustments for the observed frequencies give values of 20.08 and 6.59 mdyn Å^{-1} for the terminal and the central N–N stretching force constants, respectively. The

Table 2. Low-temperature Raman and IR bands of solid $^{14}N_5^+AsF_6^-$ and their assignments based on the calculated harmonic frequencies of free gaseous N_5^+.

Obsd frequencies [cm^{-1}][a]		Assignment (point group)		Calcd frequencies [cm^{-1}][b]	
Raman[c]	IR[d]	$^{14}N_5^+(C_{2v})$	$AsF_6^-(O_h)$	B3LYP	CCSD(T)
2271 [44]	2270 (m)	$\nu_1(A_1)$		2336 (22)	2229 (13) [215][e]
2211 [8]	2210 (s)	$\nu_7(B_2)$		2282 (147)	2175 (105) [42]
	1088 (s)	$\nu_8(B_2)$		1167 (141)	1032 (138) [2]
871 [7]	872 (w)	$\nu_2(A_1)$		850 (4)	818 (0.5) [5]
	704 (vs)		$\nu_3(F_{1u})$		
686 [100]	680 (sh)		$\nu_1(A_{1g})$		
672 [17], 669 [18]		$\nu_3(A_1)$	or part of $\nu_1(A_{1g})$ or $\nu_3(F_{1u})$	678 (1)	644 (2) [1]
579 [16]	575 (w)		$\nu_2(E_g)$		
		$\nu_5(A_2)$		502 (0)	475 (0) [1]
	420 (sh)	$\nu_6(B_1)$		424 (7)	405 (6) [0]
		$\nu_9(B_2)$		436 (0.6)	399 (1) [0.5]
	394 (vs)		$\nu_4(F_{1u})$		
372 [32]	360 (sh), 380 (sh)		$\nu_5(F_{2g})$		
209 [44]		$\nu_4(A_1)$		193 (0.5)	181 (0.3) [6]
127 [55]		lattice vibration			

[a] Relative IR and Raman intensities given in parentheses and brackets, respectively. [b] Frequencies calculated using a 6–311 + G(2d) basis set. IR intensities given in parentheses [km mol^{-1}], and Raman intensities given in brackets [Å^4 amu^{-1}]. [c] $T = -130$ °C. [d] $T = -196$ °C. [e] The Raman intensities were calculated at the RHF level.

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Table 3. Comparison of the calculated (B3LYP) and observed ^{15}N isotopic shifts for N_5^+.

N_5^+ isotopomer	Calcd frequencies (shifts) [cm^{-1}]								
	$\nu_4(A_1)$	$\nu_9(B_2)$	$\nu_6(B_1)$	$\nu_5(A_2)$	$\nu_3(A_1)$	$\nu_2(A_1)$	$\nu_8(B_2)$	$\nu_7(B_2)$	$\nu_1(A_1)$
$^{14}N1$-$^{14}N2$-$^{14}N3$-$^{14}N2$-$^{14}N1$	193.1(0)	424.1(0)	436.3(0)	502.4(0)	678.1(0)	850.0(0)	1116.9(0)	2281.7(0)	2336.3(0)
$^{14}N1$-$^{14}N2$-$^{15}N3$-$^{14}N2$-$^{14}N1$	191.8(1.3)	422.0(2.1)	436.0(.2)	502.4(0)	677.5(.7)	833.3(16.7)	1138.0(28.9)	2281.2(.5)	2336.3(.1)
$^{15}N1$-$^{14}N2$-$^{14}N3$-$^{14}N2$-$^{14}N1$	190.8(2.2)	422.3 (1.8)	434.7(1.5)	500.7(1.7)	674.4(3.7)	847.4(2.6)	1163.4(3.5)	2259.8(21.9)	2324.5(11.9)

N_5^+ isotopomer	Obsd frequencies (shifts) [cm^{-1}][a]					
	$\nu_2(A_1)$, IR	$\nu_2(A_1)$, RA	$\nu_7(B_2)$, IR	$\nu_7(B_2)$, RA	$\nu_1(A_1)$, IR	$\nu_1(A_1)$, RA
$^{14}N1$-$^{14}N2$-$^{14}N3$-$^{14}N2$-$^{14}N1$	872(0)	871(0)	2210(0)	2211(0)	2271(0)	2271(0)
$^{14}N1$-$^{14}N2$-$^{15}N3$-$^{14}N2$-$^{14}N1$	858(14)	855(16)	2209.8	2211(1)	2270.8	2271(0)
$^{15}N1$-$^{14}N2$-$^{14}N3$-$^{14}N2$-$^{14}N1$	870(2)	869(2)	2189.0(21)	2190(21)	2259.0(12)	2259(12)

[a] RA = Raman.

Table 4. Results from the normal coordinate analysis[a] of N_5^+.

Approx. mode in point group C_{2v}			Frequency [cm^{-1}]		Symmetry force constants[b] CCSD(T) (B3LYP)				Potential energy distribution[a] [%]
			obsd	calcd CCSD(T) (B3LYP)					CCSD(T)
A_1	ν_1	in-phase terminal stretches	2270	2229 (2336)	F_{11}	19.573(21.314)			93(1) + 6(2)
	ν_2	sym. central stretch	872	818 (850)	F_{22}	0.702(0.843)	5.546(6.952)		62(2) + 23(3) + 13(4) + 2(1)
	ν_3	central bending		644 (678)	F_{33}	−0.085(−0.137)	1.377(1.535)	1.540(1.427)	39(3) + 33(2) + 23(4) + 5(1)
	ν_4	in-phase terminal bends	209	181 (193)	F_{44}	0.167(0.171)	0.204(0.312)	0.120(0.108)	0.373(0.425) 64(4) + 37(3) − (2)
A_1	ν_5	torsion		475 (502)	F_{55}	0.0266(0.0281)			100(5)
B_1	ν_6	torsion		405 (424)	F_{66}	0.0236(0.0246)			100(6)
						F_{77}	F_{88}	F_{99}	
B_2	ν_7	out-of-phase term stretch	2210	2175 (2282)	F_{77}	19.491(21.272)			96(7) + 4(8)
	ν_8	asym. central stretch	1088	1032 (1167)	F_{88}	1.197(1.359)	4.780(5.927)		95(8) + 4(7)
	ν_9	out-of-phase terminal bends		399 (436)	F_{99}	0.200(0.195)	0.085(0.159)	0.358(0.423)	99(9) + 1(8)

[a] The following symmetry coordinates were used for $[N1\text{-}N2\text{-}N3\text{-}N2'\text{-}N1']^+$: $S_1 = \nu(1-2) + \nu(1'-2')$; $S_2 = \nu(2-3) + \nu(2'-3)$; $S_3 = \delta(2-3-2')$; $S4 = \delta(1-2-3) + \delta(1'-2'-3)$; $S_5 = \tau(1-2-3-2') + \tau(2-3-2'-1')$; $S_6 = \tau(1-2-3-2') - \tau(2-3-2'-1')$; $S_7 = \nu(1-2) - \nu(1'-2')$; $S_8 = \nu(2-3) - \nu(2'-3)$; $S_9 = \delta(1-2-3) - \delta(1'-2'-3)$. [b] The two most important internal force constants, estimated from the calculated symmetry force constants and the observed frequencies are $f_{(1-2)} = 20.08$ mdyn Å^{-1} and $f_{(2-3)} = 6.59$ mdyn Å^{-1}. Streching constants in mdyn Å^{-1}, deformation constants in mdyn Å^{-1} rad^{-2}, and stretch-bend interaction constants in mdyn rad^{-1}.

former value is significantly lower than the 22.4 mdyn Å^{-1} found for the N≡N bond in N_2,[15] whereas the latter value is between those found for typical N–N single (f_{N-N} = 3.6 mdyn Å^{-1}) and double bonds (f_{N-N} = 10.2 mdyn Å^{-1}).[15] The strengthening of the N–N central bonds at the expense of the terminal bonds, as suggested by the resonance structures, explains the relative stability of N_5^+ toward N_2 elimination. Reliable calculations of the energy barrier for N_2 elimination from N_5^+ will be the subject of a separate study.

Experimental Section

Caution! $N_5^+AsF_6^-$ is a highly energetic, strongly oxidizing material that can detonate violently. It should be handled only on a very small scale while using appropriate safety precautions (face shields, leather gloves, and protective clothing).

The $N_2F^+AsF_6^-$ was prepared from *cis*-N_2F_2 and AsF_5 as previously described.[16a–c] The HN_3 was generated by heating NaN_3 with a threefold excess of stearic acid to about 80 °C under a dynamic vacuum and collecting the evolved HN_3 in a trap cooled with liquid N_2. The HN_3 was purified by fractional condensation through a series of traps at −64, −95, and −196 °C, with the material retained at −95 °C being used. Singly ^{15}N-labeled NaN_3 (Cambridge Isotope Laboratories, 99 % ^{15}N label) was used for the preparation of a roughly 50:50 mixture of HN_3 that was singly ^{15}N-labeled in either the α or γ position. The HF (Matheson Co.) was dried by storage over BiF_5.[17]

The HN_3 was generated and handled on a Pyrex glass vacuum line equipped with grease-free Kontes glass-Teflon valves. The HF was handled on a previously described[18] stainless steel-Teflon FEP vacuum line. The $N_5^+AsF_6^-$ samples were handled at −196 °C in the dry N_2 atmosphere of a glove box.

Low-temperature Raman spectra were recorded on a Cary Model 83GT spectrometer using the 488-nm line of an Ar-ion laser for excitation, a previously described cooling device,[19] and quartz tubes (3 mm outer diameter) as sample containers. For measurements of the $^{14}N - ^{15}N$ isotopic shifts, the signal was scale expanded on an external strip chart recorder. The low-temperature IR spectra were recorded on a Mattson Galaxy FTIR

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spectrometer using a demountable low-temperature cell equipped with CsI windows. The ^{14}N and ^{15}N NMR spectra were recorded at 36.13 and 50.69 MHz, respectively, on a Bruker AMX 500 spectrometer using saturated solutions of $N_5^+AsF_6^-$ in HF/AsF_5 at $-63\,^\circ C$ and heat-sealed 5-mm Teflon-FEP liners (Wilmad Glass Co.) as sample containers, delay times of 60–120 s for the recording of the ^{15}N spectra, and neat CH_3NO_2 and aqueous ^{15}N-labeled urea referenced as $\delta = -305.0$ relative to CH_3NO_2 as external standards. The spectra were recorded both ^1H-coupled and ^1H-decoupled to determine if there was a nuclear Overhauser effect.

Preparation of $N_5^+AsF_6^-$: In a typical experiment, $N_2F^+AsF_6^-$ (1.97 mmol) was loaded in the drybox into a Teflon-FEP ampule (1.9 cm outer diameter) that was closed by a stainless steel valve. On the metal vacuum line, anhydrous HF (≈3 mL) was added at $-196\,^\circ C$, and the mixture was warmed to room temperature to dissolve the $N_2F^+AsF_6^-$. The ampule was connected to the glass line, and HN_3 (2.39 mmol) was added at $-196\,^\circ C$. The ampule was reconnected to the metal line and allowed to warm to $-78\,^\circ C$, where it was kept for three days with occasional gentle agitation. The ampule was then cooled to $-196\,^\circ C$ to check for the presence of volatile products. Nitrogen (0.76 mmol) was identified by mass spectrometry. All material volatile at $-64\,^\circ C$ was pumped off for 8 h, leaving behind a white solid residue that was identified by low-temperature vibrational and ^{14}N and ^{15}N NMR spectroscopy as a mixture of $N_5^+AsF_6^-$ (≈80 mol %) and $H_2N_3^+AsF_6^-$ (≈20 mol %).

Preparation of ^{15}N-labeled $N_5^+AsF_6^-$: The procedure was identical to that used for the synthesis of unlabeled $N_5^+AsF_6^-$, except for the use of a mixture of HN_3 that was ^{15}N-labeled in either the N_α or N_γ position.

Computational Methods. Hartree–Fock (HF), density functional theory (DFT), and single- and double-excitation coupled cluster calculations[20] that include a noniterative treatment of connected triple excitations (denoted CCSD(T))[21] were carried out employing several atomic basis sets. The DFT calculations employed the B3LYP functional.[22] Geometries, IR and Raman spectra, and nuclear magnetic resonance shieldings were calculated for N_5^+ as well as (for calibration purposes) N_2F^+, $H_2N_3^+$, and the standard CH_3NO_2, the geometries and NMR parameters of which are experimentally known.[12, 14, 16] The vibrational spectra reported in this work were computed using the 6-311 + G(2d) atomic basis set.[23] The NMR shieldings were computed at the CCSD(T)/6-311 + G(2d) geometries employing the gauge-including atomic orbital (GIAO) solution to the gauge-invariance problem[24] and density matrices obtained from second-order many-body perturbation theory [MBPT(2)], CCSD, or CCSD(T) calculations.[25–27] The results reported in this work used quadruple-zeta plus polarization (QZP) atomic basis sets derived from the QZ sets of Schäfer et al.,[28] supplemented with a d function with exponent 1.0. As discussed by Gauss and Stanton,[25–27] the accurate calculation of nitrogen NMR shieldings frequently requires an extensive electron correlation treatment such as that provided by the CCSD(T) method. Hartree–Fock and even MBPT(2) shielding calculations for species such as N_5^+ with many free valence electron pairs yield extremely poor results. The GAMESS,[29] Gaussian,[30] and ACES II[31] program systems were used for these calculations on IBM RS/6000 work stations.

Received: March 9, 1999 [Z 13131 IE]
German version: *Angew. Chem.* **1999**, *111*, 2112–2118

Keywords: density functional calculations · isotopic labeling · nitrogen · NMR spectroscopy · vibrational spectroscopy

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  1433-7851/99/3813-2009 $ 17.50+.50/0