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Homopolyatomic Nitrogen Compounds[**]

Thomas M. Klapötke[*]

As a consequence of the high thermodynamic stability of the N_2 molecule other homopolyatomic nitrogen species are very rare. Dinitrogen, N_2, was first isolated in 1772 by D. Rutherford and also by C. W. Scheele and H. Cavendish (Figure 1).[1] Over 100 years later hydrazoic acid, HN_3, was prepared for the first time by T. Curtius, and numerous metal azides containing the linear, isolated $[N_3]^-$ ion have been characterized (Figure 1).[2] Sodium azide can be prepared by adding powdered $NaNO_3$ to fused $NaNH_2$ at 175 °C or by passing N_2O into the same molten amide at 190 °C [Eqs. (1) and (2), respectively].[1]

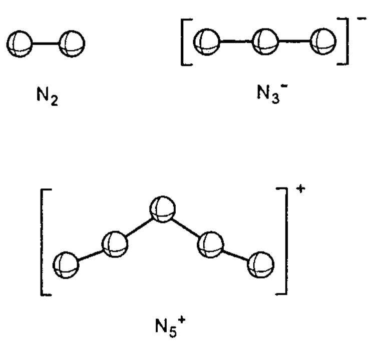

Figure 1. Structures of the isolated homopolyatomic polynitrogen species N_2, N_3^-, and N_5^+.

$$NaNO_3 + 3\,NaNH_2 \xrightarrow{175\,^\circ C} NaN_3 + 3\,NaOH + NH_3 \tag{1}$$

$$N_2O + 2\,NaNH_2 \xrightarrow{190\,^\circ C} NaN_3 + NaOH + NH_3 \tag{2}$$

In covalently bound azides the N_3 group behaves as a pseudohalogen (for example in HN_3 and the halogen azides FN_3, ClN_3, BrN_3, and IN_3),[3] and although potential allotropes of nitrogen such as N_3–N_3 (analogous to Cl_2) and $N(N_3)_3$ (analogous to NCl_3) have not been unequivocally isolated the compounds have been extensively studied by quantum chemical methods (see below). The predicted high instability of any potential homopolyatomic nitrogen species stems from the particularly strong N–N triple bond in N_2 that has a bond energy of 226 $kcal\,mol^{-1}$, which is much higher than three single bonds ($3 \times 37.8\ kcal\,mol^{-1}$), a single and a double bond ($37.8 + 99.9\ kcal\,mol^{-1}$) or 1.5 times the average N–N double bond energy ($1.5 \times 99.9\ kcal\,mol^{-1}$).[4]

Quite recently K. Christe and co-workers reported on the fundamentally and surprisingly straightforward preparation and characterization of the salt $[N_5]^+[AsF_6]^-$ in anhydrous HF [Eq. (3)]. This salt contains the novel N_5^+ cation (Figure 1), which represents only the third stable member of the N_n family made in this century.[5] Certainly, Karl Christe and co-workers deserve warm congratulations on this! The synthesis of this N_5^+ species is therefore a major breakthrough in research centered on the investigation of the elusive N_n species. The interest in the formation of the N_5^+ cation is not only that it is such a novel compound, but also for its potential to act as a precursor to many more polynitrogen systems. The new compound $[N_5]^+[AsF_6]^-$ is a white solid with marginal stability at room temperature but which can be stored for weeks at $-78\,^\circ C$.

$$N_2F^+[AsF_6]^- + HN_3 \xrightarrow{HF,\ -78\,^\circ C} N_5^+[AsF_6]^- + HF \tag{3}$$

The existence of the N_5^+ cation was first predicted by P. Pyykkö and N. Runeberg.[6] However, these authors found a $^3\sigma$ ground state $[(N{\equiv}N)\cdots(N_3)]^+$ for N_5^+. The symmetrical C_{2v} $^1\sigma$ state of N_5^+, which has now been observed experimentally by Christe et al., lies 1.962 eV above the asymmetrical triplet at the MP2 level of theory. However, Pyykkö and Runeberg had already pointed out that the very different geometry of

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the higher-lying C_{2v}-symmetric N_5^+ ion state ($^1\sigma$) might achieve local stability for the N_5^+ species, and this has now been confirmed by Christe et al. In the most recent experimental study by Christe et al. they identified the C_{2v}-symmetric N_5^+ ion ($^1\sigma$) and characterized this compound by means of ^{14}N/^{15}N NMR and vibrational (IR, Raman) data.[5a,b] The very good agreement between the computed and observed vibrational frequencies for the N_5^+ ion gives credence to the calculated structural parameters of this novel polynitrogen species (Table 1). Moreover, the agreement between experiment and theory for both the structural and vibrational parameters for the only other isolated homopolyatomic nitrogen species N_2 and N_3^- is also very good (Table 1).

Table 1. Computed (B3LYP/6-311 + G(2d)) and observed (in parentheses) structures and vibrational data for N_2, N_3^-, and N_5^+.

	N_2	N_3^-	N_5^+
symmetry	$D_{\infty h}$	$D_{\infty h}$	C_{2v}
d(N–N, terminal) [Å]	1.092 (1.098)[1]	1.181 (1.180)[1]	1.110
d(N–N, central) [Å]			1.300
$\tilde{\nu}_1$ [cm^{-1}]	2435 (2360)[7]	1345 (1344)[7]	2336 (2271)
$\tilde{\nu}_2$ [cm^{-1}]		654 (645)[7]	850 (871)
$\tilde{\nu}_3$ [cm^{-1}]		2048 (2041)[7]	678
$\tilde{\nu}_4$ [cm^{-1}]			193 (209)
$\tilde{\nu}_5$ [cm^{-1}]			502
$\tilde{\nu}_6$ [cm^{-1}]			424 (420)
$\tilde{\nu}_7$ [cm^{-1}]			2282 (2211)
$\tilde{\nu}_8$ [cm^{-1}]			1167 (1088)
$\tilde{\nu}_9$ [cm^{-1}]			436
δ (^{15}N)		N1-N2-N3	N1-N2-N3-N2-N1
	(−70.0)[8]	N1: (−277)[9]	N1: (−237.3)
		N2: (−128)[9]	N3: (−100.4)

The symmetrical triatomic azide ion N_3^- is isoelectronic with N_2O.[10] The standard Lewis (**1** and **3**) and increased-valence structures (**2** and **4**) are displayed in Figure 2.[11] The resonance between the increased-valence structures (together with their mirror-image structures) indicates more clearly than does the resonance between the standard Lewis structures that the N–N bond lengths (1.18 Å, see Table 1) are shorter than that of double bonds (estimated value 1.24 Å). The increased-valence structures (which may be derived from the standard Lewis structures through the one-electron delocalizations indicated) involve smaller formal charge separations, and are more stable than the Lewis structures.[11] Similarly, for the N_5^+ ion, which is isoelectronic with $C(N_2)_2$ and $C(CO)_2$, structures **5** and **6** are analagous standard Lewis and increased-valence structures (see ref. [12]). Inspection of structure **6** alone makes it clear why the central and terminal bonds are shorter than an N–N single bond (1.45 Å) and similar to that of N_2. There is an interesting alternative for describing double and triple bonds on the basis of valence bond theory.[11c]

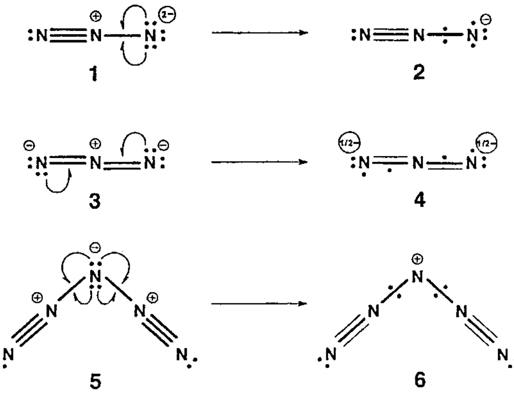

Figure 2. Standard Lewis and increased-valence structures for N_3^- and N_5^+. The thin bonds show fractional electron pair bonds.

Attempts to obtain other polynitrogen compounds experimentally have focused on the $N_3^{\bullet}$ radical[13] and also in 1995, the observation of the $N_6^{\bullet -}$ radical ion was reported.[14] Many more homopolyatomic nitrogen compounds (Figure 3), however, have been investigated by quantum chemical calculations to determine whether the potential use of polynitrogen compounds as high-energy-density materials (HEDM) could be realized.[15] In perhaps the most comprehensive theoretical study in this area, P. von R. Schleyer et al. and M. T. Nguyen et al. discovered that besides N_2, the thermodynamically most stable N_n molecules are all based on pentazole units.[15, 16] Pentazole, HN_5, and its anion N_5^- (D_{5h}), were established theoretically to be as aromatic as their isoelectronic analogues furan, pyrrole, and the cyclopentadienide anion. The azidopentazole with C_s symmetry (N_5–N_3) is calculated to be the lowest energy N_8 isomer, but is still 196.7 kcal mol^{-1} higher in energy than four N_2 molecules. It is interesting to speculate

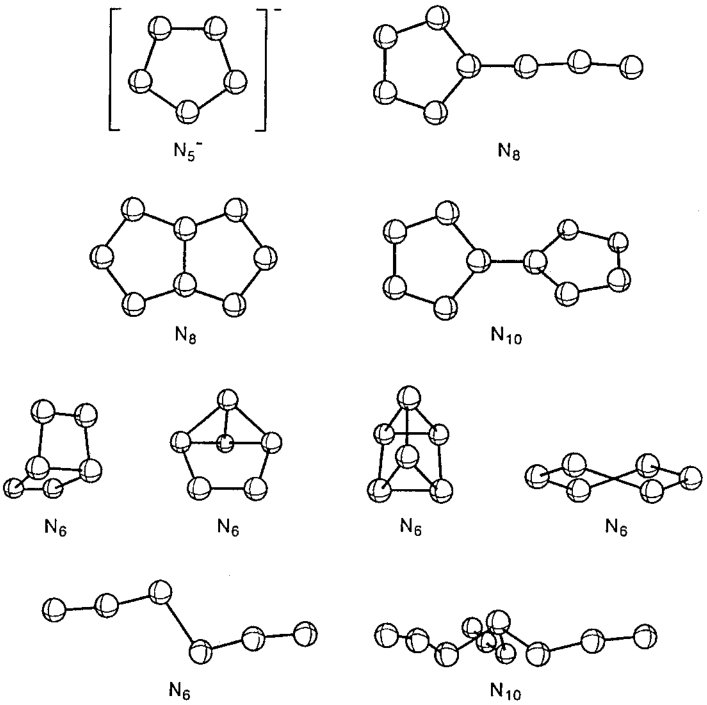

Figure 3. Structures of some theoretically investigated homopolyatomic nitrogen species. From top left to bottom right: pentazole anion (D_{5h}), azidopentazole (C_s), octaazapentalene (D_{2h}), bispentazole (D_{2d}), hexaaza Dewar benzene (C_{2v}), hexaazabenzvalene (C_{2v}), hexaazaprismane (D_{3h}), twisted boat (D_2), diazide (C_2), nitrogen triazide (C_3).

whether the reaction of the newly discovered N_5^+ ion with an ionic azide moiety may or may not provide a synthetic route to the hitherto unknown N_8 molecule. For example, the reaction of $N_5^+[AsF_6]^-$ (Christe's salt) with cesium azide should yield $Cs[AsF_6]^-$ (which is "insoluble" in anhydrous HF; [Eq. (4)]).

$$N_5^+[AsF_6]^- + CsN_3^- \xrightarrow{\text{aHF}} N_5^+N_3^- + Cs[AsF_6] \quad (4)$$

However, it seems to be doubtful whether the C_{2v}-shaped N_5^+ cation would undergo a cyclization reaction. Octaazapentalene (D_{2h}) with ten π electrons is also aromatic. Finally, the bispentazole with D_{2d} symmetry is the calculated lowest energy N_{10} isomer, but is still 260 kcal mol^{-1} higher in energy than five N_2 molecules.

Among all the possible isomers of the N_6 molecule only the analogues of Dewar benzene (C_{2v}), benzvalene (C_{2v}), prismane (D_{3h}), and a twisted D_2 form (Figure 3) have been found to represent stable minima, whereas the aromatic benzene analogue (D_{6h}) was found to be a second order saddle point. In contrast, the stability of the twisted open-chain diazide molecule (C_2) is still questionable.[17–19] Whereas P. von R. Schleyer et al. reported this to be the most stable N_6 isomer at the MP2 level of theory,[15] R. Engelke published a paper in the same year that indicated that the C_2 diazide molecule is stable at the HF level, but represents a transition state at MP2 level of theory.[17] Further high level quantum chemical computations including even higher levels of correlation such as coupled cluster calculations are necessary in order to answer conclusively the question of the stability of the N_6 isomers (see also ref. [21]). The *cis* structure (C_3) was calculated to be the most energetically favorable structure for the elusive nitrogen triazide species N_{10}, however, this structure was significantly less stable than the bispentazole (D_{2d}).[20]

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