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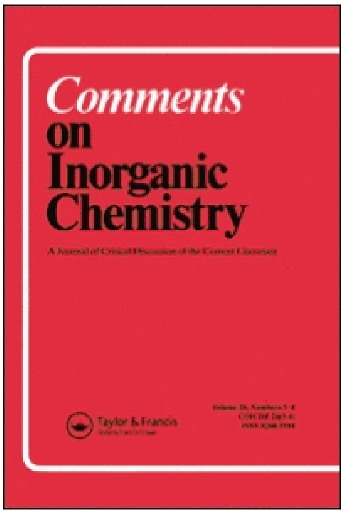

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Recent Developments in the Chemistry of Binary Nitrogen-Halogen Species

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Recent Developments in the Chemistry of Binary Nitrogen–Halogen Species

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The chemistry of the most recent years of binary nitrogen–halogen species is discussed in four chapters. Chapter I focusses on nitrogen–fluorine compounds, including NF_3, N_2F_4, N_2F_2 and the NF_4^+, $N_2F_3^+$, N_2F^+ and NF^{2+} cations. In Chapter II the trihalogeno nitrides NX_3 (X = Cl, Br, I) and the NCl_4^+ cation are described and the likely existence of heavier analogues NBr_4^+ and NI_4^+ is discussed. Whereas all halogen azides XN_3 (X = F, Cl, Br, I) are summarized in Chapter III, the ionic nitrogen iodine species $I_2N_3^+$, $I(N_3)_2^+$, $I_2N_3^-$ and $I(N_3)_2^-$ are comprised in Chapter IV.

Key Words: *nitrogen–halogen chemistry, halogen azides, nitrogen trihalogenides, quantum mechanical computations*

INTRODUCTION

This review is not exhaustive in scope but rather focusses on the most recent years of work in the field of binary nitrogen–halogen

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species. Our aim has been to give the reader a broad picture of advances in this field. This area is still currently developing. The review summarizes structure, modern methods of preparation and some aspects of reactivity of binary nitrogen–halogen species. Modern theoretical aspects (ab initio MO computations, results from local density functional theory: LDF) as well as the energetics (thermodynamics) of these species are also included.

We intend to establish perspective with respect to earlier work and to contemporary research to evaluate the present state of the subject and to cast a glance to the future.

I. NITROGEN–FLUORINE SPECIES

While *all* binary N–Cl, N–Br and N–I compounds are thermodynamically unstable ($\Delta H_f^\circ > 0$), some, but by no means all (!), of the N–F species possess a negative heat of formation and are therefore thermodynamically stable entities. In this respect NF_3 is the most stable binary halide of nitrogen. However, generally these compounds are difficult to synthesize and are often explosive. Although in the 1960s research in N–F chemistry was directed into rocket propellants and currently there is some work concerning N–F compounds as energy sources for high-powered lasers, none of the compounds studied has come into widespread use for either purpose. They are, however, powerful oxidizers and fluorinating agents and of great interest for inorganic chemistry. Moreover, because of the high electron density, accurate ab initio wavefunctions have proved difficult to obtain but are of special interest in terms of ab initio electronic structure computations.[1]

Table I summarizes the most important binary N–F species which have been reported, including all isolated compounds.

NF_3

The nitrogen fluorides were unknown until 1928 when NF_3 was prepared by electrolysis of molten $NH_4F \cdot HF$.[3] Since then there has been great interest in the chemistry of NF_3, which was reviewed in 1962[10] and 1989[3] and therefore will not be discussed in this review. In particular, NF_3 has been of interest because of its po-

TABLE I

Binary nitrogen–fluorine species

Species	Geometry	ΔH_f° (kJ mol^{-1})[a]	d(N–F) (pm)	Reference
NF_3	C_{3v}	−125	137	2, 3
NF_4^+	T_d	+211	130	4
N_2F_4	C_{2h}(trans)[b]	−7	137	2, 3
$N_2F_3^+$	C_s			5, 6
cis-N_2F_2	C_{2v}	+70	141	2, 3
trans-N_2F_2	C_{2h}	+82	140	2, 3
N_2F^+	$C_{\infty h}$	+283	122	7
NF^{2+}	$C_{\infty v}$		110[c]	8
FN_3	C_s		144	9

[a] Data for gaseous state.

[b] N_2F_4 apparently exists in both the staggered (trans) C_{2h} and gauche C_2 conformations.

[c] Calculated value.

tential applications as a high-energy oxidizer for HF–DF chemical lasers, where it can replace elemental fluorine in the reaction with hydrogen.[3]

Compared with other N-fluoroamines the N–F bond in NF_3 is relatively short and the energy required to break the first of the three N–F bonds is about 239 kJ mol^{-1}.[3] Recent studies show that the N–F bond lengths in the series H_nNF_{3-n} increase strongly from 137 pm in NF_3 via 140 pm in HNF_2 to 144 pm in H_2NF.[11,12] This bond lengthening can be rationalized by a simple electrostatic model. The Mulliken atomic charges indicate strong attractive $N^{\delta+}$–$F^{\delta-}$ interaction in NF_3, weak attraction in HNF_2 and repulsive electrostatic interaction $N^{\delta-}$–$F^{\delta-}$ in H_2NF. In the case of the methylfluoroamines (d(N–F): $MeNF_2$, 142 pm; Me_2NF, 145 pm), a still larger variation of the N–F bond lengths occurs. This effect can be explained by the strong electron-donating property of the methyl groups. Therefore, the negative charge at nitrogen will be higher in Me_2NF compared to H_2NF, resulting in stronger electrostatic repulsion and in a longer N–F bond in the methyl derivative.[11]

The nitrogen versus fluorine protonation of NF_3 was studied in the gas phase by a combined mass spectroscopic (protonation by CH_5^+ and H_3^+) and ab initio analysis.[13] The global minimum corresponds to the F-protonated isomer $F_2N{-}FH^+$ which was found to be 27 kJ mol^{-1} more stable than its N-protonated form F_3NH^+. Both isomers are separated by a significant barrier (219 kJ mol^{-1}) which prevents facile conversion.

NF_4^+

While nitrogen trifluoride, NF_3, has been known since 1928,[2] the isolation of NF_4^+ salts was not before 1966 and has proved to be a milestone in non-metal fluorine chemistry.[14-16] For a long time the synthesis of NF_4^+ salts had been discouraged by (i) the non-existence of a NF_5 parent molecule (conjugated base to NF_4^+) and (ii) the high ionization potentials of NF_3 and F_2.

The first convenient, simple and high-yield synthesis for $NF_4^+BF_4^-$ was published in 1976.[17] Low-temperature uv photosynthesis was used to synthesize the NF_4^+ salts containing the BF_4^-, AsF_6^-, PF_6^- and GeF_5^- anions:

$$\begin{gathered} NF_3 + F_2 + A \xrightarrow{\text{uv, } -196°\text{C}} NF_4^+AF^- \\ A = BF_3,\ AsF_5,\ PF_5,\ GeF_4 \end{gathered} \qquad (1)$$

Generally there are four principal routes to synthesize NF_4^+ salts on a preparative scale:

—low-temperature glow discharge[14,15];
—uv photosynthesis[17];
—direct synthesis from NF_3, F_2 and the corresponding Lewis acid BiF_5 or SbF_5 at elevated temperatures and pressures[18,19];
—microwave discharge.[20]

The BiF_6^- salt can either be prepared from NF_3, F_2 and BiF_5 [Eq. (2)] or based upon the displacement reaction between $NF_4^+BF_4^-$ and BiF_5 using either heat [Eq. (3)] or a solvent such as AHF (anhydrous HF) [Eq. (4)].[19]

$$NF_3 + F_2 + 1 + n\,BiF_5 \xrightarrow{250°\text{C, 30 h, 170 bar}} NF_4^+BiF_6^- \cdot nBiF_5, \qquad (2a)$$

$$NF_4^+BiF_6^- \cdot nBiF_5 \xrightarrow{280°\text{C, 15 h, vac.}} NF_4^+BiF_6^- + nBiF_5, \qquad (2b)$$

$$NF_4^+BF_4^- + BiF_5 \xrightarrow{180°C} NF_4^+BiF_6^- + BF_3, \qquad (3)$$

$$NF_4^+BF_4^- + BiF_5 \xrightarrow{AHF} NF_4^+BiF_6^- + BF_3 \qquad (4)$$

A one-step synthesis of $NF_4^+BiF_6^-$, however, provides the reaction according to Eq. (5) generating the Lewis acid BiF_5 as an intermediate species.[19]

$$NF_3 + 2\,F_2 + BiF_3 \xrightarrow{235°C,\ 9d,\ 200\ bar} NF_4^+BiF_6^- \qquad (5)$$

In conclusion, although a large number of NF_4^+ salts are known, only two of these salts, $NF_4^+SbF_6^-$ [18] and $NF_4^+BiF_6^-$ [19] are readily accessible by direct synthesis from NF_3, F_2 and the corresponding Lewis acids at elevated temperatures and pressure. However, by metathetical exchange of the anion in AHF or BrF_5, further salts are obtainable[21–24]:

$$2\,NF_4^+SbF_6^- + Cs_2MF_6 \xrightarrow{AHF} 2\,CsSbF_6 + (NF_4)_2MF_6 \qquad (6)$$
$$M = Ti, Ni, Sn$$

The room temperature tetragonal structure of $NF_4^+BF_4^-$ has been determined by a combination of single-crystal X-ray diffraction analysis and vibrational spectroscopy.[4] The structure is made up of an approximately tetrahedral NF_4^+ cation and a BF_4^- anion that rotates or oscillates around a 3-fold axis along one of its bonds.

In terms of applications such as NF_3–F_2 gas generators[25] and energetic formulations it is also necessary to replace the SbF_6^- anion by lighter and/or more energetic anions. Although this is also possible by a metathetical exchange reaction [Eq. (7)] the main drawbacks of this reaction include the following:

(i) the purity of the resulting $NF_4^+BF_4^-$ is only about 92%,
(ii) the yields of $NF_4^+BF_4^-$ are less than quantitative (about 80%) and
(iii) the metathetical reaction has to be carried out at low temperatures.

$$NF_4^+SbF_6^- + Cs^+BF_4^- \xrightarrow{AHF} CsSbF_6 + NF_4^+BF_4^- \qquad (7)$$

A recently reported one-step procedure under ambient conditions is the anion exchange in NF_4^+ salts using graphite salt as an oxidizer- and acid-resistant anion-exchange medium. The usefulness of graphite salts such as $C_8^+BF_4^-$ and $C_8^+AsF_6^-$ [prepared according to Eqs. (8) and (9)] as anion exchangers was demonstrated by an improved method for the production of NF_4^+ salts[26]:

$$8\,C + 1/2\,F_2 + BF_3 \rightarrow C_8^+BF_4^-, \tag{8}$$

$$8\,C + O_2^+AsF_6^- \rightarrow C_8^+AsF_6^- + O_2, \tag{9}$$

$$\begin{gathered} C_8^+AF^- + NF_4^+SbF_6^- \xrightarrow{AHF} C_8^+SbF_6^- + NF_4^+AF^- \\ A = BF_3,\ AsF_5 \end{gathered} \tag{10}$$

This method eliminates most of the drawbacks of the previously used low-temperatures metathetical process and provides the desired NF_4^+ salts in high purities and yields by a simple, one-step process under ambient conditions.

Concerning the formation and decomposition mechanism of NF_4^+ salts, there had been some doubt in the past and several mechanisms had been postulated for the formation of NF_4^+ salts. In 1972, as the result of a kinetic study of thermal decomposition of $NF_4^+AsF_6^-$, a mechanism was proposed that involved the equilibrium dissociation step of $NF_4^+AsF_6^-$ generating NF_5 and AsF_5 followed by irreversible decompositon of the unstable NF_5 to yield NF_3 and F_2.[27] However, a critical evaluation of all experimental data on the NF_4^+ salt formation and decomposition suggests that the above mechanism (involving NF_5) is *not* correct.[28] It is more likely that the salt formation and decomposition can be described by the following mechanism[28]:

$$F_2 \rightarrow 2\,F\cdot \tag{11a}$$

$$F\cdot + AsF_5 \rightarrow AsF_6\cdot \tag{11b}$$

$$AsF_6\cdot + NF_3 \rightarrow NF_3^+\cdot AsF_6^- \tag{11c}$$

$$NF_3^+\cdot AsF_6^- + F\cdot \rightarrow NF_4^+AsF_6^- \tag{11d}$$

The above mechanism is in agreement with the experimental observation that NF_4^+ salts can be synthesized by uv photolysis (cf. B.E.(F–F) = 158 kJ mol^{-1}). Moreover, ESR studies confirmed the existence of the $NF_3^+\cdot$ radical cation as an intermediate in both the low-temperature uv photosynthesis and the γ-irradiation-induced decomposition of NF_4^+ salts.[29–31] The $AsF_6\cdot$ radical species, however, has not been detected so far.[32]

Nicely in agreement with the above discussed mechanism is a very sophisticated experimental study on the existence of pentacoordinated nitrogen that confirms the previous suggestion that the lack of pentacoordinated nitrogen is mainly due to steric reasons.[33] In this investigation the thermal decomposition of $NF_4^+HF_2^-$ was studied by using ^{18}F labeled HF_2^-:

$$NF_4^+PF_6^- + Cs^+H^{18}F_2^- \xrightarrow{\text{AHF}} Cs^+PF_6^- + NF_4^+H^{18}F_2^-, \quad (12)$$

$$NF_4^+H^{18}F_2^- \xrightarrow{\Delta T,\ \text{vac.}} NF_3 + H^{18}F + F{-}^{18}F \quad (13)$$

The observed distribution of ^{18}F among the decomposition products clearly indicates that the attack of $H^{18}F_2^-$ on NF_4^+ occurs exclusively on fluorine and *not* on nitrogen, contrary to the predictions based on bond polarities.

In view of the small size of fluorine and its ability to achieve maximum coordination numbers for most elements, the existence of pentacoordinated nitrogen species containing ligands other than fluorine must be judged even less likely (except for hydrogen; cf. r,cov.: F = 54 pm, H = 30 pm).[34]

However, recent ab initio calculations suggest that covalent NF_5 and even NF_6^- are vibrationally stable and might be experimentally accessible.[1,35–37] An experimental study on the existence of nitrogen pentafluoride considering the covalent $NF_5(D_{3h})$ versus ionic $NF_4^+F^-$ allows the following conclusions: (i) ionic and covalent "NF_5" are of comparable energy, (ii) ionic $NF_4^+F^-$ should be experimentally more accessible than covalent NF_5 which should suffer from severe ligand-crowding effects and (iii) at temperatures as low as −142°C, metathetical experiments involving solvated NF_4^+ and F^- ions resulted in NF_3 and F_2 elimination, indicating that $NF_4^+F^-$ is unstable at or above −142°C.[38] The observed decomposition reaction according to Eq. (14) was calculated to be exothermic by about 134 kJ mol^{-1}.[38]

$$NF_4^+F^-(s) \rightarrow NF_3(g) + F_2(g) \tag{14}$$

Earlier studies report on the thermochemistry of NF_4^+ salts in general and on the enthalpy of formation of $NF_4^+XeF_7^-$ and the $NF_4^+SbF_6^-/BrF_3$ system.[39,40]

Recently a quantitative scale for the oxidation strength of oxidative fluorinators has been developed.[41] This scale is based on relative F^+ detachment energies (FPDE: fluor plus detachment energy). It was shown that the oxidizer strength depends not only on the number of fluorine ligands and the oxidation state and electronegativity of the central atom, but also on the presence of free valence electron pairs on the central atom and the geometry of the oxidizer. For NF_4^+ the FPDE value according to Eq. (15) was computed by local density functional calculations to be 752 kJ mol^{-1}.[41]

$$NF_4^+(g) \rightarrow NF_3(g) + F^+(g) \tag{15}$$

By this means NF_4^+ is a stronger oxidative fluorinator than IF_4^+ (886 kJ mol^{-1}) and ClF_2O^+ (807 kJ mol^{-1}) but is considerably weaker than XeF^+ (689 kJ mol^{-1}), N_2F^+ (582 kJ mol^{-1}) or KrF^+ (484 kJ mol^{-1}).[41]

The great potential of NF_4^+ salts, however, is not only that they are strong oxidative fluorinators but they also possess a remarkable capability to "store" elemental fluorine. $(NF_4^+)_2NiF_6^{2-}$ is an example of a stable salt containing both a strongly oxidizing cation and anion. As NF_5 is unknown and NiF_4 is unstable at elevated temperatures, the salt decomposes to NF_3, lower nickel fluorides and elemental fluorine[23]:

$$(NF_4^+)_2NiF_6^{2-} \xrightarrow{\Delta T} 2\ NF_3 + NiF_{2+x} + (3 - x/2)F_2 \tag{16}$$

On thermal decomposition 1 cm^3 of solid $(NF_4^+)_2NiF_6^{2-}$ is capable of producing 12% more useful fluorine values, i.e., in the form of F_2 and NF_3, than liquid fluorine at −187°C. In other terms 1 l (2.7 kg, 7.65 mol) of $(NF_4^+)_2NiF_6^{2-}$ (d_{298} = 2.7 g cm^{-3}) produces 23 moles of F_2 on thermal decomposition. This is more than 50% of the amount of fluorine in the same volume of liquid $F_2(d_{85} = 1.518$ g $cm^{-3})$. Furthermore, $(NF_4^+)_2NiF_6^{2-}$ is a stable solid at ambient temperature and pressure which can be safely stored without requiring cryogenic cooling.[23]

N_2F_4 and $N_2F_3^+$

Dinitrogentetrafluoride, N_2F_4, exists in both the staggered (trans) C_{2h} and gauche C_2 conformations.[2,3] From ^{19}F NMR data there is experimental evidence for the coexistence of both conformations in nonpolar solvents between -130 and $-180°C$.[42] The compound, which is a relatively strong fluorinating agent (cf. Ref. 3), was originally made by partial defluorination of NF_3 with Cu or Hg and is now prepared by quantitative oxidation of difluoroamine with alkaline hypochlorite [Eq. (17)].[3]

$$(NH_2)_2CO \xrightarrow{F_2,N_2} NH_2CONF_2 \xrightarrow{H_2SO_4} HNF_2 \xrightarrow{NaOCl} 1/2\ N_2F_4 \tag{17}$$

N_2F_4 dissociates to give free NF_2 radicals [Eq. (18)].[43,44]

$$\begin{gathered} N_2F_4 \rightarrow 2\ NF_2 \\ K(150°C) = 0.03\ \text{atm};\ \Delta H° = 83\ \text{kJ mol}^{-1}. \end{gathered} \tag{18}$$

Salts of the corresponding cationic acid $N_2F_3^+$ were prepared from N_2F_4 either in AHF solution (SbF_5) or reacting the neat materials (AsF_5) [Eqs. (19) and (20)].[5]

$$N_2F_4 + 2\ SbF_5 \xrightarrow{AHF} N_2F_3^+ + Sb_2F_{11}^-, \tag{19}$$

$$N_2F_4 + AsF_5 \xrightarrow{\text{neat, r.t.}} N_2F_3^+ + AsF_6^- \tag{20}$$

All experimental data (IR, Raman, ^{19}F NMR) are consistent with a planar structure of symmetry C_s (diazenium ion structure) for $N_2F_3^+$.[5,6] Moreover, this structure (C_s) has also been supported by high-level ab initio computations (Fig. 1).[45] A report (Ref. 5) that revised the originally reported vibrational assignments for C_1 sym-

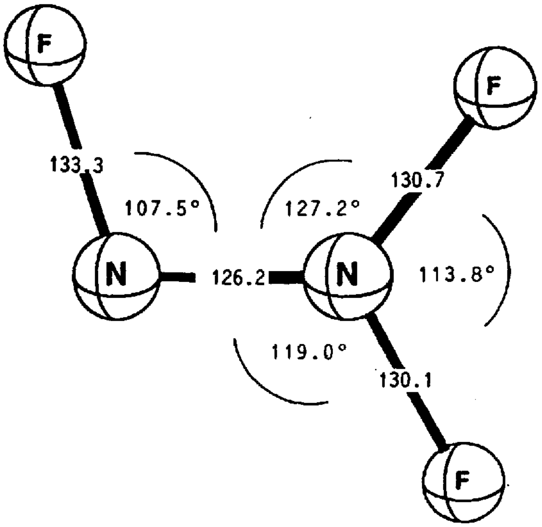


FIGURE 1 MP optimized C_s structure (diazenium ion structure) of $N_2F_3^+$ (bond lengths in pm).

metry (nitrenium structure, Ref. 46) was theoretically updated in terms of quantum-mechanical computations concerning the IR, Raman and NMR data ($^{14/15}N$, ^{19}F).[45]

N_2F_2 and N_2F^+

Dinitrogendifluoride, N_2F_2, is best prepared by passing difluoroamine, HNF_2 (for preparation, see above, N_2F_4), over KF at room temperature, the latter acting as a dehydrofluorinating agent[3]:

$$HNF_2 + KF \xrightarrow{\text{r.t.}} KHF_2 + 1/2\, N_2F_2 \tag{21}$$

N_2F_2 exists as two planar isomers, a cis and a trans form. In spite of a very small enthalpy difference of only 13 kJ mol^{-1} between the two isomers,[47] their properties and reaction chemistry are very different. For example, only the cis isomer reacts with strong Lewis acids to form N_2F^+ salts [Eq. (22)] and displacement reaction of $N_2F^+AsF_6^-$ and NOF yields exclusively cis-N_2F_2[7]:

$$\text{trans-}N_2F_2 \xrightarrow{70°\text{C, slow}} \text{cis-}N_2F_2, \tag{22a}$$

$$\text{cis-}N_2F_2 + AsF_5 \xrightarrow{\text{fast}} N_2F^+AsF_6^-, \tag{22b}$$

$$N_2F^+AsF_6^- + NOF \rightarrow \text{cis-}N_2F_2 + NO^+AsF_6^- \tag{23}$$

This great difference in the reactivity between cis- and trans-N_2F_2 cannot be due to differences in thermodynamic properties. How-

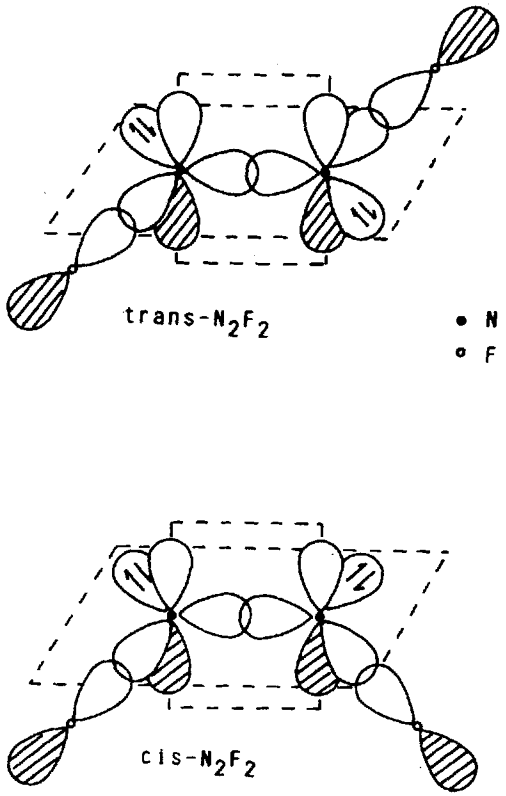


FIGURE 2 MO model for cis- and trans-N_2F_2 (Ref. 7).

ever, a semiempirical molecular orbital model can be used to explain the puzzling differences.[7] The bonding in N_2F_2 can be described by two sp^2-hybridized N atoms resulting in one N–N and two N–F σ-bonds and two sterically active, free valence electron pairs on the two nitrogen atoms. In addition, the remaining p orbitals on the nitrogen atoms form a p_π–p_π bond perpendicular to the plane of the sp^2 hybrids. In linear N_2F^+, the two nitrogens form a sp–sp σ-bond and two perpendicular p_π–p_π bonds (Fig. 2). When a Lewis acid, such as AsF_5, approaches a cis-N_2F_2 molecule, one of the fluorine ligands and thereby some electron density is pulled away from the remainder of the molecule. This removal of electron density from one of the nitrogen atoms should result in the lowering of the electron density in the antibonding orbitals of the two free valence electron pairs on the two nitrogens. This enables them to form a partial triple bond. Therefore, the energy required for the elongation of one of the N–F bonds can be compensated for by the simultaneous formation of a partial N≡N triple bond. However, the formation of such a triple bond should be possible only for the cis-isomer when the two valence electron pairs on the N atoms are on the same side. Therefore, as there is no free rotation around the N–N axis, the formation of N_2F^+ from the trans-N_2F_2 should be a high activation energy process requiring almost complete removal of one fluorine ion from N_2F_2.[7]

Similarly, the displacement reaction of $N_2F^+AsF_6^-$ [Eq. (23)] can be explained on the basis of this model. As $F{-}N^+{\equiv}N$ is the most important resonance structure for N_2F^+, the F^- (from NOF) attacks the α-N atoms resulting in the formation of an intermediate $F_2N{=}N$ molecule. The latter could easily undergo an α-F migration to give cis-N_2F_2 since in all migration steps a N=N π-bond is always retained (no free rotation).[7]

The crystal structure of $N_2F^+AsF_6^-$ was determined, indicating a N–F bond distance of 122 pm which is by far the shortest experimentally observed N–F bond.[7]

NF^{2+}

The NF^{2+} dication was experimentally observed by electron impact ionization (appearance energy: 44 eV) of NF_3 followed by mass analysis of the ionization products.[8] The direct detection of

NF^{2+} by mass spectroscopy indicates that the dication is a kinetically stable species, in agreement with recent ab initio molecular orbital calculations. A lower limit for the NF^{2+} lifetime was obtained to be $\geq 10\ \mu s$. Structurally, the NF^{2+} ion was calculated to have a short equilibrium bond length (110 pm) and a large dissociation barrier (445 kJ mol^{-1}) to the formation of N^+ and F^+.[48]

II. TRIHALOGENO NITRIDES

All binary NX_3 (X = F, Cl, Br, I) compounds are known. They are, however, with the exception of NF_3, all thermodynamically unstable and explosive species (Table II).[49,50] Whereas NF_3 and its congeners have already been discussed in the N–F section in this chapter, we focus on the trihalogeno nitrides in which nitrogen is negatively and the halogens positively polarized. This bond polarity is nicely demonstrated by the hydrolysis of NCl_3[2]:

$$NCl_3 + 3\,H_2O \rightarrow NH_3 + 3\,HOCl \qquad (24)$$

Preparation

NCl_3 can easily be obtained in H_2O/CCl_4 solution by direct chlorination of either NH_4Cl or $(NH_4)_2CO_3$.[55] The NH_4Cl route [Eq. (25)] provides an easy method for the preparation of ^{15}N labeled

TABLE II

Thermochemical and physical data of NX_3 (X = F, Cl, Br, I)

	$NF_3(g)$[3]	$NCl_3(l)$[51]	$NBr_3(g)$[52,51]	$NI_3(g)$[53,54]
ΔH_f° (kJ mol^{-1})	−125	+229	ca. + 280	+286
B.E. (N–X) (kJ mol^{-1})	278	190	ca. 176	169
b.p. (°C)	−129	+71		
m.p. (°C)	−207	−40	> −100	subl. −20°C, vac.

NCl_3 (^{15}N NMR, vibrational spectroscopy) since $^{15}NH_4Cl$ is commercially readily available.

$$NH_4Cl + 3\ Cl_2 \xrightarrow{H_2O/CCl_4} NCl_3 + 4\ HCl \qquad (25)$$

NBr_3 can be prepared as a deep-red, very temperature-sensitive, volatile solid by low temperature bromination of bistrimethylsilylbromamine with BrCl in pentane or $CFCl_3$ solution[56]:

$$(ME_3Si)_2NBr + 2\ BrCl \xrightarrow{-85°C} NBr_3 + 2\ Me_3SiCl \qquad (26)$$

NI_3 was first prepared as a polymeric adduct with one, three or five NH_3 molecules coordinated.[50] In excess of ammonia the three adducts exist in equilibrium:

$$\underset{\text{brown}}{1/n(NI_3\cdot NH_3)_n} + 4\ NH_3 \xrightleftharpoons[T\geq -30°C]{T\leq -30°C}$$

$$\underset{\text{green}}{1/n(NI_3\cdot 3\ NH_3)_n} + 2\ NH_3 \xrightleftharpoons[T\geq -75°C]{T\leq -75°C} \underset{\text{red}}{1/n(NI_3\cdot 5\ NH_3)_n} \qquad (27)$$

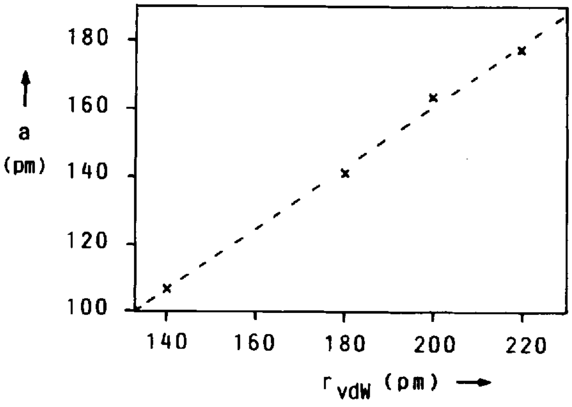
Whereas $(NI_3\cdot NH_3)_n$ is best prepared from liquid ammonia and elemental iodine (byproduct NH_4I),[51] it can also be obtained from the reaction of $I_3^+AsF_6^-$ and NH_3.[57]

The synthesis of free NI_3 can only be performed in the absence of ammonia, since $(NI_3\cdot NH_3)_n$ cannot be transferred into NI_3 by removal of NH_3, and according to thermochemical considerations the adduct $NI_3\cdot NH_3$ should be about 30 kJ mol^{-1} more stable than NH_3 and NI_3.[54] Activated boron nitride reacts with IF according to Eq. (28) to form explosive NI_3, a red-black, volatile solid, very unstable at room temperature and soluble in $CFCl_3$.[53]

$$1/n(BN)_n + 3\ IF \rightarrow NI_3 + BF_3 \qquad (28)$$

Structure

In accordance with VSEPR rules all NX_3 species possess trigonal pyramidal structure (C_{3v}); however, only NF_3 (see above) and NCl_3 have been studied experimentally.[58] The empirical relationship between the N–X bond distance d, the XNX angle θ and the



$$a = d \sin\left[\frac{\theta}{2}\right] = 0.90\, r_{vdW} - 19.3$$

correlation coefficient = 0.998; d, r_{vdW} in pm

FIGURE 3 Relationship between the structural parameters of NX_3 compounds and the halogen van der Waals radius.

TABLE III

Structural parameters for NX_3 (X = F, Cl, Br, I) compounds

	F	Cl	Br	I
r_{vdW} (pm)	140[60]	180[60]	200[60]	220[60]
θ (°)	102.5[3]	107[51]	112[a,61]	107[61,a]
d(N–X) (pm)	137[3]	176[51]	197[a,61]	221[61,a]

[a] MP2/6-31 + G*.

van der Walls radius of the corresponding halogen X shows a nearly linear correlation as shown in Fig. 3 (Table III).[59]

As there are no experimental structural data available for NI_3($NI_3 \cdot NH_3$ see below) the structure was first calculated by the use of semi-empirical molecular orbital methods AM1 and PM3.[62] These calculations suggest that NI_3 in the gas phase is close to planar in structure (μ = 0.004 D, d(N–I) = 194 pm). As this result did not fit the previously reported Raman data indicating a C_{3v} geometry for NI_3,[53] the structure was ab initio calculated and

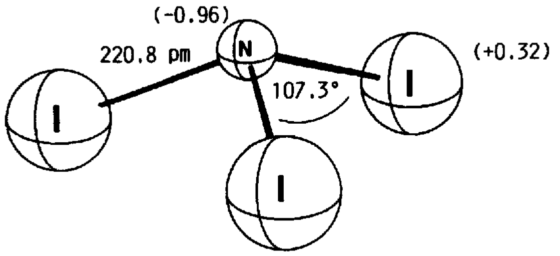


FIGURE 4 MP2 optimized structure of NI_3 (NPA charges in brackets).

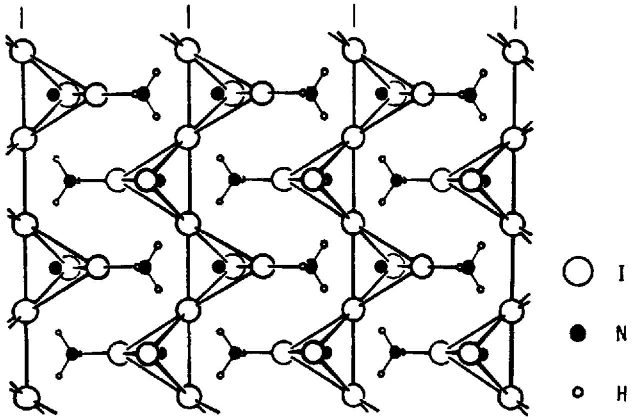


FIGURE 5 Polymeric structure of $(NI_3 \cdot NH_3)_n$. (Reprinted from N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Copyright 1993, p. 506, with kind permission from Pergamon Press Ltd., Headington Hill Hall, Oxford OX3 0BW, UK.)

fully optimized MP2(FC)/6-31G* (Fig. 4).[61] In agreement with the experimental spectroscopic results, the ab initio computation also shows a nonplanar C_{3v} structure of the isolated NI_3 molecule.

Unlike isolated NI_3, the involatile, insoluble compound $(NI_3 \cdot NH_3)_n$ has a structure in which tetrahedral NI_4 units are corner-linked into infinite chains of –N–I–N–I– (d(N–I) = 215 and 230 pm) as shown in Fig. 5. In addition one iodine atom of each NI_4 unit is also loosely attached to a NH_3 molecule ($d(I \cdots N)$ = 253 pm).[50]

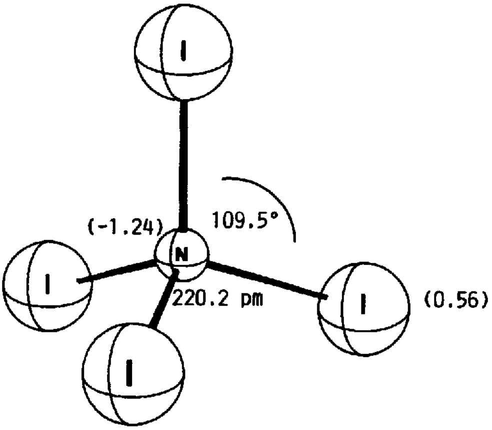


FIGURE 6 MP2 optimized structure of NI_4^+ (NPA charges in brackets).

NX_4^+ Species

Whereas NF_4^+ as the conjugated acid to the hitherto unknown NF_5 parent molecule is well established (see N–F section), only one of its heavier congeners, NCl_4^+, has been prepared.[63] The oxidative chlorination of NCl_3 [Eq. (29)] in SO_2 at low temperature led to the formation of $NCl_4^+AsF_6^-$ as a colorless, non-explosive solid which is indefinitely stable at −78°C. The salt was characterized by IR and Raman data including ^{15}N isotopic labeling experiments and foce field calculations.

$$2\,NCl_3 + Cl_2 + 3\,AsF_5 \xrightarrow{SO_2} 2\,NCl_4^+AsF_6^- + AsF_3 \quad (29)$$

Despite several attempts so far, the preparation of the NI_4^+ analogue has not been successful.[53] However, according to correlated ab initio computations (MP2(FC)/6-31G*), the NI_4^+ cation possesses a minimum in T_d symmetry (Fig. 6), and simple thermodynamic estimations predict that a salt $NI_4^+AsF_6^-$ should be assessable.[61] Therefore, NBr_4^+ also seems to be a likely candidate to be envisaged.

III. HALOGEN AZIDES

Whereas halogen azides have been known since the beginning of the 20th century, quite recently their isolation as pure compounds, their structural characterization and their thermodynamical stabilities have been reported. This is mostly due to the fact that these compounds are highly explosive and therefore their handling is difficult.[64–68]

Preparation

FN_3 is best prepared from dry hydrazoic acid and fluorine (diluted with N_2) in the gas phase[69]:

$$4\,HN_3 + 2\,F_2 \rightarrow 3\,FN_3 + N_2 + NH_4F \tag{30}$$

The most convenient method to prepare dry ClN_3 is the reaction of chlorine gas (diluted with N_2) with an aqueous solution of sodium azide [Eq. (31)] and following desiccation of the gaseous ClN_3 over P_4O_{10} prior to use.[70]

$$NaN_3 + Cl_2 \xrightarrow{0°C,\ H_2O} ClN_3 + NaCl \tag{31}$$

Pure BrN_3 can be obtained as a very explosive red liquid by passing a stream of gaseous bromine (diluted with N_2) over dry sodium azide [Eq. (32)] in a very slow reaction rate.[64]

$$NaN_3(s) + Br_2(g) \rightarrow NaBr(s) + BrN_3(l) \tag{32}$$

The best way to prepare IN_3 in nearly quantitative yield in a 0.5 g scale is the reaction of freshly prepared silver azide and iodine in $CFCl_3$ solution [Eq. (33)]. After separation of the IN_3 solution by filtration followed by slow evaporation of the solvent, very pure, bright yellow IN_3 can be isolated.[68]

$$I_2 + AgN_3 \xrightarrow{0°C,\ CFCl_3} IN_3 + AgI \tag{33}$$

Structures

All halogen azides are highly explosive compounds which can decompose violently when pressure changes or phase transitions occur, and therefore the structural characterization was hampered. The structure of FN_3 was recently determined by microwave spectroscopy and in addition FN_3 was fully characterized by its infrared spectrum.[9] Besides this, the results of ab initio calculations on FN_3 at the HF and correlated level were presented.[9]

ClN_3 was experimentally determined by uv,[71] microwave[67] and vibrational spectroscopy.[72] Some quantum mechanical calculations on ClN_3 have also been published.[66,73-75]

BrN_3 was characterized by its infrared spectrum[76] and quite recently the gas phase structure of BrN_3 was reported.[52]

IN_3 was investigated by uv[71] and vibrational spectroscopy.[77,78] In 1993 the structure of solid IN_3 was elucidated by single crystal X-ray diffraction and shown to be polymeric.[68] Several attempts to determine the structure of gaseous IN_3 have been unsuccessful[79]; However, due to ab initio calculations the structure is predicted to be similar to that of the other halogen azides.

FN_3, ClN_3 and BrN_3 (and presumably IN_3 in the gaseous state) possess monomer trans bent structures with C_s symmetry containing a slightly bent N_3 unit with two different N–N bond distances (Fig. 7). Lately a quantum mechanical ab initio study of structures

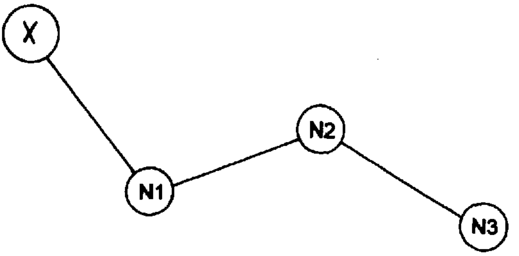


FIGURE 7 Molecular structure of XN_3 (X = F, Cl, Br).

TABLE IV

Experimental and calculated structural parameters for XN_3 (X = F, Cl, Br)

	FN_3: exp[9]/calc.[66,a]	ClN_3: exp[67]/calc.[66,a]	BrN_3: exp[52]/calc.[66,a]
d(X–N1) (pm)	144.4/143.1	174.5/175.3	190(1)/192.3
d(N1–N2) (pm)	125.3/128.0	125.2/126.5	123(2)/126.2
d(N2–N3) (pm)	113.2/115.2	113.3/115.7	113(2)/116.0
<(N1N2N3) (°)	170.9/171.7	171.9/171.3	171(2)/171.4
<(XN1N2) (°)	103.8/103.8	108.6/109.3	110(1)/108.5

[a] MP2/6-31 + G*.

and stabilities of all halogen azides was published[66] and the results concerning the calculated bond lengths and angles are in very good agreement with the experimental data. The experimental and calculated structural parameters of XN_3 species (X = F, Cl, Br) are listed in Table IV.

The X-ray diffraction determination of solid IN_3 states that IN_3 exists in I–N–I–N– chains, which are arranged along the *a* axis and in which every N atom belongs to one N_3 unit (Fig. 8). The chains lie roughly in the IN_3-plane and form layers in such a way that the iodine atoms of different layers are stacked vertically above each other and the terminal N atoms of the N_3 units are superimposed. The structural parameters of gaseous (computed) and solid (X-ray) IN_3 are compared in Table V. The bond distances in gaseous and solid IN_3 are essentially identical except the N–I bond distance. The N–I bond distance in solid IN_3 is significantly

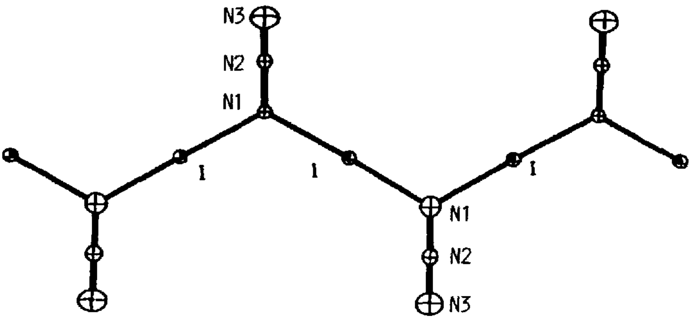


FIGURE 8 Polymeric structure of solid iodine azide.

TABLE V

Computed (isolated molecule) and experimental (X-ray) structural parameters of iodine azide.

	IN_3, solid (X-ray)[68]	IN_3, isolated molecule[a,68]
d(I–N1) (pm)	228(5)	213.3
d(N1–N2) (pm)	123(13)	125.8
d(N2–N3) (pm)	107(8)	116.7
<(N1N2N3) (°)	172(9)	171.4
<(IN1N2) (°)	116(16)	110.2

[a] MP2/6-31 + G*.

longer than in gaseous IN_3. This is due to the twofold coordination of the I atom in the polymeric chain, i.e., the iodine atom is a bridging atom. However, the N–I distance of 228 pm in solid IN_3 is in remarkable agreement with the observed N–I bond length for the $I(N_3)_2^-$ ion (227 pm).[80] Furthermore, the N_3 unit is as slightly bent as in other halogen azides.

Energetics

In recent quantum mechanical ab initio computations the calculated total energies were used to predict theoretically the bond energies and thermodynamic stabilities of the halogen azides which are (for obvious reasons) difficult to determine experimentally.[66] The X–N bond strength was derived from the calculated dissociation enthalpies according to Eq. (34)[66]:

$$XN_3 \xrightarrow{D_0} N_3 + X \qquad (34)$$

However, thermal fragmentation of XN_3 is not induced by breaking the $X–N_3$ bond but rather by dissociation into XN and N_2 [Eq. (35)] although this process is spin-symmetry forbidden.[66]

$$XN_3 \xrightarrow{D_0} N_2(^1\Sigma) + XN(^3\Sigma) \qquad (35)$$

The reaction enthalpy for dissociation of XN_3 into X_2 and N_2 [Eq. (36)] was also computed.[66]

$$2\,XN_3(g) \xrightarrow{\Delta H} 3\,N_2(g) + X_2(g) \qquad (36)$$

The calculated reaction enthalpies for the reactions according to Eqs. (34)–(36) are summarized in Table VI.[66]

The dissociation according to Eq. (34) is strongly endothermic for all halogen azides. The calculated dissociation energies $D_0(34)$ show that the $X–N_3$ bond strength decreases in the order F > Cl > Br > I. As shown experimentally for HN_3 a dissociation corresponding to Eq. (35) can take place although it is spin-symmetry forbidden. These $XN–N_2$ dissociations are predicted to be exothermic for FN_3, ClN_3 and BrN_3, but are predicted to be slightly endothermic for IN_3. The heat of reaction for a decomposition

TABLE VI

Calculated reaction enthalpies[a] for reactions (34)–(36)[66]

X	$D_0(34)$[b]	$D_0(35)$[b]	$\Delta H(36)$[b]	0.5 $\Delta H(36)$[b]	$\Delta H_f^\circ(XN_3)$[b]
F	+242	−105	−688	−343	+343
Cl	+205	−50	−778	−389	+389
Br	+196	−17	−811	−406	+426
I	+192	+29	−803	−401	+435

[a] MP2/6-31 + G*.

[b] All values in kJ mol^{-1}.

according to Eq. (36) is strongly exothermic for all halogen azides and is consistent with the positive heat of formation of XN_3 from the elements in the gaseous state. The molar heat of formation ΔH_f° for XN_3 shows that IN_3 is thermodynamically the least stable species. Nevertheless, BrN_3 was experimentally shown to be (kinetically) less stable than IN_3.[81] This observation cannot be explained by the reaction enthalpies according to Eqs. (34) and (36) because they are only insignificantly different. However, the reaction enthalpy of the dissociation of BrN_3 according to Eq. (35) is negative (exothermic process) contrary to the analogous reaction enthalpy value for the dissociation of IN_3 into IN and N_2 which is just slightly positive (endothermic). This explains why IN_3 is kinetically marginally more stable than BrN_3.

Vibrational Data

All halogen azides were characterized by vibrational spectroscopy[9,65,68,72,76–78] and the observed frequencies agree nicely with the computed wavenumbers.[66] The only exception is the ν(N–I) stretching mode of IN_3 which is still controversial. The N–I stretching mode was first observed at 338 cm^{-1} for solid IN_3 or solutions of IN_3.[77] Two years later the IR and Raman spectra of IN_3 in solid CCl_4 were presented and the N–I stretching mode was assigned to a band at 400–410 cm^{-1}.[78] The band at 338 cm^{-1} was also observed with low intensity and was attributed to solid iodine acid. This seems to be doubtful since the formation of iodine acid by hydrolysis of IN_3 is not very likely. On the other hand, the band at 400–410 cm^{-1} was better supported by ab initio calculations than the band at 338 cm^{-1}.[66] Quite recently the infrared spectra of gaseous and solid IN_3 were reinvestigated[68,82] and the observed N–I stretching mode at 338 cm^{-1} could be confirmed, whereas the band at 410 cm^{-1} was not observed. In these terms the above question must be regarded as still open and further experiments are needed to unequivocally establish the frequency of the N–I stretching mode of iodine azide.

IV. IONIC NITROGEN–IODINE SPECIES

Anionic Species

So far only two neutral binary iodine–nitrogen compounds have been described, which as a result of the very labile N–I bond[66] and the associated thermodynamic instability are both explosive: NI_3[53] (or $NI_3 \cdot NH_3$)[83] and IN_3.[68,77] The first binary anionic N–I species were synthesized by K. Dehnicke *et al.* who reacted IN_3 with Lewis bases such as N_3^- or I^- according to Eq. (37)–(40) yielding $I(N_3)_2^-$ or $I_2N_3^-$, respectively.[64,84,80]

$$NMe_4^+N_3^- + IN_3 \rightarrow NMe_4^+I(N_3)_2^-, \text{ orange red,} \quad (37)$$

$$PPh_4^+N_3^- + IN_3 \rightarrow PPh_4^+I(N_3)_2^-, \text{ orange,} \quad (38)$$

$$NMe_4^+I^- + IN_3 \rightarrow NMe_4^+I_2N_3^-, \text{ deep violet,} \quad (39)$$

$$NMe_4^+N_3^- + I_2 \rightarrow NMe_4^+I_2N_3^-, \text{ deep violet} \quad (40)$$

All these compounds are colored and explosive, except $PPh_4^+I(N_3)_2^-$, in which the anion is stabilized by the larger tetraphenylphosphonium cation. The compounds were characterized by their infrared spectra[80,84] and the structure of the thermal more stable $PPh_4^+I(N_3)_2^-$ was determined by X-ray diffraction.[80] As shown by X-ray structure analysis the $I(N_3)_2^-$ anion exists in C_2 geometry and contains a nearly linear N–I–N unit and two bent N_3 groups (Fig. 9). The structure determination suffered from severe disorder problems and the observed N1N2N3 angle of about 151° seems to be too small in comparison with the NNN angles observed for all other halogen azides of about 172°.[9,67,68,52] Also the N–N bond

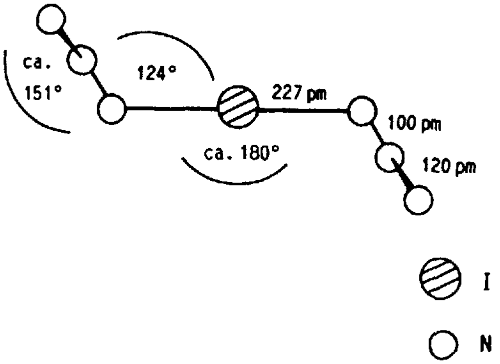


FIGURE 9 Structure of the $I(N_3)_2^-$ anion.

distances of 100 pm for d(N1–N2) and 120 pm for d(N2–N3) are in disagreement with those found for halogen azides in which d(N2–N3) is always significantly shorter (113 pm) than d(N1–N2) (125 pm). However, the N–I distance (227 pm) fits very well with the N–I bond length in solid IN_3 in which the iodine atom acts also as a bridging atom.[68]

Cationic Species

Quite recently two other binary ionic N–I species were synthesized, the $I(N_3)_2^+$ [85] and $I_2N_3^+$ [86] which have formally the same composition as the above described $I_2N_3^-$ and $I(N_3)_2^-$ anions but are, as expected, different in structure. The synthesis of the $I_2N_3^+$ cation started from freshly prepared IN_3 which was then reacted with I_2/SbF_5 or I_2/AsF_5, respectively, in order to form "$I^+EF_6^-$" (E = As, Sb) as an intermediate and then led to the formation of $I_2N_3^+$ [82,86]:

$$IN_3 + 1/2\,I_2 + 3/2\,EF_5 \xrightarrow{-90/-40^\circ C,\ CFCl_3} I_2N_3^+EF_6^- + 1/2\,EF_3 \qquad (41)$$

$$E = As, Sb$$

The resulting $I_2N_3^+$ salts are deep carmine red and insoluble in $CFCl_3$, soluble in SO_2 and highly explosive in the solid state even at low temperature.[86] The $I_2N_3^+$ cation is more easily accessible from the reaction of freshly prepared AgN_3 with $I_3^+SbF_6^-$ in liquid SO_2 [Eq. (42)] because the $I_2N_3^+$ salt could be separated from insoluble AgI and was characterized in SO_2 solution.[86]

$$AgN_3 + I_3^+SbF_6^- \xrightarrow{-50°C,\ SO_2} AgI + I_2N_3^+SbF_6^- \qquad (42)$$

The $I_2N_3^+$ cation was characterized by low-temperature Raman spectroscopy in SO_2 solution.[86] The Raman spectrum of $I_2N_3^+SbF_6^-$ shows, apart from the bands due to the N_3 unit, two intense bands which could be assigned to an I–I stretching mode (182 cm^{-1}) and to ν(N–I) (355 cm^{-1}). The presence of the I–I stretching mode gave strong evidence that the $I_2N_3^+$ cation exists in a chain-like structure. It is noteworthy that the I–I stretch in $I_2N_3{}^+SbF_6^-$ (182 cm^{-1}) in comparison to that in iodine (215 cm^{-1}) is shifted to lower wavenumbers which means that there is only a weak I–I bond. The position of the I–I vibrational band corresponds to a calculated bond distance of 272 pm and this also agrees with the empirical correlation between the I–I bond length and the wavenumber of the corresponding I–I stretching mode (Table VII).[82,86] The N–I stretch in $I_2N_3^+SbF_6^-$ (355 cm^{-1}) was observed at higher wavenumbers compared with that in IN_3 (338 cm^{-1}). This fits well with the calculated N–I bond lengths for $I_2N_3^+$ (207 pm) and IN_3 (213 pm).[82,86] The structure of the $I_2N_3^+$ cation was predicted to be in a non-planar chain due to the presence of the ν(I–I) vibration. Since the strong asymmetric N_3 vibration in the Raman spectrum made the terminal arrangement of the two iodine

TABLE VII

I–I and N–I bond lengths and vibrational frequencies

	ν(I–I) (cm^{-1}) calc.[a]/exp.	d(I–I) (pm), exp.	ν(N–I) (cm^{-1}) exp.	d(N–I) (pm) calc.
I_2^+	237/235[87]	256[87]		
I_2	208/215[87]	266[87]		
I_3^-	113/114[88]	290[2]		
IN_3			338[68,77]	213[b,68,82]
$I_2N_3^+$	182/182[82,86]	272[b,82,86]	355[82,86]	207[82,86]

[a] Estimated from: $\nu(\text{I–I, cm}^{-1}) = [-1170.8 + 13.56\, d\,(\text{pm}) - 0.03149\, d^2\,(\text{pm}^2)]$.[82]

[b] MP2/6-31 + G*.

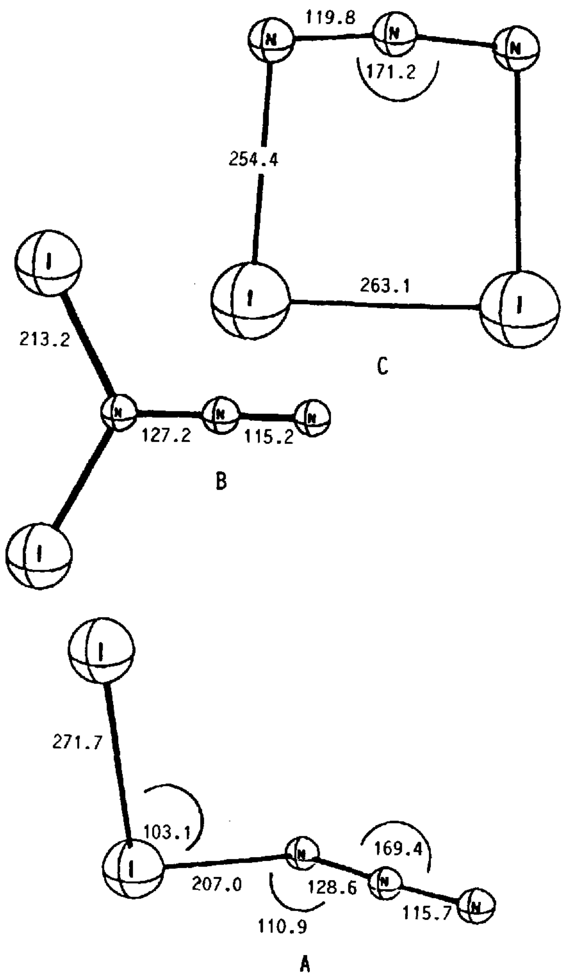


FIGURE 10 Computed structures for different isomers of $I_2N_3^+$ (bond lengths in pm, angles in degrees (Ref. 86).

atoms at the N_3 unit unlikely, the structures of the predicted isomer (A) and those of other possible isomers (B, C) were computed on the basis of ab initio MO calculations at the MP2/6-31 + G* level (Fig. 10). The results of the ab initio calculations are in conformity with the experimental spectroscopic data and show that

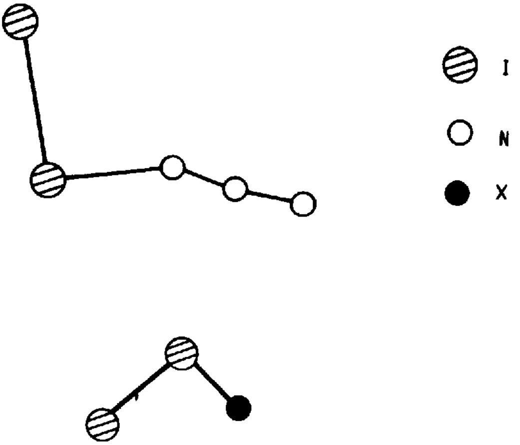


FIGURE 11 Structures of I_2X^+ (X = Cl, Br) in comparison with $I_2N_3^+$.

the proposed non-planar chain-like structure (A) of the $I_2N_3^+$ ion is favored by about 4 kJ mol^{-1} compared to the unobserved isomer B.[82,36] Also all triatomic interhalogen cations like I_2Cl^+ and I_2Br^+ exist in a bent asymmetrical constitution in which the heavier halogen occupies the central position (Fig. 11).[89] If one considers the N_3 unit as a pseudohalogen this structural principle can also be applied for the $I_2N_3^+$ cation. As shown in Fig. 11 the computed and experimentally confirmed structure for this interhalogen–pseudohalogen cation corresponds to that model.

The instability of the $I_2N_3^+$ cation was explained by some thermodynamic estimations. The enthalpy of a reaction according to Eq. (43) was roughly estimated on the basis of a simple Born–Haber cycle to be $\Delta H(43) = -83$ kJ mol^{-1}; hence the standard heat of formation of $I_2N_3^+AsF_6^-$ was estimated to be -1092 kJ mol^{-1}.[82,86]

$$IN_3(g) + 1/2\ I_2(s) + 3/2\ AsF_5(g) \rightarrow I_2N_3^+AsF_6^-(s) + 1/2\ AsF_3(l) \qquad (43)$$

The decomposition given in Eq. (44) is strongly favored with $\Delta H(44) = -464$ kJ mol^{-1} and this accounts for the low stability of

$I_2N_3^+AsF_6^-$ or $I_2N_3^+SbF_6^-$, respectively.[82,86] Moreover, I_2^+ dimerizes exothermally to give I_4^{2+}, and both decomposition products, N_2 and I_2^+/I_4^{2+}, were observed in the thermal decomposition of $I_2N_3^+$ salts.[82,86]

$$I_2N_3^+AsF_6^-(s) \rightarrow I_2^+AsF_6^-(s) + 3/2\ N_2(g) \qquad (44)$$

The synthesis of the $I(N_3)_2^+$ cation was carried out by reaction of $ICl_2^+AsF_6^-$ either with Me_3SiN_3 or AgN_3 [Eqs. (45) and (46)].[85]

$$ICl_2^+AsF_6^- + 2\ Me_3SiN_3 \rightarrow 2\ Me_3SiCl + I(N_3)_2^+AsF_6^-, \qquad (45)$$

$$ICl_2^+AsF_6^- + 2\ AgN_3 \rightarrow 2\ AgCl + I(N_3)_2^+AsF_6^-, \qquad (46)$$

$$I(N_3)_2^+AsF_6^-(s) \rightarrow IF(s) + AsF_5(g) + 3\ N_2(g) \qquad (47)$$

Based on a simple Born–Haber cycle the reaction according to Eq. (45) is thermodynamically allowed with $\Delta H(45) = -82$ kJ mol^{-1}, but a likely decomposition reaction [Eq. (47)] was estimated to be even more favorable ($\Delta H(47) = -485$ kJ mol^{-1}).[85] Therefore, the yellow $I(N_3)_2^+$ cation is thermodynamically highly unstable and it was identified by low temperature Raman spectroscopy.[85] Based on the results of ab initio calculations (HF/6-31 + G*) the structure of the $I(N_3)_2^+$ cation was predicted to be bent (C_2) with two stereochemically active lone pairs at iodine and two slightly bent N_3 units (Fig. 12).[85] The N–I bond distance (204 pm)[85] is substantially shorter than in the neutral, polymeric IN_3 (228 pm)[68] and resembles that of $I_2N_3^+$ (207 pm).[86]

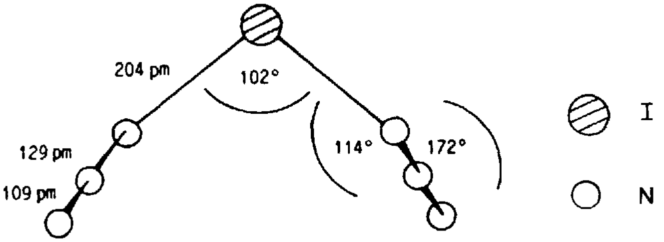


FIGURE 12 Computed structure of $I(N_3)_2^+$ (Ref. 85).

CONCLUSIONS

Binary nitrogen halogen species are well established entities. They are, however, with the exception of some nitrogen–fluorine compounds (e.g., NF_3, N_2F_4, NF_4^+, . . .) as a result of the very labile N–X bond (X = Cl, Br, I) and the associated thermodynamic instability, all explosive. In principle, the partial charge is always slightly negative at N for N–X bonds (X = Cl, Br, I) and positive for N–F bonds. In general, structures are as expected from simple valence theory (VSEPR) and the isoelectric principle. However, some special structural principles should be mentioned:

—Whereas NF_4^+ is a well-known species the NF_5 parent molecule is still non-existent and is likely not possible as the lack of pentacoordinated nitrogen is mainly due to steric reasons. (NH_5 might be more conceivable from the theoretical point of view but seems to be much more difficult to realize experimentally.)

—Contrary to ionic azides (e.g., NaN_3; N_3^-: D_{∞}) all covalent species of the XN_3 type (X = H, F, Cl, Br, I) possess a trans-bent C_s configuration with a NNN bond angle of about 172 ± 3° and two different N–N bond distances. The covalent bond order indicates that the XN–NN bond in XN_3 is intermediate between a single and a double bond and that the XNN–N bond has nearly triple bond character.

—In terms of structural predictions azides seem always to behave as pseudohalogens. This means, for example, IN_3 corresponds to ICl and therefore $I_2N_3^+$ possesses an I–I–N_3 chain-like structure and the heavy iodine atom (of IN_3) occupies the central position.

—Unexpectedly, IN_3 was found to exist in the solid state in a polymeric chain structure with linear, two-coordinated iodine. The solid state structures of all other halogen azides, and especially those of many binary species like NI_3, NCl_4^+, BrN_3, . . . , are still unknown. The structural characterization of these species should be fascinating and may present many mysteries and should therefore be a challenging problem for the future.

Recent computational work has intensified on both NX_3 and XN_3 derivatives, having the advantage of no danger of explosion in the computer. However, only high level quantum mechanical ab initio computations on correlated levels give a satisfying agreement with the available experimental data. Moreover, for the heavy halogens, especially iodine, relativistic effects have to be taken into consideration, which is, for example, possible by the use of effective quasi-relativistic (core) potentials. In particular the results of the last two years show the trend that computational chemistry becomes more and more important in combination with modern inorganic preparative chemistry, especially for thermodynamically and kinetically unstable compounds.

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