

# The $\text{N}_2\text{F}^+$ Cation. An Unusual Ion Containing the Shortest Presently Known Nitrogen–Fluorine Bond

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**Abstract:** The  $\text{N}_2\text{F}^+\text{AsF}_6^-$  salt was prepared in high yield from *trans*- $\text{N}_2\text{F}_2$  by thermal *trans*–*cis* isomerization in the presence of  $\text{AsF}_5$  at 70 °C. A displacement reaction between  $\text{N}_2\text{F}^+\text{AsF}_6^-$  and  $\text{FNO}$  yields exclusively *cis*- $\text{N}_2\text{F}_2$ . The Lewis acids  $\text{BF}_3$  and  $\text{PF}_5$  do not form a stable adduct with *cis*- $\text{N}_2\text{F}_2$  at temperatures as low as –78 °C and do not catalyze the  $\text{N}_2\text{F}_2$  *trans*–*cis* isomerization. A semiempirical molecular orbital model is used to explain the puzzling differences in the reaction chemistry of *cis*- and *trans*- $\text{N}_2\text{F}_2$ . The crystal structure of  $\text{N}_2\text{F}^+\text{AsF}_6^-$  (monoclinic,  $C2/m$ ,  $a = 9.184$  (5) Å,  $b = 5.882$  (2) Å,  $c = 5.160$  (2) Å,  $\beta = 90.47$  (4)°,  $Z = 2$ ) was determined. Alternate space groups ( $Cm$  and  $C2$ ) can be rejected on the basis of the observed vibrational spectra. Since in  $C2/m$  the  $\text{N}_2\text{F}^+$  cations are disordered, only the sum of the N–F and N–N bond distances could be determined from the X-ray data. Local density functional calculations were carried out for  $\text{N}_2\text{F}^+$  and the well-known isoelectronic FCN molecule. The results from these calculations allowed the sum of the  $\text{N}_2\text{F}^+$  bond lengths to be partitioned into the individual bond distances. The resulting N–F bond length of 1.217 Å is by far the shortest presently known N–F bond, while the N–N bond length of 1.099 Å is comparable to the shortest presently known N–N bond length of 1.0976 (2) Å in  $\text{N}_2$ . The surprising shortness of both bonds is attributed to the high s-character (*sp* hybrid) of the  $\sigma$ -bond orbitals on nitrogen and the formal positive charge on the cation. Thus, the shortening of the N–F bond on going from *sp*<sup>3</sup>-hybridized  $\text{NF}_4^+$  (1.30 Å) to *sp*-hybridized  $\text{N}_2\text{F}^+$  (1.22 Å) parallels those found for the C–H and C–F bonds in the  $\text{CH}_4$ ,  $\text{CH}_2=\text{CH}_2$ ,  $\text{CH}\equiv\text{CH}$  and  $\text{CF}_4$ ,  $\text{CF}_2=\text{CF}_2$ ,  $\text{FC}\equiv\text{N}$  series, respectively. The oxidative power of  $\text{N}_2\text{F}^+$  has also been studied. The  $\text{N}_2\text{F}^+$  cation oxidized Xe and ClF to  $\text{XeF}^+$  and  $\text{ClF}_2^+$ , respectively, but did not oxidize  $\text{ClF}_5$ ,  $\text{BrF}_5$ ,  $\text{IF}_5$ ,  $\text{XeF}_4$ ,  $\text{NF}_3$ , or  $\text{O}_2$ .

## Introduction

The chemistry of  $\text{N}_2\text{F}_2$  and its derivatives is fascinating and presents many mysteries.<sup>1</sup> Thus,  $\text{N}_2\text{F}_2$  exists as two planar  $\text{FN}=\text{NF}$  isomers, a *cis* and a *trans* form. In spite of only a small enthalpy difference of 3.04 kcal/mol between the two isomers,<sup>2</sup> their properties and reaction chemistry are very different. For example, only the *cis* isomer reacts with strong Lewis acids to form  $\text{N}_2\text{F}^+$  salts. Furthermore, some of the synthetic methods for  $\text{N}_2\text{F}_2$  produce exclusively the *trans* isomer, and its slow and erratic isomerization to the more stable *cis* isomer is poorly understood, as shown by recent *ab initio* calculations.<sup>3</sup>

The  $\text{N}_2\text{F}^+$  cation<sup>4–9</sup> is also of great interest. Force field<sup>9</sup> and *ab initio* calculations<sup>10–12</sup> suggested that this cation should possess an unusually short N–F bond. On the basis of the previously published<sup>9</sup> NF stretching force constant value of 8.16 mdyn/Å and N–F bond length–force constant plots,<sup>10,13</sup> a value of about 1.23 Å can be extrapolated for the N–F bond in  $\text{N}_2\text{F}^+$ . This surprisingly short N–F bond length value for  $\text{N}_2\text{F}^+$  was also supported by *ab initio* calculations<sup>10–12</sup> which resulted in values of 1.28, 1.24, and 1.23 Å, respectively. Considering that in covalent main group element fluorides the bond length generally decreases with an increase in the formal oxidation state of the central atom and that the shortest previously known N–F bond was 1.30 Å in  $\text{NF}_4^+$  (+V),<sup>14</sup> a value of about 1.23 Å for  $\text{N}_2\text{F}^+$  (+I) would be unique indeed.

On the other hand, if the N–F bond length in  $\text{N}_2\text{F}^+$  were considerably longer than the value predicted from the force field computations, the  $\text{N}_2\text{F}^+$  cation would be an ideal test case for “Gordy’s rule”.<sup>15</sup> According to this rule, the bond stretching force constant  $k$  is related to the bond distance  $d$  by the equation

$$k_{AB} = aN(X_A X_B / d_{AB}^2)^{3/4} + b$$

where  $X$  are the Pauling electronegativities,  $N$  the bond order, and  $a$  and  $b$  empirically determined constants. Although no *a priori* reason dictates such a relationship since bond lengths

measure the position of the potential energy minimum whereas force constants indicate its curvature, only one exception to Gordy’s rule has previously been reported.<sup>16</sup> Thus, a knowledge of the N–F bond distance in  $\text{N}_2\text{F}^+$  was of significant interest since it would either confirm the existence of an unusually short N–F bond or provide a rare example of a species not obeying Gordy’s rule.

## Experimental Section

**Materials.** The following commercial materials were used without further purification:  $\text{N}_2\text{F}_4$  (Air Products); Xe,  $\text{O}_2$ ,  $\text{IF}_5$ ,  $\text{PF}_5$ , and  $\text{BF}_3$  (Matheson);  $\text{ClF}_5$  and  $\text{NF}_3$  (Rocketdyne); and ClF (Ozark Mahoning). Literature methods were used for the syntheses of *trans*- $\text{N}_2\text{F}_2$ ,<sup>17</sup>  $\text{N}_2\text{F}^+\text{AsF}_6^-$ ,<sup>4</sup>  $\text{FNO}$ ,<sup>18</sup> and  $\text{XeF}_4$ ,<sup>19</sup> the purification of  $\text{BrF}_5$ ,<sup>20</sup> and the drying of HF.<sup>21</sup>

(1) For an exhaustive review of the properties and chemistry of  $\text{N}_2\text{F}_2$ , see: *Gmelin Handbook of Inorganic Chemistry, Fluorine*, Springer Verlag; Berlin, 1986; Suppl. Vol. 4, pp 385–403.

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**Table I.** Summary of Crystal Data and Refinement Results for  $\text{N}_2\text{F}^+\text{AsF}_6^-$ 

space group	$C2/m$ (No. 12)
<i>a</i> , Å	9.184 (5)
<i>b</i> , Å	5.882 (2)
<i>c</i> , Å	5.160 (2)
$\beta$ , deg	90.47 (4)
<i>V</i> , Å <sup>3</sup>	278.7 (2)
molecules per unit cell	2
formula weight, g	235.9
cryst dimens, mm	$0.32 \times 0.38 \times 1.08$
calcd density, g cm <sup>-3</sup>	2.82
abs coeff, mm <sup>-1</sup>	59.8
range in transmission factor (normalized to unity)	0.61–1.00
wavelength used for data collection, Å	0.71069
$\sin \theta/\lambda$ limit, Å <sup>-1</sup>	0.6497
tot no. of reflns measd	1272
no. of independent reflns	364
no. of reflns used in structural analysis $I > 3\sigma(I)$	362
no. of variable params	30
final agreement factor	0.0404

**Apparatus.** Volatile materials were handled in a well-passivated (with  $\text{ClF}_3$ ) stainless steel Teflon-FEP vacuum line.<sup>22</sup> Nonvolatile materials were manipulated under the dry nitrogen atmosphere of a glovebox. Vibrational spectra were recorded as previously described.<sup>20</sup>

**Reaction of  $\text{N}_2\text{F}^+\text{AsF}_6^-$  with FNO.** A sample of  $\text{N}_2\text{F}^+\text{AsF}_6^-$  (1.84 mmol) was placed inside the drybox into a prepassivated  $3/4$  in. Teflon-FEP ampule that was closed by a stainless steel valve. On the vacuum line, FNO (4.14 mmol) was added at  $-196^\circ\text{C}$ , and the resulting mixture was allowed to slowly warm from  $-196$  to  $-78^\circ\text{C}$  by the use of a liquid  $\text{N}_2$ -dry ice slush bath. The mixture was then allowed to slowly warm from  $-78^\circ\text{C}$  to room temperature over a 12-h period. The ampule was cooled to  $-196^\circ\text{C}$ , and the volatile material was separated during warm-up of the ampule to  $25^\circ\text{C}$  by fractional condensation through traps kept at  $-126$  and  $-210^\circ\text{C}$ . The  $-126^\circ\text{C}$  trap contained unreacted FNO (2.29 mmol) and the  $-210^\circ\text{C}$  trap contained *cis*- $\text{N}_2\text{F}_2$  (1.8 mmol). The white solid residue (401 mg, weight calcd for 1.84 mmol of  $\text{NO}^+\text{AsF}_6^- = 403$  mg) was identified by vibrational spectroscopy as  $\text{NO}^+\text{AsF}_6^-$ .<sup>23</sup>

**Oxidation Reactions of  $\text{N}_2\text{F}^+\text{AsF}_6^-$ .** All oxidation reactions of  $\text{N}_2\text{F}^+\text{AsF}_6^-$  were carried out in the same manner. About 2 mmol of  $\text{N}_2\text{F}^+\text{AsF}_6^-$  was placed in the drybox into a prepassivated 0.5 in. o.d. Teflon-FEP ampule that was closed by a stainless steel valve. On the vacuum line, about 2 mL of liquid anhydrous HF and about 5 mmol of the compound to be oxidized were added, and the resulting mixture was kept at room temperature for 24 h. The ampule was cooled to  $-196^\circ\text{C}$  and the amount of evolved nitrogen was measured by expansion into the vacuum line. The material volatile at room temperature was separated by fractional condensation through a series of cold traps kept at appropriate temperatures. The contents of these traps were measured by PVT and identified by infrared spectroscopy. The solid residues in the ampule were weighed and identified by infrared and Raman spectroscopy.

**Crystal Structure Determination of  $\text{N}_2\text{F}^+\text{AsF}_6^-$ .** Single crystals of  $\text{N}_2\text{F}^+\text{AsF}_6^-$  were obtained by slowly cooling a saturated HF solution from  $25$  to  $0^\circ\text{C}$  and separating the resulting crystals from the cold solution by decantation. A suitable crystal was selected under a microscope inside the glovebox and sealed in a quartz capillary.

Diffraction data were collected at room temperature using a Siemens/Nicolet/Syntex P2<sub>1</sub> diffractometer with  $\text{Mo K}\alpha$  radiation up to a  $2\theta$  limit of  $45^\circ$ . A total of 1272 intensity values for an entire reflection sphere was collected and the four equivalent quadrants merged to give 364 unique reflections. An empirical  $\psi$ -scan absorption correction was applied, based on the variation in intensity of an axial reflection.<sup>24</sup>

The pattern of systematic absences was consistent with any one of the following centered monoclinic space groups:  $C2$  (No. 5),  $Cm$  (No. 8), or  $C2/m$  (No. 12). The structure was solved for all three space groups. The positions of the atoms were obtained by direct methods with use of

**Table II.** Final Atomic Coordinates for  $\text{N}_2\text{F}^+\text{AsF}_6^-$ 

atom	<i>x</i>	<i>y</i>	<i>z</i>	no. <sup>a</sup>
As1	0	0	0.5	2
F2	0.1235 (6)	0	0.2574 (9)	4
F3	-0.0948 (5)	0.2027 (9)	0.3406 (9)	8
N4	0	0.5	1	2
X5 <sup>b</sup>	-0.1203 (7)	0.5	0.9313 (11)	4

<sup>a</sup> Number of times this atom appears in the unit cell. <sup>b</sup> X is the disordered terminal atom (50% N/50% F) of the  $[\text{N}_2\text{F}]^+$  cation in space group  $C2/m$ .

the computing package SHELX-86.<sup>25</sup> The structures were then refined with use of 362 reflections with  $I > 3\sigma(I)$ . Details of the data collection parameters and other crystallographic information are given in Table I. The final atomic coordinates, thermal parameters, interatomic distances, and bond angles for the preferred (see Discussion section)  $C2/m$  model are given in Tables II–IV, respectively.

**Computational Methods.** The geometry and vibrational frequencies of  $\text{N}_2\text{F}^+$  and FCN were calculated in the local density functional approximation<sup>26</sup> by using the program system DMol.<sup>27</sup> The atomic basis functions are given numerically on an atom-centered, spherical-polar mesh. The radial portion of the grid is obtained from the solution of the atomic LDF equations by numerical methods. The radial functions are stored as sets of cubic spline coefficients so that the radial functions are piecewise analytic, a necessity for the evaluation of gradients. The use of exact spherical atom results offers some advantages. The molecule will dissociate exactly to its atoms within the LDF framework, although this does not guarantee correct dissociation energies. Furthermore, because of the quality of the atomic basis sets, basis set superposition effects should be minimized and correct behavior at the nucleus is obtained.

Since the basis sets are numerical, the various integrals arising from the expression for the energy need to be evaluated over a grid. The integration points are generated in terms of angular functions and spherical harmonics. The number of radial points  $N_R$  is given as

$$N_R = 1.2 \times 14(Z - 2)^{1/3}$$

where  $Z$  is the atomic number. The maximum distance for any function is 12 au. The angular integration points  $N_\theta$  are generated at the  $N_R$  radial points to form shells around each nucleus. The value of  $N_\theta$  ranges from 14 to 302 depending on the behavior of the density.<sup>28</sup> The Coulomb potential corresponding to the electron repulsion term is determined directly from the electron density by solving Poisson's equation. In DMol, the form for the exchange-correlation energy of the uniform electron gas is that derived by von Barth and Hedin.<sup>29</sup>

All of the DMol calculations were done with a double numerical basis set augmented by polarization functions. This can be thought of in terms of size as a polarized double- $\zeta$  basis set. However, because of the use of exact numerical solutions for the atom, this basis set is of significantly higher quality than a normal molecular orbital double- $\zeta$  basis set. The fitting functions have angular momentum numbers one greater than that of the polarization function. Since all of the atoms have  $d$  polarization functions, the value of 1 for the fitting function is 3.

Geometries were optimized by using analytic gradient methods. There are two problems with evaluating gradients in the LDF framework which are due to the numerical methods that are used. The first is that the energy minimum does not necessarily correspond exactly to the point with a zero derivative. The second is that the sum of the gradients may not always be zero as required for translational invariance. These tend to introduce errors on the order of  $0.001$  Å in the calculation of the coordinates if both a reasonable grid and basis set are used. This gives bond lengths and angles with reasonable error limits. The difference of  $0.001$  Å is about an order of magnitude smaller than the accuracy of the LDF geometries when compared to the experimental ones. The frequencies

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**Table III.** Final Temperature Factors for  $N_2F^+AsF_6^-$ 

atom	$10^4U_{11}$	$10^4U_{22}$	$10^4U_{33}$	$10^4U_{12}$	$10^4U_{13}$	$10^4U_{23}$
As1	416 (5)	331 (5)	333 (4)	0 (0)	9 (4)	0 (0)
F2	745 (16)	935 (17)	659 (16)	0 (0)	312 (15)	0 (0)
F3	1220 (16)	1407 (17)	1240 (16)	715 (16)	301 (15)	716 (16)
N4	723 (18)	440 (17)	532 (17)	0 (0)	146 (17)	0 (0)
X5 <sup>a</sup>	655 (17)	750 (17)	809 (17)	0 (0)	7 (16)	0 (0)

<sup>a</sup> X is the disordered terminal atom (50% N/50% F) of the  $[N_2F]^+$  cation in space group  $C2/m$ .

**Table IV.** Bond Distances (Å) and Bond Angles (deg) in  $[N_2F]^+[AsF_6]^-$ 

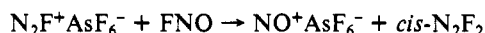
As1-F2	1.696 (4)	F2'-As1-F3	90.8 (2)
As1-F3	1.686 (4)	F3-As1-F3'	180.0 (0)
N4-X5	1.158 (6)	F3-As1-F3''	90.0 (2)
F2-As1-F3	89.2 (2)	F3'-As1-F3''	90.0 (2)
F2-As1-F2'	180.0 (0)	F3''-As1-F3'''	180.0 (0)
		X5-N4-X5'	180.0 (0)

were determined by numerical differentiation of the gradient. A two-point difference formula was used and a displacement of 0.01 au.

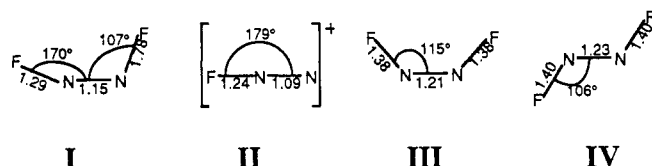
## Results and Discussion

**Trans-Cis Isomerization of  $N_2F_2$  and the Synthesis of  $N_2F^+$  Salts.** Most of the known  $N_2F_2$  syntheses produce exclusively the trans isomer.<sup>1</sup> Since the trans isomer is much less reactive than the cis isomer and, for example, does not form  $N_2F^+$  salts, conversion of the trans to the cis isomer is often required. This trans-cis isomerization is usually quite erratic. Although it proceeds at room temperature in stainless steel, it often exhibits long and irreproducible induction periods and requires numerous months to go to completion. This isomerization can be accelerated by increasing the temperature; however, the yields of *cis*- $N_2F_2$  sharply decrease at elevated temperature due to decomposition of  $N_2F_2$  to  $N_2$  +  $F_2$ .<sup>30</sup> In our study, aimed at the isomerization of  $N_2F_2$  and its subsequent conversion to  $N_2F^+AsF_6^-$ , it was found advantageous to combine the *trans*- $N_2F_2$  with an excess of  $AsF_5$  in a prepassivated, small volume stainless steel cylinder and to carry out the isomerization at about 70 °C. In this manner, any *cis*- $N_2F_2$  formed is immediately removed from the cis-trans equilibrium by complexation and thereby protected against decomposition to  $N_2$  and  $F_2$ . In this manner, yields of  $N_2F^+AsF_6^-$  as high as 80% have been obtained from *trans*- $N_2F_2$  in 3 days at 70 °C.

It was also of interest to study which  $N_2F_2$  isomer is formed in the displacement reactions of  $N_2F^+AsF_6^-$  with a strong Lewis base, such as FNO. It was found that exclusively *cis*- $N_2F_2$  is formed in quantitative yield according to



Recent ab initio calculations<sup>3</sup> on the transition-state structure for the  $N_2F_2$  trans-cis isomerization resulted in the proposition of structure I. A similar transition state might be expected for a fluoride abstraction from *cis*- $N_2F_2$  (III) by a strong Lewis acid leading to the  $N_2F^+$  cation (II).

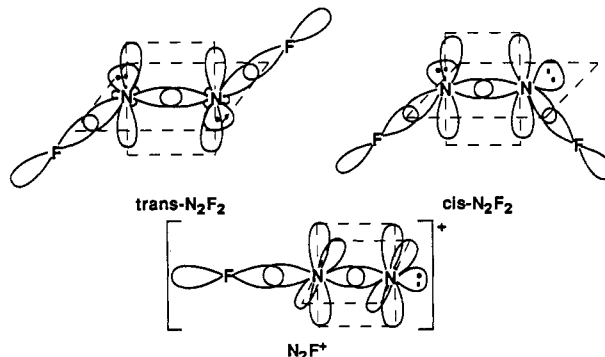


These results suggested that Lewis acids which are capable of forming  $N_2F^+$  salts might also promote the formation of the isomerization transition state and thereby catalyze the  $N_2F_2$  trans-cis isomerization. In order to be an effective isomerization catalyst, the strength of the Lewis acid should be such that it interacts with  $N_2F_2$  but does not form a stable complex at the desired isomerization temperature. To test the validity of this

approach, we have studied the interaction of *cis*- $N_2F_2$  with  $BF_3$  and  $PF_5$ . It was found that the resulting  $N_2F_2$  adducts are indeed labile enough and exhibit some dissociation pressure at temperatures as low as -78 °C. However, both  $PF_5$  and  $BF_3$  did not catalyze the isomerization of *trans*- $N_2F_2$  to *cis*- $N_2F_2$  in the temperature range of -78 to 25 °C.

Thus, the chemistry of  $N_2F_2$  raises numerous puzzling questions for which, to our best knowledge, no satisfactory answers have previously been given.<sup>1</sup> Among these questions are the following: (i) why does only *cis*- $N_2F_2$ , but not *trans*- $N_2F_2$  form  $N_2F^+$  salts, (ii) why do Lewis acids not catalyze the  $N_2F_2$  trans-cis isomerization, and (iii) why is the *cis*- $N_2F_2$  isomer exclusively formed in the displacement reaction between  $N_2F^+$  salts and FNO?

The great difference in reactivity between *cis*- and *trans*- $N_2F_2$  cannot be due to differences in thermodynamic properties or bond strengths because these values are very similar for both molecules.<sup>1</sup> Therefore, the difference in reactivity should be connected with the different spatial arrangement of the fluorine ligands and the free valence electron pairs on nitrogen. With use of a semi-empirical molecular orbital model, the bonding in  $N_2F_2$  can be described by two  $sp^2$ -hybridized nitrogen atoms resulting in one N-N and two N-F  $\sigma$ -bonds and two sterically active, free valence electron pairs on the two nitrogens. In addition, the remaining p orbitals on the nitrogen atoms form a [p-p]  $\pi$ -bond perpendicular to the plane of the  $sp^2$  hybrids. In linear  $N_2F^+$ , the two nitrogens form a [sp-sp]  $\sigma$ -bond and two perpendicular [p-p]  $\pi$ -bonds.



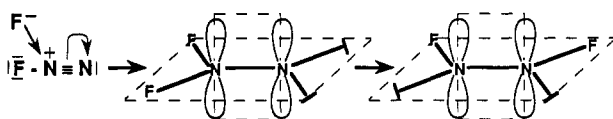
When a Lewis acid, such as  $AsF_5$ , approaches a *cis*- $N_2F_2$  molecule, one of the fluorine ligands and hereby some electron density is pulled away from the remainder of the molecule. This results in an intermediate similar to the transition state (I) of the  $N_2F_2$  trans-cis isomerization. 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, as demonstrated by the shortening of the N-N bond from 1.21 Å in *cis*- $N_2F_2$  (III) to 1.15 Å in the postulated trans-cis isomerization transition state (I). Therefore, the energy required for the elongation of one of the N-F bonds in I can be compensated for by the simultaneous formation of a partial  $N\equiv N$  triple bond thereby resulting in a very low energy barrier toward  $N_2F^+$  formation. However, the formation of such a partial  $N\equiv N$  triple bond should be possible only for *cis*- $N_2F_2$ , i.e. when the two free valence electron pairs on the nitrogens are on the same side of the molecule and can overlap. In *trans*- $N_2F_2$ , migration of a nitrogen free valence electron pair from one side of the molecule to the other is blocked in the  $N_2F_2$  plane by the fluorine ligands and in the perpendicular plane by the [p-p]  $\pi$ -bond. Furthermore, the  $N=N$  double bond in  $N_2F_2$  does not

(30) Pankratov, A. V.; Sokolov, O. M. *Russ. J. Inorg. Chem.* **1966**, *11*, 943.

permit free rotation around the N–N axis. Therefore,  $\text{N}_2\text{F}^+$  formation from *trans*- $\text{N}_2\text{F}_2$  should be a high activation energy process requiring almost complete removal of one fluoride ion from  $\text{N}_2\text{F}_2$ , before the FNN angle in the remaining  $\text{FN}_2$  fragment becomes large enough for the nitrogen free electron pair to tunnel through to the other side and form the second  $\pi$ -bond.

This rationale explains not only why *trans*- $\text{N}_2\text{F}_2$  does not form  $\text{N}_2\text{F}^+$  salts but also why Lewis acids do not catalyze the  $\text{N}_2\text{F}_2$  trans-cis isomerization. As already pointed out above, the structure of the isomerization transition state closely resembles that of an expected intermediate in the  $\text{N}_2\text{F}^+$  formation. If Lewis acids cannot abstract an  $\text{F}^-$  anion from *trans*- $\text{N}_2\text{F}_2$ , it is then not surprising at all that they also do not promote the formation of the isomerization transition state.

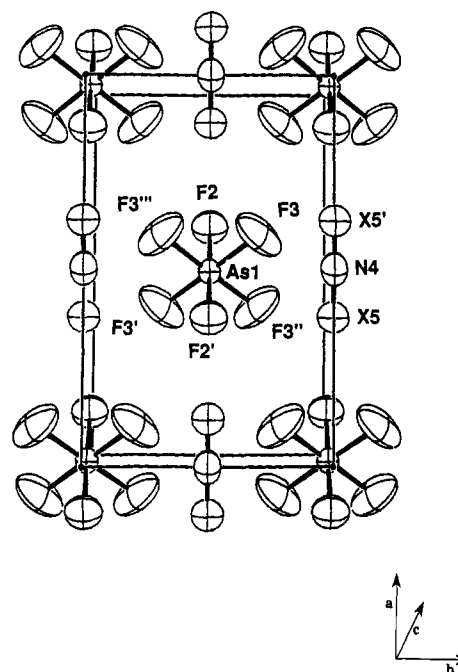
The third question remaining to be answered was why in the FNO displacement reaction of  $\text{N}_2\text{F}^+\text{AsF}_6^-$  exclusively the *cis*- $\text{N}_2\text{F}_2$  isomer is formed. In  $\text{N}_2\text{F}^+$ , the most important resonance structure is  $[\text{F}-\text{N}^+\equiv\text{N}]$  and, therefore, the formal positive charge resides mainly on the  $\alpha$ -nitrogen atom. Furthermore, the free valence electron pair on the  $\beta$ -nitrogen atom is more diffuse than the N–F bond pair orbitals. Consequently, the attack of  $\text{F}^-$  on  $\text{N}_2\text{F}^+$  should occur at the  $\alpha$ -nitrogen atom resulting in the formation of an intermediate  $\text{F}_2\text{N}=\text{N}$  molecule. The latter could easily undergo an  $\alpha$ -fluorine migration to give FNNF.



Since in all these steps a [p–p]  $\pi$ -bond between the two nitrogens is always retained, free rotation around the N–N axis is precluded and the rearrangement of the fluorine atoms and the nitrogen free valence electron pairs must take place in the plane perpendicular to the N–N  $\pi$ -bond. Therefore, the sequence of the fluorine ligands and the nitrogen free electron pairs in  $\text{F}_2\text{N}=\text{N}$  (F,F,P,P) must also be retained in FNNF, resulting exclusively in the *cis*-FNNF isomer. The general ease of this type of  $\alpha$ -migration could explain the failure to isolate the intermediate  $\text{F}_2\text{N}=\text{N}$  isomer.

**Structure of the  $\text{N}_2\text{F}^+$  Cation.** The crystal structure of  $\text{N}_2\text{F}^+\text{AsF}_6^-$  can be solved either in the non-centrosymmetric space groups  $Cm$  or  $C2$  with ordered or disordered  $\text{N}_2\text{F}^+$  cations, respectively, or the centrosymmetric space group  $C2/m$  with disordered  $\text{N}_2\text{F}^+$  cations. All three models resulted in acceptable agreement factors ( $Cm$ ,  $R = 2.96\%$ ;  $C2$ ,  $R = 2.68\%$ ;  $C2/m$ ,  $R = 4.04\%$ ) which to some extent are influenced by the number of variable parameters ( $Cm$ , 53;  $C2$ , 46;  $C2/m$ , 30). The  $Cm$  model resulted in an ordered almost linear  $\text{N}_2\text{F}^+$  cation ( $r_{\text{NF}} = 1.221$  (13) Å,  $r_{\text{NN}} = 1.099$  (13) Å,  $\angle\text{NNF} = 177.2$  (8)°) and a strongly distorted  $\text{AsF}_6^-$  anion with angles deviating by as much as 11.5° from those of an ideal octahedron. The  $C2$  model resulted in a disordered bent  $\text{N}_2\text{F}^+$  cation ( $\sum r_{\text{NF}} + r_{\text{NN}} = 2.342$  (22) Å,  $\angle\text{NNF} = 163.6$  (12)°) and again a strongly distorted  $\text{AsF}_6^-$  anion with angles deviating by as much as 13.8° from  $O_h$  symmetry. The  $C2/m$  model resulted in a disordered linear  $\text{N}_2\text{F}^+$  cation ( $\sum r_{\text{NF}} + r_{\text{NN}} = 2.316$  (12) Å) and an  $\text{AsF}_6^-$  anion which within experimental error is perfectly octahedral. Since the Raman spectra of  $\text{N}_2\text{F}^+\text{AsF}_6^-$  crystals are in perfect agreement with  $O_h$  symmetry (only three narrow bands at 689 ( $\nu_1$ ,  $A_{1g}$ ), 576 ( $\nu_2$ ,  $E_g$ ), and 376  $\text{cm}^{-1}$  ( $\nu_3$ ,  $F_{2g}$ ) with half widths of 10  $\text{cm}^{-1}$  or less at 25 °C), models  $Cm$  and  $C2$  must be rejected in spite of their lower  $R$  factors. This situation closely resembles that in isotopic  $\text{NS}_2^+\text{AsF}_6^-$  for which the alternate  $Cm$  and  $C2$  models could also be rejected on the basis of the observed vibrational spectra.<sup>31</sup> The packing diagram for  $\text{N}_2\text{F}^+\text{AsF}_6^-$  is shown in Figure 1. The  $\text{AsF}_6^-$  anions occupy the corners of the cell and the centers of the  $ab$  faces, while the  $\text{NX}_2$  cations occupy the remaining faces of the cell.

As pointed out already in the introduction, a knowledge of the exact N–F and N–N bond distances in  $\text{N}_2\text{F}^+$  is of great interest.



**Figure 1.** A unit cell plot of  $\text{N}_2\text{F}^+\text{AsF}_6^-$  viewed down the  $c$  axis. In addition to the mirror plane, 2-fold rotational axes pass through As1 (bisecting the F3–As1–F3'' angle) and N4 (perpendicular to the X5–N4–X5' axis). The  $\text{N}_2\text{F}^+$  cation is required by symmetry to be disordered, with the terminal X5, X5' positions being occupied equally by N and F atoms. This packing disorder causes the  $\text{NX}_2$  cation to be linear and symmetric, and the central nitrogen atoms to be elongated along the molecular axis.

**Table V.** Calculated and Experimental Bond Distances (Å) and Vibrational Frequencies ( $\text{cm}^{-1}$ ) for FCN

	expt	calcd (LDF)
$r_{\text{C}\equiv\text{N}}$	1.159	1.169
$r_{\text{C}-\text{F}}$	1.262	1.274
$\text{C}\equiv\text{N}$ stretch	2323	2355
$\text{C}-\text{F}$ stretch	1077	1081
$\text{F}-\text{C}\equiv\text{N}$ bend	451	465

Since the above crystal structure determination provides only a value for the sum of the N–F and N–N bond lengths, a reliable method was sought to partition this sum into its individual components. This partitioning was achieved by local density functional (LDF) calculations providing both the geometry and the vibrational frequencies.

The accuracy of the LDF calculations was tested for FCN which is isoelectronic with  $\text{FNN}^+$  and for which both the geometry<sup>32</sup> and the vibrational frequencies<sup>33</sup> are well-known (see Table V). As expected from a number of studies,<sup>34</sup> the LDF method slightly overestimates the bond distances and vibrational frequencies but otherwise excellently reproduces the experimental values (see Table V). Similarly, LDF calculations for the dinitrogen molecule,  $\text{N}_2$ , resulted in a bond length value (1.113 Å) only slightly longer than the experimental one (1.098 Å).<sup>35</sup>

The results of the LDF calculations for  $\text{N}_2\text{F}^+$  are summarized in Table VI. As expected, the  $\text{N}_2\text{F}^+$  cation is linear and the bond

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**Table VI.** Calculated and Experimental Bond Distances (Å) and Vibrational Frequencies ( $\text{cm}^{-1}$ ) for  $FNN^+$ 

	expt	calcd (LDF)				
		LDF	LDFS1	LDFS2	SCF 6-31G** <sup>a</sup>	MP-2 6-31G** <sup>a</sup>
$r_{N\equiv N}$	(1.099) <sup>b</sup>	1.121	1.111	1.106	1.072	1.138
$r_{N-F}$	(1.217) <sup>b</sup>	1.248	1.236	1.225	1.240	1.256
$\sum r_{N-N} + r_{N-F}$	2.316 (12)	2.369	2.347	2.331	2.312	2.394
$N\equiv N$ stretch	2373	2409				
$N-F$ stretch	1059	1100				
$F-N\equiv N$ bend	388	438				

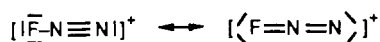
<sup>a</sup>Data from ref 11. <sup>b</sup>Values obtained by partitioning the experimentally measured sum of  $r_{N-N} + r_{N-F}$  according to their ratio in LDFS2.

lengths are, as for isoelectronic FNC, slightly too long. To obtain better estimates for the actual bond lengths, the LDF values can be scaled in the following manner. Using the scaling factors from the FCN calculations, one obtains the values labeled LDFS1. Using the  $N_2$  results for scaling  $r_{N-N}$  and the  $NF_4^+$  results for scaling  $r_{N-F}$  ( $r_{N-F}$ , LDF = 1.324 Å,<sup>36</sup> experimental = 1.297 Å<sup>14</sup>), one obtains the values labeled LDFS2. The sum of  $r_{N-N}$  and  $r_{N-F}$  of LDFS2 (2.331 Å) is very close to that obtained from the crystal structure determination (2.316 Å). If one partitions the experimentally determined sum of  $r_{N-N} + r_{N-F}$  in the same ratio as that in LDFS2, final values of 1.217 and 1.099 Å are obtained for  $r_{N-F}$  and  $r_{N-N}$ , respectively, in  $N_2F^+$  (see Table VI). The close agreement between these values and those ( $r_{NF} = 1.221$  Å,  $r_{NN} = 1.099$  Å) obtained by the rejected  $C_m$  model with ordered  $N_2F^+$  cations (see above) might be fortuitous.

Of the previously calculated<sup>10-12</sup> N-N and N-F bond lengths for  $N_2F^+$ , the SCF 6-31G\* and MP-2 6-31G\* values of Peters<sup>11</sup> (see Table VI) come the closest to the values from this study but appear to either underestimate or overestimate the  $r_{N-N}$  value. When comparing the calculated LDF vibrational frequencies of  $N_2F^+$  with the observed ones (see Table VI), the agreement is very satisfactory, particularly if it is kept in mind that the LDF values are unscaled, harmonic, gas-phase frequencies and the experimental values are anharmonic, solid-state frequencies.

As shown above, the  $N_2F^+$  cation is linear. This result confirms a recent theoretical study<sup>12</sup> which concluded that, contrary to  $P_2F^+$ , for  $N_2F^+$  the linear  $C_{\infty v}$  structure is favored by about 50–60 kcal over the symmetric, three-membered-ring structure of symmetry  $C_{2v}$ . As already pointed out in the introduction, the most interesting aspect of the  $N_2F^+$  structure is its N-F bond distance. This distance of 1.22 Å is by far the shortest distance found to date for any N-F bond. The previously known range for N-F bonds extended from 1.512 Å in FNO to 1.30 Å in  $NF_4^+$ .<sup>13,14</sup> The value of 1.22 Å found for  $N_2F^+$  is in good agreement with the value of 1.24 Å estimated from a force field calculation<sup>9</sup> and force constant-bond distance plot extrapolations.<sup>11,13</sup> The excellent agreement between our experimental value and the value extrapolated from the stretching force constant demonstrates that  $N_2F^+$  conforms with Gordy's rule.<sup>15</sup>

The nitrogen-nitrogen bond distance in  $N_2F^+$  is also of interest. Its value of 1.099 Å is comparable to those of 1.0976 (2) Å<sup>26</sup> in  $N_2$  and 1.118 Å in  $N_2^{+38}$  and confirms its triple bond character. Thus the  $N_2F^+$  cation is highly unusual. It possesses by far the shortest known N-F bond while at the same time exhibiting an N-N bond length comparable to the shortest known N-N bond. How can these unusually short bond distances be explained? It is tempting to invoke partial double bond character for the N-F bond by writing the following resonance structures:



If, however, the N-F bond assumes partial double bond character, the  $N\equiv N$  bond must lose some of its strength and lengthen accordingly. This is not the case, as evidenced by the short  $N\equiv N$  bond of 1.099 Å in  $N_2F^+$ .

**Table VII.** Influence of Hybridization on Bond Lengths (Å) in Carbon and Nitrogen Compounds

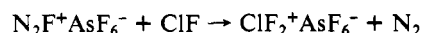
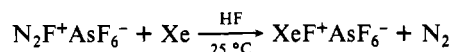
	$CH_4$ ( $sp^3$ )	$H_2C=CH_2$ ( $sp^2$ )	$HC\equiv CH$ ( $sp$ )
$r_{C-H}$	1.094 <sup>a</sup>	1.085 <sup>a</sup>	1.061 <sup>a</sup>
	$CF_4$ ( $sp^3$ )	$F_2C=CF_2$ ( $sp^2$ )	$FC\equiv N$ ( $sp$ )
$r_{C-F}$	1.323 <sup>b</sup>	1.313 <sup>b</sup>	1.262 <sup>a</sup>
	$NF_4^+$	$[FN=NF]^+$	$[FN\equiv N]^+$
$r_{N-F}$	1.30 <sup>c</sup>	?	1.22 <sup>d</sup>

<sup>a</sup>Data from ref 32. <sup>b</sup>Data from ref 39. <sup>c</sup>Data from ref 14. <sup>d</sup>This work.

Although a formal positive charge and other highly electronegative ligands generally tend to increase the strength of an X-F bond, this effect alone is insufficient to explain the unusually short N-F and  $N\equiv N$  bonds in  $N_2F^+$ . For example, the N-F bond in  $NF_4^+$  still has a value of 1.30 Å,<sup>14</sup> in spite of a formal positive charge and three additional fluorine ligands which should be more electronegative than the nitrogen ligand in  $N\equiv NF^+$ .

The most plausible explanation for the shortening of the N-F bond in  $N_2F^+$ , compared to  $NF_4^+$ , is the change in hybridization of the nitrogen molecular orbitals. From carbon chemistry it is well-known that the C-H and C-F bond lengths significantly decrease with increasing s-character of the carbon molecular orbital. Therefore, a similar bond shortening should be expected on going from  $sp^3$ -hybridized  $NF_4^+$  to  $sp$ -hybridized  $N\equiv NF^+$  (see Table VII). To our knowledge, this is the first example of hybridization-induced, dramatic bond shortening outside of carbon chemistry.

**The  $N_2F^+$  Cation as an Oxidative Fluorinator.** In view of  $N_2$  having a higher ionization potential than Kr, i.e. 15.576 vs 13.999 eV,<sup>40</sup> and  $KrF^+$  being the most powerful presently known oxidative fluorinator,<sup>41</sup> it was interesting to examine the oxidative power of the  $N_2F^+$  cation. For this purpose, the reactions of  $N_2F^+AsF_6^-$ , dissolved in anhydrous HF, were studied at 25 °C with the following substrates:  $ClF_5$ ,  $BrF_5$ ,  $IF_5$ ,  $XeF_4$ ,  $Xe$ ,  $ClF$ ,  $O_2$ , and  $NF_3$ . The  $KrF^+$  cation is capable of oxidizing all of these substrates under comparable reaction conditions. For example,  $HalF_5$  is oxidized to  $HalF_6^+$  salts,  $XeF_4$  to  $XeF_5^+$ ,  $O_2$  to  $O_2^+$ , and  $NF_3$  to  $NF_4^+$ .<sup>41</sup> In the case of  $N_2F^+$  the only substrates oxidized were Xe and  $ClF$  according to



The first reaction was briefly mentioned in a previous paper,<sup>42</sup> but no experimental details were given.

To examine whether fluorination reactions with  $N_2F^+$  might benefit from elevated temperatures,  $N_2F^+AsF_6^-$  was heated with a large excess of either  $ClF_5$  or  $BrF_5$  in a small ullage stainless steel cylinder, in the absence of HF, to 70 °C for 3 days. Again, no evidence for the formation of either  $ClF_6^+$  or  $BrF_6^+$  was detected. In the case of  $ClF_5$ , however, a small amount of the  $N_2F^+$  starting material was fluorinated by  $ClF_5$  to  $N_2F_3^+$ . A detailed

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analysis of the factors determining the relative strength of an oxidative fluorinator will be given in a separate paper.<sup>43</sup>

**Acknowledgment.** The authors thank Dr. Carl Schack for help, Dr. Konrad Seppelt for helpful comments on the crystal structure

disorder problem, and the U.S. Army Research Office and the U.S. Air Force Phillips Laboratory for financial support of the work at Rocketdyne.

**Supplementary Material Available:** Table SI listing observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

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## Preparation and Interconversion of Binuclear 2-Ferrazetine and Isomeric Ferrapyrrolinone Complexes

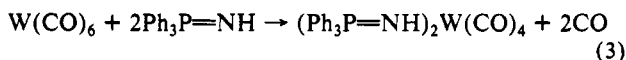
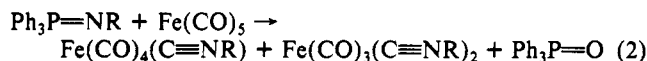
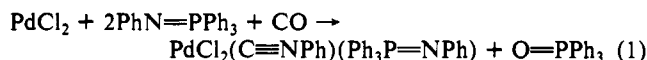
Chad A. Mirkin,<sup>†</sup> Kuang-Lieh Lu,<sup>†</sup> Thomas E. Snead,<sup>†</sup> Bruce A. Young,<sup>†</sup> Gregory L. Geoffroy,<sup>\*,†</sup> Arnold L. Rheingold,<sup>†</sup> and Brian S. Haggerty<sup>†</sup>

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**Abstract:** The complex  $\text{Fe}_2(\mu\text{-CH}_2)(\text{CO})_8$  reacts with the phosphine imides  $\text{R}'_3\text{P}=\text{NR}$  ( $\text{R}, \text{R}' = \text{Ph}$ ;  $\text{R} = \text{Bu}^t$ ,  $\text{R}' = \text{Bu}^n$ ) to form a mixture of the 3-ferra-4-pyrrolin-2-one complexes  $\text{Fe}_2(\mu\text{-CH}=\text{CHN}(\text{R})\text{C}(\text{O}))(\text{CO})_6$  and the 2-ferrazetine complexes  $\text{Fe}_2(\mu\text{-CH}=\text{CHNR})(\text{CO})_6$ . The latter complexes derive from the former by loss of CO, which is accelerated by heating (50 °C, 3 h) or by adding CO-labilizing agents (halides,  $[\text{HB}(\text{s-Bu})_3]^+$ ). This reaction is reversed by photolysis of the 2-ferrazetine complexes under 1 atm of CO. However, when the 2-ferrazetine complexes are allowed to thermally react with CO, the isomeric 2-ferra-4-pyrrolin-3-one complexes  $\text{Fe}_2(\mu\text{-C}(\text{O})\text{CH}=\text{CHNR})(\text{CO})_6$  are produced instead. These latter complexes have been found to add electrophiles ( $\text{HBF}_4$  and  $[\text{Me}_3\text{O}]\text{BF}_4$ ) to the acyl oxygen to form the cationic complexes  $[\text{Fe}_2\{\mu\text{-C}(\text{OR})=\text{CHCH}=\text{NBu}^t\}](\text{CO})_6[\text{BF}_4]$  ( $\text{R} = \text{H}, \text{Me}$ ). The 3-ferra-4-pyrrolin-2-one complexes also react with acid ( $\text{HBF}_4$ ) under 1 atm of CO to form the complexes  $[\text{Fe}_2\{\mu\text{-C}(\text{H})(\text{CH}=\text{NHR})\}](\text{CO})_6[\text{BF}_4]$ , which possess protonated  $\mu_2, \eta^1$ -azallylidene ligands. The dimethylcarbene complex  $\text{Fe}_2(\mu\text{-CMe}_2)(\text{CO})_8$  also reacts with  $(\text{Bu}^n)_3\text{P}=\text{NBu}^t$ , but this reaction stops at the acyl complex  $\text{Fe}_2(\mu\text{-CMe}_2)(\text{CO})_7\{\text{C}(\text{O})\text{N}(\text{Bu}^t)\text{P}(\text{Bu}^n)_3\}$  since this species cannot undergo the hydrogen migration needed to give entry to the ferrapyrrolinone and ferrazetine complexes. Mechanisms are proposed for these various transformations, and the following complexes have been crystallographically characterized:  $\text{Fe}_2(\mu\text{-CH}=\text{CHNPhC}(\text{O}))(\text{CO})_6$ ,  $\text{Fe}_2(\mu\text{-CH}=\text{CHNBu}^t)(\text{CO})_6$ ,  $\text{Fe}_2(\mu\text{-C}(\text{O})\text{CH}=\text{CHNPh})(\text{CO})_6$ ,  $[\text{Fe}_2(\mu\text{-CHCH}=\text{NBu}^t)(\text{CO})_6][\text{CF}_3\text{SO}_3]$ , and  $[\text{Fe}_2(\mu\text{-C}(\text{OMe})=\text{CHCH}=\text{NBu}^t)(\text{CO})_6][\text{BF}_4]$ .

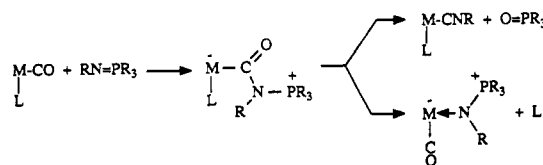
### Introduction

Phosphine imides ( $\text{R}_3\text{P}=\text{NR}$ ) are common reagents in the organic chemists repertoire for deoxygenating organic carbonyl compounds to form Schiff bases, reactions that proceed by initial addition of the nucleophilic phosphine imide nitrogen atom to the electropositive carbonyl carbon, followed by elimination of phosphine oxide. In principle, carbonyl ligands attached to transition metals should also be capable of undergoing deoxygenation by phosphine imides to form isocyanide ligands, but only two examples of this reaction have been reported (eqs 1 and 2).<sup>1–3</sup>



The predominant reaction that occurs upon reaction of carbonyl complexes with phosphine imides is ligand substitution, with the phosphine imide ligand coordinating through the nitrogen atom, e.g., eq 3.<sup>4</sup> The first step in both processes likely involves initial formation of an acyl intermediate via nucleophilic addition of the phosphine imide nitrogen to a terminal carbonyl ligand. This intermediate can then either eliminate phosphine oxide to form an isocyanide ligand or lose another ligand as the phosphine imide migrates to the metal to yield a substituted complex (Scheme I).<sup>5</sup>

### Scheme I



In our continuing studies of complexes containing ketene ligands,<sup>6</sup> we sought to determine if phosphine imides would deoxygenate a coordinated ketene ( $\text{CH}_2=\text{C}=\text{O}$ ) to form a ketenimine ( $\text{CH}_2=\text{C}=\text{NR}$ ) ligand. The complex  $\text{Fe}_2(\mu\text{-CH}_2)(\text{CO})_8$  (1) has been reported to react with nucleophiles to give products that may form via the intermediacy of a  $\mu$ -ketene complex,<sup>7</sup> and in an attempt to trap the presumed  $\mu$ -ketene intermediate, we allowed

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