# Preparation of 1-Fluoro-2,4,6-trihalogeno-*s*-triazinium Hexafluoroarsenates: Structure of $[C_3N_3Cl_3F][AsF_6]$ As Deduced by Experimental and ab Initio Methods

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The recent resurgence of nitrogen–fluorine chemistry has led to several novel N–F species with unusual properties and bonding.[1–6] For example, the $NF_4^+$ cation, prepared by Christe et al., offers new synthetic possibilities.[2] Due to its high $F^+$ detachment energy (FPDE = 180 kcal/mol),[6] $NF_4^+$ is a powerful oxidative fluorinator. Moreover, in $NF_4^+$ the N–F bond distance of 1.30 Å is exceptionally short.[2] Only two cations containing a shorter N–F bond have been described in the literature: $N_2F^+$ (1.22 Å)[3] and the metastable gas-phase species $NF^{2+}$ (1.10 Å, computed).[5] Recently we have reported the preparation of a salt containing the linear $FCNF^+$ cation, which is only stable at low temperatures.[4] The successful synthesis of the $FCNF^+$ cation, formally a product of the oxidative fluorination of cyanogen fluoride, FCN, led naturally to the attempted fluorination of the trimeric cyanuric halides, $(XCN)_3$ (X = F, Cl).

The reaction of $(FCN)_3$ or $(ClCN)_3$ with stoichiometric amounts of $F_2/AsF_5$ in $CFCl_3$ (Freon-11) led to the high-yield synthesis of two novel fluorotriazinium cations (eq 1). Neither

$$(XCN)_3 + F_2 + AsF_5 \xrightarrow{\text{Freon-11}} [C_3N_3X_3F][AsF_6] \qquad (1)$$
$$X = F\ (\mathbf{1}),\ Cl\ (\mathbf{2})$$

**1** nor **2** reacts with an excess of $F_2/AsF_5$ (50 °C, 5 bar). Therefore, we have so far been unable to prepare the corresponding di- and trications. Compounds **1** and **2** were characterized by their microanalytical data as well as by multinuclear NMR spectroscopy (for **2**; **1** is insoluble in Freon-11 and decomposes in $SO_2$ solution) and vibrational spectra (IR, Raman) (see Experimental Section). Recrystallization of **2** from liquid sulfur dioxide afforded crystals which were suitable for a single-crystal X-ray diffraction study (see Experimental Section).

The cation in compound **2** is disordered; the one fluorine atom was assigned a 33% occupancy at each nitrogen atom (Figure 1). The $AsF_6^-$ anions show undistorted octahedral symmetry without significant cation–anion interactions. The C–N bond distance (1.34 Å) and the CNC (117.6°) and NCN (122.3°) angles in **2** are similar to those in the neutral cyanuric chloride (1.33 Å, 112.7°, 127.2°).[7] The N–F bond distance in the cation in **2** is apparently very short. However, the value of 1.11 Å is unreliable, due to severe disorder problems of the cation (see above). Moreover, relatively high thermal motion of the fluorine atom out of the plane, coupled with inaccurate placing of the nitrogen atom along the N–F vector, and of both the N and F atoms perpendicular to the plane could very well be the reason for the apparently (and unreliable) shortness of the N–F bond length. Unfortunately, various attempts did not yield crystals free from disorder problems (N.B.: we changed the anions to $SbF_6^-$ and $Sb_2F_{11}^-$ and we tried to oxidize $(RCN)(ClCN)_2$ with $R = Me_3C$).

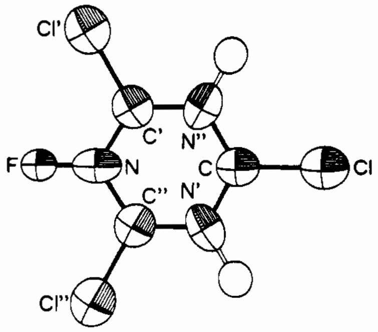

**Figure 1.** X-ray structure of the $[C_3N_3Cl_3F]^+$ cation in **2**. Bond distances (Å) and angles (deg): As-F1 = 1.718(3), Cl–C = 1.656(7), C–N = 1.341(6), N–F2 = 1.106(13); Cl–C–N = 118.8(3), N–C–N' = 122.3(6), C–N–C' = 117.6(6).

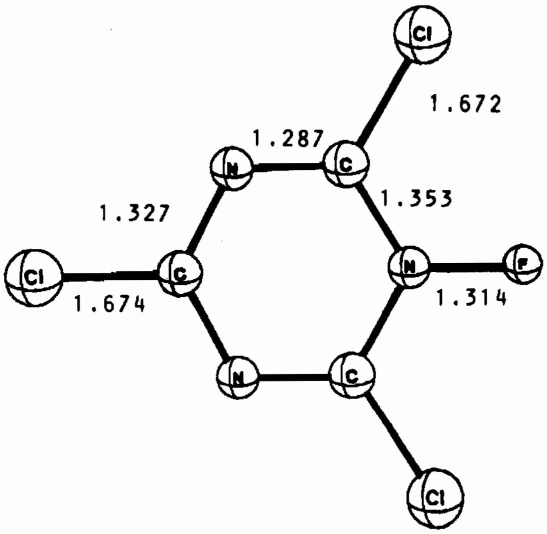

**Figure 2.** Structure of the $[C_3N_3Cl_3F]^+$ cation in **2** (HF/6-31G*). Bond distances (Å) are shown.

Therefore, ab initio calculations for the $C_{2v}$-symmetric $[C_3N_3Cl_3F]^+$ cation **2** have been carried out at the HF/6-31G* level (Figure 2). The average values of the calculated C–N and C–Cl bond lengths are 1.32 and 1.67 Å, respectively, in reasonable agreement with experiment. Higher-level geometry optimizations including electron correlation are too expensive for the trihalogenated system. Hence we chose $[C_3N_3H_3F]^+$ as a model system. At the HF level the C–N and C–F distances are the same as in **2**. At the MP2/6-31G* level the average C–N bond length increases to 1.34 Å, in perfect agreement with the experimental value. In fact, it is not so obvious that the "ortho"-chlorine has no effect on the C–N bond strengths. However, it has been reported that in $[C_3N_3F_3]$, $[C_3N_3Cl_3]$, and analogous *s*-triazines the vibrations which primarily reflect the character of a ring valence vibration are relatively constant in their position. The same observation obtains for the totally symmetric vibration near 1000 cm$^{-1}$ (cf. IR in Experimental Section) and for all nonplanar

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**Table I.** Comparison of Experimental and Computed N–F Bond Lengths (Å)

| compd | Pt group state | HF/6-31G*//6-31G* | //MP2/6-31G** | //MP2/6-311G** | expt[a] |
|---|---|---|---|---|---|
| FN | $C_{\infty v}$ 1 | 1.280 | 1.310 | 1.290 | 1.300 MW A |
| | $C_{\infty v}$ $^3\Sigma$ | 1.302 | 1.329 | 1.309 | 1.317 MW A |
| F–NH | $C_s$ 2A″ | 1.345 | 1.377 | 1.359 | 1.37 MW A |
| $F_2N$ | $C_{2v}$ 2B | 1.317 | 1.356 | 1.339 | 1.349 MW B |
| F–$NH_2$ | $C_s$ 1 | 1.386 | 1.431 | 1.412 | 1.433 MW A[b] |
| $F_2NH$ | $C_s$ | 1.353 | 1.405 | 1.386 | 1.400 MW B |
| $F_3N$ | $C_{3v}$ | 1.328 | 1.383 | 1.365 | 1.365 MW A |
| FNNF cis | $C_{2v}$ | 1.337 | 1.394 | 1.377 | 1.385 MW B |
| FNNF trans | $C_{2v}$ | 1.339 | 1.393 | 1.371 | 1.372 MW B[c] |
| F–NO | $C_s$ | 1.383 | 1.516 | 1.535 | 1.512 MW B |
| F–$NO_2$ | $C_{2v}$ | 1.344 | 1.488 | 1.497 | 1.467 MW D |
| $F_3NO$ | $C_{3v}$ | 1.350 | 1.446 | 1.437 | 1.432 X–R[d] |
| $F_4N^+$ | $T_d$ | 1.280 | 1.319 | 1.303 | 1.299 X-R[e] |
| F–$NN^+$ | $C_{\infty v}$ | 1.239 | 1.255 | 1.233 | 1.22 X-R[f] |
| F–$N_3$ | $C_s$ | 1.382 | 1.431 | 1.412 | 1.444 MW A[g] |
| $F_2NNF_2$ | $C_{2h}$ | 1.336 | 1.390 | 1.370 | 1.372 ED[h] |
| $F_2NCN$ | $C_s$ | 1.345 | 1.407 | 1.390 | 1.398 MW C |
| $F(CNCl)_3^+$ | $C_{2v}$ | 1.314 | | | 1.11 X-R |
| $F(CNH)_3^+$ | $C_{2v}$ | 1.317 | 1.356 | | |

[a] Taken, unless otherwise noted, from ref 14. [b] Reference 15. [c] Reference 16. [d] Reference 17. [e] Reference 18. [f] Reference 3. [g] Reference 19. [h] Reference 20. MW: microwave data. X-R: X-ray data. ED: electron diffraction data. Experimental uncertainties (Å): A, ≤0.002; B, ±0.002 – ±0.005; C, ±0.005 – ±0.010; D, ±0.010 – ±0.020.

modes.[10] The N–F bond becomes even longer (1.36 Å) than in the HF calculation (1.31 Å). Experimentally N–F bond lengths range from 1.30 to 1.50 Å. The reason for the uncommon behavior is due to electrostatic and anomeric effects, discussed extensively by Reed and Schleyer.[11-13] To check the accuracy of calculated N–F bond lengths, 17 compounds were calculated (Table I) at different theoretical levels and compared with experiment. The HF/6-31G* calculated N–F bond lengths are generally too short; the deviations are extremely large for oxygen-containing compounds (FNO, $FNO_2$, $F_3NO$). The inclusion of electron correlation corrects this problem; the MP2/6-31G** and the MP2/6-311G** levels give very good results. In general the N–F bond lengths are about 0.02 Å shorter for MP2/6-311G** compared to MP2/6-31G**. Both basis sets reproduce the experimental values remarkably well, but deviations do not necessarily arise from errors in the computed values. The microwave data show uncertainties up to 0.02 Å; the accuracy of high level calculations are comparable. Hence it seems very likely that the very short N–F bond length in **2** (X-ray) is unreliable (see above) and that the real value should be 1.34 Å.

Compound **2** is a promising fluorination agent. Moreover, both new species **1** and **2** can easily be prepared in high yield in one simple step from commercially readily available reagents.

## Experimental Section

**Caution**: Fluorine, chlorine trifluoride, and arsenic pentafluoride are powerful oxidizers! Suitable shielding is required, and protective clothing and face masks should be worn all times.

$F_2$ (0.128 g, 3.38 mmol; dried over NaF) and $AsF_5$ (0.574 g, 3.38 mmol) were condensed at −196 °C onto a frozen solution of $(FCN)_3$ (0.457 g, 3.38 mmol) [or $(ClCN)_3$ (0.623 g, 3.38 mmol)] in $CFCl_3$ (10 mL) in a 20-mL Kel-F reaction vessel (deactivated with $ClF_3$). The stirred reaction mixture was warmed within 12 h to room temperature. All volatile components were removed in vacuum and **1** (or **2**) was isolated as a white solid. **2** was recrystallized from $SO_2$ (10 mL).

**Analytical Data for 1.** Yield: 0.89 g (77%). $T_{dec}$ = 206 °C. Anal. Calcd for $C_3AsF_{10}N_3$ (342.96): C, 10.50; N, 12.25. Found: C, 10.41; N, 12.17. IR (powder between KBr plates, $cm^{-1}$): 1770 m; 1725 m; 1670 m and 1630 ($\nu$-$C_3N_3$); 1590 s, br ($\nu$-CF); 1415 m ($\nu$-$C_3N_3$); 1088 s ($\nu$-CF); 1030 m and 978 w ($\delta$-$C_3N_3$); 814 m ($\gamma$-$C_3N_3$); 769 m; 700 vs ($\nu_3$-$AsF_6$); 560 m ($\delta$-$C_3N_3$); 385 vs ($\nu_4$-$AsF_6$).

**Analytical Data for 2.** Yield: 1.32 g (99%). $T_{dec}$ = 172 °C. Anal. Calcd for $C_3AsCl_3F_7N_3$ (392.32): C, 9.18; N, 10.71. Found: C, 9.34; N, 10.71. $^{13}C$ NMR ($SO_2$, 25 °C, 67.5 MHz, $CDCl_3$): 136.4 s (1), 169.4 s (2). $^{14}N$ NMR ($SO_2$, 25 °C, 14.45 MHz, $MeNO_2$): −110 s, $\Delta\nu_{1/2}$ = 560 Hz. $^{19}F$ NMR ($SO_2$, 25 °C, 188.2 MHz, $CFCl_3$): −60.0 q (6), −45.2 s (1). IR (powder between KBr plates, $cm^{-1}$): 1565 s and 1480 s ($\nu$-$C_3N_3$); 1312 m ($\nu$-$C_3N_3$); 1290 m and 1270 m ($\nu$-CCl); 1135 m; 892 m; 860 m ($\nu$-CCl); 741 m ($\gamma$-$C_3N_3$); 700 vs ($\nu_3$-$AsF_6$); 395 vs ($\nu_4$-$AsF_6$).

IR and Raman data for compounds **1** and **2** are in agreement with the given structures (cf. ref 19).

**Crystal Data for 2.** $M$ = 392.32, rhombohedral, space group $R3c$, $a$ = 10.775(5) Å, $b$ = 15.453(3) Å, $\alpha$ = 90°, $\beta$ = 90°, $\gamma$ = 120°, $V$ = 1553.7 $Å^3$, $Z$ = 6, $D_c$ = 2.51 $Mg{\cdot}m^{-3}$, crystal size 0.25 × 0.35 × 0.5 $mm^3$. Data were collected at 173 K on a Syntex P2$_1$ diffractometer with graphite monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.7107 Å) using the $\omega$–$2\theta$ scan mode ($2\theta_{max}$ of 55°), and correction was made for absorption ($\mu$ = 41.3 $cm^{-1}$).[8] The structure was solved by direct methods and refined by full-matrix least-squares, SHELX76, to residuals of $R$ = 0.045 and $R_w$ = 0.046 for 333 reflections [$I > 2.0\sigma(I)$] (379 total). Scattering factors were taken from ref 9. All atoms were assigned anisotropic thermal parameters.

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**Supplementary Material Available:** Tables of crystallographic data, atomic coordinates, anisotropic thermal parameters, and long distances and angles (4 pages). Ordering information is given on any current masthead page. Additional crystallographic material may be obtained either from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information, W-7514 Eggenstein-Leopoldshafen 2, Germany, CSD No. 55866, or from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

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