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Syntheses, Properties, and Structures of Anhydrous Tetramethylammonium Fluoride and Its 1:1 Adduct with *trans*-3-Amino-2-butenenitrile

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Abstract: A simple method for the preparation of anhydrous and essentially HF_2^--free $N(CH_3)_4F$ is described. The compound was characterized by X-ray diffraction, NMR, infrared, and Raman spectroscopy. It crystallizes in the hexagonal system with a hexagonal closest packing of the $N(CH_3)_4^+$ cations. It is shown that the free F^- anion is a very strong Lewis base and chemically reacts with most of the solvents, such as CH_3CN or chlorinated hydrocarbons, previously used for studies of the fluoride anion. As a result, some of the properties previously reported for F^- were due to HF_2^- or other secondary reaction products. Its relatively simple synthesis and lower cost, combined with its good solubility and the high chemical inertness of the $N(CH_3)_4^+$ cation, make $N(CH_3)_4F$ an excellent substitute for presently used fluoride ion sources, such as either $[(CH_3)_2N]_3S^+F_2Si(CH_3)_3^-$, which is commonly referred to as tris(dimethylamino)sulfonium fluoride, or CsF. The reaction of $N(CH_3)_4F$ with CH_3CN results in the dimerization of CH_3CN and the formation of a 1:1 adduct of $N(CH_3)_4F$ with this dimer, *trans*-3-amino-2-butenenitrile. The crystal structure and vibrational spectra of this adduct are reported.

Introduction

The free fluoride anion is a very strong base and plays an important role in many organic and inorganic reactions.[1] Although alkali-metal fluorides are readily available, their low solubilities in most of the common solvents have rendered them of very limited practical use. Since the solubility of an ionic fluoride generally increases with increasing size of its countercation, the solubility limitations of the alkali-metal fluorides could be overcome by the use of a larger countercation. However, this large countercation must be chemically inert toward the fluoride anion, solvents, and other reagents, and its fluoride salt must be readily accessible to make it of practical use.

Although tetraalkylammonium fluorides would appear to be ideally suited for this purpose, they have not been developed into widely used reagents because of the great experimental difficulties encountered with their syntheses in anhydrous form. Thus, the tetraalkylammonium fluorides are generally available only as hydrates that, upon attempted water removal, undergo an E_2 elimination reaction with the formation of bifluoride and an olefin. The observation of the following reaction

$$2(n\text{-}C_4H_9)_4N^+F^- \rightarrow (n\text{-}C_4H_9)_4N^+HF_2^- + (n\text{-}C_4H_9)_3N + CH_3CH_2CH{=}CH_2$$

has prompted Sharma and Fry to conclude[2] that "it is very unlikely that pure, anhydrous tetraalkylammonium fluoride salts have ever, in fact, been produced in the case of ammonium ions susceptible to E_2 elimination; rather, reactions which have been reported to proceed in the presence of naked fluoride ion generated from such sources have probably actually been caused either by hydrated fluoride ion or by bifluoride ion". Although tetramethylammonium fluoride does not contain any carbon–carbon bond and, therefore, cannot undergo an E_2-type elimination reaction, Sharma and Fry's conclusion has also been applied to this compound, as evidenced by a recent statement[3a] that $N(CH_3)_4F$ "has never been obtained anhydrous and that removal of water results in decomposition". Similarly, Rieux and co-workers recently concluded[3b] that "the naked fluoride is still a myth and not yet a reality". In view of these reports, it is not surprising that $N(CH_3)_4F$ has not been exploited as a readily accessible, chemically inert, and highly soluble form of naked fluoride and that costly alternatives, such as tris(dimethylamino)sulfonium difluorotrimethylsilicate,[4] $[(CH_3)_2N]_3S^+F_2Si(CH_3)_3^-$, have been developed. Although the latter compound does not contain a free fluoride ion per se, the $F_2Si(CH_3)_3^-$ anion serves as an excellent fluoride ion donor toward stronger Lewis acids.

Recent work in our laboratory on the synthesis of the ClF_6^- anion[5] required a countercation that was larger and more soluble than cesium and at the same time resisted chemical attack by ClF_5. Since ClF_5 reacts violently with H_2O and is a much weaker Lewis acid than HF, incapable of displacing it from HF_2^-, we needed H_2O- and HF_2^--free $N(CH_3)_4F$.

Numerous reports[6-12] on the synthesis of tetramethylammonium fluoride can be found in the literature. They are based on two approaches. The first one dates back to 1888 and involves the neutralization of $N(CH_3)_4OH$ with HF in aqueous solution, followed by water removal in vacuo at temperatures up to 160 °C.[6] If the water is removed at various temperatures, intermediate $N(CH_3)_4F{\cdot}nH_2O$-type hydrates can be isolated with n ranging from 1 to 5.[13] The difficulty with this process is the removal of the last amounts of water from the $N(CH_3)_4F$, because at 160 °C the removal rate is still slow while the $N(CH_3)_4F$ already begins to undergo a very slow decomposition.[6] Thus, the products obtained by this method have been reported to contain significant amounts of impurities, attributed to either HF_2^-[9] or the monohydrate.[10] In a minor modification[8] of this method, the bulk of the water was removed from the aqueous $N(CH_3)_4F$ solution in vacuo on a rotating evaporator. The resulting syrupy oils were converted to an $N(CH_3)_4F{\cdot}CH_3OH$ solvate by repeated treatment

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with CH_3OH and drying in vacuo at 100 °C.

The second approach utilizes metathetical reactions,[9-12] such as

$$N(CH_3)_4Cl + KF \xrightarrow{CH_3OH} N(CH_3)_4F + KCl\downarrow$$

The resulting crude $N(CH_3)_4F$ was purified by recrystallization from isopropyl alcohol.[9] This synthetic method has frequently been used but, according to Klanberg and Muetterties,[8] the $N(CH_3)_4F$ prepared in this manner always contained at least 1-2% of chloride, while commercially available $N(CH_3)_4F$ had an even higher Cl^- content of 6.6%.

Another metathesis that has been described in a German patent[11] is based on the reaction of $N(CH_3)_4Cl$ with HF and $NaOCH_3$ in CH_3OH to give $N(CH_3)_4F\cdot2CH_3OH$. This solvate is then converted to $N(CH_3)_4F$ by vacuum pyrolysis at 150 °C. The reaction of $N(CH_3)_4Cl$ with HF and $NaOCH_3$ must be carried out in two separate steps. Reacting the $N(CH_3)_4Cl$ first with $NaOCH_3$ according to

$$N(CH_3)_4Cl + NaOCH_3 \xrightarrow{CH_3OH} N(CH_3)_4OCH_3 + NaCl\downarrow$$

$$N(CH_3)_4OCH_3 + HF + CH_3OH \xrightarrow{CH_3OH} N(CH_3)_4F\cdot2CH_3OH$$

results in a more efficient use of the starting materials than the reverse sequence

$$N(CH_3)_4Cl + 10HF \rightarrow N(CH_3)_4H_2F_3 + 7HF + HCl$$

$$N(CH_3)_4H_2F_3 + 2NaOCH_3 \xrightarrow{CH_3OH} N(CH_3)_4F\cdot2CH_3OH + 2NaF\downarrow$$

According to Klanberg and Muetterties[8] these $NaOCH_3$–HF-based processes suffer from the same drawback, i.e., Cl^- impurities, as the $N(CH_3)_4Cl$ + KF metathesis and the use of excess HF will generate HF_2^- impurities.

Although some of the above chemistry dates back for more than 100 years,[6] reliable analytical data, such as water analyses, detailed spectroscopic or structural data, and physical and chemical properties have not been reported for "anhydrous" $N(CH_3)_4F$. Therefore, it was also highly desirable to better characterize this important compound.

Experimental Section

Materials. The CH_3CN (Baker, Bio-analyzed, having a water content of 40 ppm) was treated with P_2O_5 and freshly distilled prior to use, thereby reducing its water content to <4 ppm. The $N(CH_3)_4OH$ (Baker, analyzed, 10% aqueous solution), HF (Baker, analyzed, 50% aqueous solution), CH_3OH (Baker, absolute, 0.003% H_2O), and $(CH_3)_2CHOH$ (Mallinckrodt, A.R., 0.03% H_2O) were used as received.

Apparatus. Volatile materials were handled either in a flamed-out Pyrex vacuum line equipped with Kontes Teflon valves or in the dry nitrogen atmosphere of a glovebox. Solids were manipulated exclusively in the drybox.

Raman spectra were recorded on either a Cary Model 83 or a Spex Model 1403 spectrophotometer by use of the 488-nm exciting line of an Ar ion or the 647.1-nm line of a Kr ion laser, respectively. Baked-out Pyrex melting point capillaries were used as sample holders. Infrared spectra were recorded as KBr disks on a Perkin-Elmer Model 283 spectrophotometer. For the exclusion of moisture, only KBr that had been fused and finely ground in the drybox was used. The KBr disks were pressed in a Wilks minipress inside the drybox, with the sample in a powdered KBr matrix being sandwiched between two prepressed layers of neat KBr, and the resulting sandwiches were left in the press for the recording of the spectra. The spectra obtained in this manner were identical with those obtained for pressed AgCl disks, indicating that no reaction between KBr and $N(CH_3)_4F$ had occurred during the pressing operation.

The ^{19}F and ^1H NMR spectra were measured at 84.6 and 90 MHz, respectively, on a Varian Model EM390 spectrometer, with 5-mm Teflon-FEP tubes (Wilmad Glass Co.) as sample containers and $CFCl_3$ and TMS, respectively, as internal standards, with negative shifts being upfield from the standards. A Perkin-Elmer differential scanning calorimeter, Model DSC-1B, was used to determine the thermal stability and to check for phase transitions. The samples were crimp-sealed in aluminum pans, and a heating rate of 10 °C/min in N_2 was used. The instrument was calibrated with the known melting points of *n*-octane and indium. Water contents were measured by the Karl Fischer method[14] on a Photovolt Model Aquatest IV, with Teflon ampules as sample containers and plastic syringes for the sample injection.

Table I. Summary of Crystal Data and Refinement Results for the Tetramethylammonium Fluoride–3-Amino-2-butenenitrile Adduct

space group	$P2_1/C$ (monoclinic)
a (Å)	10.252 (3)
b (Å)	8.579 (2)
c (Å)	13.324 (3)
β (deg)	111.65 (2)
V (Å^3)	1089.2 (5)
molecules/unit cell	4
molecular weight	174.99
crystal dimensions (mm)	0.5 × 2.0 × 1.2
calculated density (g cm^{-3})	1.071
wavelength (Å) used for data collection	0.71069
$(\sin\theta)/\lambda$ limit (Å^{-1})	0.539
total number of reflections measured	1493
number of independent reflections	1492
number of reflections used in structural analysis $I > 3\sigma(I)$	1141
number of variable parameters	181
final agreement factors	$R(F) = 0.0387$ $R_w(F) = 0.0529$

Table II. Bond Distances in the Tetramethylammonium Fluoride–3-Amino-2-butenenitrile Adduct

C2---N1	1.486 (2)	C3′---C2′	1.489 (2)
C3---N1	1.485 (2)	C4′---C2′	1.357 (1)
C4---N1	1.491 (2)	C5′---C4′	1.408 (2)
C5---N1	1.503 (2)	N6′---C5′	1.150 (2)
C2′---N1′	1.337 (2)		

Table III. Bond Angles (deg) in the Tetramethylammonium Fluoride–3-Amino-2-butenenitrile Adduct

C3–N1–C2	110.4 (1)	C3′–C2′–N1′	115.9 (1)
C4–N1–C2	109.3 (1)	C4′–C2′–N1′	122.6 (1)
C4–N1–C3	111.5 (1)	C4′–C2′–C3′	121.5 (1)
C5–N1–C2	108.1 (1)	C5′–C4′–C2′	121.8 (1)
C5–N1–C3	109.1 (1)	N6′–C5′–C4′	179.6 (1)
C5–N1–C4	108.3 (1)		

X-ray diffraction patterns of powdered samples in sealed 0.5-mm quartz capillaries were obtained by using a General Electric Model XRD-6 diffractometer, Ni-filtered Cu Kα radiation, and a 114.6-mm-diameter Philips camera.

Crystal Structure of $N(CH_3)_4F$-*trans*-$NH_2C(CH_3)$=CHCN. Single crystals of $N(CH_3)_4F$-*trans*-$NH_2C(CH_3)$=CHCN were grown by allowing *n*-hexane vapors to diffuse slowly into a saturated solution of $N(CH_3)_4F$ in CH_3CN. A rocklike crystal was mounted in a quartz capillary in the glovebox. A Nicolet/Syntex $P2_1$ automated four-circle diffractometer, with Mo Kα radiation and a graphite crystal monochromator, was used for the intensity data collection. The unit cell parameters were determined by least-squares refinement of 15 centered reflections. Data were collected with the ω-scan technique for all reflections such that $4.0° < 2\theta < 45.0°$. Throughout the data collection, three reflections were monitored periodically and no decay was observed. Of 1493 reflections collected, 1141 reflections with $I > 3\sigma(I)$ were retained for the ensuing structure analysis.

The structure was solved by direct methods with the SHELXS86 system[15] of crystallographic programs. The positions of all atoms were revealed after direct method analysis of the data. Subsequent least-squares refinements of the atomic coordinates, including positions of the hydrogen atoms, and thermal parameters resulted in final agreement values of R = 3.87% and R_w = 5.29%. Details of the data collection parameters and other crystallographic information are given in Table I, and the final atomic coordinates are listed in Table A (supplementary material). Interatomic distances and angles are given in Tables II and III, respectively. Figures 1 and 2 show a packing diagram for the $N(CH_3)_4F$ adduct and the interactions of the fluorine atoms, respectively.

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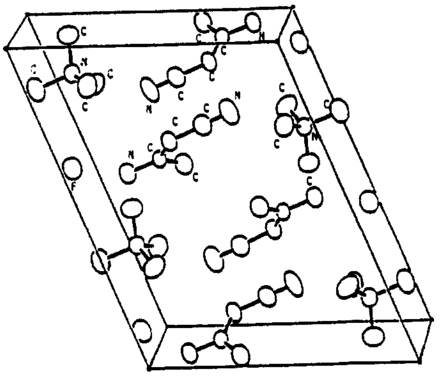

Figure 1. Packing diagram of $N(CH_3)_4F$-*trans*-$H_2NC(CH_3)CHCN$ viewed along the *b* axis.

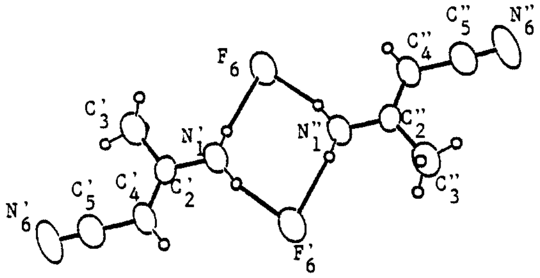

Figure 2. View of the molecular $N(CH_3)_4F$-$H_2NC(CH_3)CHCN$ unit showing the interactions of the fluorine atoms.

Synthesis of $N(CH_3)_4F$. The following generalized procedure was found to yield the purest samples of $N(CH_3)_4F$. Inside a glovebag purged by nitrogen or CO_2-free air, a measured amount of a 10% aqueous $N(CH_3)_4OH$ solution was placed into a polyethylene beaker. With a pH electrode as an indicator and a Teflon-coated magnetic stirring bar for mixing, the $N(CH_3)_4OH$ solution was titrated with 50% aqueous HF to the exact equivalence point. Plasticware was used exclusively for the handling of the HF solution. The last few percent of the required HF was added slowly with a more dilute HF solution to avoid overshooting the end point. The resulting $N(CH_3)_4F$ solution was transferred into a round-bottom Pyrex flask, and the water was pumped off with a rotary film evaporator while the temperature was slowly raised toward 150 °C. After most of the water had been removed at 150 °C, the solid white residue was finely ground in a porcelain mortar in the dry N_2 atmosphere of a glovebox and then further pumped on at 150 °C for several days until the weight became essentially constant, and the infrared absorption bands of $N(CH_3)_4F \cdot H_2O$[16] at 822 and 895 cm^{-1} showed an intensity comparable to or less than that of the weak $N(CH_3)_4^+$ band at 1203 cm^{-1} (see later text). The other main impurities present at this stage were small amounts of HF_2^- and, if glass equipment had been used, SiF_6^{2-}, which were readily monitored by their characteristic infrared absorptions[17,18] at 1256 and at 708 and 728 cm^{-1}, respectively. In the drybox, the crude $N(CH_3)_4F$ was recrystallized by dissolving it in dry isopropyl alcohol and pumping off enough of the solvent to precipitate most of the $N(CH_3)_4F$, in the form of its alcoholate, out of the solution. The $N(CH_3)_4HF_2$ and $[N(CH_3)_4]_2SiF_6$ impurities were enriched in the mother liquor, and the solvated isopropyl alcohol was removed from the recrystallized material in a dynamic vacuum at 80 °C. The yield of purified $N(CH_3)_4F$ was about 80%, and material with a water content ≤0.06 wt % and a trace of HF_2^- as the only detectable impurity was obtained in this manner. The quality of the product was checked for H_2O, isopropyl alcohol, HF_2^-, and SiF_6^{2-} contamination by Karl Fischer titration and infrared, Raman, and ^{19}F and ^1H NMR spectroscopy.

Thermal Decomposition of $N(CH_3)_4F$. Anhydrous $N(CH_3)_4F$ (7.08 mmol) was placed inside the glovebox into a flamed-out Pyrex vessel equipped with a Teflon valve. The vessel was connected to a Pyrex vacuum line and gradually heated in a dynamic vacuum to 230 °C. The volatile products were separated by passage through two cold traps kept at −126 and −196 °C. After 4 h, the pyrolysis was essentially complete. The Pyrex vessel contained 18 mg (0.06 mmol) of a white solid residue that was identified by its infrared spectrum as $[N(CH_3)_4]_2SiF_6$. The −126 °C trap contained $N(CH_3)_3$ (7.01 mmol), and the −196 °C trap contained CH_3F (7.03 mmol).

Results and Discussion

Synthesis of Anhydrous $N(CH_3)_4F$. Our synthesis of anhydrous $N(CH_3)_4F$ is based on the method of Lawson and Collie from 1888, but incorporates the following improvements: (i) the neutralization step

$$N(CH_3)_4OH + HF \xrightarrow{H_2O} N(CH_3)_4F + H_2O$$

is carried out in a CO_2-free atmosphere to avoid the formation of carbonate or bicarbonate impurities; (ii) a pH electrode is used as an indicator to titrate exactly to the equivalence point of aqueous $N(CH_3)_4F$; (iii) only plastic (polyethylene or Teflon) equipment is used for the handling of the HF solution to avoid SiF_6^{2-} formation; (iv) the water is removed in a dynamic vacuum with a rotary film evaporator; (v) the bath temperature is precisely controlled to 150 °C for the final water removal that is periodically monitored by the weight loss of the sample and by infrared spectroscopy; (vi) the crude product is azeotroped with isopropyl alcohol for additional water removal; and (vii) the azeotroped product is purified by recrystallization from dry isopropyl alcohol.

This process is capable of producing $N(CH_3)_4F$ in very high yield. The only significant loss of material is that retained in the mother liquor during the final recrystallization step. Water contents, based on Karl Fischer titrations of methanol solutions, as low as 0.06 wt % were obtained, with no detectable SiF_6^{2-} and only a trace of HF_2^- as an impurity. Since the process does not involve any chlorine-containing reagents, chloride contamination is precluded. The process is also readily scalable and was carried out on a 100-g scale without any complications.

Recrystallizations of the crude $N(CH_3)_4F$ from either CH_3CN or CH_3OH were also studied, but are inferior to that using isopropyl alcohol. Methanol does not form an azeotrope with H_2O, and its solvate with $N(CH_3)_4F$ is considerably more stable than that of isopropyl alcohol, thus rendering the CH_3OH removal more difficult. Acetonitrile reacts with the free fluoride ion (see later text), resulting in significant material losses and the formation of $N(CH_3)_4HF_2$ and $N(CH_3)_4F$-$NH_2C(CH_3){=}CHCN$ as potential contaminants.

Properties of $N(CH_3)_4F$. The compound is a white, crystallinic, hygroscopic solid that starts to decompose slowly in a dynamic vacuum at about 170 °C. The previously postulated[6] decomposition path

$$N(CH_3)_4F \rightarrow N(CH_3)_3 + CH_3F$$

was confirmed by a quantitative vacuum pyrolysis at 210–230 °C. The only byproduct obtained in the pyrolysis was a trace of $[N(CH_3)_4]_2SiF_6$ that had been formed by handling of the material in glass. The $N(CH_3)_4F$ is highly soluble in water and alcohols with which it tends to form solvates, in partially chlorinated hydrocarbons with which it undergoes a ready chlorine–fluorine exchange,[19] and in CH_3CN from which it readily abstracts a proton resulting in the formation of CH_2CN^-, $NH_2C(CH_3){=}CHCN$, and HF_2^-.[20] It is also soluble in formamide; however, the ^{19}F NMR signal in this solvent is very broad (about 200 Hz at 25 °C), indicating strong interaction with the solvent. Furthermore, $N(CH_3)_4F$ dissolves exothermically in acetone, exhibiting originally a signal at about −103.6 ppm that rapidly decays giving rise to a new signal at about −103.0 ppm. It dissolves also in nitromethane with a faint yellow color showing a ^{19}F signal at −150 ppm. It thus appears that in most solvents in which $N(CH_3)_4F$ is soluble, strong interactions with the solvent occur. The most inert solvent found to date is CHF_3 (bp −84.4 °C, mp −160 °C). At −80 °C, CHF_3 dissolves 4.4 wt % of $N(CH_3)_4F$ and the only ^{19}F signal observed in addition to the solvent peak is a singlet with a line width of about 7 Hz at −107 ppm for the fluoride ion. There was no evidence for hydrogen abstraction and HF_2^- for-

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Table IV. ^{19}F NMR Shifts (ppm Upfield from $CFCl_3$) of Tetramethylammonium Fluoride in Various Solvents

$(CH_3)_2SO$	−73	CH_3COCH_3	−103	$(CH_3)_2CHOH$	−122
CH_3CN	−74	CHF_3	−107	C_2H_5OH	−137
H_2NCHO	−96	$CHCl_3$	−113	CH_3OH	−148
CH_2Cl_2	−97	H_2O	−119	CH_3NO_2	−150

mation under these conditions. When the CHF_3 solvent is pumped off from the $N(CH_3)_4F$ at −78 °C, a CHF_3 adduct of approximately a 1:1 composition was obtained that dissociates at a higher temperature reversibly to $N(CH_3)_4F$ and CHF_3. Low-temperature Raman spectra of this adduct showed only minor frequency shifts compared to the starting materials, indicating weak interaction. In some other solvents such as hexane, dimethoxyethane, ethyl acetate, propylene carbonate, dimethylformamide, benzene, 1,2-difluorobenzene, tetrahydrofuran, dioxane, trichlorofluoromethane, sulfuryl chloride fluoride, sulfolane, or carbon disulfide, however, little or no solubility of $N(CH_3)_4F$ was observed by ^{19}F NMR spectroscopy. Whereas the proton resonance of the $N(CH_3)_4^+$ cation exhibits the expected chemical shift and coupling constant ($\delta = 3.1$, $J_{^1H^{14}N} = 0.6$ Hz),[20] the observed ^{19}F NMR shifts of the fluoride anion are highly solvent dependent,[20] as can be seen in Table IV, and strongly deviate from those previously reported.[21] The trend in chemical shifts for $^{19}F^-$ in different solvents relative to those of $^{35}Cl^-$ ions in the same solvents is similar to that observed for ^{129}Xe relative to Cl^-. Therefore, this solvent dependency cannot be attributed to varying degrees of hydrogen bonding between F^- and protons of the solvents.[22]

Chemically, the free fluoride anion in $N(CH_3)_4F$ acts, as expected, as a very strong Lewis base and readily complexes with suitable Lewis acids, such as BF_3,[23] PF_5,[23] SbF_5,[24] HF,[17] SiF_4, SF_4,[9] etc., forming the corresponding complex fluoro anions. In the absence of good fluoride acceptor molecules, it can abstract even relatively firmly bound protons from compounds such as CH_3CN.[19] The $N(CH_3)_4^+$ cation is coordinatively saturated and, due to the relatively high strength of the carbon–nitrogen bond, possesses a high activation energy toward chemical reactions. Compared to the tris(dimethylamino)sulfonium cation, TAS^+,[4] the $N(CH_3)_4^+$ cation is chemically much more inert as shown, for example, by its ability to form a stable ClF_4^- salt.[25] On the other hand, TAS^+ salts are more soluble and are also thermally more stable. This was shown by complexing $N(CH_3)_4F$ with $SiF(CH_3)_3$.

$$N(CH_3)_4F + SiF(CH_3)_3 \rightarrow N(CH_3)_4^+SiF_2(CH_3)_3^-$$

The resulting $N(CH_3)_4^+SiF_2(CH_3)_3^-$ salt was found to be of only marginal stability at room temperature, whereas $TAS^+SiF_2(CH_3)_3^-$ is stable up to its melting point of 98–101 °C.[4] Thus, the main advantages of $N(CH_3)_4^+$ over $[(CH_3)_2N]_3S^+$ are its lower cost and increased chemical inertness.

Crystal Structure of Tetramethylammonium Fluoride. Although the crystal structures of $N(CH_3)_4Cl$, $N(CH_3)_4Br$, and $N(CH_3)_4I$ are well-known[26-29] and exhibit interesting polymorphism, no crystal data were previously available for $N(CH_3)_4F$. Our attempts failed to grow single crystals of pure $N(CH_3)_4F$ that were suitable for an X-ray diffraction study. With CH_3CN, hydrogen abstraction occurs[19] resulting in the formation of CH_2CN^-

$$2F^- + CH_3CN \rightarrow HF_2^- + CH_2CN^-$$

Table V. X-ray Powder Data[a] for $N(CH_3)_4F$

d(obsd), Å	*d*(calcd), Å	intens	*h*	*k*	*l*
5.35	5.356	vs	1	0	0
4.57	4.577	s	1	0	1
4.40	4.406	ms	0	0	2
3.398	3.403	mw	1	0	2
3.092	3.092	m	1	1	0
2.677	2.678	m	2	0	0
2.565	2.562	ms	2	0	1
2.530	2.531	ms	1	1	2
2.290	2.289	mw	2	0	2
2.202	2.203	w	0	0	4
1.979	1.979	m	2	0	3
1.838	1.839	mw	2	1	2
1.794	1.794	w	1	1	4
1.751	1.750	w	3	0	1
1.667	1.667	mw	2	1	3

[a] Hexagonal; $a = 6.185$ Å, $c = 8.812$ Å; Cu Kα radiation, Ni filter.

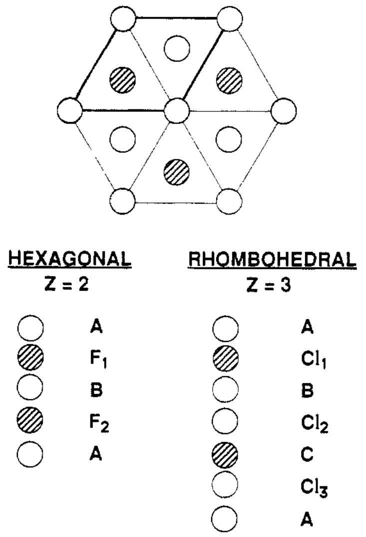
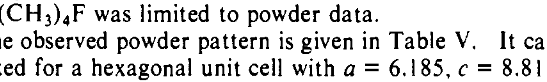


Figure 3. Packing arrangements for the hexagonal anion and cation layers in hexagonal $N(CH_3)_4F$ and rhombohedral $N(CH_3)_4Cl$, viewed along the *c* axis. The actual unit cell is marked by a heavier line.

followed by its reaction with CH_3CN to give *trans*-3-amino-2-butenenitrile[30]



which forms a 1:1 adduct with $N(CH_3)_4F$ (see later text). Thus, all the single crystals obtained during this study from CH_3CN solutions were either the tetramethylammonium bifluoride[17] or the 1:1 adduct of $N(CH_3)_4F$ with *trans*-3-amino-2-butenenitrile (see later text). In chlorinated solvents, rapid halogen exchange was observed,[20] while from alcoholic solutions only solvates of $N(CH_3)_4F$ were obtained. Therefore, our structure determination of $N(CH_3)_4F$ was limited to powder data.

The observed powder pattern is given in Table V. It can be indexed for a hexagonal unit cell with $a = 6.185$, $c = 8.812$ Å, $Z = 2$, and a calculated density of 1.058 g cm^{-3}. The *hkl* indices show no restrictions indicating a primitive lattice, and the presence of two molecules per unit cell precludes the possibility of a rhombohedral unit cell. Since the observed c/a value of 1.42 strongly deviates from 1.63, a zincite-type structure is highly unlikely[29,31] and $N(CH_3)_4F$ most likely possesses an *anti*-NiAs-type structure. In the latter, the $N(CH_3)_4^+$ cation would be surrounded by six fluoride anions located at the corners of a trigonal prism, while the fluoride anion would be surrounded by six $N(CH_3)_4^+$

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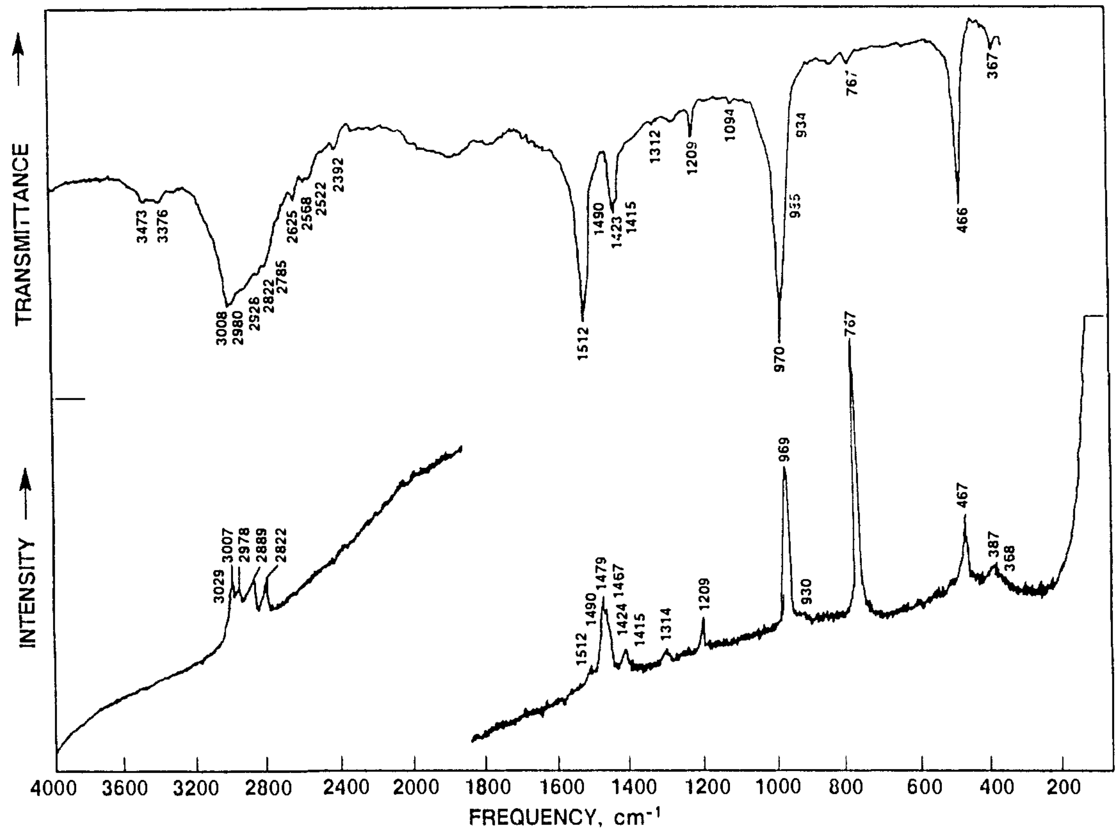

Figure 4. Infrared and Raman spectra of solid $N(CH_3)_4F$.

cations and two other fluoride anions.[29,31]

It is interesting to compare the structure of $N(CH_3)_4F$ with that of $N(CH_3)_4Cl$. The latter exhibits five phases: two low-temperature phases and a tetragonal room-temperature phase that is irreversibly transformed at 140 °C to a room-temperature stable, rhombohedral phase, which in turn reversibly changes at 263 °C to a face-centered cubic high-temperature phase.[27] The tetragonal room-temperature phase is a hydrated phase that exists only in the presence of a small amount of water.[28]

The main difference between the rhombohedral $N(CH_3)_4Cl$ and the hexagonal $N(CH_3)_4F$ phases consists of the stacking arrangements of the hexagonal anion and cation layers. In $N(CH_3)_4F$, the cations are arranged in a hexagonal closest packing with $Z = 2$ and alternating AB layers, while in rhombohedral $N(CH_3)_4Cl$ they are stacked in a cubic closest packing with $Z = 3$ and alternating ABC layers[31] (see Figure 3). In $N(CH_3)_4F$, the two fluoride anions are located above each other within the unit cell, while in $N(CH_3)_4Cl$ the three chloride anions occupy all three possible positions. This difference can be explained by the larger radius and space requirement of Cl^- versus F^-.

No evidence was found by DSC measurements between 30 and 330 °C for a phase transition from the hexagonal to a higher temperature phase. The only observed effect was the onset of endothermic decomposition at about 210 °C.

Vibrational Spectra of $N(CH_3)_4F$. The infrared and Raman spectra of solid $N(CH_3)_4F$ are shown in Figure 4. The observed frequencies and their assignments[17,32-35] are summarized in Tables VI and G (supplementary material).

The previous literature data on the vibrational spectra of $N(CH_3)_4F$ had been limited to incomplete infrared spectra of Nujol and Fluorolube mulls in the NaCl region.[10,16] Whereas the antisymmetric NC_4 stretching and the CH_3 deformation modes had been properly assigned,[10] the CH_3 rocking mode, $\nu_{17}(F_2)$, had been incorrectly attributed to an HF_2^- impurity band at 1263 cm⁻¹. As shown by our study, this mode occurs at 1312 cm⁻¹, in excellent agreement with the values of 1293, 1297, and 1299 cm⁻¹ observed for the corresponding iodide, bromide, and chloride salts.[33]

Furthermore, the previous predictions made from these partial IR data, that $N(CH_3)_4F$ should be tetragonal,[10] were ill founded,

Table VI. Vibrational Spectra of Solid $N(CH_3)_4F$ and Their Assignment

obsd freq, cm⁻¹ (rel intens)		
IR	Raman	assgnt in pt gp T_d
3473 w, br		$\nu_{CH_3} + \nu_{19}$
3376 w, br		$\nu_{CH_3} + \nu_8$
3030 sh	3029 sh	
3008	3007 (2)	
2980	2978 (1.3)	
2928 s, br		ν_{CH_3} and binary bands
	2889 (1.9)	
2822	2822 (1.4)	
2785		
2625 w		$\nu_7 + \nu_{16}$, $2\nu_{17}$
2568 w		$\nu_3 + \nu_8 + \nu_{16}$
2522 w		$\nu_7 + \nu_{17}$
2392 w		$\nu_{16} + \nu_{18}$
1880 w, vbr		$\nu_8 + \nu_{15}$
1770 w, br		$\nu_{17} + \nu_{19}$
1512 s	1512 (0.4)	ν_{15}
1490 sh	1490 sh	
	1479 (2.9)	ν_6
	1467 sh	ν_2
1423 m	1424 (0.7)	ν_{16}
1415 sh	1415 sh	
1312 vvw	1314 (0.4)	ν_{17}
1209 w	1209 (1.3)	ν_7
1094 vw		3 × 367 or ν_{11}
970 vs	969 (5.8)	ν_{18}
955 sh		
934 sh	930 (0.2)	$2\nu_{19}$
767 vw	767 (10)	ν_3
466 ms	467 (2.4)	ν_{19}
	387 (0.4)	ν_8
367 w	368 (0.3)	ν_8 or ν_{12}

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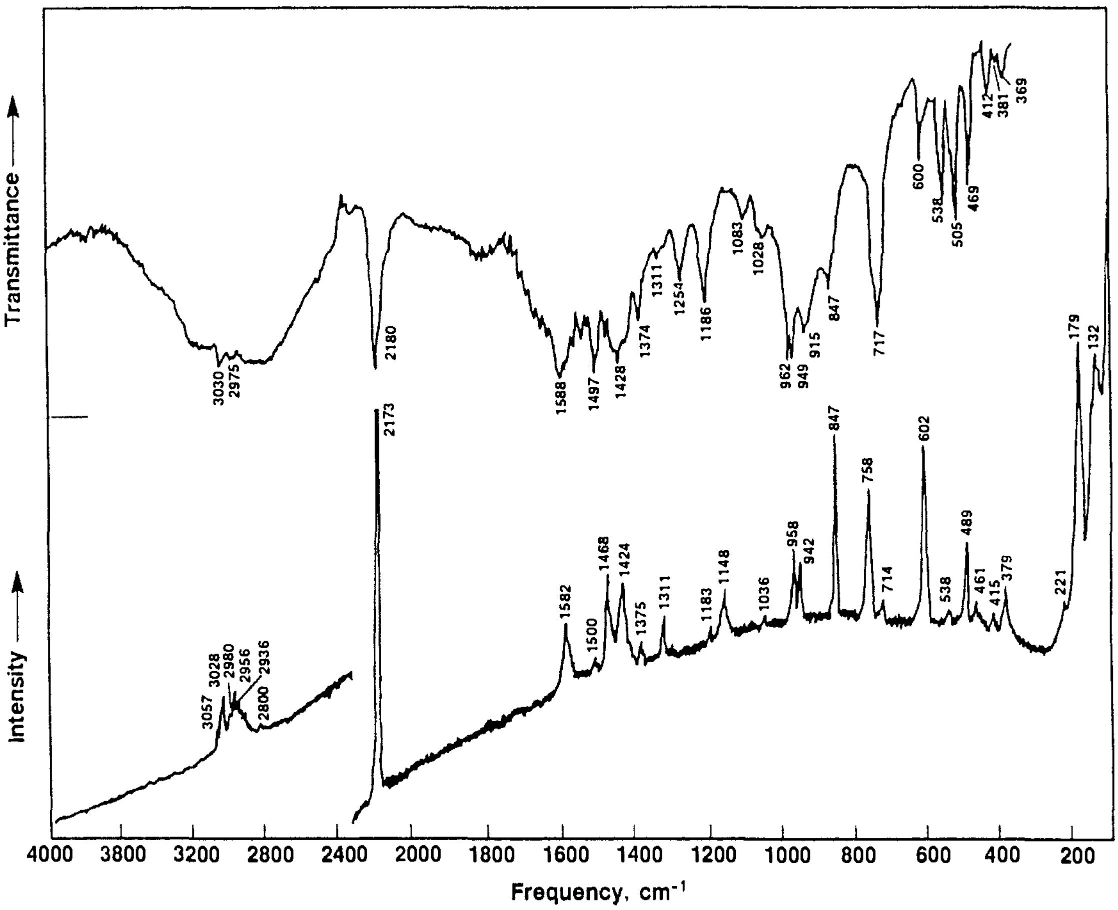


Figure 5. Infrared and Raman spectra of solid $N(CH_3)_4F-H_2NC(CH_3)CHCN$.

as demonstrated by the above X-ray diffraction data showing the compound to be hexagonal.

The assignments for $N(CH_3)_4F$ can be derived from those of the free $N(CH_3)_4^+$ cation. As a free ion, $N(CH_3)_4^+$ belongs to the point group T_d and has 19 fundamental vibrations that are classified as $3A_1 + A_2 + 4E + 4F_1 + 7F_2$. Of these, only the F_2 modes are infrared and the A_1, E, and F_2 modes Raman active.[32] In the solid state, the number of fundamentals can increase and the selection rules be violated due to effects, such as distortion of the $N(CH_3)_4^+$ tetrahedron, site symmetries lower than T_d, and factor group splittings. Thus, the deviations of the observed spectra from the T_d selection rules, coupled with crystallographic information, can be used to judge the degree of deformation of the $N(CH_3)_4^+$ from tetrahedral symmetry.[35] On the basis of a comparison of the Raman spectrum of the free $N(CH_3)_4^+$ ion with those of cubic $[N(CH_3)_4]_2SnCl_6$, hexagonal $N(CH_3)_4CdCl_3$, monoclinic $N(CH_3)_4HgCl_3$, and tetragonal $N(CH_3)_4ClO_4$, $N(CH_3)_4NO_3$, $N(CH_3)_4Cl$, $N(CH_3)_4Br$, and $N(CH_3)_4I$, Kabisch has derived empirical rules for estimating, from the vibrational spectra, the degree of distortion of the $N(CH_3)_4^+$ cation.[35]

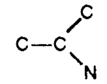
A comparison of our $N(CH_3)_4F$ spectra (see Figure 4 and Table VI) with the data[35] of Kabisch shows that the spectrum of the $N(CH_3)_4^+$ cation in solid $N(CH_3)_4F$ is very similar to those of the free $N(CH_3)_4^+$ cation and of the very weakly distorted $N(CH_3)_4^+$ cation in $[N(CH_3)_4]_2SnCl_6$. Therefore, it can be concluded that in $N(CH_3)_4F$ the distortion of the $N(CH_3)_4^+$ cation from tetrahedral symmetry must also be minimal. This finding is not unexpected since Kabisch had also shown that within the $N(CH_3)_4I$, $N(CH_3)_4Br$, and $N(CH_3)_4Cl$ series the cation distortion decreases with decreasing anion size.[35] Therefore, repulsion effects are more important than electrostatic effects, and fluoride should be the least distorting.

On the basis of the broadness of the CH_3 stretching bands in its infrared spectrum, CH···F hydrogen bonding has previously been postulated for $N(CH_3)_4F$.[10] This postulate requires further substantiation since the CH_3 deformation modes show no evidence for similar broadenings and the widths of the CH_3 stretching infrared bands can be readily explained by the Fermi resonance bands also observed in the Raman spectra of the free $N(CH_3)_4^+$ ion.[32,34,35]

Since infrared spectroscopy is a very useful technique to analyze $N(CH_3)_4F$ for impurities, we have scrutinized all the weak infrared features. In our opinion, essentially all of the weak bands shown in Figure 4 belong to $N(CH_3)_4F$. The most common impurities in $N(CH_3)_4F$ are HF_2^-, SiF_6^{2-}, $F^-\cdot nH_2O$, and different solvates. All of these are readily detected by their characteristic absorptions, most of which are given in the Experimental Section.

$N(CH_3)_4F$-*trans*-$H_2NC(CH_3){=}CHCN$ Adduct. As already mentioned, the fluoride anion can abstract a proton from CH_3CN, and the resulting CH_2CN^- anion can react with a second CH_3CN molecule and a proton to give the rearranged acetonitrile dimer, 3-amino-2-butenenitrile. During attempts to grow single crystals of $N(CH_3)_4F$ by allowing *n*-hexane to slowly diffuse into a saturated CH_3CN solution, large single crystals were obtained that were characterized by X-ray diffraction and vibrational spectroscopy as a 1:1 adduct between $N(CH_3)_4F$ and *trans*-3-amino-2-butenenitrile (I).

The crystal structure of I is shown in Figures 1 and 2, and the pertinent crystallographic data are summarized in Tables I–III and A–F. The monoclinic unit cell of I consists of layers of $N(CH_3)_4F$ that are separated by four molecules of the aminobutenenitrile. To maximize the packing density, the four aminobutenenitrile molecules are arranged in four different orientations, with the linear C—C≡N groups pointing alternatingly to the left and to the right and the



groups forward and backward (see Figure 1). The F^- anion forms two weak bridges to two hydrogen atoms from two different $-NH_2$ groups at 1.808 and 1.856 Å, respectively, with the remaining distances to other hydrogens being considerably longer than the sum of the van der Waals radii. As a result, the tetramethylammonium cation shows little distortion and is essentially tetrahedral.

The bond distances and angles found for the $H_2N{-}C(CH_3){=}CH{-}CN$ part of the adduct agree well with those predicted from the known structures of the similar molecules, CH_3CN, $NC{-}CN$, $CH_2{=}CH_2$, CH_3CHO, H_2NCHO, and CH_3COCN.[36]

The infrared and Raman spectra of the $N(CH_3)_4F{-}H_2NC(CH_3)CHCN$ adduct are given in Figure 5. The sizes of the molecules involved, the low crystal symmetry, and the large unit cell make detailed assignments difficult. However, the following vibrations can be readily assigned: $\nu(C{\equiv}N)$, 2173; $\nu(C{=}C)$, 1582; $\nu_{as}(NC_4)$, 958, 942; $\nu_s(NC_4)$, 758; $\delta_{as}(NC_4)$, 469 cm^{-1}. The intense and narrow $C{\equiv}N$ stretching vibration at 2173–2180 cm^{-1} is very useful for checking for the presence of the nitrile adduct in $N(CH_3)_4F$ that has been handled in CH_3CN.

Conclusion

Contrary to the general belief that $N(CH_3)_4F$ cannot be obtained anhydrous and that removal of water results in decomposition,[3] it was shown in this study that $N(CH_3)_4F$ with a water content of ≤ 0.06 wt % can be prepared with relative ease. This synthesis of anhydrous $N(CH_3)_4F$ provides a relatively cheap source of highly soluble fluoride containing a chemically very inert countercation. Thus, anhydrous $N(CH_3)_4F$ might become an attractive substitute for the more expensive and less inert fluoride ion source, (TAS)F, $[(CH_3)_2N]_3S^+F_2Si(CH_3)_3^-$. A characterization of anhydrous $N(CH_3)_4F$ also revealed that the properties of the "naked" fluoride ion in solution are poorly understood and that some of the properties previously attributed to the fluoride ion are due to other anions, such as HF_2^-. Furthermore, it was shown that certain solvents, such as CH_3CN or partially chlorinated hydrocarbons, which in the past have been preferred for fluoride ion reactions,[37,38] undergo chemical reactions with F^-. Finally, a novel 1:1 adduct of $N(CH_3)_4F$ with a dimer of CH_3CN was isolated from CH_3CN solution, and its crystal structure was determined.

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Supplementary Material Available: Tables A–G listing final atomic coordinates, hydrogen atom positions, N–H and C–H bond distances, hydrogen bond distances, final temperature factors, and mode descriptions for the $N(CH_3)_4^+$ cation, respectively (6 pages); observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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[3 + 3]-Carbocyclizations of Nitroallylic Esters and Enamines with Stereoselective Formation of up to Six New Stereogenic Centers

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Abstract: Enamines (**1**) from open-chain and cyclic ketones react with 2-nitro-2-propen-1-yl acetates and pivalates (nitroallylic esters **2**) to give, after aqueous workup, 4-nitrocyclohexanones (Schemes I–IV; products **3–18**). Monocyclic as well as bicyclic [4.3.1], [3.3.1], and [3.2.1] systems may be prepared. With appropriate substitution of the educt structures, up to five stereogenic centers are formed in this [3 + 3]-carbocyclization. One diastereoisomer usually prevails (60% to >95% selectivity). With enamines from (*S*)-2-(methoxymethyl)pyrrolidine (prolinol methyl ether) and cyclic ketones, enantiomerically pure compounds are obtained (see **8** and **15–18** in Scheme VI). The configuration and conformation of the products are assigned by extensive use of NMR spectroscopy. An additional stereogenic center may be formed by stereoselective borohydride reduction of the keto group in the nitrocyclohexanones, and Baeyer–Villiger oxidation introduces another functional group (see the hydroxydimethylnitrocyclooctanecarboxylic acid derivatives **23** in Scheme VII). The mechanism of the complex sequence of reactions, leading to the observed products, is discussed (Schemes VIII, X, XI). The structures of the products and intermediates, which can be trapped under certain conditions (Scheme IX), as well as previous investigations of single steps of the in situ reaction sequence involved in the carbocyclization are used to arrive at a tentative proposal for the steric course of these steps: (i) intermolecular coupling of the trigonal centers of enamine and nitroolefin with preferred relative topicity *like*, (ii) intramolecular coupling of the trigonal centers in an intermediate olefinic enamine, (iii) protonation of a nitronate anion moiety, and (iv) protonation of an enamine (in the case of the monocyclic products).

(A) Introduction

Due to their special reactivity[3] and ease of functional-group interchange,[4] aliphatic nitrocompounds have acquired an important position as intermediates in organic synthesis. Among the most commonly encountered reactions are the nitroaldol addition and condensation[5] and the Michael addition of either nitroalkanes to enones or of nucleophiles to nitroolefins.[6] Also Diels–Alder

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[1] Most of the results described here are taken from the dissertation of M. Missbach, ETH-Nr. 9152, Eidgenössische Technische Hochschule, 1990.

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