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# Observation of Perfluoromethylnitrene in Cryogenic Matrixes

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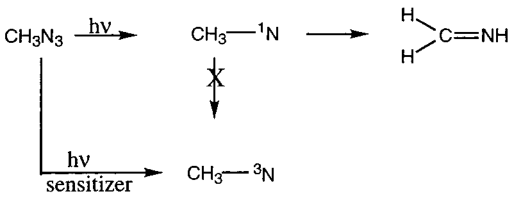
Photolysis (254 nm) of $CF_3N_3$ in pentane at 6−10 K produced a persistent electron paramagnetic resonance spectrum typical of a triplet nitrene centered at 8620 G. The spectrum ($|D/hc| = 1.736\ cm^{-1}$) is attributed to triplet $CF_3$−N, and is very similar to that of triplet NH ($|D/hc| = 1.863\ cm^{-1}$) and $CH_{3-}$N ($|D/hc| = 1.720\ cm^{-1}$) which were reported previously. $CF_3N_3$ was also deposited in an argon matrix at 14 K. The azide ($\lambda_{max} = 257$ nm) was decomposed by exposure to 254 nm light with the concurrent formation of sharp, structured absorption bands at 342, 347.5, and 354 nm. The UV bands are assigned to the triplet nitrene $CF_3N$ on the basis of its similarity to the spectrum of $CH_3N$ and time-dependent density functional theory (B3LYP) calculations.

## I. Introduction

Singlet methylnitrene has been predicted recently[1] to rearrange over a very small barrier (2.5 ± 1.0 kcal/mol) to form methyleneimine and has never been detected by spectroscopic methods. The theoretical predictions[1] are in excellent agreement with the photoelectron spectrum of the $CH_3N$ anion, which indicates that the barrier to isomerization of singlet $CH_3N$ is less than 2.6 kcal/mol.[2] Photolysis of methyl azide does not produce $^1NCH_3$ as a trappable species, nor does the singlet nitrene live long enough, even at cryogenic temperatures, to relax to the lower energy triplet state.[3] Only methyleneimine, the product of singlet $CH_3N$ isomerization, was detected in the cryogenic matrix.[4]



Triplet methylnitrene can be produced directly by sensitized photolysis[3] in the condensed phase or in a gas-phase corona discharge.[5] Larger alkylnitrenes have been formed by intramolecular sensitization.[6]

The same issues exist in the study of simple alkylcarbenes. Although methyl carbene is predicted to have a triplet ground state,[7] it is not observed on photolysis of precursors in inert cryogenic matrixes, although it can be trapped with carbon monoxide.[8] Singlet methylcarbene-$d_4$ has been trapped in solution with pyridine, and its lifetime was estimated to be 100−500 ps.[9] Triplet trifluoromethylcarbene can be formed in matrixes upon direct photolysis of diazirine precursors[10] because the strong C−F bond resists rearrangement in the nascent singlet carbene.

This led us to synthesize perfluoromethyl azide and to study its photochemistry in cryogenic matrixes. Herein we are pleased to report the results of this study.

## II. Experimental Section

**Synthesis.** Perfluoromethyl azide was prepared as described previously.[11]

**EPR Spectroscopy.** A solution of $CF_3N_3$ in pentane was transferred into a 3-mm quartz tube and degassed by three freeze−pump−thaw cycles. The sample was cooled to 6−10 K in a flow of cold helium in a Helitran model LTR-3 liquid transfer refrigerator (APD Cryogenics) in the cavity of Bruker ESP 300 spectrometer. The sample was irradiated (254 nm) with a "pen lamp" to produce the triplet nitrene.

**Spectroscopy in Argon Matrix.** A gaseous mixture of $CF_3N_3$ and argon (1:100) was deposited directly on the surface of a CsI window of a closed-cycle cryogenic system cooled by helium (Air Products). The argon matrix formed was maintained at 14 K during the entire experiment. The UV−vis spectra were measured with a Lambda 6 UV−vis spectrophotometer. Ray-O-Net 254-nm lamps were used to photolyze the samples.

**Computational Chemistry.** The geometry optimizations for triplet $CF_3N$ and $CF_2NF$ were implemented at the B3LYP[12] and CASSCF[13] levels. The geometry optimizations for singlet $CF_3N$ were performed at the CASSCF level. The local minima were confirmed by a Hessian calculation. Electronic absorption spectra were calculated using time-dependent density functional theory[14] at the B3LYP level. All the calculations were performed with the Gaussian 98 software package.[15]

## III. Results and Discussion

**III.1. EPR Spectroscopy.** A solution of $CF_3N_3$ ($\lambda_{max} = 257$ nm) in pentane was cooled to 6−10 K and exposed to 254-nm light for 10 min. This produced an electron paramagnetic resonance (EPR) spectrum typical of a triplet nitrene centered at 8620 G (available in the Supporting Information). The zero-field splitting parameter $|D/hc|$ was calculated to be 1.736 $cm^{-1}$. This value is close to that of the parent triplet NH ($|D/hc| = 1.863\ cm^{-1}$).[16] Wasserman reported a smaller value ($|D/hc| = 1.595\ cm^{-1}$)[3] for matrix isolated triplet $CH_3N$. This earlier experiment can be questioned,[5b] and a revised *D* constant of 1.720 $cm^{-1}$ was obtained[5c] for $CH_3N$ using gas-phase spectroscopy. Therefore the value of the zero-field splitting parameter of $CF_3N$ is typical of simple nitrenes, and the EPR spectrum is attributed to $CF_3N$ in its triplet ground state.

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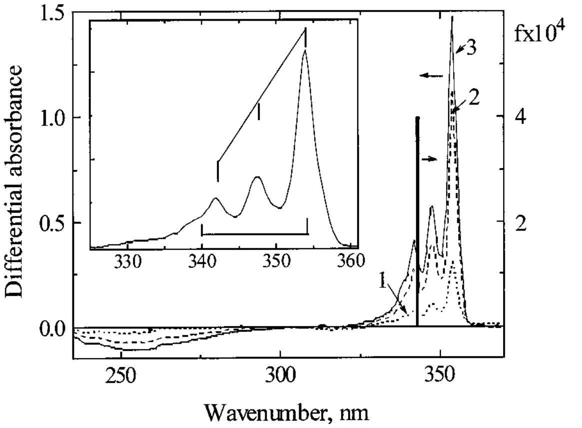


**Figure 1.** Differential electronic absorption spectra detected after irradiation of $CF_3N_3$ in an Ar matrix at 14 K with 254-nm light of 5-min (1), 25-min (2), and 45-min (3) duration. The calculated absorption bands (TD-B3LYP/6-31*) of triplet $CF_3N$ (positive) and $CF_3N_3$ (negative) are depicted as solid vertical lines. Insert: differential electronic absorption spectrum detected after 25 min of irradiation.

**TABLE 1: Electronic Absorption Spectra of Triplet $CF_3N$ ($\lambda > 170$ nm Only) and Related Species Calculated Using Time Dependent DFT Theory[14] with the Gaussian98[15] Suite of Electronic Structure Programs**

| species | $\lambda$ (nm) | $f$ ($\times 10^4$)[a] | transition | method[b] |
|---|---|---|---|---|
| $^3NCF_3$ | 343 | 4 | $^3A_2 \rightarrow {}^3E$ | A |
| $^3NCF_3$ | 339 | 6 | $^3A_2 \rightarrow {}^3E$ | B |
| $CF_2NF$ | 182 | 0 | $^1A' \rightarrow {}^1A''$ | A |
| | 171 | 25 | $^1A' \rightarrow {}^1A''$ | |
| *cis*-$CF_3N{=}NCF_3$ | 471 | 1 | $^1A_1 \rightarrow {}^1B_1$ | A |
| | 202 | 0 | $^1A_1 \rightarrow {}^1A_2$ | |
| | 175 | 1 | $^1A_1 \rightarrow {}^1A_1$ | |
| *trans*-$CF_3N{=}NCF_3$ | 421 | 0 | $^1A_g \rightarrow {}^1B_g$ | A |
| | 173 | 0 | $^1A_g \rightarrow {}^1B_g$ | |
| | 173 | 23 | $^1A_g \rightarrow {}^1B_u$ | |

[a] Oscillator strength. [b] Method A, TD-B3LYP/6-31G*//B3LYP/6-31G*; method B, TD-B3LYP/6-311+G*//B3LYP/6-31G*.

**III.2. UV Spectroscopy in Argon Matrix.** $CF_3N_3$ was condensed in an argon matrix at 14 K. Upon brief photolysis (254 nm), the azide is slightly decomposed concomitant with the appearance of absorption bands at 342, 347.5, and 354 nm (Figure 1).

The electronic absorption spectrum of Figure 1 is similar to the spectrum of triplet $CH_3N$ ($A^3E \rightarrow X^3A_2$ transition)[17] but shifted slightly (by about 37 nm) to the red. Figure 1 shows also that the experimental spectrum is in fairly good agreement with the calculated spectrum of triplet $CF_3N$ (Table 1). Note that according to our calculations the spectrum of triplet $CH_3N$ is indeed shifted to the blue (by about 47 nm at TD-B3LYP/6-311+G** level) relative to the spectrum of triplet $CF_3N$. Therefore we can unambiguously assign the experimental UV spectrum of Figure 1 to triplet $CF_3N$.

Two progressions with an average vibrational interval of 710 $cm^{-1}$ were discerned in the spectrum of triplet $CH_3N$.[5b] These progressions were offset by 1166 $cm^{-1}$. In the spectrum of triplet $CF_3N$ only one progression with an average interval of about 500 $cm^{-1}$ can be resolved (Figure 1, insert). The shoulder at about 340 nm can be tentatively assigned to the origin of the second progression (shifted by about 1160 $cm^{-1}$).

Perfluromethyl azide[11] has an absorption maximum at 258 nm with a molar absorptivity ($\epsilon$) of 17 $M^{-1}cm^{-1}$. To obtain sufficient absorption at 254 nm we had to prepare a matrix with a rather large concentration of azide ($Ar/CF_3N_3 = 100/1$). Therefore azo-compounds (*cis*- and *trans*-$CF_3N{=}NCF_3$) can be produced by a triplet nitrene dimerization reaction or by reaction of nitrene with starting azide. The products of nitrene rearrangement ($F_2C{=}NF$) and dimerization (*cis*- and *trans*-$CF_3N{=}NCF_3$) are not predicted to absorb between 300 and 400 nm (Table 1) and are not responsible for the spectrum of Figure 1.

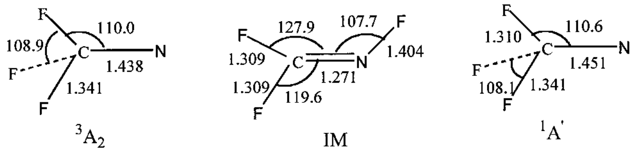


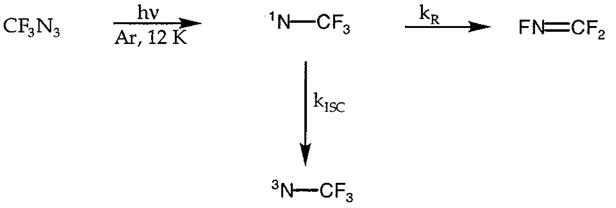
**Figure 2.** Geometries (bond lengths in Å, bond angles in degrees) of $^3CF_3N$ ($^3A_2$) and perfluoromethyleneimine (**IM**) calculated at B3LYP/6-31G* level and of $^1CF_3N$ ($^1A'$) calculated at CASSCF(8,8)/6-31G* level.

Therefore, the EPR and UV data indicate formation of triplet $CF_3N$ under direct irradiation of $CF_3N_3$. This finding confirms that singlet $CF_3N$ is indeed an energy minimum on the singlet potential energy surface.

**III.3. Calculations.** In $C_{3V}$ symmetry the lowest-energy singlet state of nitrene is a degenerate $^1E$ state. According to the Jahn–Teller theorem it should undergo Jahn–Teller distortions, giving rise to $^1A'$ and $^1A''$ states in $C_S$ symmetry. Figure 2 displays the CASSCF(8,8)/6-31G* optimized geometry for the lowest singlet ($^1A'$) of $CF_3N$. As shown in Figure 2, the $^1A'$ state has one short and two long C–F bonds similar to $CH_3N$.[1]

The singlet–triplet splitting of $N{-}CF_3$ calculated at the CASSCF (8,8)/6-31G* level of theory[13] is 43.7 kcal/mol. This value is larger than the experimentally determined singlet–triplet splitting of $N{-}CH_3$ (31.2 kcal/mol).[1,2] However, a CASSCF level of theory (CASSCF (12,11)/cc-pVDZ) predicts[1] that the ST splitting of $N{-}CH_3$ is 41.1 kcal/mol, a value that is too high by 10 kcal/mol.[1,2] Thus, our calculated ST gap of $N{-}CF_3$ is also likely to be too large by this amount.

Singlet $CF_3N$ should undergo rearrangements typical of alkylnitrenes.[18] The rearrangement of $^1N{-}CF_3$ to imine $F_2C{=}NF$ is predicted by CASSCF (8,8)/6-31G* to be exothermic by 46 kcal/mol, a value which is too high by ≈10 kcal/mol because of the error in calculating the energy of $^1N{-}CF_3$. This is much less exothermic than the rearrangement of $^1N{-}CH_3$ to $HN{=}CH_2$ (82.9 kcal/mol).[1] Unlike $^1N{-}CH_3$, however, ISC of the perfluoromethyl singlet nitrene to $^3N{-}CF_3$ ($k_{ISC}$) can compete with rearrangement ($k_R$) at cryogenic temperatures because of the greater strength of the C–F relative to the C–H bond, and the consequently greater barrier to isomerization.



Flash photolysis studies of $CF_3N_3$, matrix IR spectroscopy, and quantum chemical calculations of the potential energy surface of $^1N{-}CF_3$ are in progress and will be reported in due course.

## IV. Conclusions

EPR and UV spectroscopy unambiguously demonstrate formation of triplet $CF_3N$ upon direct irradiation of $CF_3N_3$. This confirms that singlet $CF_3N$ is indeed an energy minimum on the singlet potential energy surface.

Rearrangement of $^1N-CF_3$ to imine $F_2C=NF$ is predicted by CASSCF (8,8)/6-31G* to be exothermic by about 46 kcal/mol. This is much less exothermic than the rearrangement of $^1N-CH_3$ to $HN=CH_2$ (82.9 kcal/mol).[1] Unlike $^1N-CH_3$, ISC of the perfluoromethyl singlet nitrene to $^3N-CF_3$ can compete with rearrangement at cryogenic temperatures because of the greater strength of the C−F bond relative to the C−H bond. This is responsible for the smaller exothermicity of rearrangement of $^1N-CF_3$ relative to $^1N-CH_3$ and consequently a greater barrier to isomerization of the fluorinated nitrene.

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**Supporting Information Available:** The EPR spectrum of triplet $CF_3N$ in pentane (6−10 K) produced by 254 nm photolysis of $CF_3N_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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