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Photochemistry of Fluorinated Phenyl Nitrenes: Matrix Isolation of Fluorinated Azirines

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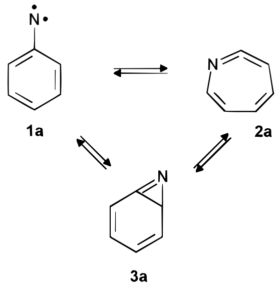
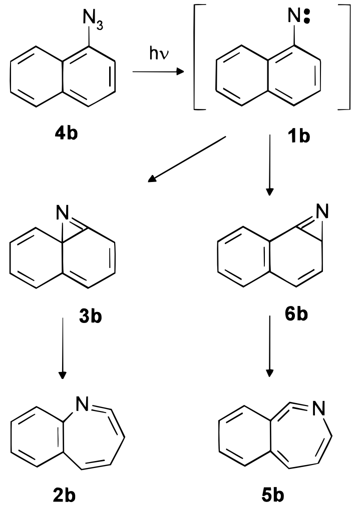
2,6-Difluorophenylnitrene and pentafluorophenylnitrene were generated in solid argon at 10 K by irradiation of the corresponding phenyl azides and characterized by IR and UV spectroscopy. Selective irradiation with $\lambda = 444$ nm results in the formation of the corresponding azirines, while ketene imines are not produced. On $\lambda = 366$ nm irradiation the azirines rearrange back to the nitrenes. The assignment of the azirines is confirmed by *ab-initio* calculations.

Phenylnitrene (**1a**) is the prototype of the arylnitrenes and has been the topic of many mechanistic studies.[1] Several reactive intermediates have to be considered to understand the thermo- and photochemistry of **1a**. Generally, the nitrene is produced from a precursor molecule—most frequently phenyl azide—in its singlet ground state S-**1a**. Platz et al. demonstrated that S-**1a** is a true intermediate in the photochemistry of the azide[2] and that the fate of the nitrene depends very much on the environment.[3] At cryogenic temperatures S-**1a** preferentially relaxes to the triplet ground state T-**1a**, which was characterized spectroscopically by IR,[4] UV,[10] and ESR[6,7] spectroscopy. The singlet−triplet splitting was determined to 18 kcal/mol.[8,9] At higher temperatures in solution rearrangement to ketene imine **2a** becomes the major path; the activation barrier (E_a) for this rearrangement is 3 kcal/mol.[10] In the gas phase the relaxation of thermally excited nitrene is slow and the rearrangement to cyanocyclopentadiene—the global energy minimum of the C_6H_5N hypersurface—becomes feasible ($E_a = 30{-}51$ kcal/mol).[11] The IR spectrum of matrix isolated ketene imine **2a** was published first by Chapman et al.[5] Later Sheridan et al. were able to demonstrate that T-**1a** and **2a** are formed in a photostationary equilibrium under the conditions of matrix isolation.[4]



A third C_6H_5N isomer, azirine **3a**, has been claimed as an intermediate in early trapping experiments;[12−14] however, it has never been observed by direct spectroscopic methods. The azirines **3b** and **6b**—but not the nitrene **1b**—were observed by IR spectroscopy during the photolysis of 1-naphthyl azide (**4b**), matrix isolated in argon at 10 K.[15] Subsequent photolysis at shorter wavelength resulted in the irreversible rearrangement of the azirines to ketene imines **2b** and **5b**. This finding clearly demonstrates the importance of substituents in the nitrene photochemistry.



Ortho-disubstituted phenylnitrenes, such as 2,6-dimethylphenylnitrene (**1c**[16]) and pentafluorophenylnitrene (**1d**),[17] were reported by Dunkin et al. to rearrange only very inefficiently, if at all, during matrix photolysis. This lack

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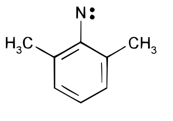
Table 1. Infrared Data of 2,6-Difluorophenylnitrene (1e), Matrix Isolated in Ar at 10 K

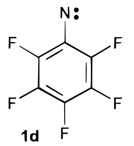
ν (cm^{-1})	I^a	ν (cm^{-1})	I^a	ν (cm^{-1})	I^a
1585.1	0.34	1242.0	0.44	767.7	0.33
1577.7	0.59	1229.3	0.36	708.3	0.13
1459.4	0.28	1002.8	0.09	699.6	0.09
1452.2	1	991.6	0.63	553.2	0.08
1411.2	0.14	850.4	0.11	501.2	0.05
1312.4	0.27	836.6	0.08		
1281.1	0.13	772.4	0.13		

[a] Relative intensities.

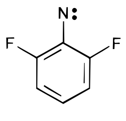
of intramolecular reactivity was attributed to the steric hindrance of the ortho positions in **1c** and **1d**. This is in line with the conclusion of Young and Platz from product studies that for S-**1d** at −78 °C ISC to T-**1d** is the primary process, while at room temperature ring expansion to the ketene imine **2d** is predominant.[18]



1c



1d



1e

Here we report on the matrix photochemistry of the fluorinated phenylnitrenes **1d** and **1e**, which on irradiation reversibly rearrange to the corresponding azirines **3d** and **3c** in high yields.

Results and Discussion

2,6-Difluorophenylnitrene (1e). Irradiation of matrix-isolated 2,6-difluorophenyl azide (**4e**)[19] in Ar at 10 K at λ > 280 nm results in the rapid decomposition of the azide. In the IR spectrum a new set of bands appears with intense absorptions at 1578, 1452, 1242, and 768 cm^{-1}, which we assign to 2,6-difluorophenylnitrene (**1e**) (Table 1, Figure 1). The UV spectrum of nitrene **1e** in argon at 10 K exhibits maxima at 312, 284, and 236 nm (Figure 2) and is in accordance with literature data (EPA glass, 77 K).[10] Prolonged irradiation at $\lambda = 444$ nm (irradiation into the long-wavelength tail of the 312 nm absorption or weak absorption which is not detected in the vis spectra) slowly leads to the appearance of new medium to strong IR absorptions at 1679, 1610, 1259, and 1180 cm^{-1} (Table 2, Figure 1). On the basis of comparison with IR spectra of other azirines[15,20,21] and on an *ab-initio* calculations, the newly formed compound is assigned the structure of 7-aza-1,5-difluoro-2,4,6-bicyclo[4.1.0]heptatriene (**3e**) and the IR absorption at 1679 cm^{-1} to the C=N stretching vibration $\nu_{C=N}$ (vide infra). There were no strong absorptions in the 1890 cm^{-1} or 2200 cm^{-1} region, indicative for cyclic ketene imines **2** or cyanocyclopentadienes, respectively. In the UV region azirine **3e** absorbs at 252 nm, but not around 350 nm (broad maximum), as frequently observed in ketene imines **2**.[22] On 366 nm irradiation the **1e** → **3e** rearrangement is reversible and the nitrene partially recovered.

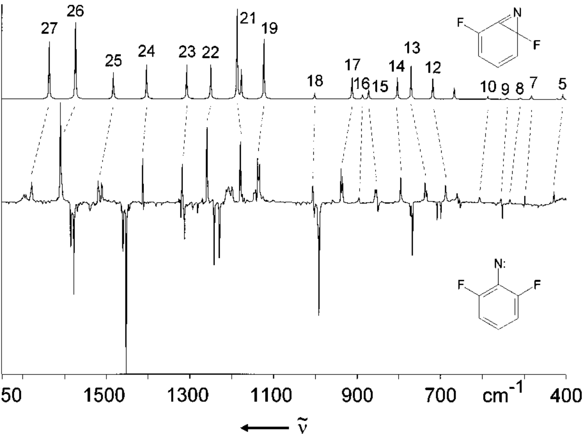


Figure 1. 1. Infrared spectrum of 7-aza-1,5-difluoro-2,4,6-bicyclo[4.1.0]heptatriene (**3e**), matrix isolated in Ar at 10 K. Bottom: difference spectrum showing the photochemical conversion of **1e** to **3e**. Irradiation ($\lambda = 444$ nm) of **1e**, matrix isolated in Ar at 10 K. Absorptions assigned to **1e** decrease and absorptions assigned to **3e** appear. Top: vibrational spectrum of **3e** calculated at the RMP2/6-31G(d) level of theory. The band positions are scaled with 0.95, and a Lorentz line shape with 2 cm^{-1} at half height is assumed.

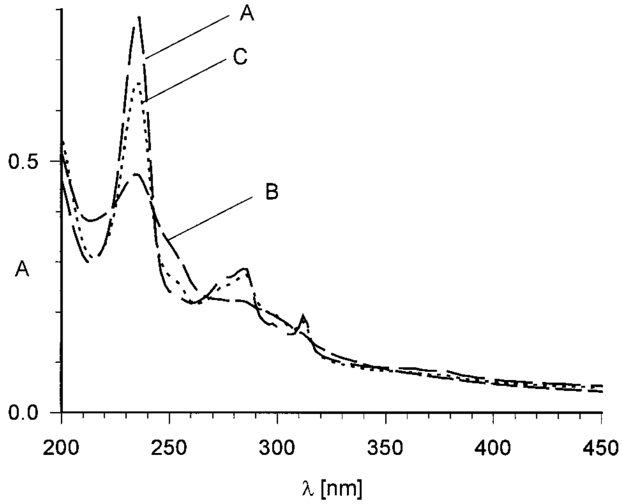
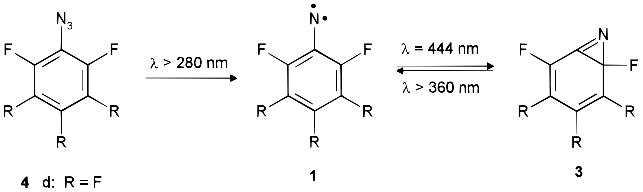


Figure 2. 2. UV–vis spectra showing the reversible conversion of **1e** to **3e**. A: 2,6-Difluorophenylnitrene (**1e**), matrix isolated in Ar at 10 K. B: Spectrum after irradiation with λ = 444 nm. C: Spectrum after prolonged irradiation with $\lambda = 366$ nm.



4 d: R = F
e: R = H

1

3

In matrix-isolated 2*H*-azirine $\nu_{C=N}$ is observed at 1669 cm^{-1},[20] in 2-phenylazirine at 1755 cm^{-1},[21] in **3b** at 1708 cm^{-1}, and in **6b** at 1730 cm^{-1} (Scheme 1).[15] This reveals that substitution shifts $\nu_{C=N}$ to higher frequencies, while the increased strain in **3b** and **6b** results in a red-shift compared to the phenylazirine. In **3e** the C=N stretching frequency of 1679 cm^{-1} is close to that of the parent 2*H*-azirine.

The calculated (RMP2/6-31G(d) level of theory) IR spectrum is in qualitative agreement with the experi-

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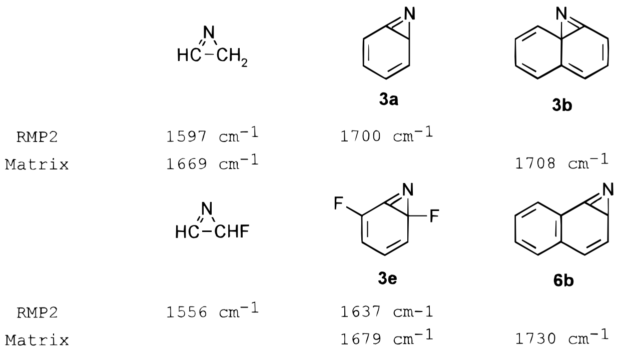
Table 2. Infrared Data of 7-Aza-1,5-difluoro-2,4,6-bicyclo[4.1.0]heptatriene (3e), Matrix Isolated in Ar at 10 K and Calculated at the RMP2/6-31G(d) Level

	matrix[a]		calcd[b]		
vib	ν (cm^{-1})	I^c	ν (cm^{-1})	I^c	assignment[d]
30			3095	0.02	CH str
29			3090	0.04	CH str
28			3076	0.03	CH str
27	1679.3	0.28	1637	0.64	C=C,C=N str
26	1609.8	1	1574	0.85	C=C str
25	1519.7	0.25	1483	0.29	C=C str
24	1412.2	0.5	1403	0.38	*c*
23	1318.0	0.45	1307	0.38	C−C str
22	1258.9	0.75	1250	0.38	C−F str
21	1179.7	0.65	1187	1	C−F str
20			1177	0.32	*c*
19	1138.3	0.45	1123	0.67	6-ring ip
18	1006.7	0.18	1002	0.06	6-ring ip
17	939.2	0.33	913	0.24	6-ring oop
16	896.1	0.1	888	0.05	CH oop
15	856.9	0.18	873	0.1	3-ring ip
14	796.0	0.28	804	0.24	*c*
13	737.4	0.23	771	0.36	*c*
12	688.2	0.15	719	0.23	*c*
11			668	0.13	3-ring ip
10	608.5	0.03	588	0.03	*c*
9	557.1	0.03	543	0.01	*c*
8	535.7	0.03	511	0.02	*c*
7	500.3	0.08	484	0.04	*c*
6			423	0.01	*c*
5	430.0	0.15	409	0.05	*c*

[a] **3e**, generated by irradiation (λ = 444 nm, argon, 10 K) of **4e**. [b] Calculated at the RMP2/6-31G(d) level, frequencies scaled by 0.95. [c] Relative intensities. [d] Approximate description. The assignment of experimental to calculated vibrations is tentative and based on band positions and relative intensities: ip, in plane deformation; oop, out of plane deformation; c, combination.

Scheme 1



mental spectrum (Figure 1, Table 2). If the usual scaling of the calculated frequencies with 0.95 is used, $\nu_{C=N}$ is found at 1637 cm^{-1}, at significantly lower frequency than the experimental value. Since the RMP2 frequency of the C=N stretching vibration of 2*H*-azirine is calculated at 1597 cm^{-1} (scaled by 0.95), it becomes clear that RMP2 theory is not adequate to correctly predict $\nu_{C=N}$.

Further *ab-initio* calculations on 3-fluoro-2*H*-azirine and azirine **3a** indicate that a fluoro substituent in the 3-position results in a red shift of the C=N-stretching mode of approximately 40−60 cm^{-1}. This nicely explains the red shift of 39 and 61 cm^{-1} in **3e** compared to **3b** and **6b**, respectively.

Pentafluorophenylnitrene (1d). The photochemistry of pentafluorophenyl azide (**4d**) is very similar to that of **4e**. Irradiation of **4d**,[22] matrix isolated in argon at 10 K, with λ > 311 nm results in the formation of pentafluorophenylnitrene **1d**, which was identified by comparison of the IR spectrum with the data published by Dunkin et al.[17] (Table 3). Photolysis with λ = 444 nm slowly leads to a decrease of the IR absorptions of the nitrene and to the appearance of new peaks of medium to strong intensity at 1664, 1395, and 1008 cm^{-1} (Table 4). This photoreaction is reversible on λ = 366 nm irradiation. We conclude from the similarities in the photochemistry of 2,6-difluoro- (**1e**) and pentafluorophenylnitrene (**1d**) that perfluoro-7-aza-2,4,6-bicyclo[4.1.0]heptatriene (**3d**) is formed. The absence of **3d** in the earlier experiments is easily explained by the long-wavelength irradiation required for the formation of **3d**. Under the conditions necessary to cleave the azide **4d** the photostationary equilibrium of **1d** and **3d** is far on the side of the nitrene.

Table 3. Infrared Data of Pentafluorophenylnitrene (1d), Matrix Isolated in Ar at 10 K

ν (cm^{-1})	I[a]	ν (cm^{-1})	I[a]	ν (cm^{-1})	I[a]
1572.4	0.12	1334.6	0.08	1000.6	0.15
1564.4	0.14	1281.4	0.15	982.3	0.84
1502.7	1	1205.5	0.08	916.1	0.05
1464.0	0.42	1151.7	0.05	610.7	0.03
1455.6	0.58	1025.5	0.59		
1359.4	0.33	1008.5	0.23		

[a] Relative intensities.

Table 4. Infrared Data of Perfluoro-7-aza-2,4,6-bicyclo[4.1.0]heptatriene (3d), Matrix Isolated in Ar at 10 K

ν (cm^{-1})	*I*[a]	ν (cm^{-1})	*I*[a]	ν (cm^{-1})	*I*[a]
1664.2	0.18	1222.6	0.12	937.3	0.14
1589.3	0.22	1187.8	0.18	816.0	0.08
1395.3	0.45	1095.3	0.2	660.6	0.03
1374.5	0.32	1007.6	1	524.8	0.01
1308.7	0.17	947.5	0.18		

[a] Relative intensities.

Conclusion

Fluorinated phenylnitrenes **1d** and **1e** are not as photochemically inert as previously anticipated. The main difference to the photochemistry of other phenylnitrenes is that the cyclic ketene imines **2** are not formed in the low-temperature photolysis. This does not rule out that **2** might be thermally formed at higher temperatures, as was observed by Platz et al.[18,22] in trapping experiments and by time-resolved spectroscopy. These authors argue that ring expansion proceeds through the π^2 configuration of the nitrene.[1b] Since this configuration is destabilized by the fluorination, ring expansion becomes less favorable compared to other reactions of the nitrene. The formation of the azirine can be looked upon as an electrophilic attack of the nitrene center at a formal double bond of the phenyl ring. Thus, a similar reasoning would explain why fluorinated nitrenes are thermally stable toward formation of azirines **3**. In our experiment the formation of **3** is a photochemical process, and the energy of a 444 nm photon (64.4 kcal/mol) should be enough to generate the π^2 nitrene.

The question remains why azirines **3d** and **3e** do not rearrange to the corresponding ketene imines **2**. The yield of intermediates obtained during matrix photolysis depends very much on the irradiation conditions (wavelength and bandwidth of the light source), since in many cases photostationary equilibria of the intermediates are formed. If the photochemistry is reversible, it is difficult to determine the primary photo product in a sequence of photochemical steps. Thus, broad band UV photolysis—as it was used in the original experiments—of **4a** leads to ketene imine **2a**[21] and of **4d** to nitrene **1d**,[17] respectively, and selective narrow band irradiation is required to obtain **1a**[4] or **3d**.

The *ab-initio* calculated relative energies at the RMP2/6-31G(d) + ZPE level of theory favor the azirine **3e** with 1.2 kcal/mol relative to the cyclic ketene imine **2e**. This is the reverse ordering compared to the unsubstituted system. Here, azirine **3a** is 0.2 kcal/mol higher in energy than **2a**. However, these differences in the relative stabilities are in the order of the error of the *ab-initio* calculations and should not be overinterpreted. More experimental and theoretical work has to be done to explain the effect of fluorine substitution on the thermo- and photochemistry of phenylnitrenes.

Experimental Section

Calculations. The geometries of **2a**, **2e**, **3a**, **3e**, 2*H*-azirine, and 3-fluoro-2*H*-azirine have been optimized at the RMP2/6-31G(d) level of theory. The vibrational frequencies and intensities of **2e**, **3a**, **3e**, 2*H*-azirine, and 3-fluoro-2*H*-azirine have been calculated at the RMP2/6-31G(d) level. The *ab-initio* calculations were carried out using standard basis sets and the program package Gaussian 92[23] on SGI and IBM workstation computers.

Matrix Spectroscopy. Matrix isolation experiments were performed by standard techniques with an APD DE-204SL and an APD DE-202 Displex closed cycle helium cryostat. Matrices were produced by deposition of argon (Linde, 99.9999%) on top of a CsI (IR) or sapphire (UV/vis) window with a rate of approximately 0.15 mmol/min. Infrared spectra were recorded by using a Bruker IFS66 FTIR spectrometer with a standard resolution of 1 cm^{-1} in the range 400−4000 cm^{-1}. UV/vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer with a resolution of 2 nm. Irradiations were carried out with use of Osram HBO 500 W/2 or Ushio USH-508SA mercury high-pressure arc lamps in Oriel housings equipped with quartz optics. IR irradiation from the lamps was absorbed by a 10-cm path of water. For broadband irradiation Schott cutoff filters were used (50% transmission at the wavelength specified). For narrow-band irradiation interference filters in combination with dichroic mirrors ("cold mirrors") were used.

^{1}H-NMR spectra were taken on a Bruker AM 400. Mass spectra (EI 70eV) were taken on a Finnigan MAT 8430.

2,6-Difluorophenyl azide (4e) was prepared from 2,6-difluoroaniline according to a literature procedure:[19] ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.88−6.95 (m, 2H), 7.00−7.08 (m, 1H); IR (Ar, 10 K) 2160.4 (0.07), 2144.5 (0.07), 2123.3 (1), 1594.0 (0.03), 1502.1 (0.14), 1487.7 (0.04), 1482.7 (0.08), 1474.5 (0.03), 1337.9 (0.05), 1330.4 (0.11), 1297.9 (0.04), 1279.6 (0.04), 1246.9 (0.05), 1154.4 (0.02), 1128.8 (0.02), 1064.1 (0.01), 1050.7 (0.01), 1030.1 (0.01), 1023.0 (0.19), 774.6 (0.06), 723.2 (0.01), 705.4 (0.02), 614.3 (0.02), 520.4 (0.01), 504.8 (0.01) cm^{-1} (rel intensity); UV/vis (Ar, 10 K) λ_{max} 278 (0.19), 248 (0.92) nm (A); MS *m*/*z* 155 (M^+), 127.

Pentafluorophenyl azide (4d) was prepared from pentafluorophenyl hydrazine according to a literature procedure:[22] IR (Ar, 10 K) 2214.0 (0.05), 2197.9 (0.09), 2148.4(0.12), 2124.4 (0.97), 1529.5 (0.42), 1521.5 (1), 1516.8 (0.87), 1474.7 (0.08), 1354.8 (0.05), 1332.3 (0.08), 1251.8 (0.12), 1107.7 (0.31), 1086.6 (0.03), 1027.8 (0.16), 1014.4 (0.19), 1002.3 (0.23), 944.0 (0.32), 925.5 (0.03), 804.8 (0.05), 672.9 (0.02) cm^{-1} (rel intensity); UV/vis (Ar, 10 K) λ_{max} 246 (0.82) nm (A); MS *m*/*z* 209 (M^+), 181.

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