Contribution No. 263
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Difluorodiazirine. I. Physical and Spectral Properties

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Sir:

It is well known that the structure of diazomethane remained in question for some years. Only recently has cyclodiazomethane (1,2) (diazirine) been synthesized and its structure determined by microwave spectroscopy (3). Although fluorocarbon derivatives of diazomethane of the following types, R_fCHN_2 and R_fCOCHN_2, are known (4,5) no perfluorinated diazoalkanes or diazirines have been reported.

We wish to report the properties (6) of the first member of a new class of compounds, difluorodiazirine (I). The identity of difluorodiazirine (I) was established

I

on the basis of its elemental analyses [*Anal.* Calcd. for CF_2N_2: C, 15.4; F, 48.7; N, 35.9; mol. wt., 78. Found: C, 15.5; F, 48.5: N, 35.8; mol. wt. (gas density method), 77] and its spectral properties. It is colorless, boils at -91.3 ± 1°C., log P_{mm} = (7.7029) - (877.08/T), exhibits a single sharp peak at +122.5 ϕ* (7) in the fluorine n.m.r. spectrum and produces the mass-spectral cracking pattern in Table I.

Table I

Mass Spectral Cracking Pattern of CF_2N_2

m/e	Pattern %	Cationic Species
12	5.8	C
14	3.9	N
26	3.0	CN
31	63.6	CF
33	2.0	NF
40	1.0	CN_2
45	4.7	CFN
50	100.0	CF_2
59	46.8	CFN_2
64	6.9	CF_2N
69	0.6	CF_3
78	0.1	CF_2N_2

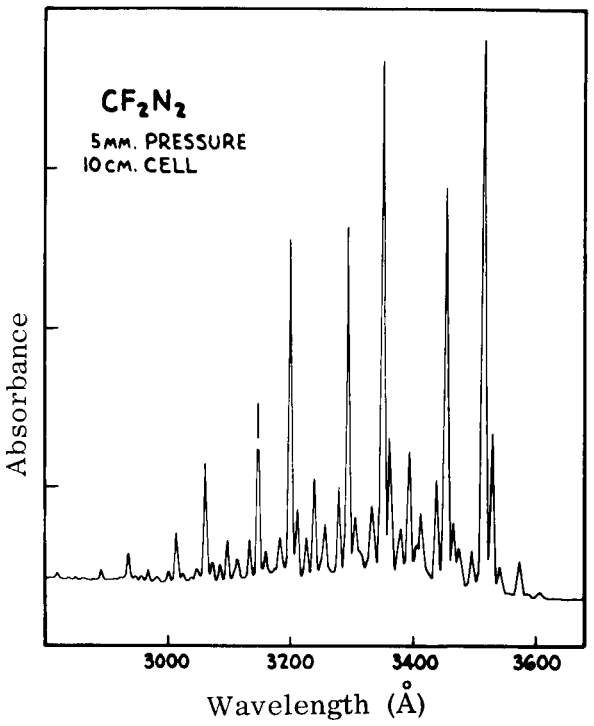

Fig. 1. Ultraviolet Spectrum of CF_2N_2

The ultraviolet spectrum (Fig. 1) is characterized by many sharp, regularly spaced peaks between 2820 and 3515 Å (ϵ = 646.9 l./mole - cm. at 3515 Å). This spectrum and that of the hydrocarbon analog, diazirine (2), are strikingly similar.

The gas phase infrared spectrum (8) of difluorodiazirine (Fig. 2) exhibits the expected carbon-fluorine absorptions as well as a strong absorption at 6.41 μ assigned to the nitrogen-nitrogen double bond stretching vibration. The corresponding absorption in the infrared spectrum of diazirine (2) is characterized by multiple peaks in the 6.03-6.22 μ region.

Chemically, difluorodiazirine (I) is much less reactive than either diazomethane or diazirine. It is stable in strong acids, storable without decomposition in glass and has been handled many times as a gas and neat liquid in the temperature range from -196° to 200°C. without incident. It is explosive, however, and therefore recommended that CF_2N_2 be handled with suitable protective equipment. Difluorodiazirine can be conveniently decomposed to difluorocarbene either thermally or by ultraviolet irradiation. In the photolysis reaction, which resulted in complete conversion of I to tetrafluoroethylene and nitrogen, a 125-watt ultraviolet lamp was used for 2.5 hours. The tetrafluoroethylene was identified by its characteristic infrared spectrum.

$$\underset{\text{I}}{CF_2N_2} \xrightarrow{h\nu} [:CF_2] + N_2 \longrightarrow \underset{\text{II}}{CF_2{=}CF_2} + N_2$$

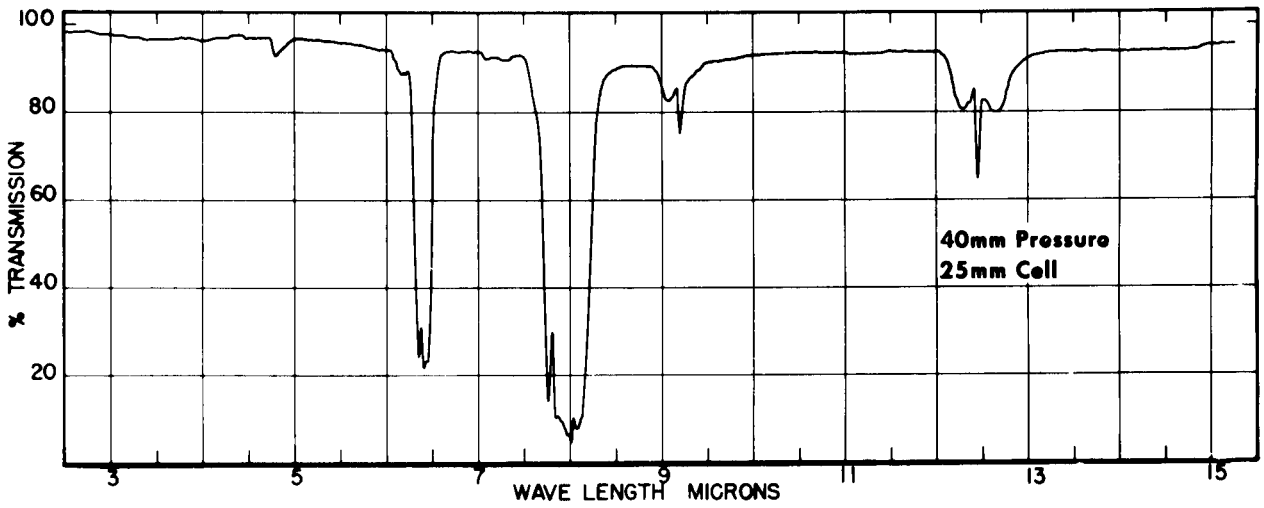

Fig. 2. Infrared Spectrum of CF_2N_2

A differential thermal analysis of I indicates a gradual exothermic decomposition beginning at about 164° C. Therefore, the pyrolysis of difluorodiazirine (0.225 g., 2.88 x 10^{-3} moles) was carried out by heating the sample at 165-180° C. in a heavy-wall glass ampoule. After three hours, preparative vapor phase chromatography was utilized to isolate tetrafluoroethylene (14%), hexafluorocyclopropane (62%) and perfluoro-2,3-diaza-1,3-butadiene (24%) from the reaction mixture (1.26 x 10^{-3} moles).

$$\underset{\text{I}}{CF_2N_2} \xrightarrow{165-180^\circ} \underset{\text{II}}{CF_2{=}CF_2} + \underset{\text{III}}{\begin{array}{c} CF_2 \\ \diagup\ \diagdown \\ CF_2 \text{---} CF_2 \end{array}} + \underset{\text{IV}}{CF_2{=}N{-}N{=}CF_2}$$

The tetrafluoroethylene and hexafluorocyclopropane were identified by infrared spectroscopy. The identity of perfluoro-2,3-diaza-1,3-butadiene (IV) was established on the basis of its elemental analyses (*Anal.* Calcd. for $C_2F_4N_2$: C, 18.7; F, 59.4; mol. wt., 128. Found: C, 18.1; F, 59.1; mol. wt., 128) as well as mass, infrared and fluorine n.m.r. spectra. The infrared absorption spectrum, exhibiting bands at 5.61 (m), 5.75 (s), 7.56 (s) and 10.50 (s) μ, bears a striking similarity to that of perfluoro-1,3-butadiene. The fluorine n.m.r. spectrum showed absorptions at 52.1 and 74.0 ϕ* (9). It is probable that the tentatively identified azine recently reported by Chambers, Tullock and Coffman (10) was not $CF_2{=}N{-}N{=}CF_2$ since the infrared spectrum and reported instability are not consistent with our observations.

The chemistry of difluorodiazirine is currently under investigation and will be the subject of future publications. Reactions of difluorocarbene, generated by photolysis and/or pyrolysis of CF_2N_2, will be described in future papers.

This research was supported by the Advanced Research Projects Agency under Contract NOrd 18688, and was monitored by the Bureau of Naval Weapons.

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(5) (a) F. Brown and W. K. R. Musgrove, *J. Chem. Soc.*, 2087, (1953). (b) J. D. Park and E. R. Larsen, 130th Meeting, American Chemical Society, Atlantic City, N. J., September, 1956.
(6) The synthesis techniques involved in the preparation of difluorodiazirine are still classified as CONFIDENTIAL by the Bureau of Naval Weapons.
(7) G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, 63, 761 (1959).
(8) Complete infrared and Raman spectroscopic studies on CF_2N_2 are currently being carried out at the University of Minnesota by Dr. John Overend. Dr. Louis Pierce (University of Notre Dame) has attempted a microwave spectroscopic structural study of CF_2N_2; however, he did not observe rotational absorption lines due to the small dipole moment of the molecule.
(9) AB type pattern analysis, J (AB) = 65 cps.
(10) W. J. Chambers, C. W. Tullock and D. D. Coffman, *J. Am. Chem. Soc.*, 84, (1962).

Received January 23, 1964

St. Paul, Minnesota