

butyllithium at  $486 \text{ m}\mu$  is  $3.0 \times 10^4$ , calculated using the extrapolated absorbance maxima. This is in good agreement with that obtained for triphenylmethylithium<sup>2</sup> ( $3.3 \times 10^4$ ) in which decomposition is not a problem.

Any inaccuracy in the extinction coefficient will appear in the values for  $k'$  listed in Table I, but the extinction coefficient has no effect on the slope of Figure 2 and, thus, cannot alter the conclusion that vinylithium is associated in THF solutions.

### Discussion

The fractional kinetic order of vinylithium for addition to DPE is evidence that vinylithium is associated in THF solution. The kinetics require that the associated vinylithium is in equilibrium with a more reactive, less associated form.<sup>4</sup> The one-third order does not require the higher aggregates to be trimers but shows that the less associated, more reactive form is one-third the size of the larger aggregates. By analogy with the findings for *n*-butyllithium, it is likely that the reactive vinylithium species is monomer, and the aggregates are trimers; *i.e.*,  $(\text{ViLi})_3 \rightleftharpoons 3\text{ViLi}$ .

*n*-Butyllithium is apparently hexameric in benzene solution over a wide range of concentration, *i.e.*,  $10^{-4}$  to  $3 \text{ M}$ . There is no indication of the average aggregate size changing with concentration. In contrast, the reactivity behavior of lithium cyclohexylamide in cyclohexylamine indicates an effective aggregate size which depends on concentration over a much smaller range.<sup>15</sup> For example, kinetic orders vary from near first order at  $5 \times 10^{-3} \text{ M}$  to near zero order at  $5 \times 10^{-1} \text{ M}$ .<sup>15</sup> Vinylithium in THF shows no indication of a

(15) A. Streitwieser, Jr., D. E. Van Sickle, and W. C. Langworthy, *J. Am. Chem. Soc.*, **84**, 244 (1962).

change in effective aggregate size over this same concentration range.

The association of vinylithium in THF, contrasted with the monomeric nature of polystyryllithium<sup>8</sup> and polyisoprenyllithium<sup>9</sup> in THF, as well as the general indication of clustering in hydrocarbon solution, illustrates that the solution behavior of organolithium compounds is both structure- and solvent-dependent.

Presumably, the excess negative charge of the vinylithium ion pair is primarily localized in a carbon  $\sigma$ -orbital. The expected high local-charge density is possibly a factor favoring association. A spreading of the excess negative charge *via* delocalization, *e.g.*, in polystyryllithium and polyisoprenyllithium, might be expected to reduce the dipolar attractive forces and favor solvation of the incipient lithium cation.

Rate constants reported for the reaction of DPE with two other organolithium compounds can be compared with that for vinylithium. The second-order rate constant for the addition of DPE to polystyrylsodium in THF<sup>16</sup> is  $1.3 \times 10^6 \text{ moles l.}^{-1} \text{ hr.}^{-1}$ . In benzene solution  $k'$  for addition of *n*-butyllithium to DPE<sup>17</sup> is  $9 \times 10^{-2} \text{ mole}^{0.18} \text{ l.}^{-0.18} \text{ hr.}^{-1}$ .

Similar kinetic measurements show that methylithium is also associated in THF solution.<sup>18</sup> The association behavior of other organolithium reagents in both olefin addition and metalation reactions in THF solution is being investigated.

*Acknowledgment.* The authors are grateful to Dr. Peter West and Miss Mary A. Doran of this laboratory for helpful discussions.

(16) J. Smid and M. Szwarc, *J. Polymer Sci.*, **61**, 31 (1962).

(17) A. G. Evans and D. B. George, *J. Chem. Soc.*, 4653 (1961). These authors state  $k' = kK$ , which, following the kinetic scheme given in this paper, should be  $k' = kK(1/n)^{1/n}$ .

(18) P. West and R. Waack, to be published.

## Infrared and Raman Spectra of $\text{CF}_2\text{N}_2$ . Evidence for a Diazirine Structure

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*The infrared spectrum of  $\text{CF}_2\text{N}_2$  has been obtained from 4000 to 250  $\text{cm.}^{-1}$ , and the Raman spectrum from 2700 to 100  $\text{cm.}^{-1}$ . Eight prominent bands in the infrared, 1563, 1282, 805, 502, 1248, 481, 1091, and 544  $\text{cm.}^{-1}$ , along with a prominent band in the Raman at 451  $\text{cm.}^{-1}$ , have been assigned as fundamentals. The spectra are interpreted as evidence for the cyclic diazirine structure rather than the linear diazomethane structure.*

### Introduction

This study of the vibrational spectrum of  $\text{CF}_2\text{N}_2$  was initiated shortly after the compound was first

synthesized; our objective was to establish the structure and to make a vibrational assignment. The hydrocarbon analog,  $\text{CH}_2\text{N}_2$ , exists in two isomeric forms. Diazomethane which has long been known has a linear structure.<sup>2</sup> The other isomer, diazirine, has only recently been prepared<sup>3,4</sup> and shown spectroscopically to have a cyclic structure.<sup>5,6</sup>

Chemistry, Oberlin College, Oberlin, Ohio 44074; (c) Minnesota Mining and Manufacturing Co.

(2) H. Zollinger, "Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds," translated by H. E. Nursten, Interscience Publishers, Inc., New York, N. Y., 1961.

(3) E. Schmitz and R. Ohme, *Tetrahedron Letters*, 612 (1961).

(4) W. H. Graham, *J. Am. Chem. Soc.*, **84**, 1063 (1962).

(5) L. Pierce and V. Dobyns, *ibid.*, **84**, 2651 (1962).

(6) R. Ettinger, *J. Chem. Phys.*, **40**, 1693 (1964).

(1) (a) University of Minnesota; (b) on leave from the Department of

In the fluorocarbon series, however, only one form of  $\text{CF}_2\text{N}_2$  is known at present,<sup>7</sup> and its structure has not been firmly established. There is some qualitative evidence for a diazirine structure: the electronic spectrum of  $\text{CF}_2\text{N}_2$ <sup>7</sup> is confined to the ultraviolet region and is rich in vibrational structure, resembling that of diazirine<sup>4</sup>; that of diazomethane is broad and diffuse and includes a weak maximum in the blue.<sup>8</sup> In addition, the chemistry of  $\text{CF}_2\text{N}_2$  resembles the more limited reactivity of diazirine rather than the great reactivity of diazomethane.<sup>9</sup>  $\text{CF}_2\text{N}_2$  is stable in strong base and in strong acid; it is also stable in the presence of boron trifluoride, a well-known catalyst for the polymerization of diazoalkanes.

**Difluorodiazirine Structure.** Before examining the observed vibrational spectra of  $\text{CF}_2\text{N}_2$ , it is useful to have on hand a summary of the expected appearance of the infrared and Raman bands for the fundamental modes of the diazirine and diazomethane structures. In Table I the predictions for difluorodiazirine are as-

**Table I.** Difluorodiazirine Structure. Predicted Infrared and Raman Spectra

Symmetry species (IR, band shape; R, p) <sup>a</sup>	—Calcd.— freq., $\text{cm}^{-1}$	Approx. description <sup>b</sup>
$A_1$ (IR, A; R, p)	$\nu_1$ 1650	$\nu_{\text{NN}}^c$
	$\nu_2$ 1247	$s\nu_{\text{CN}} + \nu_{\text{NN}} + s\nu_{\text{CF}}$
	$\nu_3$ 915	$s\nu_{\text{CF}} + \nu_{\text{CN}}$
	$\nu_4$ 591	$s\delta_{\text{CF}}$
$A_2$ (...; R, dp)	$\nu_5$ 411	Torsion
$B_1$ (IR, B; R, dp)	$\nu_6$ 1282	$a\nu_{\text{CF}}$
	$\nu_7$ 665	$a\delta_{\text{CF}}$
$B_2$ (IR, C; R, dp)	$\nu_8$ 953	$a\nu_{\text{CN}}$
	$\nu_9$ 421	$\omega_{\text{CF}_2}$

<sup>a</sup>IR = infrared; R = Raman; p = polarized; dp = depolarized. <sup>b</sup>Obtained from potential energy distribution; given in order of decreasing contribution. <sup>c</sup> $\nu$  = stretch;  $\delta$  = deformation;  $\omega$  = out-of-plane wag; s = symmetric; a = antisymmetric.

sembled, based on the molecular geometry shown in Figure 1. The principal moments of inertia in a.m.u.  $\text{\AA}^2$  are  $I_a = 57.26$ ,  $I_b = 77.23$ , and  $I_c = 113.37$ , taking  $r_{\text{CF}} = 1.30$ ,  $r_{\text{CN}} = 1.482$ ,<sup>5</sup>  $r_{\text{NN}} = 1.228 \text{\AA}$ ,<sup>5</sup> and  $\alpha_{\text{FCF}} = 117^\circ$ . It is particularly useful to recognize that, for this structure of  $C_{2v}$  symmetry, the  $A_2$  torsional mode is Raman active only.<sup>10</sup> Also, as a consequence of  $C_{2v}$  symmetry, the change in dipole moment produced by each of the normal modes takes place along one of the principal axes. This consideration leads to the expectation of type A, B, and C bands in the gas-phase infrared spectrum.<sup>11</sup> Type A bands arising from dipole moment changes parallel to the axis of least moment of inertia should have a central Q branch of intensity comparable to that of the P and R branches, whereas type C bands arising from dipole moment changes parallel to the axis of greatest moment of inertia should

(7) R. A. Mitsch, *J. Heterocyclic Chem.*, 1, 59 (1964).

(8) F. W. Kirkbride and K. G. W. Norrish, *J. Chem. Soc.*, 119 (1933).

(9) E. Schmitz, *Angew. Chem. Intern. Ed. Engl.*, 3, 333 (1964).

(10) To facilitate comparison with the diazomethane structure, the plane defined by the carbon and fluorine atoms has been chosen as the one in which vibrations of  $B_1$  symmetry occur.

(11) R. M. Badger and L. R. Zumwalt, *J. Chem. Phys.*, 6, 711 (1938); H. Allen and P. C. Cross, "Molecular Vib-rotors," John Wiley and Sons, Inc., New York, N. Y., 1963.

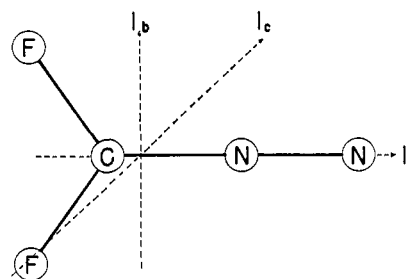


Figure 1. Assumed geometry and principal axes of difluorodiazirine structure.

have a dominant Q branch. Type B bands are expected to have only prominent P and R components.

Table I also includes calculated fundamental vibration frequencies along with approximate normal coordinates expressed in terms of valence bond stretching and bending coordinates. Of particular note is the NN stretching frequency at about  $1650 \text{ cm}^{-1}$  which appears to be characteristic of the  $\text{N}=\text{N}$  double bond.<sup>6,12</sup> This zero-order calculation of vibration frequencies followed the Wilson GF method<sup>13</sup> and was carried out with a computer program.<sup>14</sup> Symmetry coordinates were constructed in the customary way from the internal valence coordinates describing the changes in each bond length and each bond angle, except that for the NCN bond angle. The intramolecular tension<sup>15</sup> introduced by the redundancy around the carbon atom was taken to be equal to zero. Force constants, Table II, were transferred from the Urey-Bradley

**Table II.** Difluorodiazirine Structure. Transferred Force Constants<sup>a</sup>

	From diazirine <sup>b</sup>	From tetrafluoromethane <sup>c</sup>	
$K_{\text{NN}}$	11.18	$K_{\text{CF}}$	4.18
$K_{\text{CN}}$	4.14	$H_{\text{FCF}} = H_{\text{NCF}}$	0.527
$K_{\text{CN,NN}}$	-2.327	$F_{\text{FF}} = F_{\text{NF}}$	1.24

<sup>a</sup>  $H$  in  $\text{mdynes } \text{\AA}^2/\text{rad}^2$ ; others in  $\text{mdynes}/\text{\AA}^2$ . <sup>b</sup> See ref. 6. <sup>c</sup> See ref. 16.

force-field treatment of tetrafluoromethane by Shimanouchi<sup>16</sup> and from the central force-field treatment of the ring in diazirine by Ettinger.<sup>6,17</sup>

**Difluorodiazomethane Structure.** Table III summarizes the predictions for the vibrational spectra of difluorodiazomethane. Figure 2 gives the assumed geometry and the location of the principal axes.  $I_a = 43.77$ ,  $I_b = 121.25$ , and  $I_c = 165.02 \text{ a.m.u. } \text{\AA}^2$  when  $r_{\text{CF}} = 1.31$ ,  $r_{\text{CN}} = 1.30$ ,<sup>18</sup> and  $r_{\text{NN}} = 1.14 \text{\AA}$ ,<sup>18</sup> and

(12) R. J. W. LeFevre, M. F. O'Dwyer, and R. L. Werner, *Australian J. Chem.*, 6, 341 (1953); R. J. W. LeFevre, J. B. Sousa, and R. L. Werner, *ibid.*, 9, 151 (1956).

(13) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, Chapter 4.

(14) J. R. Scherer and J. Overend, *J. Chem. Phys.*, 32, 1289, 1720 (1960).

(15) B. Crawford and J. Overend, *J. Mol. Spectry.*, 12, 307 (1964).

(16) T. Shimanouchi, *J. Chem. Phys.*, 17, 848 (1949); *Nippon Kagaku Zasshi*, 74, 266 (1953).

(17) We also carried through a calculation using force constants for the  $\text{CF}_2$  group transferred from  $\text{COF}_2$  (cf. Table IV). The calculated frequencies were slightly different, in several cases by as much as  $50 \text{ cm}^{-1}$ , from those in Table I.

(18) A. P. Cox, L. F. Thomas, and J. Sheridan, *Nature*, 181, 1000

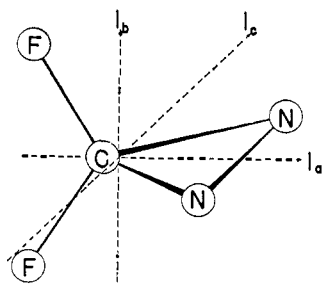


Figure 2. Assumed geometry and principal axes of difluorodiazomethane structure.

$\alpha_{\text{FCF}} = 110^\circ$ . Although the diazomethane structure has the same symmetry as that of the diazirine, it is important to note that diazomethane has no funda-

Table III. Difluorodiazomethane Structure. Predicted Infrared and Raman Spectra

Symmetry species (IR, band shape; R, p) <sup>a</sup>	Calcd. freq., cm. <sup>-1</sup>	Approx. description <sup>a</sup>
A <sub>1</sub> (IR, A; R, p)	$\nu_1$ 2161	$\nu_{\text{NN}} + \nu_{\text{CN}}$
	$\nu_2$ 1468	$\nu_{\text{CN}} + \nu_{\text{FCF}} + \nu_{\text{NN}}$
	$\nu_3$ 854	$\nu_{\text{FCF}} + \nu_{\text{CN}}$
	$\nu_4$ 561	$\delta_{\text{CF}}$
B <sub>2</sub> (IR, B; R, dp)	$\nu_5$ 1254	$\nu_{\text{FCF}}$
	$\nu_6$ 708	$\delta_{\text{CF}} + \delta_{\text{NN}}$
	$\nu_7$ 277	$\delta_{\text{NN}} + \delta_{\text{CF}}$
B <sub>2</sub> (IR, C; R, dp)	$\nu_8$ 532	$\delta_{\text{NN}}$
	$\nu_9$ 144	$\omega_{\text{CF}_2}$

<sup>a</sup> See Table I for definition of symbols.

mental of A<sub>2</sub> symmetry. In its place is a third fundamental of B<sub>1</sub> symmetry. Otherwise, the expected infrared and Raman activity and band shapes are the same for the two possible structures. The zero-order frequencies and approximate normal-coordinate descriptions were obtained in the same manner as described above for the diazirine structure. In addition to internal coordinates defined in terms of changes in bond lengths and bond angles within the plane of the molecule, out-of-plane bending coordinates were defined as the change in the angle ( $\gamma$ ) between the FCF plane and the CN bond and the change in the angle ( $\phi$ ) between the CN bond and the NN bond.<sup>19</sup> Force constants, Table IV, were transferred from the Urey-Bradley force-field treatment of carbonyl fluoride<sup>20</sup>

Table IV. Difluorodiazomethane Structure. Transferred Force Constants<sup>a</sup>

From diazomethane <sup>b</sup>		From carbonyl fluoride <sup>c</sup>	
$K_{\text{NN}}$	16.89	$K_{\text{CF}}$	4.53
$K_{\text{CN}}$	8.34	$H_{\text{FCF}}$	0.784
$H_{\text{NNC}}$	0.477	$H_{\text{NCF}}$	0.455
$H_{\phi\phi}$	0.530	$H_{\phi,\gamma}$	0.0006
$H_{\gamma\gamma}$	0.0448		
$K_{\text{NN,CN}}$	1.23		

<sup>a</sup> See Table II for units. <sup>b</sup> See ref. 19. <sup>c</sup> See ref. 20.

(1958); J. Sheridan "Molecular Spectroscopy, Report of Bologna Meeting," Pergamon Press, Inc., New York, N. Y., 1959, pp. 139-147.

(19) C. B. Moore and G. Pimentel, *J. Chem. Phys.*, **40**, 342 (1964).

(20) J. Overend and J. R. Scherer, *ibid.*, **32**, 1296 (1960).

and from the valence force-field treatment of diazomethane by Moore and Pimentel.<sup>19</sup> The characteristic NN stretching frequency of the diazomethane structure is predicted at about 2150 cm.<sup>-1</sup>.

## Experimental

**Purification of CF<sub>2</sub>N<sub>2</sub>.** CF<sub>2</sub>N<sub>2</sub> was prepared and characterized at the Minnesota Mining and Manufacturing Co. It was purified by gas chromatographic fractionation on a Beckman Megachrom. The 5/8 in. × 48 ft. column was packed with 30% Kel-F 8126 oil<sup>21</sup> on acid-washed Celite and thermostated at -30°. Carbon dioxide was removed by distillation through Ascarite, and water vapor was removed by distillation through phosphorus pentoxide. In handling CF<sub>2</sub>N<sub>2</sub> in a conventional vacuum system, the material was repeatedly exposed to Apiezon stopcock grease and to mercury. CF<sub>3</sub>NF<sub>2</sub> (0.3%; b.p. 78°<sup>22</sup>) was present in the purified sample. The infrared absorption spectrum of CF<sub>3</sub>NF<sub>2</sub> was measured, and the principal absorption bands were found to be, in cm.<sup>-1</sup> with the apparent band shapes in parentheses, 1287 vs, 1239 s (A), 1218 s (B), 1017 s (A), 951 s, 849 m, 721 s (C), 604 m, 577 m (C), 525 m (distorted A), 375 w (A), 274 m (C), and 246 m. No other impurities were known to be present.

**Infrared Spectrum.** The gas-phase infrared spectrum is shown in Figure 3 and is given in detail in Table V along with the argon-matrix spectrum obtained by Milligan, *et al.*<sup>23</sup> It was recorded on a Perkin-Elmer 521 filter-grating spectrometer over the region 4000-250 cm.<sup>-1</sup>. Samples were run in a 10-cm. cell fitted with cesium iodide windows. Pressures were measured at room temperature with a steel-scale, mercury-filled manometer and were not corrected for temperature or local gravity. Frequency accuracy was ±1 cm.<sup>-1</sup> throughout the range.<sup>24</sup>

The infrared spectrum of solid CF<sub>2</sub>N<sub>2</sub> was also recorded at liquid nitrogen temperature and was found to be fully consistent with that observed in the gas-phase and in the argon matrix.

**Raman Spectrum.** The Raman spectrum of liquid CF<sub>2</sub>N<sub>2</sub> is shown in Figure 4 and is listed in Table VI. This was recorded over the range 2700 to 100 cm.<sup>-1</sup> on a Cary 81 Raman spectrometer with excitation by the 4358-A. line of mercury, which was isolated by a filter solution containing 40 g. of Cyasorb 24 ultraviolet absorber (American Cyanamid Co.) and 2 g. of ethyl violet per gallon of isopropyl alcohol. Qualitative depolarization measurements were made by the Edsall-Wilson method.<sup>25</sup> Unfortunately, what appears to be a band, due to glass fluorescence, interfered in the crowded 500-cm.<sup>-1</sup> region of the spectrum, making depolarization measurements in this region quite uncertain. The shape of this glass band, as de-

(21) Tetramer of chlorotrifluoroethylene; source, Minnesota Mining and Manufacturing Co.

(22) J. A. Attaway, R. H. Groth, and L. A. Bigelow, *J. Am. Chem. Soc.*, **81**, 3599 (1959).

(23) D. E. Milligan, D. E. Mann, M. E. Jacox, and R. A. Mitsch, *J. Chem. Phys.*, **41**, 1199 (1964).

(24) IUPAC, "Tables of Wavenumbers for the Calibration of Infrared Spectrometers," Butterworth Inc., Washington, D. C., 1961; H. M. Randall, D. M. Dennison, N. Ginsburg, and L. R. Weber, *Phys. Rev.*, **51**, 160 (1937); P. E. Martin and E. F. Barker, *ibid.*, **41**, 291 (1932).

(25) J. T. Edsall and E. B. Wilson, *J. Chem. Phys.*, **6**, 124 (1938).

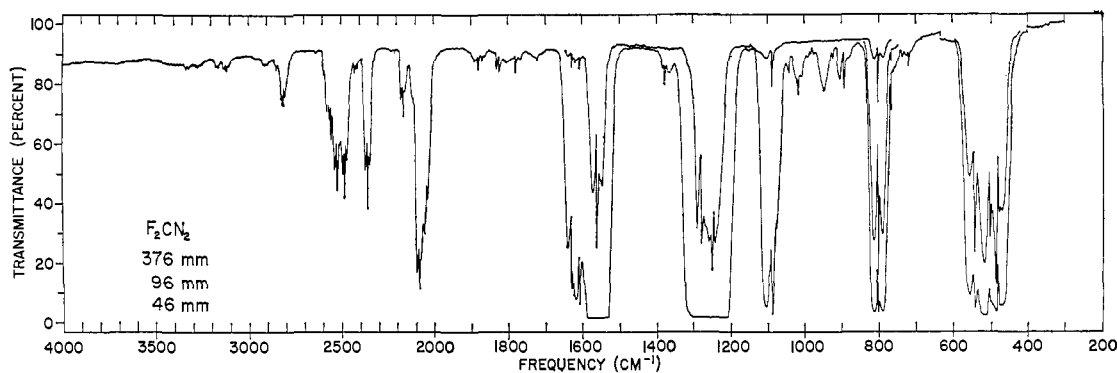


Figure 3. Gas-phase infrared spectrum of  $\text{CF}_2\text{N}_2$ .

terminated from the spectrum of the empty cell, is indicated with the dotted line in Figure 4. Careful

Table V. Infrared Spectra and Frequency Assignments for  $\text{CF}_2\text{N}_2$

Gas phase			Argon matrix <sup>a</sup>			Assignment	
Freq., cm. <sup>-1</sup>	Intens.	Band shape	Freq., cm. <sup>-1</sup>	Intens.	Freq., cm. <sup>-1</sup>	Class	
3318	vw						
3272	vw	A-C					
3158	vw						
3118	vw	A-C			3126	$2 \times \nu_1$	A <sub>1</sub>
2906	vw						
2847	vw	A-C			2845	$\nu_1 + \nu_2$	A <sub>1</sub>
2809	w	B			2811	$\nu_1 + \nu_8$	B <sub>1</sub>
2588	w	B					
2557	w	A			2564	$2 \times \nu_2$	A <sub>1</sub>
2528	m	B			2530	$\nu_2 + \nu_8$	B <sub>1</sub>
2486	m	A			2496	$2 \times \nu_6$	A <sub>1</sub>
2429	vw	A-C					
2412	vw	A-C					
2360	m	A			2368	$\nu_1 + \nu_8$	A <sub>1</sub>
2168	w	A			2182	$2 \times \nu_8$	A <sub>1</sub>
2109	w	A-C			2107	$\nu_1 + \nu_9$	B <sub>2</sub>
2084	m	A-C	2078	w	2087	$\nu_2 + \nu_8$	A <sub>1</sub>
2045	m	B	2034	w	2053	$\nu_3 + \nu_8$	B <sub>1</sub>
					2044	$\nu_1 + \nu_7$	B <sub>1</sub>
1882	vw	A-C			1896	$\nu_3 + \nu_8$	B <sub>2</sub>
1831	vw	A-C			1826	$\nu_2 + \nu_9$	B <sub>2</sub>
1780	vw	A-C			1784	$\nu_2 + \nu_4$	A <sub>1</sub>
1730	vw	Broad			1739	$\nu_6 + \nu_7$	A <sub>1</sub>
1631	m	A			1635	$\nu_8 + \nu_9$	A <sub>1</sub>
1609	m	A	1592	w	1610	$2 \times \nu_3$	A <sub>1</sub>
1563	vs	A	1560	s	$\nu_1$	Fund.	A <sub>1</sub>
1379	w	A-C					
1305	m	C	1288	m	1307	$\nu_8 + \nu_4$	A <sub>1</sub>
1282	vs	A	1277	s	$\nu_2$	Fund.	A <sub>1</sub>
			1250	w			
1248	vs	B	1240	vs	$\nu_6$	Fund.	B <sub>1</sub>
1091	m	C	1084	m	$\nu_8$	Fund.	B <sub>2</sub>
1040	vw				1046	$\nu_4 + \nu_9$	B <sub>2</sub>
1019	w	A-C			1017	$\text{CF}_3\text{NF}_2$	Im- purity
951	w	Broad			951	$\text{CF}_3\text{NF}_2$	Im- purity
927	vw				929	$\nu_5 + \nu_7$	B <sub>2</sub>
895	w	A-C			896	$2 \times \nu_5$	A <sub>1</sub>
805	m	A	804	m	$\nu_3$	Fund.	A <sub>1</sub>
770	m	A-C			779	$\nu_2 - \nu_4$	A <sub>1</sub>
736	vw				738	$\nu_2 - \nu_9$	B <sub>2</sub>
722	w	C			721	$\text{CF}_3\text{NF}_2$	Im- purity
591		A-C			589	$\nu_8 - \nu_4$	B <sub>2</sub>
544	m	A-C	541	m	$\nu_9$	Fund.	B <sub>2</sub>
502	m	A-C	501	m	$\nu_4$	Fund.	A <sub>1</sub>
481	m	B	480	m	$\nu_7$	Fund.	B <sub>1</sub>
448	w	A-C			$\nu_5$	Fund.	A <sub>2</sub>

<sup>a</sup> See ref. 23.

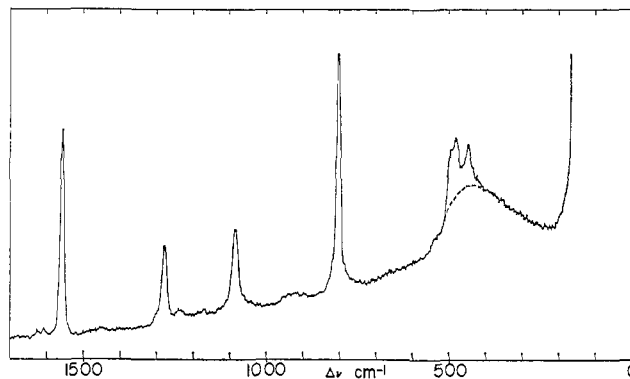


Figure 4. Liquid-phase Raman spectrum of  $\text{CF}_2\text{N}_2$ .

examination of the weak features in the Raman spectrum, particularly those in the 550- to 450- $\text{cm}^{-1}$  region, at higher resolution and higher amplifier gain led us to

Table VI. Raman Spectrum and Assignments

Freq., cm. <sup>-1</sup>	Intens.	Depol.	Assignment		Class
			Freq., cm. <sup>-1</sup>		
~1627	vw	...	1631	$\nu_8 + \nu_9$	A <sub>1</sub>
~1609	vw	...	1608	$2 \times \nu_3$	A <sub>1</sub>
1560	s	p	$\nu_1$	Fund.	A <sub>1</sub>
~1304	vw	...	1303	$\nu_3 + \nu_4$	A <sub>1</sub>
1280	m	p	$\nu_2$	Fund.	A <sub>1</sub>
~1234	vw	...	$\nu_6$	Fund.	B <sub>2</sub>
1086	m	dp	$\nu_8$	Fund.	B <sub>2</sub>
~950	vw	...	968	$2 \times \nu_7$	A <sub>1</sub>
~925	vw	...	935	$\nu_5 + \nu_7$	B <sub>2</sub>
~900	vw	...	902	$2 \times \nu_5$	A <sub>1</sub>
804	s	p	$\nu_3$	Fund.	A <sub>2</sub>
~545	vw	...	$\nu_9$	Fund.	B <sub>2</sub>
~499	w	...	$\nu_4$	Fund.	A <sub>1</sub>
484	m	dp?	$\nu_7$	Fund.	B <sub>1</sub>
451	m	dp?	$\nu_5$	Fund.	A <sub>1</sub>

believe that these are real. The centers of the well-defined bands in the spectrum were located to  $\pm 2 \text{ cm}^{-1}$ .

Because of the questionable stability of  $\text{CF}_2\text{N}_2$  toward mechanical shock, its known photolytic instability in the near-ultraviolet,<sup>7</sup> and its low boiling point of  $-91^\circ$ ,<sup>7</sup> sample handling for the Raman spectrum presented some difficulties. Following established safety procedure for this compound, we limited the sample size to 1.5 g. (19 mmoles). A light-pipe

Raman cell, which is described in detail elsewhere,<sup>26</sup> was modified in several ways. At the open end, it was fitted with a short side arm tilted at about 45° with respect to the body of the cell, with a spring-loaded stopcock, and with a ground joint. All of these appurtenances extended outside of the filter jacket of the Raman source unit and were kept compact, thereby permitting the insertion of polaroid filters without disturbing the filled, cold cell.

In the experiment, the Raman cell was mounted in the evacuated jacket, and the sample of CF<sub>2</sub>N<sub>2</sub> was distilled into the 45° side arm. Care was taken to avoid any contamination from carbon dioxide or water, which at the temperature of the experiment, would have introduced solid particles to scatter light. With the CF<sub>2</sub>N<sub>2</sub> held frozen in the side arm, the Raman cell and surrounding jacket were installed in horizontal position in the filter jacket of the Raman source and connected to a source of cold, dry nitrogen gas. When the temperature of the cell had reached about -100°, the CF<sub>2</sub>N<sub>2</sub> was carefully distilled into the body of the cell. No difficulty was encountered in getting the sample to fill the end of the nearly horizontal cell. During the course of the measurements, the temperature inside the vacuum jacket was maintained in the range of -90 to -100°.

Although no significant change in the Raman spectrum was observed from the time of the first 10-min. survey scan to the end of the depolarization measurements nearly 14 hr. later, some evidence of photolysis was found in the recovered sample. From the infrared spectrum it was found that about 0.4% of tetrafluoroethylene<sup>27</sup> and about 0.2% of perfluoro-2,3-diaza-1,3-butadiene<sup>7</sup> were formed. In addition, about 1.5% of one or more unidentified substances was also found. This residue was a yellowish liquid condensable at room temperature. Unidentified gas-phase infrared bands of notable intensity were observed at approximately 1810 s, 1785 vs, 1320 s, 1260 s, 1210 s, 1135 s, 1015 s, 975 m, 950 s, 755 m, and 715 m cm.<sup>-1</sup>. Almost all of these bands are featureless and rather sharp.

### Vibrational and Structural Assignment

In addition to the evidence advanced in the Introduction, several features of the observed vibrational spectra point toward the diazine structure; we shall therefore assume this structure and proceed with the vibrational assignment, deferring discussion of the alternative diazomethane structure.

At first glance, the Raman spectrum shows six reasonably intense lines, three of which are obviously polarized. We also find three rather weak lines, but happily these coincide with strong absorptions in the infrared spectrum. On looking at the gas-phase infrared spectrum we were immediately struck by the distorted shapes of many bands, intensity apparently having been transferred from one rotational branch to the other. This is a well-known consequence of Coriolis coupling and can result from either the coupling of a vibration with pure rotation (Herman-Wallis effect) or the rotational coupling of two vibra-

tions.<sup>28</sup> The first possibility is unlikely as the molecule apparently has a very small permanent dipole moment.<sup>29</sup> In the second case, the Coriolis operator coupling the two vibrational states,  $v_s$  and  $v_{s'}$ , is a function of the Coriolis coefficient  $\zeta_{ss'}$ , which is given by  $\zeta_{ss'} = \sum_i m_i (l_s^i \times l_{s'}^i)$ , where  $l_s^i$  is the displacement vector and  $m_i$  is the mass of the  $i$ th atom in the  $s$ th normal mode. The necessary symmetry requirement for a nonvanishing matrix element of the Coriolis operator is that the product of the symmetry species of the two vibrational states must contain the character of a rotation. Thus, we see that, for difluorodiazirine, Coriolis interaction is possible between all pairs of vibrational states of different symmetry. The magnitude of the coupling and, hence, the extent of the distortion of the band contour, is determined by the magnitude of  $\zeta_{ss'}$  and by the energy difference between the interacting levels. The vector product  $l_s^i \times l_{s'}^i$  is nonvanishing only when there is displacement of the  $i$ th atom in both vibrational modes  $v_s$  and  $v_{s'}$ . A large displacement of the  $i$ th atom in  $v_s$  and  $v_{s'}$  results in a large contribution to  $\zeta_{ss'}$ . We expect most vibrations of a diazine structure to involve considerable displacement of the central carbon atom, which is the lightest atom, and, hence, we expect the  $\zeta_{ss'}$  for this molecule to be large.<sup>30</sup> For this reason, we expect many band contours in the gas-phase infrared spectrum not to be clearly type A, B, or C, but rather to be hybrid, distorted types.

The three prominent polarized Raman lines at 1560, 1280, and 804 cm.<sup>-1</sup> are immediately identified as A<sub>1</sub> fundamentals. There is no reliable evidence for any other line being polarized although it is conceivable that either of the two weak lines at *ca.* 499 or 545 cm.<sup>-1</sup> may be. In the infrared spectrum, the bands at 1563 and 805 cm.<sup>-1</sup> have clear type A structure, but the band at 1282 cm.<sup>-1</sup> appears badly distorted by Coriolis perturbation, probably by the 1248-cm.<sup>-1</sup> vibration. The fourth A<sub>1</sub> fundamental, the symmetric CF<sub>2</sub> deformation, is almost certainly one of the vibrations close to 500 cm.<sup>-1</sup>, but there is no clear spectroscopic evidence for an assignment.

For the A<sub>2</sub> torsion we seek a Raman-active, infrared-inactive vibration at about 500 cm.<sup>-1</sup>. The Raman line at 451 cm.<sup>-1</sup> has no counterpart in the matrix infrared spectrum,<sup>31</sup> but there is a weak feature at 448 cm.<sup>-1</sup> in the gas-phase infrared spectrum. It is attractive to assign the Raman line as the torsional fundamental and to explain the gas-phase absorption as a forbidden transition made active by Coriolis interaction. No spectroscopic features lower than 450 cm.<sup>-1</sup> were detected although we scanned the infrared spectrum to 250 cm.<sup>-1</sup> and were able to work to within 100 cm.<sup>-1</sup> of the Raman exciting line. It therefore does not seem likely that the 451-cm.<sup>-1</sup> line is an overtone or combination. Further, in view of the low sample temperature, it is improbable that the 451-cm.<sup>-1</sup> Raman line results from a transition from an excited state. It is nice to find this frequency

(28) H. H. Nielsen, "Handbuch der Physik," Vol. XXXVII/1, Springer-Verlag, Berlin, 1959, p. 173.

(29) L. Pierce, private communication. See also ref. 7.

(30) Except for  $\nu_5$  which does not involve motion of the carbon atom; however, there are also contributions to the  $\zeta_{ss}$  from the fluorines and the nitrogens.

(31) D. E. Milligan, private communication.

(26) N. C. Craig and J. Overend, *Spectrochim. Acta*, 20, 1561 (1964).  
 (27) A.P.I. Research Project 44, "Catalog of Infrared Spectral Data," Carnegie Institute of Technology, Pittsburgh, Pa. 15213, spectrum No. 1006.

so close to that calculated (Table I) although, in view of the fact that most of the other calculated frequencies differ significantly from the observed ones, this agreement cannot be taken too seriously. One additional bit of support comes from the assignment of the weak, distorted type A band at 895  $\text{cm}^{-1}$  in the infrared spectrum to the overtone of the torsional mode.

There are two  $B_1$  fundamentals: an asymmetric CF stretching frequency and an asymmetric  $\text{CF}_2$  deformation. From group-frequency arguments and the zero-order calculation, we assign the former to the infrared band at 1248  $\text{cm}^{-1}$  and the weak Raman line at *ca.* 1234  $\text{cm}^{-1}$ . The infrared band should be a type B but is apparently distorted by Coriolis interaction to such an extent that there appears to be an intense Q branch. However, we took a central minimum as the band origin. A strong Coriolis interaction between  $\nu_2$  and  $\nu_6$  is quite reasonable as  $\nu_2$  is essentially a motion of the carbon atom along the  $C_2$  axis and  $\nu_6$ , a motion of the carbon atom in a perpendicular direction.  $\nu_7$ , the  $\text{CF}_2$  deformation, is assignable to one of the bands in the 500- $\text{cm}^{-1}$  region although just which band it is not clear.

In the  $B_2$  class, the asymmetric CN stretching frequency is assignable to the depolarized Raman line at 1086  $\text{cm}^{-1}$  corresponding to a Coriolis-perturbed infrared band at 1091  $\text{cm}^{-1}$ . There are again difficulties in assigning the  $B_2$  deformation frequency which apparently is at about 500  $\text{cm}^{-1}$ .

Up to this point the vibrational assignment is straightforward and can be considered well established. There remains the difficulty of sorting out the three bands at 545, 502, and 481  $\text{cm}^{-1}$  in the gas-phase infrared and at 544, 499, and 484  $\text{cm}^{-1}$  in the Raman, and assigning them as fundamentals in the symmetry species  $A_1$ ,  $B_1$ , and  $B_2$ . The close proximity of these frequencies invalidates arguments for assignment based on group frequencies or on calculations from transferred force constants. There is little help from band contours, and none of the Raman lines is apparently polarized. We have chosen to assign the 481- $\text{cm}^{-1}$  infrared band, which has a contour very similar to the distorted type B band at 1248  $\text{cm}^{-1}$ , to the  $B_1$  asymmetric  $\text{CF}_2$  deformation mode. This assignment is consistent with the expectation of a strong Coriolis interaction between all pairs of the deformation modes. It is attractive to assign the band at 1631  $\text{cm}^{-1}$  in the infrared to the combination 1091 + 544 and to postulate that it derives its considerable intensity through Fermi resonance with the  $A_1$  fundamental 1563  $\text{cm}^{-1}$ . This implies that the combination level has  $A_1$  symmetry and, hence, that the 545- $\text{cm}^{-1}$  level belongs to the  $B_2$  species, leaving the band at 502  $\text{cm}^{-1}$  in the infrared (499  $\text{cm}^{-1}$  in the Raman) to be assigned to the  $A_1$  mode  $\nu_4$ . Even though we have attributed an apparently weak Raman line to an  $A_1$  fundamental, this does appear, on the basis of present evidence, to be the most attractive assignment of the spectra in the 450–550- $\text{cm}^{-1}$  region. The most important point is, however, that this vibrational spectrum can be assigned convincingly on the assumption of a cyclic structure; this assignment is summarized in Table VII.

Turning next to a possible assignment based on the difluorodiazomethane structure, we see that there are

Table VII. Summary of Fundamental Vibration Frequencies of  $\text{F}_2\text{CN}_2$

Class	—Freq., $\text{cm}^{-1}$ —	Class	—Freq., $\text{cm}^{-1}$ —	
$A_1$	$\nu_1$	1563	$B_1$ $\nu_6$	1248
	$\nu_2$	1282	$\nu_7$	481
	$\nu_3$	805	$B_2$ $\nu_8$	1091
	$\nu_4$	502		$\nu_9$
$A_2$	$\nu_5$	451		

several difficulties. Table III shows the estimated frequency of  $\nu_1$  as 2161  $\text{cm}^{-1}$ , a typical group frequency for the  $>\text{C}=\text{N}=\text{N}$  group. This contrasts markedly with the highest fundamental frequency of 1650  $\text{cm}^{-1}$  estimated for the diazine structure. The difference apparently lies in the relative strengths of the NN bond as reflected in the force constants; *cf.* Tables II and IV. In diazine it is a fairly normal double bond; in diazomethane it is close to a triple bond. Although there is absorption in the infrared at 2084 and 2045  $\text{cm}^{-1}$  which could be assigned to an NN stretching vibration, we should then be left with an intense band at about 1560  $\text{cm}^{-1}$ , in both the infrared and the Raman, to be assigned rather inconvincingly as an overtone or combination. Corresponding to an infrared absorption in the 2060- $\text{cm}^{-1}$  region for the NN stretch we would expect an intense Raman band since the stretching of a multiple bond is involved, but no Raman line was found in this region.

Further, for a diazomethane structure we expect at least one low fundamental,  $\nu_9$ . We cannot discount entirely the possibility that there is a band which lies outside the spectroscopic range we have explored, but, by comparison of low temperature and room temperature infrared spectra, we did not identify any difference band requiring the postulate of a fundamental in the region of 150  $\text{cm}^{-1}$ , nor did we require such a frequency in the assignment of combinations and overtones.

The identification of the Raman line at 451  $\text{cm}^{-1}$ , which has no counterpart in the condensed-phase infrared spectrum, is also considered as support for the diazine structure. But perhaps the strongest structural evidence is that the over-all fit of the observed vibrational spectrum to the calculated one is much better when we assume the cyclic structure. The entire vibrational spectrum, with the exception of a few weak features at high frequency, can be assigned as fundamentals, first overtones, and binary combinations or difference tones; *cf.* Tables V and VI. Although the unassigned features are readily explained as tertiary combinations, they may also be unidentified impurity bands, and we have not attempted a specific assignment.

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