sons, Figures 1 and 2 are scaled comparably for the calculated values.

In addition to the factors discussed thus far, at least three other considerations could influence the correlation of theoretical energies and experimental charge-transfer spectra for molecular complexes. These are (1) errors in the assignment of wavelengths for correlation, (2) the influence of changes in solvent on the position of the charge-transfer band, and (3) the perturbation of donor orbital energies on complexation with TCNE. While it is impossible to adequately correct for these factors from the limited information in the literature, a reasonable estimate of their combined effects would indicate a probable correction of not more than 0.1 ev. Obviously variations of this magnitude are relatively unimportant in view of the deviations shown in correlations between theoretical and experimental charge-transfer transition energies.

Thus the method of molecular calculation seems to have a major influence on whether or not correlation is obtained. Correlation of the second charge-transfer bands for the TCNE complexes is poor with the Hückel molecular orbital method regardless of the inclusion of overlap in calculations or nonbonding terms in perturbation relationships. The use of highest occupied and penultimate orbital energies from self-consistent molecular orbital methods gives a reasonably good correlation with either first or second charge-transfer transitions.

Although a direct relationship considering only the energy of the donor orbital participating in the transition has been considered here, the variants discussed demonstrate the general means of applying this approach to other charge-transfer treatments.

Acknowledgment. The authors are indebted to Professors M. J. S. Dewar and G. J. Gleicher for the computer programs used in self-consistent molecular orbital calculations, and to the computer centers of the University of Texas and West Virginia University for CDC 1604 and IBM 7040 facilities, respectively.

The Molecular Structure of Perfluorodiazirine

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Abstract: The cyclic structure of F_2CN_2 has been confirmed by an electron diffraction experiment on the vapor. Perfluorodiazirine has C_{2v} symmetry (planes of CF_2 and CN_2 are mutually perpendicular) with C—F = 1.315 ± 0.004 A, C—N = 1.426 ± 0.004 A, N═N = 1.293 ± 0.009 A, ∠FCF = 111.84 ± 0.52°, and ∠NCN = 53.95 ± 0.36°. Comparison of the metrics of perfluorodiazirine with diazirine shows that C—N distance is shorter and the N═N distance is longer in the former than in the latter by about 0.06 A. An analysis of the structures of related molecular species underscores the observation that the attachment of two or more fluorines to a carbon atom introduces a compacting of the structure in the immediate vicinity of the carbon atom.

Study of the structures and properties of triatom ring systems has proved to be an intriguing activity for experimental as well as theoretical chemists. Exclusive of postulated transient species, diazirine and perfluorodiazirine are the smallest molecules (five atoms) which incorporate such rings. Currently there is particular interest in their structural properties because they are precursors of carbenes. Perfluorodiazirine, a precursor of CF_2, was first prepared by Mitsch.[1] That this preparation produced a compound with a cyclic structure (C_{2v} symmetry), like that for diazirine, was deduced from a detailed analysis of its infrared and Raman spectra,[2] and the assignment of the fundamental frequencies was confirmed by an analysis of its ultraviolet spectrum.[3] Preparation of the noncyclic isomer (perfluorodiazomethane) has not yet been reported.

The present electron diffraction investigation of the vapor phase structure of perfluorodiazirine was undertaken to obtain interatomic distances and bond angles for comparison with the known geometry of diazirine.[4]

Experimental Section

The gas chromatographically pure sample of CF_2N_2 was obtained from Ronald A. Mitsch, Minnesota Mining and Manufacturing Co. The sample was kept in the vapor state at 0.5 atm in a 250-ml glass bulb, which was fitted with a pressure stopcock and a cold finger. The sample was frozen out and degassed before each pattern was taken. For the diffraction runs, the sample pressure was maintained at about 5 mm by immersing the bulb in a bath at −150°. Sectored diffraction patterns were obtained with the new electron diffraction apparatus, operated in the convergent mode.[5,6] Exposures were made on 4 × 5 in. Kodak process plates. An r^3 sector was used, and diffraction patterns were obtained for three regimes: q = 3–40 A^{-1} (25 kv; L = 262.4 mm); q = 6–75 A^{-1} (75 kv; L = 262.4 mm); and q = 12–143 A^{-1} (75 kv; L = 129.4 mm) ($q = (40/\lambda) \sin \theta/2$). At each magnification four different gas diffraction exposures and one calibrating ZnO exposure were made.

The plates were microphotometered on a double-beam Jarrell–Ash microdensitometer, the stage of which was fitted with a rotating plateholder, driven at 600 rpm during the scan. A precision calibration plate (250-μ interval marks) was mounted on the second stage. Images of both plates were projected in split field onto a viewing screen, at the front of the instrument. The two plate stages were rigidly locked so that both images moved across the screen as the pattern was scanned. Motion of the calibration rulings was

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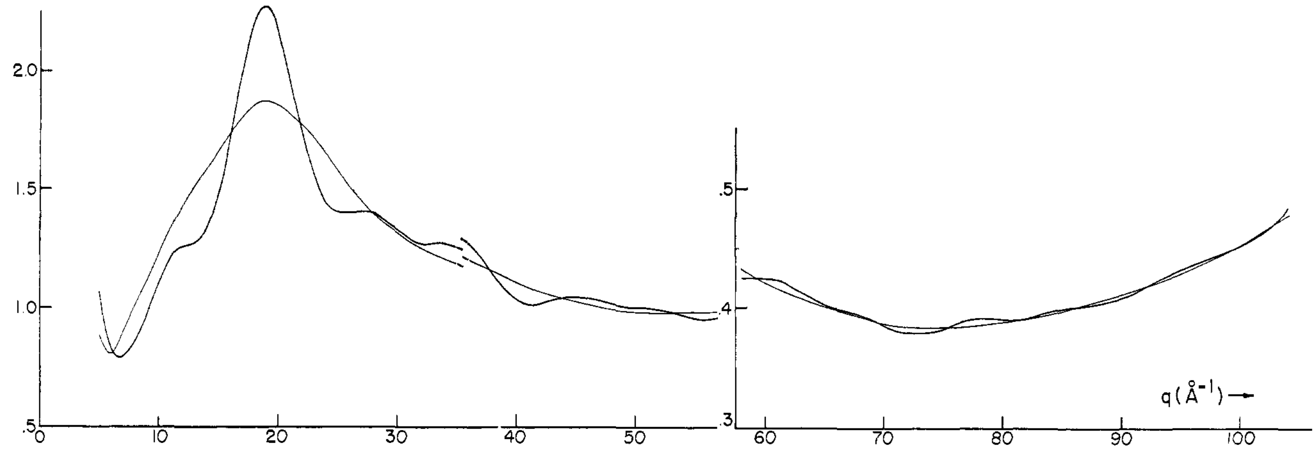

Figure 1. Experimental sectored electron diffraction intensity and refined background for three sets of data.

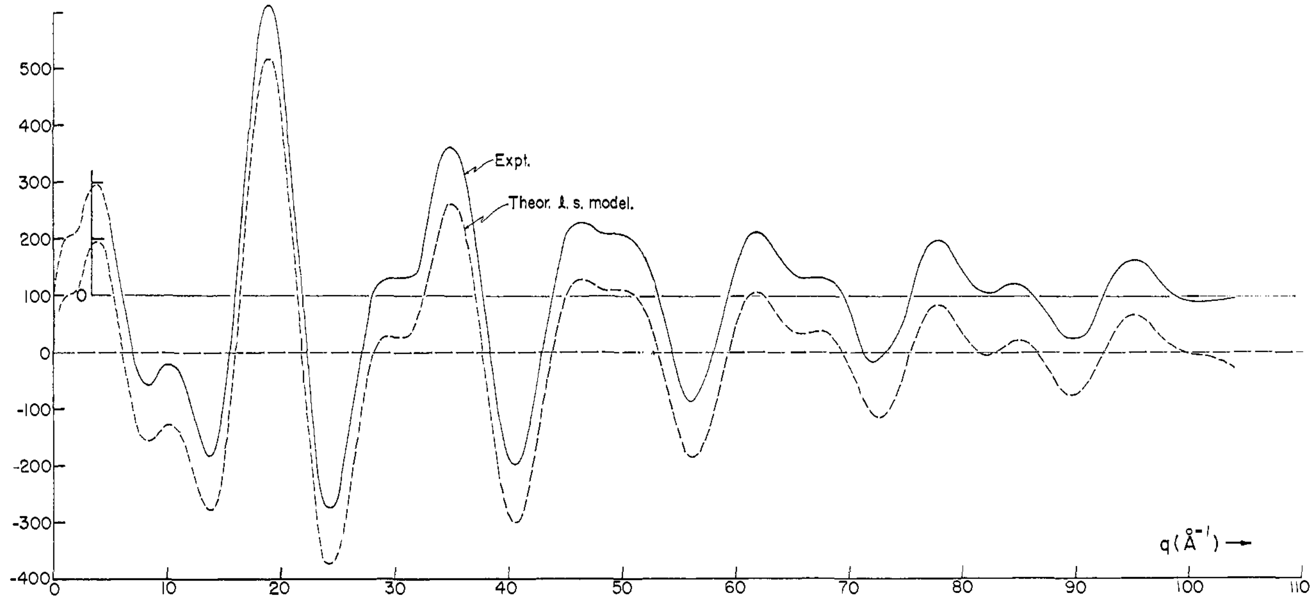

Figure 2. Comparison of $(\pi/10)qM_{\text{exptl}}(q)$ with that calculated for the final model as characterized in Table I.

sensed by a crystal detector as a periodic drop in light intensity which was fed through an amplifier and discriminator to an auxillary pen attached to the recorder. These 250-μ calibration marks at the edge of the chart paper provide data on plate position, independent of nonuniform stage or paper travel. Complete details of the modification of this instrument (including analog to digital conversion) will be given elsewhere.[7]

Optical density values were converted to intensity in the following manner. A light and a dark plate taken under identical conditions, except for exposure time, were selected. If reciprocity between exposure and intensity is assumed

$$I_d = kI_l \tag{1}$$

where the subscripts d and l refer to dark and light plates, respectively, and I is the *relative* intensity. To a first approximation (superscripts 0), for the light plate

$$I_l^{(0)} = D_l \tag{2}$$

The optical density D_l may be expressed as a power series in D_d

$$D_l = (1/k)D_d(1 + \sum_i B_i D_d^{\,i}) \tag{3}$$

and the coefficients B_i and $(1/k)$ can be determined by the method of least squares. On combining eq 1–3

$$I_d^{(0)} = D_d(1 + \sum_i B_i D_d^{\,i}) \tag{4}$$

If eq 4 is now used for the light plate intensity instead of (2), a first-order approximation in the dark plate intensity is obtained as

$$I_d^{(1)} = D_d(1 + \sum_i B_i D_l^{\,i})\,(1 + \sum_i B_i D_d^{\,i}) \tag{5}$$

Data Reduction

The experimental molecular intensity was calculated for each set of data as

$$M_{\text{exptl}}(q) = \frac{\pi q}{10}P\left[\frac{I(q)}{B(q)} - 1\right] \tag{6}$$

where $I(q)$ is the experimental sectored intensity, $B(q)$ is the *estimated* background, and $P = \Sigma_k(Z_k^{\,2} + Z_k)$. The background $B(q)$ was drawn in such a way that the zeros and relative intensities were self-consistent for all sets of data, in the regions of overlap. The $M_{\text{exptl}}(q)$'s for all data sets were scaled to $M_{\text{exptl}}(q)$ for the lowest q range, so that at the splice points, q_0, the scaling was exact. The data were then spliced such that at any given q in the splice region

$$M_{\text{exptl}}(q) = \frac{1}{2}[\{1 + \tanh(-X)\}M^{\text{a}}_{\text{exptl}}(q) + \{1 + \tanh(X)\}M^{\text{b}}_{\text{exptl}}(q)] \tag{7}$$

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[7] S. H. Bauer, in preparation.

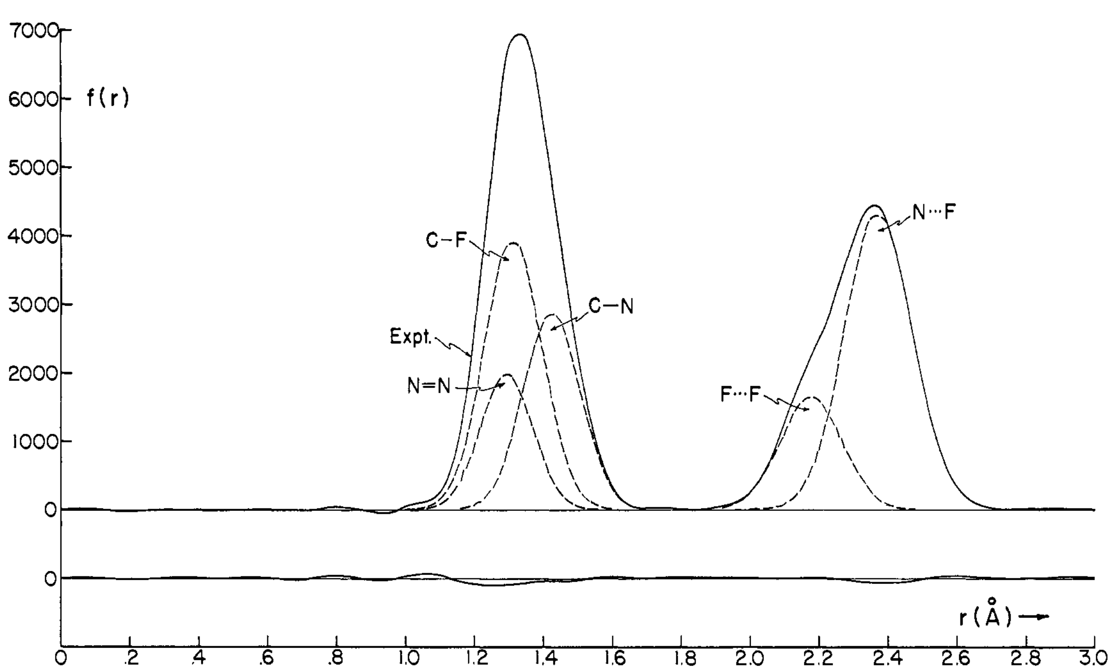

Figure 3. Experimental radial distribution curve (showing resolved atom pair contributions). The experimental curve was calculated with a damping factor $\gamma = 0.002157$.

where $X = (q_0 - q)$. The superscripts a and b refer to $M_{\text{exptl}}(q)$ for q ranges less than q_0 and greater than q_0, respectively.

The subsequent analysis followed the procedure recently described.[8] The background $B(q)$ was refined by reinverting the nonstructural regions of the radial distribution $f(r)$ until further refinement resulted in no change in $M_{\text{exptl}}(q)$. Between background refinements $f_{\text{theor}}(r)$ was calculated for various models for comparison with the curve derived from the data.

When the trial-and-error method had given reasonable agreement between $f_{\text{exptl}}(r)$ and $f_{\text{theor}}(r)$, $M_{\text{exptl}}(q)$ calculated from the best background was fitted by the method of least squares by

$$P\left(\frac{\pi}{10}\right)qM(q) = P{\sum_{ij}}' \frac{(Z_i - f_i)(Z_j - f_j)\cos\Delta\eta_{ij}\exp\left[-{}^1/_2 l_{ij}^2\left(\frac{\pi}{10}q\right)^2\right]}{\sum_k[(Z_k - f_k)^2 + S_k]}\,\frac{\sin\left(\frac{\pi}{10}qr_{ij}\right)}{r_{ij}} \qquad (8)$$

where Z_i, Z_j are the atomic numbers, f_i, f_j are the X-ray atom form factors, S_k is the incoherent scattering factor, and $\Delta\eta_{ij}$ is the scattering phase shift between atoms i and j. Instead of using r_{ij}'s as parameters, the least-squares analysis was made in terms of independent bond lengths and valence angles, following the procedure of Hedberg and Iwaski.[9]

Analysis and Results

The experimental sectored intensity and background are reproduced in Figure 1 for the three sets of data. Curves for $[(\pi/10)qM_{\text{exptl}}(q)]$ and the theoretical $[(\pi/10)\cdot qM(q)]$, calculated for the converged least-squares model, are given in Figure 2. The experimental radial distribution curve calculated with damping factor $\gamma = 0.002157$ is given in Figure 3 [γ is defined by $\exp(-\pi^2\gamma q_{\max}^2/100) = 0.1$].

From the radial distribution curve it was immediately evident that the molecule was not perfluorodiazomethane. In that case N···F distances greater than 2.7 A and an N···N distance of approximately 1.139 A (its value in diazomethane) would have been expected. Another possible isomer, perfluorocyanamide, was ruled out on a similar basis; the perfluorodiazirine model is clearly indicated. The CF_2 and CN_2 planes were then assumed to be mutually perpendicular. This left the C–F and C–N distances and the FCF and NCN angles as independent parameters. An empirical weight matrix was used.[9] $M_{\text{exptl}}(q)$ data from q = 20–95 A^{-1} were given a weight of unity; data at the extremes of q = 5 and q = 104 A^{-1} were given weights 0.1 and 0.25, respectively. Beyond q = 104 A^{-1}, $I_{\text{exptl}}(q)$ was so weak that the differences in intensity between maxima and minima were of the same order of magnitude as the experimental uncertainty; hence, the data beyond q = 104 A^{-1} were not used. $M_{\text{exptl}}(q)$ was obtained by splicing $M_{\text{exptl}}(q)$ from the three sets of data, per eq 7.

The converged values of the parameters are listed in Table I. Equation 8 is based on the assumption that the vibrational potential is harmonic. Comparison of the observed and calculated molecular intensity curves (Figure 2) reveals no apparent anharmonic phase shift. Hence it is believed that the r_{ij} values obtained here are very nearly $r_g(1)$ values, as defined by Bartell. The estimated uncertainties (taken as four times the calculated standard deviations) are given in Table I. In a preliminary test, it was found that parameter $l_{N=N}$ had large correlation coefficients with the other parameters. Because of the large correlations, the sum of the squared residuals oscillated and did not approach a minimum value. Inspection of the radial distribution

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Table I. Structural Parameters for Perfluorodiazirine Compared with Its Analog

Parameter	F_2CN_2 (this work)		H_2CN_2[4]	F_2C[a]
C—F	1.315 ± 0.004 A	l_{CF} = 0.053 ± 0.004 A		1.300 A
C—H			1.09 ± 0.02 A	
C—N	1.426 ± 0.004 A	l_{CN} = 0.050 ± 0.008 A	1.482 ± 0.003 A	
∠NCN	53.95 ± 0.36°		48.9°	
∠FCF	111.84 ± 0.52°		∠HCH = 117 ± 2°	104.9°
N═N[b]	1.293 ± 0.009 A	l_{NN} = 0.040 A (assumed)	1.228 ± 0.003 A	
F···F[b]	2.178 A	l_{FF} = 0.063 ± 0.008 A		
N···F[b]	2.374 A	l_{NF} = 0.073 ± 0.004 A		

[a] F. X. Powell and D. R. Lide, Jr., *J. Chem. Phys.*, **45**, 1067 (1966); C. W. Matthews, *ibid.*, **45**, 1068 (1966). [b] Calculated from the parameters given above.

Table II. Error Matrix[a]

	r_{CF}	r_{CN}	∠NCN	∠FCF	l_{CF}	l_{CN}	l_{FF}	l_{NF}
r_{CF}	0.0012							
r_{CN}	−0.0011	0.0014						
∠NCN	−0.0011	0.0006	0.0016					
∠FCF	−0.0011	0.0015	−0.0004	0.0020				
l_{CF}	0.0005	−0.0010	0.0011	−0.0012	0.0014			
l_{CN}	0.0010	−0.0012	0.0008	−0.0014	0.0015	0.0018		
l_{FF}	0.0003	0.0003	−0.0004	−0.0005	−0.0008	0.0020	0.0016	
l_{NF}	−0.0004	0.0002	0.0004	−0.0004	0.0001	−0.0002	0.0006	0.0007

[a] The elements in the above matrix are defined by

$$\sigma_{ij} = \mathrm{sgn}[(BJ^{-1})_{ij}][|([B]^{-1})_{ij}| \cdot \chi_R/(n_q - n_p)]^{1/2}$$

where χ_R is the sum of the squares of the residuals, n_q is the number of observations, n_p is the number of variable parameters. $[B] \equiv [J]^t[w][J]$, where $[J]$ is the Jacobian matrix and $[w]$ is the weight matrix. The distance variables are measured in angstrom units, the angle variables in radians.

curve (Figure 3) shows that arbitrary variations of the N═N peak width lead to large ambiguities in the location of the C–F and C–N peak positions. The only physically meaningful procedure is to constrain $l_{N=N}$ to a reasonable value, and indeed when its magnitude was set at 0.04 A the calculation converged. The resulting error matrix is reproduced in Table II, wherein the diagonal elements are the calculated uncertainties for the parameters and the off-diagonal elements measure the correlations for this set. The specific error limits (which include our estimate of systematic errors) were assigned at four times the calculated σ_{ij}'s.

Discussion

The above electron diffraction data confirm the conclusion that F_2CN_2 as prepared by Mitsch has a cyclic structure.[2] The contrasts between the geometric parameters of perfluorocarbene (F_2C:), perfluorodiazirine, and diazirine are presented in Table I. That the C–F bond distance and ∠FCF are less in the carbene than in the perfluorodiazirine is not surprising in view of the greater extent of delocalization of the carbon valence electrons in the radical. The relative magnitudes of the C—N and N═N distances in perfluorodiazirine as compared with those reported for diazirine did prove unexpected. To rationalize these observations we reviewed the structural data available for a variety of compounds which show changes in geometry due to successive fluorine substitution for hydrogen. The pertinent values are listed in Table III.

That the replacement of H by F onto a carbon atom generally leads to compression of the charge density around that carbon and hence to the shortening of adjacent bond lengths has been known for about 3 decades. For example, in the sequence $FCH_3 \cdots F_3CH$, the C–F bond length ranges from 1.383$_6$[10] to 1.358[11] to 1.332 A.[12] It is also established that when the carbon is involved in π bonding, the C–F distances are shorter than when all substituents are attached to the central atom by single bonds. Compare FCH_3 (1.383$_6$), $FHC{=}CH_2$ (1.344),[13] $FHC{=}CHF$ (1.335),[14] and $F_2C{=}CH_2$ (1.323),[15] but F_2CH_2 (1.358); also note $HFC{=}O$ (1.338)[16] and $F_2C{=}O$ (1.312).[17] The trend in magnitudes for the C–F distances in the sequence F_3CCH_3 (1.333$_5$),[18] $(CF_3)_3N$ (1.32 ± 0.02),[19] and $(CF_3)_2NN(CF_3)_2$ (1.325)[20] is not well defined, but the very short bonds in $FC{\equiv}N$ and $FC{\equiv}CH$[21] (1.262 and 1.279, respectively) clearly indicate that the $(2p\sigma)_F$ and $(2p\pi)_F$ orbitals interact to a significant extent with the $(\sigma^2\pi^4)$ orbitals in the triple bond. That the C—F distance in F_2CN_2 is like that in F_2CO, and somewhat smaller than in $F_2C{=}CH_2$, suggests that orbitals associated with the three-membered ring interact with the pπ orbitals associated with the C—F bonds.

The introduction of fluorine atoms affects not only the adjacent C—F bond lengths; generally, the other adjacent bonds are also somewhat shortened. This is

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Table III. Comparison of Interatomic Distances in Related Molecules

	C—F, A	∠FCF, deg	C—N, A (C—C)	N=N, A (C=C) [C=O]	Ref
FCH_3	1.383_6				10, *a*
F_2CH_2	1.358 ± 0.001	108° 14′			11, *a*
F_3CH	1.332	108° 48′			12, *a*
$HFC{=}CH_2$	1.344 ± 0.002			(1.337 ± 0.002)	13
$HFC{=}CFH$	1.335 ± 0.002			(1.324 ± 0.002)	14
$F_2C{=}CH_2$	1.321 ± 0.005			(1.311 ± 0.005)	15
	1.323 ± 0.002	109.1 ± 0.3°		(1.315 ± 0.002)	14
$HFC{=}O$	1.338 ± 0.005			[1.181]	16
$F_2C{=}O$	1.312	108.0°		[1.174]	17
CF_3CH_3	1.335 ± 0.005	107.9°			18
$(CF_3)_3N$	1.32 ± 0.020	108.5 ± 0.2°	1.43 ± 0.030		19
$(CF_3)_2NN(CF_3)_2$	1.325 ± 0.005	108.2 ± 0.5°	1.433 ± 0.010		20
$FC{\equiv}CH$	1.279				21
$FC{\equiv}N$	1.262				21
$(CH_3)_3N$			1.47 ± 0.020		22
$(CH_3)_2NNH_2$			1.47		23
$H_2C{=}CH_2$				(1.338 ± 0.005)	24
$(CH_3)_2C{=}CH_2$				(1.331)	25
$H_2C{=}O$				[1.210]	26
$H_2C{-}CH{=}CH$			(1.525 ± 0.02)	(1.286 ± 0.04)	27
$H_2C{-}CH_2{-}CH_2$			(1.509 ± 0.0015)		28
cis-N_2F_2				1.209 ± 0.011	8
				1.214 ± 0.005	*b*
trans-N_2F_2				1.224	8

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barely discernible for the acetylenes, but is quite striking in the amines. Thus, in trimethylamine C–N = 1.47 A;[22] the same value is reported for 1,1-dimethylhydrazine, $(CH_3)_2NNH_2$.[23] However, in $(CF_3)_3N$ and in the perfluorotetramethylhydrazine the C–N distance is 1.433 ± 0.010 A.[19,20] The C=C separation is 1.338 A[24] in C_2H_4 and is 1.331 A in $(CH_3)_2$ $C{=}CH_2$;[25] it remains essentially unaffected by monosubstitution of fluorine for hydrogen (in FHC=CHF it is 1.335 A[14]). However, the introduction of a terminal F_2C group, as in $F_2C{=}CH_2$, leads to C=C = 1.315 A.[14] A parallel trend holds for $H_2C{=}O$,[26] HFC=O, and $F_2C{=}O$.[17] That the C-N distance in F_2CN_2 is smaller than in H_2CN_2 (1.426 *vs.* 1.482 A)[4] is according to the established pattern. However, the magnitude of the change (0.055 A) is greater than expected. Indeed it is about the same as for the fluoro trisubstituted carbons (perfluorotrimethylamine and perfluorotetramethylhydrazine).

What appears to be most puzzling is the N=N bond length; it is 0.06 A greater in F_2CN_2 than in H_2CN_2. The magnitude in the latter is compatible with the distances found in *trans*-N_2F_2[8] and is somewhat longer than that in *cis*-N_2F_2.[8] To check the point that this difference is not primarily due to the presence of a three-atom ring, note that in cyclopropene, the C-C distance is 1.525 ± 0.02 A,[27] close to that found in cyclopropane,[28] while C=C is 1.286 ± 0.04 A, definitely less than the C=C distance in ethylene. If F_2CN_2 followed this pattern, its N=N would be shorter than in N_2F_2[16] instead of longer; data for N_2H_2 are not available for comparison.

The ∠FCF in $F_2C{=}X$ compounds are in the range 108–109° whereas in the perfluorodiazirine this angle is larger (111.8°). It is interesting to note that the reported frequencies for those vibrations which are predominantly stretching of C—N and N=N correlate with the measured bond distances. Thus $\nu_{N=N}$ is 1626 cm^{-1} in H_2CN_2[29] and 1563 cm^{-1} in F_2CN_2;[2] ν_{C-N} is 991 cm^{-1} in H_2CN_2[29] and 1091 cm^{-1} in F_2CN_2.[2]

The extended Hückel values of electron overlap populations for H_2CN_2 and F_2CN_2, calculated by Hoffmann,[30] are less for N=N in the perfluoro compound than in diazirine and inversely for the C—N bonds, correlating well with the observed relative distances.

Acknowledgments. We are particularly grateful to Dr. R. A. Mitsch for giving us the sample of perfluorodiazirine used in this study. This work was supported in part by the ONR, Contract Nonr-401(41), and the Material Science Center at Cornell University, ARPA-SD-68.

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