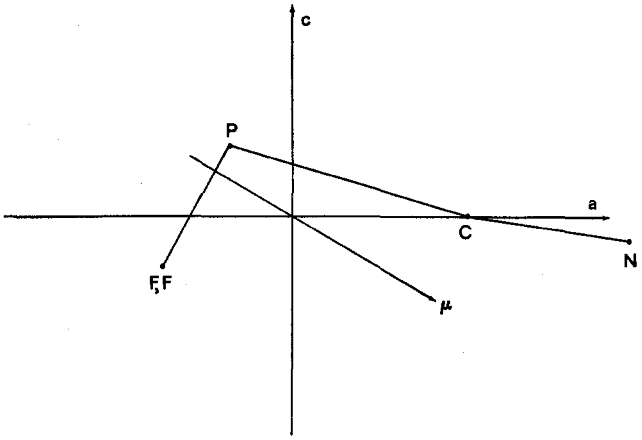

Figure 1.—A projection of PF_2CN in its *ac* plane of symmetry. The probable direction of the dipole moment is shown.

The PF_2 geometry in PF_2CN adds further confirmation to an apparent positive correlation between the PF bond length and the FPF bond angle in compounds in which the phosphorus atom is three- or four-coordinate. The correlation, shown in Figure 2, can be rationalized by considering the interactions between bonded and nonbonded pairs of electrons. In every case involving a quadruply connected phosphorus atom, the FPF bond angle is larger and the PF bond distance is shorter than in compounds of trivalent phosphorus. This suggests that in the quadruply connected compounds the electron pairs are all effectively localized in bonds and do not repel one another as strongly as they are repelled by the nonbonded electron pair in the phosphines.

Another interesting correlation is that the longest PF bonds and smallest FPF bond angles are found in compounds in which a (p → d)π bond has been proposed.[2b] An electronic interaction of this type would increase the electron density on phosphorus which, on the basis of a simple electrostatic repulsion model, would increase the PF bond lengths and decrease the FPF angles. Where the (p → d)π interaction is less likely to occur (in PF_2H and PF_3, for example), the PF bond lengths are smaller and FPF angles are larger.[2a,e] On this basis, the fact that PF_2CN has the shortest PF bond length of any triply connected PF_2 derivative suggests that in this molecule the electronic interaction which reduces electron density on phosphorus, the p → π interaction, is more important than the π → d interaction.

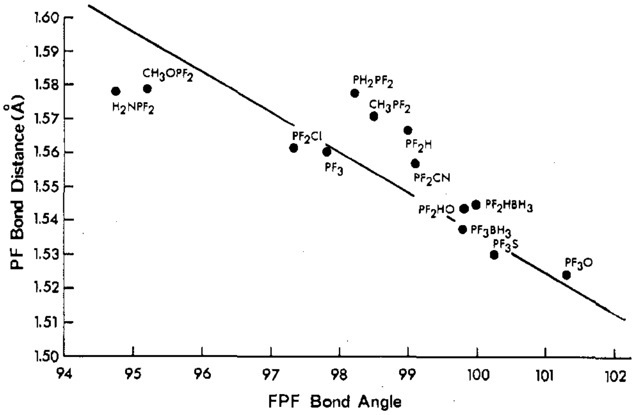

Figure 2.—Plot of PF bond distance *vs.* FPF bond angle for three- and four-coordinate difluorophosphines. The solid line joins points of constant FF distance = 2.355 Å. Data are from the papers cited in ref 2 and T. Moritani, K. Kuchitsu, and Y. Morino, *Inorg. Chem.*, **10**, 344 (1971); R. L. Kuczkowski and D. R. Lide, *J. Chem. Phys.*, **46**, 357 (1967); L. F. Centofanti and R. L. Kuczkowski, *Inorg. Chem.*, **7**, 2582 (1968); E. Codding, Ph.D. Thesis, Michigan State University, 1971.

There is another correlation between the PF bond distance and FPF bond angle in Figure 2. The solid line in the figure joins points for which the FF distance is constant (2.355 Å). It is apparent that, whatever the electronic interactions which are responsible for altering the PF bond distance and FPF bond angle in these compounds, the parameters are altered in such a way as to keep the FF distance nearly constant. No attempt was made to select a "best" FF distance in Figure 2; no single "best" FF distance is likely in these compounds.

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Microwave Spectrum, Structure, and Dipole Moment of Difluorocyanamide[1]

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Rotational transitions in the microwave spectrum of the ground and three excited vibrational states of NF_2CN and in the ground states of $^{15}NF_2CN$, $NF_2{}^{13}CN$, and $NF_2C^{15}N$ have been assigned. By analysis of the moments of inertia, bond distances and bond angles have been derived as follows: $d(CN) = 1.158 \pm 0.004$ Å, $d(NC) = 1.386 \pm 0.009$ Å, $d(NF) = 1.399 \pm 0.008$ Å, $\angle NCN = 173.9 \pm 2.2°$, $\angle CNF = 105.4 \pm 0.7°$, and $\angle FNF = 102.8 \pm 0.5°$. The tilt of the CN group is away from the fluorine atoms. The dipole moments are $\mu_a = 1.03 \pm 0.02$ D, $\mu_c = 0.39 \pm 0.10$ D, and $\mu = 1.10 \pm 0.02$ D.

Introduction

The question of multiple bonding in organic and inorganic chemistry is still a topic for discussion.[2] In H_2NCN it has been suggested that delocalization of the lone pair of electrons on the NH_2 group into the π-bonding system of the CN group leads to an increase in the bond angles about the NH_2 group and a shortened N–C bond. Although there has been considerable controversy about the exact geometry of the NH_2 group in NH_2CN, it is now generally accepted that in

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[1] (a) Supported in part by grants from the National Science Foundation. (b) Presented at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

[2] For a recent review see L. D. Pettit, *Quart. Rev., Chem. Soc.*, **25**, 1 (1971).

TABLE I

COMPARISON OF OBSERVED[a] AND CALCULATED[b] FREQUENCIES OF GROUND STATE ROTATIONAL TRANSITIONS FOR ISOTOPIC SPECIES OF NF_2CN

Transition	NF_2CN	$NF_2{}^{13}CN$	$NF_2C^{15}N$	$^{15}NF_2CN$
$1_{01} \rightarrow 2_{02}$	15,310.81 (0.12)	15,205.28 (0.17)	14,823.46 (0.26)	15,279.24 (0.17)
$1_{11} \rightarrow 2_{12}$	14,292.79 (0.21)	14,198.85 (0.41)	13,857.52 (0.10)	14,270.47 (0.04)
$1_{10} \rightarrow 2_{11}$	16,663.47 (0.34)	16,535.47 (0.01)	16,076.80 (0.22)	16,617.59 (0.12)
$2_{02} \rightarrow 3_{03}$	22,569.08 (0.04)	22,423.02 (0.38)	21,890.94 (0.31)	22,527.04 (0.15)
$2_{20} \rightarrow 3_{21}$	23,864.58 (0.06)	23,678.28 (0.06)	23,010.16 (−0.21)	
$2_{12} \rightarrow 3_{13}$	21,340.94 (0.09)	21,202.76 (0.10)	20,701.63 (0.22)	21,309.00 (0.06)
$2_{11} \rightarrow 3_{12}$	24,881.83 (0.08)	24,694.19 (0.17)	24,018.53 (0.15)	24,814.85 (0.00)
$2_{21} \rightarrow 3_{22}$	23,216.89 (0.11)	23,049.99 (−0.44)	22,450.42 (−0.08)	23,166.07 (0.14)
$3_{03} \rightarrow 4_{04}$	29,452.10 (−0.01)	29,273.31 (0.02)	28,621.06 (−0.12)	29,403.78 (0.00)
$3_{21} \rightarrow 4_{22}$	32,327.25 (−0.30)	32,066.92 (−0.09)	31,133.59 (−0.13)	32,242.03 (−0.05)
$3_{13} \rightarrow 4_{14}$	28,291.04 (0.11)	28,111.44 (0.05)	27,459.33 (0.14)	28,250.57 (0.06)
$3_{12} \rightarrow 4_{13}$	32,943.75 (0.02)	32,701.50 (0.01)	31,827.75 (0.04)	32,857.79 (−0.05)
$3_{22} \rightarrow 4_{23}$	30,824.84 (−0.21)	30,607.30 (−0.13)	29,821.47 (−0.22)	30,758.82 (−0.21)
$4_{04} \rightarrow 5_{05}$	36,039.13 (−0.21)	35,829.78 (−0.19)	35,065.97 (−0.22)	35,987.22 (−0.06)
$4_{14} \rightarrow 5_{15}$	35,138.12 (0.02)	34,919.45 (−0.10)	34,124.62 (−0.02)	35,090.30 (−0.08)

[a] In MHz; estimated uncertainty = 0.10 MHz. [b] Values in parentheses are observed minus calculated frequencies in MHz. Rotational constants for calculated frequencies are in Table II.

TABLE II

OBSERVED ROTATIONAL PARAMETERS[a] FOR THE ISOTOPIC SPECIES OF NF_2CN

Parameter	NF_2CN	$NF_2{}^{13}CN$	$NF_2{}^{15}N$	$^{15}NF_2CN$
A	10,130.61 ± 1.2	10,128.76 ± 1.6	10,127.01 ± 1.5	10,083.91 ± 1.0
B	4462.10 ± 0.04	4425.99 ± 0.05	4296.54 ± 0.04	4447.75 ± 0.03
C	3276.83 ± 0.04	3257.48 ± 0.05	3186.96 ± 0.04	3274.23 ± 0.03
I_a	49.8857	49.8950	49.9037	50.1171
I_b	113.2602	114.1835	117.6239	113.6251
I_c	154.2273	155.1436	158.5762	154.3497
P_{aa}	108.8009	109.7160	113.1482	108.9289
P_{bb}	45.4264	45.4275	45.4280	45.4208
P_{cc}	4.4593	4.4675	4.4757	4.6962
κ	−0.654135	−0.659883	−0.680238	−0.655337

[a] Conversion factor 505,376 MHz u Å². Uncertainties in the rotational constants are twice the standard deviation of the fit.

the free molecule the CNH_2 atoms form a shallow pyramid with a very low barrier to inversion (~500 cal/mol).[3]

We examined the microwave spectrum of NF_2CN for three reasons, all of them associated with the structure of the molecule. First, we wished to compare the structure of the CNF_2 group in NF_2CN with that of the CNH_2 group in NH_2CN. We also wished to compare the CN bond lengths in the two molecules. Second, we recently examined the structure of PF_2CN[4] and found that the PCN angle deviated from linearity by about 8° and was tilted toward the lone pair of electrons on the phosphorus atom. The tilt was attributed to an interaction of the phosphorus lone pair with the π system of the CN bond or to a repulsion of the π system by the fluorine atoms. We wished to see if further examples of this tilt could occur in molecules where similar interactions were possible. Difluorocyanamide, NF_2CN, was an obvious candidate for an interaction of this type. Third, an infrared study[5] of NF_2CN reported eight observed fundamentals in the 245–4000-cm^{-1} region. The remaining mode, ν_9, attributed to an a'' motion of the NF_2 out-of-plane wagging, was predicted to lie near 190 cm^{-1}. In view of the fact that the lowest frequency mode of vibration in NH_2CN is the inversion mode of the NH_2 group, it seemed worthwhile to examine the nature of the lowest frequency mode in NF_2CN by assigning rotational spectra in this mode.

In the present study the microwave spectra of the parent and three isotopically substituted species of NF_2CN have been examined and the structural parameters have been determined. Rotational transitions in several low-frequency vibrational modes have been observed, transitions in two of the modes have been assigned, and rough relative intensity measurements have been made.

Experimental Section

Difluorocyanamide was prepared by fluorination of aqueous NH_2CN in buffered solution.[6] The isotopically labeled species were prepared by fluorination of the appropriately labeled NH_2CN, which in turn was prepared by allowing BrCN to interact with NH_3.[7] Samples of $Br^{13}CN$ and $BrC^{15}N$ were obtained by the interaction of Br_2 with the appropriate KCN. We confirmed the previous report[3] that the preparation of NH_2CN from either $^{15}NH_3$ and BrCN or NH_3 and $BrC^{15}N$ yields $^{15}NH_2CN$ and $NH_2C^{15}N$ in roughly equal proportions.

The microwave spectra of the samples were observed at Dry Ice temperature with conventional Stark-modulated spectrometers of our own construction and with a Hewlett-Packard R8460A MRR spectrometer.

Spectra.—The initial assignment of the spectrum of each of the various species was made by identifying several low-*J*, R-branch, *a*-type transitions by means of their Stark effect. Rotational constants were obtained from least-squares fits of the measured frequencies. Some transitions from the normal species exhibited small quadrupole splittings but no attempt at resolution was made. Also, *c*-type transitions, which are ex-

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[3] J. K. Tyler, L. F. Thomas, and J. Sheridan, *Proc. Chem. Soc., London*, 155 (1959); D. R. Lide, Jr., *J. Mol. Spectrosc.*, **8**, 142 (1962); D. J. Millen, G. Topping, and D. R. Lide, Jr., *ibid.*, **8**, 153 (1962); W. H. Fletcher and F. B. Brown, *J. Chem. Phys.*, **39**, 2478 (1963); E. M. Popov and I. P. Yakovlev, *Zh. Strukt. Khim.*, **9**, 54 (1968); J. N. MacDonald, D. Taylor, and J. K. Tyler, *J. Mol. Spectrosc.*, **26**, 285 (1968); T. R. Jones and N. Sheppard, *Chem. Commun*, 715 (1970).

[4] P. L. Lee, K. Cohn, and R. H. Schwendeman, *Inorg. Chem.*, **11**, 1917 (1972).

[5] N. B. Colthup, *Spectrochim. Acta, Part A*, **23**, 2167 (1967).

[6] M. D. Meyers and S. Frank, *Inorg. Chem.*, **5**, 1455 (1966).

[7] A. Murry and D. H. Williams, "Organic Syntheses with Isotopes," Interscience, New York, N. Y., 1958: Part I, p 589; Part II, p 1716.

pected, were not examined because of their relative weakness. The frequencies of the observed transitions of the four species in the ground vibrational state are given in Table I, and the rotational parameters computed from these frequencies are given in Table II.

Vibrational satellites arising from several low-frequency modes of vibration accompanied each ground state line. The frequencies of the transitions in the first two excited states of the lowest energy mode (designated here as v) and in the first excited state of a second mode (v') are listed in Table III. The corresponding rotational parameters are given in Table IV. On the basis of observed out-of-plane second moments (P_{bb}) it would appear that v is an out-of-plane mode (a'') and v' is probably an in-plane mode (a'). The vibrational frequencies of v and v' estimated from rough relative intensity measurements are 150 ± 30 and 220 ± 30 cm^{-1}, respectively.

TABLE III

FREQUENCIES[a] OF OBSERVED TRANSITIONS OF THE EXCITED STATES OF NF_2CN

Transition	$v = 1$	$v = 2$	$v' = 1$
$1_{01} \rightarrow 2_{02}$	15,342.80 (0.46)[b]	15,373.76 (0.12)	
$1_{11} \rightarrow 2_{12}$	14,313.65 (0.04)		
$1_{10} \rightarrow 2_{11}$	16,716.39 (−0.19)		
$2_{02} \rightarrow 3_{03}$	22,604.43 (0.37)	22,638.66 (0.21)	
$2_{20} \rightarrow 3_{21}$	23,941.50 (0.28)	24,017.73 (0.03)	
$2_{12} \rightarrow 3_{13}$	21,369.32 (0.11)	21,397.23 (0.09)	
$2_{11} \rightarrow 3_{12}$	24,958.09 (0.13)	25,033.85 (0.18)	24,952.11 (−0.03)
$2_{21} \rightarrow 3_{22}$	23,271.83 (−0.81)	23,327.88 (−0.19)	
$3_{03} \rightarrow 4_{04}$	29,482.00 (−0.05)	29,511.15 (−0.04)	29,544.61 (0.12)
$3_{21} \rightarrow 4_{22}$	32,441.94 (−0.14)		
$3_{13} \rightarrow 4_{14}$	28,324.05 (0.19)	28,356.23 (0.05)	28,379.08 (0.05)
$3_{12} \rightarrow 4_{13}$	33,037.02 (0.21)	33,128.90 (−0.17)	
$3_{22} \rightarrow 4_{23}$	30,895.00 (−0.13)		
$4_{04} \rightarrow 5_{05}$	36,062.74 (−0.22)		36,154.30 (−0.08)
$4_{14} \rightarrow 5_{15}$	35,173.28 (0.04)	35,207.47 (−0.12)	35,248.36 (−0.04)

[a] In MHz; estimated uncertainty is ±0.10 MHz. [b] Values in parentheses are observed minus calculated frequencies in MHz.

TABLE IV

ROTATIONAL PARAMETERS[a] FOR THE EXCITED STATES[b] OF NF_2CN

Parameter	$v = 1$	$v = 2$	$v' = 1$
A	10,102.77 ± 1.5	10,076.72 ± 1.5	10,168.49 ± 1.5
B	4479.52 ± 0.05	4496.86 ± 0.05	4474.16 ± 0.05
C	3278.03 ± 0.05	3279.17 ± 0.05	3287.42 ± 0.05
P_{bb}	45.6875 ± 0.0038	45.9429 ± 0.0038	45.2379 ± 0.0038

[a] The rotational constants are in MHz. The second moment $P_{bb} = (I_a + I_c - I_b)/2$ is in u Å^2. [b] The lowest frequency vibrational mode is designated by the quantum number v and the next lowest frequency mode is designated v'.

Molecular Structure.—The rotational constants of the four isotopic species of NF_2CN shown in Table II yield nine independent moments of inertia. If a plane of symmetry is assumed, there are nine different nonzero atomic coordinates in the principal inertial axis system. The nine moments of inertia together with two center-of-mass relations ($M_a = 0$ and $M_c = 0$) and one product-of-inertia relation ($I_{ac} = 0$) are more than sufficient to determine the nine coordinates.

Two different sets of atomic coordinates were derived from the moments. One set (the "r_0" set) was obtained by adjusting the nine coordinates to provide a best fit in the least-squares sense to the experimental values of I_a, I_b, and I_c for the parent molecule, to I_b and I_c for the substituted molecules, and to zero for the two center-of-mass relations and the product-of-inertia relation. The I_a values of the substituted molecules were excluded from this calculation because they are considerably less precise than the I_b and I_c values.

A second set of coordinates (the "Kr" set) was derived by using the Kraitchman equations[8] to obtain the a and c coordinates of the carbon atom and the two nitrogen atoms. Because of the low precision of the I_a values, the Kraitchman equations used were those which involve I_b and I_c and which assume a plane of symmetry. The three coordinates of the fluorine atoms were then adjusted to give the best least-squares fit to the out-of-plane second moment of the parent molecule and the three nontrivial principal-axis relations. The coordinates of the r_0 and Kr sets are shown in Table V, and the bond distances and bond angles derived from these coordinates are compared with corresponding values for related molecules in Table VI.

TABLE V

CARTESIAN COORDINATES[a] (Å) IN THE PRINCIPAL AXIS SYSTEM OF NF_2CN

Atom	Method[b]	a	b	c
C	r_0	0.9623 ± 0.0017	0.0	0.0463 ± 0.0221
	Kr	0.9651 ± 0.0018	0.0	0.0908 ± 0.0245
N_1	r_0	2.1016 ± 0.0008	0.0	−0.1197 ± 0.0129
	Kr	2.1024 ± 0.0008	0.0	−0.1268 ± 0.0132
N_2	r_0	−0.3571 ± 0.0047	0.0	0.4903 ± 0.0034
	Kr	−0.3607 ± 0.0047	0.0	0.4940 ± 0.0034
F	r_0	−0.9468 ± 0.0017	±1.0934 ± 0.0015	−0.1512 ± 0.0099
	Kr	−0.9451 ± 0.0081	±1.0934 ± 0.0039	−0.1546 ± 0.0118

[a] The uncertainties in all the coordinates except the c coordinate of the C atom include a vibration–rotation contribution (estimated to be $\delta q = 0.0015/q$) and an experimental contribution. The uncertainty in the carbon c coordinate was estimated from the relation $\Sigma m_i c_i = 0$ and the uncertainties in the remaining c coordinates. [b] The r_0 and Kr methods are described in the text.

TABLE VI

MOLECULAR PARAMETERS[a] OF NF_2CN AND RELATED MOLECULES

Parameter	NF_2CN^b		CH_3-NF_2[e]	HNF_2[d]	NF_3[c]	NH_2-CN[f]
	r_0	Kr				
C≡N	1.151 ± 0.004	1.158 ± 0.004				1.160
N—C	1.392 ± 0.009	1.386 ± 0.009	1.449			1.346
N—F	1.398 ± 0.005	1.399 ± 0.008	1.413	1.400	1.371	
NCN	169.7 ± 2.1	173.9 ± 2.2				
CNF	104.7 ± 0.6	105.4 ± 0.7	104.6			
FNF	102.9 ± 0.4	102.8 ± 0.5	101.0	102.9		

[a] Bond distances in ångströms and bond angles in degrees. [b] The methods used to obtain the r_0 and Kr structures are described in the text. For the r_0 structure $\Sigma m_i a_i = \Sigma m_i c_i = \Sigma m_i a_i c_i = 0.0000$. For the Kr structure $\Sigma m_i a_i = 0.0581$, $\Sigma m_i c_i = -0.3554$, $\Sigma m_i a_i c_i = -0.3760$. [c] S. N. Ghosh, R. Trambarulo, and W. Gordy, *J. Chem. Phys.*, **21**, 308 (1953). [d] D. R. Lide, Jr., *ibid.*, **38**, 456 (1963). [e] Reference 12. [f] Reference 11.

It is clear from values of the coordinates in Table V that the a coordinates are considerably more precise than the c coordinates. It is known that the Kraitchman equations become increasingly more unreliable as coordinates become smaller than 0.1 Å. The Kraitchman values for the c coordinates in the atoms of the cyanide group are marginal in this regard. Consequently, several other sets of coordinates were derived (all by means of a recently developed computer program STRFIT). In one set the c coordinates of the cyanide atoms were omitted from the Kraitchman calculation and included with the fluorine coordinates in a least-squares fit of I_a, I_b, and I_c of the parent molecule and the three nontrivial principal axis relations. Although the use of first moment and cross-product relations is usually recommended for substitution coordinates which are too small, in this case the results were not satisfactory. The C≡N distance obtained was 1.146 Å and the NCN angle was 165.6°. Furthermore, the c coordinates of the C≡N atoms were considerably smaller than the substitution coordinates, whereas it is most likely that one or both of them should be larger.

The three sets of coordinates described above were also recalculated after making the Laurie corrections[9] to the moments of inertia. For these corrections the differences between moments of inertia calculated for the Kr structure in Table V and moments calculated for structures in which all distances to substituted atoms have been reduced by 0.00005 Å are added to the experimental moments of inertia. The main result of this calculation was to reduce the differences between the Kr and

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(8) J. Kraitchman, *Amer. J. Phys.*, **21**, 17 (1953).

(9) V. W. Laurie and D. R. Herschbach, *J. Chem. Phys.*, **37**, 1687 (1962).

r_0 structures. However, the mean values of the distances and angles changed only slightly (±0.001–0.004 Å and ±0.0–1.0°).

For most purposes the Kr structure in Table VI is probably more reliable than the r_0 structure. Since the nonlinear N—C≡N geometry is the most striking structural feature, we calculated the change in *c* coordinates which would be required to make the NCN angle 180°. An increase of 0.136 Å in the *c* coordinate of the cyanide nitrogen atom, a decrease of 0.073 Å in the *c* coordinate of the carbon atom, or some combination of smaller changes would increase the NCN angle to 180°.

Dipole Moment.—The Stark splitting of the 1_{01}–2_{02} and 1_{11}–2_{12} transitions were measured as a function of electric field, and the results are summarized in Table VII. The total dipole moment is 1.10 ± 0.02 D and makes an angle of 21° with the *a* axis.

In Table VIII dipole moment data are presented for molecules of the types PF_2X and NF_2X, where X is F, H, CH_3, and CN. Although the dipole moment of the phosphorus compound is greater than that of the nitrogen compound when X is F or CN, the dipole moment of the nitrogen compound is greater when X is H or CH_3. These data can be rationalized by suggesting that the lone pair of electrons in the nitrogen compounds contributes to the dipole moment to a larger extent than does the lone pair of electrons in the phosphorus compounds. This argument has been presented before to account for the trend in the dipole moments of $NH_n(CH_3)_{3-n}$ and $PH_n(CH_3)_{3-n}$, where n = 0, 1, 2, and 3.[10]

TABLE VII

STARK COEFFICIENTS AND DIPOLE MOMENT FOR NF_2CN

Transition	M	$(d\nu/dE^2)_{obsd}$[a]	$(d\nu/dE^2)_{calcd}$[a]
$1_{01} \rightarrow 2_{02}$	0	−5.05	−4.92
$1_{01} \rightarrow 2_{02}$	1	5.54	5.59
$1_{11} \rightarrow 2_{12}$	1	4.55	4.36

$\mu_a^2 = 1.060 \pm 0.032\ D^2$ $\quad\mu_a = 1.03 \pm 0.02$ D

$\mu_c^2 = 0.154 \pm 0.030\ D^2$ $\quad\mu_c = 0.39 \pm 0.10$ D

$\theta_a = 20.8°$ $\quad\mu = 1.10 \pm 0.02$ D

[a] In MHz $(kV/cm)^{-2}$; $\mu_{OCS} = 0.7152$ D assumed.

TABLE VIII

DIPOLE MOMENTS (DEBYES) OF NF_2CN AND RELATED MOLECULES

Molecule	μ_D	Molecule	μ_D
PF_3	1.03[a]	NF_3	0.23[a]
HPF_2	1.32[b]	HNF_2	1.93[c]
CH_3PF_2	2.06[d]	CH_3NF_2	2.57[e]
$CNPF_2$	2.39[f]	$CNNF_2$	1.10[g]

[a] S. N. Ghosh, R. Trambarulo, and W. Gordy, *J. Chem. Phys.*, **21,** 308 (1953). [b] R. L. Kuczkowski, *J. Amer. Chem. Soc.*, **90,** 1705 (1968). [c] D. R. Lide, Jr., *J. Chem. Phys.*, **38,** 456 (1963). [d] E. G. Codding and R. H. Schwendeman, private communication. [e] Reference 12. [f] Reference 4. [g] This work.

Discussion

The structure of NF_2CN is presented in planar projection in Figure 1, and the structural parameters are compared with those of several similar molecules in Table VI. The significant structural features are as follows: (1) the pyramidal nature of the bonds to nitrogen in NF_2CN is much more pronounced than in NH_2CN;[11] (2) the NCN angle is appreciably smaller than the expected 180°; (3) the N–C distance in NF_2CN is ~0.05 Å shorter than in CH_3NF_2[12] and ~0.05 Å longer than in NH_2CN;[11] and (4) the C≡N distance is comparable to that in NH_2CN.[11]

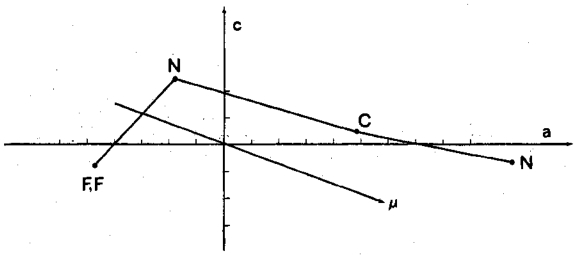

Figure 1.—A projection of NF_2CN in its *ac* plane of symmetry. The probable orientation of the dipole moment is also shown.

The pyramidal nature of the bonds to the NF_2 nitrogen in NF_2CN can be rationalized by assuming a repulsion between the nitrogen lone-pair electrons and the bonding pairs. Presumably in NH_2CN[3] there is a greater involvement of the nitrogen lone pair with the CN π system. As a result, the bonds to nitrogen form a shallower pyramid in NH_2CN than in NF_2CN and the increased double-bond character in NH_2CN leads to a shorter NC bond length. The shortened NC bond length in NF_2CN compared to CH_3NF_2 may still be explained as due to partial double-bond character in NF_2CN, or it may be the result of fewer repulsive interactions when an sp^3-hybridized atom faces an sp-hybridized atom.

As in PF_2CN,[4] the bent NCN angle in NF_2CN may be attributed to either or both of two effects. A bonding interaction between the lone-pair electrons of the NF_2 nitrogen and the CN π system, which would tend to shorten the NC bond, would also lead to a tilt in the observed direction since a tilt of the CN bond toward the lone pair would increase the interaction. Also, as in PF_2CN,[4] an electrostatic repulsion between the fluorine atoms and the CN π system would lead to the observed tilt. Detailed quantum mechanical calculations of NH_2CN and NF_2CN are needed to quantitatively characterize the interactions described here.

The present evidence obtained for the two modes of vibration tends to confirm the assignments of ν_6 and ν_9 in the infrared spectrum.[5] The NF_2 out-of-plane wagging mode (ν_9), predicted by the analysis of the infrared spectrum[5] to be at 190 cm^{-1}, may be assigned to the mode labeled v estimated here at 150 ± 30 cm^{-1}. The NF_2 rocking mode (ν_6), observed at 258 cm^{-1}, is probably the mode labeled v' which we estimate at 220 ± 30 cm^{-1}. With the structural parameters now determined experimentally, detailed force-field calculations of NF_2CN should give additional information about its electronic structure.

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