Microwave Spectrum and Structure of Dimethylaminodifluorophosphine, $PF_2N(CH_3)_2$

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Abstract: The microwave spectra of $PF_2N(CH_3)_2$ and $PF_2N(CD_3)_2$ have been measured in the frequency range 8000–40,000 MHz. The values of the rotational and distortion constants (in MHz) obtained from the measured transitions for $PF_2N(CH_3)_2$ and $PF_2N(CD_3)_2$, respectively, are as follows: A, 4315.6 ± 2.7, 3748.8 ± 1.0; B, 2164.75 ± 0.01, 1940.08 ± 0.02; C, 2090.95 ± 0.01, 1803.41 ± 0.02; D_J, 0.0009019 ± 0.0000770, 0.0006047 ± 0.0001444; D_{JK}, 0.0006928 ± 0.0003480, 0.0002452 ± 0.0003766. The structural parameters consistent with the experimental data show that the molecule has a semiplanar structure in which phosphorus, nitrogen, and the two carbons lie in the same plane, which is the symmetry plane for the molecule in good agreement with the results of the X-ray analysis for such a molecule. No reasonable fitting of rotational constants has been found for a "gauche" conformation with a "short" P–N bond length and a PNC_2 angle lower than 175° in contrast with the electron diffraction results.

Some interest has been shown in recent years for the study of the P–N bond nature. In many cases a $(p–d)\pi$-type bond has been postulated as deriving from the delocalization of the lone pair electrons of nitrogen into empty d orbitals of the phosphorus atom.[1] A recent X-ray structure of $PF_2N(CH_3)_2$ by Morris, *et al.*,[2] has shown a structure in which phosphorus, nitrogen, and the two carbons are in the same plane, which is a symmetry plane for the molecule. Moreover the P–N bond has been found to be anomalously short ($\simeq 1.625$ Å) indicating a probable adduct $(p–d)\pi$ in the solid state.

We decided to analyze the microwave spectrum of $PF_2N(CH_3)_2$ to see if the planar conformation of the molecule is maintained in the gas phase. As we were completing the structural calculations, a paper on the structure of PF_2NH_2 and $PF_2N(CH_3)_2$ obtained from electron diffraction was published by Holywell, *et al.*[3]

The results obtained by these authors led to a non-planar gauche structure for both molecules, while still finding a short P–N bond ($\simeq 1.66$ Å). Apart from the P–N bond length, these results are in contrast with the planar structure obtained by Brittain, *et al.*,[4] for PF_2NH_2 from its microwave spectrum. In fitting the structural parameters of $PF_2N(CH_3)_2$ to our experimental data we took into consideration both possible conformations.

Experimental Section

The $PF_2N(CH_3)_2$ sample and the analogous hexadeuterated compound were prepared by gas-phase reaction between $HN(CH_3)_2$

and PF_3.[5] The samples were purified by fractional distillation and their purity was tested by ir spectroscopy. The microwave spectra were obtained with an HP-MRR 8400 C-type spectrometer in the range 8000–40,000 MHz. Transition frequencies were measured with an estimated maximum error of 0.02 MHz.

A fast-scan broad-banded spectrum showed a series of nearly equidistant bands due to unresolved R^a-type transitions. This type of spectrum gives an approximate value of $B + C$ and implies that the molecule is a nearly prolate symmetric top. A search for lines outside the R^a-bands proved to be unsuccessful and a-type transitions only have been observed for both isotopic species. The high-resolution scan of each observed band showed a rather large number of excited-state lines. The ground-state lines showed up as singlets, and no analysis of the excited-state lines has been attempted. All measurements were made at Dry Ice temperature, and the intensity of the spectrum rapidly decreased at higher temperature, disappearing completely at 0°.

Owing to the complexity of the spectrum, due to the presence of a large number of excited states, the first assignments were made by double resonance experiments on the $J = 2–3$ and $J = 3–4$ bands.

For the same reason every attempt to make an analysis of the Stark effect proved to be unsuccessful, and therefore no information on the dipole moment of the molecule has been obtained.

The quadrupole hyperfine structure due to the nitrogen atom was not resolved, and because of the consequent broadening it did not prove possible to measure the lines of the $J = 1–2$ band with good accuracy. In Table I the experimental and calculated frequencies are listed for the measured transitions of both isotopic species.

In Table II the rotational and the centrifugal distortion constants obtained from the analysis of the spectrum are listed.

Molecular Structure

The experimental values were insufficient for the determination of the molecular structure using a substitution method, because of the lack of isotopic species relative to phosphorus and fluorine. Therefore an approximate method of calculation was used to obtain conformational information on this molecule. An iterative procedure was then carried out by using relations of the form

$$A_{\text{exptl}} - A_{\text{calcd}} = \sum_R \frac{\partial A}{\partial R}\delta R, \text{ etc.}$$

where the R's are the structural parameters to be fitted to the experimental values of the rotational constants.

By starting with an assumed value of the rotational

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(3) G. C. Holywell, D. W. Rankin, B. Beagley, and J. M. Freeman, *J. Chem. Soc. A*, 785 (1971).

(4) A. H. Brittain, J. E. Smith, P. L. Lee, K. Cohn, and R. H. Schwendeman, *J. Amer. Chem. Soc.*, **93**, 6772 (1971).

(5) R. G. Cavell, *J. Chem. Soc.*, 1992 (1964).

Table I. Rotational Spectrum (in MHz) of $PF_2N(CH_3)_2$ and of $PF_2N(CD_3)_2$

	PF₂N(CH₃)₂		PF₂N(CD₃)₂	
Transition	Obsd	Calcd	Obsd	Calcd
$2_{1,2} \rightarrow 3_{1,3}$			11,020.90	11,020.87
$2_{0,2} \rightarrow 3_{0,3}$			11,200.65	11,200.74
$2_{1,1} \rightarrow 3_{1,2}$			11,430.65	11,430.63
$3_{1,3} \rightarrow 4_{1,4}$	16,871.40	16,871.34	14,686.47	14,686.31
$3_{0,3} \rightarrow 4_{0,4}$	17,003.90	17,004.00	14,900.90	14,900.57
$3_{2,2} \rightarrow 4_{2,3}$			14,967.73	14,968.02
$3_{2,1} \rightarrow 4_{2,2}$			15,041.20	15,041.27
$3_{1,2} \rightarrow 4_{1,3}$	17,166.38	17,166.37	15,231.62	15,231.46
$4_{1,4} \rightarrow 5_{1,5}$	21,085.67	21,085.71	18,345.43	18,345.44
$4_{0,4} \rightarrow 5_{0,5}$	21,241.04	21,241.10	18,574.47	18,574.33
$4_{2,3} \rightarrow 5_{2,4}$	21,273.95	21,273.91		
$4_{4,0} \rightarrow 5_{4,1}$	21,282.20	21,282.27	18,733.90	18,733.76
$4_{2,2} \rightarrow 5_{2,3}$	21,310.87	21,310.89		
$4_{1,3} \rightarrow 5_{1,4}$	21,454.11	21,454.10	19,023.18	19,023.48
$5_{1,5} \rightarrow 6_{1,6}$	25,297.87	25,297.92	21,997.51	21,997.55
$5_{0,5} \rightarrow 6_{0,6}$	25,469.46	25,469.41	22,220.72	22,220.89
$5_{4,2} \rightarrow 6_{4,3}$			22,485.91	22,485.68
$5_{2,4} \rightarrow 6_{2,5}$	25,524.92	22,525.03		
$5_{2,3} \rightarrow 6_{2,4}$	25,589.11	25,589.08	22,666.04	22,666.27
$5_{1,4} \rightarrow 6_{1,5}$	25,739.28	25,739.09	22,803.43	22,803.50
$6_{1,6} \rightarrow 7_{1,7}$	29,507.77	29,507.70	25,642.41	25,642.36
$6_{0,6} \rightarrow 7_{0,7}$			25,843.47	25,843.50
$6_{2,5} \rightarrow 7_{2,6}$	29,773.94	29,774.17	26,145.73	26,145.93
$6_{6,0} \rightarrow 7_{6,1}$			26,224.37	26,224.43
$6_{5,1} \rightarrow 7_{5,2}$	29,795.15	29,795.10	26,230.03	26,230.06
$6_{2,4} \rightarrow 7_{2,5}$			26,505.42	26,505.23
$6_{4,2} \rightarrow 7_{4,3}$	29,797.81	29,797.88		
$6_{3,4} \rightarrow 7_{3,5}$	29,802.42	29,802.33		
$6_{1,5} \rightarrow 7_{1,6}$	30,020.68	30,020.61	26,568.02	26,567.77
$7_{1,7} \rightarrow 8_{1,8}$	33,715.02	33,714.83		
$7_{2,6} \rightarrow 8_{2,7}$	34,020.82	34,021.00		

Table II. Rotational and Centrifugal Distortion Constants (in MHz) of $PF_2N(CH_3)_2$ and of $PF_2N(CD_3)_2$

	PF₂N(CH₃)₂	PF₂N(CD₃)₂
A	4315.6 ± 2.7	3748.8 ± 1.0
B	2164.75 ± 0.01	1940.08 ± 0.02
C	2090.95 ± 0.01	1803.41 ± 0.02
D_J	0.0009019 ± 0.0000770	0.0006047 ± 0.0001444
D_{JK}	0.0006928 ± 0.0003480	0.0002452 ± 0.0003766

tion between calculated and observed values of the rotational constants was a minimum.

As a starting structure, that obtained by X-ray diffraction[2] was chosen. Such a structure shows a planar conformation of the P–N–C(C) group and the plane is a symmetry plane for the molecule, while the NC_2 group possesses no symmetry.

The parameters of the CH_3 groups were assumed to be

Table III. Bond Distances[a] and Bond Angles[b] for $PF_2N(CH_3)_2$

	X-Ray[2]	Electron diff[3]	This work			PF₂NH₂[4]
			Gauche structure	Semiplanar structure		
PF	1.610	1.589	1.60	1.57		1.587
FPF	91.5	99.0	93.3	95.3		94.6
NPF	101.6	97.0	98.5	99.8		100.6
PN	1.628	1.648	1.75	1.66		1.65
PNC₂		148.0	155.4			
PNC_cis	123.7			124.5		123.1 (PNH_cis)
		118.0	118.0[c]			
PNC_trans	120.4			121.3		119.7 (PNH_trans)
NC_cis	1.485			1.48[c]		
		1.448	1.45			
NC_trans	1.46			1.46[c]		
Dihedral		86.0	86.0[c]			
HCH					108.6[d]	
CH					1.09[d]	

[a] In Å. [b] In degrees. [c] Assumed values. [d] See ref 6.

constants, the derivatives $\partial A/\partial R$, $\partial B/\partial R$, and $\partial C/\partial R$ were calculated and the previous system solved for the δR's by a least-squares method. The values of the δR's so obtained were used to calculate new rotational constants and the process was iterated until the deviation

the average of those determined for the $NH(CH_3)_2$ molecule[6] (see Table III).

By such an assumption the independent parameters

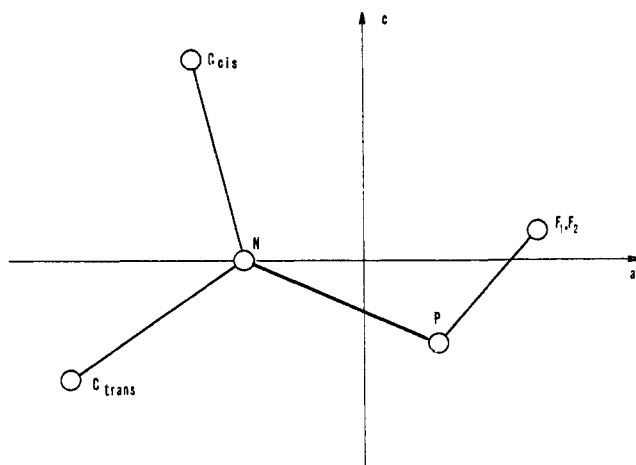(6) J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, 48, 5058 (1968).

Figure 1. Projection of $PF_2N(CH_3)_2$ in its plane of symmetry.

left to define the structure were reduced to eight: four bond lengths (PF, PN, NC_{cis}, NC_{trans}) and four bond angles (FPF, FPN PNC_{cis}, PNC_{trans}). As the experimental data available were only six, a preliminary analysis to search for parameters whose variation would produce the minimum effect on the rotational constants was carried out. The two bond lengths NC_{cis} and NC_{trans} were found to meet this condition and were kept constant throughout the calculations. The least-squares fit analysis was then performed by using three to four parameters at a time changing them in turn until the best fit was reached. While this work was being done a gauche structure for the $PF_2N(CH_3)_2$ was obtained by electron diffraction.[3] In this structure the molecule possesses no symmetry, but both PF_2 and NC_2 groups have a symmetry plane with a dihedral angle of $86 \pm 2°$. A new fitting was then tried with this structure as starting point, by using the same assumptions made for the CH_3 groups. The structural parameters were still eight: three bond lengths (PF, PN, NC) and five bond angles (FPF, FPN, PNC, CNC, dihedral). As in the previous case, two parameters were kept constant, that is the PNC and the dihedral angles. The results of the fitting for both structures are listed in Table III together with the X-ray and the electron diffraction data for comparison. In Table III the parameters obtained by Brittain, et al.,[4] for the PF_2NH_2 molecule are also listed. In Table IV the values of the

Table IV. Calculated Rotational Constants[a] of $PF_2N(CH_3)_2$ and $PF_2N(CD_3)_2$ from the Structural Parameters of Table III

		Gauche structure	Semiplanar structure
$PF_2N(CH_3)_2$	A	4309.3 $(-6.3)^b$	4313.6 (-2.0)
	B	2162.84 (-2.94)	2166.87 $(+1.09)$
	C	2088.39 (-1.82)	2090.11 $(+0.90)$
$PF_2N(CD_3)_2$	A	3757.8 $(+8.7)$	3747.3 (-1.82)
	B	1941.94 $(+1.90)$	1941.47 $(+1.42)$
	C	1807.39 $(+3.95)$	1803.75 $(+0.31)$

[a] In MHz. [b] Deviations from experimental values.

rotational constants calculated from the parameters of Table III for the semiplanar and gauche structural conformations are listed together with the deviations from the observed values.

The value of the difference ΔP_{cc} between the second

moment $P_{cc}^{(D)}$ for the deuterated species and that for the normal species $P_{cc}^{(H)}$ in the assumption of a plane of symmetry is $\Delta P_{cc} = 4c_H^2(m_D - m_H)$ with c_H the hydrogen coordinates along the c axis. Using the experimental values of the rotational constants given in Table II one obtains $\Delta P_{cc} = 3.102 \pm 0.055$ amu Å^2. With the parameters assumed for the methyl groups (see Table III) one obtains $\Delta P_{cc} = 3.139$ amu Å^2, which is in good agreement with the experimental one.

The coordinates of the atoms in the principal axis system for the $PF_2N(CH_3)_2$ molecule in the semiplanar conformation are given in Table V while the projection

Table V. Coordinates[a] of the Atoms in the Principal Axis System of $PF_2N(CH_3)_2$

Atom	a	b	c
N	−0.94	0.01	0.00
C_{cis}	−1.27	1.45	0.00
$H_{1(cis)}$	−2.35	1.60	0.00
$H_{2(cis)}$	−0.85	1.93	0.89
$H_{3(cis)}$	−0.85	1.93	−0.89
$C_{(trans)}$	−2.11	−0.87	0.00
$H_{1(trans)}$	−3.03	−0.27	0.00
$H_{2(trans)}$	−2.11	−1.50	0.89
$H_{3(trans)}$	−2.11	−1.50	−0.89
P	0.60	−0.61	0.00
F	1.23	0.25	±1.16

[a] In Å.

of the molecule on its own symmetry plane is given in Figure 1.

Discussion

By comparison of the results listed in Table III it is evident that with the presently available microwave data, the structure obtained by starting from the X-ray structure does not differ substantially from this one.

On the other hand, it did not prove possible to obtain a reasonable fitting for the "gauche" conformation with a "short" P–N bond length, which instead seems to be a characteristic result of all kinds of investigations made for these type of molecules.[2–4]

Finally the microwave results obtained for a similar molecule, PF_2NH_2, lead[4] to a semiplanar structure whose parameters are listed in Table III for comparison.

In conclusion, from the previous considerations it appears that the present experimental results can be interpreted to a good degree of confidence on the basis of the semiplanar conformation.

However, we were aware that the semiempirical calculation[7] predicts the possibility of a pyramidal structure at the nitrogen atom, and, therefore, we performed a theoretical analysis on the $PF_2N(CH_3)_2$ molecule within the framework of the CNDO scheme[8] by using the molecular parameters of Table III and allowing for several nonplanar configurations. In this way it has been confirmed that the CNDO energies are in favor of a nonplanar configuration.

Some more calculations were therefore performed using the fitting method described before; starting from the data of Table III for the semiplanar structure the

(7) Professor K. Mislow, Princeton University, private communication.

(8) J. A. Pople, D. P. Santry, and G. A. Segal, J. Chem. Phys., 43, S129 (1965); J. A. Pople and G. A. Segal, ibid., 43, S136 (1965); 44, 3289 (1966); D. P. Santry and G. A. Segal, ibid., 47, 158 (1967).

angle between the CNC and the starting P–N–C(C) planes was increased by steps.

Such calculations have clearly shown that for angles up to ±5°, the fitting of the rotational constants is unaffected. Similar results have been obtained by evaluating ΔP_{cc} for different nonplanar configurations within the error of experimental ΔP_{cc}. A maximum deviation from planarity of 4° has been found. Unfortunately variations of the methyl parameters within the values found by Wollrab[6] for the $HN(CH_3)_2$ molecule yield variations of the same order on ΔP_{cc}, and therefore the present results cannot give any information of a possible departure of the molecule from the semiplanar conformation. This uncertainty could probably be overcome if experimental data for isotopic species like PF_2N-

$(CH_3)(CD_3)$ were available. However, because of lack of symmetry in the NC_2 group, the spectrum of such a molecule would be made up by the transitions relative to the two possible isomers. Both intensity considerations and the fact that the precalculated spectra of the two isomers show partial overlapping, together with the added complexity due to the vibrational satellites, would make a successful analysis of such a spectrum rather improbable.

An Extension of the E and C Equation to Evaluate Constant Contributions to a Series of Observed "Enthalpies of Adduct Formation"

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Abstract: When an attempt was made to obtain E_A and C_A numbers for the hydrogen bonding acid 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) by computer-fitting calorimetrically measured enthalpies of interaction of HFIP with various Lewis bases, the fit was much poorer then one would anticipate. The difficulty was believed due to the demonstrated intramolecular hydrogen bonding in HFIP between the hydroxyl proton and the $-CF_3$ fluorine. If one subtracts a constant amount, -1.1 kcal mol^{-1}, to account for the intramolecular interaction, from each of the experimentally measured enthalpies, a suitable fit of the data can be obtained. E_A and C_A parameters of 5.93 and 0.623, respectively, are determined for HFIP. The use of these new parameters, which incorporate the intramolecular interaction, is described. The addition of this constant amount is justified by deriving an E and C equation to describe competitive equilibria. It is shown that when there is some effect that produces a constant contribution to a series of measured enthalpies toward donors whose E_B and C_B numbers are known, this equation can often be solved for this unknown quantity. The procedure is checked on systems where the constant amount being added can be determined independently. The procedure is invaluable for incorporating systems in which there is intramolecular association into the E and C scheme. It has the potential of extending this treatment to dimers which must be dissociated to form adducts and whose enthalpy of dissociation is not known. Displacement reactions also fall in the category of reactions containing a constant contribution to measured enthalpies.

I n the course of our studies on hydrogen bonding acids, we have had occasion to examine 1,1,1,3,3,3-hexafluoro-2-propanol, HFIP, a very interesting acid that has been previously studied extensively as a Lewis acid by Purcell and coworkers.[1,2] Upon attempting to fit their data to our E and C equation[3]

$$-\Delta H = E_A E_B + C_A C_B \qquad (1)$$

(where E_A and C_A are empirical parameters for acids and E_B and C_B are empirical parameters for bases), we did not get as good a fit as one might expect considering this is a hydrogen bonding acid. We repeated measurements on several of the reported systems, and when we

limited the attempted correlation only to our data, the expected fit still did not result.

One of the complications with HFIP is the demonstrated[4] intramolecular hydrogen bonding between the hydroxyl proton and the $-CF_3$ fluorine. In HFIP, two different rotamers are present, a and b. Infrared mea-

a   b
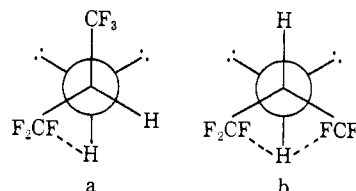
surements have been interpreted to indicate that b is the predominant species. The enthalpy of interconversion

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