Microwave Spectrum, Structure, Dipole Moment, and Quadrupole Coupling Constants of Aminodifluorophosphine[1]

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Abstract: The microwave spectrum of PF_2NH_2 is consistent with a molecule containing a planar nitrogen configuration with the hydrogen atoms in the symmetry plane. The structural parameters are: $d(PF) = 1.587 \pm 0.004$ Å, $\angle FPF = 94.6 \pm 0.2°$; $d(PN) = 1.650 \pm 0.004$ Å, $\angle FPN = 100.6 \pm 0.2°$; $d(NH_{cis}) = 1.002 \pm 0.005$ Å, $\angle HNH = 117.2 \pm 0.4°$; $d(NH_{trans}) = 0.981 \pm 0.005$ Å $\angle PNH_{cis} = 123.1 \pm 0.2°$, $\angle PNH_{trans} = 119.7 \pm 0.4°$. Quadrupole coupling constants for the ^{14}N nucleus in $PF_2{}^{14}NH_2$ have the values $\chi_{aa} = 1.7 \pm 0.1$, $\chi_{bb} = -3.5 \pm 0.3$, and $\chi_{cc} = 1.8 \pm 0.3$ MHz. The dipole moment components for $PF_2{}^{14}NH_2$ were determined to be $\mu_a = 2.570 \pm 0.007$, $\mu_c = 0.18 \pm 0.01$ D and yield a total dipole moment of 2.58 ± 0.01 D which is inclined at an angle of 25.1° to the PN bond. The proton nmr spectrum of liquid $PF_2{}^{15}NH_2$ contains a single pair of transitions. The splitting, attributed to ^{15}N–H coupling, is 83.2 Hz, which is close to the value expected for a planar $-NH_2$ group. No further splitting is observed down to −70°, suggesting that on the nmr time scale the molecule is undergoing a rapid intramolecular conversion, probably an internal rotation about the P–N bond.

In recent years there has been considerable discussion about the nature of the P–N bond. Some of the physical and chemical data for compounds containing PN bonds have been rationalized by postulating the existence of a (p–d)π bond arising from delocalization of the lone pair of electrons on the nitrogen atom into empty d orbitals of the phosphorus atom.[2–5]

The recently prepared compound aminodifluorophosphine, PF_2NH_2,[6] appeared to be an excellent example for investigation of possible effects of (p–d)π bonding. Consequently, we have examined the microwave spectrum of the parent compound and four isotopically labeled species. We also examined the proton nmr spectrum of a sample of liquid $PF_2{}^{15}NH_2$.

Table I. Hypothetical Unsplit Frequencies[a] for Isotopic Species of PF_2NH_2

Transition	$PF_2{}^{14}NH_2$		$PF_2{}^{15}NH_2$		PF_2NHD(cis)		PF_2NHD(trans)		PF_2ND_2	
0_{00}–1_{01}	11648.76	0.04[b]	11338.70	0.04	11160.72	0.06	10932.42	0.00	10514.55	0.06
1_{10}–2_{11}	25753.19	−0.09	25004.55	−0.07	24495.61	−0.12	24037.23	0.01	22962.71	−0.05
1_{11}–2_{12}	20841.47	−0.09	20349.96	−0.07	20146.3[c]	−0.6	19692.48	0.02	19095.19	−0.03
1_{01}–2_{20}	32941.17	0.05								
1_{01}–2_{02}	21421.15	−0.05	21048.36	−0.11	20827.56	−0.04	20159.48	−0.13	19943.48	−0.03
2_{02}–2_{21}			9975.72	0.10	9495.95	0.02	10526.21	0.13		
4_{23}–4_{22}	12703.83	−0.01	11838.52	0.10	11010.20	−0.29	10673.23	0.29	9177.80	−0.06
4_{13}–4_{32}	14583.47	−0.98								
5_{33}–5_{32}	11444.93	0.02	10106.93	0.18						
5_{23}–5_{42}	15510.66	−2.51								
5_{05}–5_{24}					23206.32	−0.55				
7_{44}–7_{43}									9541.35	0.28
8_{54}–8_{53}	15404.52	1.09					9065.97	1.39		

[a] In megahertz. [b] Hypothetical unsplit frequency minus calculated frequency. [c] Interference from strong line at lower frequency.

Experimental Section

The aminodifluorophosphine used in this study was prepared by the reaction of ammonia with PF_2Cl.[6] The ammonia (Matheson) was dried over sodium before use. The PF_2Cl was prepared by the reaction of $(CH_3)_2NPF_2$ with HCl.[7] Samples enriched in $PF_2{}^{15}NH_2$ and PF_2ND_2 were prepared by reaction of PF_2Cl with $^{15}NH_3$ and ND_3, respectively. A sample containing a mixture of PF_2NHD species was prepared *in situ* by exchange of PF_2NH_2 with D_2O in the waveguide sample cell. The various samples were characterized by infrared, mass, and nmr spectra.

The microwave spectra of the samples were quite rich, with a predominance of *a*-type Q-branch transitions from which initial assignments were made. The assignments were completed by the measurement of the frequencies of several *a*-type R-branch transitions. No *b*-type or *c*-type transitions were identified. The ground-state transitions were accompanied by vibrational satellites, and transitions in several excited vibrational states of $PF_2{}^{14}NH_2$ and $PF_2{}^{15}NH_2$ were assigned. Quadrupole hyperfine structure was observed on most of the transitions (except for $PF_2{}^{15}NH_2$), but complete resolution of the hyperfine components was rarely possible because of rather large line widths.

The hypothetical unsplit frequencies of the observed transitions for the ground states of the various isotopic species are given in Table I, with the exception of some intermediate *J* transitions for $PF_2{}^{14}NH_2$ which are given in Table II. The corresponding frequencies for two vibrationally excited states of $PF_2{}^{14}NH_2$ and four vibrationally excited states of $PF_2{}^{15}NH_2$ are shown in Tables III

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[2] (a) K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969); (b) A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, **92**, 5206 (1970).

[3] (a) A. B. Burg and B. J. Slota, *ibid.*, **80**, 1107 (1958); (b) G. Ewart, D. S. Payne, A. L. Porte, and A. P. Lane, *J. Chem. Soc.*, 3984 (1962).

[4] (a) R. R. Holmes and R. P. Carter, *Inorg. Chem.*, **2**, 1146 (1963); (b) W. A. Hart and H. H. Sisler, *ibid.*, **3**, 617 (1964).

[5] (a) R. Schmutzler, *ibid.*, **3**, 415 (1964); (b) A. H. Cowley and R. P. Pinnell, *J. Amer. Chem. Soc.*, **87**, 4654 (1965); (c) A. H. Cowley and M. H. Hnoosh, *ibid.*, **88**, 2545 (1966); (d) K. Cohn and R. W. Parry, *Inorg. Chem.*, **7**, 46 (1968); (e) J. F. Nixon and M. D. Sexton, *J. Chem. Soc. A.*, 1089 (1969); (f) R. M. Kren and H. H. Sisler, *Inorg. Chem.*, **9**, 836 (1970).

[6] J. E. Smith and K. Cohn, *J. Amer. Chem. Soc.*, **92**, 6185 (1970).

[7] J. G. Morse, K. Cohn, R. W. Rudolph, and R. W. Parry, *Inorg. Syn.*, **10**, 147 (1967).

Table II. Hypothetical Unsplit Frequencies[a] of Intermediate J Transitions of $PF_2{}^{14}NH_2$

Transition	ν	$\Delta\nu$[b]	Transition	ν	$\Delta\nu$[b]
$5_{33}-5_{32}$	11444.93	0.02	$4_{13}-4_{32}$	14583.47	−0.98
$6_{34}-6_{33}$	18353.18	−0.83	$5_{23}-5_{42}$	15510.66	−2.58
$6_{43}-6_{42}$	9798.84	0.46	$6_{15}-6_{34}$	24940.83	−2.13
$7_{53}-7_{52}$	7903.54	1.18	$6_{33}-6_{52}$	17230.21	−5.25
$8_{54}-8_{53}$	15404.52	1.09	$7_{34}-7_{53}$	19995.52	−6.07
$9_{64}-9_{63}$	13195.68	3.27	$7_{43}-7_{62}$	20016.76	−9.39

[a] In megahertz. [b] Hypothetical unsplit frequency minus calculated frequency (rotational constants in Table V).

Table III. Hypothetical Unsplit Frequencies[a] of Vibrationally Excited States of $PF_2{}^{14}NH_2$

Transition	$\nu_{12} = 1$		$\nu_{12} = 2$	
$0_{00}-1_{01}$	11678.55	0.01[b]	11692.30	0.03[b]
$1_{10}-2_{11}$	25852.15	−0.01	25901.31	0.17
$1_{11}-2_{12}$	20862.00	−0.01	20868.10	0.06
$1_{01}-2_{02}$	21396.98	0.01	21380.98	−0.25
$5_{33}-5_{32}$	11857.34	0.00	12063.80	−0.06
$6_{43}-6_{42}$	10387.32	0.67	10680.43	0.45
$7_{53}-7_{52}$	8647.55	1.55	9021.45	1.66

[a] In megahertz. [b] Hypothetical unsplit frequency minus calculated frequency (rotational constants in Table VI).

Table IV. Hypothetical Unsplit Frequencies[a] of Vibrationally Excited States of $PF_2{}^{15}NH_2$

Transition	$\nu_{12} = 1$		$\nu_{12} = 2$		$\nu_{11} = 1$		$\nu_8 = 1$	
$0_{00}-1_{01}$	11365.83	0.01[b]	11378.56	0.00	11346.52	0.24		
$1_{10}-2_{11}$	25095.54	−0.02	25141.99	0.00	25040.04	0.19	25011.03	0.16
$1_{11}-2_{12}$					20345.41	0.11	20279.45	−0.13
$1_{01}-2_{02}$	21030.56	−0.03	21018.08	0.00	21027.31	−0.12	20952.15	0.04
$1_{01}-2_{20}$							32561.64	0.51
$2_{02}-2_{21}$	9857.75	−0.01			9926.89	0.04		
$2_{20}-3_{21}$					32828.39	−0.04	38205.38	−0.24
$2_{21}-3_{22}$					34038 71	−0.16	33967.51	−0.33
$4_{14}-4_{13}$					19042.70	0.39	19131.09	0.57
$4_{04}-4_{23}$					19262.12	0.38	19335.10	−0.14
$4_{23}-4_{22}$	12099.84	0.02					12094.14	−0.18
$5_{24}-5_{23}$					18466.27	−0.03	18585.22	−0.24
$5_{33}-5_{32}$	10510.85	−0.02					10471.54	−0.27

[a] In megahertz. [b] Hypothetical unsplit frequency minus calculated frequency (rotational constants in Table VI).

Table V. Rotational Constants,[a] Moments of Inertia,[b] Principal Second Moments,[b] and Quadrupole Coupling Constants[a] of PF_2NH_2

	$PF_2{}^{14}NH_2$	$PF_2{}^{15}NH_2$	PF_2NHD(cis)	PF_2NHD(trans)	PF_2ND_2
A	7766.22 (0.05)[c]	7756.02 (0.05)	7580.88 (0.08)	7761.48 (0.15)	7569.63 (0.15)
B	7052.29 (0.05)	6832.98 (0.05)	6667.53 (0.05)	6552.40 (0.05)	6224.13 (0.05)
C	4596.43 (0.05)	4505.69 (0.05)	4493.12 (0.05)	4380.02 (0.05)	4290.36 (0.05)
I_a	65.0736	65.1492	66.6645	65.1134	66.7636
I_b	71.6613	73.9613	75.7966	77.1284	81.1962
I_c	109.9498	112.1640	112.4777	115.3821	117.7934
P_{aa}	58.2687	60.4830	60.8049	63.6986	66.1130
P_{bb}	51.6810	51.6809	51.6729	51.6835	51.6804
P_{cc}	13.3926	13.4783	14.9917	13.4298	15.0832
ΔP_{bb}[d]	0.0000	−0.0001	−0.0081	0.0025	−0.0006
χ_{aa}	1.65 (0.13)		1.65[e]	1.17 (0.25)	1.65[e]
χ_{bb}	−3.45 (0.25)		−3.45[e]	−3.38 (0.39)	−3.45[e]
χ_{cc}	1.80 (0.25)		1.80[e]	2.21 (0.39)	1.80[e]

[a] In megahertz. [b] In unified atomic mass units (ångströms)^2. [c] Values in parentheses are experimental uncertainties. [d] $\Delta P_{bb} = P_{bb}$(isotopic species) − $P_{bb}(PF_2{}^{14}NH_2)$. [e] Value assumed from $PF_2{}^{14}NH_2$.

and IV, respectively. The transitions were observed and the frequencies measured with a 100-kHz Stark-modulated spectrometer using backward wave oscillators as microwave sources. The R-band transitions in the excited states of $PF_2{}^{15}NH_2$ were examined with a Hewlett-Packard R8460 MRR spectrometer. A search for the spectrum of another isomer of PF_2NH_2 was unsuccessful.

Spectral Analysis

The rotational constants, moments of inertia, principal second moments, and quadrupole coupling constants obtained by analysis of the spectra of the ground-state species are given in Table V. The value of the out-of-plane second moment, $P_{bb} = \Sigma m_i b_i^2$, is seen to be almost constant for all the isotopic species, suggesting that the molecule has a plane of symmetry containing the phosphorus, nitrogen, and both hydrogen atoms. The small variations in P_{bb} are attributed to vibrational changes from one isotopic species to another, and their magnitude is consistent with a planar $P-NH_2$ group. In formamide,[8] nonplanarity of the molecule was suggested upon comparison of the out-of-plane second moments (P_{cc} in this case) of the parent, NHD(trans), NHD(cis), and ND_2 species. The values of P_{cc} for the trans-D, cis-D, and ND_2 species were larger than that of the parent by 0.0058, 0.0120, and 0.0147 uÅ^2, respectively. The corresponding changes in P_{bb} for PF_2NH_2 are 0.0025, −0.0081, and −0.0006 uÅ^2. The fact that the changes are small and in two cases negative for PF_2NH_2 is strong evidence for a planar nitrogen configuration.

The rotational constants of the two vibrationally excited $PF_2{}^{14}NH_2$ and the four vibrationally excited $PF_2{}^{15}NH_2$ species which have been assigned are given in Table VI. These constants were derived from analy-

[8] C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960).

Table VI. Rotational Constants[a] of Vibrationally Excited Species of $PF_2{}^{14}NH_2$ and $PF_2{}^{15}NH_2$

		A	B	C
$PF_2{}^{14}NH_2$	$\nu_{12} = 1$	7731.28	7086.81	4591.73
	$\nu_{12} = 2$	7716.20	7104.42	4587.87
$PF_2{}^{15}NH_2$	$\nu_{12} = 1$	7722.09	6864.91	4500.82
	$\nu_{12} = 2$	7707.43	6881.72	4496.85
	$\nu_{11} = 1$	7738.48	6846.78	4499.51
	$\nu_8 = 1$	7717.00	6844.13	4478.49

[a] In megahertz.

ses of the frequencies of spectral lines given in Tables III and IV. In Tables III, IV, and V the various vibrational states have been numbered according to the following considerations. If a plane of symmetry is assumed for the vibrational potential function, the 12 vibrational motions divide into eight motions of symmetry A′ (in plane) and four of symmetry A′′ (out of plane). The lowest frequency A′ motion has been observed[9] in the infrared spectrum at 354 cm^{-1} and is called ν_8. The lowest frequency A′′ motion has a measured vibrational frequency of 170 cm^{-1} and is called ν_{12}. The next lowest A′′ motion, seen at 235 cm^{-1}, is referred to as ν_{11}. The fourth set of vibrational satellites assigned in the microwave spectrum is attributed to $2\nu_{12}$. Rough measurements of relative intensities give values which are in accord with these assignments.

Examination of the rotational constants for the ν_{12} and $2\nu_{12}$ species in Table VI reveals that the rotational constants do not vary in a harmonic manner. We believe that this is due to a vibration–rotation interaction between $2\nu_{12}$ and ν_8; the symmetries of the two states are the same and the energy difference is not large ($\sim$15 cm^{-1}).

The absence of unusual effects in the vibrational satellite pattern appears to confirm a plane of symmetry in PF_2NH_2. The best evidence for nonplanarity in formamide is probably the identification of a severely anharmonic vibration. No such phenomenon occurs for PF_2NH_2 unless the anharmonicity is very small. Nevertheless, since some question remains, and since PF_2NH_2 is an unusual molecule, the vibrational assignment and the question of vibration–rotation interaction is currently under investigation in these laboratories.[9a]

Molecular Structure

The coordinates of the atoms in the principal inertial axis system of PF_2NH_2 were determined from the moments of inertia of the five isotropically different species in four ways. (1) The coordinates of the nitrogen and hydrogen atoms were determined by means of the Kraitchman equations[10] assuming a plane of symmetry, the *b* coordinates of the fluorine atoms were determined by means of the relation $P_{bb} = 2m_F b_F{}^2$ where m_F is the mass of a fluorine atom and P_{bb} is a principal second moment of the parent species, and the remaining coordinates (the *a* and *c* coordinates of the phosphorus and fluorine atoms) were determined by least squares from the first-moment and cross-product relations of the parent species and from the values of P_{aa} and P_{cc} for PF_2NH_2 and PF_2ND_2. (2) All the nonzero coordinates were determined by minimization of the sum of the squares of the deviations between the calculated and the experimentally derived values of the second moments of all five species. First-moment relations and the in-plane cross-product relation were included in this least-squares procedure. (3) Calculation 1 was repeated after correcting the moments of inertia of the isotopically substituted species in the manner suggested by Laurie.[11] For this calculation, the length of each bond (except those to hydrogen atoms) is assumed to be reduced by 0.00005 Å upon substitution of a heavier isotope for one of the atoms of the bond. Deuterium substitution is assumed to shorten bonds to hydrogen by 0.003 Å. The experimentally derived moments of inertia are increased by the amount necessary to compensate for this decrease of bond lengths before applying the Kraitchman and least-squares procedures. (4) Calculation 2 was repeated after making the Laurie adjustment of the moments of inertia. All of the above calculations were performed with a recently developed structure-fitting computer program.

Structures calculated by procedures 1 and 2 were essentially equivalent; all bond distances agreed within 0.002 Å and all bond angles agreed within 0.1°. For procedures 3 and 4 the PN bond distance was greater by 0.002 Å and the two NH distances were each greater by 0.005 Å than the corresponding values for procedures 1 and 2. All the other distances and angles agreed within 0.001 Å or 0.1°. The deviation between observed and calculated first and second moments was more than three times smaller for calculation 3 than for calculation 1. It will be of interest to see if this is a general result for other molecules.

Coordinates of the atoms obtained by procedure 2 are given in Table VII and the corresponding bond distances and bond angles are given in Table VIII. A projection of PF_2NH_2 in its plane of symmetry is shown in Figure 1. The structural parameters in Tables VII and VIII are r_0 parameters.[12] The uncertainties in these tables include contributions from experimental uncertainties in the moments of inertia and from vibration–rotation effects.

Table VII. Coordinates[a] of the Atoms in the Principal Axis System of $PF_2{}^{14}NH_2$

Atom	*a*	*b*	*c*
P	0.0566	0.0	−0.4980
N	1.4986	0.0	0.3035
F	−0.7021	±1.1662	0.2650
H(cis)	1.5694	0.0	1.3025
H(trans)	2.3374	0.0	−0.2058

[a] In ångströms.

Dipole Moment

The shifts in the frequencies of eight Stark components of transitions in $PF_2{}^{14}NH_2$ were measured as a

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(9) P. L. Lee, K. Cohn, and J. E. Smith, unpublished results.

(9a) Note Added in Proof. In a recent electron diffraction study [G. C. Holywell, D. W. H. Rankin, B. Beagley, and J. M. Freeman, *J. Chem. Soc. A*, 785 (1971)] of gaseous PF_2NH_2 it was concluded that the nitrogen configuration was substantially pyramidal with the HNH plane making an angle af 146° with the P–N bond. However, this result was based on a model in which both of the N–H bonds and both of the P–N–H angles were assumed to be equal. In the present paper it is shown that these assumptions are invalid and that the microwave evidence is strongly in favor of a planar PNH_2 configuration.

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

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

(12) K. Kuchitsu and S. Konaka, *ibid.*, **45**, 4342 (1966).

Table VIII. Bond Distances,[a] Bond Angles,[b] and Comparison of Moments of Inertia[c] for $PF_2{}^{14}NH_2$

PF	1.587 ± 0.004	∠FPF	94.6 ± 0.2
PN	1.650 ± 0.004	∠FPN	100.6 ± 0.2
NH(cis)	1.002 ± 0.005	∠PNH(cis)	123.1 ± 0.2
NH(trans)	0.981 ± 0.005	∠PNH(trans)	119.7 ± 0.4
		∠HNH	117.2 ± 0.4

	Calcd	Obsd
I_a	65.0727	65.0736
I_b	71.6586	71.6613
I_c	109.9455	109.9497
$\Sigma m_i a_i$, uÅ	0.0000	
$\Sigma m_i c_i$, uÅ	0.0000	
$\Sigma m_i a_i c_i$, uÅ	0.0000	

[a] In ångströms. [b] In degrees. [c] In unified atomic mass units (ångströms)^2.

function of electric field (E) in a Stark cell which was calibrated by measuring the $J = 0 \rightarrow 1$ transition in OCS ($\mu_{OCS} = 0.7152$ D[13]). The Stark coefficients for these transitions were computed by neglecting the small quadrupole interaction. The eight slopes, $d\Delta\nu/dE^2$, were first fit by least squares with the assumption that all three components of the dipole moment are nonzero. The results were $\mu_a{}^2 = 6.609 \pm 0.026$, $\mu_c{}^2 = 0.031 \pm 0.0003$, and $\mu_b{}^2 = -0.009 \pm 0.031$ D^2, where the uncertainties are standard deviations of the fit. The small negative value obtained for $\mu_b{}^2$ confirms the presence of a plane of symmetry.

The eight slopes were then refit with the assumption of nonzero values for μ_a and μ_c only. The dipole moment components obtained were $\mu_a = 2.570 \pm 0.007$, and $\mu_c = 0.18 + 0.01$ D; the total dipole moment is $\mu = 2.576 \pm 0.007$ D. Here, the uncertainties are twice the standard deviations. A comparison of the experimental and calculated Stark slopes is presented in Table IX.

Table IX. Stark Coefficients in $PF_2{}^{14}NH_2$ and PF_2NHD(cis)

Transition	M	$d\nu/dE^2$ (obsd)[a]	Obsd − calcd[a,b]
$PF_2{}^{14}NH_2$			
0_{00}–1_{01}	0	77.48	1.20
1_{10}–2_{11}	0	−16.34	0.46
	±1	−152.6	1.0
1_{11}–2_{12}	0	20.01	0.26
	±1	181.1	0.2
1_{01}–2_{02}	0	−23.62	−0.11
	±1	10.30	0.57
7_{34}–7_{53}	±7	−22.22	0.15
PF_2NHD(cis)			
1_{01}–2_{02}	±1	14.0[c]	3.3 ($\theta = 3.9°$)[d] −0.6 ($\theta = -3.9°$)

[a] In MHz/(kV/cm)^2. [b] Calculated Stark coefficients assume $\mu_a{}^2 = 6.605$, $\mu_b{}^2 = 0$, 2.570 D^2. [c] Rough measurement, ±5%. [d] $\theta = \tan^{-1}(\mu_c/\mu_a)$ in $PF_2{}^{14}NH_2$; explanation given in text.

The dipole moment vector lies very close to the a axis ($\theta = \pm 3.9°$). Since deuteration of PF_2NH_2 to give PF_2NHD(cis) rotates the principal inertial axes by 2.4°, it is possible to determine the orientation of the dipole moment by measuring a single Stark shift in PF_2NHD(cis). For this purpose the Stark shift of the $M = \pm 1$ component of the 1_{01}–2_{02} transition was measured. The results are summarized at the bottom of Table IX, where it is shown that $\theta = -3.9°$, which is the orientation of the dipole moment shown in Figure 1.

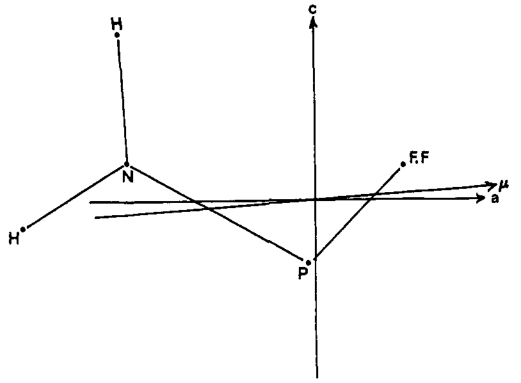

Figure 1. Projection of PF_2NH_2 in its plane of symmetry.

Discussion

The microwave and nmr data for PF_2NH_2 are consistent with the following conclusions: (a) the $-NH_2$ group is planar, (b) the plane of the $-NH_2$ group is the plane of symmetry of the PF_2 group, and (c) the molecule is undergoing an intramolecular conversion which, on the nmr time scale, is still rapid at −70°.

Stereochemical data of the sort presented here provides further support for a (p–d)π interaction. Previously, Morris and Nordman[14] showed that in the solid state the three bonds to the nitrogen in $(CH_3)_2NPF_2$ all lie in the same plane. This result could be interpreted as favoring (p–d)π bonding. Unfortunately, in the solid state it is always possible that the crystal forces may distort the geometry of the molecule. However, in PF_2NH_2 the three bonds to nitrogen are coplanar in the free molecule.

PF_2NH_2 appears to be the first case of a compound containing a planar $-NH_2$ group in the gas phase. Formamide,[8] aniline,[15] and cyanamide[16] have all been investigated in the gas phase and found to be nonplanar. The near planarity of formamide has been explained as being due to partial double bond character of the C–N bond, which is a result of conjugation of the lone-pair electrons on the nitrogen atom with the electrons in the CO π bond. Similarly, the near planarity of aniline has been explained as being the result of conjugation of the nitrogen lone pair with the π system of the ring. It is reasonable then to ascribe the planarity of the $-NH_2$ group in PF_2NH_2 to the formation of a (p–d)π bond.

Further confirmation of double bond character in the P–N bond in PF_2NH_2 is obtained by a comparison of the P–N bond length with values which are usually assumed to be typical of P–N single bonds and P=N double bonds. The P–N distance in NaH_3NPO_3 is 1.769 Å,[17] and this value is thought to be the P–N single bond length. For a typical P=N double bond, we may take $Ph_2FP{=}NMe$ where the P=N bond length is 1.641 Å.[18] The P–N bond length in PF_2NH_2 is 1.647 Å, which is seen to be considerably closer to a double bond length than to a single bond length. The P–N bond distance in $(CH_3)_2NPF_2$ is 1.628 Å in the solid,[13] which is 0.019 Å less than the P–N bond length in gaseous PF_2NH_2. It

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(13) J. S. Muenter, *J. Chem. Phys.*, **48**, 4544 (1968).

(14) E. D. Morris and C. E. Nordman, *Inorg. Chem.*, **8**, 1673 (1969).

(15) J. C. Evans, *Spectrochim. Acta*, **16**, 428 (1960).

(16) D. J. Miller, G. Topping, and D. R. Lide, *J. Mol. Spectrosc.*, **8**, 153 (1962); T. R. Jones and N. Sheppard, *Chem. Commun.*, 715 (1970).

(17) E. Hobbs, D. E. C. Corbridge, and B. Raistrick, *Acta Crystallogr.*, **6**, 621 (1953).

(18) G. W. Adamson and J. C. J. Bart, *J. Chem. Soc. A*, 1452 (1970).

is tempting to attribute this shortening to the increased inductive effect of CH_3 groups compared to H atoms, which would be expected to be important if the P–N bond in these compounds had significant π character.

Although the structural data obtained on PF_2NH_2 and $(CH_3)_2NPF_2$ add considerable support to a π-bonding model, it should be mentioned that a recent infrared and Raman investigation of $N[P(CF_3)_2]_3$ suggests that this molecule does not have a planar NP_3 skeleton.[19]

The ^{15}N–H coupling constant (83.2 Hz) obtained for $PF_2{}^{15}NH_2$ is also consistent with a planar $-NH_2$ group. A relationship between $^{1}J_{^{15}N-H}$ and the percentage 2s character in the nitrogen orbital used in the NH bond has been developed.[20] This relationship predicts 30% 2s character in the nitrogen orbitals bonded to the hydrogen atoms in PF_2NH_2; a planar $-NH_2$ group with sp^2 hybrids would require 33% 2s character.

The fact that no broadening or splitting of the lines in the nmr spectrum of $PF_2{}^{15}NH_2$ occurs down to -70° (near the freezing point) indicates that unless the chemical shifts of the two protons are accidentally identical, a rapid (on the nmr time scale) intramolecular conversion is taking place in this molecule. The conversion could be an inversion of the PF_2 group or an internal rotation about the P–N bond. Assumption of a reasonable difference in the chemical shifts of the two protons would lead to the conclusion that the potential barrier to interconversion is less than about 10 kcal/mol. This value is probably too small for a phosphorus inversion,[2b] and hence may be taken as an upper limit to the barrier to internal rotation about the P–N bond. In principle, this question can be settled by means of a vibrational analysis, and we are currently investigating the ir and Raman spectra of PF_2NH_2 with this goal in mind.

(19) P. J. Hentra, R. A. Johns, C. T. S. Miles, C. J. Vear, and A. B. Burg, *Spectrochim. Acta, Part A*, **26**, 2169 (1970).

(20) G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 5564 (1964); A. J. R. Bourn, D. G. Gillies, and E. W. Randall, *Tetrahedron*, **20**, 1871 (1964).

Raman Spectra of Schiff Bases of Retinal (Models of Visual Photoreceptors)

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Abstract: The resonance-enhanced Raman (RR) spectra of *trans*-retinal and of three of its Schiff bases in various solutions are presented and correlated with the corresponding solvent-shifted absorption spectra. The frequencies of solvent-shifted vibrational modes of the conjugated segment of retinal are plotted *vs.* the corresponding λ_{max}. The degree of π-electron delocalization in a given solvent is an implicit parameter for each point on the plot. The locus of points representing acidified Schiff bases differs from that of the unacidified ones. A single point representing preliminary data on lumirhodopsin in whole bovine retina fits well into the locus of acidified Schiff bases. Stretching modes of C=O and C=N, as well as other vibrational modes, are identified. The Raman spectrum of acidified retinal looks as if contributed by a single solute species, while the corresponding absorption spectrum is characteristic of a mixture.

There exists substantial evidence that retinal binds to opsin by Schiff base condensation of the carbonyl with ϵ-amine of lysine[2–9] or, perhaps, with the primary amine of phosphatidylethanolamine.[10–12] Model systems of *trans*-retinal bonded covalently to aliphatic amines can be readily prepared, yet it is significant that these models do not reproduce the bathochromic shift of λ_{max} observed in retinal isomers bound to opsin.[6] A possible reason for this inadequacy of the models may be in some noncovalent bonding specific to opsin, which may be studied and hopefully elucidated by vibrational Raman spectroscopy *in situ*. The feasibility of observing the Raman spectrum of pigments (*e.g.*, bound retinal) in heterogeneous media[13] (*e.g.*, frozen bovine retina[14]) is a consequence of the phenomenon of resonance enhancement (RE) of the Raman effect[15] which is operative only for pigment molecules excited close to an electronic transition.[16,17]

The vibrational modes most strongly enhanced are those contributed by the stretching deformations of C=C and C—C bonds in the conjugated chain, while a somewhat attenuated RE is extended to vibrations in-

(1) Supported by the Michigan Cancer Foundation.

(2) (a) G. Wald, *Science*, **162**, 230 (1968); (b) E. W. Abrahamson and S. E. Ostroy, *Progr. Biophys.*, **17**, 181 (1967).

(3) C. D. B. Bridges, *Compr. Biochem.*, **27**, 31 (1967).

(4) F. D. Collins, *Nature (London)*, **171**, 469 (1953).

(5) R. A. Morton and G. A. J. Pitt, *Biochem. J.*, **59**, 128 (1955).

(6) A. Kropf and R. Hubbard, *Ann. N. Y. Acad. Sci.*, **74**, 266 (1958).

(7) D. Bownds and G. Wald, *Nature (London)*, **205**, 254 (1965).

(8) D. Bownds, *ibid.*, **216**, 1178 (1967).

(9) M. Aktar, P. T. Blosse, and P. B. Dewhurst, *Chem. Commun.*, 631 (1967).

(10) N. I. Krinsky, *Arch. Ophthalmol.*, **60**, 688 (1958).

(11) R. P. Poincelot, P. G. Millar, R. L. Kimbel, Jr., and E. W. Abrahamson, *Nature (London)*, **221**, 256 (1969).

(12) R. E. Anderson and M. B. Maude, *Biochemistry*, **9**, 3624 (1970).

(13) D. Gill, R. G. Kilponen, and L. Rimai, *Nature (London)*, **227**, 743 (1970).

(14) L. Rimai, R. G. Kilponen, and D. Gill, *Biochem. Biophys. Res. Commun.*, **41**, 492 (1970).

(15) J. Behringer in "Raman Spectroscopy," H. A. Szymanski, Ed., Plenum Press, New York, N. Y., 1967, Chapter 6.

(16) L. Rimai, R. G. Kilponen, and D. Gill, *J. Amer. Chem. Soc.*, **92**, 3824 (1970).

(17) M. C. Hutley and D. J. Jacobs, *Chem. Phys. Lett.*, **6**, 269 (1970).