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Microwave Spectrum, Barrier to Internal Rotation, and Molecular Structure of *cis*-Methoxydifluorophosphine[1,2]

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Microwave spectra are reported for species of CH_3OPF_2, $^{13}CH_3OPF_2$, $CH_3{}^{18}OPF_2$, and CD_3OPF_2 in which the methyl group is cis to the fluorine atoms. The rotational transitions are split by internal rotation of the methyl group. Heights of the potential barrier to internal rotation determined from the splittings are $V_3 = 422 \pm 5$ cal/mol for CH_3OPF_2 and 404 ± 5 cal/mol for CD_3OPF_2. The structural parameters derived from the moments of inertia of the four species are $r(PF) = 1.591 \pm 0.006$ Å, $r(PO) = 1.560 \pm 0.015$ Å, $r(CO) = 1.446 \pm 0.005$ Å, $r(CH) = 1.090 \pm 0.010$ Å, $\angle FPF = 94.8 \pm 0.6°$, $\angle OPF = 102.2 \pm 1.0°$, $\angle COP = 123.7 \pm 0.5°$, and $\angle HCH = 110.5 \pm 1.0°$.

Introduction

A study of the microwave spectrum of methoxydifluorophosphine was undertaken as part of a series of investigations of difluorophosphine derivatives. In addition, a number of investigators[3] have described the bonding of phosphorus to second-row atoms in terms of so-called $(p \rightarrow d)_\pi$ bonding in which the p-orbital lone pairs of the second-row atom—here, oxygen—are delocalized into one or more vacant d orbitals on the phosphorus atom. It seemed that an investigation of the molecular structure and internal rotation in methoxydifluorophosphine would provide some data for discussion.

Upon examination of the microwave spectrum of a sample of methoxydifluorophosphine it proved possible to assign transitions to a species in which the methyl group and the fluorine atoms are in the cis configuration (Figure 1). No assignment of transitions to other conformers was made, although there are many unassigned transitions including some with resolvable Stark effect. We report here the molecular structure and the barrier to internal rotation of the methyl group for *cis*-methoxydifluorophosphine.

Experimental Section

The normal and isotopically enriched species of methoxydifluorophosphine were prepared according to

$$CH_3OH + PCl_3 \rightarrow CH_3OPCl_2 + (CH_3O)_2PCl + PCl_3 + HCl \rightarrow CH_3OPCl_2$$

$$CH_3OPCl_2 + SbF_3 \xrightarrow{SbCl_5} CH_3OPF_2$$

The methanol was added dropwise to a slight molar excess of phosphorus trichloride. A mixture of products formed initially; however, upon standing the dimethoxychlorophosphine reacts further with the excess phosphorus trichloride to give the methoxydichlorophosphine in nearly quantitative yield.

The methoxydichlorophosphine was fluorinated by slowly dropping it into solid, finely ground antimony trifluoride which had been wet by a catalytic amount of antimony pentachloride. The gaseous products were collected in a trap at −78°. The products were partially separated by distillation through traps at −78, −112, and −196°. Final purification was accomplished by low-temperature codistillation of the −112° fraction with helium as the carrier gas.

The isotopically enriched species were prepared by successively repeating the procedure with 60% $^{13}CH_3OH$, 40% CD_3OH, and 40% $CH_3{}^{18}OH$ as starting materials.

The microwave spectra of the various samples of methoxydifluorophosphine were investigated with the sample cell immersed in Dry Ice. The spectrometer was a Hewlett-Packard Model 8460A MRR spectrometer operating in R band (26.5–40.0 GHz). Frequency measurements were made by the direct application of frequency markers to the strip chart recordings.

Spectra

From preliminary estimates of the structural parameters, moments of inertia and rotational constants were calculated for species with the methyl group cis and trans to the fluorine atoms. The spectra were moderately dense and not strong. Since the frequencies of the predicted $J = 3 \rightarrow 4$, $J = 4 \rightarrow 5$, and $J = 5 \rightarrow 6$ transitions were in the R-band region covered by our Hewlett-Packard spectrometer, the spectral search was confined to these regions. It proved possible to assign transitions to the species with the methyl group cis to the fluorine atoms. These transitions were assigned to the species of A internal rotation symmetry because of their typical second-order Stark effect. Attempts to measure the Stark shifts failed because of the density of transitions and the overall weakness of the spectra. Only a-type transitions were observed, and since the frequencies are not strongly dependent on the A rotational constant, an effort was made to study those transitions with the strongest A dependence.

After the rotational transitions in the parent species were assigned, the preliminary structural parameters were used to estimate the frequencies of transitions in the isotopically labeled molecules. These transitions were subsequently assigned and the frequencies of the assigned transitions of A symmetry in the four isotopic species studied are compared with calculated values in Tables I and II. The effective rotational constants for the levels of A symmetry are given in Table III.

That the species assigned was cis or near cis was determined by comparison of the experimental rotational constants in Table III with values computed for trans or near trans structures. The A rotational constant for an assumed trans structure was 1600 MHz larger and the B and C constants were 700 MHz smaller than the experimental values. Also, an attempt was made to adjust the bond distances and bond angles of a trans structure to fit the observed rotational constants, but the structural parameters obtained were not reasonable and the fit to the rotational constants was not acceptable. The best evidence that the species assigned has a plane of symmetry and is therefore the cis conformer is the near equality of the values of $P_{bb} = (I_a + I_c - I_b)/2$ for the parent, ^{13}C, and ^{18}O species. These values are compared for effective moments of inertia in Table IV.

The transitions of E symmetry were readily assigned after internal rotation splittings were predicted on the basis of an assumed barrier height. The E-level transitions exhibited the expected fast Stark effect. The internal rotation splittings were computed by direct diagonalization of a truncated ma-

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[1] This work was supported in part by grants from the National Science Foundation.

[2] Presented at the Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June 1971.

[3] For a recent review see K. A. R. Mitchell, *Chem. Rev.*, 69, 157 (1969).

Table I. Comparison of Observed[a] and Calculated[b] Frequencies and Internal Rotation Splittings for CH_3OPF_2 and $^{13}CH_3OPF_2$

	CH_3OPF_2		$^{13}CH_3OPF_2$	
Transition	ν_A	$\nu_A - \nu_E$	ν_A	$\nu_A - \nu_E$
3_{12}–4_{13}			27225.84 (0.30)	
3_{21}–4_{22}	27692.99 (0.33)		26947.08 (0.12)	
3_{22}–4_{23}	27019.89 (0.23)			
4_{04}–5_{05}	32667.54 (0.21)	426.08 (−0.14)	31955.63 (0.24)	406.09 (−0.06)
4_{14}–5_{15}	32298.16 (0.36)	−316.29 (−0.03)	31565.68 (0.35)	−305.68 (−0.35)
4_{13}–5_{14}	34726.94 (0.08)	114.44 (0.09)	33871.43 (0.06)	99.08 (0.05)
4_{23}–5_{24}	33680.87 (−0.08)			
4_{22}–5_{23}	34857.83 (0.13)		33913.17 (−0.05)	
4_{31}–5_{32}	34182.60 (−0.68)			
5_{05}–6_{06}	38876.41 (−0.19)	424.50 (−0.01)	38035.08 (−0.13)	417.00 (−0.14)
5_{15}–6_{16}	38636.59 (−0.02)	−282.50 (−0.12)	37769.26 (−0.04)	−285.41 (−0.05)
5_{24}–6_{25}			39319.32 (−0.61)	

[a] Observed frequencies are in MHz and are ±0.05 MHz. [b] The differences between observed and calculated values are given in parentheses. Calculated ν_A values assume the parameters in Table III; calculated $\nu_A - \nu_E$ values assume the parameters in Table V.

Table II. Comparison of Observed[a] and Calculated[b] Frequencies and Internal Rotation Splittings for $CH_3{}^{18}OPF_2$ and CD_3OPF_2

	$CH_3{}^{18}OPF_2$		CD_3OPF_2	
Transition	ν_A	$\nu_A - \nu_E$	ν_A	$\nu_A - \nu_E$
4_{04}–5_{05}	32212.33 (0.26)	417.38 (0.13)	29695.57 (0.37)	23.93 (0.05)
4_{14}–5_{15}	31833.34 (0.28)	−310.26 (0.28)		
4_{13}–5_{14}	34115.97 (0.18)	105.48 (−0.13)		
4_{22}–5_{23}	34171.79 (0.09)		31172.39 (0.26)	10.24 (−0.02)
5_{05}–6_{06}	38346.71 (−0.14)	424.98 (0.17)	35367.48 (−0.10)	40.47 (−0.01)
5_{15}–5_{16}	38090.63 (−0.05)	−285.71 (0.42)	35068.90 (−0.02)	−11.59 (0.01)
5_{24}–6_{25}	39627.36 (−0.49)		36375.38 (−0.33)	5.14 (−0.06)
5_{23}–6_{24}			37584.34 (−0.09)	5.61 (−0.04)

[a] Observed frequencies are in MHz and are ±0.05 MHz. [b] The differences between observed and calculated values are given in parentheses. Calculated ν_A values assume the parameters in Table III; calculated $\nu_A - \nu_E$ values assume the parameters in Table V.

Table III. Effective Rotational Constants[a] for the A Levels for the Normal and Three Isotopically Labeled Species of CH_3OPF_2

	CH_3OPF_2	$^{13}CH_3OPF_2$	$CH_3{}^{18}OPF_2$	CD_3OPF_2
A_A	5991.04	5973.28	5935.14	5718.40
B_A	3641.81	3542.67	3566.40	3252.63
C_A	3127.86	3058.98	3086.88	2844.60

[a] In MHz. Uncertainties are as follows: A, ±2.0 MHz; B and C, ±0.06 MHz.

Table IV. Effective Rotational Constants[a] Free of Internal Rotation, Moments of Inertia,[b] and Second Moments[c] for Methoxydifluorophosphine

	CH_3OPF_2	$^{13}CH_3OPF_2$	$CH_3{}^{18}OPF_2$	CD_3OPF_2
A_0	5980.13	5962.10	5924.79	5715.34
B_0	3641.82	3542.68	3566.41	3252.64
C_0	3123.46	3054.87	3082.56	2843.72
I_a	84.5093	84.7647	85.2986	88.4244
I_b	138.7702	142.6537	141.7043	155.3740
I_c	161.8000	165.4331	163.9471	177.7166
P_{aa}	108.0305	111.6611	110.1764	122.3331
P_{bb}	53.7696	53.7721	53.7707	55.3835
P_{cc}	30.7398	30.9927	31.5279	33.0409

[a] In MHz. Uncertainties are as follows: A_0, ±2.0 MHz; B_0 and C_0, ±0.06 MHz. [b] In u Å^2. Conversion factor assumed: 505376 MHz u Å^2. [c] $P_{aa} = (I_b + I_c - I_a)/2$, etc.

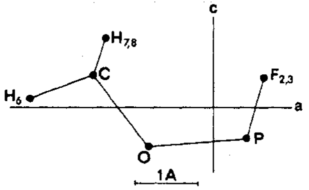

Figure 1. Projection of *cis*-methoxydifluorophosphine in the molecular plane of symmetry.

trix of the combined rigid rotator–internal rotation Hamiltonian. The internal rotation splittings are compared with calculated values in Tables I and II.

Internal Rotation

The large A-E splittings shown in Tables I and II are indicative of a rather low barrier to internal rotation. The splittings for the CD_3 species are considerably smaller than for the CH_3 species which is evidence that the splitting is a result of rotation of the methyl group about the CO bond.

The internal rotation parameters (V_3, the height of the barrier to internal rotation, I_α, the moment of inertia of the methyl group, and θ, the angle between the internal rotation axis and the a inertial axis) were determined by least-squares fitting to the observed A-E splittings. The derivatives of the splittings with respect to each of the parameters were obtained numerically. A computer program based on Herschbach's formulation[4] including perturbation coefficients to fourth order was used to compute the derivatives since it used much less computer time than the direct diagonalization and gave quite good values for the splittings. Although the splittings depend slightly on the rotational constants, the dependence was judged small enough to be ignored.

The A-E splittings of the parent, ^{18}O, and ^{13}C species were used to obtain single values of V_3 and I_α and individual values of θ for each species in one calculation. The A-E splittings for the CD_3 species were used separately to fix values of V_3, I_α, and θ for that species. The results of these two calculations are shown in Table V along with other relevant internal rotation parameters. The differences between observed and calculated A-E splittings for the best values of the internal rotation parameters are shown in parentheses in Tables I and II.

Once the internal rotation parameters were obtained, it was

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[4] D. R. Herschbach, *J. Chem. Phys.*, 31, 91 (1959).

Table V. Internal Rotation Parameters[a] for Four Isotopic Species of CH_3OPF_2

	CH_3OPF_2	$^{13}CH_3OPF_2$	$CH_3{}^{18}OPF_2$	CD_3OPF_2
V_3	422 ± 5.0			404 ± 5.0
I_α	3.179			6.425
θ	51.0	50.2	51.5	47.8
s	12.04	12.04	12.04	22.68
F	163.394	163.385	163.319	83.051

[a] V_3, I_α, and θ are defined in the text; s and F are internal rotation parameters defined in ref 4. V_3 is in cal/mol, I_α in u Å^2, θ in degrees, and F in GHz.

possible to determine rotational constants which are essentially free of the effects of internal rotation. This was done by assuming zero-order rotational constants and calculating frequencies of A- and E-level transitions by means of the internal rotation program. The computed A-level frequencies were then fit by least squares to effective A-level rotational constants in a manner which was identical with that used to obtain the effective A-level rotational constants from the experimental frequencies. The differences between the zero-order rotational constants and the A-level values were then applied as a correction to the experimental A-level constants shown in Table III. This process was repeated until by starting with assumed zero-order constants the internal rotation program gave A-level constants which were equal to those in Table III. The zero-order constants together with moments of inertia and planar second moments derived from them are given in Table IV.

In addition to being low in an absolute sense, the barrier to internal rotation in CH_3OPF_2 is also low by comparison with other methoxy compounds. A comparison of barriers to internal rotation in CH_3OPF_2 and related compounds is shown in Table VI.

Molecular Structure

Since there is only one stable isotope each for phosphorus and fluorine, a complete substitution structure for CH_3OPF_2 is out of the question. In such circumstances there are a number of ways to determine the structure and we chose two. In one procedure principal axis substitution coordinates were computed for the oxygen and carbon atoms by using the moments of inertia of the parent, ^{13}C, and ^{18}O species in the Kraitchman equations.[5] The principal axis coordinates of the remaining atoms were then obtained by least-squares fit to the moments of inertia of the parent and the CD_3 species and the three nontrivial principal axis relations (a plane of symmetry was assumed). The form of the Kraitchman equations which does not require precise values of the A rotational constants was used because of the relatively poor precision of the experimental A constants. In addition, because the CD_3 moments of inertia provide only three independent pieces of information related to the methyl group geometry and there are five independent parameters for an asymmetric methyl group straddling a plane of symmetry, a symmetric methyl group was assumed. In the early calculations the axis of the methyl group was assumed to lie along the CO bond. For all of the structure calculations the zero-order moments in Table IV were used.

Table VI. Barriers to Internal Rotation of Methyl Groups about C–O Bonds

Compd	V_3, cal/mol	Ref	Compd	V_3, cal/mol	Ref
CH_3OH	1070	*a*	$(CH_3)_2O$	2720	*d*
CH_3OCHO	1190	*b*	CH_3OCl	3060	*e*
CH_3ONO_2	2321	*c*	CH_3OPF_2	422	*f*

[a] E. V. Ivash and D. M. Dennison, *J. Chem. Phys.*, 21, 1804 (1953). [b] R. F. Curl, *ibid.*, 30, 1529 (1959). [c] W. B. Dixon and E. B. Wilson, Jr., *ibid.*, 35, 191 (1961). [d] P. H. Kasai and R. J. Myers, *ibid.*, 30, 1096 (1959). [e] J. S. Rigden and S. S. Butcher, *ibid.*, 40, 2109 (1964). [f] This work.

Table VII. Coordinates[a] of the Atoms in the Principal Axis System of CH_3OPF_2

Atom	*a*	*b*	*c*
P	−0.5305	0.0	0.5490
	−0.4968	0.0	0.5544
O	1.0400	0.0	0.6416
	1.0456	0.0	0.6295
C	1.9093	0.0	−0.5137
	1.9085	0.0	−0.5388
F	−0.7845	±1.1716	−0.4898
	−0.8059	±1.1716	−0.4821
H	2.9509	0.0	−0.1784
	2.9422	0.0	−0.1989
H	1.7116	±0.8955	−1.1109
	1.6952	±0.8951	−1.1199

[a] The coordinates in the first row for each atom are for the Kr structure and in the second are for the p-Kr structure. The methyl group was assumed to be symmetric about the CO bond for both structures. For the Kr structure $\Sigma m_i a_i = -0.2696$, $\Sigma m_i c_i = 0.0726$, $\Sigma m_i a_i c_i = 0.1165$; these values are zero for the p-Kr structure by definition.

Table VIII. Bond Distances[a] and Bond Angles[b] for Methoxydifluorophosphine

	Kr	p-Kr	p-Kr (tilt)	Best
PF	1.586	1.595	1.594	1.591 ± 0.006
PO	1.573	1.544	1.549	1.560 ± 0.020
CO	1.446	1.452	1.451	1.446 ± 0.005
CH	1.094	1.088	1.085	1.090 ± 0.010
FPF	95.2	94.6	94.6	94.8 ± 0.6
OPF	101.4	103.0	102.7	102.2 ± 1.0
COP	123.6	123.7	123.7	123.7 ± 0.5
HCH	109.8	110.7	111.1	110.5 ± 1.0

[a] In angstroms. [b] In degrees.

The calculations just described gave unreasonably small values for the CH distances, apparently as a result of the fact that relatively small changes in the PF_2 geometry were magnified many times in their effect on the CH_3 geometry. Consequently, the PF_2 and CH_3 fittings were uncoupled. Coordinates were assumed for the hydrogen atoms and the coordinates of the PF_2 group were determined by least-squares fitting to the moments of inertia of the parent and the three nontrivial principal axis relations. The coordinates of the PF_2 group were then fixed and the coordinates of the hydrogen atoms were determined by least-squares fitting to the differences in the moments of inertia of the CD_3 and the CH_3 species and the three principal axis relations. This process was repeated once to give self-consistency. The resulting principal axis coordinates are given in Table VII, and the bond distances and bond angles are shown in Table VIII. We refer to a structure obtained in this way as a Kr structure. The computer program STRFIT was used for all the calculations.

The second procedure employed to determine the structural parameters was more straightforward. In this calculation a set of internal coordinates was assumed which completely defined the structure including the restrictions of a plane of symmetry and a symmetric methyl group. The internal coordinates were defined to be compatible with the method for computing atomic coordinates described by Thompson.[6] The internal coordinates were varied to give the best fit in the least-squares sense to the moments of inertia of the parent species, the differences between the

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

(6) H. B. Thompson, *J. Chem. Phys.*, 47, 3407 (1967).

I_b and I_c moments of the ^{13}C and ^{18}O species and the corresponding moments of the parent species, and the differences between all the moments of the CD_3 species and the moments of the parent species. We refer to this type of structure calculation in which differences in moments of inertia are used as pseudo-Kraitchman calculations (p-Kr). A new computer program STRFTQ was used for this calculation. The coordinates obtained are in Table VII and the bond distances and bond angles are in Table VIII.

A third set of structural parameters was calculated in order to determine the effect of a tilt of the methyl group axis. The angle between the *a* axis and the axis of the internal rotor as determined from the internal rotation analysis is 51.0° (Table V). The corresponding angles computed from the Kr and p-Kr coordinates in Table VII are 53.0 and 53.5°. A tilt of the methyl group of approximately 2.5° is therefore indicated with the tilt such that the hydrogen atoms are moved away from the PF_2 group and toward the oxygen lone pairs. Methyl group tilts of this magnitude and direction have been reported previously.[7] The p-Kr calculation was repeated holding the methyl group tilt at 2.5°. The structure which resulted is essentially unchanged from the p-Kr structure and is shown in Table VIII.

Comparison of the structures in Table VIII shows that the PO distance is strongly affected by the type of data analysis. Several variations of the method of calculation verified this effect. Any calculation which included substitution coordinates for the oxygen and carbon atoms led to a "long" PO distance. This is probably a result of the well-documented fact that moments of inertia calculated from substitution coordinates are smaller than the moments used to compute the coordinates. Thus, in a calculation in which some substitution coordinates are used and the remaining coordinates are adjusted to fit the moments themselves it is probable that some parameter will have to take up the difference.

The "best" structure given in Table VIII is a weighted average of the parameters of the two structures. For the OC distance the Kr value is used since this is a true substitution parameter. For the remaining parameters the p-Kr structure is more heavily weighted.

Discussion

One stable conformer of methoxydifluorophosphine has a plane of symmetry with the methyl group cis to the fluorine atoms. This is of interest since in this conformation there is an opportunity for interaction between the hydrogen and fluorine atoms. Indeed, the low barrier to internal rotation of the methyl group and the apparent tilt of the methyl group away from the fluorines suggest that steric forces are operating.

Table IX. Comparison of Structures of Selected Phosphorus Compounds

Molecule	$r(PO)^a$	$r(OC)^a$	$\angle POC^b$	Ref
2,4,5-Trimethoxy-1,3,5-trimethyl-2,5,6-trioxocyclotriphosphazane	1.56	1.45	119	*c*
Methyl ethylene phosphate	1.57	1.44	118.8	*d*
Methyl diphenylthiophosphinite	1.60	1.45	118.5	*e*
Methoxydifluorophosphine	1.56	1.446	123.7	*f*

[a] In angstroms. [b] In degrees. [c] G. B. Ansell and G. J. Bullen, *J. Chem. Soc. A*, 3026 (1968). [d] T. A. Steitz and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 87, 2488 (1965). [e] G. Lepicord, D. De-Saint-Giniez-Liebig, A. Laurent, and C. Rerat, *Acta Crystallogr., Sect. B*, 25, 617 (1969). [f] This work.

The PO bond length (1.56 Å) is intermediate between the PO single- and double-bond lengths of 1.71 and 1.38 Å, respectively, as estimated by Cruickshank.[8] The structural parameters of CH_3OPF_2 from the present gas-phase study are compared with the corresponding values from several X-ray crystallographic studies in Table IX. In each of the compounds in Table IX some partial double-bond character has been attributed to the PO bond and the PO bonds are all very similar in length. The increase in bond order has been attributed to delocalization of the oxygen lone pairs into the vacant d orbitals of the phosphorus atom and a similar argument may be made for the PO bond length in CH_3OPF_2. This suggestion of oxygen to phosphorus $(p \rightarrow d)_\pi$ bonding is further supported by the large POC bond angle of 123.7°. In dimethyl ether the COC bond angle is 111.5°[9] indicating a nearly sp^3 hybridization about the oxygen atom. The POC bond angle in CH_3OPF_2 implies sp^2 hybridization on the oxygen atom, which is consistent with significant PO double bonding.

The CO bond length in CH_3OPF_2 (1.446 Å) is comparable to that in methyl nitrate (1.43 Å[10]) and somewhat larger than that in dimethyl ether (1.417 Å[9]). The PF bond distance in CH_3OPF_2 (1.591 Å) is nearly equal to that reported for PF_2NH_2 (1.587 Å[11]). Recently, PF bond lengths in PF_2X compounds have been correlated with the electronegativity of the X group.[12] In view of the similar inductive effects of the NH_2 and OCH_3 groups, it is not surprising then that the PF distances in CH_3OPF_2 and PF_2NH_2 are nearly the same.

Registry No. CH_3OPF_2, 381-65-7; $^{13}CH_3OPF_2$, 42087-60-5; $CH_3{}^{18}OPF_2$, 42087-61-6; CD_3OPF_2, 24425-01-2.

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(7) W. Gordy and R. L. Cook, "Microwave Molecular Spectra," Interscience, New York, N. Y., 1958, p 487, Table 12:9.

(8) D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).

(9) (a) K. Kimura and M. Kubo, *J. Chem. Phys.*, 30, 151 (1959); (b) P. H. Kasai and R. J. Myers, *ibid.*, 30, 1096 (1959).

(10) W. B. Dixon and E. B. Wilson, Jr., *J. Chem. Phys.*, 35, 191 (1961).

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

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