

this calculation the transition state species is assumed to have equal bond lengths with the fluorine pairs on respective sides of a plane passing through the sulfur atom (C_{2v} symmetry). In the equilibrium configurations, corresponding to the minima of the two potential wells, the fluorine atoms are all on one side of the plane.^{12,13} ($S-F_{ax}=1.646 \text{ \AA}$ and $S-F_{eq}=1.545 \text{ \AA}$.¹²) In order to estimate V_0 , we assume that the force constant f_β for the equatorial fluorine distortion is dominant in the exchange motion. A value for f_β of 0.63 mdyn-\AA is used⁷ in the expression for V_0 . Although these considerations lead to a barrier, V_0^{\max} , corresponding to the intersection of the harmonic curves, it is probably more realistic to scale the barrier because of anharmonicity.^{10,11} V_0^{\max} was scaled by replacing the intersecting parabolas with a cosine function² whose second derivative at each minimum is equivalent to those for the parabolas. Thus, $V_0^{\text{final}} = (4/\pi^2) V_0^{\max} = 10.3 \text{ kcal/mole}$. This close agreement with the barrier height from the eigenvalue fit of 10.0 kcal/mole is, perhaps, fortuitous, but it does add credence to the approach of fitting experimentally observed vibrationally excited transitions to a double minimum potential function. Finally, the barrier to intramolecular exchange in SF_4 , which we

calculate here from far-infrared data, is consistent with available NMR data for a series of pentacoordinated species in which the barriers occur between 6–12 kcal/mole.¹⁴

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⁷ I. W. Levin, "Calculation of Infrared Spectra Using CNDO/2 Techniques: An Application to SF_4 ." (unpublished) Although Frey *et al.*⁴ assign the $\nu_4(a_1)$ mode at 228 cm^{-1} to the axial bending mode, reassignment of this mode to the equatorial bending motion of SF_4 correlates better with the equatorial (in-plane) bend of PF_5 at 179 cm^{-1} . (Note that SF_4 can be considered a quasi-pentacoordinated system if the lone pair is viewed as a ligand.) For PF_5 , the 533- and 179-cm^{-1} e' modes, primarily the axial and in-plane modes, respectively [I. Levin, *J. Mol. Spectry.* **33**, 61 (1970); W. J. Adams and L. S. Bartell, *J. Mol. Struct.* **8**, 23 (1971)] correlate with two of the a_1 and one of the b_2 modes of SF_4 . Thus, for the SF_4 a_1 bending modes, the lower vibration is expected to be the equatorial bend and would probably appear at a slightly higher frequency than that of the PF_5 179-cm^{-1} transition. The weak infrared intensity for this motion in SF_4 also follows from the virtually zero infrared intensity that arises for the in-plane e' bending mode of PF_5 . Finally, an approximate force field for SF_4 supports this reassignment.

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TABLE I. Calculated excited vibrational levels ν for SF_4 from the quartic-harmonic potential function $V=14.62(x^4-31z^2)$. (obs and calc frequencies are in cm^{-1} .)

obs	calc	Δ (obs-calc)	Assignment (ν) ⁹
227.6	227.6	0	0→1
224.5	224.6	-0.1	1→2
221.0	221.6	-0.6	2→3
219.0	218.6	+0.4	3→4
215.5	215.3	+0.2	4→5
Barrier height $V_0=10.0\pm 0.5 \text{ kcal/mole}$			

Structure and Conformation of Trimethylphosphine*

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The structure of trimethylphosphine has been previously reported, but these investigations did not include the possibility of a small tilt of the methyl groups.^{1,2} Pierce *et al.*³ have pointed out that a methyl group attached to an atom possessing an unshared electron pair frequently is tilted toward the unshared pair. They further suggested that this effect might be associated with barriers to internal rotation.

Recent microwave studies of trimethylamine,⁴ monomethylphosphine,⁵ and dimethylphosphine⁶ have suggested methyl group tilts of 1° – 2° . Only in the case of Me_3N was this deduced from direct isotopic substitution. We report here evidence for methyl group tilts in Me_3P from the analysis of the spectra of several deuterated species.

Samples of $(CH_2D)(CH_3)_2P$ (97%) and $(CD_3)-$

TABLE I. Observed ground state transitions and rotational constants for some deuterated trimethylphosphine species (megacycle/second).

Transition	(CD ₃)(CH ₃) ₂ P	(CH ₂ D _a)(CH ₃) ₂ P	(CH ₂ D _s)(CH ₃) ₂ P
2 ₂₁ -1 ₁₁	21 804.06	22 913.06	22 615.71
2 ₁₁ -1 ₀₁	20 702.50	22 221.11	22 333.63
2 ₂₀ -1 ₁₀	21 370.70	22 610.60	22 482.25
3 ₂₂ -2 ₁₂	31 879.61	33 850.32	33 711.57
3 ₃₁ -2 ₂₁	32 772.98	34 394.98	33 928.07
3 ₃₀ -2 ₂₀	32 318.45	34 020.00	33 742.21
3 ₁₂ -2 ₀₂	31 441.18	33 680.84	33 680.75
3 ₂₁ -2 ₁₁	31 136.49	33 360.54	33 505.11
A	5 588.71±0.03	5 814.72±0.03	5 689.14±0.04
B	5 037.87±0.03	5 468.75±0.03	5 548.08±0.04
C	3 406.4±1	3 588±2	3 689±9

(CH₂)₂P (99%) were prepared by treating dimethylphosphine with the appropriate isotopic species of CH₃I.⁷ Their spectra were measured at approximately -78° with a conventional spectrometer⁸ and are accurate to ±0.05 MHz.

The spectra of (CD₃)(CH₃)₂P and the two isotopic species of (CH₂D)(CH₃)₂P are listed in Table I. The species possessing no symmetry element (CH₂D_a)-(CH₃)₂P, exhibited a spectrum which was approximately twice as intense as that of the species having a symmetry plane (CH₂D_s)(CH₃)₂P. The assignments were confirmed from the Stark effect and rigid rotor frequency fit ($\nu_{\text{obs}} - \nu_{\text{calc}} \leq |0.25|$ MHz for all transitions). No torsional splittings were observed.

The hydrogen substitution coordinates⁹ calculated for the two (CH₂D)(CH₃)₂P species show that each methyl group is staggered with respect to the other two PC bonds. For a symmetric top molecule, only the distance from the symmetry axis can be determined by substitution of an off-axis atom. Thus, it is impossible to calculate directly the distance between the equivalent out-of-plane H atoms in each methyl group (designated as H_a and H_{a'})⁴ from substitution coordinates alone. The distance, however, can be obtained from the expression $4(m_{\text{D}} - m_{\text{H}})b_{\text{H}_a}^2 = 2P_b[(\text{CD}_3)(\text{CH}_3)_2\text{P}] -$

$I_c[(\text{CH}_3)_3\text{P}]$ since $r(\text{H}_a\text{H}_a') = 2|b_{\text{H}_a}|$. The value of I_c for (CH₃)₃P was calculated from ($I_c + I_a - I_b$) of the (CH₂D_a)(CH₃)₂P species since these values have the least experimental error. The value of 1.763 Å obtained for $r(\text{H}_a\text{H}_a')$ compared well with other $r(\text{H}_a\text{H}_a')$ values.^{10,11}

The structure was calculated three different ways by using the rotational constants from Ref. 1 along with those in Table I. In the first method, substitution coordinates were computed for the carbon and hydrogen atoms and the first moment equation was used for the phosphorous coordinate. The resulting structure was rather unsatisfactory¹⁰ because it gave $\angle\text{HCH}$ values which were outside the range normally found for methyl groups.¹² The primary cause was the small value for c_{H_a} since small substitution coordinates are subject to large errors from both experimental uncertainty and zero-point effects.^{13,14} Consequently, a first and second moment equation were solved simultaneously to determine c_{P} and c_{H_a} and the resulting coordinates are shown in Table II. The structure calculated from these coordinates is labeled structure A in Table III.

A third calculation was also undertaken to estimate what effect the assumption of bond shortening upon deuteration would have on the final structure. It was assumed that the average CH bond shortened by

TABLE II. Coordinates of (CH₃)₃P (angstroms).^a

Atom	<i>a</i>	<i>b</i>	<i>c</i>
P	0.0	0.0	0.5514
C	1.6174	0.0	-0.3378
H _s	1.4771	0.0	-1.4307
H _a	2.1809	±0.8816	-0.0979

^a The coordinates are expressed in the principal axis system of (CH₃)₃P in which the substituted atoms in those species which possess C_s symmetry lie in the *ac* plane (*b*=0).

TABLE III. Structural parameters of (CH₃)₃P.

	Structure A	Structure B
C-H _s (Å)	1.102	1.112±0.005
C-H _a (Å)	1.073	1.090±0.010
P-C (Å)	1.846	1.843±0.003
$\angle\text{PCH}_s$	111.5°	111.4°±0.2°
$\angle\text{PCH}_a$	110.6°	109.8°±0.4°
$\angle\text{H}_s\text{CH}_a$	106.8°	108.2°±0.8°
$\angle\text{H}_a\text{CH}_a'$	110.4°	109.4°±0.4°
$\angle\text{CPC}$	98.7°	98.9°±0.2°

0.005 Å upon deuteration. The resulting structure is referred to as B in Table III

Structures A and B compare well with the electron diffraction results: $r(\text{PC}) = 1.846 \pm 0.003$ Å, $r(\text{CH}) = 1.091 \pm 0.006$ Å, $\angle \text{CPC} = 98.6^\circ \pm 0.3^\circ$ and $\angle \text{PCH} = 110.7^\circ \pm 0.5^\circ$.² The differences between structures A and B should be useful estimates of the uncertainties in the structural parameters caused by zero-point effects. The actual structure is probably closer to B. The error limits in structure B are those arising from experimental uncertainty alone.

It is interesting to compare structure B with the results for $(\text{CH}_3)_3\text{N}$.⁴ The parameters involving the hydrogens are remarkably similar. For example, in Me_3N the $r(\text{CH}_s)$ value (1.109 ± 0.008 Å) is also found to be longer than the $r(\text{CH}_a)$ value (1.088 ± 0.008 Å). The calculation of $(\angle \text{NCH}_s - \angle \text{NCH}_a)$ for Me_3N and $(\angle \text{PCH}_s - \angle \text{PCH}_a)$ for Me_3P both give 1.6° , which indicates that the methyl groups appear to be tilted slightly toward the unshared electron pair in both cases.

In conclusion, it appears that there are small methyl group tilts in Me_3P and that $r(\text{CH}_s)$ is slightly longer than $r(\text{CH}_a)$. The effect is assuredly small, but the

repeated observation of the effect in this and similar molecules suggests that it is probably real.

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Effect of Molecular Shape on the Dielectric Second Virial Coefficients of Polar Gases

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Recently, a modified Stockmayer potential of the form

$$\begin{aligned}
 U(R, \theta_1, \theta_2, \phi) = & 4\epsilon[(\sigma/R)^{12} - (\sigma/R)^6] \\
 & + C_\alpha R^{-14} - C_\alpha' R^{-8} + C_\beta R^{-13}(\cos\theta_1 + \cos\theta_2) \\
 & + C_\gamma R^{-14}(3 \cos^2\theta_1 + 3 \cos^2\theta_2 - 2) \\
 & + C_\delta R^{-14}(\sin\theta_1 \sin\theta_2 \cos\phi + 13 \cos\theta_1 \cos\theta_2) \\
 & - C_\beta' R^{-7}(\cos\theta_1 + \cos\theta_2) - C_\gamma' R^{-8}(3 \cos^2\theta_1 + 3 \cos^2\theta_2 - 2) \\
 & - C_\delta' R^{-8}(\sin\theta_1 \sin\theta_2 \cos\phi + 7 \cos\theta_1 \cos\theta_2) \\
 & + \mu_0^2 R^{-3}(2 \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos\phi) \\
 & - (\alpha_e \mu_0^2 / 2) R^{-6}(3 \cos^2\theta_1 + 3 \cos^2\theta_2 - 2)
 \end{aligned}$$

has been used to account for the effect of molecular shape on the dielectric second virial coefficients of simple gases of axially symmetric polar molecules.^{1,2} Estimating the coefficients C_α , C_β , C_γ , ... from the knowledge of the pairwise interactions among the constituent atomic groups of the molecules,^{1,3} it was reduced to a function of only two adjustable parameters, ϵ and σ , that were determined from the experimental

ordinary second virial coefficient, B . The model then predicted the correct sign of the dielectric second virial coefficient, \mathcal{B} , for CH_3F and CHF_3 . The lack of reliable experimental data made it difficult to further test the model in the previous papers. Recently, Sutter and Cole⁴ have reported experimental measurements of B and \mathcal{B} at several temperatures for two additional gases, CClF_3 and CH_3Cl , as well as more extensive measurements for CH_3F and CHF_3 . Their results show that \mathcal{B} values of the halogenated methanes are very sensitive to differences in molecular shape. In this note, the foregoing molecular model is applied to calculate \mathcal{B} for

TABLE I. Molecular and potential-energy parameters.

Molecule	L (Å)	l (Å)	μ_0 (D)	$\alpha_e \times 10^{24}$ (cm ³)	ϵ/k (°K)	σ (Å)
CHF_3	0.021	1.444	1.649	3.57	190	4.60
CClF_3	0.724	1.408	0.51	5.59	150	5.40
CH_3F	0.612	0.773	1.81	3.55	270	4.058
CH_3Cl	0.553	1.304	1.895	4.72	265	4.455