

# The Microwave Spectra, Molecular Structure, and Dipole Moment of Phosphirane<sup>1a</sup>

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**Abstract:** The microwave spectra of phosphirane, phosphirane-<sup>13</sup>C, *cis*- and *trans*-phosphirane-C-*d*<sub>1</sub>, and phosphirane-P-*d* have been studied. From these isotopes the following molecular structure was determined:  $r(\text{C-C}) = 1.502 \text{ \AA}$ ,  $r(\text{C-P}) = 1.867 \text{ \AA}$ ,  $r(\text{C-H}_{cis}) = 1.092 \text{ \AA}$ ,  $r(\text{C-H}_{trans}) = 1.093 \text{ \AA}$ ,  $r(\text{P-H}) = 1.428 \text{ \AA}$ ,  $\angle \text{CPC} = 47.4^\circ$ ,  $\angle \text{HCH} = 114.4^\circ$ ,  $\angle \text{H-PC}_2(\text{plane}) = 95.7^\circ$ ,  $\angle \text{H-P-C} = 95.2^\circ$ , and  $\angle \text{C-C-H}_{cis} = 118.0^\circ$ ,  $\angle \text{C-C-H}_{trans} = 117.5^\circ$ . A dipole moment of 1.12 D and its orientation were also obtained.

The molecular structure of the heteronuclear tricyclic compounds ethylene oxide,<sup>2</sup> ethylene sulfide,<sup>2b</sup> and ethylenimine<sup>3</sup> have been determined by microwave spectroscopy. Since the analogous phosphorus compound (see Figure 1) has recently been synthesized,<sup>4</sup> it is interesting to determine and compare its structure with the other tricyclics.

The structure of phosphirane (ethylenephosphine) has been determined by studying the rotational spectra of the normal, of the <sup>13</sup>C, and of all the singly deuterated isotopic species. The data were reduced using Kraitchman's method.<sup>5</sup> The dipole moment has been measured to be 1.12 D.

## Experimental Section

**Synthesis.** Phosphirane was prepared by a published procedure.<sup>4</sup> Phosphirane-P-*d* was prepared from PD<sub>3</sub>. In a 250-ml three-necked flask, connected through a trap cooled in liquid N<sub>2</sub> to a vacuum line, was placed a mixture of 22.0 ml (1.2 moles) of D<sub>2</sub>O and 40 ml of carefully dried ether. The flask and trap were held at a pressure of 60 cm and were flushed with dry nitrogen while 35.0 ml (0.40 mole) of phosphorus trichloride was slowly dropped in with vigorous stirring and ice cooling of the flask. Volatile materials were then pumped out of the flask at room temperature until the pressure was below 5  $\mu$ . The crystalline colorless residue (D<sub>3</sub>PO<sub>3</sub>) was then heated *in vacuo*, with stirring, to 230°. PD<sub>3</sub> was smoothly evolved and collected in the vacuum line where it was passed through a trap at -79° and condensed at -196°; yield of PD<sub>3</sub>, 0.083 mole (83%). The product was characterized by its infrared spectrum. All further operations in the synthesis of phosphirane-P-*d* were carried out in glassware conditioned by being exposed to D<sub>2</sub>O vapor before being pumped out.

Finely dispersed sodium (5  $\mu$ ) in xylene (1.1 g of sodium, 0.048 g-atom) was placed in a 1-l. bulb. The xylene was pumped out and 75 ml of hexamethylphosphoramide, distilled from sodium, was

transferred into the bulb. Then PD<sub>3</sub>, at a pressure of 60 cm, was admitted to the bulb and the dark blue mixture was shaken. PD<sub>3</sub> and D<sub>2</sub> were pumped off together with some dimethylamine from cleavage of the solvent. This process was repeated until the solution was a clear yellow with no trace of residual sodium. The solution was cooled in liquid nitrogen, 3.00 g (0.030 mole) of 1,2-dichloroethane was transferred into it, and the bulb was allowed to warm slowly. The volatile products were fractionated in the vacuum line through traps at -45, -95, and -196°. The material in the trap at -95° was refractionated twice to yield 12.8 mmoles (43%) of phosphirane-P-*d*. Gas chromatography<sup>4</sup> of this product showed that it contained less than 3% impurity (other than phosphirane). Proton magnetic resonance spectroscopy indicated a phosphirane content of approximately 5%.

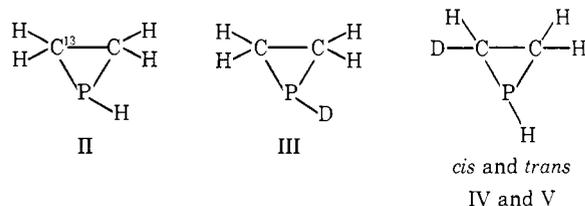
Phosphirane-C-*d*<sub>1</sub> was prepared from ethylene-*d*<sub>1</sub> (Merck Sharpe and Dohme Isotopic Products). Reaction of ethylene-*d*<sub>1</sub> (30.0 mmoles) and chlorine (30.0 mmoles), condensed together at -196° in a trap attached to the vacuum line and allowed to warm slowly to room temperature, gave a quantitative yield of 1,2-dichloroethane-*d*<sub>1</sub>. This was allowed to react with a solution of PH<sub>2</sub>Na (48.0 mmoles) in hexamethylphosphoramide (75 ml). The PH<sub>2</sub>Na was prepared from PH<sub>3</sub> in the way described above for PD<sub>2</sub>Na from PD<sub>3</sub>. The reaction yielded phosphirane-C-*d*<sub>1</sub> (34%), which was characterized by infrared and nmr spectroscopy and by gas chromatography.

Phosphirane enriched in <sup>13</sup>C was prepared from <sup>13</sup>C-enriched ethylene in essentially the same way. The yield in this preparation, carried out on a 5-mmole scale, was unaccountably low (15%). The product was characterized by infrared and nmr spectroscopy.

Phosphirane is very unstable in liquid form at room temperature.<sup>4</sup> However, we were able to keep it for 2 to 3 hr without serious decomposition in a copper waveguide at 20-50  $\mu$  of pressure. We also found that phosphirane and its decomposition products persisted in the cell for weeks after the experiments were completed. This is not uncommon with amines and phosphines.

The measurements were made on two conventional Stark-modulated microwave spectrometers, one located at the University of Southern California and the other at the Jet Propulsion Laboratory, California Institute of Technology. Each instrument was capable of obtaining precisions of 0.05 MHz.

**Spectra and Assignment.** An approximate spectrum of phosphirane was calculated using the bond distances in methylphosphine and assuming *a*- and *c*-type selection rules. The observed spectrum was found to be very intense. Both *a*- and *c*-type transitions were observed. Besides the normal species (I), the spectra of the following isotopes were assigned by their resolved stark effects. Though it was possible to assign the *a*-type transitions of the C<sup>13</sup> isotope in



(1) (a) Supported in part by National Aeronautics Space Administration under Contract NAS 7-100 extended to the Jet Propulsion Laboratory, by the Sloan Foundation under a fellowship and by the Air Force Office of Scientific Research under Grant AFOSR 749-67 extended to R. A. Beaudet, and by Public Health Service Grant No. 5 CA-07182 from the National Cancer Institute extended to H. Goldwhite. (b) U. S. Army assigned to Jet Propulsion Laboratory, California Institute of Technology, under Contract NAS 7-100 sponsored by the National Aeronautics and Space Administration; (c) University of Southern California; (d) California State College at Los Angeles.

(2) (a) T. E. Turner and J. A. Howe, *J. Chem. Phys.*, **24**, 924L (1956); (b) G. L. Cunningham, A. W. Boyd, R. J. Myers, W. D. Gwinn, and W. I. LeVan, *ibid.*, **19**, 676 (1951).

(3) T. E. Turner, V. C. Fiora, and W. M. Kendrick, *ibid.*, **23**, 1966L (1955).

(4) R. I. Wagner, L. D. Freeman, H. Goldwhite, and D. G. Roswell, *J. Am. Chem. Soc.*, **89**, 1102 (1967).

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

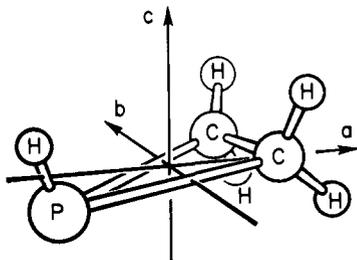


Figure 1. Orientation of principal axes in phosphirane.

natural abundance, the  $c$  types were only assigned after an enriched species was synthesized. The assigned lines of all species are given in Tables I and II. The rotational constants and moments of inertia are given in Table III. The physical mass scale using  $O^{16}$  as a mass of 16.0000 was used. The frequencies calculated from the rotational constants of Table III have been included in Table I, but only the deviations between the observed and calculated frequencies,  $\nu_{\text{obsd}} - \nu_{\text{calcd}}$ , have been included in Table II.

Table I. Comparison of Observed and Calculated Transition Frequencies in MHz for Phosphirane ( $\text{CH}_2\text{CH}_2\text{PH}$ )

Transition	$\nu_{\text{obsd}}^a$	$\nu_{\text{calcd}}$	$\Delta(\nu_{\text{obsd}} - \nu_{\text{calcd}})$
<i>a</i> Type			
$1_{01} - 0_{00}^b$	17,435.48	17,435.48	0.00
$2_{02} - 1_{01}$	34,563.42	34,563.44	-0.02
$2_{11} - 1_{10}$	37,037.63	37,038.07	-0.40
$2_{12} - 1_{11}^b$	32,703.85	22,703.85	0.00
$3_{12} - 3_{13}$	12,973.74	12,975.05	-1.31
$4_{13} - 4_{14}$	21,477.55	21,480.08	-2.53
$5_{14} - 5_{15}$	31,755.58	31,760.15	-4.57
$6_{24} - 6_{25}$	16,267.38	16,272.77	-5.39
$7_{25} - 7_{26}$	25,634.36	25,643.63	-8.27
$10_{37} - 10_{38}$	27,127.86	27,150.78	-22.92
$12_{48} - 12_{49}$	16,866.75	16,894.59	-27.84
<i>c</i> Type			
$1_{10} - 0_{00}^b$	29,896.00	29,896.00	0.00
$2_{02} - 1_{10}$	22,102.70	22,102.92	-0.22
$3_{12} - 2_{20}$	24,160.23	24,161.48	-1.25
$4_{14} - 3_{22}$	24,054.37	24,054.35	+0.02
$1_{11} - 1_{01}$	10,293.57	10,293.41	+0.16
$2_{12} - 2_{02}$	8,434.06	8,433.82	+0.24
$2_{21} - 2_{11}$	30,880.44	30,880.23	+0.21
$3_{22} - 3_{12}$	27,837.82	27,837.44	+0.38
$4_{23} - 4_{13}$	23,967.87	23,967.12	+0.75
$5_{24} - 5_{14}$	19,514.16	19,512.80	+1.36
$6_{25} - 6_{15}$	14,859.50	14,857.51	+1.99
$7_{26} - 7_{16}$	10,492.39	10,489.83	+2.56
$9_{37} - 9_{27}$	26,003.36	25,996.34	+7.02
$11_{39} - 11_{29}$	13,454.45	13,442.56	+11.89

<sup>a</sup> The estimated error in the observed frequencies is  $\pm 0.05$  MHz.

<sup>b</sup> These transitions were used to determine  $a$ ,  $b$ , and  $c$  and hence the calculated spectra.

For three transitions,  $4_{13}-4_{14}$  in II and  $5_{14}-5_{15}$  in IV and V, large discrepancies between the calculated and measured values were observed (see Table II). When an attempt was made to remeasure these lines, it was found that the samples had inadvertently decomposed. Hence, the results for these three lines may be erroneous. All other deviations can be nominally attributed to centrifugal distortion.

### Molecular Structure

The molecular structure was determined by the Kraitchman method.<sup>5</sup> As Costain<sup>6</sup> has shown, this technique tends to minimize errors in the structure due to zero-point vibrational effects. For a molecule of the size of phosphirane, it would be an insur-

(6) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).

mountable task to calculate exactly the effects of the  $(3N - 6)$  normal modes as Morino<sup>7</sup> has done for some simple molecules.

The Kraitchman method calculates the center of mass coordinates of a nuclei from the differences in the moments of inertia which arise when an isotopic substitution is made for that nuclei. Hence if the zero-point vibrational effects are the same for both isotopic species, they should cancel out in the difference of the moments of inertia.

Since the Kraitchman method determines the square of the coordinates in the principal axes system, the signs of the coordinates are not determined. Usually the assignment of the signs is unambiguous. However, since the two types of hydrogen (*cis* and *trans*) have nearly the same coordinates, the correct assignment is not immediately evident. For the two possible assignments of signs of the hydrogen coordinates, bond lengths of 1.103 and 1.082 or 1.093 and 1.092 Å were obtained for the *trans*- and *cis*-hydrogens, respectively. It seems reasonable that the second choice is correct, so it is listed in Table IV. This choice is further substantiated by comparing the relative effect of *cis* and *trans* deuteration on the moments of inertia (Table III). One can quickly satisfy oneself that the *cis*-deuterated species must have the largest increase in  $I_a$ .

The coordinates and signs of all remaining nuclei except the phosphorus nucleus and the  $c$  coordinate of the carbon nuclei can be unambiguously determined by a straightforward application of Kraitchman's method. Since phosphorus has only one stable isotopic species, the Kraitchman method cannot be used to determine its location. However, the phosphorus  $a$  coordinate can be determined from the center of mass condition  $\sum m_i a_i = 0$ . The  $b$  coordinate must be zero if a plane of symmetry is assumed. For the  $c$  coordinates of the carbon atoms a further complication arises. Because the carbon atoms are very close to the  $ab$  plane (see Figure 1), the  $c$  coordinate of the two carbons could not be accurately determined by the isotopic substitution method. In order to determine the  $c$  coordinates of the phosphorus nucleus and the two carbon nuclei, three conditions are necessary. For one condition we can assume that the  $ac$  plane is a plane of symmetry. The other two conditions are  $\sum m_i c_i = 0$  and  $\sum m_i c_i a_i = 0$  which are solved simultaneously for the carbon and phosphorus  $c$  coordinates. The results are given in Table IV.

It is impossible to calculate the effect of the zero-point vibrations on every coordinate, so the true equilibrium coordinates cannot be determined. However, it is reasonable to assume that these zero-point effects reflect less than a  $\pm 0.005$ -Å error in the bond length and  $\pm 0.5^\circ$  error in the bond angles.

### Stark Effect and Dipole Moment

The dipole moment of phosphirane was determined by studying the Stark effect of the  $M = 0$  lobes of the  $1_{01}-0_{00}$ ,  $2_{12}-1_{11}$ , and  $1_{10}-0_{00}$  transitions and the  $M = |2|$  and  $M = |3|$  lobes of the  $3_{13}-3_{12}$  line. These particular transitions were picked for their high sensitivity to either  $\mu_a$  or  $\mu_c$ . The  $\mu_b$  component was assumed to be zero by symmetry.

(7) Y. Morino, Second Austin Symposium on Gas Phase Molecular Structure, Austin, Texas, Feb 26-27, 1968.

**Table II.** Observed Rotational Frequencies in MHz and a Comparison with Calculated Frequencies for Four Isotopic Species of Phosphirane

Transition	D-P		<sup>13</sup> C		C-D ( <i>cis</i> ) <sup>b</sup>		C-D ( <i>trans</i> ) <sup>b</sup>	
	$\nu$	$\Delta\nu^a$	$\nu$	$\Delta\nu^a$	$\nu$	$\Delta\nu$	$\nu$	$\Delta\nu$
	a Type							
1 <sub>01</sub> -0 <sub>00</sub> <sup>c</sup>	16,814.30	0.00	17,135.22	0.00	16,695.09	0.00	16,693.68	0.00
2 <sub>02</sub> -1 <sub>01</sub>	33,400.98	-0.07	33,954.94	-0.14	33,065.02	-0.06	33,063.47	-0.07
2 <sub>11</sub> -1 <sub>10</sub>	35,406.02	-0.56	36,438.90	-0.41	35,488.25	-0.46	35,483.90	-0.47
2 <sub>12</sub> -1 <sub>11</sub> <sup>c</sup>	31,850.62	0.00	32,101.55	0.00	31,291.65	0.00	21,290.35	0.00
4 <sub>13</sub> -4 <sub>14</sub>	17,649.50	-2.88	21,477.50	(-10.65)	20,762.22	-2.63	20,748.36	-2.86
5 <sub>14</sub> -5 <sub>15</sub>	26,164.79	-4.66	31,744.96	-4.85	30,647.90	(27.90)	30,630.89	(27.23)
6 <sub>24</sub> -6 <sub>25</sub>	12,507.25	-4.74	16,521.81	-6.63	16,589.26	-5.17	16,546.28	-5.63
	c Type							
1 <sub>10</sub> -0 <sub>00</sub> <sup>c</sup>	28,067.92	0.00	29,327.49	0.00	27,822.76	0.00	27,846.23	0.00
2 <sub>21</sub> -2 <sub>11</sub>	28,427.30	0.21	30,070.64	0.52	27,087.73	0.31	27,166.98	0.36
3 <sub>22</sub> -3 <sub>12</sub>	25,913.06	0.38	27,031.16	0.71	24,161.67	0.53	24,242.27	0.59
4 <sub>23</sub> -4 <sub>13</sub>	22,693.91	0.75	23,171.88	1.88	20,464.47	0.87	20,545.90	1.02
5 <sub>24</sub> -5 <sub>14</sub>	18,940.47	1.36	18,745.96	1.74	16,265.96	1.41	16,346.02	1.59
6 <sub>25</sub> -6 <sub>15</sub>	14,923.88	1.99	14,149.37	2.30	11,982.90	1.93	12,057.40	2.11

<sup>a</sup>  $\Delta\nu = \nu_{\text{obsd}} - \nu_{\text{calcd}}$ . <sup>b</sup> *cis* and *trans* relative to the hydrogen on the phosphorus. <sup>c</sup> Used to determine *a*, *b*, and *c* and hence the calculated spectra.

**Table III.** Rotational Constants and Moments of Inertia of the Isotopes of Phosphirane

	—Rotational constants, MHz <sup>a</sup> —		
	<i>a</i>	<i>b</i>	<i>c</i>
Phosphirane	20,094.70	9801.29	7634.19
Phosphirane-P- <i>d</i>	18,771.85	9296.07	7518.18
<i>cis</i> -Phosphirane-C- <i>d</i> <sub>1</sub>	18,425.95	9396.81	7298.28
<i>trans</i> -Phosphirane-C- <i>d</i> <sub>1</sub>	18,450.88	9395.34	7298.335
Phosphirane- <sup>13</sup> C	19,675.43	9652.05	7483.16
	Moments of inertia, amu Å <sup>2</sup> <sup>b</sup>		
	<i>I<sub>a</sub></i>	<i>I<sub>b</sub></i>	<i>I<sub>c</sub></i>
Phosphirane-C- <i>d</i> <sub>1</sub>	25.1574	51.4780	66.2193
Phosphirane-P- <i>d</i>	26.9302	54.3811	67.2411
<i>cis</i> -Phosphirane-C- <i>d</i> <sub>1</sub>	27.4358	53.7981	69.2671
<i>trans</i> -Phosphirane-C- <i>d</i> <sub>1</sub>	27.3987	53.8066	69.2667
Phosphirane- <sup>13</sup> C	25.6935	52.3755	67.5558

<sup>a</sup> Values  $\pm 0.15$  MHz. <sup>b</sup> Values  $\pm 0.005$  amu Å<sup>2</sup>.

**Table IV.** Center of Mass Coordinates (Å) of Phosphirane<sup>a</sup>

	<i>a</i>	<i>b</i>	<i>c</i>
P	-0.815 <sup>c</sup>	0.000 <sup>b</sup>	-0.050 <sup>d</sup>
C <sub>1</sub>	0.893	0.751	0.006 <sup>d</sup>
C <sub>2</sub>	0.893	-0.751	0.006
H <sub>P</sub>	-1.003	0.000 <sup>b</sup>	1.366
H <sub>1</sub> ( <i>cis</i> )	1.190	+1.264	0.923
H <sub>2</sub> ( <i>cis</i> )	1.190	-1.264	0.923
H <sub>1</sub> ( <i>trans</i> )	1.200	1.256	-0.914
H <sub>2</sub> ( <i>trans</i> )	1.200	-1.256	-0.914

<sup>a</sup> Errors are estimated to be  $\pm 0.005$  Å due to vibrational effects. The signs of all coordinates were chosen to give reasonable values of the bond distances. <sup>b</sup> Assumed zero by symmetry. <sup>c</sup> Calculated from the condition  $\sum_i m_i a_i = 0$ . <sup>d</sup> Calculated from the conditions  $\sum_i m_i c_i = 0$  and  $\sum m_i a_i c_i = 0$ .

The measurements were carried out by measuring the shift in line frequencies when a fixed square-wave voltage was superimposed on a variable dc biasing voltage. The dc voltage was supplied by a Fluke 412B power supply. The electric field for the various settings of the decade switches on the power supply were calibrated with OCS. The dipole moment of OCS was taken to be 0.7124 D.<sup>8</sup>

The dipole moment components were obtained by

(8) S. A. Marshall and J. Weber, *Phys. Rev.*, **105**, 1502 (1957).

least-squares fitting the observed Stark effects to the relationship

$$\frac{\Delta\nu}{E^2} = A_{J_T\mu_i;J'_T\mu'_i}|\mu_a|^2 + C_{J_T\mu_i;J'_T\mu'_i}|\mu_c|^2$$

The coefficients *A* and *C* were obtained from a computer program for the asymmetric rotor which is described elsewhere.<sup>9</sup> The final values with standard deviations are  $\mu_a = 1.032 \pm 0.007$  D,  $\mu_c = 0.439 \pm 0.005$  D, and  $\mu_{\text{tot}} = 1.12 \pm 0.01$  D.

### Discussion

One interesting feature in the molecular structure of phosphirane is the apparent repulsion of the *cis*-ethylene hydrogens by the P-H group. The *cis*-hydrogens are 0.035 Å further away from the phosphorus than the *trans*. This deviation is considerably larger than the estimated uncertainty of  $\pm 0.005$  Å. In addition, the angle between the C-H bond and the plane of the ring is 2.2° larger for the *cis* than for the *trans*. Therefore, the *cis*-hydrogens appear to be bent away from the P-H group. It seems unlikely that an effect as large as 0.035 Å would be due to zero-point vibrations. It is also difficult to rationalize that this "repulsion" is due to a nonbonded hydrogen-hydrogen interaction since H<sub>P</sub> and H<sub>*cis*</sub> are separated by 2.57 Å which is greater than the sum of the van der Waals radii.

The HPC angle in phosphirane is 95.2° (Table V), indicating nearly pure p-type hybridization of the phosphorus in the P-H bond. This fact is confirmed by the high-resolution nmr data. Manatt, *et al.*,<sup>10</sup> have proposed that the P-H spin-spin coupling constant is related to the amount of s character in the phosphorus orbital making up the P-H bond by the relationship  $J_{\text{H-P}} = 29.30s_{\text{P}}$ , where  $s_{\text{P}}$  is the per cent s character of a phosphorus orbital to hydrogen.  $J_{\text{H-P}}$  for phosphirane has been determined to be<sup>11</sup>  $\sim 156$  Hz. This gives an  $s_{\text{P}}$  of 5.3%. This value of  $s_{\text{P}}$  is somewhat lower than the 6.4 and 6.5% s character in CH<sub>3</sub>PH<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>PH, respectively.<sup>10</sup>

(9) R. A. Beaudet, Doctoral Thesis, Harvard University, 1962.

(10) S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, *J. Am. Chem. Soc.*, **88**, 2689 (1966).

(11) M. T. Bowers and S. L. Manatt, to be submitted for publication.

**Table V.** Bond Distances and Angles in Phosphirane

—Bond distances, Å—		—Bond angles, deg—	
C-P	1.867	C <sub>1</sub> -P-C <sub>2</sub>	47.4
P-HP	1.428	H-P-ring plane	95.7
C <sub>1</sub> -C <sub>2</sub>	1.502	H <sub>cis</sub> -C-H <sub>trans</sub>	114.4
C <sub>1</sub> -H <sub>cis</sub>	1.092	H <sub>P</sub> -P-C	95.2
C <sub>1</sub> -H <sub>trans</sub>	1.093	∠C-C-H <sub>cis</sub>	118.0
P-H <sub>trans</sub>	2.527	∠C-C-H <sub>trans</sub>	117.5
P-H <sub>cis</sub>	2.562	∠H <sub>cis</sub> -C-ring plane	123.9 ± 0.5
H <sub>P</sub> -H <sub>cis</sub>	2.570	∠H <sub>trans</sub> -C-ring plane	121.7 ± 0.5

The CPC angle of 47.4° indicates that the P-C orbitals on the phosphorus are also nearly pure p type since the phosphorus orbitals engaged in the bonding with the carbon atoms will strive for maximum overlap with the carbon orbitals,<sup>12</sup> and, since a 90° angle signifies pure p orbitals (assuming only s,p hybridization), it appears that the phosphorus orbitals bonding with the carbon atoms are nearly pure p type.

The lone pair is thus located in a hybrid orbital which is nearly pure 3s and presumably not highly oriented, *i.e.*, unpolarized. If we assume that the lone-pair bond moment is approximately 0.8 D larger in the nitrogen compounds than in the analogous phosphorus compound, all the differences between the dipole moments can be accounted for. For example, dipole moments of phosphine (0.55 D), PF<sub>3</sub> (1.02 D), and phosphirane (1.12 D) then differ from NH<sub>3</sub> (1.47 D), NF<sub>3</sub> (0.28 D), and ethylenimine (1.89 D) by approximately 0.8 D

(12) C. A. Coulson, "Valence," Oxford University Press, New York, N. Y., 1961, pp 194-195.

**Table VI.** Comparison of Bond Lengths (Å) and Bond Angles (Degrees) for Phosphirane, Ethylene Sulfide, Ethylenimine, and Ethylene Oxide

	H P <sup>a</sup> CH <sub>2</sub> -CH <sub>2</sub>	H S <sup>b</sup> CH <sub>2</sub> -CH <sub>2</sub>	H N <sup>c</sup> CH <sub>2</sub> -CH <sub>2</sub>	H O <sup>b</sup> CH <sub>2</sub> -CH <sub>2</sub>
r(C-C)	1.502	1.472 <sup>d</sup>	1.480	1.472
r(C-H)	1.093	1.078	1.083	1.082
r(C-X)	1.867	1.819	1.488	1.436
r(X-H)	1.428		1.000	
∠CXC	47.4	48.50 <sup>e</sup>	60.0	61.4
∠HCH	114.4	116.0	116.7	116.6
∠CCH	117.5			
∠C-CH <sub>2</sub>	149.5	151.70	159.4	159.5
∠HXC	95.2			
∠HXC <sub>2</sub>	95.7		112.0	

<sup>a</sup> This work. <sup>b</sup> Reference 2<sup>b</sup>. <sup>c</sup> Reference 3. The ethylenimine structure has not been completely done by isotropic substitution. <sup>d</sup> Taken from Figure 10 of ref 2b. The reported value of 1.492 Å in Table XIV of ref 2b appears to be a typographical error. <sup>e</sup> Re-calculated from the original data in ref 2b.

when the lone-pair bond moment is added and the signs of the dipoles are taken into account.

A comparison of bond lengths and bond angles for phosphirane, ethylene sulfide, ethylenimine, and ethylene oxide is given in Table VI.

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## Spectroscopic Studies of the Solvation of Alkali Metal Ions in Dialkyl Sulfoxide Solutions<sup>1</sup>

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**Abstract:** Infrared spectra of a large number of alkali metal salts have been obtained in the 5000-100-cm<sup>-1</sup> spectral region in dimethyl sulfoxide, dipropyl sulfoxide, and dibutyl sulfoxide. In all cases, a band was obtained in the 500-100-cm<sup>-1</sup> region whose frequency is characteristic of the cation and the solvent but not of the anion. The results indicate that these low-frequency bands are due to the vibrations of the cations in a solvent cage. The study of ν<sub>S-O</sub> indicates that the solvent dipoles are oriented with the oxygen atom in direct proximity to the metal. Bands obtained with DMSO-d<sub>6</sub> and with NH<sub>4</sub>-d<sub>4</sub> show predictable spectral shifts related to the change in the reduced mass of the vibrating system.

The importance of solvation phenomena in the mechanism of reactions in solutions is patently obvious and needs no emphasis. Historically a variety of experimental techniques have been used in the determination of solvation numbers of ions. These include studies of various physicochemical properties of solutions such as refractive index, freezing and boiling points, vapor pressure, surface tension, density, specific

heat, ionic transport numbers, and solubility studies. These classical techniques have been adequately reviewed by Bockris.<sup>2</sup>

In recent years the application of nuclear magnetic resonance spectroscopy to investigations of solvation phenomena has become quite widespread. In most cases this technique has been used in studies of transition metal ions. An excellent recent review thoroughly covers the literature to 1966.<sup>3</sup>

(1) Taken in part from the Ph.D. Thesis of B. W. Maxey, Michigan State University, 1968.

(2) J. O'M. Bockris, *Quart. Rev.* (London), 3, 173 (1949).