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SPECTRA OF SILYLPHOSPHINE , SILYLARSINE ,
GERMYLOPHOSPHINE AND GERMYLARSINE**

Berkeley, California

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HIGH RESOLUTION PROTON MAGNETIC RESONANCE SPECTRA OF
SILYLPHOSPHINE, SILYLARSINE, GERMYLPHOSPHINE AND GERMYLARSINE

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ABSTRACT

The proton magnetic resonance spectra of SiH_3PH_2 , SiH_3AsH_2 ,
 GeH_3PH_2 and GeH_3AsH_2 are described and interpreted.

INTRODUCTION

We have previously¹ described the formation of "mixed hydrides" in a silent electric discharge. The proton magnetic resonance spectra of four of these hydrides: silylphosphine (SiH_3PH_2), silylarsine (SiH_3AsH_2), germylphosphine (GeH_3PH_2) and germylarsine (GeH_3AsH_2), are described in this paper.

EXPERIMENTAL

The samples were sealed, under vacuum, in 5 mm. ext. diam. Pyrex tubes. The spectra were run on a Varian Model A 60 spectrometer, with a spinning sample, at sweep widths ranging from 50-500 cps. The spectra are presented in Figs. 1-4. Tetramethylsilane (T.M.S.) was used throughout as an internal standard. With the silyl compounds, disilane was used as an additional internal reference, and with the germyl compounds, digermene was used. The relative amounts of T.M.S. and of disilane or digermene were changed, but the relative positions of the resonance frequencies never changed by more than 1%.

DESCRIPTION OF SPECTRA

Spectrum of SiH_3PH_2 (Fig. 1)

The spectrum is as might be predicted. The $-\text{SiH}_3$ resonance is split into a 1:2:1 triplet by the two hydrogen atoms on the phosphorous atom, and the $-\text{PH}_2$ resonance is split into a 1:3:3:1 quartet by the three hydrogen atoms on the silicon atom. Because phosphorous (P^{31} , 100% abundant) has a magnetic nucleus of spin $\frac{1}{2}$, there is additional splitting. The splitting of the hydrogen atoms on the phosphorous atom is large, resulting in the quartet being split into a widely separated pair of quartets of equal intensity (centered at 1.31 ppm to low field of T.M.S.) by the J_{PH} coupling. The splitting of

the hydrogen atoms on the silicon atom is much less resulting in a comparatively smaller splitting of the triplet into a pair of triplets (centered at 3.73 ppm to low field of T.M.S.) by the J_{PH} coupling. The most abundant silicon isotope (Si^{28} , 92.2% abundant) has no magnetic nucleus spin, but the isotope Si^{29} (4.7% abundant) has a magnetic nucleus of spin $\frac{1}{2}$. At high spectrum amplitude the 'satellites' caused by this spin can be seen and there is splitting of the 'double-triplet' $-SiH_3$ resonance by the J_{SiH} coupling. We were unable to detect the splitting caused by the $J_{SiH'}$ coupling. The intensity of the satellite triplets is about 4-5% that of the main triplets, and the intensities of the $-SiH_3$ triplets and the $-PH_2$ quartets are in the ratio of 3:2.

Spectrum of SiH_3AsH_2' (Fig. 2)

Because arsenic (As^{75} , 100% abundant) has a magnetic nucleus of spin $\frac{3}{2}$, one might expect the spectrum to be similar to that of SiH_3PH_2' , except that the $-SiH_3$ triplet and the $-AsH_2'$ quartet would undergo fourfold, rather than twofold, splitting. However, no splitting occurs due either to J_{AsH} or $J_{AsH'}$ coupling, probably because arsenic has a high nuclear electric quadrupole moment ($Q = 0.3 \times e \times 10^{-24} \text{ cm}^2$) and the asymmetries of the electron charge distribution about the nucleus result in line broadening rather than splitting. As a result, the $-SiH_3$ resonance is a simple 1:2:1 triplet and the $-AsH_2'$ resonance is a much broadened 1:3:3:1 quartet. At high spectrum amplitude the splitting from the J_{SiH} coupling can be seen, the intensity of the 'satellites' again being 4-5% of the main resonance peaks.

Spectra of GeH_3PH_2' and GeH_3AsH_2' (Figs. 3 and 4)

These are very similar to those of the corresponding silyl compounds, because the more abundant isotopes of germanium have no nuclear magnetic

moments. There are no 'satellite' peaks because the only isotope to have a nuclear magnetic spin (Ge^{73} , spin = $\frac{9}{2}$) is only 7.8% abundant and also have a high nuclear electric quadrupole moment ($Q = -0.2 \times e \times 10^{-24} \text{ cm}^2$).

DISCUSSION

The values of the various coupling constants are summarized in Table I. No coupling is found between hydrogen atoms on the same atom, indicating that there is no restriction to rotation. That is, the three hydrogen atoms on the silicon or germanium atoms are equivalent to one another, as are the two hydrogen atoms on the phosphorus and arsenic atoms.

For $\text{SiH}_3\text{PH}'_2$ the value of the J_{SiH} coupling constant is 204 ± 1 cps, which is close to the value reported for the pure silanes ($\text{Si}_2\text{H}_6 = 199$ cps)² and the value of the J_{PH} coupling constant is 180 ± 1 cps, which is close to the value reported for phosphine and diphosphine. ($\text{P}_2\text{H}_4 = 186$ cps)³.

The similarities of the coupling constants seems to indicate that there is not much change in hybridization, bond length or bond angle in either the P-H or the Si-H bonds. Because the differences are so slight we may only tentatively predict a slight decrease in the 's' character in the P-H bond and a corresponding increase in the 's' character of the Si-H bonds on the basis of the slightly lower value for J_{PH} and higher value for J_{SiH} in the mixed hydrides. The coupling J_{PH} (i.e. of phosphorous with a hydrogen atom on an adjacent atom) is slightly greater in the case of silylphosphine (16.2 cps) than in germylphosphine (15.3 cps) and both are greater than the value for diphosphine. The value of J_{HH} is slightly greater in the silyl compounds than in the germyl compounds. However, at this time, it is not possible to put forward any concrete explanation for these differences particularly as the differences are so small.

The relative chemical shifts of the resonance peaks (shown in Table II) may be explained, to a first approximation, by differences in electronegativity. As a phosphorus atom replaces either a silicon or germanium atom in disilane or digermane its greater electronegativity should result in a decrease in the shielding of the hydrogen atoms in $-\text{SiH}_3$ and $-\text{GeH}_3$, and shift the resonance to lower fields. The shifts are to lower field being 0.55 ppm on going from Si_2H_6 to $\text{SiH}_3\text{PH}'_2$, and 0.46 ppm on going from Ge_2H_6 to $\text{GeH}_3\text{PH}'_2$. The fact that the shift is less in the germyl compound may indicate that germanium has a higher electronegativity than silicon, as has been suggested by Rochow and Allred.⁴ The arsine compounds parallel the phosphine compounds in that there is a shift to lower field of 0.45 ppm on going from Si_2H_6 to $\text{SiH}_3\text{AsH}'_2$, and of 0.36 ppm on going from Ge_2H_6 to $\text{GeH}_3\text{AsH}'_2$. The fact that the shifts are greater for replacement with a phosphorous atom than with an arsenic atom, agrees with the generally accepted view that phosphorous has the higher value of electronegativity.

If germanium has a higher electronegativity than silicon, then the differences of electronegativity are greater between silicon and phosphorous or arsenic, than with germanium and phosphorous or arsenic, and so we should expect that the H' resonances would occur to higher field in the cases of $\text{SiH}_3\text{PH}'_2$ and $\text{SiH}_3\text{AsH}'_2$ than in $\text{GeH}_3\text{PH}'_2$ and $\text{GeH}_3\text{AsH}'_2$, respectively. This is the case. Finally, as the state of hybridization in all the compounds discussed seems to be the same, the data indicate that the order of electronegativities is $\text{P} > \text{As} > \text{Ge} > \text{Si}$.

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TABLE I
Coupling Constants (in cps)

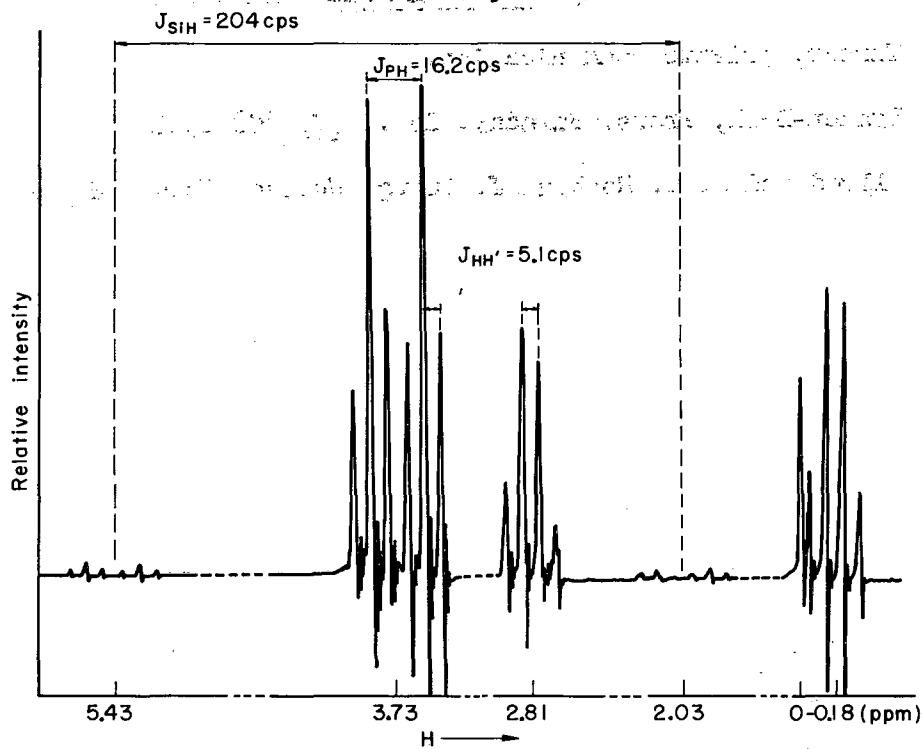
Compound	J_{SiH}	$J_{\text{HH}'}$	$J_{\text{PH}'}$	J_{PH}
$\text{SiH}_3\text{PH}'_2$	204 \pm 1	5.1 \pm .1	180 \pm 1	16.2 \pm .2
$\text{SiH}_3\text{AsH}'_2$	203 \pm 1	5.1 \pm .1	-	-
$\text{GeH}_3\text{PH}'_2$	-	4.8 \pm .1	180 \pm 1	15.3 \pm .2
$\text{GeH}_3\text{AsH}'_2$	-	4.8 \pm .1	-	-

TABLE II
Resonance Position (to low field of internal T.M.S.)
(in ppm)

	$-\text{SiH}_3$	$-\text{GeH}_3$	$-\text{PH}'_2$	$-\text{AsH}'_2$
$\text{SiH}_3\text{PH}'_2$	3.73	-	1.31	-
$\text{SiH}_3\text{AsH}'_2$	3.67	-	-	0.78
SiH_3SiH_3	3.22	-	-	-
$\text{GeH}_3\text{PH}'_2$	-	3.67	1.41	-
$\text{GeH}_3\text{AsH}'_2$	-	3.57	-	1.02
GeH_3GeH_3	-	3.21	-	-

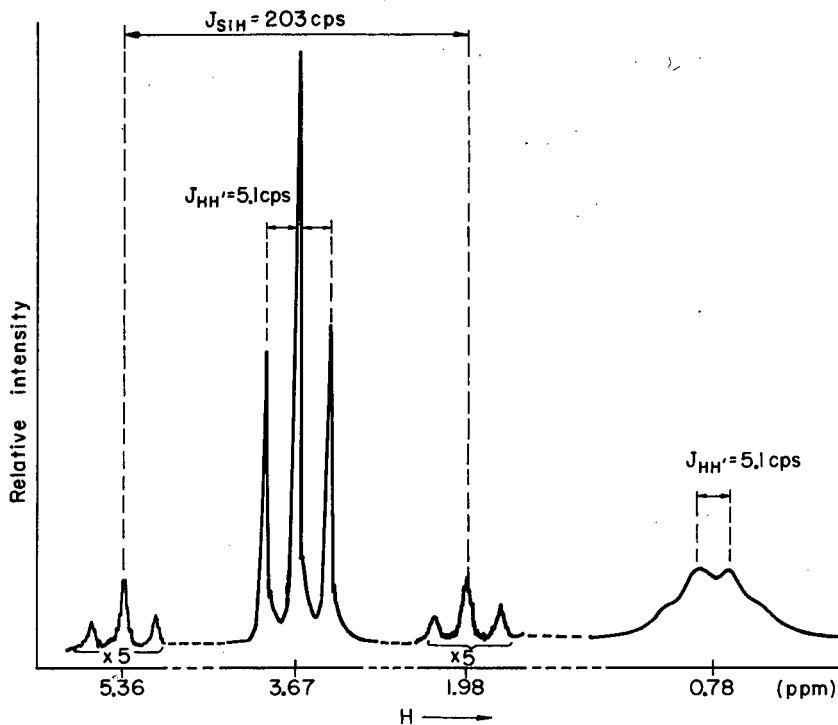
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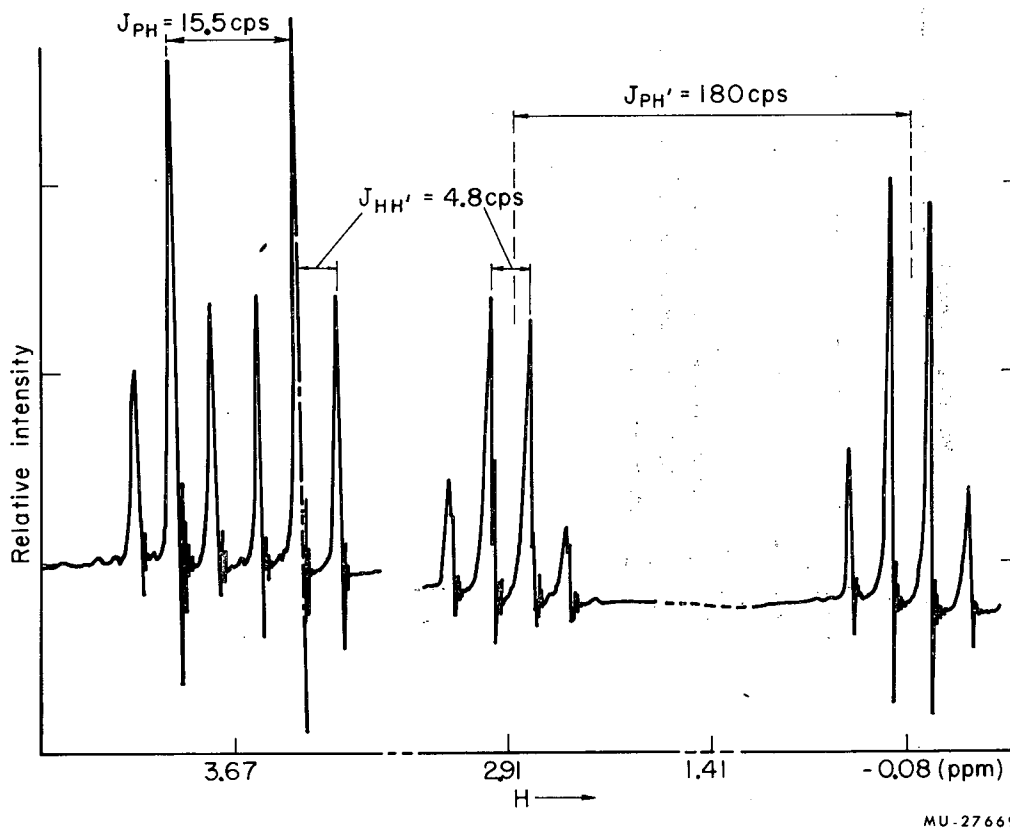
MU-27670

1. The proton magnetic resonance spectrum of silylphosphine (SiH_3PH_2) at 60 Mc/sec. with a sweep width of 500 cps. The reference compound is T.M.S. as an internal standard.

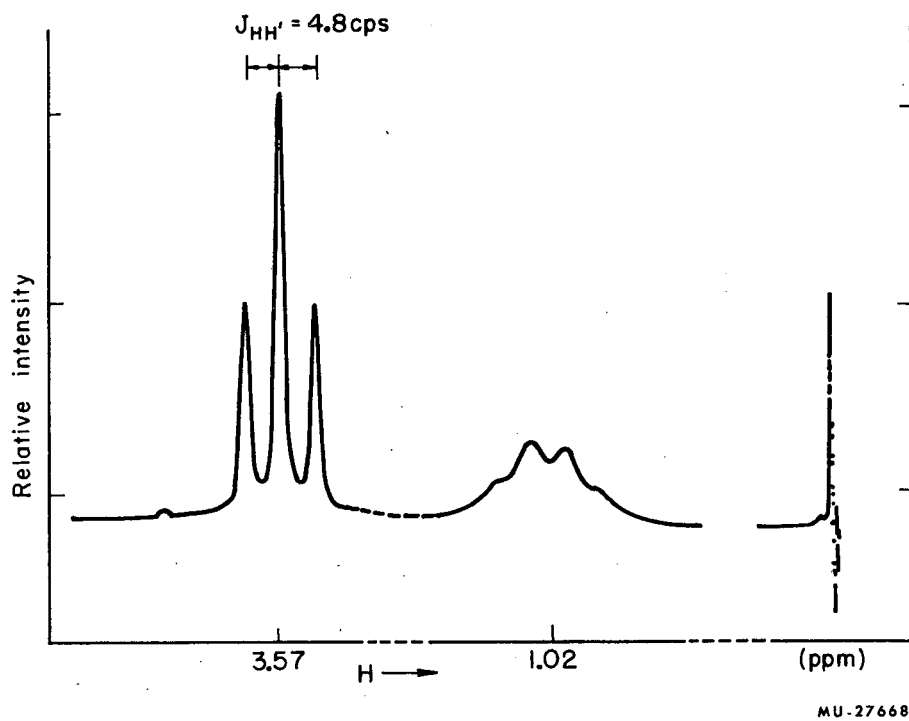


MU-27671

2. The proton magnetic resonance spectrum of silylarsine (SiH_3AsH_2) at 60 Mc/sec. with a sweep width of 250 cps. The reference compound is T.M.S. as an internal standard.



3. The proton magnetic resonance spectrum of germylphosphine (GeH_3PH_2) at 60 Mc/sec. with a sweep width of 250 cps. The reference compound is T.M.S. as an internal standard.



4. The proton magnetic resonance spectrum of germylarsine (GeH_3AsH_2) at 60 Mc/sec. with a sweep width of 250 cps. The reference compound is T.M.S. as an internal standard.

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