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The Vibrational Spectra of Digermylarsine and Digermylphosphine

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Received July 25, 1968

The infrared spectra of digermylarsine $(GeH_3)_2AsH$ and digermylphosphine $(GeH_3)_2PH$ have been recorded in the region 4000-400 cm^{-1} together with the Raman spectrum of $(GeH_3)_2AsH$. With the aid of the Raman polarisation data, tentative assignments are made to the bands observed in the expected fundamental absorption regions assuming C_s symmetry.

Introduction

Mono-, di- and trigermylarsines $(GeH_3)_nAsH_{3-n}$; n = 1,2,3, as well as the corresponding phosphines are all known.[1-3] Detailed analyses of the vibrational spectra of GeH_3AsH_2[4] and GeH_3PH_2[5] have resulted in the assignment in both molecules of 14 of the 15 fundamentals on the basis of C_s symmetry and of the trigermyl species only $(GeH_3)_3P$ has been studied in detail.[6] We wish to report the infrared spectrum of $(GeH_3)_2AsH$ in both the gaseous (Figure 1) and solid states (Table I) as well as the Raman spectrum of the liquid (Figure 2). Because $(GeH_3)_2PH$ is unstable in the condensed phase[2] only its gaseous infrared spectrum (Figure 3) could be recorded.

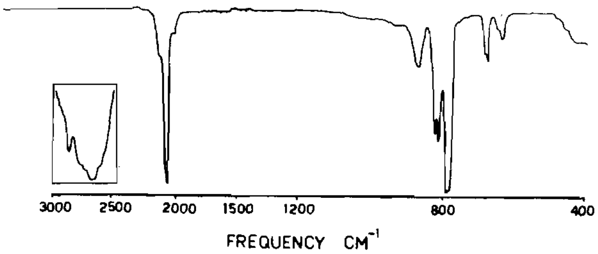

Figure 1. The gas phase infrared spectrum of $(GeH_3)_2AsH$.

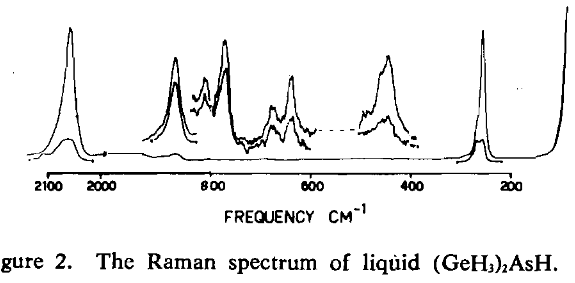

Figure 2. The Raman spectrum of liquid $(GeH_3)_2AsH$.

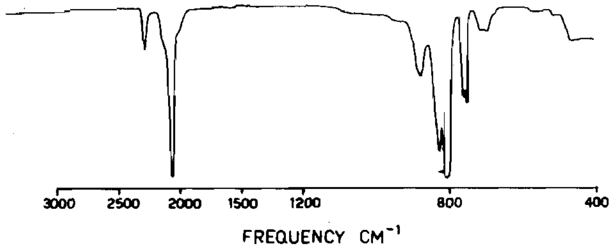

Figure 3. The gas phase infrared spectrum of $(GeH_3)_2PH$.

No structural data is available for the digermyl species but it is reasonable to assume C_s symmetry. This results in the 24 normal vibrations, all of which should be both infrared and Raman active, being divided into 13 a′ and 11 a″ modes. As was found with $(CH_3)_2NH$,[7] an approximate calculation of the moments of inertia indicates that the least moment of inertia lies along the axis at right angles to the molecular symmetry plane in both $(GeH_3)_2AsH$ and $(GeH_3)_2PH$. Consequently, mixed-contour vapour-phase infrared bands intermediate between B- and pure C-type are expected for the a′ modes and A-type bands with P,Q,R branches for the a″.[7] In the Raman effect the a′ modes should be at least partially polarised whereas the a″ modes should be depolarised.

Experimental Section

$(GeH_3)_2AsH$ and $(GeH_3)_2PH$ were formed during the self-condensation of monogermylarsine and monogermylphoshpine respectively.[2] They were separated by trap-to-trap distillation on a conventional greaseless vacuum line and their purity estimated by recording their ^1H n.m.r. spectra on a Varian A-60 high resolution spectrometer. This check was doubly important as we have shown that both hydrides tend to disproportionate.[2] However, this disproportionation is sufficiently slow in the case of $(GeH_3)_2AsH$ that the gas phase infrared spectrum of a freshly distilled sample remained constant during observation. Also, after a sample had been used for recording the Raman spectrum, its ^1H n.m.r. spectrum showed less than 5% of trigermylarsine as the only detectable impurity.

(1) J. E. Drake and W. L. Jolly, *Chem. and Ind.*, 1470, (1962).
(2) J. E. Drake and C. Riddle, *J. Chem. Soc. (A)*, 2709, (1968).
(3) S. Cradock, G. Davidson, E. A. V. Ebworth, and L. A. Woodward, *Chem. Comm.*, 515 (1966).
(4) J. E. Drake, C. Riddle, K. M. Mackay, K. J. Sutton and S. R. Stobart, *Spectrochim. Acta (A)*, in the press.
(5) K. M. Mackay, K. J. Sutton, S. R. Stobart, J. E. Drake and C. Riddle, *Spectrochim. Acta (A)*, in the press.
(6) S. Cradock, E. A. V. Ebsworth, G. Davidson and L. A. Woodward, *J. Chem. Soc. (A)*, 1229 (1967).
(7) M. J. Buttler and D. C. McMcKean, *Spectrochim. Acta*, *21*, 465 (1965).

Table I. The Observed Frequencies (cm^{-1}) for $(GeH_3)_2AsH$ and $(GeH_3)_2PH$

Approximate Description of motion	$(GeH_3)_2AsH$			$(GeH_3)_2PH$
	I.R. (vapour)	I.R. (solid)	Raman (liquid)	I.R. (vapour)
P-H stretch	—	—	—	2302 m
GeH_3 stretches	2135 sh	2100 sh	2115 br sh dep?	2140 sh
and As-H stretch	2100 sharp sh	2070 s		2080 vs
	2060)			2030 sh
	2055) s	2054 s	2056 vs pol	
	2050)			
	2045 sh			
	2010 sh			
M-H bend	$\sim$940 w	—	—	—
GeH_3 deformations	868 br m	858 s	867 m depol	880)
				871)
	820) s	815 sh	810 w depol	824 s
	811)	796 s		
	789)	772 s		804 vs
	784) vs		770 w depol	
	780)	758 s		755) m
				747)
M-H wag	681) m	668 m	675 w depol	706) w
	672)			689)
GeH_3 rocks	635 br m	630 m	638 w part. pol	? 515 br vw
	460 br w	480 w	$\sim$490 w sh	
		? 460 w	450 w pol	
As-Ge stretches	—	—	269 m depol	—
			258 vs pol	

where v = very, s = strong, m = medium, br = broad, sh = shoulder, part. = partially, w = weak, pol and depol indicate Raman polarised and depolarised bands respectively.

The disproportionation of $(GeH_3)_2PH$ is much more rapid so to estimate the purity of the freshly distilled sample at the end of one infrared scan, the sample was condensed onto tetramethylsilane and its ^1H n.m.r. spectrum in solution recorded immediately. This indicated that the decomposition of the $(GeH_3)_2PH$ had been less than 10%. However, subsequent n.m.r. spectra showed that even in solution in the sealed tubes its disproportionation to mono- and tri-germylphosphine was so rapid that a Raman spectrum would have little meaning. The figures for the gaseous spectrum of $(GeH_3)_2PH$ are listed with confidence (Table I) for although small amounts of GeH_3PH_2 and $(GeH_3)_3P$ may be present their spectra are well known.[5,6]

The infrared spectra were recorded in the region 4000-400 cm^{-1} on a Perkin-Elmer 337 spectrometer· A 5 cm. path length cell fitted with KBr windows was used for the gas samples which were run at up to 10 mm Hg pressure. The solid state spectrum was recorded by condensing a film of $(GeH_3)_2AsH$ onto a KBr plate cooled by liquid nitrogen and held in an evacuated cell fitted with KBr windows. The Raman spectrum was recorded on a Cary 81 laser Raman spectrometer using *ca.* 1 mm. diameter sealed sample tubes. The spectra were calibrated in the usual manner[8] and the positions of sharp bands are considered to be accurate to ±5 cm^{-1} (infrared, region 4000-1500 cm^{-1}), ±2 cm^{-1} (infrared, 1500-400 cm^{-1}) and ±2 cm^{-1} (Raman).

Results and Discussion

The observed frequencies for both $(GeH_3)_2AsH$ and $(GeH_3)_2PH$ are listed in Table I. The absorptions lie in regions fairly well defined as being associated with P-H, As-H and GeH_3 stretches, GeH_3 deformations, P-H or As-H wags, GeH_3 rocks and Ge-P or Ge-As stretches.

The P-H and As-H stretches. The PH stretching region, unlike that of AsH, is well separated from the GeH stretching region. The P-H stretch is clearly observed in the spectrum of $(GeH_3)_2PH$ as a basically C-type band at 2302 cm^{-1} which is similar to the value of 2310 cm^{-1} for the corresponding mode in GeH_3PH_2.[5] This region of the gaseous spectrum of $(GeH_3)_2AsH$ shows a sharp shoulder, which could be the C-type band of the As-H stretch, at 2100 cm^{-1} on the high frequency side of the main GeH_3 stretching envelope.

The Ge-H stretches. All of the six GeH_3 stretches are contained in a confined region for both hydrides. There is no clear underlying contour in the gaseous bands of $(GeH_3)_2PH$ and the situation is only slightly improved with gaseous $(GeH_3)_2AsH$ but an A-type band, possibly the a″ symmetric stretch can be picked out from the main feature. In the Raman effect there is a strong polarised band at 2056 cm^{-1} indicating that here the main contribution is possibly the a′ symmetric stretch.

Deformation modes· The GeH_3 deformation region should contain 3a′ and 3a″ vibrations with one of the a″ modes possibly very weak. In fact, five components can be seen in the solid infrared spectrum of $(GeH_3)_2AsH$ where there are three distinct peaks and two shoulders. Not surprisingly therefore, only three bands can be seen in both the gaseous infrared and Raman spectra of $(GeH_3)_2AsH$. None of the Raman bands is clearly polarised yet none of the vapour phase contours is clearly A-type so that a near coincidence

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(8) P. J. Hendra and E. J. Loader, *Chem. and Ind.*, 718 (1968).

of the a′ and a″ modes is suggested. The gaseous spectrum of $(GeH_3)_2PH$ in the main shows similar features.

The wagging modes. The bands at 699 cm^{-1} and 675 cm^{-1} in $(GeH_3)_2PH$ and $(GeH_3)_2AsH$ respectively are assigned as the a′ M-H wag. These values may be favourably compared with those of the corresponding vibration in GeH_3PH_2 (701 cm^{-1}) and GeH_3AsH_2 (646 cm^{-1}).[5,4] The weak band at 940 cm^{-1} is assumed to be the a″ wag which corresponds to the value of 960 cm^{-1}for the AsH_2 bend in GeH_3AsH_2.

The rocking modes. The weak bands around 515 cm^{-1} in $(GeH_3)_2PH$ are readily assigned to the GeH_3 rocks as they correspond to those in GeH_3PH_2 at 474 cm^{-1} where the assignment was supported by a normal coordinate calculation.[5] Similarly, by comparison with GeH_3AsH_2 in which the rocks were placed around 450 cm^{-1}, the weak band envelope centred at 460 cm^{-1} can be assigned. However, in the latter case there is some ambiguity because the weak band at 635 cm^{-1} would also appear to be a rocking mode. There is a wide variation in the position of these modes in comparable molecules which probably suggests varying degrees of coupling with other modes as was suggested by the calculations in the case of the monogermyl species.[4,5] Thus the rock has been assigned at 530 cm^{-1} in $(GeH_3)_3P$[6] and even as high as 650 cm^{-1} in $(GeH_3)_2O$.[9]

The skeletal and torsional modes. The torsional modes, which were not observed in GeH_3PH_2 or GeH_3AsH_2, and the skeletal bend are expected to be very weak in the digermyl species so it is not surprising that they were not detected· The skeletal stretches on the other hand ought to be strong in the Raman effect. In GeH_3AsH_2 the Ge-As stretch lies at 268 cm^{-1} which is the same value as has been reported for the Ge-Ge stretch in digermane.[10] In trigermane, Ge_3H_8, the symmetric and asymmetric skeletal stretches were found at 243 and 287 cm^{-1} respectively.[11] Thus the two bands observed in this region of the Raman spectrum of $(GeH_3)_2AsH$ are unambiguously assigned with the polarised band at 258 cm^{-1} as the symmetrical mode and the depolarised one at 269 cm^{-1} as the asymmetric mode.

Acknowledgements. One of us (C.R.) thanks the S.R.C. for the award of a studentship.

(9) S. Cradock, *J. Chem. Soc. (A)*, 1426 (1968).
(10) J. E. Griffiths and G. E. Walrafen, *J. Chem. Phys.*, *40*, 321 (1964).
(11) J. E. Drake and C. Riddle, unpublished obs. See also K. M. Mackay and K. J. Sutton unpublished obs. quoted in K. M. Mackay, P. Robinson and R. D. George, *Inorg. Chim. Acta.*, *1*, 236 (1967).