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The Vibrational Spectrum and Structure of Pentamethylantimony

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RECENT structural analyses of penta-co-ordinate derivatives of Group VB elements[1] have shown that the skeleton of such compounds favours a trigonal bipyramidal geometry; one important exception to this rule is provided by pentaphenylantimony,[2] which adopts a tetragonal pyramidal structure in the solid state. Since relatively little is known about the stereochemistry of simple, monomeric antimony(V) derivatives, we have investigated the vibrational spectrum of pentamethylantimony in relation to the possible shape of its heavy-atom framework.

The pentamethyl has been prepared by the method previously described,[3] and characterised by (1) elemental analysis, (2) vapour-phase chromatography, (3) proton n.m.r. spectroscopy,[4] and (4) vapour-phase molecular-weight measurements. We have confirmed that the compound is a liquid with a faint yellow tinge, m.p. $-19°$, v.p. at 25° ~8 mm., which is stable at room temperature in clean glass apparatus, but tends to decompose slowly in the presence of grease and other foreign material. Preliminary measurements of the ultraviolet-visible spectrum of cyclohexane solutions reveal at least two absorption bands at 238 (ϵ, 5×10^3) and ~250 mμ (ϵ, 10^3).

The most likely structures for the compound involve either a trigonal bipyramidal or a square pyramidal skeleton. If the vibrations of this unit are considered in isolation from those involving the methyl groups, the number of skeletal fundamental modes to be expected is 8 for a trigonal bipyramidal (I) and 9 for a square pyramidal (II) SbC_5 system (point groups D_{3h} and C_{4v}, respectively). In the spectral region below 600 cm.$^{-1}$ model (I) requires six Raman-active modes (two totally symmetric) and five infrared-active modes, only three of which are allowed in Raman scattering. In contrast, model (II) implies nine Raman-active and six infrared-active modes, and hence six coincidences between Raman- and infrared-active fundamentals; three of the Raman lines should be polarised.

We have recorded infrared spectra (4000—50 cm.$^{-1}$) of pentamethylantimony in the solid, liquid, and vapour phases, and in carbon tetrachloride and benzene solutions. Excellent quality Raman spectra were obtained using a Cary Model 81 spectrometer with Hg 4358Å excitation; the sample (volume ~8 ml.) was maintained at 30—40°. The Raman spectrum contains, besides features due to internal motions of the methyl groups (C–H stretching, CH_3 deformation, and CH_3 rocking), just six well-defined lines: 514 (strong, depolarised), 493 (very strong, polarised), 414 (medium–strong, depolarised), 239 (medium, depolarised), 199 (shoulder, depolarised), and 104 cm.$^{-1}$ (medium–strong, depolarised). In the corresponding range of the infrared spectrum five absorptions attributable to fundamental modes are observed: 516 (strong), 456 (very strong), 213 (strong), 195 (strong), and 108 cm.$^{-1}$ (weak). These results afford very strong evidence that model (I) is

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appropriate to the SbC_5 skeleton. Virtually unequivocal assignments of the observed vibrational features are possible on the strength of the (D_{3h}) selection rules, vibrations of the various species being identifiable as follows: a_1', polarised Raman lines, inactive in the infrared; a_2'', infrared absorptions, inactive in the Raman; e', coincident infrared and Raman features; e'', depolarised Raman lines, inactive in the infrared. The results of this analysis, indicated in the Table, are confirmed by analogy with the spectra of related molecules.[5] Curiously, the depolarisation ratio of the Raman line corresponding to the a_1' fundamental ν_2 (414 cm.$^{-1}$) is not measurably less than 6/7, but this appears to be an anomaly characteristic of trigonal bipyramidal molecules.[6]

Significantly, the infrared spectrum of solid pentamethylantimony shows (weakly) bands at 493 and 414 cm.$^{-1}$, which are attributed to the infrared-forbidden modes ν_1 and ν_2 appearing as the result of a breakdown of the D_{3h} selection rules. However, the results suggest that any change of symmetry is due simply to intermolecular interaction in the solid crystal and not to any gross change of molecular stereochemistry. Thus, we have no evidence that the $Sb(CH_3)_5$ molecule assumes a tetragonal pyramidal structure, and the unusual status of pentaphenylantimony[2] probably hinges on crystal packing considerations rather than on any marked alteration in the relative stabilities of the two five-co-ordinate frameworks.

TABLE. *Fundamental modes of the* SbC_5 *skeleton of pentamethylantimony.*

Species	Number	Approximate description	Raman (liquid) cm.$^{-1}$	Infrared (liquid) cm.$^{-1}$
a_1'	ν_1	SbC_3 equatorial stretch	493	Inactive
	ν_2	SbC_2 axial stretch	414	Inactive
a_2''	ν_3	SbC_2 axial stretch	Inactive	456
	ν_4	SbC_3 out-of-plane deform.	Inactive	213
e'	ν_5	SbC_3 equatorial stretch	514	516
	ν_6	SbC_3 in-plane deform.	199	195
	ν_7	SbC_2 axial deform.	104	108
e''	ν_8	SbC_4 rock	239	Inactive

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[1] See for example: J. E. Griffiths, R. P. Carter, Jr., and R. R. Holmes, *J. Chem. Phys.*, 1964, **41**, 863; L. S. Bartell and K. W. Hansen, *Inorg. Chem.*, 1965, **4**, 1777.

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