The Molecular Structures of $(SiH_3)_3P$ and $(SiH_3)_3As$

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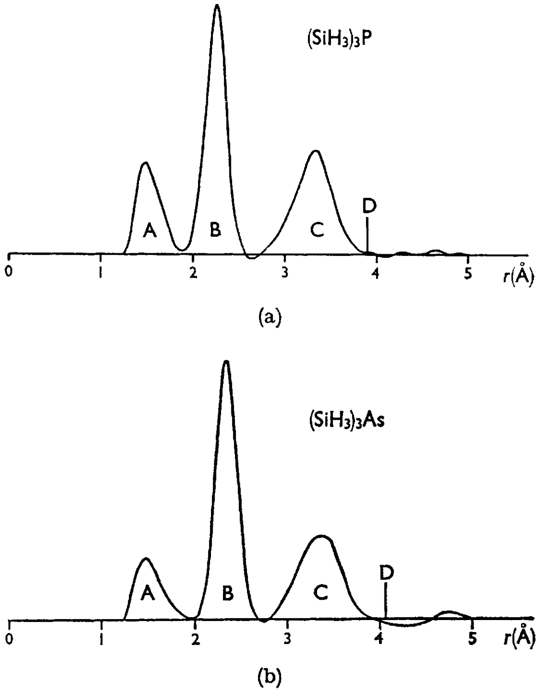
AN electron-diffraction study by Hedberg[1] established that in trisilylamine, $(SiH_3)_3N$, the heavy atoms are coplanar within experimental error. The infrared and Raman spectra of this compound agree with those predicted for a molecule of effective planar symmetry.[2] Trisilylphosphine, $(SiH_3)_3P$, and trisilylarsine, $(SiH_3)_3As$, have vibrational spectra similar to those of trisilylamine, and this led Davidson *et al.*[3] to suggest that the heavy-atom skeletons of these molecules might also be planar or nearly so. In contrast trigermylphosphine, $(GeH_3)_3P$, shows selection rules which are clearly appropriate to a nonplanar skeleton.[4] An extended Hückel molecular orbital treatment has led to a claim that the most stable configuration for trisilylphosphine should be planar.[5] McKean,[6] however, supports a nonplanar skeleton for trisilylphosphine, because the observed vibrational frequencies would, in a planar molecule, lead to somewhat unusual harmonic potential constants (subject to certain assumptions which drastically simplify the force field).

The present gas-phase electron-diffraction studies carried out in Glasgow show unequivocally that both $(SiH_3)_3P$ and $(SiH_3)_3As$ are pyramidal. The two Figures are experimental radial distribution curves for these molecules. In each case, peak A gives the Si–H bond length, peak B gives the Si–X bond length (X = P, As), and peak C gives primarily the Si $\cdots$ Si distance; point D, at $\sqrt{3}$ times the Si–X distance, marks the value of the Si $\cdots$ Si distance for a planar structure. Preliminary least-squares refinement using molecular intensity data gave the values of the main structural parameters which are listed in the Table. These results were obtained within a month of the commencement of the study. A detailed refinement is in progress. Also given in the Table for comparison are the corresponding results[7] for $(SiH_3)_2S$. The configurational difference between $(SiH_3)_3N$ and $(SiH_3)_3P$ has a parallel in the difference between $(SiH_3)_2O$, where[8] Si–O–Si = 144°, and $(SiH_3)_2S$.



(a)

(b)

FIGURES

No Si–P or Si–As bond length in an isolated molecule has been determined previously. The bond lengths are not unusual in any way, being close to those predicted for single bonds by adding the required Pauling covalent radii (Si–P 2·27 Å, Si–As 2·38 Å). Beagley's relation[9] for second-row elements predicts 2·25 Å for an Si–P single bond.

TABLE

Molecular parameters[a] *and e.s.d. from electron-diffraction studies*

	$(SiH_3)_3P$	$(SiH_3)_3As$	$(SiH_3)_2S$[b]
Si–H	1·50 ± 0·02	$1{\cdot}48_5 \pm 0{\cdot}02$	1·494 ± 0·008
Si–X (X = P,As,S)	2·247 ± 0·005	2·352 ± 0·005	2·136 ± 0·002
Si–X–Si	95 ± 2	91½ ± 2	97·4 ± 0·7
H–Si–H	110 ± 7	110 ± 7	110 ± 4

[a] Distance in Å; angles in degrees.
[b] Ref. 7.

It would be dangerous to conclude from this that 3*d*-orbitals of silicon are totally unimportant in the bonding (disilyl sulphide and trisilylphosphine are remarkably feeble bases, for example). However the stereochemistry certainly provides no direct evidence of *p–d* π-bonding in these molecules.

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