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“Heavy” Hydrogen Cyanide

Bonding in the Heavy Analogue of Hydrogen Cyanide: The Curious Case of Bridged HPSi**

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The bonding of first- and second-row elements differ dramatically. The simplest unsaturated silicon hydrides Si_2H_2 and Si_2H_4 exhibit quite unusual geometries[1] compared to the analogous hydrocarbon molecules. For example, the most stable form of Si_2H_2 is nonplanar with C_{2v} symmetry and two bridging H atoms, in sharp contrast to linear acetylene, HC≡CH. Phosphorus and nitrogen share many of the same bonding characteristics, but P prefers single over multiple bonds. For these reasons, it may be difficult to predict the most stable isomeric arrangement, even for a small molecule with a single P or Si atom and especially when it contains both.

Silicon–phosphorus bonds are important in materials science[2] and organometallic chemistry.[3] Geometries for several-hundred larger molecules containing a phosphorus–silicon single bond have been determined by X-ray crystallography,[4] but the uncertainties are typically 0.05 Å. With respect to phosphorus–silicon multiple bonds, it appears that sterically stabilized phosphasilenes[5] $R_2Si=PR'$ are the only compounds that have been isolated to date. The precise structures have been determined for only two of these species, using single-crystal X-ray crystallography.[6] Our knowledge of the Si−P bond is therefore quite inadequate.

Gas-phase investigations of phosphorus–silicon compounds have been hampered by their high reactivity; consequently the structures of only a few species with Si−P bond have been accurately characterized,[7] that is, with accuracies of at least 0.05 Å. Nevertheless, it should be noted that small molecules containing both elements are also of astronomical interest, because silicon- and phosphorus-bearing molecules[8] have been detected in the interstellar space by radio astronomy.

HPSi is perhaps the simplest unsaturated compound to have a chemical bond between silicon and phosphorus. Quantum-chemical calculations and experimental investigations[9] have shown that linear structures are by far the most stable arrangements for HCN, HNC, and the heavier analogues HNSi and HCP. Until the present investigation, no experimental data were available for HPSi, but ab initio calculations[10–12] concluded that a bridged structure with a Si−P double bond (hereafter denoted HPSi) is more stable than linear HSiP. These calculations[12] also predict an energy difference, of the order of 10 kcal mol^{-1}, between these forms; a transition state lying 13 kcal mol^{-1} above HSiP connects the two isomers. Although hydrogen bonding occurs in silicon hydrides, no phosphorus-bearing molecules with this type of bonding are known.

To determine the existence, geometry, and bonding of HPSi, a study has been undertaken to measure its rotational spectrum. Rotational spectroscopy is an ideal technique to study HPSi and other polar molecules because rotational frequencies are directly related to the moments of inertia along the three principal axes of the molecule. With sufficient isotopic substitutions, it is then possible to determine highly accurate molecular structures, that is, with bond lengths to an uncertainty on the order of 0.010 Å. When the experimental rotational constants are corrected for zero-point vibrational effects, it is possible to derive bond lengths to even higher accuracy, on the order of ±0.001 Å or better. The experimental investigations presented herein were guided by high-level coupled-cluster calculations at the same level of theory as that reported recently for silanethione, H_2SiS.[13] Details concerning the approach used to treat electron-correlation and basis-set effects in quantum-chemical calculations in a quantitative manner are given below and can also be found in Ref. [14].

HPSi was produced in the gas phase through a discharge of silane and phosphine in neon and then detected at high-

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spectral resolution by means of Fourier transform microwave and millimeter wave absorption spectroscopy. The existence of HPSi was established by the observation of its lowest energy rotational transition near a frequency of 16 GHz (see Figure 1). The spectrum shows closely spaced hyperfine structure, characteristic of a molecule containing ^{31}P with spin $I={}^{1}\!/_{2}$. Because of the high signal-to-noise ratio, the corresponding lines of the ^{29}Si and ^{30}Si isotopic species were also detected nearby in frequency, despite the low fractional abundance of these two isotopes (4.7 % for ^{29}Si and 3.1 % for ^{30}Si). Additional lines, nearly harmonic in frequency to these, were soon detected near 32 GHz. By replacing silane with SiD_4 the same two transitions were detected for DPSi, DP^{29}Si, and DP^{30}Si. Because D substitution lowers the A rotational constant by a factor of two, it was also possible to measure two additional lines of DPSi, which arise from $K_a = 1$, as opposed to $K_a = 0$. After the 16 to 32 GHz measurements, the rotational spectra of two isotopic species, HPSi and DPSi, were subsequently observed at substantially higher frequencies (287–421 GHz) to better determine their spectroscopic constants of both isotopic species.

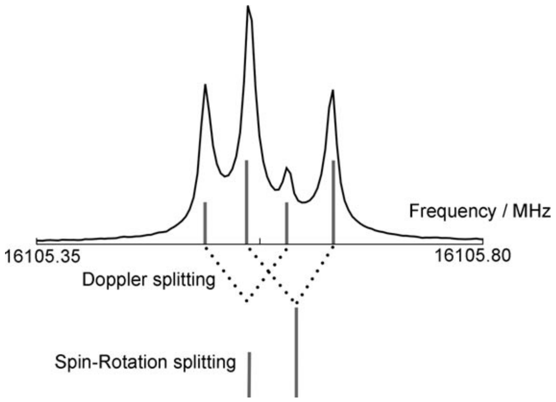

Figure 1. The lowest energy ($1_{0,1}$–$0_{0,0}$) rotational transition of HPSi showing resolved hyperfine structure from the interaction of the ^{31}P nuclear spin $I={}^{1}\!/_{2}$ with the small magnetic field induced by rotation. A best-fit stick spectrum in gray is shown beneath that observed, with the calculated relative intensities. Each rotational transition has a double-peak line shape, because of the Doppler doubling caused by the Mach 2 molecular beam expanding collinear to the two propagating directions of the molecular emission field. The integration time was 1 min.

More than 200 rotational transitions have now been measured for HPSi, and 30 for DPSi. Spectroscopic constants for both isotopic species were then determined from a nonlinear least-squares analysis using a standard asymmetric-top Hamiltonian (see Supporting Information for complete data sets). The data for both species could be reproduced with the three rotational constants, A, B, and C, and five centrifugal distortion constants, to a root mean square (rms) accuracy of only 40 kHz, that is, a fraction of the spectral line width for most of the measurements. The rotational constants, each determined to better than 0.1 %, are summarized in Table 1 and there compared to the theoretical predictions. A more complete account of the laboratory measurements, data analysis, and quantum-chemical calculations will be given elsewhere.

Table 1: Rotational constants of HPSi and DPSi (in MHz).[a]

Constant	HPSi		DPSi	
	Exp.	Calcd[b]	Exp.	Calcd[b]
A_0	297 187(20)	296 559.5	152 598(63)	152 442.0
B_0	8168.95742(81)	8170.0	8169.9398(16)	8171.5
C_0	7936.6581(11)	7939.0	7737.4098(16)	7740.0

[a] 1σ uncertainties (in parentheses) are in units of the last significant digit. [b] See text.

Because the three rotational constants are inversely proportional to the principal moments of the molecule, it is possible to precisely determine the positions of all three nuclei by a least-squares minimization of the HPSi and DPSi data. To determine the most accurate structure, the experimental rotational constants were corrected for zero-point vibration, a small but important correction, prior to minimization. The structure thus derived is shown in Figure 2. With the present data set, the three bond lengths are each determined to better than 0.006 Å, the ∡SiPH angle to better than 0.5°.

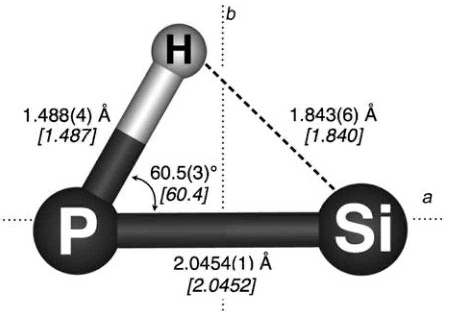

Figure 2. Molecular structure of bridged HPSi derived from the experimental rotational constants of HPSi and DPSi corrected for zero-point vibrational effects (see text). Statistical uncertainties in units of the last significant digit are in parentheses. The theoretical structure obtained using coupled-cluster methods (see text) is given in italics for comparison; the calculated dipole moment components along the two principal axes shown are $\mu_a = 0.89$ D and $\mu_b = 0.25$ D.

From a purely geometrical perspective, the SiP bond in HPSi appears to be best characterized as a strong Si=P double bond; it is 0.05 Å shorter than the value (2.094 Å) determined by X-ray crystallography on phosphasilenes,[4] but is 0.05 Å longer than that expected for a triple bond (1.993 Å).[10] The P−H distance is 5 % longer than a normal P−H bond (i.e. PH_3, 1.41 Å).[15] The Si−H distance (1.843 Å) is roughly 0.4 Å longer than in SiH_4 (1.471 Å[16]) and 0.2 Å longer than in bridged Si_2H_2 (1.668 Å[1]), but much shorter than the sum of the van der Waals radii (3.2 Å) implying significant bonding. A natural bond orbital (NBO) analysis[17] yields two bonding orbitals for the P−Si bond and one for P−H. However, no normal bonding orbital is found for H−Si. In addition, two lone-pair orbitals are identified, one at P and one at Si.

In view of these findings, HPSi does not adopt a cyclic but a bent structure, although the H-P-Si angle of 60.5(3) degrees clearly indicates significant PH–Si interactions. The bonding in HPSi can be summarized as in Figure 3 with a classical P=Si double bond, a P−H bond, and donor–acceptor interactions between PH and the empty p orbital at the Si atom.

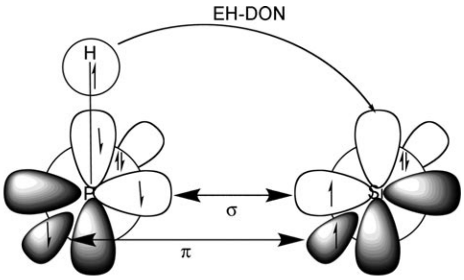

Figure 3. Schematic representation of the bonding in HPSi in terms of orbital interactions.

Contrary to HCP and HNSi, it cannot be as easily explained by qualitative arguments, why the HPSi arrangement is preferred over the HSiP form. Linear HPSi, which is not a minimum on the potential energy surface, is slightly less stable (about 1 kcal mol^{-1}) than linear HSiP, and the preference for the HPSi arrangement is solely due to the bending. The bent structure of HPSi can be rationalized by the fact that P, because of a lower tendency to form hybrid orbitals[18] favors arrangements with a lone pair over those with a triple bond. In the present case, P avoids a triple bond and instead adopts a bonding situation with a double bond and a lone pair of essentially s-orbital character. We emphasize the importance of the PH–Si donor–acceptor interactions, as they are essential for the stabilization of the non-linear structure.

It is remarkable that the most stable arrangement of H, Si, and P is bridged when the three isovalent analogues of HPSi (HCN, HNSi, and HCP) are linear. Calculations suggest that HPSi may be fairly unique among SiP compounds, as no other SiP compound with a bridged structure has been experimentally characterized to date. Similar examples have been discussed solely on the basis of quantum-chemical calculations, namely the P_2H^+ ion with a cyclic structure and HPPR with electron-withdrawing substituents R.[19] In light of the present findings, it is clearly desirable to characterize experimentally the structures of other species of greater complexity, such as $HPSiH_2$.[10,12] As the recent experimental detection of a fairly stable, new bridged isomer of Si_2H_4 demonstrates,[1c] isomers with bridging H atoms may exist for other simple SiP compounds as well. Molecules such as H_2PSiH and $HPSiH_2$, may be detectable with the present technique because HPSi is efficiently produced using PH_3 as a source of P and silane as a source of Si. If so, it should be possible to determine, at high spectral resolution, the structure and bonding properties of a number of fundamental SiP bearing molecules.

Because HCN, HCP, and other small silicon- and phosphorus-bearing compounds (i.e. CCP, PO) have been detected in circumstellar shells of evolved carbon-rich stars[8] and other astronomical sources, HPSi is also a good candidate for radio astronomical detection. Searches for HPSi have been conducted on circumstellar gas using the Arizona Radio Observatory 12 m telescope. The results of these observations will be described elsewhere.

Experimental Section

FT Microwave spectroscopy: The FT microwave spectrometer used has been described in Ref. [20]. HPSi was formed in the throat of a nozzle by applying a low-current dc discharge to a short gas pulse created by a fast mechanical valve, the gas in the present work being a mixture of phosphine (PH_3) and silane (SiH_4) heavily diluted (0.2 %) in neon. To yield the strongest lines, the discharge potential was 1.2 kV, and the flow rate was about 20 $cm^3 min^{-1}$, at the 6 Hz pulse rate of the nozzle with a stagnation pressure behind the valve of 2.5 kTorr.

Millimeter wave spectroscopy: The spectrometer used has been described in Ref. [21]. HPSi was produced in a 1 m long glass cell, from a mixture of elemental phosphorus, H_2, and SiH_4 diluted in argon, in a 200 W ac glow discharge; D_2 was used instead of H_2 to create DPSi. Typical pressures used were 20 mTorr of H_2 and 20 mTorr of 0.8 % SiH_4 in argon.

Quantum-chemical calculations: The calculations have been performed using the CFOUR suite of programs.[22] The best-estimate structure has been obtained at a level denoted as fc-CCSD(T)/cc-pV∞Z + ΔT/cc-pVTZ + ΔQ/cc-pVDZ + Δcore/cc-pCV5Z[14] with the frozen-core CCSD(T) contribution extrapolated to the basis-set limit (indicated by cc-pV∞Z) and augmented by corrections for a full CC singles, doubles, triples (CCSDT) treatment (using the cc-pVTZ basis), for the effect of quadruple excitations at the CC singles, doubles, triples, quadruples (CCSDTQ) level (using the cc-pVDZ basis), and for core-valence correlation effects treated at the CCSD(T)/cc-pCV5Z level. Vibrational corrections for the rotational constants have been obtained at the CCSD(T)/cc-pwCVQZ level of theory using second-order vibrational perturbation theory.[14] The NBO analyses have been carried out at the CCSD/cc-pVTZ level using the program package MOLPRO, version 2006.1.[23]

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