Phosphasilene ($HP{=}SiH_2$) and its Valence Isomers. A Theoretical Study

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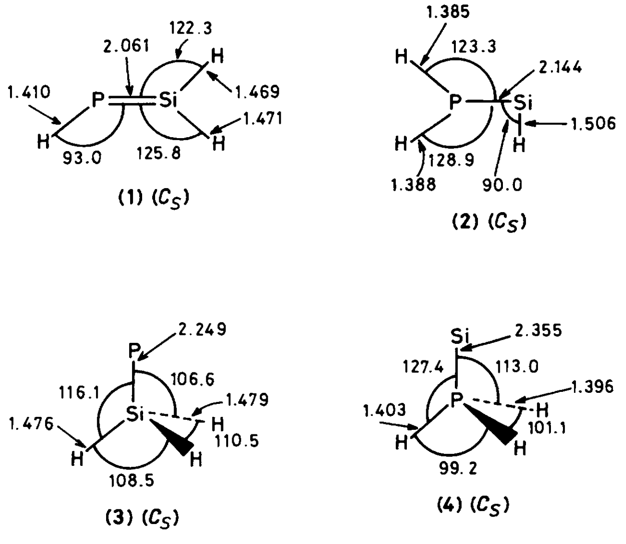
The first *ab initio* molecular orbital calculations on the phosphasilene, $HP{=}SiH_2$, and its valence isomers are reported.

Disilenes ($R_2Si{=}SiR_2$), diphosphenes (RP=PR), and their heavier congeners have attracted significant recent attention.[1] By contrast, there are only two reports of phosphasilenes ($RP{=}SiR'_2$) and so far it has not been possible to isolate such compounds in a pure state.[2,3] We have therefore undertaken a theoretical study of the prototype phosphasilene, $HP{=}SiH_2$, and its valence isomers.

Geometry optimisation using either the 6-31 G or 6-31 G** basis set revealed that the phosphasilene structure (**1**) (Figure 1) is significantly more stable than the other closed-shell valence isomers (**2**)—(**4**).† The same stability order for (**1**)—(**4**) prevailed when configuration interaction was included. For example, use of the 6-31 G basis set (at the 6-31 G optimised geometries) with 14 409 configurations for (**1**) and (**2**) and 13 369 configurations for (**3**) and (**4**) afforded the relative energies (kcal/mol; 1 cal = 4.184 J): (**1**), 0; (**2**), 11.9; (**3**), 37.8; and (**4**), 58.4. The energies of (**2**)—(**4**) increased slightly when Davidson's correlation function[8] was applied. Interestingly, the triplet state ($^3A_2$) of silylphosphinidene (**5**) is computed to be 8.42 kcal/mol more stable than the singlet phosphasilene structure, (**1**) at the SCF 6-31G** level although this may be due to the neglect of correlation. The stability order computed here contrasts with the analogous light-atom system for which singlet $HN{=}CH_2$ = 0, singlet $H_2N{-}CH$ = 39, triplet $N{-}CH_3$ = 47, and singlet $N{-}CH_3$ = 89 kcal/mol.[9] On the other hand, the (non-planar) triplet states for (**1**) and (**2**) turned out to be less stable than singlet (**1**) at the same level of calculation. These differences reflect the relative stabilities of N=C and P=Si bonds.

Using either the 6-31 G or 6-31 G** basis sets, the ground-state geometry of singlet phosphasilene (**1**) is computed to be planar. This result contrasts with several M.O. calculations on $H_2Si{=}SiH_2$ which indicate a preference for the *trans*-folded structure.[10] The P=Si bond length is computed to be 2.121 or 2.061 Å using the 6-31 G or 6-31 G** basis sets, respectively.



(**1**) (C_S) (**2**) (C_S)

(**3**) (C_S) (**4**) (C_S)

Figure 1. Equilibrium geometries for closed-shell singlet compounds of formula $PSiH_3$ using the 6-31 G** basis set. (Bond angles in degrees, bond lengths in Å.)

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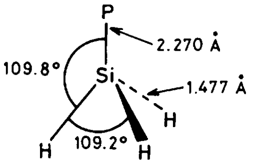
† For closed-shell systems, geometry optimisations were carried out using the *ab initio* program Texas (ref. 4) which features the gradient method (ref. 5). The 6-31 G and 6-31 G** basis sets (ref. 6) were employed. Configuration interaction (C.I.) calculations were performed with the 6-31 G basis set. The program GUGA (Graphical Unitary Group Approach) (ref. 7) was used for the calculations on triplet and C.I. singlet states.



(5)

The average experimental values for Si=Si and P=P bond lengths are 2.145 and 2.015 Å, respectively.[1] In turn, use of these values affords an estimated P=Si bond length of 2.080 Å which is closer to the 6-31 G** value.

The molecular orbitals of (**1**) are also of interest. The two highest occupied M.O.s, 3a″ (−8.61 eV) and 13a′ (−10.53 eV) correspond to the P–Si π-bond and phosphorus lone pair (n), respectively. The 4a″ LUMO is low-lying (+0.85 eV), suggesting that one-electron reduction of phosphasilenes should take place readily. For molecules of the type HP=X (X = CH_2, NH, or O) it has been shown[11] that the energies of the n and π M.O.s are close, the latter being very sensitive to the electronegativity of X. Thus, the HOMO of $HP=CH_2$ is π, while that of HP=NH and HP=O is n. Our finding that the π and n M.O.s of (**1**) are well separated is consistent with the modest electronegativity of the SiH_2 moiety. Moreover, as a consequence of this orbital sequence, phosphasilenes are expected to undergo [2 + 2] rather than [2 + 1] or [4 + 1] cycloaddition reactions.

Finally, we note that the computed 6-31 G P=Si force constant and stretching frequency for (**1**) are 3.39 mdyn/Å and 625 cm^{-1} respectively. Being of a′ symmetry, this vibration should be i.r.-inactive but Raman-active.

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