

## Bis-silylenephosphorane (Silylene = Silanediyl) versus Bis-methylenephosphorane: a Theoretical Study

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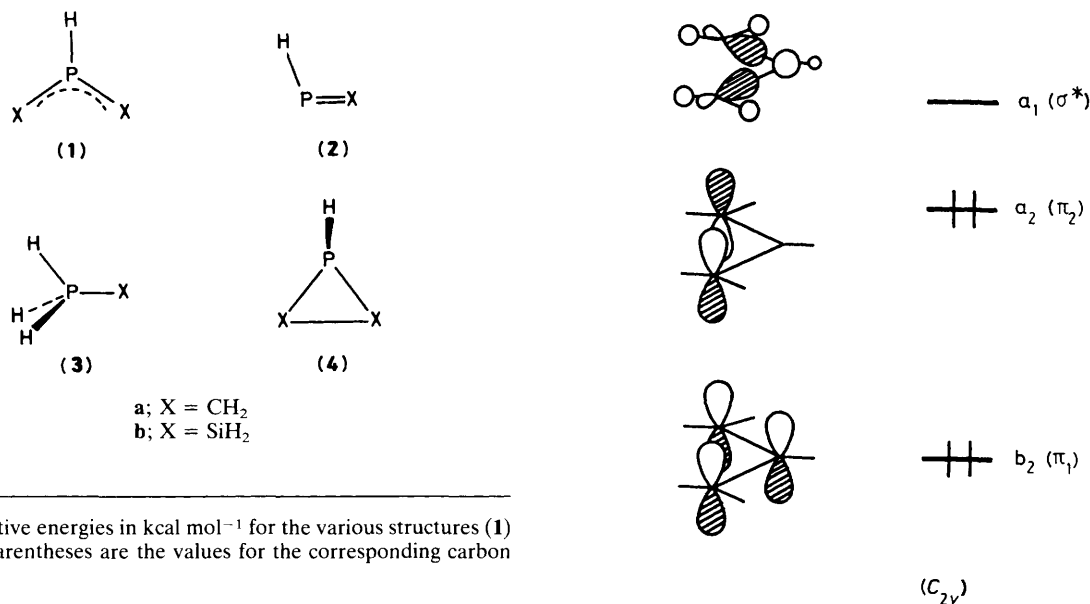
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On the basis of *ab initio* calculations bis-silylenephosphorane as compared with bis-methylenephosphorane suffers from Jahn–Teller distortion as a consequence of the stability of (nonbonding) lone pairs at the terminal SiH<sub>2</sub> units, causing a strengthening of the phosphorus–silicon bond.

While the chemistry and bonding of bis-methylenephosphorane (**1a**) has been explored in detail<sup>1,2</sup>, the synthesis of its silicon analogue bis-silylenephosphorane (**1b**) has not been recorded so far. Here we predict on the basis of *ab initio* calculations an unusual bonding situation for parent (**1b**) which result from second-order Jahn–Teller distortion. It will be shown that the P–Si bond is intermediate in length between

silylenephosphane (**2b**), and silylenephosphorane (**3b**). Hence (**1b**) should be an interesting target for synthetic verification.

Consider first the MO scheme of (**1**) (X = SiH<sub>2</sub>) in C<sub>2v</sub> symmetry (Scheme 1). It consists of an allylic  $\pi$ -system ( $\pi_1$  to  $\pi_3$ ) and an energetically low lying antibonding  $\sigma^*$  orbital. The close proximity of  $\pi_2$  and  $\sigma^*$  is a consequence of orbital nonhybridization,<sup>3</sup> a characteristic of bonding between higher



**Table 1.** Relative energies in kcal mol<sup>-1</sup> for the various structures (1) and (4). In parentheses are the values for the corresponding carbon compounds.

Structure	Symmetry	PSi (PC)/Å	SiPSi- (CPC)/°	ΔE <sup>a</sup> SCF	CEPA-1
(1)	C <sub>2v</sub>	2.096	140.6	19.8	23.4
	C <sub>2v</sub>	(1.636)	(135.4)	(0.0)	(0.0)
	C <sub>2</sub>	2.164	140.7	0.0	0.0
(4)	C <sub>s</sub>	2.290	59.7	-58.1	-42.2
	C <sub>s</sub>	(1.853)	(47.5)	(-47.2)	(-46.8)

<sup>a</sup> Conversion factor 1 a.u. = 6.275 × 10<sup>2</sup> kcal mol<sup>-1</sup>.

main group elements. The 3s valence orbitals at silicon and phosphorus are more strongly contracted than their 3p valence orbitals. Consequently the formation of energetically low lying σ\*-orbitals becomes favoured. Interaction between π<sub>2</sub> and σ\* results in the singlet state as the consequence of Jahn-Teller distortion from higher to lower symmetry (C<sub>2v</sub> → C<sub>2</sub>). Within C<sub>2v</sub> symmetry it corresponds to an a<sub>2</sub> vibration<sup>2b</sup> according to equation (1).

$$\Gamma_{\pi_2} \times \Gamma_{\sigma^*} = a_2 \times a_1 = a_2 \quad (1)$$

The various alternatives were probed by energy optimized *ab initio* calculations at a double-ξ level.† The bonding features obtained for (1) to (4) with X = SiH<sub>2</sub>, CH<sub>2</sub> at a single determinant SCF level are summarized in Figure 1.

For the lowest energy (1b) the equilibrium bond length (2.164 Å) is intermediate between that for the corresponding (2b) (2.057 Å) and (3b) (2.417 Å), whereas in the corresponding carbon analogues the P-C bond lengths are almost equal (1.636 and 1.670 Å). For (2b) and (3b) the geometrical parameters obtained are in good agreement with the results of previous investigators.<sup>5</sup> Based on the structures obtained their relative energies were computed at the CEPA-1 level using the self-consistent electron pairs (SCEP) method<sup>6a</sup> (Table 1).

Accordingly, for (1b) the C<sub>2</sub> structural alternative is lowest in energy. In contrast (1a) adopts preferentially a C<sub>2v</sub>

**Scheme 1**

structure. The change in symmetry for (1b) is accompanied by pyramidalization at the silicon atoms. Instead of a planar system the frontier orbitals are now combinations of lone pairs at the silicon atoms, either symmetric (n<sub>a</sub>) or antisymmetric (n<sub>b</sub>) with respect to the C<sub>2</sub>-axis. This gives rise to the important Slater determinants (2)–(4). <sup>1</sup>Ψ<sub>I</sub> refers to the singlet wavefunction and results from geometry optimization at the SCF level. In order to examine the possible biradical character of (1b) we carried out a 2 × 2-MCSCF calculation<sup>6b</sup> containing <sup>1</sup>Ψ<sub>I</sub> and <sup>1</sup>Ψ<sub>II</sub>. It results in a considerable contribution of <sup>1</sup>Ψ<sub>II</sub> (c<sub>I</sub> = 0.903, c<sub>II</sub> = -0.429). Multi-reference CI calculations [averaged coupled pair functional (ACPF) method<sup>6c</sup> with either the MCSCF wavefunction or <sup>3</sup>Ψ<sub>III</sub> as reference, yield 18.9 kcal mol<sup>-1</sup> (1 cal = 4.18 J) as the energy difference between singlet and triplet (at times for the singlet geometry). Hence the triplet is higher in energy. According to a 2 × 2-MCSCF calculation on the analogous carbon compound (1a) (with C<sub>2v</sub> symmetry) the contribution of an excited singlet is negligible (c<sub>I</sub> = 0.982, c<sub>II</sub> = -0.187). Here the triplet is 66.82 kcal mol<sup>-1</sup> higher in energy. Consequently C<sub>2</sub>-symmetrical (1b) compared to (1a) possesses strong biradical character. It should only be traceable by matrix isolation spectroscopy with protection of the structure by sterically demanding substituents at the terminal silicon atoms.

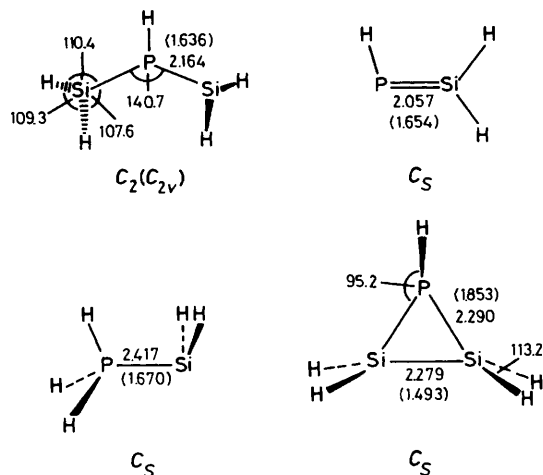
$${}^1\Psi_I = | \dots n_a \bar{n}_a | \quad (2)$$

$${}^1\Psi_{II} = | \dots n_b \bar{n}_b | \quad (3)$$

$${}^3\Psi_{III} = | \dots n_a \bar{n}_b | + | \dots \bar{n}_a n_b | \quad (4)$$

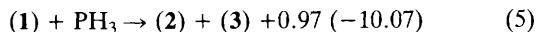
The ring closure reaction of (1) to the corresponding three-membered ring systems is exothermic (see Table 1). In both cases (1) are energy minima rather than saddle points on the energy surfaces, as revealed by corresponding analyses of the force constant matrices. For X = SiH<sub>2</sub> a stable C<sub>2</sub> structure results, even if no symmetry restrictions are assumed in the geometry optimisation. Products (4) are the most stable species on the electronic hypersurfaces. In the ring system (4b) the P-Si bond is elongated and the Si-Si bond shortened as compared with corresponding single bonds (Si-Si 2.36 Å). In addition the phosphorus atom is strongly pyramidalized.

† Huzinaga bases sets P, Si (11,7,1) in the contraction [5,6 × 1/4,3 × 1] + 1d (ξ<sub>Si</sub> = 0.4; ξ<sub>P</sub> = 0.50; ξ<sub>C</sub> = 0.8); H [3,1] were used. Geometry optimizations were performed with the Karlsruhe version of set of programs.<sup>4b</sup> The accuracy of optimization is ≤10<sup>-9</sup> a.u. in energy. Concomitantly the accuracy of bond lengths is ≤10<sup>-4</sup> Å and of bond angles ≤10<sup>-2°</sup>.



**Figure 1.** Equilibrium geometries of (1)–(4). Bond lengths are in Å, bond angles in degrees. Values in parentheses are for X = CH<sub>2</sub>.

A quantitative estimate of the energy for ylide formation of (1) from (2) is given by the energy balances of reaction (5) [computed at the CEPA-1 level]. In parentheses is the corresponding value for the carbon case. At the CEPA-1 level the energy balances are exothermic for the carbon case and slightly endothermic for the silicon compound.



Our analysis can also serve as a model for the higher homologues of the bis-methylenephosphorane-types (1), for X = GeH<sub>2</sub>, SnH<sub>2</sub>. In these structural units, the singlet stability is even more increased.<sup>7</sup> Accordingly, the lower symmetrical structures of these compounds should be even more favoured than in bis-silylenephosphorane.

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