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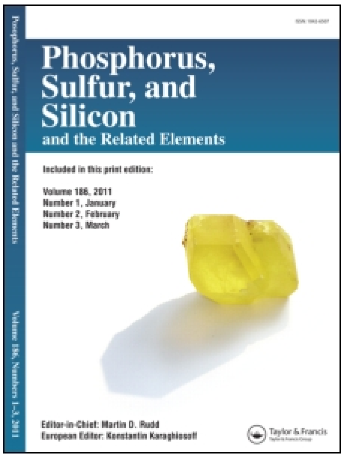

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AB Initio MO Study of P--Si π Systems: Structures and Energies

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AB INITIO MO STUDY OF P–Si π SYSTEMS: STRUCTURES AND ENERGIES

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The origin of the relative stability of isomers of 1,2-diphosphinodisilene and related compounds is discussed. The geometries of 18 isomers of $(H_2X)HE{=}EH(XH_2)$, $(H_2X)HE{=}EH(XH_2)^{2+}$, *and* $HX{=}EH{-}HE{=}XH$ $(E = C, Si; X = P, N)$ *have been optimized at the MP2/6-311++G(d,p) level of theory. Since nitrogen and phosphorus have lone-pair electrons, six electrons can delocalize in four orbitals of* $(H_2X)HE{=}EH(XH_2)$ *(6e/4o), while four electrons can delocalize in four orbitals of* $(H_2X)HE{=}EH(XH_2)^{2+}$ *and* $HX{=}EH{-}HE{=}XH$ *(4e/4o). To examine the interaction that governs the structure and relative stability of their* cis *and* trans *(or cisoid and transoid) isomers, the* π–σ^* *delocalization energies and isodesmic reaction energies of the compounds were calculated. It is concluded that the* π–σ^* *delocalization affects the bending structure of disilene derivatives, and phosphorus substituents prefer 2e/4o and 4e/4o systems.*

Keywords: Ab initio MO calculation; disilene; π–σ^* delocalization; isodesmic reaction; phosphorus

INTRODUCTION

We recently reported the dimeric structures of bis(diisopropylamino)silylene, $(i\text{-}Pr_2N)_2Si$:, determined from ab initio molecular orbital (MO) calculations and their spectroscopic characteristics.[1] In contrast to an early theoretical prediction[2] with experimental support[3,4] that silylenes carrying electronegative and π-donating substituents, such as NH_2, OH, and F, lack the doubly bonded dimer, our calculations gave a silicon–silicon bonded structure of $((i\text{-}Pr_2N)_2Si{:})_2$ as the most

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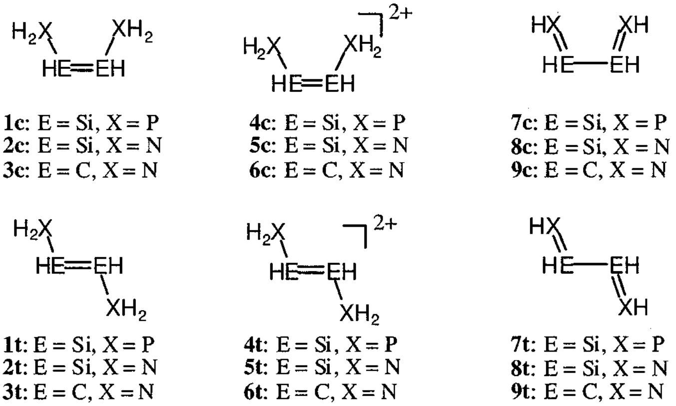
stable dimer. The calculated absorption maximum of the bonded dimer is in good agreement with UV absorption measurements.[5] The optimized structure of $((i\text{-Pr}_2\text{N})_2\text{Si:})_2$ is strongly twisted and bent, and the silicon—silicon bond distance is relatively long (2.473 Å). The unusual structure of the silicon—silicon bonded dimer of $(i\text{-Pr}_2\text{N})_2\text{Si:}$ reminds us of the interaction between the lone pairs of nitrogens and the π orbital of disilene (n–π interaction).

To examine the effects of the n–π interaction on the structure and relative stability of the isomers, in this paper we will theoretically study several disilene derivatives with substituents having lone-pair electrons and their olefin analogues (as shown in Scheme 1): $(\text{H}_2\text{X})\text{HE}{=}\text{EH}(\text{XH}_2)$ **1–3**, $(\text{H}_2\text{X})\text{HE}{=}\text{EH}(\text{XH}_2)^{2+}$ **4–6**, HX=EH–HE=XH **7–9**. Assuming the n–π interaction, six electrons can delocalize in four orbitals of $(\text{H}_2\text{X})\text{HE}{=}\text{EH}(\text{XH}_2)$ (6e/4o), while four electrons can delocalize in four orbitals of $(\text{H}_2\text{X})\text{HE}{=}\text{EH}(\text{XH}_2)^{2+}$ and HX=EH–HE=XH (4e/4o).



SCHEME 1

CALCULATIONS

Ab initio MO calculations were performed with the Gaussian 98 software package.[6] The π–σ^* delocalization energy was obtained by deleting selected antibonds in the NBO description using the NBO 4.0 module of the Gaussian 98 software package.

RESULTS AND DISCUSSION

Optimized Structures and Energies

Disilene derivatives **1** and **2** have *trans*-bent structures around the Si=Si bond. Diaminodisilene **2** is strongly *trans* bent compared with

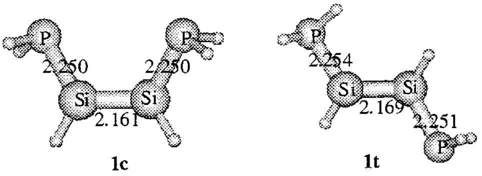


FIGURE 1 The optimized structures of compounds **1c** and **1t** at the MP2/6-311++G(d,p) level. The bond lengths are in Å.

diphosphinodisilene **1**. The *cis* isomer **2c** is twisted and bent around the Si=Si double bond. On the other hand, diaminoethylenes **3t** and **3c** have an almost planar skeleton with pyramidal NH_2 moieties. The optimized bond lengths of **1–3** are almost the same in respective *trans* and *cis* isomers. The Si=Si bond lengths of **2c** (2.297 Å) and **2t** (2.298 Å) are longer than those of **1c** (2.161 Å) and **1t** (2.169 Å). The lone pairs of **2** and **3** interact with π orbitals. However, the optimized structures of **1** show that no lone pair of the phosphorus in **1c** and only one lone pair in **1t** interact with the π orbitals of disilene: two lone pairs in **1c** and one lone pair in **1t** are almost perpendicular to the π orbital of disilene (Figure 1). In other words, **1c** and **1t** are 2e/2o and 4e/3o systems, respectively, although **2** and **3** are 6e/4o systems. The relative energies of the *trans* to *cis* isomers are listed in Table I. *Cis* isomers **2c** and **3c** are more stable than the corresponding *trans* isomers **2t** and **3t**. However, the relative stability in diphosphinodisilene **1** is opposite: *trans* isomer **1t** is more stable than *cis* isomer **1c**.

Among 4e/4o systems **4–9**, *cis* isomers **6c** and **8c** were not optimized as minimum stationary points. The Si=Si bond lengths of dications **4–6** are elongated compared with those of the corresponding neutral compounds **1–3**. Instead, the P—Si, N—Si, and N—C bond distances are shortened in **4–6**. Consequently, the structures of the dications are close to those of the corresponding dienes **7–9**. All the *cis*-isomers, **4c**, **5c**, **7c**, and **9c**, have twisted structures and all the *trans*-isomers, **5t**, **6t**, **7t**, **8t**, and **9t** but not **4t**, take planar structures. **4t** has a *trans*-bent structure. In all these 4e/4o systems, the *trans* isomers are more stable than the *cis* isomers, similar to butadiene.

TABLE I Relative Energy, ΔE (kcal/mol), of the *trans* to *cis* Isomers

Compd.	ΔE	Compd.	ΔE	Compd.	ΔE
1	−0.1	**4**	−1.3	**7**	−0.4
2	0.8	**5**	−0.8	**8**	—
3	3.6	**6**	—	**9**	−6.8

σ–π^* Delocalization and Isodesmic Reaction

The delocalization by a charge transfer between the $\pi_{\mathrm{Si-Si}}$ and $\sigma^*_{\mathrm{Si-Si}}$ bonds stabilizes disilene and affects the structure. Single point calculations of the delocalization energies between the $\pi_{\mathrm{E-E}}$ and $\sigma^*_{\mathrm{E-E}}$ bonds (E=Si, C) were performed at the MP2/6-311++G(d,p) geometry. The delocalization energy is negligible in olefin **3** (~0 kcal/mol) and is largest in diaminodisilene **2** (~40 kcal/mol). Therefore, the structure of **3** is planar, that of **2** is strongly bent, and that of **1** is moderately bent.

The following isodesmic reaction gives the stabilization energies by the formation of 6e/4o systems.

$$\mathrm{H(H_2X)E{=}E(XH_2)H + 2EH_4 \rightarrow 2E(XH_2)H_3 + H_2E{=}EH_2}$$

Although Disilene derivatives gave small stabilization energy, (1-7 kcal/mol) compared with the energy of ethylene analog (~20 kcal/mol).

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