



given in Figs. 1 and 2). The optimized planar structure of **2** has D_{2h} symmetry. However, structures **3** and **4** prefer D_{4h} symmetry and the $^1A_{1g}$ electronic configuration: $(1a_{1g})^2 (1e_u)^4 (1b_{1g})^2 (1b_{2g})^2 (2e_u)^4 (2a_{1g})^2 (1a_{2g})^2 (3e_u)^4 (3a_{1g})^2 (2b_{2g})^2 (2b_{1g})^2 (4e_u)^4 (5e_u)^4 (1a_{2u})^2 (4a_{1g})^2 (2a_{2g})^2 (3b_{2g})^2 (1e_g)^4 (6e_u)^4 (1b_{2u})^2 (3b_{1g})^2 (1b_{1u})^2 (2e_g)^4 (2a_{2u})^2 (1a_{1u})^0$. Square planar structure **2** has four fewer electrons than **3** and **4**; hence, the degenerate $2e_g$ -MO in the singlet state would be occupied by only two electrons and is not stable towards Jahn–Teller distortion to D_{2h} symmetry. While the optimized Si–C bond length in **2** (1.896 Å) is quite close to that in MeSiH_3 [1.883 Å at HF/3-21G(*)⁹], **2** is a saddle point (one imaginary frequency $\nu(b_{1g}) - 509 \text{ cm}^{-1}$). According to the vectors of the imaginary frequency, the Si atom remains in the plane but the four carbon neighbours point in opposite, *i.e.* tetrahedral directions.

Compound **3**, in which the four silicon neighbours are nitrogen atoms, is a minimum (no imaginary frequencies). Moreover, the vectors of the lowest frequency [$\nu(a_{2u}) 109 \text{ cm}^{-1}$] describe a pyramidal, rather than a tetrahedral, vibration: the Si and all N atoms move in the same direction out-of-plane. The large HOMO–LUMO energy difference, 11.5 eV, indicates that this structure should be stable towards second-order Jahn–Teller distortion.

Isoelectronic substitution of Si in **3** first by P^+ and then by Al^- leads to structures **4** and **5**. The $R(\text{Al–N})$ 1.806 Å separation in **5** is too long for Al to ‘fit’ optimally⁴ in the fenestrene ‘cavity’ (note the distances to the central atoms in **3** and **4**). As a consequence, **5** is a saddle point [one imaginary frequency $\nu(a_{2u}) 142i \text{ cm}^{-1}$]. The vectors of the imaginary frequency correspond to a pyramidal distortion (the central Al atom and all the N atoms move in the same direction). As the energy of the HOMO is negative, this anion should be stable towards

loss of an electron.

The P–N bond length in **4** (1.665 Å) is quite close to that in PH_2NH_2 [1.653 Å, also at HF/3-21G(*)⁹; the experimental value is 1.650 Å in NH_2PF_2 ¹⁰]. Hence, a P atom can be accommodated comfortably, and **4** is a minimum [lowest frequency $\nu(a_{2u}) 160 \text{ cm}^{-1}$].

An X-ray structure of phthalocyanine with a planar tetra-coordinated Si atom has been reported.¹¹ However, the experimental Si–N separation, $R(\text{Si–N})$ 1.93 Å, is much longer than that in **3** and in SiH_3NH_2 (see above). Furthermore, the formal silicon valence in the phthalocyanine is two rather than four.

When the Si in **3** is substituted by C (to give structure **6**) the square planar geometry is unstable towards in-plane distortion. This is caused by the relatively large size of the central cavity (see Figs. 1 and 2). Structure **7**, with all the nitrogens substituted by boron atoms, is not a minimum either. We have explored planar tetracoordinated carbon candidates based on **3**. The four carbon neighbours in **6** were replaced by P atoms (structure **8**) and by Al atoms (structure **9**). However, neither structures **8** nor **9** are minima.

We hope that our predictions of D_{4h} symmetry for **3** and **4** will stimulate the synthesis of molecules of this type with unusual planar tetracoordinate geometries.

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