1-Aminodiazaphosphene, Synthesis, Crystal Structure, Bonding Properties, and Reactivity of a Derivative

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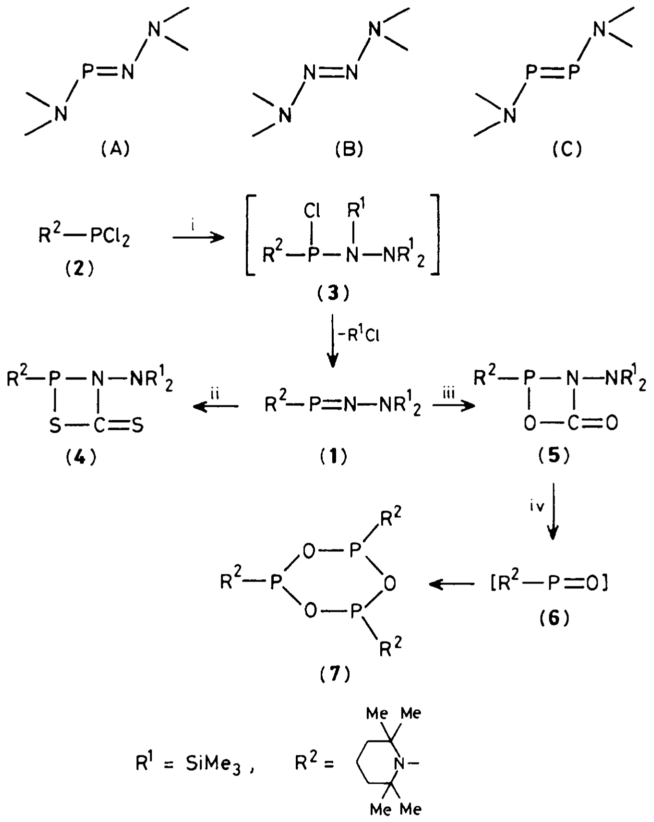
The crystal structure of a 1-aminodiazaphosphene derivative shows that it possesses an unusually long PN bond; it shows high reactivity towards CO_2 and CS_2.

Considerable interest has been shown in recent years on studies on multiple bonding between phosphorus and main group elements.[1] Here we report the first experimental and theoretical studies on the aminodiazaphosphene (A), which is the structural link between the tetrazene (B)[2] and diaminodiphosphene (C) systems.[3] We are particularly here concerned with the following aspects: (a) the synthesis of (**1**) and its crystal structure, (b) studies on its reactivity, and (c) quantum chemical investigations on its bonding properties. It will be shown that (**1**) posseses an unusually high polarity of the PN double bond, as revealed by various studies on its reactivity.

Compound (**1**) was synthesized by reaction of aminodichlorophosphane (**2**) with lithiumbis(trimethylsilyl)amide by β-elimination of trimethylchlorosilane, *i.e.*, *via* intermediate (**3**) (Scheme 1). The constitution of (**1**) was confirmed by microanalysis and spectroscopy.†

The aminodiazaphosphene (**1**) possesses a double bond system of unusually high polarity. For example, it reacts cleanly with carbon disulphide or carbon dioxide to give the corresponding [2 + 2] cycloaddition products (**4**) and (**5**). While (**4**) is quite stable at ambient temperatures, (**5**) decomposes below room temperature with elimination of R_2NNCO, and formation of the λ^3-1,3,5-trioxaphosphorine,‡ (**7**) *via* the intermediate phosphinidene oxide (**6**).

The molecular structure§ of (**1**) is shown in Figure 1, the molecule adopting a nearly planar conformation of the atoms N(3)PN(1)N(2). The short PN(3) distance of 1.66 Å and the bond angle N(3)PN(1) of 108° are in accord with previous structural findings on aminoiminophosphanes.[4] However, the



Scheme 1. *Reagents and conditions:* i, $LiN(SiMe_3)_2$ in tetrahydrofuran, 1 h at 25 °C, 3 weeks at 80 °C, then filtration, evaporation of filtrate, and distillation, 68% yield; ii, excess of CS_2, 12 h at 35 °C, evaporation, and crystallization from C_6H_6, 68% yield; iii, CO_2 in CH_2D_2 at −45 °C; iv, 3 h at 25 °C, then evaporation and crystallization from n-hexane, 35% yield.

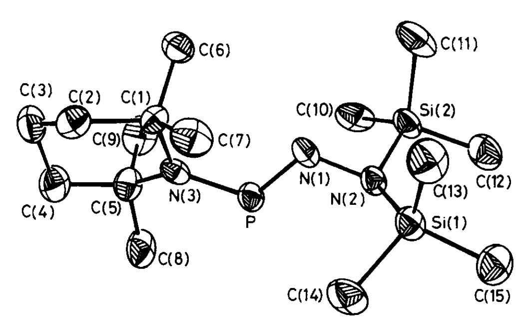


Figure 1. ORTEP view of the structure of (**1**). Important bond lengths (Å) and angles (°): P-N(1) 1.598(5), P-N(3) 1.660(5), N(1)-N(2) 1.506(6), Si(1)-N(2) 1.742(5), Si(2)-N(2) 1.751(5); N(3)-P-N(1) 107.7(2), P-N(1)-N(2) 107.1(3), N(1)-N(2)-Si(1) 107.7(3), N(1)-N(2)-Si(2) 105.8(3), Si(1)-N(2)-Si(2) 130.7(3), P-N(3)-C(5) 112.5(3), P-N(3)-C(1) 125.8(4), C(1)-N(3)-C(5) 119.4(4).

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† (**1**), m.p. 10 °C, b.p. 130—132 °C at 2 Torr; ^{31}P n.m.r. (C_6H_6) 363.9 p.p.m.; ^{13}C n.m.r. (C_6H_6) δ 1.64 (J_{CP} 3.4 Hz), 17.1, 31.7, and 41.3 (J_{CP} 1.0 Hz); $\lambda_{max.}$ (n-hexane) 304 (ε 6000, π–π*) and 398 nm (ε 720, n–π*); I.P. 7.32 (n_2'), 8.08 (π_2), and 8.89 eV (n_1). (**4**), m.p. 105 °C, ^{31}P n.m.r. (C_6D_6) 100.9 p.p.m.; ^{13}C n.m.r. (C_6D_6) δ 1.27 (J_{CP} 5.4 Hz), 1.3, 17.7 (J_{CP} 0.8 Hz), 31.9 (J_{CP} 9.1 Hz), 32.2 (J_{CP} 5.0 Hz), 32.4, 32.9, 42.5 (J_{CP} 0.5 Hz), 57.3, and 143.3 (J_{CP} 5.1 Hz). (**5**), ^{31}P n.m.r. ($CDCl_3$, −30 °C) 135.2 p.p.m.; ^{13}C n.m.r. (C_6D_6) δ 0.1, 0.2 (J_{CP} 6.5 Hz), 16.6, 31.0 (J_{CP} 1.5 Hz), 41.6, 58.4, and 154.0 (J_{CP} 7.7 Hz); (**7**), m.p. 134 °C, ^{31}P n.m.r. ($CDCl_3$) 138.4 p.p.m.; *m/z* 561 (M^+, 0.3%), 187 (R^2PO, 16%), and 172 (R^2PO-Me, 100%).

‡ The n.m.r. data of (**7**) are in accord with a chair conformation. In contrast the corresponding isopropylamino derivative preferentially adopts a boat conformation: E. Niecke, H. Zorn, B. Krebs, and G. Henkel, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 709.

§ *Crystal data:* (at −130 °C) $C_{15}H_{36}N_3PSi_2$, M = 345.62, monoclinic, space group $P2_1/c$, $a = 7.616(3)$, $b = 16.885(6)$, $c = 16.837(7)$ Å, $\beta = 92.03(3)°$, $Z = 4$, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 2.31\ cm^{-1}$. The structure was solved by direct methods and refined by full-matrix least-square refinement to a current $R_w = 0.069$, based on 2210 reflections with $F_o > 3.92\,\sigma(F_o)$. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

PN(1) distance of 1.60 Å is unusually long, and comparable with those in diaminophosphenium cations.[5] The bond angle PN(1)N(2) concomitantly becomes more acute, to lead to an almost tetrahedral environment at N(1). The N(2) amino group is twisted so as to place its lone pair orthogonal to the central π system [composed of P and N(1)]. The nitrogen N(2) is slightly pyramidalized and its lone pair points *endo* towards the phosphorus atom. Hence the structural as well as the reactivity studies of (**1**) indicate a weak PN π-bond with a high bond polarity.

The electronic bonding properties in (**1**) are in accord with previous considerations.[6] According to detailed quantum chemical calculations (not recorded here) at an *ab initio* double-zeta level, in the parent (**1**; $R^1 = R^2 = H$) a coplanar, conjugated π system is adopted. Silyl groups and to a lesser extent methyl groups at the N(2) amino group considerably reduce the energy barrier for rotation around the N(1)–N(2) bond. In other words silyl groups at N(2) promote the twisting of the p orbital at the amino group out of the π system. According to a Mulliken population analyses of the orthogonal conformations of the N(3) and/or N(2) amino group(s) the central PN σ bond is considerably weakened owing to electron donation from the (nonbonding) p orbital(s) into the PN σ* orbital. On this basis the central PN bond is longer than in planar aminoiminophosphane.

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