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FULL PAPER

New P–S–N containing ring systems. Reaction of 2,4-(naphthalene-1,8-diyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide and its 4-methoxynaphthalene derivative with hexamethyldisilazane

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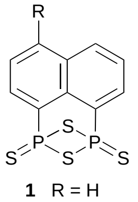
Reaction of 2,4-(naphthalene-1,8-diyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide **1** with hexamethyldisilazane (hmds) in acetonitrile gave the *N*,*N′*-bis(trimethylsilyl)acetamidinium salt of the $[(C_{10}H_6)P(S)(NHSiMe_3)SP(S)_2]^-$ anion **2**, a product of P_2S_2 ring cleavage, together with the new thiazaphosphetidine $(C_{10}H_6)P(S)SN(SiMe_3)P(S)$ **3**. Analogous (methoxy derived) products to **2** (**2a**, **2b**) and **3** (**3a**) were obtained when 2,4-(4-methoxynaphthalene-1,8-diyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide **1a** was used instead of **1**. When the reaction of **1** with hmds was performed in dichloromethane a mixture of the products was obtained, from which the hexamethyldisilazan-2-ium salt of the anion of identical structure to that in **2** has been isolated. No reaction occurred when a solventless system was used. The new compounds were studied spectroscopically (one- and two-dimensional NMR, IR spectroscopy) and by X-ray crystallography (**3**, **3a** and **4**).

Compounds with the P_2S_2 heterocyclic system continue to be of a great interest since they are widely used as thionation reagents[1] and also as sources of new organophosphorus compounds.[2] The most well known examples of compounds with such a structural motif are Lawesson's reagent 2,4-bis(*p*-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide and Davy's reagent methyl 2,4-bis(methylsulfanyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide, both of which are commercially available. Synthetic routes using the silylating agents methyl bis(trimethylsilyl)amine[3] or trimethylsilyl azide[4] towards organodithiadiphosphetane disulfides have been previously reported, which lead to new thiazadiphosphetidines. Here we report results of the study of reactions of compounds **1** and **1a** with another silylating agent hexamethyldisilazane (hmds) leading to new heterocyclic and cage compounds with electron-withdrawing groups.



1 R = H
1a R = OMe

Crystal structure analysis of compounds **1**[5] and **1a**[6] reveals a *cis* configuration of the substituents, imposed by the naphthalene-1,8-diyl, joining both phosphorus atoms and creating (together with the P_2S_2 ring) a cage structure. This backbone makes it impossible to split molecules **1** and **1a** into two fragments each having one P atom as is common in reactions of other organodithiadiphosphetane disulfides.[2]

Experimental

All manipulations were performed under dried nitrogen gas in Schlenk vessels. Compounds **1** and **1a** were prepared by the reaction of P_4S_{10} with 1-bromo- and 1-methoxynaphthalene respectively[6] and recrystallised from dichloromethane or toluene respectively. Solvents and hmds were purified and/or dried using standard methods. The IR spectra were recorded in Nujol mull in cells equipped with KBr windows on a Bruker IFS 28 spectrometer. Microanalyses were carried out by the Department of Inorganic Chemistry, Palacky University, Czech Republic.

Preparations

$[MeC(NHSiMe_3)_2]^+[(C_{10}H_6)P(S)_2SP(S)(NHSiMe_3)]^-$ 2. A suspension of compound **1** (0.50 g, 1.58 mmol) in MeCN (5 cm^3) and hmds (1.67 cm^3, 7.90 mmol) was stirred at room temperature until the reaction was finished (about 10 d), during which time it became a yellow clear solution. The dark yellow oil obtained by evaporation of solvent and residual hmds *in vacuo* was then placed in an oil-bath and evacuated/heated (15 Pa/90 °C) for 10 min to remove tris(trimethylsilyl)amine. The yellow solid obtained after cooling melted and decomposed on heating above 90 °C (determined by ^1H NMR spectroscopy). The yield of this material is apparently quantitative but purification of the crude product is difficult because of its sensitivity to moisture, extreme solubility and tendency to create oversaturated solutions in common solvents (acetonitrile, dichloromethane, benzene, toluene). Even long standing (several months) of the oily product at −20 °C did not lead to precipitation of solid. Thermal instability makes it difficult to distil off $N(SiMe_3)_3$. The purity was assessed by ^{31}P, ^1H and ^{13}C NMR spectroscopy, which revealed that the product contains about 4% (molar) of compound **3** and about 13% (molar) of $N(SiMe_3)_3$. NMR (in CD_3CN): $^{31}P-\{^1H\}$, δ 66.1 (d, P_A), 57.1 (d, P_B), $^2J(PP) = 13.6$, $^3J(P_AH) = 20.5$ Hz (from ^{31}P spectrum); ^1H, anion, δ 8.77 [1 H, ddd, $^3J(PH) = 20.5$, $^3J(HH) = 7.3$, $^4J(HH) = 1.4$, H2], 8.72 [1 H, ddd, $^3J(PH) = 20.5$, H8], 7.98 (1 H, m, H6), 7.91 (1 H, m, H4), 7.59 (1 H, m, H7), 7.52 (1 H, m, H3), 6.90 [1 H, d, $^2J(PH) = 8.7$ Hz, H11] and 0.39 (9 H, s, H12); cation, δ 8.26 (2 H, s, H11x), 2.13 (3 H, s, H1x) and 0.33 (18 H, s, H12x); $^{13}C-\{^1H\}$, anion, δ 141.2 [1 C, d, $^1J(PC) = 80.3$, C1], 136.0 [1 C, d, $^1J(PC) = 101.0$, $^3J(PC) = 3.8$, C9], 133.7 (2 C,

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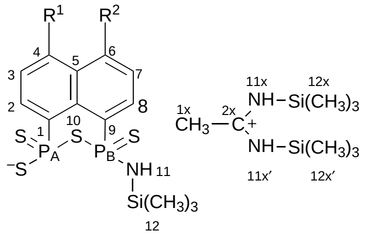
m, C5 and C6), 132.9 [1 C, d, ^2J(PC) = 13.0, C8], 132.4 (1 C, s, C4), 129.2 [1 C, d, ^2J(PC) = 13.8, C2], 127.6 [1 C, t, ^2J(PC) = 8.4 Hz, C10], 125.1 [1 C, d, ^3J(PC) = 17.6, C7], 125.0 [1 C, d, ^3J(PC) = 16.8 Hz, C3] and 1.9 (3 C, s, C12); cation, δ 174.9 (1 C, s, C2x), 20.6 (1 C, s, C1x) and −0.1 (6 C, s, C12x); ^{15}N, δ 133.1 (s, N11x and N11x′) and 68.5 (s, N11). IR ($\tilde{\nu}_{max}$/cm^{-1}): 3184s, 3125s and 3055s [ν(N–H)], 1683w and 1659w [ν(N–C$^+$–N)], 670s, 660s [ν(P=S)].



	R^1	R^2
2	H	H
2a	OMe	H
2b	H	OMe

[MeC(NHSiMe$_3$)$_2$]$^+$[(MeOC$_{10}$H$_5$)P(S)$_2$SP(S)(NHSiMe$_3$)]$^-$ 2a and 2b. A mixture of isomers (molar ratio 1.3 : 1) was prepared in the same fashion as for compound **2** from **1a** (0.50 g, 1.44 mmol) and hmds (1.52 cm^3, 7.2 mmol) in MeCN (5 cm^3). The resulting light yellow solid melts and decomposes on heating above 90 °C or when exposed to moisture. Effectively a quantitative yield was obtained; purity was assessed by ^{31}P-{^{1}H}, ^{1}H and ^{13}C-{^{1}H} NMR spectroscopy. Such mixtures of isomers contain less than 3% (molar) of **3a** and about 3% (molar) of N(SiMe$_3$)$_3$. NMR (in CD$_2$Cl$_2$): **2a**, ^{31}P-{^{1}H}, δ 65.5 (d, P$_A$), 58.0 (d, P$_B$), ^2J(PP) = 13.6 Hz; ^{1}H and ^{13}C spectra of cation identical to that of **2**; anion, ^{1}H δ 8.89 [1 H, m, ^3J(HH) = 7.5, H8], 8.83 [1 H, m, ^3J(HH) = 8.0, H2], 8.56 (1 H, m, H6), 7.69 (1 H, m, H7), 6.95 (1 H, d, H3), 6.92 [1 H, d, ^2J(PH) = 9.5 Hz, H11], 3.99 (3 H, s, OCH$_3$) and 0.51 (9 H, s, H12); ^{13}C-{^{1}H}, δ 158.0 (s, C4), 136.5 [dd, ^1J(PC) = 101, ^3J(PC) = 3.8, C9], 133.7 [d, ^2J(PC) = 12.6, C8], 133.2 [d, ^1J(PC) = 86, C1], 131.0 [d, ^2J(PC) = 15.2, C2], 129.3 [t, ^2J(PC) = 10, C10], 127.4 (s, C6), 126.2 [t, ^3J(PC) = 11.5, C5], 124.6 [d, ^3J(PC) = 16.4, C7], 103.1 [d, ^3J(PC) = 17.0 Hz, C3], 56.68 (s, OCH$_3$) and 2.6 [d, ^3J(PC) <2 Hz, C12]; **2b**, ^{31}P-{^{1}H} δ 66.4 (d, P$_A$), 56.7 (d, P$_B$), ^2J(PP) = 13.6 Hz; ^{1}H and ^{13}C spectra of cation identical to that of **2**; ^{1}H anion, δ 8.93 [1 H, m, ^3J(HH) = 7.5, H2], 8.81 [1 H, m, ^3J(HH) = 8.0, H8], 8.48 (1 H, m, H4), 7.61 (1 H, m, H3), 7.01 (1H, d, H7), 6.78 [1 H, d, ^2J(PH) = 8.8 Hz, H11], 3.97 (3 H, s, OCH$_3$) and 0.51 (9 H, s, H12); ^{13}C-{^{1}H}, δ 159.0 (s, C6), 141.3 [d, ^1J(PC) = 81, Cl], 135.1 [d, ^2J(PC) = 14.1, C8], 129.9 [d, ^2J(PC) = 13.8, C2], 129.4 [t, ^3J(PC) = 10, C10], 127.8 [dd, ^1J(PC) = 107, ^3J(PC) = 4.5, C9], 125.9 (s, C4), 125.8 [t, ^2J(PC) = 11.4, C5], 124.4 [d, ^3J(PC) = 15.8, C3], 104.0 [d, ^3J(PC) = 17.0, C7], 56.74 (s, OCH$_3$) and 2.6 [d, ^3J(PC) <2 Hz, C12].

(C$_{10}$H$_6$)P(S)SN(SiMe$_3$)P(S) 3. A suspension of compound **1** (0.50 g, 1.58 mmol) in MeCN (10 cm^3) and hmds (0.50 cm^3, 2.37 mmol) was heated under reflux for 8 h. The resulting clear yellow solution was concentrated *in vacuo* to 4 cm^3 and placed in a closed vessel inside a Dewar flask with hot water and allowed to cool slowly (10 d) to ambient temperature. Clear yellow crystals of **3** were filtered off, washed with *n*-hexane (2 × 3 cm^3) and dried *in vacuo*. Yield 218 mg (37.1%), m.p. 167–169 °C (Found: C, 42.19; H, 4.13; N, 3.50; S, 25.31. C$_{13}$H$_{15}$NP$_2$S$_3$Si requires C, 42.03; H, 4.07; N, 3.77; S, 25.89%). NMR (in CDCl$_3$, for numbering of atoms see Fig. 1): ^{31}P-{^{1}H}, δ 46.3 (s); ^{1}H, δ 8.34 (2 H, m, H2 and H8), 8.15 (2 H, m, H4 and H6), 7.69 (2 H, m, H3 and H7) and 0.05 [9 H, s, Si(CH$_3$)$_3$]; ^{13}C-{^{1}H}, δ 134.1 (s, C4 and C6), 133.3 [d, ^1J(PC) = 103.0, C1 and C9], 133.4 [t, ^3J(PC) = 11.5, C5], 131.8 (m, C2 and C8), 128.8 [t, ^2J(PC) = 9.7 Hz, C10], 125.6 (m, C3 and C7) and 0.8 [s, Si(CH$_3$)$_3$]. IR ($\tilde{\nu}_{max}$/cm^{-1}): 648s [ν(P=S)].

(MeOC$_{10}$H$_5$)P(S)SN(SiMe$_3$)P(S) 3a. A suspension of compound **2** (0.40 g, 1.15 mmol) in MeCN (5 cm^3) and hmds (0.36 cm^3, 1.72 mmol) was heated at reflux for 3 h. The resulting light yellow solution was concentrated *in vacuo* to 2 cm^3 and placed in a closed vessel in a Dewar flask with hot water and allowed to cool slowly (10 d) to ambient temperature. Colorless crystals of **3a** were filtered off, washed with MeCN (2 × 0.5 cm^3) and dried *in vacuo*. Yield 51 mg (11%), m.p. 169–171 °C (Found: C, 41.96; H, 4.02; N, 3.21; S, 24.39. C$_{14}$H$_{17}$NOP$_2$S$_3$Si requires C, 41.88; H, 4.27; N, 3.49; S, 23.96%). NMR (in CD$_2$Cl$_2$, for numbering of atoms see Fig. 2): ^{31}P-{^{1}H} (δ values calculated for AB system), δ 47.05 (d), 47.25 (d), ^2J(PP) = 17.68 Hz; ^{1}H, δ 8.58 (1 H, m, H6), 8.34 (1 H, m, H8), 8.23 (1 H, m, H2), 7.65 (1 H, m, H7), 6.99 (1 H, m, H3), 4.07 (3 H, s, H11) and 0.03 [9 H, s, Si(CH$_3$)$_3$]; ^{13}C-{^{1}H}, δ 160.5 (s, C4), 133.9 [d, ^2J(PC) = 12.2, C8], 133.0 [d, ^1J(PC) = 103.2, C9], 132.2 [d, ^2J(PC) = 10.71, C2], 130.1 [t, ^2J(PC) = 11.1, C10], 128.4 (s, C6), 125.9 [t, ^3J(PC) = 12.2, C5], 124.9 [m, ^3J(PC) = 13.8, C7], 124.2 [d, ^1J(PC) = 109.4, C1], 103.8 [m, ^3J(PC) = 14.5 Hz, C3], 56.4 (s, C11) and 0.6 [s, Si(CH$_3$)$_3$]. IR ($\tilde{\nu}_{max}$/cm^{-1}): 640s [ν(P=S)]. Raman ($\tilde{\nu}_{max}$/cm^{-1}): 639w [ν(P=S)].

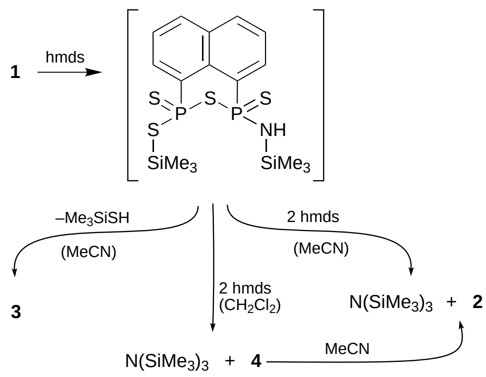
[NH$_2$(SiMe$_3$)$_2$]$^+$[(C$_{10}$H$_6$)P(S)$_2$SP(S)(NHSiMe$_3$)]$^-$·0.5CH$_2$Cl$_2$ 4. A suspension of compound **1** (0.25 g, 0.79 mmol) in CH$_2$Cl$_2$ (10 cm^3) and hmds (0.83 cm^3, 3.95 mmol) was stirred at room temperature; after 3 h it had become a clear yellow solution. Stirring was continued for several hours, the reaction mixture was then concentrated to 7 cm^3 and allowed to cool slowly to −20 °C. The clear yellow crystals of **4** were filtered off and washed with *n*-hexane before being dried *in vacuo*. Compound **4** decomposes when exposed to moisture (determined by IR spectroscopy), m.p. 133–134 °C. Yield 0.246 g (51.1%) (Found: C, 38.01; H, 6.18; N, 4.36; S, 20.94. C$_{19}$H$_{36}$N$_2$P$_2$S$_4$Si$_3$·0.5CH$_2$Cl$_2$ requires C, 38.43; H, 6.12; N, 4.60; S, 21.04%). NMR (in [^{2}H$_6$]-acetone): ^{31}P-{^{1}H}, ^{1}H and ^{13}C-{^{1}H} spectra of anion identical to those of **2** (see Discussion); ^{1}H, cation, δ 0.02 [18 H, s, Si(CH$_3$)$_3$]; ^{13}C-{^{1}H}, cation, δ 1.22 [s, Si(CH$_3$)$_3$]. IR ($\tilde{\nu}_{max}$/cm^{-1}): 3122s, 3056s [ν(N–H)], 655m, 640m [ν(P=S)].

Crystallography

Details of the data collections and refinements are summarised in Table 1. Data were collected using graphite-monochromatized Mo-Kα (λ = 0.710 73 Å) radiation on a KUMA KM-4 four circle κ-axis diffractometer equipped either with a modified Nonius low-temperature device (**3a**, **4**) or with an Oxford Cryostream Cooler (**3**). The cell parameters were determined by least-squares refinement on diffractometer coordinates of *n* centered reflections in the range ($2\theta_{min}$, $2\theta_{max}$). Data were collected in the 2θ range 4–50° with ω–2θ scan techniques. Three standard reflections tested during measurement showed no significant variation in intensity. Intensities were corrected for Lorentz-polarisation and absorption effects (DIFABS).[7] All structures were solved by direct methods (SHELXS 86).[8] All non-hydrogen atoms were refined anisotropically by full-matrix least-squares procedures based on F^2 (program SHELXL 93)[8] with weight $w^{-1} = \sigma(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$. All hydrogen atoms were located from the Fourier-difference synthesis and refined isotropically. The maximum Δ/σ after the last cycle of refinement was in all cases less than 0.001.

CCDC reference number 186/897.

See http://www.rsc.org/suppdata/dt/1998/1175/ for crystallographic files in .cif format.



Scheme 1

NMR spectroscopy

The NMR spectra were recorded on a Bruker Avance DRX-500 spectrometer. The values of small coupling constants summarised in the Experimental section were read directly from corresponding one-dimensional spectra (non-optimized). For ^{1}H and ^{13}C NMR spectroscopy SiMe$_4$ was used as an internal standard, for ^{31}P NMR 85% H_3PO_4 was used as an external standard. Homo- and hetero-nuclear chemical shift correlation spectra [double quantum filtered (DQF)-COSY,[9] GHMBC,[10] GSQMBC[11]] were recorded using a 5 mm triple resonance inverse probehead (^{1}H-{^{13}C}, {BB}, z-grad) equipped with a z-gradient coil.

For gradient-enhanced heteronuclear multiple bond correlation (GHMBC) experiments the following parameters were used: sequence $90°(^1H)–\Delta-90°(X)-t_1/2-G1-180°(^1H)-G2-t_1/2-90°(X)-G3-acq(t_2)$, for ^{1}H–^{13}C gradient ratios G1 : G2 : G3 = 30 : 18 : 24 G cm^{-1}, Δ = 60–80 ms, for ^{1}H–^{15}N gradient ratios G1 : G2 : G3 = 42 : 18 : 30 G cm^{-1}, Δ = 80–120 ms. For gradient-enhanced single-quantum multiple bond correlation (GSQMBC) experiments: sequence $90°(^1H)–\Delta/2–180°(^1H)/180°(X)-\Delta/2-90°(^1H)/90°(X)-t_1/2-180°(^1H)-t_1/2-G1-180°(X)-G2-90°(^1H)/90°(X)-acq(t_2)/G3$, evolution delays as for GHMBC spectra, gradient ratios for ^{1}H–^{13}C G1 : G2 : G3 = 12 : 36 : ±6 G cm^{-1}, for ^{1}H–^{15}N G1 : G2 : G3 = 4.8 : 52.8 : ±4.8 G cm^{-1}, for ^{1}H–^{31}P G1 : G2 : G3 = 12 : 41.6 : ±12 G cm^{-1}, Δ = 50–100 ms.

Results and Discussion

The reaction of compound **1** with hmds in acetonitrile gives products **2** and **3** depending on the molar ratio used and the temperature (Scheme 1). The proposed transition product (in square brackets) is unstable and undergoes subsequent reactions giving the products shown. The cation in **2** is probably formed from a reaction of hmds with the MeCN solvent. We speculate that $(Me_3Si)_2NH_2^+$ is formed which undergoes rapid reaction with the solvent. The reaction of **1a** with hmds gives products **2a**, **2b** and **3a**. When a great molar excess of hmds is used (1 : 5 to 1 : 10) the major products of the reaction are **2** together with $N(SiMe_3)_3$. Compound **3** was identified as a side product (4 molar %), its amount significantly increasing at higher reaction temperatures (18 molar % at reflux temperature).

The molecular structure of compound **2** was unambiguously demonstrated by both one- and two-dimensional NMR spectroscopy. The naphthalene ring hydrogen atoms were assigned using a DQF-COSY experiment. The assignment of ^{31}P signals was based on the ^{1}H–^{31}P GHMBC experiment, where interaction of P$_B$ with H11 was found. Clear interactions of P$_B$ with aromatic hydrogens H6, H7, H8 and H4 as well as weak interactions with H12 were observed. Atom P$_A$ interacted with aromatic hydrogens H2, H3 and H4 and H6, but not with any trimethylsilyl hydrogens. The ^{1}H–^{13}C GHMBC experiment allowed us to assign all ^{1}H and ^{13}C NMR signals (see Experimental section), and also the data for the *N*,*N′*-bis(trimethylsilyl)acetamidinium cation. Three-bond correlation of C1x with H11x and one-bond correlation of C1x with its hydrogens were observed as well as interaction of the least shielded carbon C2x with H11x and C1x. The proposed structure of the cation was supported also by ^{1}H–^{15}N GHMBC[12,13] and GSQMBC[11] experiments, showing one-bond correlation of hydrogen H11x with N11x [^1J(HN) = −76 Hz] as well as three-bond correlation of H11x with N11x′ [^3J(HN) = +4.3 Hz] and thus confirming the presence of two chemically equivalent NH groups bonded to one C atom.[14] The correlations of N11x with H1x [^3J(HN) = −4.8 Hz] and H12x [^{3}J(HN) = −3.5 Hz] were observed as well as one-bond interaction of nitrogen N11 with its hydrogen H11 [^1J(HN) = −71 Hz] and three-bond interaction of N11 with hydrogens H12 [^3J(HN) = −3.5 Hz]. The infrared spectrum of **2** contains characteristic bands at 1659 and 1683 cm^{-1} [ν(N–C$^+$–N)] due to the amidinium cation as well as several bands at 3055–3184 cm^{-1} [ν(N–H)], confirming the presence of more than one N–H group.

The analogous reaction of hmds with the methoxy derivative **1a** was also studied. Thus **1a** with hmds in acetonitrile in molar ratio 1 : 5 leads to a mixture of isomers **2a** and **2b** (molar ratio 1.3 : 1), differing from each other only by the position of the methoxy group on the naphthalene ring. A coproduct $N(SiMe_3)_3$ and side product **3a** were identified by NMR spectroscopy. Extreme solubility prevents purification of the crude product by recrystallisation; no attempts were made to separate isomers.

The molecular structures of compounds **2a** and **2b** were unambiguously demonstrated by both one- and two-dimensional NMR spectroscopy. A set of one-dimensional NMR experiments (^{1}H, ^{1}H-{^{31}P}, ^{13}C-{^{1}H}, ^{13}C-{^{1}H, ^{31}P}, ^{31}P-{^{1}H} allowed us to establish values of ^{1}H–^{31}P and ^{13}C–^{31}P coupling constants summarised in the Experimental section. The proposed structure and correct assignment of all signals in these spectra were confirmed also by GE-DQF-COSY{^{31}P}, ^{1}H–^{31}P GSQMBC[11] and ^{1}H–^{13}C GHMBC{^{31}P} two-dimensional experiments, where similar correlation peaks as for **2** were found. An unequivocal confirmation of the position of the methoxy group on the naphthalene ring was provided by DQF-COSY and ^{1}H–^{31}P GSQMBC experiments. The first allowed us to assign naphthalene ring hydrogen atoms, the second showed correlations of hydrogen atoms H2 and H3 (two spin system) in compound **2a** with the phosphorus atom other than that having correlation with hydrogen H11 and hydrogens, H6, H7, H8 (three-spin system). On the other hand, hydrogens H7 and H8 in compound **2b** correlated with the same phosphorus atom as that correlated with hydrogen H11.

Treatment of compound **1** with hmds in a molar ratio of 1 : 1.5 in acetonitrile leads to a mixture of products, from which the product of partial desulfuration 2,4-(naphthalene-1,8-diyl)-3-trimethylsilyl-1,3,2,4-thiazadiphosphetidine 2,4-disulfide **3** was obtained in moderate yield. Previously reported reactions of dithiadiphosphetane disulfides with methyl bis(trimethylsilyl)amine[3] (Scheme 2) resulted in the synthesis of an NH substituted ring, whereas here we obtained the NSiMe$_3$ derivative. This yellow solid is very soluble in CHCl$_3$ and poorly soluble in MeCN. Mechanistically the reaction leading to **3** and a side product SiMe$_3$(SH) requires a reactant molar ratio of 1 : 1 (Scheme 1); when the reaction was performed with only a small excess of hmds (molar ratio 1 : 1.1) unchanged **1** was observed in the mixture even after 48 h reflux. The ^{31}P-{^{1}H} NMR spectrum of **3** (singlet, δ 46.3) confirms the equivalence of both phosphorus atoms; ^{1}H NMR reveals the aromatic protons as well as confirming retention of one SiMe$_3$ group.

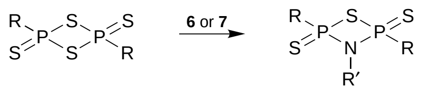
The crystal structure of compound **3** (Table 2, Fig. 1) confirms that **1** has undergone a ring-cleavage and subsequent ring-closure reaction to give a P$_2$NS ring. The asymmetric unit in **3** consists of two formula units which are slightly different from each other, as is shown in Table 2, where bond angles with

Table 1 Details of the data collections and refinements for compounds **3**, **3a** and **4**

	3	**3a**	**4**
Empirical formula	$C_{13}H_{15}NP_2S_3Si$	$C_{14}H_{17}NOP_2S_3Si$	$C_{13}H_{16}NP_2S_4Si^-C_6H_{20}NSi^+\cdot 2CH_2Cl_2$
M	371.5	401.5	609.4
Colour, habit	Yellow, rhomboid	Colourless, needle	Yellow, rhomboid
Crystal size/mm	1.00 × 1.00 × 0.15	0.80 × 0.30 × 0.30	0.8 × 0.7 × 0.4
T/K	150.0(1)	293(2)	133(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a/Å	8.944(2)	7.984(2)	17.698(9)
b/Å	11.490(2)	20.430(3)	12.841(3)
c/Å	17.165(4)	11.142(2)	14.008(4)
α/°	76.08(2)		
β/°	89.74(2)	98.53(2)	104.08(4)
γ/°	87.54(2)		
Centered reflections (*n*)	34	50	29
2θ Range of centered reflections/°	18.2–28.0	19.5–25.8	17.3–18.8
U/Å^3	1710.5(6)	1797.3(6)	3088(2)
Z	4	4	4
D_c/Mg m^{-3}	1.442	1.484	1.311
Maximum, minimum transmission	0.90, 0.51	0.82, 0.59	0.78, 0.61
μ/mm^{-1}	0.679	0.656	0.627
F(000)	768	832	1284
Index ranges	$-10 \leqslant h \leqslant 10$, $-13 \leqslant k \leqslant 13$, $-20 \leqslant l \leqslant 0$	$-9 \leqslant h \leqslant 9$, $-24 \leqslant k \leqslant 0$, $0 \leqslant l \leqslant 13$	$0 \leqslant h \leqslant 21$, $-12 \leqslant k \leqslant 0$, $-16 \leqslant l \leqslant 16$
Reflections measured	6226	3297	4736
Independent reflections (R_{int})	6008 (0.0721)	3139 (0.1000)	4591 (0.0238)
Data/parameters	6008/481	3139/266	4591/435
a, *b*	0.0939, 2.4000	0.1000, 3.1648	0.0600, 7.0000
S on F^2	0.884	0.980	0.980
Final *R*1, *wR*2 [$I > 2\sigma(I)$]	0.0391, 0.1138	0.0476, 0.1322	0.0402, 0.1091
(all data)	0.0492, 0.1242	0.0793, 0.1541	0.0484, 0.1143
Largest difference peak, hole/e Å^{-3}	0.538, −0.544	0.590, −0.611	0.349, −0.0554

Table 2 Selected bond lengths (Å) and angles (°) in compound **3**

P(1)–S(3a)	2.113(1)	P(1)–S(3b)	2.125(1)
P(2)–S(3a)	2.123(1)	P(2)–S(3b)	2.114(1)
P(1)–N	1.680(3)	P(2)–N	1.683(2)
P(1)–S(1)	1.908(1)	P(2)–S(2)	1.906(1)
P(1)–C(1)	1.796(3)	P(2)–C(9)	1.797(3)
Si–N	1.782(2)		
P(1)–S(3)–P(2)	73.55(4)	P(1)–N–P(2)	97.90(1)
N–P(1)–S(3)	89.14(9)	N–P(2)–S(3)	89.08(9)
N–P(2)–S(2a)	121.20(9)	N–P(2)–S(2b)	120.08(9)
N–P(1)–S(1)	119.01(9)	S(1)–P(1)–S(3)	121.65(5)
S(2)–P(2)–S(3a)	119.60(5)	S(2)–P(2)–S(3b)	120.18(5)
C(1)–P(1)–S(1)	117.7(1)	C(9)–P(2)–S(2)	118.2(1)
C(1)–P(1)–S(3)	101.5(1)	C(9)–P(2)–S(3)	101.6(1)
N–P(1)–C(1)	102.8(1)	N–P(2)–C(9)	102.2(1)
P(1)–N–Si(a)	126.6(1)	P(1)–N–Si(b)	130.6(1)
P(2)–N–Si(a)	133.2(2)	P(2)–N–Si(b)	129.3(1)



5a R = Me
5b R = Et
5c R = C$_6$H$_4$OMe-*p*

8a, **b**, **c** R′ = Me
(when treated with **6**)

9a, **b** R′ = SiMe$_3$
(when treated with **7**)

Scheme 2 *Reagents*: NMe(SiMe$_3$)$_2$ **6**, SiMe$_3$N$_3$ **7**

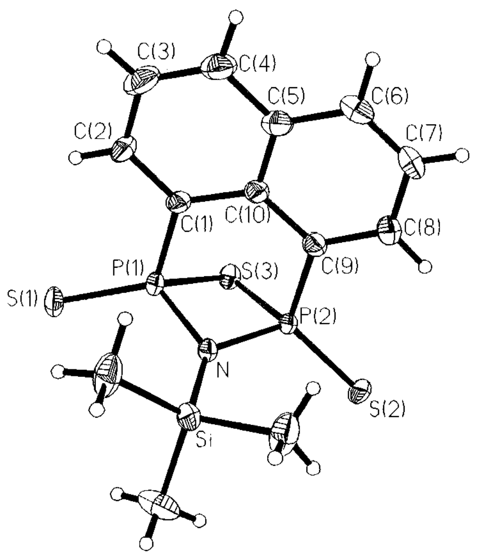


Fig. 1 Structure of the independent molecule in compound **3**

$\Delta > 3\sigma$ are listed for both independent molecules (a and b). The SiMe$_3$ group in formula unit a is slightly twisted about the N···Si axis when compared to unit b. The naphthalene part of the molecule, phosphorus and sulfur atoms S(1) and S(2) lie very close to a mean plane [maximum deviation 0.12 Å for S(1)]. There are few reports of the X-ray characterisation of P$_2$NS rings;[3,15,16] only one derivative has the *cis* configuration (*cis*-2-cyclohexylamino-3-cyclohexyl-4-methylsulfanyl-1,3,2,4-thiazadiphosphetidine 2,4-disulfide[15]), however in all of them the P$_2$NS rings are planar. In the *cis* derivative **3** the ring NP$_2$S is not planar with a dihedral angle of 146° about the P···P axis. The transannular P···P and S···N distances are 2.54 and 2.69 Å respectively. The internal P–S–P angle is noticeably reduced [73.55(4)°] relative to that in **1** [80.0(1)°][5] and to those in known NP$_2$S rings, both *cis* and *trans* derivatives (78–80°).[3,15,16] Similarly the internal P–N–P angle in **3** [97.90(1)°] is significantly reduced *vs.* that in other known NP$_2$S ring derivatives (104–106°). Similar trends could be seen in derivatives containing the P$_2$N$_2$ ring. In *cis*-PhP(S)(NEt)$_2$P(S)Ph, where the dihedral angle about the P···P axis is 168.5°, the P–N–P angle (95.0°) is slightly reduced *vs.* that in the *trans* derivative (96.7°), where the P$_2$N$_2$ ring is planar.[17] On the other hand the internal P–S and P–N bond lengths in **3** are comparable to those in

Table 3 Selected bond lengths (Å) and angles (°) in compound **3a**

P(1)–S(3)	2.127(2)	P(2)–S(3)	2.116(2)
P(1)–N	1.691(3)	P(2)–N	1.689(3)
P(1)–S(1)	1.909(1)	P(2)–S(2)	1.905(2)
P(1)–C(1)	1.783(4)	P(2)–C(9)	1.804(4)
Si–N	1.792(4)		
P(1)–S(3)–P(2)	73.49(5)	P(1)–N–P(2)	97.4(2)
N–P(1)–S(3)	88.1(1)	N–P(2)–S(3)	88.5(1)
N–P(1)–S(1)	122.2(1)	N–P(2)–S(2)	120.5(1)
S(1)–P(1)–S(3)	120.42(7)	S(2)–P(2)–S(3)	120.82(7)
C(1)–P(1)–S(1)	115.2(1)	C(9)–P(2)–S(2)	116.1(1)
C(1)–P(1)–S(3)	102.7(1)	C(9)–P(2)–S(3)	102.6(1)
N–P(1)–C(1)	103.6(2)	N–P(2)–C(9)	103.6(2)
P(1)–N–Si	131.2(2)	P(2)–N–Si	127.0(2)

Table 4 Selected bond lengths (Å) and angles (°) in compound **4**

P(1)–S(1)	2.111(1)	P(2)–S(1)	2.082(1)
P(1)–S(3)	1.970(1)	P(1)–S(4)	1.978(1)
P(2)–S(2)	1.942(1)	P(2)–N(1)	1.626(3)
P(1)–C(1)	1.812(3)	P(2)–C(9)	1.817(3)
Si(1)–N(1)	1.748(3)	Si(2)–N(2)	1.850(3)
Si(3)–N(2)	1.804(3)		
P(1)–S(1)–P(2)	100.44(6)	P(2)–N(1)–Si(1)	132.1(2)
S(3)–P(1)–S(4)	116.98(6)	N(1)–P(2)–S(2)	113.1(2)
S(3)–P(1)–S(1)	103.07(6)	S(4)–P(1)–S(1)	112.66(6)
S(2)–P(2)–S(1)	106.80(6)	N(1)–P(2)–S(1)	110.2(1)
C(1)–P(1)–S(1)	102.8(1)	C(9)–P(2)–S(1)	105.7(1)
C(1)–P(1)–S(3)	111.9(1)	C(1)–P(1)–S(4)	108.5(1)
C(9)–P(2)–S(2)	113.8(1)	C(9)–P(2)–N(1)	107.1(2)
Si(2)–N(2)–Si(3)	127.1(2)		

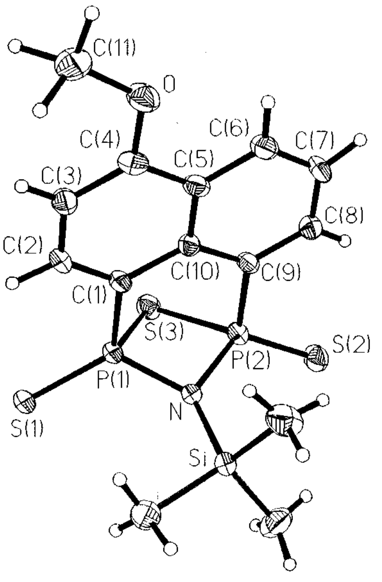


Fig. 2 Molecular structure of compound **3a**

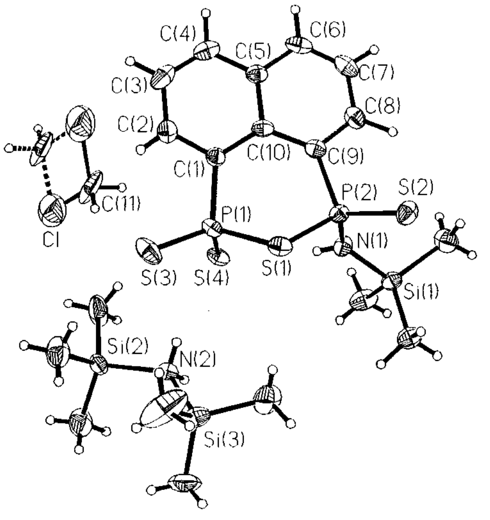


Fig. 3 Molecular structure of compound **4**

other known NP_2S ring derivatives. In **3** the molecules pack with the naphthalene rings face to face in a typical π–π overlap with an interplanar separation of 3.49 Å. The closest non-bonded intermolecular S···S distance 3.56 Å is between S(1) and S(2).

A methoxy-derived relative **3a** was obtained in a similar fashion to **3**. This white air-stable compound is soluble in dichloromethane and acetonitrile. The reaction was completed in a shorter time because of the higher solubility of **1a** *vs.* **1**. The chemical shifts of both phosphorus atoms in **3a** (δ 47.05, 47.25) are similar to that of **3** (δ 46.3) and suggest that the two compounds have similar structures. The ^{31}P-{^{1}H} NMR spectrum (AB system) is as expected, where the methoxy group has an electronic effect through the aromatic naphthalene system. Substitution of one of the internal S atoms by an N atom resulted in a substantial increase in the magnitude of the ^2J(PP) coupling constant to 17.7 Hz (6.5 Hz for **1**,[18] 7.4 Hz for **1a**). The ^{1}H and ^{13}C-{^{1}H} NMR signals were assigned by analogy of **3a** with **2a** and **2b**.

The crystal structure of compound **3a** (Table 3, Fig. 2) reveals a very similar geometry to that of **3**, as was expected on the basis of comparison between **1** and **1a**,[6] where the methoxy group does not exert any steric effect on the P_2NS ring system. The naphthalene part of the molecule, phosphorus, sulfur atoms S(1) and S(2) and methoxy O and C(11) lie very close to a mean plane [maximum deviation 0.09 Å for C(11) and P(2)]. The ring NP_2S is non-planar with a dihedral angle of 142.6° about the P···P axis (about 3° more hinged than that in **3**). All corresponding bond lengths and almost all bond angles are not substantially different from those in **3**. The only exceptions are angles C(1)–P(1)–S(1) and C(9)–P(2)–S(2), however the difference from those in **3** is less than 2°. As in **3** the molecules pack with the naphthalene rings face to face.

In an attempt to exclude formation of the *N*,*N*′-bis(trimethylsilyl)acetamidinium cation we performed the reaction of compound **1** with hmds in dichloromethane (Scheme 1). The reaction in 1 : 5 molar ratio is completed in a much shorter time than that where acetonitrile is used, probably because of the much higher solubility of **1** in dichloromethane. From a complex mixture of products compound **4** crystallizes on cooling in good yield and purity. It is soluble in acetonitrile, but its solution is unstable and turns into **2** (conversion is completed after several days), also in dichloromethane and chloroform. However in the latter solvents it undergoes decomposition to an equilibrium mixture of **4** and two unidentified products (present also in the reaction mixture before as well as after precipitation of **4**), each containing two chemically inequivalent phosphorus atoms. The ^{31}P-{^{1}H}, ^{1}H and ^{13}C-{^{1}H} NMR spectra of the anion are, as expected, very similar to those of **2**, slight differences in chemical shifts occurring because of the presence of a different cation and solvent ([$^2H_6$]acetone). We were unable to identify peaks belonging to NH_2^+ hydrogens in the ^{1}H NMR spectrum of **4**, probably due to fast chemical exchange.

The crystal structure of **4** (Table 4, Fig. 3) reveals that **1** has undergone a ring-cleavage reaction to give a product with an ionic structure. Its anionic part is identical to that in **2**, the structure of which was solved by NMR techniques. The structure of the cation is noteworthy; to our knowledge no report of the X-ray characterisation of the hexamethyldisilazan-2-ium ion has been previously published. The $C_{10}H_6P_2$ part of molecule is noticeably distorted from planar; atoms P(1) and P(2) lie 0.25 and 0.21 Å above and below the mean plane respectively. The C_3P_2S ring is hinged with the C_3P_2 and P_2S planes inclined by 51.2° with respect to each other. The opening of the P_2S_2 ring results in substantial lengthening of the P···P distance *vs.* that in **1** (3.22 *vs.* 2.73 Å) and widening of P(1)–S(1)–P(2) angle [100.44(6) *vs.* 80.0(1)°]. However, this angle is comparable to that in related molecules $(C_{10}H_6)P(S)(SMe)$-SP(S)(OMe)[19] [103.0(1)°] and $(C_{10}H_6)P(S)(OCH_2CH_2OH)SP$-$(S)(OCH_2CH_2OH)$[20] [101.8(1)°]. The P(1)–S(3) [1.9689(14) Å] and P(1)–S(4) [1.9785(13) Å] distances indicate delocalisation of the negative charge in the PS_2 group. Hydrogen bonds link the S(4) atom to an NH (anion) hydrogen (2.60 Å) and to one of the NH_2 (cation) hydrogens (2.54 Å).

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