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New P–S–N containing ring systems. Reaction of 2,4-(naphthalene-1,8-diyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide with methylbis(trimethylsilyl)amine

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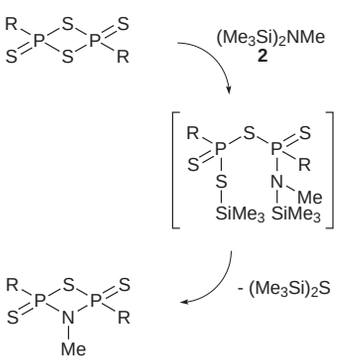
From the reaction of 2,4-(naphthalene-1,8-diyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide **1** with methylbis(trimethylsilyl)amine **2** in dichloromethane a product of the P_2S_2 ring cleavage, $(C_{10}H_6)P(S)(SSiMe_3)(\mu\text{-}S)P(S)(NMeSiMe_3)$ **3**, was isolated, existing in an equilibrium between two diastereomeric forms in solution. Compound **3** was also obtained when toluene was used as a solvent. Its subsequent reaction with pyridine (py) led to the desilylated ionic product $[Hpy^+][(C_{10}H_6)P(S)(NHMe)(\mu\text{-}S)PS_2^-]$ **4**, which reacts with tetraphenylphosphonium chloride to give $[PPh_4^+][(C_{10}H_6)P(S)(NHMe)(\mu\text{-}S)PS_2^-]$ **5**. When acetonitrile was used as a solvent a cage compound 2,6-(naphthalene-1,8-diyl)-3,4-dimethyl-1,3,5,2λ^5,6λ^5-thiadiazadiphosphinine 2,6-disulfide **6** containing a six-membered CN_2P_2S heterocycle was obtained. The new compounds were studied spectroscopically (1- and 2-D high resolution NMR, IR, MS) and in the cases of **3**, **5** and **6** by X-ray crystallography.

The reaction of *trans*-diorganodithiadiphosphetane disulfides $(RPS_2)_2$ (R = Me, Et or C_6H_4OMe-*p*) with methylbis(trimethylsilyl)amine when performed in dichloromethane leads to N-alkylated thiazadiphosphetidine disulfides (Scheme 1), and



Scheme 1

the unstable intermediate in square brackets has been proposed.[1] We have previously reported on the synthesis of *cis*-2,4-(naphthalene-1,8-diyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide[2,3] **1** from the reaction of 1-bromonaphthalene with P_4S_{10} and have noted some striking differences in reactivity between this cage compound and the more well established *trans* systems. Here we describe some studies to determine how the structural anomaly of this compound (a bridge created by organic substituent naphthalene-1,8-diyl, joining both phosphorus atoms) affects the reaction and structure of the products. We have found that the reaction of **1** with $NMe(SiMe_3)_2$ **2** gives a product **3** which has an analogous structure to that of the unstable intermediate proposed in the case of the above described reactions of $(RPS_2)_2$ with **2** (Scheme 1). Even prolonged heating of **3** in boiling toluene or addition of base (pyridine) did not lead to elimination of bis(trimethylsilyl) sulfide and formation of the thiazadiphosphetidine disulfide; in the latter case a desilylated pyridinium salt **4** was obtained instead, which was for easier purification converted into its tetraphenylphosphonium salt. Moreover we studied the reaction of **1** with **2** in acetonitrile, leading to a new cage compound 2,6-(naphthalene-1,8-diyl)-3,4-bis(methyl)-1,3,5,2λ^5,6λ^5-thiadiazadiphosphinine 2,6-disulfide containing a six-membered unsaturated heterocycle CN_2P_2S.

Experimental

All manipulations were performed under dried nitrogen gas in Schlenk vessels. Compound **1** was prepared by the reaction of P_4S_{10} with 1-bromonaphthalene[3] and recrystallized from dichloromethane. Anhydrous pyridine, tetraphenylphosphonium chloride and **2** were obtained from Aldrich; **2** was distilled before use. Solvents were purified and/or dried using standard methods. The IR spectra were recorded in Nujol mull in cells equipped with KBr windows or as pellets with KBr on a Bruker IFS 28 spectrometer or on a Perkin-Elmer system 2000, mass spectra by the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea. Microanalyses were carried out by the Department of Chemistry, Palacky University, CZ, and Loughborough Chemistry Departmental service, UK.

Preparations

$(C_{10}H_6)P(S)(SSiMe_3)(\mu\text{-}S)P(S)(NMeSiMe_3)$ 3. A suspension of compound **1** (0.50 g, 1.58 mmol) in 5 cm^3 CH_2Cl_2 and **2** (0.52 cm^3, 2.37 mmol) was stirred at room temperature for 8 h. The resulting clear yellow solution was concentrated *in vacuo* to 3 cm^3 and cooled to −20 °C for 1d. The resulting yellow crystals of **3** (some of them suitable for X-ray crystallography) were filtered off, washed with hexane and dried *in vacuo*. A further portion of less pure **3** was obtained from the mother-liquor: the oily product obtained after evaporation of the solvent *in vacuo* was stirred for several hours with 10 cm^3 *n*-hexane, the resulting suspension was filtered off, washed with 5 cm^3 of *n*-hexane and dried *in vacuo*. Compound **3** decomposes very fast when exposed to air moisture. Yield of the 1st fraction 228 mg (29.3%), mp 156–158 °C (Found: C, 41.8; H, 5.5; N, 2.7; S, 25.3. $C_{17}H_{27}NP_2S_4Si_2$ requires C, 41.5; H, 5.5; N, 2.8; S, 26.1%). IR

($\tilde{\nu}_{max}$/cm^{-1}) 682vs and 645s [ν(P=S)]. NMR (500 MHz, ^{31}P-{^{1}H} and ^{1}H in $CDCl_3$, ^{13}C-{^{1}H} in CH_2Cl_2, for numbering of atoms see Fig. 1): major isomer, ^{31}P-{^{1}H} δ 67.8 [d, P(9)], 55.1 [d, P(1)], ^{2}J(PP) = 13.0 Hz; ^{1}H δ 8.82 [1 H, dd, ^{3}J(PH) = 21.8, ^{3}J(HH) = 7.2, H2], 8.50 [1 H, dd, ^{3}J(PH) = 19.0, ^{3}J(HH) = 7.2, H8], 8.10 (2 H, m, H4 and H6), 7.69 (2 H, m, H3 and H7), 2.45 [3 H, d, ^{3}J(PH) = 17.3 Hz, NMe], 0.61 (9 H, s, $SSiMe_3$) and 0.26 (9 H, s, $NSiMe_3$); ^{13}C-{^{1}H} δ 135.8–125.1 (naphthalene ring carbons), 33.9 (s, NMe), 2.1 [d, ^{4}J(PC) = 3.5 Hz, $SSiMe_3$] and 1.8 (s, $NSiMe_3$); ^{15}N δ 52.1; minor isomer, ^{31}P-{^{1}H} δ 66.1 [d, P(9)], 57.2 [d, P(1)], ^{2}J(PP) = 15.5 Hz; ^{1}H δ 8.89 [1 H, m, H8], 8.86 [1 H, m, H2], 8.10 (2 H, m, H4 and H6), 7.69 (2 H, m, H3 and H7), 2.78 [3 H, d, ^{3}J(PH) = 16.9 Hz, NMe], 0.71 (9 H, s, $SSiMe_3$) and −0.12 (9 H, s, $NSiMe_3$); ^{13}C-{^{1}H} δ 135.8–125.1 (naphthalene ring carbons), 33.6 (s, NMe), 2.4 [d, ^{4}J(PC) = 3.5 Hz, $SSiMe_3$] and 0.7 (s, $NSiMe_3$); ^{15}N δ 50.6.

[Hpy$^+$][($C_{10}H_6$)P(S)(NHMe)(μ-S)PS_2^-] 4. A suspension of compound **1** (1.0 g, 3.16 mmol) in 10 cm^3 toluene and **2** (0.80 cm^3, 3.64 mmol) was stirred at room temperature for two days. Pyridine (0.38 cm^3, 4.74 mmol) was slowly added to the resulting clear yellow solution with stirring. The resulting suspension was stirred for 5 h, the solid was filtered off, washed with cold toluene (5 cm^3) and dried *in vacuo*. Yield 1.135 g (84.1%), decomp. above 120 °C (Found : C, 44.6; H, 4.3; N, 5.7. $C_8H_8NPS_2$ requires C, 45.1; H, 3.8; N, 6.6%). IR ($\tilde{\nu}_{max}$/cm^{-1}) 1607m, 1485m [ν_{ring}(py)], 1589 (sh) [δ(NH)], 655vs and 673vs [ν(P=S)]. NMR [400 MHz, ^{31}P-{^{1}H} in py, ^{1}H and ^{13}C-{^{1}H} in d_6-dimethyl sulfoxide (d_6-dmso)]: ^{31}P-{^{1}H} (δ values calculated for AB system) δ 70.47 (d), 70.09 (d), ^{2}J(PP) = 12.0 Hz; ^{1}H δ 8.88 (2 H, m, H13), 8.69 (1 H, m, H2), 8.58–8.51 (2 H, two overlapping multiplets, H8 and H15), 8.19 (1 H, m, H6), 8.04–7.97 (3 H, two overlaping multiplets, H4 and H14), 7.70 (1 H, m, H7), 7.60 (1 H, m, H3), 6.2 (2 H, br s, H12 and H16), 2.61 [3 H, d, ^{3}J(PH) = 20.0 Hz, H11]; ^{13}C-{^{1}H} δ 146.1 (br s, C13), 143.6 (br s, C15), 142.7 [d, ^{1}J(PC) = 81.5, C1], 135.2–134.9 (m, C6 and C8], 134.2 [dd, ^{3}J(PC) = 9.5, 11.3, C5), 132.5 (m, C4), 132.0 [dd, ^{1}J(PC) = 110, ^{3}J(PC) = 2.1, C9], 129.8 [d, ^{2}J(PC) = 13.3 Hz, C2], 128.6 [dd, ^{2}J(PC) = 8.0, 9.8, C10], 127.7 (br s, C14), 125.9–125.5 (m, C3 and C7) and 27.0 [d, ^{2}J(PC) = 4.0 Hz, C11]. Mass spectrum (FAB+): *m*/*z* 427 (M + H$^+$), 370 (M − py + Na), 348 (M − py + H) and 317 (M − Hpy − S).

[PPh_4^+][($C_{10}H_6$)P(S)(NHMe)(μ-S)PS_2^-] 5. A solution of compound **4** (0.25 g, 0.58 mmol) in 3 cm^3 pyridine was added to a stirred solution of PPh_4Cl (0.24 cm^3, 0.64 mmol) in 4 cm^3 pyridine. The volume of the solvent was reduced to half by its evaporating *in vacuo* and 60 cm^3 of cool water were added with vigorous stirring. The resulting white solid was filtered off, washed with cool water and dried *in vacuo*. Recrystallized from dry $CHCl_3$–hexane. Yield 0.297 g (74.0%), mp 195–197 °C (Found : C, 61.1; H, 4.5; N, 1.9. $C_{35}H_{30}NP_3S_4$ requires C, 61.3; H, 4.4; N, 2.0%). IR ($\tilde{\nu}_{max}$/cm^{-1}) 3133w [ν(NH)], 1586w [δ(NH)], 689s, 659vs [ν(P=S)]. NMR [400 MHz, ^{31}P-{^{1}H} in d_6-dmso, ^{1}H and ^{13}C-{^{1}H} in $CDCl_3$; for numbering of atoms see Fig. 2]: ^{31}P-{^{1}H} (δ values of anion calculated for AB system) δ 73.03 (d), 72.23 (d), ^{2}J(PP) = 11.6 Hz, 25.6 (s, PPh_4^+); ^{1}H δ 8.79 (1 H, m, H2), 8.59 (1 H, m, H8), 7.82 (1 H, m, H6), 7.72–7.41 (21 H, three partially overlapping multiplets, H4 and hydrogens of PPh_4^+ cation), 7.38 (1 H, m, H7), 7.27 (1 H, m, H3), 6.19 (1 H, m, NH), 2.60 [3 H, dd, ^{3}J(PH) = 20.1, ^{3}J(HH) = 5.60 Hz, H11]; ^{13}C-{^{1}H} δ 142.8–124.7 (carbons of naphthalene entity), 136.1–117.2 (carbons of PPh_4^+ cation) and 27.2 (s, C11). Mass spectrum: (ES+) *m*/*z* 339 (PPh_4^+) and 261 (PPh_3 + H); (ES−) *m*/*z* 346 (anion).

$C_{13}H_{12}N_2P_2S_3$ 6. A suspension of compound **1** (0.50 g, 1.58 mmol) in 40 cm^3 CH_3CN and **2** (0.38 cm^3, 1.74 mmol) was heated under reflux for 5 h. The resulting clear brown solution was concentrated *in vacuo* to 15 cm^3, placed in a closed vessel in a Dewar flask with hot water and allowed to cool slowly (10 d) to ambient temperature. Yellow clear needles of **4** (some of them suitable for X-ray crystallography) were filtered off, washed with 2 × 2 cm^3 CH_3CN and dried *in vacuo*. Yield 195 mg (34.8%), mp 218–220 °C (Found: C, 43.9; H, 3.4; N, 7.7; S, 27.9. $C_{13}H_{12}N_2P_2S_3$ requires C, 44.1; H, 3.4; N, 7.9; S, 27.1%). IR ($\tilde{\nu}_{max}$/cm^{-1}) 1582vs [ν(C=N)], 655s, 639s [ν(P=S)]. NMR (500 MHz, in CD_2Cl_2; for numbering of atoms see Fig. 3): ^{31}P-{^{1}H} δ 56.9 (d, P9), 28.6 (d, P1), ^{2}J(PP) = 11.2 Hz; ^{1}H δ 8.70 (2 H, m), 8.10 (2 H, m), 7.66 (2 H, m, H3 and H7), 3.48 [3 H, d, ^{3}J(PH) = 11.0, H13] and 2.28 [3 H, d, ^{4}J(PH) = 2 Hz, H12]; ^{13}C-{^{1}H} δ 165.1 [d, ^{2}J(PC) = 19.8, C11], 135.2 (s), 134.3 [d, J(PC) = 13.5], 134.1 [d, J(PC) = 15.3], 133.9 (s), 133.7 [t, J(PC) = 10.8], 131.2 [dd, ^{1}J(PC) = 97, ^{3}J(PC) = 8.1], 130.7 [d, ^{1}J(PC) = 102], 130.4 [t, J(PC) = 9.0], 125.7 [d, J(PC) = 17.1], 125.5 [d, J(PC) = 18.0], 33.8 [d, ^{3}J(PC) = 8.1, C13] and 28.3 [d, ^{3}J(PC) = 18.9 Hz, C12]. Mass spectrum (FAB+): *m*/*z* 377 (M + Na) and355 (M + H).

Crystallography

Details of the data collections and refinements are summarised in Table 1. Data for compounds **3** and **6** were collected using graphite-monochromatized Mo-Kα (λ = 0.71073 Å) radiation on a KUMA KM-4 four circle κ-axis diffractometer equipped with an Oxford Cryostream Cooler. Data were collected in the 2θ range 4–50° with ω–2θ scan techniques. The application of semiempirical correction of intensities (program DIFABS)[4] was in the case **3** negligible, whilst in the case **6** led to increased *R* factors. Data for **5** were collected using graphite-monochromatized Mo-Kα radiation and a 0.7 mm collimator on a KUMA KM4CCD four circle diffractometer. A total of 830 frames were recorded. The exposure time was 30 s for each 0.5° step. Data reduction was processed by 3D profile analysis software (KM4RED)[5] which corrects intensities for Lorentz-polarization effects too. All structures were solved by direct methods (SHELXS 86).[6] Non-hydrogen atoms were refined anisotropically by the full-matrix least-squares procedure based on F^2 (SHELXL 93).[7] All hydrogen atoms were found from the Fourier-difference synthesis and refined isotropically, except in the case of **5** where the hydrogen atoms on C(11), as well as hydrogens on the disordered carbon atoms in one of the phenyl rings in the cation, were fixed in idealized CH_3 and aromatic positions respectively; their *U* and site occupation factor (s.o.f.) were driven by riding C atoms.

CCDC reference number 186/1471.

See http://www.rsc.org/suppdata/dt/1999/2231/ for crystallographic files in .cif format.

NMR

NMR Spectra were recorded either on a Bruker Avance DRX-500 or DPX-400 spectrometer. Direct measurement of ^{1}H, ^{13}C and ^{31}P spectra was carried out on a 5 mm (^{13}C/^{19}F/^{31}P-{^{1}H}) probehead. Homonuclear and heteronuclear chemical shift correlation spectra (DQF-COSY,[8] NOESY,[9] GHMBC,[10] GSQMBC,[11] ^{31}P–^{15}N GHMQC[12]) were recorded either on a 5 mm triple resonance inverse probehead (^{1}H-{^{13}C} {BB} *z*-grad) equipped with a *z*-gradient coil or a 5 mm inverse probehead (^{1}H-{^{13}C} {^{15}N} {^{31}P} *x,y,z*-grad). For ^{1}H and ^{13}C NMR spectroscopy TMS was used as an internal standard; for ^{31}P NMR 85% H_3PO_4 was used as an external standard.

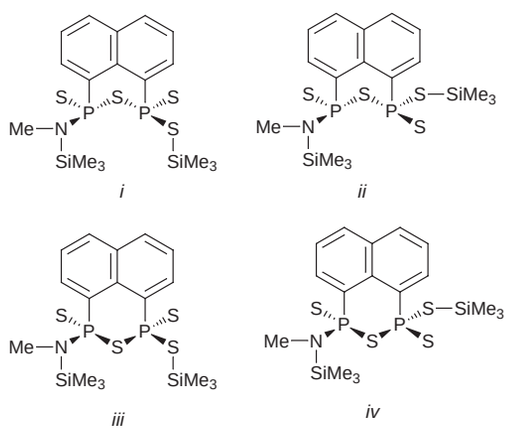
Gradient-enhanced heteronuclear multiple bond correlation (GHMBC) experiments used the following parameters: sequence published elsewhere;[13] for ^{1}H–^{15}N correlation, gradient ratio G1 : G2 : G3 = 42 : 18 : 30 G cm^{-1}; for ^{1}H–^{31}P correlation, G1 : G2 : G3 = 36 : 6 : 14.9 G cm^{-1}; delay for evolution of long-range coupling constants, 60–120 ms. Gradient-enhanced single-quantum multiple bond correlation (GSQMBC) experiments: sequence;[11,13] for ^{1}H–^{15}N correlation, gradient ratio

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}; evolution delays were as for GHMBC spectra. ^{31}P–^{15}N Gradient-enhanced heteronuclear multiple quantum correlation (^{31}P–^{15}N GHMQC) experiment: sequence;[14] gradient ratio, G1 : G2 : G3 = 30 : 18 : 24 G cm^{-1}; evolution delay, 20 ms.

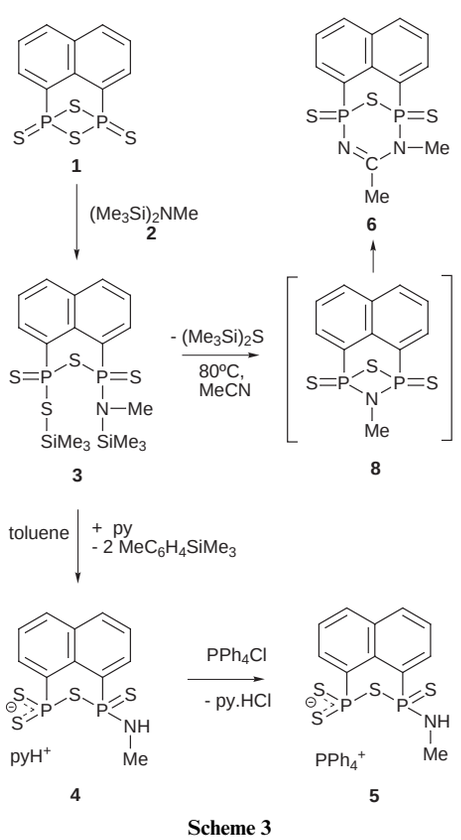
Results and discussion

The ^{31}P-{^{1}H} NMR spectrum of the reaction mixture of compound **1** with **2** in dichloromethane showed two distinct AX signals. The spectra indicate asymmetrical substitution of the phosphorus atoms, whilst the similar chemical shifts and coupling constants of both sets of doublets indicates the presence of two diastereomers. The ^{1}H NMR spectrum was in accord with these facts. The two stereogenic phosphorus centers and the existence of planar chirality in the proposed structure give rise to 4 possible diastereomers (Schemes 2 and 3).

We performed semiempirical quantum chemical computations (AM1 method[15]) which revealed that the isomers *iii* and *iv* converge to *i* and *ii* when minimized. The ΔH^{f} of the thermodynamically stable isomers *i* and *ii* are almost equal (−20.432 and −20.436 kcal mol^{-1}).



Scheme 2



Scheme 3

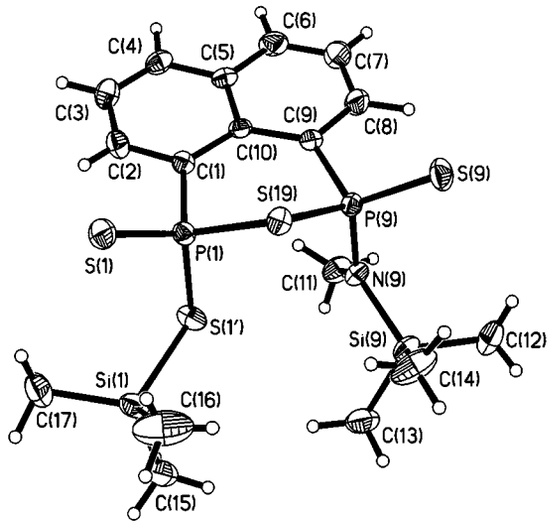


Fig. 1 Molecular diagram of compound *cis*-**3** (diastereomer *i*).

The proposed structure of the diastereomer *i* was confirmed by a crystal structure determination (Table 2, Fig. 1). Several crystals of the same type as these used for X-ray measurement (diastereomer *i*) were examined by ^{31}P-{^{1}H} and ^{1}H NMR. After their dissolution in various solvents (*e.g.* dichloromethane, chloroform, diethyl ether, benzene) a mixture of both diastereomers was observed in solution. We suppose that chemical migration of the trimethylsilyl group bonded to the sulfur atom in the solution leads to an equilibrium mixture of diastereomers *i* and *ii*, as the stability of S–Si bond is rather low[16] and the existence of the related anion **7** has been demonstrated by an X-ray diffraction determination.[13] Moreover the presence of **1** and **2** was detected by ^{31}P-{^{1}H} and ^{1}H NMR in the solution prepared from analytically pure crystals of **3**, suggesting a second equilibrium between starting compounds and products. This equilibrium is pushed to the right hand products side by use of an excess of **1** during the synthesis. Distinct signals due to both diastereomers were found in the NMR spectra at ambient temperature. On the other hand, exchange "cross-peaks" found in standard phase-sensitive ^{1}H–^{1}H NOESY spectrum (700 ms mixing time) as well as in the ^{31}P–^{31}P NOESY spectrum (700 and 300 ms mixing time) indicate relatively fast interconversion. We found that the molar ratios of diastereomers depend on the solvent, *e.g.* in dichloromethane 1 : 3 and in decalin 1 : 5 molar ratios were observed by ^{31}P NMR . A set of 2-D NMR experiments (^{1}H–^{1}H COSY, ^{1}H–^{15}N, ^{1}H–^{31}P GHMBC, ^{1}H–^{31}P, ^{1}H–^{15}N GSQMBC, ^{31}P–^{15}N GHMQC) was made allowing us to assign ^{1}H, ^{31}P-{^{1}H} and ^{15}N NMR signals of both major and minor isomers and to find their connectivities. However it was impossible to distinguish which arrangement (*i*, *ii*) corresponds with the major and minor isomer. Correlations of major and minor isomer observed in ^{1}H–^{31}P, ^{1}H–^{15}N and ^{31}P–^{15}N 2-D spectra are demonstrated in Fig. 4. Four-bond correlations of the P atom with methyl hydrogens of its $SSiMe_3$ group found for both isomers confirm that neither of them is present as the anion (with analogous structure to **7**) in solution.

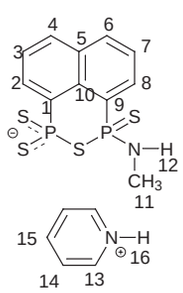
The crystal structure of compound **3** (diastereomer *i*) reveals that the naphthalene part of the molecule and phosphorus atoms lie very close to the mean plane fitted to these atoms [maximum deviation 0.03 Å for C(8)]. Exocyclic substituents lie in a *cis* position relative to the naphthalene ring, atoms S(1), S(9) and S(19) lie above the plane, $S(SiMe_3)$ and $N(Me)(SiMe_3)$ groups lie below the plane. The C_3P_2S ring is hinged with the C_3P_2 and P_2S planes inclined by 47.3° 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**[2] (3.27 *vs.* 2.73 Å) and broad-

Table 1 Details of the data collections and refinements for compounds **3**, **5** and **6**

	3	**5**	**6**
Empirical formula	$C_{17}H_{27}NP_2S_4Si_2$	$C_{35}H_{30}NP_3S_4$	$C_{13}H_{12}N_2P_2S_3$
M	491.8	685.75	354.4
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a/Å	7.178(2)	9.8665(7)	7.038(3)
b/Å	10.502(3)	10.4165(8)	27.939(3)
c/Å	17.184(5)	17.131(2)	7.891(2)
α/°	105.81(2)	105.217(8)	
β/°	93.25(2)	102.994(7)	103.81(3)
γ/°	100.94(2)	90.777(6)	
U/Å^3	1215.6(6)	1650.4(2)	1506.8(8)
T/K	150(2)	150(2)	293(2)
Z	2	2	4
μ/mm^{-1}	0.625	0.460	0.693
Reflections measured	4439	8096	2888
Reflections independent (R_{int})	4289 (0.0821)	5459 (0.0372)	2668 (0.0318)
Final *R*1, *wR*2 [$I > 2\sigma(I)$]	0.0430, 0.1140	0.0466, 0.1196	0.0347, 0.0874

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

P(1)–S(19)	2.084(1)	P(9)–S(19)	2.109(1)
P(1)–S(1)	1.936(1)	P(1)–S(1′)	2.074(1)
P(9)–S(9)	1.940(1)	P(9)–N(9)	1.647(2)
P(1)–C(1)	1.815(3)	P(9)–C(9)	1.815(3)
S(1′)–Si(1)	2.187(1)	N(9)–Si(9)	1.794(2)
N(9)–C(11)	1.456(4)		
P(1)–S(19)–P(9)	102.69(4)		
S(1)–P(1)–S(19)	106.58(5)	S(1′)–P(1)–S(19)	110.59(5)
S(9)–P(9)–S(19)	104.76(5)	N(9)–P(9)–S(19)	110.35(9)
P(1)–S(1′)–Si(1)	106.23(5)	P(9)–N(9)–Si(9)	123.0(1)
C(1)–P(1)–S(19)	105.85(9)	C(9)–P(9)–S(19)	104.62(9)
C(1)–P(1)–S(1)	114.57(9)	C(1)–P(1)–S(1′)	102.53(9)
C(9)–P(9)–S(9)	114.55(9)	C(9)–P(9)–N(9)	107.1(1)
S(1)–P(1)–S(1′)	116.31(5)	N(9)–P(9)–S(9)	115.00(9)
C(11)–N(9)–P(9)	120.1(2)	C(11)–N(9)–Si(9)	115.0(2)



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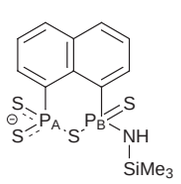

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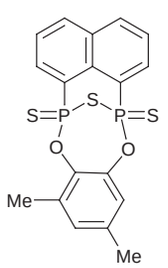

9

ening of the P(1)–S(19)–P(9) angle [102.69(4) *vs.* 80.0(1)°]. However, the value of the P–S–P angle in **3** is comparable to that in the related molecules $C_{10}H_6P(S)(SMe)(\mu\text{-}S)P(S)(OMe)$[17] [103.0(1)°], $C_{10}H_6P(S)(OCH_2CH_2OH)(\mu\text{-}S)P(S)(OCH_2CH_2OH)$[18] [101.8(1)°], $[C_{10}H_6P(S)(NHSiMe_3)(\mu\text{-}S)P(S)_2]^-$ anion **7**[13] [100.44(6)°] as well as that in the anion of **5** [100.21(4)°]. As expected, the terminal P=S bond lengths are significantly shorter than those to the bridging sulfur. The molecules pack with partial face-to-face overlap of the naphthyl rings to form stacks along the *a* axis.

The ^{31}P-{^{1}H} NMR spectrum of a mixture of compound **1** with **2** in toluene after prolonged heating to reflux temperature does not show the presence of any product other than **3**. The ring-closure reaction leading to the thiazadiphosphetidine disulfide does not occur. Even addition of base (anhydrous pyridine) to the solution of **3** in toluene did not lead to the four membered PSPN ring-closure reaction with elimination of $(Me_3Si)_2S$, but product **4** was isolated instead. The structure of **4** was determined by ^{31}P-{^{1}H}, ^{1}H and ^{13}C-{^{1}H} NMR, IR and mass spectroscopy; its purity was assessed by elemental analysis. No signals due to $SiMe_3$ groups were found in the ^{1}H and ^{13}C-{^{1}H} NMR spectrum. Pyridine thus acted as a proton-transfer catalyst; the protons are transferred from the solvent to **3**, providing desilylated ionic compound **4** (which precipitated as a solid from the reaction mixture) and a side product, trimethylsilylated toluene. The ^{31}P NMR spectrum of **4** in pyridine is an AB system [δ 70.47 and 70.09, ^2J(PP) = 12.0 Hz], whilst in dmso the difference in chemical shifts of both phosphorus atoms is so small, that only a singlet at δ 67.1 is observed; we have no ready explanation for the solvent dependence of the AB spectrum. For comparison, the chemical shifts of phosphorus atoms in anion **7**[13] are δ 66.1 (P_A) and 57.1 (P_B), ^2J(PP) = 13.6 Hz. The ^{1}H and ^{13}C NMR signals of the naphthalene entity of **4** are assigned on the basis of its analogy with anion **7**.[13] In the IR spectrum of **4** a broad unresolved multiplet of overlapping bands between 3700 and 2300 cm^{-1} is present, which makes assignment of vibrations in this region difficult. Compound **4** is very soluble in pyridine, dmso and dmf; it decomposes slowly in the latter two. We were unable to prepare single crystals of it suitable for X-ray analysis.

To improve the solubility of compound **4** we substituted its pyridinium cation by a larger organic cation, tetraphenylphosphonium, to give **5** which is soluble in more organic solvents, *e.g.* in chlorinated alkanes. This feature allowed for easier purification of **5** by crystallization, and also allowed us to obtain crystals suitable for structure analysis by diffusion of hexane into a diluted solution of **5** in dichloromethane. The ^{31}P-{^{1}H} NMR spectrum of the anionic part of **5** in dmso is an AB system [δ 73.03 and 72.23, ^2J(PP) = 11.6 Hz], whilst in $CDCl_3$ or py it shows only a singlet, as a result of the very similar chemical shifts of its two obviously magnetically non-equivalent phosphorus atoms. The ^{1}H NMR signals of the naphthalene entity were assigned on the basis of its analogy with anion **7**.[13]

The crystal structure of compound **5** (Table 3, Fig. 2) reveals the close similarity of its anionic part to the structure of the anion **7**, determined in the form of its hexamethyldisilazan-2-onium salt.[13] The only significant differences between these two structures are in the environment of P(9) and N(9), due to change of the bulky $SiMe_3$ group bonded to the nitrogen atom in **7** to a methyl group in **5**. The $C_{10}H_6P_2$ part of anion of **5** is significantly distorted from planar; atoms P(1) and P(9) lie 0.34 and 0.29 Å above and below the mean plane respectively, with additional small deviation for the sulfur atom S(1) which lies 0.36 Å below this plane. The C_3P_2S ring is hinged with the C_3P_2 and P_2S planes inclined by 49.5° with respect to each other, corresponding to a value in **7** of 51.2°. The transanular P···P distance and internal P–S–P angle in **5** [3.24 Å, 100.21(4)°] are quite similar to the corresponding values in **7** [3.22 Å, 100.44(6)°]. The P(1)–S(1) [1.967(1) Å] and P(1)–S(1′) [1.981(1)

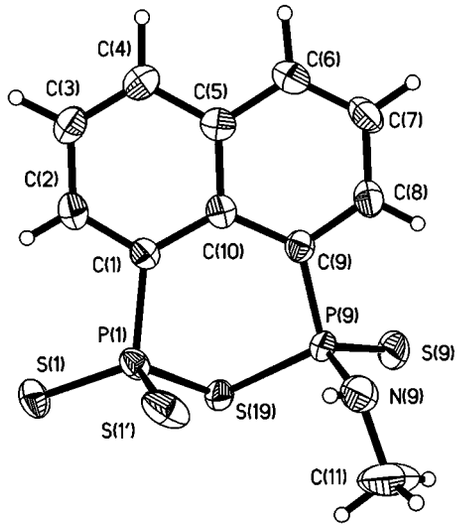

Fig. 2 Molecular diagram of the anionic part of compound **5**; PPh_4^+ cation omitted for clarity.

Table 3 Selected bond lengths (Å) and angles (°) in compound **5**

P(1)–S(19)	2.132(1)	P(9)–S(19)	2.087(1)
P(1)–S(1)	1.967(1)	P(1)–S(1′)	1.981(1)
P(9)–S(9)	1.946(1)	P(9)–N(9)	1.651(4)
P(1)–C(1)	1.819(3)	P(9)–C(9)	1.804(3)
N(9)–C(11)	1.450(6)		
P(1)–S(19)–P(9)	100.21(4)	P(9)–N(9)–C(11)	118.6(4)
S(1)–P(1)–S(19)	103.18(4)	S(1′)–P(1)–S(19)	111.30(5)
S(9)–P(9)–S(19)	107.04(5)	N(9)–P(9)–S(19)	111.8(1)
C(1)–P(1)–S(19)	101.84(9)	C(9)–P(9)–S(19)	107.67(9)
C(1)–P(1)–S(1)	112.19(9)	C(1)–P(1)–S(1′)	108.18(9)
C(9)–P(9)–S(9)	115.4(1)	C(9)–P(9)–N(9)	102.6(2)
S(1)–P(1)–S(1′)	118.79(5)	N(9)–P(9)–S(9)	112.3(2)

Å] distances indicate delocalization of the negative charge in the PS_2 group; these distances are slightly, but significantly, longer than P(9)–S(9) [1.946(1) Å], due to their lower bond order. The hydrogen atom bonded to nitrogen N(9) is not involved in any intra- or inter-molecular hydrogen bonds.

Use of hot acetonitrile as a solvent for the reaction of compound **1** with **2** gives rise to **6** containing in its cage structure the unsaturated CN_2P_2S heterocycle. We suppose that the first two reaction steps of formation of **6** are analogous to that in the reaction of *trans*-diorganodithiadiphosphetane disulfides $(RPS_2)_2$ (R = Me, Et or C_6H_4OMe-*p*) with **2** (Scheme 1).[1] Thus the first reaction product is **3**, which in hot acetonitrile undergoes a ring closure reaction giving compound **8** containing a four-membered heterocycle NP_2S and $(Me_3Si)_2S$ as a co-product. Consequent nucleophilic attack of the acetonitrile nitrogen atom at a phosphorus centre results in formation of a new heterocycle CN_2P_2S and thus gives **6** as a final product (Scheme 3). Yellow compound **6** is indefinitely stable at room temperature and shows a good solubility in hot acetonitrile. However in cold acetonitrile it is much less soluble, which enabled us to isolate the compound from a crude mixture of products by crystallization. The infrared spectrum of **6** contains a characteristic band due to the ν(C=N) at 1582 cm^{-1} as well as two ν(P=S) bands at 655 and 639 cm^{-1}.

The crystal structure of compound **6** (Table 4, Fig. 3) reveals that the planarity of the $C_{10}H_6P_2$ part of molecule is noticeably distorted; atoms P(1) and P(9) lie 0.20 and 0.15 Å above and below the mean plane respectively, with additional small deviation for the sulfur atom S(1), which lies 0.16 Å below this plane. Sulfur atoms S(9) and S(19) lie 1.02 and 1.16 Å below the mean plane. The CN_2P_2 part of the CN_2P_2S ring is almost planar [maximum deviation from mean plane 0.09 Å for N(9)]; the internal sulfur atom S(19) lies 1.09 Å below this plane,

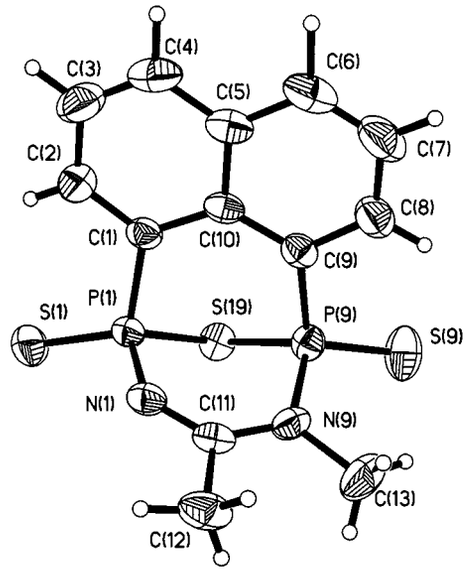

Fig. 3 Molecular diagram of compound **6**.

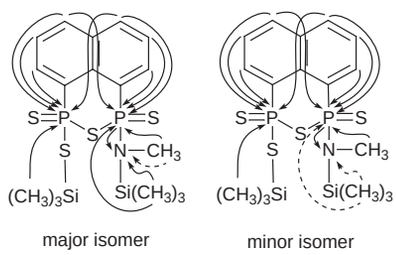

Fig. 4 Heteronuclear interactions observed for major and minor isomers (dashed lines are for weak correlations).

Table 4 Selected bond lengths (Å) and angles (°) in compound **6**

P(1)–S(19)	2.105(1)	P(9)–S(19)	2.060(1)
P(1)–N(1)	1.626(2)	P(9)–N(9)	1.714(2)
N(1)–C(11)	1.284(3)	N(9)–C(11)	1.365(4)
P(1)–S(1)	1.919(1)	P(9)–S(9)	1.918(1)
P(1)–C(1)	1.793(3)	P(9)–C(9)	1.809(3)
C(11)–C(12)	1.503(4)	N(9)–C(13)	1.470(4)
P(1)–S(19)–P(9)	93.06(4)	N(1)–C(11)–N(9)	126.2(2)
C(11)–N(1)–P(1)	133.4(2)	C(11)–N(9)–P(9)	122.3(2)
N(9)–P(9)–S(19)	106.11(9)	N(1)–P(1)–S(19)	106.95(9)
N(1)–P(1)–C(1)	105.4(1)	N(9)–P(9)–C(9)	105.1(1)
N(1)–P(1)–S(1)	114.48(9)	N(9)–P(9)–S(9)	112.91(9)
C(9)–P(9)–S(19)	106.69(9)	C(1)–P(1)–S(19)	104.13(9)
C(9)–P(9)–S(9)	115.2(1)	C(1)–P(1)–S(1)	115.5(1)
S(1)–P(1)–S(19)	109.57(5)	S(9)–P(9)–S(19)	110.21(5)
N(1)–C(11)–C(12)	116.3(3)	N(9)–C(11)–C(12)	117.5(3)
C(11)–N(9)–C(13)	119.4(3)	P(9)–N(9)–C(13)	117.9(3)

whilst C(12) and C(13) are coplanar with this plane. The planes fitted to CN_2P_2 and $C_{10}H_6P_2$ atoms are inclined by 74.6° with respect to each other. The internal P–S–P angle in **6** [93.06(4)°] is as expected significantly reduced *vs.* that in *cis*-**3** [102.69(4)°] and relative to that in the seven-membered $C_2O_2P_2S$ heterocycle **9**[19] (about 97.1°), whilst in comparison with that angle in the P_2S_2 ring of **1**[2] [80.0(1)°] it is substantially enlarged. The N(1)–C(11) distance [1.284(3) Å] is reasonable for a formal C=N double bond. The transannular P···P distance is 3.02 Å. Molecules pack with naphthalene rings parallel to each other along the *b* axis. To our best knowledge, **6** is the first reported example of a six membered heterocycle containing the internal atom sequence PSPNCN; no example of it even in its saturated form has been previously reported, although several compounds containing related six membered rings with atom sequence POPNCN have been reported.[20]

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Paper 9/01698H