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A new synthetic route to cyclophosphadithiatriazenes: synthesis and X-ray structural characterization of the first spirocycle containing thiadiazaphosphetidine and phosphadithiatriazene heterocycles

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The phosphetidine 2,4-Di-*tert*-butyl-3-chloro-$1\lambda^6$-thia-2,4-diaza-3-phosphetidine-1,1-dioxide, $O_2S({}^tBuN)_2PCl$, reacts with tetrasulfur tetranitride, S_4N_4, in benzene under reflux to afford the novel 4,6-spirocycle in moderate yield. The deep-blue crystals of the spirocycle are airstable and high melting in nature. The spiro phosphorus atom subtends a four-membered $P^VS^{VI}N_2$ ring which is saturated, and a six-membered $P^VS_2^{IV}N_3$ ring which is unsaturated. The single-crystal X-ray structure of this first example of the spirocycle reveals a planar PSN_2 ring and a puckered PS_2N_3 ring and the molecule is symmetric in nature. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: spirocycle; 4,6-spirocycle; inorganic heterocycle; cyclophosphathiazene; cyclophosphadithiatriazene; phosphetidine; X-ray structure

INTRODUCTION

Continued interest in inorganic heterocyclic chemistry has proved advantageous in recent years to inorganic polymer,[1–4] transition metal coordination[5–10] and theoretical chemistry.[11,12] The rapid development of synthetic methods[13] have led to the discovery of new types of inorganic heterocycles.[14–17] Their unique structures have also recently led to several applications in materials science.[18] Different types of inorganic heterocycles have resulted[19–24] from the reactions of S_4N_4 with phosphines. One such heterocycle obtained is cyclophosphathiazene (P–S–N heterocycle) and its derivatives assume biological importance as anti-tumor agents.[25–27]

Only a few synthetic routes are available in the literature.[21,28–30] In all cases, the syntheses were restricted to the preparation of $R_2PS_2N_3$ where R = Ph, PhO, CF_3, C_2F_5 and Me_3SiNH. In the early 1990s, Rao and coworkers[23] reported a new route for synthesizing *monoamino* derivatives of phosphathiazene heterocycles starting from 2-aminopyridyl phosphine derivatives and tetrasulfur tetranitride, S_4N_4. They succeeded in preparing $(Ph)[(C_6H_{11})_2N]PS_2N_3$, which was the first example of heterocycle bearing two different substituents. Our recent investigations[31] on the reactions of monochloro(amino)phosphines, [R][R′]PCl (R = Ph, R_2N; R′ = R'_2N) and S_4N_4 have led to the discovery of *new* and *high yield synthetic route* for the preparation of *bis(amino)* derivatives of phosphathiazene heterocycles.

For the first time, we have isolated a 4,6-spirocyclic compound from the reaction of S_4N_4 and a monochlorophosphine (Scheme 1). Details of the synthesis and X-ray structural characterization of the spirocycle, which is the first example of its kind, is reported here.

EXPERIMENTAL

All manipulations were done under inert atmosphere (dry N_2 or Ar gas) conditions. Solvents were purified by

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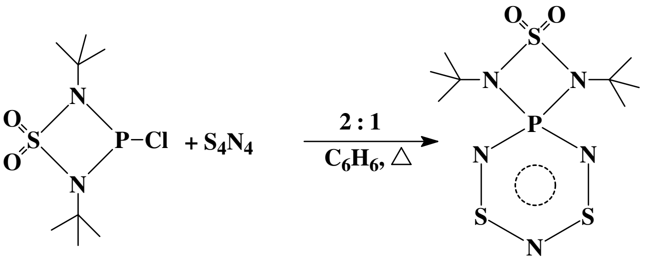


Scheme 1. Preparation of 4,6-spirocycle from the reaction of S_4N_4 and $O_2S(^tBuN)_2PCl$.

standard methods.[32] Reported procedures were employed for the preparation of the sulfamide, $O_2S(^tBuNH)_2$,[33] monochloro(amino)phosphine, $O_2S(^tBuN)_2PCl$[34] and S_4N_4.[35] (*Caution*— S_4N_4 may cause explosion. Safety precautions have to be employed.[36]) PCl_3 (Aldrich, 98%) was used as received. The spectral and other facilities used for the characterization of compounds have been described elsewhere.[37]

Synthesis of $O_2S(^tBuN)_2PS_2N_3$

To a stirred benzene (*caution*—potential carcinogen) solution (40 ml) of $O_2S(^tBuN)_2PCl$ (3.36 g, 12.3 mmol) at room temperature, S_4N_4 (1.14 g, 6.2 mmol) was added in aliquots over 15 min and the contents heated under reflux for 12 h. The resultant dark blue-green solution was evacuated to dryness *in vacuo* and the hexane extract (15 × 5 ml) of the oily residue was concentrated to *ca* 20 ml and cooled at 0 °C for 8 h to isolate dark-blue crystals of $O_2S(^tBuN)_2PS_2N_3$ (0.86 g, 41% yield). M.p.: 158–160 °C; anal. calculated for $C_8H_{18}N_5O_2PS_3$: C 27.97, H 5.29, N 20.39%. Found: C 27.26, H 5.20, N 19.98%; IR (KBr): 1456, 1370, 1344, 1325, 1258, 1184, 1075, 1040, 1005, 941, 922, 810, 746, 608, 550, 502 and 480 cm^{-1}; UV–Vis λ_{max} (ε): 603.0 (1.64×10^3), 351.7 (0.42×10^3) and 249.5 nm (6.04×10^3 $l\,mol^{-1}\,cm^{-1}$); ^1H NMR (400 MHz, $CDCl_3$) δ 1.53 ppm (s); ^{13}C NMR ($CDCl_3$) δ 29.3 [$C(\underline{C}H_3)_3$] and 59.7 ppm [$\underline{C}(CH_3)_3$]; ^{31}P NMR (CH_2Cl_2) δ, −4.9 ppm (s, 1P); mass: *m/e* 343 (11%, M^+), 287 (35%, $[M - {}^tBu + H]^+$), 231 (100%, $[M - 2{}^tBu + 2H]^+$) and 57 (12%, $^tBu^+$).

Using the above synthetic route, two other heterocycles were prepared, namely $(Ph)[(C_6H_{11})_2N]PS_2N_3$ and $[(i\text{-}C_3H_7)_2N][(n\text{-}C_4H_9)_2N]PS_2N_3$, of which the latter is the first example of the PS_2N_3 heterocycle containing two different amino groups. Since the former is known, the characterization data of the latter alone is given below:

M.p.: 127–129 °C; IR (KBr): 1460, 1380, 1260, 1150, 1090, 1020, 930, 800 and 725 cm^{-1}; UV–Vis λ_{max}: 575 nm; ^{31}P NMR (CH_2Cl_2) δ −3.6 ppm (s, 1P); mass: *m/e* 365 (50%, M^+), 319 (30%, $[M - SN]^+$), 305 (5%, $[M - SN_2]^+$), 296 (20%, $[M - {}^nBu]^+$), 292 (25%, $[M - {}^nBuNH_2]^+$), 287 (28%, $[M - S_2N]^+$), 128 (64%, $[{}^nBu_2N]^+$) and 100 (70%, $[{}^iPr_2N]^+$).

Reaction of 4,6-spirocycle with norbornadiene, C_7H_8 (NBD)

To a stirred ethereal solution (25 ml) of the spirocycle (0.08 g, 0.2 mmol) at room temperature, NBD (0.43 g, 4.6 mmol) was added dropwise through a syringe. The blue colour of the solution was discharged instantaneously. After 1 h, the clear solution was concentrated to ∼5 ml and hexane (50 ml) was added with stirring which led to a white precipitate formation identified as the 1 : 1 adduct, $O_2S(^tBuN)_2PS_2N_3 \cdot C_7H_8$ (0.08 g, 79% yield). M.p. 218 °C (decomposes); IR (KBr): 1466, 1366, 1312, 1254, 1187, 1136, 1069, 1037, 925, 858, 800, 755, 739, 707, 691, 656, 643, 547, 493 and 467 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.50 (s, 9H), 1.60 (S, 9H), 1.27, 1.80 (AB, 2H), 3.25 (s, 2H), 4.50 (s, 2H) and 6.40 ppm (s, 2H); ^{13}C NMR ($CDCl_3$) δ 28.7 [$C(\underline{C}H_3)_3$], 29.0 [$C(\underline{C}H_3)_3$]′, 41.4 [bridge $\underline{C}H$], 43.7 [bridge head $\underline{C}H_2$], 59.8 ppm [$\underline{C}(CH_3)_3$], 59.9 ppm [$\underline{C}(CH_3)_3$]′, 83.8 [$\underline{C}H$ adjacent to PS_2N_3 ring] and 139.2 ppm [olefinic $\underline{C}H$]; ^{31}P NMR (CH_2Cl_2) δ, −32.6 ppm (s, 1P).

$[(i\text{-}C_3H_7)_2N][(n\text{-}C_4H_9)_2N]PS_2N_3 \cdot C_7H_8$ was prepared similarly to above procedure and the characterization data is as follows. M.p. 139–141 °C (melts to blue liquid); IR (KBr): 1453, 1398, 1363, 1254, 1181, 1037, 989, 928, 803, 726, 560 and 528 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, 6H), 1.21–1.32 (m, 16H), 1.45 (m, 4H), 1.48 (AB, 2H), 2.95 (m, 4H), 3.15 (s, 2H), 3.35 (m, 2H), 4.20 (s, 2H) and 6.35 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 46.3 [$\underline{C}H(CH_3)_2$], 22.8 [$CH(\underline{C}H_3)_2$], 44.5 [$N\text{-}\underline{C}H_2$], 30.8 [$NCH_2\underline{C}H_2$], 20.5 [$NCH_2CH_2\underline{C}H_2$], 14.0 [$N(CH_2)_3\underline{C}H_3$], 43.6 [bridge $\underline{C}H$], 41.7 [bridge head $\underline{C}H_2$], 81.1 [$\underline{C}H$ adjacent to PS_2N_3 ring] and 139.4 ppm [olefinic $\underline{C}H$]; ^{31}P NMR (CH_2Cl_2) δ −19.3 ppm (s, 1P).

X-ray analyses

Data were collected at 293(2) K on a Bruker AXS Kappa Apex II. Formula = $C_8H_{18}N_5O_2PS_3$, M = 343.42, tetragonal, space group = $I - 42d$, $a = 13.1821(1)$, $c = 17.9785(3)$ Å, $V = 3124.08(6)$ $Å^3$, $Z = 8$, $D_x = 1.460$ g cm^{-3}, $\mu = 0.582$ mm^{-1}, R [3234 data with $I > 2\sigma(I)$; θ_{max} 38.4°] = 0.035, wR (all 4334 data) = 0.103. Programs used: SIR92,[38] WinGX,[39] SHELXL-97[40] and ORTEP32.[41] CCDC deposition number: 293289.

RESULTS AND DISCUSSION

Synthetic and characterization aspects

Contrary to our expectation,[22] 2,4-di-*tert*-butyl-3-chloro-1λ^6-thia-2,4-diaza-3-phosphetidine-1,1-dioxide, $O_2S(^tBuN)_2PCl$, reacted with tetrasulfur tetranitride, S_4N_4, in benzene under reflux to afford an intense blue-green reaction mixture from which deep-blue crystals of 1,1-(N,N′-di-*tert*-butylsulfamido)cyclo-1λ^5-phospha-3,5-dithia-2,4,6-triazene, $O_2S(^tBuN)_2PS_2N_3$, were obtained in moderate yield. However, the yield was found to be higher compared with other available synthetic routes.[21,23,28,30] Attraction of a sulfur atom from S_4N_4 by the attacking phosphine (highly thiophilic in nature; two moles of phosphine are added during the reaction) leads to both a stable phosphine sulfide molecule and a labile phosphine-bound SN open chain species, $[O_2S(^tBuN)_2](Cl)P{=}N{-}S{-}N{=}S{=}N{-}S{-}N{:}$[42] whose multifaceted role in subsequent reactions has been reported to produce diverse products from such reactions (Scheme 2). Evidence for the formation of $(R_1)(R_2)(Cl)P{=}N{-}S_3N_3$ (Scheme 2) comes from the UV–Vis spectrum of the red-purple reaction mixture (recorded 1 h from the start of the reaction), which exhibits a strong absorption around 470 nm (typical value for $(R_1)(R_2)(R_3)P{=}N{-}S_3N_3$ derivatives is *ca.* 480 nm[44]). The open chain species loses an 'NSCl' fragment and cyclizes to the PS_2N_3 heterocycle. The lost NSCl fragment probably trimerizes to the highly sensitive cyclotrithiazyl chloride, $(NSCl)_3$ which could not be isolated. Loss of such simple fragments is very well documented in the literature.[42,43]

Unlike the reaction of S_4N_4 with Ph_2PH reported earlier,[21] this reaction gave a relatively simple reaction mixture as revealed by its ^{31}P-NMR spectrum (major signals at −4.9 and 24.9 ppm; minor signals at −9.0 and −13.6 ppm). Fortunately, the blue hexane extract upon cooling at 0 °C affords the spirocycle as a high melting point and airstable solid. The melting point is found to be unusually high compared with the known PS_2N_3 heterocycles,[19,23] clearly indicating its high stability. This fact is also confirmed by thermogravimetric analysis and evolved gas analysis of the spirocyclic compound.[31] These studies reveal that the decomposition starts only around 150 °C.

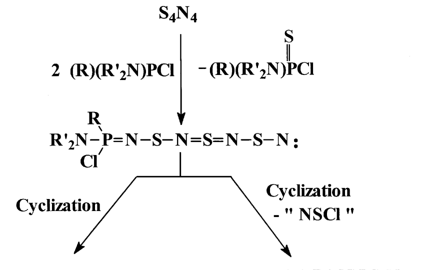
Intense visible absorption (λ_{max}: 603 nm) and an upfield phosphorus signal (δ_P: −4.9 ppm) observed for the blue spirocycle are typical of the known π-electron-rich PS_2N_3 heterocycles[45] and thus suggest that it is better regarded as a derivative of the cyclophosphadithiatriazene rather than thiadiazaphosphetidine. The visible absorption band at 603 nm is attributed to $\pi^*(\text{HOMO}) \rightarrow \pi^*$ (LUMO) transition.[28] The electron impact mass spectrum of the spirocycle shows, apart from the molecular ion, the diamide derivative of the spirocycle, $O_2S(NH)_2PS_2N_3$, as the base peak which indicates the possibility of its isolation. The other major ^{31}P-NMR signal at 24.9 ppm observed for the reaction mixture is presumably due to the corresponding sulfide of the chlorophosphetidine, $O_2S(^tBuN)_2P(S)Cl$, which has eluded isolation.[34]

Prompted by the realization of a stable addition product at 1,3-sulfur positions of the PS_2N_3 heterocycles reported earlier,[23] adduct formation reaction was attempted with the strained olefin, norbornadiene (NBD). The band at 603 nm vanishes upon derivatization with norbornadiene which conforms with previous observations and the accompanying change in the π-manifold of the inorganic heterocycle (that is, $8\pi \rightarrow 6\pi$). Phosphorus chemical shifts observed for the parent spirocycle and its NBD adduct present an interesting difference. In almost all the reported cases of PS_2N_3 ring systems,[23,28] the δ_P value is higher for the parent heterocycle compared with the corresponding NBD adduct, but the difference is not significant. However, in the present case, the phosphorus atom of the NBD adduct is found to be significantly more shielded (δ_P: −32.6 ppm) than that in the spirocycle (δ_P: −4.9 ppm) and this is probably due to the spirocyclic effect.

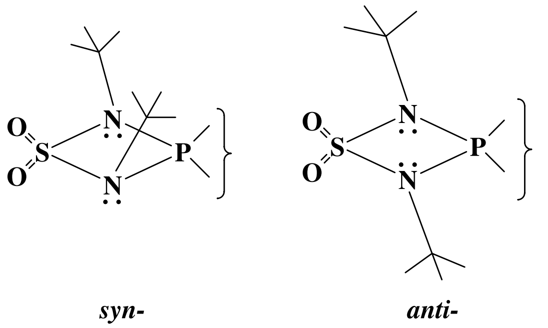
Interestingly, both ^{1}H- and ^{13}C-NMR spectra of the adduct[31] reveal that the two *tert*-butyl groups, which are equivalent in the spirocycle, are no longer equivalent in the adduct. The two signals of equivalent intensity are seen in both the spectra for the methyl signals and carbon signals of the *tert*-butyl groups. This observation indicates that norbornadiene facilitates the formation of different conformers of the compound with respect to the two *tert*-butyl groups (Fig. 1). Isolation of X-ray quality single crystals of the 1 : 1 adduct is underway.

Structural aspects

The X-ray structure (Fig. 2) establishes the spirocyclic nature of the compound. In literature, only three examples of spirocycles (6,6-, 6,8- and 8,8-) with sulfur as the spiro atom[46–48] and two others (6,6-) with phosphorus as the spiro atom[49,50] have been reported so far. Out of these, only three have been structurally characterized. The 4,6-spirocycle reported in this paper is the first example containing a four-membered saturated phosphetidine ring (PSN_2) and a six-membered unsaturated π-electron rich (8π) phosphathiazene ring (PS_2N_3) fused at phosphorus as the spiro atom. Selected



Scheme 2. Mechanism proposed for the formation of PS_2N_3 ring.



syn- *anti-*

Figure 1. Possible conformers of the 1 : 1 adduct, $O_2S(^tBuN)_2PS_2N_3{\cdot}C_7H_8$ (only PN_2S part is shown).

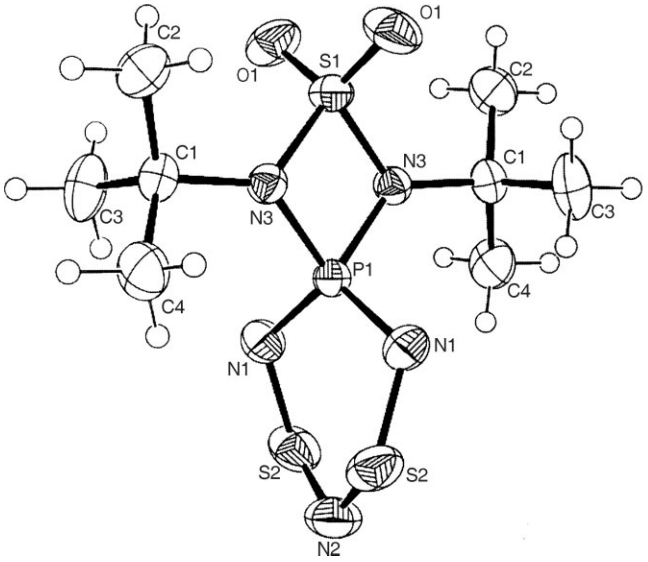


Figure 2. ORTEP plot (50% probability ellipsoids) and atomic numbering scheme for $O_2S(^tBuN)_2PS_2N_3$. Symmetry operation *i*: $x + 1/2, y + 0, -z - 1/4$.

geometric data of the dark blue spirocycle are given in Table 1. The compound crystallizes in body centered tetragonal unit cell with space group of *I-42d*. Half of the molecule forms crystallographic asymmetric unit with a two-fold axis passing through the N_2–P–S backbone of the molecule.

Structurally, the thiadiazaphosphetidine (PN_2S) part of the spirocycle for which no x-ray structural data was available presents many interesting features. While the four-membered phosphetidine rings (cyclodiphosphazane, P_2N_2) are frequently found in a puckered conformation,[51,52] the present PN_2S ring is planar (internal angles sum 360°) with all its skeletal bonds (P1–N3 and S1–N3) shorter than expected [average values: 1.6817(11) and 1.6568(11) Å respectively; single bond lengths, P–N 1.79 ´Å, S–N 1.74 Å]. However, these P–N and S–N bonds are longer compared with the six-membered PSN ring and describe a distorted square.

Table 1. Selected bond lengths (Å) and bond angles (deg) for $O_2S(^tBuN)_2PS_2N_3$[a]

Bond lengths (Å)			
S1–O1	1.4282(13)	S1–N3	1.6568(11)
S2–N1	1.6209(14)	S2–N2	1.5906(11)
P1–N1	1.5930(13)	P1–N3	1.6817(11)
N3–C1	1.4955(16)		
Bond angles (deg)			
O1–S1–N3	113.50(7)	O1–S1–O1^i	116.22(13)
N3–S1–N3^i	85.37(7)	N1–S2–N2	112.06(8)
N1–P1–N3	118.38(6)	N1–P1–N1^i	112.35(10)
N3–P1–N3^i	83.81(7)	S2–N1–P1	119.30(9)
S2–N2–S2^i	120.27(12)	S1–N3–P1	95.41(5)
S1–N3–C1	127.64(9)	P1–N3–C1	131.95(9)

[a] Symmetry transformations used to generate equivalent atoms *i*: $x + 1/2, y + 0, -z - 1/4$.

The two nitrogens, N3 and N3^i assume a near-planar geometry (ΣN: ~355°). The tetracoordinate sulfur atom, S3, is within a distorted tetrahedral geometry and exhibits a strong bonding interaction with the spiro P1 atom as revealed by the short P···S(3) distance of 2.4694(5) Å (cf. the sum of Van der Waals radii of 3.60 Å[53]).

The PN_4 moiety describes an irregular tetrahedral geometry with two types of P–N bonds [1.6817(11) and 1.5930(13) Å]. Expectedly, the shorter P–N bonds are seen with the unsaturated PS_2N_3 heterocycle, which exhibits a highly puckered structure (Fig. 3). Here, the puckering is found to be symmetric in nature, which also reflects the highly symmetric nature of the molecule. Varying

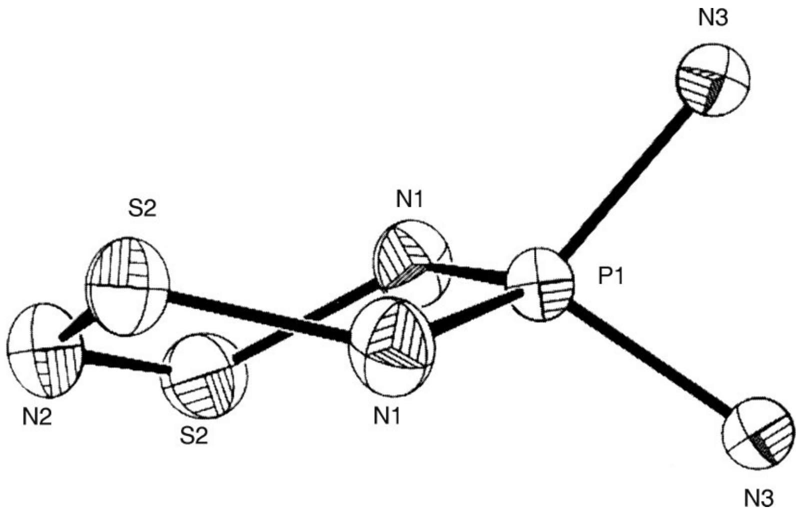


Figure 3. Highly puckered nature of the PS_2N_3 part of $O_2S(^tBuN)_2PS_2N_3$.

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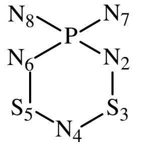
Table 2. A comparison of bond lengths (Å) and bond angles (deg) at the PS$_2$N$_3$ portion of O$_2$S(^{t}BuN)$_2$PS$_2$N$_3$ and related structures



	Ph$_2$PS$_2$N$_3$	Ph(DCA) PS$_2$N$_3$	(Me$_3$SiNH)$_2$ PS$_2$N$_3$	O$_2$S(^{t}BuN)$_2$ PS$_2$N$_3$
		Bond lengths (Å)		
P–N2	1.621(4)	1.628(3)	1.637(6)	**1.5930(13)**
N2–S3	1.560(3)	1.578(4)	1.564(7)	**1.6209(14)**
S3–N4	1.580(4)	1.574(4)	1.570(7)	**1.5906(11)**
N4–S5	**1.583(5)**	1.606(4)	1.615(8)	1.5906(11)
S5–N6	1.575(3)	1.594(3)	**1.630(5)**	1.6209(14)
N6–P	1.625(3)	1.607(3)	1.605(6)	**1.5930(13)**
P–N7	—	1.629(3)	1.623(5)	**1.6817(11)**
P–N8	—	—	1.635(7)	**1.6817(11)**
		Bond angles (deg)		
P	115.8(2)	113.2(2)	**112.1(3)**	112.35(10)
N2	121.3(2)	123.2(2)	122.9(4)	**119.30(9)**
S3	116.9(2)	116.4(2)	115.0(4)	**112.06(8)**
N4	124.6(3)	122.3(2)	122.3(5)	**120.27(12)**
S5	116.3(2)	114.4(2)	**110.9(3)**	112.06(8)
N6	120.3(2)	119.2(2)	**115.8(3)**	119.30(9)

Bold font indicates either a smaller or a larger value compared with the other values.

degrees of puckering of the heterocycle have been observed with the reported structures of PS$_2$N$_3$ heterocycles.[19,23,54] A comparison of the P–N bond lengths of the phosphetidine ring and those in (Me$_3$SiNH)2PS2N$_3$[55] [average values 1.6817(11) and 1.629(6) Å, respectively] indicates a much shorter exocyclic P–N bond in the latter, suggesting limited delocalization of π-electron density between phosphorus and nitrogen (N3) when the phosphorus atom assumes a spirocyclic state. The endocyclic P–N bonds in the PS$_2$N$_3$ heterocyclic part are distinctly shorter and appear to be slightly shorter compared with the corresponding distances in similar structures available in literature.[21,23,53] The bonding parameters of PS$_2$N$_3$ part of spirocycle have been compared (Table 2) with the three other structures of this type reported so far. The S–N bonds of the unsaturated ring are of two kinds [1.5906(11) and 1.6209(14) ´Å], unlike in the reported structures,[21,23] where the bond distances are approximately same. Interestingly, endocyclic bond length variation in case of (Me$_3$SiNH)$_2$PS$_2$N$_3$ does not present a discernable trend. The endocyclic angle at phosphorus on the side of the unsaturated ring is around 112° and the angle at nitrogen opposite to this is around 120°. These angles are slightly larger in the previously reported PS$_2$N$_3$ heterocycles. The two P–N bonds of the PS$_2$N$_3$ ring are found to be shorter [1.5930(13) ´Å] compared with the same in other known PS$_2$N$_3$ heterocycles [1.605(6)–1.637(6) Å].

CONCLUSIONS

From this study, new observations were made and new, hitherto unknown ring relationships were established. The isolation of 4,6-spirocycle from the reaction reported here appears to have opened up a hitherto unknown avenue for obtaining different types of spirocyclic and heterocyclic compounds.

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