

## Cyclic S-N compounds and phosphorus reagents-XVII. Synthesis and X-ray structural characterization of (Ph)(DCA)(Me<sub>2</sub>N)P = N-S<sub>3</sub>N<sub>3</sub> heterocycle

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**Abstract.** The phosphiniminocyclotrithiazene, (Ph)(DCA)(Me<sub>2</sub>N)PN-S<sub>3</sub>N<sub>3</sub> (II) [DCA = dicyclohexylamino] was obtained in ≈ 70% yield from room temperature reaction of S<sub>4</sub>N<sub>4</sub> with the corresponding phosphine, (Ph)(DCA)(Me<sub>2</sub>N)P (I). Single crystal X-ray structure determination of (II) reveals slightly different P-N bond lengths around phosphorus [P-N(4): 1.607; P-N(5): 1.645 and P-N(6): 1.638 Å] and almost planar configuration around both N(5) and N(6). The tricoordinate sulphur [S(1)] substantially deviates (0.663 Å) from the mean plane of the heterocycle. The structural parameters of (II) are compared with the recently reported diethylamino and di-*n*-butylamino analogues. (II) affords (Ph)(DCA)(Me<sub>2</sub>N)P = N-S<sub>3</sub>N (IV) in ≈ 60% yield on thermolysis in solution.

**Keywords.** Phosphiniminocyclotrithiazene; synthesis; X-ray structure.

### 1. Introduction

A large variety of phosphiniminocyclotrithiazenes,  $\rightarrow P = N-S_3N_3$  which are stable examples of  $8\pi$  electron-rich inorganic ring system have been synthesized from our laboratory<sup>1-4</sup> and in many cases, single crystal X-ray structures have been solved<sup>5-8</sup> to identify several interesting features. In a recent study, we have reported<sup>8</sup> X-ray structures of (Ph)(DCA)(R<sub>2</sub>N)P = N-S<sub>3</sub>N<sub>3</sub> [R = ethyl and *n*-butyl] which showed marked structural difference in changing from ethyl to *n*-butyl group. This observation, as well as our continued interest in evaluating substituent effect on structural features of  $\rightarrow P = N-S_3N_3$  heterocycles prompted us to undertake the synthesis and X-ray structural investigation of the title compound that contains 'methyl' group, the simplest of the aliphatic moieties. The details of this study along with a comparison of the structure of (II) with those of ethyl and *n*-butyl analogues are reported here.

### 2. Experimental

#### 2.1 Materials and methods

All the reactions and subsequent work-up were done under an inert atmosphere of dry N<sub>2</sub> gas. Solvents such as C<sub>6</sub>H<sub>6</sub>, *n*-C<sub>6</sub>H<sub>14</sub>, CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub> were purified and

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distilled by reported procedures<sup>9</sup>.  $S_4N_4$  was synthesized by the standard procedure<sup>10</sup> and recrystallized from toluene before use [Caution!  $S_4N_4$  may cause explosion. Safety precautions recommended<sup>11</sup> have to be employed]. Phenyl dichlorophosphine (Fluka), dicyclohexylamine (E-Merck) and dimethylamine, 40% aqueous solution (sd) were used as received. The spectral facilities and the operations made use of for the characterization of compounds are the same as described earlier<sup>12</sup>.

## 2.2 Syntheses

**2.2a (Ph)(DCA)(Me<sub>2</sub>N)P (I):** "(Ph)(DCA)PCl" (7.16 g, 22.0 mmol) prepared by the reported procedure<sup>13</sup> was subsequently reacted with dimethylamine (5.81 g, 129.0 mmol) [generated from aq. Me<sub>2</sub>NH (35 ml) and KOH pellets] for 30 min at 0°C. After 20 h of stirring at room temperature, it was filtered to separate Me<sub>2</sub>NH.HCl and the filtrate on removal of solvent gave (I) as colourless viscous liquid which solidified at 0°C (3.60 g, 46%) m.p. 87–89°C. Anal. Calcd. for C<sub>20</sub>H<sub>33</sub>N<sub>2</sub>P: C, 72.23; H, 10.02; N, 8.42. Found: C, 72.46; H, 9.89; N, 8.21. IR (1600–600 cm<sup>-1</sup>): 1480(vs), 1400(s), 1360(m), 1310(m), 1280(s), 1200(s), 1170(s), 1120(s), 1065(vs), 1040(s), 980(vs), 910(vs), 865(s), 830(s), 760(vs), 720(vs) and 670(vs) cm<sup>-1</sup>; <sup>1</sup>H-NMR (ppm): 1.0–1.8 (m, 20H), 2.6 (d, 6H), 2.6–3.0 (m, 2H), 7.3–7.5 (m, 3H) and 7.7–7.9 (m, 2H); <sup>13</sup>C-NMR (ppm): 24.9, 26.2, 33.5 (methylene carbons), 37.0 (methyl carbon), 56.6 (methyne carbon), 127.5, 130.5, 131.3 and 134.9 (phenyl carbons); <sup>31</sup>P-NMR (ppm): 79.5 (s, 1P); MS [m/z (%): 332 (M<sup>+</sup>, 28), 228 [(M-Me<sub>2</sub>N)<sup>+</sup>, 26], 180 [(DCA)<sup>+</sup>, 89] and 152 [(M-DCA)<sup>+</sup>, 100].

**2.2b (Ph)(DCA)(Me<sub>2</sub>N)P = N-S<sub>3</sub>N<sub>3</sub> (II):** To a stirred slurry of (I) (3.00 g, 9.0 mmol) in CH<sub>3</sub>CN (25 ml) at room temperature, S<sub>4</sub>N<sub>4</sub> (0.83 g, 4.5 mmol) was added in aliquots for 15 min. The resultant mixture was stirred for 24 h and filtered to get a red precipitate which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN mixture (3:1) at 0°C to obtain dark red crystals of (II) (1.13 g, 67%), m.p. 115–17°C. Anal. Calcd. for C<sub>20</sub>H<sub>33</sub>N<sub>6</sub>PS<sub>3</sub>: C, 49.54; H, 6.87; N, 18.40. Found: C, 49.89; H, 6.42; N, 18.30. IR (1600–400 cm<sup>-1</sup>): 1446(s), 1126(vs), 1088(s), 1046(vs), 992(vs), 941(s), 890(m), 851(w), 803(m), 733(vs), 694(s), 618(m), 550(m) and 531(m) cm<sup>-1</sup>; UV-Vis [λ, nm (ε, x10<sup>3</sup> dm<sup>3</sup>mol<sup>-1</sup>cm<sup>-1</sup>): 486 (4.00), 330 (3.06) and 290, sh (3.06); <sup>1</sup>H-NMR (ppm): 1.2–1.7 (m, 20H), 2.6 (d, 6H), 3.0–3.2 (m, 2H), 7.4–7.5 (m, 3H) and 7.9–8.0 (m, 2H); <sup>13</sup>C-NMR (ppm): 25.3, 26.6, 33.4 (methylene carbons), 38.0 (methyl carbon), 57.0 (methyne carbon), 128.3, 130.0, 131.5 and 132.4 (phenyl carbons); <sup>31</sup>P-NMR (ppm): 31.4 (s, 1P); MS [m/z (%): 484 [M<sup>+</sup>, ~1], 456 [(M-N<sub>2</sub>)<sup>+</sup>, 3], 392 [(M-S<sub>2</sub>N<sub>2</sub>)<sup>+</sup>, 10], 346 [(M-S<sub>3</sub>N<sub>3</sub>)<sup>+</sup>, 5], 180 [(DCA)<sup>+</sup>, 100] and 152 [(M-(DCA)S<sub>3</sub>N<sub>4</sub>)<sup>+</sup>, 24].

The residual filtrate was concentrated and cooled at 0°C for 2 days to isolate the corresponding phosphine sulphide (III) as a pale pinkish white solid which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN mixture (1:1) (1.15 g, 70%). m.p. 108–10°C; Anal. Calcd. for C<sub>20</sub>H<sub>33</sub>N<sub>2</sub>PS: C, 65.88; H, 9.14; N, 7.68. Found: C, 65.20; H, 8.91; N, 7.23. IR (1600–600 cm<sup>-1</sup>): 1470(vs), 1380(vs), 1310(m), 1250(m), 1150(s), 1100(s), 1045(s), 970(m), 940(s), 890(s), 850(s), 820(m), 800(m), 725(vs) and 620(s) cm<sup>-1</sup>; <sup>1</sup>H-NMR (ppm): 0.9–2.0 (m, 20H), 2.5 (d, 6H), 3.2 (m, 2H), 7.3–7.4 (m, 3H) and 7.9–8.0 (m, 2H); <sup>13</sup>C-NMR (ppm): 25.5, 26.7, 33.6 (methylene carbons), 37.3 (methyl carbon), 57.2 (methyne carbon), 127.9, 130.6, 131.3 and 136.2 (phenyl carbons); <sup>31</sup>P-NMR (ppm): 73.6 (s, 1P); MS [m/z (%): 364 [M<sup>+</sup>, 24], 331 [(M-S)<sup>+</sup>, 2], 320 [(M-Me<sub>2</sub>N)<sup>+</sup>, 3], 184 [(M-DCA)<sup>+</sup>, 26], 180 [(DCA)<sup>+</sup>, 100] and 152 [(M-(DCA)S)<sup>+</sup>, 20].

2.2c (Ph)(DCA)(Me<sub>2</sub>N)P = N-S<sub>3</sub>N (IV): A solution of (II) (0.25 g, 0.5 mmol) in C<sub>6</sub>H<sub>6</sub> (30 ml) was refluxed for 9 h. The resultant dark pinkish red solution was concentrated to 10 ml, CH<sub>3</sub>CN (5 ml) added and cooled at 0°C for 3 days to isolate the title compound (IV) as a dark pinkish red solid with green metallic lustre (0.14 g, 59%). Melting point 157–59°C; Anal. Calcd. for C<sub>20</sub>H<sub>33</sub>N<sub>4</sub>PS<sub>3</sub>: C, 52.58; H, 7.29; N, 12.26. Found: C, 52.31; H, 7.46; N, 12.12. IR (1600–400 cm<sup>-1</sup>): 1347(s), 1254(m), 1120(vs), 1098(s), 1046(vs), 982(m), 893(m), 749(m), 723(s), 694(m), 582(s) and 544(m) cm<sup>-1</sup>; UV-Vis [ $\lambda$ , nm ( $\epsilon$ , dm<sup>3</sup>mol<sup>-1</sup>cm<sup>-1</sup>): 499 (3.80 × 10<sup>3</sup>) and 324 (5.97 × 10<sup>2</sup>); <sup>1</sup>H-NMR (ppm): 1.0–1.8 (m, 20H), 2.7 (d, 6H), 3.0 (m, 2H), 7.4–7.6 (m, 3H) and 7.7–7.9 (m, 2H); <sup>13</sup>C-NMR (ppm): 25.4, 26.9, 33.2 (methylene carbons), 37.9 (methyl carbon), 58.0 (methyne carbon), 128.1, 129.6, 131.9 and 134.8 (phenyl carbons); <sup>31</sup>P-NMR (ppm): 31.4 (s, 1P).

### 2.3 X-ray crystallographic analysis

Single crystals suitable for X-ray study were grown from CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (3:1, v/v) mixture at 0°C. Crystal and refinement data are summarized in table 1. The procedure for both collection and analysis of data are the same as described elsewhere<sup>8</sup>.

**Table 1.** Crystal and refinement data for (Ph)(DCA)(Me<sub>2</sub>N)P = N-S<sub>3</sub>N<sub>3</sub> (II).

Identification code	:	(II)
Empirical formula	:	C <sub>20</sub> H <sub>33</sub> N <sub>4</sub> PS <sub>3</sub>
Molecular weight	:	484.67
Temperature (K)	:	293(2)
Wavelength (Å)	:	1.5418
Crystal system	:	Monoclinic
Space group	:	P2 <sub>1</sub> /n
a (Å)	:	9.4410(10)
b (Å)	:	27.983(5)
c (Å)	:	9.5050(10)
$\alpha$ (°)	:	90
$\beta$ (°)	:	106.080(10)
$\gamma$ (°)	:	90
V (Å <sup>3</sup> )	:	2412.9(6)
Z	:	4
Density, calc. (mgm <sup>-3</sup> )	:	1.334
Absorption coefficient (mm <sup>-1</sup> )	:	3.589
F(000)	:	1032
Crystal dimensions (mm)	:	0.15 × 0.28 × 0.29
$\theta$ range scanned (°)	:	3–68
Reflections collected	:	3219
Index ranges	:	0 ≤ h ≤ 11 0 ≤ k ≤ 33 –11 ≤ l ≤ 11
Independent reflections	:	3047 [R(int) = 0.0395]
No. of parameters refined	:	403
Final 'R' indices [I > 2 $\sigma$ (I)]	:	R <sub>1</sub> = 0.0449; wR <sub>2</sub> = 0.1139
GOF	:	1.085
Largest difference peak and hole (eÅ <sup>-3</sup> )	:	0.531 and –0.469

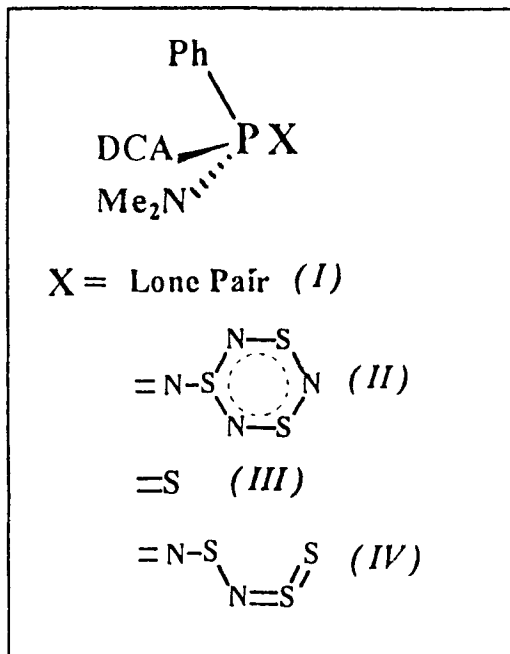


Figure 1. Structure of (Ph)(DCA)(Me<sub>2</sub>N)P and its derivatives.

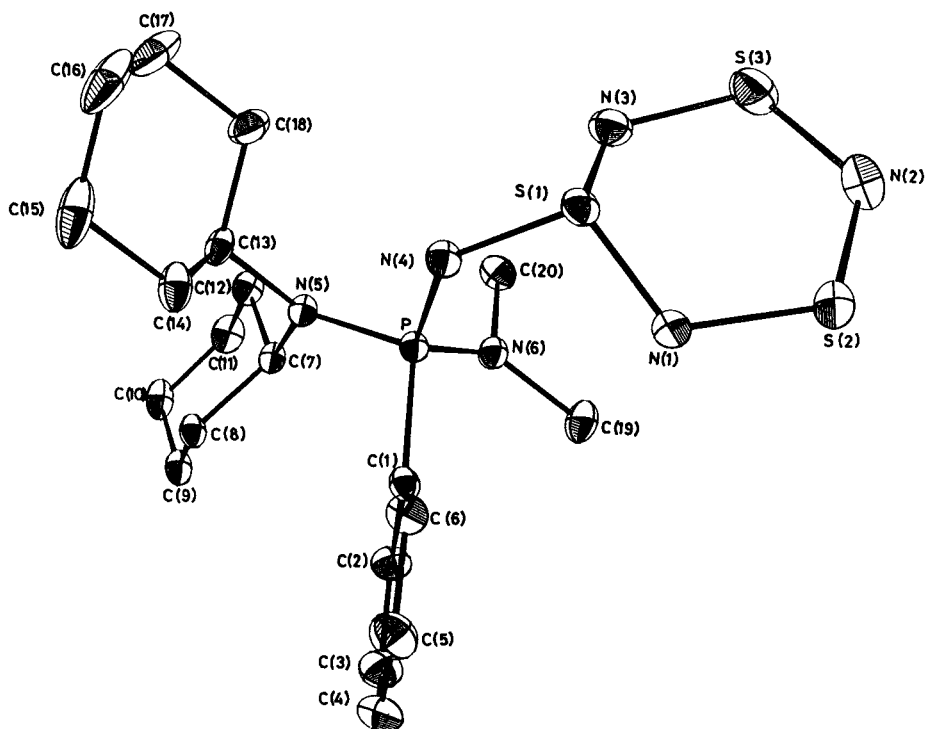
### 3. Results and discussion

The phosphine, (Ph)(DCA)(Me<sub>2</sub>N)P, (I) reacts with S<sub>4</sub>N<sub>4</sub> in accordance with previous observation<sup>1,2,4,14</sup> to give both phosphiniminocyclotrithiazene (II) and the corresponding phosphine sulphide (III) (figure 1) in moderate yield.

The new compounds (I) to (IV) are stable crystalline solids. (II) and (IV) exhibit typical electronic absorptions<sup>2,4</sup>. Interestingly, their NMR spectra revealed (i) quite similar <sup>31</sup>P-chemical shifts of (I) and (III) ( $\delta_p$  79.5 and 73.6 ppm respectively) and identical value for (II) and (IV) ( $\delta_p$  31.4 ppm) and (ii) a clean doublet for methyl protons due to coupling with phosphorus with a <sup>3</sup>J<sub>P-H</sub> value of 12 Hz in all the cases.

#### 3.1 X-ray structure

Figure 2 gives the ORTEP plot of (II). Its bond lengths and bond angles with those of ethyl and *n*-butyl analogues are given in table 2. All the three compounds show (i) primarily two kinds of endocyclic S-N bonds; those of tricoordinate sulphur [S(1)-N(1) & S(1)-N(3), avg. value: 1.65 Å], and the remaining ones [N(3)-S(3), S(3)-N(2), N(2)-S(2) & S(2)-N(1), avg. value 1.60 Å] (ii) half-chair conformations of the -S<sub>3</sub>N<sub>3</sub> heterocycles and (iii) significant deviation (0.70 Å) of the tricoordinate sulphur [S(1)] from the mean plane of the ring defined by 'N(1)-S(2)-N(2)-S(3)-N(3)' moiety. Another noteworthy feature is that the exocyclic S(1)-N(4) bond is (i) shortest of all the S-N bonds and (ii) considerably shorter to the adjacent endocyclic S-N bonds [S(1)-N(1) and S(1)-N(3)] in all the cases. Interestingly, P-N(5) and P-N(6) distances arising due to the presence of amino substituents (DCA and R<sub>2</sub>N respectively) also show bond shortening. These features imply the existence of some kind of conjugative interactions



**Figure 2.** ORTEP plot (50% probability thermal ellipsoids) of  $(Ph)(DCA)(Me_2N)P=N-S_3N_3$  (II) with atomic numbering in parentheses.

involving the phosphinimino substituent [ $\rightarrow P=N$ ] and the  $-S_3N_3$  heterocycle in all the cases.

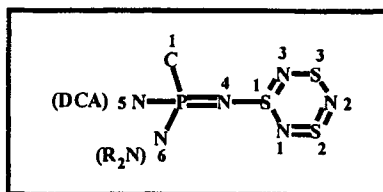
A comparison of the bond length and bond angle variation in the three structures (table 2) reveals different angle subtended at the imino nitrogen [N(4)] whereas their P-N bond lengths [P-N(5) and P-N(6)] do not show any noticeable variation. A value of  $\approx 126^\circ$  found for (II) lies in between those found for ethyl ( $135^\circ$ ) and *n*-butyl ( $119^\circ$ ) derivatives. This variation is also reflected in the observed non-bonded but significant P...S(1) distance which is least as expected for *n*-butyl case.

The angular disposition of N(5), N(6) and S(1) also reveal some interesting features for comparison. N(5) assumes a planar configuration ( $\Sigma N(5)$ :  $358-359^\circ$ ) in all the cases. But both N(6) and S(1) show differences. It is maximum for ethyl derivative ( $\approx 359^\circ$  and  $319^\circ$  respectively) and minimum for *n*-butyl derivative ( $\approx 350^\circ$  and  $311^\circ$  respectively).

On the whole, it can be said that structurally methyl and ethyl analogues resemble while *n*-butyl derivative stands out. In all the cases, the cyclohexyl groups of dicyclohexylamino substituent is found to be in chair conformation.

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**Table 2.** A comparison of the X-ray structural parameters of (Ph)(DCA)(R<sub>2</sub>N)PN-S<sub>3</sub>N<sub>3</sub> [R = Me, Et and *n*-Bu].

	R		
	Me	Et	<i>n</i> -Bu
<u>Angstroms</u>			
P.....S(1)	2·824	2·899	2·750
S(1) Deviation	0·663	0·701	0·664
P-C(1)	1·806(4)	1·808(3)	1·807(5)
P-N(4)	1·607(3)	1·601(3)	1·618(4)
P-N(5)	1·645(3)	1·640(3)	1·641(4)
P-N(6)	1·638(3)	1·641(2)	1·654(4)
N(4)-S(1)	1·567(3)	1·537(3)	1·569(4)
S(1)-N(1)	1·655(3)	1·641(3)	1·642(5)
N(1)-S(2)	1·610(3)	1·592(4)	1·615(5)
S(2)-N(2)	1·591(4)	1·581(6)	1·593(8)
N(2)-S(3)	1·589(4)	1·604(6)	1·582(7)
S(3)-N(3)	1·602(4)	1·607(4)	1·604(5)
N(3)-S(1)	1·658(3)	1·647(3)	1·649(6)
<u>Degrees</u>			
Σ N(5)	358·4	358·8	358·1
Σ N(6)	357·3	358·7	350·2
N(4)-P-N(5)	105·59(4)	106·45(14)	106·7(2)
N(4)-P-N(6)	120·4(2)	120·0(2)	117·4(2)
N(5)-P-N(6)	105·48(14)	107·75(13)	107·1(2)
N(4)-P-C(1)	108·2(2)	108·2(2)	109·7(3)
N(5)-P-C(1)	111·9(2)	107·96(13)	109·7(2)
N(6)-P-C(1)	105·4(2)	105·94(14)	106·2(2)
P-N(4)-S(1)	125·7(2)	135·0(2)	119·3(3)
N(1)-S(1)-N(3)	107·0(2)	107·2(2)	107·4(3)
S(1)-N(1)-S(2)	117·8(2)	116·7(2)	115·9(3)
N(1)-S(2)-N(2)	114·3(2)	115·6(2)	113·7(3)
S(2)-N(2)-S(3)	125·0(2)	123·8(3)	124·6(4)
N(2)-S(3)-N(3)	115·0(2)	114·5(2)	115·4(3)
S(3)-N(3)-S(1)	118·3(2)	115·9(2)	118·4(4)
N(4)-S(1)-N(1)	105·3(2)	105·3(2)	101·0(3)
N(4)-S(1)-N(3)	104·0(0)	106·1(2)	102·9(3)
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