

Crystal structure analysis of norbornadiene adduct of diphenyl hexamethylenimino phosphiniminocyclotrithiazene

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The title compound $(C_6H_{12}N)Ph_2P=N-S_3N_3 \cdot C_7H_8$ crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions: $a = 9.9200(5)$, $b = 16.3316(11)$, $c = 15.7009(17)$ Å, $\beta = 91.99(1)^\circ$, and $Z = 4$. The cyclotrithiazene ring adopts a chair conformation with equal bond distances and the norbornadiene is fused in an *exo, exo* fashion to the heterocycle. Norbornadiene addition to the cyclotrithiazene influences the bonding pattern in the ring as well as the P–N–S moiety.

KEY WORDS: Cyclotrithiazene; aryl phosphine; crystal structure; norbornadiene adduct.

Introduction

In recent years, several examples of phosphiniminocyclotrithiazenes ($\rightarrow PNS_3N_3$) with phosphorus carrying different substituents have been synthesized^{1–6} and crystal structures for a few of them have been determined.^{7–11} We have embarked on a systematic study of the structural aspects of these phosphiniminocyclotrithiazenes featuring a variety of substituents on the phosphorus atom.^{12–18} In general, it has been observed that the size and the nature of the substituents attached to the phosphorus atom have a pronounced effect

on the conformation of the cyclotrithiazene ring. In all the cases cited above the substitution is at the phosphorus atom and not on the thiazene ring. However, this heterocyclic variety has the ability to undergo an addition reaction with norbornadiene involving the dicoordinate sulfur atoms of the S_3N_3 ring. The single crystal X-ray structure of $Ph_3P=N-S_3N_3 \cdot C_7H_8$ ⁸ is the first of its kind in which a molecule of norbornadiene is added to the S_3N_3 heterocycle to create two new C–S bonds. Herein, we report the crystal structure of the title compound $(C_6H_{12}N)Ph_2P=N-S_3N_3 \cdot C_7H_8$ with a view to verify the structural changes accompanying the norbornadiene addition. The results have been compared with the precursor cyclotrithiazene namely, hexamethylenimino diphenyl phosphiniminocyclotrithiazene¹⁹ and $Ph_3P=N-S_3N_3 \cdot C_7H_8$.⁸ Incidentally, our structure is the first example in the $\rightarrow PNS_3N_3$ family where the norbornadiene adduct features mixed substituents on the phosphorus atom.

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Experimental

The title compound was prepared by the reaction of $(\text{C}_6\text{H}_{12}\text{N})\text{Ph}_2\text{P}=\text{N}-\text{S}_3\text{N}_3$ with norbornadiene in the CH_2Cl_2 medium at room temperature.¹⁹ Colorless needle-shaped crystals were obtained when the product was recrystallized from CH_3CN at 22°C . The intensity data were collected on an Enraf–Nonius CAD-4 diffractometer in the ω - 2θ scan mode using graphite monochromated $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) from a single crystal of dimensions $0.1 \times 0.1 \times 0.3 \text{ mm}$. The unit cell parameters were obtained by least-squares refinement of 25 carefully selected reflections in the range $9 \leq \theta \leq 14^\circ$. A total of 4282 reflections in the range $0 \leq h \leq 11$, $0 \leq k \leq 18$, $-17 \leq l \leq 17$ were measured up to θ equal to 60° , of which 3391 were unique reflections with $I \geq 3\sigma(I)$. The measured intensity data were corrected for Lorentz-polarization effects. The presence of Renninger reflections in the intensity data led to an ambiguity in fixing the space group. A few reflections violating the systematic absences— $0k0$: $k = 2n + 1$ and $h0l$: $h + l = 2n + 1$ —were noticed. The space group was fixed as $P2_1/n$ from the Harker section ($u^{1/2}w$) and the Harker line ($^{1/2}v^{1/2}$) peaks. Direct methods were employed for structure solution (SHELXS-86²⁰) and the full matrix least-squares refinement was carried out using the program SHELXL-97.²¹ Hydrogen atoms could be located from successive electron density maps. Large anisotropy in thermal motion was noticed for one carbon atom of the hexamethylenimino group and subsequent refinement led to two positions with different occupancies. No attempt was made to fix the hydrogen atoms for these disordered atoms.

Results and discussion

The crystal data along with the details of the structure refinement have been listed in Table 1. The final atomic fractional coordinates and equivalent isotropic thermal parameters of all the non-hydrogen atoms are in Table 2. The ORTEP²² diagram of the molecule along with the number-

Table 1. Crystal Data, Summary of Intensity Data Collection and Structure Refinement

Compound	$\text{C}_{25}\text{H}_{30}\text{N}_5\text{S}_3\text{P}$
Shape/color	Needle/colorless
Crystal dimensions, mm	$0.1 \times 0.1 \times 0.3$
Melting point, $^\circ\text{C}$	160
Data collected at, $^\circ\text{C}$	25
Crystal system	Monoclinic
Space group	$P2_1/n$
Cell constants	$a = 9.9200(5) \text{ \AA}$ $b = 16.3316(11) \text{ \AA}$ $c = 15.7009(17) \text{ \AA}$ $\beta = 91.99(1)^\circ$
Cell volume, \AA^3	2542.2(3)
Z	4
$D_{\text{calc.}}$, mg m^{-3}	1.379
μ calc., mm^{-1}	0.345
$F(000)$	1112
Diffractometer/scan	Enraf–Nonius/ ω - 2θ
Radiation employed	$\text{Cu K}\alpha$ (1.5418 \AA)
Standard reflections	(3 4 3) (3 3 2)
Decay of standards	3%
No. of reflections measured	4282
θ range ($^\circ$)	2–60
Index ranges	$0 \leq h \leq 11, 0 \leq k \leq 18,$ $-17 \leq l \leq 17$
Reflections observed [$I \geq 3\sigma(I)$]	3697
No. of unique reflections	3391
No. of parameters refined	431
R	0.0633
wR_2	0.1750
GOF	1.090
Max. shift/e.s.d.	0.007
Largest peak and hole (e \AA^{-3})	0.73 and -0.40
CCDC#	204912

ing scheme is shown in Fig. 1. The crystal structure of $(\text{C}_6\text{H}_5)_3\text{P}=\text{N}-\text{S}_3\text{N}_3 \cdot \text{C}_7\text{H}_8$ (abbreviated as NTRPPC) is the first example of phosphiniminocyclotrithiazenes in which the cyclotrithiazene ring is fused with norbornadiene.⁸ The title compound (abbreviated as NHDPPC), being second in this series, shows similar conformational features in the cyclotrithiazene ring. However, the sulphur–nitrogen bond distances and angles in the S_3N_3 ring are distinct from those of the parent molecule $(\text{C}_6\text{H}_{12}\text{N})\text{Ph}_2\text{P}=\text{N}-\text{S}_3\text{N}_3$ (abbreviated as HEDPPC).¹⁹ The endocyclic S–N bond distances and angles along with the exocyclic P–N–S moiety values of these three compounds have been compared in Table 3. Almost

Table 2. Atomic Fractional Coordinates (10⁴) and Equivalent Thermal Parameters (10³ Å²) of Non-Hydrogen Atoms With Their esd's in Parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
P	1317(1)	7137(1)	5278(1)	44(1)
N4	1977(3)	6592(2)	6018(2)	57(1)
S1	2551(1)	6996(1)	6913(1)	69(1)
N1	4199(4)	6935(2)	6861(3)	79(1)
S2	4943(1)	6091(1)	7162(1)	81(1)
N2	4386(5)	5772(3)	8075(3)	92(1)
S3	2779(1)	5578(2)	7913(1)	73(1)
N3	1950(4)	6401(2)	7645(2)	78(1)
N5	2149(3)	7933(2)	4920(2)	48(1)
C1	1105(3)	6455(2)	4386(2)	50(1)
C2	716(5)	6759(3)	3587(3)	70(1)
C3	508(6)	6239(4)	2915(3)	91(2)
C4	661(6)	5409(5)	3035(4)	98(2)
C5	1035(6)	5098(4)	3815(5)	87(2)
C6	1268(4)	5619(2)	4503(3)	63(1)
C7	−333(3)	7509(2)	5513(2)	45(1)
C8	−922(4)	7268(2)	6262(3)	54(1)
C9	−2217(4)	7490(3)	6422(3)	70(1)
C10	−2959(4)	7950(3)	5835(3)	71(1)
C11	−2376(5)	8197(3)	5095(3)	68(1)
C12	−1086(4)	7995(2)	4932(3)	56(1)
C13	2099(5)	8716(2)	5393(3)	59(1)
C14	1870(6)	9453(3)	4808(4)	76(1)
C15	2865(11)	9598(5)	4143(6)	133(3)
C16A	4135(10)	9191(5)	4130(7)	74(2)
C16B	3167(16)	8842(8)	3539(8)	100(4)
C17	3915(7)	8241(5)	3879(5)	116(2)
C18	3491(5)	7732(3)	4589(4)	70(1)
C19	4174(4)	5290(2)	6482(3)	56(1)
C20	5019(5)	4487(4)	6386(4)	90(2)
C21	4747(7)	4054(4)	7244(5)	104(2)
C22	3249(6)	4054(3)	7070(4)	81(1)
C23	2933(4)	4983(2)	6926(2)	52(1)
C24	4203(7)	3968(3)	5786(5)	94(2)
C25	3166(8)	3713(3)	6169(4)	96(2)

^a*U*_{eq} = one third of the trace of the orthogonalized *U*_{*ij*} tensor. Occupancies of A and B fragments of C16 are 0.55 and 0.45, respectively.

equal S—N bond distances, distinctly different from those of HEDPPC¹⁹ and the other examples of reported phosphiniminocyclotrithiazenes,^{12–18} are observed. The main difference between the norbornadiene-fused cyclotrithiazene and the others is that there are three tricoordinated sulphur atoms in the former against one in the latter. The addition of norbornadiene results in the conversion of the 8π ring system to a 6π system and equal S—N bond distances occur in NHDPPC

as the three sulphur atoms have the same orbital bonding arrangement. The average S—N bond distance 1.634 Å (rms deviation of 0.008 Å) is less than the S—N single bond distance of 1.76 Å²³ (structural data at 78 K) and longer than the S=N double bond distance of 1.55 Å²⁴ (study by neutron diffraction). Equal S—N bonds in the present heterocycle are short when compared to NTRPPC.⁸ This situation of approximately equal endocyclic S—N bonds and distances shorter than the single bond distance can be compared to the existence of an analogous situation present in benzene and cyclophosphazenes. It seems that in the title compound the ring delocalization expectedly gets better as it has also been noticed in (SNF)₃²⁵ and (SNCl)₃²⁶ (structural data at −130°C) in which all the sulfur atoms are tricoordinated in nature.

The endocyclic N—S—N angles in the cyclotrithiazene ring (Table 3) of NHDPPC agree well with those in NTRPPC⁸ but differ from HEDPPC.¹⁹ The angle at N2 has reduced from 123.8(5)° (HEDPPC) to 106.4(2)° (NHDPPC) whereas, at S1 it has increased from 108.7(4)° to 112.8(2)°. Further in NHDPPC the angles at S2 and S3 are almost equal and less than those of HEDPPC. Similar variations have also been evidenced in NTRPPC and its parent compound (C₆H₁₂N)Ph₂P=N—S₃N₃.⁷ The torsion angles in the cyclotrithiazene ring indicate that the heterocycle adopts a chair conformation in contrast to the approximate sofa arrangement observed in the other phosphiniminocyclotrithiazenes.^{12–18} The atoms N1, S2, S3, and N3 lie exactly in a plane while S1 and N2 deviate by −0.363(4) and 0.814(4) Å, respectively. The chair conformation of the heterocycle could possibly be due to the strain produced by the norbornadiene fusing. Phosphinimino moiety and the norbornadiene are on the same side of the heterocycle and the norbornadiene has been fused in an *exo, exo* fashion at the S2 and S3 atoms. The sulphur–carbon distances (S2—C19 = 1.840(4) Å and S3—C23 = 1.839(4) Å) are in good agreement with those of Ph₂PS₂N₃ · C₇H₈ (1.844(5) Å),²⁷ S₄N₄ ··· 2C₇H₈ (1.851(5) Å),²⁸ and NTRPPC (1.844(3) Å).⁸

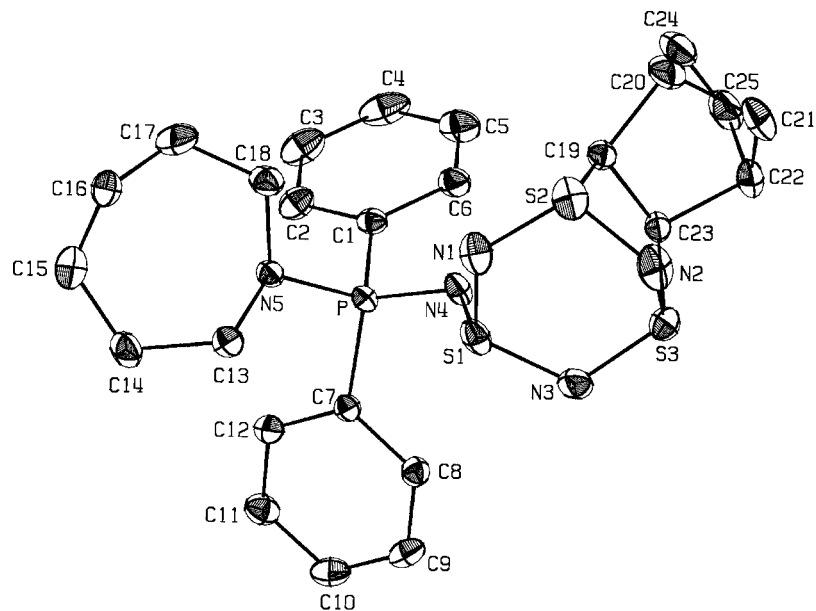


Fig. 1. The ORTEP of $(C_6H_{12}N)Ph_2P=N-S_3N_3 \cdot C_7H_8$. The thermal ellipsoids are at 50% probability level.

The P—N4 distance (1.586 Å) is close to the double bond distance of 1.55 Å and the adjoining S1—N4 bond length also indicates partial multiple bond character. Interestingly, a reverse of this trend is evidenced in the phosphininocyclotrithiazene structures with substituents attached to the phosphorus atom.^{12–18} In NHDPPC, the S1—N4—P bond angle 121.7(2)° is less than that of HEDPPC (126.5(3)°). This results in the reduction of the nonbonded P...S1 distance from 2.86(2) Å (in HEDPPC) to 2.813(8) Å (in NHDPPC). Reported phosphininocyclotrithiazene structures indicate that the nature and size of the substituents attached to the phosphorus atom have a significant effect on the bonding pattern in the cyclotrithiazene ring as well as P—N—S moiety.^{12–18} Whilst, the present study illustrates that fusing of the norbornadiene to the heterocycle influences the bonding in the P—N—S moiety in addition to that in the cyclotrithiazene ring. The imino nitrogen atom with a predicted bond angle of 120° is sp^2 hybridized, where its lone pair of electrons is occupying an sp^2 hybrid orbital and the remaining two electrons are used in the forma-

tion of sigma bonds to the neighboring sulfur and phosphorus atoms. The phosphorus atom has an approximate tetrahedral arrangement with bond angles close to 109°. The P—C1 and P—C7 bond distances 1.796(4) and 1.796(3) Å, respectively, agree well with the tetrahedral hybridization of the tetracoordinate pentavalent phosphorus atom. The two phenyl rings are planar and the seven-membered hexamethylenimino ring has chair conformation. No intermolecular short contacts less than 3.0 Å are observed and the molecules are held together by van der Waals contacts in the unit cell.

Supplementary material

CCDC 204912 contains the supplementary crystallographic data and can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk

Table 3. Comparison of Bond Lengths (Å) and Angles (°) in (a) NHDPPC (This Study), (b) NTRPPC,⁸ and (c) HEDPPC¹⁹

Bond lengths/angles	a	b	c
S1–N1	1.643(4)	1.646(3)	1.647(6)
S1–N3	1.633(4)	1.649(3)	1.651(7)
S2–N1	1.625(4)	1.617(3)	1.600(6)
S2–N2	1.641(5)	1.640(3)	1.599(9)
S3–N2	1.636(5)	1.634(3)	1.574(8)
S3–N3	1.624(4)	1.631(3)	1.608(7)
N1–S1–N3	112.8(2)	112.0(2)	108.7(4)
N1–S2–N2	111.1(3)	111.3(2)	113.5(4)
N2–S3–N3	111.2(2)	111.8(2)	117.1(4)
S2–N1–S1	118.7(2)	118.9(2)	118.7(4)
S2–N2–S3	106.4(2)	106.2(2)	123.8(5)
S3–N3–S1	118.7(2)	118.2(2)	117.9(4)
P–C1	1.796(4)	1.810(3)	1.774(7)
P–C7	1.796(3)	1.803(3)	1.821(5)
P–N5	1.649(3)	1.805(3)	1.622(5)
P–N4	1.586(3)	1.583(3)	1.641(7)
S1–N4	1.636(3)	1.634(4)	1.558(6)
N4–P–N5	119.6(2)	113.8(2)	122.0(3)
N4–P–C1	104.9(2)	104.6(2)	110.7(3)
N5–P–C1	105.6(2)	107.6(1)	106.9(3)
N4–P–C7	113.3(2)	115.5(2)	102.3(3)
N5–P–C7	105.9(2)	106.9(1)	107.5(3)
C1–P–C7	106.7(2)	108.0(1)	106.4(3)
P–N4–S1	121.7(2)	123.5(2)	126.5(3)
P...S1	2.813(8)	2.834(9)	2.86(2)

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