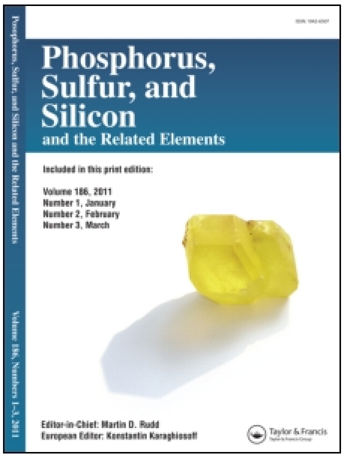

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

CRYSTAL STRUCTURE OF THE NOVEL COMPOUND (1α, 3bT, 5α)-1,3-DIPHENYL-5-HYDRIDO-5-ISOPROPOXY-1λ^6, 3λ^6,2,4,6,5λ^5-DITHIATRIAZAPHOSPHORINE-1,3-DIOXIDE. A COMPARISON WITH RELATED STRUCTURES

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To cite this Article Winter, H. , Van De Grampel, J. C. , De Boer, J. L. , Meetsma, A. and Spek, A. L.(1987) 'CRYSTAL STRUCTURE OF THE NOVEL COMPOUND (1α, 3bT, 5α)-1,3-DIPHENYL-5-HYDRIDO-5-ISOPROPOXY-1λ^6, 3λ^6,2,4,6,5λ^5-DITHIATRIAZAPHOSPHORINE-1,3-DIOXIDE. A COMPARISON WITH RELATED STRUCTURES', Phosphorus, Sulfur, and Silicon and the Related Elements, 32: 3, 145 — 151

To link to this Article: DOI: 10.1080/03086648708074271

URL: http://dx.doi.org/10.1080/03086648708074271

Phosphorus and Sulfur, 1987, Vol. 32, pp. 145–151
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(Received November 13, 1986)

The title compound (1α, 3β, 5α)-$(NSOPh)_2NP(H)O$-*i*-Pr crystallizes in the spacegroup $P2_1/n$ with cell dimensions: $a = 12.150(2)$, $b = 8.911(1)$, $c = 17.614(3)$ Å, $\beta = 107.52(1)°$; $Z = 4$. The structure was solved by direct methods and refined by least-squares techniques to an R value of 0.048 for 2420 independent reflections (collected at room temperature) with $I > 2.5\ \sigma(I)$. The unit cell contains dimeric units which are formed by unprecedented P—H···O═S bridges. The conformation of the inorganic ring skeleton can be described as a boat; phosphorus and sulfur atoms show a distorted tetrahedral geometry. The S—N bond lengths differ slightly, ranging from 1.547(3) to 1.588(2) Å. The exocyclic bond lengths are P—H = 1.34(2), P—O = 1.553(2), S—O = 1.439(2) (mean value), and S—C = 1.767(4) (mean value) Å. From a comparison with analogous structures the degree of asymmetry (Δl = {[P—N] − [S—N]} Å) in the SNP unit is related to the difference in electronegativity between the sulfur and phosphorus centres.

INTRODUCTION

In their studies on reactions of the cyclic compound $(NPCl_2)_3$ with organometallic reagents Allcock and Harris have shown that hydrido-alkyl substituted cyclophosphazenes can be prepared by using an alkyl Grignard reagent in the presence of $[(n\text{-}Bu)_3PCuI]_4$ and followed by treatment with 2-propanol.[1,2]

Very recently we have described the reactivity of chlorocyclo(thia)phosphazenes $(NSOPh)_n(NPCl_2)_{3-n}$ ($n = 0, 1, 2$) towards alkyllithium reagents.[3,4] It has been demonstrated that reactions of these compounds with MeLi followed by treatment with an excess of 2-propanol leads to the formation of a new class of

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hydrido(thia)phosphazenes with general formula $(NSOPh)_n(NPCl_2)_{2-n}NP(H)O$-*i*-Pr ($n = 0, 1, 2$).

$$(NPCl_2)_3 \xrightarrow[\text{ii}]{\text{i}} (NPCl_2)_2NP(H)O\text{-}i\text{-Pr}$$

$$NSOPh(NPCl_2)_2 \xrightarrow[\text{ii}]{\text{i}} cis\text{-and } trans\text{-}NSOPhNPCl_2NP(H)O\text{-}i\text{-Pr}$$

$$cis\text{-}(NSOPh)_2NPCl_2 \xrightarrow[\text{ii}]{\text{i}} (1\alpha, 3\alpha, 5\alpha)\text{-}(NSOPh)_2NP(H)O\text{-}i\text{-Pr}^{**}$$

$$trans\text{-}(NSOPh)_2NPCl_2 \xrightarrow[\text{ii}]{\text{i}} (1\alpha, 3\beta, 5\alpha)\text{-}(NSOPh)_2NP(H)O\text{-}i\text{-Pr}$$

i = MeLi; ii = *i*-PrOH
** for use of α and β prefixes see ref. 5.

Structures were assigned from NMR data ($^{31}P, ^{1}H$). In particular the large values of the P—H coupling constant (719–732 Hz) pointed to the presence of a direct P—H bond. In order to prove this assignment a crystal structure determination was carried out for one of the hydrido derivatives prepared. Because its facile isolation and high stability the compound $(1\alpha, 3\beta, 5\alpha)$-$(NSOPh)_2NP(H)O$-*i*-Pr was chosen for this study. Moreover, its structure fitted in with the recently determined structures of $(1\alpha, 3\beta, 5\alpha)$-$(NSOPh)_2NPI$-*i*-Pr[6], *cis*-$(NSOPh)_2NPCl_2$[7], $(1\alpha, 3\beta, 5\alpha)$-$(NSOPh)_2NP$-*n*-Pr-*i*-Pr[8], thus providing more insight into the correlation between electronegativity of the P-bonded ligands and the asymmetry in the SNP ring segment.

RESULTS AND DISCUSSION

Molecular structure

The crystal structure of the title compound consists of dimeric units (Figure 1) around crystallographic inversion centres. Selected data on the geometry are presented in Table I. The description of the structure as dimeric units is based on the interaction of the P-bonded hydrogen atom to a S-bonded oxygen atom. The H(1)···O(1′) distance* amounts to 2.37(2)Å (sum of the van der Waals radii is 2.72 Å[9]), which is typical for hydrogen bonds. The angle P(1)—H(1)···O(1′) is 171(2)°, whereas the angle H(1)···O(1′)—S(1′) amounts to 105.5(4)°. The PH···OS type interaction has no precedents for four-coordinated phosphorus systems of the type $A^1A^2A^3PH$ ($A^1, A^2, A^3 = C, N, O$) according to the 1985 release of the Cambridge Data Base.[10] The P—H bond length of 1.34(2) Å is shorter than the value of 1.44 Å in PH_3,[11] but consistent with those reported for $(C_6H_4O_2)_2PH$ (1.31, 1.38 Å),[12] $(C_6H_4O_2)(C_6H_5NO)PH$ (1.32(2) Å),[13] $(C_6H_4O_2)(C_7H_7NO)PH$ (1.36(3) Å),[13] $(NPCl_2)_2NP(i\text{-Pr})H$ (1.26(7) Å),[14] and $(C_6H_5NH)_2P(O)H$ (1.29(4), 1.32(3) Å).[15] The P—O distance of 1.553(2) Å is in the range as reported for the spiro compounds $(NPCl_2)_2NP[O(CH_2)_nO]$

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* Atoms marked with a prime are related by an inversion centre.

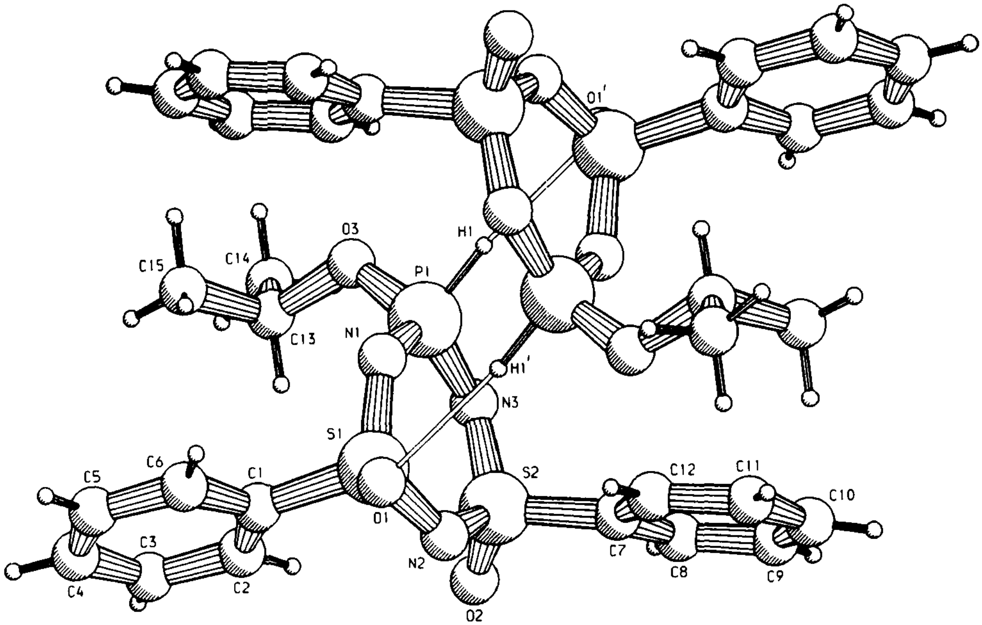

FIGURE 1 Dimeric structure of the hydrido-isopropoxy derivative, (1α, 3β, 5α)-$(NSOPh)_2NP(H)O$-*i*-Pr. Discrete molecules related by a centre of inversion are connected by PH···OS bridges.

(1.551(3)–1.574(3) Å)[16] and 1α, 3α, 5β-$(NSOCl)_2NP[O(CH_2)_2NH]$ (1.567(6) Å),[17] but longer than the P—O "double" bonds in the anions $[(NSOCl)_2NPClO]^-$ (1.438(6) Å)[18] and $[NHSOClNPCl_2NPO_2]^-$ (1.428(2) Å).[19] The S—O and S—C bond lengths, mean values 1.438(2) Å and 1.767(2) Å,[20] respectively, can be compared with those reported for the corresponding iodo-isopropyl[6] and propyl-isopropyl derivatives[8] and in *cis*- and *trans*-$(NSOPh)_2NPCl_2$.[7,21]

TABLE I

Selected data on the geometry of (1α, 3β, 5α)-$(NSOPh)_2NP(H)O$-*i*-Pr. Estimated standard deviations are given in parentheses

Bond distances (Å)			Bond angles (°)			
			O(1)	—S(1)	—C(1)	107.0(1)
S(1)	—O(1)	1.440(2)	N(1)	—S(1)	—N(2)	113.7(1)
S(1)	—N(1)	1.551(3)	O(2)	—S(2)	—C(7)	107.1(1)
S(1)	—N(2)	1.568(3)	N(2)	—S(2)	—N(3)	114.4(1)
S(1)	—C(1)	1.771(3)	O(3)	—P(1)	—H(1)	99(1)
S(2)	—N(2)	1.558(2)	N(1)	—P(1)	—N(3)	113.4(1)
S(2)	—N(3)	1.547(3)	S(1)	—N(1)	—P(1)	124.2(2)
S(2)	—O(2)	1.436(3)	S(1)	—N(2)	—S(2)	124.3(2)
S(2)	—C(7)	1.763(3)	S(2)	—N(3)	—P(1)	125.0(1)
P(1)	—H(1)	1.34(2)				
P(1)	—N(1)	1.594(2)				
P(1)	—O(3)	1.553(2)				
P(1)	—N(3)	1.598(3)				
O(3)	—C(13)	1.477(4)				

The conformation of the PNS ring approaches that of a boat[22] with torsion angles ranging from 5.2(2) to 24.5(2)°. The lowest asymmetry parameter value is $\Delta C_s = 3.5(2)°$ for S(1) and N(3).[23] Puckering parameters are $Q = 0.238(2)$ Å, $\theta = 105.9(5)°$, $\phi = 187.0(5)°$. Both phosphorus and sulfur show a distorted tetrahedral geometry, nitrogen has a sp^2 configuration. The endocyclic bond lengths will be discussed below. The phenyl rings display normal geometry, average C—C distance is 1.371(3) Å and 1.359(6) Å, respectively. Large anisotropic thermal motion is observed for C(9), C(10) and C(11). The angles between the phenyl plane and the related NSN segment plane are 74.0(2)° and 74.1(2)°, respectively. The angle between the bisectrice of the angle O(1)—S(1)—C(1) and the plane of the segment N(1)—S(1)—N(2) is 4.2(2)°. In the equivalent configuration about S(2) this angle amounts to 6.2(2)°. The nearly symmetrical position of the exocyclic S—X bonds (X = O, C) towards the related NSN plane seems to be valid for all S-phenyl derivatives, but differs from the asymmetric arrangement when X = halogen. In that case the SO bond is more or less equatorial and S-halogen axial; see for examples the molecular structure of *cis*-$(NSOF)_2NPCl_2$,[24] *cis*-$(NSOCl)_2NPCl_2$,[25] and $(1\alpha, 3\alpha, 5\alpha)$-$(NSOCl)_2$-NPClNHMe.[26]

Endocyclic bond lengths; comparison with related structure

The SN and PN bond lengths given in Table I are shorter than the so-called single bond lengths, S—N = 1.76 Å,[27] P—N = 1.77 Å.[28] The difference can be partly explained from an additional π-bonding system. As put forward by Craig and Paddock[30] for the cyclophosphazenes the degree of π-bonding arising from a phosphorus centre depends on the electronegativity (χ) of the ligands attached to it: the larger the electronegativity the greater the π-bonding ability. This means that in an inhomogeneously substituted PNP segment the P—N bond to the more electronegative phosphorus centre is shortened, whereas the other is lengthened. The same concept can be applied to the cyclothiaphosphazenes where for a PNS segment, even in case of homogeneous substitution, unequal bond lengths can be expected as $\chi(P) \neq \chi(S)$. The structural parameters of compounds $(NSOX)_2NPYZ$ (Table II) are in line with this approach. It is possible to correlate the asymmetry of a PNS segment with the electronegativity of the P and S centre: the difference Δl (in Å) between the P—N and S—N bond lengths increases with an increasing difference $\Delta\chi$ between the total χ values of the SOX and PYZ centres. For compounds *cis*-$(NSOX)_2NPYZ$ the graph of Δl versus $\Delta\chi$ has a parabolic shape; for compounds with the phenyl group in *trans*-position a linear relationship is found, $\Delta l = -0.080 + 0.036(6)\ \Delta\chi$ with a correlation coefficient of 0.97.

From the reasoning given above one should expect that in an equally substituted SNS segment the S—N bond lengths are equal. Indeed, for all compounds given in Table II no differences are observed within the experimental error, except for $(1\alpha, 3\beta, 5\alpha)$-$(NSOPh)_2NP(H)O$-*i*-Pr and *trans*-$(NSOPh)_2NPCl_2$. For the title compound the hydrogen bond formation, giving rise to partially "localized" double bonds, might be a possible cause. Lattice effects other than hydrogen bonding may disturb the symmetry of the SNS unit in the latter compound.

TABLE II

Comparison of endocyclic bond lengths (in Å) in neutral molecules $(NSOX)_2NPYZ$. E.s.d. in parentheses

Compound	Ref.	PNS-unit Mean P—N	PNS-unit Mean S—N	Δl	$\Delta\chi$[a]	SNS unit Mean S—N
$(1\alpha, 3\beta, 5\alpha)$-$(NSOPh)_2NPPr$-*i*-Pr	8	1.608(3)	1.544(3)	0.064	3.89	1.568(4)
$(1\alpha, 3\beta, 5\alpha)$-$(NSOPh)_2NP(H)O$-*i*-Pr	present paper	1.595(2)	1.549(2)	0.046	3.71	1.568(3); 1.588(2)
$(1\alpha, 3\beta, 5\alpha)$-$(NSOPh)_2NPI$-*i*-Pr	6	1.609(4)	1.556(4)	0.053	3.65	1.591(11)
trans-$(NSOPh)_2NPCl_2$	21	1.567(6)	1.555(7)	0.012	2.55	1.549(5); 1.591(7)
cis-$(NSOF)_2NPCl_2$	24	1.596(6)	1.528(6)	0.068	3.96	1.568(7)
cis-$(NSOCl)_2NPClNHMe$	26	1.593(5)	1.526(5)	0.067	3.51	1.566(5)
cis-$(NSOCl)_2NPCl_2$	25	1.585(9)	1.540(9)	0.045	3.01	1.578(9)
cis-$(NSOPh)_2NPCl_2$	7	1.573(3)	1.569(4)	0.004	2.55	1.581(2)

[a] χ-values used: H 2.21, O 5.54, F 3.90, P 2.79, S 3.21, Cl 2.95;[29a] I 2.52;[29b] Pr, *i*-Pr 2.28, NHMe 2.45, O-*i*-Pr 2.53;[29c] Ph 2.49.[29d]

EXPERIMENTAL

The synthesis of the title compound has been described elsewhere.[4] Suitable crystals (m.p. 77.5–79.5°C) were obtained by careful crystallization from Et_2O. For the structure determination a crystal ($0.27 \times 0.27 \times 0.23$ mm) was glued on top of a glass fiber and mounted on an ENRAF-NONIUS CAD-4F diffractometer. Precise lattice parameters were derived from the angular settings of 21 reflections with $23.9° < \theta < 25.6°$. The space group was determined as $P2_1/n$ from the systematic absences observed, *hol*, $h + l = 2n + 1$; *oko*, $k = 2n + 1$. The three reference reflections, measured every two hours showed a long term variation less than 1% during the 72 hours of X-ray exposure time. The intensities were corrected for Lorentz and polarization effects and the small long term

TABLE III

Crystal data and details of the structure determination

a. Crystal data

Formula	$C_{15}H_{18}N_3O_3S_2P$	V, Å^3	1818.6(5)
Mol. wt.	383.43	Z	4
Space group (no.)	$P2_1/n$ (14)	D_{calc}, g cm^{-3}	1.400
a, Å	12.150(2)	$F(000)$	800
b, Å	8.911(1)	μ(Mo$K\alpha$), cm^{-1}	3.80
c, Å	17.614(3)		
β, deg	107.52(1)		

b. Data collection

Radiation, Å	Mo$K\alpha$, 0.71073	Data Set	$h = -14 \rightarrow 14$; $k = 0 \rightarrow -10$
Monochromator	graphite		$l = -21 \rightarrow 21$
Temperature, K	295	Total data	7587
θ range; min., max., deg.	1.21, 26	Total unique	3552
$\omega/2\theta$ scan, deg.	$\Delta\omega = 0.85 + 0.35 tg\theta$	Obsd $I > 2.5\sigma(I)$	2424
		R(int)	0.054

c. Refinement

Number of reflections	2420
Number of refined parameters	272
Weighting scheme	$1/\sigma^2(F)$
Final $R_F = \sum(\lvert F_0\rvert - \lvert F_c\rvert)/\sum F_0$	0.048
Final $wR_F = [\sum w(\lvert F_0\rvert - \lvert F_c\rvert)^2/\sum wF_0^2]^{1/2}$	0.031
R.m.s. deviation of refl. on unit weight	2.09
Min. and max. densities in final Fourier map, e/Å^3	−0.39, 0.27
Max. (shift/sigma)	0.25
Average (shift/sigma)	0.016

TABLE IV

Final positional parameters (except for the phenyl hydrogen atoms) with their e.s.d. in parentheses

ATOM	X/A	Y/B	Z/C
S(1)	0.13217(7)	0.4115(1)	0.40458(5)
S(2)	0.28168(7)	0.3054(1)	0.54768(5)
P(1)	0.18613(7)	0.5919(1)	0.53950(5)
O(1)	0.0272(2)	0.3523(3)	0.3509(1)
O(2)	0.3982(2)	0.2583(3)	0.5575(1)
O(3)	0.2475(2)	0.7460(2)	0.5439(1)
N(1)	0.1089(2)	0.5484(3)	0.4519(1)
N(2)	0.2019(2)	0.2826(3)	0.4587(1)
N(3)	0.2777(2)	0.4653(3)	0.5810(1)
C(1)	0.2179(2)	0.4744(3)	0.3455(2)
C(2)	0.3356(2)	0.4612(4)	0.3716(2)
C(3)	0.3988(2)	0.5194(4)	0.3249(2)
C(4)	0.3451(3)	0.5896(4)	0.2546(2)
C(5)	0.2280(3)	0.6020(4)	0.2293(2)
C(6)	0.1631(2)	0.5446(4)	0.2743(2)
C(7)	0.2238(2)	0.1813(4)	0.6037(2)
C(8)	0.2955(3)	0.1260(4)	0.6734(2)
C(9)	0.2528(3)	0.0312(5)	0.7189(2)
C(10)	0.1402(4)	−0.0042(5)	0.6963(2)
C(11)	0.0690(3)	0.0505(6)	0.6279(3)
C(12)	0.1104(3)	0.1459(5)	0.5802(2)
C(13)	0.3434(3)	0.7693(4)	0.5098(2)
C(14)	0.4395(3)	0.8438(4)	0.5720(2)
C(15)	0.3004(3)	0.8594(4)	0.4359(2)
H(1)	0.113(2)	0.626(3)	0.581(1)

variation. No absorption corrections were applied. The variance $\sigma^2(I)$ was calculated based on counting statistics plus a term (P^2I^2), where P (=0.018) is the instability constant.[31] The structure was solved by direct methods[32] and refined on F by block-diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms, located in a difference Fourier map, were included in the final refinement with one overall isotropic temperature factor. Details on the structure determination are listed in Table III.b and c. Four low order reflections $\bar{2}00$, 002, $\bar{2}12$, and 022 were excluded from the final refinement cycles, because they probably suffered from secondary extinction. Scattering factors from Cromer and Mann[33] corrected for anomalous dispersion[34] were used. Calculations were carried out on the Cyber 180–855 of the University of Utrecht Computer Center with program packages XTAL[35] and EUCLID[36] (calculation of geometric data and preparation of illustrations including an extended version of the program PLUTO). Final positional parameters except for the phenyl hydrogen atoms are given in Table IV.

Note. A full list of final positional and thermal parameters and of bond distances, angles, and torsion angles, including their estimated standard deviations are deposited with the Cambridge Crystallographic Data Centre (CCDC), UK.

ACKNOWLEDGEMENT

The investigation was supported in part (ALS, HW) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Advancement of Pure Research (ZWO). One of us (AM) is indebted to the Department of Crystal and Structure Chemistry, University of Utrecht, for the support of this research at their laboratory.

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