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Formation and Crystal Structure of 4,4'-Oxybis(2,6bis(dimethylamino)-4H-1,3,5,4thiadiazaphosphinine 4-Oxide)

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FORMATION AND CRYSTAL STRUCTURE OF 4,4'-OXYBIS(2,6-BIS(DIMETHYLAMINO)-4H-1,3,5,4-THIADIAZAPHOSPHININE 4-OXIDE)

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GRAPHICAL ABSTRACT



Abstract The reaction of P_4S_{10} with dimethyl cyanamide as solvent yields a complex mixture of products, from which the new compound 4,4'-oxybis(2,6-bis(dimethylamino)-4H-1,3,5,4-thiadiazaphosphinine 4-oxide) (1) was isolated. In this pyrophosphate derivative, the phosphorus atoms are part of the, otherwise rarely encountered, 1,3,5,4-thiadiaza-phosphinine ring. The molecular structure of the new compound was elucidated by single-crystal X-ray diffraction, showing an almost planar thiadiazaphosphinine ring and a cis-like arrangement of the heterocycles at the two phosphorus atoms.

Keywords Phosphorus(V) sulfide; dimethyl cyanamide; synthesis; crystal structure; thiadiazaphosphinine ; phosphoric acid anhydride

INTRODUCTION

The reaction of P_4S_{10} with nitrogen-containing nucleophiles represents a challenge for chemists since several years. Roesky et al.¹ investigated the nucleophilic attack of different

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This paper is dedicated to Professor Louis D. Quin on the occasion of his 86th birthday.

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Compound	$\delta(P1)$ (ppm)	$\delta(P2)$ (ppm)	$^{2}J_{\mathrm{PP}}$ (Hz)
$\overline{P_4 S_9 N^- (2)^1}$	67.8	32.8	21.5
$P_4S_8(NC(S)Ph)_2 (3)^2$	67	30	21
$P_4S_{10} + 2 PhCN^3$	67.6	32.8	21.5
$\alpha - P_4 S_9^4$	64.6	48.8	96.3
$\beta - P_4 S_9^5$	52.0	44.2	30.5
$P_4S_{10}^4$	56.1	_	_

Table 1 Comparison of ³¹P NMR shifts and coupling constants for 2, 3, P₄S₉ and P₄S₁₀ (for comparison)

anions on P_4S_{10} already in 1970. Mainly, alkali metal salts of cyanide, azide, and thiocyanate were allowed to react with phosphorus(V) sulfide in acetonitrile. The reaction with $[(n-C_3H_7)_4N][(N_3)_2PS_2]$ in MeCN yielded a white precipitate, which was characterized using IR- and ³¹P NMR spectroscopy. The ³¹P NMR spectrum of this compound showed two triplets of equal intensity (Table 1). For its structure, a P_4S_{10} motive with one endocyclic sulfur being substituted by a nitrogen atom, resulting in the $(n-C_3H_7)_4N^+$ salt of the anion $P_4S_9N^-$ (I) was proposed (Figure 1).

Eight years later, Retuert et al.² observed nearly identical ³¹P NMR signals, when they investigated a suspension of P_4S_{10} in PhCN. They claimed the structure of the orange crystalline product, resulting from this reaction, to be a neutral P_4S_{10} adamantane-like cage, with two exocyclic sulfur atoms being substituted by =N-CS-C₆H₅ groups (Figure 2).

Neels and coworkers³ tried to answer the question, to which of the above-mentioned compounds the observed ³¹P NMR shift can be assigned. For the formation of the product, acetonitrile was used as solvent, so it is likely, that it is generally formed by reaction of P_4S_{10} with nitriles. They reproduced the synthesis of Retuert and isolated crystals of the 3,5-diphenyl-1,2,4-dithiazolium salt of **2** and determined the structure using single-crystal X-ray diffraction.

In the course of our investigations on the reactivity of P_4S_{10} , we took a closer look at the influence of different nitrogen-containing basic solvents on its reaction behavior.

RESULTS AND DISCUSSION

 P_4S_{10} was dissolved in benzonitrile or propionitrile on prolonged heating. ³¹P NMR spectra of the reaction solutions showed the formation of complex mixtures of products. In both cases, also ³¹P NMR signals indicating the presence of compound **2** were observed. This was also the case, when pyridine and 2,2'-bipyridine was added to the solution.

 $S = P \\ S = S$

Figure 1 Structure of the $P_4S_9N^-$ anion (2) by Roesky.¹



Figure 2 Structure of $P_4S_8(NC(S)C_6H_5)$ (3) by Retuert.²

The reaction of P_4S_{10} with dimethyl cyanamide resulted in the isolation of an unexpected product. Refluxing P_4S_{10} in dimethyl cyanamide yields a brown reaction solution. Here, also a complex mixture of different products could be observed in the ³¹P NMR. From this solution, a small amount of colorless crystals could be obtained. The product was identified by single-crystal X-ray diffraction as the novel compound 4,4'-oxybis(2,6-bis(dimethylamino)-4*H*-1,3,5,4-thiadiazaphosphinine 4-oxide) (1) (Figure 3).

In the literature, only one compound has been reported, containing a 1,3,5,4-thiadiazaphosphinine ring, which has been characterized in terms of single-crystal X-ray diffraction. Woollins et al.⁶ described the formation of the *P*-ferrocenyl-substituted 2,6-bis(dimethylamino)-1,3,5,4-thiadiazaphosphorine-4-sulfide (**5**) in good yield together with small amounts of the thiocyanate (**6**) from the reaction of the corresponding ferrocenyl perthiophosphonic acid anhydride (**4**) with an excess of dimethyl cyanamide as shown in Scheme 1.

Compound 1 crystallizes in the orthorhombic space group *Pbcn* with four formula units in the unit cell. Half of the molecule is symmetry generated, so it adopts perfect twofold symmetry. Figure 4 shows the molecular structure and selected atom distances and bond angles are listed.

The terminal N–C entities of two dimethyl cyanamide molecules are connected by a phosphorus atom at the nitrogen end and by a sulfur atom at the carbon end of the former CN group, forming a 1,3,5,4-thiadiazaphosphinine ring. In contrast to the thiadiazaphosphinine ring in **5**, which adopts a distorted boat conformation,⁶ the phosphinine ring in **1** deviates only slightly from planarity with values of the torsion angles within the ring between -3.9(4) and $1.1(5)^{\circ}$. A comparison of atom distances and bond angles of the thiadiazaphosphinine ring in **1** and **5** is presented in Table 2.

What attracts attention is that the bond lengths found in 1 and 5 are all in about the same range. The P–N bond distances in 1 are in the range, expected for P–N single bonds and are slightly shorter compared with those in 5. The C–S bond lengths in both compounds are practically equal. The endocyclic C–N bond lengths within the ring of 1 and 5 correspond to double bonds. The exocyclic C–N distances to the dimethylamino groups are clearly



Figure 3 Chemical structure of 4,4'-oxybis(2,6-bis(dimethylamino)-4*H*-1,3,5,4-thiadiazaphosphinine 4-oxide) (1).



Scheme 1 Synthesis of compound 5.6

shortened compared with C–N single bonds. Together with the coplanarity of the methyl groups, this indicates a delocalization of the nitrogen lone pair as shown in Scheme 2.

For a discussion of the structural parameters of the diphosphate moiety, the closely related pyrophosphate derivative 7^8 and the diphosphoric tetraamides $8^{,9-11}$ 9^{12} (Figure 5)



Figure 4 Molecular structure of **1** (two different viewing directions). Thermal ellipsoids are set at 50% probability level. Hydrogen atoms are omitted for clarity. Symmetry operation: i = 1-x, y, 0.5–z. Selected atom distances (Å) and bond angles (°) (standard uncertainties are given in brackets): P1–O1 1.496(2), P1–O2 1.607(2), P1–N1/P1–N2 1.626(3)/1.617(3), N1–C1/N2–C2 1.273(4)/1.295(4), S1–C1/S1–C2 1.786(3)/1.774(3), C1–N4/C2–N3 1.348(4)/1.342(4); O1–P1–O2 108.0(2), P1–O2–P1ⁱ 134.2(2), O1–P1–N1 123.9(2), O1–P1–N2 113.6(2), O2–P1–N1 105.2(2), O2–P1–N2 104.5(2).

	1 ^a	5 ^a	Ref. ⁷
P–N	1.626(3)/1.617(3)	1.648(6)/1.664(4)	1.652(24)
N–C	1.273(4)/1.295(4)	1.289(6)/1.290(6)	1.279(8)
C-NMe ₂	1.348(4)/1.342(4)	1.365(6)/1.335(6)	1.419(17)
C–S	1.786(3)/1.774(3)	1.788(5)/1.771(5)	1.712(13)
N-P-N	111.7(2)	108.2(2)	
P-N-C	125.6(3)/126.4(3)	122.6(4)/121.0(4)	
N-C-S	126.8(3)/127.1(3)	125.4(5)/127.3(4)	
C–S–C	102.2(2)	101.0(2)	

Table 2 Comparison of atom distances (Å) and bond angles ($^{\circ}$) within the thiadiaza-phosphinine ring in compounds **1** and **5**⁶ and standard values compiled by Allen⁷

^aStandard uncertainties are given in brackets.



Scheme 2 Mesomerism in the 1,3,5,4-thiadiazaphosphinine rings of 1.

can be consulted for comparative reasons. In the bridging O–P–O–P–O entity, the bond lengths between phosphorus and the terminal oxygen atoms (1.496(2) Å) are shorter as compared with the P–O distance to the bridging oxygen atom (1.607(2) Å) as was to be expected. Both values are in good accordance with those of 1.444-1.497 Å and 1.591-1.627 Å, respectively, reported for compounds **7**–**9**.^{8–12} The P–O–P angle $(134.2(2)^{\circ})$ is smaller compared to that observed in **7**, probably as consequence of the bulkier substituents of the latter. The value of **1**, however, fits well to those found in the tetraamides **8** and **9** $(125.1-133.8^{\circ})$.^{9–12}

The three-dimensional buildup of the structure is affected by several intra- and intermolecular interactions. An overview can be found in Table 3.

One would expect the two thiadiazaphosphinine rings in 1 to be oriented *trans* to each other as they are rather bulky. However, a *cis* orientation of the two phosphinine rings is observed. A similar arrangement in the solid state is found for the triazaphosphinine rings in $7.^8$ The observed orientation is most probably caused by three different electrostatic interactions in the molecular unit (Figure 6).

Hydrogen bonds between H3A and N3, as well as between H6A and N2 are observed within one asymmetric unit. The donor–acceptor distances are with 2.717(5) and 2.715(5) Å

D–H···A	d(D–H) (Å)	$d(H\cdots A)$ (Å)	$d(D \cdots A) (Å)$	< D-H…A (°)
С3–Н3А…N3	0.98(1)	2.37(1)	2.717(5)	100(1)
C6-H6A…N2	0.98(1)	2.47(1)	2.715(5)	94(1)
C3-H3C···N5 ⁱ	0.98(1)	2.58(1)	3.492(6)	155(1)
C3 ⁱⁱ –H3B ⁱⁱ …O1	0.98(1)	2.31(1)	3.260(5)	165(1)

Table 3 Intra- and intermolecular interactions in 1 (van der Waals radii [Å]: H: 1.20; C: 1.70; N: 1.55; O: 1.52)¹³

Symmetry codes: i = 1-x, y, 0.5-z; ii = 1.5-x, 0.5-y, z. Standard uncertainties are given in brackets.





Figure 5 Structurally characterized diphosphoric tetraamides.^{8–12}

well below the sum of the van der Waals radii of carbon and nitrogen (3.25 Å). These are rather strong interactions and have therefore a great influence on the structure, prohibiting rotation of the methyl groups. This allows the heterocycles to move closer together. The interaction between H3C and N5 connects both rings with a D…A distance of 3.492(6) Å. This electrostatic interaction is rather weak but nevertheless results in the rings being kept together.

In the crystal of **1**, one molecule is connected to four others via C3–H3B···O1 interactions (Figure 7). The contact of the carbon to the acceptor oxygen atom has a D···A distance of 3.260(5) Å and the D–H···A angle of $164.6(3)^{\circ}$.

These intermolecular interactions lead to the formation of chains along the *c*-axis (Figure 8, upper picture). The molecules are further interconnected to form layers perpendicular to the direction of propagation of these chains (Figure 8, lower picture).

Possible Mechanism of Formation

Regarding the formation mechanism of compound 1, we can only speculate (Scheme 3). Obviously, traces of water are responsible for the presence of the oxygen atoms.



Figure 6 C-H…N interactions in 1.

The compound may have formed from the reactive species (I). This species is analogous to the bis(pyridine) adduct of P_2S_5 ,¹⁴ which is known to be stable and isolatable. In contrast, I contains a reactive $-C \equiv N$ bond, which undergoes cyclization with one of the terminal sulfur atoms, yielding the intermediate II. A similar intermediate has been considered for the formation of the thiadiazaphosphinine ring in 5.⁶ This species reacts further with more dimethyl cyanamide, which is formally inserted into the P–S bond of the four-membered ring in II yielding III. In the presence of water, III is converted to the isolated product 1.



Figure 7 C-H···O interactions, connecting the molecules in 1. Symmetry operation: ii = 1.5-x, 0.5-y, z.



Figure 8 Layers perpendicular and chains along the *c*-axis in 1.

CONCLUSION

Here, the new pyrophosphate derivative 4,4'-oxybis(2,6-bis(dimethylamino)-4*H*-1,3,5,4-thiadiazaphosphinine 4-oxide) (1) is presented. Its unexpected formation in the course of the reaction of P_4S_{10} and dimethyl cyanamide shows the variable reactivity of P_4S_{10} depending on the nitrogen base employed. Compound 1 is the second representative with a 1,3,5,4-thiadiazaphosphinine ring, which could be characterized using single-crystal X-ray diffraction. The presence of a planar thiadiazaphosphinine ring in 1, in contrast to the boat conformation in 5, points to a structurally flexible ring system. The conformation of 1 is mainly influenced by electrostatic C–H…N and C–H…O interactions. These intraand intermolecular hydrogen bonds lead to a layered arrangement in the crystal.

EXPERIMENTAL

Dimethyl cyanamide was obtained from Sigma–Aldrich Inc. and used as supplied without further purification. P_4S_{10} was commercially obtained (Riedel-de Häen) and was



Scheme 3 Proposed mechanism for the formation of 1.

purified by extraction with CS_2 before use. ³¹P NMR spectra were recorded using a Jeol EX 400 Eclipse instrument operating at 161.997 MHz. Chemical shifts are referred to 85% H₃PO₄ as external standard. All spectra were measured, if not mentioned otherwise, at 25 °C.

X-ray Crystallography. An Oxford XCalibur3 diffractometer equipped with a CCD area detector was employed for data collection using Mo-K_{α} radiation ($\lambda = 0.71073$ Å). The structures were solved using direct methods (SIR2004)¹⁵ and refined by full-matrix least-squares on F^2 (SHELXL-97).¹⁶ All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in difference Fourier maps and placed with a C–H distance of 0.98 Å for C–H bonds. Intra- and intermolecular contacts were analyzed with DIA-MOND (Version 3.2i), thermal ellipsoids are drawn at the 50% probability level. Selected crystallographic data and refinement details for the structure determination of compound 1 are summarized in Table 4. CCDC 966235 contains the supplementary crystallographic data for compound 1. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Reaction of P₄S₁₀ with Benzonitrile and Propionitrile

 P_4S_{10} (0.25 mmol, 111 mg) in 1.5 mL of benzonitrile was heated to 120°C for 3 h, when a dark yellow solution was obtained. The ³¹P NMR spectrum of the reaction solution showed the signals of an $A_2 \times_2$ spin system as main product (86%): $\delta_A = 68.9$, $\delta_X = 33.9$, $J_{AX} = 21.5$ Hz.

Similarly, P_4S_{10} (0.27 mmol, 121 mg) in propionitrile (1.5 mL) was heated to 100°C for 4 h. After cooling to ambient temperature, the remaining P_4S_{10} was separated by filtration. The ³¹P NMR spectrum of the dark yellow filtrate showed a series of signals in

	1
Empirical formula	$C_{12}H_{24}N_8O_3P_2S_2$
Formula mass	454.45
T (K)	173(2)
Crystal size (mm)	$0.4 \times 0.35 \times 0.05$
Crystal description	Colorless block
Crystal system	Orthorhombic
Space group	Pbcn
a (Å)	11.4631(8)
b (Å)	12.4813(8)
c (Å)	14.0977(11)
V (Å ³)	2017.0(2)
Z	4
$\rho_{\text{calc}} (\text{g/cm}^{-3})$	1.497
$\mu \text{ (mm}^{-1})$	0.454
F(000)	952
θ range (°)	4.17-26.00
Index ranges	$-14 \le h \le 14$
	$-15 \le k \le 15$
	$-17 \le l \le 13$
Reflns. collected	9648
Refins. obsd.	1233
Reflns. unique	1952
R (int)	0.0920
$R_1, wR_2 \ (2\sigma \ \text{data})$	0.0519, 0.1024
R_1, wR_2 (all data)	0.0983, 0.1218
GOOF on F^2	0.997
Large diff. peak/hole (e/Å)	0.333/-0.260

Table 4 Crystallographic and refinement data for 1

the range of $\delta = 155-20$ ppm and with a relative intensity of 38% the signals of an A₂X₂ spin system: $\delta_A = 70.2$, $\delta_X = 34.4$, $J_{AX} = 21.5$ Hz.

Reaction of P₄S₁₀ with Dimethyl Cyanamide

 P_4S_{10} (0.37 mmol, 168 mg) was refluxed for 3 h of dimethyl cyanamide (1.5 mL) yielding a dark yellow solution. The ³¹P NMR spectrum of the reaction solution indicated the presence of a complex mixture of products and displayed main signals at $\delta = 64.8, 61.1, 18.2, 16.9, and 11.6$ ppm. After 7 days, a small amount of colorless block-shaped crystals of **1** were obtained from the solution.

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