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The Crystal and Molecular Structures of 2-Thiono-2-*N*-(diisopropylamino)-1,3,2-dithiaphosphorinane and of 2-Thiono-2-aziridino-1,3,2-dithiaphosphorinane

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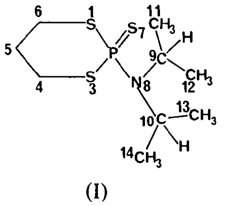
The structures of 2-thiono-2-*N*-(diisopropylamino)-1,3,2-dithiaphosphorinane (I) and of 2-thiono-2-aziridino-1,3,2-dithiaphosphorinane (II) have been determined from X-ray data by direct methods. Crystals of I are monoclinic, space group $P2_1/c$, $a = 14{\cdot}027(1)$, $b = 7{\cdot}535(1)$, $c = 13{\cdot}661(1)$ Å, $\beta = 102{\cdot}41(1)°$, $Z = 4$. Crystals of II are orthorhombic, space group *Pnma*, $a = 11{\cdot}064(5)$, $b = 10{\cdot}044(4)$, $c = 8{\cdot}508(7)$ Å, $Z = 4$. The two molecules adopt a chair conformation, with the P=S bond axial in I, and equatorial in II. The sum of the angles around the N atom in I is 360° and the plane defined by the atoms attached to this N almost bisects the SPS angle of the ring. II has a plane of symmetry which bisects the aziridine ring.

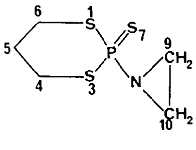
Introduction

Only a few X-ray structural studies have been reported of six-membered-ring dithiaphosphorinanes compared with numerous studies of 1,3,2-dioxaphosphorinanes (Corbridge, 1974; Khaikin & Vilkov, 1972; Silver & Rudman, 1972; Dutasta, Grand, Robert & Taieb, 1974; Grand & Robert, 1975; Grand, Martin, Robert & Tordjman, 1975; Bartczak, Christensen, Kinas & Stec, 1975; Cameron, Gałdecki & Karolak-Wojciechowska, 1976). In a previous paper (Grand, Martin & Robert, 1975) it was shown that, in the solid state, the 2-*R*-2-thiono-1,3,2-dithiaphosphorinanes (R = CH_3, Cl) adopt a chair conformation with the P—*R* bond oriented in the axial position. As it is known from NMR studies at room temperature (Hutchins & Maryanoff, 1972; Martin, Robert & Taieb, 1976) that in 2-*R*-1,3,2-dithiaphosphorinanes the P—*R* bond can adopt either axial (R = Cl, CH_3, C_6H_5, OCH_3, N◁) or equatorial orientations [N(*i*-Pr)$_2$, *t*-Bu-*N*-*i*-Pr] it was interesting to check if such a situation can occur in the corresponding 2-thiono derivatives.

The 2-thiono-2-*N*-(diisopropylamino)-1,3,2-dithiaphosphorinane (I) and the 2-thiono-2-aziridino-1,3,2-dithiaphosphorinane (II) have been chosen for X-ray analysis because one can expect from NMR studies an equatorial orientation of the P—N bond in I and an axial orientation in II. An additional factor of interest was to provide a better understanding of the P—N rotation barrier in various 1,3,2-dithiaphosphorinanes bearing an extracyclic P—N bond (Martin & Robert, 1976).



(I)



(II)

Experimental

I and II are readily obtained by reacting 2-chloro-1,3,2-dithiaphosphorinane with the corresponding secondary amine (Martin, Robert & Taieb, 1976) followed by addition of elemental sulphur (Edmundson, 1962). The crystals of I used in this investigation were recrystallized from a 9:1 hot hexane–benzene mixture, the crystals of II from benzene.

Table 1. *Crystal data*

2-Thiono-2-*N*-(diisopropylamino)-1,3,2-dithiaphosphorinane
$C_9H_{20}NPS_3$

FW 269·43	a =	14·027 (1) Å
$F(000)$ = 576	b =	7·535 (1)
Monoclinic, space group $P2_1/c$	c =	13·661 (1)
$D_m = 1{\cdot}27\,(2)$ g cm^{-3}	β	102·41 (1)°
$D_x = 1{\cdot}269$	V	1410·04 Å^3
	Z =	4

2-Thiono-2-aziridino-1,3,2-dithiaphosphorinane
$C_5H_{10}NPS_3$

FW 211·30	a =	11·064 (5) Å
$F(000)$ = 440	b	10·044 (4)
Orthorhombic, space group *Pnma*	c =	8·508 (7)
$D_m = 1{\cdot}45\,(2)$ g cm^{-3}	V =	945·47 Å^3
$D_x = 1{\cdot}48$	Z =	4

The crystals of I are monoclinic, space group $P2_1/c$ ($h0l$ absent for l odd, $0k0$ for k odd). For II the crystal was assigned to the orthorhombic system on the basis of the Weissenberg photographs. The observed systematic absences ($0kl$ for $k + l$ odd, $hk0$ for h odd) suggested that the space group was either $Pnma$ or $Pn2_1a$. The intensity statistics and the refinement of the structure revealed that the correct choice was $Pnma$. The cell dimensions and their standard deviations determined by least squares from 15 reflexions are given in Table 1 with other crystal data.

The intensities of 2986 independent reflexions ($3° < \theta < 70°$) for I and of 1180 for II were recorded with Ni-filtered Cu $K\alpha$ radiation on the four-circle Siemens diffractometer of the Laue–Langevin Institute at Grenoble. The intensity of a standard reflexion ($31\bar{4}$ for I, and $4\bar{4}3$ for II) was measured periodically and showed no decrease during data collection. The intensities were measured by the five-point method (Troughton, 1969) and corrected for Lorentz and polarization factors, but not for absorption.

Both structures were solved with *MULTAN* (Germain, Main & Woolfson, 1971). For I, the solution was based on 200 reflexions with $E > 1·77$. The E map with the best figure of merit revealed the positions of all the non-hydrogen atoms. The structure was refined with *ORFLS* (Busing & Levy, 1959) (P, S, N, C anisotropic) until $R_w = [\Sigma\, w(F_o - F_c)^2/\Sigma\, wF_o^2]^{1/2}$ had converged to 0·067 and $R = (\Sigma\,|F_o - F_c|/\Sigma\,|F_o|)$ to 0·050. For II a set of 100 reflexions with $E > 1·64$ was used. The set of phases with the highest figures of merit proved to give a sensible structure in which all the non-hydrogen atoms were located. In $Pn2_1a$, R and R_w reached 0·091 and 0·132 respectively; but some important discrepancies appeared in corresponding bond lengths and angles.

Table 2. *Fractional coordinates* (×10⁴)

	x	y	z
2-Thiono-2-*N*-(diisopropylamino)-1,3,2-dithiaphosphorinane			
P	7097 (1)	9229 (2)	3762 (1)
S(1)	6121 (1)	10525 (2)	2612 (1)
S(3)	6497 (1)	7292 (2)	4332 (1)
C(4)	6368 (1)	1182 (10)	5068 (6)
C(5)	5637 (5)	12587 (9)	4139 (6)
C(6)	5228 (5)	11262 (9)	3335 (6)
S(7)	6497 (1)	7292 (2)	4332 (1)
N(8)	8037 (3)	8802 (5)	3281 (3)
C(9)	8454 (4)	6998 (7)	3159 (4)
C(10)	8513 (4)	1036 (8)	2877 (4)
C(11)	8887 (6)	6118 (10)	4171 (5)
C(12)	7716 (6)	5779 (9)	2478 (6)
C(13)	9557 (5)	10588 (11)	3457 (6)
C(14)	8446 (6)	10096 (10)	1731 (5)
2-Thiono-2-aziridino-1,3,2-dithiaphosphorinane			
P	2050 (1)	2500	9098 (1)
S(1)	2269 (1)	840 (1)	7706 (2)
C(6)	1170 (4)	1215 (5)	6140 (6)
C(5)	1145 (7)	2500	5240 (8)
S(7)	3161 (2)	2500	10849 (2)
N	570 (4)	2500	9463 (6)
C(9)	104 (5)	1754 (5)	10839 (7)

Table 3. *Bond distances* (Å) *with standard deviations in parentheses*

2-Thiono-2-*N*-(diisopropylamino)-1,3,2-dithiaphosphorinane			
P–S(1)	2·086 (2)	P–S(3)	2·092 (2)
S(1)–C(6)	1·853 (7)	S(3)–C(4)	1·839 (7)
C(4)–C(5)	1·504 (10)	C(5)–C(6)	1·562 (11)
P–S(7)	1·930 (2)	P–N(8)	1·627 (4)
N–C(9)	1·503 (7)	N–C(10)	1·499 (6)
C(9)–C(11)	1·536 (9)	C(9)–C(12)	1·539 (9)
C(10)–C(13)	1·558 (8)	C(10)–C(14)	1·519 (9)
2-Thiono-2-aziridino-1,3,2-dithiaphosphorinane			
P–S(1)	2·059 (1)	P–S(7)	1·932 (2)
S(1)–C(6)	1·843 (5)	C(6)–C(5)	1·531 (6)
P–N	1·667 (5)	N–C(9)	1·482 (6)
C(9)–C(10)	1·497 (11)		

Table 4. *Bond angles* (°) *with standard deviations in parentheses*

2-Thiono-2-*N*-(diisopropylamino)-1,3,2-dithiaphosphorinane			
P–S(1)–C(6)	97·7 (0·2)	P–S(3)–C(4)	98·5 (0·2)
S(1)–C(6)–C(5)	112·7 (0·5)	S(3)–C(4)–C(5)	113·3 (0·5)
S(1)–P–S(3)	103·1 (0·1)	C(4)–C(5)–C(6)	115·3 (0·5)
S(7)–P–S(1)	112·6 (0·1)	S(7)–P–S(3)	112·6 (0·1)
N–P–S(1)	104·5 (0·2)	N–P–S(3)	104·2 (0·2)
P–N–C(9)	126·3 (0·4)	P–N–C(10)	117·4 (0·3)
N–C(9)–C(11)	112·3 (0·5)	N–C(9)–C(12)	112·2 (0·5)
N–C(10)–C(13)	111·1 (0·5)	N–C(10)–C(14)	110·2 (0·5)
C(11)–C(9)–C(12)	111·9 (0·5)	C(13)–C(10)–C(14)	112·5 (0·5)
N–P–S(7)	118·3 (0·1)	C(9)–N–C(10)	116·2 (0·4)
2-Thiono-2-aziridino-1,3,2-dithiaphosphorinane			
P–S(1)–C(6)	100·0 (0·2)	S(1)–C(6)–C(5)	113·8 (0·4)
S(1)–P–S(3)	108·1 (0·1)	S(1)–P–S(7)	111·7 (0·1)
S(7)–P–N	118·8 (0·2)	S(1)–P–N	102·9 (0·1)
C(4)–C(5)–C(6)	114·8 (0·6)	N–C(9)–C(10)	59·6 (0·2)
P–N–C(9)	119·2 (0·4)	C(9)–N–C(10)	60·7 (0·5)

Refinement in $Pnma$, with the molecule in special position 4(c), reduced R and R_w to 0·054 and 0·071 respectively. The intensity statistics confirm the centrosymmetric space group.

Fractional coordinates are listed in Table 2;* Tables 3 and 4 contain bond distances and angles.

Discussion

In I and II the ring adopts, in the solid state, a chair conformation (Figs. 1 and 2). The flattening of the ring at the P end is less pronounced than in the dioxa-

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* A list of structure factors and thermal parameters has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32283 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

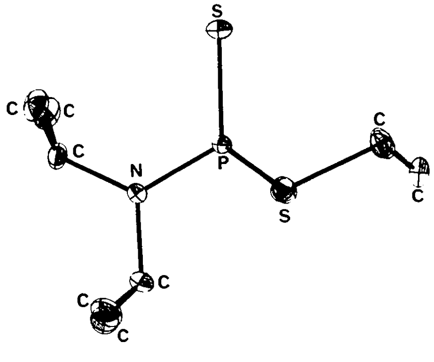

Fig. 1. Structure of 2-thiono-2-*N*-diisopropylamino-1,3,2-dithiaphosphorinane.

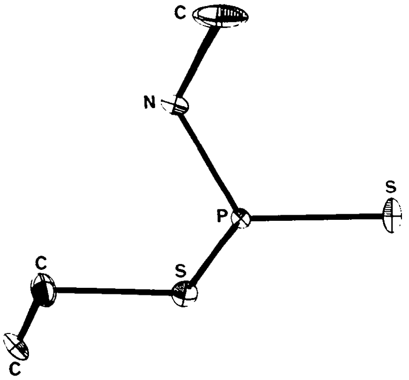

Fig. 2. Structure of 2-thiono-2-aziridino-1,3,2-dithiaphosphorinane.

phosphorinanes and is smaller in I where the P—N bond is equatorial. For comparison, the angles between the least-squares plane defined by S(3), C(4), C(6), S(1) and the planes containing S(1), P, S(3) and C(4), C(5), C(6) (α_1 and α_2 respectively) in four different 1,3,2-dithiaphosphorinanes are shown in Table 5.

The change of the P—N bond orientation observed in the three-coordinated P dithiaphosphorinanes when the amino group is changed from aziridine to an acyclic amine (Martin, Robert & Taieb, 1976) is also observed here with the corresponding 2-thiono compounds in the solid state. The P—N bond is equatorial in I and axial in II. P—N is slightly longer in II (1·667 Å), where the N is pyramidal, than in I (1·627 Å), where it is planar. Such a tendency has been observed in other molecules (Khaikin & Vilkov, 1971) and could be indicative of π bonding (Cotton, Troup, Casabianca & Riess, 1974).

In I the trigonal exocyclic N and the atoms to which it is bonded form a planar system. Such planarity is common in amino-phosphorus compounds in which an acyclic amino group is in α position to a three- (Morris & Nordman, 1969; Brittain, Smith, Lee, Cohn & Schwendeman, 1971; Forti, Damiani & Favero, 1973) or four-coordinate (Camerman & Camerman, 1973; García-Blanco & Perales, 1972; Sternglanz, Einspahr & Bugg, 1974; Clardy, Mosbo & Verkade, 1974) P compound. The plane of the C—N bonds bisects the S(1)—P—S(3) angle and N—C(9) eclipses the P=S double bond. This stereochemistry around the P—N bond seems to be quite general in three- and four-coordinated P compounds and can explain the equatorial orientation of the P—N bond. An axial orientation of P—N will give severe 1–3 interactions of the amino group with the ring protons. The two CNP bond angles are quite different (126·2 and 117·5°). The larger, C(9)—N—P, can be explained as due to the S(7)···C(9) interaction, which also increases the S(7)—P—N angle (118·3°).

Table 5. *Puckering of the six-membered ring in various 2-thiono-2R-1,3,2-dithiaphosphorinanes*

R	CH_3	Cl	N(*i*-Pr)$_2$	N◁
α_1(°)	54·0	52·0	62·1	54·0
α_2(°)	61·5	62·0	63·4	64·1

In II where the N is pyramidal, the P=S double bond bisects exactly the aziridine ring. Such a staggered stereochemistry around the P—N bond is similar to that observed for two of the three P—N bonds in triethylenethiophosphoramide (Subramanian & Trotter, 1969).

The P=S lengths are equal within the limit of errors in I and II although the P=S bond adopts a different orientation in the two molecules, axial in I, equatorial in II. These values may be compared to those found in 2-thiono-1,3,2-dithiaphospholanes (Lee & Goodacre, 1971) and in 2-thiono-1,3,2-dithiaphosphorinanes (Grand, Martin & Robert, 1975).

All interatomic distances up to 4 Å were calculated. With the van der Waals radii of Pauling (1960), no abnormal contacts were detected.

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The Structure of Monoclinic Cadmium Oxydiacetate Trihydrate

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The structure of monoclinic $CdO(CH_2COO)_2.3H_2O$ has been determined and refined to $R = 0·069$. The crystals are monoclinic, space group $P2_1/c$, with $a = 6·3848$ (7), $b = 10·2093$ (9), $c = 14·0470$ (16) Å, $\beta = 101·753$ (10)°, $Z = 4$. The crystal structure consists of discrete units of composition $2CdO(CH_2COO)_2.6H_2O$ held together by hydrogen bonds. In each unit, the two Cd atoms are bridged by two O atoms, one from each oxydiacetate ion, the remaining coordination sites about the seven-coordinate Cd atom being occupied by two more O atoms from one of the bridging oxydiacetate ions, giving a tridentate chelate, and by three water O atoms. The coordination polyhedron is a pentagonal bipyramid and within each unit the two bipyramids have one equatorial edge in common. The Cd—O distances range from 2·236 (7) to 2·492 (8) Å; the Cd—Cd distance in a unit is 3·968 (1) Å. The non-hydrogen atoms are coplanar in each oxydiacetate half with an angle of 8° between the planes.

Introduction

In this paper the structure of CDOXY II, one of the three Cd oxydiacetate hydrates reported by Boman (1974), is described in detail. Descriptions of the other two, CDOXY III and CDOXY I, have already been given (Boman, 1977*a*,*b*). A brief comparison between the three structures, as well as their relations to some similar Cd structures, is included.

Crystal data

Cadmium oxydiacetate trihydrate or di-μ-oxydiacetato-bis(triaquacadmium), $CdC_4H_{10}O_8$ (CDOXY II); FW 298·5 g mol^{-1}; monoclinic, space group $P2_1/c$; $a = 6·3848$ (7), $b = 10·2093$ (9), $c = 14·0470$ (16) Å, $\beta = 101·753$ (10)°; $V = 896·4$ Å^3; $Z = 4$; μ(Cu $K\alpha$) = 204·8 cm^{-1}; $D_m = 2·18$, $D_x = 2·21$ g cm^{-3}.