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Dichloro(dimethylsulfoximino)-phosphane

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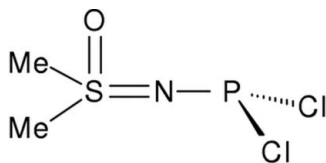
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Key indicators: single-crystal X-ray study; $T = 143$ K; mean $\sigma(\text{P-N}) = 0.002$ Å; R factor = 0.025; wR factor = 0.066; data-to-parameter ratio = 22.6.

The title compound, $\text{C}_2\text{H}_6\text{Cl}_2\text{NOP}$ S, crystallizes as dimers *via* C—H \cdots O hydrogen bonds. S—N [1.5446 (16) Å] is shorter than P—N [1.618 (2) Å], although the latter is a short phosphorus–nitrogen single bond.

Related literature

For related literature, see: Bond *et al.* (1985); Desiraju (1996); Scholz *et al.* (1989).



Experimental

Crystal data

$\text{C}_2\text{H}_6\text{Cl}_2\text{NOP}$ S
 $M_r = 194.01$
 Triclinic, $P\bar{1}$
 $a = 5.987$ (2) Å
 $b = 7.723$ (3) Å
 $c = 8.716$ (3) Å
 $\alpha = 71.59$ (3)°
 $\beta = 79.73$ (3)°
 $\gamma = 78.25$ (3)°
 $V = 371.5$ (2) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 1.28$ mm⁻¹
 $T = 143$ (2) K
 $0.45 \times 0.25 \times 0.25$ mm

Data collection

Stoe Stadi-4 diffractometer
 Absorption correction: none
 3100 measured reflections
 1716 independent reflections
 1554 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.012$
 3 standard reflections
 frequency: 90 min
 intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.066$
 $S = 1.11$
 1716 reflections
 76 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.48$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.46$ e Å⁻³

Data collection: *DIF4* (Stoe & Cie, 1992); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS90* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Bruker, 1997); software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2385).

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supplementary materials

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Dichloro(dimethylsulfoximino)phosphane

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Comment

The title compound has been used as a starting material in a research project devoted to the synthesis and structural characterization of novel diphosphenes [Scholz *et al.* (1989)]. However, single crystals of dichloro-(dimethylsulfoximino)phosphane have not been obtained until now due to the exceedingly moisture-sensitive nature of the compound. Such crystals have now been obtained by slow cooling of a saturated solution in diethyl ether to -78°C .

The sulfur atom is essentially tetrahedrally coordinated with angles between $104.16(9)^{\circ}$ [N—S—C2] and $117.27(9)^{\circ}$ [O—S—N]. A comparison with the structures of the *N*-(diisopropylphosphoryl)-, *N*-(diphenyldiphosphoryl)-, and *N*-(2,2-dimethylpropylenephosphoryl)-dimethylsulfoximides [Bond *et al.* (1985)] reveals similar distortions from an ideal tetrahedron with the widest angle always being O—S—N [$119.3(5)$, $118.0(7)$, $119.3(2)^{\circ}$]. The S—O bond length of $1.4426(14)\text{\AA}$ is typical of the relatively invariable S—O bond lengths in sulfonyl derivatives.

In accordance with the phosphoryl- sulfoximides, the S—N bond [$1.5446(16)\text{\AA}$] is shorter than the P—N bond [$1.6172(16)\text{\AA}$] implying a higher bond order between nitrogen and sulfur than between nitrogen and phosphorus. The P—N bond, however, is considerably shorter than a "regular" phosphorus nitrogen single bond, indicating a strong N \rightarrow P back bonding effect. Probably associated with this effect, the S—N—P angle [$134.40(10)^{\circ}$] is significantly widened beyond the normal value for trigonal geometry; the corresponding values for the phosphoryl-dimethylsulfoximides range from $123.8(6)$ to $128.5(3)^{\circ}$.

The phosphorus-chlorine bond distances are almost equal [P—Cl1 $2.1249(11)$, P—Cl2 $2.1086(10)\text{\AA}$] and are considerably longer than those in *N,N*-bis(dichlorophosphino)phenylamine [ranging from $2.009(9)$ to $2.056(9)\text{\AA}$] but shorter than those in dichloro(1,3-dimethyl-2-imidazole-2-ylideneimino)phosphane [$2.207(1)$ and $2.151(1)\text{\AA}$].

The O—S—N—P backbone of the title compound [torsion angle $66.43(17)^{\circ}$] adopts a conformation comparable to those of two of the linear phosphoryl-dimethylsulfoximides [63.36 , -69.84°]. The *N*-(2,2-dimethylpropylenephosphoryl)dimethylsulfoximide featuring an endocyclic phosphorus displays a corresponding O—S—N—P angle of 37.76° .

Two intermolecular C—H \cdots O hydrogen bonds are observed. The accumulation of inductive electron-withdrawing effects of the oxygen-sulfur-nitrogen triade presumably polarizes the methyl H atoms and enables them to form this often neglected type of intermolecular interaction, leading to dimers [Desiraju (1996)].

Experimental

The title compound is synthesized by reacting $\text{Me}_2\text{S}(\text{O})=\text{NSiMe}_3$ with excess phosphorus trichloride [Scholz *et al.* (1989)].

Refinement

H-atoms: rigid methyl. Absorption correction was based on delta-F (SHELXA, anonymous). An appropriate number of extra parameters was allowed for in calculating e.s.d.'s.

Figures

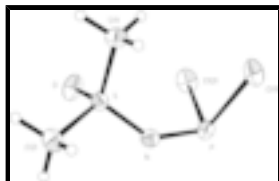


Fig. 1. The molecule of the title compound in the crystal. Thermal ellipsoids represent 50% probability levels. H-Atom radii are arbitrary.

Dichloro(dimethylsulfoximino)phosphane

Crystal data

$C_2H_6Cl_2NOPS$

$M_r = 194.01$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 5.987(2) \text{ \AA}$

$b = 7.723(3) \text{ \AA}$

$c = 8.716(3) \text{ \AA}$

$\alpha = 71.59(3)^\circ$

$\beta = 79.73(3)^\circ$

$\gamma = 78.25(3)^\circ$

$V = 371.5(2) \text{ \AA}^3$

$Z = 2$

$F_{000} = 196$

$D_x = 1.734 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 52 reflections

$\theta = 10\text{--}12.5^\circ$

$\mu = 1.28 \text{ mm}^{-1}$

$T = 143(2) \text{ K}$

Prism, yellow

$0.45 \times 0.25 \times 0.25 \text{ mm}$

Data collection

Stoe Stadi-4
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 143(2) \text{ K}$

ω/θ scans

Absorption correction: none

3100 measured reflections

1716 independent reflections

1554 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.012$

$\theta_{\text{max}} = 27.5^\circ$

$\theta_{\text{min}} = 3.2^\circ$

$h = -7 \rightarrow 5$

$k = -10 \rightarrow 10$

$l = -11 \rightarrow 11$

3 standard reflections

every 90 min

intensity decay: none

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.025$	$w = 1/[\sigma^2(F_o^2) + (0.0313P)^2 + 0.211P]$
$wR(F^2) = 0.066$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{\max} < 0.001$
1716 reflections	$\Delta\rho_{\max} = 0.48 \text{ e } \text{\AA}^{-3}$
76 parameters	$\Delta\rho_{\min} = -0.46 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: SHELXL97, $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.045 (4)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S	0.17482 (7)	0.29180 (6)	0.38517 (5)	0.01912 (12)
P	0.17739 (8)	0.05458 (6)	0.18258 (6)	0.02318 (13)
Cl1	0.30371 (9)	0.23989 (8)	-0.03857 (6)	0.03325 (14)
Cl2	-0.17262 (8)	0.16726 (8)	0.16807 (6)	0.03424 (14)
O	-0.0580 (2)	0.3199 (2)	0.46329 (18)	0.0316 (3)
N	0.2501 (3)	0.1195 (2)	0.32344 (18)	0.0223 (3)
C1	0.2263 (4)	0.4939 (3)	0.2292 (2)	0.0315 (4)
H1A	0.1222	0.5191	0.1471	0.038*
H1B	0.3859	0.4774	0.1783	0.038*
H1C	0.1996	0.5980	0.2751	0.038*
C2	0.3699 (4)	0.2653 (3)	0.5220 (2)	0.0295 (4)
H2A	0.3353	0.3710	0.5663	0.035*
H2B	0.5267	0.2588	0.4651	0.035*
H2C	0.3568	0.1512	0.6112	0.035*

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S	0.0170 (2)	0.0212 (2)	0.0189 (2)	-0.00231 (15)	-0.00131 (15)	-0.00641 (15)
P	0.0234 (2)	0.0232 (2)	0.0244 (2)	-0.00273 (17)	-0.00211 (18)	-0.01004 (18)
Cl1	0.0312 (3)	0.0456 (3)	0.0228 (2)	-0.0105 (2)	0.00312 (18)	-0.01045 (19)
Cl2	0.0200 (2)	0.0500 (3)	0.0353 (3)	-0.0084 (2)	-0.00360 (18)	-0.0140 (2)
O	0.0198 (7)	0.0409 (8)	0.0393 (8)	-0.0066 (6)	0.0059 (6)	-0.0231 (7)
N	0.0220 (7)	0.0218 (7)	0.0231 (7)	-0.0001 (6)	-0.0048 (6)	-0.0071 (6)
C1	0.0455 (12)	0.0204 (8)	0.0248 (9)	-0.0049 (8)	-0.0012 (8)	-0.0030 (7)
C2	0.0310 (10)	0.0333 (10)	0.0277 (9)	-0.0026 (8)	-0.0120 (8)	-0.0109 (8)

Geometric parameters (\AA , $^\circ$)

S—O	1.4438 (14)	C1—H1A	0.9800
S—N	1.5442 (16)	C1—H1B	0.9800
S—C2	1.753 (2)	C1—H1C	0.9800
S—C1	1.757 (2)	C2—H2A	0.9800
P—N	1.6177 (16)	C2—H2B	0.9800
P—Cl2	2.1087 (10)	C2—H2C	0.9800
P—Cl1	2.1247 (11)		
O—S—N	117.23 (9)	S—C1—H1B	109.5
O—S—C2	110.04 (10)	H1A—C1—H1B	109.5
N—S—C2	104.12 (9)	S—C1—H1C	109.5
O—S—C1	109.06 (10)	H1A—C1—H1C	109.5
N—S—C1	111.17 (10)	H1B—C1—H1C	109.5
C2—S—C1	104.38 (11)	S—C2—H2A	109.5
N—P—Cl2	105.63 (7)	S—C2—H2B	109.5
N—P—Cl1	104.32 (7)	H2A—C2—H2B	109.5
Cl2—P—Cl1	95.84 (4)	S—C2—H2C	109.5
S—N—P	134.40 (10)	H2A—C2—H2C	109.5
S—C1—H1A	109.5	H2B—C2—H2C	109.5
O—S—N—P	66.44 (17)	Cl2—P—N—S	-31.77 (15)
C2—S—N—P	-171.78 (14)	Cl1—P—N—S	68.62 (15)
C1—S—N—P	-59.94 (17)		

Fig. 1

