Dichloro(dimethylsulfoximino)-phosphane

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Received 29 May 2007; accepted 13 June 2007

Key indicators: single-crystal X-ray study; T = 143 K; mean |P–N| = 0.002 Å; R factor = 0.025; wR factor = 0.066; data-to-parameter ratio = 22.6.

The title compound, C2H6Cl2NOPS, crystallizes as dimers via C—H···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

C2H6Cl2NOPS  
M = 194.01  
Triclinic, P̅  
a = 5.987 (2) Å  
b = 7.722 (3) Å  
c = 8.716 (3) Å  
a = 71.59 (3)°  
β = 79.73 (3)°  
P = 1.28 mm−1  
T = 143 (2) K  
0.45 × 0.25 × 0.25 mm

Data collection

Stoe Stadi-4 diffractometer  
Absorption correction: none  
3100 measured reflections  
1716 independent reflections  
1554 reflections with I > 2σ(I)

Refinement

R[F2 > 2σ(F2)] = 0.025  
wr(RF) = 0.086  
S = 1.11  
1716 reflections  
76 parameters  
H-atom parameters constrained

Δρmax = 0.48 e Å−3  
Δρmin = −0.46 e Å−3

Data collection: DIF4 (Stoe & Cie, 1992); cell refinement: DIF4; data reduction: DIF4; 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.

Support of this work by the Otto-von-Guericke-Universität Magdeburg is gratefully acknowledged.

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

References

supplementary materials
Dichloro(dimethylsulfoximino)phosphane

S. Blaurock, M. Scholz, H. W. Roesky and F. T. Edelmann

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) [N—S—C2] and 117.27 (9)° [O—S—N]. A comparison with the structures of the N-(diisopropylphosphoryl)-, N-(diphenylphosphoryl)-, and N-(2,2-dimethylpropylene phosphoryl)-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)°]. The S—O bond length of 1.4426 (14)Å 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) Å] is shorter than the P—N bond [1.6172 (16) Å] 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 → P back bonding effect. Probably associated with this effect, the S—N—P angle [134.40 (10)°] 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)°.

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

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

Two intermolecular C—H···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 Me₂S(O)≡NSiMe₃ with excess phosphorus trichloride [Scholz et al. (1989)].
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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

C₂H₆Cl₂NOPS

Z = 2

F₀₀₀ = 196

Triclinic, P₁

Hall symbol: -P 1

Dₚ = 1.734 Mg m⁻³

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 52 reflections

θ = 10–12.5º

α = 71.59 (3)º

T = 143 (2) K

β = 79.73 (3)º

γ = 78.25 (3)º

V = 371.5 (2) Å³

Data collection

Stoe Stadi-4

diffractometer

Rint = 0.012

Radiation source: fine-focus sealed tube

θmax = 27.5º

0 = 10–12.5º

Cell parameters from 52 reflections

µ = 1.28 mm⁻¹

Mo Kα radiation

λ = 0.71073 Å

h = −7→5

θmin = 3.2º

k = −10→10

0 = 10–12.5º

l = −11→11

3100 measured reflections

3 standard reflections

1716 independent reflections

every 90 min

1554 reflections with I > 2σ(I)

intensity decay: none
Refinement

Refinement on $F^2$

Hydrogen site location: inferred from neighbouring sites

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.025$

$wR(F^2) = 0.066$

$S = 1.11$

1716 reflections

76 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

$U_{iso}$/*$U_{eq}$

### 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 ($Å^2$)

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Atomic displacement parameters (Å²)

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Geometric parameters (Å, °)

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Fig. 1