

Acta Cryst. (1999). **C55**, 1525–1526

Chloro(diisopropylamino)(phenyl)-phosphine sulfide

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(Received 6 April 1999; accepted 6 May 1999)

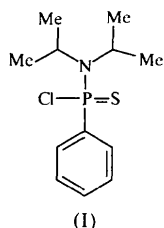
Abstract

The P atom of the title compound, C₁₂H₁₉ClNPS, has a slightly distorted tetrahedral geometry. The P—Cl and P=S bond lengths are 2.071 (1) and 1.923 (1) Å, respectively. The presence of C—H···π interactions appears to supplement van der Waals interactions in stabilizing the crystal packing.

Comment

Organophosphorous thionic esters containing the P=S group have been found to be useful nematicides on the worms which damage plant roots (Emsley & Hall, 1976). These compounds are also useful as insecticides, bactericides, flame retardants and lubricants (Ismail, 1975).

The phosphine sulfide is used as a ligand in metal coordination chemistry. Such compounds find applications as pesticides. The structure determination of the title compound, (I), was undertaken to study the effect of substitution on significant features of the conformation of the phosphorus.



The P—N bond length is considerably shorter than the reported values of 1.77 Å (Cruickshank, 1964) and 1.78 (6) Å (*cf.* Table 4.1.4 in *International Tables for X-ray Crystallography*, 1968). The P—N bond length has been correlated with the orbital electronegativity of groups of atoms (Bullen & Tucker, 1972). The length of this bond depends on the electronegativities of the substituents. The P atom is in a slightly distorted

tetrahedral geometry with the bond angles around P varying from 102.5 (1) to 117.9 (1)°, the average value being 109.3 (5)°.

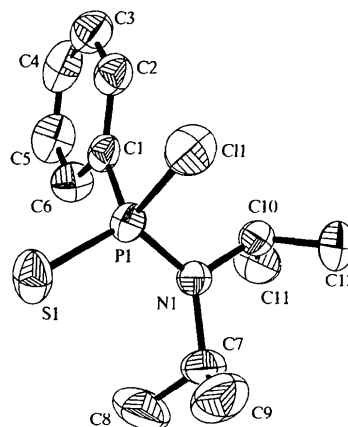


Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.

The two isopropyl groups make interplanar angles of 39.2 (3) and 73.9 (3)° with the phenyl ring, while they are mutually inclined at an angle of 67.0 (5)°. The methyl-H atoms of the isopropyl group participate in C—H···π type of interaction (Spek, 1990) that may provide additional stability along with van der Waals interactions in the packing of the molecules in the unit cell. An intramolecular C—H···Cl short contact is also observed.

Experimental

Diisopropylamine (8.90 g, 88.3 mmol) in hexane was added dropwise to a stirred solution of phenyldichlorophosphine (7.91 g, 44.2 mmol) at 273 K over a period of 45 min. After 15 h of stirring, the reaction mixture was filtered and the diisopropylamine hydrochloride precipitate was washed with hexane (40 ml). The filtrate along with the washings was pumped off completely to give a pale yellow liquid identified as pure chloro(diisopropylamino)(phenyl)phosphine (8.62 g, 80%). To a benzene solution (25 ml) of the chloro(diisopropylamino)(phenyl)phosphine (2.0 g, 8.2 mmol) at room temperature, elemental sulfur (0.26 g, 8.2 mmol) was added all at once and the resultant clear solution was heated under reflux for 4 h and brought to room temperature and pumped off. The residue was extracted with hexane (30 ml). The hexane solution was concentrated and cooled at 273 K for a day to isolate colourless, stable, needle-shaped crystals of the title compound (1.58 g, 70 mmol).

Crystal data

C₁₂H₁₉ClNPS
M_r = 275.76

Mo Kα radiation
λ = 0.71073 Å

Monoclinic

$P2_1/c$
 $a = 8.6086$ (3) Å
 $b = 11.5661$ (4) Å
 $c = 14.7650$ (5) Å
 $\beta = 91.554$ (1)°
 $V = 1469.58$ (9) Å³
 $Z = 4$
 $D_x = 1.246$ Mg m⁻³
 D_m not measured

Cell parameters from 3243 reflections

$\theta = 1.12$ – 28.35 °
 $\mu = 0.487$ mm⁻¹
 $T = 293$ (2) K
 Block
 $0.28 \times 0.12 \times 0.10$ mm
 Colourless

thanks the Universiti Sains Malaysia for a Visiting Post-doctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1290). Services for accessing these data are described at the back of the journal.

Data collection

Siemens SMART CCD area-detector diffractometer

1757 reflections with $I > 2\sigma(I)$

ω scans

$R_{\text{int}} = 0.082$

Absorption correction:

$\theta_{\text{max}} = 28.32$ °

empirical (SADABS; Sheldrick, 1996)

$h = -11 \rightarrow 11$

$T_{\text{min}} = 0.876$, $T_{\text{max}} = 0.953$

$k = 0 \rightarrow 15$

11 387 measured reflections

$l = 0 \rightarrow 19$

3622 independent reflections

Refinement

Refinement on F^2

$w = 1/[\sigma^2(F_o^2) + (0.042P)^2]$

$R[F^2 > 2\sigma(F^2)] = 0.062$

where $P = (F_o^2 + 2F_c^2)/3$

$wR(F^2) = 0.125$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$S = 1.000$

$\Delta\rho_{\text{max}} = 0.278$ e Å⁻³

3622 reflections

$\Delta\rho_{\text{min}} = -0.385$ e Å⁻³

221 parameters

Extinction correction: none

All H-atom parameters refined

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

P1—N1	1.629 (2)	P1—C11	2.071 (1)
P1—C1	1.802 (3)	N1—C10	1.492 (4)
P1—S1	1.923 (1)	N1—C7	1.505 (4)
N1—P1—C1	105.1 (1)	N1—P1—C11	106.5 (1)
N1—P1—S1	117.9 (1)	C1—P1—C11	102.5 (1)
C1—P1—S1	113.4 (1)	S1—P1—C11	110.2 (1)

Table 2. Hydrogen-bonding geometry (Å, °)

C_g is the centroid of the C1—C6 ring.

D—H...A	D—H	H...A	D...A	D—H...A
C2—H2...C11	0.85 (2)	2.70 (3)	3.180 (4)	117 (2)
C11—H11C...C _g 1 ⁱ	0.90 (4)	2.93	3.577	130
C12—H12C...C _g 1 ⁱⁱ	0.93 (4)	3.03	3.897	156

Symmetry codes: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $-x, 1 - y, -z$.

Data collection: SMART (Siemens, 1996). Cell refinement: SAINT (Siemens, 1996). Data reduction: SAINT. Program(s) used to solve structure: SHELXTL (Sheldrick, 1997). Program(s) used to refine structure: SHELXTL. Molecular graphics: XP in SHELXTL. Software used to prepare material for publication: SHELXTL, PLATON (Spek, 1990) and PARST (Nardelli, 1995).

SR and ES thank Dr M. N. S. Rao and Janardhanan, Indian Institute of Technology, Chennai, for the synthesis and supply of the compound. HKF thanks the Malaysian Government and Universiti Sains Malaysia for research grant R&D No. 190-9609-2801. SSSR

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9-(4H-1,2,4-Triazol-4-ylimino)-4,5-diazafluorene

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(Received 12 May 1999; accepted 8 June 1999)

Abstract

The title molecule, C₁₃H₈N₆, is non-planar. The dihedral angle between the planes of the diazafluorene moiety and the triazole ring is 61.0 (1)°. The molecules are arranged as chains running along the *c* axis and along the normal to the *bc* plane through C—H...N hydrogen bonds.

Comment

The aroyl Schiff bases of 4,5-diazafluorene-9-one have received considerable attention over the past few decades