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Key indicators

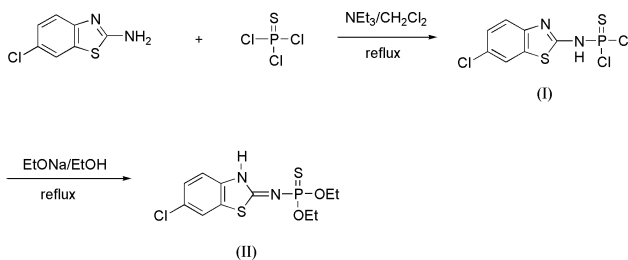
Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
R factor = 0.043
wR factor = 0.112
Data-to-parameter ratio = 17.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Diethyl [(6-chlorobenzothiazol-2-yl)-
amino]thiophosphateThe molecule of the title compound, $\text{C}_{11}\text{H}_{14}\text{ClN}_2\text{O}_2\text{PS}_2$, is essentially planar, the ethoxy groups being on opposite sides of the plane. Two molecules related by an inversion center are connected through $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds, resulting in a dimeric structure.

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Comment

Owing to their biological activities (Li *et al.*, 1998; Schuster, 1989), benzothiazoles have attracted considerable attention. In order to look for biologically active compounds containing both benzothiazolyl and dialkyl thiophosphate groups, we have designed and synthesized the title compound, (II).

A perspective view of (II), with the atom-labeling scheme, is shown in Fig. 1. It can be seen that the title compound results from the substitution of one H atom of the amino group of the starting 2-amino-6-chlorobenzothiazole by the dialkyl thiophosphate group and migration of the second to the atom N1 in the benzothiazole ring.

The benzothiazolyl group, together with atoms N2 and Cl1, form a nearly perfect plane, the largest deviation being 0.018 (2) Å for N2. Atoms S1 and P1 are slightly out of this plane by 0.589 (1) and 0.204 (1) Å, respectively. The ethoxy groups are located on each side of the plane, atoms O1 and O2 being, respectively, 1.261 (3) and 1.141 (3) Å above and below this plane.

The P1–N2 bond length, 1.629 (2) Å, is shorter than the value observed for a normal P–N single bond (1.76 Å; Ress, 1986; Chi & Chen, 2002), indicative of electron delocalization between N2 and P1. In addition, the N2–C7 bond length, 1.300 (3) Å, is close to that of an N=C double bond (1.280 Å; Gao, 1982), whereas N1–C4 [1.389 (3) Å] and N1–C7 [1.348 (3) Å] are both longer than a double bond but significantly shorter than an N–C single bond (1.470 Å; Gao, 1982).

The sums of the three bond angles around N1 and C7, close to 360°, and the P1–N2–C7 angle of 126.75 (18)° indicate

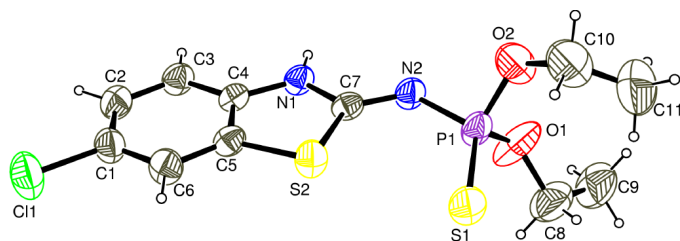


Figure 1
A view of the title compound. Displacement ellipsoids are drawn at 50% probability level.

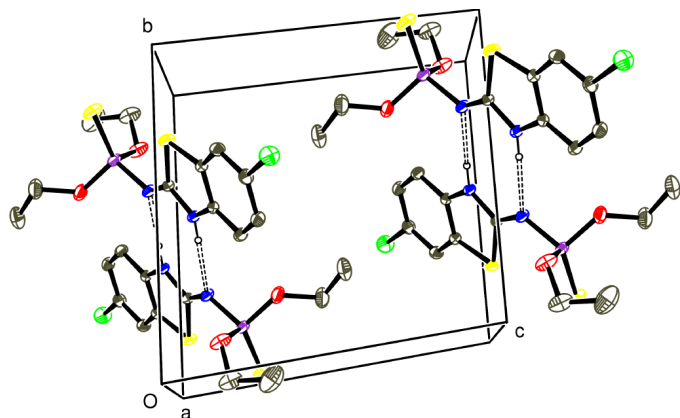


Figure 2
View showing the packing of the dimers.

that N2, C7 and N1 have sp^2 hybridization. Thus we suggest that there is complete delocalization over the whole thiazole ring.

Two molecules, related by an inversion center, are connected through $N-H \cdots N$ hydrogen bonds (Table 2). The packing in the cell results from the stacking of these dimers (Fig. 2).

Experimental

The title compound, (II), was synthesized as described as shown in the Scheme. A dichloromethane solution of 2-amino-6-chlorobenzothiazole, thiophosphoryl chloride and triethylamine was refluxed for 15 h. After evaporation of the solvent, the residue was purified by flash chromatography (petroleum-acetone 4:1) to give compound (I); m.p. 473–476 K. ^1H NMR (CDCl_3 , δ_{H}): 7.42 (s, 2H, Ar-H), 7.60 (s, 1H, Ar-H); ^{31}P NMR (CDCl_3 , 85% H_3PO_4 as external standard): δ 51.69. A mixture of compound (I) and sodium ethoxide was stirred and refluxed in ethanol. After evaporation of the ethanol, the residue was washed with water/ether and the ether layer was dried over MgSO_4 . Finally, the ether was evaporated, and the product was recrystallized from a mixed solvent of petroleum and acetone (4:1). White prismatic crystals of compound (II) were obtained, m.p. 406–408 K. Analysis calculated for $\text{C}_{11}\text{H}_{14}\text{ClN}_2\text{O}_2\text{PS}_2$: C 39.23, H 4.19, N 8.32%; found: C 39.19, H 4.14, N 8.35%; ^1H NMR (CDCl_3 , δ_{H}): 7.41–7.40 (m, 2H, Ar-H), 7.22–7.17 (m, 1H, Ar-H),

4.12–4.04 (m, 4H, CH_2), 1.25–1.18 (m, 6H, CH_3); ^{31}P (CDCl_3 , 85% H_3PO_4 as external standard): δ 58.25.

Crystal data

$\text{C}_{11}\text{H}_{14}\text{ClN}_2\text{O}_2\text{PS}_2$
 $M_r = 336.78$
 Triclinic, $P\bar{1}$
 $a = 7.605$ (3) Å
 $b = 10.288$ (4) Å
 $c = 10.568$ (4) Å
 $\alpha = 78.311$ (6)°
 $\beta = 70.600$ (6)°
 $\gamma = 77.163$ (6)°
 $V = 752.9$ (5) Å³

$Z = 2$
 $D_x = 1.486$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 749 reflections
 $\theta = 2.9$ – 26.3 °
 $\mu = 0.64$ mm⁻¹
 $T = 293$ (2) K
 Prism, white
 $0.32 \times 0.20 \times 0.18$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.780$, $T_{\text{max}} = 0.892$
 4506 measured reflections

3051 independent reflections
 2289 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$
 $\theta_{\text{max}} = 26.4$ °
 $h = -7 \rightarrow 9$
 $k = -12 \rightarrow 12$
 $l = -8 \rightarrow 13$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.112$
 $S = 1.02$
 3050 reflections
 176 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2 + 0.5081P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.63$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.40$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cl1–C1	1.744 (3)	N1–C4	1.389 (3)
S1–P1	1.9228 (11)	N1–H1	0.8600
S2–C5	1.744 (3)	N2–C7	1.300 (3)
S2–C7	1.767 (3)	N2–P1	1.629 (2)
O2–P1	1.583 (2)	C4–C5	1.386 (3)
N1–C7	1.348 (3)	P1–O1	1.563 (2)
C5–S2–C7	90.80 (12)	N1–C7–S2	109.82 (18)
C7–N1–C4	116.2 (2)	O1–P1–O2	102.66 (16)
C7–N2–P1	126.75 (18)	O1–P1–N2	100.67 (13)
C5–C4–N1	111.8 (2)	O2–P1–N2	100.77 (12)
C4–C5–S2	111.4 (2)	O1–P1–S1	115.64 (10)
C6–C5–S2	127.5 (2)	O2–P1–S1	114.28 (10)
N2–C7–N1	121.7 (2)	N2–P1–S1	120.19 (9)
N2–C7–S2	128.52 (19)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1–H1 \cdots N2 ⁱ	0.86	2.14	2.996 (3)	175

Symmetry code: (i) $-x, 1-y, 2-z$.

The H atoms were generated theoretically and refined as riding with fixed displacement parameters.

Data collection: SMART (Bruker, 1997); cell refinement: SMART; data reduction: SAINT (Bruker, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1998); software used to prepare material for publication: SHELXTL.

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