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Diisopropyl {(4-methylbenzothiazol-2-ylamino)[4-(trifluoromethyl)phenyl]methyl}phosphonate

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Key indicators

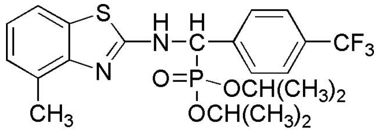
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.011 Å
Disorder in main residue
R factor = 0.062
wR factor = 0.228
Data-to-parameter ratio = 15.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $C_{22}H_{26}F_3N_2O_3PS$, there are two independent molecules in the asymmetric unit. The two molecules differ in the orientation of the benzene ring with respect to the benzothiazole group [dihedral angles 58.6 (2) and 71.6 (2)°]. In the crystal structure, symmetry-related molecules are linked by N—H···O hydrogen bonds.

Comment

As isosteres of aminocarboxylic acids, α-aminoalkylphosphonates have attracted an increasing amount of attention in the past two decades because some of them are of considerable chemical and pharmacological importance. α-Aminoalkylphosphonates with a benzothiazole group exhibit good biological activity (Li *et al.*, 1998). In our previous work, we have synthesized a series of α-aminoalkylphosphonates with fluorine (Song, Wu, He *et al.*, 2003; Song, Jiang *et al.*, 2003; Song, Wu, Yang *et al.*, 2003; Song & Jiang, 2004; Yang *et al.*, 2004), which showed significant *anti*-TMV (Tobacco Mosaic Virus) activity. As part of our ongoing programme in the development of new biologically active organophosphorus compounds, we report here the synthesis and X-ray crystal structure of the title compound, (I).



(I)

The asymmetric unit consists of two independent molecules, *A* and *B* (Fig. 1). In both molecules, the P atom exhibits a distorted tetrahedral configuration. The O═P—O and O═P—C bond angles are significantly wider than the O—P—

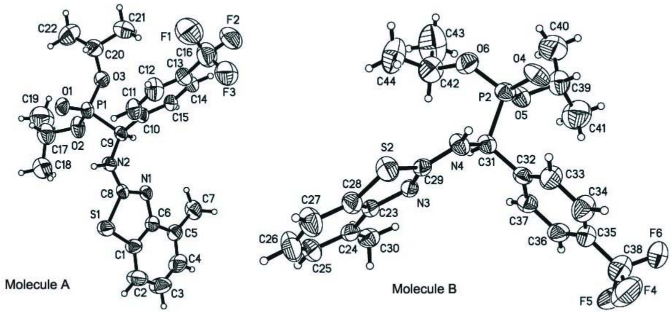


Figure 1
The structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Only one component of the disordered trifluoromethyl and isopropyl groups are shown.

O and O—P—C angles (Table 1). The C(sp^2)—N bond lengths are intermediate between the normal C—N single bond (1.47 Å; Sasada, 1984) and C═N double bond (1.28 Å; Wang *et al.*, 1998) distances, which is indicative of partial double bond character. In *A*, the dihedral angle between the planes of benzothiazole and benzene rings is 58.6 (2)°, whereas in *B*, it is 71.6 (2)°. The two molecules also differ in the orientation of the isopropyl groups.

The crystal structure is stabilized by intermolecular N—H···O hydrogen bonds (Table 2) involving the —NH group of A and the P═O group of symmetry-related *B* or *vice versa* (Fig. 2).

Experimental

A mixture of 2-amino-4-methylbenzothiazole (4 mmol) and 4-trifluoromethylbenzoaldehyde (4 mmol) in anhydrous acetonitrile (5 ml) and di-i-propyl phosphite (4 mmol) and boron fluoride-ether (0.4 mmol) was added into an oven-dried three-necked 50 ml round-bottom flask. The mixture was irradiated in an ultrasound cleaning bath (50 kHz, 250 W) at 351–353 K for 1 h. The mixture was washed with water and then filtered and dried. The crude solid was recrystallized from ethanol and water (1:1 *v*/*v*) to give compound (I) (yield: 80.12%; m.p. 466–468 K). Crystals of (I) were obtained as prisms by recrystallization from ethanol. Analysis found: C 54.40, H 5.10, N 5.53%; calculated for $C_{22}H_{26}F_3N_2O_3PS$: C 54.32, H 5.39, N5.76%. FT–IR (KBr, cm^{-1}): 3221.1 (NH), 1589.3, 1537.2 (Ar), 1234.4 (P═O), 1122.5, 1068.5 (P—O—C). ^{1}H NMR ($CDCl_3$, δ, p.p.m.): 0.984–1.222 (*m, J* = 88.8 Hz, 6H, 2CH_3), 1.281–1.332 (*m, J* = 14.0 Hz, 6H, 2CH_3), 2.456 (*s*, 3H, Ar-CH_3), 4.559–4.846 (*m*, 2H, 2CHO), 5.815 (*dd, J* = 22.8, 5.6 Hz, 1H, CHP), 6.923 (*t, J* = 7.6 Hz, NH), 7.038–7.897 (*m*, 7H, Ar-H). ^{13}CNMR(δ): 142.435, 131.729, 130.127, 130.073, 129.425, 127.135, 125.808, 122.504, 119.017, 72.691, 57.026, 55.484, 30.372, 30.182, 29.991, 29.800, 29.602, 29.411, 29.220, 24.306, 23.970, 23.474, 18.217.

Crystal data

$C_{22}H_{26}F_3N_2O_3PS$
$M_r = 486.49$
Monoclinic, $P2_1/c$
$a = 13.819\ (2)$ Å
$b = 21.354\ (3)$ Å
$c = 21.991\ (3)$ Å
$\beta = 128.931\ (6)^\circ$
$V = 5048.1\ (12)$ Å^3
$Z = 8$
$D_x = 1.280$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3118 reflections
$\theta = 2.3$–19.3°
$\mu = 0.24$ mm^{-1}
$T = 293\ (2)$ K
Prism, colourless
0.30 × 0.26 × 0.22 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.918$, $T_{max} = 0.949$
29353 measured reflections
10401 independent reflections
3429 reflections with $I > 2\sigma(I)$
$R_{int} = 0.083$
$\theta_{max} = 26.5^\circ$
$h = -15 \rightarrow 17$
$k = -23 \rightarrow 26$
$l = -27 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.228$
$S = 0.93$
10401 reflections
667 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1048P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

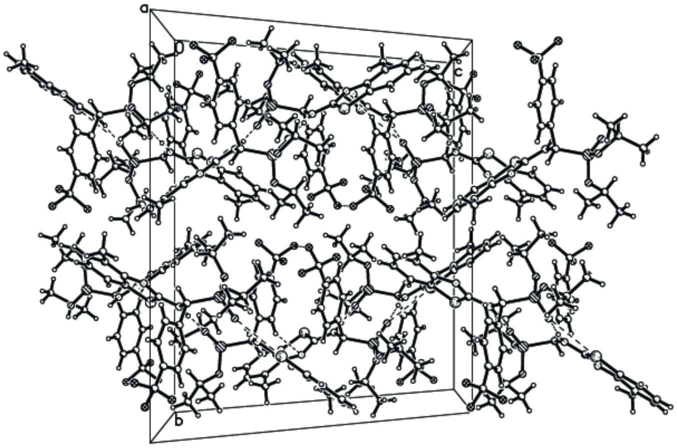


Figure 2
Packing of (I), viewed down the *a* axis. Dashed lines represent intermolecular hydrogen bonds.

Table 1
Selected geometric parameters (Å, °).

P1—O1	1.458 (3)	S2—C28	1.745 (5)
P1—O3	1.547 (4)	S2—C29	1.751 (5)
P1—O2	1.556 (4)	N1—C8	1.303 (5)
P1—C9	1.802 (5)	N1—C6	1.384 (6)
P2—O4	1.469 (3)	N2—C8	1.344 (6)
P2—O6	1.530 (4)	N2—C9	1.451 (6)
P2—O5	1.552 (3)	N3—C29	1.295 (5)
P2—C31	1.808 (4)	N3—C23	1.398 (5)
S1—C1	1.730 (5)	N4—C29	1.346 (6)
S1—C8	1.753 (5)	N4—C31	1.453 (6)
O1—P1—O3	115.1 (2)	O4—P2—C31	113.8 (2)
O1—P1—O2	115.5 (2)	O6—P2—C31	107.4 (2)
O3—P1—O2	104.4 (2)	O5—P2—C31	102.5 (2)
O1—P1—C9	113.9 (2)	N2—C9—C10	114.1 (4)
O3—P1—C9	104.4 (2)	N2—C9—P1	108.6 (3)
O2—P1—C9	102.0 (2)	C10—C9—P1	111.4 (3)
O4—P2—O6	108.0 (2)	N4—C31—C32	113.3 (4)
O4—P2—O5	114.9 (2)	N4—C31—P2	109.3 (3)
O6—P2—O5	109.8 (2)	C32—C31—P2	112.3 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O4^{i}	0.87 (5)	1.91 (6)	2.779 (7)	170 (5)
N4—H4*A*···O1^{ii}	0.90 (5)	1.90 (6)	2.774 (7)	167 (6)

Symmetry codes: (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (ii) $x, \frac{3}{2} - y, \frac{1}{2} + z$.

The F atoms of the trifluoromethyl groups are found to be disordered over two positions with occupancies of 0.416 (16) and 0.584 (16) in *A*, and 0.689 (19) and 0.311 (19) in *B*. In *A*, one of the isopropyl groups (C17–C19) is disordered over two orientations with occupancies of 0.538 (13) and 0.462 (13). During the refinement, C—F, C—O and C—C distances involving the disordered atoms were restrained to 1.37, 1.45 and 1.54 Å, respectively, and the F···F distances were restrained to be equal within 0.03 Å. In addition, the U_{ij} components of the disordered atoms were approximated to isotropic behaviour. H atoms attached to the N atoms were located in a difference Fourier map and their positional parameters were

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refined. The remaining H atoms were placed in calculated positions (C—H = 0.93–0.98 Å) and refined using a riding model with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) for methyl H atoms and 1.2$U_{\rm eq}$(C/N) for other H atoms. One of the methyl groups (C43) is disordered over two positions rotated from each other by 60°.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; 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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