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O,O′-Diisopropyl (4-methyl-7-coumarinyloxy)-phosphonothioate

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Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.004 Å
R factor = 0.055
wR factor = 0.140
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.

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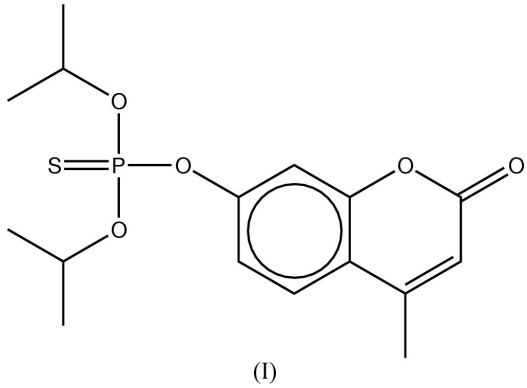
The asymmetric unit of the title compound, $C_{16}H_{21}O_5PS$, contains two symmetry-independent molecules. The overall molecular geometry of both molecules is very similar. The coumarin ring systems are only insignificantly distorted from planarity. In the structure, C—H···O and C—H···π weak intermolecular hydrogen bonds can be found. In addition, stacking interactions between the rings are present.

Comment

During recent decades, coumarin derivatives have been extensively studied due to their photochemical properties (Hammond *et al.*, 1964; Krauch *et al.*, 1966) and pesticidal activity (Lopes *et al.*, 1995; Kochansky, 2000). Furthermore, they act as natural carcinogens (Wogan & Newberne, 1967) and as skin photosensitizers (Musajo & Rodighiero, 1970). The close chemical similarity between coumarin and vitamin K (Kralt & Claassen, 1972) is the origin of physiological research on coumarin derivatives. During our investigations on the toxicity of phosphorothioic acid esters to humans, we synthesized *O,O′*-diisopropyl (4-methyl-7-coumarinyloxy)-phosphonothioate, (I), *via* the reaction of 4-methylcoumarinyl sodium salt and thiophosphorochloric acid *O,O′*-diisopropyl ester in DMSO (Losco & Peri, 1959). This reaction has a high yield.



(I)

A perspective view of (I) together with the atom-numbering scheme is shown in Fig. 1. The asymmetric unit contains two independent molecules (molecule 1 contains atom P1, and molecule 2 atom P2). The overall molecular geometry of both molecules is very similar. The weighted r.m.s. deviation for a least-squares fit of all atoms is 0.068 (3) Å, and the maximum difference of 0.149 (3) Å exists between C13 and C63 (Fig. 2). One isopropyl substituent of molecule 2 (C65 and C66) shows signs of a slight dynamic disorder, expressed in relatively large displacement ellipsoids. The coumarin ring systems of both molecules are only insignificantly distorted from planarity

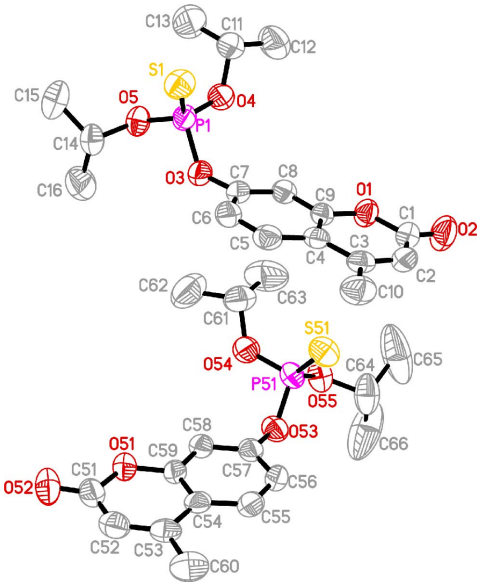


Figure 1
The structure of the asymmetric unit of the title compound, (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

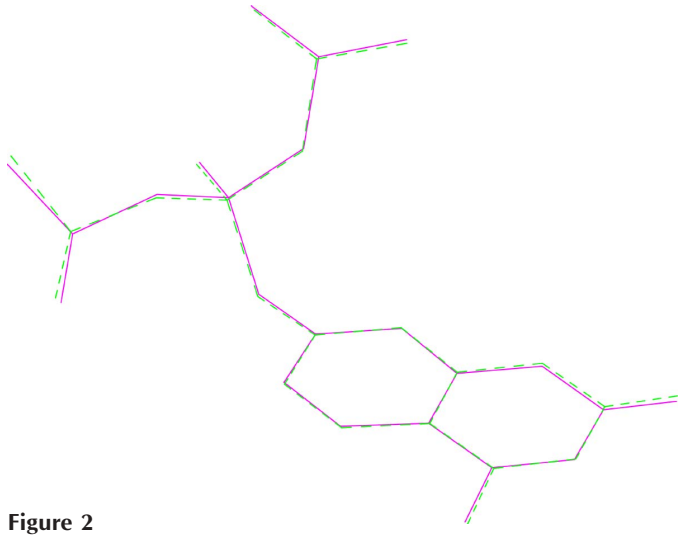


Figure 2
Superposition of the two molecules in the asymmetric unit. H atoms have been omitted for clarity.

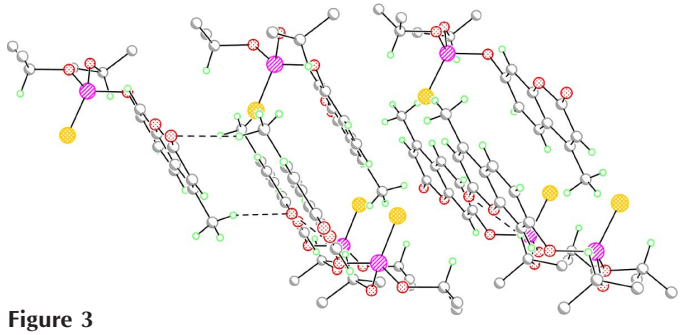


Figure 3
A part of the molecular packing of the title compound, showing intermolecular hydrogen bonds and stacking interactions. Hydrogen bonds are indicated by dashed lines. H atoms of the isopropyl methyl groups not involved in hydrogen bonding have been omitted for clarity.

[maximum deviation: 0.020 (2) Å for C3 and 0.0159 (17) Å for O51]. The ketone O atoms deviate from the above planes by 0.053 (3) and 0.034 (3) Å (respectively for molecules 1 and 2). The P—O—coumarin O atoms deviate by 0.115 (2) and 0.146 (5) Å and the methyl C atoms by −0.006 (4) and −0.007 (4) Å from the above-mentioned planes, which enclose an angle of 8.09 (6)°. The conformation of the *O,O′*-diisopropyl phosphorothioic substituents is described by the torsion angles in Table 1.

In the structure, three C—H···O short intermolecular interactions (Table 2 and Fig. 3) can be found (Taylor & Kennard, 1982; Desiraju & Steiner, 1999). In this way, hydrogen-bonded chains along the *b* axis are created. Furthermore, three short contacts can be found in the structure. One is a stacking interaction between the ring system of molecule 1 and that of molecule 2 (symmetry transformation for the generation of molecule 2: $1-x, y+\frac{1}{2}, -z+\frac{1}{2}$). The ring systems are inclined at an angle of 0.51 (9)°. The last two are C—H···π intermolecular interactions: C11—H11···(C54^{i}–C59^{i}) [symmetry code: (i) $x-1, y, z$] and C61—H61···(C4–C9), with *D*—H distances of 0.98 Å, H···*A* distances of 3.19 and 3.05 Å, and *D*—H···*A* angles of 162 and 159°, respectively.

Experimental

To a dimethyl sulfoxide solution (5 ml) of 4-methylcoumarin (0.405 g, 2.3 mmol) and thiophosphorochloric acid *O,O′*-diisopropyl ester (0.498 g, 2.3 mmol), sodium hydride (0.055 g, 2.3 mmol) was added slowly, keeping the temperature below 298 K. The mixture was stirred at room temperature for 24 h. The solvent was evaporated at low pressure (0.4 mm Hg). To the residue, water (2 ml) was added and the resulting solution was extracted twice with CH_3Cl (10 ml). The extract was dried with $MgSO_4$ and evaporated. The fine crystalline powder which was produced was recrystallized from methanol, giving colourless prismatic crystals (yield 0.78 g, 95%; m.p. 352–353 K). ^{1}H NMR ($CDCl_3$, 250 Hz Bruker): δ 1.39 [6H, *d*, $^3J_{HH}$ = 6.2 Hz, $CH(CH_3)_2$], 1.41 [6H, *d*, $^3J_{HH}$ = 6.2 Hz, $CH(CH_3)_2$], 2.42 (3H, *d*, $^4J_{HH}$ = 1.2 Hz, CH_3), 4.88 [2H, *m*, $^3J_{HH}$ = 9.6 Hz, $^3J_{PH}$ = 6.2 Hz, $CH(CH_3)_2$], 6.25 (1H, *q*, $^4J_{HH}$ = 1.2 Hz, H3), 7.16 (1H, *dd*, $^3J_{H5H6}$ = 8.6 Hz, $^4J_{H6H7}$ = 2.3 Hz, $^4J_{PH6}$ = 1.4 Hz, H6), 7.20 (1H, *m*, $^4J_{H6H7}$ = 2.3 Hz, $^4J_{PH7}$ = 1.8 Hz, H7), 7.57 (1H, *d*, $^4J_{H5H6}$ = 8.6 Hz, H5).

Crystal data

$C_{16}H_{21}O_5PS$
M_r = 356.36
Monoclinic, $P2_1/c$
a = 14.0994 (7) Å
b = 9.5999 (5) Å
c = 28.0432 (13) Å
β = 102.249 (4)°
V = 3709.3 (3) Å^3
Z = 8
D_x = 1.276 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7573 reflections
θ = 2–25°
μ = 0.28 mm^{-1}
T = 291.0 (5) K
Prism, colourless
0.59 × 0.46 × 0.17 mm

Data collection

Kuma *KM*4-CCD diffractometer
ω scans
Absorption correction: numerical (*X-RED32*; Stoe & Cie, 1999)
T_{min} = 0.837, T_{max} = 0.948
51 730 measured reflections
6610 independent reflections
5609 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 25.1°
$h = -16 \rightarrow 16$
$k = -11 \rightarrow 11$
$l = -33 \rightarrow 33$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0597P)^2 + 1.1587P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.055$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.141$	$\Delta\rho_{max} = 0.23$ e Å^{-3}
$S = 1.19$	$\Delta\rho_{min} = -0.26$ e Å^{-3}
6610 reflections	
425 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

S1—P1	1.9159 (9)	S51—P51	1.9131 (9)
P1—O5	1.5634 (18)	P51—O55	1.5647 (19)
P1—O4	1.5682 (19)	P51—O54	1.5681 (19)
P1—O3	1.5937 (17)	P51—O53	1.5928 (18)
O1—C9	1.377 (3)	O51—C59	1.376 (3)
O1—C1	1.387 (3)	O51—C51	1.392 (3)
C1—O2	1.210 (3)	C51—O52	1.202 (3)
C1—C2	1.434 (4)	C51—C52	1.434 (4)
C2—C3	1.343 (4)	C52—C53	1.338 (4)
C3—C4	1.450 (3)	C53—C54	1.452 (4)
C4—C9	1.396 (3)	C54—C59	1.396 (3)
O5—P1—O4	102.55 (10)	O55—P51—O54	102.48 (10)
O5—P1—O3	100.34 (10)	O55—P51—O53	100.29 (10)
O4—P1—O3	101.67 (10)	O54—P51—O53	101.48 (10)
O5—P1—S1	117.62 (8)	O55—P51—S51	117.78 (8)
O4—P1—S1	116.48 (8)	O54—P51—S51	116.63 (8)
O3—P1—S1	115.61 (8)	O53—P51—S51	115.54 (8)
C7—O3—P1—S1	−43.7 (2)	C57—O53—P51—S51	44.8 (2)
C7—O3—P1—O4	83.5 (2)	C57—O53—P51—O54	−82.4 (2)
O3—P1—O4—C11	−162.78 (19)	O53—P51—O54—C51	37.56 (8)
P1—O4—C11—C12	164.1 (2)	P51—O54—C51—C52	15.52 (19)
P1—O4—C11—C13	−70.6 (3)	P51—O54—C51—C53	9.96 (11)
C7—O3—P1—O5	−171.25 (18)	C57—O53—P51—O55	172.49 (18)
O3—P1—O5—C14	75.69 (19)	O53—P51—O55—C54	−6.69 (10)
P1—O5—C14—C15	119.2 (2)	P51—O55—C54—C55	−106.9 (2)
P1—O5—C14—C16	−118.2 (2)	P51—O55—C54—C56	−111.45 (19)

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

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14···O2^{i}	0.98	2.58	3.420 (4)	144
C60—H60C···O52^{ii}	0.96	2.51	3.444 (4)	165
C64—H64···O52^{iii}	0.98	2.55	3.399 (4)	145

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

All H atoms were placed in calculated positions (C—H = 0.93–0.98 Å) and were refined as riding on the carrier atom, with U_{iso}(H) = 1.2 or 1.5 times U_{eq}(C). The methyl groups were allowed to rotate about their local threefold axis.

Data collection: *CrysAlisCCD* (Kuma, 2000); cell refinement: *CrysAlisRED* (Kuma, 2000); data reduction: *CrysAlisRED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1990*b*) and *ORTEP-3* (Version 1.062; Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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