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Organophosphorus Insecticides. 16.
**Azinphos Ethyl: *O,O*-Diethyl *S*-{[4-
 Oxo-1,2,3-benzotriazin-3(4*H*)-yl]methyl}
 Phosphorodithioate, C₁₂H₁₆N₃O₃PS₂**

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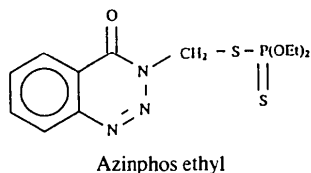
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Abstract

In the title compound, a P···δ(+)-C-atom distance is observed in the solid state which falls within the range of literature values for the span of δ(−)···δ(−) charges in the active site of insect acetylcholinesterase (AChE), but is outside the range for mammalian AChE. The structure of azinphos ethyl is comparable to that of the methyl analog.

Comment

The crystal and molecular structure of azinphos ethyl (ethyl guthion, *O,O*-diethyl *S*-{[4-oxo-1,2,3-benzotriazin-3(4*H*)-yl]methyl} phosphorodithioate) was undertaken as part of an ongoing study of the structures of organophosphorus (OP) insecticides (Baughman & Yu, 1982, and references therein). The determination of accurate three-dimensional structures of a series of OP's should give better insight into any structure–activity related interactions between P···δ(+) centers in the insecticide and δ(−)···δ(−) centers in acetylcholinesterase (AChE).



As in azinphos methyl (Rohrbaugh, Meyers & Jacobson, 1976), the ring system of azinphos ethyl is essentially planar (see Fig. 1 and Table 1). Both the methylene groups in azinphos ethyl and the methyl groups in

azinphos methyl generally point towards the S2 atom which is common to both molecules. The S2—P—O—C torsion angles are between ±65° [−50.4 (3) and 44.6 (5)° in azinphos ethyl; −62 and −36° in azinphos methyl]. In both molecules, S1 is just on the O1 side of the molecule [N2—N3—C8—S1 = −94.3 (3)° for azinphos ethyl and −119° for azinphos methyl]. However, the thiophosphate groups are twisted away from the O1 side of each molecule [P—S1—C8—N3 = 127.5 (3) for azinphos ethyl, 110° for azinphos methyl]. Both azinphos molecules have a nearly planar zigzag S2—P—S1—C8 group [torsion angles −179.0 (3) (azinphos ethyl) and −178° (azinphos methyl)]. In azinphos ethyl, the P—O3—C9—C10 group is essentially in a zigzag configuration, but P—O2—C11—C12 is not [torsion angles 167.9 (4) and 105.9 (4)°, respectively].

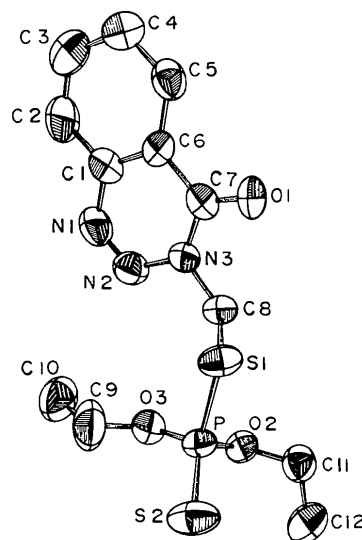


Fig. 1. The azinphos ethyl molecule showing 50% probability ellipsoids for the non-H atoms.

As noted previously (Baughman & Jacobson, 1978), certain P···δ(+)-center distances may give some insight into the toxicity and activity of OP's. For insect AChE, the range of δ(−) site separations (*i.e.* active-site distances) in AChE is 5.0–5.5 Å (Hollingworth, Fukuto & Metcalf, 1967) or 4.5–5.9 Å (O'Brien, 1963). P and C7 appear to be the most likely atoms in azinphos ethyl to be both electron deficient and at a distance within these ranges. The P···C7 separation in the solid state of azinphos ethyl is 5.21 Å, while the corresponding distance for the methyl analog is 4.83 Å. The fact that the azinphos ethyl molecule has at least one P···δ(+) distance in the 'tighter' of the two cited ranges may have an influence on the insect toxicity of the title compound.

Since azinphos ethyl has a low mammalian LD50 value of 9 mg kg^{−1} (Thompson, 1984), a comparison with the δ(−) site-separation distance in mammalian

AChE is also appropriate. P···C7 is the only likely P···δ(+) combination; however, this distance of 5.21 Å is not compatible with the δ(−)···δ(−) site-separation distance in mammalian AChE, which was found by Hollingworth *et al.* (1967) and O'Brien (1963) to be in the range 4.3–4.7 Å. It seems, therefore, quite probable that azinphos ethyl would become twisted *in vivo* from the solid-state structure.

Experimental

Crystal data

C₁₂H₁₆N₃O₃PS₂

M_r = 345.38

Monoclinic

*P*2₁/*c*

a = 12.325 (4) Å

b = 8.553 (3) Å

c = 16.299 (7) Å

β = 103.39 (3)°

V = 1671 (1) Å³

Z = 4

D_x = 1.373 Mg m^{−3}

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25

reflections

θ = 8.3–18.4°

μ = 0.419 mm^{−1}

T = 293 K

Prism

0.40 × 0.25 × 0.25 mm

Colorless

Crystal source: EPA,
recrystallized from ethanol

Data collection

Siemens P3 diffractometer

ω/2θ scans

Absorption correction:
not applied

6156 measured reflections

3323 independent reflections

3265 observed reflections

[*F* ≥ 3σ(*F*)]

*R*_{int} = 0.022

θ_{max} = 25°

h = 0 → 14

k = −10 → 10

l = −19 → 19

3 standard reflections

monitored every 50

reflections

intensity decay: 4.7%

Refinement

Refinement on *F*

R = 0.050

wR = 0.044

S = 1.50

1768 reflections

190 parameters

H-atom parameters not

refined

w = 1/σ²(*F*)

(Δ/σ)_{max} = 0.01

Δρ_{max} = 0.4 e Å^{−3}

Δρ_{min} = −0.1 e Å^{−3}

Extinction correction: none

Table 1. Fractional atomic coordinates, equivalent isotropic displacement parameters (Å²) and distances (Å) of atoms from the least-squares plane

The least-squares plane from which the atomic displacements were measured is defined by all ten non-H ring atoms, and O1 and C8.

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}	Distance
S1	0.3381 (1)	0.6765 (1)	0.07105 (8)	4.2	−1.62
S2	0.2589 (2)	0.8818 (2)	−0.09900 (8)	5.7	−3.36
P	0.2477 (1)	0.8705 (1)	0.01629 (7)	3.6	−1.64
O1	0.4412 (3)	0.4284 (4)	0.2388 (2)	5.4	−0.10
O2	0.2895 (2)	1.0143 (3)	0.0746 (2)	4.1	−0.38
O3	0.1284 (3)	0.8593 (4)	0.0352 (2)	5.4	−1.16
N1	0.1081 (3)	0.4134 (6)	0.2029 (3)	5.2	−0.03
N2	0.1543 (4)	0.5335 (5)	0.1850 (3)	5.4	0.00
N3	0.2730 (3)	0.5366 (4)	0.2019 (2)	3.7	0.03

C1	0.1706 (4)	0.2819 (5)	0.2393 (3)	4.4	−0.03
C2	0.1117 (4)	0.1551 (7)	0.2583 (4)	6.0	−0.03
C3	0.1676 (5)	0.0263 (6)	0.2957 (4)	5.6	0.01
C4	0.2827 (5)	0.0230 (5)	0.3146 (3)	5.1	0.05
C5	0.3423 (4)	0.1465 (5)	0.2952 (3)	4.3	0.04
C6	0.2860 (3)	0.2784 (4)	0.2569 (2)	3.5	0.00
C7	0.3433 (4)	0.4151 (5)	0.2335 (3)	4.0	−0.03
C8	0.3143 (4)	0.6854 (5)	0.1785 (3)	3.9	0.08
C9	0.0445 (6)	0.752 (1)	−0.0142 (4)	9.7	−2.08
C10	−0.0482 (5)	0.7386 (9)	0.0266 (5)	8.5	−1.32
C11	0.4003 (4)	1.0824 (6)	0.0797 (4)	4.9	−0.30
C12	0.3881 (5)	1.2338 (7)	0.0332 (4)	7.4	−0.49

Table 2. Selected geometric parameters (Å, °)

S1—P	2.081 (2)	N3—C7	1.374 (5)
S1—C8	1.843 (4)	N3—C8	1.454 (5)
S2—P	1.918 (2)	C1—C2	1.380 (7)
P—O2	1.567 (3)	C1—C6	1.384 (6)
P—O3	1.573 (3)	C2—C3	1.366 (8)
O1—C7	1.194 (5)	C3—C4	1.381 (8)
O2—C11	1.470 (6)	C4—C5	1.364 (6)
O3—C9	1.473 (7)	C5—C6	1.393 (6)
N1—N2	1.241 (6)	C6—C7	1.462 (6)
N1—C1	1.414 (6)	C9—C10	1.45 (1)
N2—N3	1.426 (5)	C11—C12	1.490 (7)
P—S1—C8	100.8 (1)	N1—C1—C6	122.6 (4)
S1—P—S2	107.90 (8)	C2—C1—C6	120.3 (4)
S1—P—O2	107.3 (1)	C1—C2—C3	119.8 (8)
S1—P—O3	107.4 (1)	C2—C3—C4	120.2 (4)
S2—P—O2	117.8 (1)	C3—C4—C5	120.8 (4)
S2—P—O3	118.5 (1)	C4—C5—C6	119.5 (4)
O2—P—O3	96.9 (2)	C1—C6—C5	119.4 (4)
P—O2—C11	121.0 (2)	C1—C6—C7	117.6 (4)
P—O3—C9	120.0 (4)	C5—C6—C7	123.0 (4)
N2—N1—C1	121.5 (4)	O1—C7—C6	126.7 (4)
N1—N2—N3	118.4 (4)	O1—C7—N3	119.6 (4)
N2—N3—C8	111.8 (3)	N3—C7—C6	113.7 (4)
N2—N3—C7	126.1 (3)	S1—C8—N3	110.9 (3)
C7—N3—C8	122.1 (4)	O3—C9—C10	109.1 (6)
N1—C1—C2	117.4 (4)	O2—C11—C12	109.4 (4)
P—S1—C8—N3	127.5 (3)	P—O2—C11—C12	105.9 (4)
C8—S1—P—S2	−179.0 (3)	P—O3—C9—C10	167.9 (4)
S2—P—O2—C11	−50.4 (3)	N2—N3—C8—S1	−94.3 (3)
S2—P—O3—C9	44.6 (5)	C7—N3—C8—S1	83.5 (4)

18 of 21 non-H atoms were located by *MULTAN* (Main, Woolfson & Germain, 1976) using approximate (two-dimensional) coordinates for azinphos ethyl and a *K* curve to compute the *E* values. Aromatic H atoms were set at 1.00 Å from the respective C atoms while bisecting the C—C—C angle; methyl and ethyl H atoms were placed in tetrahedral positions with C—H 1.10 Å. Anisotropic displacement parameters were used for all but the H atoms, which were assigned the *B*_{eq} value of the C atom to which they are bonded.

Atomic scattering factors for non-H atoms were taken from Hanson, Herman, Lea & Skillman (1964) and for H atoms from Stewart, Davidson & Simpson (1965). Δ*f*' and Δ*f*" were calculated using *International Tables for X-ray Crystallography* (1962, Vol. III).

Programs used: *MULTAN*; *ALLS* (Lapp & Jacobson, 1979); *FOUR* (Powell & Jacobson, 1980); *ORFFE* (Busing, Martin & Levy, 1964); *ORTEPII* (Johnson, 1971).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: BK1007). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2'-(Diphenylphosphino)propiophenone, a Functionalized Tertiary Phosphine

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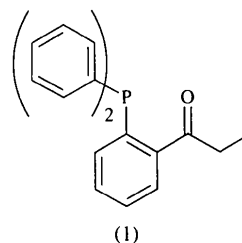
Abstract

The structure of the title compound, $\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4\text{—CO—C}_2\text{H}_5)$, shows significant distortions from tetrahedral geometry around the P atom; the C21—P1—C31 angle between the two unsubstituted rings [99.69 (9)°] is smaller than the other two C—P—C angles [104.37 (9)

and 102.24 (9)°]. The P—C distances are 1.828 (2), 1.846 (2) and 1.851 (2) Å. The C=O group does not lie in the plane of the ring to which it is bonded but is rotated $-11.2(2)^\circ$ out of the ring plane; the P...O intramolecular distance is 2.669 (3) Å. The dihedral angles which define the rotations of the phenyl ring planes relative to the lone-pair direction on the P atom are 49.3 (1), 37.7 (1) and 34.9 (1)°, and are closer to those of a regular propeller conformation than was found in triphenylphosphine.

Comment

Functionalized tertiary phosphines play an important role in the chemistry of transition metal coordination complexes. A recent review on so-called 'hemilabile' phosphorus–oxygen ligands (Bader & Lindner, 1991) describes how an oxygen-containing functional group in a tertiary phosphine ligand can influence the catalytic chemistry of the phosphine complex. As a part of a research program directed toward the study of transition-metal–enolate complexes, we were interested in the preparation of ligands in which one of the donor moieties is an enolizable carbonyl group. Although 2-formylphenyl- and 2-acylphenyldiphenylphosphine have been prepared (Schiemenz & Kaack, 1973), to our knowledge there have been no structural studies of the free ligands or of any structurally related molecules. We have thus prepared the title compound, (1), in 56% yield by the addition of ethylmagnesium bromide (Cannone, Foscolos & Caron, 1982) to (2-cyanophenyl)diphenylphosphine (Ravindar, Hemling, Schumann & Blum, 1992). Although (1) was fully characterized by IR and ^1H and ^{13}C NMR spectroscopy (Rasley & Kulawiec, 1994), the crystal structure analysis was performed in order to establish the geometry of the uncomplexed ligand for use in future studies of the geometric deformations in its transition metal complexes.



The compound consists of discrete molecules; a perspective view showing the atomic labelling scheme is shown in Fig. 1. The labelling scheme is similar to that used for the low-temperature structure of triphenylphosphine (Dunne & Orpen, 1991) and atoms C11–C16 will be referred to as ring 1, C21–C26 as ring 2, and C31–C36 as ring 3. A comparison of these two structures