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5-Ethyl-6-oxo-4-thioxo-1,3,2-oxazaphospholidino[3,2-*a*][1,3,2]benzodiazaphosphorine

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Key indicators

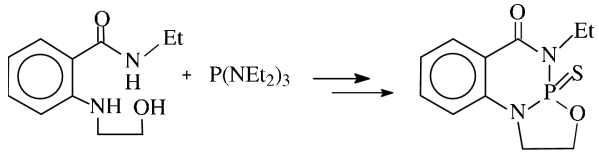
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.004 Å
R factor = 0.041
wR factor = 0.118
Data-to-parameter ratio = 14.3

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

The title fused tricyclic phosphoroheterocycle, $C_{11}H_{13}N_2O_2PS$, was unexpectedly synthesized by the reaction of a multifunctional compound, 2-[*N*-(2′-hydroxy)ethyl]amino-*N*′-ethylbenzamide, with tris(diethylamino)phosphine in the presence of iodine as catalyst. The crystallographic data analysis reveals that the title compound is triclinic with space group $P\overline{1}$ and there are three rings in the molecule. The phenyl ring, the two N atoms and the carbonyl C atom are coplanar; the P atom and the carbonyl C atom deviate by −0.692 (2) and 0.1116 (13) Å, respectively, from the phenyl ring plane. The five-membered ring exists in an boat conformation.

Comment

In new pharmaceuticals and agrochemicals, the incorporation of heterocycles is recommended to improve the biological activity. In particular, phospha-heterocycles, such as benzoannulated and related analogs of cyclophosphamide, have shown antitumor activity, and have received considerable interest in the fields of chemistry, medicine and agricultural science (Rao *et al.*, 2000; Neda *et al.*, 1996; Viljanen *et al.*, 1998; Huang & Chen, 2000).



(1) (2)

Among numerous methods for the synthesis of phosphorus heterocycles, tris(diethylamino)phosphine is frequently used as a cyclizing reagent (Nifantev *et al.*, 1990, 1991; Burilov *et al.*, 1995; Chen & Wang, 1990; Terenteva *et al.*, 1983; Jurkschat *et al.*, 1982). However, $P(NEt_2)_3$ has seldom been reported as a cyclocondensation reagent for compounds with multifunctional groups of different reactivity. Usually, the fused phospha-heterocycles have been prepared step by step for the ring closure (Chen & Bao, 1989, 1990). However, utilization of $P(NEt_2)_3$ for the synthesis of the title heterocycle, (2), through reaction with multifunctional 2-[*N*-(2′-hydroxy)-ethyl]amino-*N*′-ethylbenzamide has been successful in a one-pot procedure in the presence of iodine as catalyst. Isolation of the product becomes difficult in the absence of catalyst as the reaction gives a more complex mixture. Using PCl_3 instead of $P(NEt_2)_3$, leads only to chlorinated products (Deng *et al.*, 2000). The preliminary bioassays indicate that (2) possesses herbicidal activity. In order to study the structural properties of this novel fused phospha-heterocycle and study its struc-

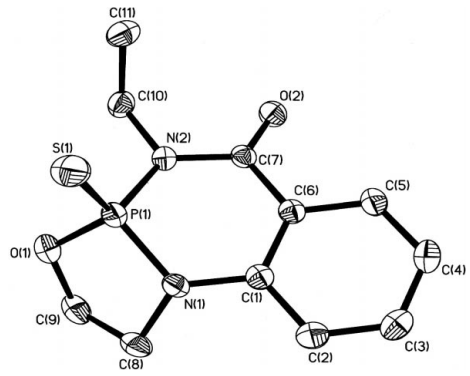


Figure 1
View of the title molecule, with the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.

ture–activity relationship, a single crystal of (2) was subjected to X-ray diffraction analysis.

This analysis reveals that there are three rings in the molecule. The phenyl ring and three atoms (N1, C7 and N2) are coplanar, and atoms P1 and C7 are on different sides of this plane at distances of −0.692 (2) and 0.1116 (13) Å, respectively. This is different from the observation regarding the structure of *N*-(1-ethoxycarbonylethyl)-1-(ethoxycarbonylmethyl)-3-ethyl-1,2,3,4-tetrahydro-4-oxo-1,3,2-benzodiazaphosphorine-2-carboxamide 2-oxide, in which the phosphorus-containing bicyclic moiety is planar, except for the P atom on one side of the plane (Huang *et al.*, 2001). It is also observed that atoms P1, N1, C8 and O1 are coplanar, with atom C9 displaced from this plane. The five-membered ring exists in a boat conformation with C9 at one tip, hence the ^{1}H NMR spectrum of the protons on atom C9 appears magnetically non-equivalent.

A comparable tricyclic compound, namely 6,12-dioxo-1-(*p*-chlorophenyl)imino-11-ethyl-1,4,3-thiazaphospha-cyclohexano[3,4]-1,3,2-benzodiazaphosphorine, has been reported previously, with a planar structure for the benzodiazaphosphorine moiety and a chair conformation for the six-membered 1,4,3-thiazaphosphorine (Chen *et al.*, 1991). That compound has an anthracene-like structure and shows some herbicidal activity at 100 p.p.m. In contrast, the title compound is phenanthrene-like with similar planar characteristics and boat conformation as in the five-membered 1,3,2-oxazaphospholidine, showing inhibition against oil rape root by 25% at 10 p.p.m.

Experimental

0.55 g (2.2 mmol) of $P(NEt_2)_3$ was dropped into 30 ml anhydrous benzene at room temperature, and then 0.051 g (0.2 mmol) of iodine was added at 343 K. After stirring for 15 min, 0.42 g (2 mmol) of 2-[*N*-(2′-hydroxy)ethylamino]-*N*′-ethylbenzamide, (1), was added, and the solution was heated to 348 K for 2.5 h. After the addition of an equivalent amount of S_8, the reaction mixture was allowed to reflux for another 1.5 h. The product was then isolated by flash chromatography with ethyl acetate-petroleum ether (1/1, *v*/*v*) as eluant, and purified by recrystallization from a mixture of chloroform and petroleum ether. 0.25 g of the title compound, (2), was obtained. Yield: 46.6%, m.p. 384 K. ^{1}H NMR ($CDCl_3$ as solvent, TMS as internal reference, δ): 8.13–7.03 (*m*, 4 H, Ar—H), 4.64–4.16 (*m*, 3 H), 3.98–3.64 (*m*, 3H), 1.36–1.29 (*t*, $^3J_{H-H}$ = 7.86 Hz, 3H). ^{31}P NMR ($CDCl_3$, 85% H_3PO_4 as external standard): 71.94 p.p.m. Analysis calculated for $C_{11}H_{13}N_2O_2PS$: C 49.25, H 4.85, N 10.44%; found: C 49.12; H 4.95, N 10.36%.

Crystal data

$C_{11}H_{13}N_2O_2PS$	Z = 2
M_r = 268.26	D_x = 1.422 Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
a = 6.9347 (7) Å	Cell parameters from 231 reflections
b = 9.9827 (10) Å	θ = 2.8–22.8°
c = 10.4868 (11) Å	μ = 0.38 mm^{-1}
α = 61.633 (2)°	T = 298 (2) K
β = 78.828 (2)°	Prism, colorless
γ = 83.139 (2)°	0.30 × 0.25 × 0.20 mm
V = 626.38 (11) Å^3	

Data collection

Bruker CCD area-detector diffractometer	2208 independent reflections
φ and ω scans	1940 reflections with $I > 2\sigma(1)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	R_{int} = 0.017
T_{min} = 0.564, T_{max} = 0.927	θ_{max} = 25.0°
2621 measured reflections	$h = -8 \rightarrow 6$
	$k = -11 \rightarrow 11$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0718P)^2 + 0.2182P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.041	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.118	$\Delta\rho_{max}$ = 0.44 e Å^{-3}
S = 1.04	$\Delta\rho_{min}$ = −0.29 e Å^{-3}
2208 reflections	
154 parameters	
H-atom parameters constrained	

The H atoms were positioned geometrically and refined with riding-model positional parameters and fixed isotropic displacement parameters.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997) and *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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