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Ethyl 3-(2-chlorophenyl)-5-(diethoxyphosphinoyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole-5-carboxylate

Ting-Ting Wang,[a] Feng Gao,[a] Mei Xue,[b] Ying-Jun Song[a] and Wen-Hu Wang[a]*

[a]State Key Laboratory of Elemental-Organic Chemistry, Institute of Elemental-Organic Chemistry, Nankai University, Tianjin, People's Republic of China, and [b]Chemistry and Chemical Engineering College, Shihezi University, Shihezi, Xinjiang, People's Republic of China

Correspondence e-mail: whwang@nankai.edu.cn

Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.005 Å
R factor = 0.047
wR factor = 0.137
Data-to-parameter ratio = 14.6

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

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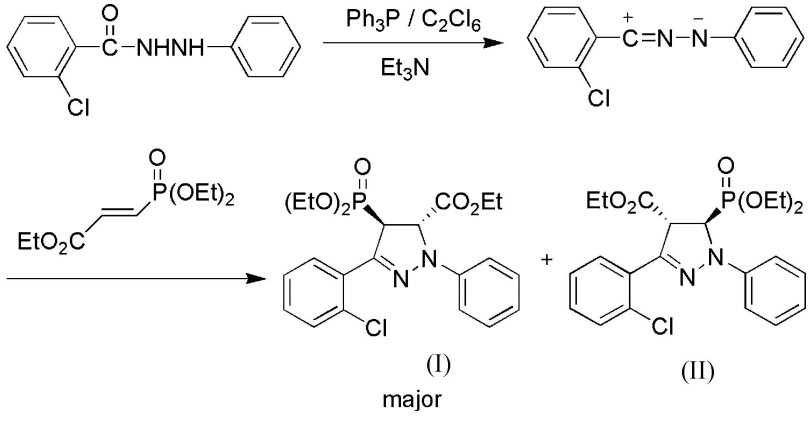
The title compound, $C_{22}H_{26}ClN_2O_5P$, was obtained from the cycloaddition reaction of 3-(2-chlorophenyl)-1-phenylnitrilimine (generated *in situ*) with ethyl *E*-2-(diethylphosphinoyl)acrylate. The pyrazoline ring adopts an envelope conformation. The molecules are linked by a pair of C—H···O hydrogen bonds into a centrosymmetric dimer.

Comment

Pyrazoline derivatives have been found to possess a broad spectrum of biological activities. They are used as anti-inflammatory and anticoagulating agents (Garanti *et al.*, 2002). 1,3-Dipolar cycloaddition of nitrilimines with alkenyl dipolarophiles offers a versatile route for the synthesis of substituted pyrazolines (Gothelf & Jorgensen, 2002; Kanemasa, 2002), and a number of reports have been published on this route (Buttero *et al.*, 2005; Molteni *et al.*, 2002; Benassuti *et al.*, 2004; Song & Zhu, 2003; Broggini *et al.*, 2001; Krajsovszky *et al.*, 2000; Nagarajan *et al.*, 1996; Molteni & Ponti, 2003). However, there have been fewer reports published on the cycloaddition of nitrilimines with phosphonyl alkenes (Kolokoltseva *et al.*, 1968). We report here the synthesis and crystal structure of the title compound, (I), obtained by the cycloaddition of 3-(2-chlorophenyl)-1-phenylnitrilimine with ethyl *E*-2-(diethylphosphinoyl)acrylate.



(I) (II)

As shown in Fig. 1, the phosphonyl and ethoxycarbonyl groups adopt a *trans* configuration with respect to the pyrazoline ring. This result is dictated by the stereoconservative nature of cycloaddition reactions (Bertrand & Wentrup, 1994). The pyrazoline ring adopts an envelope conformation with the flap atom C13 deviating by 0.401 (4) Å from the plane defined by the other four atoms. The C2–C7 and C17–C22 rings form dihedral angles of 26.4 (2) and 9.5 (2)°, respectively, with the N1/N2/C1/C8 plane. The N2—C1 distance of 1.288 (3) Å

confirms its double-bond character (Thirumurugan *et al.*, 1998).

In the solid state, C—H···O hydrogen bonds (Table 1) link the molecules into cyclic centrosymmetric dimers.

Experimental

2-Chlorobenzoylphenylhydrazine (0.27 g, 1.1 mmol), triphenylphosphine (0.53 g 2.0 mmol) and hexachloroethane (0.48 g, 2.0 mmol) were dissolved in acetonitrile (15 ml). To this mixture was added dropwise a solution of *E*-2-diethoxyphosphonyl acrylic acid ethyl ester (0.24 g, 1.0 mmol) and triethylamine (0.30 g, 3.0 mmol) in acetonitrile (5 ml). The mixture was stirred at room temperature for 30 min. The solvent was removed under vacuum and the residue was dissolved in chloroform (20 ml), washed with water and dried over anhydrous magnesium sulfate. After removing the solvent *in vacuo*, a yellow oil was obtained. It was subjected to column chromatography over silica gel, eluted with a mixture of ethyl acetate and petroleum ether (1:2), to obtain pure compound (I) (0.3 g, 64.5%) and compound (II) (0.08 g, 17.2%), both as thick oils. Single crystals of (I) were obtained by slow evaporation of a solution in chloroform and dichloromethane (1:3).

Crystal data

$C_{22}H_{26}ClN_2O_5P$
$M_r = 464.87$
Triclinic, $P\overline{1}$
$a = 10.195$ (2) Å
$b = 10.986$ (2) Å
$c = 11.409$ (3) Å
$\alpha = 82.434$ (4)°
$\beta = 84.994$ (4)°
$\gamma = 68.390$ (4)°
$V = 1176.7$ (4) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.27$ mm^{-1}
$T = 294$ (2) K
0.40 × 0.28 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.910$, $T_{max} = 0.948$
6011 measured reflections
4133 independent reflections
2759 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.137$
$S = 1.00$
4133 reflections
283 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C13—H13···O1^{i}	0.98	2.40	3.348 (4)	163

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

H atoms were placed in calculated positions, with C—H = 0.93–0.98 Å, and included in the final cycles of refinement using a riding model, with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); 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, 1999); software used to prepare material for publication: *SHELXTL*.

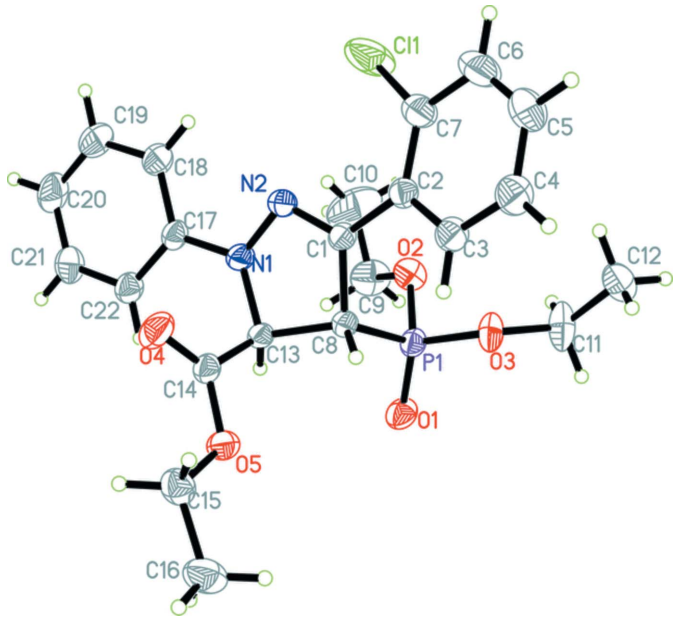


Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids and the atomic numbering.

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