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4-[(2,6-Dichlorophenyl)(hydroxyimino)methyl]-1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one

Xiao-Fang Li,[a] Ya-Qing Feng,[a]* Jun-Peng Zhuang[b] and Xiao-Fen Hu[a]

[a]School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, People's Republic of China, and [b]School of Science, Tianjin University, Tianjin 300072, People's Republic of China

Correspondence e-mail: lxf7213@eyou.com

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The title compound, $C_{18}H_{15}Cl_2N_3O_2$, was derived from the product of the intermolecular [3 + 2]-cycloaddition reaction of 2,6-dichlorobenzonitrile oxide and 1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one. The hydroxy group and the 2,6-dichlorophenyl ring of the oxime are in a *trans* conformation and the C═N—O angle is 113.90 (15) Å. Pairs of molecules form centrosymmetric O—H···N hydrogen-bonded dimers, with an O···N distance of 2.821 (2) Å. The pyrazole ring is nearly planar, with a mean deviation from the plane of 0.0246 (3) Å and a dihedral angle between the pyrazole and the unsubstituted phenyl ring of 131.7 (4)°.

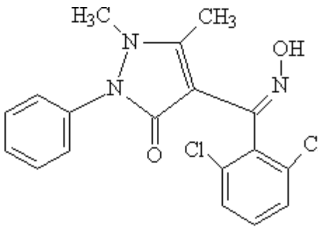
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.035
wR factor = 0.090
Data-to-parameter ratio = 13.2

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

Comment

1,3-Dipolar cycloadditions offer a convenient one-step route for the construction of a variety of complex five-membered heterocycles that are synthetically useful compounds (Caramella & Grunanger, 1984). 1,3-Dipolar cycloadditions of nitrile oxide are well documented and provide efficient methods for the synthesis of 2-isoxazolines, which are easily converted to amino ketones, oxo alcohols and a number of natural products by using different reduction reagents (Huisgen, 1984). Furthermore, 1,3-dipolar cycloaddition reactions can be used to synthesize bicyclic compounds, which are interesting structures for organic chemists because of their different practical applications. The intermolecular [3 + 2]-cycloaddition of 2,6-dichlorobenzonitrile oxide and 1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one gave the bicyclic compound 6,6a-dimethyl-3,5-diphenyl-3a,5,6,6a-tetrahydrocyclopenta[*d*]isoxazol-4-one (CPO). In this paper, the structure of 4-[(2,6-dichlorophenyl)(hydroxyimino)methyl]-1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one, (I), derived from CPO (see *Experimental*), is reported.



(I)

The molecular structure of (I) is illustrated in Fig. 1. The X-ray structure reveals that the hydroxy group and 2,6-dichlorophenyl ring of the oxime are in a *trans* configuration. Atoms C13/C12/C8/N3 are nearly coplanar, the mean deviation from the plane being 0.0051 (3) Å. Atom O2 is 0.0819 (3) Å from the C13/C12/C8/N3 mean plane and the C12—N3—O2 angle is 113.90 (15)°. The bond length C12—

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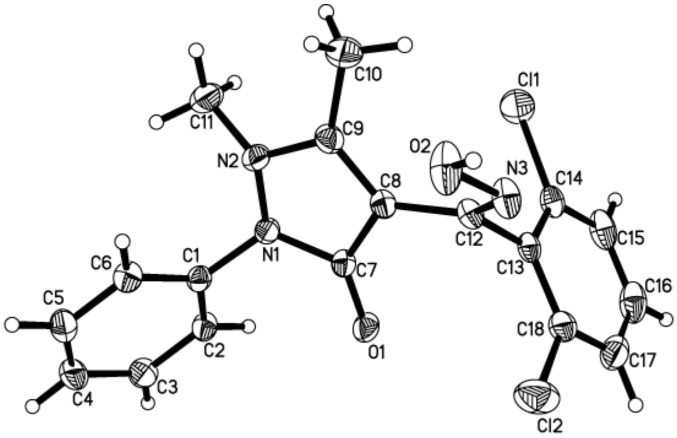

Figure 1
A view of the molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

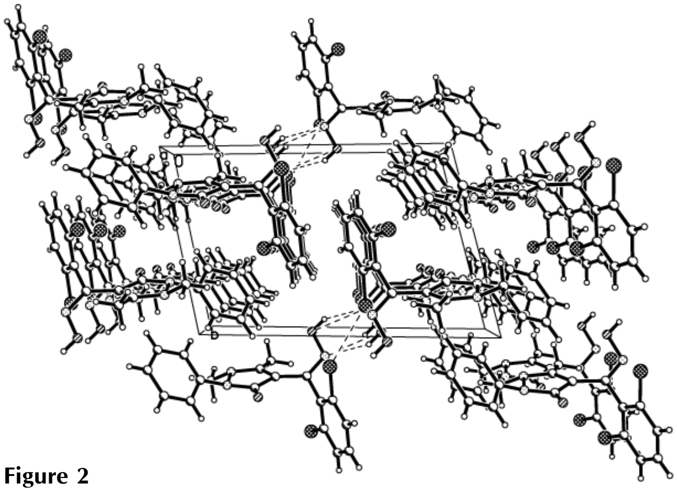

Figure 2
The crystal structure of (I), viewed along the *a* axis.

N3, which is 1.276 (2) Å, is similar to the value of 1.274 (2) Å determined in 4-(antipyrin-4-yliminomethyl)benzoic acid [(II); Zhang *et al.*, 2002] and corresponds to a double bond between C12 and N3. The dihedral angle between C13/C12/C8/N3 and the 2,6-dichlorophenyl ring (C13—C18) is 108.9 (2)° and that between C13/C12/C8/N3 and the pyrazole ring (C8/C7/N1/N2/C9) is 138.8 (3)°. The pyrazole ring is nearly planar, with a mean deviation from the plane of 0.0246 (3) Å. The C7—O1 and N1—N2 bond lengths are 1.218 (2) and 1.402 (2) Å and N1—C7—C8 and C7—N1—N2 angles are 104.95 (15) and 108.85 (14)°, respectively; these are comparable with values of 1.248 (2)/1.391(2) Å and 105.13 (18)/108.90(16)° reported in the literature (Zhang *et al.*, 2002). The C8—C9 bond length and C9—N2—N1 angle are 1.362 (3) Å and 107.48 (14)°, respectively, which compare well with the values of 1.357 (2) Å and 106.2 (1)° in the literature (Lui *et al.*, 2002). The dihedral angle between the pyrazole ring (C7/C8/C9/N2/N1) and the benzene ring (C1–C6) is 131.7 (4)°, but the corresponding value in (II) is 70.25 (4)° (Zhang *et al.*, 2002). The C—Cl bond lengths in the 2,6-dichlorophenyl ring are 1.727 (2) and 1.729 (2) Å, which are in good agreement with the values reported in the literature (Busetti *et al.*, 1980; Sutherland & Ali-Adib, 1987). Pairs of molecules of (I) form centrosymmetric O—H···N hydrogen-bonded dimers, where the O2···N3^{i} distance is 2.821 (2) Å, H2···N3^{i} is 2.11 Å, and the O2—H2···N3^{i} angle is 146° [symmetry code: (i) $1 - x, -y, 1 - z$].

Experimental

A mixture of 2,6-dichlorobenzonitrile oxide (2 mmol) and 1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one (2 mmol) in dry benzene (30 ml) was heated under reflux for 6 h. After evaporation of the solvent, the residue was separated by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give the product CPO. The structure of CPO was determined by ^{1}H NMR. CPO was unstable and underwent a decomposition reaction in solution, during recrystallization, to give crystals of (I). A crystal suitable for X-ray analysis was obtained by slow evaporation of a solution of CPO in chloroform over a period of 30 d. M.p. 475–476 K; IR (KBr): 3452 (OH), 1701 (C=O), 1595, 1578 (C=N, C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$, p.p.m.): 1.84 (3H, *s*), 2.74 (3H, *s*), 10.39 (1H, *b*), 7.21–7.58 (8H, *m*).

Crystal data

$C_{18}H_{15}Cl_2N_3O_2$
$M_r = 376.23$
Triclinic, $P\overline{1}$
$a = 7.804$ (2) Å
$b = 9.123$ (4) Å
$c = 13.523$ (5) Å
$\alpha = 74.313$ (8)°
$\beta = 78.473$ (8)°
$\gamma = 74.265$ (8)°
$V = 883.7$ (6) Å^3
$Z = 2$
$D_x = 1.414$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 985 reflections
$\theta = 2.5$–26.4°
$\mu = 0.38$ mm^{-1}
$T = 293$ (2) K
Plate, colorless
0.34 × 0.20 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.746$, $T_{max} = 0.940$
6966 measured reflections
3028 independent reflections
2537 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 25.0$°
$h = -6 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.090$
$S = 1.02$
3028 reflections
230 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.084P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.008 (2)

Table 1
Selected geometric parameters (Å, °).

Cl1—C14	1.729 (2)	N3—C12	1.276 (2)
N1—N2	1.402 (2)	N3—O2	1.400 (2)
N1—C1	1.423 (2)	O1—C7	1.218 (2)
N2—C9	1.360 (2)	C8—C9	1.362 (3)
N2—C11	1.458 (3)		
N2—N1—C7	108.85 (14)	N1—C7—C8	104.95 (15)
C9—N2—N1	107.48 (14)	C9—C8—C12	129.27 (17)
C12—N3—O2	113.90 (15)		

All H atoms were included in calculated positions, with C—H distances of 0.93 Å (for phenyl), 0.98 Å (for methyl) and 0.82 Å for O—H. They were included in the refinement in riding-motion approximation, with $U_{iso} = 1.2U_{eq}$ ($1.5U_{eq}$ for methyl and O—H) of the carrier atom.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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