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4,11-Bis(4-chlorophenyl)-3,10-bis(2,6-dichlorophenyl)-1,8-dioxa-2,9-diazadispiro[4.1.4.3]tetradeca-2,9-dien-6-one 0.75-hydrate

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Key indicators

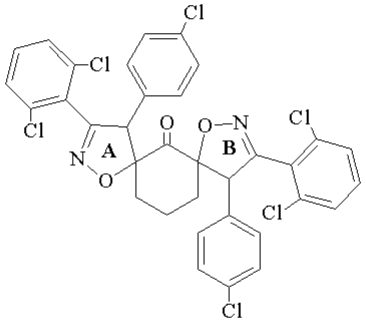
Single-crystal X-ray study
T = 293 K
Mean *σ*(C–C) = 0.008 Å
H-atom completeness 94%
Disorder in solvent or counterion
R factor = 0.068
wR factor = 0.186
Data-to-parameter ratio = 14.1

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

The title compound, $C_{34}H_{22}Cl_6N_2O_3\cdot 0.75H_2O$, was synthesized by the intermolecular [3+2]-cycloaddition of 2,6-dichlorobenzonitrile oxide and 2,6-bis(4-chlorobenzylidene)cyclohexanone. There are three rings linked by two spiro-C atoms, with approximate C_2 symmetry. The cyclohexane ring has a chair conformation and the two five-membered isoxazoline rings adopt envelope conformations.

Comment

Spiro-compounds represent an important class of naturally occurring substances characterized by highly pronounced biological properties (Kobayashi *et al.*, 1991; James *et al.*, 1991). They are found as pheromones, antibiotics, alkaloids (Gore *et al.*, 1990), and antitumor agents (Tietze *et al.*, 1998; Araki *et al.*, 2002). 1,3-Dipolar cycloaddition reactions are considered the most important process for the construction of spiro-compounds containing five-membered rings, due to the high regio- and stereoselective properties of these reactions (Caramella & Grunanger, 1984).



(I)

The structure of the title compound, (I), is reported here. The molecular structure of (I) is illustrated in Fig. 1. Compound (I) contains three spiro-linked rings, *viz*. a cyclohexanone ring and two isoxazoline rings. The six-membered cyclohexanone ring has the usual chair conformation. The two isoxazoline rings are attached to this central ring through spiro-C atoms, giving approximate C_2 symmetry. Attached to the isoxazoline rings are 4-chlorophenyl and 2,6-dichlorophenyl substituents.

The two isoxazoline rings (*A* and *B*) are non-planar, with envelope conformations. Rings O2/N1/C8/C7 (ring *A*) and O3/N2/C10/C9 (ring *B*) form almost exactly planar arrangements; the torsion angles O2—N1—C8—C7 of −0.9 (5)° and O3—N2—C10—C9 of 1.9 (5)° are similar to that of 1.4 (3)° in a related structure (Feng *et al.*, 1997). The spiro-atom C2 lies 0.190 (3) Å from the O2/N1/C8/C7 plane in ring *A* and atom C6 is 0.419 (3) Å from the O3/N2/C10/C9 plane in ring *B*, these two atoms forming the flaps of the envelopes. The

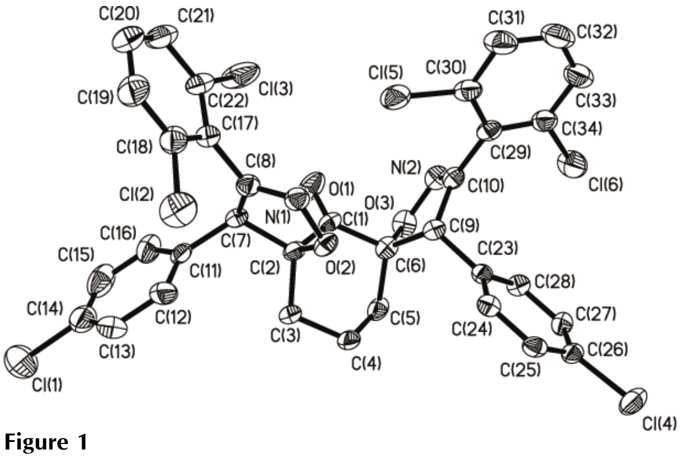


Figure 1
The molecular structure of (I), drawn with 30% probability ellipsoids.

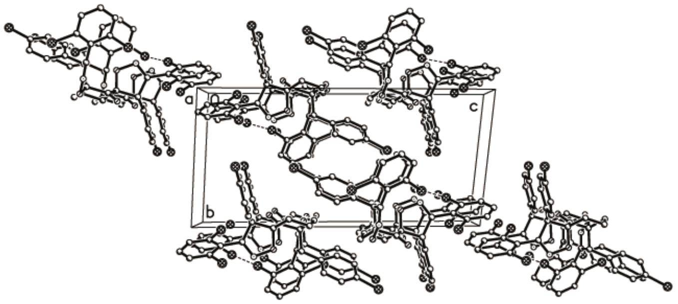


Figure 2
The crystal packing of (I), viewed along the *a* axis, without the disordered water molecules.

dihedral angle between the C7/C2/O2 plane and the C7/C8/N1/O2 mean plane is 12.0 (4)°, and that between the C9/C6/O3 plane and the C9/C10/N2/O3 mean plane is 26.7 (4)°. The bond lengths O2—N1 and O3—N2 are 1.427 (5) and 1.416 (5) Å, respectively, and are comparable to that of 1.413 (2) Å in the related structure (Feng *et al.*, 1997).

The dihedral angle between the two substituted phenyl rings on ring *A* is 95.5 (2)°, while that between the two subsituted phenyl rings on ring *B* is 91.2 (2)°; in each case, the 2,6-dichlorophenyl ring is oriented approximately perpendicular to the 4-chlorophenyl ring. The dihedral angle between the planar part (O2/N1/C8/C7) of ring *A* and its 4-chlorophenyl substituent ring is 88.2 (3)° and that between the planar part of ring *B* and its 4-chlorophenyl substituent ring is 89.2 (3)°. The dihedral angle between the two isoxazoline ring envelope flaps (C7/C2/O2 and C9/C6/O3), which form the spiro linkages with the central ring, is 66.2 (3)°.

The Cl—C bond lengths are in the range 1.732 (6)–1.746 (7) Å, in agreement with values reported in the literature (Busetti *et al.*, 1980; Sutherland & Ali-Adib, 1987).

Experimental

A mixture of 2,6-dichlorobenzonitrile oxide (3 mmol) and 2,6-bis(4-chlorobenzylidene)cyclohexanone (1.5 mmol) in dry benzene (30 ml) was heated under reflux for 40 h. After evaporation of the solvent, the residue was separated by column chromatography (silica gel, petroleum ether–ethyl acetate = 5:1) to give the title compound, (I). M.p. 498–499 K; IR (KBr): 1736 (C═O), 1602, 1580 (C═N, C═C) cm^{-1}; ^1H NMR ($CDCl_3$, p.p.m.): 1.57 (4H, *m*), 1.94 (2H, *m*), 6.18 (2H, *s*), 7.13–7.34 (14H, *m*); ^{13}C NMR ($CDCl_3$, p.p.m.): 17.71, 30.78, 57.39, 94.87, 126.71, 128.71, 130.08, 131.11, 132.34, 132.67, 134.54, 135.32, 135.97, 136.74, 156.36, 198.62, 206.84. 20 mg of (I) was dissolved in 15 ml chloroform, and the solution was kept at room temperature for 10 d, to give colorless single crystals of (I) by evaporation.

Crystal data

$C_{34}H_{22}Cl_6N_2O_3 \cdot 0.75H_2O$
$M_r = 732.75$
Triclinic, $P\overline{1}$
$a = 8.834\ (3)$ Å
$b = 10.304\ (3)$ Å
$c = 20.576\ (6)$ Å
$\alpha = 91.915\ (7)°$
$\beta = 96.371\ (7)°$
$\gamma = 110.718\ (10)°$
$V = 1735.7\ (10)$ Å^3
$Z = 2$
$D_x = 1.402$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 747 reflections
$\theta = 2.8$–$21.4°$
$\mu = 0.53$ mm^{-1}
$T = 293\ (2)$ K
Block, colorless
0.24 × 0.20 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{min} = 0.770$, $T_{max} = 0.918$
8673 measured reflections
5928 independent reflections
3052 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 25.0°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -12 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.186$
$S = 1.02$
5928 reflections
421 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.084P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C8	1.267 (6)	C1—C2	1.547 (7)
N1—O2	1.427 (5)	C2—C3	1.524 (6)
O1—C1	1.187 (5)	C2—C7	1.546 (6)
O2—C2	1.450 (5)	C7—C8	1.497 (7)
Cl1—C14	1.746 (7)	C7—C11	1.523 (6)
Cl2—C18	1.740 (6)		
C8—N1—O2	108.7 (4)	O3—C6—C9	103.0 (4)
C10—N2—O3	108.6 (4)	C5—C6—C9	118.4 (4)
N1—O2—C2	109.3 (3)	C1—C6—C9	111.5 (4)
N2—O3—C6	108.8 (3)	C8—C7—C11	114.8 (4)
O1—C1—C6	120.8 (4)	C8—C7—C2	99.7 (4)
O1—C1—C2	121.5 (4)	C11—C7—C2	117.0 (4)
C6—C1—C2	117.3 (4)	N1—C8—C7	115.9 (4)
O2—C2—C3	107.9 (4)	N1—C8—C17	118.9 (4)
O2—C2—C7	105.0 (3)	C7—C8—C17	125.2 (4)
C3—C2—C7	117.1 (4)	C10—C9—C23	112.8 (4)
O2—C2—C1	107.8 (3)	C10—C9—C6	98.0 (3)
C3—C2—C1	108.6 (4)	C23—C9—C6	115.0 (4)
C7—C2—C1	110.1 (4)	N2—C10—C29	119.8 (4)
O3—C6—C5	107.3 (4)	N2—C10—C9	114.3 (4)
O3—C6—C1	108.5 (4)	C29—C10—C9	126.0 (4)
C5—C6—C1	107.6 (4)		

H atoms were positioned geometrically and refined with riding-model constraints. Residual electron-density features were interpreted as water molecules, disordered over three partially occupied sites, one of them on an inversion center and the other two related by it. Occupancies of 0.5 were assigned on the basis of reasonable refined displacement parameters, corresponding to 0.75 molecules of water in the asymmetric unit. H atoms were not included for these water molecules, which are presumed to derive from the undried chloroform solvent used for recrystallization.

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

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