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2-(2,4-Dichlorophenoxy)-*N*′-[2-(2,4-dichlorophenoxy)acetyl]acetohydrazide

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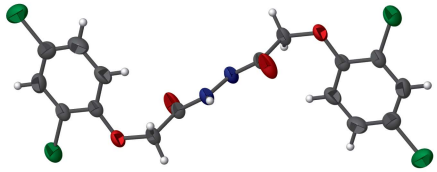
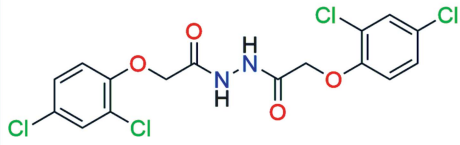
The complete molecule of the title compound, $C_{16}H_{12}Cl_4N_2O_4$, is generated by a crystallographic centre of symmetry. In the crystal, N—H···O hydrogen bonds link the molecules into [010] chains featuring $R_2^2(10)$ loops. The chains are cross-linked by short Cl···N contacts [3.224 (2) Å].

3D view



Chemical scheme



Structure description

Diacylhydrazines have insecticidal activities (Wang *et al.*, 2017) and can also be used to recover metal ions from solution (Chekanova *et al.*, 2004; Radushev *et al.*, 2007). In addition, they are precursors in the synthesis of biologically active heterocycles (Zarei 2017; Stabile *et al.*, 2010). As part of our studies in this area, we now describe the synthesis and structure of the title compound, $C_{16}H_{12}Cl_4N_2O_4$ (**I**). The asymmetric unit consists of half a molecule, which is completed by inversion symmetry centred in the middle of the central N—N bond (Fig. 1).

The twist angle between the 2,4-dichlorophenoxy ring system and the *N*′-acetylacetohydrazide group in (**I**) is 77.8 (1)°; the latter has a crystallographically imposed *trans* conformation, in a manner similar to 2-[5-methyl-2-(propan-2-yl)phenoxy]-*N*′-{2-[5-methyl-2-(propan-2-yl)phenoxy]acetyl}acetohydrazide (Fun *et al.*, 2011). The C—N—N—C torsion angles in the structures of 2-(4-chlorophenoxy)-*N*′-[2-(4-chlorophenoxy)acetyl]acetohydrazide monohydrate (Chen & Tan, 2010) and *N,N*′-*bis*[2-(quinolin-8-yloxy)acetoyl]hydrazine dihydrate (Zheng *et al.*, 2007) are 72.7 and 117.6°, respectively, compared to 180.0° in (**I**).

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2^{i}	0.86	1.94	2.774 (3)	164

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

In the crystal, each molecule is involved in four N—H···O hydrogen-bonding contacts, donating two and accepting two bonds, leading to the formation of ribbons propagating parallel to [010] (Table 1, Fig. 2). The ribbons are linked by short Cl···N contacts perpendicular to the plane of the ribbons and roughly in the *c*-axis direction. The contact involves the *para* Cl atom of the 2,4-dichlorophenoxy group and the nitrogen atom of the *N*′-acetylacetohydrazide group, with a Cl2···N1 distance of 3.224 (2) Å (sum of van der Waals' radii = 3.30 Å).

Synthesis and crystallization

A mixture of 2-(naphthalen-2-yloxy)acetohydrazide (0.47 g, 2.0 mmol) and ethyl 2-cyano-3-ethoxyacrylate (0.34 g, 2.0 mmol) in anhydrous ethanol (10 ml) was heated under reflux for 2 h. The solid obtained on cooling was collected by filtration, washed with ethanol, dried, and recrystallized from dimethylformamide solution to give colourless plates of (**I**) in 67% yield; m.p. 249–250°C (lit. m.p. 250°C; Abdel-Wahab *et al.*, 2017).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Funding information

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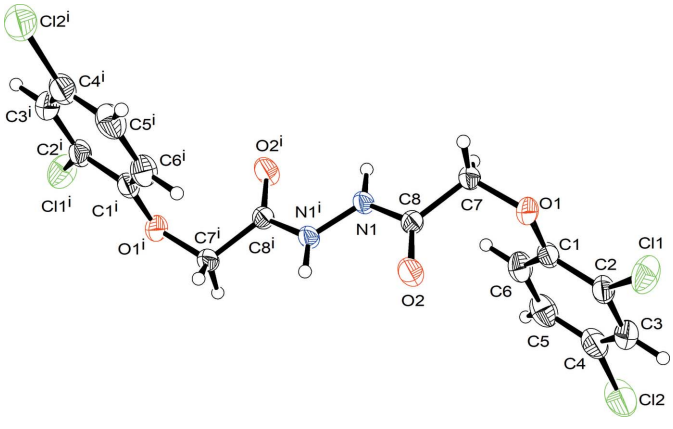

Figure 1
The molecular structure of (**I**) showing 50% displacement ellipsoids. Symmetry code: (i) $1-x, 2-y, 1-z$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{12}Cl_4N_2O_4$
M_r	438.08
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	9.7398 (4), 4.6540 (2), 20.1866 (9)
β (°)	100.842 (4)
V (Å^3)	898.71 (7)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	6.22
Crystal size (mm)	0.16 × 0.10 × 0.01
Data collection	
Diffractometer	Rigaku Oxford Diffraction SuperNova, Dual, Cu at home/near, Atlas
Absorption correction	Gaussian (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.869, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5415, 1797, 1504
R_{int}	0.040
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.624
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.053, 0.153, 1.03
No. of reflections	1797
No. of parameters	118
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.51, −0.42

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXS* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2020) and *CHEMDRAW Ultra* (Cambridge Soft, 2016).

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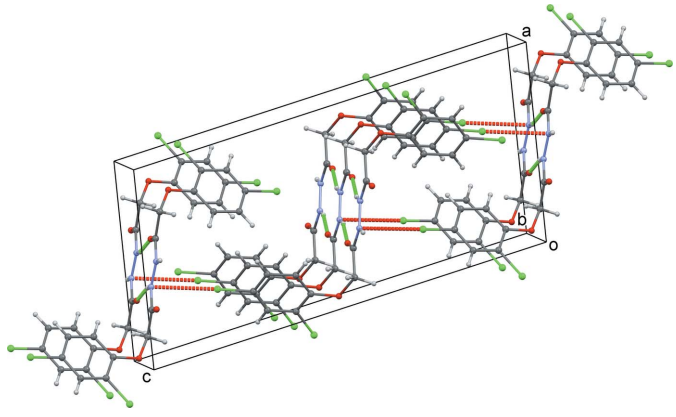

Figure 2
The crystal structure viewed down [010] showing N—H···O hydrogen bonds (green dotted lines) and short Cl···N interactions (red dotted lines).

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full crystallographic data

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Crystal data

$C_{16}H_{12}Cl_4N_2O_4$
M_r = 438.08
Monoclinic, $P2_1/c$
a = 9.7398 (4) Å
b = 4.6540 (2) Å
c = 20.1866 (9) Å
β = 100.842 (4)°
V = 898.71 (7) Å^3
Z = 2
$F(000)$ = 444
D_x = 1.619 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 2218 reflections
θ = 4.6–73.9°
μ = 6.22 mm^{-1}
T = 293 K
Plate, colourless
0.16 × 0.10 × 0.01 mm

Data collection

Rigaku Oxford Diffraction SuperNova, Dual, Cu at home/near, Atlas diffractometer
ω scans
Absorption correction: gaussian (CrysalisPro; Rigaku OD, 2015)
T_{min} = 0.869, T_{max} = 1.000
5415 measured reflections
1797 independent reflections
1504 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 74.2°, θ_{min} = 4.5°
h = −11→8
k = −5→5
l = −24→24

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.153
S = 1.03
1797 reflections
118 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0898P)^2 + 0.4345P]$ 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}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. The H atoms were positioned geometrically (N—H = 0.86, C—H = 0.93–0.96 Å) and refined using a riding model with U_{iso}(H) = 1.2U_{eq}(C,*N*).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.8216 (2)	0.7834 (5)	0.36947 (12)	0.0365 (5)
C2	0.8980 (3)	0.5906 (6)	0.33765 (14)	0.0412 (6)
C3	0.8527 (3)	0.5101 (7)	0.27100 (16)	0.0526 (7)
H3	0.903880	0.379893	0.250485	0.063*
C4	0.7314 (3)	0.6258 (8)	0.23597 (15)	0.0557 (7)
C5	0.6554 (3)	0.8206 (8)	0.26484 (16)	0.0571 (8)
H5	0.574178	0.899439	0.239873	0.069*
C6	0.7006 (3)	0.8997 (7)	0.33185 (15)	0.0479 (6)
H6	0.649162	1.032065	0.351606	0.057*
C7	0.7949 (3)	1.0250 (5)	0.47047 (14)	0.0381 (6)
H7A	0.771884	1.200592	0.444919	0.046*
H7B	0.850851	1.075711	0.513877	0.046*
C8	0.6610 (2)	0.8789 (5)	0.48107 (12)	0.0333 (5)
N1	0.5616 (2)	1.0565 (4)	0.49304 (10)	0.0322 (4)
H1	0.573575	1.239427	0.492170	0.039*
O1	0.87343 (17)	0.8420 (4)	0.43541 (9)	0.0396 (4)
O2	0.6471 (2)	0.6192 (4)	0.48048 (13)	0.0548 (6)
Cl1	1.05074 (8)	0.44859 (19)	0.38265 (4)	0.0618 (3)
Cl2	0.67176 (10)	0.5161 (3)	0.15306 (4)	0.0858 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0307 (11)	0.0369 (12)	0.0445 (12)	−0.0022 (9)	0.0135 (9)	0.0014 (10)
C2	0.0338 (12)	0.0442 (13)	0.0488 (14)	0.0016 (10)	0.0161 (10)	−0.0001 (11)
C3	0.0470 (16)	0.0622 (17)	0.0533 (17)	−0.0043 (13)	0.0219 (13)	−0.0117 (13)
C4	0.0448 (15)	0.077 (2)	0.0469 (14)	−0.0155 (14)	0.0116 (12)	−0.0015 (14)
C5	0.0383 (14)	0.074 (2)	0.0575 (17)	−0.0014 (14)	0.0044 (12)	0.0117 (15)
C6	0.0338 (13)	0.0547 (15)	0.0561 (16)	0.0079 (11)	0.0109 (11)	0.0034 (13)
C7	0.0318 (11)	0.0326 (11)	0.0535 (14)	−0.0028 (9)	0.0172 (10)	−0.0078 (10)
C8	0.0323 (11)	0.0279 (10)	0.0419 (12)	0.0012 (9)	0.0124 (9)	−0.0020 (9)
N1	0.0296 (9)	0.0240 (8)	0.0459 (11)	−0.0006 (7)	0.0142 (8)	−0.0006 (7)
O1	0.0296 (8)	0.0439 (9)	0.0474 (9)	0.0059 (7)	0.0125 (7)	−0.0047 (8)
O2	0.0464 (11)	0.0265 (9)	0.1008 (17)	0.0003 (7)	0.0374 (11)	−0.0041 (9)
Cl1	0.0481 (4)	0.0707 (5)	0.0672 (5)	0.0257 (3)	0.0128 (3)	−0.0051 (4)
Cl2	0.0647 (6)	0.1438 (10)	0.0484 (5)	−0.0318 (6)	0.0094 (4)	−0.0157 (5)

Geometric parameters (Å, º)

C1—O1	1.359 (3)	C5—H5	0.9300
C1—C6	1.386 (4)	C6—H6	0.9300
C1—C2	1.397 (3)	C7—O1	1.419 (3)
C2—C3	1.386 (4)	C7—C8	1.521 (3)
C2—Cl1	1.723 (3)	C7—H7A	0.9700
C3—C4	1.368 (5)	C7—H7B	0.9700

C3—H3	0.9300	C8—O2	1.216 (3)
C4—C5	1.368 (5)	C8—N1	1.329 (3)
C4—Cl2	1.742 (3)	N1—N1^{i}	1.386 (4)
C5—C6	1.391 (4)	N1—H1	0.8600
O1—C1—C6	125.4 (2)	C1—C6—H6	119.7
O1—C1—C2	116.6 (2)	C5—C6—H6	119.7
C6—C1—C2	118.0 (2)	O1—C7—C8	111.03 (19)
C3—C2—C1	121.4 (3)	O1—C7—H7A	109.4
C3—C2—Cl1	119.6 (2)	C8—C7—H7A	109.4
C1—C2—Cl1	119.1 (2)	O1—C7—H7B	109.4
C4—C3—C2	118.8 (3)	C8—C7—H7B	109.4
C4—C3—H3	120.6	H7A—C7—H7B	108.0
C2—C3—H3	120.6	O2—C8—N1	122.4 (2)
C3—C4—C5	121.6 (3)	O2—C8—C7	122.6 (2)
C3—C4—Cl2	118.8 (3)	N1—C8—C7	114.89 (19)
C5—C4—Cl2	119.6 (3)	C8—N1—N1^{i}	119.3 (2)
C4—C5—C6	119.5 (3)	C8—N1—H1	120.4
C4—C5—H5	120.3	N1^{i}—N1—H1	120.4
C6—C5—H5	120.3	C1—O1—C7	118.22 (19)
C1—C6—C5	120.7 (3)		

Symmetry code: (i) $-x+1, -y+2, -z+1$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2^{ii}	0.86	1.94	2.774 (3)	164

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