

**(E)-3-(2,6-Dichlorobenzylidene)indolin-2-one**

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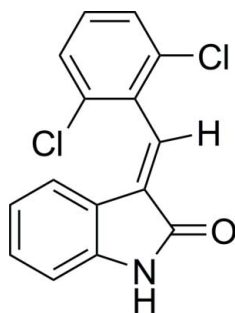
Received 13 October 2009; accepted 21 October 2009

Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  
R factor = 0.052; wR factor = 0.134; data-to-parameter ratio = 18.8.

There are two independent molecules in the asymmetric unit of the title compound,  $\text{C}_{15}\text{H}_9\text{Cl}_2\text{NO}$ . The dihedral angles between the oxindolyl and dichlorophenyl rings are essentially identical for the two independent molecules [63.4 (1) and 63.2 (1)°]. Dimers linked by amide-carbonyl  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds are formed from each symmetry-independent molecule and the respective symmetry equivalent created by inversion.

**Related literature**

For the syntheses and structures of related compounds, see: Ankati *et al.* (2009); Zhang *et al.* (2008, 2009a,b,c). For the pharmacological properties of 3-(substituted-benzylidene)-1,3-dihydro-indolin derivatives, see: Andreani *et al.* (2006); Balderamos *et al.* (2008); Johnson *et al.* (2005); Olgen *et al.* (2005, 2007); Sun *et al.* (2003)

**Experimental***Crystal data* $\text{C}_{15}\text{H}_9\text{Cl}_2\text{NO}$  $M_r = 290.13$ Triclinic,  $P\bar{1}$  $a = 8.3908$  (5) Å $b = 12.6079$  (7) Å $c = 12.7635$  (7) Å $\alpha = 99.334$  (1)° $\beta = 91.188$  (1)° $\gamma = 96.338$  (1)° $V = 1323.2$  (1) Å<sup>3</sup> $Z = 4$ Mo  $K\alpha$  radiation $\mu = 0.48$  mm<sup>-1</sup> $T = 296$  K $0.35 \times 0.17 \times 0.08$  mm*Data collection*Bruker APEX diffractometer  
Absorption correction: multi-scan  
(SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.849$ ,  $T_{\max} = 0.964$ 16946 measured reflections  
6459 independent reflections  
4669 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.024$ *Refinement* $R[F^2 > 2\sigma(F^2)] = 0.052$  $wR(F^2) = 0.134$  $S = 1.03$ 

6459 reflections

343 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.33$  e Å<sup>-3</sup> $\Delta\rho_{\text{min}} = -0.23$  e Å<sup>-3</sup>**Table 1**

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$                                    | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|-------|-------------|-------------|---------------|
| $\text{N21}-\text{H21}\cdots\text{O22}^i$        | 0.86  | 2.03        | 2.854 (2)   | 159           |
| $\text{N1}-\text{H1}\cdots\text{O2}^{\text{ii}}$ | 0.86  | 1.99        | 2.837 (2)   | 171           |

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x + 2, -y + 1, -z + 1$ .

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL and publCIF (Westrip, 2009).

The authors are grateful for the grants from the Welch Foundation (N-118) and the DARPA (HR0011-06-1-0032).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2152).

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**supplementary materials**

*Acta Cryst.* (2009). E65, o2887 [ doi:10.1107/S1600536809043487 ]

## (*E*)-3-(2,6-Dichlorobenzylidene)indolin-2-one

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### Comment

3-(Substituted-benzylidene)-1,3-dihydro-indolin derivatives show a variety of pharmacologically important properties such as being protein and tyrosine kinase inhibitors (Olgen *et al.*, 2005, 2007; Sun *et al.*, 2003) as well as antitumor (Andreani *et al.*, 2006) and neuroprotective agents (Johnson *et al.*, 2005). We have designed, synthesized and crystallized several 3-substituted indolin-2-one derivatives to study their neuroprotective properties (Balderamos *et al.*, 2008 and Ankati *et al.*, 2009). In relation of structure-activity of 3-substituted indolin-2-ones, the title compound was synthesized and its crystal structure is reported here. It is similar to the structure of 5-bromo substituted (*E*)-5-bromo-3-(2,6-dichlorobenzylidene)indolin-2-one (Zhang *et al.* 2009c). The X-ray crystal structure shows the title compound to show an *E* configuration.

For studying the biological properties a series of 3-substituted indolin-2-one derivatives have been synthesized in our lab and their neuroprotective activities have been tested (Balderamos *et al.* 2008). As a part of our research on the relationship between the biological activities and solid structures a couple of crystal structures of the derivatives have been carried out (Zhang, *et al.*, 2008, 2009a, 2009b, 2009c). The title compound consists of an oxindolyl and a dichlorophenyl unit (Fig 1). The dihedral angles between the two aromatic rings are basically identical for the two independent molecules and measure to 63.4°(1) and 63.2°(1), respectively. The crystal structure revealed that intermolecular H-bonds (Table 1), linking two symmetry related inverted molecules, form an eight membered dimeric ring system (Fig 2).

### Experimental

The title compound was synthesized by the condensation of 2,6-dichlorobenzaldehyde (1 mmol) with 2-oxindole (1 mmol) in ethanol (10 ml) in the presence of catalytic amount of piperidine (0.1 mmol) with a yield of 83%. After refluxing for 3 hr, the reaction mixture was left to stand overnight. The resulting crude solid was filtered, washed with cold ethanol (10 ml) and dried. Red single crystals of the compound suitable for X-ray structure determination obtained by recrystallization from ethanol.

### Refinement

All H atom were placed in calculated positions and included in the final cycles of refinement using a riding model, with distances N–H = 0.86 Å and C–H = 0.93 Å, and displacement parameters  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N},\text{C})$ .

## Figures

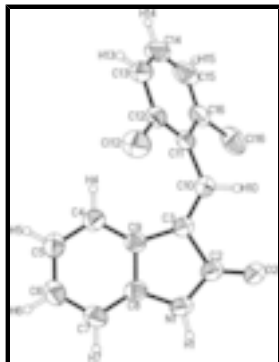


Fig. 1. : A view of one of the independent molecules with displacement ellipsoids drawn at the 40% probability level. H atoms are presented as open circles with arbitrary radii. Atoms of another independent molecule were labeled as N21 H21 C22 O22 through C36 Cl36.

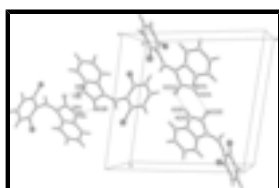


Fig. 2. : A unit cell packing view of the title compound. Dashed lines indicate hydrogen bonds. For clarity, H atoms are presented as open circles with arbitrary radii.

## (*E*)-3-(2,6-Dichlorobenzylidene)indolin-2-one

### Crystal data

$C_{15}H_9Cl_2NO$

$M_r = 290.13$

Triclinic,  $P\bar{1}$

Hall symbol: -P 1

$a = 8.3908$  (5) Å

$b = 12.6079$  (7) Å

$c = 12.7635$  (7) Å

$\alpha = 99.334$  (1)°

$\beta = 91.188$  (1)°

$\gamma = 96.338$  (1)°

$V = 1323.2$  (1) Å<sup>3</sup>

$Z = 4$

$F_{000} = 592$

$D_x = 1.456$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 6257 reflections

$\theta = 2.8$ – $27.9$ °

$\mu = 0.48$  mm<sup>-1</sup>

$T = 296$  K

Plates, orange

$0.35 \times 0.17 \times 0.08$  mm

### Data collection

Bruker APEX  
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 83.33 pixels mm<sup>-1</sup>

$T = 296$  K

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.849$ ,  $T_{\max} = 0.964$

6459 independent reflections

4669 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\text{max}} = 28.3$ °

$\theta_{\text{min}} = 1.6$ °

$h = -11 \rightarrow 11$

$k = -16 \rightarrow 16$

$l = -16 \rightarrow 16$

16946 measured reflections

*Refinement*

|  |  |
|--|--|
| Refinement on $F^2$  | Secondary atom site location: difference Fourier map     |
| Least-squares matrix: full                                     | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.052$                                | H-atom parameters constrained                            |
| $wR(F^2) = 0.134$  | $w = 1/[\sigma^2(F_o^2) + (0.0619P)^2 + 0.2428P]$        |
| $S = 1.03$   | where $P = (F_o^2 + 2F_c^2)/3$                           |
| 6459 reflections   | $(\Delta/\sigma)_{\max} < 0.001$                         |
| 343 parameters   | $\Delta\rho_{\max} = 0.33 \text{ e } \text{Å}^{-3}$      |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{\min} = -0.23 \text{ e } \text{Å}^{-3}$     |
|  | Extinction correction: none                              |

*Special details*

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

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{Å}^2$ )*

|     | $x$        | $y$          | $z$          | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|------------|--------------|--------------|----------------------------------|
| N1  | 0.8867 (2) | 0.59180 (14) | 0.44745 (13) | 0.0561 (4)                       |
| H1  | 0.9144     | 0.5842       | 0.5108       | 0.067*                           |
| C2  | 0.9182 (3) | 0.52439 (18) | 0.35853 (16) | 0.0548 (5)                       |
| O2  | 0.9914 (2) | 0.44512 (13) | 0.35421 (12) | 0.0729 (5)                       |
| C3  | 0.8476 (2) | 0.56692 (16) | 0.26602 (15) | 0.0480 (5)                       |
| C4  | 0.6896 (3) | 0.73604 (17) | 0.27271 (17) | 0.0537 (5)                       |
| H4  | 0.6677     | 0.7285       | 0.2000       | 0.064*                           |
| C5  | 0.6374 (3) | 0.82040 (18) | 0.3414 (2)   | 0.0609 (6)                       |
| H5  | 0.5800     | 0.8698       | 0.3146       | 0.073*                           |
| C6  | 0.6698 (3) | 0.83215 (18) | 0.44947 (19) | 0.0613 (6)                       |
| H6  | 0.6343     | 0.8898       | 0.4944       | 0.074*                           |
| C7  | 0.7538 (3) | 0.76009 (18) | 0.49217 (17) | 0.0575 (5)                       |
| H7  | 0.7760     | 0.7684       | 0.5649       | 0.069*                           |
| C8  | 0.8033 (2) | 0.67554 (16) | 0.42338 (16) | 0.0487 (5)                       |
| C9  | 0.7750 (2) | 0.66252 (16) | 0.31353 (15) | 0.0461 (4)                       |
| C10 | 0.8627 (3) | 0.51431 (17) | 0.16770 (16) | 0.0520 (5)                       |
| H10 | 0.9152     | 0.4526       | 0.1636       | 0.062*                           |

## supplementary materials

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|      |             |               |               |              |
|------|-------------|---------------|---------------|--------------|
| C11  | 0.8090 (2)  | 0.53923 (16)  | 0.06520 (15)  | 0.0478 (5)   |
| C12  | 0.8584 (2)  | 0.63401 (17)  | 0.02580 (16)  | 0.0511 (5)   |
| Cl12 | 0.99044 (8) | 0.73448 (5)   | 0.10073 (5)   | 0.07059 (19) |
| C13  | 0.8105 (3)  | 0.6502 (2)    | -0.07446 (18) | 0.0665 (6)   |
| H13  | 0.8441      | 0.7148        | -0.0979       | 0.080*       |
| C14  | 0.7137 (3)  | 0.5705 (3)    | -0.13847 (19) | 0.0764 (8)   |
| H14  | 0.6818      | 0.5810        | -0.2059       | 0.092*       |
| C15  | 0.6628 (3)  | 0.4751 (2)    | -0.10437 (19) | 0.0747 (7)   |
| H15  | 0.5965      | 0.4211        | -0.1482       | 0.090*       |
| C16  | 0.7111 (3)  | 0.46028 (18)  | -0.00474 (17) | 0.0570 (5)   |
| Cl16 | 0.64687 (9) | 0.33919 (5)   | 0.03774 (6)   | 0.0858 (2)   |
| N21  | 0.6215 (2)  | 0.38621 (13)  | 0.51019 (13)  | 0.0534 (4)   |
| H21  | 0.6146      | 0.4447        | 0.5543        | 0.064*       |
| C22  | 0.5593 (3)  | 0.36652 (16)  | 0.40938 (16)  | 0.0513 (5)   |
| O22  | 0.4820 (2)  | 0.42554 (12)  | 0.36706 (12)  | 0.0687 (5)   |
| C23  | 0.6022 (2)  | 0.25727 (15)  | 0.36049 (15)  | 0.0461 (4)   |
| C24  | 0.7577 (3)  | 0.12452 (17)  | 0.44962 (18)  | 0.0558 (5)   |
| H24  | 0.7547      | 0.0704        | 0.3904        | 0.067*       |
| C25  | 0.8278 (3)  | 0.1109 (2)    | 0.5444 (2)    | 0.0666 (6)   |
| H25  | 0.8720      | 0.0473        | 0.5491        | 0.080*       |
| C26  | 0.8328 (3)  | 0.1911 (2)    | 0.6324 (2)    | 0.0684 (6)   |
| H26  | 0.8808      | 0.1805        | 0.6957        | 0.082*       |
| C27  | 0.7682 (3)  | 0.28678 (19)  | 0.62897 (17)  | 0.0602 (6)   |
| H27  | 0.7717      | 0.3405        | 0.6885        | 0.072*       |
| C28  | 0.6985 (2)  | 0.29923 (16)  | 0.53382 (16)  | 0.0491 (5)   |
| C29  | 0.6920 (2)  | 0.21915 (15)  | 0.44319 (15)  | 0.0461 (4)   |
| C30  | 0.5491 (2)  | 0.21366 (15)  | 0.26238 (15)  | 0.0481 (5)   |
| H30  | 0.4870      | 0.2549        | 0.2276        | 0.058*       |
| C31  | 0.5768 (2)  | 0.10769 (15)  | 0.20232 (14)  | 0.0461 (4)   |
| C32  | 0.4491 (3)  | 0.02878 (16)  | 0.16894 (16)  | 0.0518 (5)   |
| Cl32 | 0.25656 (7) | 0.05641 (5)   | 0.20230 (6)   | 0.0764 (2)   |
| C33  | 0.4683 (3)  | -0.07053 (18) | 0.10949 (18)  | 0.0655 (6)   |
| H33  | 0.3801      | -0.1218       | 0.0890        | 0.079*       |
| C34  | 0.6194 (4)  | -0.0920 (2)   | 0.08132 (18)  | 0.0710 (7)   |
| H34  | 0.6337      | -0.1587       | 0.0415        | 0.085*       |
| C35  | 0.7498 (3)  | -0.0170 (2)   | 0.11093 (19)  | 0.0692 (7)   |
| H35  | 0.8519      | -0.0322       | 0.0910        | 0.083*       |
| C36  | 0.7281 (3)  | 0.08203 (18)  | 0.17090 (17)  | 0.0562 (5)   |
| Cl36 | 0.89345 (8) | 0.17731 (6)   | 0.20621 (6)   | 0.0860 (2)   |

### Atomic displacement parameters ( $\text{\AA}^2$ )

|    | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$    | $U^{13}$     | $U^{23}$    |
|----|-------------|-------------|-------------|-------------|--------------|-------------|
| N1 | 0.0754 (12) | 0.0573 (11) | 0.0375 (9)  | 0.0106 (9)  | -0.0024 (8)  | 0.0117 (8)  |
| C2 | 0.0685 (14) | 0.0529 (12) | 0.0444 (11) | 0.0080 (10) | -0.0019 (10) | 0.0122 (9)  |
| O2 | 0.1095 (14) | 0.0638 (10) | 0.0513 (9)  | 0.0352 (10) | -0.0080 (9)  | 0.0110 (7)  |
| C3 | 0.0548 (11) | 0.0485 (11) | 0.0418 (10) | 0.0073 (9)  | -0.0001 (8)  | 0.0099 (8)  |
| C4 | 0.0568 (12) | 0.0541 (12) | 0.0520 (12) | 0.0080 (10) | 0.0024 (9)   | 0.0128 (10) |

|      |             |             |             |              |              |              |
|------|-------------|-------------|-------------|--------------|--------------|--------------|
| C5   | 0.0615 (13) | 0.0540 (13) | 0.0704 (15) | 0.0139 (10)  | 0.0091 (11)  | 0.0136 (11)  |
| C6   | 0.0663 (14) | 0.0517 (12) | 0.0647 (15) | 0.0066 (11)  | 0.0176 (11)  | 0.0042 (11)  |
| C7   | 0.0677 (14) | 0.0572 (13) | 0.0451 (11) | 0.0011 (11)  | 0.0086 (10)  | 0.0043 (10)  |
| C8   | 0.0525 (11) | 0.0490 (11) | 0.0443 (11) | -0.0009 (9)  | 0.0015 (8)   | 0.0116 (9)   |
| C9   | 0.0490 (11) | 0.0462 (11) | 0.0434 (10) | 0.0035 (8)   | 0.0030 (8)   | 0.0095 (8)   |
| C10  | 0.0614 (13) | 0.0488 (11) | 0.0481 (11) | 0.0164 (10)  | -0.0007 (9)  | 0.0084 (9)   |
| C11  | 0.0518 (11) | 0.0534 (12) | 0.0386 (10) | 0.0184 (9)   | 0.0017 (8)   | 0.0004 (8)   |
| C12  | 0.0529 (12) | 0.0584 (12) | 0.0437 (11) | 0.0180 (10)  | 0.0048 (9)   | 0.0053 (9)   |
| Cl12 | 0.0724 (4)  | 0.0672 (4)  | 0.0680 (4)  | -0.0048 (3)  | 0.0039 (3)   | 0.0073 (3)   |
| C13  | 0.0767 (16) | 0.0827 (17) | 0.0482 (13) | 0.0330 (14)  | 0.0112 (11)  | 0.0175 (12)  |
| C14  | 0.0839 (18) | 0.109 (2)   | 0.0389 (12) | 0.0392 (17)  | -0.0063 (11) | 0.0035 (13)  |
| C15  | 0.0667 (15) | 0.097 (2)   | 0.0513 (14) | 0.0177 (14)  | -0.0086 (11) | -0.0180 (14) |
| C16  | 0.0572 (12) | 0.0594 (13) | 0.0507 (12) | 0.0134 (10)  | 0.0053 (10)  | -0.0062 (10) |
| Cl16 | 0.0954 (5)  | 0.0576 (4)  | 0.0953 (5)  | -0.0016 (3)  | 0.0205 (4)   | -0.0090 (3)  |
| N21  | 0.0712 (11) | 0.0381 (9)  | 0.0460 (10) | 0.0049 (8)   | -0.0040 (8)  | -0.0062 (7)  |
| C22  | 0.0656 (13) | 0.0391 (10) | 0.0470 (11) | 0.0052 (9)   | 0.0022 (9)   | 0.0009 (8)   |
| O22  | 0.1060 (13) | 0.0475 (8)  | 0.0536 (9)  | 0.0290 (9)   | -0.0097 (8)  | -0.0010 (7)  |
| C23  | 0.0558 (11) | 0.0354 (9)  | 0.0457 (11) | 0.0053 (8)   | 0.0030 (9)   | 0.0020 (8)   |
| C24  | 0.0636 (13) | 0.0454 (11) | 0.0568 (13) | 0.0091 (10)  | -0.0043 (10) | 0.0029 (9)   |
| C25  | 0.0698 (15) | 0.0580 (14) | 0.0739 (16) | 0.0116 (11)  | -0.0136 (12) | 0.0158 (12)  |
| C26  | 0.0715 (15) | 0.0714 (16) | 0.0608 (14) | 0.0008 (12)  | -0.0205 (12) | 0.0145 (12)  |
| C27  | 0.0659 (14) | 0.0593 (13) | 0.0485 (12) | -0.0037 (11) | -0.0092 (10) | -0.0024 (10) |
| C28  | 0.0502 (11) | 0.0421 (10) | 0.0509 (11) | -0.0026 (8)  | -0.0017 (9)  | 0.0019 (8)   |
| C29  | 0.0488 (11) | 0.0423 (10) | 0.0454 (10) | 0.0008 (8)   | -0.0010 (8)  | 0.0046 (8)   |
| C30  | 0.0578 (12) | 0.0420 (10) | 0.0450 (11) | 0.0141 (9)   | 0.0004 (9)   | 0.0038 (8)   |
| C31  | 0.0609 (12) | 0.0435 (10) | 0.0346 (9)  | 0.0146 (9)   | -0.0012 (8)  | 0.0030 (8)   |
| C32  | 0.0658 (13) | 0.0482 (11) | 0.0414 (10) | 0.0149 (10)  | -0.0065 (9)  | 0.0028 (9)   |
| Cl32 | 0.0616 (4)  | 0.0763 (4)  | 0.0860 (5)  | 0.0078 (3)   | -0.0018 (3)  | -0.0020 (3)  |
| C33  | 0.0947 (18) | 0.0446 (12) | 0.0544 (13) | 0.0137 (12)  | -0.0129 (12) | -0.0020 (10) |
| C34  | 0.115 (2)   | 0.0513 (13) | 0.0489 (13) | 0.0359 (15)  | -0.0008 (13) | -0.0040 (10) |
| C35  | 0.0865 (18) | 0.0728 (16) | 0.0558 (13) | 0.0412 (14)  | 0.0129 (12)  | 0.0105 (12)  |
| C36  | 0.0642 (13) | 0.0562 (12) | 0.0503 (12) | 0.0174 (10)  | 0.0042 (10)  | 0.0082 (10)  |
| Cl36 | 0.0609 (4)  | 0.0907 (5)  | 0.1046 (6)  | 0.0068 (3)   | 0.0163 (4)   | 0.0106 (4)   |

*Geometric parameters (Å, °)*

|        |           |         |           |
|--------|-----------|---------|-----------|
| N1—C2  | 1.353 (3) | N21—C22 | 1.353 (3) |
| N1—C8  | 1.399 (3) | N21—C28 | 1.403 (3) |
| N1—H1  | 0.8600    | N21—H21 | 0.8600    |
| C2—O2  | 1.224 (2) | C22—O22 | 1.220 (3) |
| C2—C3  | 1.510 (3) | C22—C23 | 1.502 (3) |
| C3—C10 | 1.336 (3) | C23—C30 | 1.330 (3) |
| C3—C9  | 1.460 (3) | C23—C29 | 1.457 (3) |
| C4—C5  | 1.381 (3) | C24—C25 | 1.378 (3) |
| C4—C9  | 1.390 (3) | C24—C29 | 1.382 (3) |
| C4—H4  | 0.9300    | C24—H24 | 0.9300    |
| C5—C6  | 1.381 (3) | C25—C26 | 1.381 (3) |
| C5—H5  | 0.9300    | C25—H25 | 0.9300    |
| C6—C7  | 1.380 (3) | C26—C27 | 1.383 (3) |

## supplementary materials

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|             |             |             |             |
|-------------|-------------|-------------|-------------|
| C6—H6       | 0.9300      | C26—H26     | 0.9300      |
| C7—C8       | 1.375 (3)   | C27—C28     | 1.376 (3)   |
| C7—H7       | 0.9300      | C27—H27     | 0.9300      |
| C8—C9       | 1.397 (3)   | C28—C29     | 1.402 (3)   |
| C10—C11     | 1.468 (3)   | C30—C31     | 1.473 (3)   |
| C10—H10     | 0.9300      | C30—H30     | 0.9300      |
| C11—C12     | 1.395 (3)   | C31—C32     | 1.389 (3)   |
| C11—C16     | 1.401 (3)   | C31—C36     | 1.395 (3)   |
| C12—C13     | 1.386 (3)   | C32—C33     | 1.382 (3)   |
| C12—Cl12    | 1.732 (2)   | C32—Cl32    | 1.737 (2)   |
| C13—C14     | 1.365 (4)   | C33—C34     | 1.369 (4)   |
| C13—H13     | 0.9300      | C33—H33     | 0.9300      |
| C14—C15     | 1.372 (4)   | C34—C35     | 1.369 (4)   |
| C14—H14     | 0.9300      | C34—H34     | 0.9300      |
| C15—C16     | 1.374 (3)   | C35—C36     | 1.387 (3)   |
| C15—H15     | 0.9300      | C35—H35     | 0.9300      |
| C16—Cl16    | 1.736 (3)   | C36—Cl36    | 1.733 (2)   |
| C2—N1—C8    | 111.47 (17) | C22—N21—C28 | 111.48 (16) |
| C2—N1—H1    | 124.3       | C22—N21—H21 | 124.3       |
| C8—N1—H1    | 124.3       | C28—N21—H21 | 124.3       |
| O2—C2—N1    | 126.48 (19) | O22—C22—N21 | 126.61 (19) |
| O2—C2—C3    | 126.87 (19) | O22—C22—C23 | 126.87 (19) |
| N1—C2—C3    | 106.64 (18) | N21—C22—C23 | 106.52 (18) |
| C10—C3—C9   | 136.10 (19) | C30—C23—C29 | 133.96 (18) |
| C10—C3—C2   | 118.73 (18) | C30—C23—C22 | 120.05 (18) |
| C9—C3—C2    | 105.17 (17) | C29—C23—C22 | 105.84 (16) |
| C5—C4—C9    | 119.3 (2)   | C25—C24—C29 | 119.5 (2)   |
| C5—C4—H4    | 120.4       | C25—C24—H24 | 120.2       |
| C9—C4—H4    | 120.4       | C29—C24—H24 | 120.2       |
| C4—C5—C6    | 120.6 (2)   | C24—C25—C26 | 120.4 (2)   |
| C4—C5—H5    | 119.7       | C24—C25—H25 | 119.8       |
| C6—C5—H5    | 119.7       | C26—C25—H25 | 119.8       |
| C7—C6—C5    | 121.3 (2)   | C25—C26—C27 | 121.7 (2)   |
| C7—C6—H6    | 119.3       | C25—C26—H26 | 119.2       |
| C5—C6—H6    | 119.3       | C27—C26—H26 | 119.2       |
| C8—C7—C6    | 117.7 (2)   | C28—C27—C26 | 117.3 (2)   |
| C8—C7—H7    | 121.2       | C28—C27—H27 | 121.4       |
| C6—C7—H7    | 121.2       | C26—C27—H27 | 121.4       |
| C7—C8—C9    | 122.4 (2)   | C27—C28—C29 | 122.23 (19) |
| C7—C8—N1    | 128.23 (19) | C27—C28—N21 | 128.52 (19) |
| C9—C8—N1    | 109.37 (17) | C29—C28—N21 | 109.23 (17) |
| C4—C9—C8    | 118.71 (19) | C24—C29—C28 | 118.90 (18) |
| C4—C9—C3    | 133.96 (19) | C24—C29—C23 | 134.09 (18) |
| C8—C9—C3    | 107.33 (17) | C28—C29—C23 | 106.90 (17) |
| C3—C10—C11  | 129.73 (19) | C23—C30—C31 | 127.71 (18) |
| C3—C10—H10  | 115.1       | C23—C30—H30 | 116.1       |
| C11—C10—H10 | 115.1       | C31—C30—H30 | 116.1       |
| C12—C11—C16 | 115.33 (19) | C32—C31—C36 | 116.07 (18) |
| C12—C11—C10 | 125.09 (19) | C32—C31—C30 | 120.65 (18) |



|              |             |              |             |
|--------------|-------------|--------------|-------------|
| C16—C11—C10  | 119.4 (2)   | C36—C31—C30  | 123.21 (19) |
| C13—C12—C11  | 122.4 (2)   | C33—C32—C31  | 122.9 (2)   |
| C13—C12—C112 | 117.53 (19) | C33—C32—C132 | 118.52 (19) |
| C11—C12—C112 | 120.03 (16) | C31—C32—C132 | 118.61 (15) |
| C14—C13—C12  | 119.5 (2)   | C34—C33—C32  | 118.8 (2)   |
| C14—C13—H13  | 120.3       | C34—C33—H33  | 120.6       |
| C12—C13—H13  | 120.3       | C32—C33—H33  | 120.6       |
| C13—C14—C15  | 120.7 (2)   | C33—C34—C35  | 121.0 (2)   |
| C13—C14—H14  | 119.7       | C33—C34—H34  | 119.5       |
| C15—C14—H14  | 119.7       | C35—C34—H34  | 119.5       |
| C14—C15—C16  | 119.2 (2)   | C34—C35—C36  | 119.3 (2)   |
| C14—C15—H15  | 120.4       | C34—C35—H35  | 120.3       |
| C16—C15—H15  | 120.4       | C36—C35—H35  | 120.3       |
| C15—C16—C11  | 122.9 (2)   | C35—C36—C31  | 122.0 (2)   |
| C15—C16—C116 | 118.9 (2)   | C35—C36—C136 | 118.96 (19) |
| C11—C16—C116 | 118.12 (17) | C31—C36—C136 | 119.08 (16) |

*Hydrogen-bond geometry* ( $\text{\AA}$ ,  $^\circ$ )

| <i>D</i> —H $\cdots$ <i>A</i>     | <i>D</i> —H | H $\cdots$ <i>A</i> | <i>D</i> $\cdots$ <i>A</i> | <i>D</i> —H $\cdots$ <i>A</i> |
|-----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N21—H21 $\cdots$ O22 <sup>i</sup> | 0.86        | 2.03                | 2.854 (2)                  | 159                           |
| N1—H1 $\cdots$ O2 <sup>ii</sup>   | 0.86        | 1.99                | 2.837 (2)                  | 171                           |

Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $-x+2, -y+1, -z+1$ .

Fig. 1

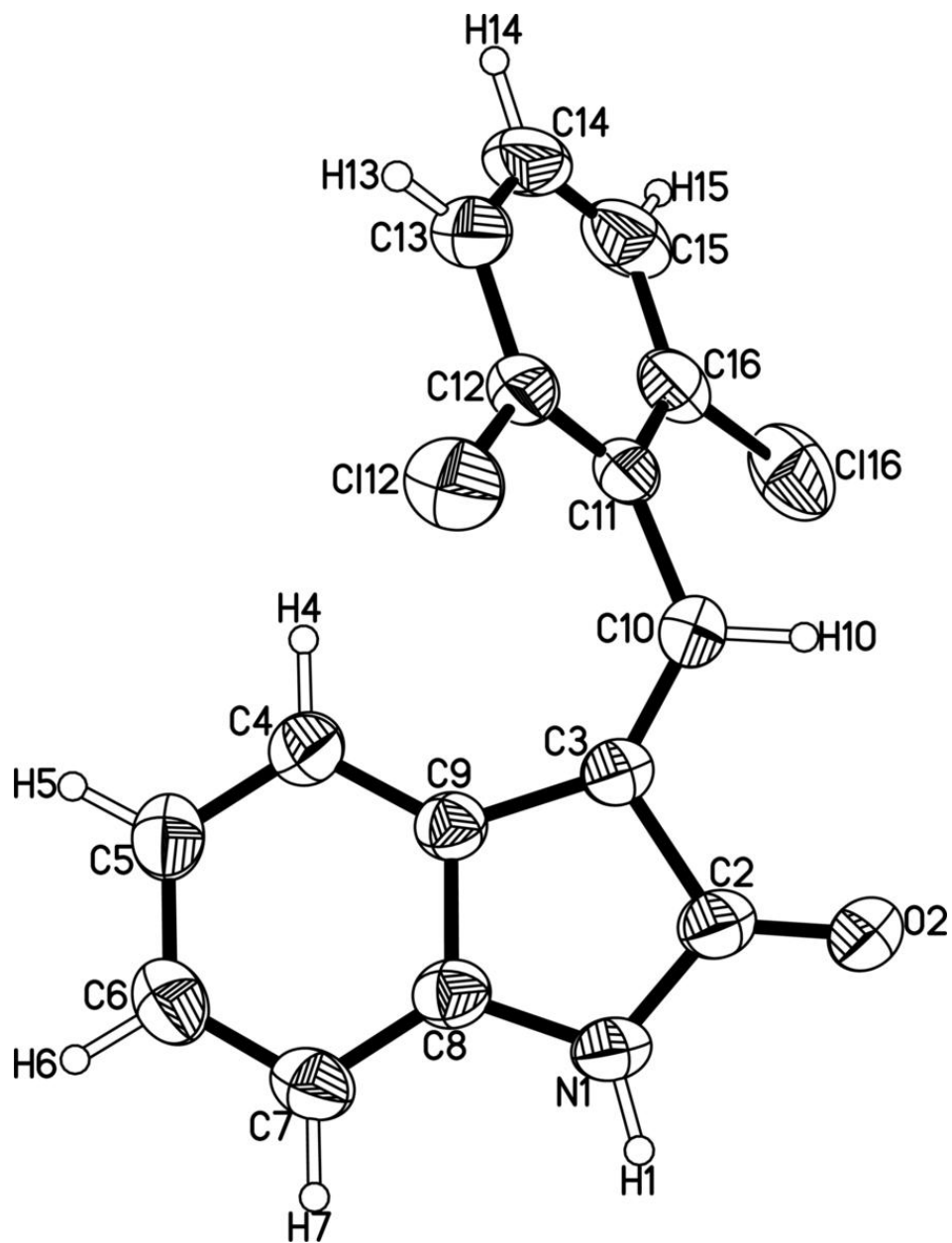


Fig. 2

