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3-(4-Chlorophenyl)-2,1-benzisoxazole-5-carbonyl chloride

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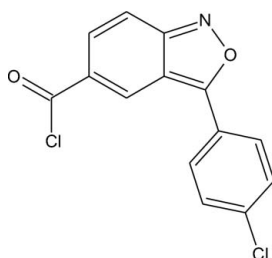
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.044; wR factor = 0.126; data-to-parameter ratio = 13.9.

The molecule of the title compound, $\text{C}_{14}\text{H}_7\text{Cl}_2\text{NO}_2$, is not planar; the dihedral angle between the mean planes of the chlorophenyl and benzisoxazole rings is $20.32(7)^\circ$. The carbonyl chloride group is twisted with respect to the benzisoxazole ring by $2.5(1)^\circ$. The molecular conformation is stabilized by an intramolecular $\text{C}-\text{H}\cdots\text{Cl}$ hydrogen bond. In the crystal packing, adjacent molecules are linked into dimers by intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds. The dimers are further stacked into columns along the unique axis direction by $\pi-\pi$ stacking interactions, with a centroid \cdots centroid distance of $3.828(5)$ Å. Other weak intermolecular $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{Cl}$ interactions are also present.

Related literature

For the applications and biological activities of benzo[*c*]-isoxazoles, see: McEvoy *et al.* (1968); Hester *et al.* (1989); Walsh *et al.* (1990); Angibaud *et al.* (2003). For details of the synthesis, see: Davis & Pizzini (1960). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$\text{C}_{14}\text{H}_7\text{Cl}_2\text{NO}_2$
 $M_r = 292.11$
 Monoclinic, $C2/c$
 $a = 30.337(6)$ Å
 $b = 3.828(1)$ Å
 $c = 21.000(4)$ Å
 $\beta = 100.67(3)^\circ$

$V = 2396.6(9)$ Å³
 $Z = 8$
 Cu $K\alpha$ radiation
 $\mu = 4.85$ mm⁻¹
 $T = 100(2)$ K
 $0.80 \times 0.15 \times 0.12$ mm

Data collection

Oxford Xcalibur PX κ -geometry diffractometer with Onyx CCD camera

Absorption correction: analytical (*CrysAlis RED*; Oxford)

Diffraction, 2006
 $T_{\min} = 0.21$, $T_{\max} = 0.66$
 9609 measured reflections
 2413 independent reflections
 2131 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.068$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.126$
 $S = 1.05$
 2413 reflections

173 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.30$ e Å⁻³
 $\Delta\rho_{\min} = -0.60$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|--------------|--------------------|-------------|----------------------|
| $\text{C4}-\text{H4}\cdots\text{Cl1}$ | 0.95 | 2.58 | 3.015 (2) | 108 |
| $\text{C6}-\text{H6}\cdots\text{O1}^{\text{i}}$ | 0.95 | 2.53 | 3.378 (2) | 149 |
| $\text{C9}-\text{H9}\cdots\text{Cl1}^{\text{ii}}$ | 0.95 | 2.96 | 3.813 (2) | 150 |
| $\text{C13}-\text{H13}\cdots\text{O2}^{\text{iii}}$ | 0.95 | 2.69 | 3.492 (2) | 142 |

Symmetry codes: (i) $-x + \frac{1}{2}, -y + \frac{5}{2}, -z$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 1, y, -z + \frac{1}{2}$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *publCIF* (Westrip, 2008).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2265).

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supporting information

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3-(4-Chlorophenyl)-2,1-benzisoxazole-5-carbonyl chloride

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S1. Comment

Our interest in benzo[*c*]isoxazoles is concerned with their biological activity and their application as precursors of the variety of bioactive compounds (Angibaud *et al.*, 2003; Walsh *et al.*, 1990; Hester *et al.*, 1989; McEvoy *et al.*, 1968). The title compound will be used in our further investigations as a building block for modifications by nucleophiles.

The asymmetric unit of the title compound is shown in Figure 1. The planarity of the molecule is disturbed by intramolecular attractive and repulsive interactions of the C–H···Cl, C–H···O and C–H···H–C types. The dihedral angle between the least-square mean planes of the chlorophenyl and benzisoxazole rings is 20.32 (7)°. The carbonyl chloride group is rotated by 2.5 (1)° with respect to the benzisoxazole ring. An intramolecular C—H···Cl hydrogen bonding interactions is observed (Table 1). The crystal packing (Fig. 2) is governed by intermolecular interactions of the C–H···O type and by π - π stacking interactions. The C–H···O type hydrogen bonds connect adjacent molecules into dimers, forming ten-membered rings of graph set motif $R^2_2(10)$ (Bernstein *et al.*, 1995). The dimers are further linked along the unique axis direction by π - π stacking interactions: $Cg1\cdots Cg1^i = Cg2\cdots Cg2^i = 3.828$ (5) Å ($Cg1$ and $Cg2$ are the centroids of the C1/C2/C4–C7 and C8–C13 aromatic rings, respectively; symmetry code: (i) $x, 1+y, z$); the corresponding perpendicular interplanar distances are 3.429 (4) and 3.475 (4) Å, respectively, and the centroid-centroid offsets are 1.702 (4) and 1.605 (3) Å, respectively. Additionally, two weak C–H···O and C—H···Cl interactions are present in the structure (shown as dotted lines in Figure 2).

S2. Experimental

To 40 ml of an ethanol solution of potassium hydroxide (4 g, 0.1 mol) *p*-nitrobenzoic acid (1.67 g, 10 mmol) was added with stirring. Then 5 ml of an ethanol solution of 4-chlorophenylacetonitrile (1.82 g, 12 mmol) was added to the reaction mixture. The suspension was stirred for 4 h at 323 K and left overnight at room temperature. The reaction mixture was poured into 150 ml of water and acidified with hydrochloric acid. The precipitate was isolated by filtration, washed with water and dried. Crude acid was added to a solution of thionyl chloride (1.19 ml, 20 mmol) in benzene (15 ml) and heated under reflux until a clear solution was obtained. Yellow needles of the title compound were obtained by slow cooling of the reaction solution (m.p. 453–454 K; 2 g, yield 70%).

S3. Refinement

All H atoms were found in difference-Fourier maps. In the final refinement cycles, H atoms were positioned geometrically and treated as riding atoms, with C–H = 0.95 Å and with $U_{iso}(H) = 1.2 U_{eq}(C)$.

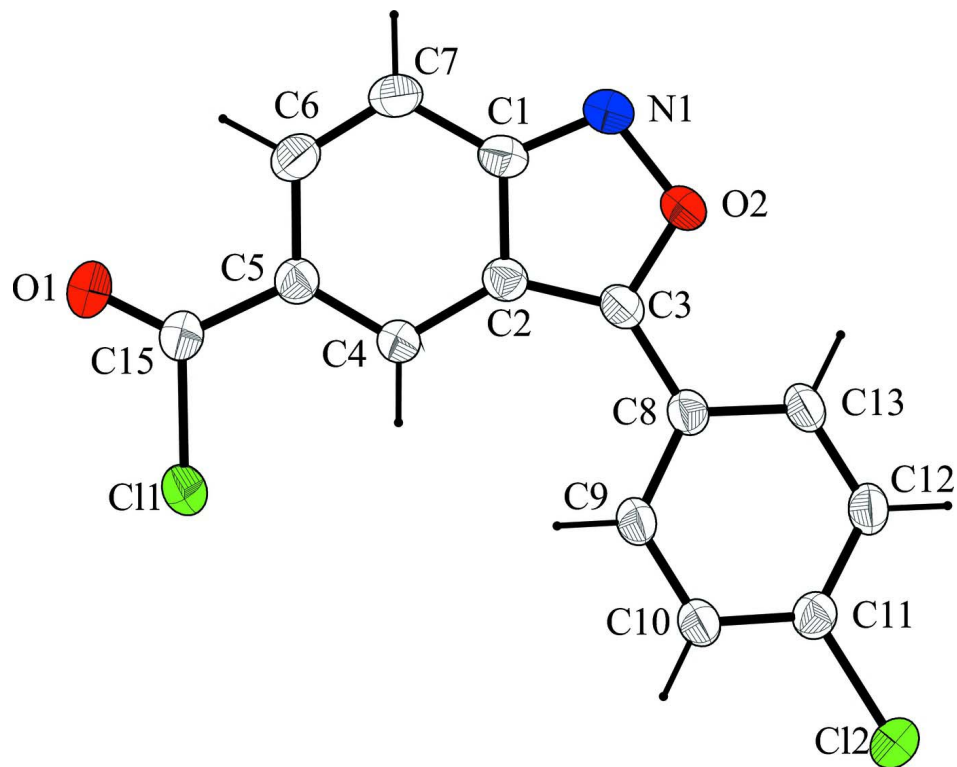
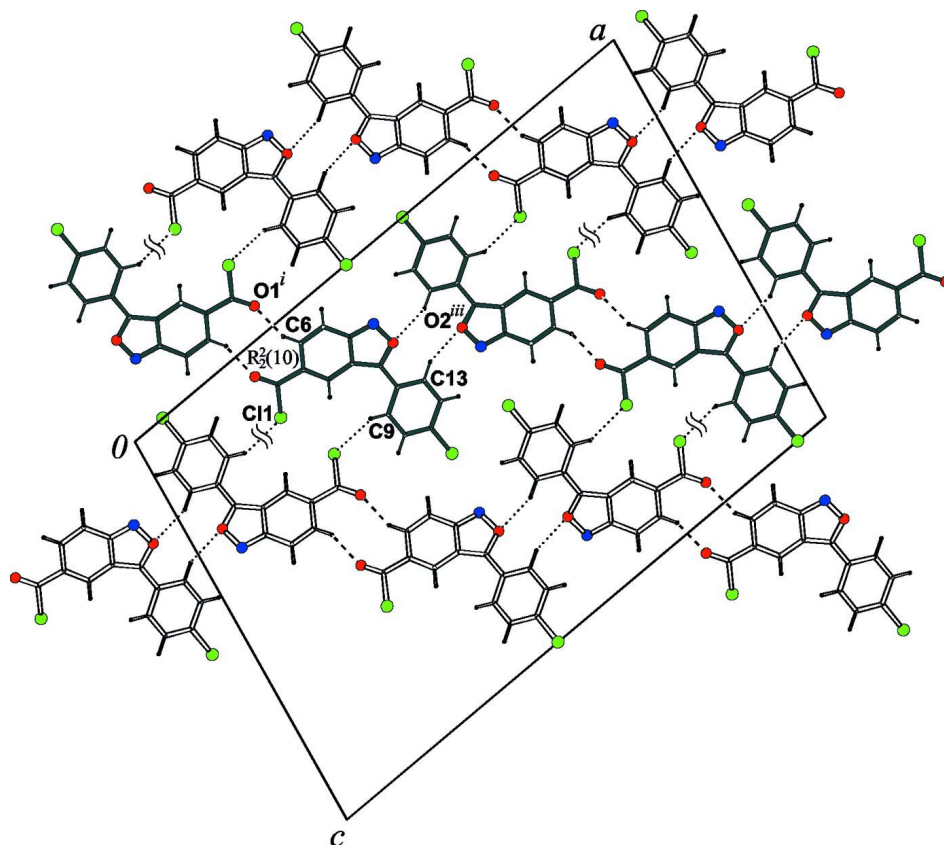


Figure 1

The molecular structure of the title compound with the atom labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**

Packing diagram of the title compound viewed along the *b* axis, showing intermolecular hydrogen bonds (dashed lines) and weak hydrogen interactions (dotted lines). Symmetry codes are as in Table 1.

3-(4-Chlorophenyl)-2,1-benzisoxazole-5-carbonyl chloride

Crystal data

$C_{14}H_7Cl_2NO_2$

$M_r = 292.11$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 30.337 (6) \text{ \AA}$

$b = 3.828 (1) \text{ \AA}$

$c = 21.000 (4) \text{ \AA}$

$\beta = 100.67 (3)^\circ$

$V = 2396.6 (9) \text{ \AA}^3$

$Z = 8$

$F(000) = 1184$

$D_x = 1.619 \text{ Mg m}^{-3}$

Melting point: 453–454 K K

Cu $K\alpha$ radiation, $\lambda = 1.54180 \text{ \AA}$

Cell parameters from 9042 reflections

$\theta = 2.2\text{--}76.9^\circ$

$\mu = 4.85 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Needle, yellow

$0.80 \times 0.15 \times 0.12 \text{ mm}$

Data collection

Xcalibur PX κ -geometry

diffractometer with CCD Onyx camera

Radiation source: fine-focus sealed tube

Graphite monochromator

ω and ϕ scans

Absorption correction: analytical

(*CrysAlis RED*; Oxford Diffraction, 2006)

$T_{\min} = 0.21$, $T_{\max} = 0.66$

9609 measured reflections

2413 independent reflections

2131 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.068$

$\theta_{\max} = 76.7^\circ$, $\theta_{\min} = 4.3^\circ$

$h = -38 \rightarrow 21$

$k = -4 \rightarrow 4$

$l = -20 \rightarrow 26$

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.044$ $wR(F^2) = 0.126$ $S = 1.05$

2413 reflections

173 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.1002P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.60 \text{ e } \text{\AA}^{-3}$ Extinction correction: *SHELXL*, $F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.00084 (17)

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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|---------------|--------------|-------------|----------------------------------|
| C11 | 0.226537 (14) | 0.66461 (14) | 0.17672 (2) | 0.0394 (2) |
| C12 | 0.440884 (15) | 0.22145 (13) | 0.50018 (2) | 0.0379 (2) |
| O2 | 0.44488 (4) | 0.9282 (4) | 0.21086 (6) | 0.0344 (3) |
| O1 | 0.22228 (5) | 0.9426 (5) | 0.06384 (7) | 0.0531 (4) |
| N1 | 0.43252 (5) | 1.0756 (5) | 0.14821 (8) | 0.0373 (4) |
| C3 | 0.40860 (5) | 0.8178 (5) | 0.23358 (8) | 0.0276 (4) |
| C1 | 0.38838 (6) | 1.0480 (5) | 0.13517 (8) | 0.0305 (4) |
| C2 | 0.37105 (5) | 0.8870 (5) | 0.18709 (8) | 0.0272 (4) |
| C7 | 0.35923 (6) | 1.1558 (5) | 0.07744 (9) | 0.0348 (4) |
| H7 | 0.3706 | 1.2660 | 0.0433 | 0.042* |
| C6 | 0.31470 (6) | 1.0960 (5) | 0.07275 (8) | 0.0341 (4) |
| H6 | 0.2946 | 1.1668 | 0.0347 | 0.041* |
| C5 | 0.29704 (5) | 0.9272 (5) | 0.12426 (8) | 0.0286 (4) |
| C4 | 0.32426 (5) | 0.8258 (5) | 0.18041 (8) | 0.0277 (4) |
| H4 | 0.3122 | 0.7171 | 0.2141 | 0.033* |
| C8 | 0.41646 (5) | 0.6636 (5) | 0.29788 (8) | 0.0277 (4) |
| C9 | 0.38161 (5) | 0.6433 (5) | 0.33305 (8) | 0.0312 (4) |
| H9 | 0.3526 | 0.7261 | 0.3143 | 0.037* |
| C10 | 0.38894 (5) | 0.5044 (5) | 0.39469 (8) | 0.0325 (4) |
| H10 | 0.3652 | 0.4905 | 0.4183 | 0.039* |
| C11 | 0.43141 (6) | 0.3854 (5) | 0.42168 (8) | 0.0297 (4) |
| C12 | 0.46655 (5) | 0.3991 (5) | 0.38806 (8) | 0.0316 (4) |
| H12 | 0.4954 | 0.3148 | 0.4072 | 0.038* |

| | | | | |
|-----|-------------|------------|-------------|------------|
| C13 | 0.45895 (5) | 0.5378 (5) | 0.32618 (8) | 0.0314 (4) |
| H13 | 0.4828 | 0.5478 | 0.3026 | 0.038* |
| C15 | 0.24813 (6) | 0.8697 (5) | 0.11157 (9) | 0.0338 (4) |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|------------|-------------|------------|---------------|--------------|--------------|
| C11 | 0.0264 (2) | 0.0502 (4) | 0.0408 (3) | -0.00458 (17) | 0.00416 (19) | 0.00756 (19) |
| C12 | 0.0379 (3) | 0.0451 (3) | 0.0291 (3) | 0.00141 (18) | 0.00193 (19) | 0.00423 (17) |
| O2 | 0.0246 (6) | 0.0479 (8) | 0.0318 (6) | -0.0032 (5) | 0.0085 (5) | 0.0005 (5) |
| O1 | 0.0335 (7) | 0.0836 (13) | 0.0381 (8) | -0.0006 (8) | -0.0038 (6) | 0.0134 (8) |
| N1 | 0.0319 (8) | 0.0487 (10) | 0.0329 (8) | -0.0029 (7) | 0.0102 (6) | 0.0036 (7) |
| C3 | 0.0230 (7) | 0.0322 (9) | 0.0288 (8) | -0.0031 (6) | 0.0074 (6) | -0.0050 (6) |
| C1 | 0.0315 (8) | 0.0325 (9) | 0.0296 (8) | -0.0017 (7) | 0.0112 (7) | -0.0012 (7) |
| C2 | 0.0268 (8) | 0.0288 (9) | 0.0268 (8) | -0.0006 (6) | 0.0069 (6) | -0.0022 (6) |
| C7 | 0.0394 (9) | 0.0377 (10) | 0.0292 (9) | 0.0014 (7) | 0.0116 (7) | 0.0045 (7) |
| C6 | 0.0373 (9) | 0.0380 (10) | 0.0268 (8) | 0.0056 (7) | 0.0050 (7) | 0.0033 (7) |
| C5 | 0.0275 (8) | 0.0311 (9) | 0.0271 (8) | 0.0003 (6) | 0.0045 (6) | -0.0016 (7) |
| C4 | 0.0250 (8) | 0.0327 (9) | 0.0256 (8) | -0.0003 (6) | 0.0054 (6) | 0.0001 (6) |
| C8 | 0.0228 (7) | 0.0328 (9) | 0.0270 (8) | -0.0023 (6) | 0.0035 (6) | -0.0034 (6) |
| C9 | 0.0211 (7) | 0.0429 (10) | 0.0293 (8) | 0.0034 (7) | 0.0037 (6) | -0.0020 (7) |
| C10 | 0.0232 (7) | 0.0445 (11) | 0.0298 (8) | 0.0001 (7) | 0.0051 (6) | -0.0034 (7) |
| C11 | 0.0290 (8) | 0.0323 (9) | 0.0268 (8) | -0.0007 (7) | 0.0028 (6) | -0.0023 (7) |
| C12 | 0.0231 (7) | 0.0381 (10) | 0.0320 (8) | 0.0036 (7) | 0.0006 (6) | -0.0013 (7) |
| C13 | 0.0197 (7) | 0.0416 (10) | 0.0331 (8) | -0.0006 (7) | 0.0054 (6) | -0.0041 (7) |
| C15 | 0.0293 (8) | 0.0410 (10) | 0.0296 (8) | 0.0010 (7) | 0.0016 (7) | 0.0007 (8) |

Geometric parameters (Å, °)

| | | | |
|----------|-------------|-----------|-------------|
| C11—C15 | 1.803 (2) | C6—H6 | 0.9500 |
| C12—C11 | 1.7373 (18) | C5—C4 | 1.365 (2) |
| O2—C3 | 1.3461 (19) | C5—C15 | 1.475 (2) |
| O2—N1 | 1.417 (2) | C4—H4 | 0.9500 |
| O1—C15 | 1.186 (2) | C8—C9 | 1.400 (2) |
| N1—C1 | 1.320 (2) | C8—C13 | 1.401 (2) |
| C3—C2 | 1.382 (2) | C9—C10 | 1.379 (3) |
| C3—C8 | 1.452 (2) | C9—H9 | 0.9500 |
| C1—C7 | 1.423 (3) | C10—C11 | 1.385 (2) |
| C1—C2 | 1.434 (2) | C10—H10 | 0.9500 |
| C2—C4 | 1.420 (2) | C11—C12 | 1.384 (2) |
| C7—C6 | 1.356 (3) | C12—C13 | 1.383 (2) |
| C7—H7 | 0.9500 | C12—H12 | 0.9500 |
| C6—C5 | 1.446 (2) | C13—H13 | 0.9500 |
| C3—O2—N1 | 111.15 (13) | C2—C4—H4 | 120.9 |
| C1—N1—O2 | 104.15 (13) | C9—C8—C13 | 118.86 (16) |
| O2—C3—C2 | 108.11 (15) | C9—C8—C3 | 120.21 (15) |
| O2—C3—C8 | 116.92 (15) | C13—C8—C3 | 120.92 (15) |

| | | | |
|-----------|-------------|-------------|-------------|
| C2—C3—C8 | 134.97 (15) | C10—C9—C8 | 120.70 (16) |
| N1—C1—C7 | 126.85 (16) | C10—C9—H9 | 119.6 |
| N1—C1—C2 | 112.17 (16) | C8—C9—H9 | 119.6 |
| C7—C1—C2 | 120.98 (15) | C9—C10—C11 | 119.16 (16) |
| C3—C2—C4 | 135.77 (16) | C9—C10—H10 | 120.4 |
| C3—C2—C1 | 104.42 (14) | C11—C10—H10 | 120.4 |
| C4—C2—C1 | 119.77 (16) | C12—C11—C10 | 121.64 (16) |
| C6—C7—C1 | 117.82 (16) | C12—C11—Cl2 | 119.33 (14) |
| C6—C7—H7 | 121.1 | C10—C11—Cl2 | 119.02 (13) |
| C1—C7—H7 | 121.1 | C13—C12—C11 | 118.92 (15) |
| C7—C6—C5 | 121.57 (17) | C13—C12—H12 | 120.5 |
| C7—C6—H6 | 119.2 | C11—C12—H12 | 120.5 |
| C5—C6—H6 | 119.2 | C12—C13—C8 | 120.72 (15) |
| C4—C5—C6 | 121.66 (15) | C12—C13—H13 | 119.6 |
| C4—C5—C15 | 122.78 (16) | C8—C13—H13 | 119.6 |
| C6—C5—C15 | 115.56 (16) | O1—C15—C5 | 127.12 (18) |
| C5—C4—C2 | 118.18 (15) | O1—C15—Cl1 | 117.88 (15) |
| C5—C4—H4 | 120.9 | C5—C15—Cl1 | 115.00 (13) |

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------------|-------|-------------|-------------|---------------|
| C4—H4 \cdots C11 | 0.95 | 2.58 | 3.015 (2) | 108 |
| C6—H6 \cdots O1 ⁱ | 0.95 | 2.53 | 3.378 (2) | 149 |
| C9—H9 \cdots C11 ⁱⁱ | 0.95 | 2.96 | 3.813 (2) | 150 |
| C13—H13 \cdots O2 ⁱⁱⁱ | 0.95 | 2.69 | 3.492 (2) | 142 |

Symmetry codes: (i) $-x+1/2, -y+5/2, -z$; (ii) $-x+1/2, y+1/2, -z+1/2$; (iii) $-x+1, y, -z+1/2$.