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4-(2-Chlorophenylamino)-pent-3-en-2-one

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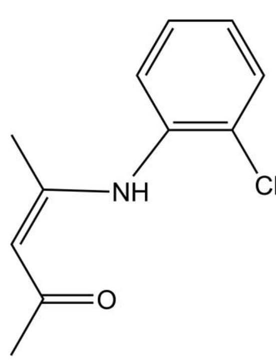
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.025; wR factor = 0.068; data-to-parameter ratio = 17.9.

In the title compound, $C_{11}H_{12}ClNO$, intramolecular N—H⋯O hydrogen bonding is present. The dihedral angle between the benzene ring and the pentenone unit is 46.52 (5)°. In the crystal, C—H⋯O interactions between hydrogen atoms of the aryl moiety and two separate oxygen atoms occur, leading to a three-dimensional network.

Related literature

For synthetic background and similar compounds, see: Shaheen *et al.* (2006); Venter *et al.* (2010, 2012*b*). For applications, see: Brink *et al.* (2010); Pyżuk *et al.* (1993); Roodt & Steyn (2000); Tan *et al.* (2008); Xia *et al.* (2008). For related ligand systems, see: Damoense *et al.* (1994), Venter *et al.* (2012*a*).



Experimental

Crystal data

$C_{11}H_{12}ClNO$
M_r = 209.67
Orthorhombic, $P2_12_12_1$
a = 7.3264 (3) Å
b = 8.7103 (4) Å
c = 16.1960 (7) Å
V = 1033.55 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.33 mm^{-1}
T = 100 K
0.6 × 0.42 × 0.21 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.825, T_{max} = 0.933
17399 measured reflections
2259 independent reflections
2211 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.068
S = 1.06
2259 reflections
126 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Absolute structure: Flack (1983), 932 Friedel pairs
Flack parameter: 0.01 (5)

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N11—H11⋯O12	0.82	1.95	2.6317 (16)	139
C113—H113⋯O12^{i}	0.95	2.42	3.3536 (18)	166
C115—H115⋯O12^{ii}	0.95	2.43	3.3217 (18)	157

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Financial assistance from the University of the Free State is gratefully acknowledged. We also express our gratitude towards SASOL, the South African National Research Foundation (SA-NRF/THRIP) and the Inkaba yeAfrica initiative for financial support of this project. Part of this material is based on work supported by the SA-NRF/THRIP under grant No. GUN 2068915. Opinions, findings, conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the SA-NRF.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2444).

References

Brandenburg, K. & Putz, H. (2005). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Brink, A., Visser, H. G., Steyl, G. & Roodt, A. (2010). *Dalton Trans.* **39**, 5572–5578.
Bruker (2004). *SAINT-Plus* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2005). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
Damoense, L. J., Purcell, W., Roodt, A. & Leipoldt, J. G. (1994). *Rhodium Express*, **5**, 10–13.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Pyżuk, W., Krówczynsk, A. & Górecka, E. (1993). *Mol. Cryst. Liq. Cryst.* **237**, 75–84.
Roodt, A. & Steyn, G. J. J. (2000). *Recent Research Developments in Inorganic Chemistry*. Vol. 2, pp. 1–23. Trivandrum: Transworld Research Network.

Shaheen, F., Marchio, L., Badshah, A. & Khosa, M. K. (2006). *Acta Cryst.* E**62**, o873–o874.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Tan, H. Y., Loke, W. K., Tan, Y. T. & Nguyen, N.-T. (2008). *Lab Chip*, **8**, 885–891.
Venter, G. J. S., Steyl, G. & Roodt, A. (2010). *Acta Cryst.* E**66**, o3011–o3012.
Venter, G. J. S., Steyl, G. & Roodt, A. (2012*a*). *Acta Cryst.* E**68**, m666–m667.
Venter, G. J. S., Steyl, G. & Roodt, A. (2012*b*). *Acta Cryst.* E**68**, o2930–o2931.
Xia, M., Wu, B. & Xiang, G. (2008). *J. Fluor. Chem.* **129**, 402–408.

supplementary materials

Acta Cryst. (2012). E**68**, o3101–o3102   [doi:10.1107/S1600536812042043]

4-(2-Chlorophenylamino)-pent-3-en-2-one

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Comment

The β-diketone compound AcacH (acetylacetone; or when coordinated acetylacetonato, $acac^-$) has been studied extensively, with a multitude of derivatives synthesized to date. One such derivative type, known as enaminoketones, contains both nitrogen and oxygen atoms with an unsaturated C═C bond, and is of interest in various fields including liquid crystals [Pyżuk *et al.* (1993)], fluorescence studies [Xia *et al.* (2008)], medicine [Tan *et al.* (2008)] and catalysis [Roodt & Steyn (2000); Brink *et al.* (2010)].

The title compound (Fig. 1) crystallizes in the orthorhombic space group $P2_12_12_1$ with $Z = 4$. This enaminoketone is a derivative of 4-(phenylamino)pent-3-en-2-one [PhonyH; Shaheen *et al.* (2006)]. Bond distances differ significantly from compounds coordinated to rhodium [Venter *et al.* (2012*a*); Damoense *et al.* (1994)], but share characteristics with other enaminoketones of this type [Venter *et al.* (2010; 2012*b*). An unsaturated bond in the pentenone backbone is indicated by the difference in distance between the C_2═C_3 bond [1.379 (2) Å] and the C_3–C_4 bond [1.428 (2) Å]. The distance, $N_{11}\cdots O_{12}$, is greatly increased (~ 0.2 Å) upon coordination. Intramolecular N_{11}—$H_{11}\cdots O_{12}$ bonding (D—A distance = 2.632 (2) Å was observed, as well as intermolecular interactions for C_{113}—$H_{113}\cdots O_{12}$i [i = x-0.5, 0.5-y, 1-z; distance = 3.3536 (18) Å] and C_{115}—$H_{115}\cdots O_{12}$ii [ii = x, y+1, z; distance = 3.3217 (18) Å]. These interactions are illustrated in Fig. 2. The dihedral angle between the benzene ring and pentenone moieties is 46.52 (5)° and is dependent on the position of the substituent on the benzene ring, where *para* substituents usually display the smallest angles (Venter *et al.*, 2010).

Experimental

A solution of acetylacetone (11.07 g, 0.1106 mol), 2-chloro-aniline (10.73 g, 0.1008 mol) and 2 drops of H_2SO_4 (conc.) in 150 ml benzene was refluxed for 6 h in a Dean-Stark trap, filtered and left to crystallize. Crystals suitable for X-ray diffraction were obtained in 17.86 g (94.32%) yield. This compound is stable in air and light over a period of several months.

Refinement

The methyl and aromatic H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.95 Å and 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C) and 1.2U_{eq}(C), respectively. The methyl groups were generated to fit the difference electron density and the groups were then refined as rigid rotors.

Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

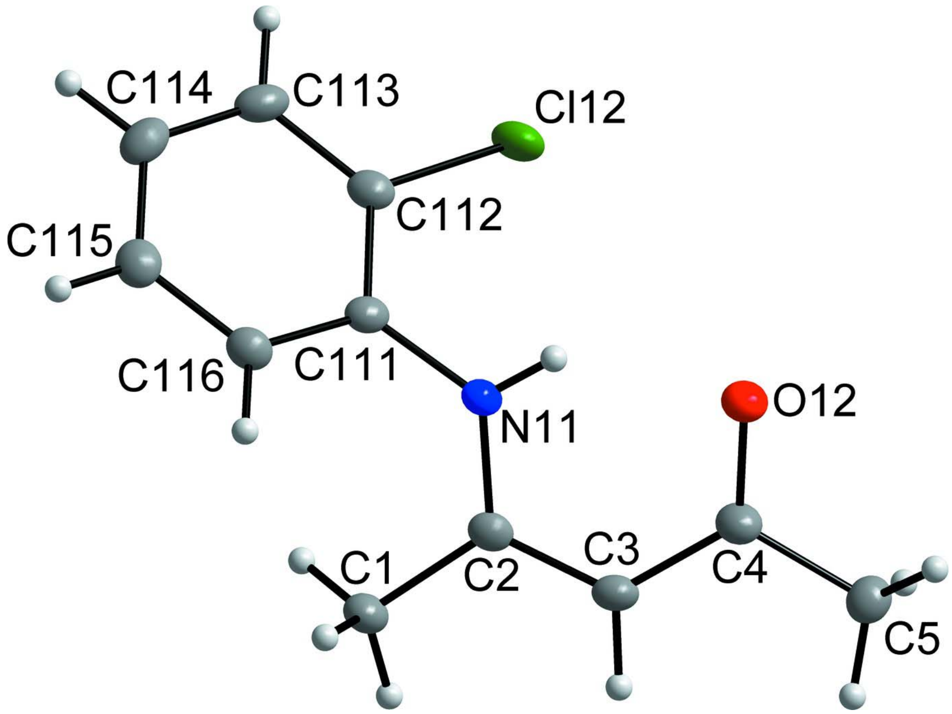

Figure 1

Molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radius.

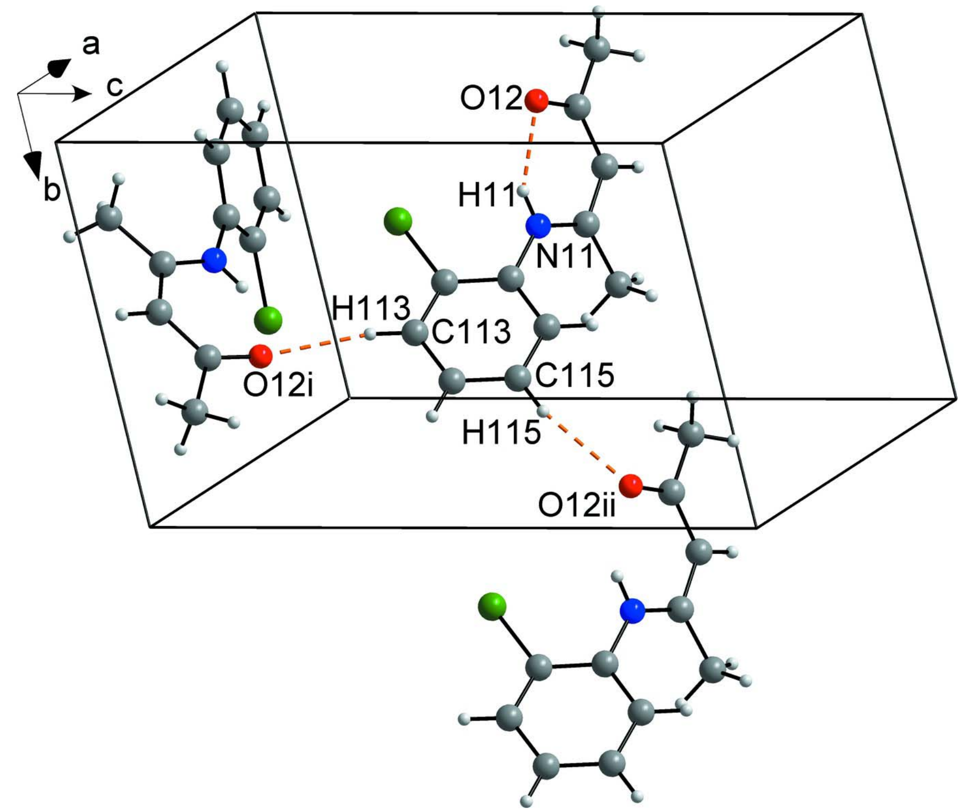

Figure 2

Partially filled unit cell illustrating the intra- and intermolecular hydrogen bonding interactions in the title compound, indicated with dashed lines.

4-(2-Chlorophenylamino)-pent-3-en-2-one

Crystal data

$C_{11}H_{12}ClNO$
M_r = 209.67
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
a = 7.3264 (3) Å
b = 8.7103 (4) Å
c = 16.1960 (7) Å
V = 1033.55 (8) $Å^3$
Z = 4

F(000) = 440
D_x = 1.347 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 5717 reflections
θ = 2.7–28.3°
μ = 0.33 mm^{-1}
T = 100 K
Cuboid, yellow
0.6 × 0.42 × 0.21 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and *ω* scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.825, T_{max} = 0.933

17399 measured reflections
2259 independent reflections
2211 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 27.0°, θ_{min} = 2.5°
h = −9→9
k = −11→11
l = −20→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.068$
$S = 1.06$
2259 reflections
126 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 0.2837P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.013$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Absolute structure: Flack (1983), 932 Friedel pairs
Flack parameter: 0.01 (5)

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cl12	0.00235 (5)	0.20519 (4)	0.531562 (19)	0.02339 (10)
N11	0.21805 (15)	0.28866 (14)	0.67897 (7)	0.0174 (2)
H11	0.2500 (8)	0.209 (2)	0.6556 (6)	0.027 (5)*
O12	0.33003 (14)	0.00171 (12)	0.68371 (6)	0.02136 (18)
C3	0.24678 (18)	0.14426 (16)	0.80149 (9)	0.0178 (3)
H3	0.2362	0.1411	0.8599	0.021*
C2	0.20915 (17)	0.28095 (16)	0.76209 (8)	0.0169 (3)
C111	0.18055 (18)	0.41335 (16)	0.62662 (8)	0.0166 (3)
C116	0.2464 (2)	0.56091 (16)	0.64159 (9)	0.0197 (3)
H116	0.3191	0.5797	0.6891	0.024*
C4	0.3006 (2)	0.00740 (18)	0.75983 (9)	0.02136 (18)
C113	0.04201 (19)	0.50725 (19)	0.49974 (9)	0.0229 (3)
H113	−0.0264	0.4881	0.451	0.027*
C5	0.3168 (2)	−0.13853 (17)	0.80936 (9)	0.0227 (3)
H5A	0.2032	−0.1974	0.8047	0.034*
H5B	0.339	−0.1131	0.8674	0.034*
H5C	0.4185	−0.2	0.7881	0.034*
C112	0.08035 (18)	0.38927 (17)	0.55421 (9)	0.0184 (3)
C115	0.20717 (19)	0.68074 (17)	0.58791 (9)	0.0226 (3)
H115	0.2505	0.7812	0.5996	0.027*
C1	0.1554 (2)	0.41966 (16)	0.81135 (9)	0.0203 (3)
H1A	0.2628	0.4845	0.8205	0.03*
H1B	0.1056	0.3871	0.8647	0.03*
H1C	0.0627	0.478	0.7811	0.03*

C114	0.1048 (2)	0.65395 (18)	0.51727 (9)	0.0243 (3)
H114	0.0776	0.7363	0.4808	0.029*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl12	0.02513 (17)	0.02720 (17)	0.01784 (17)	−0.00589 (15)	−0.00152 (14)	−0.00549 (12)
N11	0.0194 (5)	0.0181 (5)	0.0146 (5)	0.0016 (5)	−0.0004 (4)	−0.0024 (5)
O12	0.0232 (4)	0.0229 (4)	0.0180 (4)	−0.0007 (3)	0.0032 (3)	−0.0004 (3)
C3	0.0158 (6)	0.0234 (7)	0.0140 (7)	−0.0011 (5)	−0.0006 (5)	−0.0012 (5)
C2	0.0122 (6)	0.0218 (6)	0.0167 (6)	−0.0010 (5)	−0.0007 (5)	−0.0026 (5)
C111	0.0136 (6)	0.0216 (6)	0.0145 (6)	0.0013 (5)	0.0015 (5)	−0.0012 (5)
C116	0.0168 (6)	0.0224 (6)	0.0198 (7)	−0.0008 (5)	0.0010 (5)	−0.0028 (5)
C4	0.0232 (4)	0.0229 (4)	0.0180 (4)	−0.0007 (3)	0.0032 (3)	−0.0004 (3)
C113	0.0202 (7)	0.0333 (7)	0.0152 (6)	0.0025 (6)	0.0003 (5)	0.0019 (6)
C5	0.0211 (6)	0.0230 (7)	0.0241 (8)	0.0020 (6)	0.0011 (6)	0.0025 (6)
C112	0.0151 (6)	0.0236 (7)	0.0165 (7)	−0.0019 (5)	0.0026 (5)	−0.0027 (5)
C115	0.0212 (7)	0.0224 (7)	0.0242 (7)	−0.0013 (6)	0.0062 (5)	0.0008 (6)
C1	0.0212 (6)	0.0221 (7)	0.0175 (7)	0.0018 (5)	0.0007 (5)	−0.0032 (5)
C114	0.0228 (7)	0.0276 (7)	0.0224 (8)	0.0032 (6)	0.0042 (6)	0.0077 (6)

Geometric parameters (Å, º)

Cl12—C112	1.7412 (15)	C4—C5	1.508 (2)
N11—C2	1.3494 (18)	C113—C112	1.383 (2)
N11—C111	1.4049 (18)	C113—C114	1.387 (2)
N11—H11	0.8243	C113—H113	0.95
O12—C4	1.2524 (18)	C5—H5A	0.98
C3—C2	1.3787 (19)	C5—H5B	0.98
C3—C4	1.425 (2)	C5—H5C	0.98
C3—H3	0.95	C115—C114	1.388 (2)
C2—C1	1.5005 (19)	C115—H115	0.95
C111—C116	1.3942 (19)	C1—H1A	0.98
C111—C112	1.3994 (19)	C1—H1B	0.98
C116—C115	1.389 (2)	C1—H1C	0.98
C116—H116	0.95	C114—H114	0.95
C2—N11—C111	129.12 (13)	C4—C5—H5A	109.5
C2—N11—H11	115.4	C4—C5—H5B	109.5
C111—N11—H11	115.4	H5A—C5—H5B	109.5
C2—C3—C4	123.95 (13)	C4—C5—H5C	109.5
C2—C3—H3	118	H5A—C5—H5C	109.5
C4—C3—H3	118	H5B—C5—H5C	109.5
N11—C2—C3	119.67 (12)	C113—C112—C111	121.98 (13)
N11—C2—C1	120.21 (13)	C113—C112—Cl12	118.89 (11)
C3—C2—C1	120.11 (12)	C111—C112—Cl12	119.13 (11)
C116—C111—C112	117.74 (13)	C114—C115—C116	120.12 (13)
C116—C111—N11	122.69 (12)	C114—C115—H115	119.9
C112—C111—N11	119.50 (12)	C116—C115—H115	119.9
C115—C116—C111	120.82 (13)	C2—C1—H1A	109.5

C115—C116—H116	119.6	C2—C1—H1B	109.5
C111—C116—H116	119.6	H1A—C1—H1B	109.5
O12—C4—C3	123.13 (14)	C2—C1—H1C	109.5
O12—C4—C5	118.48 (14)	H1A—C1—H1C	109.5
C3—C4—C5	118.35 (13)	H1B—C1—H1C	109.5
C112—C113—C114	119.11 (14)	C113—C114—C115	120.18 (14)
C112—C113—H113	120.4	C113—C114—H114	119.9
C114—C113—H113	120.4	C115—C114—H114	119.9

C111—N11—C2—C3	177.99 (12)	C114—C113—C112—C111	0.1 (2)
C111—N11—C2—C1	−0.9 (2)	C114—C113—C112—Cl12	−179.63 (11)
C4—C3—C2—N11	1.8 (2)	C116—C111—C112—C113	−1.8 (2)
C4—C3—C2—C1	−179.31 (13)	N11—C111—C112—C113	−178.91 (12)
C2—N11—C111—C116	46.2 (2)	C116—C111—C112—Cl12	177.84 (10)
C2—N11—C111—C112	−136.84 (15)	N11—C111—C112—Cl12	0.77 (17)
C112—C111—C116—C115	2.6 (2)	C111—C116—C115—C114	−1.5 (2)
N11—C111—C116—C115	179.53 (13)	C112—C113—C114—C115	1.1 (2)
C2—C3—C4—O12	4.7 (2)	C116—C115—C114—C113	−0.3 (2)
C2—C3—C4—C5	−173.14 (12)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11···O12	0.82	1.95	2.6317 (16)	139
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Symmetry codes: (i) *x*−1/2, −*y*+1/2, −*z*+1; (ii) *x*, *y*+1, *z*.