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3-(4-Bromoanilino)-3-(4-chlorophenyl)-1-phenylpropan-1-one

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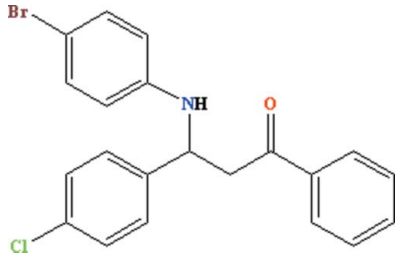
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.033; wR factor = 0.084; data-to-parameter ratio = 17.3.

The asymmetric C atom in the title compound, $C_{21}H_{17}BrClNO$, is in a slightly distorted tetrahedral environment and the NH unit adopts a *gauche* orientation with respect to the CO group. In the crystal, pairs of intermolecular N—H···O hydrogen bonds form centrosymmetric dimers.

Related literature

For background to β-amino ketones, see: Scettri *et al.* (2008). For related structures, see: Shobeiri *et al.* (2011); Zhang *et al.* (2008). For hydrogen-bond motifs and their graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{21}H_{17}BrClNO$
M_r = 414.72
Monoclinic, $P2_1/n$
a = 10.6571 (4) Å
b = 17.2432 (6) Å
c = 10.8602 (4) Å
β = 113.571 (2)°
V = 1829.19 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.40 mm^{-1}
T = 296 K
0.35 × 0.31 × 0.11 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.589, T_{max} = 0.746
69312 measured reflections
3983 independent reflections
3274 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.084
S = 1.03
3983 reflections
230 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.71 e Å^{-3}
$\Delta\rho_{min}$ = −0.86 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H···O1^{i}	0.81 (3)	2.23 (3)	2.992 (3)	156 (2)

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); 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) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXTL*.

Support of this investigation by Ferdowsi University of Mashhad is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: QM2027).

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supporting information

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3-(4-Bromoanilino)-3-(4-chlorophenyl)-1-phenylpropan-1-one

Mehrdad Pourayoubi, Zohreh Shobeiri, Giuseppe Bruno and Hadi Amiri Rudbari

S1. Comment

β-Amino ketones, of the formula [R^1]CH[NHR^2][$CH_2C(O)R^3$], such as the title compound have attracted attention because of their roles as important intermediates for the synthesis of natural products and chiral auxiliaries (Scettri *et al.*, 2008). In the previous work, the structure determination of 3-(4-bromophenylamino)-1-phenyl-3-*p*-tolylpropan-1-one (Shobeiri *et al.*, 2011) has been investigated. Here, we report the synthesis and crystal structure of the title molecule, [4-Cl—C_6H_4]CH[NHC_6H_4-4-Br][$CH_2C(O)C_6H_5$]. The asymmetric C atom has a slightly distorted tetrahedral configuration (Fig 1) with the bond angles in the range of 107.92 (16)° [N(1)—C(9)—C(8)] to 114.69 (16)° [N(1)—C(9)—C(10)]. In the crystal, pairs of intermolecular N—H···O(C) hydrogen bonds (Table 1) form centrosymmetric dimers as $R_2^2(12)$ rings (for graph-set notation, see Bernstein *et al.*, 1995). A view of crystal packing is shown in Fig. 2.

S2. Experimental

To a magnetically stirred mixture of 3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (0.24 g, 1.0 mmol) and $Ag_3PW_{12}O_{40}$ (0.32 g, 0.10 mmol) as catalyst, in ethanol (5 ml), 4-bromoaniline (0.20 g, 1.2 mmol) was added at room temperature. The reaction completion was monitored by thin layer chromatography (TLC). The catalyst $Ag_3PW_{12}O_{40}$ was collected by centrifugation. The reaction mixture was extracted with distilled water and ether (2×10 ml). The combined organic layer was evaporated to obtain crude product which was washed with hexane to give pure product. Single crystals of the product were obtained from a solution of $CHCl_3$/CH_3OH at room temperature.

S3. Refinement

H atoms of N—H was found in a difference Fourier map and refined isotropically with a distance restraint of N1—H = 0.81 (3) Å. The other H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93(aromatic CH), 0.97(CH2) and 0.98 (aliphatic CH) Å and with U_{iso}(H) = 1.2 and 1.5 U_{eq}(C).

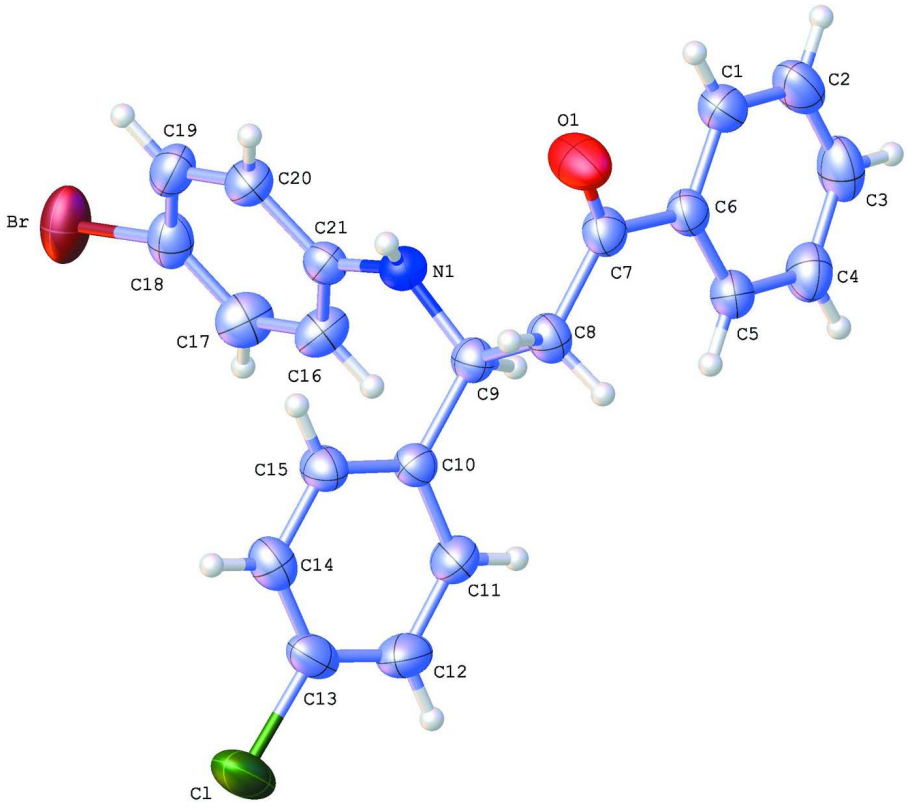

Figure 1

An *ORTEP*-style plot of title compound with labeling. Ellipsoids are given at the 50% probability level.

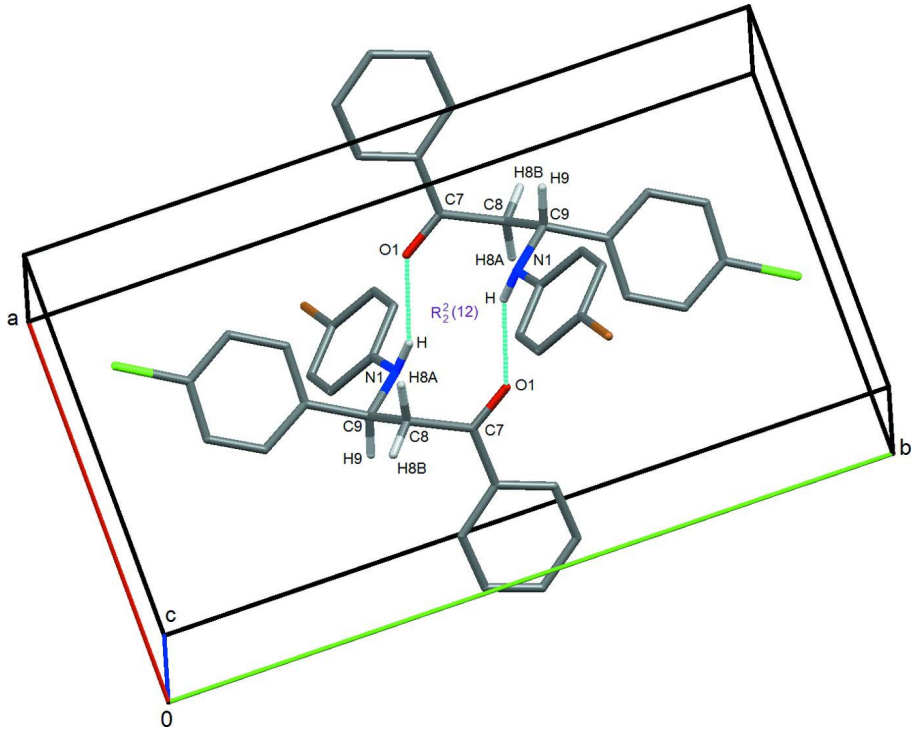

Figure 2

Part of the crystal packing of the title compound showing a centrosymmetric H-bonded (dashed lines) dimer. Only H atoms involving in hydrogen bonds are shown.

3-(4-Bromoanilino)-3-(4-chlorophenyl)-1-phenylpropan-1-one

Crystal data

$C_{21}H_{17}BrClNO$
$M_r = 414.72$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 10.6571$ (4) Å
$b = 17.2432$ (6) Å
$c = 10.8602$ (4) Å
$\beta = 113.571$ (2)°
$V = 1829.19$ (12) Å^3
$Z = 4$

$F(000) = 840$
$D_x = 1.506$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9986 reflections
$\theta = 2.4$–$23.8°$
$\mu = 2.40$ mm^{-1}
$T = 296$ K
Irregular, colorless
0.35 × 0.31 × 0.11 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
$T_{min} = 0.589$, $T_{max} = 0.746$

69312 measured reflections
3983 independent reflections
3274 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 27.0°$, $\theta_{min} = 2.3°$
$h = -13 \rightarrow 13$
$k = -22 \rightarrow 22$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.084$
$S = 1.03$
3983 reflections
230 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
$w = 1/[\sigma^2(F_o^2) + (0.0314P)^2 + 1.4336P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.71$ e Å^{-3}
$\Delta\rho_{min} = -0.86$ e Å^{-3}

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br	−0.04722 (3)	0.80334 (2)	−0.19048 (3)	0.06568 (12)
Cl	−0.16806 (9)	0.56173 (4)	0.49694 (7)	0.0721 (2)
O1	0.17572 (18)	1.03398 (10)	0.6206 (2)	0.0634 (5)
N1	0.08682 (19)	0.90054 (10)	0.38597 (18)	0.0371 (4)
C18	−0.0066 (2)	0.83266 (15)	−0.0093 (2)	0.0450 (5)
C17	0.0762 (3)	0.78643 (15)	0.0933 (2)	0.0494 (6)
H17	0.1118	0.7409	0.0743	0.059*
C16	0.1072 (2)	0.80736 (13)	0.2259 (2)	0.0450 (5)
H16	0.1635	0.7757	0.2953	0.054*
C21	0.0549 (2)	0.87508 (12)	0.2558 (2)	0.0351 (4)
C9	0.1518 (2)	0.85036 (11)	0.5014 (2)	0.0341 (4)
H9	0.2417	0.8351	0.5049	0.041*
C8	0.1731 (2)	0.89759 (12)	0.6286 (2)	0.0385 (5)
H8A	0.0848	0.9064	0.6323	0.046*
H8B	0.2281	0.8673	0.7069	0.046*
C7	0.2419 (2)	0.97478 (12)	0.6350 (2)	0.0389 (5)
C6	0.3887 (2)	0.97840 (12)	0.65830 (19)	0.0358 (4)
C5	0.4741 (2)	0.91441 (13)	0.6986 (2)	0.0405 (5)
H5	0.4400	0.8672	0.7132	0.049*
C4	0.6101 (2)	0.92042 (15)	0.7171 (2)	0.0498 (6)
H4	0.6673	0.8774	0.7450	0.060*
C3	0.6605 (2)	0.98986 (17)	0.6944 (3)	0.0556 (6)
H3	0.7514	0.9934	0.7053	0.067*
C20	−0.0291 (2)	0.92111 (13)	0.1491 (2)	0.0437 (5)

H20	−0.0654	0.9667	0.1670	0.052*
C19	−0.0594 (2)	0.90066 (15)	0.0179 (2)	0.0486 (5)
H19	−0.1149	0.9323	−0.0520	0.058*
C10	0.0717 (2)	0.77732 (11)	0.5009 (2)	0.0336 (4)
C11	0.1383 (2)	0.70874 (13)	0.5539 (2)	0.0455 (5)
H11	0.2335	0.7072	0.5888	0.055*
C12	0.0668 (3)	0.64243 (14)	0.5562 (3)	0.0538 (6)
H12	0.1129	0.5967	0.5926	0.065*
C13	−0.0743 (3)	0.64527 (13)	0.5035 (2)	0.0460 (5)
C14	−0.1434 (2)	0.71292 (14)	0.4522 (2)	0.0460 (5)
H14	−0.2385	0.7144	0.4188	0.055*
C15	−0.0702 (2)	0.77871 (12)	0.4507 (2)	0.0409 (5)
H15	−0.1166	0.8246	0.4156	0.049*
C2	0.5775 (3)	1.05403 (16)	0.6559 (3)	0.0565 (6)
H2	0.6125	1.1010	0.6417	0.068*
C1	0.4420 (2)	1.04882 (13)	0.6382 (2)	0.0463 (5)
H1	0.3862	1.0924	0.6129	0.056*
H	0.031 (3)	0.9290 (15)	0.396 (3)	0.046 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.04927 (16)	0.1060 (3)	0.03996 (14)	−0.00352 (14)	0.01597 (11)	−0.00835 (13)
Cl	0.0956 (5)	0.0517 (4)	0.0638 (4)	−0.0335 (4)	0.0266 (4)	0.0014 (3)
O1	0.0462 (10)	0.0427 (9)	0.0988 (15)	0.0070 (8)	0.0262 (10)	−0.0028 (9)
N1	0.0382 (9)	0.0331 (9)	0.0392 (9)	0.0026 (8)	0.0145 (8)	0.0021 (7)
C18	0.0366 (11)	0.0616 (14)	0.0372 (11)	−0.0081 (10)	0.0153 (9)	−0.0005 (10)
C17	0.0552 (14)	0.0516 (13)	0.0476 (13)	0.0056 (11)	0.0271 (11)	−0.0006 (11)
C16	0.0483 (12)	0.0469 (13)	0.0403 (11)	0.0105 (10)	0.0183 (10)	0.0080 (10)
C21	0.0319 (10)	0.0349 (10)	0.0376 (10)	−0.0048 (8)	0.0129 (8)	0.0024 (8)
C9	0.0296 (9)	0.0346 (10)	0.0368 (10)	0.0004 (8)	0.0117 (8)	0.0005 (8)
C8	0.0347 (10)	0.0433 (11)	0.0375 (11)	−0.0052 (9)	0.0144 (9)	−0.0027 (9)
C7	0.0371 (11)	0.0393 (11)	0.0370 (10)	−0.0010 (9)	0.0114 (9)	−0.0042 (9)
C6	0.0348 (10)	0.0375 (11)	0.0324 (10)	−0.0048 (8)	0.0106 (8)	−0.0037 (8)
C5	0.0361 (10)	0.0406 (11)	0.0395 (11)	−0.0032 (9)	0.0094 (9)	0.0001 (9)
C4	0.0366 (11)	0.0565 (14)	0.0495 (13)	0.0017 (10)	0.0100 (10)	−0.0039 (11)
C3	0.0380 (12)	0.0771 (18)	0.0495 (14)	−0.0132 (12)	0.0151 (10)	−0.0062 (13)
C20	0.0407 (11)	0.0390 (11)	0.0453 (12)	0.0026 (9)	0.0107 (10)	0.0040 (9)
C19	0.0398 (11)	0.0565 (14)	0.0406 (12)	0.0000 (10)	0.0068 (9)	0.0100 (10)
C10	0.0356 (10)	0.0316 (10)	0.0327 (9)	−0.0010 (8)	0.0127 (8)	−0.0009 (8)
C11	0.0405 (12)	0.0405 (12)	0.0484 (13)	0.0045 (9)	0.0104 (10)	0.0056 (10)
C12	0.0652 (16)	0.0361 (12)	0.0516 (14)	0.0019 (11)	0.0143 (12)	0.0081 (10)
C13	0.0624 (15)	0.0373 (12)	0.0386 (11)	−0.0157 (10)	0.0206 (11)	−0.0041 (9)
C14	0.0410 (12)	0.0478 (13)	0.0486 (13)	−0.0085 (10)	0.0173 (10)	−0.0052 (10)
C15	0.0363 (11)	0.0341 (10)	0.0493 (12)	0.0005 (8)	0.0141 (9)	0.0003 (9)
C2	0.0559 (15)	0.0589 (16)	0.0519 (14)	−0.0240 (13)	0.0186 (12)	0.0009 (12)
C1	0.0491 (13)	0.0408 (12)	0.0441 (12)	−0.0060 (10)	0.0134 (10)	0.0007 (10)

Geometric parameters (Å, º)

Br—C18	1.906 (2)	C5—C4	1.385 (3)
Cl—C13	1.738 (2)	C5—H5	0.9300
O1—C7	1.215 (3)	C4—C3	1.374 (4)
N1—C21	1.386 (3)	C4—H4	0.9300
N1—C9	1.451 (3)	C3—C2	1.374 (4)
N1—H	0.81 (3)	C3—H3	0.9300
C18—C17	1.367 (3)	C20—C19	1.375 (3)
C18—C19	1.382 (4)	C20—H20	0.9300
C17—C16	1.391 (3)	C19—H19	0.9300
C17—H17	0.9300	C10—C11	1.381 (3)
C16—C21	1.387 (3)	C10—C15	1.388 (3)
C16—H16	0.9300	C11—C12	1.380 (3)
C21—C20	1.395 (3)	C11—H11	0.9300
C9—C10	1.520 (3)	C12—C13	1.379 (4)
C9—C8	1.540 (3)	C12—H12	0.9300
C9—H9	0.9800	C13—C14	1.373 (3)
C8—C7	1.507 (3)	C14—C15	1.381 (3)
C8—H8A	0.9700	C14—H14	0.9300
C8—H8B	0.9700	C15—H15	0.9300
C7—C6	1.483 (3)	C2—C1	1.381 (4)
C6—C5	1.385 (3)	C2—H2	0.9300
C6—C1	1.394 (3)	C1—H1	0.9300
C21—N1—C9	121.99 (17)	C3—C4—C5	120.0 (2)
C21—N1—H	115.5 (18)	C3—C4—H4	120.0
C9—N1—H	111.7 (18)	C5—C4—H4	120.0
C17—C18—C19	120.4 (2)	C2—C3—C4	120.4 (2)
C17—C18—Br	119.53 (19)	C2—C3—H3	119.8
C19—C18—Br	120.11 (17)	C4—C3—H3	119.8
C18—C17—C16	120.1 (2)	C19—C20—C21	121.5 (2)
C18—C17—H17	119.9	C19—C20—H20	119.3
C16—C17—H17	119.9	C21—C20—H20	119.3
C21—C16—C17	120.6 (2)	C20—C19—C18	119.5 (2)
C21—C16—H16	119.7	C20—C19—H19	120.3
C17—C16—H16	119.7	C18—C19—H19	120.3
N1—C21—C16	123.20 (19)	C11—C10—C15	118.5 (2)
N1—C21—C20	118.79 (19)	C11—C10—C9	120.90 (19)
C16—C21—C20	117.9 (2)	C15—C10—C9	120.61 (18)
N1—C9—C10	114.69 (16)	C12—C11—C10	121.4 (2)
N1—C9—C8	107.92 (16)	C12—C11—H11	119.3
C10—C9—C8	108.81 (16)	C10—C11—H11	119.3
N1—C9—H9	108.4	C13—C12—C11	118.8 (2)
C10—C9—H9	108.4	C13—C12—H12	120.6
C8—C9—H9	108.4	C11—C12—H12	120.6
C7—C8—C9	113.74 (17)	C14—C13—C12	121.2 (2)
C7—C8—H8A	108.8	C14—C13—Cl	118.75 (19)

C9—C8—H8A	108.8	C12—C13—Cl	120.06 (19)
C7—C8—H8B	108.8	C13—C14—C15	119.3 (2)
C9—C8—H8B	108.8	C13—C14—H14	120.4
H8A—C8—H8B	107.7	C15—C14—H14	120.4
O1—C7—C6	120.3 (2)	C14—C15—C10	120.9 (2)
O1—C7—C8	119.32 (19)	C14—C15—H15	119.6
C6—C7—C8	120.35 (18)	C10—C15—H15	119.6
C5—C6—C1	119.1 (2)	C3—C2—C1	120.0 (2)
C5—C6—C7	122.37 (19)	C3—C2—H2	120.0
C1—C6—C7	118.56 (19)	C1—C2—H2	120.0
C4—C5—C6	120.2 (2)	C2—C1—C6	120.2 (2)
C4—C5—H5	119.9	C2—C1—H1	119.9
C6—C5—H5	119.9	C6—C1—H1	119.9

C19—C18—C17—C16	0.4 (4)	C16—C21—C20—C19	−0.2 (3)
Br—C18—C17—C16	179.65 (18)	C21—C20—C19—C18	0.6 (3)
C18—C17—C16—C21	0.0 (4)	C17—C18—C19—C20	−0.7 (4)
C9—N1—C21—C16	−14.4 (3)	Br—C18—C19—C20	−179.93 (17)
C9—N1—C21—C20	168.47 (19)	N1—C9—C10—C11	145.8 (2)
C17—C16—C21—N1	−177.2 (2)	C8—C9—C10—C11	−93.3 (2)
C17—C16—C21—C20	−0.1 (3)	N1—C9—C10—C15	−36.2 (3)
C21—N1—C9—C10	−59.1 (2)	C8—C9—C10—C15	84.8 (2)
C21—N1—C9—C8	179.46 (17)	C15—C10—C11—C12	0.8 (3)
N1—C9—C8—C7	−50.4 (2)	C9—C10—C11—C12	178.8 (2)
C10—C9—C8—C7	−175.40 (17)	C10—C11—C12—C13	0.3 (4)
C9—C8—C7—O1	109.1 (2)	C11—C12—C13—C14	−1.5 (4)
C9—C8—C7—C6	−70.7 (2)	C11—C12—C13—Cl	176.77 (19)
O1—C7—C6—C5	168.4 (2)	C12—C13—C14—C15	1.5 (4)
C8—C7—C6—C5	−11.8 (3)	Cl—C13—C14—C15	−176.77 (18)
O1—C7—C6—C1	−11.9 (3)	C13—C14—C15—C10	−0.4 (3)
C8—C7—C6—C1	167.93 (19)	C11—C10—C15—C14	−0.7 (3)
C1—C6—C5—C4	−0.7 (3)	C9—C10—C15—C14	−178.8 (2)
C7—C6—C5—C4	179.0 (2)	C4—C3—C2—C1	−0.7 (4)
C6—C5—C4—C3	−0.6 (4)	C3—C2—C1—C6	−0.5 (4)
C5—C4—C3—C2	1.3 (4)	C5—C6—C1—C2	1.2 (3)
N1—C21—C20—C19	177.1 (2)	C7—C6—C1—C2	−178.5 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H···O1^{i}	0.81 (3)	2.23 (3)	2.992 (3)	156 (2)

Symmetry code: (i) −*x*, −*y*+2, −*z*+1.