organic compounds

(1S,4S,5S,6R)-6-(4-Bromophenyl)-5-nitrobicyclo[2.2.2]octan-2-one

Aibao Xia, Jie Tang, Yifeng Wang, Junrong Jiang and Shuping Luo*

State Key Laboratory Breeding Base of Green Chemistry–Synthesis Technology, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China
Correspondence e-mail: xiaaibao1983@163.com

The title compound, $C_{14}H_{14}BrNO_3$, contains a bicyclic ring system with four chiral centers. The absolute structure was established by the Flack method.

Related literature

For the asymmetric Diels-Alder reaction, which in principle allows the formation of four contiguous asymmetric centers, see: Anrendt *et al.* (2000); Northrup & MacMillan (2002); Xu *et al.* (2007); Xu *et al.* (2008).
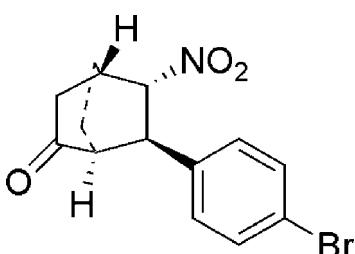
Experimental

Crystal data

$C_{14}H_{14}BrNO_3$

M_r = 324.17

Orthorhombic, $P2_12_12_1$
a = 6.4675 (8) Å
b = 10.0007 (13) Å
c = 20.108 (3) Å
V = 1300.6 (3) Å^3

Z = 4
Mo $K\alpha$ radiation
μ = 3.16 mm^{-1}
T = 293 (2) K
$0.38 \times 0.33 \times 0.27$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.758, T_{max} = 1.000
(expected range = 0.325–0.428)

7669 measured reflections
2823 independent reflections
2201 reflections with $I > 2\sigma(I)$
R_{int} = 0.057

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.084
S = 0.90
2823 reflections
173 parameters
H-atom parameters constrained

$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}
Absolute structure: Flack (1983), 1161 Friedel pairs
Flack parameter: 0.024 (12)

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2000); 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*.

References

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supporting information

(1*S*,4*S*,5*S*,6*R*)-6-(4-Bromophenyl)-5-nitrobicyclo[2.2.2]octan-2-one

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S1. Comment

There has been growing interest in the study of asymmetric Diels-Alder reaction because it allows in principle the formation of four contiguous asymmetric centers (Anrendt *et al.*, 2000; Northrup & MacMillan, 2002; Xu *et al.*, 2007, 2008). Consequently, we have synthesized a series of Diels-Alder products in our laboratory and the crystal structure and absolute configuration of one of these, the title compound, (I), is reported in this article.

In the title compound (Fig. 1), the nitryl and the 4-bromophenyl groups lie on different sides of the plane defined by C3/C4/C5 atoms with O2—N1—C4—C5 and N1—C4—C5—C9 torsion angles of 141.4 (4) and 92.5 (5)°, respectively. The C5—H5 bond and 4-bromophenyl group are almost coplanar with H5—C5—C9—C10 torsion angle of -2.3°. The structure is devoid of any classical hydrogen bonding and the molecules of (I) are separated by normal van der Waal's forces (Fig. 2).

S2. Experimental

A THF (1.0 ml) solution of *trans*-nitrostyrene (0.75 mmol) and cyclohex-2-enone (1.0 mmol) in the presence of (*S*)-1-methyl-2-(pyrrolidin-2-ylmethylthio)-1*H*-imidazole (0.15 mmol) as amine catalyst and benzoic acid (0.15 mmol) as additive at room temperature was subjected to vigorous stirring. After completion of the reaction, the mixture was washed with water (appoximately 300 ml) and extracted with ethyl acetate. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluent: petroleum ether-ethoxyethane). Single crystals were obtained by slow evaporation of an ethyl acetate solution.

S3. Refinement

H atoms were placed in calculated position with C—H = 0.98, 0.97 and 0.93 Å for methine, methylene and aryl H-atoms. All H atoms were included in the final cycles of refinement in riding mode, with $U_{iso}(H) = 1.2U_{eq}$ of the carrier atoms. An absolute structure was established using 1226 Friedel pairs and has been presented in this article.
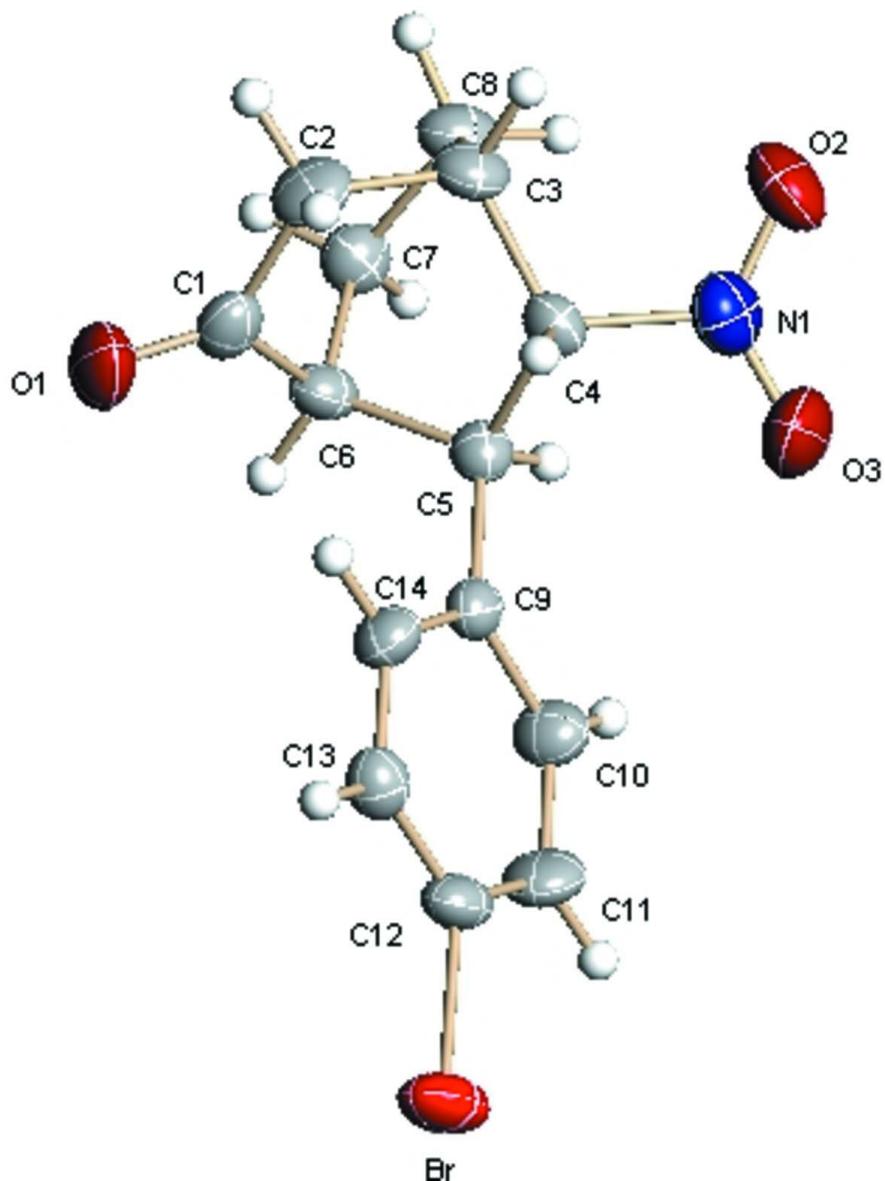
Figure 1

Molecular structure of the title compound with atomic labeling scheme; displacement ellipsoids are drawn at the 30% probability level.
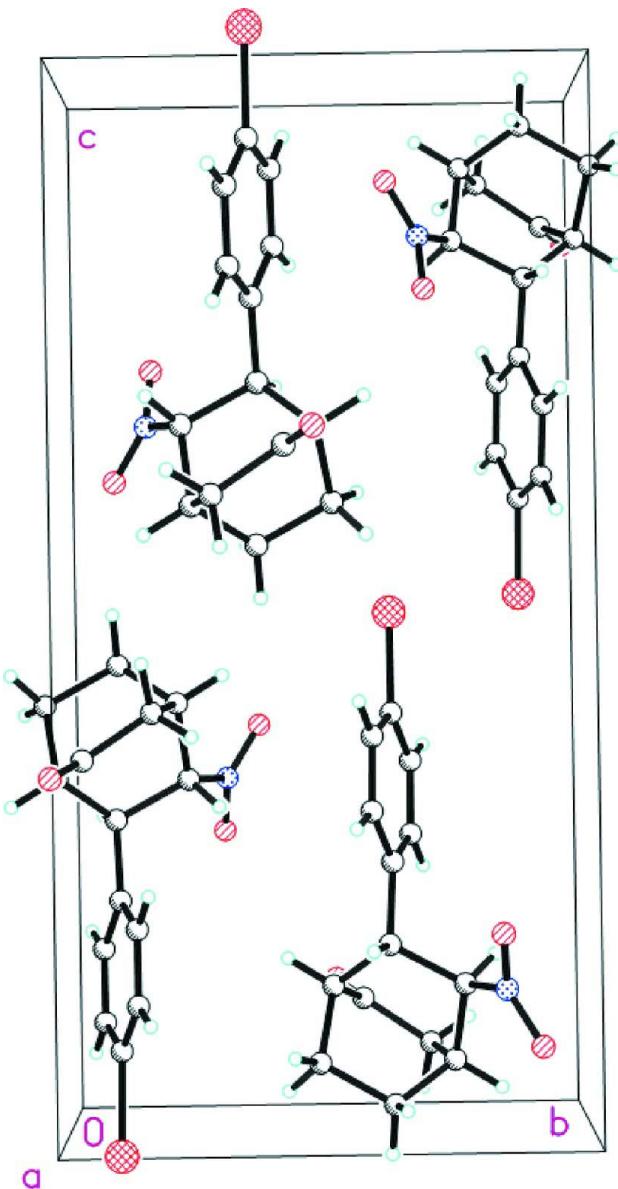
Figure 2

Unit cell packing of the title compound.

(1*S*,4*S*,5*S*,6*R*)-6-(4-Bromophenyl)-5-nitrobicyclo[2.2.2]octan-2-one

Crystal data

$C_{14}H_{14}BrNO_3$	$F(000) = 656$
$M_r = 324.17$	$D_x = 1.656$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 2565 reflections
$a = 6.4675$ (8) Å	$\theta = 4.6$–48.7°
$b = 10.0007$ (13) Å	$\mu = 3.16$ mm^{-1}
$c = 20.108$ (3) Å	$T = 293$ K
$V = 1300.6$ (3) Å^3	Prismatic, colorless
$Z = 4$	$0.38 \times 0.33 \times 0.27$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	7669 measured reflections
Radiation source: fine-focus sealed tube	2823 independent reflections
Graphite monochromator	2201 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.057$
Absorption correction: multi-scan	$\theta_{max} = 27.0°$, $\theta_{min} = 2.0°$
(*SADABS*; Sheldrick, 1996)	$h = -8 \rightarrow 8$
$T_{min} = 0.758$, $T_{max} = 1.000$	$k = -12 \rightarrow 12$
	$l = -25 \rightarrow 18$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.038$	$w = 1/[\sigma^2(F_o^2) + (0.043P)^2]$
$wR(F^2) = 0.084$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.90$	$(\Delta/\sigma)_{max} = 0.010$
2823 reflections	$\Delta\rho_{max} = 0.63$ e Å^{-3}
173 parameters	$\Delta\rho_{min} = -0.53$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0251 (15)
Secondary atom site location: difference Fourier map	Absolute structure: Flack (1983), 1161 Friedel pairs
	Absolute structure parameter: 0.024 (12)

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br	0.60615 (7)	0.37916 (4)	0.992203 (17)	0.05507 (17)
N1	0.1712 (5)	0.1860 (3)	0.66087 (18)	0.0450 (8)
O1	0.8682 (4)	0.4856 (3)	0.64840 (13)	0.0589 (8)
O2	0.1115 (4)	0.1257 (3)	0.61231 (14)	0.0583 (7)
O3	0.0748 (5)	0.1934 (4)	0.71214 (16)	0.0764 (10)
C1	0.7048 (6)	0.4361 (4)	0.63535 (17)	0.0390 (9)
C2	0.6837 (6)	0.3111 (4)	0.5941 (2)	0.0446 (10)
H2A	0.7602	0.2389	0.6148	0.054*
H2B	0.7415	0.3264	0.5502	0.054*
C3	0.4587 (5)	0.2721 (4)	0.58773 (18)	0.0381 (9)
H3	0.4457	0.1883	0.5628	0.046*
C4	0.3809 (5)	0.2536 (3)	0.65847 (16)	0.0321 (7)
H4	0.4797	0.1964	0.6821	0.038*

C5	0.3716 (5)	0.3892 (3)	0.69495 (14)	0.0306 (7)
H5	0.2273	0.4190	0.6935	0.037*
C6	0.4991 (6)	0.4916 (4)	0.65427 (17)	0.0353 (8)
H6	0.5158	0.5749	0.6793	0.042*
C7	0.3820 (6)	0.5176 (3)	0.58930 (16)	0.0394 (8)
H7A	0.4634	0.5755	0.5608	0.047*
H7B	0.2523	0.5623	0.5989	0.047*
C8	0.3387 (5)	0.3837 (4)	0.55301 (16)	0.0432 (9)
H8A	0.1918	0.3642	0.5541	0.052*
H8B	0.3815	0.3902	0.5069	0.052*
C9	0.4318 (4)	0.3813 (4)	0.76760 (14)	0.0316 (7)
C10	0.2904 (6)	0.4189 (3)	0.81598 (18)	0.0405 (9)
H10	0.1590	0.4467	0.8033	0.049*
C11	0.3406 (6)	0.4160 (4)	0.88210 (17)	0.0454 (10)
H11	0.2429	0.4391	0.9140	0.054*
C12	0.5348 (5)	0.3790 (4)	0.90080 (15)	0.0384 (8)
C13	0.6804 (6)	0.3425 (3)	0.85488 (17)	0.0374 (9)
H13	0.8123	0.3169	0.8681	0.045*
C14	0.6269 (5)	0.3446 (3)	0.78835 (16)	0.0365 (8)
H14	0.7252	0.3207	0.7567	0.044*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.0759 (3)	0.0602 (3)	0.0292 (2)	−0.0056 (2)	−0.00768 (18)	−0.00532 (18)
N1	0.049 (2)	0.0307 (16)	0.055 (2)	−0.0033 (14)	−0.0048 (17)	0.0069 (15)
O1	0.0375 (17)	0.081 (2)	0.0584 (18)	−0.0188 (17)	−0.0023 (14)	0.0023 (15)
O2	0.0513 (15)	0.0495 (16)	0.0741 (18)	−0.0076 (18)	−0.0139 (15)	−0.0171 (16)
O3	0.076 (2)	0.090 (2)	0.062 (2)	−0.040 (2)	0.0159 (18)	0.0028 (18)
C1	0.038 (2)	0.048 (2)	0.031 (2)	−0.0038 (18)	0.0005 (16)	0.0104 (16)
C2	0.041 (2)	0.049 (2)	0.044 (2)	0.0109 (18)	0.0129 (17)	−0.0059 (18)
C3	0.049 (2)	0.033 (2)	0.0330 (19)	0.0027 (17)	−0.0010 (15)	−0.0093 (15)
C4	0.0306 (17)	0.0311 (18)	0.0344 (17)	−0.0006 (17)	−0.0064 (16)	−0.0025 (13)
C5	0.0308 (16)	0.0275 (16)	0.0335 (16)	0.0018 (18)	0.0013 (14)	−0.0029 (15)
C6	0.047 (2)	0.0310 (19)	0.0283 (19)	−0.0028 (18)	−0.0020 (15)	−0.0039 (15)
C7	0.043 (2)	0.0356 (19)	0.0392 (19)	0.0000 (18)	−0.0011 (19)	0.0051 (15)
C8	0.060 (2)	0.0377 (19)	0.0321 (17)	0.002 (2)	−0.0035 (15)	−0.0038 (17)
C9	0.0344 (18)	0.0287 (16)	0.0317 (16)	−0.0055 (18)	0.0025 (12)	−0.0006 (15)
C10	0.0364 (18)	0.047 (2)	0.038 (2)	0.0073 (17)	0.0027 (16)	−0.0044 (16)
C11	0.052 (3)	0.050 (3)	0.034 (2)	0.0054 (18)	0.0104 (17)	−0.0127 (16)
C12	0.053 (2)	0.0354 (19)	0.0268 (16)	−0.0065 (19)	0.0000 (14)	−0.0052 (18)
C13	0.0367 (18)	0.035 (2)	0.041 (2)	−0.0027 (15)	−0.0031 (15)	0.0042 (15)
C14	0.0351 (19)	0.042 (2)	0.0323 (17)	0.0020 (16)	0.0073 (16)	−0.0009 (14)

Geometric parameters (Å, º)

Br—C12	1.895 (3)	C6—C7	1.532 (5)
N1—O3	1.207 (4)	C6—H6	0.9800

N1—O2	1.211 (4)	C7—C8	1.550 (5)
N1—C4	1.516 (4)	C7—H7A	0.9700
O1—C1	1.196 (4)	C7—H7B	0.9700
C1—C6	1.491 (5)	C8—H8A	0.9700
C1—C2	1.506 (5)	C8—H8B	0.9700
C2—C3	1.512 (5)	C9—C14	1.379 (5)
C2—H2A	0.9700	C9—C10	1.387 (4)
C2—H2B	0.9700	C10—C11	1.369 (5)
C3—C4	1.520 (5)	C10—H10	0.9300
C3—C8	1.529 (5)	C11—C12	1.362 (5)
C3—H3	0.9800	C11—H11	0.9300
C4—C5	1.543 (4)	C12—C13	1.368 (5)
C4—H4	0.9800	C13—C14	1.382 (5)
C5—C9	1.514 (4)	C13—H13	0.9300
C5—C6	1.549 (5)	C14—H14	0.9300
C5—H5	0.9800		
O3—N1—O2	123.7 (3)	C1—C6—H6	110.4
O3—N1—C4	117.5 (3)	C7—C6—H6	110.4
O2—N1—C4	118.8 (3)	C5—C6—H6	110.4
O1—C1—C6	125.3 (3)	C6—C7—C8	110.1 (3)
O1—C1—C2	123.0 (4)	C6—C7—H7A	109.6
C6—C1—C2	111.6 (3)	C8—C7—H7A	109.6
C1—C2—C3	110.4 (3)	C6—C7—H7B	109.6
C1—C2—H2A	109.6	C8—C7—H7B	109.6
C3—C2—H2A	109.6	H7A—C7—H7B	108.1
C1—C2—H2B	109.6	C3—C8—C7	108.9 (3)
C3—C2—H2B	109.6	C3—C8—H8A	109.9
H2A—C2—H2B	108.1	C7—C8—H8A	109.9
C2—C3—C4	105.7 (3)	C3—C8—H8B	109.9
C2—C3—C8	109.8 (3)	C7—C8—H8B	109.9
C4—C3—C8	110.4 (3)	H8A—C8—H8B	108.3
C2—C3—H3	110.3	C14—C9—C10	117.6 (3)
C4—C3—H3	110.3	C14—C9—C5	122.8 (3)
C8—C3—H3	110.3	C10—C9—C5	119.6 (3)
N1—C4—C3	112.4 (3)	C11—C10—C9	121.3 (3)
N1—C4—C5	110.0 (3)	C11—C10—H10	119.4
C3—C4—C5	110.5 (3)	C9—C10—H10	119.4
N1—C4—H4	107.9	C12—C11—C10	119.5 (3)
C3—C4—H4	107.9	C12—C11—H11	120.3
C5—C4—H4	107.9	C10—C11—H11	120.3
C9—C5—C4	113.7 (3)	C11—C12—C13	121.4 (3)
C9—C5—C6	114.1 (3)	C11—C12—Br	119.5 (3)
C4—C5—C6	108.0 (3)	C13—C12—Br	119.2 (3)
C9—C5—H5	106.9	C12—C13—C14	118.5 (3)
C4—C5—H5	106.9	C12—C13—H13	120.7
C6—C5—H5	106.9	C14—C13—H13	120.7
C1—C6—C7	106.7 (3)	C9—C14—C13	121.7 (3)

C1—C6—C5	111.3 (3)	C9—C14—H14	119.1
C7—C6—C5	107.4 (3)	C13—C14—H14	119.1
O1—C1—C2—C3	178.7 (4)	C9—C5—C6—C7	−163.8 (3)
C6—C1—C2—C3	−4.0 (4)	C4—C5—C6—C7	68.7 (3)
C1—C2—C3—C4	−58.0 (4)	C1—C6—C7—C8	65.1 (4)
C1—C2—C3—C8	61.1 (4)	C5—C6—C7—C8	−54.4 (4)
O3—N1—C4—C3	−163.6 (3)	C2—C3—C8—C7	−52.1 (4)
O2—N1—C4—C3	17.8 (4)	C4—C3—C8—C7	64.1 (4)
O3—N1—C4—C5	−40.0 (4)	C6—C7—C8—C3	−9.6 (4)
O2—N1—C4—C5	141.4 (3)	C4—C5—C9—C14	63.5 (4)
C2—C3—C4—N1	−167.8 (3)	C6—C5—C9—C14	−61.0 (4)
C8—C3—C4—N1	73.5 (3)	C4—C5—C9—C10	−120.1 (3)
C2—C3—C4—C5	68.9 (3)	C6—C5—C9—C10	115.4 (3)
C8—C3—C4—C5	−49.8 (4)	C14—C9—C10—C11	−1.9 (5)
N1—C4—C5—C9	92.5 (3)	C5—C9—C10—C11	−178.5 (3)
C3—C4—C5—C9	−142.8 (3)	C9—C10—C11—C12	1.8 (6)
N1—C4—C5—C6	−139.8 (3)	C10—C11—C12—C13	−1.0 (6)
C3—C4—C5—C6	−15.1 (4)	C10—C11—C12—Br	178.5 (3)
O1—C1—C6—C7	119.8 (4)	C11—C12—C13—C14	0.4 (6)
C2—C1—C6—C7	−57.4 (4)	Br—C12—C13—C14	−179.1 (3)
O1—C1—C6—C5	−123.4 (4)	C10—C9—C14—C13	1.2 (5)
C2—C1—C6—C5	59.5 (4)	C5—C9—C14—C13	177.7 (3)
C9—C5—C6—C1	79.8 (3)	C12—C13—C14—C9	−0.5 (5)
C4—C5—C6—C1	−47.7 (4)		