3,6-Dibromo-9-(4-chlorobenzyl)-9*H*-carbazole

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The title compound, $C_{19}H_{12}Br_2ClN$, was synthesized by *N*-alkylation of 1-chloro-4-(chloromethyl)benzene with 3,6-dibromo-9*H*-carbazole. The carbazole ring system is essentially planar (mean deviation of 0.028 Å) and makes a dihedral angle of 74.6 (3)° with the plane of the benzene ring.

Related literature

For the pharmaceutical properties of carbazoles, see: Buu-Hoï & Royer (1950); Caulfield *et al.* (2002); Harfenist & Joyner (1983); Harper *et al.* (2002). For bond length data, see: Allen *et al.* (1987). For the synthesis of the title compound, see: Duan *et al.* (2005a,b); Smith *et al.* (1992). For related literature, see: Borzatta & Carrozza (1991). For a related compound, see: Cui *et al.* (2009).
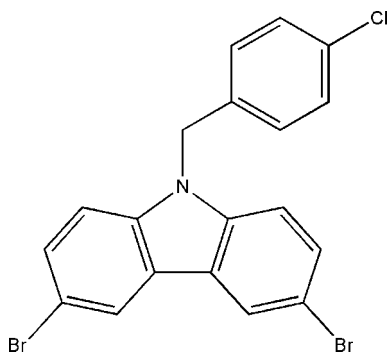
Experimental

Crystal data

$C_{19}H_{12}Br_2ClN$	V = 3164.8 (10) Å^3
M_r = 449.57	Z = 8
Orthorhombic, *Pbca*	Mo *K*α radiation
a = 8.7673 (18) Å	μ = 5.29 mm^{-1}
b = 16.732 (3) Å	T = 113 (2) K
c = 21.574 (4) Å	$0.06 \times 0.02 \times 0.02$ mm

Data collection

Rigaku Saturn diffractometer	18205 measured reflections
Absorption correction: multi-scan	2794 independent reflections
(*CrystalClear*; Rigaku/MSC, 2005)	2369 reflections with $I > 2\sigma(I)$
T_{min} = 0.742, T_{max} = 0.902	R_{int} = 0.090

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047	208 parameters
$wR(F^2)$ = 0.108	H-atom parameters constrained
S = 1.10	$\Delta\rho_{max}$ = 0.54 e Å^{-3}
2794 reflections	$\Delta\rho_{min}$ = −0.53 e Å^{-3}

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RN2052).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Borzatta, V. & Carrozza, P. (1991). European Patent EP 0 462 069.
Buu-Hoï, N. P. & Royer, R. (1950). *J. Org. Chem.* **15**, 123–130.
Caulfield, T., Cherrier, M. P., Combeau, C. & Mailliet, P. (2002). European Patent No. 1 253 141.
Cui, J.. Duan, M. & Cai, L. (2009). *Acta Cryst.* E**65**, o216
Duan, X. M., Han, J., Chen, L. G., Xu, Y. J. & Li, Y. (2005a). *Fine Chem.* **22**, 39–40.
Duan, X. M., Han, J., Chen, L. G., Xu, Y. J. & Li, Y. (2005b). *Fine Chem.* **22**, 52.
Harfenist, M. & Joyner, C. T. (1983). US Patent No. 4 379 160.
Harper, R. W., Lin, H. S. & Richett, M. E. (2002). World Patent No. 02 079 154.
Rigaku/MSC (2005). *CrystalClear* and *CrystalStructure*. Rigaku/MSC, The Woodlands, Texas,.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Smith, K., James, D. M., Mistry, A. G., Bye, M. R. & Faulkner, D. J. (1992). *Tetrahedron*, **48**, 7479–7488.

supporting information

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S1. Comment

Carbazole derivatives substituted by *N*-alkylation possess valuable pharmaceutical properties (Buu-Hoï & Royer, 1950; Harfenist & Joyner, 1983; Caulfield *et al.*, 2002; Harper *et al.*, 2002). In this paper, we report the structure of 3,6-di-bromo-9-(4-chlorobenzyl)-9*H*-carbazole (I), which was synthesized by *N*-alkylation of 1-chloro-4-(chloromethyl)benzene with 3,6-dibromo-9*H*-carbazole. The carbazole ring system is essentially planar with mean deviations of 0.0277Å. The carbazole plane is inclined to the benzene ring planes at dihedral angle of 74.6 (3)°. The C—Br distances fall in the range 1.883 (4) to 1.905 (5) Å, consistent with the literature (Allen *et al.*, 1987).

S2. Experimental

The title compound was prepared according to the procedure of Duan *et al.* (2005*a*,*b*) from 3,6-dibromo-carbazole (Smith *et al.* 1992) and 1-chloro-4-(chloromethyl)benzene. Compound (I) (40 mg) was dissolved in mixture of chloro-form (10 ml) and ethanol (5 ml) and the solution was kept at room temperature for 18 d. Natural evaporation of the solution gave colourless crystals suitable for X-Ray analysis. (m.p. 451–452 K).

S3. Refinement

All H atoms were included in the riding model approximation with C—H distances = 0.93 (aromatic) and 0.97 (methyl-ene) Å, and with $U_{iso}(H) = 1.2 \times U_{eq}(C)$.
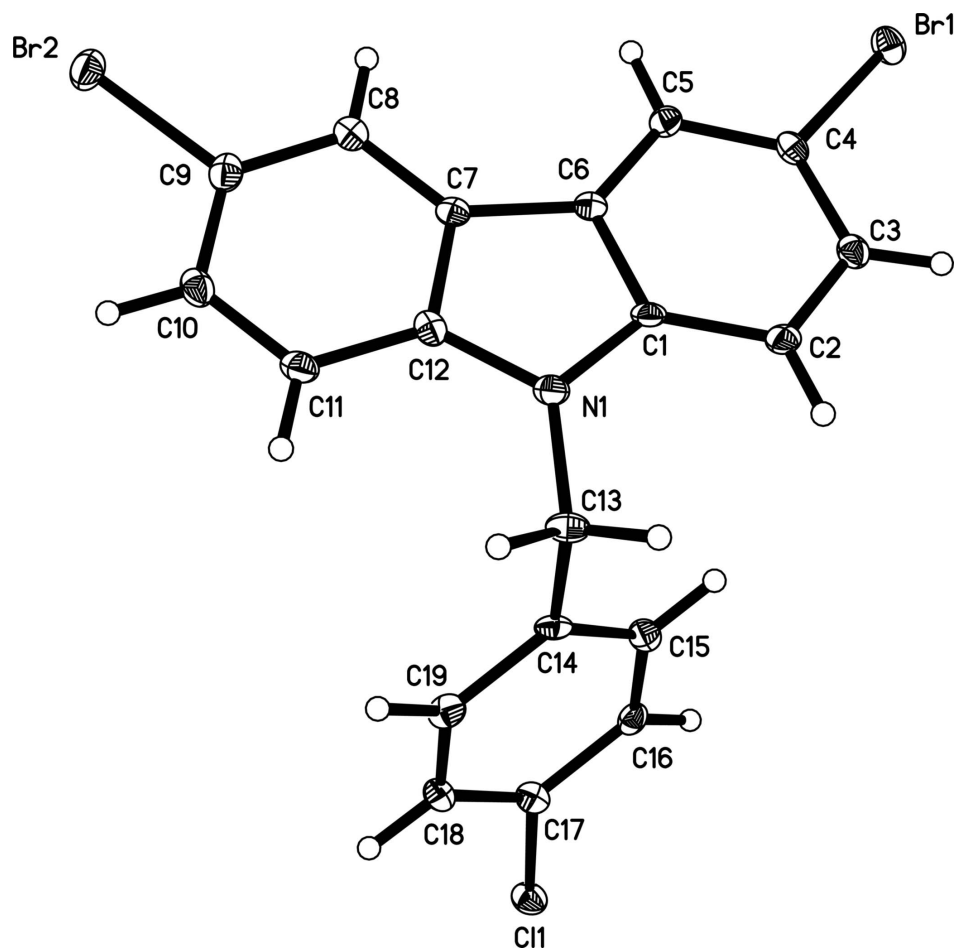
Figure 1

A perspective view of (I) with displacement ellipsoids drawn at the 30% probability level.
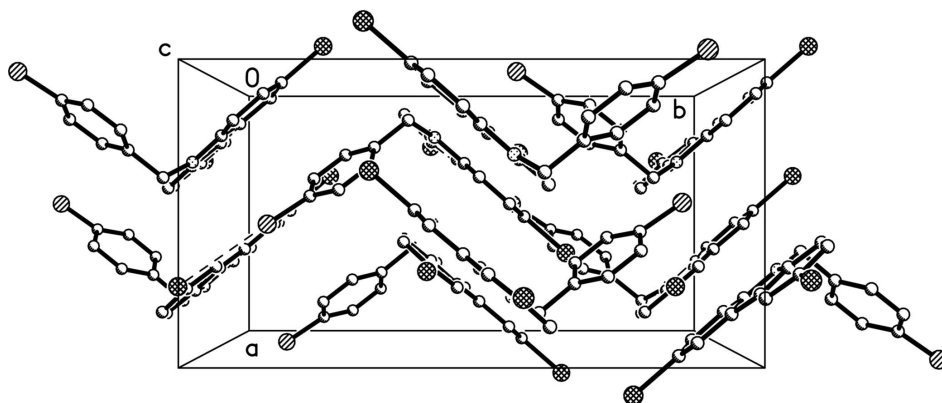
Figure 2

Crystal packing of (I), viewed down the a axis with H atoms omitted for clarity.

3,6-Dibromo-9-(4-chlorobenzyl)-9*H*-carbazole

Crystal data

$C_{19}H_{12}Br_2ClN$	$D_x = 1.887$ Mg m^{-3}
$M_r = 449.57$	Melting point = 451–452 K
Orthorhombic, *Pbca*	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ac 2ab	Cell parameters from 5270 reflections
$a = 8.7673$ (18) Å	$\theta = 2.4$–27.9°
$b = 16.732$ (3) Å	$\mu = 5.29$ mm^{-1}
$c = 21.574$ (4) Å	$T = 113$ K
$V = 3164.8$ (10) Å^3	Prism, colorless
$Z = 8$	$0.06 \times 0.02 \times 0.02$ mm
$F(000) = 1760$	

Data collection

Rigaku Saturn diffractometer	18205 measured reflections
Radiation source: rotating anode	2794 independent reflections
Confocal monochromator	2369 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.090$
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)	$\theta_{max} = 25.0°$, $\theta_{min} = 1.9°$
$T_{min} = 0.742$, $T_{max} = 0.902$	$h = -10 \rightarrow 10$
	$k = -19 \rightarrow 13$
	$l = -25 \rightarrow 25$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.047$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.108$	
$S = 1.10$	H-atom parameters constrained
2794 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 2.2242P]$ where $P = (F_o^2 + 2F_c^2)/3$
208 parameters	
0 restraints	$(\Delta/\sigma)_{max} = 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.54$ e Å^{-3}
	$\Delta\rho_{min} = -0.53$ e Å^{-3}

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 (Å²)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Br1	0.22114 (6)	0.09041 (3)	0.56121 (2)	0.02566 (18)
Br2	0.65417 (6)	−0.19402 (3)	0.84401 (2)	0.02964 (19)
Cl1	0.54034 (14)	0.40983 (8)	0.94634 (5)	0.0248 (3)
N1	0.2015 (4)	0.0764 (3)	0.83555 (17)	0.0200 (9)

C1	0.1896 (5)	0.0868 (3)	0.7726 (2)	0.0181 (10)
C2	0.1017 (5)	0.1422 (3)	0.7406 (2)	0.0205 (11)
H2	0.0388	0.1783	0.7611	0.025*
C3	0.1123 (5)	0.1410 (3)	0.6772 (2)	0.0208 (11)
H3	0.0562	0.1771	0.6536	0.025*
C4	0.2067 (5)	0.0860 (3)	0.6482 (2)	0.0193 (11)
C5	0.2911 (5)	0.0299 (3)	0.6790 (2)	0.0193 (11)
H5	0.3511	−0.0071	0.6580	0.023*
C6	0.2827 (5)	0.0308 (3)	0.7433 (2)	0.0163 (10)
C7	0.3559 (5)	−0.0160 (3)	0.7902 (2)	0.0170 (10)
C8	0.4580 (5)	−0.0795 (3)	0.7888 (2)	0.0198 (11)
H8	0.4890	−0.1020	0.7515	0.024*
C9	0.5117 (6)	−0.1080 (3)	0.8443 (2)	0.0236 (12)
C10	0.4625 (5)	−0.0769 (3)	0.9006 (2)	0.0240 (12)
H10	0.4999	−0.0977	0.9375	0.029*
C11	0.3590 (5)	−0.0155 (3)	0.9018 (2)	0.0224 (11)
H11	0.3259	0.0052	0.9395	0.027*
C12	0.3041 (5)	0.0154 (3)	0.8466 (2)	0.0182 (11)
C13	0.1391 (6)	0.1292 (3)	0.8828 (2)	0.0230 (12)
H13A	0.1194	0.0985	0.9201	0.028*
H13B	0.0425	0.1505	0.8683	0.028*
C14	0.2447 (5)	0.1977 (3)	0.8982 (2)	0.0190 (11)
C15	0.2722 (5)	0.2589 (3)	0.8562 (2)	0.0208 (11)
H15	0.2264	0.2568	0.8174	0.025*
C16	0.3654 (5)	0.3226 (3)	0.8703 (2)	0.0198 (11)
H16	0.3825	0.3628	0.8414	0.024*
C17	0.4333 (5)	0.3259 (3)	0.9281 (2)	0.0220 (11)
C18	0.4101 (6)	0.2650 (3)	0.9700 (2)	0.0237 (11)
H18	0.4579	0.2666	1.0084	0.028*
C19	0.3168 (5)	0.2020 (3)	0.9553 (2)	0.0214 (11)
H19	0.3018	0.1614	0.9841	0.026*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0279 (3)	0.0322 (4)	0.0169 (3)	−0.0001 (2)	0.00008 (19)	0.0030 (2)
Br2	0.0277 (3)	0.0238 (4)	0.0375 (3)	0.0038 (2)	−0.0060 (2)	0.0027 (2)
Cl1	0.0296 (7)	0.0222 (8)	0.0225 (6)	−0.0055 (5)	−0.0011 (5)	−0.0009 (5)
N1	0.025 (2)	0.018 (3)	0.0176 (19)	−0.0014 (18)	0.0005 (16)	−0.0021 (18)
C1	0.023 (2)	0.013 (3)	0.018 (2)	−0.003 (2)	−0.0011 (19)	−0.005 (2)
C2	0.019 (2)	0.016 (3)	0.027 (3)	−0.003 (2)	−0.003 (2)	−0.005 (2)
C3	0.021 (3)	0.020 (3)	0.021 (2)	−0.004 (2)	−0.004 (2)	0.001 (2)
C4	0.017 (2)	0.023 (3)	0.017 (2)	−0.004 (2)	−0.0016 (19)	0.000 (2)
C5	0.021 (2)	0.016 (3)	0.021 (2)	−0.001 (2)	0.0007 (19)	0.000 (2)
C6	0.016 (2)	0.016 (3)	0.017 (2)	−0.003 (2)	0.0019 (18)	−0.002 (2)
C7	0.017 (2)	0.015 (3)	0.019 (2)	−0.006 (2)	0.0002 (18)	−0.001 (2)
C8	0.018 (2)	0.022 (3)	0.020 (2)	−0.003 (2)	0.0014 (19)	0.001 (2)
C9	0.021 (3)	0.020 (3)	0.030 (3)	−0.003 (2)	−0.004 (2)	0.004 (2)

C10	0.027 (3)	0.023 (3)	0.022 (2)	−0.007 (2)	−0.006 (2)	0.004 (2)
C11	0.028 (3)	0.021 (3)	0.019 (2)	−0.005 (2)	−0.001 (2)	−0.003 (2)
C12	0.017 (2)	0.018 (3)	0.019 (2)	−0.008 (2)	−0.0026 (18)	0.003 (2)
C13	0.025 (3)	0.026 (3)	0.018 (2)	0.000 (2)	0.008 (2)	−0.007 (2)
C14	0.019 (2)	0.020 (3)	0.018 (2)	0.001 (2)	0.0044 (19)	−0.008 (2)
C15	0.017 (2)	0.028 (3)	0.017 (2)	0.003 (2)	0.0022 (19)	−0.002 (2)
C16	0.019 (2)	0.020 (3)	0.020 (2)	0.006 (2)	0.0042 (19)	0.002 (2)
C17	0.023 (3)	0.024 (3)	0.020 (2)	−0.001 (2)	0.000 (2)	−0.001 (2)
C18	0.032 (3)	0.024 (3)	0.015 (2)	0.003 (2)	−0.002 (2)	0.001 (2)
C19	0.027 (3)	0.016 (3)	0.021 (2)	−0.002 (2)	0.008 (2)	0.004 (2)

Geometric parameters (Å, º)

Br1—C4	1.883 (4)	C8—H8	0.9300
Br2—C9	1.905 (5)	C9—C10	1.390 (7)
Cl1—C17	1.734 (5)	C10—C11	1.370 (7)
N1—C1	1.373 (6)	C10—H10	0.9300
N1—C12	1.382 (6)	C11—C12	1.384 (6)
N1—C13	1.455 (6)	C11—H11	0.9300
C1—C2	1.390 (7)	C13—C14	1.510 (7)
C1—C6	1.393 (7)	C13—H13A	0.9700
C2—C3	1.370 (6)	C13—H13B	0.9700
C2—H2	0.9300	C14—C19	1.386 (7)
C3—C4	1.387 (7)	C14—C15	1.389 (7)
C3—H3	0.9300	C15—C16	1.377 (7)
C4—C5	1.368 (7)	C15—H15	0.9300
C5—C6	1.389 (6)	C16—C17	1.383 (6)
C5—H5	0.9300	C16—H16	0.9300
C6—C7	1.431 (7)	C17—C18	1.376 (7)
C7—C8	1.390 (7)	C18—C19	1.372 (7)
C7—C12	1.402 (6)	C18—H18	0.9300
C8—C9	1.371 (6)	C19—H19	0.9300
C1—N1—C12	108.3 (4)	C9—C10—H10	119.9
C1—N1—C13	126.0 (4)	C10—C11—C12	119.6 (5)
C12—N1—C13	124.9 (4)	C10—C11—H11	120.2
N1—C1—C2	128.2 (4)	C12—C11—H11	120.2
N1—C1—C6	108.6 (4)	N1—C12—C11	130.7 (4)
C2—C1—C6	123.2 (4)	N1—C12—C7	109.7 (4)
C3—C2—C1	116.7 (5)	C11—C12—C7	119.6 (5)
C3—C2—H2	121.7	N1—C13—C14	112.6 (4)
C1—C2—H2	121.7	N1—C13—H13A	109.1
C2—C3—C4	119.9 (5)	C14—C13—H13A	109.1
C2—C3—H3	120.0	N1—C13—H13B	109.1
C4—C3—H3	120.0	C14—C13—H13B	109.1
C5—C4—C3	124.1 (4)	H13A—C13—H13B	107.8
C5—C4—Br1	118.3 (4)	C19—C14—C15	117.5 (5)
C3—C4—Br1	117.6 (4)	C19—C14—C13	121.0 (5)

C4—C5—C6	116.6 (5)	C15—C14—C13	121.5 (4)
C4—C5—H5	121.7	C16—C15—C14	122.0 (4)
C6—C5—H5	121.7	C16—C15—H15	119.0
C5—C6—C1	119.5 (4)	C14—C15—H15	119.0
C5—C6—C7	132.5 (5)	C15—C16—C17	119.1 (5)
C1—C6—C7	108.1 (4)	C15—C16—H16	120.5
C8—C7—C12	120.9 (4)	C17—C16—H16	120.5
C8—C7—C6	133.9 (4)	C18—C17—C16	119.9 (5)
C12—C7—C6	105.3 (4)	C18—C17—Cl1	122.1 (4)
C9—C8—C7	118.0 (5)	C16—C17—Cl1	118.0 (4)
C9—C8—H8	121.0	C19—C18—C17	120.4 (5)
C7—C8—H8	121.0	C19—C18—H18	119.8
C8—C9—C10	121.7 (5)	C17—C18—H18	119.8
C8—C9—Br2	119.0 (4)	C18—C19—C14	121.2 (5)
C10—C9—Br2	119.3 (4)	C18—C19—H19	119.4
C11—C10—C9	120.2 (5)	C14—C19—H19	119.4
C11—C10—H10	119.9		
C12—N1—C1—C2	−178.9 (5)	Br2—C9—C10—C11	−179.4 (4)
C13—N1—C1—C2	−8.9 (8)	C9—C10—C11—C12	−0.1 (7)
C12—N1—C1—C6	1.3 (5)	C1—N1—C12—C11	177.3 (5)
C13—N1—C1—C6	171.2 (4)	C13—N1—C12—C11	7.2 (8)
N1—C1—C2—C3	178.8 (5)	C1—N1—C12—C7	−1.8 (5)
C6—C1—C2—C3	−1.3 (7)	C13—N1—C12—C7	−171.9 (4)
C1—C2—C3—C4	0.4 (7)	C10—C11—C12—N1	−179.6 (5)
C2—C3—C4—C5	1.2 (8)	C10—C11—C12—C7	−0.5 (7)
C2—C3—C4—Br1	−177.8 (4)	C8—C7—C12—N1	−178.6 (4)
C3—C4—C5—C6	−1.8 (7)	C6—C7—C12—N1	1.7 (5)
Br1—C4—C5—C6	177.2 (3)	C8—C7—C12—C11	2.1 (7)
C4—C5—C6—C1	0.8 (7)	C6—C7—C12—C11	−177.6 (4)
C4—C5—C6—C7	−178.1 (5)	C1—N1—C13—C14	−85.7 (6)
N1—C1—C6—C5	−179.4 (4)	C12—N1—C13—C14	82.7 (6)
C2—C1—C6—C5	0.7 (7)	N1—C13—C14—C19	−111.0 (5)
N1—C1—C6—C7	−0.2 (5)	N1—C13—C14—C15	69.5 (6)
C2—C1—C6—C7	179.9 (4)	C19—C14—C15—C16	−1.0 (7)
C5—C6—C7—C8	−1.5 (9)	C13—C14—C15—C16	178.4 (4)
C1—C6—C7—C8	179.5 (5)	C14—C15—C16—C17	−0.2 (7)
C5—C6—C7—C12	178.2 (5)	C15—C16—C17—C18	1.6 (7)
C1—C6—C7—C12	−0.9 (5)	C15—C16—C17—Cl1	−176.0 (4)
C12—C7—C8—C9	−2.9 (7)	C16—C17—C18—C19	−1.7 (8)
C6—C7—C8—C9	176.7 (5)	Cl1—C17—C18—C19	175.8 (4)
C7—C8—C9—C10	2.3 (7)	C17—C18—C19—C14	0.4 (8)
C7—C8—C9—Br2	−179.1 (4)	C15—C14—C19—C18	1.0 (7)
C8—C9—C10—C11	−0.8 (8)	C13—C14—C19—C18	−178.5 (5)