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Crystal structure of 1,3,6,8-tetrabromo-9-ethyl-9*H*-carbazole

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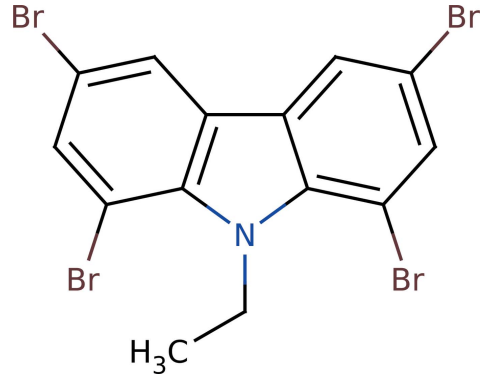
In the title compound, $C_{14}H_9Br_4N$, the tricyclic ring system is almost planar (r.m.s. deviation for the 13 non-H atoms = 0.017 Å) and the methyl C atom deviates from the mean plane of the ring system by 1.072 (17) Å. In the crystal, Br···Br contacts [3.636 (3) and 3.660 (3) Å] slightly shorter than the van der Waals contact distance of 3.70 Å are seen.

Keywords: crystal structure; carbazole; halogen–halogen contact.

CCDC reference: 1402621

1. Related literature

For applications of *N*-substituted carbazole derivatives in anticancer research, see: Caulfield *et al.* (2002). For their use in optoelectronic devices, see: Niu *et al.* (2011); Miyazaki *et al.* (2014); Grigalevicius *et al.* (2002).



2. Experimental

2.1. Crystal data

$C_{14}H_9Br_4N$
M_r = 510.85
Monoclinic, $P2_1$
a = 4.202 (2) Å
b = 14.654 (6) Å
c = 12.245 (6) Å
β = 92.758 (18)°
V = 753.1 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 10.70 mm^{-1}
T = 293 K
0.40 × 0.13 × 0.12 mm

2.2. Data collection

Rigaku XtaLAB mini diffractometer
Absorption correction: multi-scan (*REQAB*; Rigaku, 1998)
T_{min} = 0.115, T_{max} = 0.277
2755 measured reflections
2599 independent reflections
2071 reflections with $F^2 > 2.0\sigma(F^2)$
R_{int} = 0.021

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.130
S = 1.01
2600 reflections
172 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.74 e Å^{-3}
$\Delta\rho_{min}$ = −0.66 e Å^{-3}
Absolute structure: Flack (1983), 868 Friedel Pairs
Absolute structure parameter: 0.05 (4)

Data collection: *CrystalClear-SM Expert* (Rigaku, 2011); cell refinement: *CrystalClear-SM Expert*; data reduction: *CrystalClear-SM Expert*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CrystalStructure* (Rigaku, 2010); software used to prepare material for publication: *CrystalStructure*.

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7428).

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supporting information

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Crystal structure of 1,3,6,8-tetrabromo-9-ethyl-9*H*-carbazole

Mykola Bezuglyi, Gintare Grybauskaite, Gintautas Bagdziunas and Juozas Vidas Grazulevicius

S1. Synthesis and crystallization

9-Ethyl-9*H*-carbazole (0.904 g, 4.63 mmol) was added to the solution of *N*-bromosuccinimide (NBS) (3.708 g, 20.83 mmol) in 30 ml of DMF. The reaction mixture was heated at 60°C for 24 hours. When the reaction completed (monitored *via* TLC) the solution was poured into a large amount of water with ice. The precipitate was filtered off and crystallized from the mixture of isopropanol and DMF (volume ratio about 5:1) to isolate the product as needles. The bulk sample appears yellowish, but individual crystals are colourless. Yield 1.80 g (76 %), m.p. 155–156°C. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.92 (d, J = 1.8 Hz, 2H), 7.69 (d, J = 1.8 Hz, 2H), 5.10 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H).

S2. Refinement

All hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.930 Å for aromatic C—H, with 0.969 Å for methylene C—H, 0.957 Å for methyl distances and U_{iso}(H) = 1.2 U_{eq}.

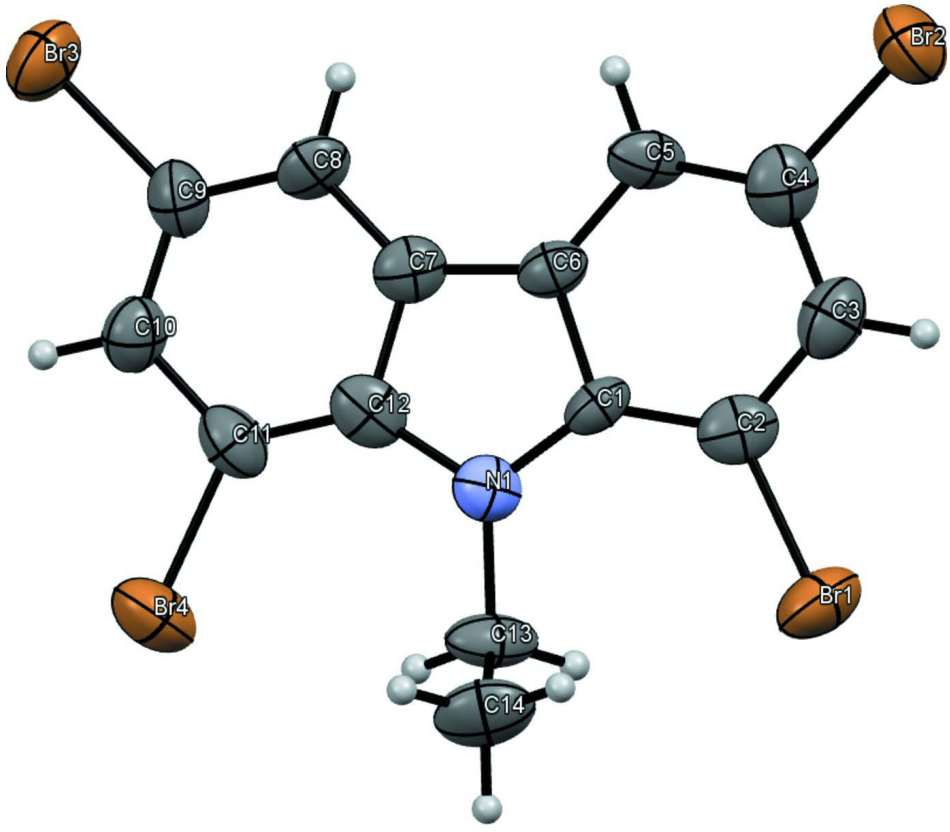

Figure 1

The molecular structure of the title molecule with displacement ellipsoids drawn at the 50% probability level.

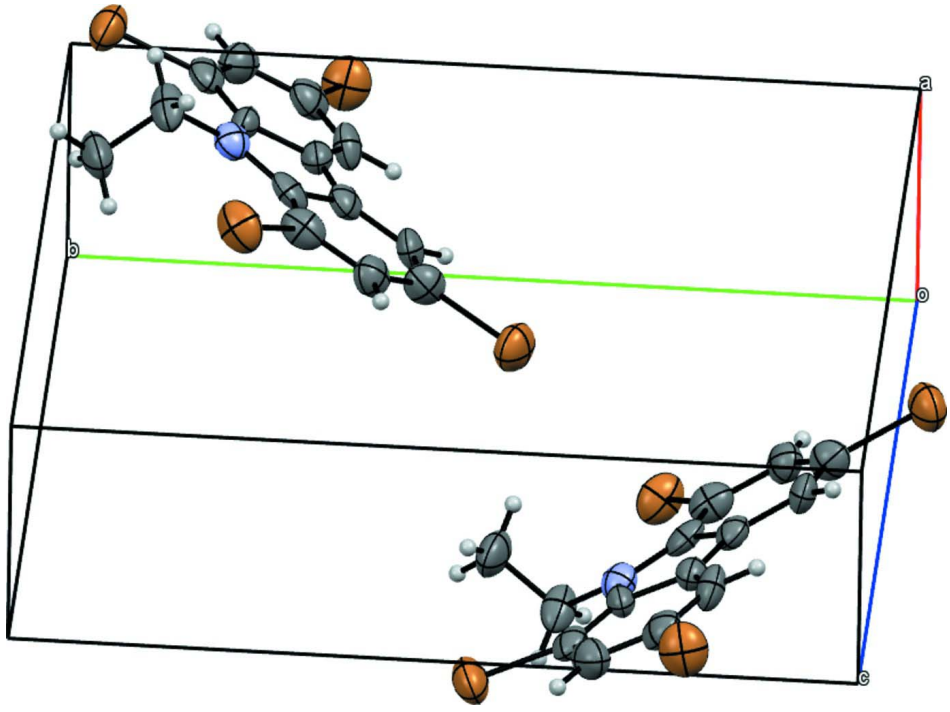

Figure 2

The crystal packing of the title compound.

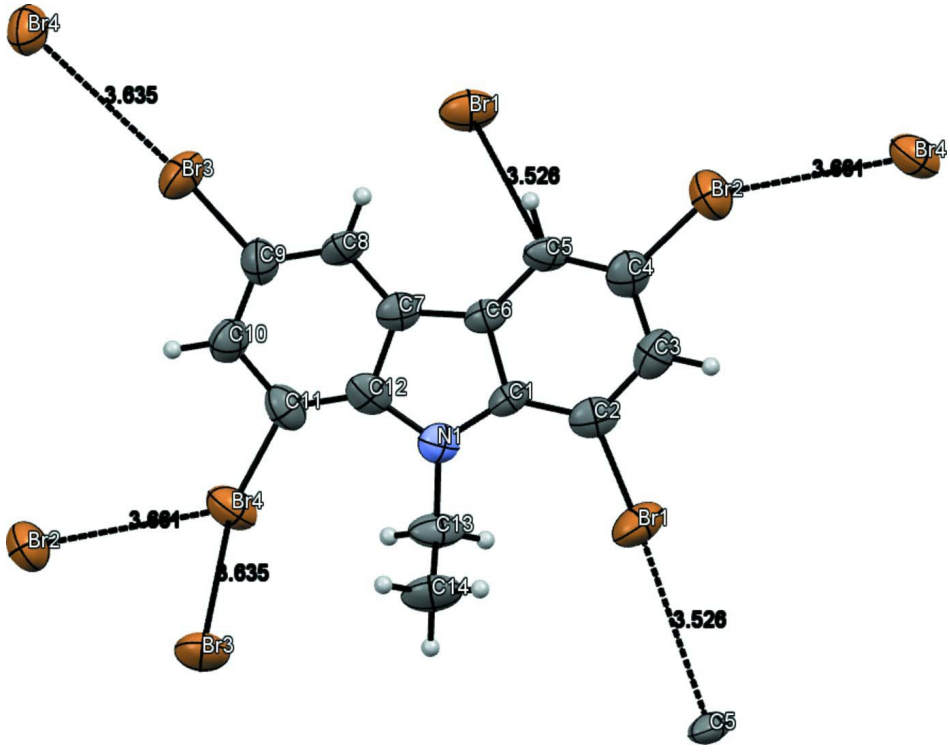

Figure 3

C—Br···Br and Br···π intermolecular contacts.

1,3,6,8-Tetrabromo-9-ethyl-9*H*-carbazole

Crystal data

$C_{14}H_9Br_4N$
M_r = 510.85
Monoclinic, $P2_1$
Hall symbol: P 2yb
a = 4.202 (2) Å
b = 14.654 (6) Å
c = 12.245 (6) Å
β = 92.758 (18)°
V = 753.1 (6) Å^3
Z = 2
$F(000)$ = 480.00
D_x = 2.253 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71075 Å
Cell parameters from 2306 reflections
θ = 3.2–27.5°
μ = 10.70 mm^{-1}
T = 293 K
Chip, colorless
0.40 × 0.13 × 0.12 mm

Data collection

Rigaku XtaLAB mini diffractometer
Detector resolution: 6.827 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*REQAB*; Rigaku, 1998)
T_{min} = 0.115, T_{max} = 0.277
2755 measured reflections
2599 independent reflections
2071 reflections with $F^2 > 2.0\sigma(F^2)$
R_{int} = 0.021
θ_{max} = 27.5°
h = −5→5
k = −18→18
l = −15→4

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.130
S = 1.01
2600 reflections
172 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.74 e Å^{-3}
$\Delta\rho_{min}$ = −0.66 e Å^{-3}
Absolute structure: Flack (1983), 868 Friedel Pairs
Absolute structure parameter: 0.05 (4)

Special details

Refinement. Refinement was performed using all reflections. The weighted *R*-factor (*wR*) and goodness of fit (*S*) are based on F^2. *R*-factor (gt) are based on *F*. The threshold expression of $F^2 > 2.0\ \sigma(F^2)$ is used only for calculating *R*-factor (gt).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	1.0896 (3)	0.54414 (9)	0.00371 (12)	0.0652 (4)
Br2	0.4335 (4)	0.80930 (10)	−0.24666 (11)	0.0710 (4)
Br3	0.3881 (3)	1.05176 (9)	0.38945 (12)	0.0657 (4)
Br4	1.0717 (3)	0.73324 (10)	0.49105 (11)	0.0654 (4)
N1	0.9560 (19)	0.7062 (6)	0.2062 (8)	0.041 (2)
C1	0.854 (3)	0.7148 (7)	0.0995 (9)	0.037 (3)
C2	0.893 (3)	0.6617 (8)	0.0045 (10)	0.046 (3)
C3	0.768 (3)	0.6924 (8)	−0.0998 (10)	0.051 (3)

C4	0.598 (3)	0.7757 (8)	−0.1069 (10)	0.048 (3)
C5	0.556 (3)	0.8265 (7)	−0.0176 (9)	0.042 (3)
C6	0.682 (3)	0.7978 (7)	0.0871 (9)	0.039 (3)
C7	0.671 (3)	0.8383 (7)	0.1907 (9)	0.039 (3)
C8	0.533 (3)	0.9191 (7)	0.2281 (10)	0.044 (3)
C9	0.566 (3)	0.9430 (8)	0.3353 (9)	0.047 (3)
C10	0.729 (3)	0.8854 (8)	0.4117 (10)	0.048 (3)
C11	0.869 (3)	0.8032 (8)	0.3764 (9)	0.046 (3)
C12	0.845 (3)	0.7785 (8)	0.2676 (9)	0.041 (3)
C13	1.178 (3)	0.6333 (8)	0.2518 (11)	0.051 (3)
C14	1.008 (3)	0.5530 (9)	0.2926 (12)	0.067 (4)
H3	0.7995	0.6581	−0.1623	0.0616*
H5	0.4442	0.8811	−0.0240	0.0498*
H8	0.4181	0.9565	0.1791	0.0524*
H10	0.7444	0.9015	0.4852	0.0581*
H13A	1.3166	0.6139	0.1951	0.0616*
H13B	1.3104	0.6590	0.3111	0.0616*
H14A	0.8767	0.5270	0.2342	0.0802*
H14B	0.8768	0.5712	0.3508	0.0802*
H14C	1.1601	0.5084	0.3193	0.0802*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0604 (7)	0.0431 (7)	0.0918 (11)	0.0099 (7)	0.0024 (7)	−0.0126 (7)
Br2	0.0871 (9)	0.0752 (10)	0.0491 (7)	0.0044 (9)	−0.0140 (7)	−0.0013 (7)
Br3	0.0759 (8)	0.0475 (7)	0.0738 (9)	0.0015 (8)	0.0042 (7)	−0.0187 (7)
Br4	0.0710 (9)	0.0678 (9)	0.0557 (8)	−0.0063 (8)	−0.0143 (7)	0.0171 (6)
N1	0.039 (5)	0.037 (5)	0.047 (5)	−0.009 (4)	−0.002 (4)	0.000 (4)
C1	0.034 (5)	0.026 (5)	0.051 (6)	0.003 (5)	0.004 (5)	−0.004 (5)
C2	0.031 (5)	0.040 (6)	0.066 (8)	−0.010 (5)	−0.001 (5)	0.003 (5)
C3	0.052 (6)	0.048 (7)	0.055 (7)	−0.009 (6)	0.007 (5)	−0.017 (6)
C4	0.050 (6)	0.040 (6)	0.054 (7)	−0.013 (6)	0.004 (6)	−0.006 (5)
C5	0.049 (6)	0.020 (5)	0.054 (7)	−0.003 (5)	−0.011 (5)	0.002 (4)
C6	0.037 (5)	0.033 (6)	0.046 (6)	−0.001 (5)	0.005 (4)	−0.002 (5)
C7	0.038 (5)	0.030 (5)	0.048 (6)	−0.017 (5)	0.002 (5)	0.002 (4)
C8	0.049 (6)	0.032 (6)	0.051 (7)	−0.007 (5)	0.001 (5)	0.002 (5)
C9	0.057 (7)	0.048 (6)	0.037 (6)	−0.015 (6)	0.002 (5)	−0.004 (5)
C10	0.054 (6)	0.042 (6)	0.049 (7)	−0.008 (6)	0.002 (6)	−0.007 (5)
C11	0.047 (6)	0.047 (7)	0.043 (6)	−0.012 (6)	−0.009 (5)	0.007 (5)
C12	0.036 (5)	0.041 (6)	0.047 (6)	−0.020 (5)	−0.002 (5)	0.004 (5)
C13	0.039 (6)	0.037 (6)	0.076 (9)	0.002 (5)	−0.019 (6)	0.007 (6)
C14	0.066 (7)	0.030 (6)	0.106 (11)	−0.004 (7)	0.013 (7)	0.018 (7)

Geometric parameters (Å, º)

Br1—C2	1.912 (11)	C7—C12	1.458 (15)
Br2—C4	1.880 (12)	C8—C9	1.359 (16)

Br3—C9	1.894 (12)	C9—C10	1.412 (16)
Br4—C11	1.906 (11)	C10—C11	1.418 (16)
N1—C1	1.361 (14)	C11—C12	1.379 (15)
N1—C12	1.393 (14)	C13—C14	1.476 (17)
N1—C13	1.507 (14)	C3—H3	0.930
C1—C2	1.415 (16)	C5—H5	0.930
C1—C6	1.418 (14)	C8—H8	0.930
C2—C3	1.429 (17)	C10—H10	0.930
C3—C4	1.417 (16)	C13—H13A	0.970
C4—C5	1.340 (16)	C13—H13B	0.970
C5—C6	1.426 (15)	C14—H14A	0.960
C6—C7	1.404 (15)	C14—H14B	0.960
C7—C8	1.403 (15)	C14—H14C	0.960
Br2···Br4^{i}	3.660 (3)	Br3···Br4^{ii}	3.636 (3)
C1—N1—C12	110.4 (8)	Br4—C11—C12	125.5 (9)
C1—N1—C13	125.6 (9)	C10—C11—C12	120.3 (10)
C12—N1—C13	123.8 (9)	N1—C12—C7	106.2 (9)
N1—C1—C2	134.0 (9)	N1—C12—C11	135.2 (10)
N1—C1—C6	108.5 (9)	C7—C12—C11	118.5 (10)
C2—C1—C6	117.5 (10)	N1—C13—C14	113.0 (9)
Br1—C2—C1	124.5 (8)	C2—C3—H3	120.413
Br1—C2—C3	114.7 (9)	C4—C3—H3	120.407
C1—C2—C3	120.7 (10)	C4—C5—H5	119.576
C2—C3—C4	119.2 (11)	C6—C5—H5	119.568
Br2—C4—C3	116.3 (9)	C7—C8—H8	119.725
Br2—C4—C5	122.8 (9)	C9—C8—H8	119.729
C3—C4—C5	120.9 (11)	C9—C10—H10	119.964
C4—C5—C6	120.9 (10)	C11—C10—H10	119.962
C1—C6—C5	120.9 (10)	N1—C13—H13A	108.986
C1—C6—C7	107.8 (9)	N1—C13—H13B	108.988
C5—C6—C7	131.3 (9)	C14—C13—H13A	108.984
C6—C7—C8	133.2 (10)	C14—C13—H13B	108.981
C6—C7—C12	106.9 (9)	H13A—C13—H13B	107.779
C8—C7—C12	119.9 (10)	C13—C14—H14A	109.473
C7—C8—C9	120.5 (10)	C13—C14—H14B	109.466
Br3—C9—C8	122.1 (9)	C13—C14—H14C	109.472
Br3—C9—C10	117.2 (9)	H14A—C14—H14B	109.470
C8—C9—C10	120.6 (11)	H14A—C14—H14C	109.470
C9—C10—C11	120.1 (11)	H14B—C14—H14C	109.476
Br4—C11—C10	114.2 (8)		
C1—N1—C12—C7	−2.6 (10)	C3—C4—C5—C6	−0.3 (16)
C1—N1—C12—C11	178.7 (10)	C4—C5—C6—C1	−0.2 (15)
C12—N1—C1—C2	−179.2 (9)	C4—C5—C6—C7	−179.9 (9)
C12—N1—C1—C6	3.2 (10)	C1—C6—C7—C8	−179.3 (9)
C1—N1—C13—C14	−92.7 (12)	C1—C6—C7—C12	0.9 (10)

C13—N1—C1—C2	4.9 (16)	C5—C6—C7—C8	0.4 (18)
C13—N1—C1—C6	−172.6 (8)	C5—C6—C7—C12	−179.4 (9)
C12—N1—C13—C14	91.9 (11)	C6—C7—C8—C9	−178.4 (10)
C13—N1—C12—C7	173.4 (8)	C6—C7—C12—N1	1.0 (10)
C13—N1—C12—C11	−5.3 (17)	C6—C7—C12—C11	179.9 (8)
N1—C1—C2—Br1	6.9 (16)	C8—C7—C12—N1	−178.9 (8)
N1—C1—C2—C3	−176.1 (9)	C8—C7—C12—C11	0.1 (14)
N1—C1—C6—C5	177.7 (8)	C12—C7—C8—C9	1.4 (15)
N1—C1—C6—C7	−2.5 (10)	C7—C8—C9—Br3	179.4 (8)
C2—C1—C6—C5	−0.3 (13)	C7—C8—C9—C10	−2.4 (16)
C2—C1—C6—C7	179.4 (8)	Br3—C9—C10—C11	−179.7 (7)
C6—C1—C2—Br1	−175.7 (7)	C8—C9—C10—C11	2.0 (16)
C6—C1—C2—C3	1.3 (13)	C9—C10—C11—Br4	−178.9 (9)
Br1—C2—C3—C4	175.5 (7)	C9—C10—C11—C12	−0.5 (16)
C1—C2—C3—C4	−1.7 (15)	Br4—C11—C12—N1	−3.7 (17)
C2—C3—C4—Br2	−178.4 (8)	Br4—C11—C12—C7	177.7 (6)
C2—C3—C4—C5	1.2 (16)	C10—C11—C12—N1	178.1 (10)
Br2—C4—C5—C6	179.4 (6)	C10—C11—C12—C7	−0.5 (15)

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