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(2*S*,4*S*)-2-[(*S*,*E*)-2-Bromo-1-nitromethyl-3-phenylallyl]-4-methylcyclohexanone

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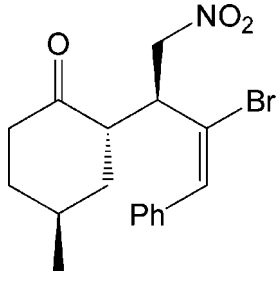
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.006 Å; R factor = 0.040; wR factor = 0.106; data-to-parameter ratio = 19.1.

The crystal structure of the title compoud, $C_{17}H_{20}BrNO_3$, contains three chiral centers, which all exhibit an *S* configuration. The C=C double bond has an *E* conformation. The cyclohexane ring is in a chair conformation. In the crystal, molecules are linked by weak N—O···Br interactions [O···Br = 3.136 (4) Å].

Related literature

For related compounds, see: Li *et al.* (2009); Wu *et al.* (2011). For the asymmetric Michael reaction, which allows for the formation of three contiguous asymmetric centers, see: Agarwal & Peddinti (2011); Lu *et al.* (2010); Luo *et al.* (2007).



Experimental

Crystal data

$C_{17}H_{20}BrNO_3$
M_r = 366.25
Orthorhombic, $P2_12_12_1$
a = 7.0942 (5) Å
b = 13.7920 (11) Å
c = 17.3108 (13) Å
V = 1693.7 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.44 mm^{-1}
T = 296 K
0.40 × 0.38 × 0.30 mm

Data collection

Rigaku R-AXIS RAPID/ZJUG diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.377, T_{max} = 0.481
13310 measured reflections
3829 independent reflections
1967 reflections with $I > 2\sigma(I)$
R_{int} = 0.092

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.106
S = 0.91
3829 reflections
200 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}
Absolute structure: Flack (1983), 1625 Friedel pairs
Flack parameter: −0.019 (14)

Data collection: *PROCESS-AUTO* (Rigaku, 2006); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BH2424).

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supplementary materials

Acta Cryst. (2012). E**68**, o1253 [doi:10.1107/S1600536812013098]

(2*S*,4*S*)-2-[(*S*,*E*)-2-Bromo-1-nitromethyl-3-phenylallyl]-4-methylcyclohexanone

Long Zhao, Chao Wu, Wen-Zeng Weng, Chu-Xia Yan and Ai-Bao Xia

Comment

Asymmetric Michael additions of aldehydes or ketones to nitroalkenes represent fundamental transformations which have wide applications in organic synthesis (Luo *et al.*, 2007; Lu *et al.*, 2010; Agarwal & Peddinti, 2011). On the other hand, alkenyl halides are present in a variety of natural products as well as in bioactive compounds. The title compound (Fig. 1) was obtained from the Michael addition of 4-methyl-cyclohexanone to (2-bromo-4-nitro-buta-1,3-dienyl)-benzene in our laboratory. The geometry compares well with other related structures (Li *et al.*, 2009; Wu *et al.*, 2011). In the title compound, the cyclohexyl ring adopts a chair conformation. The plane of the phenyl ring and the least-squares plane of the cyclohexyl moiety enclose an angle of 69.80 (3)°, while the plane through the nitro group and the adjacent C17 atom encloses an angle of 87.12 (3)° with the phenyl ring. The Br1—C9—C10—C11 torsion angle of 175.8 (4)° confirms the *E* configuration of the molecule with respect to the C9=C10 double bond. The molecules are linked by weak intermolecular N—O···Br interactions, the O···Br distance being 3.136 (4) Å.

Experimental

A saturated brine (0.5 mL) solution of (2-bromo-4-nitrobuta-1,3-dienyl) benzene (1 mmol) and 4-methyl-cyclohexanone (1.2 mmol) was stirred with (*S*)-2-(pyrrolidin-2-ylmethylthio)pyridine (0.3 mmol) as catalyst and benzoic acid (0.3 mmol) as cocatalyst, at room temperature. After completion of the reaction, the mixture was extracted with ethyl acetate. Solvents were removed under vacuum and the residue was purified by column chromatography on silica gel (eluent: petroleum ether-ether). Suitable crystals were obtained by slow evaporation of an ethyl acetate solution.

Refinement

H atoms were placed in calculated positions with C—H ranging from 0.93 to 0.98 Å and refined using riding model with U_{iso}(H)=1.2U_{eq} or 1.5U_{eq} of the carrier atoms.

Computing details

Data collection: *PROCESS-AUTO* (Rigaku, 2006); cell refinement: *PROCESS-AUTO* (Rigaku, 2006); data reduction: *CrystalStructure* (Rigaku, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

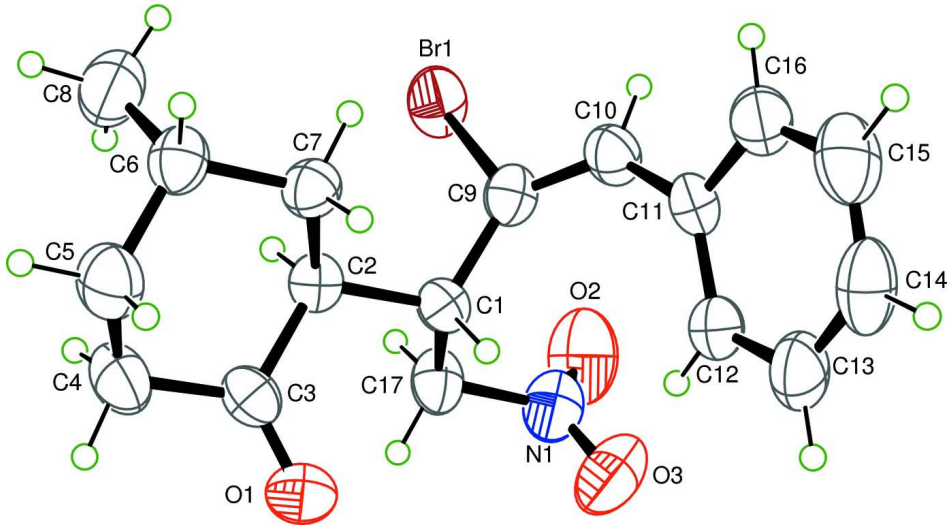

Figure 1

The asymmetric unit of the structure of the title compound, with displacement ellipsoids for non-H atoms at the 40% probability level.

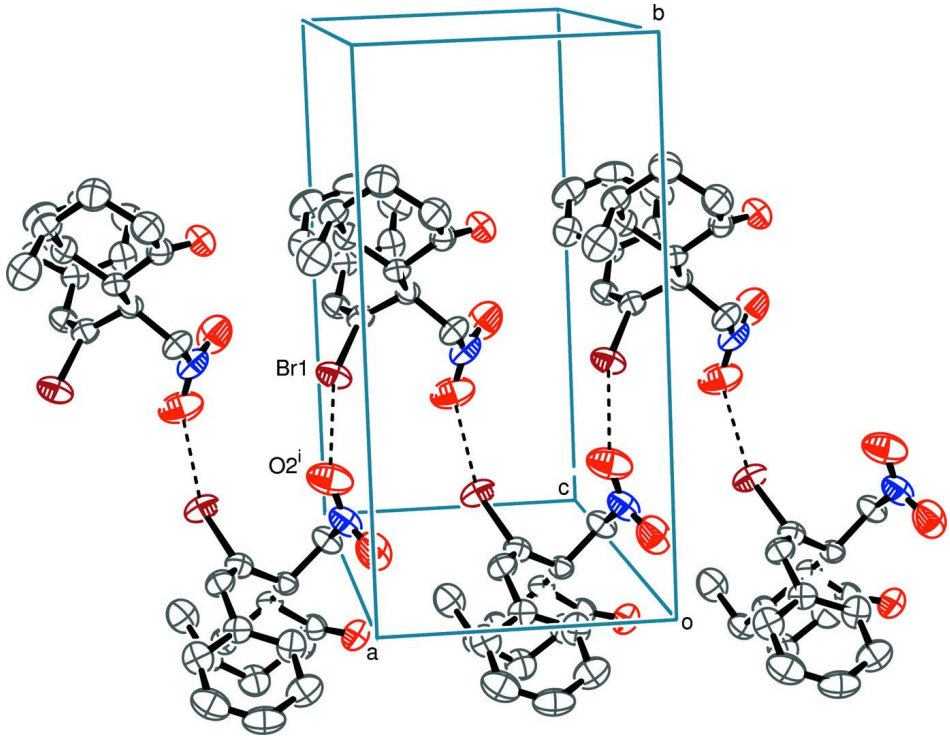

Figure 2

Unit cell packing of the title compound.

(2*S*,4*S*)-2-[(*S*,*E*)-2-Bromo-1-nitromethyl- 3-phenylallyl]-4-methylcyclohexanone

Crystal data

$C_{17}H_{20}BrNO_3$
M_r = 366.25
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
a = 7.0942 (5) Å
b = 13.7920 (11) Å
c = 17.3108 (13) Å
V = 1693.7 (2) Å^3
Z = 4
$F(000)$ = 752
D_x = 1.436 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8068 reflections
θ = 3.1–27.4°
μ = 2.44 mm^{-1}
T = 296 K
Chunk, colourless
0.40 × 0.38 × 0.30 mm

Data collection

Rigaku R-AXIS RAPID/ZJUG diffractometer
Radiation source: rotating anode
Graphite monochromator
Detector resolution: 10.00 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.377, T_{max} = 0.481
13310 measured reflections
3829 independent reflections
1967 reflections with $I > 2\sigma(I)$
R_{int} = 0.092
θ_{max} = 27.4°, θ_{min} = 3.1°
h = −9→7
k = −17→17
l = −22→21

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.106
S = 0.91
3829 reflections
200 parameters
0 restraints
0 constraints
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
$w = 1/[\sigma^2(F_o^2) + (0.030P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}
Absolute structure: Flack (1983), 1625 Friedel pairs
Flack parameter: −0.019 (14)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	1.02011 (8)	0.36551 (3)	0.51179 (3)	0.0761 (2)
O1	0.4791 (5)	0.6330 (2)	0.46539 (18)	0.0755 (8)
O2	0.5698 (8)	0.3042 (3)	0.6070 (2)	0.1185 (17)
O3	0.4316 (6)	0.4334 (4)	0.6423 (2)	0.1077 (15)
N1	0.5198 (7)	0.3865 (3)	0.5965 (2)	0.0757 (12)
C2	0.7862 (6)	0.5611 (3)	0.4626 (2)	0.0501 (11)
H2	0.8173	0.5116	0.4240	0.060*
C1	0.7353 (6)	0.5087 (3)	0.5385 (2)	0.0483 (11)
H1	0.6865	0.5576	0.5744	0.058*
C3	0.6255 (7)	0.6214 (3)	0.4309 (2)	0.0579 (12)
C4	0.6690 (7)	0.6733 (4)	0.3565 (3)	0.0762 (15)
H4A	0.5633	0.7141	0.3422	0.091*

H4B	0.6880	0.6261	0.3156	0.091*
C5	0.8469 (8)	0.7357 (4)	0.3653 (3)	0.0817 (17)
H5A	0.8806	0.7624	0.3154	0.098*
H5B	0.8197	0.7894	0.3997	0.098*
C6	1.0146 (7)	0.6786 (3)	0.3972 (2)	0.0627 (11)
H6	1.1128	0.7259	0.4101	0.075*
C7	0.9604 (6)	0.6279 (3)	0.4720 (2)	0.0565 (10)
H7A	0.9335	0.6764	0.5111	0.068*
H7B	1.0663	0.5896	0.4899	0.068*
C8	1.0995 (8)	0.6087 (4)	0.3388 (3)	0.0883 (18)
H8A	1.2033	0.5748	0.3620	0.132*
H8B	1.1435	0.6443	0.2947	0.132*
H8C	1.0055	0.5629	0.3228	0.132*
C9	0.9023 (7)	0.4616 (3)	0.5761 (2)	0.0563 (12)
C10	0.9783 (7)	0.4757 (3)	0.6453 (2)	0.0599 (11)
H10	1.0773	0.4343	0.6576	0.072*
C11	0.9294 (7)	0.5474 (3)	0.7059 (2)	0.0537 (12)
C12	0.7487 (7)	0.5782 (4)	0.7244 (2)	0.0666 (14)
H12	0.6465	0.5530	0.6974	0.080*
C13	0.7176 (8)	0.6451 (4)	0.7817 (3)	0.0798 (16)
H13	0.5954	0.6654	0.7925	0.096*
C14	0.8649 (10)	0.6819 (4)	0.8232 (3)	0.0842 (18)
H14	0.8432	0.7277	0.8616	0.101*
C15	1.0436 (9)	0.6515 (4)	0.8081 (3)	0.0895 (18)
H15	1.1443	0.6762	0.8363	0.107*
C16	1.0753 (7)	0.5830 (4)	0.7500 (2)	0.0720 (14)
H16	1.1973	0.5611	0.7410	0.086*
C17	0.5758 (6)	0.4353 (3)	0.5233 (2)	0.0625 (12)
H17A	0.4679	0.4686	0.5014	0.075*
H17B	0.6182	0.3871	0.4863	0.075*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.1030 (4)	0.0633 (3)	0.0619 (3)	0.0246 (3)	−0.0012 (3)	−0.0079 (2)
O1	0.067 (2)	0.076 (2)	0.083 (2)	0.016 (2)	0.0017 (18)	−0.0001 (17)
O2	0.175 (5)	0.079 (3)	0.101 (3)	−0.029 (3)	0.004 (3)	0.017 (2)
O3	0.105 (3)	0.132 (4)	0.086 (2)	−0.027 (3)	0.031 (2)	−0.021 (3)
N1	0.083 (3)	0.078 (3)	0.066 (2)	−0.029 (3)	0.000 (3)	−0.005 (2)
C2	0.060 (3)	0.041 (3)	0.049 (2)	−0.001 (2)	−0.001 (2)	−0.0039 (19)
C1	0.052 (3)	0.044 (3)	0.049 (2)	−0.002 (2)	−0.006 (2)	−0.0027 (19)
C3	0.057 (3)	0.058 (3)	0.059 (3)	−0.003 (3)	−0.014 (2)	−0.002 (2)
C4	0.084 (4)	0.078 (4)	0.067 (3)	0.004 (3)	−0.016 (3)	0.017 (3)
C5	0.089 (4)	0.077 (4)	0.079 (3)	−0.003 (3)	−0.001 (3)	0.022 (3)
C6	0.070 (3)	0.059 (3)	0.059 (2)	−0.010 (3)	0.002 (3)	0.003 (2)
C7	0.054 (3)	0.060 (3)	0.056 (2)	−0.004 (2)	0.002 (2)	−0.002 (2)
C8	0.092 (4)	0.105 (5)	0.068 (3)	−0.014 (3)	0.010 (3)	0.001 (3)
C9	0.066 (3)	0.052 (3)	0.051 (2)	−0.007 (2)	0.002 (2)	−0.001 (2)
C10	0.067 (3)	0.056 (3)	0.056 (2)	0.012 (3)	−0.005 (3)	0.0023 (19)
C11	0.065 (3)	0.054 (3)	0.042 (2)	0.001 (2)	−0.010 (2)	0.0020 (19)

C12	0.066 (4)	0.088 (4)	0.047 (3)	0.002 (3)	−0.003 (2)	−0.008 (2)
C13	0.103 (4)	0.084 (4)	0.052 (3)	0.017 (4)	−0.001 (3)	−0.011 (3)
C14	0.140 (6)	0.061 (4)	0.052 (3)	0.000 (4)	−0.001 (4)	−0.008 (3)
C15	0.116 (6)	0.089 (4)	0.064 (3)	−0.026 (4)	−0.016 (3)	−0.014 (3)
C16	0.073 (4)	0.082 (4)	0.061 (3)	−0.004 (3)	−0.005 (3)	0.003 (3)
C17	0.073 (3)	0.063 (3)	0.051 (2)	−0.020 (2)	−0.005 (2)	0.002 (2)

Geometric parameters (Å, º)

Br1—C9	1.923 (4)	C7—H7A	0.9700
O1—C3	1.208 (5)	C7—H7B	0.9700
O2—N1	1.203 (5)	C8—H8A	0.9600
O3—N1	1.199 (5)	C8—H8B	0.9600
N1—C17	1.490 (5)	C8—H8C	0.9600
C2—C3	1.514 (6)	C9—C10	1.328 (5)
C2—C1	1.542 (5)	C10—C11	1.483 (6)
C2—C7	1.551 (5)	C10—H10	0.9300
C2—H2	0.9800	C11—C16	1.377 (6)
C1—C9	1.500 (6)	C11—C12	1.387 (6)
C1—C17	1.541 (6)	C12—C13	1.374 (7)
C1—H1	0.9800	C12—H12	0.9300
C3—C4	1.506 (6)	C13—C14	1.365 (8)
C4—C5	1.535 (7)	C13—H13	0.9300
C4—H4A	0.9700	C14—C15	1.361 (8)
C4—H4B	0.9700	C14—H14	0.9300
C5—C6	1.530 (6)	C15—C16	1.397 (7)
C5—H5A	0.9700	C15—H15	0.9300
C5—H5B	0.9700	C16—H16	0.9300
C6—C8	1.521 (6)	C17—H17A	0.9700
C6—C7	1.520 (5)	C17—H17B	0.9700
C6—H6	0.9800		
O3—N1—O2	124.3 (5)	C6—C7—H7B	109.1
O3—N1—C17	117.3 (5)	C2—C7—H7B	109.1
O2—N1—C17	118.4 (5)	H7A—C7—H7B	107.8
C3—C2—C1	112.9 (4)	C6—C8—H8A	109.5
C3—C2—C7	108.1 (3)	C6—C8—H8B	109.5
C1—C2—C7	112.0 (3)	H8A—C8—H8B	109.5
C3—C2—H2	107.8	C6—C8—H8C	109.5
C1—C2—H2	107.8	H8A—C8—H8C	109.5
C7—C2—H2	107.8	H8B—C8—H8C	109.5
C9—C1—C17	111.7 (4)	C10—C9—C1	130.5 (4)
C9—C1—C2	112.9 (3)	C10—C9—Br1	116.5 (4)
C17—C1—C2	109.5 (3)	C1—C9—Br1	113.0 (3)
C9—C1—H1	107.5	C9—C10—C11	129.8 (4)
C17—C1—H1	107.5	C9—C10—H10	115.1
C2—C1—H1	107.5	C11—C10—H10	115.1
O1—C3—C4	122.4 (4)	C16—C11—C12	117.2 (4)
O1—C3—C2	122.7 (4)	C16—C11—C10	117.0 (4)
C4—C3—C2	114.6 (4)	C12—C11—C10	125.7 (4)

C3—C4—C5	110.4 (4)	C13—C12—C11	121.3 (5)
C3—C4—H4A	109.6	C13—C12—H12	119.3
C5—C4—H4A	109.6	C11—C12—H12	119.3
C3—C4—H4B	109.6	C14—C13—C12	120.5 (5)
C5—C4—H4B	109.6	C14—C13—H13	119.8
H4A—C4—H4B	108.1	C12—C13—H13	119.8
C6—C5—C4	112.7 (4)	C15—C14—C13	119.8 (5)
C6—C5—H5A	109.0	C15—C14—H14	120.1
C4—C5—H5A	109.0	C13—C14—H14	120.1
C6—C5—H5B	109.0	C14—C15—C16	119.8 (5)
C4—C5—H5B	109.0	C14—C15—H15	120.1
H5A—C5—H5B	107.8	C16—C15—H15	120.1
C8—C6—C7	112.1 (4)	C11—C16—C15	121.3 (5)
C8—C6—C5	113.2 (4)	C11—C16—H16	119.4
C7—C6—C5	110.3 (4)	C15—C16—H16	119.4
C8—C6—H6	107.0	N1—C17—C1	110.3 (3)
C7—C6—H6	107.0	N1—C17—H17A	109.6
C5—C6—H6	107.0	C1—C17—H17A	109.6
C6—C7—C2	112.7 (3)	N1—C17—H17B	109.6
C6—C7—H7A	109.1	C1—C17—H17B	109.6
C2—C7—H7A	109.1	H17A—C17—H17B	108.1

C3—C2—C1—C9	−171.2 (3)	C17—C1—C9—Br1	63.8 (4)
C7—C2—C1—C9	−48.7 (5)	C2—C1—C9—Br1	−60.0 (4)
C3—C2—C1—C17	63.8 (5)	C1—C9—C10—C11	−4.4 (8)
C7—C2—C1—C17	−173.8 (3)	Br1—C9—C10—C11	175.8 (4)
C1—C2—C3—O1	5.7 (6)	C9—C10—C11—C16	−146.0 (5)
C7—C2—C3—O1	−118.9 (5)	C9—C10—C11—C12	37.3 (8)
C1—C2—C3—C4	−179.6 (4)	C16—C11—C12—C13	3.2 (7)
C7—C2—C3—C4	55.8 (5)	C10—C11—C12—C13	179.9 (5)
O1—C3—C4—C5	120.0 (5)	C11—C12—C13—C14	−1.1 (9)
C2—C3—C4—C5	−54.7 (6)	C12—C13—C14—C15	−0.7 (9)
C3—C4—C5—C6	52.3 (6)	C13—C14—C15—C16	0.3 (9)
C4—C5—C6—C8	73.0 (5)	C12—C11—C16—C15	−3.6 (7)
C4—C5—C6—C7	−53.5 (5)	C10—C11—C16—C15	179.4 (4)
C8—C6—C7—C2	−71.2 (5)	C14—C15—C16—C11	1.9 (8)
C5—C6—C7—C2	55.9 (5)	O3—N1—C17—C1	73.0 (5)
C3—C2—C7—C6	−56.0 (4)	O2—N1—C17—C1	−104.9 (5)
C1—C2—C7—C6	178.9 (4)	C9—C1—C17—N1	56.4 (5)
C17—C1—C9—C10	−115.9 (5)	C2—C1—C17—N1	−177.9 (4)
C2—C1—C9—C10	120.2 (5)		