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3,6-Dichloro-9-(prop-2-yn-1-yl)-9H-carbazole

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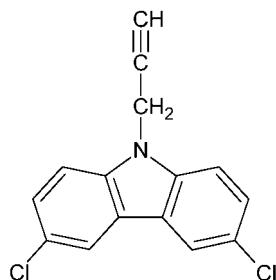
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.026; wR factor = 0.068; data-to-parameter ratio = 13.6.

The tricyclic aromatic ring system of the title compound, $\text{C}_{15}\text{H}_9\text{Cl}_2\text{N}$, is essentially planar (r.m.s. deviation = 0.002 Å). The two Cl atoms lie slightly out of the plane of the carbazole ring system, with the C—Cl bonds forming angles of 1.23 (8) and 1.14 (8)° with the plane. The acetylene group has a *syn* orientation with respect to the ring system. In the crystal, no weak hydrogen bonds nor any π – π stacking interactions are observed.

Related literature

For industrial applications of carbazole-containing compounds, see: Zhang *et al.* (1998). For pharmaceutical properties of carbazoles, see: Liu & Larock (2007); Hussain *et al.* (2011); Zhang *et al.* (2010); Conchon *et al.* (2006). For a related structure, see: Xie *et al.* (2012).



Experimental

Crystal data

 $\text{C}_{15}\text{H}_9\text{Cl}_2\text{N}$ $M_r = 274.13$ Orthorhombic, $P2_12_12_1$ $a = 3.9825$ (1) Å $b = 11.1705$ (4) Å $c = 27.4417$ (9) Å $V = 1220.79$ (7) Å³ $Z = 4$ Cu $K\alpha$ radiation $\mu = 4.59$ mm⁻¹ $T = 100$ K $0.18 \times 0.05 \times 0.02$ mm

Data collection

Bruker D8 VENTURE PHOTON

100 CMOS diffractometer

Absorption correction: multi-scan

(SADABS; Bruker, 2013)

 $T_{\min} = 0.74$, $T_{\max} = 0.91$

10712 measured reflections

2224 independent reflections

2160 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.088$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.026$ $wR(F^2) = 0.068$ $S = 1.05$

2224 reflections

163 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.22$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.18$ e Å⁻³

Absolute structure: Flack

parameter determined using 817 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons *et al.*, 2013)

Absolute structure parameter: -0.002 (12)

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT*; program(s) used to solve structure: *SHELXT* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5674).

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supplementary materials

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3,6-Dichloro-9-(prop-2-yn-1-yl)-9H-carbazole

Joel T. Mague, Mehmet Akkurt, Shaaban K. Mohamed, Asmaa H. Mohamed and Mustafa R. Albayati

1. Comment

In recent years, carbazoles have been used as photoconductors, semiconductors and for their light-emitting properties, making them interesting organic tools for physics experiments (Zhang *et al.*, 1998). Moreover, several alkaloids based on a carbazole structure are known to possess interesting biological activities such as antitumor, antibacterial, anti-inflammatory, psychotropic and anti-histamine properties (Liu & Larock, 2007). Many synthetic carbazole derivatives are of significant pharmacological relevance because of their antifungal, antibiotic, and antitumor activities (Hussain *et al.*, 2011; Zhang *et al.*, 2010; Conchon *et al.*, 2006). The introduction of functional groups onto the carbazole scaffold is essential to generate compounds suitable for biological and physical investigations. Based on such facts we herein report the crystal structure of the title compound.

In the title compound (Fig. 1), the carbazole ring system is essentially planar (r.m.s. deviation = 0.002 Å). The Cl1 and Cl2 atoms lie slightly out of the plane of the carbazole ring system which makes angles of 1.23 (8) and 1.14 (8)° with the Cl1—C4 and Cl2—C9 bonds, respectively. The values of the geometric parameters of the title compound are within normal ranges (Xie *et al.*, 2012).

In the crystal, no classical hydrogen bonds are observed. The crystal packing is stabilized by weak van der Waals interactions. The packing of the title compound viewed along the *a* axis are shown in Fig. 2.

2. Experimental

Propargyl bromide (1.1 g, 9 mmol) was added to a suspension solution of 3,6-dichloro-9H-carbazole (0.7 g, 3 mmol) and K₂CO₃ (0.82 g, 6 mmol) in DMF (15 ml) and stirred at room temperature for 6 h. The excess solvent was evaporated to dryness *in vacuo*. The residue was diluted with water and then extracted with CH₂Cl₂ (3 x 30 ml). The combined organic extracts were dried over anhydrous Na₂SO₄, filtered and evaporated under reduced pressure to give the corresponding product as colourless crystals (0.61 g, 75%) yield, mp 469–471 K.

3. Refinement

All H atoms were placed geometrically and refined using a riding model with C—H = 0.95 - 0.99 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{C})$.

Computing details

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELXT* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

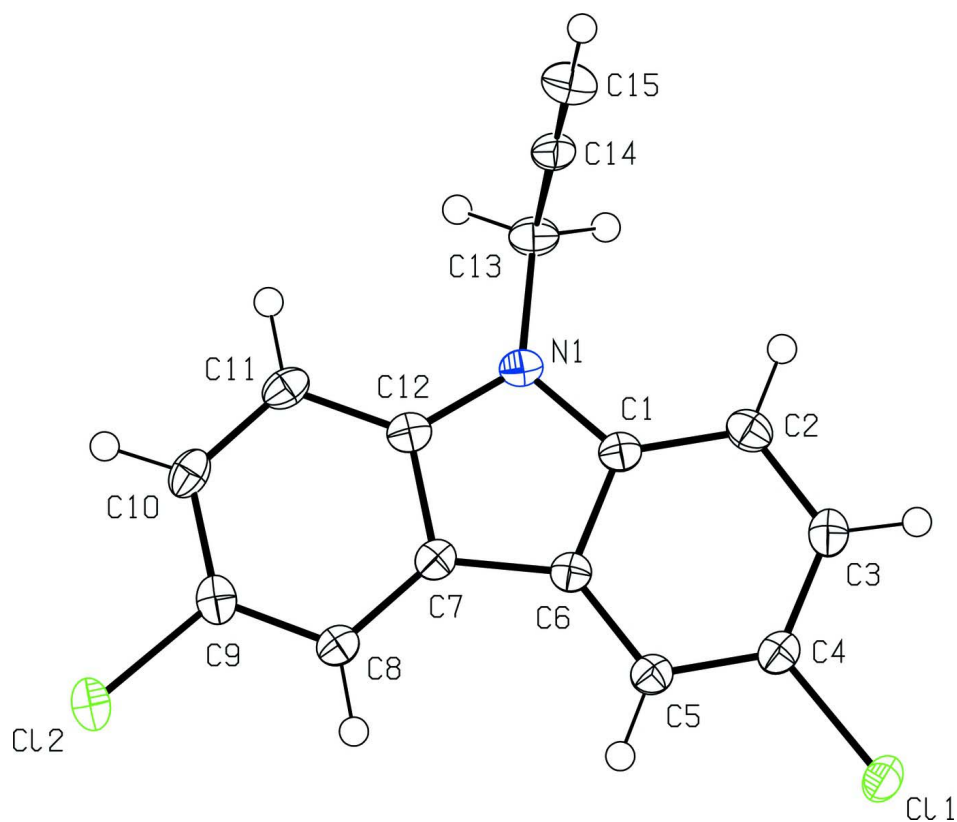


Figure 1

Perspective view of the title compound with 50% probability ellipsoids.

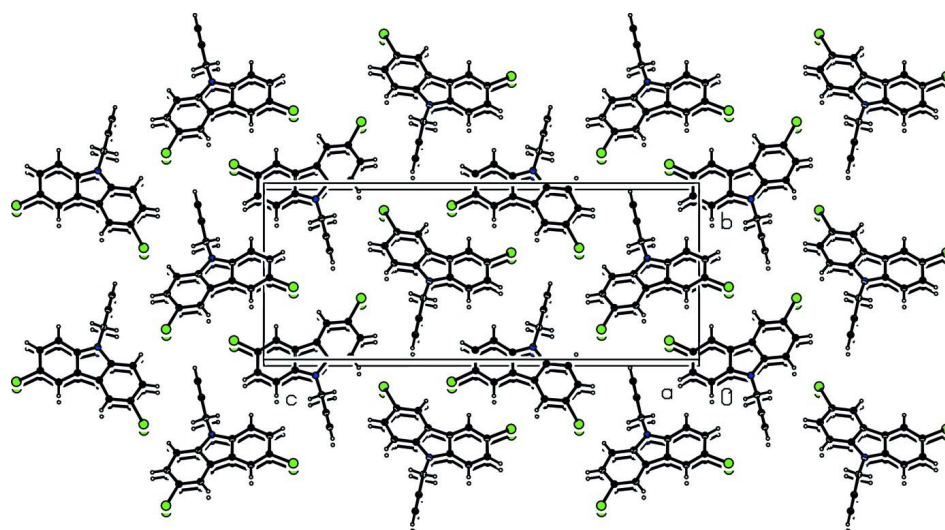


Figure 2

Packing of the title compound viewed along the *a* axis.

3,6-Dichloro-9-(prop-2-yn-1-yl)-9H-carbazole

Crystal data

C₁₅H₉Cl₂N
 $M_r = 274.13$
 Orthorhombic, $P2_12_12_1$
 Hall symbol: P 2ac 2ab
 $a = 3.9825 (1) \text{ \AA}$
 $b = 11.1705 (4) \text{ \AA}$
 $c = 27.4417 (9) \text{ \AA}$
 $V = 1220.79 (7) \text{ \AA}^3$
 $Z = 4$

$F(000) = 560$
 $D_x = 1.492 \text{ Mg m}^{-3}$
 Cu $K\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$
 Cell parameters from 9151 reflections
 $\theta = 4.3\text{--}68.0^\circ$
 $\mu = 4.59 \text{ mm}^{-1}$
 $T = 100 \text{ K}$
 Column, colourless
 $0.18 \times 0.05 \times 0.02 \text{ mm}$

Data collection

Bruker D8 VENTURE PHOTON 100 CMOS
 diffractometer
 Radiation source: INCOATEC I μ S micro-focus
 source
 Mirror monochromator
 Detector resolution: $10.4167 \text{ pixels mm}^{-1}$
 ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2013)

$T_{\min} = 0.74$, $T_{\max} = 0.91$
 10712 measured reflections
 2224 independent reflections
 2160 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.088$
 $\theta_{\max} = 68.1^\circ$, $\theta_{\min} = 3.2^\circ$
 $h = -4 \rightarrow 4$
 $k = -13 \rightarrow 13$
 $l = -32 \rightarrow 33$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.068$
 $S = 1.05$
 2224 reflections
 163 parameters
 0 restraints
 Hydrogen site location: inferred from
 neighbouring sites

H-atom parameters constrained
 $W = 1/[\Sigma^2(FO^2) + (0.0351P)^2 + 0.195P]$
 where $P = (FO^2 + 2FC^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.22 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.18 \text{ e \AA}^{-3}$
 Absolute structure: Flack parameter determined
 using 817 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons
et al., 2013)
 Absolute structure parameter: $-0.002 (12)$

Special details

Experimental. ¹H-NMR (300 MHz, CDCl₃): d 3.31 (s, 1H, C—CH), 5.34 (d, 2H, J=2.4 Hz, CH₂—C), 7.54 (m, 2H, Ar—H), 7.74 (m, 2H, Ar—H), 8.34 (s, 2H, Ar—H). ¹³C-NMR (75 MHz, CDCl₃): d 32.2 (CH₂), 74.8 (C—CH), 78.5 (C—CH), 111.4, 120.5, (4CH-Ar), 122.9, 124.2 (4 C-Ar), 126.4 (2CH-Ar), 138.6 (2 C-Ar). MS: (EI) m/z (%): 275 ($M+2$, 70), 274 ($M+1$, 74), 273 (M^+ , 100), 247 (10), 233 (44), 201 (4), 174 (2), 164 (14), 150 (2), 122 (2), 98 (2), 75 (4). Anal. for C₁₅H₉Cl₂N: calcd. C, 65.72; H, 3.31; Cl, 25.86; N, 5.11. Found: C, 65.38; H, 3.11; N, 4.95%.

Geometry. Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted R -factors wR and all goodnesses 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 observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating $-R$ -factor-obs *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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.52328 (16)	0.39290 (5)	−0.06840 (2)	0.0240 (2)
Cl2	0.52780 (15)	0.15240 (5)	0.22392 (2)	0.0252 (2)
N1	0.0291 (5)	0.57255 (17)	0.11884 (6)	0.0190 (5)
C1	0.1356 (6)	0.5462 (2)	0.07181 (8)	0.0180 (6)
C2	0.0865 (6)	0.6107 (2)	0.02874 (8)	0.0218 (7)
C3	0.2076 (6)	0.5615 (2)	−0.01405 (8)	0.0214 (7)
C4	0.3762 (6)	0.4513 (2)	−0.01335 (8)	0.0197 (6)
C5	0.4309 (6)	0.3879 (2)	0.02890 (8)	0.0190 (6)
C6	0.3072 (6)	0.4360 (2)	0.07226 (8)	0.0175 (6)
C7	0.3067 (6)	0.3947 (2)	0.12215 (8)	0.0177 (6)
C8	0.4327 (6)	0.2920 (2)	0.14472 (8)	0.0188 (6)
C9	0.3751 (6)	0.2800 (2)	0.19418 (8)	0.0208 (7)
C10	0.2040 (6)	0.3660 (2)	0.22166 (8)	0.0217 (7)
C11	0.0803 (6)	0.4677 (2)	0.19960 (8)	0.0213 (7)
C12	0.1317 (6)	0.4812 (2)	0.14950 (8)	0.0183 (6)
C13	−0.1714 (6)	0.6755 (2)	0.13263 (9)	0.0219 (7)
C14	0.0264 (6)	0.7838 (2)	0.14305 (8)	0.0216 (6)
C15	0.1835 (7)	0.8710 (2)	0.15139 (10)	0.0284 (7)
H2	−0.02610	0.68560	0.02880	0.0260*
H3	0.17640	0.60250	−0.04400	0.0260*
H5	0.54890	0.31400	0.02860	0.0230*
H8	0.55280	0.23300	0.12690	0.0230*
H10	0.17270	0.35420	0.25560	0.0260*
H11	−0.03610	0.52690	0.21790	0.0260*
H13A	−0.30450	0.65470	0.16190	0.0260*
H13B	−0.33110	0.69340	0.10600	0.0260*
H15	0.31000	0.94120	0.15810	0.0340*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0287 (3)	0.0266 (3)	0.0167 (2)	−0.0027 (3)	0.0020 (2)	−0.0015 (2)
Cl2	0.0256 (3)	0.0274 (3)	0.0226 (3)	−0.0015 (3)	−0.0015 (2)	0.0073 (2)
N1	0.0184 (9)	0.0176 (9)	0.0209 (9)	−0.0002 (9)	0.0008 (8)	−0.0031 (7)
C1	0.0165 (11)	0.0170 (11)	0.0206 (11)	−0.0036 (9)	−0.0012 (9)	−0.0023 (9)
C2	0.0201 (11)	0.0185 (11)	0.0269 (12)	−0.0009 (10)	−0.0024 (9)	0.0002 (9)
C3	0.0221 (11)	0.0228 (12)	0.0192 (11)	−0.0057 (10)	−0.0024 (9)	0.0016 (10)
C4	0.0191 (11)	0.0212 (11)	0.0189 (11)	−0.0052 (9)	0.0009 (9)	−0.0023 (9)
C5	0.0186 (11)	0.0180 (11)	0.0204 (10)	−0.0036 (10)	0.0004 (9)	−0.0017 (9)
C6	0.0157 (10)	0.0174 (11)	0.0195 (11)	−0.0028 (9)	−0.0017 (9)	−0.0014 (9)
C7	0.0155 (10)	0.0188 (11)	0.0188 (11)	−0.0045 (9)	0.0006 (8)	−0.0018 (9)
C8	0.0168 (11)	0.0201 (10)	0.0194 (10)	−0.0028 (9)	−0.0008 (9)	−0.0028 (9)
C9	0.0178 (12)	0.0235 (12)	0.0211 (11)	−0.0056 (10)	−0.0038 (9)	0.0031 (10)
C10	0.0194 (11)	0.0291 (13)	0.0167 (10)	−0.0066 (10)	0.0015 (9)	−0.0024 (10)
C11	0.0193 (12)	0.0238 (12)	0.0207 (11)	−0.0041 (10)	0.0017 (9)	−0.0064 (9)
C12	0.0143 (11)	0.0188 (11)	0.0219 (11)	−0.0034 (9)	−0.0008 (9)	−0.0031 (9)
C13	0.0173 (11)	0.0208 (12)	0.0276 (12)	0.0012 (10)	0.0005 (9)	−0.0043 (10)

C14	0.0212 (12)	0.0219 (11)	0.0217 (10)	0.0062 (11)	0.0028 (10)	−0.0018 (9)
C15	0.0276 (12)	0.0206 (12)	0.0369 (14)	0.0005 (11)	0.0004 (11)	−0.0031 (11)

Geometric parameters (Å, °)

C11—C4	1.747 (2)	C9—C10	1.399 (3)
C12—C9	1.751 (2)	C10—C11	1.378 (3)
N1—C1	1.390 (3)	C11—C12	1.398 (3)
N1—C12	1.384 (3)	C13—C14	1.472 (3)
N1—C13	1.450 (3)	C14—C15	1.180 (3)
C1—C2	1.398 (3)	C2—H2	0.9500
C1—C6	1.408 (3)	C3—H3	0.9500
C2—C3	1.383 (3)	C5—H5	0.9500
C3—C4	1.402 (3)	C8—H8	0.9500
C4—C5	1.376 (3)	C10—H10	0.9500
C5—C6	1.395 (3)	C11—H11	0.9500
C6—C7	1.445 (3)	C13—H13A	0.9900
C7—C8	1.397 (3)	C13—H13B	0.9900
C7—C12	1.408 (3)	C15—H15	0.9500
C8—C9	1.383 (3)		
C1—N1—C12	108.55 (18)	N1—C12—C7	109.15 (19)
C1—N1—C13	125.32 (19)	N1—C12—C11	129.3 (2)
C12—N1—C13	126.05 (18)	C7—C12—C11	121.5 (2)
N1—C1—C2	129.3 (2)	N1—C13—C14	114.1 (2)
N1—C1—C6	108.97 (19)	C13—C14—C15	179.7 (3)
C2—C1—C6	121.7 (2)	C1—C2—H2	121.00
C1—C2—C3	117.7 (2)	C3—C2—H2	121.00
C2—C3—C4	120.3 (2)	C2—C3—H3	120.00
C11—C4—C3	118.46 (17)	C4—C3—H3	120.00
C11—C4—C5	118.91 (17)	C4—C5—H5	121.00
C3—C4—C5	122.6 (2)	C6—C5—H5	121.00
C4—C5—C6	117.7 (2)	C7—C8—H8	121.00
C1—C6—C5	120.0 (2)	C9—C8—H8	121.00
C1—C6—C7	106.67 (19)	C9—C10—H10	120.00
C5—C6—C7	133.3 (2)	C11—C10—H10	120.00
C6—C7—C8	133.0 (2)	C10—C11—H11	121.00
C6—C7—C12	106.66 (19)	C12—C11—H11	121.00
C8—C7—C12	120.3 (2)	N1—C13—H13A	109.00
C7—C8—C9	117.1 (2)	N1—C13—H13B	109.00
C12—C9—C8	118.59 (17)	C14—C13—H13A	109.00
C12—C9—C10	118.49 (17)	C14—C13—H13B	109.00
C8—C9—C10	122.9 (2)	H13A—C13—H13B	108.00
C9—C10—C11	120.2 (2)	C14—C15—H15	180.00
C10—C11—C12	117.9 (2)		
C12—N1—C1—C2	178.9 (2)	C3—C4—C5—C6	1.0 (4)
C12—N1—C1—C6	0.4 (3)	C4—C5—C6—C1	−0.5 (3)
C13—N1—C1—C2	1.9 (4)	C4—C5—C6—C7	177.8 (2)
C13—N1—C1—C6	−176.6 (2)	C1—C6—C7—C8	179.0 (3)

C1—N1—C12—C7	0.0 (3)	C1—C6—C7—C12	0.6 (3)
C1—N1—C12—C11	−179.3 (2)	C5—C6—C7—C8	0.6 (5)
C13—N1—C12—C7	177.0 (2)	C5—C6—C7—C12	−177.8 (3)
C13—N1—C12—C11	−2.4 (4)	C6—C7—C8—C9	−177.8 (2)
C1—N1—C13—C14	−86.6 (3)	C12—C7—C8—C9	0.4 (3)
C12—N1—C13—C14	97.0 (3)	C6—C7—C12—N1	−0.4 (3)
N1—C1—C2—C3	−177.2 (2)	C6—C7—C12—C11	179.0 (2)
C6—C1—C2—C3	1.1 (4)	C8—C7—C12—N1	−179.1 (2)
N1—C1—C6—C5	178.1 (2)	C8—C7—C12—C11	0.3 (4)
N1—C1—C6—C7	−0.6 (3)	C7—C8—C9—C12	179.84 (17)
C2—C1—C6—C5	−0.6 (4)	C7—C8—C9—C10	−1.0 (4)
C2—C1—C6—C7	−179.3 (2)	C12—C9—C10—C11	179.94 (18)
C1—C2—C3—C4	−0.7 (3)	C8—C9—C10—C11	0.8 (4)
C2—C3—C4—C11	179.85 (18)	C9—C10—C11—C12	0.0 (3)
C2—C3—C4—C5	−0.4 (4)	C10—C11—C12—N1	178.7 (2)
C11—C4—C5—C6	−179.26 (18)	C10—C11—C12—C7	−0.6 (4)