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9-Butyl-3-nitro-9*H*-carbazole

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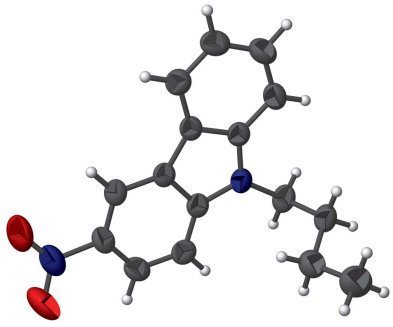
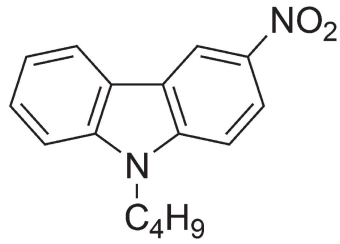
The title compound, $C_{16}H_{16}N_2O_2$, is a carbazole derivative with the 3-position substituted by a nitro group and the 9-position substituted by an *n*-butyl group. The nitro group is inclined to the benzene ring to which it is attached by 4.4 (2)°. The *n*-butyl substituent has an extended conformation and lies almost normal to the plane of the carbozole ring. In the crystal, inversion-related molecules stack along the *a* axis and are linked *via* offset π–π interactions, forming columns [shortest intercentroid distance = 3.773 (1) Å].

3D view



Chemical scheme



Structure description

Carbazole-based materials are well known for their excellent thermal stability, hole-transporting properties, versatile structural derivatization, and their ability to form amorphous films. Such compounds have also been used to produce high-performance blue phosphorescent organic light-emitting diodes (Ye *et al.*, 2010). When a *n*-butyl group is introduced into the molecule, it enhances the solubility and film-forming ability. A nitro group can form non-covalent interactions, especially hydrogen bonds, and exhibits a diversity of chemical and biological actions (Trzesowska-Kruszynska, 2015). The synthesis and crystal structure of the title compound, with both a butyl and a nitro substituent, is described herein.

In the title compound, Fig. 1, the bond lengths and angles are similar to those in the related compound 1-nitro-9*H*-carbazole (Kautny & Stöger, 2014). The carbazole ring system is, as expected, almost planar (r.m.s. deviation = 0.01 Å) and the nitro group is inclined by 4.4 (2)° to the benzene ring to which it is attached. The *n*-butyl substituent has an extended conformation and lies almost normal to the plane of the carbozole ring system. Its mean plane is inclined to the central five-membered ring by 77.6 (2) °.

In the crystal, inversion-related molecules stack along the *a* axis and are linked *via* offset π–π interactions, forming columns (Fig. 2). The shortest intercentroid distance is

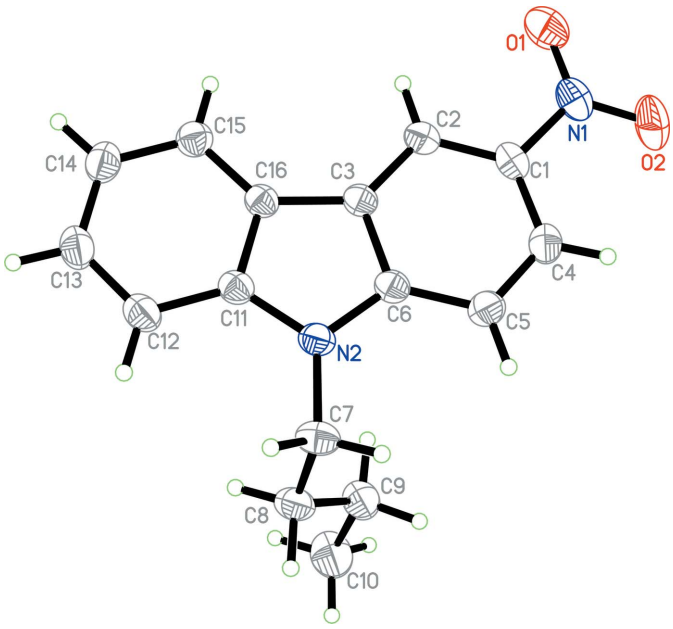


Figure 1
The molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

$Cg1\cdots Cg3^{i}$ = 3.773 (1) Å [$Cg1$ and $Cg3$ are the centroids of rings N2/C3/C6/C11/C16 and C11–C16, respectively, interplanar distance = 3.536 (1) Å, slippage = 1.316 Å, symmetry code: (i) $-x+1, -y, -z+2$].

Synthesis and crystallization

The precursor *N*-(*n*-butyl)-carbazole was prepared in accord with the literature method (Yang *et al.*, 2005). Carbazole (3.3 g, 20 mmol) was added to a mixture of NaOH (1.3 g, 32 mmol), Bu_4NBr (0.3 g) as phase-transfer catalyst in 20 ml CH_3COCH_3. The mixture was stirred for 1 h and then 1-bromobutane was slowly added. After refluxing for 24 h, no carbazole was present (monitoring by TLC). The solvents were removed under reduced pressure, and 20 ml water was added to the flask and a white solid precipitated out. The white solid was filtered and washed several times with water, dried and recrystallized from ethanol solution giving white needle-shaped crystals (yield: 4.1 g, 90.1%).

The title compound was prepared in accord with the literature methods (Shufen *et al.*, 1995; Zhang *et al.*, 2014). *N*-(*n*-butyl)-carbazole (5.6 g, 25 mmol) was dissolved in dichloromethane (50 ml) and the solution cooled (ice–water bath) to 273–275 K. Concentrated nitric acid (65–68%, 2.2 ml, 32 mmol) was added dropwise over one hour with vigorous stirring. Stirring was continued for a further hour at 283 K, after which time all of the *N*-(*n*-butyl)-carbazole had reacted. The liquor was steam distilled to remove dichloromethane, then the mixture was cooled and filtered and the product obtained was washed several times with water. The residue was purified by flash chromatography on silica gel using dichloroethane as eluent (yield: 5.8 g, 86.5%). Yellow block-like crystals of the title compound, suitable for X-ray diffraction analysis, were grown from ethanol solution by slow evaporation at room temperature in about one week.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{16}N_2O_2$
M_r	268.31
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	296
a, b, c (Å)	8.1948 (9), 9.5630 (11), 9.7528 (11)
α, β, γ (°)	68.106 (1), 73.141 (1), 85.379 (1)
V (Å^3)	678.37 (13)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.18 × 0.17 × 0.16
Data collection	
Diffractometer	Bruker SMART CCD area detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2007)
T_{min}, T_{max}	0.984, 0.986
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4867, 2372, 2080
R_{int}	0.014
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.594
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.113, 1.09
No. of reflections	2372
No. of parameters	183
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.24, −0.15

Computer programs: *SMART* and *SAINT* (Bruker, 2007), *SHELXS97*, *SHELXL97* and *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2008).

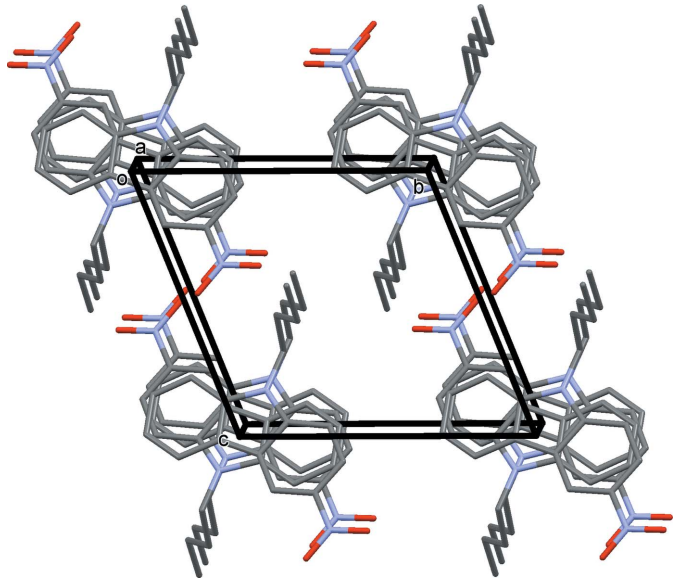


Figure 2
Crystal packing of the title compound, viewed along the *a* axis. H atoms have been omitted for clarity.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Acknowledgements

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References

Bruker (2007). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Kautny, P. & Stöger, B. (2014). *Acta Cryst.* E**70**, o28.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Shufen, Z., Danhong, Z. & Jinzong, Y. (1995). *Dyes Pigments*, **27**, 287–296.

Trzesowska-Kruszynska, A. T. (2015). *CrystEngComm*, **17**, 7702–7716.

Yang, J.-X., Tao, X.-T., Yuan, C. X., Yan, Y. X., Wang, L., Liu, Z., Ren, Y. & Jiang, M. H. (2005). *J. Am. Chem. Soc.* **127**, 3278–3279.

Ye, S. H., Liu, Y. Q., Chen, J. M., Lu, K., Wu, W. P., Du, C. Y., Liu, Y., Wu, T., Shuai, Z. G. & Yu, G. (2010). *Adv. Mater.* **22**, 4167–4171.

Zhang, P., Liu, J., Huang, J. Y. & Yang, J. X. (2014). *Chin. J. Appl. Chem.* **31**, 1171–1176.

full crystallographic data

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9-Butyl-3-nitro-9*H*-carbazole

Crystal data

$C_{16}H_{16}N_2O_2$
M_r = 268.31
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 8.1948 (9) Å
b = 9.5630 (11) Å
c = 9.7528 (11) Å
α = 68.106 (1)°
β = 73.141 (1)°
γ = 85.379 (1)°
V = 678.37 (13) Å^3
Z = 2
$F(000)$ = 284
D_x = 1.314 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3094 reflections
θ = 2.3–26.8°
μ = 0.09 mm^{-1}
T = 296 K
Block, light yellow
0.18 × 0.17 × 0.16 mm

Data collection

Bruker SMART CCD area detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2007)
T_{min} = 0.984, T_{max} = 0.986
4867 measured reflections
2372 independent reflections
2080 reflections with $I > 2\sigma(I)$
R_{int} = 0.014
θ_{max} = 25.0°, θ_{min} = 2.3°
h = −9→9
k = −11→11
l = −11→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.113
S = 1.09
2372 reflections
183 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0524P)^2 + 0.1519P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}
Extinction correction: SHELXL97 (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.029 (5)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ 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}
N2	0.37033 (15)	0.13986 (14)	0.84237 (13)	0.0458 (3)
N1	−0.13392 (18)	0.18235 (19)	1.34577 (17)	0.0603 (4)
O2	−0.18313 (17)	0.30664 (17)	1.34766 (18)	0.0832 (5)
O1	−0.19381 (19)	0.06376 (19)	1.45000 (16)	0.0867 (5)
C11	0.37310 (18)	−0.01575 (16)	0.88088 (16)	0.0432 (3)
C2	0.04843 (19)	0.03728 (17)	1.20382 (17)	0.0455 (4)
H2	−0.0023	−0.0514	1.2821	0.055*
C3	0.17430 (17)	0.03417 (16)	1.07446 (16)	0.0410 (3)
C6	0.24994 (18)	0.17125 (16)	0.95749 (16)	0.0425 (3)
C1	0.00093 (19)	0.17611 (18)	1.21260 (17)	0.0477 (4)
C16	0.25369 (17)	−0.08540 (16)	1.02448 (16)	0.0413 (3)
C4	0.0748 (2)	0.31103 (18)	1.09844 (19)	0.0520 (4)
H4	0.0393	0.4021	1.1094	0.062*
C12	0.4732 (2)	−0.09885 (19)	0.79835 (18)	0.0528 (4)
H12	0.5521	−0.0521	0.7035	0.063*
C7	0.4756 (2)	0.24856 (19)	0.69959 (17)	0.0533 (4)
H7A	0.5905	0.2119	0.6782	0.064*
H7B	0.4814	0.3434	0.7130	0.064*
C5	0.2000 (2)	0.31044 (17)	0.96963 (18)	0.0509 (4)
H5	0.2501	0.4001	0.8927	0.061*
C15	0.2343 (2)	−0.24194 (17)	1.08728 (18)	0.0499 (4)
H15	0.1560	−0.2899	1.1822	0.060*
C13	0.4502 (2)	−0.2532 (2)	0.8634 (2)	0.0591 (4)
H13	0.5146	−0.3116	0.8107	0.071*
C8	0.4070 (2)	0.2762 (2)	0.56171 (17)	0.0561 (4)
H8A	0.4875	0.3420	0.4695	0.067*
H8B	0.4003	0.1809	0.5495	0.067*
C9	0.2347 (2)	0.3454 (2)	0.5750 (2)	0.0598 (4)
H9A	0.2426	0.4447	0.5783	0.072*
H9B	0.1551	0.2839	0.6706	0.072*
C14	0.3336 (2)	−0.32454 (19)	1.0057 (2)	0.0575 (4)
H14	0.3223	−0.4292	1.0465	0.069*
C10	0.1674 (3)	0.3591 (3)	0.4412 (2)	0.0808 (6)
H10A	0.2381	0.4300	0.3478	0.121*
H10B	0.0526	0.3935	0.4592	0.121*

H10C	0.1688	0.2625	0.4321	0.121*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N2	0.0465 (7)	0.0483 (7)	0.0367 (6)	0.0007 (5)	−0.0075 (5)	−0.0123 (5)
N1	0.0487 (8)	0.0790 (10)	0.0608 (9)	0.0037 (7)	−0.0083 (7)	−0.0396 (8)
O2	0.0679 (8)	0.0907 (10)	0.1034 (11)	0.0107 (7)	−0.0029 (7)	−0.0669 (9)
O1	0.0833 (10)	0.0943 (11)	0.0613 (8)	−0.0012 (8)	0.0146 (7)	−0.0306 (8)
C11	0.0415 (7)	0.0503 (8)	0.0391 (7)	0.0050 (6)	−0.0145 (6)	−0.0160 (6)
C2	0.0446 (8)	0.0507 (9)	0.0396 (7)	−0.0024 (6)	−0.0092 (6)	−0.0159 (6)
C3	0.0411 (7)	0.0457 (8)	0.0377 (7)	0.0008 (6)	−0.0132 (6)	−0.0152 (6)
C6	0.0431 (8)	0.0474 (8)	0.0383 (7)	0.0014 (6)	−0.0134 (6)	−0.0155 (6)
C1	0.0438 (8)	0.0598 (9)	0.0460 (8)	0.0043 (7)	−0.0116 (6)	−0.0280 (7)
C16	0.0406 (7)	0.0474 (8)	0.0387 (7)	0.0025 (6)	−0.0137 (6)	−0.0171 (6)
C4	0.0559 (9)	0.0503 (9)	0.0575 (9)	0.0081 (7)	−0.0192 (7)	−0.0272 (8)
C12	0.0477 (8)	0.0665 (11)	0.0442 (8)	0.0101 (7)	−0.0112 (7)	−0.0231 (8)
C7	0.0451 (8)	0.0620 (10)	0.0426 (8)	−0.0063 (7)	−0.0068 (7)	−0.0103 (7)
C5	0.0570 (9)	0.0448 (8)	0.0482 (8)	−0.0009 (7)	−0.0150 (7)	−0.0134 (7)
C15	0.0512 (9)	0.0485 (9)	0.0486 (8)	0.0001 (7)	−0.0135 (7)	−0.0163 (7)
C13	0.0601 (10)	0.0648 (11)	0.0615 (10)	0.0185 (8)	−0.0199 (8)	−0.0347 (9)
C8	0.0540 (9)	0.0622 (10)	0.0401 (8)	0.0013 (7)	−0.0052 (7)	−0.0114 (7)
C9	0.0602 (10)	0.0641 (11)	0.0574 (10)	0.0065 (8)	−0.0157 (8)	−0.0262 (8)
C14	0.0650 (10)	0.0488 (9)	0.0645 (10)	0.0082 (8)	−0.0234 (8)	−0.0247 (8)
C10	0.0859 (14)	0.0962 (15)	0.0755 (13)	0.0283 (12)	−0.0423 (12)	−0.0388 (12)

Geometric parameters (Å, º)

N2—C6	1.3730 (19)	C12—H12	0.9300
N2—C11	1.3924 (19)	C7—C8	1.531 (2)
N2—C7	1.4601 (19)	C7—H7A	0.9700
N1—O1	1.225 (2)	C7—H7B	0.9700
N1—O2	1.2290 (19)	C5—H5	0.9300
N1—C1	1.458 (2)	C15—C14	1.381 (2)
C11—C12	1.393 (2)	C15—H15	0.9300
C11—C16	1.406 (2)	C13—C14	1.391 (2)
C2—C1	1.380 (2)	C13—H13	0.9300
C2—C3	1.387 (2)	C8—C9	1.502 (2)
C2—H2	0.9300	C8—H8A	0.9700
C3—C6	1.418 (2)	C8—H8B	0.9700
C3—C16	1.442 (2)	C9—C10	1.517 (2)
C6—C5	1.398 (2)	C9—H9A	0.9700
C1—C4	1.391 (2)	C9—H9B	0.9700
C16—C15	1.393 (2)	C14—H14	0.9300
C4—C5	1.374 (2)	C10—H10A	0.9600
C4—H4	0.9300	C10—H10B	0.9600
C12—C13	1.376 (2)	C10—H10C	0.9600

C6—N2—C11	108.59 (12)	N2—C7—H7B	109.0
C6—N2—C7	126.97 (13)	C8—C7—H7B	109.0
C11—N2—C7	124.40 (13)	H7A—C7—H7B	107.8
O1—N1—O2	123.01 (15)	C4—C5—C6	118.11 (14)
O1—N1—C1	118.64 (15)	C4—C5—H5	120.9
O2—N1—C1	118.35 (16)	C6—C5—H5	120.9
N2—C11—C12	128.91 (14)	C14—C15—C16	118.65 (15)
N2—C11—C16	109.18 (13)	C14—C15—H15	120.7
C12—C11—C16	121.91 (14)	C16—C15—H15	120.7
C1—C2—C3	117.88 (14)	C12—C13—C14	122.02 (15)
C1—C2—H2	121.1	C12—C13—H13	119.0
C3—C2—H2	121.1	C14—C13—H13	119.0
C2—C3—C6	119.72 (13)	C9—C8—C7	114.26 (14)
C2—C3—C16	133.72 (14)	C9—C8—H8A	108.7
C6—C3—C16	106.56 (12)	C7—C8—H8A	108.7
N2—C6—C5	129.60 (14)	C9—C8—H8B	108.7
N2—C6—C3	109.16 (13)	C7—C8—H8B	108.7
C5—C6—C3	121.24 (14)	H8A—C8—H8B	107.6
C2—C1—C4	122.71 (14)	C8—C9—C10	111.91 (15)
C2—C1—N1	118.87 (14)	C8—C9—H9A	109.2
C4—C1—N1	118.42 (15)	C10—C9—H9A	109.2
C15—C16—C11	119.52 (14)	C8—C9—H9B	109.2
C15—C16—C3	133.98 (14)	C10—C9—H9B	109.2
C11—C16—C3	106.50 (12)	H9A—C9—H9B	107.9
C5—C4—C1	120.34 (15)	C15—C14—C13	120.85 (15)
C5—C4—H4	119.8	C15—C14—H14	119.6
C1—C4—H4	119.8	C13—C14—H14	119.6
C13—C12—C11	117.05 (15)	C9—C10—H10A	109.5
C13—C12—H12	121.5	C9—C10—H10B	109.5
C11—C12—H12	121.5	H10A—C10—H10B	109.5
N2—C7—C8	112.79 (13)	C9—C10—H10C	109.5
N2—C7—H7A	109.0	H10A—C10—H10C	109.5
C8—C7—H7A	109.0	H10B—C10—H10C	109.5

C6—N2—C11—C12	179.28 (14)	N2—C11—C16—C3	0.38 (15)
C7—N2—C11—C12	1.2 (2)	C12—C11—C16—C3	−179.68 (13)
C6—N2—C11—C16	−0.79 (16)	C2—C3—C16—C15	−0.2 (3)
C7—N2—C11—C16	−178.82 (13)	C6—C3—C16—C15	−179.70 (15)
C1—C2—C3—C6	0.4 (2)	C2—C3—C16—C11	179.60 (15)
C1—C2—C3—C16	−179.01 (14)	C6—C3—C16—C11	0.15 (15)
C11—N2—C6—C5	−179.23 (14)	C2—C1—C4—C5	0.4 (2)
C7—N2—C6—C5	−1.3 (2)	N1—C1—C4—C5	−178.75 (14)
C11—N2—C6—C3	0.89 (16)	N2—C11—C12—C13	−179.99 (14)
C7—N2—C6—C3	178.85 (13)	C16—C11—C12—C13	0.1 (2)
C2—C3—C6—N2	179.82 (12)	C6—N2—C7—C8	−99.63 (18)
C16—C3—C6—N2	−0.64 (15)	C11—N2—C7—C8	78.03 (18)
C2—C3—C6—C5	−0.1 (2)	C1—C4—C5—C6	0.0 (2)
C16—C3—C6—C5	179.47 (13)	N2—C6—C5—C4	−179.98 (14)

C3—C2—C1—C4	−0.5 (2)	C3—C6—C5—C4	−0.1 (2)
C3—C2—C1—N1	178.57 (13)	C11—C16—C15—C14	−0.1 (2)
O1—N1—C1—C2	4.2 (2)	C3—C16—C15—C14	179.74 (15)
O2—N1—C1—C2	−175.23 (14)	C11—C12—C13—C14	−0.5 (2)
O1—N1—C1—C4	−176.61 (15)	N2—C7—C8—C9	63.5 (2)
O2—N1—C1—C4	3.9 (2)	C7—C8—C9—C10	−175.61 (15)
N2—C11—C16—C15	−179.74 (12)	C16—C15—C14—C13	−0.3 (2)
C12—C11—C16—C15	0.2 (2)	C12—C13—C14—C15	0.6 (3)