Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

(3*R*,4*S*)-2-Isopropyl-3-methyl-4-phenyl-3,4-dihydroisoquinolinium iodide

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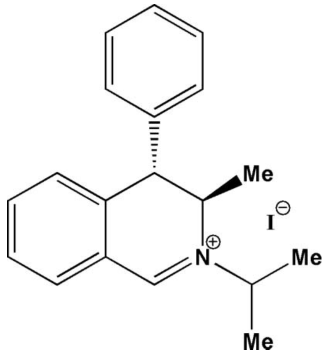
Received 18 June 2007; accepted 22 June 2007

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.008 Å; R factor = 0.038; wR factor = 0.086; data-to-parameter ratio = 19.1.

The title compound, $C_{19}H_{22}N^+\cdot I^-$, is a new dihydroisoquinolinium salt, used as a catalyst in asymmetric epoxidation. It was characterized by NMR spectroscopy and X-ray crystallographic techniques. The absolute configurations of the two stereogenic centres were established by the refinement of the Flack parameter to be 3*R* and 4*S*.

Related literature

For general background, see: Bohé *et al.* (1999); Xia *et al.* (2005). For related literature, see: Cremer & Pople (1975).



Experimental

Crystal data

$C_{19}H_{22}N^+\cdot I^-$	Z = 6
M_r = 391.28	Mo $K\alpha$ radiation
Hexagonal, $P6_1$	μ = 1.77 mm^{-1}
a = 9.773 (4) Å	T = 293 (2) K
c = 32.630 (12) Å	0.40 × 0.35 × 0.35 mm
V = 2699.0 (19) Å^3	

Data collection

Nonius KappaCCD diffractometer	6545 measured reflections
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)	3694 independent reflections
T_{min} = 0.491, T_{max} = 0.540	2992 reflections with $I > 2\sigma(I)$
	R_{int} = 0.014

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038	H-atom parameters constrained
$wR(F^2)$ = 0.086	$\Delta\rho_{max}$ = 0.55 e Å^{-3}
S = 1.02	$\Delta\rho_{min}$ = −1.01 e Å^{-3}
3694 reflections	Absolute structure: Flack (1983), with 1602 Friedel pairs
193 parameters	Flack parameter: 0.01 (3)
1 restraint	

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The authors thank Dr Pascal Retailleau for his help and advice.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2204).

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doi:10.1107/S1600536807030565

supplementary materials

Acta Cryst. (2007). E**63**, o3355 [**doi:10.1107/S1600536807030565**]

(3*R*,4*S*)-2-Isopropyl-3-methyl-4-phenyl-3,4-dihydroisoquinolinium iodide

K. Ben Ali, **A. Chiaroni** and **L. Bohe**

Comment

Catalytic asymmetric epoxidation of alkenes is an exceptionally valuable synthetic transformation (Xia *et al.*,2005). The development of efficient methods for asymmetric epoxidation of simple, 'unfunctionalized' alkenes is a particular challenge, and some of the most spectacular progress in recent years has come from the use of oxaziridinum salts generated *in situ* by oxidation of chiral iminium salts (Bohé *et al.*, 1999). As part of our interest in oxaziridinium chemistry and particularly in the rational design of dihydroisoquinolinium-derived catalysts able to improve the catalytic oxygen transfer process, we examined the influence of the exocyclic substituent on the nitrogen atom on the ee induced in an epoxidation reaction. Thus we prepared the iminium salt (2) and evaluated its behavior in the catalytic system (Fig. 1). We report herein the synthesis and the crystal structure determination of the title compound. Synthesis of the title compound involved heating a mixture of the corresponding diydroisoquinoline (2) and isopropyl iodide for 24 h. Imine (2) was prepared as described by Bohé *et al.*(1999), in four steps from (1*S*, 2*R*)-norephedrine (1).

In the title compound, the tetrahydroisoquinoline unit is substituted by a methyl group in position 3, a phenyl substituent in position 4, and a cyclohexane ring at the nitrogen (Fig. 2). The heterocyclic ring adopts a half-chair conformation as indicated by puckering analysis [QT= 0.458 (5)Å and θ= 62.1 (6)°] (Cremer & Pople, 1975). The substituents in positions 3 and 4 of the heterocyclic ring are in axial conformation with respect to this ring and the X-ray analyses allowed to define the absolute configuration of C3(*R*) and C4(*S*).

Experimental

Compound (3) was prepared by reaction of imine (2) (3.470 g, 16 mmol), and isopropyl iodide (8 ml, 80 mmol) in acetonitrile (80 ml)·The mixture was heated at reflux for 24 h. On completion of the reaction, as monitored by TLC, the solvent was removed in vacuum and the product purified by flash chromatography on silica, with dichloromethane/methanol (90/10) as eluent (yield 95%). m.p. 457 K. $[\alpha]_D^{22}$ – 62 (c 1; CHCl3). Spectroscopic analysis, 1H NMR (400 MHz; CDCl3, p.p.m): 1.23 (d, J = 6.2, 3H, Me20); 1.24 (d, J = 6.2,3*H*, Me19); 1.58 (d, J = 6.7, 3H, Me11); 4.37 (q, J = 6.7, 1H, H3); 4.47 (s,1*H*, H4); 4.54 (dq, J = 6.2, J = 6.2, 1H, H18); 6.87 (d, J = 6.5, 2H, aromatic H); 7.30 (m, 3H, aromatic H); 7.40 (d, J = 7.5, 1H, aromatic H); 7.63 (t, J = 7.3, 1H, aromatic H); 7.80 (t, J = 7.6, 1H, aromatic H); 8.70 (d, J = 7.2, 1H, aromatic H); 10.54 (s, 1H, H1). 13 C NMR (62.5 MHz; CDCl3): 18.92, 20.33,21.12, 48.12, 61.61, 62.67, 125.10, 127.69, 128.51, 129.48, 129.74, 130.16, 135.75, 136.22, 138.78, 163.74. m/*z* (ESI+): 264 (M—I)+. Anal.: Calcd for C19H22NI: C 58.32%; H 5.67%; N 3.58%. Found: C 58.44%; H 5.79%; N 3.44% Recrystallization from acetone afford yellow crystals suitable for diffraction.

Refinement

All H atoms were positioned geometrically and treated as riding, with C—H = 0.93 (aromatic), 0.96 (methyl), or 0.98 Å (methine), with $U_{\rm iso}$(H) = $xU_{\rm eq}$(C) where x = 1.5 for methyl H and 1.2 for all other H atoms. Friedel opposites were not merged. The absolute configuration C3(*R*),C4(*S*) was determined from the anomalous scattering contribution of the iodide anion, using 1602 Friedel pairs.

Figures

Fig. 1. Chemical pathway of the formation of (3).

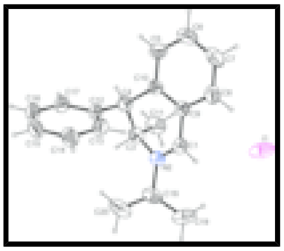


Fig. 2. Molecular view of the title compound showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level·H atoms are represented as small spheres of arbitrary radii.

(3*R*,4*S*)-2-Isopropyl-3-methyl-4-phenyl-3,4-dihydroisoquinolinium iodide

Crystal data

$C_{19}H_{22}N^{+}\cdot I^{-}$
$M_r = 391.28$
Hexagonal, $P6_1$
Hall symbol: P 61
$a = 9.773$ (4) Å
$b = 9.773$ (4) Å
$c = 32.630$ (12) Å
$\alpha = 90°$
$\beta = 90°$
$\gamma = 120°$
$V = 2699.0$ (19) Å^3

$Z = 6$
$F_{000} = 1176$
$D_x = 1.444$ Mg m^{-3}
Melting point: 457 K
Mo *K*α radiation
$\lambda = 0.71073$ Å
Cell parameters from 3639 reflections
$\theta = 1.0–27.5°$
$\mu = 1.77$ mm^{-1}
$T = 293$ (2) K
Prism, yellow
0.40 × 0.35 × 0.35 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Monochromator: graphite
$T = 293(2)$ K
φ and ω scans
Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997)
$T_{\min} = 0.491$, $T_{\max} = 0.540$
6545 measured reflections

3694 independent reflections
2992 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.014$
$\theta_{\max} = 27.5°$
$\theta_{\min} = 2.4°$
$h = -12\rightarrow12$
$k = -10\rightarrow10$
$l = -42\rightarrow34$

Refinement

Refinement on F^2	Hydrogen site location: difference Fourier map
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.038$	$w = 1/[\sigma^2(F_o^2) + (0.0277P)^2 + 2.172P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.086$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.02$	$\Delta\rho_{max} = 0.55$ e Å^{-3}
3694 reflections	$\Delta\rho_{min} = -1.01$ e Å^{-3}
193 parameters	Extinction correction: none
1 restraint	Absolute structure: Flack (1983), 1602 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.01 (3)
Secondary atom site location: difference Fourier map	

Special details

Refinement. Refinement of F^2 against ALL reflections except one truncated by the beamstop. 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 $F^2 >$ 2sigma(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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	0.64454 (5)	0.68377 (4)	0.139072 (16)	0.1060 (2)
C1	0.7788 (5)	0.4692 (5)	0.20412 (13)	0.0535 (10)
H1	0.8142	0.5730	0.2121	0.060*
N2	0.8719 (4)	0.4388 (4)	0.18374 (10)	0.0528 (8)
C3	0.8106 (5)	0.2778 (5)	0.16614 (15)	0.0599 (11)
H3	0.9006	0.2622	0.1610	0.067*
C4	0.7003 (5)	0.1521 (5)	0.19702 (15)	0.0606 (11)
H4	0.6446	0.0516	0.1822	0.068*
C5	0.4251 (6)	0.0766 (6)	0.22239 (18)	0.0740 (14)
H5	0.3941	−0.0298	0.2198	0.083*
C6	0.3199 (6)	0.1186 (8)	0.23685 (19)	0.0853 (17)
H6	0.2183	0.0406	0.2440	0.096*
C7	0.3627 (6)	0.2737 (9)	0.24090 (19)	0.0837 (17)
H7	0.2898	0.3009	0.2505	0.094*
C8	0.5150 (6)	0.3917 (6)	0.23068 (16)	0.0692 (13)
H8	0.5454	0.4976	0.2341	0.078*
C9	0.6205 (5)	0.3492 (5)	0.21536 (13)	0.0508 (9)
C10	0.5777 (5)	0.1908 (5)	0.21141 (14)	0.0543 (10)
C11	0.7318 (7)	0.2690 (7)	0.12538 (15)	0.0827 (16)
H11A	0.6999	0.1688	0.1127	0.099*
H11B	0.8049	0.3525	0.1078	0.099*

H11C	0.6407	0.2800	0.1298	0.099*
C12	0.7885 (5)	0.1284 (5)	0.23205 (16)	0.0582 (11)
C13	0.8437 (6)	0.2279 (6)	0.26558 (16)	0.0666 (12)
H13	0.8217	0.3098	0.2678	0.075*
C14	0.9315 (6)	0.2078 (7)	0.29619 (18)	0.0766 (14)
H14	0.9722	0.2789	0.3179	0.086*
C15	0.9572 (7)	0.0836 (9)	0.2941 (2)	0.094 (2)
H15	1.0137	0.0679	0.3147	0.105*
C16	0.8997 (7)	−0.0179 (8)	0.2617 (3)	0.096 (2)
H16	0.9167	−0.1033	0.2605	0.108*
C17	0.8179 (6)	0.0037 (6)	0.2311 (2)	0.0740 (14)
H17	0.7812	−0.0663	0.2091	0.083*
C18	1.0400 (5)	0.5578 (6)	0.17395 (16)	0.0718 (13)
H18	1.0601	0.5393	0.1456	0.080*
C19	1.0690 (7)	0.7252 (6)	0.1764 (2)	0.097 (2)
H19A	1.1722	0.7972	0.1659	0.116*
H19B	1.0622	0.7510	0.2044	0.116*
H19C	0.9908	0.7333	0.1604	0.116*
C20	1.1482 (6)	0.5291 (9)	0.2014 (2)	0.097 (2)
H20A	1.1392	0.5570	0.2291	0.116*
H20B	1.2554	0.5927	0.1923	0.116*
H20C	1.1185	0.4196	0.2003	0.116*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0964 (3)	0.0813 (3)	0.0739 (2)	−0.00536 (18)	−0.0301 (2)	0.0212 (2)
C1	0.064 (3)	0.052 (2)	0.047 (2)	0.031 (2)	−0.0024 (19)	−0.0007 (18)
N2	0.0505 (19)	0.0547 (19)	0.0459 (19)	0.0208 (16)	−0.0008 (15)	−0.0027 (15)
C3	0.062 (3)	0.071 (3)	0.050 (2)	0.036 (2)	−0.004 (2)	−0.018 (2)
C4	0.062 (3)	0.050 (2)	0.067 (3)	0.026 (2)	−0.010 (2)	−0.020 (2)
C5	0.057 (3)	0.063 (3)	0.082 (4)	0.016 (2)	−0.006 (3)	0.010 (3)
C6	0.052 (3)	0.111 (5)	0.081 (4)	0.031 (3)	0.007 (3)	0.027 (3)
C7	0.066 (3)	0.128 (5)	0.075 (4)	0.061 (4)	0.010 (3)	0.020 (3)
C8	0.079 (3)	0.082 (3)	0.065 (3)	0.053 (3)	0.012 (3)	0.013 (3)
C9	0.052 (2)	0.057 (2)	0.046 (2)	0.030 (2)	0.0008 (17)	0.0041 (18)
C10	0.049 (2)	0.058 (2)	0.054 (3)	0.025 (2)	−0.0067 (19)	0.0007 (19)
C11	0.081 (3)	0.103 (4)	0.051 (3)	0.036 (3)	−0.013 (2)	−0.019 (3)
C12	0.057 (2)	0.048 (2)	0.076 (3)	0.030 (2)	0.004 (2)	0.002 (2)
C13	0.078 (3)	0.061 (3)	0.068 (3)	0.039 (2)	−0.011 (3)	−0.002 (2)
C14	0.070 (3)	0.096 (4)	0.070 (4)	0.045 (3)	0.000 (2)	0.018 (3)
C15	0.061 (3)	0.119 (5)	0.116 (5)	0.057 (3)	0.027 (3)	0.063 (4)
C16	0.083 (4)	0.083 (4)	0.151 (7)	0.062 (3)	0.032 (4)	0.040 (4)
C17	0.070 (3)	0.059 (3)	0.101 (4)	0.038 (3)	0.015 (3)	0.002 (3)
C18	0.052 (3)	0.094 (4)	0.050 (3)	0.023 (2)	0.003 (2)	−0.005 (2)
C19	0.082 (4)	0.073 (3)	0.081 (4)	−0.002 (3)	0.005 (3)	0.004 (3)
C20	0.057 (3)	0.141 (6)	0.083 (4)	0.042 (3)	−0.009 (3)	−0.019 (4)

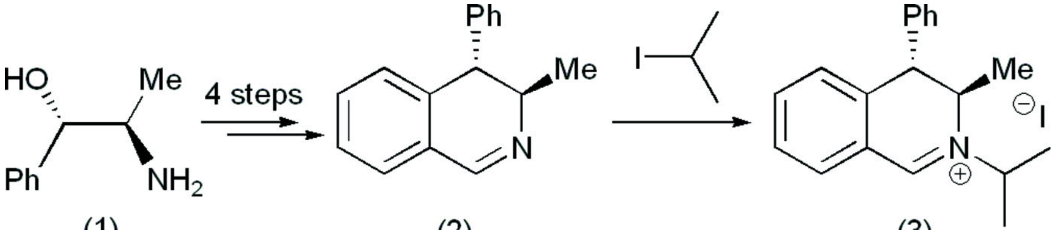
Geometric parameters (Å, °)

C1—N2	1.276 (5)	C11—H11B	0.9600
C1—C9	1.445 (6)	C11—H11C	0.9600
C1—H1	0.9300	C12—C13	1.381 (7)
N2—C3	1.491 (5)	C12—C17	1.385 (6)
N2—C18	1.497 (5)	C13—C14	1.393 (7)
C3—C11	1.517 (7)	C13—H13	0.9300
C3—C4	1.537 (7)	C14—C15	1.359 (8)
C3—H3	0.9800	C14—H14	0.9300
C4—C10	1.501 (6)	C15—C16	1.364 (9)
C4—C12	1.518 (7)	C15—H15	0.9300
C4—H4	0.9800	C16—C17	1.361 (9)
C5—C6	1.367 (8)	C16—H16	0.9300
C5—C10	1.391 (6)	C17—H17	0.9300
C5—H5	0.9300	C18—C20	1.516 (8)
C6—C7	1.362 (8)	C18—C19	1.516 (8)
C6—H6	0.9300	C18—H18	0.9800
C7—C8	1.393 (8)	C19—H19A	0.9600
C7—H7	0.9300	C19—H19B	0.9600
C8—C9	1.383 (6)	C19—H19C	0.9600
C8—H8	0.9300	C20—H20A	0.9600
C9—C10	1.393 (6)	C20—H20B	0.9600
C11—H11A	0.9600	C20—H20C	0.9600
N2—C1—C9	122.8 (4)	C3—C11—H11C	109.5
N2—C1—H1	118.6	H11A—C11—H11C	109.5
C9—C1—H1	118.6	H11B—C11—H11C	109.5
C1—N2—C3	119.3 (4)	C13—C12—C17	117.2 (5)
C1—N2—C18	124.3 (4)	C13—C12—C4	122.8 (4)
C3—N2—C18	116.3 (4)	C17—C12—C4	120.0 (5)
N2—C3—C11	108.8 (4)	C12—C13—C14	121.3 (5)
N2—C3—C4	110.0 (3)	C12—C13—H13	119.3
C11—C3—C4	113.3 (4)	C14—C13—H13	119.3
N2—C3—H3	108.2	C15—C14—C13	119.5 (6)
C11—C3—H3	108.2	C15—C14—H14	120.3
C4—C3—H3	108.2	C13—C14—H14	120.3
C10—C4—C12	112.9 (4)	C14—C15—C16	119.7 (6)
C10—C4—C3	109.4 (4)	C14—C15—H15	120.2
C12—C4—C3	113.0 (4)	C16—C15—H15	120.2
C10—C4—H4	107.1	C17—C16—C15	121.1 (5)
C12—C4—H4	107.1	C17—C16—H16	119.4
C3—C4—H4	107.1	C15—C16—H16	119.4
C6—C5—C10	120.9 (5)	C16—C17—C12	121.0 (6)
C6—C5—H5	119.5	C16—C17—H17	119.5
C10—C5—H5	119.5	C12—C17—H17	119.5
C7—C6—C5	120.6 (5)	N2—C18—C20	109.0 (4)
C7—C6—H6	119.7	N2—C18—C19	111.5 (4)
C5—C6—H6	119.7	C20—C18—C19	113.4 (5)

C6—C7—C8	120.2 (5)	N2—C18—H18	107.5
C6—C7—H7	119.9	C20—C18—H18	107.5
C8—C7—H7	119.9	C19—C18—H18	107.5
C9—C8—C7	119.1 (5)	C18—C19—H19A	109.5
C9—C8—H8	120.4	C18—C19—H19B	109.5
C7—C8—H8	120.4	H19A—C19—H19B	109.5
C8—C9—C10	120.8 (4)	C18—C19—H19C	109.5
C8—C9—C1	120.2 (4)	H19A—C19—H19C	109.5
C10—C9—C1	118.9 (4)	H19B—C19—H19C	109.5
C5—C10—C9	118.3 (4)	C18—C20—H20A	109.5
C5—C10—C4	123.3 (4)	C18—C20—H20B	109.5
C9—C10—C4	118.4 (4)	H20A—C20—H20B	109.5
C3—C11—H11A	109.5	C18—C20—H20C	109.5
C3—C11—H11B	109.5	H20A—C20—H20C	109.5
H11A—C11—H11B	109.5	H20B—C20—H20C	109.5

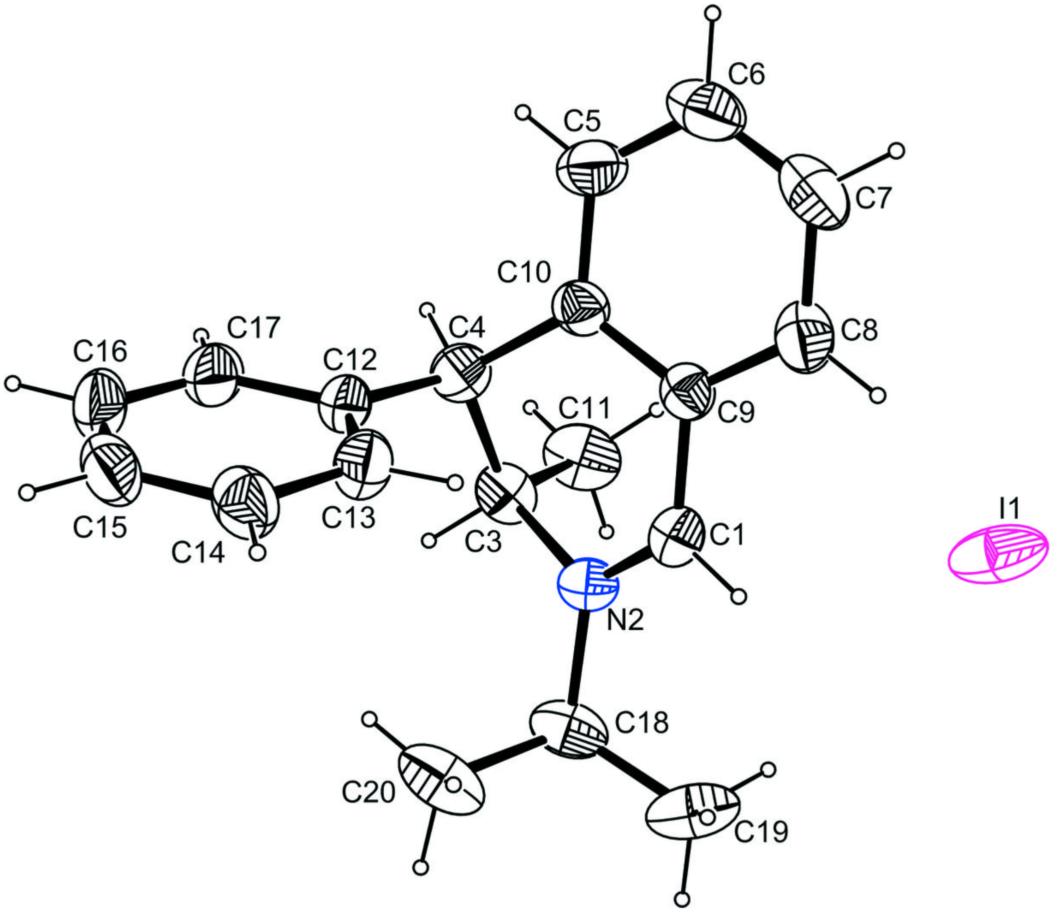
C9—C1—N2—C3	7.8 (6)	C1—C9—C10—C4	2.1 (6)
C9—C1—N2—C18	−175.7 (4)	C12—C4—C10—C5	−85.0 (6)
C1—N2—C3—C11	83.8 (5)	C3—C4—C10—C5	148.2 (5)
C18—N2—C3—C11	−92.9 (5)	C12—C4—C10—C9	92.6 (5)
C1—N2—C3—C4	−40.9 (5)	C3—C4—C10—C9	−34.1 (5)
C18—N2—C3—C4	142.4 (4)	C10—C4—C12—C13	−44.2 (6)
N2—C3—C4—C10	51.6 (5)	C3—C4—C12—C13	80.7 (5)
C11—C3—C4—C10	−70.5 (5)	C10—C4—C12—C17	136.4 (4)
N2—C3—C4—C12	−75.1 (5)	C3—C4—C12—C17	−98.8 (5)
C11—C3—C4—C12	162.8 (4)	C17—C12—C13—C14	2.9 (7)
C10—C5—C6—C7	−0.1 (9)	C4—C12—C13—C14	−176.6 (5)
C5—C6—C7—C8	−0.7 (9)	C12—C13—C14—C15	−3.2 (8)
C6—C7—C8—C9	1.8 (9)	C13—C14—C15—C16	1.4 (8)
C7—C8—C9—C10	−2.2 (7)	C14—C15—C16—C17	0.6 (9)
C7—C8—C9—C1	179.3 (5)	C15—C16—C17—C12	−0.9 (9)
N2—C1—C9—C8	−168.1 (5)	C13—C12—C17—C16	−0.9 (7)
N2—C1—C9—C10	13.4 (6)	C4—C12—C17—C16	178.6 (5)
C6—C5—C10—C9	−0.3 (8)	C1—N2—C18—C20	104.5 (5)
C6—C5—C10—C4	177.4 (5)	C3—N2—C18—C20	−79.0 (5)
C8—C9—C10—C5	1.5 (7)	C1—N2—C18—C19	−21.5 (6)
C1—C9—C10—C5	179.9 (4)	C3—N2—C18—C19	155.0 (4)
C8—C9—C10—C4	−176.3 (4)		

Fig. 1



(1) (2) (3)

Fig. 2


C6
C5
C7
C10
C8
C17
C4
C16
C12
C11
C9
I1
C15
C13
C1
C14
C3
N2
C18
C20
C19