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3-(3-Chloro-3-methyl-1,2,3,4-tetrahydrocarbazole-2-yl)propanenitrile

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.035
wR factor = 0.107
Data-to-parameter ratio = 13.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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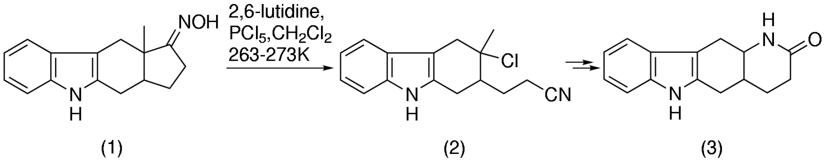
In the structure of the title compound, $C_{16}H_{17}ClN_2$, all the bond lengths and angles have normal values. The aromatic indole ring is planar.

Comment

Tetrahydrocarbazole derivatives have an important role in the synthesis of indole alkaloids (Magnus *et al.*, 1992). Neurotransmitter serotonin analogues (3) (Langlois *et al.*, 1993) are a type of potent agonist of 5-HT receptor function both *in vitro* and *in vivo*. These compounds and related derivatives contain the tetrahydrocarbazole moiety, which may be a suitable target for new drug design. A simple synthetic access route to derivatives of (3), starting from racemic Hajos–Parish ketone (Hajos & Parrish, 1985), has been designed. Conversion of (1) to the title compound, (2), is the key step, involving Beckmann fragmentation with displacement (Hassner & Nash, 1965) in the presence of phosphorus pentachoride and 2,6-lutidine in dichloromethane. It is expected that (2) could be used as an important synthetic intermediate in serotonin and other natural product syntheses. Compound (2) has not been reported in the literature. The structure of (2) has been confirmed by ^{1}H NMR, ^{13}C NMR and X-ray single-crystal diffraction analysis.



The molecular structure of (2) is shown in Fig. 1. The cyanoethyl and methyl groups on the cyclohexane ring are both equatorial, whereas the Cl atom is in an axial position.

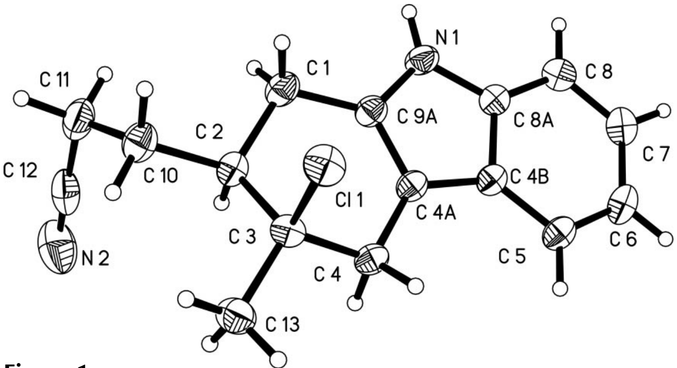


Figure 1
The molecular structure of (2), shown with 30% probability displacement ellipsoids.

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The cyclohexane ring has a half-chair conformation. All bond lengths and angles have values comparable with those reported in the literature for related structures (Allen & Trotter, 1970, Gatilov *et al.*, 1981).

Experimental

Oxime (1) (0.8 mmol) in anhydrous dichloromethane (10 ml) was added dropwise to a stirred suspension of phosphorus pentachoride (1.2 mmol) and 2,6-lutidine (2.5 mmol) in dichloromethane (15 ml). The reaction mixture was stirred at 263–273 K in an atmosphere of nitrogen for 5 min (monitored by thin-layer chromatography), then quenched with a saturated ammonium chloride solution. The separated aqueous phase was extracted twice with dichloromethane, the combined organic extracts were washed with water, and then with saturated sodium bicarbonate solution. After drying and concentration, the crude product was purified by column chromatography [silica gel (10 g); petroleum ether–ethyl acetate = 6:1) afforded (2) as colorless crystals. Single crystals of (2) suitable for X-ray crystallographic analysis were obtained by recrystallization from dichloromethane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (*s*, H1), 7.46–7.44 (*d, J* = 7.80 Hz, H8), 7.34–7.31 (*m*, H5), 7.19–7.10 (*m*, H6, H7), 3.31–3.27 (*d, J* = 16.50 Hz, H4*A*), 3.12–3.11 (*tt, J*1 = 1.90 Hz, *J*2 = 1.56 Hz, *J*1′ = 1.83 Hz, *J*2′ = 1.61 Hz, H4*B*), 2.98–2.92 (*dd*, 1H, *J*1 = 7.48 Hz, *J*2 = 5.38 Hz, H2), 2.77–2.70 (*m*, H1*A*), 2.61–2.54 (*m*, H1*B*), 2.50–2.43 (*m*, H11*B*), 2.33–2.30 (*m*, H11*A*), 2.17–2.15 (*m*, H2), 1.84–1.79 (*m*, H10*B*), 1.81 (*s*, H10*A*, H13*A*, H13*B*, H13*C*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.2, 130.4, 127.0, 121.7, 119.5, 119.3, 117.7, 110.7, 107.4, 71.8, 44.1, 38.5, 30.7, 25.8, 25.76, 15.2.

Crystal data

$C_{16}H_{17}ClN_2$
$M_r = 272.77$
Monoclinic, $P2_1/c$
$a = 14.810$ (3) Å
$b = 7.940$ (10) Å
$c = 12.049$ (2) Å
$\beta = 99.99$ (10)°
$V = 1395.4$ (18) Å^3
$Z = 4$

$D_x = 1.298$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.0$–13.4°
$\mu = 0.26$ mm^{-1}
$T = 293$ (2) K
Plate, colorless
0.40 × 0.25 × 0.08 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.925$, $T_{max} = 0.979$
3055 measured reflections
2512 independent reflections
1499 reflections with $I > 2\sigma(I)$

$R_{int} = 0.038$
$\theta_{max} = 25.2°$
$h = -17 \rightarrow 17$
$k = -9 \rightarrow 1$
$l = -14 \rightarrow 0$
3 standard reflections
frequency: 3600 min
intensity decay: 1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.107$
$S = 1.05$
2512 reflections
189 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0479P)^2 + 0.3507P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

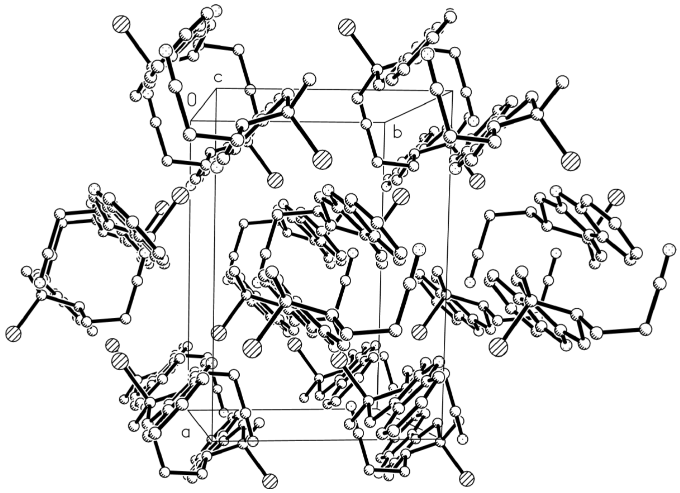

Figure 2
A view, approximately down the *c* axis, of the packing of (2).

Table 1
Selected geometric parameters (Å, °).

Cl1—C3	1.839 (2)	N2—C12	1.130 (4)
C4*A*—C9*A*—C1	125.6 (2)	C4—C3—C2	110.87 (18)
C4—C3—C2—C1	−58.0 (2)	C13—C3—C2—C10	50.0 (3)

All H atoms were positioned geometrically and refined as riding, with isotropic displacement parameters 1.2–1.5 times U_{eq} of the parent atom. The distances to H atoms were in the range 0.86–0.98 Å.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1996); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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