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Ethyl 9*H*-1,2,3,4-tetrahydrocarbazole-3-carboxylate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.043
wR factor = 0.115
Data-to-parameter ratio = 9.5

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

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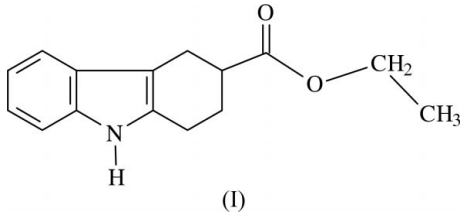
The title compound, $C_{15}H_{17}NO_2$, consists of a tetrahydrocarbazole skeleton with a carboxyethyl group at position 3. Molecules are linked about inversion centres by N—H···O hydrogen bonds [N···O 2.908 (4) Å] to form centrosymmetric dimers.

Comment

Tetrahydrocarbazole derivatives can be considered to be synthetic precursors of cyclic indole-type alkaloids of biological interest (Phillipson & Zenk, 1980; Saxton, 1983; Abraham, 1975). They have tricyclic ring systems, as in the strychnose type of indole alkaloids (Bosch & Bonjoch, 1988).

The structures of tetrahydrocarbazole derivatives having different substituents at different positions of the carbazole core have been the subject of much interest in our laboratory. These include ethyl 4-methyl-9*H*-carbazole-3-carboxylate, (II) (Hökelek *et al.*, 2002), 2-(1,2,3,4-tetrahydrocarbazol-2-yl)-butylamine, (III) (Hökelek *et al.*, 2001*a*), 4-methylcarbazole-3-carboxylic acid, (IV) (Hökelek *et al.*, 2001*b*), 1-benzyloxy-1,2,3,4-tetrahydrocarbazole, (V) (Hökelek *et al.*, 2000), *N*-(1,2,3,4-tetrahydrocarbazole-1-yl)-2-methoxyacetamide, (VI) (Hökelek & Patır, 2000*a*), 2,3-dihydro-3-ethyl-9-(phenylsulfonyl)carbazole-4(1*H*)-one, (VII) (Hökelek & Patır, 2000*b*), *N*-(2,2-dimethoxyethyl)-*N*-(9-methoxymethyl-1,2,3,4-tetrahydrospiro[carbazole-1,2′-[1,3]dithiolan]-4-yl)benzamide, (VIII) (Hökelek & Patır, 1999), 9-acetonyl-3-ethylidene-1,2,3,4-tetrahydrospiro[carbazole-1,2′-[1,3]dithiolan]-4-one, (IX) (Hökelek *et al.*, 1999), spiro[carbazole-1(2*H*),2′-[1,3]dithiolan]-4(3*H*)-one, (X) (Hökelek *et al.*, 1998), *N*-(2-methoxymethyl)-*N*-(2,3,4,9-tetrahydrospiro[1*H*-carbazole-1,2-(1,3) dithiolan]-4-yl)benzenesulfonamide, (XI) (Patır *et al.*, 1997), 2,3-dihydro-9-(phenylsulfonyl)carbazole-4(1*H*)-one, (XII) (Hökelek *et al.*, 1994) and 1,2,3,4-tetrahydrocarbazole-1-spiro-2′-[1,3]dithiolane (XIII) (Hökelek *et al.*, 1994).



(I)

Tetrahydrocarbazole derivatives have an important role in the synthesis of indole alkaloids (Fritz *et al.*, 1993; Magnus *et al.*, 1992; Ergün *et al.*, 2000). Synthesizing indole-type alkaloids by substitution at different positions is currently under investigation (Patır *et al.*, 1997). Ellipticine, olivacine and their analogues have attracted much interest due to their anti-

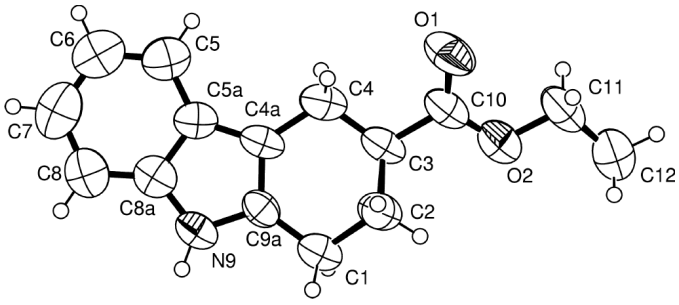


Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of the title molecule, with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

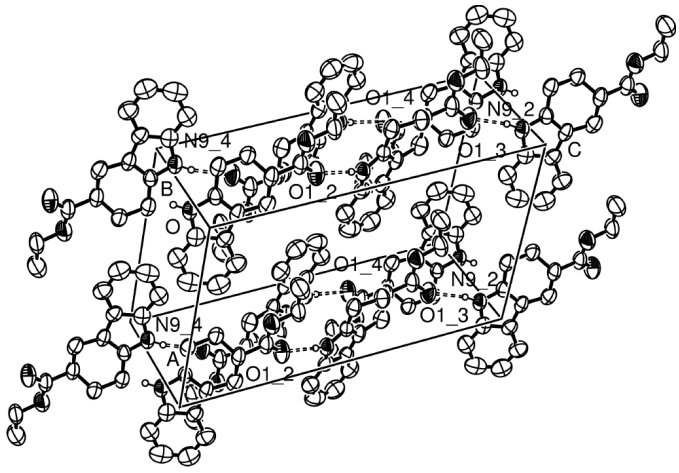


Figure 2
A packing diagram for (I). Hydrogen bonds are shown as dashed lines and H atoms not involved in hydrogen bonding have been omitted.

tumour and antileukaemic activities (Svoboda *et al.*, 1968) and many elegant methods for the synthesis of ellipticine and related pyrido-carbazole alkaloids have been reported (Kansal & Potier, 1986; Ishikura *et al.*, 2000; Ergün *et al.*, 1998). The title compound, (I), may be a useful precursor for the synthesis of pyrido-carbazole alkaloids.

The present structure determination of (I) was undertaken in order to understand the effects of the carboxyethyl group on the geometry of the carbazole skeleton, and to compare the results with those obtained for previously reported tetrahydrocarbazole derivatives.

Compound (I) (Fig. 1) contains a tetrahydrocarbazole skeleton with a carboxyethyl group as substituent at position 3. The carboxyethyl group has an electron-withdrawing effect. As can be seen from the packing diagram (Fig. 2), there are intermolecular hydrogen bonds between the carbonyl O atoms and NH groups of neighbouring molecules [$O1^{i}\cdots H9(N9)$ 2.09 (3) Å and $N9-H9\cdots O1^{i}$ 168 (3)°; symmetry code: (i) x, $-y+\frac{3}{2}$, $z+\frac{1}{2}$]. These intermolecular hydrogen bonds cause dimerization of the substituted carbazole molecules. Dipole-dipole and van der Waals interactions are also effective in the molecular packing. Intermolecular interactions may also cause increases in the angles C5*A*—C8*A*—C8 [122.7 (4)°], C1—C9*A*—N9 [125.1 (4)°], C8—C8*A*—N9 [130.8 (4)°], C5—C5*A*—C4*A* [133.8 (4)°], C4—C4*A*—C5*A* [129.1 (4)°], C4—C4*A*—C9*A* [123.9 (5)°], C1—C9*A*—C4*A* [125.3 (4)°] and decreases in the angles C9*A*—C1—C2 [108.7 (3)°], C1—C2—C3 [112.6 (3)°], C2—C3—C4 [112.4 (3)°] and C3—C4—C4*A* [111.2 (4)°].

The absence of any protecting group at atom N9 causes shortening of the C—N bonds [N9—C8*A* 1.377 (5) and N9—C9*A* 1.378 (4) Å]. These may be compared with the corresponding values [1.397 (4) and 1.360 (4) Å] in (II), [1.376 (4) and 1.391 (4) Å] in (VIII), [1.377 (2) and 1.396 (2) Å] in (IX), [1.382 (10) and 1.355 (3) Å] in (X), [1.390 (10) and 1.404 (9) Å] in (XI), [1.423 (5) and 1.412 (5) Å] in (XII) and [1.372 (5) and 1.392 (5) Å] in (XIII).

The carboxyethyl group in (I) cause notable changes in the geometry of the carbazole core, leading to increases in the angles C2—C3—C4, C4—C4*A*—C5*A*, C3—C4—C4*A*, C1—C9*A*—N9, C4*A*—C5*A*—C5 and decreases in C4—C4*A*—C9*A*, N9—C8*A*—C8 angles (Table 1), compared with the corresponding values in compounds (II), (IX), (X), and (XII) (Table 2).

In conclusion, the types of groups, depending on their electron-releasing or electron-donating properties, and their substitution positions, have a significant effect on the geometry of the carbazole system.

An examination of the deviations from the least-squares planes through the individual rings shows that rings *A* (C5*A*/C5–C8/C8*A*) and *B* (C4*A*/C5*A*/C8*A*/N9/C9*A*) are nearly planar, while ring *C* (C1–C4/C4*A*/C9*A*) is, of course, non-planar. The dihedral angles between the least-squares planes are *A*/*B* = 1.54 (13)°, *A*/*C* = 6.72 (12)° and *B*/*C* = 5.57 (12)°. Ring *C* has a local pseudo-twofold axis running through the midpoints of the C2—C3 and C9*A*—C4*A* bonds.

Experimental

The title compound, (I), was prepared from an ethyl 4-oxocyclohexane carboxylate (2.5 g, 14.70 mmol) and phenylhydrazine hydrochloride (2.33 g, 16.11 mmol) mixture in absolute ethanol (50 ml), which was refluxed for 6 h under an argon atmosphere. The solvent was removed under reduced pressure. The crude product was dissolved in chloroform and washed with hydrochloric acid (50 ml, 50%) and sodium carbonate (50 ml, 10%). After the organic layer was dried with anhydrous magnesium sulfate, the solvent was evaporated and the residue was crystallized from ethanol (yield 2.80 g, 78%), m.p. 369 K.

Crystal data

$C_{15}H_{17}NO_2$
M_r = 243.30
Monoclinic, $P2_1/c$
a = 10.2221 (10) Å
b = 7.5133 (10) Å
c = 17.539 (2) Å
β = 101.603 (9)°
V = 1319.5 (3) Å^3
Z = 4
D_x = 1.225 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10–18°
μ = 0.08 mm^{-1}
T = 293 (2) K
Rod, colourless
0.30 × 0.15 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.976, T_{max} = 0.988
2686 measured reflections
2686 independent reflections
653 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 26.3°
$h = -12 \rightarrow 0$
$k = 0 \rightarrow 9$
$l = -18 \rightarrow 21$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.115
S = 0.92
1583 reflections
167 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0459P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.11 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C9*A*—C4*A*	1.352 (4)	C3—C2	1.516 (4)
C9*A*—N9	1.378 (4)	C8*A*—C8	1.381 (5)
C9*A*—C1	1.478 (4)	C8*A*—C5*A*	1.407 (5)
O2—C10	1.329 (4)	C4*A*—C5*A*	1.419 (5)
O2—C11	1.448 (4)	C4*A*—C4	1.477 (4)
N9—C8*A*	1.377 (5)	C5*A*—C5	1.391 (5)
C10—O1	1.206 (4)	C5—C6	1.372 (5)
C10—C3	1.503 (5)	C11—C12	1.475 (5)
C1—C2	1.528 (4)	C7—C8	1.384 (5)
C3—C4	1.516 (5)	C7—C6	1.400 (5)
C4*A*—C9*A*—C1	125.3 (4)	C9*A*—C4*A*—C4	123.9 (5)
N9—C9*A*—C1	125.1 (4)	C5*A*—C4*A*—C4	129.1 (4)
C9*A*—C1—C2	108.7 (3)	C4*A*—C4—C3	111.2 (4)
C4—C3—C2	112.4 (3)	C3—C2—C1	112.6 (3)
N9—C8*A*—C8	130.8 (4)	C5—C5*A*—C8*A*	118.4 (5)
C8—C8*A*—C5*A*	122.7 (4)	C5—C5*A*—C4*A*	133.8 (4)
C9*A*—C4*A*—C5*A*	107.0 (4)	C8*A*—C5*A*—C4*A*	107.8 (4)
C4*A*—C9*A*—C1—C2	17.6 (4)	C1—C9*A*—C4*A*—C4	−0.6 (5)
O1—C10—C3—C4	8.8 (5)	C9*A*—C4*A*—C4—C3	11.7 (4)
O2—C10—C3—C4	−172.3 (3)	C2—C3—C4—C4*A*	−40.3 (4)
O1—C10—C3—C2	−118.6 (4)	C4—C3—C2—C1	60.3 (4)
O2—C10—C3—C2	60.4 (4)	C9*A*—C1—C2—C3	−46.1 (4)

Table 2
Comparison of the bond angles (°) in the carbazole core of (I) with the corresponding values in the related compounds (II), (IX), (X) and (XII).

Angles	(I)	(II)	(IX)	(X)	(XII)
C2—C3—C4	112.4 (3)	119.4 (3)	115.1 (2)	114.7 (2)	114.6 (5)
C4—C4*A*—C5*A*	129.1 (4)	133.6 (2)	127.5 (2)	130.9 (2)	130.4 (4)
C3—C4—C4*A*	111.2 (4)	117.6 (2)	114.6 (2)	115.9 (2)	116.5 (4)
C1—C9*A*—N9	125.1 (4)	128.7 (3)	127.5 (2)	126.4 (2)	126.8 (4)
C4*A*—C5*A*—C5	133.8 (4)	135.1 (3)	134.0 (3)	134.7 (2)	132.2 (4)
C4—C4*A*—C9*A*	123.9 (5)	120.8 (3)	124.5 (2)	122.0 (2)	121.5 (4)
N9—C8*A*—C8	130.8 (4)	128.1 (3)	129.4 (3)	129.8 (2)	131.0 (4)

Atom H9 was located in a difference map and refined isotropically; the positions of the other H atoms were calculated geometrically at distances of 0.93 and 0.98 (CH), 0.97 (CH_2) and 0.96 (CH_3) Å from the attached C atoms, and a riding model was used during the refinement process.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

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