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4-Methylcarbazole-3-carboxylic acid

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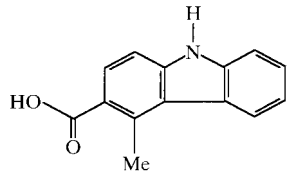
The title compound, $C_{14}H_{11}NO_2$, consists of a carbazole skeleton with carboxylic acid and methyl groups at positions 3 and 4, respectively. Molecules are linked about inversion centres by O—H···O hydrogen bonds [O···O 2.620 (3) Å] to form centrosymmetric dimers.

Comment

The structures of 1,2,3,4-tetrahydrocarbazole derivatives with different substituents bonded at different positions of the carbazole core have been the subject of much interest in our laboratory. Examples include 1-benzyloxy-1,2,3,4-tetrahydrocarbazole, (II) (Hökelek *et al.*, 2000), *N*-(1,2,3,4-tetrahydrocarbazole-1-yl)-2-methoxyacetamide, (III) (Hökelek & Patır, 2000), *N*-(2,2-dimethoxyethyl)-*N*-{9-methoxymethyl-1,2,3,4-tetrahydro-spiro[carbazole-1,2′-[1,3]dithiolan]-4-yl}benzamide, (IV) (Hökelek & Patır, 1999), 9-acetonyl-3-ethylidene-1,2,3,4-tetrahydrospiro[carbazole-1,2′-[1,3]dithiolan]-4-one, (V) (Hökelek *et al.*, 1999), spiro[carbazole-1(2*H*),2′-[1,3]dithiolan]-4(3*H*)-one, (VI) (Hökelek *et al.*, 1998), *N*-(2-methoxymethyl)-*N*-{2,3,4,9-tetrahydrospiro[1*H*-carbazole-1,2-[1,3]dithiolan]-4-yl}benzenesulfonamide, (VII) (Patır *et al.*, 1997), and 2,3-dihydro-9-(phenylsulfonyl)carbazole-4(1*H*)-one and 1,2,3,4-tetrahydrocarbazole-1-spiro-2′-[1,3]dithiolane, (VIII) and (IX), respectively (Hökelek *et al.*, 1994).

Tetrahydrocarbazole derivatives are present in the framework of indole-type alkaloids of biological interest (Phillipson & Zenk, 1980; Saxton, 1983; Abraham, 1975). Olivacine, ellipcitine and their 9-oxygenated derivatives have attracted much interest due to their antitumour activities, and many elegant methods for the synthesis of ellipcitine and related pyrido–carbazole alkaloids have been reported (Harada *et al.*, 1997). The title compound, (I), is an intermediate in the total synthesis of 5-demethylellipcitine (Ergün *et al.*, 1998). The present structure determination of (I) was undertaken in order to understand the effects of carboxylic acid and methyl groups on the geometry of the carbazole skeleton, and to compare the results obtained with those of previously reported tetrahydrocarbazole derivatives.



(I)

Compound (I) (Fig. 1) contains a carbazole skeleton with a carboxylic acid and a methyl group bonded as substituents at positions 3 and 4, respectively. It is known that the carboxylic acid group has a strong electron-withdrawing effect, while the methyl group interacts with atoms H51(C5) [H51···H101(C10) 1.894 (3) Å] and O2 [O2···H103(C10) 2.586 (2) Å], causing increases in the exocyclic angles C4—C4a—C5a [133.2 (2)°], C5—C5a—C4a [136.2 (2)°], C3—C4—C10 [124.6 (2)°] and C4—C3—C11 [123.0 (2)°], and decreases in the endocyclic angles C3—C4—C4a [117.1 (2)°] and C5—C5a—C8a [117.9 (2)°]. As can be seen from the packing diagram (Fig. 2), there are intermolecular hydrogen bonds between the carbonyl O atoms and the hydroxy H atoms of neighbouring molecules [$O2^{i}\cdots H1(O1)$ 1.59 (5) Å and O1—$H1\cdots O2^{i}$ 171 (5)°; symmetry code: (i) $-x-1, -y, 1-z$]. These strong intermolecular hydrogen bonds cause dimerization of the substituted carbazole molecules. Dipole–dipole and van der Waals interactions are also effective in the molecular packing.

The absence of any protecting group at atom N9 causes shortening of the C—N bonds. In the carbazole skeleton, the N9—C8a [1.376 (3) Å] and N9—C9a [1.373 (3) Å] bond lengths are shorter than the corresponding values in compounds (VII) [1.390 (10) and 1.404 (9) Å] and (VIII) [1.423 (5) and 1.412 (5) Å]. On the other hand, N9—C9a is nearly the same and N9—C8a is shorter when compared with the corresponding values in compounds (IV) [1.376 (4) and 1.391 (4) Å], (V) [1.377 (2) and 1.396 (2) Å] and (IX) [1.372 (5) and 1.392 (5) Å], and N9—C9a is a little longer than in compound (VI) [1.381 (2) and 1.355 (2) Å].

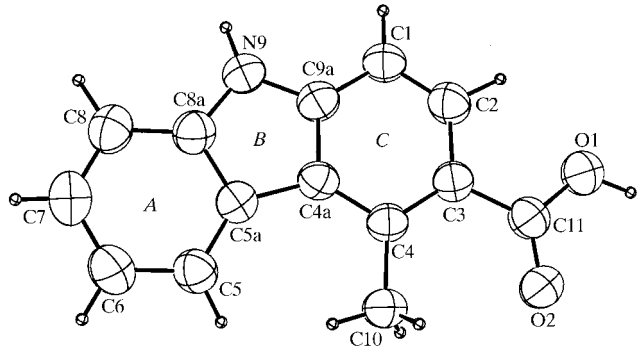


Figure 1
An *ORTEP*II (Johnson, 1976) drawing of (I) with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

The carboxylic acid and methyl groups in (I) cause notable changes in the geometry of the carbazole core, leading to increases in the angles C2—C3—C4, C4—C4a—C5a, C3—C4—C4a, C1—C9a—N9 and C4a—C5a—C5, and decreases in the angles C4—C4a—C9a and N9—C8a—C8 (Table 1), compared with the corresponding values in compounds (IV), (V), (VI), (VIII) and (IX) (Table 2).

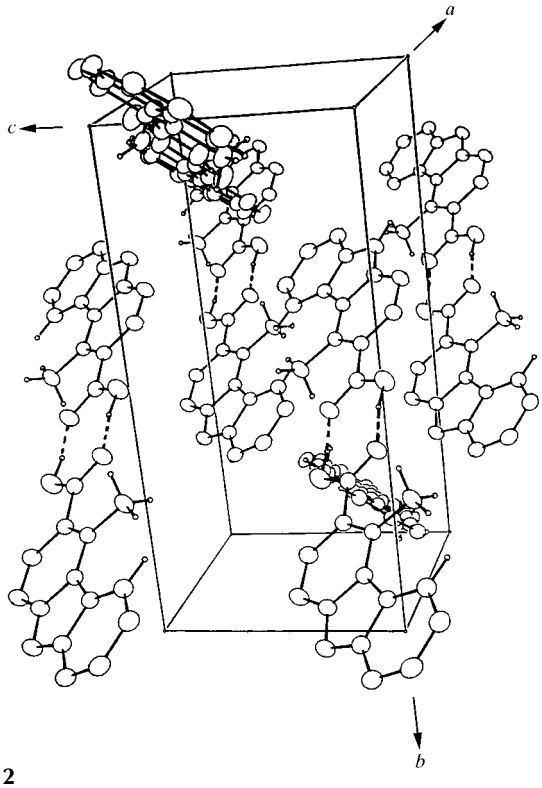


Figure 2
The packing diagram for (I). Hydrogen bonds are shown as dotted lines and H atoms not involved in hydrogen bonding have been omitted.

In conclusion, the types of substituent groups, depending on their electron-releasing or electron-donating properties and their bonding 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*, *B* and *C* are nearly coplanar. Ring *C* has a local pseudo-mirror running along C3···C9a.

Experimental

The title compound, (I), was prepared from ethyl 4-methylcarbazole-3-carboxylate (2.0 g, 7.90 mmol) and potassium hydroxide solution (20 ml, 20%) in methanol–water (1:1). The mixture was refluxed for 3 h. After evaporation of the methanol, the residue was acidified with HCl (10%) and extracted with ethyl acetate. The organic layer was dried with magnesium sulfate and the solvent was evaporated. The product was recrystallized from a dichloromethane–cyclohexane solution.

Crystal data

$C_{14}H_{11}NO_2$
M_r = 225.25
Monoclinic, $P2_1/c$
a = 7.573 (1) Å
b = 17.750 (1) Å
c = 8.277 (1) Å
β = 93.53 (1)°
V = 1110.5 (2) Å^3
Z = 4
D_x = 1.347 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 21–43°
μ = 0.737 mm^{-1}
T = 298 K
Rod, yellow
0.3 × 0.2 × 0.2 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (*MolEN*; Fair, 1990)
T_{min} = 0.731, T_{max} = 0.863
2532 measured reflections
2268 independent reflections
1833 reflections with $F > 3\sigma(F)$
R_{int} = 0.015
θ_{max} = 74.35°
$h = -9 \rightarrow 0$
$k = 0 \rightarrow 22$
$l = -10 \rightarrow 10$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F
R = 0.061
wR = 0.071
S = 0.87
1833 reflections
182 parameters
H atoms treated by a mixture of independent and constrained refinement
$(\Delta/\sigma)_{max}$ = 0.01
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C4a—C5a	1.461 (3)	N9—C8a	1.376 (3)
C5a—C5	1.394 (4)	N9—C9a	1.373 (3)
C11—O2	1.238 (3)	C8a—C8	1.397 (4)
C11—O1	1.293 (3)	C7—C8	1.369 (4)
C1—C2	1.366 (4)	C7—C6	1.390 (4)
C1—C9a	1.393 (4)	C5—C6	1.384 (4)
C4—C4a—C5a	133.2 (2)	C4a—C5a—C5	136.2 (2)
C4—C4a—C9a	120.6 (2)	C8a—C5a—C5	117.9 (2)
C5a—C4a—C9a	106.2 (2)	C3—C11—O2	123.6 (2)
C4a—C4—C3	117.1 (2)	C3—C11—O1	115.5 (2)
C4a—C4—C10	118.3 (2)	N9—C8a—C8	128.2 (2)
C4—C3—C2	120.4 (2)	C1—C9a—N9	128.7 (2)
C4a—C5a—C8a	105.9 (2)		

Table 2
Comparison of the bond angles (°) in the carbazole core of (I) with the corresponding values in the related compounds (IV), (V), (VI), (VIII) and (IX).

Note that one of the rings of the carbazole skeleton in (IV) is aliphatic.

Angles	(I)	(IV)	(V)	(VI)	(VIII)	(IX)
C2—C3—C4	120.4 (2)	109.9 (2)	115.1 (2)	114.7 (2)	114.6 (5)	110.5 (4)
C4—C4a—C5a	133.2 (2)	128.6 (2)	127.5 (2)	130.9 (2)	130.4 (4)	129.9 (4)
C3—C4—C4a	117.1 (2)	109.0 (2)	114.6 (2)	115.9 (2)	116.5 (4)	110.1 (4)
C1—C9a—N9	128.7 (2)	126.7 (2)	127.5 (2)	126.4 (2)	126.8 (4)	125.0 (3)
C4a—C5a—C5	136.2 (2)	134.7 (2)	134.0 (3)	134.7 (2)	132.2 (4)	133.6 (4)
C4—C4a—C9a	120.6 (2)	124.2 (3)	124.5 (2)	122.0 (2)	121.5 (4)	124.0 (4)
N9—C8a—C8	128.2 (2)	129.1 (2)	129.4 (3)	129.8 (2)	131.0 (4)	130.8 (4)

Most of the H atoms were located from the difference map and were refined isotropically. The positions of the remaining H atoms were calculated geometrically at a distance of 0.95 Å from the corresponding C atom, and a riding model was used during their refinement.

Data collection: *MolEN* (Fair, 1990); cell refinement: *MolEN*; data reduction: *MolEN*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *MolEN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *MolEN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1060). Services for accessing these data are described at the back of the journal.

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