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Form II of monoclinic methyl β-carboline-3-carboxylate

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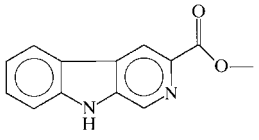
The crystal structure of the second monoclinic $P2_1/c$ form of the β-carboline-3-carboxylate, $C_{13}H_{10}N_2O_2$, has been determined. Very small changes in the packing scheme lead to a different unit cell; the role of weak C—H···O hydrogen bonds seems to be crucial.

Comment

The crystal structure of monoclinic methyl β-carboline-3-carboxylate (hereinafter referred to as BCCM) was reported twice (Bertolasi *et al.*, 1984, hereinafter BFGB; Muir & Codding, 1985, hereinafter MC). Both independent determinations were of comparable quality (reported R factors are 0.058 and 0.049 for BFGB and MC, respectively), and they described exactly the same form of BCCM; monoclinic $P2_1/c$, with mean unit-cell parameters of a = 11.477 (2), b = 5.806 (1), c = 32.400 (4) Å, β = 97.11 (2)° and Z = 8 (*i.e.* there are two symmetry-independent molecules in the asymmetric part of the unit cell).



BCCM

The discussion of the biological activity of β-carbolines and similar compounds at the benzodiazepine receptor, as well as the results of structure-activity studies of these compounds, can be found in Codding *et al.* (1988). Here, we report the crystal and molecular structure of another monoclinic form of BCCM (Fig. 1). The different unit cell [a = 9.6550 (5), b = 20.8077 (8), c = 11.0793 (5) Å and β = 102.388 (5)°] of the same space group $P2_1/c$ also contains eight molecules of BCCM, very similar to those reported earlier. The bond-length and angle patterns agree within experimental error, and on the basis of the results of the normal probability plot (Abrahams & Keve, 1971; *International Tables for X-ray Crystallography*, 1969, Vol. IV) it can be stated that the differences are random rather than systematic in nature. In both molecules, three fused rings are essentially coplanar [maximum deviations are 0.040 (2) and 0.051 (2) Å for molecules *A* and *B*, respectively], and the methyl carboxylate groups are close to coplanarity with the carboline planes [the appropriate dihedral angles are 3.9 (1) and 5.0 (1)° for both symmetry-independent molecules].

The hydrogen-bonding scheme is exactly the same in both forms: the molecules form infinite planar sheets that expand

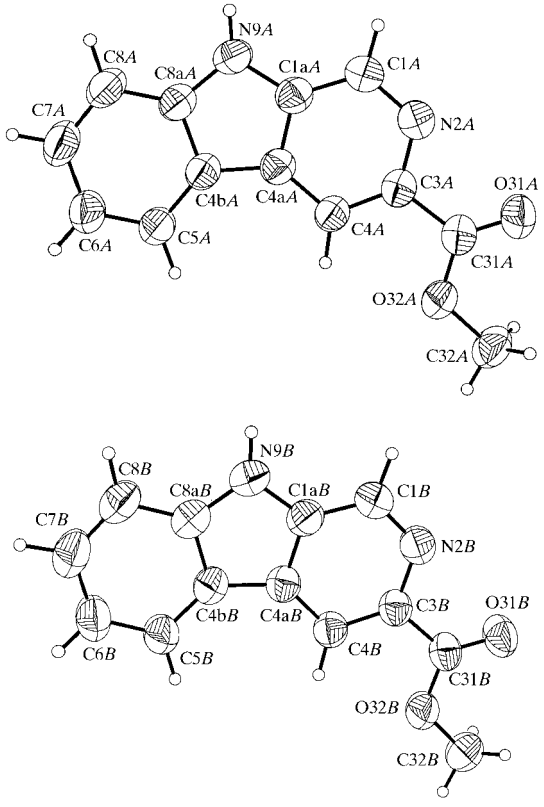


Figure 1
The molecular structure of the two independent molecules of (I) with displacement ellipsoids drawn at the 50% probability level.

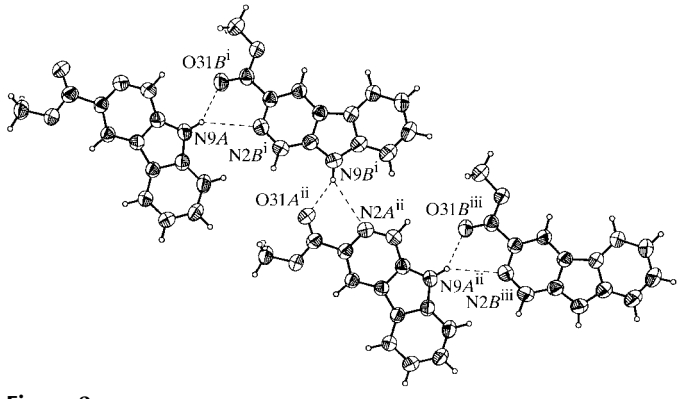


Figure 2
The hydrogen-bonded sheet (Siemens, 1989) in (I). Displacement ellipsoids are drawn at the 50% probability level and the H atoms are depicted as spheres of arbitrary radii. Hydrogen bonds are drawn as dashed lines. [Symmetry codes: (i) 1 + *x*, *y*, *z*; (ii) 1 + *x*, *y*, 1 + *z*; (iii) 2 + *x*, *y*, 1 + *z*.]

along the axis of *ca* 13 Å length ([110] in BFGB and MC , and [101] in present case, see Fig. 2). It might be noted that only the unit-cell translations are used in the formation of the sheet. The inter-sheet interactions are weak, mainly of van der Waals nature, and there is therefore a certain degree of flexibility in the orientation of the sheets with respect to the symmetry elements, hence two forms are possible within the same space group. In the present case, the neighbouring non-coplanar sheets are joined by weak C6—H6···O hydrogen bonds, while in MC and BFGB, weak C—H···O hydrogen bonds connect the parallel sheets into a centrosymmetric bilayer. This may also explain the large differences in the unit-cell parameters in MC and BFGB (longest to shortest parameter ratio of *ca* 6) compared with the present form (ratio of 2).

The geometrical parameters of the strong hydrogen bonds are quite similar; the only remarkable difference is a lack of asymmetry between the N—H···O bonds in the present case, and consequently, much longer N—H···N contacts, and the absence of a 'slip of one molecule past the other in the hydrogen-bonding plane' (Muir & Codding, 1985).

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N9A—H9A···O31B^{i}	0.88 (2)	2.06 (2)	2.840 (2)	146 (2)
N9A—H9A···N2B^{i}	0.88 (2)	2.73 (2)	3.492 (2)	145 (1)
N9B—H9B···O31A^{ii}	0.88 (2)	2.05 (2)	2.835 (2)	147 (2)
N9B—H9B···N2A^{ii}	0.88 (2)	2.72 (2)	3.476 (2)	144 (1)
C6A—H6A···O32B^{iii}	0.97 (2)	2.58 (2)	3.431 (2)	147 (1)
C6B—H6B···O31B^{iv}	0.96 (2)	2.61 (2)	3.473 (2)	150 (1)

Symmetry codes: (i) $1+x, y, z$; (ii) $x, y, 1+z$; (iii) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iv) $1+x, \frac{1}{2}-y, \frac{1}{2}+z$.

Experimental

The title compound was provided by Drs R. Coutts and R. Micetish of the Faculty of Pharmacy, University of Alberta. Colourless prismatic crystals were grown from an ethanol solution by slow evaporation.

Crystal data

$C_{13}H_{10}N_2O_2$
M_r = 226.23
Monoclinic, $P2_1/c$
a = 9.6550 (5) Å
b = 20.8077 (8) Å
c = 11.0793 (5) Å
β = 102.388 (5)°
V = 2173.99 (16) Å^3
Z = 8
D_x = 1.382 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10–38°
μ = 0.78 mm^{-1}
T = 293 (2) K
Prism, colourless
0.35 × 0.25 × 0.20 mm

Data collection

CAD-4F four-circle diffractometer
$\omega/2\theta$ scans
8604 measured reflections
4113 independent reflections
3280 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 69.9°
$h = -8 \rightarrow 11$
$k = -25 \rightarrow 25$
$l = -13 \rightarrow 11$
2 standard reflections
frequency: 33 min
intensity decay: 2%

Table 1
Selected geometric parameters (Å, °).

C1aA—N9A	1.371 (2)	C1aB—N9B	1.370 (2)
C1A—N2A	1.327 (2)	C1B—N2B	1.322 (2)
N2A—C3A	1.356 (2)	N2B—C3B	1.353 (2)
C31A—O31A	1.201 (2)	C31B—O31B	1.203 (2)
C8aA—N9A	1.375 (2)	C8aB—N9B	1.377 (2)
C1A—N2A—C3A	118.0 (1)	C1B—N2B—C3B	118.2 (1)
C1aA—N9A—C8aA	108.8 (1)	C1aB—N9B—C8aB	108.6 (1)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.099
S = 1.22
4113 reflections
393 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0300P)^2 + 0.1443P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

The H atoms of the methyl group in molecule A were found to be disordered over two positions with site-occupation factors of 0.5 each. The positional parameters of all these H atoms were refined, as was one common isotropic displacement parameter for each three-atom group.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *ENPROC* (Rettig, 1978); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1458). Services for accessing these data are described at the back of the journal.

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