# Benzyl 5-carboxy-4-ethyl-3-methyl-pyrrole-2-carboxylate

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In the title compound, $C_{16}H_{17}NO_4$, the benzyloxycarbonyl group is *anti* to the pyrrolic N atom. The molecules are joined into head-to-head dimers by hydrogen bonds involving the carboxylic acid groups. There is orientational disorder of these groups over two positions with approximately equal occupancy. A weaker hydrogen bond between the pyrrolic N atom and the carbonyl O atom of the benzyloxycarbonyl group joins the dimers into chains running parallel to the [110] direction.

## Comment

The class of pyrrole derivatives has many members and includes naturally occurring compounds with important biological functions (Battersby & McDonald, 1976). Synthesized pyrroles have been used widely in the pharmaceutical industry and are precursors in the synthesis of porphyrins and other macrocycles which are finding increasing use in the medical (Bonnet, 1995) and material sciences (Hudson *et al.*, 1993; Grieve, Hudson *et al.*, 1994; Grieve, Richardson *et al.*, 1994). The incorporation of one or several fused-pyrrole rings at the $\beta$-pyrrolic positions of porphyrins is considered to afford an efficient pathway to a molecular architecture based on fused porphyrins. With this objective in mind, the title compound, (I), was synthesized and an X-ray diffraction study was undertaken to clarify the conformation of the molecule.

(I)
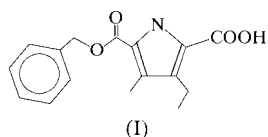
The endocyclic angles of the pyrrole ring add up to exactly 540°, indicating that the heterocycle is almost perfectly planar; in fact, no atom deviates by more than 0.0010 (15) Å from the least-squares plane. The two $Nsp^2$—C bonds are consistent with the reported average value [1.372 (16) Å; Allen *et al.*, 1987]. The largest bond distance within the heterocyclic ring is
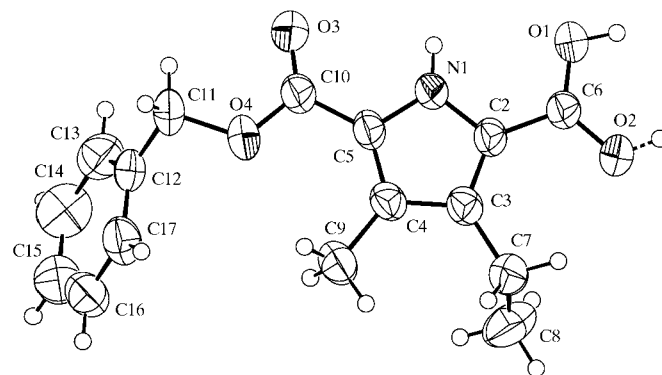


**Figure 1**
*ORTEP*II (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

that opposite the N atom [1.400 (3) Å]. Whereas the methyl C9 atom is practically within the ring plane, with a deviation of just 0.015 (5) Å, the C6, C7 and C10 atoms have small but significant deviations [C6 −0.025 (5), C7 −0.063 (5) and C10 −0.058 (5) Å].

The benzyloxycarbonyl group bonds to the pyrrole ring adopting an *anti* conformation with respect to the N atom, as shown by the N1—C5—C10—O4 torsion angle of −178.4 (2)°. The phenyl ring is planar and makes an angle of 60.89 (11)° with the carboxylate group.

The carboxylic acid group exhibits disorder around the C2—C6 single bond, as shown by the similar C6—O1 [1.264 (3) Å] and C6—O2 [1.272 (3) Å] bond lengths. This group is twisted around the C2—C6 bond by 8.2 (2)°.

The plane formed by the ethyl group and the C3 atom is almost orthogonal to the pyrrole ring, a conformation that minimizes the steric interaction between the ethyl group and the adjacent methyl and carboxylic acid groups. The observed deviation of the C2—C3—C7—C8 torsion angle [−97.9 (3)°]
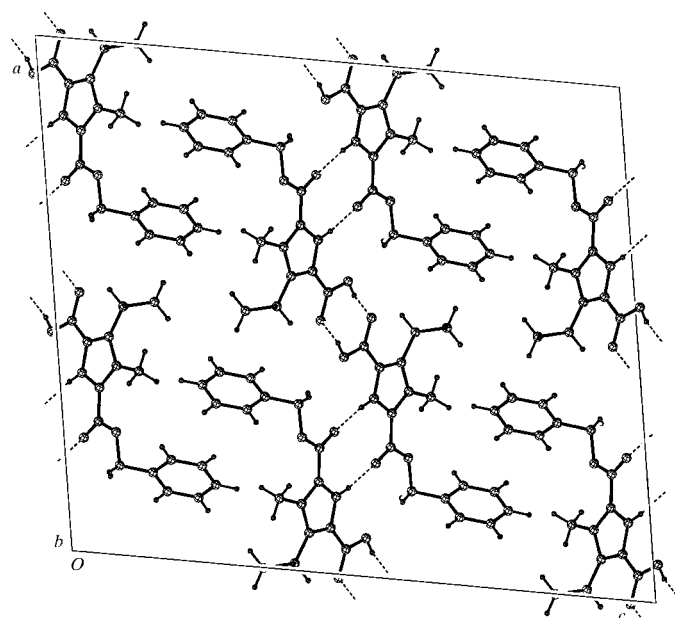


**Figure 2**
Packing of the molecules of (I) viewed down the *b* axis. The carboxylic acid H atom is disordered and only one of the alternate positions is shown for clarity.

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from orthogonality and the small observed asymmetry between the exocyclic angles at C3 appear to indicate that the steric interaction is stronger with the carboxylic acid group.

The molecules are joined into head-to-head dimers by strong hydrogen bonds involving two carboxylic acid groups [O1···O2 2.621 (3) Å]. Weaker hydrogen bonds exist between the N1 atom and the carbonyl O3 atom of the benzyloxy-carbonyl group of a neighbouring molecule. This hydrogen-bond pattern joins the molecules into infinite chains running parallel to the [110] direction. C—H···O interactions have been recognized as important secondary interactions and, in many cases, play a dominant role in the molecular confor-mation (Steiner, 1997). Two such intramolecular interactions can be identified in the present structure, *i.e.* a weak C7···O2 [3.037 (4) Å] interaction and a strong C11···O3 [2.691 (4) Å] interaction.

## Experimental

The title compound was prepared according to Archibald *et al.* (1966) from the parent 2,4-dimethyl-3-ethyl-5-carbobenzoxypyrrole by methyl chlorination with sulfuryl chloride followed by hydrolysis, giving the title compound in 60% yield. The compound was crystal-lized by slow evaporation from dichloromethane/methanol (1:1), giving small translucent plate-shaped crystals. A large number of crystals were examined by photographic methods until a specimen suitable for data collection was found. The crystal was still weakly diffracting (only ~50% of the measured reflections up to $\theta = 25°$ have $I > 2\sigma$). M.p. 437–438 K [literature 439 K (Archibald *et al.*, 1966)]; elemental analysis: calculated for $C_{16}H_{17}NO_4$: C 66.8, H 5.9, N 4.8%; found: C 65.9, H 6.0, N 4.1%.

*Crystal data*

| | |
|---|---|
| $C_{16}H_{17}NO_4$ | $D_x = 1.302$ Mg m$^{-3}$ |
| $M_r = 287.31$ | Mo $K\alpha$ radiation |
| Monoclinic, $C2/c$ | Cell parameters from 25 |
| $a = 22.195$ (6) Å | reflections |
| $b = 5.2607$ (13) Å | $\theta = 6.01$–$13.07°$ |
| $c = 25.413$ (3) Å | $\mu = 0.094$ mm$^{-1}$ |
| $\beta = 98.938$ (15)° | $T = 293$ (2) K |
| $V = 2931.3$ (11) Å$^3$ | Plate, colourless translucent |
| $Z = 8$ | $0.37 \times 0.37 \times 0.10$ mm |

*Data collection*

| | |
|---|---|
| Enraf–Nonius CAD-4 diffract-ometer | $\theta_{max} = 24.97°$ |
| $\omega$–$2\theta$ scans | $h = 0 \rightarrow 26$ |
| 2638 measured reflections | $k = 0 \rightarrow 6$ |
| 2568 independent reflections | $l = -30 \rightarrow 29$ |
| 1253 reflections with $I > 2\sigma(I)$ | 3 standard reflections |
| $R_{int} = 0.045$ | frequency: 180 min |
| | intensity decay: 1% |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0669P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.041$ | $+ 0.6191P]$ |
| $wR(F^2) = 0.129$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 0.964$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 2568 reflections | $\Delta\rho_{max} = 0.16$ e Å$^{-3}$ |
| 199 parameters | $\Delta\rho_{min} = -0.17$ e Å$^{-3}$ |
| H atoms treated by a mixture of independent and constrained refinement | |

The H atoms were placed at calculated positions and refined as riding using *SHELXL*97 defaults (N—H = 0.86 Å and C—H = 0.93–0.97 Å), except for the carboxylic acid H atom. Inspection of a

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| N1—C5 | 1.359 (3) | O4—C11 | 1.457 (3) |
| N1—C2 | 1.367 (3) | C2—C3 | 1.386 (3) |
| O3—C10 | 1.190 (3) | C3—C4 | 1.400 (3) |
| O4—C10 | 1.312 (3) | C5—C4 | 1.385 (3) |
| | | | |
| C10—O4—C11 | 119.3 (2) | O4—C10—C5 | 111.7 (3) |
| O3—C10—O4 | 123.1 (2) | O4—C11—C12 | 107.8 (2) |
| O3—C10—C5 | 125.2 (3) | | |
| | | | |
| C11—O4—C10—C5 | −176.4 (3) | C10—C5—C4—C9 | −3.8 (5) |
| N1—C5—C10—O3 | 0.8 (4) | C7—C3—C4—C9 | 3.7 (4) |
| C10—O4—C11—C12 | 129.5 (3) | | |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1···O3$^i$ | 0.86 | 2.09 | 2.942 (3) | 175 |
| O1—H1$A$···O2$^{ii}$ | 0.87 (12) | 1.77 (13) | 2.621 (3) | 168 (8) |

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

difference Fourier map showed the carboxylic acid H atom to be disordered. Refinement of the occupancy gave a 53 (8):47 (8)% occupancy ratio of the two alternate positions (attached to O1 or O2). Examination of the crystal structure with *PLATON* (Spek, 1995) showed that there are no solvent-accessible voids in the crystal lattice.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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