

# Dimer Formation in 4-Benzyl-5-Methoxymethyl-3-Methyl-1*H*-Pyrrole-2-Carboxylic Acid Benzyl Ester

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**Abstract** A new substituted pyrrole, a precursor of meso-free-porphyrins, has been synthesised and characterised by single-crystal X-ray diffraction: monoclinic,  $P2_1/c$  with  $a = 14.607(9)$  Å,  $b = 5.136(2)$  Å,  $c = 25.832(17)$  Å,  $\beta = 108.14(5)^\circ$ ,  $M_r = 349.41$ ,  $V = 1841.6(18)$  Å<sup>3</sup>,  $Z = 4$ . The molecules are assembled in centrosymmetric dimers via strong N–H...O hydrogen bonds. The dimers are gathered into chains via C–H... $\pi$  intermolecular interactions.

**Keywords** Pyrrole · Porphyrin · Hydrogen bond · Dimer

## Introduction

Pyrroles are important bio-molecules with significant roles in human metabolism and are also preferred synthons in macromolecular chemistry [1, 2] with large applicability in medicinal chemistry [3–5] and materials science [6–8].

As a continuation of our work in pyrrole [9–13] and dipyrromethane [14, 15] chemistry, we have prepared the title compound. This new compound is going to be used in the synthesis of catalysts (heme related meso-free-porphyrins) of oxidation reactions. Previous studies have

shown that the corresponding manganese metallocomplexes presented an exceptional activity as epoxidation catalysts [16, 17]. That activity was not fully exploited due to their short lifetime in the reaction medium, opening the way to more research. Efforts are now being made to keep the high catalytic activity of porphyrins and improve their lifetime in the reaction medium by changing the chemical motifs inserted at the pyrrolic peripheral positions of the porphyrin macrocycle.

## Experimental

Preparation of 4-Benzyl-5-Methoxymethyl-3-Methyl-1*H*-Pyrrole-2-Carboxylic Acid Benzyl Ester

The title compound 4-benzyl-5-methoxymethyl-3-methyl-1*H*-pyrrole-2-carboxylic acid benzyl ester was prepared by acid solvolysis in methanol/HCl (5% w/w) of the 5-acetoxymethyl-4-benzyl-3-methyl-1*H*-pyrrole-2-carboxylic acid benzyl ester. This acetoxyated pyrrole was obtained by acetoxylation, with lead tetra-acetate in acetic acid, of the parent 4-benzyl-3,5-dimethyl-1*H*-pyrrole-2-carboxylic acid benzyl ester, prepared by the Knorr reaction of benzil acetoacetate and 3-methylphenyl-2,4-pentanedione.

The title compound was then recrystallized by slow evaporation of solvent from a dichloromethane/ethanol (1:1) solution, giving pale yellow rectangular crystals. Before data collection, the quality of the crystal was checked by photographic methods (Lauegrams).

## Crystal Structure Determination

A crystal of the title compound with thin plate shape and having approximate dimensions of 0.42 mm × 0.22 mm × 0.02 mm

**Electronic supplementary material** The online version of this article (doi:10.1007/s10870-007-9234-5) contains supplementary material, which is available to authorized users.

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was glued on a glass fibre and mounted on a Enraf-Nonius CAD4 diffractometer. Diffraction data were collected at room temperature 293(2) K using graphite monochromated Mo K $\alpha$  ( $\lambda = 0.71073$  Å). The unit cell parameters were determined by least-squares refinement of diffractometer angles ( $6.37 < \theta < 17.16^\circ$ ) for 24 automatically centred reflections.

Data were processed using PLATON [18] and an absorption correction [19] (psi scan) was applied which resulted in transmission factors ranging from 0.800 to 0.958. Data were corrected for Lorentz and Polarization effects. Reflections with  $2\theta \leq 51^\circ$  were used for structure solution and refinement.

The structure was solved by direct methods using SHELXS-97 [20] and refined anisotropically (non-H atoms) by full-matrix least-squares on  $F^2$  using the SHELXL-97 [20] program. All the hydrogen atoms were placed at calculated positions and allowed to ride on their parent atoms using SHELXL-97 defaults. The final least-squares cycle was based on 1,694 observed reflections [ $I > 2\sigma(I)$ ] and 237 variable parameters, converged with  $R = 0.077$  and  $wR = 0.241$ . Crystallographic details and selected interatomic distances and angles are given in Tables 1 and 2.

## Results and Discussion

### Crystal Structure of the Complex

The structure of the title compound together with the atom-numbering scheme, is illustrated in Fig. 1. The packing diagram and the formation of dimers are shown in Figs. 2 and 3 shows the assembling of the molecules in chains. Selected bond lengths and angles are listed in Table 2.

The pyrrole ring is almost planar (Fig. 1) and all intra ring torsion angles are less than  $0.6(2)^\circ$ . The intra-ring bond angles range from  $106.3(4)$  to  $110.3(4)^\circ$  which indicates that the ring is slightly distorted from  $C_{2v}$  symmetry. There is a shortening of the C1–C5 bond ( $1.421$  Å) compared to the usual  $C_{sp^2}$ – $C_{aryl}$  bonds [21] [ $1.483(15)$  Å] certainly due to the  $\pi$ -electron distribution along the pyrrole ring and the carboxylate group.

The non-H atoms of the benzyloxycarbonyl substituent, of the methyl substituent and C14 and C21 share the pyrrolic plane with a maximum deviation of  $0.166(4)$  Å (for O1) from the least-squares plane containing all of the above atoms.

On the contrary, in the related compound benzyl 5-carboxy-4-ethyl-3-methyl-pyrrole-2-carboxylate [12], the phenyl ring of the benzyloxycarbonyl group is almost perpendicular to the pyrrole ring mean plane. This difference cannot be explained by changes in the steric

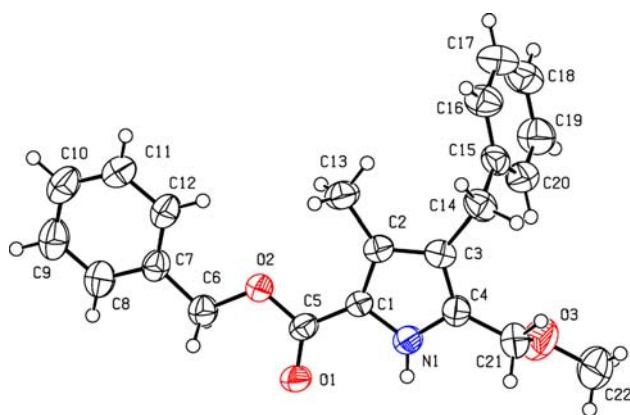
**Table 1** Summary of crystallographic results

Temperature (K)	293(2)
Empirical formula	C <sub>22</sub> H <sub>23</sub> NO <sub>3</sub>
Formula weight	349.41
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /c
<i>a</i> (Å)	14.607(9)
<i>b</i> (Å)	5.136(2)
<i>c</i> (Å)	25.832(17)
$\beta$ (°)	108.14(5)
Volume (Å <sup>3</sup> )	1841.6(18)
<i>Z</i>	4
Calculated density (g/cm <sup>3</sup> )	1.260
Absorption coefficient (mm <sup>-1</sup> )	0.084
<i>F</i> (000)	744
Crystal size (mm <sup>3</sup> )	0.39 × 0.34 × 0.16
$\theta$ Range for data collection (deg.)	1.66 – 25.48
Index ranges	–17 ≤ <i>h</i> ≤ 17, –6 ≤ <i>k</i> ≤ 6, –31 ≤ <i>l</i> ≤ 31
Reflections collected/unique	9903/3424
Completeness to $\theta = 51^\circ$	99.8%
Transmission factors (min/max)	0.800/0.958
Data/restraints/parameters	3424/0/237
Goodness-of-fit on $F^2$	1.060
Final <i>R</i> indices [ $I > 2\sigma(I)$ ]	0.077/0.180
<i>R</i> indices (all data)	0.174/0.216
Largest diff. peak and hole (e Å <sup>-3</sup> )	–0.217/0.230
CCDC Number	CCDC 649444

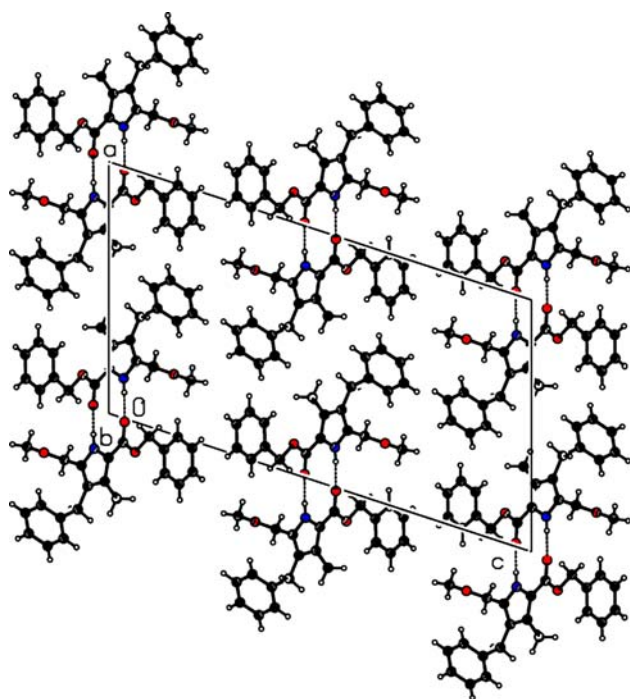
**Table 2** Selected bond lengths (Å) and angles (°)

C1–C2	1.400(6)
C2–C3	1.416(7)
C3–C4	1.386(6)
C4–N1	1.342(6)
N1–C1	1.372(6)
C4–N1–C1	110.3(4)
N1–C1–C2	107.5(4)
C1–C2–C3	106.3(4)
C4–C3–C2	107.6(4)
N1–C4–C3	108.3(4)
O1–C5–O2	121.2(4)
C2–C3–C14–C15	–77.0(6)
C3–C4–C21–O3	–96.6(6)

interaction with intramolecular neighbouring groups (they are the same in both cases) but may be attributed to different intermolecular interactions and packing efficiency.



**Fig. 1** ORTEP plot of the title compound. Displacement ellipsoids are drawn at the 50% level

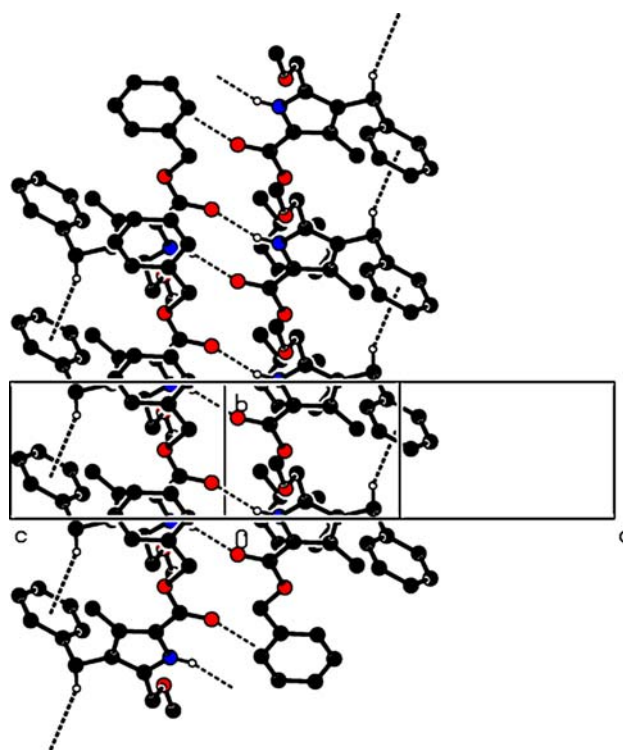


**Fig. 2** Packing diagram of the title compound showing the dimer formation. Hydrogen bonds are shown as dashed lines

However, in both compounds, the benzyloxycarbonyl group bonds to the pyrrole ring adopting an anti conformation with respect to the N atom.

The phenyl ring C15–C20 makes an angle of  $79.1(2)^\circ$  with the main molecular plane, and also adopts an anti conformation with respect to the N atom. O3 is  $1.328(4)$  Å above the main molecular plane.

The molecules are joined in head to head centrosymmetric dimers by strong hydrogen bonds, where the nitrogen atom acts as donor and the carboxylate O atom as the acceptor, a supramolecular synthon that is often observed in related compounds [9, 10, 12, 13]. These hydrogen bonds



**Fig. 3** One of the chains formed by the C–H... $\pi$  intermolecular interactions

form rings with a graph-set [22] motif of  $R_2^2(10)$  [donor-acceptor distance of  $2.842(5)$  Å and bond angle  $162.2^\circ$ ].

The dimers are aggregated in chains running along the *b* axis through C–H... $\pi$  intermolecular interactions. H14A (bonded to C14) is positioned above the phenyl  $\pi$  ring system that acts as the acceptor. The H14A-centroid distance is  $2.93$  Å and the C–H... $\pi$  angle is  $157.0^\circ$  corresponding to a geometry described as type I by Malone et al. [23], with the classical T-shaped geometry.

### Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC 649444. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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