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Key indicators

Single-crystal X-ray study

T = 130 K

Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$

R factor = 0.060

wR factor = 0.134

Data-to-parameter ratio = 14.5

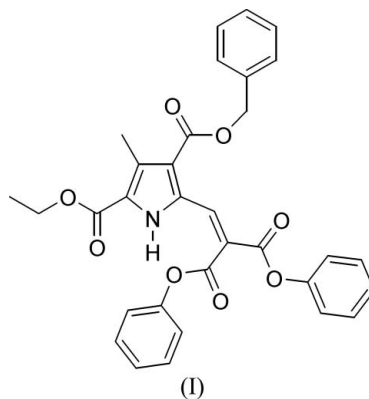
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Ethyl 4-benzyloxycarbonyl-5-[2,2-bis(benzyloxy-carbonyl)vinyl]-3-methylpyrrole-2-carboxylate

The crystal structure of the title compound, $\text{C}_{34}\text{H}_{31}\text{NO}_8$, is stabilized by intramolecular $\text{C}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds, and $\text{C}-\text{H}\cdots\pi$ and $\pi-\pi$ interactions.

Comment

Pyrroles are both important natural products and crucial starting materials for the synthesis of porphyrins (Gossauer, 1974). In the context of ongoing studies on the hydrogen-bonding pattern in pyrroles (Senge & Smith, 2005), dipyrromethanes (Senge, 2005) and porphyrins (Senge & Kalisch, 1999; Senge, 2000), we were interested in elucidating to what extent a compound such as (I), with many dipolar groups around the pyrrole ring, will participate in hydrogen-bonding interactions.



The compound forms one strong intramolecular hydrogen bond between the pyrrole NH group and atom O5 from one of the two benzyl ester groups at the vinyl substituent (Fig. 1 and Table 1). The seven-membered ring thus formed (H1/N1/C5/C51–C53/O5) is almost planar, with an average deviation from the least-squares plane of 0.046 Å. Atom O2 of the ethyl ester lies also in this plane and is separated by only 2.37 Å from H1. However, the O2–H1–N1 angle is 96° and outside the usual limits for a bonding interaction (Steiner, 1997). Thus, this orientation might be more the result of the C31–H···O1 interaction (Table 1). The other benzyl ester at the vinyl group is also fixed in a relatively coplanar arrangement with the vinyl group and the pyrrole ring. Here two weaker $\text{C}-\text{H}\cdots\text{O}$ interactions play a role. The stronger one of these is the interaction between the vinylic H51A and O3. Other close contacts, albeit with small bond angles, are C31–H31B···O4, C51–H51A···O8 and C518–H51I···O8 (see Table 1).

In the crystal structure, the molecules are arranged in polymeric chains which are connected by a close inter-

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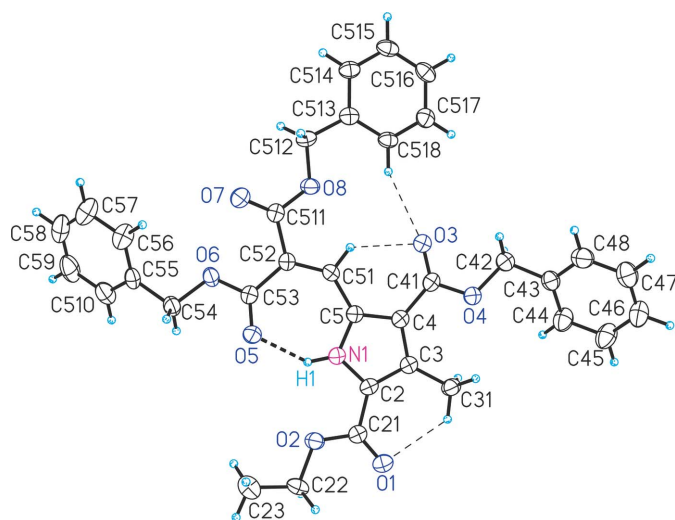


Figure 1

The molecular structure of (I). Displacement ellipsoids for the non-H atoms are drawn at the 50% probability level. The thick dashed line indicates a classical hydrogen bond $N-H\cdots O$; thin dashed lines indicate the intramolecular $C-H\cdots O$ interactions according to the criteria given by Steiner (1997).

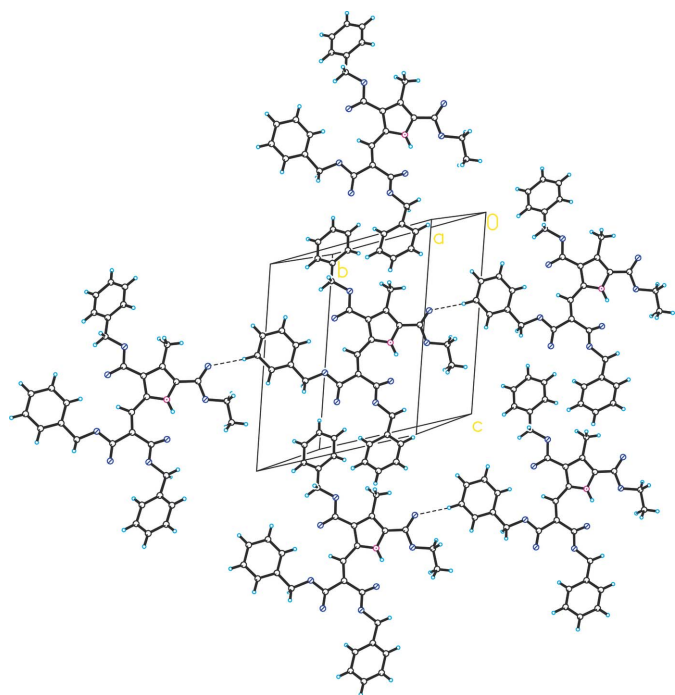


Figure 2

View of the molecular arrangement of (I) in the crystal structure. Dashed lines indicate intermolecular $C-H\cdots O$ bonding interactions within a layer.

molecular contact (2.50 Å) between the aromatic hydrogen of C515 and O1ⁱⁱ and a $C22\cdots O1^i$ contact. Table 1 ranks the different hydrogen-bonding motifs in the order suggested by Etter *et al.* (1990). In this order the nine different motifs can be described by the following graph sets: $N_1 = S(7)$, $N_2 = C(5)$, $N_3 = C(14)$, $N_4 = S(12)$, $N_5 = S(5)$, $N_6 = S(6)$, $N_7 = S(5)$, $N_8 = S(6)$, $N_9 = S(6)$. Further stabilization is achieved *via* π - π stacking of the pyrrole rings whose least-squares planes are separated by

3.32 Å and a benzylic CH_2 benzene π -ring interaction. H54A is separated from the center of the C43–C48 phenyl ring by 2.69 Å.

Experimental

Crystals were handled as described by Hope (1994). The compound was prepared as described by Senge & Smith (2005) and crystallized from CH_2Cl_2/n -hexane.

Crystal data

$C_{34}H_{31}NO_8$
 $M_r = 581.60$
 Triclinic, $P\bar{1}$
 $a = 8.966$ (3) Å
 $b = 12.037$ (3) Å
 $c = 14.349$ (4) Å
 $\alpha = 72.09$ (2)°
 $\beta = 83.67$ (2)°
 $\gamma = 82.02$ (2)°

$V = 1455.5$ (8) Å³
 $Z = 2$
 $D_x = 1.327$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.10$ mm⁻¹
 $T = 130$ (2) K
 Needle, colorless
 $0.40 \times 0.20 \times 0.16$ mm

Data collection

Siemens R3m/V diffractometer
 ω scans
 Absorption correction: none
 5965 measured reflections
 5727 independent reflections
 3812 reflections with $I > 2\sigma(I)$

$R_{int} = 0.032$
 $\theta_{max} = 26.1^\circ$
 2 standard reflections
 every 198 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.060$
 $wR(F^2) = 0.134$
 $S = 1.02$
 5727 reflections
 394 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 0.4579P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.20$ e Å⁻³
 $\Delta\rho_{min} = -0.22$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1\cdots O5$	0.91 (3)	1.89 (3)	2.668 (3)	142 (2)
$C22-H22B\cdots O1^i$	0.99	2.59	3.570 (3)	171
$C515-H51F\cdots O1^{ii}$	0.95	2.50	3.445 (3)	173
$C518-H51I\cdots O3$	0.95	2.42	3.297 (3)	154
$C518-H51I\cdots O8$	0.95	2.41	2.750 (3)	101
$C51-H51A\cdots O3$	0.95	2.27	2.961 (3)	129
$C51-H51A\cdots O8$	0.95	2.18	2.655 (3)	110
$C31-H31A\cdots O1$	0.98	2.38	3.109 (3)	131
$C31-H31B\cdots O4$	0.98	2.53	2.859 (3)	100
$C54-H54A\cdots Cg$	0.99	2.69	3.607 (3)	154

Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $x - 1, y - 1, z$. Cg is the centroid of the C43–C48 ring.

The pyrrole H atom was refined with isotropic displacement parameters. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with $C-H$ distances in the range 0.95–0.99 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for CH and CH_2 groups and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl groups.

Data collection: *P3* (Siemens, 1995); cell refinement: *P3*; data reduction: *XDISK* and *XPREP* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

XP (Siemens, 1995); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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