organic papers

Dibenzyl 5-(2-chloroethyl)-3,7-diethyl-2,8-dimethyldipyrromethane-1,9-dicarboxylate

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The structure of the title compound [systematic name: dibenzyl 3,3′-diethyl-4,4′-dimethyl-2,2′-(3-chloropropane-1,1-diyl)dipyrrole-5,5′-dicarboxylate], $C_{33}H_{37}ClN_2O_4$, was determined by single-crystal X-ray diffraction at 130 K. In the crystal structure, the compound forms hydrogen-bonded dimers. The two pyrrole H atoms are bonded to one carbonyl O atom of a symmetry-related molecule. Additional, weaker, C—H···O interactions further stabilize the dimers. The two pyrrole rings are inclined to one another by 63.57 (7)°.

Comment

Dipyrromethanes are important building blocks for porphyrin synthesis. Their chemical synthesis in the laboratory often involves the so-called 2 + 2 synthesis, where two dipyrromethane units are condensed (Lindsey, 2000). In nature, porphyrins are prepared by attaching pyrrole units to a dipyrromethane co-factor of porphobilinogen deaminase (Louie *et al.*, 1992; Hädener *et al.*, 1999). Dipyrromethane units are structural building blocks of many bilanes (Zhang *et al.*, 1998; Senge *et al.*, 2001) and calixphyrins (Sessler *et al.*, 2003).

(I)
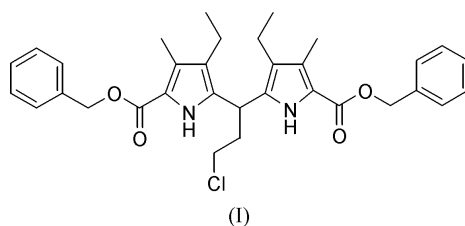
The molecular structure of the title compound, (I), is illustrated in Fig. 1 and selected bond distances and angles are given in Table 1. The two pyrrole rings are inclined to one another by 63.57 (7)°. The molecules form hydrogen-bonded dimers in the crystal structure, utilizing both pyrrole H atoms, but only one of the two carbonyl O atoms. As shown in Fig. 2, carbonyl atom O1 forms two classical hydrogen bonds with the NH units of a neighboring dipyrromethane (N1—H1···O1[i] and N2—H2···O1[i]). A search for weaker hydrogen-bonding interactions (Steiner, 1997) revealed that atom O1 is involved in a third weaker hydrogen bond involving the C51H$_2$ unit. Thus, each dimer is held together by four classical N—H···O hydrogen bonds and has two C—H···O contacts. Additional close contacts are found within each individual dipyrromethane. Ether atom O2 of one benzyl ester group is separated from the neighboring 2-methyl group by only 2.886 (3) Å, while carbonyl atom O3 of the other benzyl ester group has a close contact to C92 [2.692 (3) Å] and is weakly coordinated to the C81-methyl group. The dimers are further

connected by another weak C—H···O interaction. Besides the two intramolecular contacts, O3 is also connected inter-molecularly to aromatic atom H14 (H···A = 2.45 Å and D—H···A = 157°) to form infinite chains of the dimers (not shown). Full details of the hydrogen bonding are given in Table 2.

Related crystal structures almost exclusively involve α-unsubstituted dipyrromethanes (Lin *et al.*, 1996; Bennis & Gallagher, 1998; Gallagher & Moriarty, 1999; Arumugam *et al.*, 2001; Patra *et al.*, 2002).

Experimental

The compound was prepared as described by Lee & Smith (1997); a sample of the material was kindly provided by Kevin M. Smith (LSU, Baton Rouge) and crystallized from CH_2Cl_2/n-hexane. Crystals were handled as described by Hope (1994).

Crystal data

$C_{33}H_{37}ClN_2O_4$	$Z = 2$
$M_r = 561.10$	$D_x = 1.248$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.514$ (4) Å	Cell parameters from 40
$b = 13.361$ (6) Å	reflections
$c = 14.020$ (5) Å	$\theta = 19$–23°
$\alpha = 92.84$ (3)°	$\mu = 0.17$ mm^{-1}
$\beta = 101.53$ (3)°	$T = 130$ (2) K
$\gamma = 105.96$ (3)°	Block, colorless
$V = 1493.2$ (11) Å^3	$0.50 \times 0.45 \times 0.39$ mm

Data collection

Siemens $R3m/V$ diffractometer	$R_{int} = 0.041$
ω scans	$\theta_{max} = 27.5°$
Absorption correction: refined from	$h = -11 \rightarrow 10$
ΔF (XABS2; Parkin *et al.*, 1995)	$k = -17 \rightarrow 17$
$T_{min} = 0.909$, $T_{max} = 0.939$	$l = 0 \rightarrow 18$
7317 measured reflections	2 standard reflections
6854 independent reflections	every 198 reflections
5327 reflections with $I > 2\sigma(I)$	intensity decay: 1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.048P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.045$	$+ 0.6397P]$
$wR(F^2) = 0.117$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
6854 reflections	$\Delta\rho_{max} = 0.26$ e Å^{-3}
365 parameters	$\Delta\rho_{min} = -0.35$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

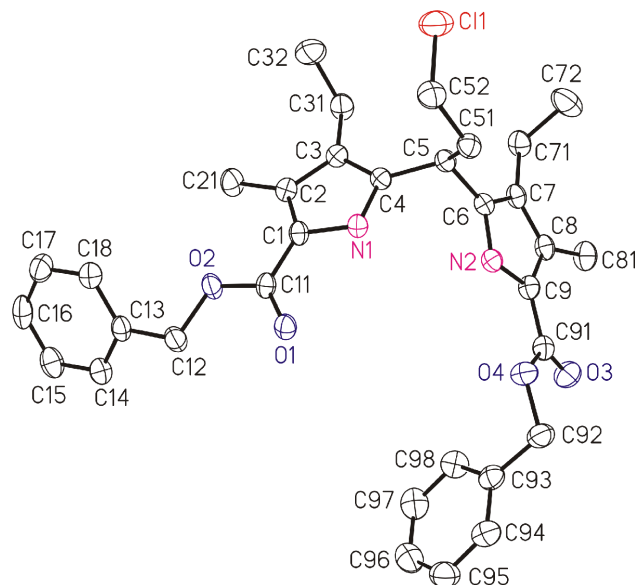|			
N1—C4	1.362 (2)	N2—C6	1.356 (2)
N1—C1	1.3793 (19)	N2—C9	1.380 (2)
C1—C2	1.387 (2)	C6—C7	1.391 (2)
C2—C3	1.416 (2)	C7—C8	1.415 (2)
C3—C4	1.389 (2)	C8—C9	1.391 (2)
C4—C5	1.508 (2)	C51—C52	1.506 (2)
C5—C6	1.506 (2)	C52—Cl1	1.796 (2)
C5—C51	1.538 (2)		
C4—N1—C1	109.47 (13)	C6—N2—C9	109.64 (13)
N1—C4—C5—C6	71.21 (18)	C51—C5—C6—N2	62.76 (19)
C3—C4—C5—C6	−105.77 (18)	C4—C5—C6—C7	116.31 (17)
N1—C4—C5—C51	−56.19 (19)	C51—C5—C6—C7	−115.74 (18)
C3—C4—C5—C51	126.83 (17)	C5—C51—C52—Cl1	−62.05 (17)

Figure 1
A view of (I). Displacement ellipsoids are drawn at the 50% probability level; and H atoms have been omitted for clarity.
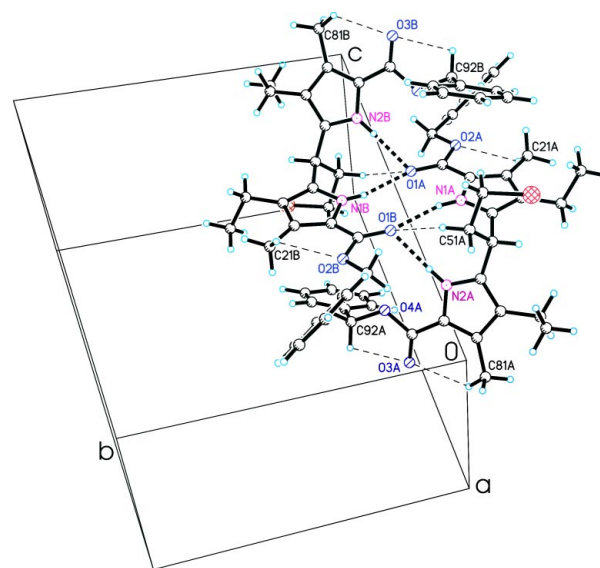

Figure 2
View of the hydrogen-bonded dimers of (I) in the crystal structure. Full dashed lines indicate strong N—H···O hydrogen bonds, thin dashed lines indicate C—H···O bonding interactions (see Table 2 for details).

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^i	0.88	2.10	2.966 (2)	167
N2—H2···O1^i	0.88	2.03	2.893 (2)	166
C5—H5···Cl1	1.00	2.75	3.204 (2)	108
C14—H14···O3^{ii}	0.95	2.45	3.340 (3)	157
C21—H21A···O2	0.98	2.51	2.886 (2)	103
C51—H51A···O1^i	0.99	2.57	3.489 (3)	154
C81—H81C···O3	0.98	2.47	3.141 (3)	125
C92—H92B···O3	0.99	2.31	2.692 (3)	102

Symmetry codes: (i) $2 - x, 2 - y, 1 - z$; (ii) $3 - x, 2 - y, 1 - z$.

H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.95–1.00 Å and N—H distances of 0.88 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$ for CH, CH$_2$ and pyrrole H atoms, and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl groups.

Data collection: *P3* (Siemens, 1995); cell refinement: *P3*; data reduction: *XDISK* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); 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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