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Ethyl 4-dodecyl-3,5-dimethyl-1*H*-pyrrole-2-carboxylate: intermolecular interactions in an amphiphilic pyrrole

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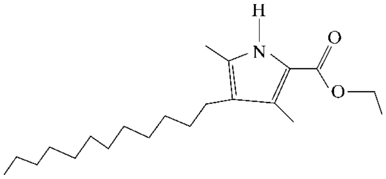
The title compound, $C_{21}H_{37}NO_2$, is a new amphiphilic pyrrole with a long hydrocarbon chain, which will be used as a precursor for the synthesis of Langmuir–Blodgett films of porphyrins. Molecules related by an inversion centre are joined head-to-head into dimers by strong N—H···O hydrogen bonds. The dimers pack in the structure with their carbon chains parallel to one another, thereby forming alternating layers of carbon chains and pyrrole heads. The structure is further stabilized by two weak C—H···π intermolecular interactions, thereby saturating the hydrogen-bonding capability of the aromatic π-electron clouds.

Comment

Pyrroles are important as pharmaceutical agents, monomers for polymer chemistry, and precursors of porphyrins and related macrocycles, and have been studied intensely in recent decades (Baltazzi & Krimen, 1963; Chadwick, 1990). The porphyrin core is a system of four pyrrole rings. This ring system plays an important role in the chemistry of living organisms, appearing in chlorophylls, haemoglobin and myoglobin proteins. New and exciting research into porphyrin materials seeks to design novel polymers with the potential to behave as electrical conductors and semiconductors (Reimers *et al.*, 1996, 1999). Studies in the areas of molecular switching devices, molecular shift-registers and non-linear optics (Hush *et al.*, 1998, Kadish *et al.*, 2002) are also flourishing. For instance, the possibility of using redox-active organic monolayers as molecular-scale information storage systems is being considered (Crossley *et al.*, 1995), where the information is stored in the oxidation state. For many of these applications, molecular films of porphyrins are required. Assembling highly ordered molecular films is easiest with the Langmuir–Blodgett technique, which involves transferring monolayers of molecules with an amphiphilic tail, floating on a water surface, to a solid substrate (Pitt & Walpita, 1980; Vincent & Roberts, 1980; Ruaudel-Teixier *et al.*, 1983; Ohtake *et al.*, 1992; Palto *et al.*, 1992). Porphyrins substituted with long hydrocarbon chains have already been shown to form stable films (Hudson *et al.*, 1993). Following previous structural studies on pyrrole chemistry (Ramos Silva *et al.*, 2000*b*) and on the deposition of porphyrins in Langmuir–Blodgett films (Richardson *et al.*, 1998), the title compound, (I), was synthesized with the intention of using it as a precursor of new amphiphilic porphyrins, and its structure is now reported.



(I)

The pyrrole ring in (I) is almost planar (Fig. 1) and all intra-ring torsion angles are less than 0.1 (2)°. The intra-ring bond angles range from 106.83 (16) to 109.95 (15)°, which indicates that the ring is slightly distorted from C_{2v} symmetry. The non-H atoms of the two methyl and ethoxycarbonyl substituents share the pyrrole plane, with a maximum deviation of 0.038 (3) Å (for O1) from the least-squares plane of the pyrrole ring. Atom C10 of the dodecyl chain is also only 0.032 (3) Å from this plane. Although rotation around the C1—C5 bond is possible, the conformation adopted by the ethoxycarbonyl group is that which is usually found in similar compounds (Bonnet *et al.*, 1972, Yamamoto *et al.*, 1986), with the ethyl group *trans* to atom N1.

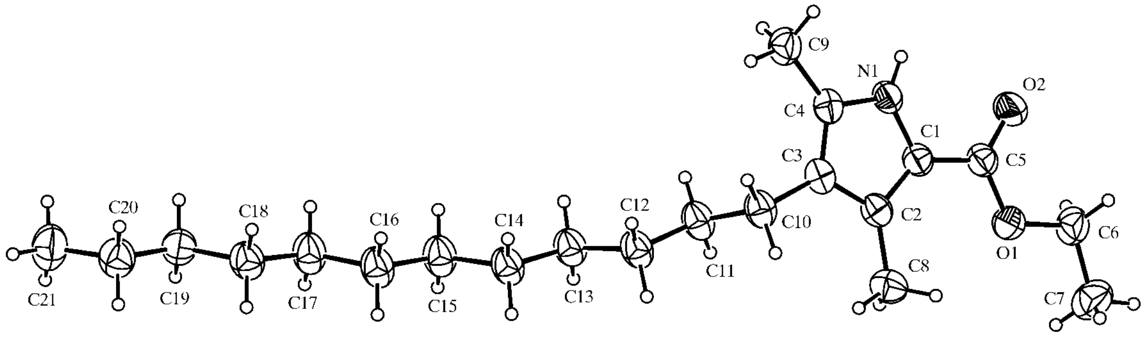


Figure 1
*ORTEP*II (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

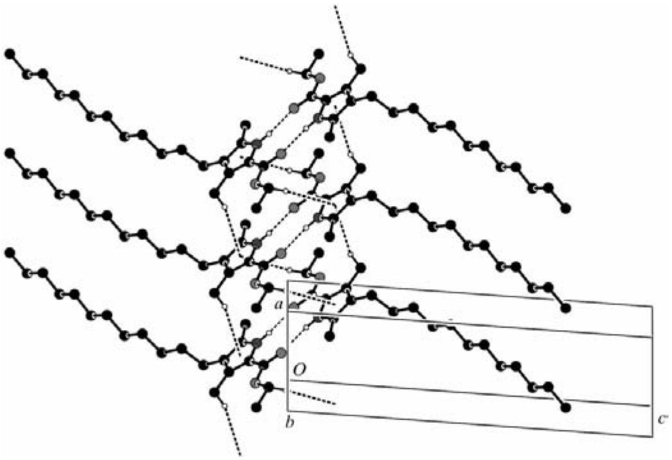


Figure 2
View of the unit-cell packing, with the hydrogen-bonding scheme shown as dashed lines. H atoms not partipating in hydrogen bonding have been omitted for clarity.

The conformation of the dodecyl chain is that most often found for larger alkanes, *i.e.* staggered with the largest substituents at any C—C bond *anti* to each other. The largest deviation from the ideal 180° torsion angle is 12.58 (18)° for C10—C11—C12—C13. The average C—C bond length in the chain is 1.500 (9) Å and the average valence angle is 116 (1)°. These values are similar to those found in related compounds already studied by us [1.516 (3) Å and 113.8 (8)° for 9-(*n*-dodecylaminomethyl)anthracene (Ramos Silva *et al.*, 2000*a*), and 1.511 (6) Å and 114.3 (4)° for *N*-*n*-dodecylbis(9-anthrylmethyl)amine (Matos Beja *et al.*, 2001)]. The zigzag dodecyl backbone is less planar than in the above-mentioned compounds, being bent towards atom C9. Atom C13 is a transition atom between the two planar parts of the chain, deviating by 0.295 (4) Å from the plane defined by atoms C10, C11 and C12, and by 0.224 (3) Å from the least-squares plane defined by atoms C14–C21. The mean deviation of atoms C14–C21 from their least-squares plane is 0.021 (2) Å [maximum deviation 0.047 (2) Å for C19]. The angle between the planar sections of the chain is 20.5 (3)°.

A strong intermolecular hydrogen bond exists between atoms N1 and $O2^i$ [symmetry code: (i) $-x+1$, $-y$, $-z$; Table 2]. This joins the molecules head-to-head across crystallographic inversion centres to give dimers. The molecular packing is such that the hydrocarbon chains lie side-by-side, thereby forming alternating layers of carbon chains and pyrrole heads. The structure is stabilized by two C—H$\cdots\pi$ intermolecular interactions, thereby saturating the hydrogen-bonding capability of the aromatic π-electron clouds (Fig. 2). One of the bonds belongs to a geometric type-II interaction, according to the classification of Malone *et al.* (1997), with the C6—H6*A* bond pointing in the direction of the ring centre ($\alpha \simeq 164°$ and $\theta \simeq 60°$). The other has a type-III interaction, with the H atom above the centre of the pyrrole ring and the C8—H8*C* bond pointing towards a ring atom. Both C—H$\cdots\pi$ bonds have a slightly long H$\cdots$*Cg* distance (*Cg* is the ring centroid), compared with the limit of 3.05 Å, which is based on the sum of the van der Waals radii of the atoms concerned (Malone *et al.*, 1997). C—H$\cdots\pi_{\rm arene}$ interactions have been shown previously to have a profound effect on the molecular packing patterns of macrocycles (Ferguson *et al.*, 1996).

Experimental

The title compound was prepared by a Knorr-type reaction (Paine, 1978) in 22% yield. Small single crystals (m.p. 303–308 K) were grown from a dichloromethane–hexane (1:1) solution. IR (cm^{-1}): 1697 (νC=O), 2854 (νC—H), 3313 (νN—H); MS (FAB+): M^+ *m*/*z* 335; ^{1}H NMR (CDCl$_3$, δ, p.p.m.): 0.88 [*t*, 3H, CH$_3$–(CH$_2$)$_{10}$, *J* = 6.69 Hz], 1.25 [*m*, 20H, CH$_3$–(CH$_2$)$_{10}$–C], 2.13 (*s*, 3H, ring^5-CH$_3$), 2.26 (*s*, 3H, ring^3-CH$_3$), 2.35 (*t*, 3H, CH$_3$–CH$_2$O, *J* = 7.11 Hz), 3.61 [*t*, 2H, ring–CH$_2$–(CH$_2$)$_{10}$–CH$_3$], 4.28 (*q*, 2H, O–CH$_2$–CH$_3$, *J* = 7.11 Hz), 8.7 (*m*, 1H, NH).

Crystal data

$C_{21}H_{37}NO_2$
M_r = 335.52
Triclinic, $P\bar{1}$
a = 5.4778 (6) Å
b = 9.8774 (10) Å
c = 20.4090 (16) Å
α = 98.79 (7)°
β = 94.06 (8)°
γ = 99.93 (9)°
V = 1069.6 (5) Å^3
Z = 2
D_x = 1.042 Mg m^{-3}
Cu *K*α radiation
Cell parameters from 25 reflections
θ = 21.7–29.2°
μ = 0.50 mm^{-1}
T = 293 (2) K
Block, translucent light yellow
0.49 × 0.37 × 0.31 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\rm min}$ = 0.812, $T_{\rm max}$ = 0.984
8228 measured reflections
4238 independent reflections
2953 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.022
$\theta_{\rm max}$ = 72.4°
$h = -6 \rightarrow 6$
$k = -12 \rightarrow 12$
$l = -25 \rightarrow 25$
3 standard reflections
frequency: 180 min
intensity decay: 4%

Table 1
Selected geometric parameters (Å, °).

N1—C4	1.356 (2)	C2—C3	1.414 (2)
N1—C1	1.374 (2)	C3—C4	1.385 (3)
C1—C2	1.385 (3)		
N1—C1—C5	117.84 (16)	C3—C4—C9	131.27 (16)
C1—C2—C8	127.29 (17)	O2—C5—O1	122.00 (16)
C3—C2—C8	125.87 (17)	O1—C6—C7	107.22 (19)
N1—C4—C9	120.97 (16)		
N1—C1—C2—C3	−0.10 (17)	N1—C1—C5—O1	179.02 (14)
N1—C1—C2—C8	179.87 (15)	C5—O1—C6—C7	−178.67 (16)
C1—N1—C4—C9	−179.84 (15)	C10—C11—C12—C13	167.42 (18)
C2—C3—C4—C9	179.74 (17)	C11—C12—C13—C14	−171.63 (18)
C10—C3—C4—C9	1.3 (3)	C12—C13—C14—C15	172.76 (18)
N1—C1—C5—O2	−1.6 (3)		

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

Cg is the centroid of the pyrrole ring.

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
N1—H1$\cdots$O2$^{\rm i}$	0.875 (19)	1.996 (19)	2.850 (3)	164.9 (18)
C6—H6*A*$\cdots$*Cg*$^{\rm ii}$	0.97	3.18	4.119 (2)	164
C8—H8*C*$\cdots$*Cg*$^{\rm iii}$	0.96	3.18	3.872 (2)	130

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

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.156$
$S = 1.14$
4238 reflections
225 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0647P)^2 + 0.1001P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.013$
$\Delta\rho_{\max} = 0.17$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0043 (8)

The position of the amine H atom was determined from a difference Fourier map and was refined freely, with its isotropic displacement parameter constrained to $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm N})$. The methyl H atoms were constrained to an ideal geometry (C—H = 0.96 Å), with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$, but were allowed to rotate freely about the C—C bonds. All remaining H atoms were placed in geometrically idealized positions (C—H = 0.97 Å) and constrained to ride on their parent atoms, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. 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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1145). Services for accessing these data are described at the back of the journal.

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