

Jose Antonio Paixão,^a Manuela Ramos Silva,^{a*} Ana Matos Beja,^a Abilio J. F. N. Sobral,^b Susana H. Lopes^b and A. M. d'A. Rocha Gonsalves^b

^aCEMDRX, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, P-3004-516 Coimbra, Portugal, and

^bDepartamento de Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, P-3004-535 Coimbra, Portugal

Correspondence e-mail:
manuela@pollux.fis.uc.pt

Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

R factor = 0.044

wR factor = 0.144

Data-to-parameter ratio = 15.1

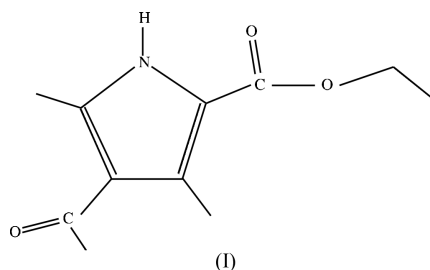
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Ethyl 4-acetyl-3,5-dimethyl-1*H*-pyrrole-2-carboxylate

In the title compound, $\text{C}_{11}\text{H}_{15}\text{NO}_3$, the molecules are joined into dimers by a pair of strong hydrogen bonds between the pyrrole N atom and the carbonyl O atom of the carboxylate substituent [$\text{N}\cdots\text{O}$ 2.861 (2) Å and $\text{N}-\text{H}\cdots\text{O}$ 168 (2)°]. A single $\text{C}-\text{H}\cdots\pi$ intermolecular interaction is observed, with an $\text{H}\cdots\pi$ distance of 3.04 Å, linking the dimers together.

Comment

Pyrroles are important pharmaceutical agents (Baltazzi & Krimen, 1963). Some 2-(alkoxycarbonyl)pyrrole derivatives exhibit analgesic, morphine agonist, antipyretic, anti-inflammatory, spasmolytic and even anti-HIV-1 properties (Artico *et al.*, 1996; Gribble, 1996). Pyrroles are also very useful precursors in porphyrin synthesis (Sobral & Rocha Gonsalves, 2001*a,b*), and as monomers for polymer chemistry (Brockmann & Tour, 1995; Cosnier *et al.*, 1998), with applications ranging from non-linear optical materials (Suslick *et al.*, 1992) to electronic noses (Di Natale *et al.*, 1998). Following our studies on the synthesis of pyrrole derivatives, we report here the structure of the title compound, (I), intended to be used as a building block of porphyrins and polypyrroles.



The weighted average of the absolute torsion angles of the pyrrole ring is 0.22 (9)°, indicating that the heterocycle is almost perfectly planar. The internal ring angles range from 107.31 (16) to 110.48 (18)°, showing a small distortion from ideal C_{2v} symmetry. Although rotation around the C2—C6 bond is possible, the conformation adopted by the ethoxycarbonyl group has the ethyl group *trans* to the N1 atom, as is usually found (Bonnet *et al.*, 1972; Yamamoto *et al.*, 1986; Paixão *et al.*, 2002*a,b*). In this group, the torsion angle C6—O2—C7—C8 [−173.90 (18)°] shows that atom C8 deviates slightly from the plane defined by atoms O1, C6, O2 and C7. This deviation from the ideal value of 180°, determined by *ab initio* HF-LCAO quantum-mechanical calculation of the geometry of the isolated molecule using the GAMESS program (Schmidt *et al.*, 1993) and a 631(*d,p*) basis set, is probably due to packing effects.

A strong hydrogen bond between the pyrrole N—H group and the carbonyl O atom links the molecules into dimers, in a

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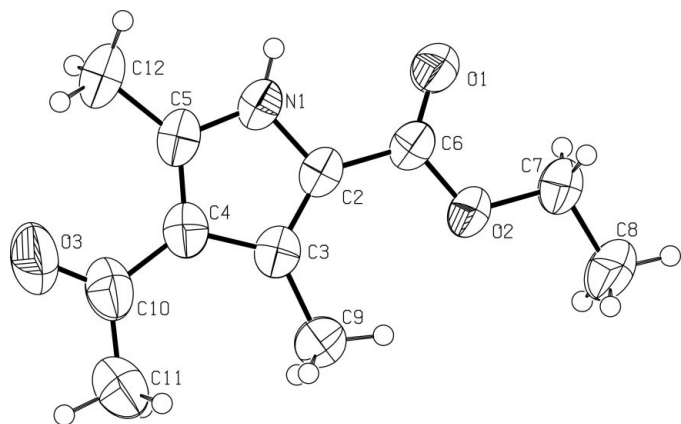


Figure 1
ORTEP (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

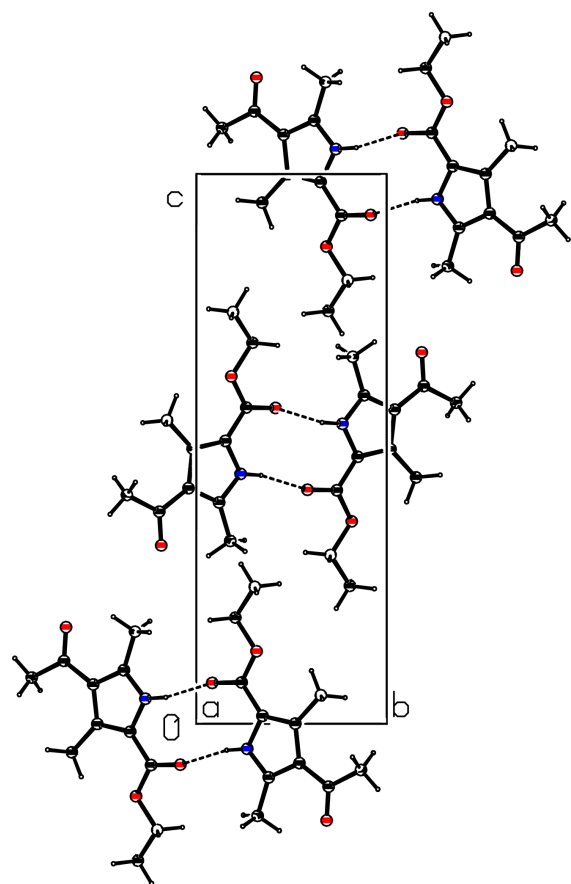


Figure 2
View of the unit-cell packing, with the hydrogen-bonding scheme shown as dashed lines.

manner similar to that found in the related compounds ethyl 3,5-dimethyl-4-phenyl-1*H*-pyrrole-2-carboxylate (Paixão *et al.*, 2002*a*) and 4-ethyl-3,5-dimethyl-1*H*-pyrrole-2-carboxylic acid (Paixão *et al.*, 2002*b*). A single C—H··· π intermolecular interaction of type II, according to the definition of Malone *et al.* (1997), is observed, with an H··· π distance of 3.04 Å. This interaction, with the proton shared between C9 and the π -electron system of the pyrrole ring, links the dimers together.

Experimental

The title compound was prepared by a Knorr-type reaction (Paine, 1978) from the condensation of acetylacetone and ethyl oximinoacetoacetate. Small single crystals (m.p. 409.5–410.9 K) were grown from a solution of dichloromethane/hexane (1:1). IR (cm^{-1} ; group): (1649, C=O ketone form), (2933, aromatic C—C), (3375, $\nu\text{N—H}$); ^1H NMR, CDCl_3 , δ (p.p.m.): 1.38 (*t*, $\text{CH}_3\text{—CH}_2\text{—}$), 2.46 (*s*, $\text{CH}_3\text{—}$), 2.54 (*s*, $\text{CH}_3\text{—}$), 2.59 (*s*, $\text{CH}_3\text{—}$), 4.36 (*q*, $\text{CH}_3\text{—CH}_2\text{—}$), 9.80 (*ls*, —NH—). Elemental analysis: calculated for $\text{C}_{11}\text{H}_{15}\text{NO}_3$: C 63.14, H 7.23, N 6.69%; found: C 62.03, H 7.29, N 5.91%.

Crystal data

$\text{C}_{11}\text{H}_{15}\text{NO}_3$	$D_x = 1.258 \text{ Mg m}^{-3}$
$M_r = 209.24$	Cu $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 8.0985 (10) \text{ \AA}$	$\theta = 21.0\text{--}35.3^\circ$
$b = 6.8757 (15) \text{ \AA}$	$\mu = 0.76 \text{ mm}^{-1}$
$c = 20.406 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 103.607 (8)^\circ$	Prism, colourless
$V = 1104.4 (3) \text{ \AA}^3$	$0.49 \times 0.22 \times 0.17 \text{ mm}$
$Z = 4$	

Data collection

Enraf–Nonius MACH3 diffractometer	$R_{\text{int}} = 0.013$
ω – 2θ scans	$\theta_{\text{max}} = 72.4^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 10$
$T_{\text{min}} = 0.90$, $T_{\text{max}} = 0.98$	$k = -8 \rightarrow 0$
3600 measured reflections	$l = -25 \rightarrow 24$
2187 independent reflections	3 standard reflections
1678 reflections with $I > 2\sigma(I)$	frequency: 180 min
	intensity decay: 5%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0687P)^2 + 0.281P]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.144$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$
2187 reflections	$\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$
145 parameters	Extinction correction: <i>SHELXL97</i>
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.0204 (17)

Table 1
Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
$\text{N1—H1}\cdots\text{O1}^i$	0.88 (2)	2.00 (2)	2.861 (2)	168 (2)

Symmetry code: (i) $2 - x, -y, -z$.

The methyl H atoms were constrained to an ideal geometry (C—H = 0.96 Å), with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, but were allowed to rotate freely about the C—C bonds. H atoms attached to atom C7 were placed in geometrically idealized positions and constrained to ride on their parent atom, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C7})$. The H atom bonded to the N atom was freely refined. Examination of the crystal structure with *PLATON* (Spek, 2003) 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, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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