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Methyl (4-formyl-2-methoxycarbonylpyrrol-1-yl)-acetate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.058
wR factor = 0.106
Data-to-parameter ratio = 16.9

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

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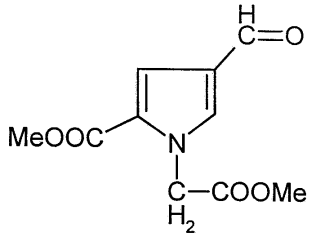
The title compound, $C_{10}H_{11}NO_5$, belongs to a broad class of nitrogen heterocycles widely used in medicinal chemistry as well as the pharmaceutical and chemical industries and was selected for crystal structure determination in order to elucidate the conformation of the substituents bonded to the pyrrole ring and the extent of π-electron delocalization. There is structural evidence that both the 2-methoxycarbonyl and 4-formyl groups interact with the π-cloud of the pyrrole ring. The second methoxycarbonyl group at N1 is twisted out of the pyrrole plane due to rotations around the methylene bonds.

Comment

Polysubstituted and polycondensed pyrrolyl derivatives have found widespread applications as drugs, polymers, dyes, agrochemicals *etc.* (Gribble, 1996). The title compound, (I), has also been exploited in the synthesis of other heterocyclic derivatives, such as 4-pyrrolyl-1,4-dihydropyridines or glutaric acid derivatives (Milata *et al.*, 2001), which are of interest because of their calcium channel blocking activity. The present crystal structure determination was undertaken in order to establish the conformation of the substituents bonded to the pyrrole ring and the degree of π-electron conjugation.



(I)

A drawing of the molecule is shown in Fig. 1. As expected, the central pyrrole ring is planar within experimental error (r.m.s. deviation 0.003 Å). The distortion of the pyrrole ring from C_{2v} symmetry is considerable and concerns mainly the two N—C bonds which differ by a very significant amount, *viz.* 18σ. The 2-methoxycarbonyl group (at C5) is roughly coplanar with the mean plane of the pyrrole ring [dihedral angle 7.0 (2)°]; similarly, the formyl group lies exactly in the pyrrole plane [torsion angle C4—C3—C11—O12 = −0.4 (4)°]. Furthermore, the C3—C11 and C5—C13 bond distances of 1.434 (3) and 1.449 (3) Å, respectively, are significantly shorter than the value of 1.487 (5) Å reported for a Csp^2—Csp^2 single bond (Shmueli *et al.*, 1973). These results indicate that there is some degree of π-electron delocalization from the heterocyclic ring into the C11—O12 and C13—O14 carbonyl bonds.

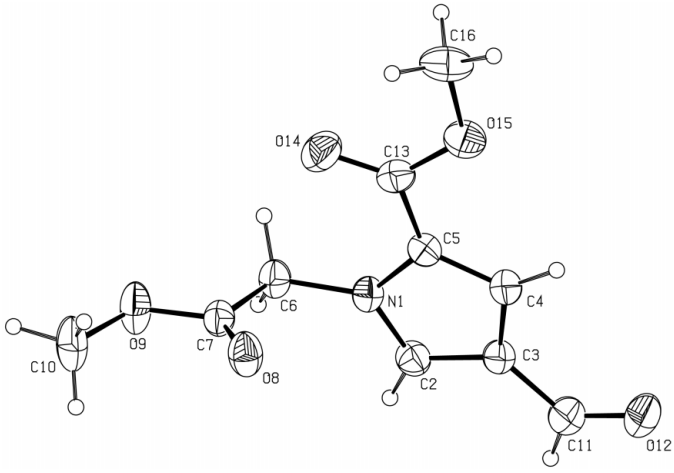


Figure 1
View of a molecule of the title compound with its numbering scheme. Displacement ellipsoids are shown at the 35% probability level and H atoms are drawn as spheres of arbitrary radii.

As revealed by the Cambridge Structural Database (Allen & Kennard, 1993), similar features have also been observed for compounds having electron-withdrawing substituents in the 2- and/or 4-positions of the pyrrole ring. The second methoxycarbonyl group of the molecule is rotated around the N1—C6 and C6—C7 bonds [torsion angles C5—N1—C6—C7 = 79.5 (3)° and N1—C6—C7—O8 = −3.7 (3)°], so that it makes an angle of 76.5 (3)° with the pyrrole plane.

As the molecule has no potential hydrohen-bond donor, the packing is governed by van der Waals interactions.

Experimental

The title compound was prepared by a two-step reaction. In the first step, to a stirred solution of methyl 2-pyrrolylcarbocylate (0.1 mol) in CH_2Cl_2 (300 ml), CH_3NO_2 (20 ml) and $AlCl_3$ (30 g) was added dropwise a solution of 1,1-dichloromethyl methyl ether in CH_2Cl_2 (150 ml) at 273 K. After 1 h, the reaction mixture was poured on to ice/water, extracted with chloroform, dried with sodium sulfate, evaporated to dryness and recrystallized from CCl_4. To a stirred solution of methyl 4-formylpyrrolyl-2-carboxylate (50 mmol) obtained above in 20 ml of dimethylformamide (DMF) was added potassium *tert*-butoxide (55 mmol) and tetrabutylammonium bromide (5 mmol) in 20 ml of DMF at 313 K. After 3 h a solution of alkyl bromoacetate (60 mmol) in 20 ml of DMF was added dropwise and stirred for 3 h. The DMF was evaporated, the residue dissolved in 80 ml of H_2O, neutralized with concentrated hydrochloric acid and extracted with chloroform. The extract was dried with Na_2SO_4 and crystallized from toluene–cyclohexane (m.p. 343–345 K).

Crystal data

$C_{10}H_{11}NO_5$
M_r = 225.20
Monoclinic, $P2_1/c$
a = 5.101 (1) Å
b = 20.098 (4) Å
c = 10.461 (2) Å
β = 90.31 (3)°
V = 1072.4 (4) Å^3
Z = 4
D_x = 1.395 Mg m^{-3}
D_m = 1.39 (1) Mg m^{-3}
D_m measured by flotation in bromoform/methanol
Mo $K\alpha$ radiation
Cell parameters from 15 reflections
θ = 7–18°
μ = 0.11 mm^{-1}
T = 293 (2) K
Prism, light yellow
0.35 × 0.28 × 0.25 mm

Data collection

Syntex $P2_1/c$ diffractometer
$\theta/2\theta$ scans
2623 measured reflections
2485 independent reflections
1469 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 27.6°
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 26$
$l = -13 \rightarrow 13$
2 standard reflections
every 98 reflections
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.106
S = 1.04
2485 reflections
147 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0356P)^2 + 0.4874P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.338 (3)	C3—C11	1.434 (3)
N1—C5	1.383 (2)	C4—C5	1.359 (3)
N1—C6	1.446 (2)	C5—C13	1.449 (3)
C2—C3	1.370 (3)	C11—O12	1.199 (3)
C3—C4	1.404 (3)	C13—O14	1.196 (3)
C2—N1—C5	108.48 (16)	C4—C3—C11	128.47 (19)
C2—N1—C6	122.77 (17)	C5—C4—C3	107.42 (18)
C5—N1—C6	128.75 (17)	C4—C5—N1	108.03 (17)
N1—C2—C3	109.23 (19)	C4—C5—C13	129.62 (19)
C2—C3—C4	106.84 (18)	N1—C5—C13	122.35 (18)
C2—C3—C11	124.7 (2)		
C5—N1—C6—C7	79.5 (3)	C4—C3—C11—O12	−0.4 (4)
N1—C6—C7—O8	−3.7 (3)	N1—C5—C13—O14	−7.6 (3)

Although the H atoms were located in a difference Fourier map, they were refined with fixed geometry, riding on their carrier atoms, with U_{iso} set to 1.2 (or 1.5 for the methyl H atoms) times U_{eq} of the parent atom. Both methyl groups were allowed to rotate about their local threefold axis.

Data collection: *Syntex Software* (Syntex, 1973); cell refinement: *Syntex Software*; data reduction: *XP*21 (Pavelčík, 1987); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL*97.

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