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 Methyl 1*H*-pyrrole-2-carboxylate

Tobias Kerscher, Peter Mayer and Peter Klüfers*

Department Chemie und Biochemie, Ludwig-Maximilians-Universität, Butenandtstrasse 5–13, 81377 München, Germany

Correspondence e-mail: kluef@cup.uni-muenchen.de

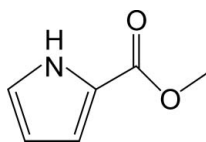
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 Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.070; wR factor = 0.176; data-to-parameter ratio = 13.3.

The title compound, $\text{C}_6\text{H}_7\text{NO}_2$, is essentially planar with a dihedral angle of $3.6(3)^\circ$ between the pyrrole ring and the methoxycarbonyl O/C/O/C plane. In the crystal structure, the N atom is a hydrogen-bond donor to the carboxylate C=O O atom of the neighboring molecule. These intermolecular hydrogen bonds lead to the formation of helical chains along the b axis.

Related literature

For related structures, see: Kerscher, Klüfers, Kügel & Müller (2007); Kerscher, Klüfers & Kügel (2007). For graph-set analysis, see: Bernstein *et al.* (1995); Etter *et al.* (1990).



Experimental

Crystal data

$\text{C}_6\text{H}_7\text{NO}_2$
 $M_r = 125.13$
 Monoclinic, $P2_1/c$
 $a = 7.5346(19)$ Å
 $b = 5.4598(14)$ Å
 $c = 14.730(4)$ Å
 $\beta = 100.55(2)^\circ$

$V = 595.7(3)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.11$ mm⁻¹
 $T = 200$ K
 $0.38 \times 0.16 \times 0.06$ mm

Data collection

Oxford Xcalibur KappaCCD diffractometer
 Absorption correction: none
 2591 measured reflections

1103 independent reflections
 528 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.112$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.070$
 $wR(F^2) = 0.176$
 $S = 0.95$
 1103 reflections

83 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.27$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.26$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|-------|-------------|-------------|---------------|
| $\text{N1}-\text{H1}\cdots\text{O2}^{\text{i}}$ | 0.88 | 2.06 | 2.933 (4) | 171 |
| $\text{C4}-\text{H4}\cdots\text{Cg1}^{\text{ii}}$ | 0.95 | 2.63 | 3.401 (5) | 139 |

Symmetry codes: (i) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$. Cg1 is the centroid of the pyrrole ring.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-III* (Burnett & Johnson, 1996), *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2445).

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supplementary materials

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Methyl 1*H*-pyrrole-2-carboxylate

T. Kerscher, P. Mayer and P. Klüfers

Comment

The title compound was prepared, in the attempt to create new complexing ligands, as a byproduct. The compound is quite similar to other compounds already published by our group (Kerscher, Klüfers, Kügel & Müller, 2007; Kerscher, Klüfers & Kügel, 2007).

In the molecule, a formic acid methyl ester is in the 2 position of the pyrrole ring (Fig. 1). With a torsion angle for C2–C1–C5–O1 of only about 2.9°, the molecule is, with the exception of the H atoms of the methyl group, nearly planar. Because of this small torsion angle, the molecule is not C_s symmetric.

The hydrogen bonds of the nitrogen to the carboxylate oxygen lead to a chain like hydrogen bonding system which can be described according to graph-set analysis (Etter *et al.*, 1990; Bernstein *et al.*, 1995) with a C(5) descriptor on the unitary level [the rpluto program (Cambridge Crystallographic Data Centre, England) was used for the graph set analyses; one of these strands is shown in Fig. 2].

Considering contacts whose range falls below the sum of van der Waals radii by only about 0.1 Å, a set of weak C–H $\cdots\pi$ interactions leads to the formation of a second system of strands along [0 1 0] which can be described by a C(2) descriptor (see Fig. 3).

The two strand systems alternate, which means two hydrogen bonding strands are interconnected by a strand of weak C–H $\cdots\pi$ contacts (this situation is illustrated in Fig. 4) and *vice versa*, two strands made of weak C–H $\cdots\pi$ contacts are interconnected by hydrogen bonding strands. This bonding pattern leads to sheet like structures normal to [0 0 1].

The molecular packing of the title compound is shown in Figure 5.

Experimental

The title compound was obtained by reaction of 228 mg (3.40 mmol) of pyrrole with 280 mg (1.70 mmol) phosgene imminium chloride in 6 ml of dry acetonitrile. After removal of the solvent, the remaining green solid was purified by column chromatography on silica with chloroform as eluent. Sublimation of fraction five yielded the title compound as colorless crystals.

Refinement

H atoms were calculated in ideal geometry, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C or N})$ for all aromatic C- and N-bound H atoms, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for the methylgroup H atoms.

Figures

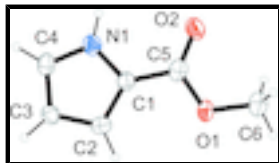


Fig. 1. The molecular structure of the title compound with atom labels and anisotropic displacement ellipsoids (drawn at 50% probability level) for non-H atoms.

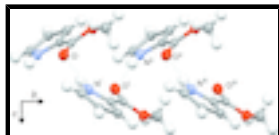


Fig. 2. Strands formed by N-H...O hydrogen bonds along [0 1 0] in the crystal structure of the title compound, viewed along [1 0 0]. Symmetry codes: (i) $-x, y + 1/2, 1/2 - z$; (ii) $x, y + 1, z$; (iii) $-x, y + 3/2, 1/2 - z$.

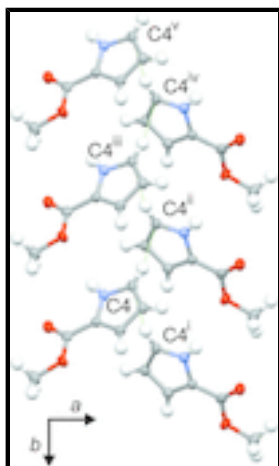


Fig. 3. Strands formed by C-H... π contacts along [0 1 0] in the crystal structure of the title compound, viewed along [0 0 1]. Symmetry codes: (i) $1 - x, y + 1/2, 1/2 - z$; (ii) $1 - x, y - 1/2, z - 1/2$; (iii) $x, y - 1, z$; (iv) $1 - x, y - 3/2, 1/2 - z$; (v) $x, y - 2, z$.

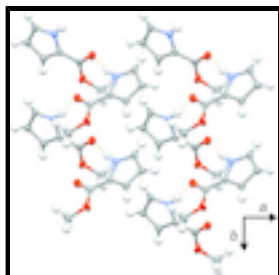


Fig. 4. The strands formed by hydrogen bonding in the crystal structure are interconnected by the strands formed by C-H... π contacts.

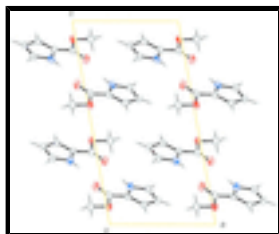


Fig. 5. The packing of the title compound, viewed along [0 1 0].

Methyl 1H-pyrrole-2-carboxylate

Crystal data

$C_6H_7NO_2$

$M_r = 125.13$

Monoclinic, $P2_1/c$

$F_{000} = 264$

$D_x = 1.395 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Hall symbol: -P 2ybc
 $a = 7.5346$ (19) Å
 $b = 5.4598$ (14) Å
 $c = 14.730$ (4) Å
 $\beta = 100.55$ (2)°
 $V = 595.7$ (3) Å³
 $Z = 4$

Cell parameters from 1091 reflections
 $\theta = 4.0$ – 27.5 °
 $\mu = 0.11$ mm⁻¹
 $T = 200$ K
 Platelet, colourless
 $0.38 \times 0.16 \times 0.06$ mm

Data collection

Oxford Xcalibur KappaCCD
 diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 200$ K

ω -scans

Absorption correction: none

2591 measured reflections

1103 independent reflections

528 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.112$

$\theta_{\text{max}} = 25.5$ °

$\theta_{\text{min}} = 4.0$ °

$h = -9 \rightarrow 9$

$k = -6 \rightarrow 6$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.070$

$wR(F^2) = 0.176$

$S = 0.95$

1103 reflections

83 parameters

Primary atom site location: structure-invariant direct
 methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring
 sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0745P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.27$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.26$ e Å⁻³

Extinction correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|------------|--------------|----------------------------------|
| O1 | 0.0203 (3) | 0.7534 (4) | 0.08955 (19) | 0.0312 (8) |
| O2 | -0.0644 (3) | 0.4755 (5) | 0.18723 (19) | 0.0331 (8) |
| N1 | 0.2637 (4) | 0.2221 (6) | 0.1856 (2) | 0.0286 (9) |
| H1 | 0.1960 | 0.1417 | 0.2183 | 0.034* |
| C1 | 0.2176 (5) | 0.4370 (7) | 0.1405 (3) | 0.0248 (10) |
| C5 | 0.0452 (5) | 0.5519 (7) | 0.1425 (3) | 0.0276 (10) |
| C6 | -0.1459 (5) | 0.8847 (7) | 0.0877 (3) | 0.0378 (12) |
| H6A | -0.2475 | 0.7701 | 0.0753 | 0.057* |
| H6B | -0.1594 | 1.0093 | 0.0391 | 0.057* |
| H6C | -0.1439 | 0.9640 | 0.1476 | 0.057* |

supplementary materials

| | | | | |
|----|------------|------------|------------|-------------|
| C3 | 0.4923 (5) | 0.3236 (7) | 0.1182 (3) | 0.0275 (10) |
| H3 | 0.6054 | 0.3212 | 0.0984 | 0.033* |
| C4 | 0.4295 (5) | 0.1506 (7) | 0.1726 (3) | 0.0300 (10) |
| H4 | 0.4914 | 0.0065 | 0.1967 | 0.036* |
| C2 | 0.3585 (5) | 0.5042 (7) | 0.0975 (3) | 0.0276 (10) |
| H2 | 0.3638 | 0.6461 | 0.0608 | 0.033* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|-------------|-------------|-------------|--------------|--------------|--------------|
| O1 | 0.0235 (16) | 0.0309 (17) | 0.0388 (19) | 0.0084 (12) | 0.0042 (12) | 0.0051 (13) |
| O2 | 0.0241 (16) | 0.0352 (17) | 0.041 (2) | 0.0013 (13) | 0.0090 (14) | -0.0012 (14) |
| N1 | 0.025 (2) | 0.0251 (19) | 0.036 (2) | -0.0002 (15) | 0.0059 (15) | -0.0020 (16) |
| C1 | 0.024 (2) | 0.022 (2) | 0.028 (2) | -0.0012 (18) | 0.0041 (18) | -0.0015 (17) |
| C5 | 0.028 (2) | 0.022 (2) | 0.030 (2) | 0.0005 (18) | -0.0009 (19) | -0.0072 (18) |
| C6 | 0.034 (3) | 0.037 (3) | 0.041 (3) | 0.009 (2) | 0.004 (2) | 0.001 (2) |
| C3 | 0.026 (2) | 0.031 (2) | 0.026 (2) | 0.0016 (18) | 0.0079 (17) | -0.0016 (19) |
| C4 | 0.023 (2) | 0.029 (2) | 0.035 (3) | 0.0024 (19) | -0.0013 (18) | -0.0029 (19) |
| C2 | 0.030 (2) | 0.026 (2) | 0.026 (3) | -0.0026 (19) | 0.0051 (19) | 0.0019 (19) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|-------------|------------|-------------|------------|
| O1—C5 | 1.341 (4) | C6—H6A | 0.9800 |
| O1—C6 | 1.439 (4) | C6—H6B | 0.9800 |
| O2—C5 | 1.221 (5) | C6—H6C | 0.9800 |
| N1—C4 | 1.356 (5) | C3—C4 | 1.377 (5) |
| N1—C1 | 1.362 (5) | C3—C2 | 1.403 (5) |
| N1—H1 | 0.8800 | C3—H3 | 0.9500 |
| C1—C2 | 1.382 (5) | C4—H4 | 0.9500 |
| C1—C5 | 1.447 (5) | C2—H2 | 0.9500 |
| C5—O1—C6 | 116.6 (3) | O1—C6—H6C | 109.5 |
| C4—N1—C1 | 109.8 (3) | H6A—C6—H6C | 109.5 |
| C4—N1—H1 | 125.1 | H6B—C6—H6C | 109.5 |
| C1—N1—H1 | 125.1 | C4—C3—C2 | 107.4 (3) |
| N1—C1—C2 | 107.7 (3) | C4—C3—H3 | 126.3 |
| N1—C1—C5 | 120.9 (3) | C2—C3—H3 | 126.3 |
| C2—C1—C5 | 131.4 (4) | N1—C4—C3 | 108.0 (3) |
| O2—C5—O1 | 123.9 (4) | N1—C4—H4 | 126.0 |
| O2—C5—C1 | 124.1 (4) | C3—C4—H4 | 126.0 |
| O1—C5—C1 | 112.0 (4) | C1—C2—C3 | 107.2 (3) |
| O1—C6—H6A | 109.5 | C1—C2—H2 | 126.4 |
| O1—C6—H6B | 109.5 | C3—C2—H2 | 126.4 |
| H6A—C6—H6B | 109.5 | | |
| C4—N1—C1—C2 | 0.0 (4) | C2—C1—C5—O1 | 2.9 (6) |
| C4—N1—C1—C5 | 179.3 (3) | C1—N1—C4—C3 | 0.3 (4) |
| C6—O1—C5—O2 | 0.7 (5) | C2—C3—C4—N1 | -0.4 (4) |
| C6—O1—C5—C1 | -179.0 (3) | N1—C1—C2—C3 | -0.2 (4) |
| N1—C1—C5—O2 | 4.1 (6) | C5—C1—C2—C3 | -179.4 (4) |

| | | | |
|-------------|------------|-------------|---------|
| C2—C1—C5—O2 | -176.8 (4) | C4—C3—C2—C1 | 0.4 (4) |
| N1—C1—C5—O1 | -176.2 (3) | | |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N1—H1 \cdots O2 ⁱ | 0.88 | 2.06 | 2.933 (4) | 171 |
| C4—H4 \cdots Cg1 ⁱⁱ | 0.95 | 2.63 | 3.401 (5) | 139 |

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

Fig. 1

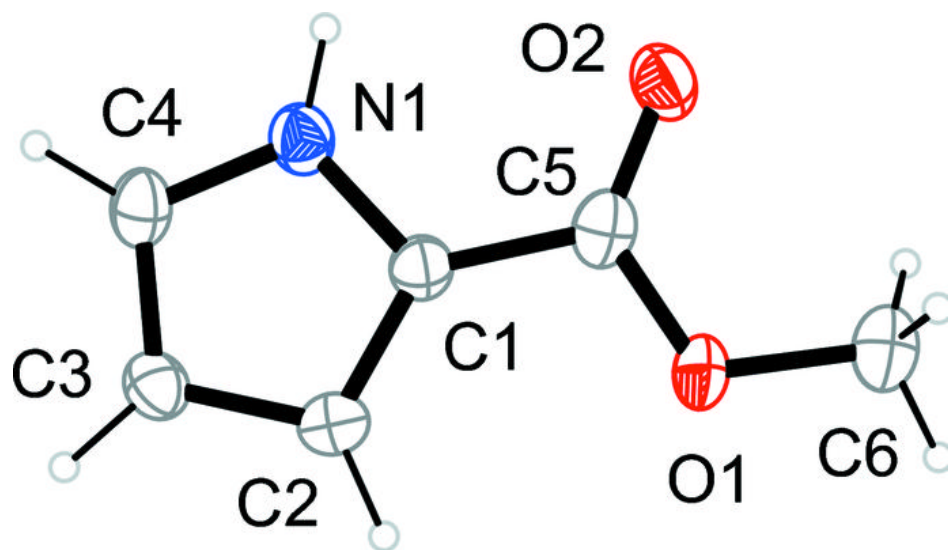


Fig. 2

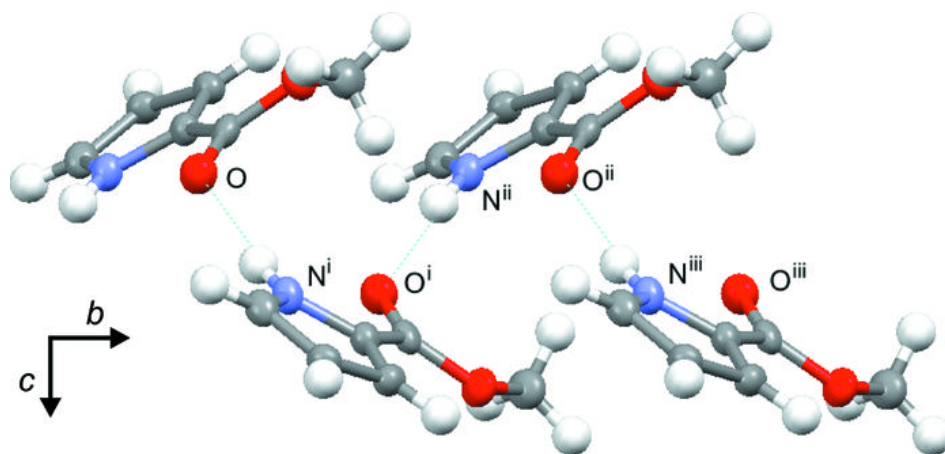


Fig. 3

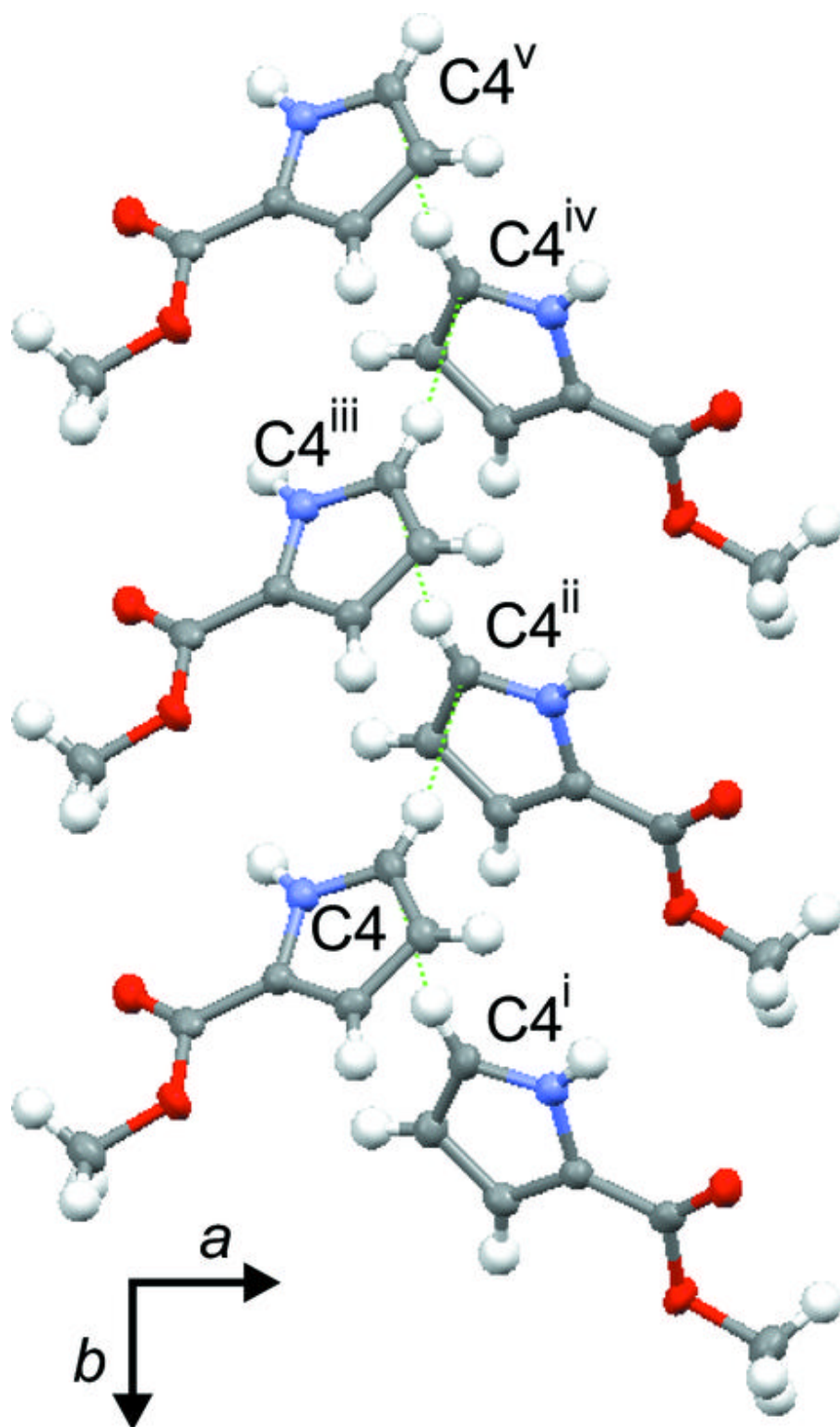


Fig. 4

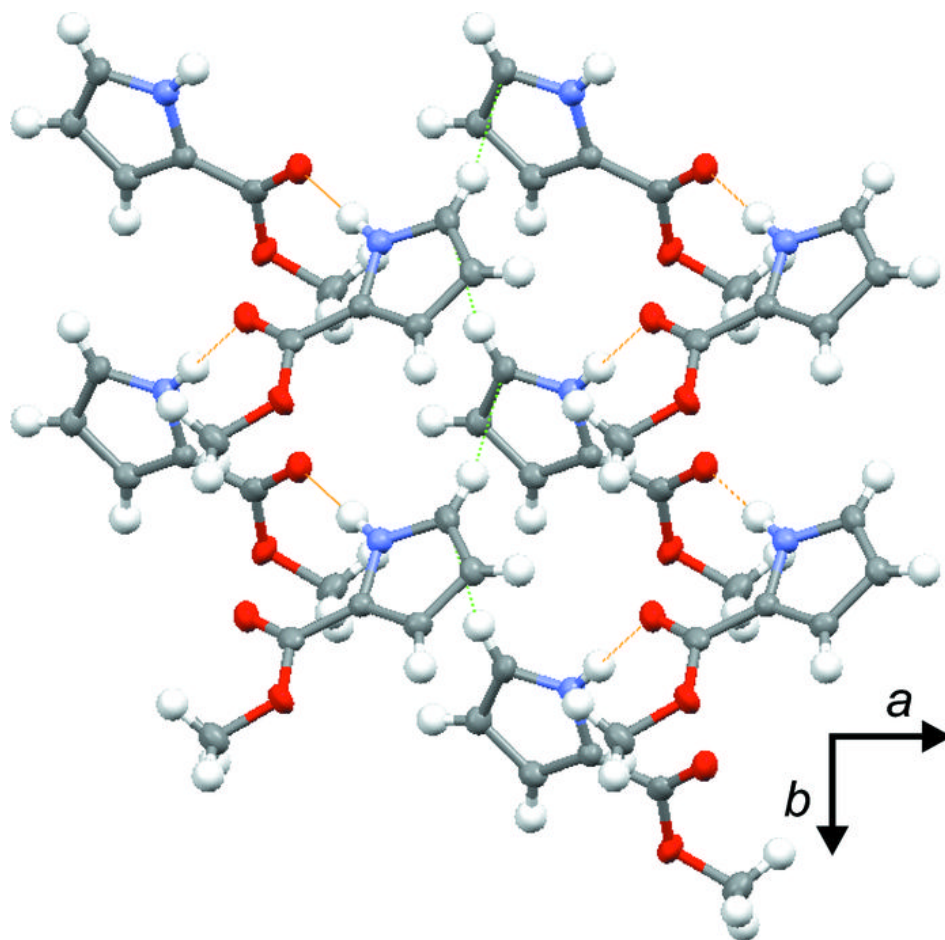


Fig. 5

