

Hydrogen-bonding patterns in six derivatives of 2,4-dimethylpyrrole

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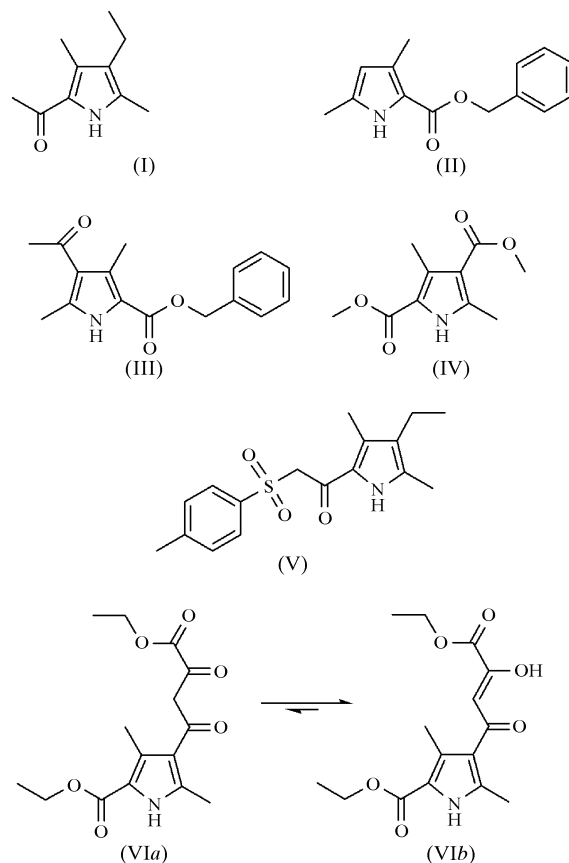
The crystal and molecular structures of 4-ethyl-3,5-dimethylpyrrole-2-carbaldehyde, C₁₀H₁₅NO, (I), benzyl 3,5-dimethylpyrrole-2-carboxylate, C₁₄H₁₅NO₂, (II), benzyl 4-acetyl-3,5-dimethylpyrrole-2-carboxylate, C₁₆H₁₇NO₃, (III), dimethyl 3,5-dimethylpyrrole-2,4-dicarboxylate, C₁₀H₁₃NO₄, (IV), 4-ethyl-3,5-dimethyl-2-(*p*-tosylacetyl)pyrrole, C₁₇H₂₁NO₃S, (V), and ethyl 4-(2-ethoxycarbonyl-2-hydroxyacryloyl)-3,5-dimethylpyrrole-2-carboxylate, C₁₅H₁₉NO₆, (VI), were determined at 130 K. Compounds (I), (II), (IV), (V) and (VI) form hydrogen-bonded dimers [N—H···O=C = 1.97 (2)–2.03 (3) Å]. Four dimers, *viz.* (I) and (IV)–(VI), have inversion symmetry, while the dimer of (II) has twofold symmetry. Only (III) forms polymeric chains involving hydrogen bonds between the pyrrole H atom and the acetyl carbonyl group [H···O = 1.97 (2) Å] and is further stabilized by CH₃···O interactions (C—H···O = 2.28–2.49 Å). Compound (VI) was found to occur as the enol ether in the crystal.

Comment

Pyrroles are both important natural products and crucial starting materials for the synthesis of porphyrins (Gossauer, 1974). Nevertheless, a brief survey of the crystallographic literature shows that few crystal structures of aromatic *N*-unsubstituted monopyrroles have been reported. Some representative and recent examples are given by Goddard *et al.* (1997), Despinoy *et al.* (1998), Senge *et al.* (2001), Light *et al.* (2001), Smith *et al.* (2001), Paixão *et al.* (2002), Ramos Silva *et al.* (2002) and Zhang *et al.* (2003). In an extension of ongoing studies on the hydrogen-bonding patterns in porphyrins (Senge *et al.*, 1994; Senge & Kalisch, 1999; Senge, 2000) and dipyrromethanes (Senge, 2005), we were interested in the strengths and types of hydrogen bonding of isolated pyrrole units. For initial studies we choose a series of 2,4-dimethylpyrroles with different numbers and types of carbonyl acceptor groups.

The simplest compound is (I), with one potential hydrogen-bond donor and one acceptor group (Fig. 1). As expected, this compound forms strongly hydrogen-bonded dimers, held

together by two N—H···O bonds. A similar type of hydrogen bonding with similar geometrical parameters is found for (II) (Fig. 2). Again, hydrogen-bonded dimers are the characteristic feature of the crystal structure. The structure also contains a second, weaker, H···O contact connecting the C31 methyl group with ether atom O2. Although the contact is short and less than 2.7 Å, as suggested by Steiner (1997) (H31B···O2 = 2.59 Å), the bond angle for this intramolecular contact is rather small (104°). An essentially identical structure of (II) at 150 K has been published by Thompson *et al.* (2000).



In contrast, compound (III), with carbonyl acceptor groups at both ends of the N—H vector, forms polymeric chains (Fig. 3). The main feature is a classical hydrogen bond invol-

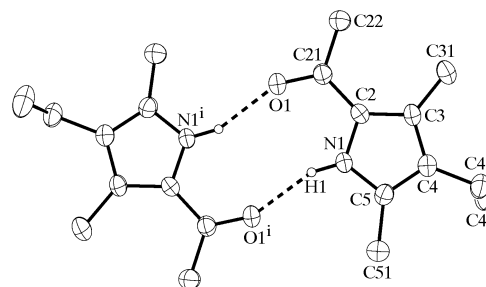


Figure 1

A view of the dimer formed in (I). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines and H atoms not involved in the motifs shown have been omitted. See Table 1 for symmetry code.

ving the pyrrole H atom and the acetyl carbonyl group (N1—H1···O3ⁱⁱⁱ, symmetry code as in Table 1) (Fig. 4). This N—H···O bond is the shortest [1.971 (18) Å] found in the present structures. Carbonyl atom O3 is tightly coordinated by the C51 methyl group (H51C···O3 = 2.49 Å). Likewise, the acetyl methyl group C42 has a short H42C···O1 contact of 2.30 Å.

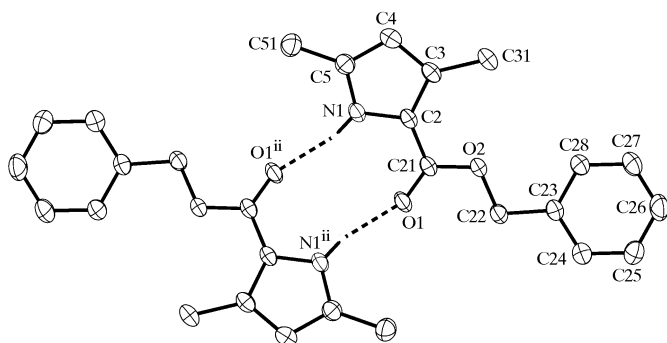


Figure 2
A view of the dimer formed in (II). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines and H atoms not involved in the motifs shown have been omitted. See Table 1 for symmetry code.

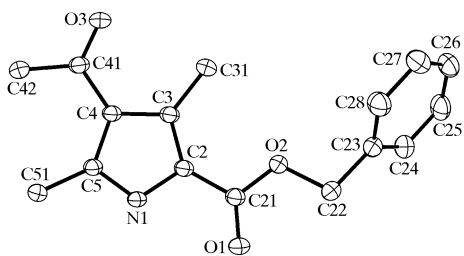


Figure 3
A view of (III). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted.

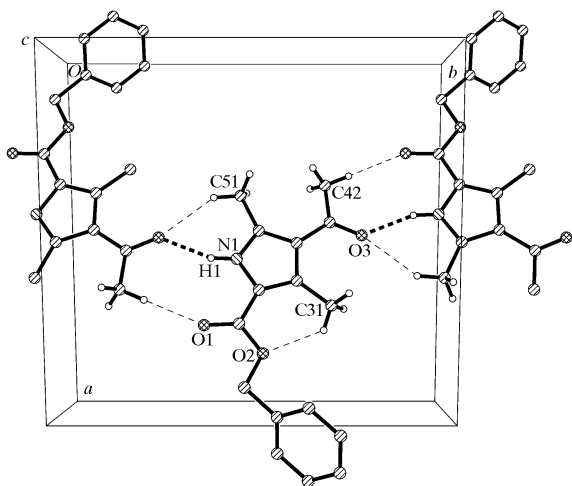


Figure 4
A view of the hydrogen-bonded chain formed in (III) (view down the *c* axis). Heavy dashed lines indicate classical hydrogen bonds and dashed lines indicate C—H···O interactions. Other H atoms have been omitted.

Thus, each pyrrole unit in the polymeric structure in the crystal is held by six hydrogen-bonding interactions as defined by Steiner & Desiraju (1998). Additionally, a short intramolecular contact of 2.28 Å is observed for H31C···O2, involving the ether O atom of the benzyl ester. Note that simple exchange of the benzyl ester for an ethyl ester results in the formation of simple dimers (Paixão *et al.*, 2002).

Compound (IV), despite having two ester groups on two ends of the pyrrole, forms only hydrogen-bonded dimers in the crystal structure (Fig. 5). Like (III), this compound has a short intramolecular contact (H31···O2 = 2.31 Å). Pyrrole (V), with a bulkier group in the side chain (*viz.* tosyl), forms crystals with a molecular arrangement dominated by the formation of standard hydrogen-bonded dimers involving N1—H1···O1^{vi} bonding [1.98 (3) Å and 161 (3)°; Fig. 6]. Compound (VI) again forms standard hydrogen-bonded dimers in the crystal structure (Fig. 7). Here, the pyrrole H atom is bonded to the carbonyl group of the 2-ethyl ester group [N1—H1···O1^{viii};

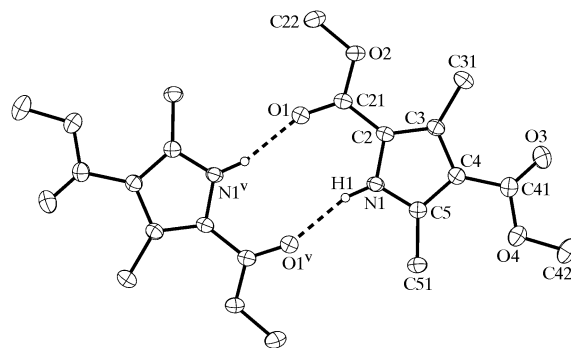


Figure 5
A view of the dimer formed in (IV). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines and H atoms not involved in the motifs shown have been omitted. See Table 1 for symmetry code.

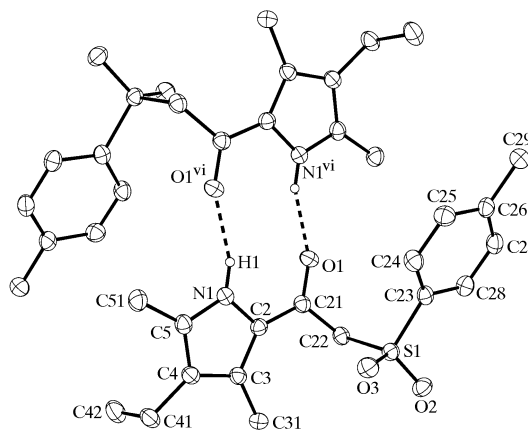


Figure 6
A view of the dimer formed in (V). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines and H atoms not involved in the motifs shown have been omitted. See Table 1 for symmetry code.

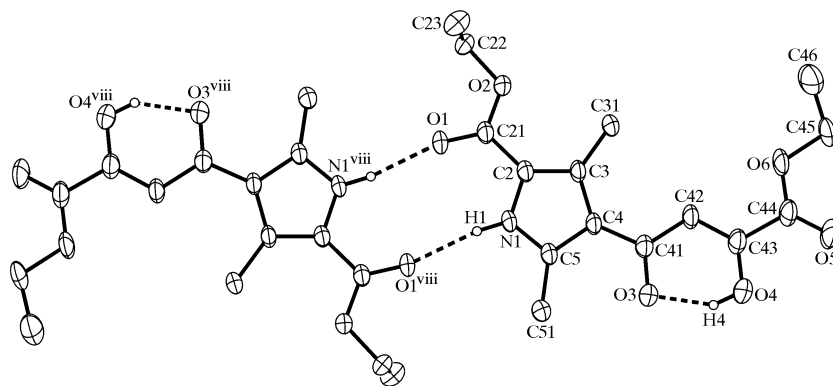


Figure 7

A view of the dimer formed in (VIb). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines and H atoms not involved in the motifs shown have been omitted. See Table 1 for symmetry code.

2.03 (3) Å and 169 (2)°]. Intriguingly, the butanoic acid side chain does not exist in keto form (VIa) but rather as the enol ether (VIb). This is clearly evidenced by the fact that the C41–C42 bond [1.440 (3) Å] is longer than the C42–C43 bond [1.371 (3) Å], by differences in the C–O bond lengths [C41–O3 = 1.280 (3) Å and C43–O4 = 1.301 (3) Å] and by the unequivocal location of the relevant H atoms. The regiochemistry of the enol ether formation is in line with chemical expectations, and the hydroxy group forms an intramolecular hydrogen bond with the neighboring carbonyl group (O4–H4...O3; 1.72 Å and 145°). The six-membered ring system thus formed is almost flat, with an average deviation of the atoms from their least-squares plane of 0.019 (3) Å, and is almost coplanar with the pyrrole ring (the angle between the two planes is 5°). A weak intramolecular methyl–oxygen contact (C31...O2) was also observed for this compound.

Some of the compounds discussed have served as important building blocks for porphyrins for more than a century (Fischer & Stern, 1940; Omote *et al.*, 1997). They have been investigated for their herbicidal activity (Church *et al.*, 1973), used in cyclophane synthesis (Lai *et al.*, 1994) and used as test cases in various physicochemical studies (Abraham *et al.*, 1974; Tappa & Smith, 1984; Thompson *et al.*, 2000).

Experimental

Crystals were handled as described by Hope (1994). The compounds were prepared as described previously (Küster, 1922; Fischer & Stern, 1940; Hayes *et al.*, 1958; Johnson *et al.*, 1958; Kenner *et al.*, 1977) and crystallized from CH₂Cl₂/*n*-hexane.

Compound (I)

Crystal data

C₁₀H₁₅NO
M_r = 165.23
 Monoclinic, *C2/c*
a = 28.513 (12) Å
b = 9.007 (5) Å
c = 7.471 (3) Å
 β = 99.83 (3)°
V = 1890.5 (15) Å³
Z = 8

D_x = 1.161 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 42 reflections
 θ = 18–24°
 μ = 0.08 mm⁻¹
T = 130 (2) K
 Block, colorless
 0.55 × 0.41 × 0.40 mm

Data collection

Siemens *R3m/V* diffractometer
 ω scans
 2493 measured reflections
 2174 independent reflections
 1343 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.041
 θ_{\max} = 27.5°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.064
wR(*F*²) = 0.174
S = 1.04
 2174 reflections
 117 parameters
 H atoms treated by a mixture of independent and constrained refinement

h = -36 → 36
k = 0 → 11
l = 0 → 9
 2 standard reflections
 every 198 reflections
 intensity decay: none

$w = 1/[\sigma^2(F_o^2) + (0.0777P)^2 + 0.1515P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.26 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.32 \text{ e } \text{Å}^{-3}$

Compound (II)

Crystal data

C₁₄H₁₅NO₂
M_r = 229.27
 Monoclinic, *C2/c*
a = 31.793 (18) Å
b = 7.308 (2) Å
c = 10.553 (3) Å
 β = 97.02 (3)°
V = 2433.5 (17) Å³
Z = 8

D_x = 1.252 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 38 reflections
 θ = 19–25°
 μ = 0.08 mm⁻¹
T = 130 (2) K
 Plate, colorless
 0.50 × 0.50 × 0.08 mm

Data collection

Siemens *R3m/V* diffractometer
 ω scans
 3086 measured reflections
 2799 independent reflections
 2120 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.017
 θ_{\max} = 27.5°

h = 0 → 41
k = 0 → 9
l = -13 → 13
 2 standard reflections
 every 198 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.050
wR(*F*²) = 0.144
S = 1.01
 2799 reflections
 160 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0911P)^2 + 0.3712P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.31 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.28 \text{ e } \text{Å}^{-3}$

Compound (III)

Crystal data

C₁₆H₁₇NO₃
M_r = 271.31
 Monoclinic, *P*₂₁/*c*
a = 13.473 (3) Å
b = 14.359 (3) Å
c = 7.489 (2) Å
 β = 100.47 (2)°
V = 1424.7 (6) Å³
Z = 4
D_x = 1.265 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 44 reflections
 θ = 18–23°
 μ = 0.09 mm⁻¹
T = 143 (2) K
 Cube, colorless
 0.35 × 0.35 × 0.35 mm

Data collection

Siemens *R3m/V* diffractometer
 ω scans
 3519 measured reflections
 3268 independent reflections
 2871 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.044
 θ_{\max} = 27.5°

h = -17 → 17
k = -18 → 0
l = 0 → 9
 2 standard reflections
 every 198 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.043
wR(*F*²) = 0.120
S = 1.04
 3268 reflections
 189 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0692P)^2 + 0.3279P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.001
 $\Delta\rho_{\max} = 0.41 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.22 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.027 (3)

Compound (IV)

Crystal data

C₁₀H₁₃NO₄
M_r = 211.21
 Monoclinic, *P*₂₁/*c*
a = 8.150 (4) Å
b = 16.040 (6) Å
c = 7.908 (4) Å
 β = 95.31 (3)°
V = 1029.3 (8) Å³
Z = 4
D_x = 1.363 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 41 reflections
 θ = 20–25°
 μ = 0.11 mm⁻¹
T = 130 (2) K
 Plate, colorless
 0.40 × 0.38 × 0.10 mm

Data collection

Siemens *R3m/V* diffractometer
 ω scans
 2521 measured reflections
 2354 independent reflections
 2214 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.084
 θ_{\max} = 27.5°

h = -10 → 10
k = -20 → 0
l = 0 → 10
 2 standard reflections
 every 198 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.047
wR(*F*²) = 0.134
S = 1.08
 2354 reflections
 145 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0783P)^2 + 0.3875P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.006
 $\Delta\rho_{\max} = 0.43 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.29 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.046 (7)

Compound (V)

Crystal data

C₁₇H₂₁NO₃S
M_r = 319.41
 Monoclinic, *P*₂₁/*c*
a = 5.179 (2) Å
b = 13.986 (4) Å
c = 22.315 (13) Å
 β = 90.09 (4)°
V = 1616.4 (12) Å³
Z = 4

D_x = 1.321 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 32 reflections
 θ = 19–23°
 μ = 0.21 mm⁻¹
T = 130 (2) K
 Block, colorless
 0.30 × 0.25 × 0.25 mm

Data collection

Siemens *R3m/V* diffractometer
 ω scans
 4753 measured reflections
 3730 independent reflections
 2761 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.025
 θ_{\max} = 27.6°

h = -6 → 6
k = 0 → 18
l = 0 → 29
 2 standard reflections
 every 198 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.048
wR(*F*²) = 0.123
S = 1.05
 3730 reflections
 207 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 0.3777P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.003
 $\Delta\rho_{\max} = 0.31 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.35 \text{ e } \text{Å}^{-3}$

Compound (VIb)

Crystal data

C₁₅H₁₉NO₆
M_r = 309.31
 Triclinic, *P* $\bar{1}$
a = 7.281 (3) Å
b = 10.363 (6) Å
c = 11.003 (7) Å
 α = 65.11 (5)°
 β = 84.61 (5)°
 γ = 86.65 (4)°
V = 749.6 (8) Å³

Z = 2
D_x = 1.370 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 18–22°
 μ = 0.11 mm⁻¹
T = 130 (2) K
 Parallelepiped, colorless
 0.40 × 0.10 × 0.10 mm

Table 1

Hydrogen-bond parameters (Å, °) for compounds (I)–(VIb).

Compound	D—H...A	D—H	H...A	D...A	D—H...A
(I)	N1—H1...O1 ⁱ	0.95 (3)	1.99 (3)	2.882 (3)	156 (2)
(II)	N1—H1...O1 ⁱⁱ	0.87 (2)	2.02 (3)	2.862 (3)	164 (2)
(III)	N1—H1...O3 ⁱⁱⁱ	0.936 (18)	1.971 (18)	2.8624 (14)	158.5 (15)
	C51—H51C...O3 ⁱⁱⁱⁱ	0.98	2.49	3.3292 (16)	143
	C42—H42C...O1 ^{iv}	0.98	2.30	3.2401 (16)	160
	C31—H31C...O2	0.98	2.28	3.0127 (16)	130
(IV)	N1—H1...O1 ^v	0.88 (2)	2.01 (2)	2.8628 (17)	163.6 (18)
	C31—H31C...O2	0.98	2.31	3.027 (2)	129
(V)	N1—H1...O1 ^{vi}	0.88 (3)	1.98 (3)	2.826 (3)	161 (3)
	C29—H29B...O2 ^{vii}	0.98	2.34	3.299 (4)	164
(VIb)	N1—H1...O1 ^{viii}	0.88 (3)	2.03 (3)	2.895 (3)	169 (2)
	O4—H4...O3	0.84	1.72	2.459 (3)	145
	C31—H31A...O2	0.98	2.30	3.034 (3)	131

Symmetry codes: (i) $\frac{1}{2} - x, \frac{3}{2} - y, -z$; (ii) $1 - x, y, \frac{1}{2} - z$; (iii) $1 - x, y, -\frac{1}{2} - z$; (iv) $1 - x, \frac{1}{2} + y, -\frac{1}{2} - z$; (v) $1 - x, 1 - y, -z$; (vi) $-x, -y, 1 - z$; (vii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (viii) $-x, 1 - y, 1 - z$.

Data collection

Siemens R3m/V diffractometer
 ω scans
 3686 measured reflections
 3414 independent reflections
 2279 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.073$
 $\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.066$
 $wR(F^2) = 0.192$
 $S = 1.02$
 3414 reflections
 207 parameters
 H atoms treated by a mixture of independent and constrained refinement

$h = 0 \rightarrow 9$
 $k = -13 \rightarrow 13$
 $l = -14 \rightarrow 14$
 2 standard reflections
 every 198 reflections
 intensity decay: none

$$w = 1/[\sigma^2(F_o^2) + (0.1091P)^2 + 0.0847P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.29 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.33 \text{ e } \text{Å}^{-3}$

H atoms were typically placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.95–0.99 Å, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{O})$ for CH, OH and CH₂ groups or pyrrole H atoms, and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl groups. The pyrrole H atoms in all six structures were refined with isotropic displacement parameters. The H atom at O4 in (VIb) was located in a difference map and refined using a standard riding model (O—H = 0.84 Å).

For all compounds, data collection: P3 (Siemens, 1995); cell refinement: P3; data reduction: XDISK (Siemens, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990) for (I), (II), (III), (IV) and (VIb), and SIR92 (Altomare *et al.*, 1994) for (V); 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) for (I), (II) and (VIb), and SHELXL97 for (III), (IV) and (V).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1869). Services for accessing these data are described at the back of the journal.

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