

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

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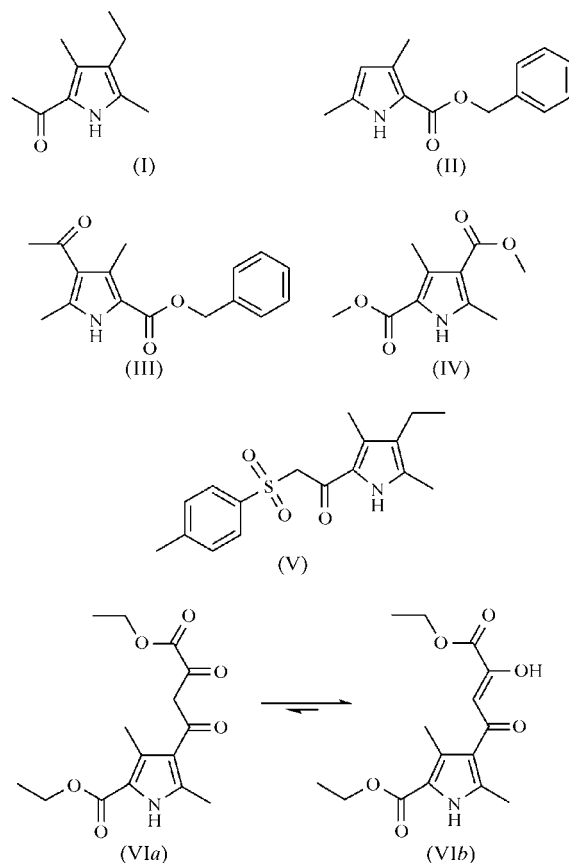
The crystal and molecular structures of 4-ethyl-3,5-dimethylpyrrole-2-carbaldehyde, C<sub>10</sub>H<sub>15</sub>NO, (I), benzyl 3,5-dimethylpyrrole-2-carboxylate, C<sub>14</sub>H<sub>15</sub>NO<sub>2</sub>, (II), benzyl 4-acetyl-3,5-dimethylpyrrole-2-carboxylate, C<sub>16</sub>H<sub>17</sub>NO<sub>3</sub>, (III), dimethyl 3,5-dimethylpyrrole-2,4-dicarboxylate, C<sub>10</sub>H<sub>13</sub>NO<sub>4</sub>, (IV), 4-ethyl-3,5-dimethyl-2-(*p*-tosylacetyl)pyrrole, C<sub>17</sub>H<sub>21</sub>NO<sub>3</sub>S, (V), and ethyl 4-(2-ethoxycarbonyl-2-hydroxyacryloyl)-3,5-dimethylpyrrole-2-carboxylate, C<sub>15</sub>H<sub>19</sub>NO<sub>6</sub>, (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 CH<sub>3</sub>···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-

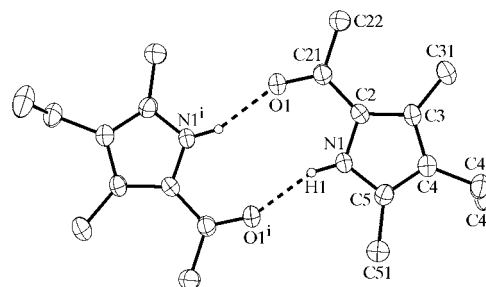
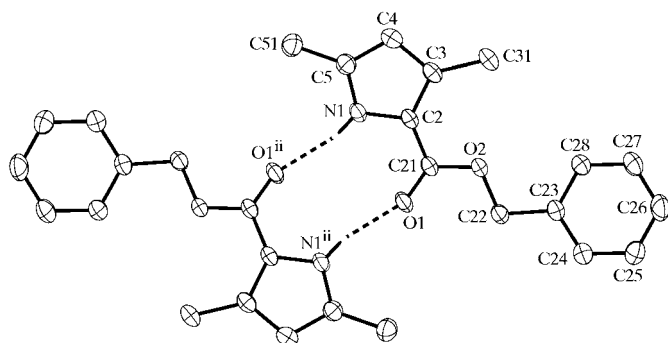


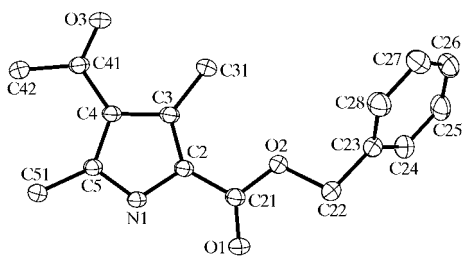
Figure 1

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.

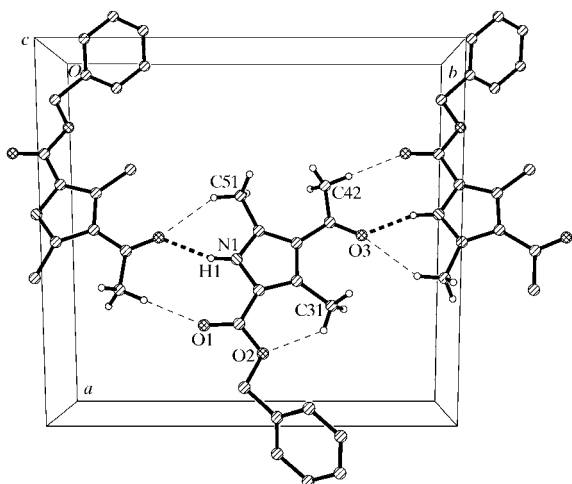
ving the pyrrole H atom and the acetyl carbonyl group (N1—H1···O3<sup>iii</sup>, symmetry code as in Table 1) (Fig. 4). This N—H···O bond is the shortest [1.971 (18) Å] found in the present structures. Carbonyl atom O3 is tightly coordinated by the C51 methyl group (H51C···O3 = 2.49 Å). Likewise, the 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.



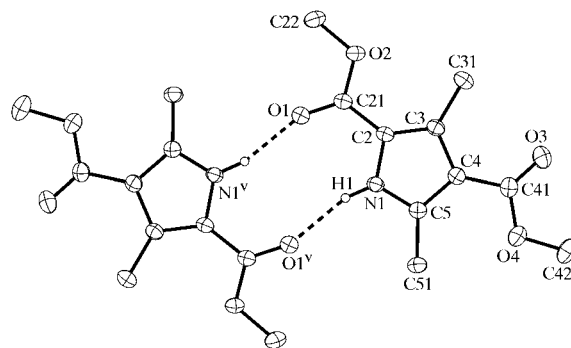
**Figure 3**  
A view of (III). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted.



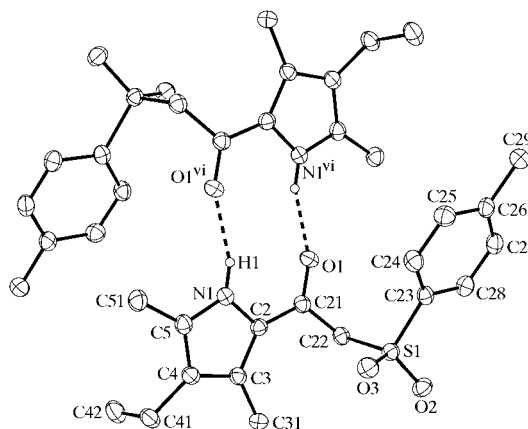
**Figure 4**  
A view of the hydrogen-bonded chain formed in (III) (view down the *c* axis). Heavy dashed lines indicate classical hydrogen bonds and dashed lines indicate C—H···O interactions. Other H atoms have been omitted.

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<sup>vi</sup> 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<sup>viii</sup>;



**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.

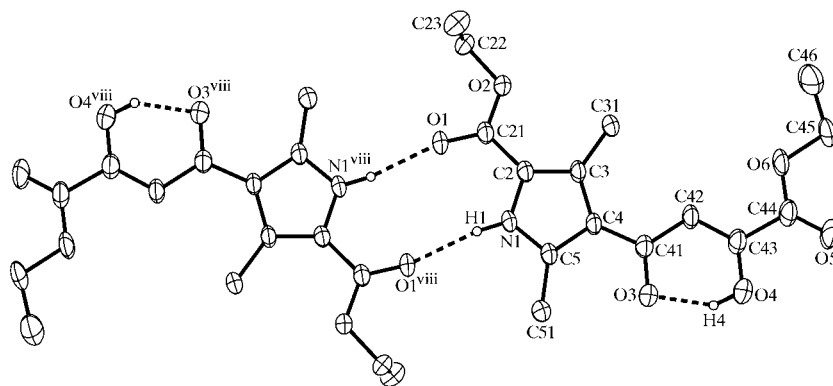


Figure 7

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; Tabba & 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 CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane.

### Compound (I)

#### Crystal data

C<sub>10</sub>H<sub>15</sub>NO  
*M<sub>r</sub>* = 165.23  
 Monoclinic, *C*2/*c*  
*a* = 28.513 (12) Å  
*b* = 9.007 (5) Å  
*c* = 7.471 (3) Å  
 $\beta$  = 99.83 (3)°  
*V* = 1890.5 (15) Å<sup>3</sup>  
*Z* = 8

*D<sub>x</sub>* = 1.161 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 42 reflections  
 $\theta$  = 18–24°  
 $\mu$  = 0.08 mm<sup>-1</sup>  
*T* = 130 (2) K  
 Block, colorless  
 0.55 × 0.41 × 0.40 mm

#### Data collection

Siemens *R3m/V* diffractometer  
 $\omega$  scans  
 2493 measured reflections  
 2174 independent reflections  
 1343 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.041  
 $\theta_{\max}$  = 27.5°

#### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.064  
*wR*(*F*<sup>2</sup>) = 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

C<sub>14</sub>H<sub>15</sub>NO<sub>2</sub>  
*M<sub>r</sub>* = 229.27  
 Monoclinic, *C*2/*c*  
*a* = 31.793 (18) Å  
*b* = 7.308 (2) Å  
*c* = 10.553 (3) Å  
 $\beta$  = 97.02 (3)°  
*V* = 2433.5 (17) Å<sup>3</sup>  
*Z* = 8

*D<sub>x</sub>* = 1.252 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 38 reflections  
 $\theta$  = 19–25°  
 $\mu$  = 0.08 mm<sup>-1</sup>  
*T* = 130 (2) K  
 Plate, colorless  
 0.50 × 0.50 × 0.08 mm

#### Data collection

Siemens *R3m/V* diffractometer  
 $\omega$  scans  
 3086 measured reflections  
 2799 independent reflections  
 2120 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.017  
 $\theta_{\max}$  = 27.5°

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

#### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.050  
*wR*(*F*<sup>2</sup>) = 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

C<sub>16</sub>H<sub>17</sub>NO<sub>3</sub>  
*M<sub>r</sub>* = 271.31  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>/*c*  
*a* = 13.473 (3) Å  
*b* = 14.359 (3) Å  
*c* = 7.489 (2) Å  
 $\beta$  = 100.47 (2)°  
*V* = 1424.7 (6) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.265 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 44 reflections  
 $\theta$  = 18–23°  
 $\mu$  = 0.09 mm<sup>-1</sup>  
*T* = 143 (2) K  
 Cube, colorless  
 0.35 × 0.35 × 0.35 mm

Data collection

Siemens *R3m/V* diffractometer  
 $\omega$  scans  
 3519 measured reflections  
 3268 independent reflections  
 2871 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.044  
 $\theta_{\max}$  = 27.5°

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

Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.043  
*wR*(*F*<sup>2</sup>) = 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)<sub>max</sub> = 0.001  
 Δρ<sub>max</sub> = 0.41 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.22 e Å<sup>-3</sup>  
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.027 (3)

Compound (IV)

Crystal data

C<sub>10</sub>H<sub>13</sub>NO<sub>4</sub>  
*M<sub>r</sub>* = 211.21  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>/*c*  
*a* = 8.150 (4) Å  
*b* = 16.040 (6) Å  
*c* = 7.908 (4) Å  
 $\beta$  = 95.31 (3)°  
*V* = 1029.3 (8) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.363 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 41 reflections  
 $\theta$  = 20–25°  
 $\mu$  = 0.11 mm<sup>-1</sup>  
*T* = 130 (2) K  
 Plate, colorless  
 0.40 × 0.38 × 0.10 mm

Data collection

Siemens *R3m/V* diffractometer  
 $\omega$  scans  
 2521 measured reflections  
 2354 independent reflections  
 2214 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.084  
 $\theta_{\max}$  = 27.5°

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

Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.047  
*wR*(*F*<sup>2</sup>) = 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)<sub>max</sub> = 0.006  
 Δρ<sub>max</sub> = 0.43 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.29 e Å<sup>-3</sup>  
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.046 (7)

Compound (V)

Crystal data

C<sub>17</sub>H<sub>21</sub>NO<sub>3</sub>S  
*M<sub>r</sub>* = 319.41  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>/*c*  
*a* = 5.179 (2) Å  
*b* = 13.986 (4) Å  
*c* = 22.315 (13) Å  
 $\beta$  = 90.09 (4)°  
*V* = 1616.4 (12) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.321 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 32 reflections  
 $\theta$  = 19–23°  
 $\mu$  = 0.21 mm<sup>-1</sup>  
*T* = 130 (2) K  
 Block, colorless  
 0.30 × 0.25 × 0.25 mm

Data collection

Siemens *R3m/V* diffractometer  
 $\omega$  scans  
 4753 measured reflections  
 3730 independent reflections  
 2761 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.025  
 $\theta_{\max}$  = 27.6°

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

Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.048  
*wR*(*F*<sup>2</sup>) = 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)<sub>max</sub> = 0.003  
 Δρ<sub>max</sub> = 0.31 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.35 e Å<sup>-3</sup>

Compound (VIb)

Crystal data

C<sub>15</sub>H<sub>19</sub>NO<sub>6</sub>  
*M<sub>r</sub>* = 309.31  
 Triclinic, *P* $\bar{1}$   
*a* = 7.281 (3) Å  
*b* = 10.363 (6) Å  
*c* = 11.003 (7) Å  
 $\alpha$  = 65.11 (5)°  
 $\beta$  = 84.61 (5)°  
 $\gamma$  = 86.65 (4)°  
*V* = 749.6 (8) Å<sup>3</sup>

*Z* = 2  
*D<sub>x</sub>* = 1.370 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 25 reflections  
 $\theta$  = 18–22°  
 $\mu$  = 0.11 mm<sup>-1</sup>  
*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 <sup>i</sup>	0.95 (3)	1.99 (3)	2.882 (3)	156 (2)
(II)	N1—H1...O1 <sup>ii</sup>	0.87 (2)	2.02 (3)	2.862 (3)	164 (2)
(III)	N1—H1...O3 <sup>iii</sup>	0.936 (18)	1.971 (18)	2.8624 (14)	158.5 (15)
	C51—H51C...O3 <sup>iii</sup>	0.98	2.49	3.3292 (16)	143
	C42—H42C...O1 <sup>iv</sup>	0.98	2.30	3.2401 (16)	160
	C31—H31C...O2	0.98	2.28	3.0127 (16)	130
(IV)	N1—H1...O1 <sup>v</sup>	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 <sup>vi</sup>	0.88 (3)	1.98 (3)	2.826 (3)	161 (3)
	C29—H29B...O2 <sup>vii</sup>	0.98	2.34	3.299 (4)	164
(VIb)	N1—H1...O1 <sup>viii</sup>	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)  $1 - x, y, -\frac{1}{2}, -\frac{1}{2} - z$ ; (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	$h = 0 \rightarrow 9$
$\omega$ scans	$k = -13 \rightarrow 13$
3686 measured reflections	$l = -14 \rightarrow 14$
3414 independent reflections	2 standard reflections
2279 reflections with $I > 2\sigma(I)$	every 198 reflections
$R_{\text{int}} = 0.073$	intensity decay: none
$\theta_{\text{max}} = 27.5^\circ$	

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.1091P)^2 + 0.0847P]$
$R[F^2 > 2\sigma(F^2)] = 0.066$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.192$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.29 \text{ e } \text{\AA}^{-3}$
3414 reflections	$\Delta\rho_{\text{min}} = -0.33 \text{ e } \text{\AA}^{-3}$
207 parameters	
H atoms treated by a mixture of independent and constrained refinement	

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 CH<sub>2</sub> 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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