

H-atom positions were calculated and confirmed in difference Fourier maps. The H atoms were refined as riding atoms with fixed isotropic displacement parameters. The program PLATON94 (Spek, 1994) with the module MISSYM (Le Page, 1987, 1988) was used to check for missed symmetry and found no extra crystallographic symmetry. PARST95 (Nardelli, 1996) located a pseudosymmetry between molecules A and B (pseudo-twofold axis, pseudo inversion centre). The reflection data were analyzed and it was observed that the reflections  $0kl$  are systematically absent for  $l = 2n + 1$ . This indicates the monoclinic space group  $P2_1/c$  (interchanging  $a$  and  $b$ ). However, the unit-cell angles are clearly different from  $90^\circ$  for two of the angles and the program TRACER (Lawton & Jacobson, 1965), which checks for other possible unit cell options, did not find any new solution. The conclusion is that the correct space group is  $P\bar{1}$ , but pseudosymmetry elements show that it is close to the monoclinic space group  $P2_1/c$ .

Data reduction: DREADD (Blessing, 1987, 1989). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1102). Services for accessing these data are described at the back of the journal.

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## Four Methyl Azolyl-3-propenoates

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## Abstract

The structures of four azolyl-3-propenoic esters, methyl (*E*)-3-(imidazol-4-yl)propenoate, (2), as its hemihydrate,  $C_7H_8N_2O_2 \cdot 0.5H_2O$ , methyl (*E*)-3-(pyrrol-2-yl)propenoate,  $C_8H_9NO_2$ , (3), methyl (*E*)-3-(imidazol-2-yl)propenoate,  $C_7H_8N_2O_2$ , (4), and methyl (*Z*)-3-(imidazol-2-yl)propenoate,  $C_7H_8N_2O_2$ , (5), are reported. In the pyrrole and imidazole derivatives, (3) and (4), the N—H function has an *s*-*Z* configuration with respect to the propenoate chain, whereas in the urocanate, (2), protonation has occurred at the N atom further from the side chain. In (5), an intramolecular N—H···O hydrogen bond causes a relative widening of the angles in the side chain. In all four compounds, both the azole rings and the side chains are almost planar. In the hemihydrate of (2), there is extensive hydrogen bonding, primarily of the type N—H···O but supplemented by much longer C—H···O interactions. In (3) and (4), the hydrogen bonding is much simpler, with molecules linked into ribbons via N—H···O contacts.

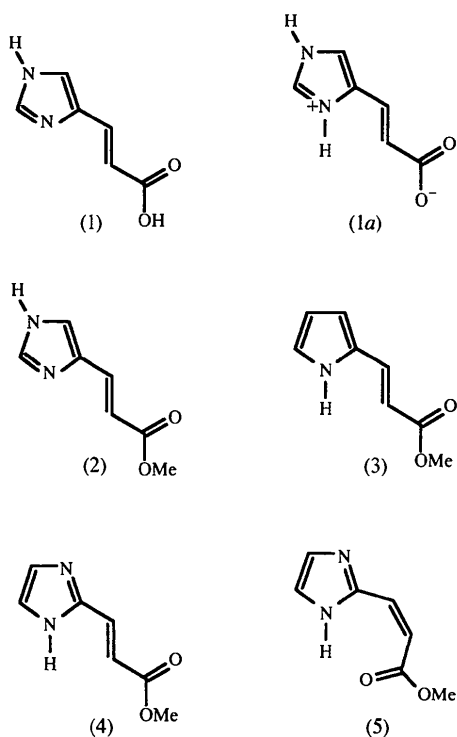
## Comment

(*E*)-Urocanic acid, (1), is a naturally occurring metabolite of histidine, which comprises *ca* 0.5% of the dry weight of the epidermis. It is thought that (1) acts as a natural photoprotecting agent (Morrison, 1985) and for this reason there are many recent patents covering the uses of esters of (1) as components of sunscreens. Although the structure of (1) itself has been known for 20 years (Hawkinson, 1977; Svinning & Sørum, 1979), it occurs in the solid state as a zwitterion, (1a), and so is not directly relevant to the corresponding ester structure. In this paper, we report structural data for a series of four azolyl-3-propenoic esters comprising methyl (*E*)-urocanate, (2) (as the hemihydrate), the corresponding pyrrol-2-yl and imidazol-2-yl derivatives, (3) and (4), and the imidazol-2-yl (*Z*)-propenoate, (5) (McNab & Thornley, 1997; Campbell *et al.*, 1997).

In the structure of (3), there are two molecules per asymmetric unit and in (5) there are three molecules;

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no significant differences between the independent molecules in the asymmetric unit in each of these were noted, except as detailed below. In the pyrrole and imidazole derivatives, (3) and (4), the N—H bond adopts an *s*-*Z* configuration with respect to the propenoate chain, whereas in the urocanate, (2), it is the N atom remote from the side chain which is protonated. The absence of an adjacent N—H bond allows the angle C4—C6—C7 in (2) to become more acute [125.68 (13)°] than in the other *E* esters (>127°). The (*Z*)-propenoate, (5), forms an intramolecular hydrogen bond between the N—H bond and the carbonyl O atom of the ester moiety [average parameters N—H 0.89 (3), O··H 1.84 (3) Å, N—H··O 149 (3)° and O··N 2.653 (3) Å]. This causes all the angles in the side chain to be widened (by 1.4–6.8°) with respect to the *E* esters, with the major differences occurring at C6 and C7.

A comparison of the bond lengths in the four structures reveals few significant differences. The parameters for the azole rings are little different from typical values for these systems. However, the small difference, in (3), between the N1—C5 and N1—C2 lengths is common in pyrroles with electron-withdrawing substituents in the 2-position (Blake, McNab & Thornley, 1995) and the N3—C4 bond in (2) is particularly long by comparison with the other structures. Both of these minor features may reflect the conjugative pathway from the N1 lone pair to the ester carbonyl function.

In all the structures, (2)–(5), the azole rings are planar [greatest ring deviations 0.003 Å in (2), (3) and (4)]; the propenoate chains as a whole are also close to being

planar, although the average deviations are *ca* one order of magnitude greater. The angles between the normals to these planes are small but significant, ranging from 0.85 (11)° in molecule *B* of (5), to 9.97 (9) and 9.2 (2)° in (2) and (4), respectively.

In (2), which crystallizes as the hemihydrate with the water molecule on a twofold axis (Fig. 1), there is extensive hydrogen bonding; each water molecule acts as a double donor and double acceptor to four symmetry-related molecules of (2). Each molecule of (2) forms one long and two short hydrogen bonds; the long contact involves C5—H5··O9<sup>i</sup> [H5··O9<sup>i</sup> 2.48 (2) Å and C5—H5··O9<sup>i</sup> 154 (2)°; symmetry code: (i)  $x - \frac{1}{2}, y - \frac{1}{2}, z$ ]. The short contacts involve the water molecules and are (a) an N1—H1··O1W interaction within the same asymmetric unit, with H1··O1W 1.99 (2) Å and N1—H1··O1W 176 (2)°, and (b) an N3··H1W<sup>ii</sup>—O1W<sup>ii</sup> contact with N3··H1W<sup>ii</sup> 2.03 (2) Å and N3··H1W<sup>ii</sup>—O1W<sup>ii</sup> 164 (2)° [symmetry code: (ii)  $-\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$ ]. The structure may be visualized as alternating shells of water and (2), which are shown in Fig. 1.

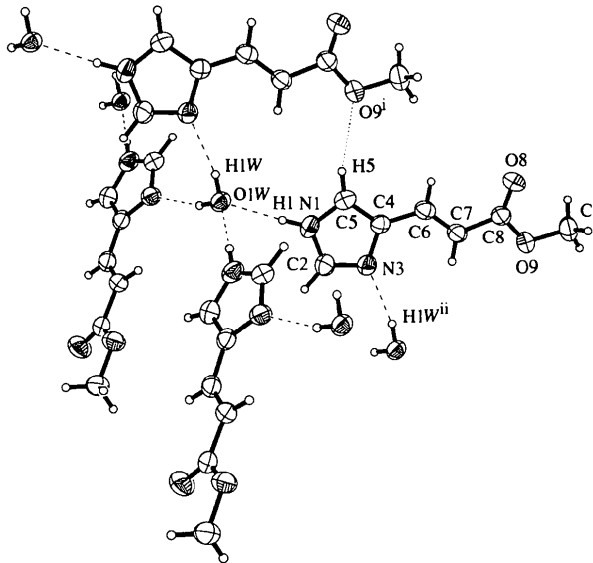


Fig. 1. A view of the structure of (2)·0.5H<sub>2</sub>O, showing the atom-numbering scheme and part of the hydrogen-bonded network. Displacement ellipsoids enclose 50% probability surfaces and H atoms are shown as spheres of arbitrary radii. [Symmetry codes: (i)  $x - \frac{1}{2}, y - \frac{1}{2}, z$ ; (ii)  $-\frac{1}{2} + x, \frac{1}{2} + y, \frac{3}{2} - z$ ].

The asymmetric unit of (3) contains two independent molecules (Fig. 2) which are hydrogen bonded [O8··H1'—N1', with O8··H1' 2.03 (2) Å and O8··H1'—N1' 166 (4)°]. These pairs of molecules are further linked by N1—H1··O8<sup>i</sup> contacts [H1··O8<sup>i</sup> 1.98 (2) Å and N1—H1··O8<sup>i</sup> 169 (4)°; symmetry code: (i)  $x - 1, y, z$ ] to form infinite ribbons running parallel to *a*.

In (4) (Fig. 3), molecules related by the *a* glide plane are linked into ribbons running in the *a* direction, in this

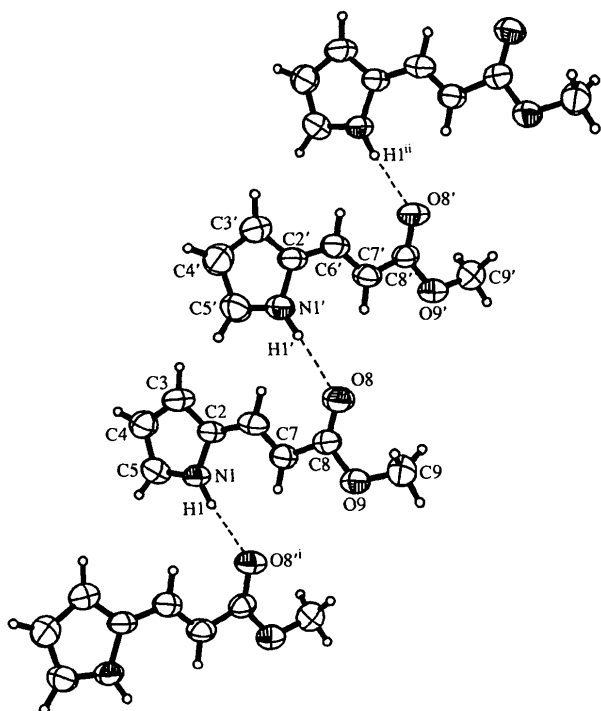


Fig. 2. A view of the structure of (3) showing the atom-numbering scheme for the two independent molecules, which are hydrogen bonded and alternate to form ribbons of molecules in the *a* direction. Displacement ellipsoids enclose 50% probability surfaces and H atoms are shown as spheres of arbitrary radii. [Symmetry codes: (i)  $x + 1, y, z$ ; (ii)  $x - 1, y, z$ .]

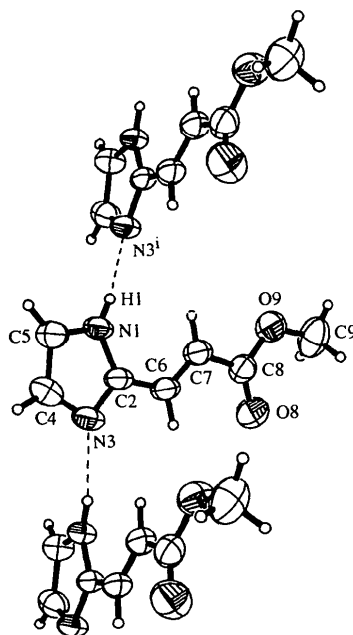


Fig. 3. A view of the structure of (4) showing the atom-numbering scheme. The hydrogen-bonded molecules are related by the  $2_1$  screw axis parallel to *a* and form ribbons running in that direction. Displacement ellipsoids enclose 50% probability surfaces and H atoms are shown as spheres of arbitrary radii. [Symmetry code: (i)  $x - \frac{1}{2}, y, \frac{1}{2} - z$ .]

case by  $N1-H1 \cdots N3^i$  contacts [ $H1 \cdots N3^i$  2.04 (3) Å and  $N1-H1 \cdots N3^i$  171 (3)°; symmetry code: (i)  $x - \frac{1}{2}, y, \frac{1}{2} - z$ ].

There are no significant intermolecular hydrogen bonds in (5), only the intramolecular contact described above (see Fig. 4).

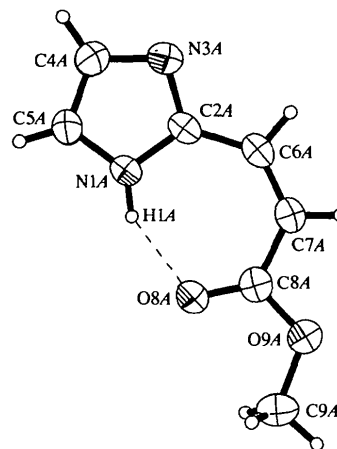


Fig. 4. A view of one of the three independent molecules of (5) showing the atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces and H atoms are shown as spheres of arbitrary radii. The intramolecular  $N-H \cdots O$  hydrogen bond closes a seven-membered ring.

## Experimental

The urocanate, (2), was prepared by esterification of commercially available urocanic acid (Kimoto, Fujii & Cohen, 1984; McNab & Thornley, 1997). The esters, (3)–(5), were made by Wittig reactions of the appropriate azolyaldehyde as described previously [(3) according to Campbell *et al.*, 1997; (4) and (5) according to McNab & Thornley, 1997]. Compound (2) was crystallized from ethyl acetate, (3) from toluene/hexane, (4) from benzene and (5) from hexane.

### Compound (2)

#### Crystal data

$C_7H_8N_2O_2 \cdot 0.5H_2O$

$M_r = 161.16$

Monoclinic

$C2/c$

$a = 7.498$  (3) Å

$b = 12.564$  (4) Å

$c = 16.296$  (13) Å

$\beta = 93.36$  (4)°

$V = 1532.5$  (15) Å<sup>3</sup>

$Z = 8$

$D_x = 1.397$  Mg m<sup>-3</sup>

$D_m$  not measured

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 18

reflections

$\theta = 15$ – $16^\circ$

$\mu = 0.108$  mm<sup>-1</sup>

$T = 173$  (2) K

Tablet

$0.77 \times 0.77 \times 0.42$  mm

Colourless

**Data collection**

Stoe Stadi-4 four-circle diffractometer with Oxford Cryosystems open-flow cryostat (Cosier & Glazer, 1986)  
 $\omega$ - $2\theta$  scans  
 Absorption correction: none  
 1345 measured reflections  
 1345 independent reflections

1234 reflections with  $I > 2\sigma(I)$   
 $\theta_{\max} = 25.05^\circ$   
 $h = -8 \rightarrow 8$   
 $k = 0 \rightarrow 14$   
 $l = 0 \rightarrow 19$

3 standard reflections  
 frequency: 60 min  
 intensity variation:  $\pm 1.5\%$

**Refinement**

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.096$   
 $S = 1.057$   
 1345 reflections  
 142 parameters  
 H atoms freely refined with common  $U_{\text{iso}} = 0.042(2) \text{ \AA}^2$   
 $w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 0.924P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.20 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.16 \text{ e \AA}^{-3}$   
 Extinction correction: SHELXL96 (Sheldrick, 1996)  
 Extinction coefficient: 0.0044 (12)  
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (2)

|          |             |          |             |
|----------|-------------|----------|-------------|
| N1—C2    | 1.3523 (19) | C6—C7    | 1.330 (2)   |
| N1—C5    | 1.362 (2)   | C7—C8    | 1.473 (2)   |
| C2—N3    | 1.3147 (19) | C8—O8    | 1.2063 (18) |
| N3—C4    | 1.3873 (19) | C8—O9    | 1.3486 (17) |
| C4—C5    | 1.3690 (19) | O9—C9    | 1.4452 (18) |
| C4—C6    | 1.445 (2)   |          |             |
| C2—N1—C5 | 107.03 (12) | C7—C6—C4 | 125.68 (13) |
| N3—C2—N1 | 112.23 (13) | C6—C7—C8 | 121.16 (13) |
| C2—N3—C4 | 104.95 (12) | O8—C8—O9 | 123.36 (12) |
| C5—C4—N3 | 109.45 (12) | O8—C8—C7 | 126.20 (13) |
| C5—C4—C6 | 127.22 (12) | O9—C8—C7 | 110.44 (11) |
| N3—C4—C6 | 123.31 (12) | C8—O9—C9 | 116.36 (11) |
| N1—C5—C4 | 106.33 (12) |          |             |

**Compound (3)***Crystal data*

C<sub>8</sub>H<sub>9</sub>NO<sub>2</sub>  
 $M_r = 151.16$   
 Monoclinic  
 $P2_1/n$   
 $a = 10.795(3) \text{ \AA}$   
 $b = 8.271(1) \text{ \AA}$   
 $c = 17.803(3) \text{ \AA}$   
 $\beta = 92.957(15)^\circ$   
 $V = 1587.5(6) \text{ \AA}^3$   
 $Z = 8$   
 $D_x = 1.265 \text{ Mg m}^{-3}$   
 $D_m$  not measured

*Data collection*

Stoe Stadi-4 four-circle diffractometer  
 $\omega$ - $2\theta$  scans  
 Absorption correction: none

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 27 reflections  
 $\theta = 12-13^\circ$   
 $\mu = 0.092 \text{ mm}^{-1}$   
 $T = 298(2) \text{ K}$   
 Lath  
 $0.930 \times 0.175 \times 0.078 \text{ mm}$   
 Colourless

2589 measured reflections  
 2589 independent reflections  
 918 reflections with  $I > 2\sigma(I)$

*Refinement*

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.058$   
 $wR(F^2) = 0.215$   
 $S = 1.014$   
 2589 reflections  
 206 parameters  
 H atoms freely refined (for H1 and H1', on N1 and N1', respectively) and riding model for all others  
 $w = 1/[\sigma^2(F_o^2) + (0.079P)^2 + 0.352P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

3 standard reflections  
 frequency: 120 min  
 intensity decay: 16%

$(\Delta/\sigma)_{\max} = 0.005$   
 $\Delta\rho_{\max} = 0.17 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.18 \text{ e \AA}^{-3}$   
 Extinction correction: SHELXL96 (Sheldrick, 1996)  
 Extinction coefficient: 0.0038 (13)  
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (3)

|          |           |          |           |
|----------|-----------|----------|-----------|
| N1—C5    | 1.352 (6) | C6—C7    | 1.322 (6) |
| N1—C2    | 1.366 (6) | C7—C8    | 1.459 (7) |
| C2—C3    | 1.365 (6) | C8—O8    | 1.213 (5) |
| C2—C6    | 1.433 (7) | C8—O9    | 1.343 (5) |
| C3—C4    | 1.389 (7) | O9—C9    | 1.437 (6) |
| C4—C5    | 1.359 (6) |          |           |
| C5—N1—C2 | 108.6 (4) | C7—C6—C2 | 128.1 (5) |
| C3—C2—N1 | 107.0 (5) | C6—C7—C8 | 121.4 (5) |
| C3—C2—C6 | 129.2 (5) | O8—C8—O9 | 122.1 (5) |
| N1—C2—C6 | 123.7 (5) | O8—C8—C7 | 125.9 (5) |
| C2—C3—C4 | 108.8 (5) | O9—C8—C7 | 112.0 (4) |
| C5—C4—C3 | 106.2 (5) | C8—O9—C9 | 116.1 (4) |
| N1—C5—C4 | 109.3 (5) |          |           |

**Compound (4)***Crystal data*

C<sub>7</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>  
 $M_r = 152.15$   
 Orthorhombic  
 $Pbca$   
 $a = 9.706(2) \text{ \AA}$   
 $b = 8.9898(9) \text{ \AA}$   
 $c = 17.714(3) \text{ \AA}$   
 $V = 1545.6(4) \text{ \AA}^3$   
 $Z = 8$   
 $D_x = 1.308 \text{ Mg m}^{-3}$   
 $D_m$  not measured

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 30 reflections  
 $\theta = 13-14^\circ$   
 $\mu = 0.098 \text{ mm}^{-1}$   
 $T = 277(2) \text{ K}$   
 Plate  
 $0.68 \times 0.54 \times 0.05 \text{ mm}$   
 Colourless

*Data collection*

Stoe Stadi-4 four-circle diffractometer with Oxford Cryosystems open-flow cryostat (Cosier & Glazer, 1986)  
 $\omega$ - $2\theta$  scans  
 Absorption correction: none  
 1365 measured reflections  
 1365 independent reflections

747 reflections with  $I > 2\sigma(I)$   
 $\theta_{\max} = 25.02^\circ$   
 $h = 0 \rightarrow 11$   
 $k = 0 \rightarrow 10$   
 $l = -21 \rightarrow 0$   
 3 standard reflections  
 frequency: 120 min  
 intensity decay: none

**Refinement**Refinement on  $F^2$ 

$$R[F^2 > 2\sigma(F^2)] = 0.044$$

$$wR(F^2) = 0.137$$

$$S = 1.108$$

1365 reflections

104 parameters

H atoms riding, except for  
H1 (bound to N1) which  
was refined freely

$$w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 1.04P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

Table 3. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (4)

|          |           |          |           |
|----------|-----------|----------|-----------|
| N1—C2    | 1.342 (3) | C6—C7    | 1.318 (4) |
| N1—C5    | 1.354 (4) | C7—C8    | 1.465 (4) |
| C2—N3    | 1.333 (3) | C8—O8    | 1.194 (4) |
| C2—C6    | 1.433 (4) | C8—O9    | 1.340 (4) |
| N3—C4    | 1.361 (4) | O9—C9    | 1.452 (4) |
| C4—C5    | 1.353 (4) |          |           |
| C2—N1—C5 | 108.1 (2) | C7—C6—C2 | 127.3 (3) |
| N3—C2—N1 | 110.2 (2) | C6—C7—C8 | 121.5 (3) |
| N3—C2—C6 | 124.3 (3) | O8—C8—O9 | 123.7 (3) |
| N1—C2—C6 | 125.5 (3) | O8—C8—C7 | 125.5 (3) |
| C2—N3—C4 | 105.6 (2) | O9—C8—C7 | 110.8 (3) |
| C5—C4—N3 | 110.0 (3) | C8—O9—C9 | 116.7 (3) |
| C4—C5—N1 | 106.1 (3) |          |           |

**Compound (5)***Crystal data*

$$M_r = 152.15$$

Monoclinic

 $P2_1/c$ 

$$a = 15.700 (13) \text{\AA}$$

$$b = 18.927 (16) \text{\AA}$$

$$c = 7.311 (5) \text{\AA}$$

$$\beta = 100.13 (6)^\circ$$

$$V = 2139 (3) \text{\AA}^3$$

$$Z = 12$$

$$D_x = 1.418 \text{ Mg m}^{-3}$$

 $D_m$  not measured*Data collection*

Stoe Stadi-4 four-circle  
diffractometer with  
Oxford Cryosystems  
open-flow cryostat  
(Cosier & Glazer, 1986)

 $\omega$ - $2\theta$  scans

Absorption correction: none  
2782 measured reflections  
2782 independent reflections

**Refinement**Refinement on  $F^2$ 

$$R[F^2 > 2\sigma(F^2)] = 0.039$$

$$wR(F^2) = 0.118$$

$$S = 1.036$$

2782 reflections

308 parameters

H atoms riding

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

$$\Delta\rho_{\text{max}} = 0.16 \text{ e \AA}^{-3}$$

$$\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$$

Extinction correction:

*SHELXL96* (Sheldrick,  
1996)

Extinction coefficient:

$$0.0054 (11)$$

Scattering factors from

*International Tables for  
Crystallography* (Vol. C)

$$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 0.63P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

Scattering factors from

*International Tables for  
Crystallography* (Vol. C)

Table 4. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (5)

|             |           |             |           |
|-------------|-----------|-------------|-----------|
| N1A—C2A     | 1.342 (3) | C6A—C7A     | 1.330 (4) |
| N1A—C5A     | 1.343 (3) | C7A—C8A     | 1.448 (4) |
| C2A—N3A     | 1.322 (3) | C8A—O8A     | 1.206 (3) |
| C2A—C6A     | 1.420 (4) | C8A—O9A     | 1.323 (3) |
| N3A—C4A     | 1.348 (3) | O9A—C9A     | 1.428 (3) |
| C4A—C5A     | 1.337 (4) |             |           |
| C2A—N1A—C5A | 107.9 (2) | C7A—C6A—C2A | 133.3 (2) |
| N3A—C2A—N1A | 110.3 (2) | C6A—C7A—C8A | 127.8 (2) |
| N3A—C2A—C6A | 122.5 (2) | O8A—C8A—O9A | 122.0 (2) |
| N1A—C2A—C6A | 127.2 (2) | O8A—C8A—C7A | 127.1 (3) |
| C2A—N3A—C4A | 105.1 (2) | O9A—C8A—C7A | 110.9 (2) |
| C5A—C4A—N3A | 110.9 (2) | C8A—O9A—C9A | 115.8 (2) |
| C4A—C5A—N1A | 105.9 (2) |             |           |

For all compounds, data collection: *DIF4* (Stoe & Cie, 1990a); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1990b); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL96* (Sheldrick, 1996); molecular graphics: *SHELXTL* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL96*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1192). Services for accessing these data are described at the back of the journal.

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1953 reflections with

$$I > 2\sigma(I)$$

$$\theta_{\text{max}} = 22.53^\circ$$

$$h = 0 \rightarrow 16$$

$$k = -20 \rightarrow 0$$

$$l = -7 \rightarrow 7$$

3 standard reflections

frequency: 120 min

intensity variation: &lt;1%