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## The Effect of 3-Substitution on the Structures of Pyrrole-2-carbaldehydes

XAVIER L. M. DESPINOY, STEVEN G. HARRIS, HAMISH McNAB, SIMON PARSONS AND KIRSTI WITHELL

*Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland. E-mail: s.parsons@ed.ac.uk*

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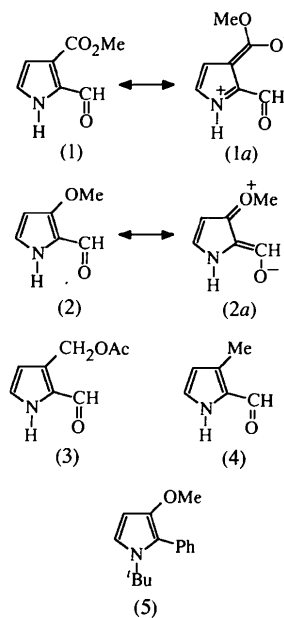
### Abstract

In the title compounds, methyl 2-formylpyrrole-3-carboxylate,  $C_7H_7NO_3$ , and 3-methoxypyrrole-2-carbaldehyde,  $C_6H_7NO_2$ , the pyrrole rings show little distortion ascribable to the electronic properties of the substituents, whether they are electron donating or electron withdrawing.

### Comment

The electronic properties of substituents on unsaturated systems is often found to influence geometry (*e.g.* Blake *et al.*, 1996). We now report the crystal structures of two pyrrole-2-carbaldehydes, one substituted in the 3-position by a strongly electron-withdrawing methoxy-carbonyl group, (1), the other similarly substituted with an electron-donating methoxy group, (2), in which the substituents have minimal effect on the structural parameters of the pyrrole ring. Two 3-substituted pyrrole-2-

carbaldehydes have been reported previously [(3): Blake *et al.*, 1995; (4): Smith *et al.*, 1985], although (2) is only the third example of a 3-methoxypyrrole to have been structurally characterized (Hunter *et al.*, 1991; Boger & Baldino, 1993).



The aldehyde group is *s*-Z with respect to the N atom of the pyrrole in both (1) and (2), at least in part due to the presence of intermolecular hydrogen bonding. The methoxy substituent at C3 and the methyl ester group are both twisted away from the aldehyde function. Both (1) and (2) are planar; maximum deviations are 0.101 Å for O11 in (1) and 0.046 Å for C9 in (2).

The bond lengths in compounds (1)–(3) are compared in Table 1 and surprisingly there is no significant difference between corresponding bonds in the pyrrole rings, with the exception of N1–C2. Here, the distance increases as a function of the substituent in the order  $CO_2Me$  [(1), 1.365 (3) Å] <  $CH_2OAc$  [(3), 1.377 (4) Å] <  $OMe$  [(2), 1.383 (3) Å]. This is consistent with delocalization of the N-atom lone pair into the ester (1a). There is a corresponding decrease in the C2–C(aldehyde) bond lengths [1.444 (3), 1.433 (4) and 1.423 (3) Å in (1), (3) and (2), respectively], consistent with delocalization of the methoxy-based lone pair into the aldehyde function (2a). In agreement with this, the C3–O8 bond in (2), at 1.348 (3) Å, is significantly shortened in comparison with the model methoxypyrrole (5), where the corresponding bond length is 1.383 (4) Å.

There are no significant differences in the endocyclic bond angles in (1)–(3). The exocyclic bond angles C2–C3–X [X =  $CO_2Me$  in (1),  $OMe$  in (2) and  $CH_2OAc$  in (3)] increase in the order (2) < (1) < (3) (see Table 1), in accord with the steric bulk of X.

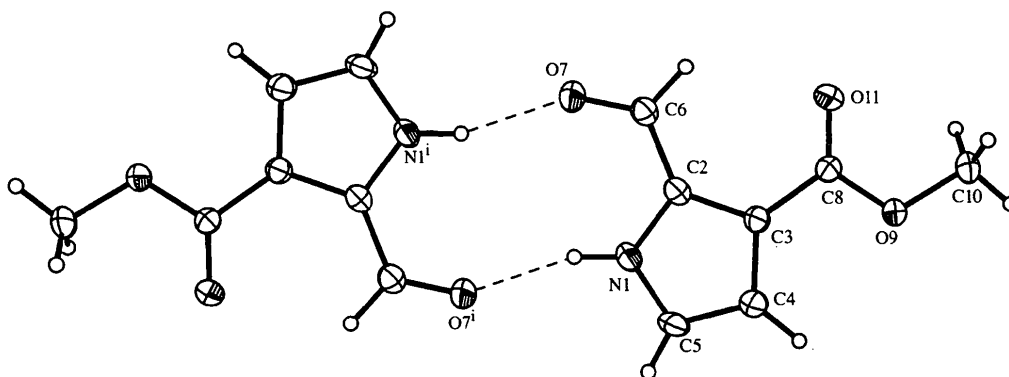


Fig. 1. View of (1) showing the formation of a hydrogen-bonded dimer in the solid state. Distance O7 $\cdots$ N1<sup>i</sup> is 2.842(3) Å, where (i) is 2 - x, -1 - y, 2 - z. Ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

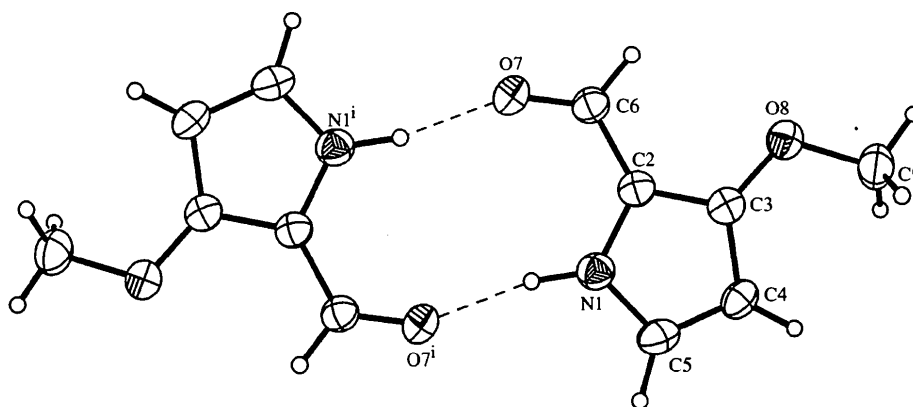


Fig. 2. View of (2) showing the formation of a hydrogen-bonded dimer in the solid state. Distance O7 $\cdots$ N1<sup>i</sup> is 2.797(3) Å, where (i) is 2 - x, 1 - y, 2 - z. Ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Packing in the crystal structures of (1) and (2) is characterized by the formation of hydrogen-bonded dimers *via* N—H $\cdots$ O=C interactions. In terms of Etter's graph-set formalism (Etter, 1990), this interaction can be described as an  $R_2^2(10)$  system and is consistent with the formation of hydrogen bonds between the most effective donor and acceptor sites.

### Experimental

Compounds (1) and (2) were obtained by photochemical ring contraction of the appropriate 4-substituted pyridine-*N*-oxide in aqueous copper(II) sulfate solution (Bisagni *et al.*, 1968; Bellamy *et al.*, 1975). Crystals of (1) and (2) were grown from toluene and chloroform, respectively.

### Compound (1)

#### Crystal data

C<sub>7</sub>H<sub>7</sub>NO<sub>3</sub>  
*M<sub>r</sub>* = 153.14

Mo *K*α radiation  
 $\lambda$  = 0.71073 Å

#### Triclinic *P*1

*a* = 5.6240(11) Å  
*b* = 7.765(2) Å  
*c* = 8.569(2) Å  
 $\alpha$  = 73.85(3)°  
 $\beta$  = 83.62(3)°  
 $\gamma$  = 88.93(3)°  
*V* = 357.19(12) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.424 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

#### Cell parameters from 25 reflections

$\theta$  = 12.5–16.0°  
 $\mu$  = 0.113 mm<sup>-1</sup>  
*T* = 150.0(2) K  
Block  
0.43 × 0.39 × 0.12 mm  
Colourless

#### Data collection

Stoe Stadi-4 diffractometer  
equipped with an Oxford  
Cryosystems low-  
temperature device (Cosier  
& Glazer, 1986)  
 $\omega$ -2 $\theta$  scans  
Absorption correction: none

976 reflections with  
 $I > 2\sigma(I)$   
*R<sub>int</sub>* = 0.059  
 $\theta_{\text{max}}$  = 25.06°  
*h* = -6 → 6  
*k* = -8 → 9  
*l* = 0 → 10

1271 measured reflections  
1264 independent reflections

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.046$   
 $wR(F^2) = 0.129$   
 $S = 1.054$   
1259 reflections  
121 parameters  
H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.0779P)^2 + 0.0235P]$   
where  $P = (F_o^2 + 2F_c^2)/3$

### Compound (2)

#### Crystal data

$C_6H_7NO_2$   
 $M_r = 125.13$   
Monoclinic  
 $P2_1/c$   
 $a = 6.9093$  (9) Å  
 $b = 12.380$  (2) Å  
 $c = 7.3256$  (11) Å  
 $\beta = 107.781$  (10)°  
 $V = 596.7$  (2) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.393$  Mg m<sup>-3</sup>  
 $D_m$  not measured

#### Data collection

Stoe Stadi-4 diffractometer  
equipped with an Oxford  
Cryosystems low-  
temperature device (Cosier  
& Glazer, 1986)  
 $\omega$ - $\theta$  scans  
Absorption correction: none  
2891 measured reflections  
887 independent reflections

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.042$   
 $wR(F^2) = 0.103$   
 $S = 1.097$   
887 reflections  
111 parameters  
All H atoms refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0572P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

3 standard reflections  
frequency: 60 min  
intensity decay: 2%

$(\Delta/\sigma)_{\max} = -0.002$   
 $\Delta\rho_{\max} = 0.23$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.22$  e Å<sup>-3</sup>  
Extinction correction:  
*SHELXTL*  
Extinction coefficient:  
0.037 (14)  
Scattering factors from  
*International Tables for  
Crystallography* (Vol. C)

Cu  $K\alpha$  radiation  
 $\lambda = 1.54184$  Å  
Cell parameters from 40  
reflections  
 $\theta = 20$ – $22^\circ$   
 $\mu = 0.888$  mm<sup>-1</sup>  
 $T = 220.0$  (2) K  
Needle  
 $0.51 \times 0.12 \times 0.12$  mm  
Colourless

689 reflections with  
 $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.075$   
 $\theta_{\max} = 60.16^\circ$   
 $h = -7 \rightarrow 7$   
 $k = -13 \rightarrow 13$   
 $l = -7 \rightarrow 8$   
3 standard reflections  
frequency: 60 min  
intensity decay: none

$\Delta\rho_{\max} = 0.25$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.20$  e Å<sup>-3</sup>  
Extinction correction:  
*SHELXTL*  
Extinction coefficient:  
0.023 (3)  
Scattering factors from  
*International Tables for  
Crystallography* (Vol. C)

C4—C5	1.374 (3)	1.371 (4)	1.370 (5)
N1—C5	1.352 (3)	1.352 (3)	1.351 (4)
C2—C6	1.444 (3)	1.423 (3)	1.433 (4)
C6—O7	1.226 (3)	1.223 (3)	1.225 (4)
C3—C8/O8	1.466 (3)	1.348 (3)	1.502 (4)
C2—N1—C5	110.0 (2)	108.7 (2)	109.0 (3)
N1—C2—C6	121.6 (2)	123.7 (2)	121.9 (3)
C3—C2—C6	131.5 (2)	129.4 (2)	130.6 (3)
N1—C2—C3	106.9 (2)	106.8 (2)	107.4 (3)
C2—C3—C8/O8	125.2 (2)	122.2 (2)	127.1 (3)
C4—C3—C8/O8	127.5 (2)	129.7 (2)	125.7 (3)
C2—C3—C4	107.3 (2)	108.1 (2)	107.2 (3)
C3—C4—C5	107.1 (2)	106.5 (2)	107.3 (3)
N1—C5—C4	108.7 (2)	109.9 (2)	109.1 (3)

Note: (a) the numbering scheme has been changed slightly from the original publication to be consistent with those of (1) and (2).

For (1), all H atoms were freely refined with isotropic displacement parameters, except those comprising the methyl group at C10, which was treated as a rotating rigid group. For compound (2), the presence of the low-temperature device during data collection limited the maximum value of  $2\theta$  to  $120^\circ$ .

For both compounds, data collection: *DIF4* (Stoe & Cie, 1990a); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1990b). Program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990) for (1); *SHELXTL* (Sheldrick, 1994) for (2). For both compounds, program(s) used to refine structures: *SHELXTL*; molecular graphics: *SHELXTL*.

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Supplementary data for this paper are available from the IUCR electronic archives (Reference: BM1194). Services for accessing these data are described at the back of the journal.

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Table 1. Comparison of bond lengths (Å) and angles (°) for compounds (1), (2) and (3)

	(1)	(2)	(3) <sup>a</sup>
N1—C2	1.365 (3)	1.383 (3)	1.377 (4)
C2—C3	1.401 (3)	1.393 (3)	1.389 (4)
C3—C4	1.405 (3)	1.400 (3)	1.402 (4)