Acta Crystallographica Section C
**Crystal Structure Communications**
ISSN 0108-2701

# Three $N^2$-benzoyloxybenzamidines: sheet structures built from hard and soft hydrogen bonds and aromatic π–π stacking interactions

**Carlos E. M. Carvalho,[a] Solange M. S. V. Wardell,[a] James L. Wardell,[b] Janet M. S. Skakle,[c] John N. Low[c] and Christopher Glidewell[d]***

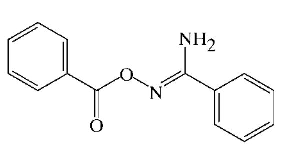
[a]Instituto de Química, Universidade Federal Fluminense, 24020-150 Niterói, Rio de Janeiro, RJ, Brazil, [b]Instituto de Química, Departamento de Química Inorgânica, Universidade Federal do Rio de Janeiro, 21945-970 Rio de Janeiro, RJ, Brazil, [c]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and [d]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

Received 29 October 2003
Accepted 4 November 2003
Online 6 December 2003

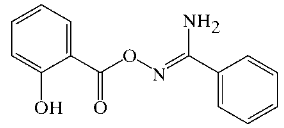
Molecules of the title compounds $N^2$-(benzoyloxy)benzamidine, $C_{14}H_{12}N_2O_2$, (I), $N^2$-(2-hydroxybenzoyloxy)benzamidine, $C_{14}H_{12}N_2O_3$, (II), and $N^2$-benzoyloxy-2-hydroxybenzamidine, $C_{14}H_{12}N_2O_3$, (III), all have extended chain conformations, with the aryl groups remote from one another. In (I), the molecules are linked into chains by a single N—H···N hydrogen bond [H···N = 2.15 Å, N···N = 3.029 (2) Å and N—H···N = 153°] and these chains are linked into sheets by means of aromatic π–π stacking interactions. There is one intramolecular O—H···O hydrogen bond in (II), and a combination of one three-centre N—H···(N,O) hydrogen bond [H···N = 2.46 Å, H···O = 2.31 Å, N···N = 3.190 (2) Å, N···O = 3.146 (2) Å, N—H···N = 138° and N—H···O = 154°] and one two-centre C—H···O hydrogen bond [H···O = 2.46 Å, C···O = 3.405 (2) Å and C—H···O = 173°] links the molecules into sheets. In (III), an intramolecular O—H···N hydrogen bond and two N—H···O hydrogen bonds [H···O = 2.26 and 2.10 Å, N···O = 2.975 (2) and 2.954 (2) Å, and N—H···O = 138 and 163°] link the molecules into sheets.

## Comment

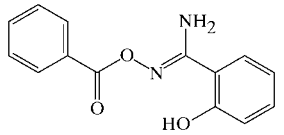
Acyloxyarylamidines, $Ar^1C(O)ON{=}C(NH_2)Ar^2$, can in principle adopt a wide range of conformations, depending on both the configuration at the C═N double bond, and the rotational freedom about the C—O and N—O single bonds. On the basis of *ab initio* calculations on the simple model compound $HC(O)ON{=}CHNH_2$ and qualitative estimates of 1,4-interactions in the aryl analogues $Ar^1C(O)ON{=}C(NH_2)Ar^2$, it has been suggested (Tucker *et al.*, 2000) that the two most stable conformers, at least in the vapour phase, are those with chain-extended C(Ar)—C—O—N═C—C(Ar) spacer units. Consistent with this prediction, the structures of three derivatives [$Ar^1$ is 1-naphthyl and $Ar^2$ is 2-methylphenyl, Cambridge Structural Database (CSD; Allen, 2002) refcode QUNMER; $Ar^1$ is 1-naphthyl and $Ar^2$ is 2,6-dichlorophenyl, CSD refcode QUNMOB; $Ar^1$ is 2-methylphenyl and $Ar^2$ is 2,4-dichlorophenyl, CSD refcode QUNMIV] were all found to adopt nearly planar chain-extended conformations, with the aryl groups remote from one another. In this paper, we report the structure of three more compounds of this type, including the unsubstituted parent compound, namely $N^2$-(benzoyloxy)benzamidine, (I), and two isomeric hydroxy compounds, $N^2$-(2-hydroxybenzoyloxy)benzamidine, (II), and $N^2$-benzoyloxy-2-hydroxybenzamidine, (III). In these three compounds, there exists the possibility that the overall conformation may be influenced by intermolecular hydrogen bonding involving the substituted aryl rings.



(I)



(II)



(III)

The molecules of (I)–(III) (Figs. 1–3) all have chain-extended conformations, with the aryl groups remote from one another. In (III), the non-H atoms in the central spacer unit between atoms C11 and C21 are almost coplanar, as shown by the key torsion angles (Table 4), whereas in both (I)

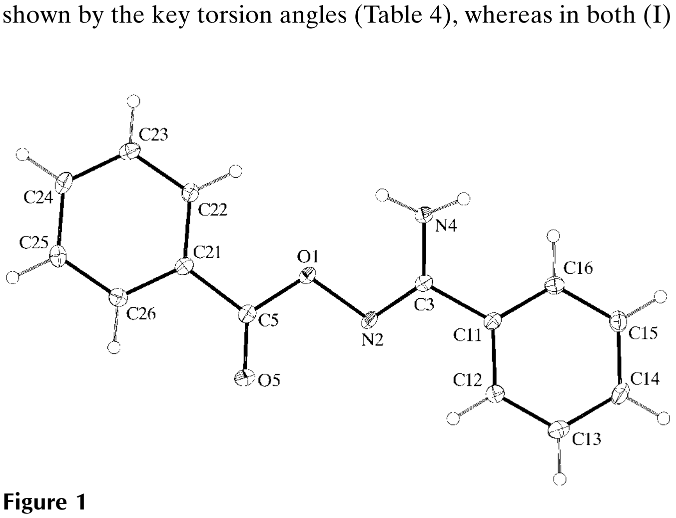


**Figure 1**
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

DOI: 10.1107/S0108270103025435

and (III), there is a modest twist about the central N2—O1 bond. The C—N and C—O distances in the spacer unit distinguish clearly between the formal single and double bonds; the C—N distances are, in addition, fully consistent with the location of the H atoms bonded to atom N4, as deduced from a difference map. The remaining bond distances and interbond angles show no unusual features.

Despite their very similar constitutions and their similar molecular geometries, the supramolecular structures of (I)–(III) are all different, with significant differences even between the isomeric compounds (II) and (III). No two structures employ the same combination of hard and soft (Desiraju & Steiner, 1999) interactions between the molecules.

In (I) (Fig. 1), where both aryl rings are unsubstituted, there are no intramolecular hydrogen bonds and only a single intermolecular hydrogen bond (N—H···O; Table 1). Amino atom N4 in the molecule at ($x$, $y$, $z$) acts as a hydrogen-bond donor, *via* atom H41, to imino atom N2 in the molecule at ($\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$), so producing a zigzag $C(4)$ chain (Bernstein *et al.*, 1995) running parallel to the [101] direction and generated by the *n*-glide plane at $y=\frac{1}{4}$ (Fig. 4). The second N—H bond plays no role in the supramolecular aggregation, forming neither a hard N—H···O hydrogen bond nor a soft N—H···$\pi$(arene) hydrogen bond. Neither of the two O atoms plays any role in the supramolecular structure.

However, the chains in (I) are weakly linked into sheets by a single aromatic $\pi$–$\pi$ stacking interaction. Phenyl rings C11–C16 and C21–C26 in the molecules at ($x$, $y$, $z$) and ($\frac{1}{2}+x$, $\frac{1}{2}-y$, $-\frac{1}{2}+z$), respectively, are nearly parallel, with an interplanar angle of only 5.1 (2)°; the ring-centroid separation is 3.852 (2) Å and the interplanar spacing is ~3.50 Å, giving a centroid offset of ~1.61 Å. Propagation of this interaction thus generates a chain running parallel to the [$10\overline{1}$] direction (Fig. 5), and the combination of [101] and [$10\overline{1}$] chains generates a (010) sheet. Two sheets pass through each unit cell, in the domains $-0.02 < y < 0.52$ and $0.48 < y < 1.02$, but there are no direction-specific interactions between adjacent sheets.

There is one intramolecular hydrogen bond in (II) (Fig. 2) and there are two intermolecular hydrogen bonds, *viz*. one

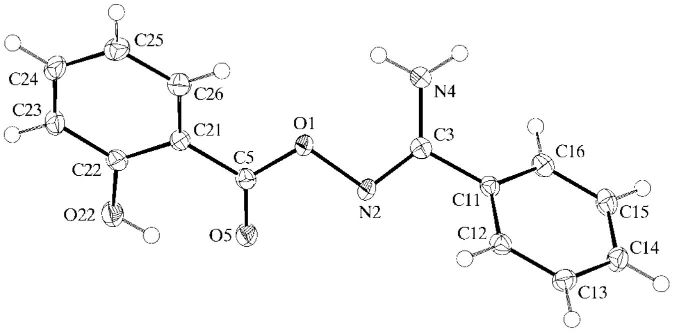


**Figure 2**
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

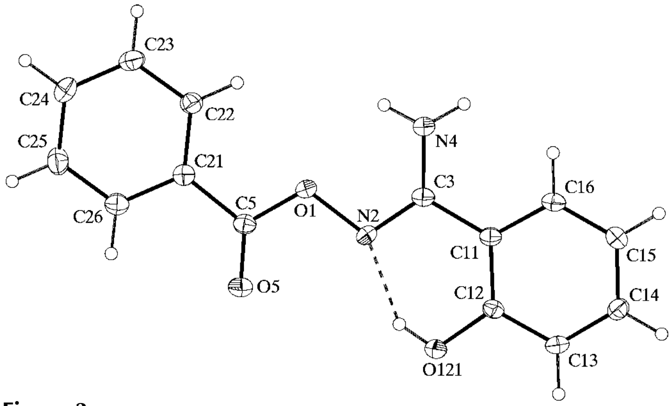


**Figure 3**
The molecule of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

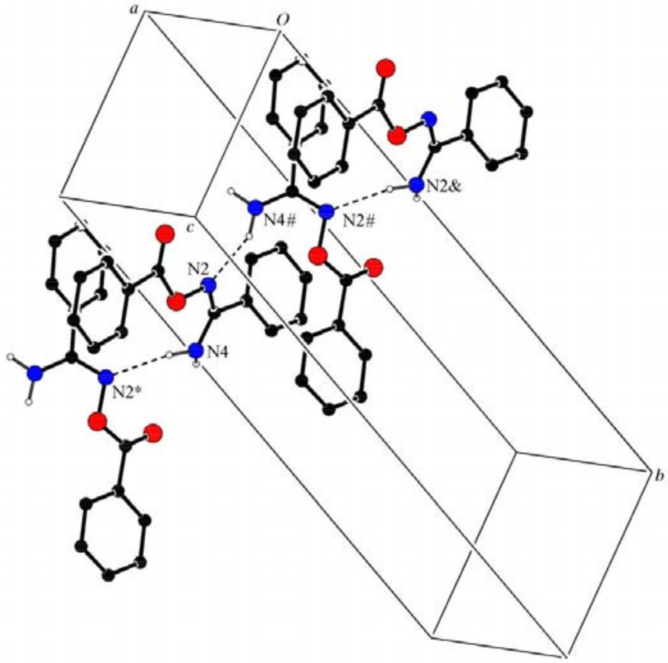


**Figure 4**
Part of the crystal structure of (I), showing the formation of a $C(4)$ hydrogen-bonded chain along [101]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), a hash (#) or an ampersand (&) are at the symmetry positions ($\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$), ($-\frac{1}{2}+x$, $\frac{1}{2}-y$, $-\frac{1}{2}+z$) and ($-1+x$, $y$, $-1+z$), respectively.

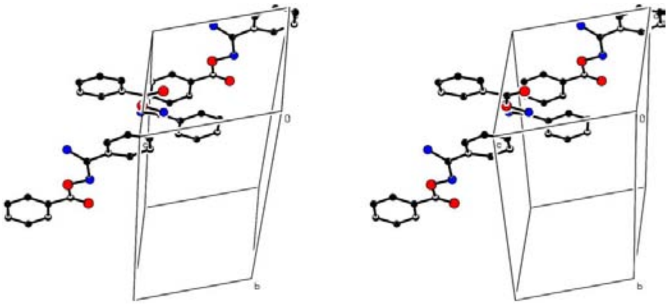


**Figure 5**
A stereoview of part of the crystal structure of (I), showing the formation of a $\pi$-stacked chain along [$10\overline{1}$]. For the sake of clarity, H atoms bonded to C atoms have been omitted.

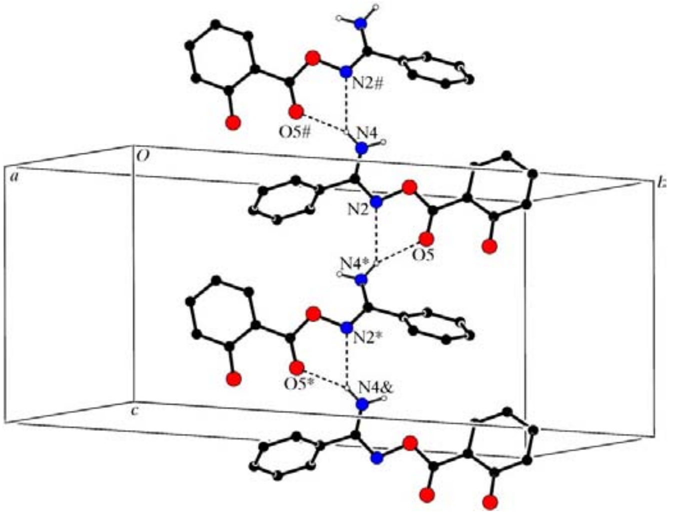


**Figure 6**
Part of the crystal structure of (II), showing the formation of a chain of rings along [001] built from hard hydrogen bonds. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), a hash (#) or an ampersand (&) are at the symmetry positions $(\frac{1}{2} - x, 1 - y, \frac{1}{2} + z)$, $(\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z)$ and $(x, y, 1 + z)$, respectively.

three-centre N—H$\cdots$(N,O) bond and one two-centre C—H$\cdots$O bond, both of which utilize the same O acceptor atom (Table 2). Amino atom N4 in the molecule at $(x, y, z)$ acts as a hydrogen-bond donor, *via* atom H42, to imino atom N2 and to carbonyl atom O5, both in the molecule at $(\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z)$, thereby producing a $C(4)C(7)[R_1^2(5)]$ chain of rings running parallel to the [001] direction and generated by the $2_1$ screw axis along $(\frac{1}{4}, \frac{1}{2}, z)$ (Fig. 6). At the same time, atom C12 at $(x, y, z)$ acts as a hydrogen-bond donor to atom O5 in the molecule at $(\frac{1}{2} + x, y, \frac{1}{2} - z)$, so producing a zigzag $C(8)$ chain parallel to [100] and generated by the *a*-glide plane at $z = \frac{1}{4}$ (Fig. 7). The combination of the [100] and [001] chains generates (010) sheets, two of which pass through each unit cell in the domains $0.26 < y < 0.74$ and $0.76 < y < 1.24$. There are no direction-specific interactions between adjacent sheets, although there is a single C—H$\cdots\pi$(arene) hydrogen bond within the sheet (Table 2).

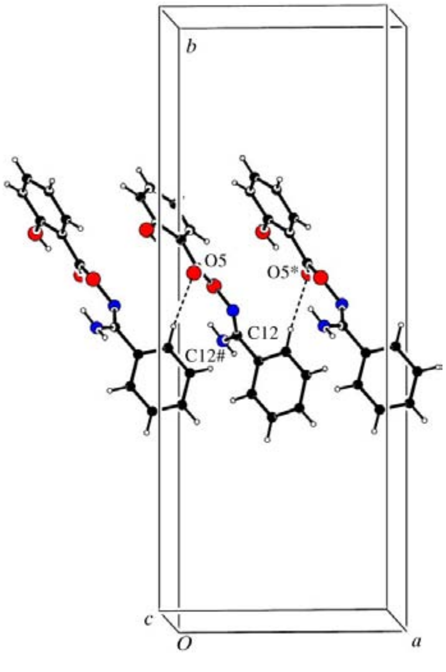


**Figure 7**
Part of the crystal structure of (II), showing the formation of a $C(8)$ chain along [100] built from soft hydrogen bonds. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{1}{2} + x, y, \frac{1}{2} - z)$ and $(-\frac{1}{2} + x, y, \frac{1}{2} - z)$, respectively.

In (III), an intramolecular O—H$\cdots$N hydrogen bond (Fig. 3) forms an $S(6)$ motif and the supramolecular aggregation is dominated by two intermolecular N—H$\cdots$O hydrogen bonds (Table 3). Amino atom N4 in the molecule at $(x, y, z)$ acts as a hydrogen-bond donor, *via* atoms H41 and H42, respectively, to phenol atom O121 in the molecule at $(-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$ and to carbonyl atom O5 in the molecule at $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$, thereby producing $C(6)$ and $C(7)$ chains running parallel to the $[\bar{1}01]$ and [101] directions, respectively. The combination of these two chains produces a (010) sheet in the form of a (4,4)-net (Batten & Robson, 1998) containing equal numbers of $S(6)$ and $R_5^4(22)$ rings (Fig. 8). This sheet, which is generated by the *n*-glide plane at $y = \frac{1}{4}$, lies in the domain $-0.02 < y < 0.52$. A second such sheet, related to the first by inversion, lies in the domain $0.48 < y < 1.02$, this sheet being generated by the *n*-glide plane at $y = \frac{3}{4}$. However, there are no direction-specific interactions between adjacent sheets; in particular, there are neither $X$—H$\cdots\pi$(arene) hydrogen bonds ($X$ = C, N or O) nor aromatic $\pi$–$\pi$ stacking interactions in the structure.

In summary, the overall conformations adopted by (I)–(III) are similar to those of the analogues reported previously. This conformation appears to be independent of the presence or absence of intermolecular hydrogen bonding involving the carbonyl O atom, a mechanism that was previously suggested as a contributory factor in the determination of molecular conformation (Tucker *et al.*, 2000).

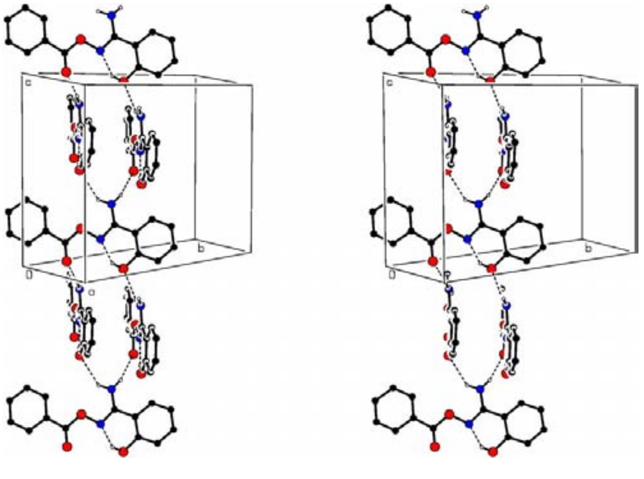


**Figure 8**
A stereoview of part of the crystal structure of (III), showing the formation of a (010) sheet of $S(6)$ and $R_5^4(22)$ rings. For the sake of clarity, H atoms bonded to C atoms have been omitted.

## Experimental

Samples of (I)–(III) were prepared by heating under reflux for 1 h a mixture containing equimolar quantities of the appropriate acyl chloride and the appropriate benzamidoxime in dry tetrahydrofuran solution, in the presence of triethylamine. After removal of triethylammonium chloride and evaporation of the solvent, the solid products were crystallized from acetonitrile.

### Compound (I)

*Crystal data*

$C_{14}H_{12}N_2O_2$
$M_r = 240.26$
Monoclinic, $P2_1/n$
$a = 7.0415$ (2) Å
$b = 21.4704$ (7) Å
$c = 8.0570$ (3) Å
$\beta = 108.4804$ (16)°
$V = 1155.27$ (7) Å$^3$
$Z = 4$

$D_x = 1.381$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 2614 reflections
$\theta = 3.2$–27.5°
$\mu = 0.09$ mm$^{-1}$
$T = 120$ (2) K
Plate, colourless
0.25 × 0.20 × 0.08 mm

*Data collection*

Nonius KappaCCD diffractometer
$\varphi$ scans, and $\omega$ scans with $\kappa$ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.967$, $T_{\max} = 0.993$
10 316 measured reflections

2614 independent reflections
1708 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.056$
$\theta_{\max} = 27.5°$
$h = -9 \rightarrow 9$
$k = -27 \rightarrow 27$
$l = -10 \rightarrow 10$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.129$
$S = 0.96$
2614 reflections
165 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0719P)^2 + 0.0022P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.21$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.27$ e Å$^{-3}$

**Table 1**
Hydrogen-bonding geometry (Å, °) for (I).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N4—H41···N2$^{\rm i}$ | 0.95 | 2.15 | 3.029 (2) | 153 |

Symmetry code: (i) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

### Compound (II)

*Crystal data*

$C_{14}H_{12}N_2O_3$
$M_r = 256.26$
Orthorhombic, $Pbca$
$a = 9.3808$ (1) Å
$b = 24.9553$ (4) Å
$c = 10.3277$ (1) Å
$V = 2417.72$ (5) Å$^3$
$Z = 8$
$D_x = 1.408$ Mg m$^{-3}$

Mo $K\alpha$ radiation
Cell parameters from 2758 reflections
$\theta = 3.1$–27.5°
$\mu = 0.10$ mm$^{-1}$
$T = 120$ (2) K
Block, colourless
0.55 × 0.32 × 0.28 mm

*Data collection*

Nonius KappaCCD diffractometer
$\varphi$ scans, and $\omega$ scans with $\kappa$ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.966$, $T_{\max} = 0.972$
17 440 measured reflections

2758 independent reflections
2308 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.065$
$\theta_{\max} = 27.5°$
$h = -12 \rightarrow 9$
$k = -32 \rightarrow 32$
$l = -13 \rightarrow 12$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.105$
$S = 0.97$
2758 reflections
175 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0581P)^2 + 1.0166P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.23$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.28$ e Å$^{-3}$

**Table 2**
Hydrogen-bonding geometry (Å, °) for (II).

$Cg1$ is the centroid of the C21–C26 ring.

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O22—H22···O5 | 0.84 | 1.90 | 2.632 (2) | 144 |
| N4—H42···O5$^{\rm ii}$ | 0.91 | 2.31 | 3.146 (2) | 154 |
| N4—H42···N2$^{\rm ii}$ | 0.91 | 2.46 | 3.190 (2) | 138 |
| C12—H12···O5$^{\rm iii}$ | 0.95 | 2.46 | 3.405 (2) | 173 |
| C16—H16···$Cg1^{\rm iv}$ | 0.95 | 2.68 | 3.529 (2) | 149 |

Symmetry codes: (ii) $\frac{1}{2}-x, 1-y, z-\frac{1}{2}$; (iii) $\frac{1}{2}+x, y, \frac{1}{2}-z$; (iv) $-x, 1-y, -z$.

### Compound (III)

*Crystal data*

$C_{14}H_{12}N_2O_3$
$M_r = 256.26$
Monoclinic, $P2_1/n$
$a = 4.6463$ (3) Å
$b = 22.1280$ (13) Å
$c = 11.9551$ (9) Å
$\beta = 99.202$ (3)°
$V = 1213.33$ (14) Å$^3$
$Z = 4$

$D_x = 1.403$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 2549 reflections
$\theta = 3.3$–27.5°
$\mu = 0.10$ mm$^{-1}$
$T = 120$ (2) K
Plate, colourless
0.25 × 0.10 × 0.01 mm

*Data collection*

Nonius KappaCCD diffractometer
$\varphi$ scans, and $\omega$ scans with $\kappa$ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.970$, $T_{\max} = 0.998$
8910 measured reflections

2549 independent reflections
1412 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.065$
$\theta_{\max} = 27.5°$
$h = -5 \rightarrow 5$
$k = -27 \rightarrow 28$
$l = -15 \rightarrow 15$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.133$
$S = 0.98$
2549 reflections
173 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0626P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.32$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.22$ e Å$^{-3}$

**Table 3**
Hydrogen-bonding geometry (Å, °) for (III).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N4—H41···O121$^{\rm v}$ | 0.88 | 2.26 | 2.975 (2) | 138 |
| N4—H42···O5$^{\rm i}$ | 0.88 | 2.10 | 2.954 (2) | 163 |
| O121—H121···N2 | 0.84 | 1.82 | 2.550 (2) | 144 |

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$.

For compounds (I) and (III), space group $P2_1/n$ was uniquely assigned from the systematic absences; space group $Pbca$ was likewise assigned for (II). All H atoms were located from difference maps, which showed clearly that the $NH_2$ groups are all pyramidal; all H atoms were then treated as riding atoms with C—H distances of 0.95 Å, N—H distances of 0.88–0.95 Å and O—H distances of 0.84 Å.

**Table 4**
Selected geometric parameters (Å, °) for compounds (I)–(III).

| Parameter | (I) | (II) | (III) |
|---|---|---|---|
| C3—N2 | 1.297 (2) | 1.302 (2) | 1.303 (2) |
| C3—N4 | 1.352 (2) | 1.354 (2) | 1.344 (2) |
| N2—O1 | 1.452 (2) | 1.460 (2) | 1.442 (2) |
| O1—C5 | 1.356 (2) | 1.340 (2) | 1.351 (2) |
| C5—O5 | 1.206 (2) | 1.222 (2) | 1.208 (2) |
| | | | |
| C11—C3—N2—O1 | 179.8 (2) | 174.47 (9) | 180.0 (2) |
| C3—N2—O1—C5 | −160.0 (2) | 152.4 (2) | 178.8 (2) |
| N2—O1—C5—C21 | −175.0 (2) | 171.77 (9) | 176.3 (2) |

For all compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants that have provided computing facilities for this work. CEMC, SMSVW and JLW thank CNPq for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1677). Services for accessing these data are described at the back of the journal.

## References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1460–1494.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond*, pp. 86–89. Oxford University Press.
Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
Nonius (1997). *KappaCCD Server Software.* Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Tucker, J. A., Clayton, T. L., Chidester, C. G., Shulz, M. W., Harrington, L. E., Conrad, S. J., Yagi, Y., Oien, N. L., Yurek, D. & Kuo, M.-S. (2000). *Bioorg. Med. Chem.* **8**, 601–615.