Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# 4-Aza-1-azoniabicyclo[2.2.2]octane–2-aminobenzoate–2-aminobenzoic acid (1/1/1)

**Hadi D. Arman,[a] Trupta Kaulgud[a] and Edward R. T. Tiekink[b]***

[a]Department of Chemistry, The University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249-0698, USA, and [b]Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia
Correspondence e-mail: edward.tiekink@gmail.com

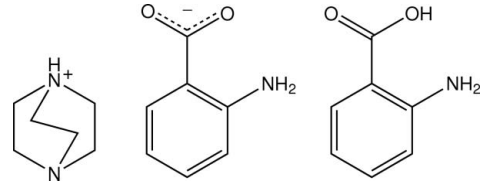
Received 7 October 2011; accepted 10 October 2011

Key indicators: single-crystal X-ray study; $T$ = 98 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.056; $wR$ factor = 0.128; data-to-parameter ratio = 16.6.

A 4-aza-1-azoniabicyclo[2.2.2]octane cation, a 2-aminobenzoate anion and a neutral 2-aminobenzoic acid molecule comprise the asymmetric unit of the title compound, $C_6H_{13}N_2^+\cdot C_7H_6NO_2^-\cdot C_7H_7NO_2$. An intramolecular N—H···O hydrogen bond occurs in the anion and in the neutral 2-aminobenzoic acid molecule. The cation provides a charge-assisted N—H···O hydrogen bond to the anion, and the 2-aminobenzoic acid molecule forms an O—H···N hydrogen bond to the unprotonated amino N atom in the cation. In this way, a three-component aggregate is formed. These are connected into a three-dimensional network by amino–carboxylate N—H···O hydrogen bonds. N—H···N hydrogen bonds are also observed.

## Related literature

For related studies on co-crystal formation, see: Arman *et al.* (2010); Arman & Tiekink (2010); Wardell & Tiekink (2011). For examples of multi-component crystals containing the 2-aminobenzoate anion, see: Lynch *et al.* (1998); Chen & Peng (2011). For a description of the Cambridge Structural Database, see: Allen (2002).



## Experimental

### Crystal data

$C_6H_{13}N_2^+\cdot C_7H_6NO_2^-\cdot C_7H_7NO_2$ $M_r$ = 386.45
Monoclinic, $P2_1/c$
$a$ = 9.285 (3) Å
$b$ = 16.843 (5) Å
$c$ = 12.660 (4) Å
$\beta$ = 102.127 (6)°
$V$ = 1935.7 (10) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.09 mm$^{-1}$
$T$ = 98 K
0.34 × 0.17 × 0.07 mm

### Data collection

Rigaku AFC12/SATURN724 diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min}$ = 0.731, $T_{max}$ = 1.000
16911 measured reflections
4440 independent reflections
3929 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.054

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.128
$S$ = 1.13
4440 reflections
268 parameters
7 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.30 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.23 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1O···N3 | 0.84 | 1.77 | 2.597 (2) | 168 |
| N4—H5*n*···O3 | 0.93 | 1.64 | 2.546 (2) | 166 |
| N1—H2*n*···O2 | 0.88 | 2.03 | 2.725 (2) | 135 |
| N2—H3*n*···O3 | 0.88 | 2.04 | 2.696 (2) | 131 |
| N1—H1*n*···O4$^{i}$ | 0.88 | 2.08 | 2.941 (2) | 165 |
| N2—H4*n*···N1$^{ii}$ | 0.88 | 2.38 | 3.256 (2) | 171 |

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+2, y+\frac{1}{2}, -z+\frac{3}{2}$.

Data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPII* (Johnson, 1976) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

The Ministry of Higher Education, Malaysia, is thanked for the award of a research grant in crystal engineering (RG125/10AFR).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6440).

## References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Arman, H. D., Kaulgud, T. & Tiekink, E. R. T. (2010). *Acta Cryst.* E**66**, o2117.
Arman, H. D. & Tiekink, E. R. T. (2010). *Acta Cryst.* E**66**, o2188.
Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Chen, Z.-Y. & Peng, M.-X. (2011). *J. Chem. Crystallogr.* **41**, 137–142.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Lynch, D. E., Smith, G., Byriel, K. A. & Kennard, C. H. L. (1998). *Aust. J. Chem.* **51**, 587–592.
Molecular Structure Corporation & Rigaku (2005). *CrystalClear*. MSC, The Woodlands, Texas, USA, and Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Wardell, J. L. & Tiekink, E. R. T. (2011). *J. Chem. Crystallogr.* **41**, 1418–1424.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

# supporting information

*Acta Cryst.* (2011). E**67**, o2933 [doi:10.1107/S1600536811041559]

## 4-Aza-1-azoniabicyclo[2.2.2]octane–2-aminobenzoate–2-aminobenzoic acid (1/1/1)

**Hadi D. Arman, Trupta Kaulgud and Edward R. T. Tiekink**

### S1. Comment

As a part of on-going studies into co-crystallization experiments of carboxylic acids with N-containing molecules (Arman *et al.* 2010; Arman & Tiekink, 2010; Wardell & Tiekink, 2011), the 1:2 co-crystallization of 1,4-diazabicyclo[2.2.2]octane (DABCO) and 2-aminobenzoic was investigated, leading to the isolation of (I).

The crystallographic asymmetric unit of (I) comprises a 4-aza-1-azoniabicyclo(2.2.2)octane cation, Fig. 1, a 2-aminobenzoate anion, Fig. 2, and a neutral 2-aminobenzoic acid molecule, Fig. 3. While there are many examples of 4-aza-1-azoniabicyclo(2.2.2)octane cations and neutral 2-aminobenzoic acid molecules in the crystallographic literature (Allen, 2002), examples of 2-aminobenzoate anions are comparatively rare in all-organic molecules (Lynch *et al.*, 1998; Chen & Peng, 2011). The ions and neutral benzoic acid derivative associate into a three-molecule aggregate *via* $N^+$—H···O and O—H···N hydrogen bonds formed by and to the cation, Fig. 4 and Table 1; intramolecular N—H···O hydrogen bonds are also noted in the benzoate and benzoic acid species, Table 1.

The three component aggregates are connected into the three-dimensional architecture by hydrogen bonds involving the amino-H atoms not participating in intramolecular N—H···O interactions, Fig. 5 and Table 1.

### S2. Experimental

Colourless crystals of (I) were isolated from the 1:2 co-crystallization of 1,4-diazabicyclo[2.2.2]octane (Sigma-Aldrich, 0.089 mmol) and anthranilic acid (Sigma-Aldrich, 0.19 mmol) in chloroform solution (6 ml); *M*.pt. 427–430 K.

### S3. Refinement

The C-bound H-atoms were placed in calculated positions (C—H 0.95–0.99 Å) and were included in the refinement in the riding model approximation with $U_{iso}$(H) set to 1.2$U_{eq}$(C). The O– and N-bound H-atoms were located in a difference Fourier map and were refined with distance restraints of O—H 0.840±0.001 Å and N—H = 0.088±0.001 Å, respectively, and with $U_{iso}$(H) = 1.5$U_{eq}$(O, N).

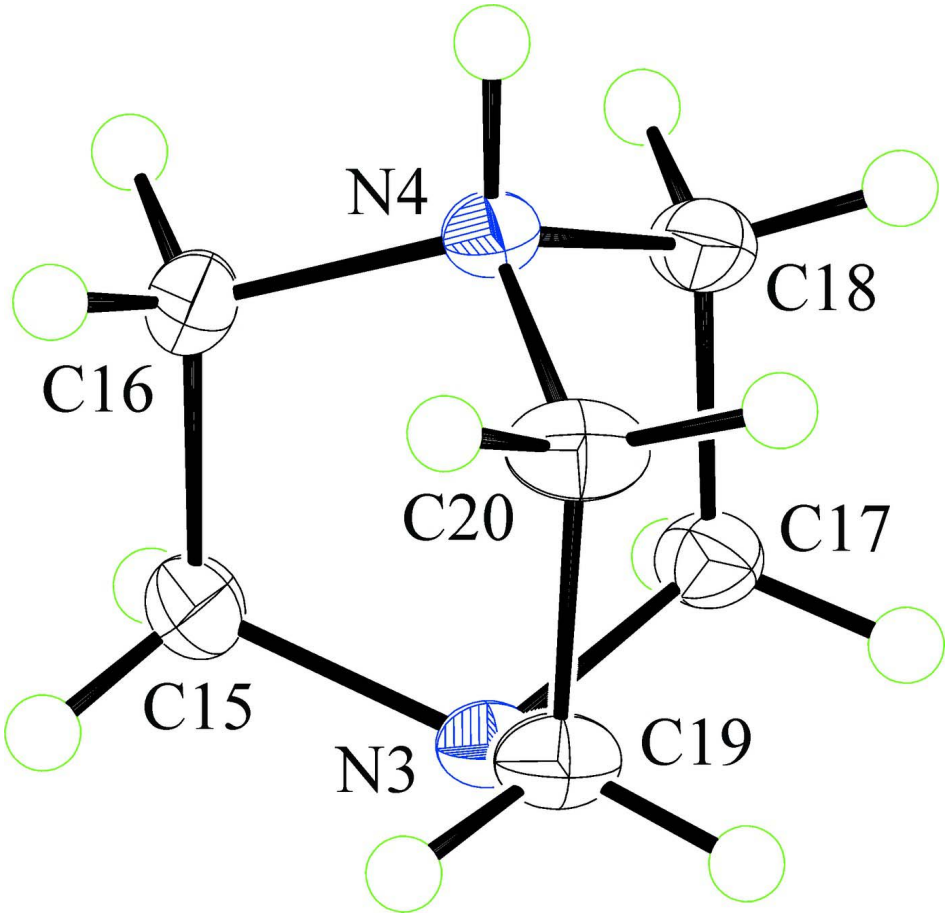



**Figure 1**

Molecular structure of the 4-aza-1-azoniabicyclo(2.2.2)octane cation in (I) showing atom-labelling scheme and displacement ellipsoids at the 50% probability level.

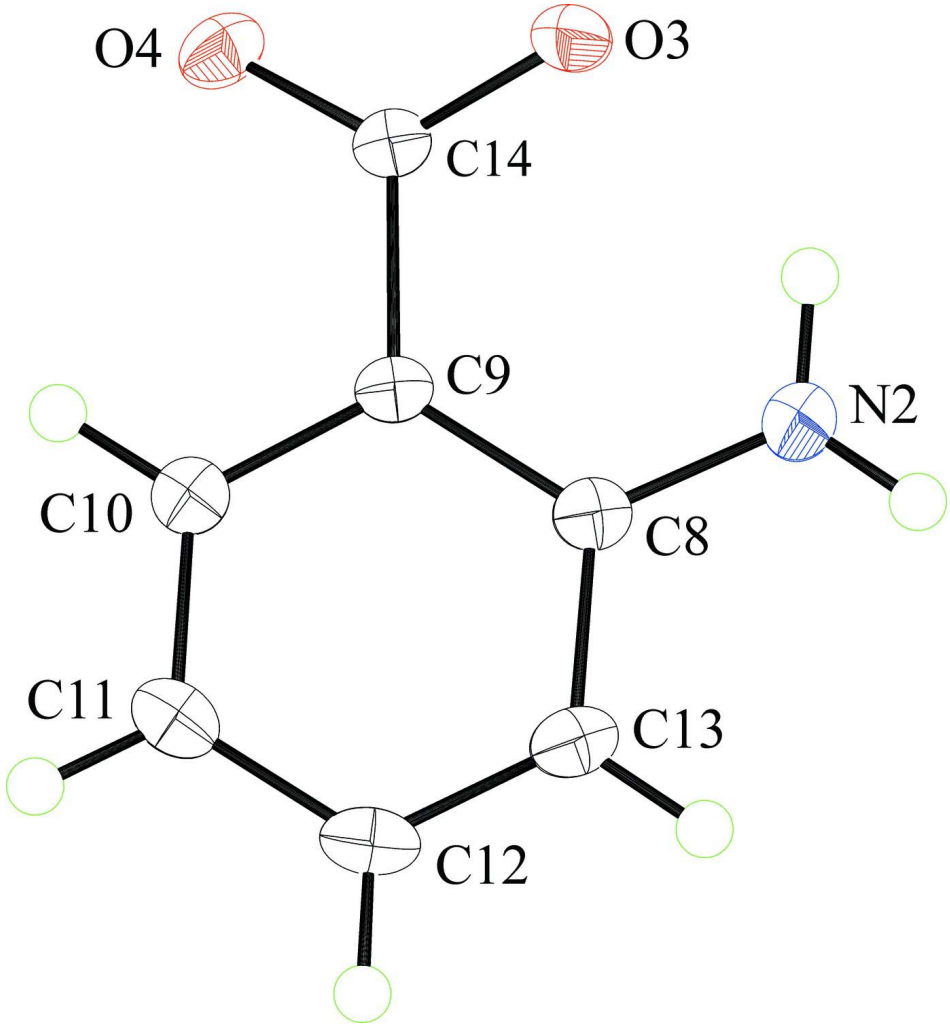



**Figure 2**

Molecular structure of the 2-aminobenzoate anion in (I) showing atom-labelling scheme and displacement ellipsoids at the 50% probability level.

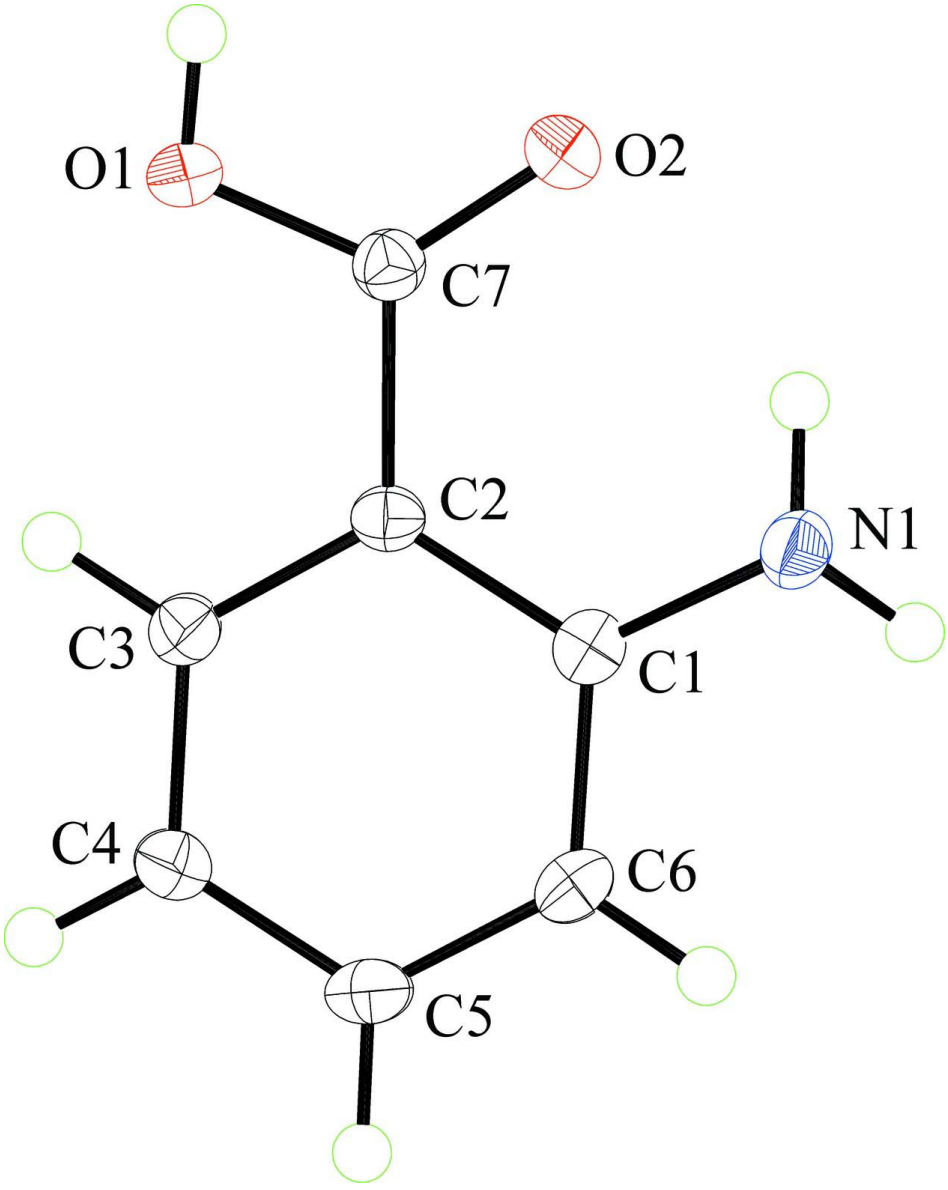



**Figure 3**

Molecular structure of the neutral 2-aminobenzoic acid molecule in (I) showing atom-labelling scheme and displacement ellipsoids at the 50% probability level.

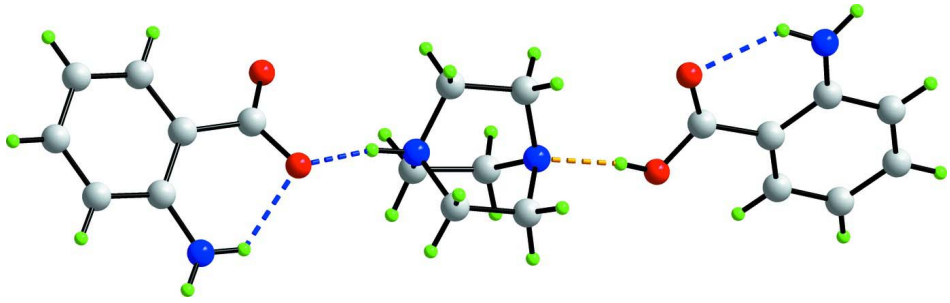


**Figure 4**

Three component aggregate in (I) held together by O—H···N and N—H···O hydrogen bonds shown as orange and blue dashed lines, respectively.

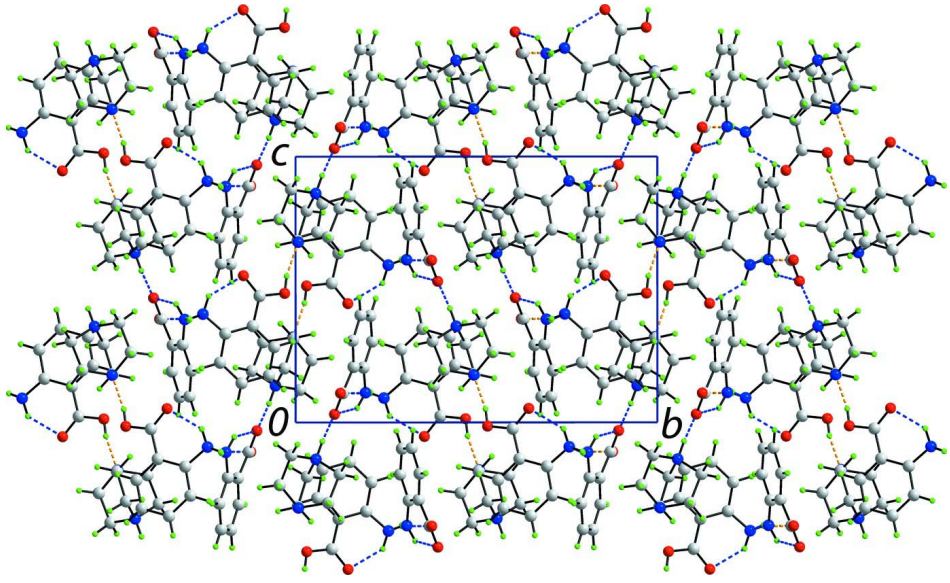



**Figure 5**

View in projection down the *a* axis of the unit-cell contents of (I). The O—H···N and N—H···O hydrogen bonds are shown as orange and blue dashed lines, respectively.

### 4-Aza-1-azoniabicyclo[2.2.2]octane–2-aminobenzoate–2-aminobenzoic acid (1/1/1)

*Crystal data*

$C_6H_{13}N_2^+·C_7H_6NO_2^-·C_7H_7NO_2$
$M_r$ = 386.45
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a$ = 9.285 (3) Å
$b$ = 16.843 (5) Å
$c$ = 12.660 (4) Å
$\beta$ = 102.127 (6)°
$V$ = 1935.7 (10) Å$^3$
$Z$ = 4
$F(000)$ = 824
$D_x$ = 1.326 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 8162 reflections
$\theta$ = 2.0–40.6°
$\mu$ = 0.09 mm$^{-1}$
$T$ = 98 K
Block, colourless
0.34 × 0.17 × 0.07 mm

*Data collection*

Rigaku AFC12K/SATURN724 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega$ scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min}$ = 0.731, $T_{max}$ = 1.000
16911 measured reflections
4440 independent reflections
3929 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.054
$\theta_{max}$ = 27.5°, $\theta_{min}$ = 2.0°
$h$ = −12→12
$k$ = −19→21
$l$ = −15→16

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.128
$S$ = 1.13
4440 reflections
268 parameters
7 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0473P)^2 + 0.9109P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.23 e Å$^{-3}$

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.73506 (15) | 0.46965 (8) | 1.01396 (10) | 0.0286 (3) |
| H1o | 0.7433 | 0.4752 | 0.9495 | 0.043* |
| O2 | 0.63182 (15) | 0.35565 (8) | 0.94734 (10) | 0.0280 (3) |
| O3 | 0.87552 (13) | 0.60731 (8) | 0.46906 (9) | 0.0255 (3) |
| O4 | 0.63909 (13) | 0.62403 (7) | 0.38987 (10) | 0.0245 (3) |
| N1 | 0.58477 (16) | 0.24385 (8) | 1.09196 (12) | 0.0225 (3) |
| H1n | 0.5262 | 0.2075 | 1.1100 | 0.034* |
| H2n | 0.5710 | 0.2596 | 1.0243 | 0.034* |
| N2 | 1.07213 (17) | 0.69313 (11) | 0.38788 (13) | 0.0320 (4) |
| H3n | 1.0547 | 0.6697 | 0.4460 | 0.048* |
| H4n | 1.1631 | 0.7060 | 0.3850 | 0.048* |
| N3 | 0.76627 (15) | 0.50739 (8) | 0.82113 (11) | 0.0203 (3) |
| N4 | 0.79912 (15) | 0.55587 (8) | 0.63832 (11) | 0.0207 (3) |
| H5n | 0.8114 | 0.5735 | 0.5712 | 0.025* |
| C1 | 0.61784 (17) | 0.30546 (9) | 1.16546 (13) | 0.0184 (3) |
| C2 | 0.66288 (17) | 0.38151 (9) | 1.13704 (12) | 0.0175 (3) |

| | | | | |
|---|---|---|---|---|
| C3 | 0.69563 (17) | 0.44053 (10) | 1.21593 (13) | 0.0200 (3) |
| H3 | 0.7229 | 0.4918 | 1.1959 | 0.024* |
| C4 | 0.68936 (19) | 0.42613 (11) | 1.32282 (13) | 0.0232 (3) |
| H4 | 0.7110 | 0.4671 | 1.3754 | 0.028* |
| C5 | 0.65063 (18) | 0.35033 (10) | 1.35151 (13) | 0.0228 (3) |
| H5 | 0.6493 | 0.3392 | 1.4249 | 0.027* |
| C6 | 0.61417 (17) | 0.29115 (10) | 1.27466 (13) | 0.0209 (3) |
| H6 | 0.5863 | 0.2402 | 1.2957 | 0.025* |
| C7 | 0.67418 (17) | 0.40032 (10) | 1.02372 (13) | 0.0192 (3) |
| C8 | 0.96688 (18) | 0.68766 (10) | 0.29348 (13) | 0.0211 (3) |
| C9 | 0.82171 (17) | 0.66015 (9) | 0.29093 (13) | 0.0185 (3) |
| C10 | 0.72053 (18) | 0.65777 (10) | 0.19229 (13) | 0.0211 (3) |
| H10 | 0.6227 | 0.6407 | 0.1912 | 0.025* |
| C11 | 0.7582 (2) | 0.67941 (10) | 0.09614 (14) | 0.0253 (4) |
| H11 | 0.6883 | 0.6759 | 0.0298 | 0.030* |
| C12 | 0.9008 (2) | 0.70645 (10) | 0.09858 (14) | 0.0259 (4) |
| H12 | 0.9283 | 0.7215 | 0.0333 | 0.031* |
| C13 | 1.00247 (19) | 0.71146 (10) | 0.19520 (14) | 0.0243 (4) |
| H13 | 1.0983 | 0.7313 | 0.1955 | 0.029* |
| C14 | 0.77248 (18) | 0.62962 (9) | 0.38957 (13) | 0.0190 (3) |
| C15 | 0.92485 (19) | 0.50551 (11) | 0.81698 (14) | 0.0254 (4) |
| H15A | 0.9641 | 0.4512 | 0.8332 | 0.031* |
| H15B | 0.9806 | 0.5420 | 0.8721 | 0.031* |
| C16 | 0.94441 (19) | 0.53077 (12) | 0.70394 (15) | 0.0289 (4) |
| H16A | 1.0154 | 0.5753 | 0.7103 | 0.035* |
| H16B | 0.9837 | 0.4858 | 0.6682 | 0.035* |
| C17 | 0.71221 (19) | 0.58987 (10) | 0.80251 (14) | 0.0241 (4) |
| H17A | 0.7639 | 0.6242 | 0.8620 | 0.029* |
| H17B | 0.6055 | 0.5916 | 0.8022 | 0.029* |
| C18 | 0.7387 (2) | 0.62134 (10) | 0.69428 (14) | 0.0262 (4) |
| H18A | 0.6450 | 0.6406 | 0.6491 | 0.031* |
| H18B | 0.8091 | 0.6662 | 0.7070 | 0.031* |
| C19 | 0.6829 (2) | 0.45573 (11) | 0.73500 (13) | 0.0255 (4) |
| H19A | 0.5780 | 0.4541 | 0.7403 | 0.031* |
| H19B | 0.7224 | 0.4010 | 0.7443 | 0.031* |
| C20 | 0.6952 (2) | 0.48755 (11) | 0.62315 (14) | 0.0294 (4) |
| H20A | 0.7318 | 0.4452 | 0.5813 | 0.035* |
| H20B | 0.5972 | 0.5048 | 0.5826 | 0.035* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0416 (7) | 0.0283 (7) | 0.0170 (6) | −0.0134 (5) | 0.0084 (5) | 0.0005 (5) |
| O2 | 0.0388 (7) | 0.0268 (7) | 0.0190 (6) | −0.0089 (5) | 0.0072 (5) | −0.0038 (5) |
| O3 | 0.0244 (6) | 0.0334 (7) | 0.0195 (6) | −0.0001 (5) | 0.0065 (5) | 0.0052 (5) |
| O4 | 0.0217 (6) | 0.0242 (6) | 0.0305 (7) | 0.0010 (5) | 0.0116 (5) | 0.0023 (5) |
| N1 | 0.0269 (7) | 0.0176 (7) | 0.0247 (7) | −0.0022 (5) | 0.0093 (6) | −0.0011 (6) |
| N2 | 0.0226 (7) | 0.0477 (10) | 0.0253 (8) | −0.0078 (7) | 0.0038 (6) | 0.0046 (7) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N3 | 0.0226 (7) | 0.0212 (7) | 0.0176 (6) | −0.0018 (5) | 0.0052 (5) | 0.0014 (5) |
| N4 | 0.0224 (7) | 0.0229 (7) | 0.0181 (6) | 0.0010 (5) | 0.0072 (5) | 0.0027 (5) |
| C1 | 0.0162 (7) | 0.0179 (8) | 0.0214 (8) | 0.0017 (6) | 0.0048 (6) | 0.0006 (6) |
| C2 | 0.0168 (7) | 0.0196 (8) | 0.0164 (7) | 0.0012 (6) | 0.0044 (6) | 0.0009 (6) |
| C3 | 0.0210 (7) | 0.0192 (8) | 0.0203 (8) | −0.0014 (6) | 0.0057 (6) | 0.0006 (6) |
| C4 | 0.0265 (8) | 0.0257 (9) | 0.0179 (8) | −0.0038 (6) | 0.0055 (6) | −0.0018 (7) |
| C5 | 0.0230 (8) | 0.0286 (9) | 0.0173 (8) | 0.0001 (6) | 0.0051 (6) | 0.0046 (7) |
| C6 | 0.0213 (8) | 0.0185 (8) | 0.0236 (8) | 0.0013 (6) | 0.0067 (7) | 0.0049 (6) |
| C7 | 0.0195 (7) | 0.0191 (8) | 0.0193 (8) | 0.0001 (6) | 0.0046 (6) | 0.0001 (6) |
| C8 | 0.0225 (8) | 0.0192 (8) | 0.0226 (8) | 0.0023 (6) | 0.0069 (6) | 0.0009 (6) |
| C9 | 0.0220 (8) | 0.0151 (7) | 0.0199 (8) | 0.0015 (6) | 0.0074 (6) | 0.0004 (6) |
| C10 | 0.0233 (8) | 0.0164 (8) | 0.0237 (8) | 0.0013 (6) | 0.0053 (6) | −0.0014 (6) |
| C11 | 0.0321 (9) | 0.0232 (9) | 0.0199 (8) | 0.0047 (7) | 0.0040 (7) | 0.0001 (7) |
| C12 | 0.0362 (9) | 0.0215 (8) | 0.0229 (8) | 0.0053 (7) | 0.0127 (7) | 0.0044 (7) |
| C13 | 0.0254 (8) | 0.0220 (8) | 0.0283 (9) | 0.0011 (6) | 0.0117 (7) | 0.0035 (7) |
| C14 | 0.0226 (8) | 0.0150 (7) | 0.0206 (8) | 0.0006 (6) | 0.0073 (6) | −0.0009 (6) |
| C15 | 0.0221 (8) | 0.0312 (9) | 0.0215 (8) | 0.0024 (7) | 0.0011 (7) | 0.0047 (7) |
| C16 | 0.0202 (8) | 0.0394 (11) | 0.0284 (9) | 0.0058 (7) | 0.0084 (7) | 0.0089 (8) |
| C17 | 0.0294 (9) | 0.0230 (8) | 0.0222 (8) | 0.0026 (7) | 0.0106 (7) | 0.0007 (7) |
| C18 | 0.0319 (9) | 0.0216 (8) | 0.0288 (9) | 0.0050 (7) | 0.0146 (8) | 0.0047 (7) |
| C19 | 0.0305 (9) | 0.0251 (9) | 0.0203 (8) | −0.0082 (7) | 0.0036 (7) | −0.0004 (7) |
| C20 | 0.0396 (10) | 0.0300 (10) | 0.0173 (8) | −0.0114 (8) | 0.0028 (7) | −0.0022 (7) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C7 | 1.315 (2) | C6—H6 | 0.9500 |
| O1—H1O | 0.8402 | C8—C13 | 1.411 (2) |
| O2—C7 | 1.223 (2) | C8—C9 | 1.419 (2) |
| O3—C14 | 1.290 (2) | C9—C10 | 1.397 (2) |
| O4—C14 | 1.243 (2) | C9—C14 | 1.507 (2) |
| N1—C1 | 1.384 (2) | C10—C11 | 1.384 (2) |
| N1—H1N | 0.8800 | C10—H10 | 0.9500 |
| N1—H2N | 0.8802 | C11—C12 | 1.394 (3) |
| N2—C8 | 1.379 (2) | C11—H11 | 0.9500 |
| N2—H3N | 0.8800 | C12—C13 | 1.382 (3) |
| N2—H4N | 0.8799 | C12—H12 | 0.9500 |
| N3—C17 | 1.479 (2) | C13—H13 | 0.9500 |
| N3—C19 | 1.480 (2) | C15—C16 | 1.540 (2) |
| N3—C15 | 1.485 (2) | C15—H15A | 0.9900 |
| N4—C18 | 1.483 (2) | C15—H15B | 0.9900 |
| N4—C20 | 1.488 (2) | C16—H16A | 0.9900 |
| N4—C16 | 1.489 (2) | C16—H16B | 0.9900 |
| N4—H5N | 0.9300 | C17—C18 | 1.536 (2) |
| C1—C6 | 1.411 (2) | C17—H17A | 0.9900 |
| C1—C2 | 1.417 (2) | C17—H17B | 0.9900 |
| C2—C3 | 1.397 (2) | C18—H18A | 0.9900 |
| C2—C7 | 1.494 (2) | C18—H18B | 0.9900 |
| C3—C4 | 1.388 (2) | C19—C20 | 1.541 (2) |

| | | | |
|---|---|---|---|
| C3—H3 | 0.9500 | C19—H19A | 0.9900 |
| C4—C5 | 1.395 (2) | C19—H19B | 0.9900 |
| C4—H4 | 0.9500 | C20—H20A | 0.9900 |
| C5—C6 | 1.384 (2) | C20—H20B | 0.9900 |
| C5—H5 | 0.9500 | | |

| | | | |
|---|---|---|---|
| C7—O1—H1O | 108.5 | C10—C11—H11 | 120.6 |
| C1—N1—H1N | 114.1 | C12—C11—H11 | 120.6 |
| C1—N1—H2N | 113.2 | C13—C12—C11 | 120.57 (16) |
| H1N—N1—H2N | 119.4 | C13—C12—H12 | 119.7 |
| C8—N2—H3N | 118.3 | C11—C12—H12 | 119.7 |
| C8—N2—H4N | 119.5 | C12—C13—C8 | 121.35 (16) |
| H3N—N2—H4N | 119.5 | C12—C13—H13 | 119.3 |
| C17—N3—C19 | 109.10 (14) | C8—C13—H13 | 119.3 |
| C17—N3—C15 | 108.67 (13) | O4—C14—O3 | 123.47 (15) |
| C19—N3—C15 | 109.31 (14) | O4—C14—C9 | 120.27 (15) |
| C18—N4—C20 | 109.67 (14) | O3—C14—C9 | 116.19 (14) |
| C18—N4—C16 | 109.51 (14) | N3—C15—C16 | 109.79 (13) |
| C20—N4—C16 | 109.83 (14) | N3—C15—H15A | 109.7 |
| C18—N4—H5N | 109.3 | C16—C15—H15A | 109.7 |
| C20—N4—H5N | 109.3 | N3—C15—H15B | 109.7 |
| C16—N4—H5N | 109.3 | C16—C15—H15B | 109.7 |
| N1—C1—C6 | 118.89 (15) | H15A—C15—H15B | 108.2 |
| N1—C1—C2 | 122.85 (14) | N4—C16—C15 | 109.08 (13) |
| C6—C1—C2 | 118.18 (15) | N4—C16—H16A | 109.9 |
| C3—C2—C1 | 119.56 (14) | C15—C16—H16A | 109.9 |
| C3—C2—C7 | 119.14 (14) | N4—C16—H16B | 109.9 |
| C1—C2—C7 | 121.29 (14) | C15—C16—H16B | 109.9 |
| C4—C3—C2 | 121.70 (15) | H16A—C16—H16B | 108.3 |
| C4—C3—H3 | 119.2 | N3—C17—C18 | 110.71 (13) |
| C2—C3—H3 | 119.2 | N3—C17—H17A | 109.5 |
| C3—C4—C5 | 118.66 (16) | C18—C17—H17A | 109.5 |
| C3—C4—H4 | 120.7 | N3—C17—H17B | 109.5 |
| C5—C4—H4 | 120.7 | C18—C17—H17B | 109.5 |
| C6—C5—C4 | 120.95 (15) | H17A—C17—H17B | 108.1 |
| C6—C5—H5 | 119.5 | N4—C18—C17 | 108.48 (13) |
| C4—C5—H5 | 119.5 | N4—C18—H18A | 110.0 |
| C5—C6—C1 | 120.87 (15) | C17—C18—H18A | 110.0 |
| C5—C6—H6 | 119.6 | N4—C18—H18B | 110.0 |
| C1—C6—H6 | 119.6 | C17—C18—H18B | 110.0 |
| O2—C7—O1 | 123.04 (15) | H18A—C18—H18B | 108.4 |
| O2—C7—C2 | 123.56 (15) | N3—C19—C20 | 110.12 (14) |
| O1—C7—C2 | 113.39 (14) | N3—C19—H19A | 109.6 |
| N2—C8—C13 | 119.39 (16) | C20—C19—H19A | 109.6 |
| N2—C8—C9 | 122.57 (15) | N3—C19—H19B | 109.6 |
| C13—C8—C9 | 118.03 (15) | C20—C19—H19B | 109.6 |
| C10—C9—C8 | 119.14 (15) | H19A—C19—H19B | 108.2 |
| C10—C9—C14 | 117.83 (15) | N4—C20—C19 | 108.78 (14) |

| | | | |
|---|---|---|---|
| C8—C9—C14 | 122.98 (15) | N4—C20—H20A | 109.9 |
| C11—C10—C9 | 122.13 (16) | C19—C20—H20A | 109.9 |
| C11—C10—H10 | 118.9 | N4—C20—H20B | 109.9 |
| C9—C10—H10 | 118.9 | C19—C20—H20B | 109.9 |
| C10—C11—C12 | 118.74 (16) | H20A—C20—H20B | 108.3 |
| | | | |
| N1—C1—C2—C3 | −179.44 (14) | C11—C12—C13—C8 | 1.6 (3) |
| C6—C1—C2—C3 | −2.8 (2) | N2—C8—C13—C12 | 179.51 (17) |
| N1—C1—C2—C7 | 1.4 (2) | C9—C8—C13—C12 | −1.6 (2) |
| C6—C1—C2—C7 | 178.02 (14) | C10—C9—C14—O4 | −19.9 (2) |
| C1—C2—C3—C4 | 1.9 (2) | C8—C9—C14—O4 | 162.91 (15) |
| C7—C2—C3—C4 | −178.95 (15) | C10—C9—C14—O3 | 157.33 (15) |
| C2—C3—C4—C5 | 0.6 (2) | C8—C9—C14—O3 | −19.9 (2) |
| C3—C4—C5—C6 | −2.2 (3) | C17—N3—C15—C16 | −62.35 (18) |
| C4—C5—C6—C1 | 1.2 (3) | C19—N3—C15—C16 | 56.62 (19) |
| N1—C1—C6—C5 | 178.09 (15) | C18—N4—C16—C15 | 57.55 (19) |
| C2—C1—C6—C5 | 1.3 (2) | C20—N4—C16—C15 | −62.94 (19) |
| C3—C2—C7—O2 | −171.35 (16) | N3—C15—C16—N4 | 5.0 (2) |
| C1—C2—C7—O2 | 7.8 (2) | C19—N3—C17—C18 | −62.15 (18) |
| C3—C2—C7—O1 | 9.0 (2) | C15—N3—C17—C18 | 56.95 (18) |
| C1—C2—C7—O1 | −171.82 (15) | C20—N4—C18—C17 | 57.54 (18) |
| N2—C8—C9—C10 | 178.78 (16) | C16—N4—C18—C17 | −63.04 (18) |
| C13—C8—C9—C10 | −0.1 (2) | N3—C17—C18—N4 | 4.8 (2) |
| N2—C8—C9—C14 | −4.0 (3) | C17—N3—C19—C20 | 55.90 (18) |
| C13—C8—C9—C14 | 177.12 (15) | C15—N3—C19—C20 | −62.81 (18) |
| C8—C9—C10—C11 | 1.8 (2) | C18—N4—C20—C19 | −63.53 (19) |
| C14—C9—C10—C11 | −175.57 (15) | C16—N4—C20—C19 | 56.86 (19) |
| C9—C10—C11—C12 | −1.8 (3) | N3—C19—C20—N4 | 5.3 (2) |
| C10—C11—C12—C13 | 0.0 (3) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1O···N3 | 0.84 | 1.77 | 2.597 (2) | 168 |
| N4—H5*n*···O3 | 0.93 | 1.64 | 2.546 (2) | 166 |
| N1—H2*n*···O2 | 0.88 | 2.03 | 2.725 (2) | 135 |
| N2—H3*n*···O3 | 0.88 | 2.04 | 2.696 (2) | 131 |
| N1—H1*n*···O4$^{i}$ | 0.88 | 2.08 | 2.941 (2) | 165 |
| N2—H4*n*···N1$^{ii}$ | 0.88 | 2.38 | 3.256 (2) | 171 |

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+3/2; (ii) −*x*+2, *y*+1/2, −*z*+3/2.