Title
Acridinium 6-carb-oxy-pyridine-2-carboxyl-ate monohydrate.

Permalink
https://escholarship.org/uc/item/4ks1v0g2

Journal
Acta crystallographica. Section E, Structure reports online, 67(Pt 2)

ISSN
1600-5368

Authors
Derikvand, Zohreh
Olmstead, Marilyn M
Attar Gharamaleki, Jafar

Publication Date
2011-01-15

DOI
10.1107/S1600536810053791

Peer reviewed
Acridinium 6-carboxypyridine-2-carboxylate monohydrate

Zohreh Derikvand, Marilyn M. Olmstead and Jafar Attar Gharamaleki

*Acta Cryst.* (2011). *E67*, o416

This open-access article is distributed under the terms of the Creative Commons Attribution Licence http://creativecommons.org/licenses/by/2.0/uk/legalcode, which permits unrestricted use, distribution, and reproduction in any medium, provided the original authors and source are cited.

*Acta Crystallographica Section E: Structure Reports Online* is the IUCr's highly popular open-access structural journal. It provides a simple and easily accessible publication mechanism for the growing number of inorganic, metal-organic and organic crystal structure determinations. The electronic submission, validation, refereeing and publication facilities of the journal ensure very rapid and high-quality publication, whilst key indicators and validation reports provide measures of structural reliability. In 2007, the journal published over 5000 structures. The average publication time is less than one month.

Crystallography Journals Online is available from journals.iucr.org
The title compound, C_{13}H_{10}N^{+}\cdot C_7H_4NO_4^{-}\cdot H_2O or (acrH)^{+}\cdot (pydH)^{-}\cdot H_2O, is a monohydrate of acridinium cations and a mono-deprotonated pyridine-2,6-dicarboxylic acid. The structure contains a range of non-covalent interactions, such as O—H···O, O—H···N and N—H···O hydrogen bonds, as well as π–π stacking [range of centroid–centroid distances = 3.4783 (5)–3.8059 (5) \AA{}]. The N—H···O hydrogen bond between the donor acridinium cation and the carboxylate acceptor is particularly strong. The average separation between the \pi-stacked acridinium planes is 3.42 (3) \AA{}.

Related literature

For structures of acridinium salts, see: Aghabozorg et al. (2010); Attar Gharamaleki et al. (2010); Derikvand et al. (2009, 2010); Shaameri et al. (2001); Tabatabae et al. (2009).

Table 1

Hydrogen-bond geometry (\AA, °).

\begin{tabular}{cccccc}
D—H···A & D—H & H···A & D···A & D—H···A \\
\hline
O4—H4A···O5 & 0.869 (17) & 1.958 (17) & 2.7604 (10) & 152.9 (16) \\
O4—H4A···N2 & 0.869 (17) & 2.182 (17) & 2.6664 (10) & 114.6 (14) \\
O5—H5A···O1 & 0.849 (18) & 2.016 (18) & 2.8421 (10) & 164.0 (16) \\
O5—H5B···O2′ & 0.845 (18) & 2.134 (18) & 2.9255 (10) & 155.8 (16) \\
N1—H1···O2 & 1.031 (17) & 1.555 (18) & 2.5859 (9) & 178.6 (16) \\
\end{tabular}

Symmetry code: (i) x+1, y, z.

Data collection

APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: XP in SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXL97.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2777).

References

Aghabozorg, H., Attar Gharamaleki, J., Parvizi, M. & Derikvand, Z. (2010). Acta Cryst. E66, m83–m84.
Attar Gharamaleki, J., Derikvand, Z. & Stoeckli-Evans, H. (2010). Acta Cryst. E66, o2231.
Bruker (2009). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
Derikvand, Z., Aghabozorg, H. & Attar Gharamaleki, J. (2009). Acta Cryst. E65, o1173.
Derikvand, Z., Attar Gharamaleki, J. & Stoeckli-Evans, H. (2010). Acta Cryst. E66, m1316–m1317.
Shaameri, Z., Shan, N. & Jones, W. (2001). Acta Cryst. E57, o945–o946.
Sheldrick, G. M. (1996). SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2008). Acta Cryst. A64, 112–122.
Tabatabae et al., M., Aghabozorg, H., Attar Gharamaleki, J. & Sharif, M. A. (2009). Acta Cryst. E65, m473–m474.
supplementary materials
supplementary materials

Acta Cryst. (2011). E67, o416 [doi:10.1107/S1600536810053791]

Acridinium 6-carboxypyridine-2-carboxylate monohydrate

Z. Derikvand, M. M. Olmstead and J. Attar Gharamaleki

Comment

We have reported a number of crystal structures of protonated acridine and pyridine dicarboxylates (Derikvand et al., 2009, 2010; Aghabozorg et al., 2010; Attar Gharamaleki et al., 2010; Tabatabae et al., 2009). Many other examples of acridinium salts are known, and they have π–π stacking of the acridinium ions and various types of hydrogen bonding in common. The molecular structure of the title compound, the 1:1 salt of acridinium and pyridine-2,6-dicarboxylate is illustrated in Fig. 1. The crystal structure shows one of the protons of the two carboxylic groups has been transferred to the nitrogen atom of the acride molecule.

As expected, bond lengths of the –CO₂ groups reflect the presence or lack of an acidic H atom. At distances of 1.2403 (11) Å and 1.2806 (11) Å, respectively, the O1—C19 and O2—C19 bond lengths are much closer to equality than O3—C20 and O4—C20, at 1.226 (11) Å and 1.3305 (11) Å. However, we can also point out that the O2—C19 bond is slightly longer than the O1—C19 bond, possibly due to there being two classical hydrogen bonds involving O2 and only one involving O1 (see Table 1). In fact, one of the hydrogen bonds for O2 can be classified as a very strong hydrogen bond, with an N···O distance of 2.5859 (9) Å. In a similar structure involving the acridinium salt of isophthalate (Shaameri et al., 2001), the analogous arrangement of cation and anion gives rise to a similar short hydrogen bond with N···O distance of 2.553 (2) Å. A depiction of the hydrogen bonded motif involving anion and cation fragments and water molecules is presented in Fig. 2. The hydrogen bonds between the water molecule and O2 serve to link the anions into a chain along the a axis direction. Symmetry code: i = x - 1, y, z.

Additional noncovalent interactions cause the structure to form a self assembled system. In the structure π–π stacking interactions between the acridinium ions average 3.42[3]Å (average deviation in square brackets). Sideways strong hydrogen bonds between O2 and the the proton of acidine gather the π-stack and the anionic chain together as shown in Fig. 3.

Experimental

A solution of pyridine-2,6-dicarboxylic acid (167 mg, 1 mmol) in water (10 ml) was added to a solution of acridine(179 mg, 1 mmol) in methanol (5 ml) and stirring for 30 minutes, a clear solution was obtained (Scheme 1). Yellow-gold block crystals suitable for X-ray crystallography were produced by slow evaporation of the solvent at room temperature after a week.

Refinement

All hydrogen atoms were freely refined.
supplementary materials

Figures

Fig. 1. Molecular structure of (acrH)$^\dagger$(pydcH)$^-$. H$_2$O. Displacement ellipsoids are drawn at 50% probability level.

Fig. 2. Hydrogen bonding interactions. Symmetry code: i = x - 1, y, z.

Fig. 3. π-π Stacking interactions between cationic fragments and their link to anionic chains as viewed along [0 1 1].

Acridinium 6-carboxypyridine-2-carboxylate monohydrate

Crystal data

\[
\begin{align*}
C_{13}H_{16}N^+\cdot C_7H_4NO_4^-\cdot H_2O & \\
M_r & = 364.35 \\
\text{Triclinic, } \overline{P} & 1 \\
\text{Hall symbol: } P & 1 \\
a & = 7.4842 (3) \text{ Å} \\
b & = 8.6850 (3) \text{ Å} \\
c & = 13.0305 (4) \text{ Å} \\
\alpha & = 100.266 (3)^\circ \\
\beta & = 93.851 (2)^\circ \\
\gamma & = 97.766 (2)^\circ \\
V & = 822.16 (5) \text{ Å}^3 \\
Z & = 2 \\
F(000) & = 380 \\
\rho_x & = 1.472 \text{ Mg m}^{-3} \\
\text{Mo } K\alpha \text{ radiation, } \lambda & = 0.71073 \text{ Å} \\
\theta & = 2.6--32.9^\circ \\
\mu & = 0.11 \text{ mm}^{-1} \\
T & = 90 \text{ K} \\
V_{\text{block}} & = 0.32 \times 0.23 \times 0.17 \text{ mm} \\
V_{\text{cell}} & = 822.16 (5) \text{ Å}^3 \\
\end{align*}
\]

Data collection

Bruker SMART APEXII \\
diffraclorimeter \\
Radiation source: fine-focus sealed tube \\
graphe \\
Detector resolution: 8.3 pixels mm$^{-1}$ \\
\[ \omega \text{ scans} \]

4403 independent reflections \\
4034 reflections with $I > 2\sigma(I)$ \\
$R_{\text{int}} = 0.011$ \\
$\theta_{\text{max}} = 29.1^\circ$, $\theta_{\text{min}} = 2.6^\circ$ \\
$h = -10\rightarrow10$
Absorption correction: multi-scan
(*SADABS; Sheldrick, 1996)

\(k = -11 \rightarrow 11\)

\(T_{\text{min}} = 0.966, T_{\text{max}} = 0.982\)

11632 measured reflections

Refinement

Primary atom site location: structure-invariant direct
methods

Least-squares matrix: full

Secondary atom site location: difference Fourier map

\(R[F^2 > 2\sigma(F^2)] = 0.035\)

\(wR(F^2) = 0.105\)

\(S = 1.07\)

4403 reflections

308 parameters

0 restraints

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 \(F^2 > 2\sigma(F^2)\) 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 (Å\(^2\))

|   | \(x\)       | \(y\)       | \(z\)       | \(U_{iso}/U_{eq}\) |
|---|-------------|-------------|-------------|---------------------|
| O1| 0.49045 (9) | 0.63220 (8) | 0.25575 (5) | 0.02109 (15)        |
| O2| 0.19185 (9) | 0.63670 (8) | 0.23357 (5) | 0.01783 (14)        |
| O3| 0.62172 (10)| 0.08319 (8) | -0.08226 (5)| 0.02271 (16)        |
| O4| 0.75469 (9) | 0.23901 (8) | 0.06409 (6) | 0.02201 (15)        |
| H4A| 0.735 (2)  | 0.320 (2)   | 0.1097 (13) | 0.043 (4)*          |
| O5| 0.81245 (10)| 0.49602 (9) | 0.22739 (6) | 0.02321 (16)        |
| H5A| 0.721 (2)  | 0.544 (2)   | 0.2252 (13) | 0.044 (4)*          |
| H5B| 0.907 (2)  | 0.560 (2)   | 0.2244 (13) | 0.043 (4)*          |
| N1| 0.22761 (10)| 0.86086 (8) | 0.39668 (6) | 0.01351 (15)        |
| H1| 0.215 (2)  | 0.771 (2)   | 0.3318 (14) | 0.049 (5)*          |
| N2| 0.46280 (10)| 0.38054 (8) | 0.09346 (5) | 0.01356 (15)        |
| C1| 0.29254 (11)| 0.83725 (10)| 0.49119 (6) | 0.01346 (16)        |
| C2| 0.33756 (12)| 0.68689 (11)| 0.50193 (7) | 0.01783 (18)        |
| H2| 0.3209 (19) | 0.6010 (17) | 0.4401 (11) | 0.029 (3)*          |
supplementary materials

|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| C3 | 0.40456 (13) | 0.66579 (12) | 0.59791 (8) | 0.02161 (19) |   |   |
| H3 | 0.432 (2) | 0.5632 (18) | 0.6068 (11) | 0.034 (4)* |   |   |
| C4 | 0.43460 (13) | 0.79225 (13) | 0.68579 (8) | 0.0226 (2) |   |   |
| H4 | 0.486 (2) | 0.7719 (18) | 0.7514 (12) | 0.034 (4)* |   |   |
| C5 | 0.39282 (12) | 0.93759 (12) | 0.67742 (7) | 0.01935 (18) |   |   |
| H5 | 0.418 (2) | 1.0241 (17) | 0.7378 (11) | 0.031 (4)* |   |   |
| C6 | 0.31603 (11) | 0.96397 (10) | 0.57969 (6) | 0.01448 (16) |   |   |
| C7 | 0.26325 (11) | 1.10795 (10) | 0.56689 (7) | 0.01559 (17) |   |   |
| H7 | 0.2804 (19) | 1.1941 (17) | 0.6252 (11) | 0.028 (3)* |   |   |
| C8 | 0.19056 (11) | 1.12820 (10) | 0.46937 (7) | 0.01433 (17) |   |   |
| C9 | 0.13152 (12) | 1.27198 (11) | 0.45221 (8) | 0.01948 (18) |   |   |
| H9 | 0.139 (2) | 1.3590 (17) | 0.5148 (11) | 0.031 (3)* |   |   |
| C10 | 0.06669 (13) | 1.28604 (12) | 0.35436 (9) | 0.0227 (2) |   |   |
| H10 | 0.026 (2) | 1.3839 (18) | 0.3435 (12) | 0.037 (4)* |   |   |
| C11 | 0.05946 (13) | 1.15875 (12) | 0.26824 (8) | 0.02219 (19) |   |   |
| H11 | 0.016 (2) | 1.1712 (18) | 0.1989 (12) | 0.037 (4)* |   |   |
| C12 | 0.11412 (12) | 1.01882 (11) | 0.28081 (7) | 0.01838 (18) |   |   |
| H12 | 0.1125 (19) | 0.9325 (17) | 0.2221 (11) | 0.028 (3)* |   |   |
| C13 | 0.17760 (11) | 1.00027 (10) | 0.38252 (6) | 0.01340 (16) |   |   |
| C14 | 0.31558 (11) | 0.44843 (9) | 0.11517 (6) | 0.01310 (16) |   |   |
| C15 | 0.14892 (12) | 0.39585 (11) | 0.05742 (7) | 0.01748 (17) |   |   |
| H15 | 0.0454 (18) | 0.4460 (16) | 0.0776 (10) | 0.025 (3)* |   |   |
| C16 | 0.13303 (13) | 0.26913 (12) | −0.02620 (7) | 0.0224 (2) |   |   |
| H16 | 0.015 (2) | 0.2304 (19) | −0.0658 (12) | 0.039 (4)* |   |   |
| C17 | 0.28452 (13) | 0.19891 (11) | −0.04975 (7) | 0.02011 (19) |   |   |
| H17 | 0.280 (2) | 0.1079 (17) | −0.1077 (11) | 0.032 (4)* |   |   |
| C18 | 0.44547 (11) | 0.25928 (10) | 0.01274 (6) | 0.01459 (16) |   |   |
| C19 | 0.33787 (12) | 0.58364 (10) | 0.20896 (6) | 0.01463 (16) |   |   |
| C20 | 0.61355 (12) | 0.18562 (10) | −0.00691 (7) | 0.01689 (17) |   |   |

Atomic displacement parameters (Å²)

|   | U¹¹ | U²² | U³³ | U¹² | U¹³ | U²³ |
|---|---|---|---|---|---|---|
| O1 | 0.0156 (3) | 0.0221 (3) | 0.0213 (3) | 0.0021 (2) | −0.0019 (2) | −0.0053 (2) |
| O2 | 0.0154 (3) | 0.0174 (3) | 0.0187 (3) | 0.0044 (2) | 0.0012 (2) | −0.0031 (2) |
| O3 | 0.0247 (3) | 0.0232 (3) | 0.0206 (3) | 0.0092 (3) | 0.0066 (3) | −0.0007 (3) |
| O4 | 0.0159 (3) | 0.0220 (3) | 0.0267 (4) | 0.0062 (2) | 0.0003 (3) | −0.0013 (3) |
| O5 | 0.0150 (3) | 0.0245 (4) | 0.0307 (4) | 0.0020 (3) | 0.0008 (3) | 0.0078 (3) |
| N1 | 0.0133 (3) | 0.0131 (3) | 0.0137 (3) | 0.0024 (2) | 0.0012 (2) | 0.0011 (2) |
| N2 | 0.0139 (3) | 0.0140 (3) | 0.0130 (3) | 0.0031 (2) | 0.0014 (2) | 0.0025 (2) |
| C1 | 0.0110 (3) | 0.0146 (4) | 0.0150 (4) | 0.0015 (3) | 0.0024 (3) | 0.0034 (3) |
| C2 | 0.0157 (4) | 0.0162 (4) | 0.0233 (4) | 0.0040 (3) | 0.0048 (3) | 0.0060 (3) |
| C3 | 0.0154 (4) | 0.0251 (5) | 0.0297 (5) | 0.0067 (3) | 0.0061 (3) | 0.0153 (4) |
| C4 | 0.0149 (4) | 0.0363 (5) | 0.0199 (4) | 0.0036 (4) | 0.0020 (3) | 0.0145 (4) |
| C5 | 0.0147 (4) | 0.0290 (5) | 0.0139 (4) | 0.0005 (3) | 0.0011 (3) | 0.0052 (3) |
| C6 | 0.0117 (4) | 0.0182 (4) | 0.0127 (4) | −0.0002 (3) | 0.0014 (3) | 0.0025 (3) |
| C7 | 0.0145 (4) | 0.0149 (4) | 0.0153 (4) | −0.0005 (3) | 0.0025 (3) | −0.0012 (3) |
| C8 | 0.0124 (4) | 0.0128 (4) | 0.0173 (4) | 0.0006 (3) | 0.0028 (3) | 0.0020 (3) |
|     |          |          |          |          |          |          |
|-----|----------|----------|----------|----------|----------|----------|
| C9  | 0.0169 (4)| 0.0134 (4)| 0.0286 (5)| 0.0026 (3)| 0.0049 (3)| 0.0040 (3) |
| C10 | 0.0172 (4)| 0.0194 (4)| 0.0352 (5)| 0.0051 (3)| 0.0037 (4)| 0.0126 (4) |
| C11 | 0.0169 (4)| 0.0288 (5)| 0.0237 (4)| 0.0034 (3)| 0.0001 (3)| 0.0132 (4) |
| C12 | 0.0164 (4)| 0.0230 (4)| 0.0158 (4)| 0.0024 (3)| -0.0001 (3)| 0.0045 (3) |
| C13 | 0.0112 (3)| 0.0141 (4)| 0.0149 (4)| 0.0015 (3)| 0.0017 (3)| 0.0029 (3) |
| C14 | 0.0145 (4)| 0.0134 (4)| 0.0114 (3)| 0.0028 (3)| 0.0012 (3)| 0.0020 (3) |
| C15 | 0.0147 (4)| 0.0221 (4)| 0.0145 (4)| 0.0056 (3)| -0.0003 (3)| -0.0011 (3) |
| C16 | 0.0162 (4)| 0.0297 (5)| 0.0172 (4)| 0.0049 (3)| -0.0026 (3)| -0.0062 (3) |
| C17 | 0.0188 (4)| 0.0231 (4)| 0.0156 (4)| 0.0041 (3)| 0.0012 (3)| -0.0042 (3) |
| C18 | 0.0156 (4)| 0.0152 (4)| 0.0135 (4)| 0.0041 (3)| 0.0031 (3)| 0.0022 (3) |
| C19 | 0.0159 (4)| 0.0135 (4)| 0.0139 (4)| 0.0023 (3)| 0.0011 (3)| 0.0009 (3) |
| C20 | 0.0161 (4)| 0.0170 (4)| 0.0185 (4)| 0.0040 (3)| 0.0041 (3)| 0.0038 (3) |

**Geometric parameters (Å, °)**

| Bond | Length (Å) | Angle (°) |
|------|------------|-----------|
| O1—C9 | 1.2403 (11) | C6—C7 1.3952 (12) |
| O2—C19 | 1.2806 (10) | C7—C8 1.3980 (12) |
| O3—C20 | 1.2126 (11) | C7—H7 0.955 (14) |
| O4—C20 | 1.3305 (11) | C8—C13 1.4256 (11) |
| O4—H4A | 0.869 (17) | C8—C9 1.4282 (12) |
| O5—H5A | 0.849 (18) | C9—C10 1.3655 (14) |
| O5—H5B | 0.845 (18) | C9—H9 1.002 (14) |
| N1—C1 | 1.3533 (11) | C10—C11 1.4204 (15) |
| N1—C13 | 1.3538 (11) | C10—H10 0.972 (16) |
| N1—H1 | 1.031 (17) | C11—C12 1.3665 (13) |
| N2—C18 | 1.3350 (11) | C11—H11 0.970 (16) |
| N2—C14 | 1.3415 (11) | C12—C13 1.4215 (12) |
| C1—C2 | 1.4199 (12) | C12—H12 0.969 (14) |
| C1—C6 | 1.4283 (11) | C14—C15 1.3885 (12) |
| C2—C3 | 1.3680 (13) | C14—C19 1.5194 (11) |
| C2—H2 | 0.984 (14) | C15—C16 1.3901 (12) |
| C3—C4 | 1.4208 (15) | C15—H15 0.968 (14) |
| C3—H3 | 0.966 (15) | C16—C17 1.3850 (13) |
| C4—C5 | 1.3617 (14) | C16—H16 0.977 (16) |
| C4—H4 | 0.969 (15) | C17—C18 1.3908 (12) |
| C5—C6 | 1.4303 (12) | C17—H17 0.987 (15) |
| C5—H5 | 0.975 (14) | C18—C20 1.5032 (12) |
| C20—O4—H4A | 112.1 (11) | C9—C10—C11 120.43 (9) |
| H5A—O5—H5B | 109.3 (16) | C9—C10—H10 119.8 (9) |
| C1—N1—C13 | 122.44 (7) | C11—C10—H10 119.7 (9) |
| C1—N1—H1 | 120.2 (10) | C12—C11—C10 121.37 (9) |
| C13—N1—H1 | 117.3 (10) | C12—C11—H11 119.0 (9) |
| C18—N2—C14 | 117.75 (7) | C10—C11—H11 119.6 (9) |
| N1—C1—C2 | 119.91 (8) | C11—C12—C13 119.08 (9) |
| N1—C1—C6 | 119.81 (8) | C11—C12—H12 121.8 (8) |
| C2—C1—C6 | 120.28 (8) | C13—C12—H12 119.1 (8) |
| C3—C2—C1 | 119.03 (9) | N1—C13—C12 119.76 (8) |
| C3—C2—H2 | 121.8 (8) | N1—C13—C8 119.91 (7) |
| C1—C2—H2 | 119.2 (8) | C12—C13—C8 120.32 (8) |
supplementary materials

C2—C3—C4  121.31 (9)  N2—C14—C15  122.24 (8)
C2—C3—H3  119.9 (9)  N2—C14—C19  116.69 (7)
C4—C3—H3  118.8 (9)  C15—C14—C19  121.05 (7)
C5—C4—C3  120.73 (8)  C14—C15—C16  119.29 (8)
C5—C4—H4  121.3 (9)  C14—C15—H15  119.3 (8)
C3—C4—H4  118.0 (9)  C16—C15—H15  121.4 (8)
C4—C5—C6  120.05 (9)  C17—C16—C15  118.93 (8)
C4—C5—H5  119.8 (9)  C17—C16—H16  121.7 (9)
C6—C5—H5  120.1 (9)  C15—C16—H16  119.3 (9)
C7—C6—C1  118.53 (8)  C16—C17—C18  117.69 (8)
C7—C6—C5  122.96 (8)  C16—C17—H17  122.0 (9)
C1—C6—C5  118.52 (8)  C18—C17—H17  120.3 (9)
C6—C7—C8  120.73 (8)  N2—C18—C17  124.10 (8)
C6—C7—H7  119.2 (9)  N2—C18—C20  115.58 (7)
C8—C7—H7  120.0 (9)  C17—C18—C20  120.31 (8)
C7—C8—C13  118.48 (8)  O1—C19—O2  125.44 (8)
C7—C8—C9  123.10 (8)  O1—C19—C14  119.23 (8)
C13—C8—C9  118.42 (8)  O2—C19—C14  115.33 (7)
C10—C9—C8  120.32 (9)  O3—C20—O4  121.35 (8)
C10—C9—H9  122.8 (8)  O3—C20—C18  122.73 (8)
C8—C9—H9  116.9 (8)  O4—C20—C18  115.92 (7)
C13—N1—C1—C2  178.05 (7)  C11—C12—C13—N1  178.23 (8)
C13—N1—C1—C6  −2.15 (12)  C11—C12—C13—C8  −2.42 (13)
N1—C1—C2—C3  179.41 (8)  C7—C8—C13—N1  2.91 (12)
C6—C1—C2—C3  −0.39 (13)  C9—C8—C13—N1  −178.14 (7)
C1—C2—C3—C4  −1.84 (13)  C7—C8—C13—C12  −176.43 (8)
C2—C3—C4—C5  1.74 (14)  C9—C8—C13—C12  2.51 (12)
C3—C4—C5—C6  0.66 (14)  C18—N2—C14—C15  0.51 (12)
N1—C1—C6—C7  2.80 (12)  C18—N2—C14—C19  178.61 (7)
C2—C1—C6—C7  −177.40 (8)  N2—C14—C15—C16  −0.32 (14)
N1—C1—C6—C5  −177.12 (7)  C19—C14—C15—C16  −178.35 (8)
C2—C1—C6—C5  2.68 (12)  C14—C15—C16—C17  −0.15 (15)
C4—C5—C6—C7  177.28 (8)  C15—C16—C17—C18  0.39 (15)
C4—C5—C6—C1  −2.80 (13)  C14—N2—C18—C17  −0.24 (13)
C1—C6—C7—C8  −0.59 (12)  C14—N2—C18—C20  −178.89 (7)
C5—C6—C7—C8  179.32 (8)  C16—C17—C18—N2  −0.21 (15)
C6—C7—C8—C13  −2.20 (12)  C16—C17—C18—C20  178.38 (9)
C6—C7—C8—C9  178.91 (8)  N2—C14—C19—O1  5.15 (12)
C7—C8—C9—C10  178.03 (8)  C15—C14—C19—O1  −176.72 (8)
C13—C8—C9—C10  −0.87 (13)  N2—C14—C19—O2  −173.96 (7)
C8—C9—C10—C11  −0.86 (14)  C15—C14—C19—O2  4.17 (12)
C9—C10—C11—C12  0.97 (14)  N2—C18—C20—O3  −173.96 (8)
C10—C11—C12—C13  0.68 (14)  C17—C18—C20—O3  7.33 (14)
C1—N1—C13—C12  178.61 (7)  N2—C18—C20—O4  6.37 (11)
C1—N1—C13—C8  −0.74 (12)  C17—C18—C20—O4  −172.34 (8)

Hydrogen-bond geometry (Å, °)

\[
\begin{array}{cccc}
D—H—A & D—H & H···A & D···A & D—H···A \\
\end{array}
\]

sup-6
supplementary materials

|          |       |       |       |       |
|----------|-------|-------|-------|-------|
| O4—H4A···O5 | 0.869 (17) | 1.958 (17) | 2.7604 (10) | 152.9 (16) |
| O4—H4A···N2 | 0.869 (17) | 2.182 (17) | 2.6646 (10) | 114.6 (14) |
| O5—H5A···O1 | 0.849 (18) | 2.016 (18) | 2.8421 (10) | 164.0 (16) |
| O5—H5B···O2i | 0.845 (18) | 2.134 (18) | 2.9255 (10) | 155.8 (16) |
| N1—H1···O2  | 1.031 (17) | 1.555 (18) | 2.5859 (9)  | 178.6 (16) |

Symmetry codes: (i) x+1, y, z.
Fig. 2
supplementary materials

Fig. 3