The missing crystal structure in the series of $N,N',N''$-tris(pyridinyl)benzene-1,3,5-tricarboxamides: the 2-pyridinyl derivative

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The missing crystal structure in the series of \( \text{N}, \text{N}', \text{N}'' \)-tris(pyridinyl)benzene-1,3,5-tricarboxamides: the 2-pyridinyl derivative

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In the first reported crystal structure involving the potential ligand \( \text{N}, \text{N}', \text{N}'' \)-tris(pyridin-2-yl)benzene-1,3,5-tricarboxamide, \( \text{C}_{24}\text{H}_{18}\text{N}_{6}\text{O}_{3} \), intermolecular \( \text{N—H—O} \) hydrogen bonds link the molecules via their amide groups into slanted ladder-like chains, in which the uprights of the ladder are formed by the hydrogen-bonding interactions and the benzene ring cores of the molecules act as the rungs of the ladder. Only two of the three amide groups in the molecule are involved in hydrogen bonding and this influences the degree of out-of-plane twisting at each amide group, with the twist being more significant for those amide groups participating in hydrogen bonds.

1. Chemical context

Branched coordinating ligands with potential donor atoms on each branch can be useful as spacers in the synthesis of coordination polymers and metal–organic frameworks. A frequently used starting material is benzene-1,3,5-tricarboxylic acid (trimesic acid), which can act as a three-way planar node-connector. A related, less frequently employed, ligand system is \( \text{N}, \text{N}', \text{N}'' \)-tris(\( n \)-pyridinyl)-1,3,5-benzenetricarboxamide (\( n = 2, 3 \) or 4), which has potential donor atoms on each pyridinyl ring and at the amide function.

![Image of crystal structure]

We are interested in constructing bismuth(III) coordination polymers (Senior & Linden, 2020a,b) and have synthesized the above three amides as potential spacer ligands, although, so far, experiments involving these have not produced any Bi\(^{\text{III}} \) coordination polymers. The crystal structure of the 2-pyridinyl derivative, \( \text{N}, \text{N}', \text{N}'' \)-tris(2-pyridinyl)-1,3,5-benzenetricarboxamide, \( \text{C}_{24}\text{H}_{18}\text{N}_{6}\text{O}_{3} \), (I), has not previously been reported and is described here.
2. Structural commentary

The asymmetric unit of (I), shown in Fig. 1, contains one molecule, which, despite its chemical threefold symmetry, does not adopt any crystallographic symmetry, nor does it have a propeller-like conformation in which the orientations of the amide groups all lie with the same relative orientation as one progresses around the benzene ring. This may be related to the absence of any hydrogen-bonding interactions at one of the amide groups, while the other amide groups act as both hydrogen-bond donors and acceptors (see Supramolecular features). The 2-pyridinyl rings all lie with the ring N atom approximately cis to the amide N—H group.

The bond lengths and angles in the molecule have normal values and the bond lengths around the amide groups (Table 1) are not significantly influenced by the presence or absence of hydrogen-bonding interactions. Of more interest are the deviations from the central benzene ring plane of the amide and 2-pyridinyl groups. The torsion angles listed in Table 1 indicate that each of the amide C(O)—N bonds is twisted by approximately 27° out of the plane of the benzene ring. On the other hand, for the amide group not involved in hydrogen bonding, the amide C7(O1)—N1 bond is twisted by less than 8° from the plane of the 2-pyridinyl ring, while for the other two amide groups, the magnitude of the C(O)—N twist is in the range 25–34°. This suggests that the hydrogen-bonding interactions significantly influence the orientation of the adjacent 2-pyridinyl ring; where interactions occur, the ring is rotated more to accommodate the intermolecular hydrogen bonds. The dihedral angles between the planes of the benzene ring and the 2-pyridinyl rings adjacent to the amide groups involving atoms N1, N3 and N5 are 20.41 (5), 3.11 (5) and 7.50 (5)°, respectively, which again highlights the difference attributable to the absence of hydrogen-bonding interactions at the amide group involving atom N1.

3. Supramolecular features

In the extended structure of (I), the molecules are linked into slanted ladder-like chains by N—H···O hydrogen bonds, which involve the amide groups as donors and acceptors (Table 2, Fig. 2). The 2-pyridinyl N atoms are not involved in these interactions. The ladders progress parallel to the [100] direction. The uprights of the ladder are formed by the hydrogen-bonding interactions and the benzene ring cores of the molecules act as the rungs of the ladder. Considered separately, amide group N2—H interacts with the O atom of the N3—H amide group of an adjacent molecule and continuing the same path brings one back to the original molecule, thereby completing a loop that can be described by a graph-set motif (Bernstein et al., 1995) of \( R_2^2(16) \). Similarly, the amide group N3—H interacts with the O atom of the N2—H amide group...
group of the adjacent molecule on the other side to give the same loop motif. These two loops alternate as one progresses along the ladder. The rungs of the ladder can be described by the chain graph-set motif of \( C_2^2 \), because it involves the N2—H and N3—H amide groups in an alternating sequence.

The slanted stacking of the molecules as the rungs of the hydrogen-bonded ladder only allow weak \( \pi-\pi \) interactions, which occur between the central benzene ring and the 2-pyridinyl ring containing atom N5 in the centrosymmetrically related adjacent molecule on one side at \( 1-x, 1-y, 1-z \), and with the 2-pyridinyl ring containing atom N6 in the centrosymmetrically related adjacent molecule on the other side at \(-x, 1-y, 1-z\). These interactions reinforce the ladder structure, rather than linking adjacent ladders. For the interactions involving the 2-pyridinyl rings containing atoms N5 and N6, respectively, the distances between the centroids of the benzene and 2-pyridinyl rings are 3.8956 (6) and 3.8409 (6) \( \AA \), the perpendicular distances between the centroid of the benzene ring and the planes of the 2-pyridinyl rings are 3.4522 (5) and 3.4610 (4) \( \AA \), while the slippages of centroids of the benzene ring and the planes of the 2-pyridinyl side at centrosymmetrically related adjacent molecule on the other side at \( 1-x, 1-y, 1-z \). These interactions reinforce the ladder structure, rather than linking adjacent ladders.

### Table 3

| Experimental details. |
|------------------------|
| Crystal data          |
| Chemical formula      | \( \text{C}_{22}\text{H}_{19}\text{N}_{5}\text{O}_{3} \) |
| \( M_w \)             | 438.44 |
| Crystal system, space group | Monoclinic, \( P_{2_1}/n \) |
| Temperature (K)       | 160 |
| \( a, b, c(\AA) \)    | 8.2807 (1), 14.1554 (1), 17.5020 (2) |
| \( \beta(\degree) \)  | 98.920 (1) |
| \( V(\AA^3) \)        | 2026.71 (4) |
| \( Z \)               | 4 |
| Radiation type        | Cu K\( \alpha \) |
| \( \mu(\text{mm}^{-1}) \) | 0.81 |
| Crystal size (mm)     | 0.24 \( \times \) 0.09 \( \times \) 0.09 |

### 4. Database survey

The Cambridge Structural Database (CSD, version 5.41, update of March 2020; Groom et al., 2016) has no entries for (I), its salts, nor for its use as a ligand. There are six crystal structures reported for the tris(3-pyridinyl) analogue; the pure anisolvate (Palmons et al., 1997), and five reports of the monohydrate, which occurs in two polymorphic forms with space groups \( \text{Cc} \) and \( \text{Pbca} \) (Rajput & Biradha, 2008, 2011; Jia et al., 2009; Zhang et al., 2016). In the anisolvate, the 3-pyridinyl rings all lie with the ring N atom approximately \( \text{cis} \) to the adjacent amide N—H group, as in (I), but is the only example among the 2- and 3-pyridinyl analogues where a propeller-like sequence of the three arms of the molecule is observed. In the \( \text{Cc} \) polymorph of the monohydrate, two of the 3-pyridinyl rings lie approximately \( \text{trans} \) to their adjacent amide N—H groups, while in the \( \text{Pbca} \) polymorph, all three of the 3-pyridinyl rings have the \( \text{trans} \) arrangement. Surprisingly, there are only three crystal structures reported for the tris(4-pyridinyl) analogue; the monohydrate (Rajput & Biradha, 2011), its chloroform solvate monohydrate (Luo et al., 2013) and its dimethylsulfoxide methanol solvate (Kumar et al., 2004). Only the latter two display a propeller-like sequence of the three arms of the molecule.

The CSD contains 28 entries for coordination complexes where the tris(3-pyridinyl) analogue acts as a ligand. In most of these, the ligand coordinates through the pyridinyl N atom, although the amide O atom is involved in a few examples. The tris(4-pyridinyl) analogue occurs as a ligand in six coordination complexes, all of which involve coordination through the pyridinyl N atom. Given the propensity of the pyridinyl N atom to act as the coordinating atom in these examples, the steric congestion between the 2-pyridinyl ring and the adja-
overnight. A small quantity of orange–yellow crystals was recovered from a yellow oil. $^1$H NMR $\delta$: 11.03 (s, 3H), 8.76 (s, 3H), 8.44 (d, 3H, $J = 4.82$), 8.28 (d, 3H, $J = 8.48$), 7.90 (t, 3H, $J = 7.90$), 7.22 (t, 3H, $J = 6.16$); ESI $m/z$: 438.14335 (predicted 438.14).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The amide H atoms were located in a difference-Fourier map and their positions were refined together with individual isotropic displacement parameters. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms (C–H = 0.95 Å) with $U_{\text{iso}}(H) = 1.2 U_{\text{eq}}(C)$.

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Computing details

Data collection: CrysAlis PRO (Rigaku OD, 2017); cell refinement: CrysAlis PRO (Rigaku OD, 2017); data reduction: CrysAlis PRO (Rigaku OD, 2017); program(s) used to solve structure: SHELXT2018 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018 (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov et al., 2009), Mercury (Macrae et al., 2020); software used to prepare material for publication: SHELXL2018 (Sheldrick, 2015b) and PLATON (Spek, 2015, 2020).

N,N',N''-Tris(pyridinyl)benzene-1,3,5-tricarboxamide

Crystal data

C$_24$H$_{18}$N$_6$O$_3$  
$M_r$ = 438.44  
Monoclinic, $P2_1/n$  
a = 8.2807 (1) Å  
b = 14.1554 (1) Å  
c = 17.5020 (2) Å  
$\beta$ = 98.920 (1)$^\circ$  
$V$ = 2026.71 (4) Å$^3$  
Z = 4

Data collection

Oxford Diffraction SuperNova, dual radiation diffractometer  
Radiation source: micro-focus sealed X-ray tube, SuperNova (Cu) X-ray source  
Mirror monochromator  
Detector resolution: 10.3801 pixels mm$^{-1}$  
$\omega$ scans  
(CrysAlisPro; Rigaku OD, 2017)

Refinement

Refinement on $F^2$  
Least-squares matrix: full  
$R[F^2 > 2\sigma(F^2)] = 0.031$  
wR($F^2$) = 0.088  
$S$ = 1.05  
4020 reflections  
311 parameters  
0 restraints

Primary atom site location: dual  
Secondary atom site location: difference Fourier map  
Hydrogen site location: difference Fourier map  
H atoms treated by a mixture of independent and constrained refinement  
w = 1/[$(\sigma^2(F_c^2) + (0.0474P)^2 + 0.5699P)]$  
where $P = (F_c^2 + 2F_s^2)/3$
supporting information

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

$\Delta \rho_{\text{max}} = 0.27 \text{ e Å}^{-3}$

$\Delta \rho_{\text{min}} = -0.17 \text{ e Å}^{-3}$

Extinction correction: SHELXL-2018 (Sheldrick, 2015b),

$F_c^2 = k F_c [1 + 0.001 x F_c^2 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0012 (2)

Special details

Experimental. Data collection and full structure determination done by Prof. Anthony Linden: anthony.linden@chem.uzh.ch

Solvent used: methanol

Cooling Device: Oxford Instruments Cryojet XL

Crystal mount: on a glass fibre

Frames collected: 1718

Seconds exposure per frame: 1.0-5.0

Degrees rotation per frame: 1.0

Crystal-detector distance (mm): 55.0

Client: Levi Senior

Sample code: LS002

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

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

|     | x       | y       | z       | U_{iso}*/U_{eq} |
|-----|---------|---------|---------|-----------------|
| O1  | 0.36342 (11) | 0.88417 (6) | 0.60262 (5) | 0.0380 (2)     |
| O2  | 0.64957 (8)  | 0.57226 (5)  | 0.62868 (4) | 0.02469 (18)   |
| O3  | -0.13032 (8) | 0.61942 (5)  | 0.39693 (4) | 0.02547 (18)   |
| N1  | 0.22689 (12) | 0.90845 (6)  | 0.48097 (6) | 0.0286 (2)     |
| H1  | 0.1826 (19)  | 0.8797 (11)  | 0.4388 (9)  | 0.044 (4)*     |
| N2  | 0.47719 (10) | 0.44612 (6)  | 0.62364 (5) | 0.02113 (19)   |
| H2  | 0.3752 (17)  | 0.4245 (10)  | 0.6088 (8)  | 0.034 (4)*     |
| N3  | 0.02167 (10) | 0.49006 (6)  | 0.37699 (5) | 0.02058 (19)   |
| H3  | 0.1165 (18)  | 0.4642 (10)  | 0.3849 (8)  | 0.033 (4)*     |
| N4  | 0.12823 (13) | 1.03623 (7)  | 0.41011 (6) | 0.0330 (2)     |
| N5  | 0.53774 (11) | 0.28992 (6)  | 0.64545 (6) | 0.0271 (2)     |
| N6  | -0.07968 (11)| 0.34722 (6)  | 0.32839 (5) | 0.0249 (2)     |
| C1  | 0.27688 (12) | 0.74907 (7)  | 0.52677 (6) | 0.0211 (2)     |
| C2  | 0.39380 (12) | 0.69079 (7)  | 0.56837 (6) | 0.0208 (2)     |
| H201| 0.481926     | 0.717841     | 0.602596   | 0.025*         |
| C3  | 0.38289 (11) | 0.59313 (7)  | 0.56032 (5) | 0.0185 (2)     |
| C4  | 0.25660 (11) | 0.55341 (7)  | 0.50819 (6) | 0.0183 (2)     |
| H4  | 0.249923     | 0.486807     | 0.501836   | 0.022*         |
| C5  | 0.14014 (11) | 0.61163 (7)  | 0.46542 (6) | 0.0187 (2)     |
| C6  | 0.14907 (12) | 0.70904 (7)  | 0.47598 (6) | 0.0205 (2)     |
| H6  | 0.067381     | 0.748521     | 0.448346   | 0.025*         |
| C7  | 0.29370 (12) | 0.85343 (7)  | 0.54121 (6) | 0.0245 (2)     |
| C8  | 0.21855 (13) | 1.00767 (7)  | 0.47569 (6) | 0.0250 (2)     |
| C9  | 0.29662 (15) | 1.06853 (8)  | 0.53146 (7) | 0.0338 (3)     |
| H9  | 0.360791     | 1.045229     | 0.577297   | 0.041*         |
| C10 | 0.27774 (16) | 1.16473 (8)  | 0.51797 (8) | 0.0375 (3)     |
| H10 | 0.329125     | 1.208782     | 0.554908   | 0.045*         |
| C11 | 0.18406 (15) | 1.19619 (8)  | 0.45073 (7) | 0.0333 (3)     |
| H11 | 0.169393     | 1.261778     | 0.440413   | 0.040*         |
| C12 | 0.11257 (15) | 1.12956 (8)  | 0.39909 (7) | 0.0351 (3)     |
**Atomic displacement parameters (Å²)**

|     | $U_11$     | $U_22$     | $U_33$     | $U_{12}$   | $U_{13}$   | $U_{23}$   |
|-----|------------|------------|------------|------------|------------|------------|
| O1  | 0.0526 (5) | 0.0223 (4) | 0.0315 (5) | 0.0017 (3) | −0.0178 (4)| −0.0036 (3) |
| O2  | 0.0165 (3) | 0.0221 (4) | 0.0330 (4) | 0.0004 (3) | −0.0039 (3)| −0.0040 (3) |
| O3  | 0.0167 (3) | 0.0225 (4) | 0.0345 (4) | 0.0024 (3) | −0.0045 (3)| −0.0016 (3) |
| N1  | 0.0375 (5) | 0.0185 (4) | 0.0254 (5) | −0.0017 (4)| −0.0088 (4)| −0.0016 (4) |
| N2  | 0.0151 (4) | 0.0218 (4) | 0.0246 (4) | 0.0011 (3) | −0.0029 (3)| 0.0014 (3)  |
| N3  | 0.0142 (4) | 0.0212 (4) | 0.0243 (4) | 0.0006 (3) | −0.0033 (3)| −0.0009 (3) |
| N4  | 0.0390 (5) | 0.0252 (5) | 0.0306 (5) | 0.0004 (4) | −0.0080 (4)| 0.0027 (4)  |
| N5  | 0.0246 (4) | 0.0237 (5) | 0.0316 (5) | 0.0024 (3) | 0.0002 (4) | 0.0032 (4)  |
| N6  | 0.0235 (4) | 0.0226 (4) | 0.0269 (5) | −0.0015 (3)| −0.0011 (3)| −0.0019 (3) |
| C1  | 0.0214 (5) | 0.0191 (5) | 0.0220 (5) | −0.0002 (4)| 0.0010 (4) | −0.0009 (4) |
| C2  | 0.0187 (4) | 0.0217 (5) | 0.0211 (5) | −0.0012 (4)| −0.0002 (4)| −0.0021 (4) |
| C3  | 0.0157 (4) | 0.0208 (5) | 0.0184 (5) | 0.0016 (4) | 0.0011 (3) | −0.0003 (4) |
| C4  | 0.0167 (4) | 0.0181 (4) | 0.0198 (5) | −0.0003 (3)| 0.0017 (4) | −0.0006 (4) |
| C5  | 0.0152 (4) | 0.0209 (5) | 0.0194 (5) | −0.0008 (3)| 0.0007 (4) | 0.0002 (4)  |
| C6  | 0.0187 (4) | 0.0200 (5) | 0.0217 (5) | 0.0020 (4) | −0.0002 (4)| 0.0016 (4)  |
| C7  | 0.0250 (5) | 0.0203 (5) | 0.0260 (5) | 0.0008 (4) | −0.0033 (4)| −0.0013 (4) |
| C8  | 0.0264 (5) | 0.0199 (5) | 0.0271 (5) | −0.0004 (4)| −0.0010 (4)| 0.0007 (4)  |
| C9  | 0.0409 (6) | 0.0229 (5) | 0.0330 (6) | −0.0010 (5)| −0.0090 (5)| −0.0006 (4) |
| C10 | 0.0456 (7) | 0.0224 (6) | 0.0411 (7) | −0.0032 (5)| −0.0042 (5)| −0.0048 (5) |
| C11 | 0.0385 (6) | 0.0201 (5) | 0.0419 (7) | 0.0033 (4) | 0.0064 (5) | 0.0044 (5)  |
| C12 | 0.0399 (6) | 0.0283 (6) | 0.0344 (6) | 0.0050 (5) | −0.0032 (5)| 0.0074 (5)  |
| C13 | 0.0166 (4) | 0.0206 (5) | 0.0185 (5) | 0.0022 (3) | 0.0000 (3) | −0.0039 (4) |
| C14 | 0.0181 (5) | 0.0244 (5) | 0.0209 (5) | 0.0025 (4) | 0.0020 (4) | 0.0033 (4)  |
Geometric parameters (Å, °)

|    | C7—N1—C8 | C8—N1—H1 | C12—C11—C10 | N4—C12—H12 | C13—N2—C14 | C14—N2—H2 | N5—C14—C18 | C15—C16—C17 | C16—H16 | C17—C18 | N6—C20 | C15—C16 | C16—H16 | C17—C18 | N7—C20 | C18—H18 | C18—C21 | C19—N3—C20 | C20—C24 | C21—C22 | C22—C23 | C23—H23 | C24—H24 |
|----|-----------|-----------|--------------|-------------|-------------|-----------|-------------|-------------|---------|---------|--------|----------|----------|---------|--------|---------|---------|------------|--------|---------|---------|---------|---------|
| O1—C7 | 1.2189 (13) | C5—C6 | 1.3916 (13) |
| O2—C13 | 1.2325 (12) | C5—C19 | 1.5032 (13) |
| O3—C19 | 1.2334 (12) | C6—H6 | 0.9500 |
| N1—C7 | 1.3578 (14) | C8—C9 | 1.3846 (15) |
| N1—C8 | 1.4085 (14) | C9—C10 | 1.3867 (16) |
| N1—H1 | 0.872 (16) | C9—H9 | 0.9500 |
| N2—C13 | 1.3499 (13) | C10—C11 | 1.3792 (18) |
| N2—C14 | 1.4163 (12) | C10—H10 | 0.9500 |
| N2—H2 | 0.898 (14) | C11—C12 | 1.3751 (17) |
| N3—C19 | 1.3468 (13) | C11—H11 | 0.9500 |
| N3—C20 | 1.4195 (12) | C12—H12 | 0.9500 |
| N3—H3 | 0.857 (14) | C14—C15 | 1.3923 (14) |
| N4—C8 | 1.3319 (14) | C15—C16 | 1.3864 (16) |
| N4—C12 | 1.3384 (15) | C15—H15 | 0.9500 |
| N5—C14 | 1.3304 (14) | C16—C17 | 1.3798 (19) |
| N5—C18 | 1.3395 (14) | C16—H16 | 0.9500 |
| N6—C20 | 1.3295 (14) | C17—C18 | 1.3778 (18) |
| N6—C24 | 1.3406 (14) | C17—H17 | 0.9500 |
| C1—C2 | 1.3890 (14) | C18—H18 | 0.9500 |
| C1—C6 | 1.3927 (13) | C20—C21 | 1.3883 (14) |
| C1—C7 | 1.5015 (14) | C21—C22 | 1.3855 (16) |
| C2—C3 | 1.3910 (14) | C21—H21 | 0.9500 |
| C2—H201 | 0.9500 | C22—C23 | 1.3795 (18) |
| C3—C4 | 1.3951 (13) | C22—H22 | 0.9500 |
| C3—C13 | 1.4996 (13) | C23—C24 | 1.3795 (16) |
| C4—C5 | 1.3949 (13) | C23—H23 | 0.9500 |
| C4—H4 | 0.9500 | C24—H24 | 0.9500 |
| C7—N1—C8 | 129.27 (9) | C12—C11—C10 | 117.85 (11) |
| C7—N1—H1 | 117.2 (10) | C12—C11—H11 | 121.1 |
| C8—N1—H1 | 113.5 (10) | C10—C11—H11 | 121.1 |
| C13—N2—C14 | 126.40 (8) | N4—C12—C11 | 124.06 (11) |
| C13—N2—H2 | 119.8 (9) | N4—C12—H12 | 118.0 |
| C14—N2—H2 | 113.8 (9) | C11—C12—H12 | 118.0 |
| C19—N3—C20 | 126.29 (8) | O2—C13—N2 | 123.84 (9) |
| Bond                    | Bond Angle (°) |
|------------------------|----------------|
| C19—N3—H3              | 119.8 (9)      |
| C20—N3—H3              | 113.7 (9)      |
| C8—N4—C12              | 116.92 (10)    |
| C14—N5—C18             | 117.19 (10)    |
| C20—N6—C24             | 116.60 (9)     |
| C2—C1—C6               | 119.46 (9)     |
| C2—C1—C7               | 117.21 (9)     |
| C6—C1—C7               | 123.31 (9)     |
| C1—C2—C3               | 120.54 (9)     |
| C1—C2—H201             | 119.7          |
| C3—C2—H201             | 119.7          |
| C2—C3—C4               | 119.81 (9)     |
| C2—C3—C13              | 116.71 (8)     |
| C4—C3—C13              | 123.44 (9)     |
| C5—C4—C3               | 119.91 (9)     |
| C5—C4—H4               | 120.0          |
| C3—C4—H4               | 120.0          |
| C6—C5—C4               | 119.73 (9)     |
| C6—C5—C19              | 117.15 (8)     |
| C4—C5—C19              | 123.07 (9)     |
| C5—C6—C1               | 120.49 (9)     |
| C5—C6—H6               | 119.8          |
| C1—C6—H6               | 119.8          |
| O1—C7—N1               | 124.07 (10)    |
| O1—C7—C1               | 121.24 (9)     |
| N1—C7—C1               | 114.69 (9)     |
| N1—C7—H9               | 121.2          |
| N4—C8—C9               | 123.85 (10)    |
| N4—C8—N1               | 111.99 (9)     |
| C9—C8—N1               | 124.15 (10)    |
| C8—C9—C10              | 117.58 (11)    |
| C8—C9—H9               | 121.2          |
| C10—C9—H9              | 121.2          |
| C11—C10—C9             | 119.74 (11)    |
| C11—C10—H10            | 120.1          |
| C9—C10—H10             | 120.1          |
| C6—C1—C2—C3            | −0.78 (15)     |
| C7—C1—C2—C3            | 177.55 (9)     |
| C1—C2—C3—C4            | 2.12 (14)      |
| C1—C2—C3—C13           | −179.99 (9)    |
| C2—C3—C4—C5            | −1.17 (14)     |
| C13—C3—C4—C5           | −178.92 (9)    |
| C3—C4—C5—C6            | −1.09 (14)     |
| C3—C4—C5—C19           | −178.46 (9)    |
| C4—C5—C6—C1            | 2.44 (14)      |
| C19—C5—C6—C1           | 179.97 (9)     |
| C2—C1—C6—C5            | −1.51 (15)     |
| C7—C1—C6—C5            | −179.73 (9)    |
C8—N1—C7—O1  
C8—N1—C7—C1  178.72 (10)  
C2—C1—C7—O1  −25.98 (15)  
C2—C1—C7—N1  153.59 (10)  
C6—C1—C7—O1  152.27 (11)  
C6—C1—C7—N1  153.27 (11)  
N1—C7—C1—C6  −28.16 (15)  
C12—N4—C8—C9  −0.62 (18)  
C12—N4—C8—N1  −179.82 (11)  
C7—N1—C8—N4  −173.33 (11)  
C7—N1—C8—C9  7.5 (2)  
N4—C8—C9—C10  0.56 (19)  
N1—C8—C9—C10  179.66 (11)  
C8—C9—C10—C11  −0.2 (2)  
C9—C10—C11—C12  −0.1 (2)  
C8—N4—C12—C11  0.30 (19)  
C10—C11—C12—N4  0.1 (2)  
C14—N2—C13—O2  −3.35 (16)  
C14—N2—C13—C3  175.81 (9)  

Hydrogen-bond geometry (\(\AA\), \(^{\circ}\))

|            | \(D—H\)  | \(H···A\)  | \(D···A\)  | \(D—H···A\) |
|------------|---------|-----------|-----------|-------------|
| N2—H2···O3\(^i\) | 0.898 (14) | 2.108 (14) | 2.9866 (11) | 165.6 (13) |
| N3—H3···O2\(^i\) | 0.857 (14) | 2.054 (14) | 2.8781 (11) | 160.9 (13) |

Symmetry codes: (i) \(-x, -y+1, -z+1\); (ii) \(-x+1, -y+1, -z+1\).