Syntheses and crystal structures of 2-(p-tolyl)-1H-perimidine hemihydrate and 1-methyl-2-(p-tolyl)-1H-perimidine

Paulina Kalle, Sergei V. Tatarin, Marina A. Kiseleva, Alexander Yu. Zakharov, Daniil E. Smirnov and Stanislav I. Bezzubov

The title compounds, 2-(4-methylphenyl)-1H-perimidine hemihydrate (1, C_{18}H_{14}N_{2}·0.5H_{2}O) and 1-methyl-2-(4-methylphenyl)-1H-perimidine (2, C_{19}H_{16}N_{2}), were prepared and characterized by ^1H NMR and single-crystal X-ray diffraction. The organic molecule of the hemihydrate lies on a twofold rotation axis while the water molecule lies on the intersection of three twofold rotation axes (point group symmetry 222). As a consequence, the hydrogen atoms that are part of the N—H group and the water molecule as well as the CH_{3} group of the p-tolyl ring are disordered over two positions. In compound 1, the perimidine and the 2-aryl rings are slightly twisted while its N-methylated derivative 2 has a more distorted conformation because of the steric repulsion between the N-methyl group and the 2-aryl ring. In the crystal structures, molecules of perimidine 2 are held together only by C—H···π contacts while the parent perimidine 1 does not exhibit this type of interaction. Its crystal packing is established by intermolecular N—H···O hydrogen bonds with the solvent water molecules and additionally stabilized by π—π stacking.

1. Chemical context

Perimidines have found applications in industry as dyes and pigments because of their finely tunable optical properties (Pozharskii et al., 2020). The introduction of electron-donating/withdrawing groups to the perimidine system dramatically affects its electronic structure and allows the color as well as color intensity of the perimidine to be varied. Additionally, a significant deepening of the color of perimidines can be achieved by decorating them with aromatic rings at position 2 while their optical characteristics can be modulated by varying the N-substituent (Sahiba & Agarwal, 2020). Recently, we have studied the effect of the N-substituent(s) on the structures of 2-(pyridin-2-yl)-1H-perimidines (Kalle et al., 2021). Herein, we report structural studies of 1-H-2-(p-tolyl)-perimidine hemihydrate (1) and 1-methyl-2-(p-tolyl)-perimidine (2).
2. Structural commentary

The perimidine molecule of 1 possesses C2 symmetry with the twofold rotation axis passing through carbon atoms C3–C6, C11 and C12 (Fig. 1). This perimidine exhibits a C6—N1 bond length of 1.3345 (12) Å, a value intermediate between the average C—N single [1.366 (13) Å] and double [1.293 (11) Å] bond lengths in perimidines according to the Cambridge Crystal Structure Database (CSD version 5.43 November 2021; Groom et al., 2016). The perimidine core of 1 is flat while the p-tolyl ring (C1–C5) forms a dihedral angle of 34.47 (5)° with the core, which is likely an effect of the crystal packing.

The asymmetric unit of crystal 2 contains two molecules, which are N-methylated analogs of compound 1 (Fig. 2). Steric pressure exerted by the N-methyl group causes an increase of the interplanar angle between the p-tolyl ring and the perimidine system [53.51 (10)° for one molecule and 55.96 (9)° for the other]. Additionally, in the first molecule, the angle between the N1—C19 bond and the centroid of the perimidine plane is as large as 8.7 (2)°; while the corresponding angle in the second molecule is 6.1 (2)°.

Table 1

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| O1—H1B···N1 | 0.89 (3) | 2.13 (3) | 2.9826 (10) | 162 (3) |
| N1—H1···O1 | 0.87 (3) | 2.15 (3) | 2.9826 (10) | 160 (3) |

3. Supramolecular features

Recrystallization of 1 from toluene, dichloromethane, chloroform or methanol gives crystals having an identical structure. An X-ray study of the crystals grown from hot toluene shows that compound 1 crystallizes as a hemihydrate in which the solvent molecule plays a dominant role in the crystal packing. Each water molecule, located at the intersection of three twofold rotation axes (Wyckoff position 8a; point group symmetry 222), arranges four 2-(p-tolyl)perimidines by mutual O—H···N and N—H···O interactions involving the O1 and N1 atoms as well as disordered hydrogen atoms H1 and H1B (Fig. 3, Table 1). These hydrogen-bonded associates containing the included water molecule are additionally stabilized by π—π contacts between the aromatic units [d(C1···N1–C12centroid) = 3.3276 (11) Å, centroid-centroid shift of 1.591 (1) Å, d(C7···C1–C5centroid) = 3.5950 (11) Å, centroid-centroid shift of 1.433 (1) Å]. The same interactions combine the associates into infinite stacks along the a axis, forming two-dimensional structural arrays. The alignment of the arrays along the c axis by weak van der Waals interactions between perimidine C9—H9 and C10—H10 bonds and the methyl group (C4) of the p-tolyl ring completes the crystal packing of 1.

In the crystal structure of 2 (Fig. 4), the two crystallographically independent molecules are held together by C—H···π interactions between the p-tolyl and perimidine systems involving the H5 atom and the centroid of the C32–C37 ring [2.8226 (13) Å, 144.85 (18)°] and the H21 atom and the centroid of the C9–C13/C18 ring [2.6199 (12) Å, 145.74 (19)°]. The resulting dimers form stacks via similar non-covalent bonds involving the H24 atom and the centroid of the C9–C13/C18 ring [2.8676 (12) Å, 151.1 (2)°] and the H2 atom and the

Figure 2

Molecular structure of 1-methyl-2-(p-tolyl)-perimidine (2), with displacement ellipsoids drawn at the 50% probability level.

Figure 3

Hydrogen bonding and π—π stacking interactions in the crystal structure of 1-H-2-(p-tolyl)-perimidine (1), with displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms of the minor disorder component are omitted for clarity.
centroïd of the C32–C37 ring [3.1727 (13) Å, 142.3 (2)°]. The resulting layers are grafted together by weak C—H···N contacts involving the H19A and N4 atoms [d(H···N) = 2.624 (2) Å, C—H···N angle = 166.86 (18)°], forming arrays in the ab plane. The three-dimensional crystal packing is organized by the alignment of the arrays along the c axis by weak van der Waals interactions in the same manner as in the crystal of 1. It is interesting that compound 2, in contrast to the parent perimidine 1, crystallizes without notable π–π interactions.

4. Database survey
A database search in the CSD (version 5.43 November 2021; Groom et al., 2016) found only one crystal structure, a 2-arylperimidine hydrate in which one water molecule combines two 2-(2-methoxyphenyl)-1-H-perimidines by O—H···N hydrogen bonds whereas the H atom at the second nitrogen atom cannot interact with the oxygen atom of the water molecule because it participates in an intramolecular N—H···O bond with the methoxy group (PEKRIG; Foces-Foces et al., 1993). A pseudo-tetrahedral pattern of hydrogen-bonded organic molecules around the included water molecule is formed by 2-aminoo-4-(4-pyridyl)-6-phenylamino-1,3,5-triazine, which bears many more donor and acceptor hydrogen-bonding groups than compound 1 (TETRIT; Chan et al., 1996). The crystal structures of organic hydrates including N—H···O interactions have also been published [KIJPUO (Black et al., 1991); FAZRED (Rosling et al., 1999)].

5. Synthesis and crystallization
The title compounds were prepared as follows:

1H-2-(p-tolyl)perimidine (1)
A mixture of 1.8-diaminonaphthalene (1.58 g, 0.01 mol), 4-methylbenzaldehyde (1.18 ml, 0.01 mol) and sodium metabisulfite (5.7 g, 0.03 mol) in ethanol (40 ml) was refluxed under Ar for 2 h. The reaction mixture was cooled, filtered and the filtrate was evaporated to dryness and washed with water. The crude solid was recrystallized from toluene and dried in vacuo. Yield 2.20 g (85%). Single crystals suitable for X-ray analysis were grown from hot toluene.

1H NMR (DMSO-d6, ppm, 400 MHz): δ 2.34 (s, 3H, CH3), 6.65 (d, J = 7.2 Hz, 2H, H naph), 7.04 (d, J = 8.0 Hz, 2H, H naph), 7.15 (t, J = 7.2 Hz, 2H, H naph), 7.30 (d, J = 7.2 Hz, 2H, H tol), 7.95 (d, J = 8.0 Hz, 2H, H tol). See supplementary Fig. S1.

1-Methyl-2-(p-tolyl)perimidine (2)
To a mixture of (1) (0.258 g, 1.0 mmol), solid KOH (0.056 g, 1.0 mmol) and anhydrous K2CO3 (0.138 g, 1.0 mmol) in anhydrous Ar-saturated acetonitrile methyl iodide (0.062 ml, 1.0 mmol) were added dropwise upon stirring and the resulting suspension was heated at 323 K for 1 h and at room temperature for 1 h. The reaction mixture was evaporated to dryness and the crude product was purified by column chromatography (elucent hexane/ethyl acetate 1/1 → 1/5 v/v), recrystallized from a mixture of toluene/hexane and dried in vacuo. Yield 125 mg (46%). Single crystals suitable for X-ray analysis were grown by slow evaporation of the solvent from a solution of the substance in toluene.

1H NMR (CDCl3, ppm, 400 MHz): δ 2.42 (s, 3H, CH3), 3.17 (s, 3H, N—CH3), 6.28 (d, J = 7.2 Hz, 1H, H naph), 6.94 (d, J = 7.3 Hz, 1H, H naph), 7.17–7.24 (m, 3H, H naph), 7.28–7.32 (m, 3H, H naph + H tol), 7.44 (d, J = 7.7 Hz, 2H, H tol). See supplementary Fig. S2.

6. Refinement
Crystal data, data collection and structure refinement details are summarized in Table 2. All C—H hydrogen atoms in the structures of 1 and 2 were placed in calculated positions and refined using a riding model [C—H = 0.94–0.97 Å with Uiso(H) = 1.2–1.5Ueq(C)]. N—H and O—H hydrogen atoms (structure 1) were located in difference electron-density maps and were refined with a fixed occupancy of 0.5. para-Methyl groups in both crystallographically independent molecules of 2 were found to be rotationally disordered with occupancy ratios of 0.6/0.4 and 0.7/0.3. The same group in the structure of 1 was similarly disordered with an occupancy ratio of 0.5/0.5. The SIMU instruction was used to restrain the Uiso components of the neighboring C6 and N1 atoms in the structure of 1. The most disagreeable reflections with an error/s.u. of more than 10 (0 0 4 in the structure of 1; 5 0 34 and 6 1 33 in the structure of 2) were omitted using the OMIT instruction in SHELXL (Sheldrick, 2015).

Acknowledgements
X-ray diffraction studies were performed at the Centre of Shared Equipment of IGIC RAS.

Figure 4
Fragment of the crystal packing of 1-methyl-2-(p-tolyl)-perimidine (2), with displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms of the minor parts of the disordered methyl groups are omitted for clarity.
Table 2
Experimental details.

| Crystal data | C_{18}H_{14}N_{2}·0.5H_{2}O | C_{19}H_{16}N_{2} |
|--------------|---------------------------|------------------|
| M (g/mol)    | 267.32                    | 272.34           |
| Crystal system, space group | Orthorhombic, Fddd | Orthorhombic, Pbc a |
| Temperature (K) | 100               | 100              |
| a, b, c (Å)   | 7.2131 (2), 13.8648 (5), 53.4532 (18) | 11.6878 (4), 18.0941 (6), 26.9604 (8) |
| V (Å³)        | 5345.8 (3)               | 5701.6 (3)       |
| Z             | 16                        | 16               |
| Radiation type | Mo Kα                    | Mo Kα            |
| μ (mm⁻¹)      | 0.08                      | 0.08             |
| Crystal size (mm) | 0.13 × 0.1× 0.1 | 0.12 × 0.09 × 0.08 |
| Data collection | | |
| Diffractometer | Bruker D8 Venture | Bruker D8 Venture |
| Absorption correction | Multi-scan (SADABS; Krause et al., 2015) | Multi-scan (SADABS; Krause et al., 2015) |
| Tₘᵦₘ,max (°) | 0.672, 0.746             | 0.676, 0.746     |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 14708, 2138, 1630 | 53425, 5047, 3857 |
| Rint | 0.044 | 0.093 |
| (sin θ/λ)max (Å⁻¹) | 0.725 | 0.596 |
| Refinement | | |
| R[F² > 2σ(F²)], wR(F²), S | 0.049, 0.140, 1.04 | 0.073, 0.157, 1.14 |
| No. of reflections | 2138 | 5047 |
| No. of parameters | 126 | 383 |
| No. of restraints | 6 | 0 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement | H-atom parameters constrained |
| Δρ max, Δρ min (e Å⁻³) | 0.42, –0.34 | 0.23, –0.29 |

Computer programs: APEX3 and SAINT (Bruker, 2017), SHELXS (Sheldrick, 2008), SHELXL (Sheldrick, 2015) and OLEX2 (Dolomanov et al., 2009).

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Computing details
For both structures, data collection: APEX3 (Bruker, 2017); cell refinement: SAINT (Bruker, 2017); data reduction: SAINT (Bruker, 2017); program(s) used to solve structure: SHELXS (Sheldrick, 2008); program(s) used to refine structure: SHELXL (Sheldrick, 2015); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

2-(4-Methylphenyl)-1H-perimidine hemihydrate (1)

Crystal data

$D_{x} = 1.329$ Mg m$^{-3}$  
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å  
Cell parameters from 4300 reflections  
$\theta = 3.0$–$31.5^{\circ}$  
$\mu = 0.08$ mm$^{-1}$  
$T = 100$ K  
Block, orange  
$0.13 \times 0.1 \times 0.1$ mm

Data collection

$T_{\text{min}} = 0.672$, $T_{\text{max}} = 0.746$  
14708 measured reflections  
2138 independent reflections  
1630 reflections with $I > 2\sigma(I)$  
$\theta_{\text{max}} = 31.0^{\circ}$, $\theta_{\text{min}} = 3.0^{\circ}$  
$h = -9 \rightarrow 10$  
$k = -20 \rightarrow 16$  
$l = -77 \rightarrow 77$

Refinement

Refinement on $F^{2}$  
Least-squares matrix: full  
$R[F^{2} > 2\sigma(F^{2})] = 0.049$  
w$R(F^{2}) = 0.140$  
$S = 1.04$  
2138 reflections  
126 parameters  
6 restraints

Primary atom site location: structure-invariant direct methods

Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/\sigma^{2}(F_{o}^{2}) + (0.0761P)^{2} + 4.7998P$  
where $P = (F_{o}^{2} + 2F_{c}^{2})/3$  
$(\Delta\sigma)_{\text{max}} = 0.001$
\[ \Delta \rho_{\text{max}} = 0.42 \text{ e Å}^{-3} \quad \Delta \rho_{\text{min}} = -0.34 \text{ e Å}^{-3} \]

**Special details**

**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      | Uiso*/Ueq | Occ. (<1) |
|--------|--------|--------|-----------|-----------|
| O1     | 0.8750 | 0.3750 | 0.3750    | 0.0216 (4) |
| H1B    | 0.790 (4) | 0.335 (2) | 0.3693 (6) | 0.036 (9)* | 0.5 |
| N1     | 0.65901 (13) | 0.20824 (7) | 0.35517 (2) | 0.0176 (2) |
| H1     | 0.708 (4) | 0.253 (2) | 0.3644 (6) | 0.026 (8)* | 0.5 |
| C1     | 0.55996 (16) | 0.20495 (8) | 0.40781 (2) | 0.0177 (2) |
| H1A    | 0.508 (2) | 0.2610 (11) | 0.3988 (3) | 0.024 (4)* |
| C2     | 0.55826 (15) | 0.20393 (8) | 0.43382 (2) | 0.0181 (3) |
| H2     | 0.503 (2) | 0.2585 (11) | 0.4429 (3) | 0.022 (3)* |
| C3     | 0.6250 | 0.1250 | 0.44720 (3) | 0.0171 (3) |
| C4     | 0.6250 | 0.1250 | 0.47536 (3) | 0.0226 (4) |
| H4A    | 0.6649 | 0.1883 | 0.4815 | 0.034* | 0.5 |
| H4B    | 0.7105 | 0.0754 | 0.4815 | 0.034* | 0.5 |
| H4C    | 0.4996 | 0.1113 | 0.4815 | 0.034* | 0.5 |
| C5     | 0.6250 | 0.1250 | 0.39454 (3) | 0.0155 (3) |
| C6     | 0.6250 | 0.1250 | 0.36684 (3) | 0.0182 (3) |
| C7     | 0.65540 (15) | 0.21186 (8) | 0.32902 (2) | 0.0148 (2) |
| C8     | 0.68100 (16) | 0.29750 (8) | 0.31632 (2) | 0.0188 (3) |
| H8     | 0.705 (2) | 0.3573 (10) | 0.3255 (3) | 0.022 (4)* |
| C9     | 0.67686 (17) | 0.29749 (8) | 0.28998 (2) | 0.0210 (3) |
| H9     | 0.697 (2) | 0.3594 (11) | 0.2812 (3) | 0.031 (4)* |
| C10    | 0.65083 (16) | 0.21420 (8) | 0.27653 (2) | 0.0193 (3) |
| H10    | 0.654 (2) | 0.2141 (10) | 0.2581 (3) | 0.029 (4)* |
| C11    | 0.6250 | 0.1250 | 0.28908 (3) | 0.0162 (3) |
| C12    | 0.6250 | 0.1250 | 0.31562 (3) | 0.0144 (3) |

**Atomic displacement parameters (Å²)**

|      | U¹¹  | U²²  | U³³  | U¹²  | U¹³  | U²³  |
|------|------|------|------|------|------|------|
| O1   | 0.0249 (9) | 0.0176 (8) | 0.0222 (8) | 0.000 | 0.000 | 0.000 |
| N1   | 0.0173 (4) | 0.0223 (5) | 0.0133 (4) | -0.0015 (3) | -0.0005 (3) | 0.0017 (3) |
| C1   | 0.0172 (5) | 0.0200 (5) | 0.0160 (5) | -0.0012 (4) | 0.0005 (4) | 0.0013 (4) |
| C2   | 0.0172 (5) | 0.0210 (5) | 0.0160 (5) | -0.0009 (4) | 0.0021 (4) | -0.0015 (4) |
| C3   | 0.0153 (7) | 0.0230 (8) | 0.0128 (7) | -0.0030 (6) | 0.000 | 0.000 |
| C4   | 0.0244 (8) | 0.0294 (9) | 0.0141 (7) | 0.0001 (7) | 0.000 | 0.000 |
| C5   | 0.0126 (6) | 0.0209 (7) | 0.0130 (7) | -0.0034 (5) | 0.000 | 0.000 |
| C6   | 0.0150 (6) | 0.0261 (7) | 0.0134 (6) | -0.0007 (5) | 0.000 | 0.000 |
| C7   | 0.0140 (5) | 0.0167 (5) | 0.0137 (5) | -0.0007 (4) | -0.0005 (4) | 0.0009 (4) |
| C8   | 0.0222 (5) | 0.0163 (5) | 0.0179 (5) | -0.0023 (4) | -0.0002 (4) | 0.0010 (4) |

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Geometric parameters (Å, °)

|        |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
|--------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| O1—H1B| 0.89 | C5—C1 | 1.3971 | (14)  |
| N1—H1 | 0.87 | C5—C6 | 1.481  | (2)   |
| N1—C6 | 1.3345 | C6—N1 | 1.3345 | (12)  |
| N1—C7 | 1.3993 | C7—C8 | 1.3801 | (15)  |
| C1—H1A| 0.987| C7—C12| 1.4182 | (13)  |
| C1—C2 | 1.3901 | C8—H8 | 0.978  | (15)  |
| C1—C5 | 1.3972 | C8—C9 | 1.4083 | (16)  |
| C2—H2 | 0.983 | C9—H9 | 0.988  | (16)  |
| C2—C3 | 1.3932 | C9—C10| 1.3734 | (17)  |
| C3—C2 | 1.3932 | C10—H10| 0.987  | (16)  |
| C3—C4 | 1.505 | C10—C11| 1.4192 | (13)  |
| C4—H4A| 0.980| C11—C10| 1.4194 | (13)  |
| C4—H4B| 0.980| C11—C12| 1.419  | (2)   |
| C4—H4C| 0.980| C12—C7  | 1.4181 | (13)  |

C6—N1—H1                      116 (2) C5—C1 | 118.28 | (14)  |
C6—N1—C7                      119.64 (10) N1—C6—C5 | 117.86 | (7)   |
C7—N1—H1                      123 (2)   N1—C6—C5 | 117.86 | (7)   |
C2—C1—H1A                     119.4 (9)  N1—C7—C12| 118.49 | (10)  |
C2—C1—C5                      120.17 (11) C8—C7—N1 | 121.32 | (10)  |
C5—C1—H1A                     120.3 (9)   C8—C7—C12| 120.19 | (10)  |
C1—C2—H2                      119.4 (8)  C7—C8—H8 | 120.5  | (9)   |
C1—C2—C3                      121.22 (11) C7—C8—C9 | 119.26 | (11)  |
C3—C2—H2                      119.3 (8)   C9—C8—H8 | 120.2  | (9)   |
C2—C3—C2                      118.23 (14) C8—C9—H9 | 118.1  | (9)   |
C2—C3—C4                      120.88 (7)  C10—C9—C8 | 121.76 | (11)  |
C3—C4—C2                      120.89 (7)  C10—C9—H9 | 120.2  | (9)   |
C3—C4—H4A                     109.5     C9—C10—H10| 121.5  | (9)   |
C3—C4—H4B                     109.5     C9—C10—C11| 120.21 | (11)  |
C3—C4—H4C                     109.5     C11—C10—H10| 118.3  | (9)   |
H4A—C4—H4B                    109.5     C10—C11—C10i | 123.58 | (14)  |
H4A—C4—H4C                    109.5     C12—C11—C10i | 118.21 | (7)   |
H4B—C4—H4C                    109.5     C12—C11—C10i | 118.21 | (7)   |
C1—C5—C1                      111.86 (14) C7—C12—C7  | 119.34 | (13)  |
C1—C5—C6                      120.51 (7)  C7—C12—C11| 120.33 | (7)   |
C1—C5—C6                      120.51 (7)  C7—C12—C11| 120.33 | (7)   |
N1—C7—C8—C9                   179.77 (10) C7—N1—C6—N1i | 1.69  | (7)   |
N1—C7—C12—C7i                 1.61 (6)    C7—N1—C6—C5 | −178.31 | (7)   |
N1—C7—C12—C11                 −178.39 (6) C7—C8—C9—C10 | −1.02 | (18)  |
C1—C2—C3—C2i                  −0.82 (7)    C8—C7—C12—C7i | −178.51 | (12)  |
Symmetry code: (i) \(-x+5/4, -y+1/4, z\).

Hydrogen-bond geometry (Å, °)

| D—H···A     | D—H | H···A | D···A | D—H···A |
|-------------|------|-------|-------|---------|
| O1—H1B···N1| 0.89 (3) | 2.13 (3) | 2.9826 (10) | 162 (3) |
| N1—H1···O1 | 0.87 (3) | 2.15 (3) | 2.9826 (10) | 160 (3) |

1-Methyl-2-(p-tolyl)-1-H-perimidine (2)

Crystal data

C\(_{19}\)H\(_{16}\)N\(_2\)

\(M_r = 272.34\)

Orthorhombic, \(Pbca\)

\(a = 11.6878\) (4) Å

\(b = 18.0941\) (6) Å

\(c = 26.9604\) (8) Å

\(V = 5701.6\) (3) Å\(^3\)

\(Z = 16\)

\(F(000) = 2304\)

Data collection

Bruker D8 Venture diffractometer

Radiation source: microfocus sealed X-ray tube, \(\mu\)s

Focusing mirrors monochromator

Detector resolution: 10.4 pixels mm\(^{-1}\)

\(\omega\)-scan

Absorption correction: multi-scan (\(SADABS;\) Krause \textit{et al.}, 2015)

Refinement

Reefinement on \(F^2\)

Least-squares matrix: full

\(|R(F^2 > 2\sigma(F^2))| = 0.073\)

\(wR(F^2) = 0.157\)

\(S = 1.14\)

5047 reflections

383 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

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

\(\Delta \rho_{\text{max}} = 0.23\) e Å\(^{-3}\)

\(\Delta \rho_{\text{min}} = -0.29\) e Å\(^{-3}\)

\(D_x = 1.269\) Mg m\(^{-3}\)

Mo \(K\alpha\) radiation, \(\lambda = 0.71073\) Å

Cell parameters from 7540 reflections

\(\theta = 2.2–28.3^\circ\)

\(\mu = 0.08\) mm\(^{-1}\)

\(T = 100\) K

Block, yellow

\(0.12 \times 0.09 \times 0.08\) mm

53425 measured reflections

5047 independent reflections

3857 reflections with \(I > 2\sigma(I)\)

\(R_{\text{int}} = 0.093\)

\(\theta_{\text{max}} = 25.1^\circ, \theta_{\text{min}} = 2.2^\circ\)

\(h = -13\rightarrow 13\)

\(l = -31\rightarrow 21\)

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**Special details**

**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)**

| Atom | x      | y      | z      | U(eq)  | Occ. (<1) |
|------|--------|--------|--------|--------|-----------|
| N1   | 0.43727(19) | 0.18405(12) | 0.31230(8)  | 0.0175(5) |
| N2   | 0.2447(2)   | 0.21911(12)  | 0.29690(8)  | 0.0185(5) |
| C1   | 0.3882(2)   | 0.11253(15)  | 0.21059(10) | 0.0209(6) |
| H1   | 0.4128      | 0.0760       | 0.2335      | 0.025*   |
| C2   | 0.3842(3)   | 0.09595(15)  | 0.16034(11) | 0.0233(7) |
| H2   | 0.4038      | 0.0477       | 0.1493      | 0.028*   |
| C3   | 0.3516(2)   | 0.14950(16)  | 0.12585(10) | 0.0217(7) |
| C4   | 0.3475(3)   | 0.13008(18)  | 0.07119(11) | 0.0325(8) |
| H4AA | 0.4255      | 0.1230       | 0.0588      | 0.049*   |
| H4AB | 0.3107      | 0.1703       | 0.0528      | 0.049*   |
| H4AC | 0.3036      | 0.0844       | 0.0667      | 0.049*   |
| H4BD | 0.2695      | 0.1372       | 0.0587      | 0.049*   |
| H4BE | 0.3702      | 0.0784       | 0.0667      | 0.049*   |
| H4BF | 0.4002      | 0.1622       | 0.0528      | 0.049*   |
| C5   | 0.3240(2)   | 0.21969(16)  | 0.14290(10) | 0.0224(7) |
| H5   | 0.3035      | 0.2571       | 0.1199      | 0.027*   |
| C6   | 0.3261(2)   | 0.23577(15)  | 0.19325(10) | 0.0197(6) |
| H6   | 0.3066      | 0.2840       | 0.2043      | 0.024*   |
| C7   | 0.3567(2)   | 0.18187(15)  | 0.22769(10) | 0.0166(6) |
| C8   | 0.3451(2)   | 0.19748(14)  | 0.28191(10) | 0.0167(6) |
| C9   | 0.2275(2)   | 0.22857(14)  | 0.34790(10) | 0.0175(6) |
| C10  | 0.1229(3)   | 0.25252(16)  | 0.36522(11) | 0.0239(7) |
| H10  | 0.0632      | 0.2635       | 0.3425      | 0.029*   |
| C11  | 0.1044(3)   | 0.26077(16)  | 0.41622(11) | 0.0270(7) |
| H11  | 0.0322      | 0.2779       | 0.4277      | 0.032*   |
| C12  | 0.1890(3)   | 0.24445(16)  | 0.45006(11) | 0.0258(7) |
| H12  | 0.1742      | 0.2496       | 0.4845      | 0.031*   |
| C13  | 0.2973(3)   | 0.22019(15)  | 0.43391(10) | 0.0215(7) |
| C14  | 0.3895(3)   | 0.20256(16)  | 0.46636(11) | 0.0268(7) |
| H14  | 0.3798      | 0.2075       | 0.5012      | 0.032*   |
| C15  | 0.4915(3)   | 0.17867(16)  | 0.44797(11) | 0.0261(7) |
| H15  | 0.5510      | 0.1663       | 0.4705      | 0.031*   |
| C16  | 0.5117(3)   | 0.17171(16)  | 0.39662(10) | 0.0233(7) |
| H16  | 0.5840      | 0.1556       | 0.3846      | 0.028*   |
| C17  | 0.4243(2)   | 0.18870(14)  | 0.36411(10) | 0.0184(6) |
| C18  | 0.3162(2)   | 0.21197(14)  | 0.38191(10) | 0.0174(6) |
| C19  | 0.5531(2)   | 0.17366(16)  | 0.29268(10) | 0.0229(7) |
| H19A | 0.5765      | 0.1221       | 0.2973      | 0.034*   |
| H19B | 0.6063      | 0.2062       | 0.3104      | 0.034*   |
| H19C | 0.5540 | 0.1857 | 0.2572 | 0.034* |
| N3   | 0.2012 (2) | 0.42161 (12) | 0.21218 (8) | 0.0219 (6) |
| N4   | 0.3830 (2) | 0.47987 (13) | 0.20977 (8) | 0.0226 (6) |
| C20  | 0.2838 (3) | 0.40519 (16) | 0.32035 (10) | 0.0259 (7) |
| H20  | 0.2647 | 0.3582 | 0.3071 | 0.031* |
| C21  | 0.2985 (3) | 0.41308 (16) | 0.37083 (11) | 0.0287 (7) |
| H21  | 0.2901 | 0.3711 | 0.3917 | 0.034* |
| C22  | 0.3253 (3) | 0.48092 (16) | 0.39184 (11) | 0.0258 (7) |
| C23  | 0.3434 (3) | 0.48919 (19) | 0.44674 (11) | 0.0387 (9) |
| H23A | 0.4250 | 0.4843 | 0.4543 | 0.058* |
| H23B | 0.3005 | 0.4507 | 0.4643 | 0.058* |
| H23C | 0.3164 | 0.5379 | 0.4574 | 0.058* |
| H23D | 0.3890 | 0.5336 | 0.4532 | 0.058* |
| H23E | 0.3838 | 0.4457 | 0.4593 | 0.058* |
| C24  | 0.3369 (3) | 0.54109 (16) | 0.36007 (11) | 0.0255 (7) |
| H24  | 0.3546 | 0.5883 | 0.3735 | 0.031* |
| C25  | 0.3231 (3) | 0.53364 (15) | 0.30924 (11) | 0.0238 (7) |
| H25  | 0.3318 | 0.5756 | 0.2884 | 0.029* |
| C26  | 0.2967 (2) | 0.46554 (15) | 0.28853 (10) | 0.0205 (6) |
| C27  | 0.2939 (3) | 0.45635 (14) | 0.23366 (10) | 0.0208 (7) |
| C28  | 0.3886 (3) | 0.46785 (15) | 0.15836 (11) | 0.0250 (7) |
| C29  | 0.4843 (3) | 0.49011 (17) | 0.13268 (11) | 0.0291 (7) |
| H29  | 0.5461 | 0.5130 | 0.1496 | 0.035* |
| C30  | 0.4989 (3) | 0.47866 (17) | 0.08107 (12) | 0.0359 (8) |
| H30  | 0.5562 | 0.4935 | 0.0634 | 0.043* |
| C31  | 0.4011 (3) | 0.44640 (17) | 0.05601 (11) | 0.0347 (8) |
| H31  | 0.4064 | 0.4400 | 0.0211 | 0.042* |
| C32  | 0.3017 (3) | 0.42245 (16) | 0.08105 (11) | 0.0300 (8) |
| C33  | 0.2067 (3) | 0.38821 (17) | 0.05775 (12) | 0.0350 (8) |
| H33  | 0.2070 | 0.3814 | 0.0228 | 0.042* |
| C34  | 0.1150 (3) | 0.36494 (17) | 0.08484 (12) | 0.0356 (8) |
| H34  | 0.0530 | 0.3414 | 0.0684 | 0.043* |
| C35  | 0.1098 (3) | 0.37489 (16) | 0.13666 (11) | 0.0291 (7) |
| H35  | 0.0449 | 0.3586 | 0.1549 | 0.035* |
| C36  | 0.2001 (3) | 0.40848 (15) | 0.16054 (11) | 0.0241 (7) |
| C37  | 0.2970 (3) | 0.43318 (15) | 0.13339 (11) | 0.0241 (7) |
| C38  | 0.0958 (3) | 0.40401 (19) | 0.23934 (12) | 0.0341 (8) |
| H38A | 0.0888 | 0.3503 | 0.2429 | 0.051* |
| H38B | 0.0297 | 0.4231 | 0.2210 | 0.051* |
| H38C | 0.0985 | 0.4269 | 0.2723 | 0.051* |

Atomic displacement parameters (Å²)

\[
\begin{array}{cccccccc}
U_{11} & U_{22} & U_{33} & U_{12} & U_{13} & U_{23} \\
N1 & 0.0187 (13) & 0.0200 (12) & 0.0137 (12) & 0.0014 (10) & 0.0004 (10) & -0.0016 (9) \\
N2 & 0.0223 (13) & 0.0151 (12) & 0.0180 (13) & -0.0003 (10) & 0.0015 (10) & -0.0008 (9) \\
C1 & 0.0273 (17) & 0.0156 (14) & 0.0198 (16) & -0.0042 (12) & 0.0009 (13) & 0.0021 (11) \\
\end{array}
\]
### Geometric parameters (Å, °)

| Bond                  | Distance  | Angle  |
|-----------------------|-----------|--------|
| N1—C8                 | 1.375 (3) | N3—C27 | 1.380 (4) |
| N1—C17                | 1.407 (3) | N3—C36 | 1.412 (4) |
| N1—C19                | 1.466 (4) | N3—C38 | 1.468 (4) |
| N2—C8                 | 1.301 (4) | N4—C27 | 1.297 (4) |
| N2—C9                 | 1.400 (3) | N4—C28 | 1.404 (4) |
| C1—H1                 | 0.9500    | C20—H20| 0.9500    |

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C1—C2 1.388 (4) C1—C7 1.386 (4) C20—C21 1.379 (4)
C1—C7 1.386 (4) C20—C26 1.397 (4) C21—H21 0.9500
C2—H2 0.9500 C21—C22 1.388 (4) C2—C3 1.396 (4)
C2—C3 1.396 (4) C22—C23 1.503 (4) C3—C4 1.389 (4)
C3—C4 1.389 (4) C22—C24 1.392 (4) C4—H4AA 0.9800
C4—H4AC 0.9800 C4—H4AB 0.9800 C4—H4AC 0.9800
C4—H4AC 0.9800 C4—H4BD 0.9800 C4—H4BD 0.9800
C4—H4BE 0.9800 C4—H4BE 0.9800 C4—H4BF 0.9800
C4—H4BF 0.9800 C5—H5 0.9500 C5—C6 1.388 (4)
C5—C6 1.388 (4) C6—H6 0.9500 C6—C7 1.393 (4)
C6—C7 1.393 (4) C7—C8 1.495 (4) C9—C10 1.378 (4)
C7—C8 1.495 (4) C9—C10 1.378 (4) C9—C10 1.417 (4)
C9—C18 1.417 (4) C10—H10 0.9500 C10—C11 1.400 (4)
C10—H10 0.9500 C10—C11 1.400 (4) C11—H11 0.9500
C11—H11 0.9500 C11—C12 1.378 (4) C11—C12 1.378 (4)
C12—C13 1.409 (4) C12—C13 1.409 (4) C12—H12 0.9500
C12—H12 0.9500 C12—C13 1.409 (4) C13—C14 1.424 (4)
C13—C14 1.424 (4) C13—C18 1.427 (4) C14—H14 0.9500
C14—H14 0.9500 C14—C15 1.361 (4) C14—H14 0.9500
C14—C15 1.361 (4) C15—C16 1.410 (4) C15—H15 0.9500
C15—H15 0.9500 C15—C16 1.410 (4) C16—H16 0.9500
C16—H16 0.9500 C16—C17 1.381 (4) C16—C17 1.381 (4)
C16—C17 1.381 (4) C17—C18 1.416 (4) C17—C18 1.416 (4)
C17—C18 1.416 (4) C18—C19 1.380 (4) C18—C19 1.380 (4)
C18—C19 1.380 (4) C19—H19A 0.9800 C19—H19B 0.9800
C19—H19A 0.9800 C19—H19B 0.9800 C19—H19C 0.9800
C19—H19C 0.9800 C20—C21 1.379 (4) C20—C26 1.397 (4)
C20—C26 1.397 (4) C21—H21 0.9500 C21—C22 1.388 (4)
C21—C22 1.388 (4) C22—C23 1.503 (4) C22—C24 1.392 (4)
C22—C24 1.392 (4) C23—H23A 0.9800 C23—H23B 0.9800
C23—H23A 0.9800 C23—H23B 0.9800 C23—H23C 0.9800
C23—H23C 0.9800 C23—H23D 0.9800 C23—H23E 0.9800
C23—H23E 0.9800 C23—H23F 0.9800 C24—H24 0.9500
C24—H24 0.9500 C24—C25 1.386 (4) C25—H25 0.9500
C25—H25 0.9500 C25—C26 1.388 (4) C26—C27 1.489 (4)
C26—C27 1.489 (4) C27—C28 1.376 (4) C27—C36 1.19.8 (3)
C27—C36 1.19.8 (3) C27—N3—C36 119.8 (3) C28—C29 1.376 (4)
C28—C29 1.376 (4) C29—H29 0.9500 C29—C30 1.408 (4)
C29—C30 1.408 (4) C30—H30 0.9500 C30—C31 1.369 (5)
C30—C31 1.369 (5) C31—H31 0.9500 C31—C32 1.412 (5)
C31—C32 1.412 (5) C32—C33 1.418 (5) C32—C37 1.425 (4)
C32—C37 1.425 (4) C33—C34 1.364 (5) C33—H33 0.9500
C33—H33 0.9500 C34—H34 0.9500 C34—C35 1.410 (4)
C34—C35 1.410 (4) C35—H35 0.9500 C35—C36 1.377 (4)
C35—C36 1.377 (4) C36—C37 1.421 (4) C36—C37 1.421 (4)
C36—C37 1.421 (4) C37—H38A 0.9800 C37—H38B 0.9800
C37—H38A 0.9800 C37—H38B 0.9800 C37—H38C 0.9800
C37—H38C 0.9800 C27—N3—C36 119.8 (3) C27—N3—C38 123.2 (2)
C27—N3—C38 123.2 (2) C8—N1—C17 119.8 (2) C8—N1—C19 122.1 (2)
C8—N1—C17 119.8 (2) C8—N1—C19 119.8 (2) C8—N1—C19 119.8 (2)
C9—C18 1.427 (4) C17—C18 1.416 (4) C1—C2 1.378 (4)
C1—C2 1.378 (4) C1—C2 1.378 (4) C1—C2 1.378 (4)
C1—C2 1.378 (4) C1—C2 1.378 (4) C1—C2 1.378 (4)
C16—C17 1.381 (4) C17—C18 1.416 (4) C19—H19A 0.9800
C2—C3—C4 119.7 (3)  C21—C22—C23 121.5 (3)
C5—C3—C2 118.5 (3)  C21—C22—C24 117.6 (3)
C5—C3—C4 121.8 (3)  C24—C22—C23 121.0 (3)
C3—C4—H4AA 109.5  C22—C23—H23A 109.5
C3—C4—H4AB 109.5  C22—C23—H23B 109.5
C3—C4—H4AC 109.5  C22—C23—H23C 109.5
C3—C4—H4BD 109.5  C22—C23—H23D 109.5
C3—C4—H4BE 109.5  C22—C23—H23E 109.5
C3—C4—H4BF 109.5  C22—C23—H23F 109.5
H4AA—C4—H4AB 109.5  H23A—C23—H23B 109.5
H4AA—C4—H4AC 109.5  H23A—C23—H23C 109.5
H4AC—C4—H4AC 109.5  H23B—C23—H23C 109.5
H4BD—C4—H4BE 109.5  H23D—C23—H23E 109.5
H4BD—C4—H4BF 109.5  H23D—C23—H23F 109.5
H4BE—C4—H4BF 109.5  H23E—C23—H23F 109.5
C3—C5—H5 119.6  C22—C24—H24 119.3
C6—C5—C3 120.7 (3)  C25—C24—C22 121.4 (3)
C6—C5—H5 119.6  C25—C24—H24 119.3
C5—C6—H6 119.7  C24—C25—H25 119.7
C5—C6—C7 120.6 (3)  C24—C25—C26 120.7 (3)
C7—C6—H6 119.7  C26—C25—H25 119.7
C7—C6—C7 118.7 (2)  C20—C26—C27 121.4 (2)
C1—C7—C6 121.3 (2)  C25—C26—C20 118.1 (3)
C1—C7—C8 119.7 (2)  C25—C26—C27 120.3 (3)
C6—C7—C8 118.6 (2)  N3—C27—C26 119.0 (3)
C6—C7—C9 125.1 (2)  N4—C27—N3 124.9 (3)
N1—C8—C7 116.2 (2)  N4—C27—C26 116.0 (3)
N2—C8—N1 119.9 (3)  N4—C28—C37 120.3 (3)
N2—C8—C7 120.3 (2)  C29—C28—N4 119.3 (3)
N2—C8—C9 119.9 (3)  C29—C28—C37 120.4 (3)
C10—C9—N2 120.3 (3)  C28—C29—C30 119.5 (3)
C10—C9—C18 119.9 (3)  C28—C29—H29 120.3
C9—C10—H10 119.5  C30—C29—H29 120.3
C9—C10—C11 119.9  C30—C29—C30 119.5
C11—C10—H10 119.9  C30—C29—H29 120.3
C10—C11—H11 119.5  C30—C31—C32 121.2 (3)
C12—C11—C10 121.1 (3)  C32—C31—H31 119.4
C12—C11—H11 119.5  C32—C31—C32 121.2 (3)
C11—C12—H12 119.8  C32—C31—H31 119.4
C12—C12—C13 120.5 (3)  C30—C31—C32 121.2 (3)
C12—C12—H12 119.8  C32—C31—H31 119.4
C12—C13—C14 124.0 (3)  C31—C30—H30 119.5
C12—C13—C18 118.4 (3)  C31—C30—C32 121.0 (3)
C14—C13—C18 117.6 (3)  C31—C30—C30 119.5
C13—C14—H14 119.7  C31—C30—H30 119.5
C15—C14—C13 120.7 (3)  C31—C30—H31 119.4
C15—C14—H14 119.7  C31—C30—C30 119.5
C14—C15—H15 118.9  C31—C30—H30 119.5
C14—C15—C16 122.2 (3)  C33—C34—C35 121.7 (3)
C16—C15—H15 118.9  C35—C34—H34 119.2

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| Bond                  | Value 1 | Bond                  | Value 2 |
|----------------------|---------|----------------------|---------|
| C15—C16—H16         | 120.7   | C34—C35—H35         | 120.4   |
| C17—C16—C15         | 118.7 (3)| C36—C35—C34         | 119.1 (3)|
| C17—C16—H16         | 120.7   | C36—C35—H35         | 120.4   |
| N1—C17—C18          | 116.8 (2)| N3—C36—C37          | 116.6 (3)|
| C16—C17—N1          | 122.5 (3)| C35—C36—N3          | 122.8 (3)|
| C16—C17—C18         | 120.7 (3)| C35—C36—C37         | 120.6 (3)|
| C9—C18—C13          | 120.0 (3)| C28—C37—C32         | 120.2 (3)|
| C17—C18—C9          | 119.8 (2)| C28—C37—C36         | 119.9 (3)|
| C17—C18—C13         | 120.1 (3)| C36—C37—C32         | 119.9 (3)|
| N1—C19—H19A         | 109.5   | N3—C38—H38A         | 109.5   |
| N1—C19—H19B         | 109.5   | N3—C38—H38B         | 109.5   |
| N1—C19—H19C         | 109.5   | N3—C38—H38C         | 109.5   |
| H19A—C19—H19B       | 109.5   | H38A—C38—H38B       | 109.5   |
| H19A—C19—H19C       | 109.5   | H38A—C38—H38C       | 109.5   |
| N1—C17—C18—C9      | 0.5 (4)  | N3—C36—C37—C28     | 0.9 (4) |
| N1—C17—C18—C13     | −178.1 (2)| N3—C36—C37—C32     | −179.5 (2)|
| N2—C9—C10—C11      | 178.8 (3)| N4—C28—C29—C30     | −179.5 (3)|
| N2—C9—C18—C13      | −178.6 (2)| N4—C28—C37—C32     | 178.7 (2) |
| N2—C9—C18—C17      | 2.7 (4)  | N4—C28—C37—C36     | −1.7 (4) |
| C1—C2—C3—C4        | −179.8 (3)| C20—C21—C22—C23    | −178.9 (3)|
| C1—C2—C3—C5        | 0.4 (4)  | C20—C21—C22—C24    | 0.0 (5) |
| C1—C7—C8—N1        | 56.1 (4) | C20—C26—C27—N3     | 54.3 (4) |
| C1—C7—C8—N2        | −120.2 (3)| C20—C26—C27—N4     | −123.2 (3)|
| C2—C1—C7—C6        | −3.0 (4) | C21—C20—C26—C25    | −0.9 (5) |
| C2—C1—C7—C8        | 171.5 (3)| C21—C20—C26—C27    | 173.2 (3) |
| C2—C3—C5—C6        | −1.5 (4) | C21—C22—C24—C25    | −0.5 (5) |
| C3—C5—C6—C7        | 0.4 (4)  | C22—C24—C25—C26    | 0.2 (5) |
| C4—C3—C5—C6        | 178.7 (3)| C23—C22—C24—C25    | 178.4 (3)|
| C5—C6—C7—C1        | 1.9 (4)  | C24—C25—C26—C20    | 0.4 (4) |
| C5—C6—C7—C8        | −172.8 (3)| C24—C25—C26—C27    | −173.7 (3)|
| C6—C7—C8—N1        | −129.4 (3)| C25—C26—C27—N3     | −131.8 (3)|
| C6—C7—C8—N2        | 54.3 (4) | C25—C26—C27—N4     | 50.7 (4) |
| C7—C1—C2—C3        | 2.0 (4)  | C26—C20—C21—C22    | 0.7 (5) |
| C8—N1—C17—C16      | 176.2 (2)| C27—N3—C36—C35     | −179.2 (3)|
| C8—N1—C17—C18      | −3.9 (4) | C27—N3—C36—C37     | −0.5 (4) |
| C8—N2—C9—C10       | 179.0 (3)| C27—N4—C28—C29     | −177.7 (3)|
| C8—N2—C9—C18       | −2.5 (4) | C27—N4—C28—C37     | 2.1 (4) |
| C9—N2—C8—N1        | −1.1 (4) | C28—N4—C27—N3      | −1.8 (4) |
| C9—N2—C8—C7        | 174.9 (2)| C28—N4—C27—C26     | 175.5 (2) |
| C9—C10—C11—C12     | −0.8 (4) | C28—C29—C30—C31    | 0.7 (5) |
| C10—C9—C18—C13     | −0.1 (4) | C29—C28—C37—C32    | −1.5 (4) |
| C10—C9—C18—C17     | −178.8 (3)| C29—C28—C37—C36    | 178.1 (3) |
| C10—C11—C12—C13    | 1.1 (4)  | C29—C30—C31—C32    | −1.0 (5) |
| C11—C12—C13—C14    | 179.7 (3)| C30—C31—C32—C33    | −179.6 (3)|
| C11—C12—C13—C18    | −0.9 (4) | C30—C31—C32—C37    | 0.1 (4) |
| C12—C13—C14—C15    | 179.3 (3)| C31—C32—C33—C34    | 178.3 (3)|
| Bond            | Dihedral Angle (°) (e) | Bond            | Dihedral Angle (°) (e) |
|-----------------|------------------------|-----------------|------------------------|
| C12—C13—C18—C9 | 0.5 (4)                | C31—C32—C37—C28 | 1.1 (4)                |
| C12—C13—C18—C17| 179.1 (3)              | C31—C32—C37—C36 | −178.5 (3)             |
| C13—C14—C15—C16| 1.3 (5)                | C32—C33—C34—C35 | 1.0 (5)                |
| C14—C13—C18—C9 | 179.9 (2)              | C33—C32—C37—C28 | −179.2 (3)             |
| C14—C13—C18—C17| −1.4 (4)               | C33—C32—C37—C36 | 1.2 (4)                |
| C14—C15—C16—C17| −1.0 (4)               | C33—C34—C35—C36 | −0.5 (5)               |
| C15—C16—C17—N1 | 179.3 (2)              | C34—C35—C36—N3  | 179.0 (3)              |
| C15—C16—C17—C18| −0.6 (4)               | C34—C35—C36—C37 | 0.3 (4)                |
| C16—C17—C18—C9 | −179.5 (2)             | C35—C36—C37—C28 | 179.7 (3)              |
| C16—C17—C18—C13| 1.8 (4)                | C35—C36—C37—C32 | −0.7 (4)               |
| C17—N1—C8—N2   | 4.4 (4)                | C36—N3—C27—N4  | 1.0 (4)                |
| C17—N1—C8—C7   | −171.5 (2)             | C36—N3—C27—C26 | −176.3 (2)             |
| C18—C9—C10—C11 | 0.3 (4)                | C37—C28—C29—C30 | 0.6 (4)                |
| C18—C13—C14—C15| −0.1 (4)               | C37—C32—C33—C34 | −1.4 (4)               |
| C19—N1—C8—N2   | −168.0 (3)             | C38—N3—C27—N4  | −172.2 (3)             |
| C19—N1—C8—C7   | 16.1 (4)               | C38—N3—C27—C26 | 10.6 (4)               |
| C19—N1—C17—C16 | −11.1 (4)              | C38—N3—C36—C35 | −5.7 (4)               |
| C19—N1—C17—C18 | 168.9 (2)              | C38—N3—C36—C37 | 173.1 (3)              |