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Abstract: In the crystal structure of the title ketoamine systematic name: (E)-1,7,7-trimethyl-3-[(1-naphthylamino)methylene]bicyclo[2.2.1]heptan-2-one, C21H23NO, there are two independent molecules in the asymmetric unit. Both molecules have an E configuration about the alkene function. The main conformational difference between the molecules is in the orientation of the plane of the naphthyl rings with respect to the camphor fragment. The torsion angle about the enamine C-N bond is 21.3 (7)° for molecule A, but -24.4 (8)° for molecule B. Intermolecular N-H...O hydrogen bonds between the amino and ketone groups of adjacent independent molecules sustain the crystal, and the resulting extended chains, containing an alternating sequence of the two independent molecules, run parallel to the [001] direction and can be described by a graph-set motif of C22(12).

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(E)-3-(1-Naphthylamino)methylene- (+)-camphor

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In the crystal structure of the title ketoamine [systematic name: (E)-7,7,7-trimethyl-3-[(1-naphthylamino)methylenecyclo[2.2.1]heptan-2-one], C_{21}H_{23}NO, there are two independent molecules in the asymmetric unit. Both molecules have an E configuration about the alkene function. The main conformational difference between the molecules is in the orientation of the plane of the naphthyl rings with respect to the camphor fragment. The torsion angle about the enamine C—N bond is 21.3 (7)° for molecule A, but −24.4 (8)° for molecule B. Intermolecular N—H···O hydrogen bonds between the amino and ketone groups of adjacent independent molecules sustain the crystal, and the resulting extended chains, containing an alternating sequence of the two independent molecules, run parallel to the [001] direction and can be described by a graph-set motif of $C_2(12)$. 

Related literature

For the conformations of $\beta$-ketoamines, see: Zharkova et al. (2009). For chiral camphor-derived $\beta$-aminoketone ligands, see: Everett & Powers (1970); Casella et al. (1979). For reactions involving aminoketone complexes, see: Hsu, Chang et al. (2004); Hsu, Li et al. (2007); Lai et al. (2005); Pan et al. (2008); Wang et al. (2006). For the coordination chemistry of $\beta$-aminoketone ligands, see: Lesikar et al. (2008); Sedai et al. (2008). For the synthesis of (+)-hydroxymethylenecamphor, see: Lintvedt & Fatta (1968). For related (1-naphthylamino)methylene structures, see: Li et al. (2009); Özek et al. (2005). For graph-set theory, see: Bernstein et al. (1995).
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supplementary materials
Comment

Β-Ketoamines are the neutral protic form of β-aminoketonate bidentate anionic ligands that have been used in the coordination chemistry of transition and main group metals (Lesikar et al., 2008; Sedai et al., 2008). The electronic and steric disymmetry of these ligands is easily modified in order to tune the reactivity of the metal centre. β-Aminoketonate complexes have been used effectively in stoichiometric (Hsu, Chang et al., 2004; Hsu, Li et al., 2007) and catalytic processes, such as Suzuki cross-coupling (Lai et al., 2005), polymerization (Wang et al., 2006) and copolymerization (Pan et al., 2008) reactions. Interestingly, there are only a few reports on chiral camphor-derived β-aminoketonate ligands (Everett & Powers, 1970; Casella et al., 1979). Generally, β-ketoamines have Z conformations that are stabilized by intramolecular hydrogen bonding (Zharkova et al., 2009). The structure of the title compound was determined in order to confirm the anticipated E conformation about the alkene bond for the major product of the synthesis.

There are two molecules (A and B) of the title compound in the asymmetric unit (Fig. 1). The slightly twisted conformations of the (1-naphthylamino)methylene fragments are similar to that in the structure of 2,2-dimethyl-5-(1-naphthylaminomethylene)-1,3-dioxane-4,6-dione (Li et al., 2009): the absolute values of the torsion angle about the enamine C—N bond for the two structures lie in the narrow range of 21–25°. In contrast, the same group in 2-hydroxy-6-\{(1-naphthylamino)methylene\}cyclohexa-2,4-dien-1-one is almost planar (Özek et al., 2005).

The preference for the E conformation during the synthesis of the title compound may be attributed to the large size of the naphthyl group, whose steric pressure overcomes the competing intramolecular N—H···O hydrogen bonding, which is facilitated in the Z conformer. The observed intermolecular N—H···O hydrogen bonds between the amino and keto groups of adjacent independent molecules, which link the molecules into extended chains running parallel to [001] (Fig. 2), are an additional stabilizing factor of the E conformation. They can be described by a graph-set motif of $C_2^2(12)$ [Bernstein et al., 1995].

While the chirality of the (+)-camphor fragment means that both symmetry-independent molecules are of the same enantiomer, it is interesting to note that there is significant pseudo-inversion symmetry in the structure, with 82% of the atoms in one molecule matching closely with those of the inverted structure of the other molecule; the r.m.s. fit of 21 atoms from each molecule is 1.14 Å. Slight in-plane disorder of the naphthyl groups leads to enlarged displacement ellipsoids for some of the atoms of these groups with the direction of elongation being in the naphthyl plane.

Experimental

The title compound was prepared by refluxing 1-naphthylamine (6.77 g, 37.6 mmol) with (+)-hydroxymethylene camphor (Lintvedt & Fatta, 1968) (5.92 g, 41.3 mmol) in dry ethanol (200 ml) and formic acid (2.5 ml) for 48 h. After removing the solvent under reduced pressure, the resulting yellow solid was dried in vacuo for 4 h. The crude product contained both conformers, which after washing with hexane and HV drying afforded 6.53 g (57%) of the pure (E)-conformer [the (Z)-conformer being more soluble in alkanes]. Yellow single crystals suitable for an X-ray analysis were grown from a
saturated and filtered ethanol solution that was cooled slowly to 263 K (m.p. 351–353 K). Elemental analysis calculated for C_{21}H_{23}NO: C 82.58, H 7.59, N 4.59%; found: C 85.26, H 7.99, N 4.61%. NMR and IR Spectroscopic data are available in the archived CIF.

**Refinement**

In the final cycles of refinement, in the absence of significant anomalous scattering effects, 2643 Friedel pairs were merged and Δf " set to zero. The enantiomer used in the refinement model was chosen to match the known configuration of the (+)-camphor fragment. The amine H atoms were located in a difference Fourier map and their positions were refined freely with U_{iso}(H) = 1.2U_{eq}(N). The C-bound H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms: C—H = 0.95, 0.98, 1.00 Å, for CH, CH{sub 3} and CH{sub 2} H-atoms, respectively, with U_{iso}(H) = k × U_{eq}(C), where k = 1.5 for CH{sub 3} H-atoms and k = 1.2 for all other H-atoms.

**Figures**

Fig. 1. View of molecule A and molecule B of the title compound, showing the atom-labelling scheme. The molecules are oriented independently so as to have the camphor fragments in approximately the same orientation and emphasise the conformational differences between the molecules. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

Fig. 2. Molecular packing of compound compound projected down the b axis, showing the hydrogen bonding as thin lines [see Table 1 for details]. Hydrogen atoms not involved in hydrogen bonding have been omitted for clarity.

**(E)-1,7,7-trimethyl-3-[(1-naphthylamino)methylidene]bicyclo[2.2.1]heptan-2-one**

**Crystal data**

| C_{21}H_{23}NO | F(000) = 1312 |
|----------------|--------------|
| M_r = 305.42   | D_x = 1.190 Mg m^{-3} |
| Monoclinic, C2 | Melting point: 352 K |
| Hall symbol: C 2y | Mo Kα radiation, λ = 0.71073 Å |
| a = 23.807 (2) Å | Cell parameters from 3158 reflections |
| b = 11.9688 (12) Å | θ = 2.0–25.0° |
c = 12.0192 (8) Å
β = 95.672 (5)°
V' = 3408.1 (5) Å³
Z = 8

\[ \mu = 0.07 \text{ mm}^{-1} \]
\[ T = 160 \text{ K} \]

Prism, yellow

0.25 \times 0.20 \times 0.12 \text{ mm}

**Data collection**

Nonius KappaCCD area-detector
diffractometer

2227 reflections with \( I > 2\sigma(I) \)

Radiation source: Nonius FR590 sealed tube generator

\[ R_{int} = 0.092 \]

horizontally mounted graphite crystal

\( \theta_{\text{max}} = 25.0°, \theta_{\text{min}} = 2.5° \)

Detector resolution: 9 pixels mm\(^{-1}\)

\( h = 0 \rightarrow 28 \)

\( k = 0 \rightarrow 14 \)

21618 measured reflections

3170 independent reflections

**Refinement**

Refinement on \( F^2 \)

Least-squares matrix: full

\[ R[F^2 > 2\sigma(F^2)] = 0.059 \]

\[ wR(F^2) = 0.155 \]

\[ S = 1.05 \]

3170 reflections

428 parameters

1 restraint

\[ \Delta \rho_{\text{max}} = 0.24 \text{ e Å}^{-3} \]

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

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

\[ w = \frac{1}{(\sigma(F_o^2) + (0.0737P)^2 + 1.1311P} \]

where \( P = (F_o^2 + 2F_c^2)/3 \)

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

Extinction correction: \( SHELXL97 \) (Sheldrick, 2008),

\[ F_c^* = kF_c[1+0.001xF_c^2\lambda^2\sin(2\theta)]^{-1/4} \]

Extinction coefficient: 0.0040 (7)

**Special details**

**Experimental.** Solvent used: EtOH. Cooling Device: Oxford Cryosystems Cryostream 700. Crystal mount: glued on a glass fibre. Mosaicity: 1.498 (4)°. Frames collected: 273. Seconds exposure per frame: 88. Degrees rotation per frame: 1.4. Crystal-Detector distance: 30.0 mm.

Spectroscopic data:

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \( \delta \) 10.77 (d, \( J = 12.0 \) Hz, 1H), 8.09 (d, \( J = 8.0 \) Hz, 1H), 7.80 (d, \( J = 12.0 \) Hz, 1H), 7.54–7.45 (m, 3H), 7.40–7.36 (t, 1H), 7.20 (d, \( J = 12.0 \) Hz, 1H), 7.11 (d, \( J = 8.0 \) Hz, 1H), 2.53–2.52 (d, \( J = 4.0 \) Hz, 1H), 2.11–2.05 (m, 1H), 1.73–1.66 (m, 1H), 1.49–1.41 (m, 2H), 1.03 (s, 3H), 0.94 (s, 3H), 0.89 (s, 3H); \(^{13}\)C \((^1\)H)-NMR (101 MHz, CDCl\(_3\)): \( \delta \) 209.4, 136.9, 134.5, 132.9, 128.5, 126.4, 126.2, 125.9, 123.9, 121.9, 120.7, 116.3, 107.6, 58.9, 49.9, 49.1, 30.4, 28.5, 20.7, 19.1, 9.2; FT—IR (\( \nu \), cm\(^{-1}\), KBr): 3300 (N—H), 1681 (C=O).
supplementary materials

**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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)

| Atom | x     | y     | z     | U$_{iso}$/U$_{eq}$ |
|------|-------|-------|-------|--------------------|
| O1   | 0.68329 (13) | 0.4955 (3) | 0.5734 (2) | 0.0597 (10) |
| N1   | 0.76542 (16) | 0.5821 (4) | 0.2820 (3) | 0.0467 (10) |
| H1   | 0.7453 (18) | 0.563 (4) | 0.204 (4) | 0.056* |
| C1   | 0.82420 (18) | 0.6018 (4) | 0.2844 (4) | 0.0457 (12) |
| C2   | 0.8445 (2) | 0.6690 (4) | 0.1988 (4) | 0.0454 (12) |
| C3   | 0.8088 (2) | 0.7267 (5) | 0.1164 (4) | 0.0542 (14) |
| H3   | 0.7691 | 0.7240 | 0.1190 | 0.065* |
| C4   | 0.8307 (2) | 0.7866 (5) | 0.0329 (4) | 0.0624 (15) |
| H4   | 0.8064 | 0.8257 | −0.0211 | 0.075* |
| C5   | 0.8888 (3) | 0.7982 (5) | 0.0282 (5) | 0.0674 (16) |
| H5   | 0.9036 | 0.8278 | −0.0316 | 0.081* |
| C6   | 0.9245 (2) | 0.7388 (5) | 0.1057 (4) | 0.0584 (15) |
| H6   | 0.9641 | 0.7438 | 0.1009 | 0.070* |
| C7   | 0.9041 (2) | 0.6780 (5) | 0.1950 (4) | 0.0508 (13) |
| C8   | 0.9406 (2) | 0.6296 (5) | 0.2821 (5) | 0.0575 (14) |
| H8   | 0.9802 | 0.6378 | 0.2817 | 0.069* |
| C9   | 0.9198 (2) | 0.5715 (5) | 0.3664 (4) | 0.0569 (13) |
| H9   | 0.9449 | 0.5412 | 0.4251 | 0.068* |
| C10  | 0.86094 (19) | 0.5562 (4) | 0.3669 (4) | 0.0514 (13) |
| C11  | 0.8468 | 0.5140 | 0.4250 | 0.062* |
| C12  | 0.74053 (18) | 0.5505 (4) | 0.3731 (4) | 0.0435 (12) |
| H11  | 0.7592 | 0.5701 | 0.4439 | 0.052* |
| C13  | 0.69145 (18) | 0.4934 (4) | 0.3731 (3) | 0.0436 (12) |
| C14  | 0.65587 (19) | 0.4306 (4) | 0.2821 (3) | 0.0454 (12) |
| C15  | 0.6557 (2) | 0.4624 | 0.2051 | 0.054* |
| C16  | 0.6757 (2) | 0.3084 (4) | 0.2953 (4) | 0.0574 (14) |
| H141 | 0.7173 | 0.3028 | 0.2978 | 0.069* |
| H142 | 0.6583 | 0.2611 | 0.2336 | 0.069* |
| C17  | 0.6547 (2) | 0.2746 (5) | 0.4094 (4) | 0.0595 (14) |
| H151 | 0.6869 | 0.2576 | 0.4654 | 0.071* |
| H152 | 0.6297 | 0.2084 | 0.4008 | 0.071* |
| C18  | 0.62158 (19) | 0.3793 (4) | 0.4453 (3) | 0.0469 (12) |
| C19  | 0.66827 (19) | 0.4636 (4) | 0.4773 (4) | 0.0467 (13) |
| C18  | 0.59773 (18) | 0.4275 (4) | 0.3300 (3) | 0.0459 (12) |
| C19  | 0.5713 (2) | 0.5429 (5) | 0.3385 (4) | 0.0590 (14) |
| H191 | 0.5393 | 0.5382 | 0.3836 | 0.088* |
| H192 | 0.5581 | 0.5699 | 0.2634 | 0.088* |
|     | x     | y     | z     | U (eV) |
|-----|-------|-------|-------|--------|
| H193| 0.5995| 0.5948| 0.3738| 0.088* |
| C20 | 0.5540 (2)| 0.3515 (5)| 0.2652 (4)| 0.0624 (15)|
| H201| 0.5440 | 0.3824 | 0.1903 | 0.094* |
| H202| 0.5202 | 0.3469 | 0.3051 | 0.094* |
| H203| 0.5700 | 0.2766 | 0.2586 | 0.094* |
| C21 | 0.5823 (2)| 0.3569 (6)| 0.5342 (4)| 0.0631 (15)|
| H211| 0.5603 | 0.4243 | 0.5460 | 0.095* |
| H212| 0.6044 | 0.3362 | 0.6042 | 0.095* |
| H213| 0.5566 | 0.2956 | 0.5099 | 0.095* |
| O2  | 0.69132 (15)| 0.5802 (3)| 1.0744 (3)| 0.0673 (11)|
| N2  | 0.76421 (18)| 0.5057 (4)| 0.7714 (3)| 0.0564 (12)|
| H2  | 0.743 (2) | 0.502 (5)| 0.712 (4)| 0.068* |
| C31 | 0.8225 (2)| 0.4882 (5)| 0.7702 (4)| 0.0512 (13)|
| C32 | 0.8415 (2)| 0.4213 (5)| 0.6840 (4)| 0.0554 (14)|
| C33 | 0.8049 (2)| 0.3591 (5)| 0.6054 (4)| 0.0588 (14)|
| H33 | 0.7653 | 0.3617 | 0.6100 | 0.071* |
| C34 | 0.8253 (3)| 0.2968 (5)| 0.5246 (5)| 0.0674 (16)|
| H34 | 0.7998 | 0.2569 | 0.4732 | 0.081* |
| C35 | 0.8829 (3)| 0.2900 (6)| 0.5154 (5)| 0.0750 (17)|
| H35 | 0.8965 | 0.2475 | 0.4569 | 0.090**|
| C36 | 0.9189 (3)| 0.3432 (5)| 0.5889 (5)| 0.0700 (16)|
| H36 | 0.9582 | 0.3376 | 0.5822 | 0.084* |
| C37 | 0.8998 (2)| 0.4094 (5)| 0.6788 (5)| 0.0572 (14)|
| C38 | 0.9397 (2)| 0.4604 (5)| 0.7578 (5)| 0.0621 (15)|
| H38 | 0.9791 | 0.4515 | 0.7537 | 0.075* |
| C39 | 0.9195 (2)| 0.5234 (5)| 0.8409 (5)| 0.0708 (17)|
| H39 | 0.9455 | 0.5581 | 0.8952 | 0.085* |
| C40 | 0.8608 (2)| 0.5376 (5)| 0.8472 (4)| 0.0582 (14)|
| H40 | 0.8480 | 0.5817 | 0.9054 | 0.070* |
| C41 | 0.7408 (2)| 0.5355 (5)| 0.8651 (4)| 0.0575 (14)|
| H41 | 0.7626 | 0.5197 | 0.9339 | 0.069* |
| C42 | 0.68961 (18)| 0.5857 (4)| 0.8730 (4)| 0.0452 (12)|
| C43 | 0.6461 (2)| 0.6346 (5)| 0.7896 (4)| 0.0547 (14)|
| H43 | 0.6592 | 0.6503 | 0.7146 | 0.066* |
| C44 | 0.5941 (2)| 0.5569 (6)| 0.7881 (4)| 0.0674 (16)|
| H441| 0.5651 | 0.5764 | 0.7263 | 0.081* |
| H442| 0.6049 | 0.4775 | 0.7811 | 0.081* |
| C45 | 0.5733 (2)| 0.5810 (5)| 0.9029 (4)| 0.0621 (14)|
| H451| 0.5747 | 0.5127 | 0.9495 | 0.075* |
| H452| 0.5341 | 0.6097 | 0.8944 | 0.075* |
| C46 | 0.6151 (2)| 0.6717 (5)| 0.9562 (4)| 0.0524 (13)|
| C47 | 0.6699 (2)| 0.6078 (4)| 0.9813 (4)| 0.0458 (12)|
| C48 | 0.62762 (19)| 0.7388 (5)| 0.8533 (4)| 0.0556 (14)|
| C49 | 0.6746 (2)| 0.8251 (5)| 0.8770 (5)| 0.0661 (15)|
| H491| 0.6821 | 0.8616 | 0.8070 | 0.099* |
| H492| 0.7090 | 0.7877 | 0.9098 | 0.099* |
| H493| 0.6630 | 0.8812 | 0.9295 | 0.099* |
| C50 | 0.5761 (2)| 0.8006 (6)| 0.7922 (5)| 0.0802 (18)|
| H501| 0.5461 | 0.7466 | 0.7704 | 0.120* |
supplementary materials

|      |      |      |      |      |      |      |
|------|------|------|------|------|------|------|
| H502 | 0.5875 | 0.8377 | 0.7253 | 0.120* |
| H503 | 0.5622 | 0.8565 | 0.8423 | 0.120* |
| C51  | 0.5939 (3) | 0.7335 (6) | 1.0546 (4) | 0.0796 (18) |
| H511 | 0.6229 | 0.7860 | 1.0858 | 0.119* |
| H512 | 0.5857 | 0.6796 | 1.1123 | 0.119* |
| H513 | 0.5594 | 0.7747 | 1.0292 | 0.119* |

Atomic displacement parameters (Å\(^2\))

|      |      |      |      |      |      |      |
|------|------|------|------|------|------|------|
| O1   | 0.059 (2) | 0.080 (3) | 0.0400 (18) | −0.0056 (19) | 0.0018 (15) | −0.0112 (19) |
| N1   | 0.043 (2) | 0.055 (3) | 0.041 (2) | −0.004 (2) | −0.0013 (17) | 0.000 (2) |
| C1   | 0.038 (3) | 0.045 (3) | 0.054 (3) | −0.0002 (3) | 0.004 (2) | −0.004 (2) |
| C2   | 0.051 (3) | 0.041 (3) | 0.046 (3) | −0.009 (3) | 0.014 (2) | −0.011 (2) |
| C3   | 0.055 (3) | 0.053 (3) | 0.054 (3) | −0.014 (3) | 0.007 (2) | −0.008 (3) |
| C4   | 0.076 (4) | 0.063 (4) | 0.048 (3) | −0.022 (3) | 0.005 (3) | −0.002 (3) |
| C5   | 0.078 (4) | 0.072 (4) | 0.054 (3) | −0.037 (4) | 0.019 (3) | −0.012 (3) |
| C6   | 0.055 (3) | 0.063 (4) | 0.061 (3) | −0.022 (3) | 0.021 (3) | −0.017 (3) |
| C7   | 0.047 (3) | 0.046 (3) | 0.061 (3) | −0.008 (3) | 0.010 (2) | −0.017 (3) |
| C8   | 0.040 (3) | 0.049 (3) | 0.085 (4) | −0.005 (3) | 0.013 (3) | −0.015 (3) |
| C9   | 0.049 (3) | 0.040 (3) | 0.079 (3) | 0.004 (3) | −0.005 (3) | −0.003 (3) |
| C10  | 0.047 (3) | 0.043 (3) | 0.065 (3) | −0.005 (3) | 0.009 (2) | −0.003 (3) |
| C11  | 0.045 (3) | 0.044 (3) | 0.041 (2) | −0.001 (2) | 0.002 (2) | −0.003 (2) |
| C12  | 0.040 (3) | 0.050 (3) | 0.041 (2) | −0.001 (2) | 0.0016 (19) | 0.001 (2) |
| C13  | 0.048 (3) | 0.054 (3) | 0.035 (2) | −0.007 (2) | 0.0080 (19) | 0.005 (2) |
| C14  | 0.064 (3) | 0.057 (4) | 0.053 (3) | −0.006 (3) | 0.013 (2) | −0.007 (3) |
| C15  | 0.071 (3) | 0.049 (3) | 0.059 (3) | −0.006 (3) | 0.008 (3) | 0.004 (3) |
| C16  | 0.050 (3) | 0.050 (3) | 0.041 (2) | −0.008 (3) | 0.007 (2) | 0.001 (2) |
| C17  | 0.045 (3) | 0.054 (3) | 0.040 (3) | 0.006 (2) | 0.000 (2) | 0.000 (2) |
| C18  | 0.045 (3) | 0.051 (3) | 0.041 (2) | −0.011 (2) | 0.0043 (19) | −0.001 (2) |
| C19  | 0.047 (3) | 0.066 (4) | 0.063 (3) | −0.003 (3) | −0.001 (2) | 0.002 (3) |
| C20  | 0.046 (3) | 0.085 (4) | 0.057 (3) | −0.024 (3) | 0.009 (2) | −0.013 (3) |
| C21  | 0.063 (3) | 0.078 (4) | 0.051 (3) | −0.007 (3) | 0.019 (2) | 0.001 (3) |
| O2   | 0.077 (2) | 0.076 (3) | 0.0455 (18) | −0.020 (2) | −0.0127 (17) | 0.0087 (19) |
| N2   | 0.049 (3) | 0.064 (3) | 0.055 (2) | 0.006 (2) | 0.0027 (19) | −0.001 (2) |
| C31  | 0.049 (3) | 0.047 (3) | 0.058 (3) | 0.002 (3) | 0.006 (2) | 0.000 (3) |
| C32  | 0.054 (3) | 0.040 (3) | 0.072 (3) | 0.005 (3) | 0.007 (3) | 0.017 (3) |
| C33  | 0.058 (3) | 0.052 (4) | 0.066 (3) | −0.003 (3) | 0.004 (3) | 0.009 (3) |
| C34  | 0.089 (5) | 0.054 (4) | 0.060 (3) | 0.013 (3) | 0.011 (3) | 0.002 (3) |
| C35  | 0.095 (5) | 0.065 (4) | 0.066 (4) | 0.010 (4) | 0.013 (3) | 0.006 (3) |
| C36  | 0.067 (4) | 0.062 (4) | 0.084 (4) | 0.017 (3) | 0.022 (3) | 0.020 (4) |
| C37  | 0.048 (3) | 0.045 (3) | 0.079 (3) | 0.005 (3) | 0.009 (3) | 0.017 (3) |
| C38  | 0.056 (3) | 0.051 (4) | 0.082 (4) | 0.006 (3) | 0.020 (3) | 0.013 (3) |
| C39  | 0.058 (4) | 0.051 (4) | 0.101 (4) | −0.011 (3) | −0.004 (3) | 0.015 (4) |
| C40  | 0.051 (3) | 0.052 (3) | 0.072 (3) | 0.003 (3) | 0.006 (3) | 0.002 (3) |
| C41  | 0.061 (3) | 0.063 (4) | 0.048 (3) | −0.010 (3) | 0.001 (2) | 0.003 (3) |
| C42  | 0.039 (3) | 0.053 (3) | 0.043 (3) | 0.004 (2) | 0.003 (2) | 0.000 (2) |
| C43  | 0.057 (3) | 0.064 (4) | 0.042 (3) | 0.004 (3) | 0.000 (2) | 0.007 (3) |
|   | 0.056 (3) | 0.083 (4) | 0.060 (3) | 0.013 (3) | −0.012 (2) | −0.004 (3) |
|---|---|---|---|---|---|---|
| C45 | 0.046 (3) | 0.063 (4) | 0.078 (3) | 0.005 (3) | 0.010 (3) | 0.002 (3) |
| C46 | 0.055 (3) | 0.053 (3) | 0.051 (3) | 0.004 (3) | 0.015 (2) | 0.001 (2) |
| C47 | 0.050 (3) | 0.047 (3) | 0.039 (3) | −0.004 (2) | −0.004 (2) | 0.003 (2) |
| C48 | 0.050 (3) | 0.058 (4) | 0.060 (3) | 0.011 (3) | 0.007 (2) | 0.012 (3) |
| C49 | 0.066 (3) | 0.058 (4) | 0.076 (3) | −0.002 (3) | 0.016 (3) | 0.009 (3) |
| C50 | 0.073 (4) | 0.083 (5) | 0.085 (4) | 0.021 (4) | 0.009 (3) | 0.013 (4) |
| C51 | 0.093 (4) | 0.077 (5) | 0.073 (4) | 0.002 (4) | 0.031 (3) | −0.006 (3) |

**Geometric parameters (Å, °)**

|   | 1.235 (5) | O2—C47 | 1.229 (5) |
|---|---|---|---|
| O1—C17 | 1.351 (6) | N2—C41 | 1.353 (6) |
| N1—C11 | 1.416 (6) | N2—C31 | 1.404 (6) |
| N1—H1 | 1.03 (4) | N2—H2 | 0.83 (5) |
| C1—C10 | 1.370 (6) | C31—C40 | 1.368 (7) |
| C1—C2 | 1.427 (6) | C31—C32 | 1.419 (7) |
| C2—C3 | 1.419 (7) | C32—C37 | 1.404 (7) |
| C2—C7 | 1.429 (6) | C32—C33 | 1.430 (7) |
| C3—C4 | 1.378 (7) | C33—C34 | 1.353 (7) |
| C3—H3 | 0.9500 | C33—H33 | 0.9500 |
| C4—C5 | 1.391 (8) | C34—C35 | 1.390 (8) |
| C4—H4 | 0.9500 | C34—H34 | 0.9500 |
| C5—C6 | 1.341 (8) | C35—C36 | 1.331 (8) |
| C5—H5 | 0.9500 | C35—H35 | 0.9500 |
| C6—C7 | 1.421 (7) | C36—C37 | 1.449 (8) |
| C6—H6 | 0.9500 | C36—H36 | 0.9500 |
| C7—C8 | 1.416 (7) | C37—C38 | 1.413 (8) |
| C8—C9 | 1.362 (7) | C38—C39 | 1.375 (7) |
| C8—H8 | 0.9500 | C38—H38 | 0.9500 |
| C9—C10 | 1.414 (6) | C39—C40 | 1.418 (7) |
| C9—H9 | 0.9500 | C39—H39 | 0.9500 |
| C10—H10 | 0.9500 | C40—H40 | 0.9500 |
| C11—C12 | 1.353 (6) | C41—C42 | 1.371 (7) |
| C11—H11 | 0.9500 | C41—H41 | 0.9500 |
| C12—C17 | 1.462 (6) | C42—C47 | 1.451 (6) |
| C12—C13 | 1.516 (6) | C42—C43 | 1.488 (6) |
| C13—C14 | 1.541 (7) | C43—C44 | 1.547 (8) |
| C13—C18 | 1.551 (6) | C43—C48 | 1.551 (7) |
| C13—H13 | 1.0000 | C43—H43 | 1.0000 |
| C14—C15 | 1.559 (7) | C44—C45 | 1.540 (7) |
| C14—H141 | 0.9900 | C44—H441 | 0.9900 |
| C14—H142 | 0.9900 | C44—H442 | 0.9900 |
| C15—C16 | 1.563 (7) | C45—C46 | 1.566 (8) |
| C15—H151 | 0.9900 | C45—H451 | 0.9900 |
| C15—H152 | 0.9900 | C45—H452 | 0.9900 |
| C16—C21 | 1.512 (6) | C46—C47 | 1.516 (7) |
| C16—C17 | 1.522 (7) | C46—C51 | 1.523 (7) |
| C16—C18 | 1.555 (6) | C46—C48 | 1.528 (7) |
| Bond          | Distance (Å) | Bond          | Distance (Å) |
|---------------|--------------|---------------|--------------|
| C18—C19       | 1.526 (7)    | C48—C49       | 1.529 (7)    |
| C18—C20       | 1.535 (6)    | C48—C50       | 1.553 (7)    |
| C19—H191      | 0.9800       | C49—H491      | 0.9800       |
| C19—H192      | 0.9800       | C49—H492      | 0.9800       |
| C19—H193      | 0.9800       | C49—H493      | 0.9800       |
| C20—H201      | 0.9800       | C50—H501      | 0.9800       |
| C20—H202      | 0.9800       | C50—H502      | 0.9800       |
| C20—H203      | 0.9800       | C50—H503      | 0.9800       |
| C21—H211      | 0.9800       | C51—H511      | 0.9800       |
| C21—H212      | 0.9800       | C51—H512      | 0.9800       |
| C21—H213      | 0.9800       | C51—H513      | 0.9800       |
| C11—N1—C1     | 122.8 (4)    | C41—N2—C31    | 122.4 (4)    |
| C11—N1—H1     | 118 (3)      | C41—N2—H2     | 117 (4)      |
| C1—N1—H1      | 115 (2)      | C31—N2—H2     | 120 (4)      |
| C10—C1—N1     | 120.5 (4)    | C40—C31—N2    | 121.5 (5)    |
| C10—C1—C2     | 120.6 (4)    | C40—C31—C32   | 119.9 (5)    |
| N1—C1—C2      | 118.9 (4)    | N2—C31—C32    | 118.6 (4)    |
| C3—C2—C1     | 123.7 (4)    | C37—C32—C31   | 118.6 (5)    |
| C3—C2—C7     | 118.0 (5)    | C37—C32—C33   | 117.4 (5)    |
| C1—C2—C7     | 118.3 (5)    | C31—C32—C33   | 124.0 (5)    |
| C4—C3—C2     | 121.2 (5)    | C34—C33—C32   | 121.5 (5)    |
| C4—C3—H3     | 119.4        | C34—C33—H33   | 119.2        |
| C2—C3—H3     | 119.4        | C32—C33—H33   | 119.2        |
| C3—C4—C5     | 119.4 (5)    | C33—C34—C35   | 121.1 (6)    |
| C3—C4—H4     | 120.3        | C33—C34—H34   | 119.4        |
| C5—C4—H4     | 120.3        | C35—C34—H34   | 119.4        |
| C6—C5—C4     | 121.8 (5)    | C36—C35—C34   | 119.7 (6)    |
| C6—C5—H5     | 119.1        | C36—C35—H35   | 120.1        |
| C4—C5—H5     | 119.1        | C34—C35—H35   | 120.1        |
| C5—C6—C7     | 121.0 (5)    | C35—C36—C37   | 121.9 (6)    |
| C5—C6—H6     | 119.5        | C35—C36—H36   | 119.1        |
| C7—C6—H6     | 119.5        | C37—C36—H36   | 119.1        |
| C8—C7—C6     | 122.5 (5)    | C32—C37—C38   | 121.9 (5)    |
| C8—C7—C2     | 118.9 (5)    | C32—C37—C36   | 118.2 (5)    |
| C6—C7—C2     | 118.5 (5)    | C38—C37—C36   | 119.9 (5)    |
| C9—C8—C7     | 121.3 (5)    | C39—C38—C37   | 117.7 (5)    |
| C9—C8—H8     | 119.4        | C39—C38—H38   | 121.1        |
| C7—C8—H8     | 119.4        | C37—C38—H38   | 121.1        |
| C8—C9—C10    | 120.1 (5)    | C38—C39—C40   | 121.5 (5)    |
| C8—C9—H9     | 119.9        | C38—C39—H39   | 119.3        |
| C10—C9—H9    | 119.9        | C40—C39—H39   | 119.3        |
| C1—C10—C9    | 120.5 (5)    | C31—C40—C39   | 120.5 (5)    |
| C1—C10—H10   | 119.7        | C31—C40—H40   | 119.8        |
| C9—C10—H10   | 119.7        | C39—C40—H40   | 119.8        |
| N1—C11—C12   | 126.1 (4)    | N2—C41—C42    | 128.0 (5)    |
| N1—C11—H11   | 116.9        | N2—C41—H41    | 116.0        |
| C12—C11—H11  | 116.9        | C42—C41—H41   | 116.0        |
| C11—C12—C17  | 121.5 (4)    | C41—C42—C47   | 120.8 (4)    |
| C11—C12—C13  | 132.2 (4)    | C41—C42—C43   | 133.6 (4)    |
C17—C12—C13 105.4 (4)  
C12—C13—C14 104.7 (4)  
C12—C13—C18 101.5 (3)  
C14—C13—C18 102.4 (4)  
C12—C13—H13 115.5  
C14—C13—H13 115.5  
C18—C13—H13 115.5  
C13—C14—C15 102.4 (4)  
C13—C14—H141 111.3  
C14—C13—H13 115.5  
C14—C13—H13 115.5  
C15—C14—H142 111.3  
C15—C14—H142 111.3  
H141—C14—H142 109.2  
C14—C15—C16 104.5 (4)  
C14—C15—H151 110.9  
C16—C15—H151 110.9  
C14—C15—H152 110.9  
C16—C15—H152 110.9  
H151—C15—H152 108.9  
C21—C16—C17 115.2 (4)  
C21—C16—C18 119.9 (4)  
C17—C16—C18 99.9 (4)  
C21—C16—C15 114.7 (5)  
C17—C16—C15 103.0 (4)  
C18—C16—C15 101.6 (4)  
O1—C17—C12 128.8 (5)  
O1—C17—C12 128.7 (5)  
C12—C17—C16 125.3 (4)  
C17—C16—C18 105.9 (4)  
C19—C18—C20 107.9 (4)  
C19—C18—C13 113.1 (4)  
C20—C18—C13 114.2 (4)  
C19—C18—C16 113.2 (4)  
C20—C18—C16 113.7 (4)  
C13—C18—C16 94.5 (3)  
C18—C19—H191 109.5  
C18—C19—H192 109.5  
H191—C19—H192 109.5  
C18—C19—H193 109.5  
H191—C19—H193 109.5  
C19—C19—H193 109.5  
H192—C19—H193 109.5  
C18—C20—H201 109.5  
C18—C20—H202 109.5  
H201—C20—H202 109.5  
C18—C20—H203 109.5  
H201—C20—H203 109.5  
C16—C21—H211 109.5  
C16—C21—H212 109.5  
H211—C21—H212 109.5
| Bond          | Angle (°) | Bond          | Angle (°) |
|--------------|----------|--------------|----------|
| C16—C21—H213 | 109.5    | C46—C51—H513 | 109.5    |
| H211—C21—H213 | 109.5    | H511—C51—H513 | 109.5    |
| H212—C21—H213 | 109.5    | H512—C51—H513 | 109.5    |
| C11—N1—C1—C10 | 21.3 (7) | C41—N2—C31—C40 | −24.4 (8) |
| C11—N1—C1—C2  | −159.3 (4) | C41—N2—C31—C32 | 158.1 (5) |
| C10—C1—C2—C3  | −174.3 (5) | C40—C31—C32—C37 | −1.3 (7) |
| N1—C1—C2—C3  | 6.2 (7) | N2—C31—C32—C37 | 176.1 (5) |
| C10—C1—C2—C7  | 6.2 (7) | C40—C31—C32—C33 | 174.7 (5) |
| N1—C1—C2—C7  | −173.2 (4) | N2—C31—C32—C33 | −7.8 (8) |
| C1—C2—C3—C4  | −177.2 (5) | C37—C32—C33—C34 | −4.1 (7) |
| C7—C2—C3—C4  | 2.2 (7) | C31—C32—C33—C34 | 179.9 (5) |
| C2—C3—C4—C5  | 0.9 (8) | C32—C33—C34—C35 | 0.5 (8) |
| C3—C4—C5—C6  | −2.8 (9) | C33—C34—C35—C36 | 1.8 (9) |
| C4—C5—C6—C7  | 1.5 (9) | C34—C35—C36—C37 | −0.4 (9) |
| C5—C6—C7—C8  | −176.0 (5) | C31—C32—C33—C37 | 1.2 (8) |
| C5—C6—C7—C2  | 1.7 (8) | C32—C33—C34—C35 | −175.2 (5) |
| C3—C2—C7—C8  | 174.3 (5) | C31—C32—C33—C37 | −178.5 (5) |
| C1—C2—C7—C8  | −6.2 (7) | C33—C32—C31—C40 | 5.2 (7) |
| C3—C2—C7—C6  | −3.5 (7) | C35—C36—C37—C32 | −3.1 (8) |
| C1—C2—C7—C6  | 176.0 (4) | C35—C36—C37—C38 | 177.2 (6) |
| C6—C7—C8—C9  | −179.8 (5) | C32—C33—C34—C35 | −0.3 (8) |
| C2—C7—C8—C9  | 2.5 (8) | C36—C37—C38—C39 | 179.3 (5) |
| C7—C8—C9—C10 | 1.5 (8) | C37—C38—C39—C40 | −0.4 (8) |
| N1—C1—C10—C9 | 177.1 (5) | N2—C31—C40—C39 | −176.7 (5) |
| C2—C1—C10—C9 | −2.4 (8) | C32—C31—C40—C39 | 0.7 (8) |
| C8—C9—C10—C1 | −1.6 (8) | C38—C39—C40—C31 | 0.2 (9) |
| C1—N1—C11—C12 | −155.0 (5) | C31—N2—C41—C42 | 159.3 (5) |
| N1—C11—C12—C17 | −179.9 (5) | N2—C41—C42—C47 | 177.4 (5) |
| N1—C11—C12—C13 | 12.9 (9) | N2—C41—C42—C43 | −7.6 (10) |
| C11—C12—C13—C14 | 94.2 (6) | C41—C42—C43—C44 | 112.2 (6) |
| C17—C12—C13—C14 | −74.5 (4) | C47—C42—C43—C44 | −72.2 (5) |
| C11—C12—C13—C18 | −159.5 (5) | C41—C42—C43—C48 | −140.7 (6) |
| C17—C12—C13—C18 | 31.8 (5) | C47—C42—C43—C48 | 34.8 (5) |
| C12—C13—C14—C15 | 67.9 (4) | C42—C43—C44—C45 | 70.0 (5) |
| C18—C13—C14—C15 | −37.7 (4) | C48—C43—C44—C45 | −35.9 (5) |
| C13—C14—C15—C16 | 3.6 (5) | C43—C44—C45—C46 | 1.1 (5) |
| C14—C15—C16—C21 | 162.2 (4) | C44—C45—C46—C47 | −70.1 (5) |
| C14—C15—C16—C17 | −71.8 (4) | C44—C45—C46—C51 | 163.3 (5) |
| C14—C15—C16—C18 | 31.4 (5) | C44—C45—C46—C48 | 34.5 (5) |
| C11—C12—C17—O1 | 10.6 (8) | C41—C42—C47—O2 | −5.9 (9) |
| C13—C12—C17—O1 | −179.2 (5) | C43—C42—C47—O2 | 177.8 (5) |
| C11—C12—C17—C16 | −167.4 (5) | C41—C42—C47—C46 | 175.3 (5) |
| C13—C12—C17—C16 | 2.8 (5) | C43—C42—C47—C46 | 0.9 (6) |
| C21—C16—C17—O1 | 15.9 (7) | C51—C46—C47—O2 | 17.8 (8) |
| C18—C16—C17—O1 | 145.8 (5) | C48—C46—C47—O2 | 147.4 (5) |
| C15—C16—C17—O1 | −109.7 (5) | C45—C46—C47—O2 | −107.8 (6) |
| C21—C16—C17—C12 | −166.0 (4) | C51—C46—C47—C42 | −163.4 (5) |
| C18—C16—C17—C12 | −36.1 (5) | C48—C46—C47—C42 | −33.8 (5) |
| C15—C16—C17—C12 | 68.4 (4) | C45—C46—C47—C42 | 71.0 (5) |
supplementary materials

|          | D—H···A              | D—H      | H···A    | D···A    | D—H···A |
|----------|----------------------|----------|----------|----------|----------|
| N1—H1···O2<sup>i</sup> | 1.03 (4)             | 1.93 (4) | 2.909 (5) | 157 (4)  |          |
| N2—H2···O1       | 0.83 (5)             | 2.08 (5) | 2.913 (5) | 174 (5)  |          |

Hydrogen-bond geometry (Å, °)

Symmetry codes: (i) x, y, z−1.
Fig. 2