4-30-2008

4-Anilino-1-benzyl-piperidine-4-carbo-nitrile

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4-Anilino-1-benzylpiperidine-4-carbonitrile

Kiran K. Allam,‡ Frank R. Fronczek* and M. Graca H. Vicente

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Received 25 March 2008; accepted 3 April 2008

Key indicators: single-crystal X-ray study; R = 0.045; wR = 0.124; data-to-parameter ratio = 33.7.

The title molecule, C_{19}H_{21}N_{3}, an important precursor in the synthesis of porphyrin–fentanyl conjugates, has its piperidine ring in the chair conformation, with endocyclic torsion-angle magnitudes in the range 53.26 (8)–60.63 (9)°. The C≡N group is axial, while the CH_{2}Ph and NHPh groups are equatorial. The NH group does not engage in strong hydrogen bonding, but forms an intermolecular N—H···N interaction.

Related literature

For background literature, see: Barth et al. (2005); Deguchi et al. (2004); Henriksen et al. (2005); Terasaki et al. (2003); Vicente, (2001). For a related structure, see: Brine et al. (1994).

Data collection

Nonius KappaCCD diffractometer with an Oxford Cryosystems Cryostream cooler
Absorption correction: none
24180 measured reflections
6842 independent reflections
5189 reflections with I > 2σ(I)
R_{int} = 0.025

Refinement

R[F^2 > 2σ(F^2)] = 0.044
wR(F^2) = 0.124
S = 1.03
6842 reflections
203 parameters

H atoms treated by a mixture of independent and constrained refinement
Δρ_{max} = 0.49 e Å^{-3}
Δρ_{min} = −0.27 e Å^{-3}

Table 1

Hydrogen-bond geometry (Å, °).

<table>
<thead>
<tr>
<th>D—H···A</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
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<tbody>
<tr>
<td>N2—H2N···N3</td>
<td>0.847 (14)</td>
<td>2.756 (13)</td>
<td>3.5044 (12)</td>
<td>148.2 (11)</td>
</tr>
</tbody>
</table>

Symmetry code: (i) −x + 1/2, y − 1/2, z − 1/2.

Data collection: COLLECT (Nonius, 2000); cell refinement: DENZO and SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO and SCALEPACK; program(s) used to solve structure: SIR97 (Altomare et al., 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

The purchase of the diffractometer was made possible by grant No. LEQSF(1999–2000)-ENH-TR-13, administered by the Louisiana Board of Regents.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2222).

References


‡ Deceased 13 December 2007.
4-Anilino-1-benzylpiperidine-4-carbonitrile

Kiran K. Allam, Frank R. Fronczek and M. Graça H. Vicente

S1. Comment

1-Benzyl-4-phenylamino-4-piperidinedecarbonitrile is an important precursor in the synthesis of porphyrin-fentanyl conjugates that might be used as sensitizers in photodynamic therapy (PDT) (Vicente, 2001) and/or in boron neutron capture therapy (BNCT) (Barth et al., 2005) of brain tumors. One of the obstacles for treating brain tumors using chemotherapy is the presence of the blood brain barrier (BBB), which protects the central nervous system from drugs and endogenous molecules (Terasaki et al., 2003). Porphyrin-fentanyl conjugates could potentially cross the BBB due to the affinity of fentanyl derivatives for the opioid receptors highly expressed in the BBB (Deguchi et al., 2004), and thus selectively accumulate within brain tumors.

The structure of the title compound is shown in Fig 1. The piperidine ring is in the chair conformation, with the C≡N group axial and the CH2Ph and NHPh groups equatorial. The conformation of the CH2Ph group with respect to the piperidine is described by torsion angles C5—N1—C6—C7 - 168.52 (6) and N1—C6—C7—C8 62.28 (10)°. The conformation of the NHPh group with respect to the piperidine is described by torsion angles C2—C3—N2—C13 179.19 (8) and C3—N2—C13—C18 172.56 (8)°. The pyramidal nature of N1 can be seen by the near-tetrahedral C—N1—C angles, which all fall within the narrow range 110.18 (6) - 110.76 (7)°, such that N1 lies 0.465 (1) Å from the plane defined by C1, C5, and C6.

Despite the presence of both a potential hydrogen-bond donor and potential hydrogen-bond acceptors, the compound exhibits no strong hydrogen bonding, nor any short C—H···N interactions. The nearest distance of the N—H group to a hydrogen-bond acceptor is to nitrile N3i (at i = 3/2 - x, 1/2 + y, 3/2 - z), having N2···N3i distance 3.5044 (12) Å, H2N···N3i distance 2.756 (13) Å, and angle about H2N 148.2 (11)°.

S2. Experimental

The title compound was prepared in 89.5% yield from N-benzyl-4-piperidone, using an optimized procedure from that previously published (Henriksen et al., 2005), as follows. To a 100 ml round-bottom flask under an argon atmosphere were added N-benzyl-4-piperidone (1.89 g, 10 mmol), aniline (3.7 g, 40 mmol), KCN (2.6 g, 40 mmol) and dry dichloromethane (40 ml). The reaction mixture was cooled to 0° C and stirred under argon for 20 minutes. Acetic acid (1.8 g, 30 mmol) was added to the reaction mixture over a period of 10 minutes and the final mixture heated at 50° C for 24 h. After cooling to room temperature the reaction mixture was poured into crushed ice (50 g), neutralized with 25% aqueous NaOH and the pH of the mixture was adjusted to about 10 using 40% aqueous K2CO3. The organic phase was collected and the water layer was extracted with dichloromethane (2 x 25 ml). The organic extracts were dried over anhydrous sodium bicarbonate and concentrated under reduced pressure to give a yellow solid. The yellow crystals were purified by re-crystallization from dichloromethane/hexane to give 2.6 g (89.5%) yield of colorless crystals. Spectroscopic analysis, 1H NMR (250 MHz, CDCl3): 1.92 (td, \( J_1 = 3.6 \text{ Hz}, J_2 = 10.8 \text{ Hz}, 2H, CH_2 \)), 2.29–2.53 (m, 4H, CH_2), 2.79–2.85 (m, 2H, CH_2), 3.56 (s, 2H, CH_2Ph), 3.64 (s, 1H, NH), 6.88–6.95 (m, 3H, ArH), 7.20–7.33 (m, 7H, ArH). 13C NMR (CDCl_3):
36.09, 49.27, 59.06, 62.58, 117.78, 120.93, 127.26, 128.96, 129.00, 129.31, 134.02, 138.00, 143.29. MS MALDI-TOF m/z 290.9 (M⁺).

S3. Refinement

H atoms on C were placed in idealized positions with C—H distances 0.95 - 0.99 Å and thereafter treated as riding. Coordinates of the N—H hydrogen atom were refined. \( U_{iso} \) for H was assigned as 1.2 times \( U_{eq} \) of the attached atoms.

Figure 1

Ellipsoids at the 50% level, with H atoms having arbitrary radius.

4-Anilino-1-benzylpiperidine-4-carbonitrile

Crystal data

\[ \text{C}_{19}\text{H}_{21}\text{N}_{3} \]

\( M_r = 291.39 \)

Monoclinic, \( P2_1/n \)

Hall symbol: -P 2yn

\( a = 9.7718 (13) \, \text{Å} \)

\( b = 10.0415 (14) \, \text{Å} \)

\( c = 15.9519 (15) \, \text{Å} \)

\( \beta = 94.532 (9)^\circ \)

\( V = 1560.4 (3) \, \text{Å}^3 \)

\( Z = 4 \)

Data collection

Nonius KappaCCD

diffractometer with an Oxford Cryosystems

Cryostream cooler

Radiation source: fine-focus sealed tube

Graphite monochromator

\( \omega \) scans with \( \kappa \) offsets

24180 measured reflections

6842 independent reflections

5189 reflections with \( I > 2\sigma (I) \)

\( R_{int} = 0.025 \)

\( \theta_{max} = 35.0^\circ, \theta_{min} = 2.5^\circ \)

\( h = -15 \rightarrow 15 \)

\( k = -12 \rightarrow 16 \)

\( l = -25 \rightarrow 25 \)

\( F(000) = 624 \)

\( D_\text{x} = 1.240 \, \text{Mg} \, \text{m}^{-3} \)

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

Cell parameters from 5228 reflections

Fragment, colorless

0.37 × 0.25 × 0.23 mm

Acta Cryst. (2008). E64, o839
**Refinement**

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.124$

$S = 1.04$

6842 reflections

203 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0605P)^2 + 0.3181P]$

where $P = (F^2 + 2F_c^2)/3$

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

$\Delta\rho_{\text{max}} = 0.49 \text{ e Å}^{-3}$

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

Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^e = kF_c[1+0.001xF_c^2\lambda^3/\sin(2\theta)]^{1/4}$

Extinction coefficient: 0.0081 (18)

**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 $F^2 > \alpha(F^2)$ 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 ($Å^2$)**

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<td>N2 0.68233 (8)</td>
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<td>H2N 0.6447 (13)</td>
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<td>N3 0.86941 (8)</td>
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<td>0.44146 (9)</td>
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<tr>
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### Atomic displacement parameters (Å²)

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<td>$-0.0008$ (2)</td>
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<td>0.0015 (2)</td>
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### Geometric parameters (Å, °)

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<th>Distance</th>
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<td>C16—C17</td>
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<tr>
<td>C6—H6B</td>
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<table>
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<th>Distance</th>
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</tr>
<tr>
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<td>110.34 (6)</td>
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<tr>
<td>C5—N1—C6</td>
<td>110.76 (7)</td>
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C19—C3—C4 110.37 (7)   C14—C13—C18 118.43 (7)
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C5—C4—C3 112.06 (6)   C15—C14—H14 120.0
C5—C4—H4A 109.2   C13—C14—H14 120.0
C3—C4—H4A 109.2   C16—C15—C14 121.12 (8)
C5—C4—H4B 109.2   C16—C15—H15 119.4
C3—C4—H4B 109.2   C14—C15—H15 119.4
H4A—C4—H4B 107.9   C15—C16—C17 118.91 (7)
N1—C5—C4 110.80 (7)   C15—C16—H16 120.5
N1—C5—H5A 109.5   C17—C16—H16 120.5
C4—C5—H5B 109.5   C18—C17—C16 120.59 (8)
C4—C5—H5B 109.5   C18—C17—H17 119.7
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N1—C6—C7 111.21 (7)   C17—C18—C13 120.88 (8)
N1—C6—H6A 109.4   C17—C18—H18 119.6
C7—C6—H6A 109.4   C13—C18—H18 119.6
N1—C6—H6B 109.4   N3—C19—C3 177.73 (8)
N1—C6—H6B 109.4

C5—N1—C1—C2 60.63 (9)   C12—C7—C8—C9 179.10 (8)
C6—N1—C1—C2 −176.75 (6)   C6—C7—C8—C9 0.10 (13)
N1—C1—C2—C3 −58.68 (9)   C7—C8—C9—C10 1.61 (14)
C13—N2—C3—C19 63.33 (10)   C8—C9—C10—C11 1.61 (14)
C13—N2—C3—C2 179.19 (8)   C9—C10—C11—C12 −1.57 (14)
C13—N2—C3—C4 −61.08 (11)   C8—C7—C12—C11 1.86 (13)
C1—C2—C3—N2 177.84 (6)   C6—C7—C12—C11 −179.09 (8)
C1—C2—C3—C19 −64.94 (8)   C10—C11—C12—C7 −0.17 (14)
C1—C2—C3—C4 53.51 (8)   C3—N2—C13—C14 −9.65 (13)
N2—C3—C4—C5 60.63 (9)   C3—N2—C13—C18 −177.6 (6)
C6—N1—C1—C2 −176.75 (6)   C3—N2—C13—C18 172.56 (8)
C2—C3—C4—C5 −53.26 (8)   C6—C7—C12—C11 1.86 (13)
C1—N1—C5—C4 −59.98 (8)   C13—C14—C15—C16 0.09 (12)
C6—N1—C5—C4 177.65 (6)   C13—C14—C15—C16 0.65 (12)
C3—C4—C5—N1 57.77 (8)   C14—C15—C16—C17 −0.77 (12)
C1—N1—C6—C7 69.20 (8)   C15—C16—C17—C18 0.15 (12)
C5—N1—C6—C7 177.65 (6)   C16—C17—C18—C13 0.59 (12)
N1—C6—C7—C12 −116.76 (9)   C2—C3—C4—C5 −53.26 (8)
N1—C6—C7—C8 62.28 (10)   N2—C3—C4—C5 60.63 (9)

Hydrogen-bond geometry (Å, °)

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Symmetry code: (i) −x+3/2, y+1/2, −z+3/2.