Crystal Structure of *N,N'*-Bis(4-hexyloxybenzoyl)piperazine

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The structure of *N,N'*-bis(4-hexyloxybenzoyl)piperazine was determined by X-ray crystallography. It crystallizes in the space group $P2_1/c$ (#14) with cell parameters $a = 27.234(7)\text{\AA}$, $b = 7.496(2)\text{\AA}$, $c = 6.820(2)\text{\AA}$, $\beta = 93.80(2)^\circ$, $Z = 2$, and $V = 1389.3(6)\text{\AA}^3$. The molecule sits on a center of symmetry, such that the two benzoyl groups are in an *anti* conformation with respect to one another across the piperazine ring. Intermolecular C–H $\cdots$ O and C–H $\cdots\pi$ interactions were observed in the crystal lattice.

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Self-assembled systems are of great significance, particularly for their potential applications to nanomaterials, such as liquid crystals and gelators.^{1,2} Numerous studies have been dedicated to structural investigations and determinations of the molecular-aggregation mechanisms. Materials containing a piperazine component have been useful in many fields, such as anthelmintic, drugs, plastics, resins, pesticides, brake fluid, and liquid crystals. The structures of *N,N'*-dibenzoylpiperazine,³ *N,N'*-bis(4-chlorobenzoyl)piperazine,⁴ and *N,N'*-bis(2,3,4,5-tetrafluorobenzoyl)piperazine⁵ have been reported. However, the synthesis and crystal structure of *N,N'*-bis(4-hexyloxybenzoyl)piperazine (**1**) (Fig. 1) has not. We now present the structures of **1** with the aim to contribute to a deeper understanding of the substituent effect at the 4-position of *N,N'*-dibenzoylpiperazine concerning the structure and crystal packing.

1 was prepared by the condensation of piperazine and 4-(hexyloxy)benzoyl chloride in a DMAP (*N,N*-dimethyl-4-aminopyridine) and pyridine solution. **1**: m.p. 154°C, colorless crystals, ¹H NMR (CDCl₃) δ 0.92 (6H, t, $J = 7.0$ Hz), 1.32 – 1.50 (12H, m), 1.79 (4H, quint, $J = 7.0$ Hz), 3.65 (8H, brs), 3.98 (4H, t, $J = 7.0$ Hz), 6.90 (4H, d, $J = 8.7$ Hz), 7.38 (2H, d, $J = 8.7$ Hz). ¹³C NMR (CDCl₃) δ 14.0 (2C), 22.5 (2C), 25.6 (4C),

29.0 (2C), 31.5 (2C), 68.1 (4C), 114.3 (4C), 126.8 (2C), 129.2 (4C), 160.6 (2C), 170.7 (2C). FAB-MS: m/z , 495 (M+H⁺). Found: C, 72.73; H, 8.57; N, 5.60%. Calcd for C₃₀H₄₂N₂O₄: C, 72.84; H, 8.56; N, 5.66%. Single crystals of **1** were grown in a mixture of chloroform–ethanol (1:1 v/v) at room temperature. The data collection and refinement parameters are listed in Table 1. The H atoms were positioned with the idealized geometry, and were refined to be isotropic ($U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$

Table 1 Crystal and experimental data

Chemical formula: C ₃₀ H ₄₂ N ₂ O ₄	
Formula weight = 494.67	
$T = 123\text{K}$	
Crystal system: Monoclinic	Space group: $P2_1/c$
$a = 27.234(7)\text{\AA}$	
$b = 7.496(2)\text{\AA}$	$\beta = 93.80(2)^\circ$
$c = 6.820(2)\text{\AA}$	
$V = 1389.3(6)\text{\AA}^3$	$Z = 2$
$D_x = 1.182\text{ g/cm}^3$	
Radiation: Cu K_α ($\lambda = 1.54187\text{\AA}$) graphite monochromated	
$\mu(\text{Cu } K_\alpha) = 6.181\text{ cm}^{-1}$	$F(0\ 0\ 0) = 536.00$
Crystal size = $0.200 \times 0.180 \times 0.060\text{ mm}^3$	
No. of reflections collected = 8286	
No. of independent reflections = 2466	
θ range for data collection: 3.25° to 68.25°	
Data/Restraints/Parameters = 2466/0/164	
R indices [$I \geq 2\sigma(I)$]: $R1 = 0.0633$	
R indices (all data): $R1 = 0.1208$, $wR2 = 0.1337$	
Goodness-of-fit on $F^2 = 0.829$	
$(\Delta/\sigma)_{\text{max}} = 0.000$	
$(\Delta\rho)_{\text{max}} = 0.35\text{ e}\text{\AA}^{-3}$	$(\Delta\rho)_{\text{min}} = -0.22\text{ e}\text{\AA}^{-3}$
Measurement: Rigaku R-Axis RAPID diffractometer	
Data collection & cell refinement program: CrystalClear	
Data reduction program: CrystalStructure 4.0	
Structure solving program: SIR2008	
Structure refinement program: CRYSTALS	
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Fig. 1 Chemical diagram of the title compound (**1**).

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Table 2 Selected bond distances, bond angles, and torsion angles (Å, °)

N1-C7	1.371(4)	O1-C7	1.234(4)
C1-C7	1.501(4)	O2-C4	1.375(4)
O2-C10	1.445(3)	C7-N1-C8	119.7(3)
C7-N1-C9	126.5(3)	C8-N1-C9	112.4(2)
C4-O2-C10-C11	169.41(17)	C10-O2-C4-C3	-169.22(18)
C10-O2-C4-C5	9.7(4)	C8-N1-C9-C8 ⁱ	-57.5(3)
C2-C12-C7-O1	-46.2(4)	C2-C1-C7-N1	135.0(3)
C6-C1-C2-O1	128.9(3)	C6-C1-C7-N1	-49.9(4)
N1-C8-C9 ⁱ -N1 ⁱ	-55.9(3)	O2-C10-C11-C12	179.49(16)
C10-C11-C12-C13	-176.79(17)	C11-C12-C13-C14	179.91(17)
C12-C13-C14-C15	179.75(18)

Fig. 2 ORTEP structure of **1**, showing 50% probability ellipsoids. Symmetry code: (i) $1-x, -y, 1-z$.

(C)) using a riding model with C-H = 0.95 Å for aromatic H atoms, C-H = 0.99 Å for methylene H atoms, and C-H = 0.98 Å for methyl H atoms. The selected bond distances and torsion angles are collected in Table 2.

An ORTEP drawing of molecule of **1** is shown in Fig. 2. The molecule of **1** sits on a center of symmetry with the two benzoyl groups in an *anti* conformation with a piperazine ring that has a normal chair conformation. Each paraffin chain has an all-*trans* conformation, thus forming an almost planar zigzag chain; the deviation of the atom from the least-squares planes, defined by atoms C10/C11/C12/C13/C14/C15, is within 0.0031(2)Å. The sum [358.6(3)°] of the angles around atom N1 and the N1-C7 bond length are similar to those [360.0(1)°, 1.354(18)Å] of *N,N'*-dibenzoylpiperazine.³ The N1-C7 bond length is in accordance with the Nsp^2-Csp^2 (N planar) in acyclic amides [1.346 Å].⁶ The two phenyl rings [C1/C2/C3/C4/C5/C6 and the related by the inversion center C1ⁱ/C2ⁱ/C3ⁱ/C4ⁱ/C5ⁱ/C6ⁱ (symmetry code (i) $1-x, -y, 1-z$)] are parallel. The angle between the phenyl (defined by C1/C2/C3/C4/C5/C6) and the amide plane (defined by O1/C7/N1) is 48.0(1)°, which is close to that [54°]³ of *N,N'*-dibenzoylpiperazine. The molecular length of the compound is 27.692(3)Å for the C15...C15ⁱ distance (symmetry code: (i) $1-x, -y, 1-z$). Compound (**1**) has a tilted layer structure (Fig. 3). Intermolecular C-H...O and C-H... π interactions are observed in the crystal structure of **1** (Table 3, Fig. 4), with distances typical of these types of interactions. C-H...O = 2.5 – 2.7 Å and C-H... π = 2.8 – 3.1 Å.^{2,7,8} These intermolecular C-H...O and CH... π interactions help to stabilize the crystal packing.

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Fig. 3 Packing diagram of **1** viewed down the *b* axis.Table 3 Hydrogen-bond geometry (Å, °) of **1**

D-H...A	D-H	H...A	D...A	D-H...A
C5-H8...Cg ⁱⁱ	0.950	2.961	3.789(4)	146
C6-H12...O1 ⁱⁱ	0.950	2.472	3.303(4)	146
C8-H4B...O1 ⁱⁱⁱ	0.990	2.554	3.118(3)	116
C9-H13B...O1 ^{iv}	0.990	2.654	3.395(4)	132

Symmetry codes: (ii) $x, -y-1/2, z-1/2$, (iii) $1-x, -y, 2-z$, (iv) $x, 1/2-y, z-1/2$.

Fig. 4 Intermolecular C-H...O and C-H... π interactions of **1**. Symmetry codes: (i) $1-x, -y, 1-z$, (ii) $x, -y-1/2, z-1/2$, (iii) $1-x, -y, 2-z$, (iv) $x, 1/2-y, z-1/2$.

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