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N-(2-Aminobenzyl)-*N,N*-bis(quinolin-2-ylmethyl)amine

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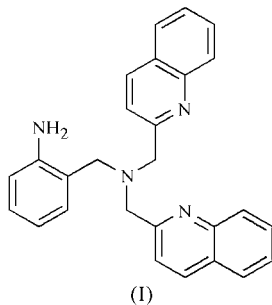
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The title new diquinaldine derivative, C₂₇H₂₄N₄, forms molecular assemblies organized by intermolecular quinoline π - π stacking [3.356 (3) and 3.440 (3) Å] and both inter- and intramolecular N—H...N hydrogen bonds [3.039 (3)–3.104 (3) Å and 129 (2)–172 (2)°]. The combination of such interactions provides readily definable contacts that propagate along each crystallographic axis.

Comment

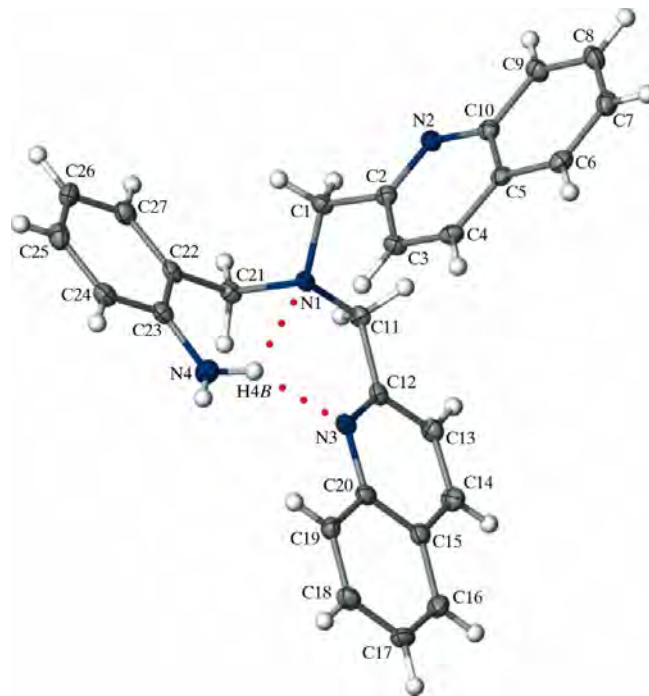
Different types of arene–arene non-covalent interactions lead to fascinating molecular architectures and supramolecular structure in solids. We have recently shown by NMR spectroscopy (Mitra, Seaton, Assarpour & Williamson *et al.*, 1998; Mitra, Seaton, Capitani & Assarpour, 1998) that such interactions can also be a prevalent theme in solutions. In our continuing study of π - π interactions and their effect on ¹H NMR spectra, we wanted to study the consequence of interactions between aromatic and heteroaromatic groups. To this end, we synthesized a molecule that contains both arene and



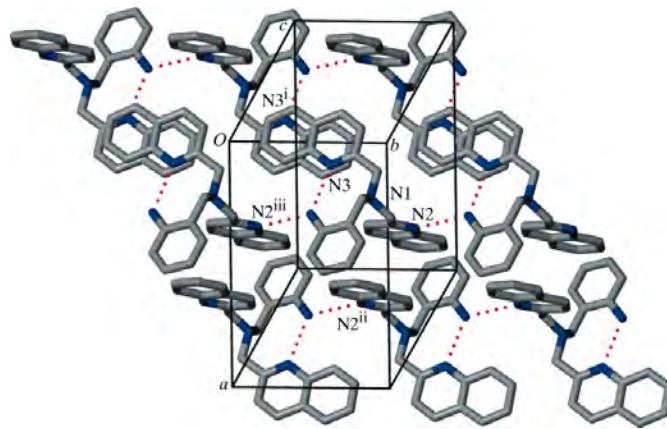
quinoline components. 2-Aminobenzylamine is an interesting molecule that consists of two amino groups that have different reactivity profiles. Selective N-alkylation of the benzylic amine with two equivalents of 2-(bromomethyl)quinoline gave the title compound, (I).

The molecular conformation of (I), as it exists in the crystal, is influenced by several close intramolecular contacts. As shown in Fig. 1, the anilino H4B atom participates in a bifurcated contact with nearby tertiary amino (N1) and quinoline (N3) acceptor groups (Table 1). This hydrogen-bond motif results in the anilino and quinoline fragments adopting a roughly planar alignment with an interplanar angle of 16.66 (8)°. Selected geometric parameters are given in Table 2.

Inspection of the crystal structure reveals translationally related molecules linked by N—H...N hydrogen bonds to

**Figure 1**

The molecular structure and labeling scheme of (I) (50% probability displacement ellipsoids), showing the intramolecular bifurcated interaction (dotted lines).

**Figure 2**

A view of the packing of (I), showing the catemeric hydrogen-bond network and π -stacking of the quinoline fragments. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $-x + 1, -y + 2, -z$; (iii) $x, y - 1, z$.]

form a catemeric motif along the *b* axis (Fig. 2). These molecular assemblies, described by *C*(9) graph-set notation (Bernstein *et al.*, 1995), result from the association of neighboring anilino (H4A) and quinoline (N2) groups. Another noteworthy feature of this structure is the contribution of π - π interactions to the crystal packing. As shown in Fig. 2, each of the quinoline groups forms centrosymmetric dimeric motifs [for example quinoline(N3)-quinoline(N3ⁱ) = 3.356 (3) Å and quinoline(N2)-quinoline(N2ⁱⁱ) = 3.440 (3) Å; symmetry codes as in Fig. 2] that link the hydrogen-bonded molecular chains along the *a* and *c* axes. Since molecules of (I) contain two nearly orthogonally positioned quinoline fragments [the interplanar angle is 81.75 (4)°], the combination of such π - π interactions and hydrogen bonds provides readily definable contacts that contribute to the overall three-dimensional organization.

Experimental

2-(Bromomethyl)quinoline (0.222 g, 1.0 mmol) was reacted with 2-aminobenzylamine (0.0061 g, 0.5 mmol) in CH₃CN (5 ml) in the presence of anhydrous K₂CO₃ (0.152 g, 1.1 mmol) under N₂ at room temperature for 16 h. The reaction mixture was concentrated under reduced pressure and directly chromatographed by flash column chromatography (SiO₂ gel) using a solvent gradient from 5 to 10% MeOH/CH₂Cl₂. Fractions containing the pure product were combined, concentrated under reduced pressure and recrystallized from CHCl₃/*n*-heptane to give (I) (0.110 g, 55% yield) as a colorless powder (m.p. 473–476 K). UV-Vis [MeOH, λ_{max} , nm, (ϵ): 232 (56200), 303 (6570), 316 (6940). IR (KBr, cm⁻¹): 3351, 3186, 1602, 1565, 743. ¹H NMR (0.005 M in CDCl₃): δ 3.82 (*s*, 2H, benzyl-CH₂), 4.01 (*s*, 4H, quinolyl-CH₂), 5.20 (*br s*, 2H, NH₂), 6.64 (*t*, *J* = 7.5 Hz, H-5'), 6.66 (*d*, *J* = 6.9 Hz, 1H, H-3'), 7.07 (*t*, *J* = 7.5 Hz, 1H, H-4'), 7.11 (*d*, *J* = 7.5 Hz, 1H, H-6'), 7.50 (*m*, 2H, H-6), 7.51 (*d*, *J* = 8.1 Hz, 2H, H-3'), 7.69 (*ddd*, 2H, *J* = 8.3, 6.9 and 1.4 Hz, 2H, H-7), 7.75 (*d*, *J* = 8.1 Hz, 2H, H-5), 8.04 (*d*, *J* = 8.1 Hz, 2H, H-4), 8.06 (*d*, *J* = 8.3 Hz, 2H, H-8). ¹³C NMR (CDCl₃): δ 159.2 (C2), 147.6 (C8a), 147.0 (C2'), 136.3 (C4), 131.5 (C6'), 129.4 (C7), 128.9 (C8), 128.6 (C4'), 127.5 (C5), 127.3 (C4a), 126.2 (C6), 122.2 (C1'), 121.3 (C3), 117.1 (C5'), 115.4 (C3'), 60.9 (CH₂), 58.4 (CH₂').

Table 1
Hydrogen-bond geometry (Å, °).

<i>D</i> -H... <i>A</i>	<i>D</i> -H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> -H... <i>A</i>
N4-H4B...N3	0.95 (3)	2.17 (3)	3.039 (3)	152 (2)
N4-H4B...N1	0.95 (3)	2.42 (3)	3.104 (3)	129 (2)
N4-H4A...N2 ⁱⁱⁱ	0.96 (3)	2.15 (3)	3.100 (2)	172 (2)

Symmetry code: (iii) *x*, *y* - 1, *z*.

Table 2
Selected geometric parameters (Å, °).

N1-C1	1.457 (3)	N1-C21	1.469 (2)
N1-C11	1.458 (3)	N4-C23	1.370 (3)
C1-N1-C11	111.7 (2)	C11-N1-C21	111.5 (2)
C1-N1-C21	112.1 (2)		

Crystal data

C ₂₇ H ₂₄ N ₄	<i>Z</i> = 4
<i>M_r</i> = 404.50	<i>D_x</i> = 1.282 Mg m ⁻³
Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Mo <i>K</i> α radiation
<i>a</i> = 12.4071 (16) Å	μ = 0.08 mm ⁻¹
<i>b</i> = 7.9834 (10) Å	<i>T</i> = 100 (2) K
<i>c</i> = 21.376 (3) Å	Transparent needle, colorless
β = 98.041 (2)°	0.38 × 0.04 × 0.03 mm
<i>V</i> = 2096.5 (5) Å ³	

Data collection

Bruker APEX-II CCD area-detector diffractometer	14852 measured reflections
φ and ω scans	4699 independent reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Bruker, 2000)	3089 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T_{min}</i> = 0.971, <i>T_{max}</i> = 0.998	<i>R_{int}</i> = 0.058
	θ_{max} = 27.5°

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0569P)^2 + 0.5447P]$
$R[F^2 > 2\sigma(F^2)] = 0.057$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.134$	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.02	$\Delta\rho_{\text{max}} = 0.40 \text{ e } \text{Å}^{-3}$
4699 reflections	$\Delta\rho_{\text{min}} = -0.23 \text{ e } \text{Å}^{-3}$
288 parameters	
H atoms treated by a mixture of independent and constrained refinement	

The anilino H atoms (H4A and H4B) were located in a difference density map and their parameters were refined freely. The remaining H atoms were treated as riding, with C-H distances of 0.95 (aromatic) and 0.99 Å (CH₂) [*U*_{iso}(H) = 1.2*U*_{eq}(C)].

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 2002) and *XPREP* (Bruker, 2001); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *X-SEED*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3012). Services for accessing these data are described at the back of the journal.

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