organic compounds

N,N'-Bis(2-quinolylcarbonyl)hydrazine

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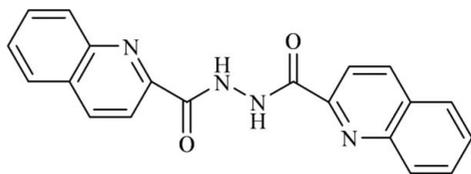Correspondence e-mail: zhudr@njut.edu.cn

The title compound, $C_{20}H_{14}N_4O_2$, crystallizes in the orthorhombic system with a crystallographic twofold axis through the N—N bond. The molecule is non-planar and the dihedral angle between two amide groups is 74.9 (2)°. An intramolecular N—H···N hydrogen bond is present. In the crystal, the molecules are packed in chains running along the c axis through intermolecular N—H···O hydrogen bonds. These chains are further stabilized by intermolecular C—H···O hydrogen bonds and C—H···π interactions leading to the formation of a three-dimensional network.

Related literature

For general background to the chemistry of N,N'-diacyl-hydrazines, see: Zhao & Bruke (1997); Knödler et al. (2004); Bernhardt et al. (2005). For the syntheses and structures of related compounds, see: Jasinskas et al. (1975); Shao et al. (1999); Xu et al. (2006); Zheng et al. (2007); Shanmuga Sundara Raj et al. (2000). For the synthesis of the title compound, see: Xie et al. (2009). For hydrogen-bond motifs, see: Bernstein et al. (1995);

Experimental

Crystal data

$C_{20}H_{14}N_4O_2$	a = 11.649 (4) Å
M_r = 342.35	b = 17.023 (6) Å
Orthorhombic, $Pccn$	c = 8.349 (3) Å

V = 1655.6 (10) Å³	μ = 0.09 mm⁻¹
Z = 4	T = 296 K
Mo $K\alpha$ radiation	$0.26 \times 0.12 \times 0.08$ mm

Data collection

Bruker APEXII CCD diffractometer	10346 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2005)	1629 independent reflections
T_{min} = 0.976, T_{max} = 0.993	816 reflections with $I > 2\sigma(I)$
	R_{int} = 0.082

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046	119 parameters
$wR(F^2)$ = 0.115	H-atom parameters constrained
S = 0.95	$\Delta\rho_{max}$ = 0.17 e Å⁻³
1629 reflections	$\Delta\rho_{min}$ = −0.19 e Å⁻³

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···N1	0.86	2.31	2.689 (2)	107
N2—H2A···O1ⁱⁱ	0.86	2.35	2.978 (3)	130
C5—H5A···O1ⁱⁱⁱ	0.93	2.45	3.177 (3)	135
C8—H8A···Cg1ⁱᵛ	0.93	2.64	3.449	146

Symmetry codes: (ii) $-x + \frac{3}{2}, y, z - \frac{1}{2}$; (iii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x - \frac{1}{2}, y, z - \frac{3}{2}$. $Cg1$ is the centroid of the N1/C1–C4/C9 ring.

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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supporting information

N,*N*′-Bis(2-quinolylcarbonyl)hydrazine

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S1. Comment

(Un)symmetrical *N*,*N*′-diacylhydrazines are of interest because they are the basic structural components in heterocyclic chemistry and may be used as bridging ligands in coordination chemistry (Zhao & Bruke, 1997; Knödler *et al.*, 2004; Bernhardt *et al.*, 2005). We have reported the structure of *N*,*N*′-bis(2-picolinoyl)hydrazine (Shao *et al.*, 1999). As a continuation of our investigations of the structure of *N*,*N*′-diacylhydrazines and their derivatives, herein, we report the crystal structure of the title compound. It was first prepared by aroylation of 2-quinolylcarbonylhydrazine with 2-quinolinecarbonyl chloride in dry pyridine (Jasinskas *et al.*, 1975).

The X-ray analysis of the title compound (Fig. 1) indicates that the molecule is non-planar. The dihedral angle between the quinolyl ring and the amide group is 15.3 (2)° and that between the amide groups is 74.9 (2)°. Similarly to *N*,*N*′-bis(2-picolinoyl)hydrazine, the asymmetric unit contains half the molecule and the other half is related by a crystallographic twofold axis passing through the N2—N2^i bond [symmetry code: (i) 3/2 - *x*, 1/2 - *y*, *z*]. The bond lengths and angles (Table 1) in the structure are in the normal ranges (Xu *et al.*, 2006; Zheng *et al.*, 2007). The C10—N2—N2^i—C10^i torsion angle is -87.7 (2)°. The two carbonyl groups and the H atoms of the N—N bond are in a *trans* orientation with respect to each other. This conformation is due mainly to the intramolecular N—H⋯N hydrogen bonds.

In the crystal (Fig. 2), each molecule is connected to another by a pair of intermolecular N—H⋯O hydrogen bonds (Table 2) between the amide H atoms and the O atoms of neighbouring carbonyl groups to form a ten-membered ring with the graph-set motif $C4R^2_2(10)$ (Bernstein *et al.*, 1995). The same feature is also found in *N*,*N*′-bis(2-picolinoyl)hydrazine and 1,2-dibenzoylhydrazine (Shanmuga Sundara Raj *et al.*, 2000). Due to presence of these intermolecular N—H⋯O hydrogen bonds, the molecules are packed into chains running along the *c* axis. These chains are further stabilized by intermolecular C—H⋯O hydrogen bonds and C—H⋯π interactions (Table 2) leading to the formation of a three-dimensional network.

S2. Experimental

The title compound was obtained unexpectedly in the synthesis of 3-methyl-4-(*p*-methylphenyl)-5-(2-quinolyl)-1,2,4-triazole by the reaction of *N*-formyl-*N*′-(2-quinolylcarbonyl)hydrazine (1 mmol) with 4,4′-dimethylphenyl-phosphazoanilide (1 mmol) in *N*,*N*-dimethylaniline (20 ml) at 463–473 K (Xie *et al.*, 2009). It also can be prepared by literature method (Jasinskas *et al.*, 1975). Diffraction quality crystals were obtained by recrystallization from ethanol (yield 31%).

S3. Refinement

All H atoms were located in a difference Fourier map and allowed to ride on their parent atoms at distances of 0.96Å (aromatic), 0.93Å (pyridyl), and with U_{iso}(H) values of 1.2 or 1.5 times of U_{eq}(C).
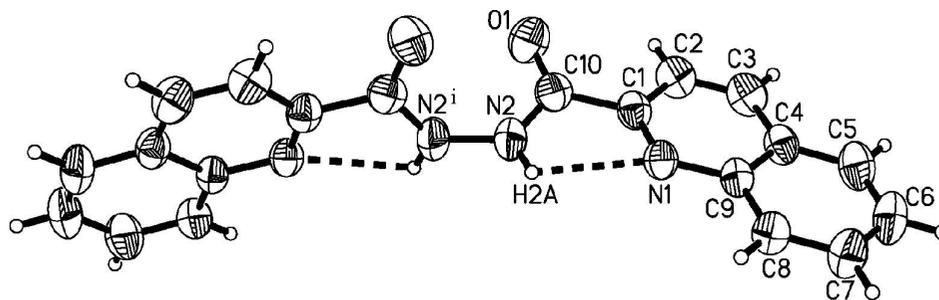
Figure 1

The structure of the title compound showing 50% probability displacement ellipsoids and atom-numbering scheme [symmetry code: (i) 3/2 - x, 1/2 - y, z].
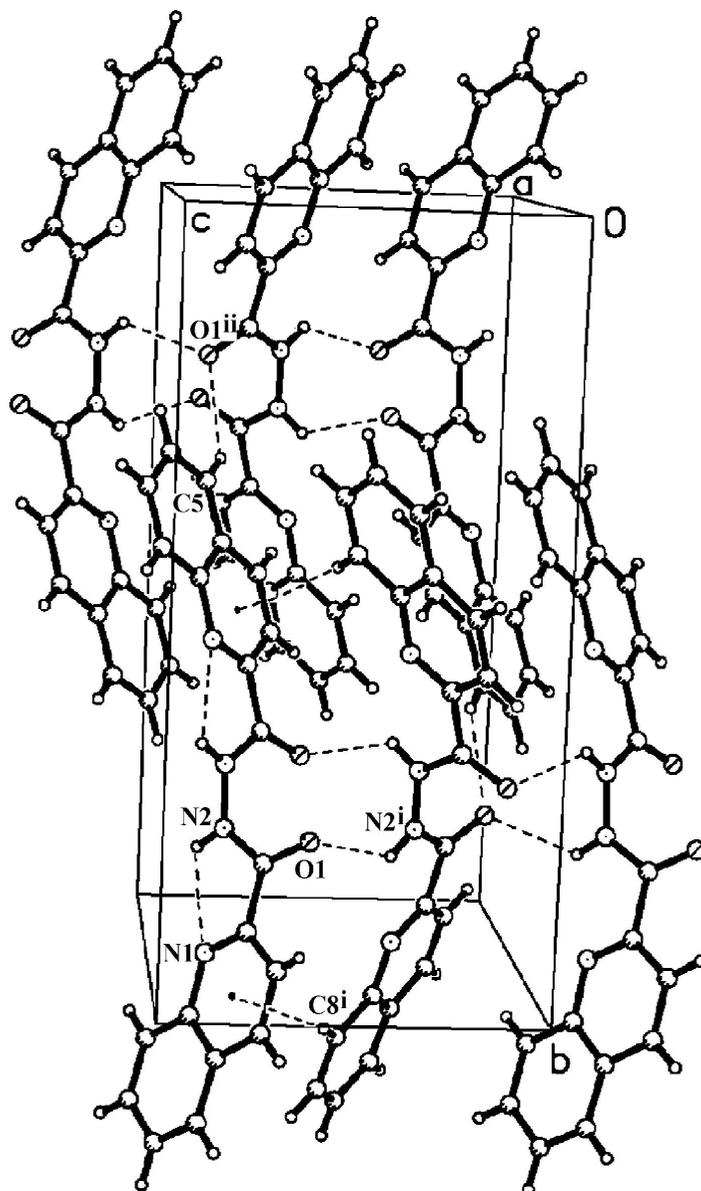
Figure 2

The three-dimensional network formed *via* hydrogen bonds (dashed lines) and C—H⋯π interactions [symmetry code: (i) 1 - *x*, 1/2 + *y*, 1/2 - *z*].

N,N′-Bis(2-quinolylcarbonyl)hydrazine

Crystal data

$C_{20}H_{14}N_4O_2$	$F(000) = 712$
$M_r = 342.35$	$D_x = 1.374$ Mg m^{-3}
Orthorhombic, *Pccn*	Mo *Kα* radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ab 2ac	Cell parameters from 28 reflections
$a = 11.649$ (4) Å	$\theta = 2.1–26.6°$
$b = 17.023$ (6) Å	$\mu = 0.09$ mm^{-1}
$c = 8.349$ (3) Å	$T = 296$ K
$V = 1655.6$ (10) Å^3	Block, colourless
$Z = 4$	$0.26 \times 0.12 \times 0.08$ mm

Data collection

Bruker APEXII CCD diffractometer	10346 measured reflections
Radiation source: fine-focus sealed tube	1629 independent reflections
Graphite monochromator	816 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.082$
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$\theta_{max} = 26.0°$, $\theta_{min} = 2.1°$
	$h = -14 \rightarrow 14$
	$k = -21 \rightarrow 18$
$T_{min} = 0.976$, $T_{max} = 0.993$	$l = -9 \rightarrow 10$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.046$	H-atom parameters constrained
$wR(F^2) = 0.115$	$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2]$
$S = 0.95$	where $P = (F_o^2 + 2F_c^2)/3$
1629 reflections	$(\Delta/\sigma)_{max} < 0.001$
119 parameters	$\Delta\rho_{max} = 0.17$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.19$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc*=kFc[1+0.001xFc²λ³/sin(2θ)]$^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.011 (2)

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 $F^2 > \sigma(F^2)$ 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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
O1	0.61559 (14)	0.28662 (9)	0.3812 (2)	0.0651 (5)
N1	0.69622 (14)	0.44375 (10)	0.1318 (2)	0.0424 (5)
N2	0.73777 (18)	0.28973 (9)	0.1733 (2)	0.0605 (6)
H2A	0.7745	0.3197	0.1080	0.073*
C1	0.62868 (17)	0.40522 (13)	0.2314 (3)	0.0432 (6)
C2	0.52811 (18)	0.43630 (14)	0.2994 (3)	0.0520 (7)
H2B	0.4841	0.4063	0.3694	0.062*
C3	0.49611 (18)	0.51056 (15)	0.2615 (3)	0.0549 (7)
H3A	0.4290	0.5317	0.3037	0.066*
C4	0.56521 (18)	0.55552 (12)	0.1576 (3)	0.0450 (6)
C5	0.5394 (2)	0.63312 (13)	0.1127 (3)	0.0599 (7)
H5A	0.4739	0.6573	0.1530	0.072*
C6	0.6091 (2)	0.67300 (14)	0.0114 (3)	0.0663 (8)
H6A	0.5908	0.7243	−0.0172	0.080*
C7	0.7083 (2)	0.63781 (14)	−0.0508 (3)	0.0615 (7)

H7A	0.7552	0.6658	−0.1205	0.074*
C8	0.73620 (19)	0.56297 (13)	−0.0097 (3)	0.0498 (6)
H8A	0.8025	0.5401	−0.0509	0.060*
C9	0.66544 (17)	0.51985 (12)	0.0947 (3)	0.0401 (6)
C10	0.65956 (19)	0.32223 (14)	0.2702 (3)	0.0471 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0692 (11)	0.0517 (10)	0.0743 (13)	−0.0141 (9)	0.0059 (10)	0.0116 (10)
N1	0.0396 (11)	0.0382 (11)	0.0495 (12)	−0.0009 (8)	−0.0004 (9)	−0.0006 (9)
N2	0.0861 (15)	0.0349 (10)	0.0605 (14)	0.0080 (12)	0.0094 (12)	0.0031 (10)
C1	0.0407 (13)	0.0388 (13)	0.0501 (15)	−0.0023 (11)	−0.0059 (11)	−0.0051 (11)
C2	0.0404 (14)	0.0547 (17)	0.0610 (17)	−0.0066 (12)	0.0063 (12)	−0.0029 (13)
C3	0.0387 (13)	0.0605 (18)	0.0657 (17)	0.0031 (12)	0.0043 (12)	−0.0063 (14)
C4	0.0379 (13)	0.0428 (14)	0.0543 (16)	0.0046 (10)	−0.0049 (11)	−0.0065 (12)
C5	0.0508 (15)	0.0484 (16)	0.080 (2)	0.0138 (13)	−0.0026 (14)	−0.0058 (15)
C6	0.0691 (18)	0.0403 (15)	0.089 (2)	0.0079 (13)	−0.0075 (16)	0.0060 (15)
C7	0.0599 (16)	0.0489 (16)	0.076 (2)	−0.0021 (13)	0.0032 (14)	0.0091 (14)
C8	0.0459 (14)	0.0458 (15)	0.0577 (16)	0.0004 (11)	0.0014 (11)	0.0027 (12)
C9	0.0362 (12)	0.0358 (12)	0.0483 (14)	0.0012 (10)	−0.0064 (11)	−0.0033 (11)
C10	0.0489 (14)	0.0433 (15)	0.0491 (15)	−0.0100 (12)	−0.0030 (12)	−0.0013 (12)

Geometric parameters (Å, º)

O1—C10	1.220 (3)	C3—H3A	0.9300
N1—C1	1.319 (3)	C4—C5	1.406 (3)
N1—C9	1.379 (2)	C4—C9	1.417 (3)
N2—C10	1.338 (3)	C5—C6	1.354 (3)
N2—N2^i	1.382 (3)	C5—H5A	0.9300
N2—H2A	0.8600	C6—C7	1.401 (3)
C1—C2	1.405 (3)	C6—H6A	0.9300
C1—C10	1.493 (3)	C7—C8	1.359 (3)
C2—C3	1.355 (3)	C7—H7A	0.9300
C2—H2B	0.9300	C8—C9	1.406 (3)
C3—C4	1.409 (3)	C8—H8A	0.9300
C1—N1—C9	116.98 (18)	C6—C5—H5A	119.7
C10—N2—N2^i	123.0 (2)	C4—C5—H5A	119.7
C10—N2—H2A	118.5	C5—C6—C7	120.7 (2)
N2^i—N2—H2A	118.5	C5—C6—H6A	119.6
N1—C1—C2	124.4 (2)	C7—C6—H6A	119.6
N1—C1—C10	117.6 (2)	C8—C7—C6	120.3 (2)
C2—C1—C10	118.0 (2)	C8—C7—H7A	119.8
C3—C2—C1	119.1 (2)	C6—C7—H7A	119.8
C3—C2—H2B	120.5	C7—C8—C9	120.3 (2)
C1—C2—H2B	120.5	C7—C8—H8A	119.8
C2—C3—C4	119.5 (2)	C9—C8—H8A	119.8

C2—C3—H3A	120.2	N1—C9—C8	118.5 (2)
C4—C3—H3A	120.2	N1—C9—C4	122.2 (2)
C5—C4—C3	123.5 (2)	C8—C9—C4	119.3 (2)
C5—C4—C9	118.7 (2)	O1—C10—N2	122.7 (2)
C3—C4—C9	117.8 (2)	O1—C10—C1	122.3 (2)
C6—C5—C4	120.6 (2)	N2—C10—C1	115.1 (2)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···N1	0.86	2.31	2.689 (2)	107
N2—H2*A*···O1ii	0.86	2.35	2.978 (3)	130
C5—H5*A*···O1iii	0.93	2.45	3.177 (3)	135
C8—H8*A*···*Cg*1iv	0.93	2.64	3.449	146

Symmetry codes: (ii) −*x*+3/2, *y*, *z*−1/2; (iii) −*x*+1, *y*+1/2, −*z*+1/2; (iv) −*x*−1/2, *y*, *z*−3/2.