

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

Hui-Min Cheng, Lang Chen, Wei Lu, Xuan Shen and Dun-Ru Zhu*

College of Chemistry and Chemical Engineering, State Key Laboratory of Materials-oriented Chemical Engineering, Nanjing University of Technology, Nanjing 210009, People's Republic of China

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

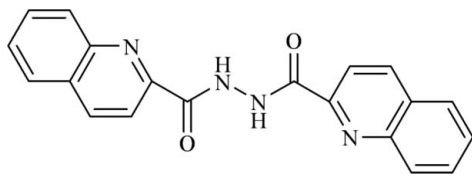
Received 10 September 2009; accepted 18 September 2009

Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.046; wR factor = 0.115; data-to-parameter ratio = 13.7.

The title compound, $\text{C}_{20}\text{H}_{14}\text{N}_4\text{O}_2$, 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 $74.9(2)^\circ$. An intramolecular N–H \cdots N hydrogen bond is present. In the crystal, the molecules are packed in chains running along the c axis through intermolecular N–H \cdots O hydrogen bonds. These chains are further stabilized by intermolecular C–H \cdots O hydrogen bonds and C–H $\cdots\pi$ interactions leading to the formation of a three-dimensional network.

Related literature

For general background to the chemistry of *N,N'*-diacylhydrazines, 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

$\text{C}_{20}\text{H}_{14}\text{N}_4\text{O}_2$
 $M_r = 342.35$
 Orthorhombic, *Pccn*

$a = 11.649(4)$ Å
 $b = 17.023(6)$ Å
 $c = 8.349(3)$ Å

$V = 1655.6(10)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation

$\mu = 0.09$ mm⁻¹
 $T = 296$ K
 $0.26 \times 0.12 \times 0.08$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{\min} = 0.976$, $T_{\max} = 0.993$

10346 measured reflections
 1629 independent reflections
 816 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.082$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.115$
 $S = 0.95$
 1629 reflections

119 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.17$ e Å⁻³
 $\Delta\rho_{\min} = -0.19$ e Å⁻³

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2–H2A \cdots N1	0.86	2.31	2.689 (2)	107
N2–H2A \cdots O1 ⁱⁱ	0.86	2.35	2.978 (3)	130
C5–H5A \cdots O1 ⁱⁱⁱ	0.93	2.45	3.177 (3)	135
C8–H8A \cdots Cg1 ^{iv}	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.

This work was funded by the National Natural Science Foundation of China (No. 20771059) and the Natural Science Foundation of Jiangsu Province (BK2008371).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2361).

References

- Bernhardt, P. V., Chin, P., Sharpe, P. C., Wang, J.-Y. C. & Richardson, D. R. (2005). *J. Biol. Inorg. Chem.* **10**, 761–777.
 Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed.* **34**, 1555–1573.
 Bruker (2005). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
 Jasinskas, L., Urbonas, A. & Latakas, V. (1975). *Liet. TSR Aukš. Mokyklu Mokslo Darb. Chem. Chem. Technol.* **17**, 143–145.
 Knödler, K., Fiedler, J. & Kaim, W. (2004). *Polyhedron*, **23**, 701–707.
 Shanmuga Sundara Raj, S., Yamin, B. M., Boshala, A. M. A., Tarafder, M. T. H., Crouse, K. A. & Fun, H.-K. (2000). *Acta Cryst.* **C56**, 1011–1012.
 Shao, S., Zhu, D., Song, Y., You, X. Z., Shanmuga Sundara Raj, S. & Fun, H.-K. (1999). *Acta Cryst.* **C55**, 1841–1843.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Xie, D.-J., Lu, W., Wang, Z.-X. & Zhu, D.-R. (2009). *Acta Cryst.* **E65**, o1177–o1178.
 Xu, R.-H., Zhou, J., Xu, Y., Qi, L., Shen, X. & Zhu, D.-R. (2006). *Acta Cryst.* **E62**, o5234–o5235.
 Zhao, H. & Bruke, T. R. J. (1997). *Tetrahedron*, **53**, 4219–4230.
 Zheng, Z.-B., Wu, R.-T., Li, J.-K. & Sun, Y.-F. (2007). *Acta Cryst.* **E63**, o4658.

supplementary materials

Acta Cryst. (2009). E65, o2526 [doi:10.1107/S1600536809037842]

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

H.-M. Cheng, L. Chen, W. Lu, X. Shen and D.-R. Zhu

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-quinolylylcarbonylhydrazine 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 two-fold axis passing through the N2—N2ⁱ 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—N2ⁱ—C10ⁱ 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*²₂(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.

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-quinolylylcarbonyl)hydrazine (1 mmol) with 4,4'-dimethylphenylphosphazoanilide (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%).

Refinement

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

Figures

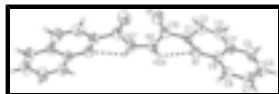


Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids and atom-numbering scheme [symmetry code: (i) $3/2 - x, 1/2 - y, z$].

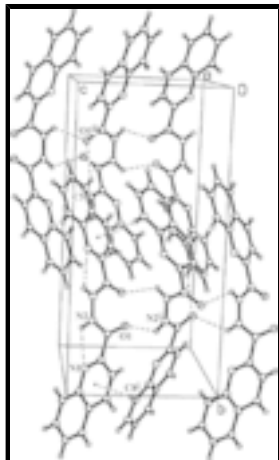


Fig. 2. The three-dimensional network formed *via* hydrogen bonds (dashed lines) and C—H... π interactions [symmetry code: (i) $1 - x, 1/2 + y, 1/2 - z$].

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

Crystal data

$C_{20}H_{14}N_4O_2$

$M_r = 342.35$

Orthorhombic, *Pccn*

Hall symbol: $-P\ 2ab\ 2ac$

$a = 11.649\ (4)\ \text{\AA}$

$b = 17.023\ (6)\ \text{\AA}$

$c = 8.349\ (3)\ \text{\AA}$

$V = 1655.6\ (10)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 712$

$D_x = 1.374\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 28 reflections

$\theta = 2.1\text{--}26.6^\circ$

$\mu = 0.09\ \text{mm}^{-1}$

$T = 296\ \text{K}$

Block, colourless

$0.26 \times 0.12 \times 0.08\ \text{mm}$

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 296\ \text{K}$

ω scans

Absorption correction: Multi-scan
(SADABS; Bruker, 2005)

$T_{\min} = 0.976, T_{\max} = 0.993$

10346 measured reflections

1629 independent reflections

816 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.082$

$\theta_{\max} = 26.0^\circ$

$\theta_{\min} = 2.1^\circ$

$h = -14 \rightarrow 14$

$k = -21 \rightarrow 18$

$l = -9 \rightarrow 10$

Refinement

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

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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*

supplementary materials

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 (\AA^2)

	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 (\AA , $^\circ$)

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 codes: (i) $-x+3/2, -y+1/2, z$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N2—H2A \cdots N1	0.86	2.31	2.689 (2)	107
N2—H2A \cdots O1 ⁱⁱ	0.86	2.35	2.978 (3)	130
C5—H5A \cdots O1 ⁱⁱⁱ	0.93	2.45	3.177 (3)	135
C8—H8A \cdots Cg1 ^{iv}	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) $-x-1/2, y, z-3/2$.

Fig. 1

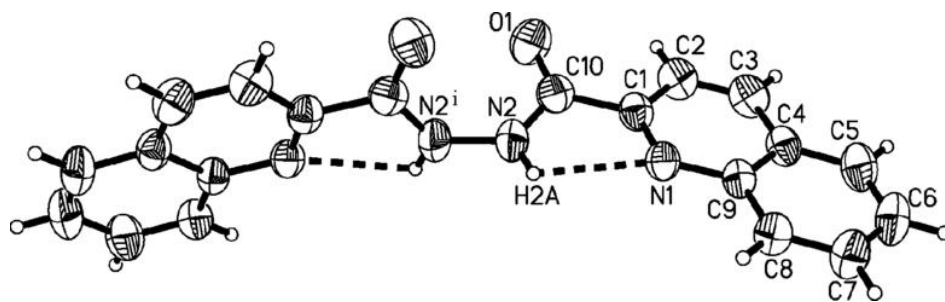


Fig. 2

