

N''-N'''*-Bis(di-2-pyridylmethylene)carbonic dihydrazide*E. Manoj,^a
M. R. Prathapachandra Kurup,^a
Hoong-Kun Fun^{b*} and
Suchada Chantrapromma^{c*}**^aDepartment of Applied Chemistry, Cochin University of Science and Technology, Kochi 682022, Kerala, India, ^bX-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and ^cDepartment of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand

Correspondence e-mail: hkfun@usm.my, suchada.c@psu.ac.th

Key indicatorsSingle-crystal X-ray study
T = 297 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.045
wR factor = 0.116
Data-to-parameter ratio = 15.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound {alternative name: 1,3-bis(di-2-pyridylmethylene)amino]urea}, $\text{C}_{23}\text{H}_{18}\text{N}_8\text{O}$, adopts an *EE* configuration about the hydrazine bonds and exists in the ketone form. Intramolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds are observed. Molecules translated by one unit cell along the *a*-axis direction are linked by $\text{C}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions, forming a chain. In addition, $\text{C}-\text{H}\cdots\pi$ and $\pi-\pi$ interactions are observed.

Comment

Carbohydrazones and thiocarbohydrazones are the next highest homolog of potential biologically important compounds after semicarbazones and thiosemicarbazones. Thiocarbohydrazones and some carbohydrazones are reported to have antimicrobial activity towards bacteria and fungi (Abu-Hussen & Emara, 2004; Bacchi *et al.*, 1999); bis-thiocarbohydrazones possess the highest antibacterial activity and are potentially useful as antimicrobial agents against Gram positive bacteria (Bacchi *et al.*, 1999). As inactivators of HSV-1 ribonucleotide reductase, a series of 2-acetylpyridine thiocarbohydrazones are found to possess better activity than that of the corresponding thiosemicarbazones (Blumenkopf *et al.*, 1992; Spector *et al.*, 1989). Owing to the presence of different kinds of potential donor sites, thiocarbohydrazones are interesting ligand species and generate mononuclear, dinuclear and even tetranuclear complexes (Bacchi *et al.*, 1996; Moubaraki *et al.*, 1999; Bustos *et al.*, 1990; Cheng *et al.*, 2000), which provide a new dimension to supramolecular chemistry. Single-crystal X-ray structure determinations of these types of compounds are interesting, especially regarding the extensive delocalization of the thiocarbonyl group (Cheng *et al.*, 2000). Compared to studies on thiocarbohydrazones, there are only a few reports on carbohydrazones, and only one crystal structure of a carbohydrazone, *viz* bis(methyl 2-pyridyl ketone)-carbohydrazone (Bacchi *et al.*, 1996), has been reported; this could act as an N_5O ligand towards the Cu^{II} ion after enolization. A similar compound, tetra(2-pyridyl)thiocarbohydrazone, was reported but without any crystallographic study (Duan *et al.*, 1997).

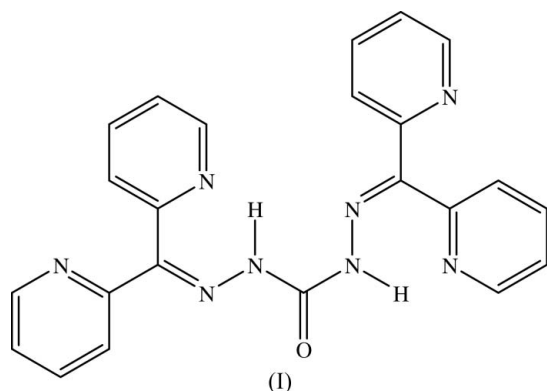
The title compound, (I), is a potential ligand with flexible coordination ability. The bond lengths and angles in (I) show normal values (Allen *et al.*, 1987). Selected bond lengths and angles are given in Table 1. As shown in Fig. 1, atom O1 is in a *cis* configuration with respect to the azomethine atom N3 [$\text{N3}-\text{N4}-\text{C12}-\text{O1} = 3.9 (3)^\circ$], and a *trans* configuration with respect to the azomethine atom N6 [$\text{N6}-\text{N5}-\text{C12}-\text{O1} = 170.20 (16)^\circ$], similar to that reported for bis(methyl 2-pyridyl ketone)carbohydrazone (Bacchi *et al.*, 1996). As also observed in bis(methyl 2-pyridyl ketone)carbohydrazone (Bacchi *et al.*,

Received 1 November 2005

Accepted 8 November 2005

Online 16 November 2005

1996) and in bithiocarbohydrazones (Bacchi *et al.*, 1996; Cheng *et al.*, 2000; Chantrapromma *et al.*, 2001), the C13–N6 and N5–C12 bonds are in an *E* configuration with respect to the N5–N6 bond and, similarly, the C6–N3 and N4–C12 bonds are in an *E* configuration about the N3–N4 bond. The C6–N3–N4–C12 [176.23 (14) $^\circ$] and C13–N6–N5–C12 [–179.44 (15) $^\circ$] torsion angles confirm the *EE* configuration. The C12=O1 distance of 1.2116 (18) Å indicates a typical double-bond nature and the ketone form. The N–N and C–N bond lengths of the thiocarbzone group (Table 1), which are comparable to the corresponding lengths in bis(methyl 2-pyridyl ketone)carbohydrazone (Bacchi *et al.*, 1996), indicate some electron delocalization in the N3/N4/C12/N5/N6 moiety.



The thiocarbzone moiety (C6/N3/N4/C12/O1/N5/N6/C13) is approximately planar (r.m.s deviation 0.043 Å), similar to bis(methyl 2-pyridyl ketone)carbohydrazone. The N2/C7–C11 and N7/C14–C18 pyridine ring planes are twisted away from the thiocarbzone plane by 40.88 (5) and 50.10 (4) $^\circ$, respectively, while the N1/C1–C5 and N8/C19–C23 pyridine ring planes are twisted by 23.92 (7) and 21.45 (7) $^\circ$, respectively. The decrease in the twisting may be attributed to intramolecular N–H \cdots N hydrogen bonds (Fig. 1). The dihedral angle between the N1/C1–C5 and N2/C7–C11 planes is 55.75 (6) $^\circ$ and that between the N7/C14–C18 and N8/C19–C23 planes is 71.03 (5) $^\circ$.

Intramolecular N–H \cdots N hydrogen bonds (Table 2) involving H1N4 generate rings of graph-set motifs *S*(5) and *S*(6) (Bernstein *et al.*, 1995), similar to those in bis(methyl 2-pyridyl ketone)carbohydrazone (Bacchi *et al.*, 1996) and in

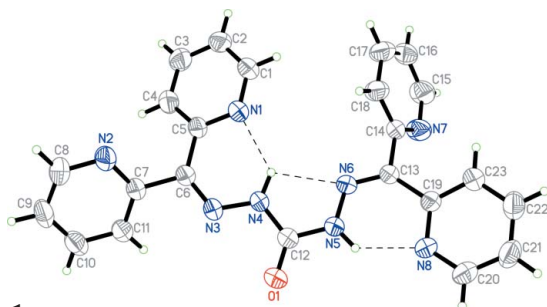


Figure 1
The structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines denote intramolecular hydrogen bonds.

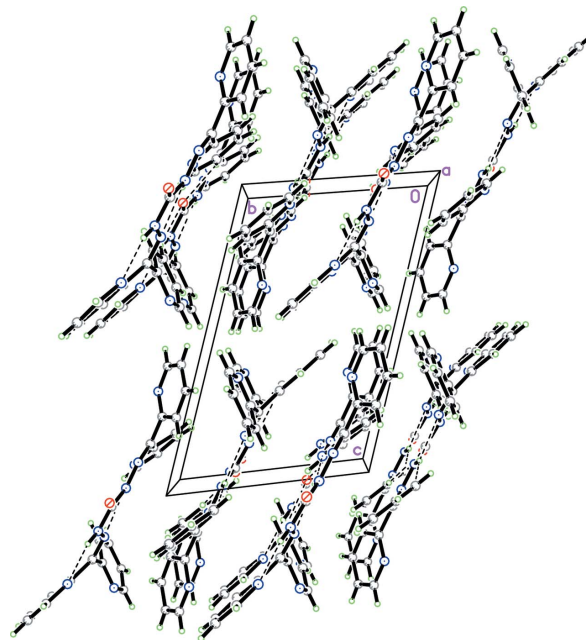


Figure 2
The crystal packing of (I), viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

bithiocarbohydrazones (Bacchi *et al.*, 1996; Cheng *et al.*, 2000), while the N–H \cdots N hydrogen bond involving H1N5 generates a graph-set motif *S*(6), as seen in bithiocarbohydrazone (Cheng *et al.*, 2000). Molecules translated by one unit cell along the *a*-axis direction are linked by C2–H2A \cdots O1 i and C17–H17A \cdots O1 i [symmetry code: (i) 1 + *x*, *y*, *z*] hydrogen-bonding interactions, forming a chain (Fig. 2). These interactions together constitute a pair of bifurcated acceptor bonds. In addition, the crystal packing is reinforced by a weak C–H \cdots π interaction involving the N8/C19–C23 pyridine ring (centroid *Cg*) and π \cdots π stacking interactions involving the N1/C1–C5 pyridine rings at (*x*, *y*, *z*) and (2 – *x*, 2 – *y*, –*z*) [centroid \cdots centroid distance = 3.5804 (9) Å].

Experimental

Dipyridyl ketone (0.3908 g, 2.1 mmol) in methanol (10 ml) was added to carbohydrazone (0.0918 g, 1 mmol) dissolved in hot methanol (30 ml). After adding glacial acetic acid (2 ml), the resulting solution was refluxed for 2 h and, on cooling, yellow crystals were precipitated. These crystals were isolated, washed with methanol and diethyl ether, and dried over P₄O₁₀ *in vacuo*. Single crystals of (I) suitable for X-ray analysis were obtained by slow evaporation of a methanol solution of (I) (yield 85%).

Crystal data

C₂₃H₁₈N₈O
M_r = 422.45
 Triclinic, *P*1
a = 9.0963 (2) Å
b = 9.1215 (2) Å
c = 13.6215 (3) Å
 α = 71.136 (1) $^\circ$
 β = 86.899 (1) $^\circ$
 γ = 72.431 (1) $^\circ$
V = 1018.42 (4) Å³

Z = 2
D_x = 1.378 Mg m^{–3}
 Mo *K* α radiation
 Cell parameters from 4652 reflections
 θ = 2.5–27.5 $^\circ$
 μ = 0.09 mm^{–1}
T = 297 (2) K
 Block, colourless
 0.31 × 0.26 × 0.19 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer	4652 independent reflections
φ and ω scans	3235 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2005)	$R_{\text{int}} = 0.038$
$T_{\text{min}} = 0.972$, $T_{\text{max}} = 0.983$	$\theta_{\text{max}} = 27.5^\circ$
17391 measured reflections	$h = -11 \rightarrow 11$
	$k = -11 \rightarrow 11$
	$l = -16 \rightarrow 17$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0475P)^2 + 0.1398P]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.116$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.15 \text{ e } \text{\AA}^{-3}$
4652 reflections	$\Delta\rho_{\text{min}} = -0.21 \text{ e } \text{\AA}^{-3}$
297 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (\AA , $^\circ$).

N3—C6	1.2945 (19)	N6—C13	1.2950 (18)
N3—N4	1.3662 (17)	C5—C6	1.489 (2)
N4—C12	1.367 (2)	C6—C7	1.4903 (19)
N5—N6	1.3556 (17)	C13—C19	1.482 (2)
N5—C12	1.3799 (19)	C13—C14	1.493 (2)
N3—C6—C5	128.10 (13)	N4—C12—N5	113.51 (13)
N3—C6—C7	112.55 (13)	N6—C13—C19	128.00 (13)
O1—C12—N4	125.56 (14)	N6—C13—C14	113.27 (12)

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N4—H1N4 \cdots N1	0.92 (2)	2.03 (2)	2.707 (2)	130 (2)
N4—H1N4 \cdots N6	0.92 (2)	2.25 (2)	2.613 (2)	103 (1)
N5—H1N5 \cdots N8	0.87 (2)	2.04 (2)	2.702 (2)	132 (2)
C2—H2A \cdots O1 ⁱ	0.93	2.55	3.213 (2)	128
C4—H4A \cdots N2	0.93	2.60	2.982 (2)	105
C17—H17A \cdots O1 ⁱ	0.93	2.53	3.348 (2)	146
C8—H8A \cdots Cg ⁱⁱ	0.93	2.78	3.466 (2)	131

Symmetry codes: (i) $x + 1, y, z$; (ii) $x, y, z + 1$. Cg is the centroid of the N8/C19—C23 pyridine ring.

H atoms attached to N atoms were located in a difference map and refined isotropically. C-bound H atoms were placed in calculated

positions and allowed to ride on their parent C atoms, with C—H = 0.93 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: APEX2 (Bruker, 2005); cell refinement: APEX2; data reduction: SAINT (Bruker, 2005); program(s) used to solve structure: SHELXTL (Sheldrick, 1998); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2003).

MRPK and EM thank Kerala State Council for Science Technology and Environment, Thiruvananthapuram, India, for financial support. The authors also thank the Malaysian Government and Universiti Sains Malaysia for the Scientific Advancement Grant Allocation (SAGA; grant No. 304/PFIZIK/635003/A118).

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