

Polymorphic di-2-pyridyl ketone 4-nitrophenylhydrazone (dpknph): the structure of β -dpknph

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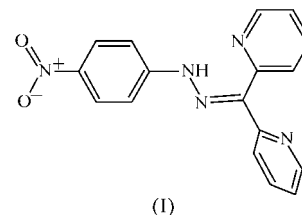
A new polymorph of di-2-pyridyl ketone 4-nitrophenylhydrazone [alternative name: *N*-(dipyridin-2-ylmethylene)-*N'*-(4-nitrophenyl)hydrazine], C₁₇H₁₃N₅O₂, isolated from the filtrate of a sonicated acetonitrile solution of dpknph and CdCl₂, was found to crystallize in the monoclinic space group *P*2₁/*c*, in contrast to the known form which crystallizes in *P*2₁/*n*. The non-coplanar molecules pack in parallel stacks without any intermolecular hydrogen-bonding interactions. This packing pattern contrasts with the interlocked interdigitated packing seen in the previously known polymorph.

Comment

In recent reports (Bakir & Abdur-Rashid, 1999; Bakir, 2001; Bakir & Brown, 2002; Bakir & Gyles, 2002; Bakir *et al.*, 2000, 2003, 2005) we described the syntheses, structures and reactions of di-2-pyridyl ketone 4-nitrophenylhydrazone (dpknph) and its metal complexes; these investigations revealed a high sensitivity of dpknph and its metal compounds to slight variations in their surroundings. Optosensing measurements on dpknph show a reversible interconversion between two charge transfer electronic states, and substrates with concentrations as low as 1.00×10^{-7} M can be detected and measured using dpknph in DMSO (dimethyl sulfoxide). Thermo-optical measurements on dpknph in DMSO confirmed the reversible interconversion between high- and low-energy electronic states of dpknph, and allowed for the calculations of their thermodynamic activation parameters. Thus, changes in enthalpy (ΔH°) of 249.05 ± 1.25 kJ mol⁻¹, entropy (ΔS°) of $+0.16 \pm 0.04$ kJ mol⁻¹ and free energy (ΔG°) of -96.30 ± 2.45 kJ mol⁻¹ were determined at 295 K.

Although several attempts were made to explore the polymorphic behavior of di-2-pyridyl ketone hydrazones and their metal compounds, prior to this report we were only able to isolate one polymorphic form of di-2-pyridyl ketone hydrazone (Bakir & Brown, 2002). In the course of exploring

the optosensing behavior and reactions of dpknph with group 12 metal halides in acetonitrile, a new polymorphic form of dpknph was isolated when the filtrate of a sonicated acetonitrile solution of dpknph and CdCl₂ was allowed to stand at room temperature for several days. We have designated this polymorph β -dpknph, (I).



A view of the molecular structure of β -dpknph is shown in Fig. 1. With the exception of slight variations of less than 4° in bond angles about atom C01 of the di-2-pyridyl ketone (dpk) moiety, there are no significant variations in bond distances and valence angles between the molecules in the α - and β -dpknph forms. However, pronounced differences between α - and β -dpknph are apparent in the conformation of the pyridine rings about atom C1 (see Table 1). In the case of β -dpknph, atom N1 is in close proximity to atom N4, and atom N2 is in close proximity to atom C14 (see Fig. 1). This orientation is the result of a classical intramolecular N—H···N hydrogen bond between atoms N1 and N4. The bond distances and angle of the hydrogen bonds (see Table 2) are similar to those in a variety of compounds containing such bonds; for example, in di-2-pyridyl ketone *p*-aminobenzoylhydrazone monohydrate (dpkbz·H₂O; Bakir & Green, 2002), hydrogen-bonding parameters *D*—H, H···*A*, *D*···*A* and *D*—H···*A* of 0.86, 2.01, 2.656 (2) Å and 131° were observed for the classical N—H···N hydrogen bond, and values of 0.93, 2.52, 3.325 (2) Å and 142° were observed for a non-classical C—

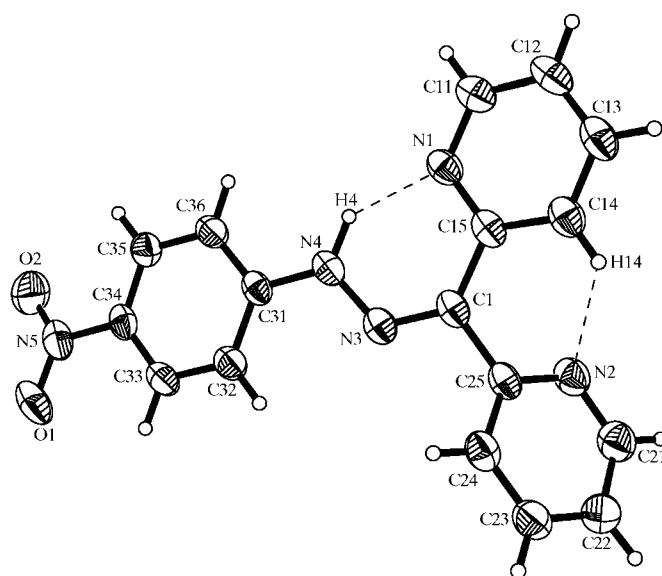


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level. The intramolecular hydrogen bonds are shown as dashed lines.

H···O hydrogen bond. In the case of α -dpknp, the 4-nitrophenylhydrazone moiety and the N1-pyridine ring are coplanar and orthogonal to the N2-pyridine ring, and hence do not allow for the formation of any suitable intramolecular hydrogen bonding.

In β -dpknp, torsion angles of -12.55 (19) and 131.90 (12) $^\circ$ were observed for N3—C1—C15—N1 and N3—C1—C25—N2, respectively, while for α -dpknp, the analogous angles are 94.4 (3) and 176.1 (2) $^\circ$. The pyridine rings in α -dpknp are nearly perpendicular, with a dihedral angle of 94.4 (3) $^\circ$, while in the case of β -dpknp, the dihedral angle between the pyridine ring planes is 56.36 (12) $^\circ$.

The packing of β -dpknp molecules along the c axis, shown in Fig. 2, reveals parallel stacks of β -dpknp molecules along the a axis and the absence of intermolecular interactions such

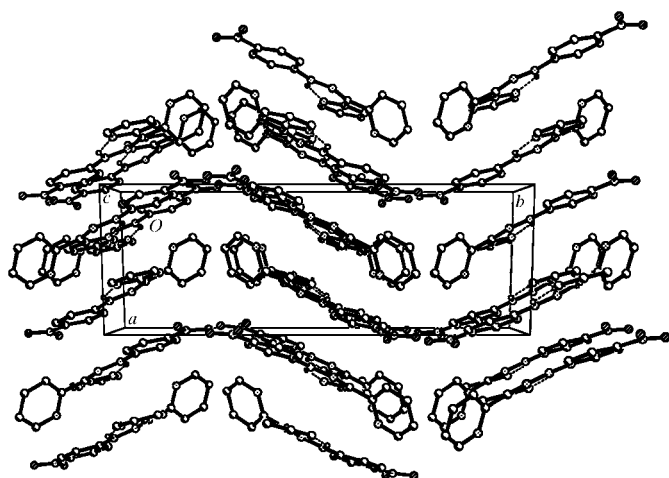


Figure 2
The packing in β -dpknp.

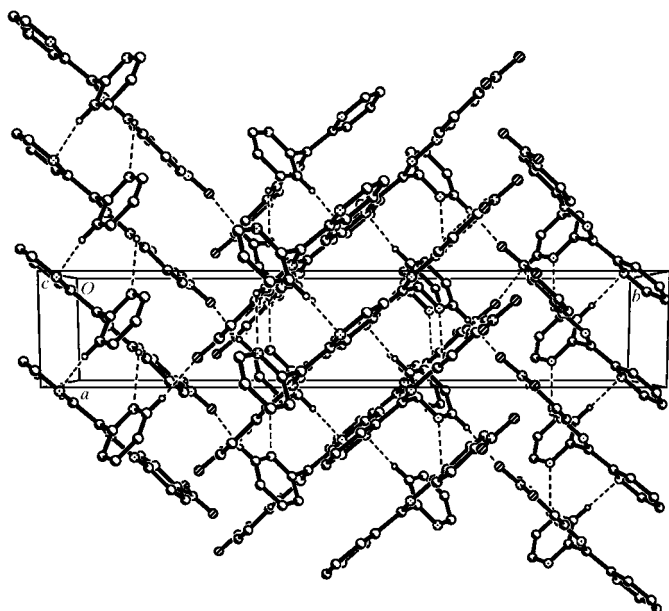


Figure 3
The packing in α -dpknp.

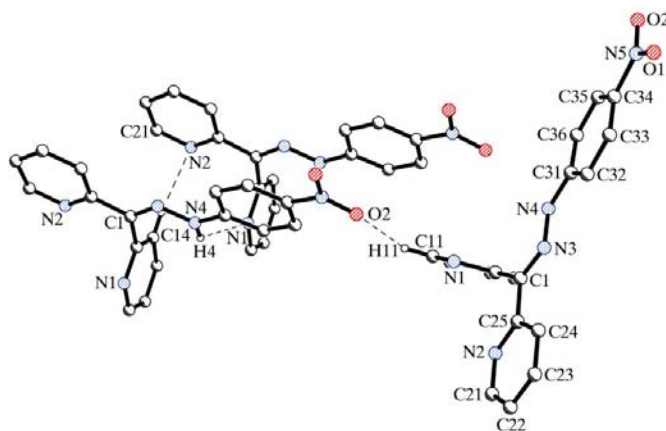


Figure 4
The intermolecular hydrogen bonds in α -dpknp.

as hydrogen bonding between stacks. Alternate molecules in the stacks are related by inversion. This packing pattern contrasts with the interlocked interdigitated packing behavior of α -dpknp (see Fig. 3), which also displayed an extensive network of non-covalent intermolecular interactions, namely N4···N1, C14···N2 and C11···O2 (see Fig. 4).

In conclusion, a second polymorphic form of dpknp has been isolated, and the solid-state structural analysis reveals significant conformational differences between α - and β -dpknp, as manifested in the orientation of the pyridine rings around the bridging C atom of dpk and the differing types of intermolecular hydrogen-bonding interactions. The rich physicochemical properties of hydrazones and their metal complexes allow a number of possible applications in, for example, non-linear optics and molecular sensing. We are therefore actively exploring the structures of a variety of di-2-pyridyl ketone hydrazones.

Experimental

When an equimolar mixture of dpknp and CdCl₂ dissolved in acetonitrile was subjected to ultrasonic radiation for an hour, and the filtrate of the reaction mixture was allowed to stand at room temperature for several days, an orange crystal of (I), originally thought to be Cd(dpknp)Cl₂, was isolated.

Crystal data

C₁₇H₁₃N₅O₂
M_r = 319.32
 Monoclinic, *P*2₁/*c*
a = 7.9415 (9) Å
b = 22.123 (3) Å
c = 8.9747 (10) Å
 β = 103.606 (2) $^\circ$
V = 1532.5 (3) Å³
Z = 4

D_x = 1.384 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 2735 reflections
 θ = 2.5–23.0 $^\circ$
 μ = 0.10 mm⁻¹
T = 296 (2) K
 Plate, orange
 0.32 × 0.22 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 ω scans
 13621 measured reflections
 3630 independent reflections
 1961 reflections with $I > 2\sigma(I)$

*R*_{int} = 0.053
 θ_{\max} = 28.2 $^\circ$
h = -10 → 10
k = -28 → 28
l = -11 → 11

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.095$
 $S = 0.87$
 3630 reflections
 221 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0426P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.13 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.12 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

N3—N4	1.3574 (16)	C01—N3	1.2983 (16)
N5—O1	1.2200 (17)	C01—C25	1.4873 (19)
C11—N1	1.3334 (17)	C25—N2	1.3474 (16)
C11—C12	1.372 (2)	C31—N4	1.3767 (16)
C15—N1	1.3450 (17)	C34—N5	1.4539 (19)
C15—C01	1.4757 (19)		
C14—C15—C01	121.19 (15)	N4—C31—C32	122.05 (14)
N3—C01—C15	127.77 (14)	C01—N3—N4	119.94 (12)
N3—C01—C25	112.55 (13)	N3—N4—C31	118.79 (13)
C15—C01—C25	119.66 (12)	O1—N5—O2	122.91 (15)
N2—C25—C01	116.03 (12)		
N1—C15—C01—N3	−12.55 (19)	C15—C01—C25—N2	−46.65 (16)
C14—C15—C01—N3	165.38 (13)	N3—C01—C25—C24	−45.90 (17)
N1—C15—C01—C25	165.75 (11)	C15—C01—N3—N4	3.48 (19)
C14—C15—C01—C25	−16.32 (18)	C25—C01—N3—N4	−174.92 (10)
N3—C01—C25—N2	131.90 (12)	C01—N3—N4—C31	174.98 (11)

Table 2

Hydrogen-bond and short intramolecular contact geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N4—H4 \cdots N1	0.96 (2)	1.87 (2)	2.6389 (16)	136 (1)
C14—H14 \cdots N2	0.93	2.52	2.982 (2)	111

All H atoms of β -dpknph were assigned by assuming idealized geometry, with C—H distances of 0.93 Å and $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{carrier})$. The N-bound atom H4 was refined freely.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1616). Services for accessing these data are described at the back of the journal.

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