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1-(2-Pyridyl)ethan-1-one 8-quinolylhydrazone and 1-(1*H*-pyrrol-2-yl)ethan-1-one 8-quinolylhydrazone

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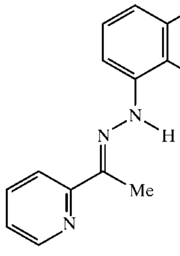
The structures of the title compounds, $C_{16}H_{14}N_4$, (I), and $C_{15}H_{14}N_4$, (II), respectively, have been determined, and their molecular packing arrangements compared. Both are essentially flat molecules, with respective dihedral angles between the quinoline and heterocyclic rings of 19.0 (1) and 8.5 (2)°. The pyridyl derivative, (I), packs in a $P2_1/c$ unit cell, while in the pyrrolyl compound, (II), the molecules pack in $Pca2_1$ and form a crinkled ribbon arrangement through the association of pyrrole NH groups with the quinoline N atoms.

Comment

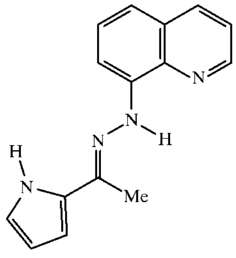
The Fischer indole synthesis, discovered in 1883 by Emil Fischer, occurs when phenylhydrazine is heated in acidic solution with an aldehyde or ketone (Clayden *et al.*, 2001). The first step involves the formation of the phenylhydrazone, which is itself stable and can be isolated. The next three steps involve cyclization and the loss of ammonia to produce the aromatic indole. Substituents on the aldehyde or ketone are important because 4-methyl-2-phenyl-2*H*-phthalazin-1-one is produced by reacting phenylhydrazine with, respectively, 2-acetylbenzoic acid (Rowe & Peters, 1931), 2-acetylbenzonitrile (Helberger & von Rebay, 1937) or 3-(2-carboxyphenyl)-3-oxopropionic acid (Roser, 1885) in an analogous reaction to the indole synthesis. We have recently been studying the potential of 8-hydrazinoquinoline and produced 4-methyl-2-(8-quinolyl)phthalazin-1-one in a reaction containing 2-acetylbenzoic acid (Lynch & McClenaghan, 2002*a*).

The title compounds, (I) and (II), were synthesized by refluxing 8-hydrazinoquinoline dihydrochloride hydrate (Lynch & McClenaghan, 2002*b*) with the relevant 2-acetyl heterocycle. The structure of an analogous product, (*E*)-1-(2-thienyl)ethanone 8-quinonylhydrazone, has been reported (Lynch & McClenaghan, 2001) and was found to be planar [the dihedral angle between the quinoline and thiophene rings is 2.6 (2)°]. Each of these products can undergo additional cyclization to the corresponding pyrrolo[3,2-*h*]quinoline [see, for example, Lynch *et al.* (2001) and Lynch & McClenaghan (2002*c*)] (see reaction scheme below).

Such molecules have potential as metal binding agents, although we have yet to study this possibility. In the quinonylhydrazone form, molecules such as (I) and (II) have one strong hydrogen-bond donor and two strong hydrogen-bond acceptors, as well as any similar atoms on the attached *R* group. The structure of the thienyl derivative showed that an intramolecular association with the adjacent quinoline N atom influenced the position of the hydrazone NH group. The subsequent arrangement (and steric hindrance) of the thienyl 'tail' thus prevented any further intermolecular associations to the sp^2 N atom of the hydrazone moiety.

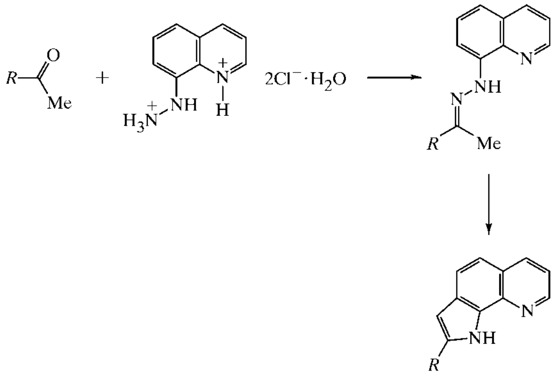


(I)



(II)

As part of an overall study of the structural aspects of both quinonylhydrazones and pyrrolo[3,2-*h*]quinolines, we decided to study the structures of quinonylhydrazone analogues with varying numbers of hydrogen-bond acceptor and donor atoms within the *R* group. Here, we compare two structures, one with a single hydrogen-bond acceptor (pyridine) in the *R* group, (I), and one with a single hydrogen-bond donor (pyrrole), (II), with both hydrogen-bond components contained within heterocyclic rings.



The structure of compound (I) (Fig. 1) is very similar to that of the thienyl derivative, being an essentially flat molecule [the dihedral angle between the quinoline and pyridine rings is 19.0 (1)°] and having essentially the same *trans* conformation for the two ring systems. Similarities extend to the packing of both compounds, in that both exist in centrosymmetric space groups; $P2_1/c$ for (I) (Fig. 2) and *Pbca* for the thienyl derivative. In addition to the (hydrazone)N—H···N(quinoline) association, in (I), there is also an intramolecular C—H···N close contact from one of the methyl H atoms to the pyridine

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N atom. Two possible intermolecular close contacts (not listed in Table 1) are both from different quinoline H atoms to the quinoline N atom (H4···N1 = 2.74 Å and 135°) and the pyridine N atom (H2···N15 = 2.69 Å and 135°).

Compound (II) (Fig. 3) is also essentially flat [dihedral angle 8.5 (2)°] and exists in the previously mentioned *trans* conformation. However, the additional strong hydrogen-bond donor atom, and its requirement to be involved in a formal hydrogen bond when there are hydrogen-bond acceptors available for association, significantly influences the solid-state packing of (II). The subsequent N—H···N interaction between the pyrrole NH group and the quinoline N atom creates a crinkled ribbon arrangement that propagates along the *a* axis (Fig. 4), with the overall packing being non-centrosymmetric. The dihedral angle between associated pyrrole and quinoline rings is 83 (1)°.

The production and control of non-centrosymmetric space groups by hydrogen-bonding interactions is still an area of crystal engineering that is little understood, but it is worth pursuing because of the resultant non-linear optical properties that any non-centrosymmetric material may possess. For this reason, we have decided to investigate further the solid-state structure and properties of quinonylhydrazone analogues,

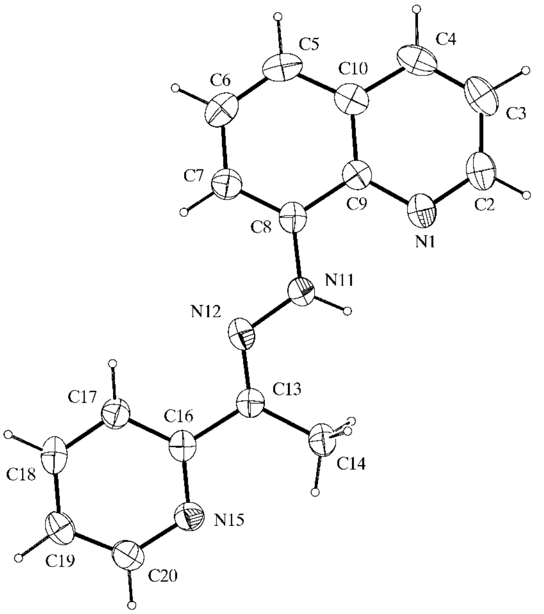

Figure 1
The molecular configuration and atom-numbering scheme for (I), shown with 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

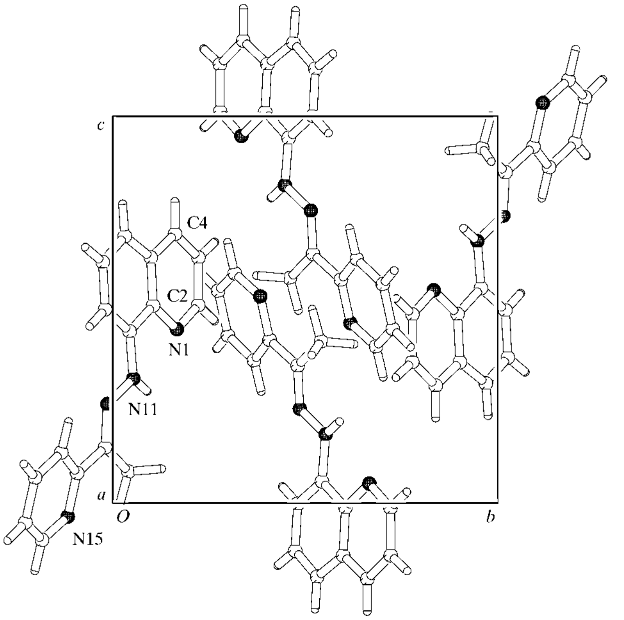

Figure 2
The molecular packing for (I).

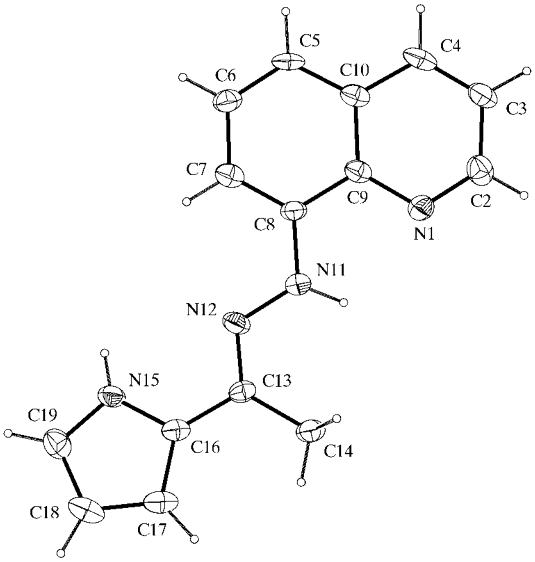

Figure 3
The molecular configuration and atom-numbering scheme for (II), shown with 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

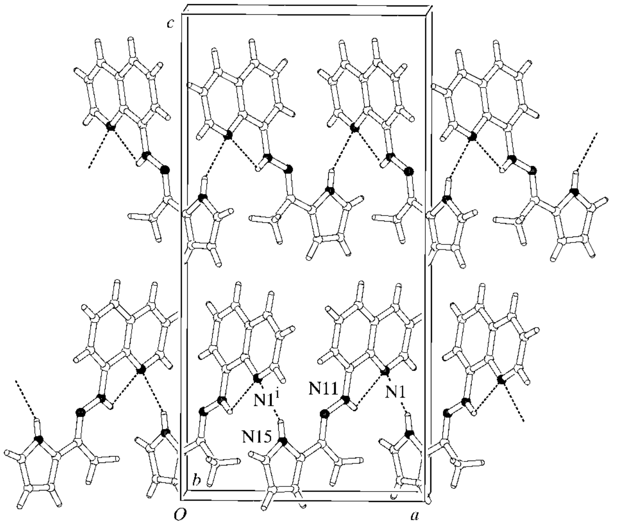

Figure 4
The molecular packing for (II). Hydrogen-bond associations are indicated by dotted lines [symmetry code: (i) $x + \frac{1}{2}, 1 - y, z$].

such as (II), containing additional hydrogen-bond donor elements in the *R* group.

Experimental

The title compounds were obtained from Key Organics Ltd and crystals were grown from ethanol solutions.

Compound (I)

Crystal data

$C_{16}H_{14}N_4$
$M_r = 262.31$
Monoclinic, $P2_1/c$
$a = 10.1678\ (4)$ Å
$b = 11.2970\ (6)$ Å
$c = 11.3566\ (6)$ Å
$\beta = 90.284\ (3)^\circ$
$V = 1304.47\ (11)$ Å^3
$Z = 4$
$D_x = 1.336$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 13 136 reflections
$\theta = 2.9$–27.5°
$\mu = 0.08$ mm^{-1}
$T = 150\ (2)$ K
Needle, yellow
0.20 × 0.08 × 0.07 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{\min} = 0.984$, $T_{\max} = 0.994$
17 166 measured reflections
2987 independent reflections
1709 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.095$
$\theta_{\max} = 27.5^\circ$
$h = -13 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.154$
$S = 0.96$
2987 reflections
186 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0853P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}

Table 1
Hydrogen-bonding and contact geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11···N1	0.93 (2)	2.31 (2)	2.688 (2)	104 (3)
C14—H142···N15	0.98	2.38	2.855 (2)	109

Compound (II)

Crystal data

$C_{15}H_{14}N_4$
$M_r = 250.30$
Orthorhombic, $Pca2_1$
$a = 10.690\ (2)$ Å
$b = 5.5066\ (11)$ Å
$c = 21.363\ (4)$ Å
$V = 1257.5\ (4)$ Å^3
$Z = 4$
$D_x = 1.322$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4172 reflections
$\theta = 2.9$–27.5°
$\mu = 0.08$ mm^{-1}
$T = 150\ (2)$ K
Plate, yellow
0.32 × 0.24 × 0.01 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{\min} = 0.974$, $T_{\max} = 0.999$
7258 measured reflections
1445 independent reflections
876 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.111$
$\theta_{\max} = 27.4^\circ$
$h = -13 \rightarrow 13$
$k = -7 \rightarrow 7$
$l = -27 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.113$
$S = 0.97$
1445 reflections
181 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0497P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}

Table 2
Hydrogen-bonding and contact geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11···N1	0.92 (4)	2.30 (3)	2.726 (4)	107 (3)
N15—H15···N1$^{\rm i}$	0.83 (5)	2.20 (5)	2.990 (5)	159 (4)

Symmetry code: (i) $\frac{1}{2}+x, 1-y, z$.

H atoms on N atoms were located in difference syntheses and had both positional and displacement parameters refined. All other H atoms were included at calculated positions and refined using a riding model, with C—H distances set to 0.95 (aryl H) and 0.98 Å (CH_3). The high $R_{\rm int}$ values of 0.095 and 0.111 for (I) and (II), respectively, were the result of poor diffraction and weak high-angle data. For (II), Friedel reflections were merged before refinement.

For both compounds, data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLUTON*94 (Spek, 1994) and *PLATON*97 (Spek, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1136). Services for accessing these data are described at the back of the journal.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Clayden, J., Greeves, N., Warren, S. & Wothers, P. (2001). *Organic Chemistry*, pp. 1204–1205. Oxford University Press.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Helberger, J. H. & von Rebay, A. (1937). *Justus Liebigs Ann. Chem.* **531**, 279–287.
Lynch, D. E. & McClenaghan, I. (2001). *Acta Cryst.* E**57**, o52–o53.
Lynch, D. E. & McClenaghan, I. (2002*a*). *Acta Cryst.* E**58**, o1051–o1052.
Lynch, D. E. & McClenaghan, I. (2002*b*). *Acta Cryst.* E**58**, o1070–o1071.
Lynch, D. E. & McClenaghan, I. (2002*c*). *Acta Cryst.* E**58**, o1150–o1151.
Lynch, D. E., McClenaghan, I. & Light, M. E. (2001). *Acta Cryst.* E**57**, o56–o57.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Roser, W. (1885). *Chem. Ber.* **18**, 804.
Rowe, F. M. & Peters, A. T. (1931). *J. Chem. Soc.* pp. 1918–1925.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (1994). *PLUTON*94. University of Utrecht, The Netherlands.
Spek, A. L. (1997). *PLATON*97. University of Utrecht, The Netherlands.