

A diastereoisomer of pyrano[3,2-*c*]quinolineK. Ravikumar,^{a*} B. Sridhar,^a
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Key indicators

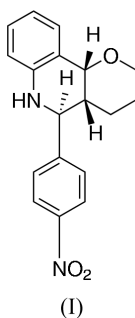
Single-crystal X-ray study
T = 273 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
R factor = 0.061
wR factor = 0.139
Data-to-parameter ratio = 13.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, 5-(4-nitrophenyl)-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano[3,2-*c*]quinoline, $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_3$, was obtained from the Diels–Alder reaction of *N*-benzylideneaniline and dihydropyran, catalyzed by zirconium tetrachloride. This molecule is an *exo*-cycloadduct isomer. The pyran ring adopts a chair conformation, while the *N*-heterocyclic ring prefers a half-chair conformation. Molecules are associated into centrosymmetric dimers by $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds.

Received 20 December 2004
Accepted 21 January 2005
Online 29 January 2005Imino Diels–Alder adducts.
Part V

Comment

Quinoline derivatives, an important class of pharmaceuticals, exhibit psychotropic, anti-allergenic and anti-inflammatory activities (Nesterova *et al.*, 1995; Yamada *et al.*, 1992; Faber *et al.*, 1984). In addition, the pyranoquinoline moiety is present in many alkaloids. For the synthesis of pyranoquinolines, the imino Diels–Alder reaction between *N*-arylimines and dienophile dihydropyran is probably one of the most successful synthetic tools (Mahesh *et al.*, 2004). We report here the structure of a diastereoisomer, namely 5-(4-nitrophenyl)-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano[3,2-*c*]quinoline, (I), as part of our ongoing structure elucidation studies.



The molecular dimensions of (I) are normal and compare well with similar structures reported in the literature (Ravikumar *et al.*, 2004; Wang *et al.*, 2004). The orientation of atoms H4 and H5, the characteristic differentiating the diastereoisomers, results in a *trans* (*exo*) configuration, the H4–C4–C5–H5 torsion angle [$-169.8(2)^\circ$] being in accordance with the coupling constant $J = 10.7 \text{ Hz}$. Furthermore, atoms H4 and H12 are oriented in a *cis* configuration [$\text{H4}-\text{C4}-\text{C12}-\text{H12} = 49.8(3)^\circ$].

The strain exerted during the cycloaddition process, in forming the *N*-heterocyclic ring, may be seen from the torsion angles C6–C11–C12–C4 [$-15.0(3)^\circ$] and C6–N1–C5–C4 [$53.5(3)^\circ$]. The *N*-heterocyclic ring is in a half-chair conformation, with atoms C6 and C11 displaced by 0.057(3) and $-0.088(2) \text{ \AA}$, respectively, from the plane formed by the other four atoms.

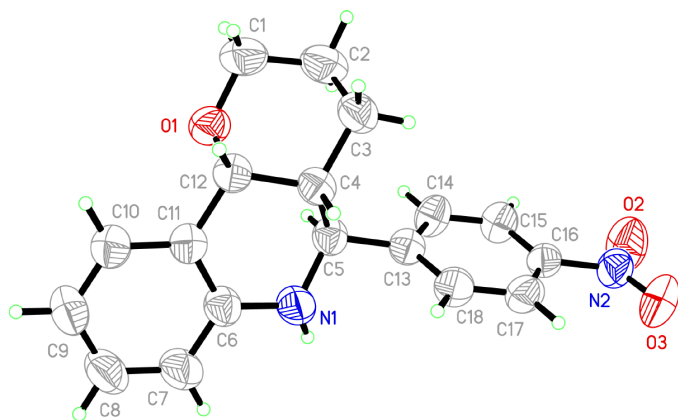


Figure 1
A view of the molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

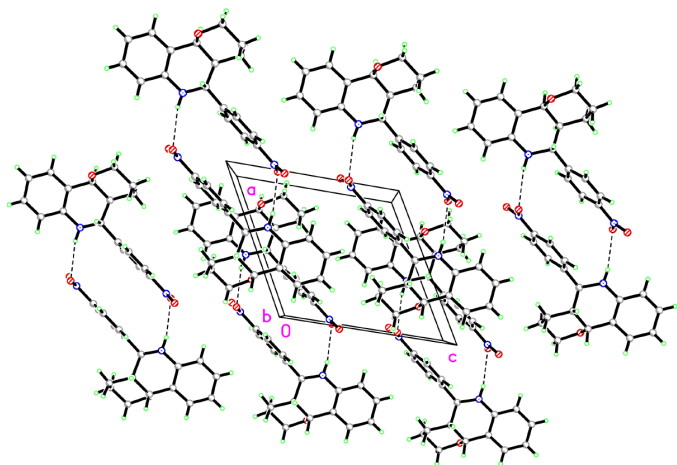


Figure 2
Packing diagram viewed down the *b* axis. Dashed lines indicate N—H...O hydrogen bonds.

Interestingly, the pyran ring is oriented perpendicular to the quinoline ring, with the torsion angle C6—C11—C12—O1 = 108.3 (2)°. The pyran ring adopts a chair conformation, as expected, with asymmetry parameter (Nardelli, 1983) $\Delta C_2(C4—C2) = 0.034$ (3). Atoms C3 and O1 are displaced by 0.602 (3) Å above and 0.647 (2) Å below the plane defined by atoms C1/C2/C4/C12 of the pyran ring.

The sum of the angles around atom N2 (359°) shows a planar configuration, with an average N—O bond length of 1.216 (3) Å. The absence of steric effects between the NO₂ group and the quinoline moiety accounts for the small dihedral angle of 4.4 (1)° between the nitro group and its attached ring. The benzene ring C13—C18 is rotated with respect to the plane of the quinoline ring by 74.5 (1)° about the C5—C13 bond.

Intermolecular hydrogen bonds between the NO₂ and quinoline groups are responsible for the formation of dimers between molecules related by an inversion centre. A possible weak interaction of the type C—H...O is present (Table 2). Edge-to-edge stacking of the benzene ring is also observed, as

indicated by the distance of 3.766 (2) Å between the C16...C18ⁱ atoms [symmetry code: (i) 2 - *x*, 2 - *y*, 2 - *z*].

Experimental

To a solution of the appropriate *N*-benzylideneaniline (5.5 mmol) in dichloromethane (5 ml) at room temperature were added 2,3-dihydrofuran (5.5 mmol) and ZrCl₄ (10 mol%) and the resulting mixture was stirred for 90 min. The completed reaction was quenched with water and the crude product was purified by column chromatography using 2% ethyl acetate and hexane to yield the title compound. Crystals for X-ray study were obtained by recrystallization from a methanol–water (3:1) solution.

Crystal data

C ₁₈ H ₁₈ N ₂ O ₃	<i>Z</i> = 2
<i>M_r</i> = 310.34	<i>D_x</i> = 1.309 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Mo K α radiation
<i>a</i> = 9.5001 (10) Å	Cell parameters from 2569 reflections
<i>b</i> = 9.8823 (10) Å	θ = 2.2–26.7°
<i>c</i> = 9.9403 (10) Å	μ = 0.09 mm ⁻¹
α = 98.039 (2)°	<i>T</i> = 273 (2) K
β = 115.157 (2)°	Block, colorless
γ = 104.092 (2)°	0.20 × 0.15 × 0.10 mm
<i>V</i> = 787.18 (14) Å ³	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	2344 reflections with <i>I</i> > 2σ(<i>I</i>)
ω scans	<i>R</i> _{int} = 0.021
Absorption correction: none	θ_{\max} = 25.0°
7650 measured reflections	<i>h</i> = -11 → 11
2770 independent reflections	<i>k</i> = -11 → 11
	<i>l</i> = -11 → 11

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2 + 0.2373P]$
$R[F^2 > 2\sigma(F^2)] = 0.061$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.139$	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.15	$\Delta\rho_{\max} = 0.19 \text{ e \AA}^{-3}$
2770 reflections	$\Delta\rho_{\min} = -0.16 \text{ e \AA}^{-3}$
212 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

N1—C6	1.385 (3)	N2—O3	1.217 (3)
N1—C5	1.457 (3)	N2—C16	1.466 (3)
N2—O2	1.214 (3)		
C6—N1—C5	118.0 (2)	O2—N2—C16	118.6 (2)
O2—N2—O3	122.9 (2)	O3—N2—C16	118.5 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1N...O3 ⁱ	0.84 (3)	2.38 (3)	3.200 (3)	165 (2)
C1—H1B...O3 ⁱⁱ	0.97	2.59	3.535 (3)	166

Symmetry codes: (i) 2 - *x*, 2 - *y*, 2 - *z*; (ii) *x* - 1, *y* - 1, *z*.

The H atom attached to the N atom was located in a difference density map and refined isotropically. All other H atoms were positioned geometrically and refined as riding, with C—H distances in the range 0.93–0.98 Å and with *U*_{iso} = 1.5*U*_{eq}(C) for methyl H and 1.2*U*_{eq}(C) for other H atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

MM thanks the Council of Scientific and Industrial Research (CSIR), India, for the award of a Senior Research Fellowship.

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