

Thermal isomerization pathway of 1-(4-nitrophenyl)-2-phenylimino-2,5-dihydro-1*H*-pyrido[3,2-*b*]indole-3-carbonitrile discovered by laboratory powder data

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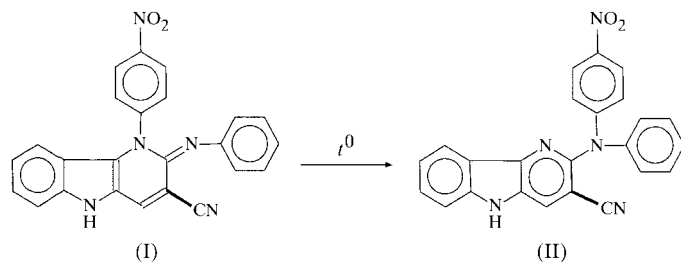
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The evidence for thermal isomerization of the title compound, C₂₄H₁₅N₅O₂, into 2-[(4-nitrophenyl)phenylamino]-5*H*-pyrido[3,2-*b*]indole-3-carbonitrile has been obtained as a consequence of crystal structure determinations from laboratory powder data.

Comment

As has recently been demonstrated (Ryabova *et al.*, 2001), the title compound, (I), irreversibly transforms into a new isomer with distinct properties on increasing the temperature to greater than 603 K, or after boiling in a solution of *N,N*-dimethylformamide in the presence of *t*-BuOK. Ryabova *et al.* (2001) assumed that this distinction in properties of the two isomers can be explained by the unexpected transformation of (I) into (II). However, the NMR and mass spectral data allow



two possible molecular structures, (I) and (II), for the new isomer. In the cases where several isomers are indistinguishable by spectroscopic methods, the crystal structure solution can help to determine the correct molecular structure even from laboratory powder data (Masciocchi *et al.*, 1998; Chernyshev, Yatsenko *et al.*, 1998; Chernyshev, Fitch *et al.*, 1999;

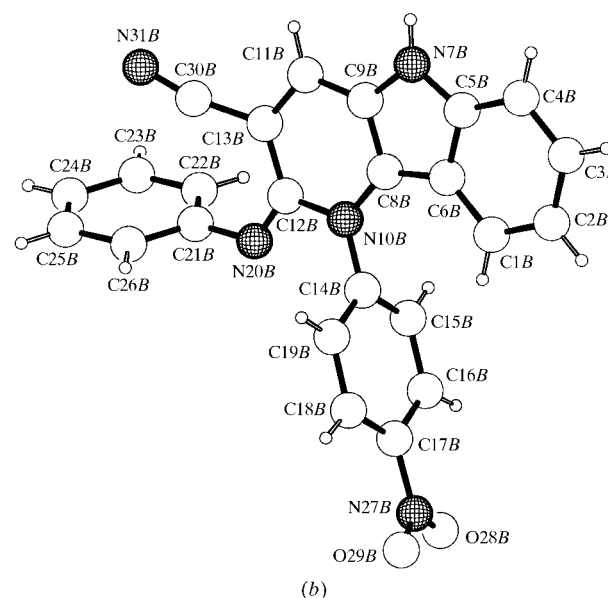
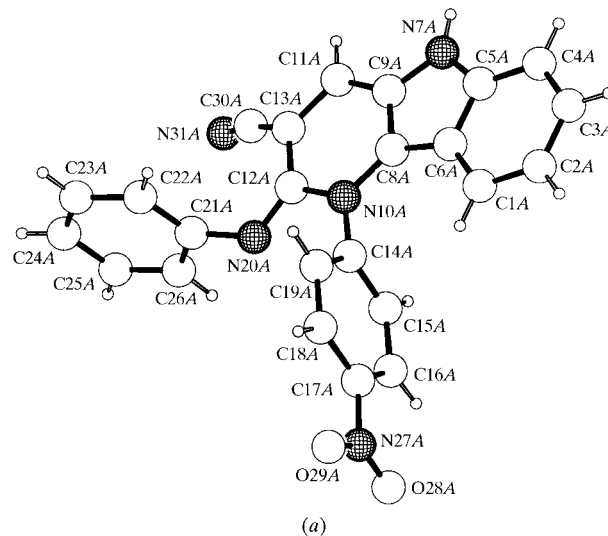


Figure 1
The two independent molecules of (I) with the atomic numbering.

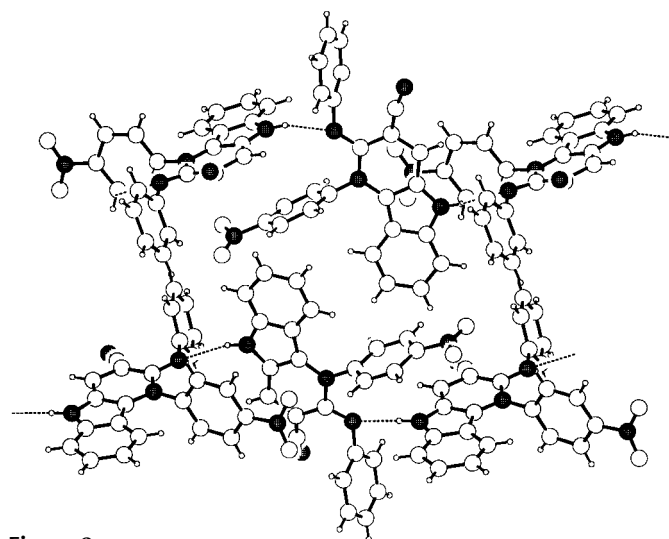


Figure 2
The hydrogen bonds in (I).

Chernyshev, Yatsenko *et al.*, 1999). Therefore, the present X-ray powder diffraction study was carried out.

The monoclinic crystal structure of (I) contains two independent molecules, *A* and *B* (Fig. 1), in the asymmetric unit. Molecules *A* and *B* are connected into chains *via* N—H...N hydrogen bonds between the imino H atoms and the azomethyne N atoms of adjacent molecules (Fig. 2 and Table 1). The conformations of molecules *A* and *B* are slightly different. The torsion angles C16*A*—C17*A*—N27*A*—O28*A* and C16*B*—C17*B*—N27*B*—O28*B* are 3 (3) and -19 (3)°, respectively. The phenyl planes of the nitrophenyl groups are inclined to the planes of the tricyclic fragments at 85.6 (5) and 91.2 (6)° for *A*

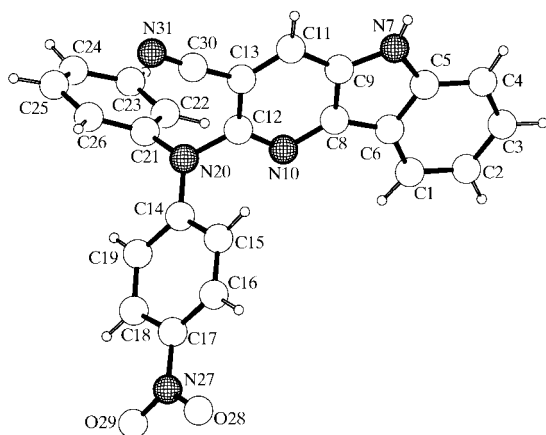


Figure 3
The molecular structure of (II) with the atomic numbering.

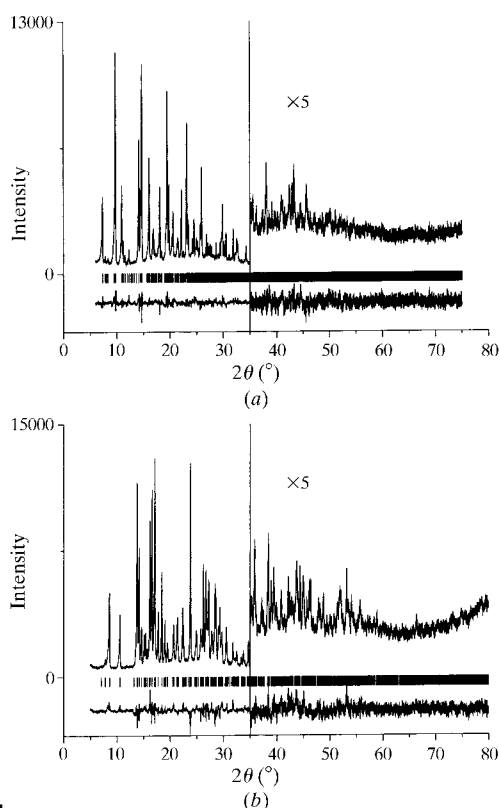


Figure 4
The Rietveld plots, showing the observed and difference profiles for (a) (I) and (b) (II). The reflection positions are shown above the difference profile.

and *B*, respectively. The decrease of the π -electron density at atoms C14*A* and C14*B* results from the almost planar geometry of the nitrophenyl groups and the absence of conjugation between the electronic pairs of N10*A* and N10*B* and the attached phenyl rings (due to their perpendicularity to the tricyclic fragments). The torsional angles C13*A*—C12*A*—N20*A*—C21*A* and C13*B*—C12*B*—N20*B*—C21*B* are 28 (4) and -3 (4)°, respectively. This means that the lone pair of the N20*A* atom is situated near the plane formed by atoms C14*A*, N10*A*, C12*A* and N20*A*, which assists the interaction between this lone pair and the π -deficient atom C14*A*. The same situation is valid for molecule *B*. It is possible to say that the space geometry of the *A* and *B* molecules is favourable for the isomerization reaction which results in compound (II). The exocyclic C=N double bond disappears in (II) (Fig. 3), causing the formation of the thermodynamically more stable pyridinium cycle and the irreversibility of this isomerization.

Experimental

Compounds (I) and (II) were prepared in polycrystalline form in the Department of Medicinal Chemistry under Professor V. G. Granik, State Scientific Center 'NIOPIK', according to the procedure of Ryabova *et al.* (2001).

Compound (I)

Crystal data

C₂₄H₁₅N₅O₂
M_r = 405.41
 Monoclinic, *P*2₁/*n*
a = 16.131 (7) Å
b = 18.070 (8) Å
c = 14.349 (6) Å
 β = 91.95 (2)°
V = 4180 (3) Å³
Z = 8

D_x = 1.288 Mg m⁻³
 Cu *K*α₁ radiation
 μ = 0.70 mm⁻¹
T = 295 (2) K
 Specimen shape: flat sheet
 7 × 7 × 1.5 mm
 Particle morphology: parallelepiped, red

Data collection

Enraf–Nonius Guinier Johansson camera FR 552 diffractometer (University of Amsterdam)
 Specimen mounting: pressed as a thin layer in the specimen holder of the camera

Specimen mounted in transmission mode
h = 0 → 12
k = 0 → 14
l = -11 → 11
 $2\theta_{\min}$ = 4.00, $2\theta_{\max}$ = 75.00°
 Increment in 2θ = 0.01°

Refinement

R_p = 0.060
R_{wp} = 0.084
R_{exp} = 0.034
S = 2.50
 $2\theta_{\min}$ = 6, $2\theta_{\max}$ = 75°
 Increment in 2θ = 0.01°
 Wavelength of incident radiation: 1.54059 Å
 Excluded region(s): 4.00–5.99
 Profile function: split-type pseudo-Voigt (Toraya, 1986)

312 parameters
 H atoms treated by a mixture of independent and constrained refinement
 Weighting scheme based on measured s.u.'s
 $(\Delta/\sigma)_{\max}$ = 0.025
 $\Delta\rho_{\max}$ = 0.6 e Å⁻³
 $\Delta\rho_{\min}$ = -0.4 e Å⁻³

Table 1

Hydrogen-bonding geometry (Å, °) for (I).

<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>
N7 <i>A</i> —H32 <i>A</i> ...N20 <i>B</i> ⁱ	0.86 (18)	2.16 (18)	2.99 (3)	162 (16)
N7 <i>B</i> —H32 <i>B</i> ...N20 <i>A</i> ⁱⁱ	0.86 (17)	2.15 (17)	2.99 (3)	166 (16)

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

Compound (II)

Crystal data

$C_{24}H_{15}N_5O_2$
 $M_r = 405.41$
 Orthorhombic, *Pbca*
 $a = 22.466$ (8) Å
 $b = 24.859$ (9) Å
 $c = 6.906$ (3) Å
 $V = 3857$ (3) Å³
 $Z = 8$

$D_x = 1.396$ Mg m⁻³
 Cu $K\alpha_1$ radiation
 $\mu = 0.76$ mm⁻¹
 $T = 295$ (2) K
 Specimen shape: flat sheet
 $7 \times 7 \times 1.5$ mm
 Particle morphology: needle, yellow

Data collection

Enraf–Nonius Guinier Johansson camera FR 552 diffractometer (University of Amsterdam)
 Specimen mounting: pressed as a thin layer in the specimen holder of the camera

Specimen mounted in transmission mode
 $h = 0 \rightarrow 18$
 $k = 0 \rightarrow 20$
 $l = 0 \rightarrow 5$
 $2\theta_{\min} = 4.00$, $2\theta_{\max} = 80.00^\circ$
 Increment in $2\theta = 0.01^\circ$

Refinement

$R_p = 0.060$
 $R_{wp} = 0.082$
 $R_{exp} = 0.030$
 $S = 2.72$
 $2\theta_{\min} = 5$, $2\theta_{\max} = 80^\circ$
 Increment in $2\theta = 0.01^\circ$
 Wavelength of incident radiation: 1.54059 Å
 Excluded region(s): 4.00–4.99
 Profile function: split-type pseudo-Voigt (Toraya, 1986)

179 parameters
 H atoms treated by a mixture of independent and constrained refinement
 Weighting scheme based on measured s.u.'s
 $(\Delta/\sigma)_{\max} = 0.02$
 $\Delta\rho_{\max} = 0.4$ e Å⁻³
 $\Delta\rho_{\min} = -0.5$ e Å⁻³
 Preferred orientation correction: March–Dollase (Dollase, 1986)

During the exposures, each specimen was spun in its plane to improve particle statistics. The unit-cell dimensions were determined from the Guinier photographs with the indexing program *ITO* (Visser, 1969) and refined with the program *LSPALD* (Visser, 1986) to $M_{20} = 20$ and $F_{30} = 49$ (0.010, 57) for (I), and to $M_{20} = 37$ and $F_{30} = 89$ (0.008, 43) for (II), using the first 50 peak positions. The space groups $P2_1/n$ and *Pbca* were chosen on the basis of systematic extinction rules for (I) and (II), respectively. Intensities for the structure determination and refinement were measured from the Guinier photographs in 0.01° steps using a Johansson LS18 line scanner. The structures of (I) and (II) were solved by the grid search procedure (Chernyshev & Schenk, 1998). Preliminary information about the possible structures of (I) and (II) was obtained from IR and NMR spectroscopy and mass spectrometry. The approximate models of the molecules were built up with the program *MOPAC6.0* (Stewart, 1990). There are two independent molecules in the crystal structure of (I). However, careful inspection of the results of full-pattern-decomposition procedure show the presence of pseudo-C centering. The full-pattern-decomposition procedure was undertaken again in space group *C2/c* to take into account the intensities of most of the peaks, though gave the worse profile *R* factor, $R_{wp} = 0.089$ compared with $R_{wp} = 0.064$ for $P2_1/n$. The crystal structure of (I) was solved in space group *C2/c* and refined in the correct space group $P2_1/n$. The conformations of two independent molecules of (I) and one molecule of (II) changed during the subsequent bond-restrained Rietveld refinements. The strength of the restraints was a function of inter-

atomic separation and for intramolecular bond lengths corresponds to an r.m.s. deviation of 0.03 Å. The additional restraints were applied to the planarity of the phenyl rings and tricyclic fragments. The diffraction profiles and the differences between the measured and calculated profiles are shown in Fig. 4. No atomic displacement parameters were refined for (I), and the overall U_{iso} parameter for non-H atoms was refined for (II). H atoms were placed in geometrically calculated positions and allowed to refine using bond restraints, with a common isotropic displacement parameter U_{iso} fixed to 0.05 Å². The March–Dollase texture formalism (Dollase, 1986) with 100 as a direction of preferred orientation was applied for (II). The texture parameter r refined to 1.26 (2). The crystal structure of (I) contains a void centered at (0,0,0) with a volume of 44 Å³. However, no peaks in the difference Fourier map were located in this area and when the O atom was placed in this position, its occupancy factor was refined to zero.

For both compounds, data collection: Johansson LS18 line-scanner data collection program; cell refinement: *LSPALD* (Visser *et al.*, 1986); data reduction: *Philips Profile Fit* (Philips, 1996); program(s) used to solve structure: *MRIA* (Zlokazov & Chernyshev, 1992); program(s) used to refine structure: *MRIA*; molecular graphics: *PLUTON* (Spek, 1992); software used to prepare material for publication: *MRIA*, *SHELXL93* (Sheldrick, 1993) and *PARST* (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1336). Services for accessing these data are described at the back of the journal.

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