

3-Amino-1-(4-fluorophenyl)-3a,3b,6,7-tetrahydrobenz[4,5]indene-2-carbonitrile

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Key indicators

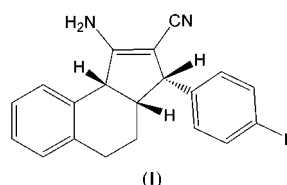
Single-crystal X-ray study
 $T = 291\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.038
 wR factor = 0.091
Data-to-parameter ratio = 14.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{20}\text{H}_{17}\text{FN}_2$, has been synthesized by the reductive cyclization induced by a low-valent titanium reagent. The cyclopentene ring adopts an envelope conformation, while the partially saturated six-membered ring adopts a distorted half-chair conformation. Intermolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds between the amino and cyano groups result in the formation of a dimer structure.

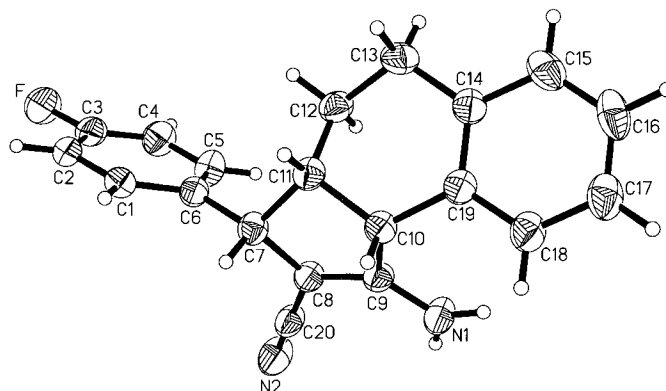
Received 16 September 2003
Accepted 19 September 2003
Online 24 September 2003

Comment

In the early 1970s, three groups of investigators (Tyreik & Wolochowicz, 1973; Mukaiyama *et al.*, 1973; McMurry & Fleming, 1974) established that low-valent titanium can abstract oxygen from ketones or aldehydes, leading to formation of olefins. The reactions induced by low-valent titanium reagents have been studied, revealing that a large number of functional groups can be reduced (Shi *et al.*, 1993, 1998, 2003). We report here the crystal structure of the title compound, (I), which has been synthesized by the cyclization reaction using a low-valent titanium reagent.



In (I), the five-membered C7–C11 ring adopts an envelope conformation, with atom C11 deviating from the C7–C10 plane by 0.566 (1) Å. The six-membered C10–C14/C19 ring adopts a distorted half-chair conformation. Atoms C13, C14,

**Figure 1**

The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

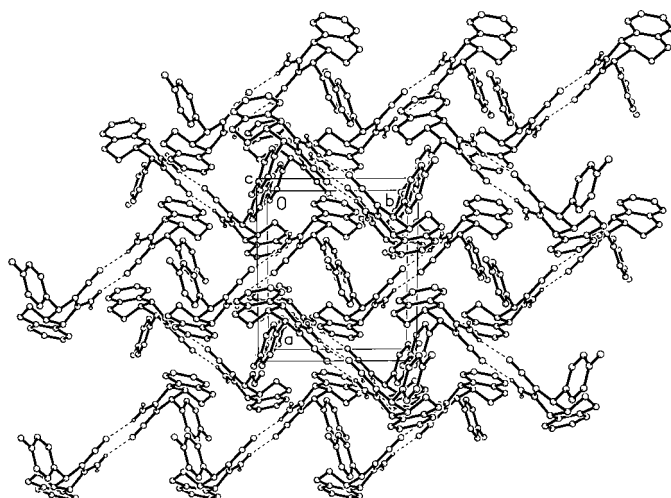


Figure 2
The molecular packing in the crystal, projected along the *c* axis.

C19 and C10 are coplanar, while atoms C11 and C12 deviate from the plane by 0.233 (1) and -0.490 (2) Å, respectively. Molecules show a dimer structure formed by an intermolecular N1—H1A \cdots N2(1 - *x*, -*y*, 1 - *z*) hydrogen bond between the amino and cyano groups (Table 2 and Fig. 2).

Experimental

The title compound, (I), was prepared by the reaction of 2-cyano-3-(4-fluorophenyl)-3-(1-tetralon-2-yl)propionitrile induced by a low-valent titanium reagent (TiCl₄/Zn) in tetrahydrofuran (m.p. 472–473 K). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of an ethanol solution.

Crystal data

C ₂₀ H ₁₇ FN ₂	$D_x = 1.249$ Mg m ⁻³
$M_r = 304.36$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 30 reflections
$a = 11.516$ (2) Å	$\theta = 2.9$ – 14.4°
$b = 9.710$ (1) Å	$\mu = 0.08$ mm ⁻¹
$c = 14.914$ (2) Å	$T = 291$ (2) K
$\beta = 103.97$ (1) $^\circ$	Block, colorless
$V = 1618.4$ (4) Å ³	$0.52 \times 0.42 \times 0.30$ mm
$Z = 4$	

Data collection

Siemens $P4$ diffractometer	$h = 0 \rightarrow 13$
ω scans	$k = 0 \rightarrow 11$
3487 measured reflections	$l = -18 \rightarrow 17$
3005 independent reflections	3 standard reflections
1534 reflections with $I > 2\sigma(I)$	every 97 reflections
$R_{\text{int}} = 0.009$	intensity decay: 2.9%
$\theta_{\text{max}} = 25.5^\circ$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0443P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.091$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.83$	$\Delta\rho_{\text{max}} = 0.12$ e Å ⁻³
3005 reflections	$\Delta\rho_{\text{min}} = -0.09$ e Å ⁻³
209 parameters	Extinction correction: <i>SHELXTL</i>
H-atom parameters constrained	Extinction coefficient: 0.0113 (12)

Table 1
Selected geometric parameters (Å, $^\circ$).

F—C3	1.367 (2)	C8—C9	1.349 (2)
N1—C9	1.343 (2)	C8—C20	1.407 (2)
N2—C20	1.145 (2)	C9—C10	1.514 (2)
C7—C8	1.515 (2)	C10—C11	1.540 (2)
C7—C11	1.549 (2)		
C6—C7—C8	116.5 (1)	N1—C9—C10	121.3 (1)
C8—C7—C11	101.0 (1)	C8—C9—C10	110.0 (1)
C9—C8—C7	111.1 (1)	C9—C10—C11	101.8 (1)
C20—C8—C7	124.7 (1)	C10—C11—C7	102.8 (1)
N1—C9—C8	128.6 (2)		
C5—C6—C7—C8	-35.8 (2)	N1—C9—C10—C19	33.5 (2)
C5—C6—C7—C11	83.6 (2)	N1—C9—C10—C11	161.3 (2)
C20—C8—C9—N1	4.6 (3)	C6—C7—C11—C12	-42.9 (2)
C7—C8—C9—N1	176.29 (17)		

Table 2
Hydrogen-bonding geometry (Å, $^\circ$).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1A \cdots N2 ⁱ	0.86	2.19	3.019 (2)	163

Symmetry code: (i) 1 - *x*, -*y*, 1 - *z*.

H atoms were positioned geometrically and treated as riding on their parent atoms, with C—H distances in the range 0.93–0.97 Å and N—H distances of 0.86 Å; the $U_{\text{iso}}(\text{H})$ values were set equal to $1.2U_{\text{iso}}(\text{parent atom})$.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1997); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We thank the Foundation of the ‘Surpassing Project’ of Jiangsu Province and the Natural Science Foundation of the Education Committee of Jiangsu Province (grant No. 03KJB150136) for financial support.

References

- McMurry, J. E. & Fleming, M. P. (1974). *J. Am. Chem. Soc.* **96**, 4708–4709.
 Mukaiyama, T., Sato, T. & Hanna, J. (1973). *Chem. Lett.* **10**, 1041–1044.
 Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
 Shi, D. Q., Chen, J. X., Chai, W. Y., Chen, W. X. & Kao, T. Y. (1993). *Tetrahedron Lett.* **34**, 2963–2964.
 Shi, D. Q., Lu, Z. S., Mu, L. L. & Dai, G. Y. (1998). *Synth. Commun.* **28**, 1073–1078.
 Shi, D. Q., Rong, L. C., Wang, J. X., Zhuang, Q. Y., Wang, X. S. & Hu, H. W. (2003). *Tetrahedron Lett.* **44**, 3199–3201.
 Siemens (1994). *XSCANS*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Tyreik, S. & Wolochowicz, I. (1973). *Bull. Soc. Chim. Fr.* **6**, 2147–2148.