# organic compounds

## Dimorphism of ethyl 1,4-dihydro-2,4,6-triphenylpyridine-3-carboxylate

**Michael Bolte**

Institut für Organische Chemie, J. W. Goethe-Universität Frankfurt, Marie-Curie-Straße 11, 60439 Frankfurt/Main, Germany
Correspondence e-mail: bolte@chemie.uni-frankfurt.de

The title compound, $C_{26}H_{23}NO_2$, (I$a$) and (I$b$), shows polymorphism with crystals obtained from different solvents displaying different crystal structures. However, it is not the geometry of the single molecules nor the hydrogen-bond pattern that is different in (I$a$) and (I$b$), but the way in which the hydrogen-bonded chains, running along the $a$-axis direction, are arranged with respect to each other.

## Comment

The 1,4-dihydropyridine ring system is of biological importance because it occurs in the reduced forms of nicotinamide adenine dinucleotide (NADH) and NADPH (Kosower & Sorensen, 1962). Since very little information is available on the geometry of aryl-substituted 1,4-dihydropyridines, the title compound, (I), was synthesized and its conformation was determined by means of an X-ray structure analysis. Surprisingly, crystals of (I) obtained from two different solvents showed two different crystal structures, (I$a$) and (I$b$). Thus, compound (I) shows polymorphism. However, since only two polymorphs have been characterized to date, one might speak of dimorphism.



(I$a$) and (I$b$)
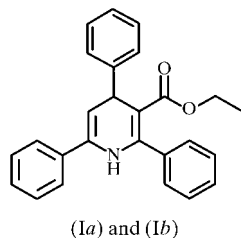
Polymorphism is a well known phenomenon in crystallography (Mitscherlich, 1822) and it is extensively described in crystallographic textbooks (*e.g.* Dunitz, 1979; Glusker, 1994). In the case of (I), two polymorphs, (I$a$) (Fig. 1) and (I$b$) (Fig. 2), were obtained *via* crystallization from different solvents. Although both polymorphs crystallize in space group $P\bar{1}$ (No. 2) with $Z = 2$, they have slightly different unit-cell volumes and their unit-cell dimensions, apart from the $a$ axis, are significantly different.

The Niggli values (Spek, 1990; Table 5) demonstrate clearly that the reduced cells are definitely different. The molecular structures of (I) found in the two polymorphs are very similar, indeed nearly identical. A least-squares fit of all non-H atoms in (I$a$) and (I$b$) gives an r.m.s. deviation of 0.263 Å. Bond lengths and angles are typical of their types (Allen *et al.*, 1987). The 1,4-dihydropyridine ring system is essentially planar [r.m.s. deviations 0.082 and 0.098 Å for (I$a$) and (I$b$), respectively]. The phenyl ring in the *para* position to the NH group is almost perpendicular to the heterocycle [80.54 (5)° in (I$a$) and
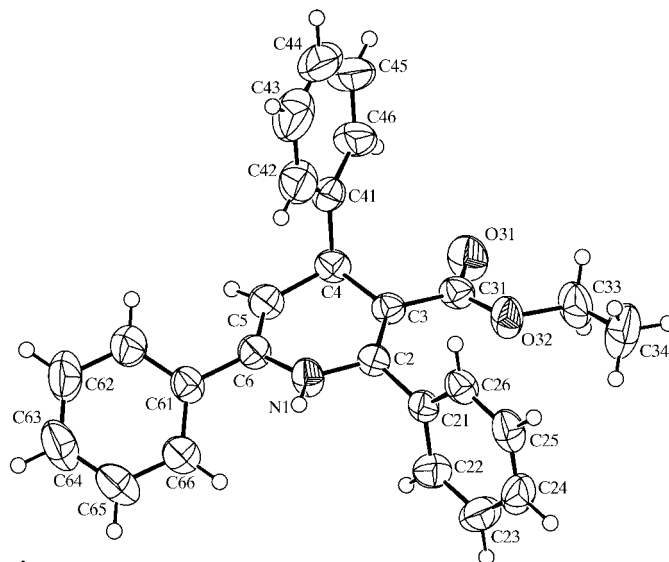


**Figure 1**
The molecular structure of (I$a$) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.



**Figure 2**
The molecular structure of (I$b$) 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.
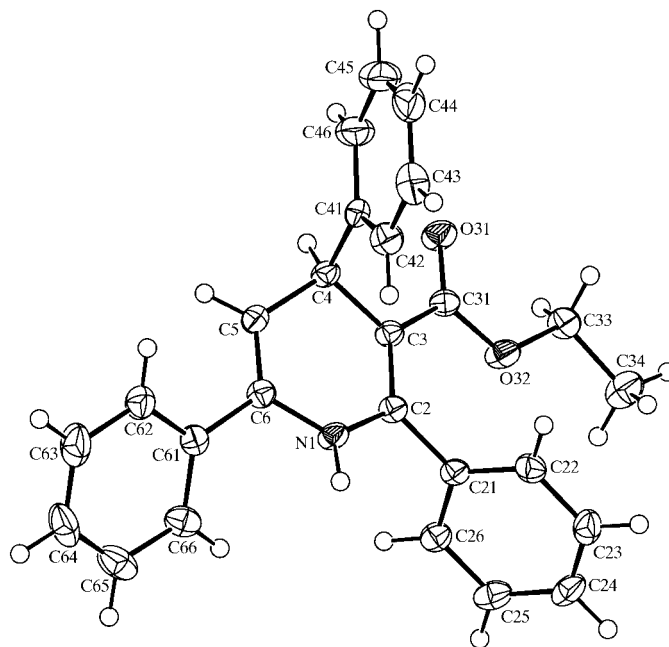
87.13 (3)° in (I*b*)]. The phenyl rings in the *ortho* positions with respect to the NH group form smaller dihedral angles with the central ring: C21–C26 71.37 (6)° in (I*a*) and 68.07 (4)° in (I*b*), and C61–C66 36.96 (9)° in (I*a*) and 35.58 (5)° in (I*b*). Since the C21–C26 aryl ring is *ortho* with respect to the ester group, it is obvious that its dihedral angle with the heterocycle is increased due to steric repulsion with the ester group. This ester group is also planar [r.m.s. deviation 0.040 Å in (I*a*) and 0.021 Å in (I*b*)] and more or less coplanar with the heterocycle [17.6 (1)° in (I*a*) and 7.57 (6)° in (I*b*)].
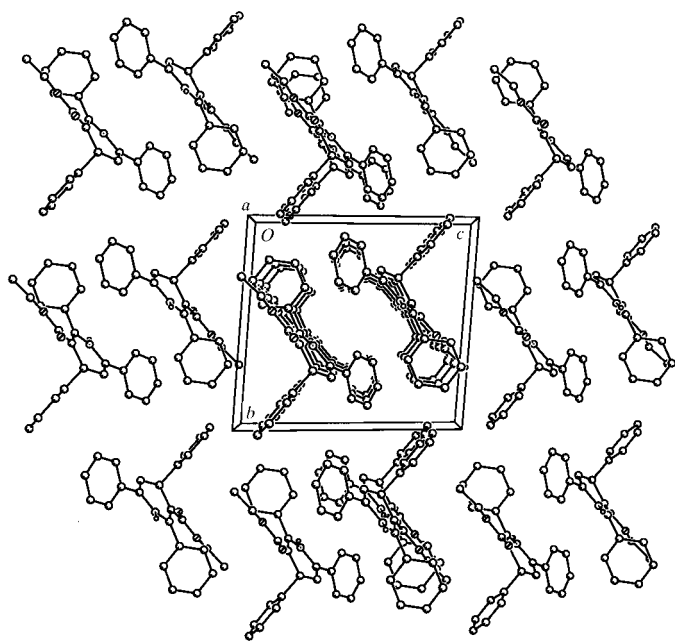


**Figure 3**
The packing diagram of (I*a*) viewed down the *a* axis.
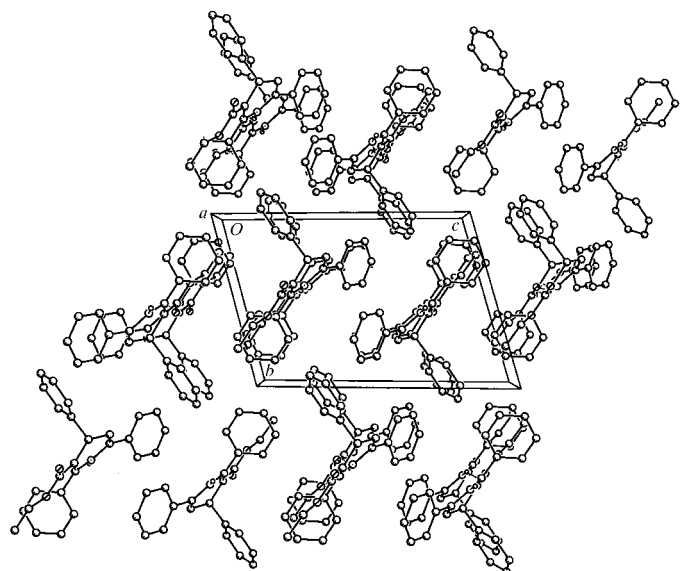


**Figure 4**
The packing diagram of (I*b*) viewed down the *a* axis.

In the crystal, the molecules form infinite chains which are stabilized by a hydrogen bond from the NH group to the carbonyl O atom. The remarkable feature of (I*a*) and (I*b*), however, is their different crystal packing (Figs. 3 and 4).

## Experimental

Compound (I) was synthesized according to the reaction described by Weiss (1952). Crystals of (I*a*) were obtained from ethyl acetate and those of (I*b*) were obtained from acetone. Having discovered that (I*b*) was a polymorph of (I*a*), the cell parameters of several further crystals of (I*b*) were checked at room temperature and at 163 K. They all turned out to be identical with those found for the first crystal of (I*b*).

### Compound (I*a*)

*Crystal data*

| | |
|---|---|
| $C_{26}H_{23}NO_2$ | $Z = 2$ |
| $M_r = 381.45$ | $D_x = 1.168$ Mg m$^{-3}$ |
| Triclinic, $P\bar{1}$ | Mo $K\alpha$ radiation |
| $a = 7.5083$ (2) Å | Cell parameters from 6287 |
| $b = 11.6140$ (3) Å | reflections |
| $c = 12.6644$ (3) Å | $\theta = 1$–26° |
| $\alpha = 93.862$ (1)° | $\mu = 0.07$ mm$^{-1}$ |
| $\beta = 98.759$ (1)° | $T = 293$ K |
| $\gamma = 94.527$ (1)° | Block, colourless |
| $V = 1084.53$ (5) Å$^3$ | $0.5 \times 0.4 \times 0.3$ mm |

*Data collection*

| | |
|---|---|
| Siemens CCD three-circle diffrac-tometer | $R_{int} = 0.038$ |
| | $\theta_{max} = 26.1°$ |
| $\omega$ scans | $h = -9 \rightarrow 9$ |
| 9841 measured reflections | $k = -14 \rightarrow 14$ |
| 3961 independent reflections | $l = -15 \rightarrow 15$ |
| 3332 reflections with $I > 2\sigma(I)$ | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0510P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.053$ | $+ 0.3729P]$ |
| $wR(F^2) = 0.141$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.10$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 3961 reflections | $\Delta\rho_{max} = 0.22$ e Å$^{-3}$ |
| 262 parameters | $\Delta\rho_{min} = -0.28$ e Å$^{-3}$ |
| H-atom parameters constrained | |

**Table 1**
Selected geometric parameters (Å, °) for (I*a*).

| | | | |
|---|---|---|---|
| N1—C2 | 1.388 (2) | C3—C4 | 1.541 (2) |
| N1—C6 | 1.411 (2) | C4—C5 | 1.514 (3) |
| C2—C3 | 1.378 (2) | C5—C6 | 1.349 (2) |
| | | | |
| C2—N1—C6 | 122.03 (14) | C5—C4—C3 | 110.26 (13) |
| C3—C2—N1 | 120.25 (15) | C6—C5—C4 | 123.29 (16) |
| C2—C3—C4 | 121.10 (15) | C5—C6—N1 | 119.41 (16) |

**Table 2**
Hydrogen-bonding geometry (Å, °) for (I*a*).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| N1—H1$\cdots$O31$^i$ | 0.86 | 2.17 | 3.0103 (19) | 164 |

Symmetry code: (i) $1 + x, y, z$.

# organic compounds

## Compound (I*b*)

### Crystal data

$C_{26}H_{23}NO_2$
$M_r = 381.45$
Triclinic, $P\bar{1}$
$a = 7.5178\ (1)$ Å
$b = 10.0669\ (2)$ Å
$c = 14.6364\ (2)$ Å
$\alpha = 73.534\ (1)°$
$\beta = 80.826\ (1)°$
$\gamma = 81.478\ (1)°$
$V = 1042.46\ (3)$ Å$^3$

$Z = 2$
$D_x = 1.215$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 5616
 reflections
$\theta = 1–25°$
$\mu = 0.08$ mm$^{-1}$
$T = 163$ K
Block, colourless
$0.6 \times 0.4 \times 0.2$ mm

### Data collection

Siemens CCD three-circle diffrac-
 tometer
$\omega$ scans
15 858 measured reflections
4188 independent reflections
3545 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$

$\theta_{max} = 26.5°$
$h = -9 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -18 \rightarrow 17$
260 standard reflections
 frequency: 720 min
 intensity decay: none

### Refinement

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.095$
$S = 1.03$
4188 reflections
263 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2 + 0.2564P]$
 where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.27$ e Å$^{-3}$
$\Delta\rho_{min} = -0.15$ e Å$^{-3}$
Extinction correction: SHELXL97
 (Sheldrick, 1997)
Extinction coefficient: 0.017 (2)

### Table 3
Selected geometric parameters (Å, °) for (I*b*).

| | | | |
|---|---|---|---|
| N1—C2 | 1.3773 (14) | C3—C4 | 1.5310 (15) |
| N1—C6 | 1.4042 (14) | C4—C5 | 1.5186 (15) |
| C2—C3 | 1.3696 (15) | C5—C6 | 1.3401 (15) |
| | | | |
| C2—N1—C6 | 121.81 (9) | C5—C4—C3 | 109.82 (9) |
| C3—C2—N1 | 120.25 (10) | C6—C5—C4 | 122.36 (10) |
| C2—C3—C4 | 120.69 (9) | C5—C6—N1 | 119.72 (10) |

### Table 4
Hydrogen-bonding geometry (Å, °) for (I*b*).

| $D—H\cdots A$ | $D—H$ | $H\cdots A$ | $D\cdots A$ | $D—H\cdots A$ |
|---|---|---|---|---|
| N1—H1$\cdots$O31$^{ii}$ | 0.88 | 2.17 | 2.9912 (12) | 155 |

Symmetry code: (ii) $x - 1, y, z$.

### Table 5
Comparative table of reduced (Niggli) cell parameters of the two polymorphs, (I*a*) and (I*b*) (Å$^2$).

| Polymorph | a.a | b.b | c.c | b.c | a.c | a.b |
|---|---|---|---|---|---|---|
| (I*a*) | 56.370 | 134.890 | 160.390 | −9.905 | −14.480 | −6.885 |
| (I*b*) | 56.520 | 101.340 | 214.220 | 41.765 | 17.545 | 11.215 |

All H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [$U(H) = 1.5U_{eq}(C_{methyl})$, $1.2U_{eq}(C)$ or $1.2U_{eq}(N)$], using a riding model with N—H = 0.86 and 0.88 Å, C—H(aromatic) = 0.93 and 0.95 Å, C—H(methyl) = 0.96 and 0.98 Å, C—H(secondary) = 0.97 and 0.99 Å, and C—H(tertiary) = 0.98 and 1.00 Å, for (I*a*) and (I*b*), respectively.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990) and *XP* in *SHELXTL-Plus* (Siemens, 1991).

## References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Dunitz, J. D. (1979). In *X-ray Analysis and the Structure of Organic Molecules.* Ithaca, NY: Cornell University Press.
Glusker, J. P. (1994). *Crystal Structure Analysis for Chemists and Biologists,* New York: VCH Publishers, Inc., edited by A. P. Marchand, pp. 321–323.
Kosower, E. M. & Sorensen, T. S. (1962). *J. Org. Chem.* **27**, 3764–3771.
Mitscherlich, E. (1822). *Ann. Chim. Phys.* **19**, 350–419.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Siemens (1991). *SHELXTL-Plus.* Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1995). *SMART* and *SAINT.* Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Weiss, M. (1952). *J. Am. Chem. Soc.* **74**, 200–202.