

Peter G. Jones,^{a*} Holger
Thönnessen,^a Reinhard
Schmutzler^a and Axel K. Fischer^b^aInstitut für Anorganische und Analytische
Chemie, Technische Universität Braunschweig,
Postfach 3329, 38023 Braunschweig, Germany,
and ^bInstitut für Chemie, Universität Magdeburg,
Universitätsplatz 2, 39106 Magdeburg,
GermanyCorrespondence e-mail:
jones@xray36.anchem.nat.tu-bs.de

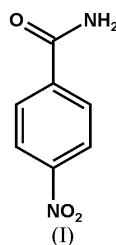
Key indicators

Single-crystal X-ray study
 $T = 173$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.049
 wR factor = 0.120
Data-to-parameter ratio = 14.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.A second polymorph of *p*-nitrobenzamide

The title compound, $\text{C}_7\text{H}_6\text{N}_2\text{O}_3$, crystallizes as a second $P2_1/c$ polymorph. Compared to the previously known form [Di Rienzo *et al.* (1977). *Acta Cryst.* B33, 3854–3858], the amide group is rotated much further out of the ring plane (*ca* 20°). The molecules are linked by symmetric three-centre $\text{N}-\text{H}(\cdots\text{O}_{\text{nitro}})_2$, and $\text{N}-\text{H}\cdots\text{O}_{\text{amide}}$ hydrogen bonds to form layers parallel to the *bc* plane.

Comment

The structure of the title compound, (I), was first determined by Di Rienzo *et al.* (1977) [space group $P2_1/c$, cell constants $a = 7.643$ (1), $b = 6.766$ (1), $c = 13.847$ (2) Å and $\beta = 91.34$ (1) $^\circ$] and was redetermined more precisely, using a high-angle refinement, by Tonogaki *et al.* (1993). The packing was shown to consist of centrosymmetric pairs of molecules, hydrogen-bonded through their $-\text{CONH}_2$ groups; the pairs were further linked by $\text{N}-\text{H}\cdots\text{O}_{\text{nitro}}$ hydrogen bonds, giving rise to an undulating layer structure. The apparently limited tendency of amides to form centrosymmetric hydrogen-bonded dimers has been discussed by Allen *et al.* (1998).



By chance, we have now discovered a new polymorph of (I) (see *Experimental*), which also crystallizes in $P2_1/c$, but with different unit-cell parameters. The molecule is shown in Fig. 1. The bond lengths and angles (Table 1) are similar in both polymorphs; in particular, the angles $\text{C}3-\text{C}4-\text{C}5$ and $\text{C}6-\text{C}1-\text{C}7$ are appreciably wider than 120° . The torsion angles, however, show that the substituents are rotated to different extents out of the ring plane. In the previous polymorph, the amide group was rotated by only *ca* 2° , but the nitro group by *ca* 7° ; in the current structure, the corresponding interplanar angles are 2.15 (7) $^\circ$ for the nitro group but 20.17 (4) $^\circ$ for the amide group.

The molecular packing is completely different from that of the first polymorph (Fig. 2 and Table 2). The molecules are first linked by a symmetric three-centre $\text{N}1-\text{H}1'(\cdots\text{O}_{\text{nitro}})_2$ hydrogen bond to form chains parallel to the *b* axis; Allen *et al.* (1997) showed, in an analysis of hydrogen bonding to nitro groups, that such symmetric systems are far from common. Next, the chains are crosslinked *via* the *c*-glide operator by

Received 12 November 2002
Accepted 19 November 2002
Online 30 November 2002

N1—H2'...O_{amide} hydrogen bonds to form layers parallel to the *bc* plane. Finally, three 'weak' hydrogen bonds of the form C—H...O join adjacent layers (not shown in Fig. 2); this is facilitated by the rotation of the molecules relative to the *bc* plane and of the amide groups relative to the rings.

Experimental

Attempts to crystallize the phosphinimide 2,3-diphenyl-2-(nitrobenzoylimido)-3,4-dihydro-2*H*-2σ⁴2λ⁵-naphtho[2,3-*e*][1,3,2]-oxazaphosphorin-4-one by slow evaporation from dichloromethane led to crystals of the title compound, presumably by slow hydrolysis by adventitious water (Thönnessen, 2000).

Crystal data

C ₇ H ₆ N ₂ O ₃	$D_x = 1.543 \text{ Mg m}^{-3}$
$M_r = 166.14$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2576 reflections
$a = 7.0993 (15) \text{ \AA}$	$\theta = 1.6\text{--}28^\circ$
$b = 10.183 (2) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$c = 10.1298 (15) \text{ \AA}$	$T = 173 (2) \text{ K}$
$\beta = 102.417 (10)^\circ$	Plate, colourless
$V = 715.2 (2) \text{ \AA}^3$	$0.5 \times 0.4 \times 0.2 \text{ mm}$
$Z = 4$	

Data collection

Siemens SMART diffractometer	$R_{\text{int}} = 0.042$
ω scans	$\theta_{\text{max}} = 28.2^\circ$
Absorption correction: none	$h = -9 \rightarrow 9$
4603 measured reflections	$k = -9 \rightarrow 13$
1746 independent reflections	$l = -12 \rightarrow 13$
1438 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 0.429P]$
$R[F^2 > 2\sigma(F^2)] = 0.049$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.120$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.09$	$\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
1746 reflections	$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$
117 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (\AA , $^\circ$).

C6—C1—C7	122.70 (14)	C3—C4—C5	123.23 (14)
C2—C1—C7—O1	−19.2 (2)	C3—C4—N2—O2	−0.8 (2)
C6—C1—C7—O1	158.62 (15)	C5—C4—N2—O2	179.50 (15)
C2—C1—C7—N1	162.03 (14)	C3—C4—N2—O3	178.81 (14)
C6—C1—C7—N1	−20.1 (2)	C5—C4—N2—O3	−0.9 (2)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
N1—H1'...O3 ⁱ	0.86 (3)	2.47 (3)	3.257 (2)	153 (2)
N1—H1'...O2 ⁱ	0.86 (3)	2.55 (3)	3.349 (2)	156 (2)
N1—H2'...O1 ⁱⁱ	0.90 (2)	2.06 (2)	2.951 (2)	172 (2)
C3—H3...O1 ⁱⁱⁱ	0.95	2.53	3.305 (2)	139
C2—H2...O2 ^{iv}	0.95	2.66	3.552 (2)	156
C6—H6...O3 ^v	0.95	2.54	3.358 (2)	145

Symmetry codes: (i) $x, 1 + y, z$; (ii) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (iii) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (iv) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (v) $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

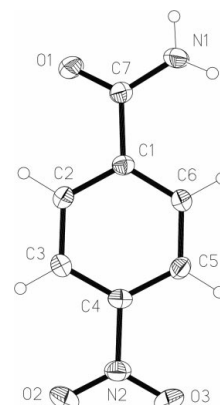


Figure 1

The molecule of the title compound in the crystal. Displacement ellipsoids are drawn at the 50% probability level. H-atom radii are arbitrary.

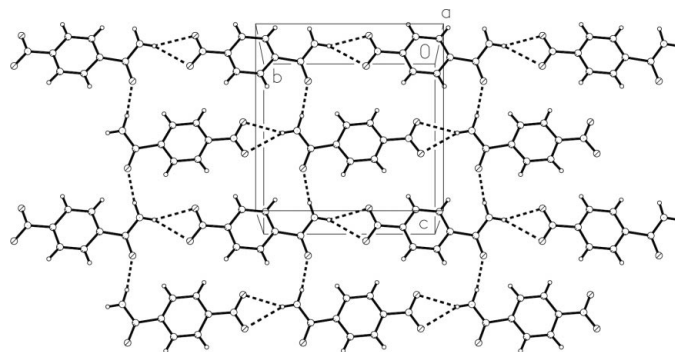


Figure 2

Packing diagram of the title compound, viewed perpendicular to the *bc* plane. Hydrogen bonds are indicated by dashed lines.

The H atoms of the NH₂ group were refined freely; other H atoms were included using a riding model with fixed C—H bond lengths of 0.95 \AA ; $U_{\text{iso}}(\text{H})$ values were fixed at 1.2 times the U_{eq} value of the parent atom.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

Financial support from the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Mr A. Weinkauff for technical assistance.

References

- Allen, F. H., Baalham, C. A., Lommerse, J. P. M., Raithby, P. R. & Sparr, E. (1997). *Acta Cryst.* **B53**, 1017–1024.
- Allen, F. H., Raithby, P. R., Shields, G. P. & Taylor, R. (1998). *Chem. Commun.* pp. 1043–1044.
- Di Rienzo, F., Domenicano, A. & Serantoni, E. F. (1977). *Acta Cryst.* **B33**, 3854–3858.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Siemens (1994). *XP*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1995). *SMART* (Version 4.05) and *SAINT* (Version 4.02). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Thönnessen, H. (2000). PhD Thesis, Technical University of Braunschweig, Germany.
Tonogaki, M., Kawata, T., Ohba, S., Iwata, Y. & Shibuya, I. (1993). *Acta Cryst.* **B49**, 1031–1039.