

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

4-Nitrophenyl *N*-phenylcarbamateYun-Hua Xu^a and Fanqi Qu^{b*}

^aSchool of Science, Beijing Jiaotong University, Beijing 100044, People's Republic of China, and ^bCollege of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei 430072, People's Republic of China

Correspondence e-mail: fanqiqu@whu.edu.cn

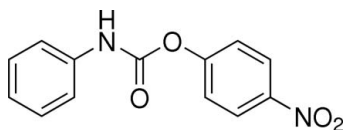
Received 9 December 2007; accepted 24 December 2007

Key indicators: single-crystal X-ray study; $T = 90$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.038; wR factor = 0.104; data-to-parameter ratio = 8.6.

The title compound, $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_4$, was synthesized as an intermediate for the preparation of ureas. The two aromatic rings are twisted about the central carbamate group with a C—C—N—C torsion angle of $139.6(2)^\circ$ and a C—C—O—C torsion angle of $95.9(2)^\circ$. The molecules are linked into one-dimensional chains by N—H \cdots O hydrogen bonds along the b axis. Weak interactions between O atoms of the nitro groups (O \cdots O = 3.012 Å) connect two adjacent chains.

Related literature

For related literature, see: Allen *et al.* (1987); Izdebski & Pawlak (1989); Olma *et al.* (2006); Tye *et al.* (2002).



Experimental

Crystal data

 $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_4$ $M_r = 258.23$ Monoclinic, $P2_1$ $a = 6.0170(2)$ Å $b = 5.0650(1)$ Å $c = 18.8960(5)$ Å $\beta = 92.538(1)^\circ$ $V = 575.31(3)$ Å³ $Z = 2$ Mo $K\alpha$ radiation $\mu = 0.11$ mm⁻¹ $T = 90(2)$ K $0.50 \times 0.40 \times 0.26$ mm

Data collection

Nonius KappaCCD diffractometer

Absorption correction: multi-scan

(SCALEPACK; Otwinowski &

Minor, 1997)

 $T_{\min} = 0.946$, $T_{\max} = 0.971$

2630 measured reflections

1473 independent reflections

1363 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.020$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.037$ $wR(F^2) = 0.104$ $S = 1.14$

1473 reflections

172 parameters

1 restraint

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.24$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.32$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{O1}^i$	0.88	2.05	2.903 (3)	164

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

Data collection: COLLECT (Nonius, 2002); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO-SMN (Otwinowski & Minor, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: XP in SHELXTL/PC (Sheldrick, 1995); software used to prepare material for publication: SHELXL97 and local procedures.

FQ and Y-HX thank Dr Sihui Long for helpful discussions during the preparation of this paper.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2180).

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.
- Izdebski, J. & Pawlak, D. (1989). *Synthesis*, **6**, 423–425.
- Nonius (2002). COLLECT. Nonius BV, Delft, The Netherlands.
- Olma, S., Ermert, J. & Coenen, H. H. (2006). *J. Label. Compd. Radiopharm.* **49**, 1037–1050.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (1995). XP in SHELXTL/PC. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Tye, H., Eldred, C. & Wills, M. (2002). *Tetrahedron Lett.* **43**, 155–158.

supporting information

Acta Cryst. (2008). E64, o404 [doi:10.1107/S1600536807068274]

4-Nitrophenyl *N*-phenylcarbamate

Yun-Hua Xu and Fanqi Qu

S1. Comment

The title compound (I), along with other 4-nitrophenyl carbamates, are important intermediates for the synthesis of ureas (Olma, *et al.* 2006; Izdebski & Pawlak, 1989). Although it has been used in organic synthesis for a long time, the crystal structure, as far as we know, is reported here for the first time.

The compound, two aromatic rings connected by a carbamate group, is not planar as would be expected. This is evidenced by the dihedral angles between the nitrophenyl ring and the carbamate, C13—C8—O2—C7=95.9 (2)°, and the benzyl ring and the carbamate, C2—C1—N1—C7=139.6 (2)°. Bond lengths and angles for (I) are within normal ranges (Allen *et al.*, 1987). The molecules form one-dimensional chains formed through N—H···O hydrogen bonds along the *b* axis (Table 1). In addition, intermolecular O···O interactions exists between nitro groups in neighboring chains (Fig. 2).

S2. Experimental

Aniline (1.0 g, 10.7 mmol) was added dropwise to a round-bottom flask containing 4-nitrophenyl chloroformate (2.2 g, 10.9 mmol) and pyridine (0.9 ml, 11.1 mmol) in 20 ml methylene chloride cooled with ice water. After the solution was warmed to ambient temperature, the mixture was refluxed overnight with stirring. The solution was then washed with 1 N NaHCO₃, water and brine, and then dried with anhydrous Na₂SO₄. After removal of the solvent, the product was recovered as a yellow solid (2.5 g, 90%) (Tye, *et al.* 2002). Colorless crystals of (I) were obtained by recrystallization from ethyl acetate.

S3. Refinement

H atoms were found in difference Fourier maps and subsequently placed in idealized positions with constrained C—H distances of 0.95 Å (C_{Ar}H), and 0.88 Å (NH₁). *U*_{iso}(H) values were set to 1.2*U*_{eq} for all H atoms. In the absence of significant anomalous scattering effects, Friedel pairs were merged prior to refinement.

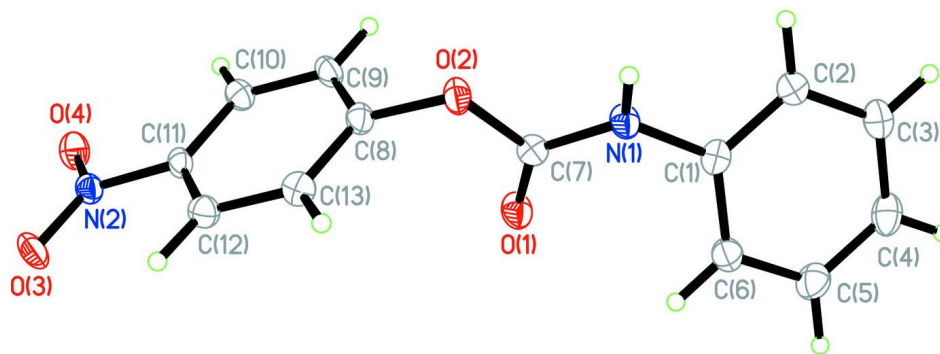


Figure 1

The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level (arbitrary spheres for the H atoms).

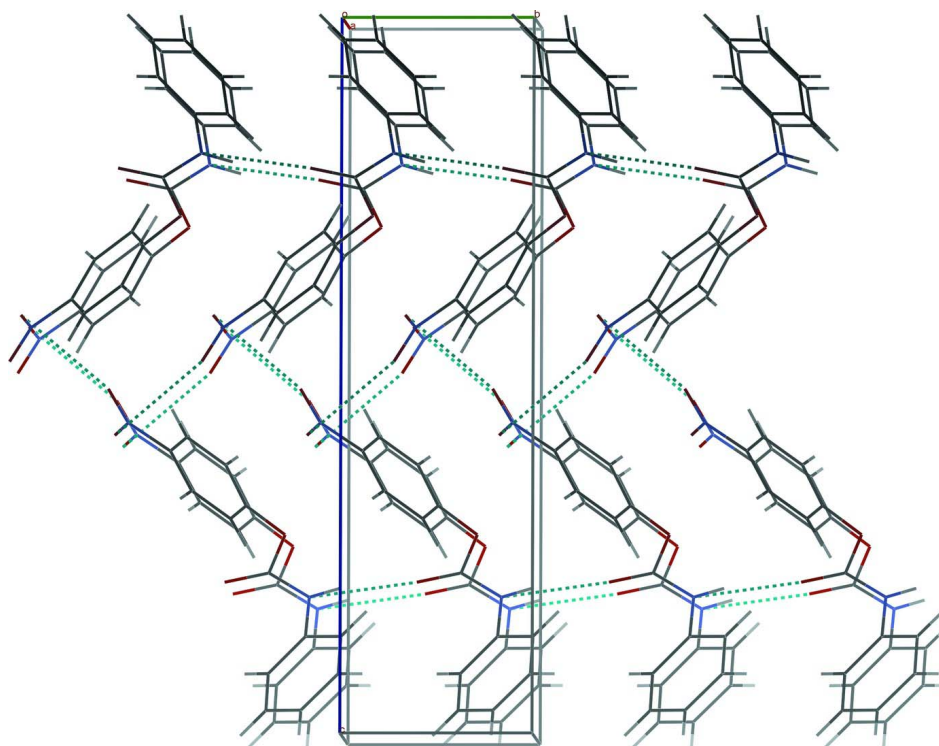


Figure 2

A packing diagram of (I) along *a* axis.

4-Nitrophenyl *N*-phenylcarbamate

Crystal data

$C_{13}H_{10}N_2O_4$

$M_r = 258.23$

Monoclinic, $P2_1$

Hall symbol: $P2_1yb$

$a = 6.0170 (2) \text{ \AA}$

$b = 5.0650 (1) \text{ \AA}$

$c = 18.8960 (5) \text{ \AA}$

$\beta = 92.538 (1)^\circ$

$V = 575.31 (3) \text{ \AA}^3$

$Z = 2$

$F(000) = 268$

$D_x = 1.491 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1469 reflections

$\theta = 1\text{--}27.5^\circ$

$\mu = 0.11 \text{ mm}^{-1}$

$T = 90$ K $0.50 \times 0.40 \times 0.26$ mm
 Block, colorless

Data collection

Nonius KappaCCD diffractometer	2630 measured reflections
Radiation source: fine-focus sealed tube	1473 independent reflections
Graphite monochromator	1363 reflections with $I > 2\sigma(I)$
Detector resolution: 18 pixels mm^{-1}	$R_{\text{int}} = 0.020$
ω scans at fixed $\chi = 55^\circ$	$\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 1.1^\circ$
Absorption correction: multi-scan	$h = -7 \rightarrow 7$
(SCALEPACK; Otwinowski & Minor, 1997)	$k = -6 \rightarrow 6$
$T_{\text{min}} = 0.946$, $T_{\text{max}} = 0.971$	$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.038$	H-atom parameters constrained
$wR(F^2) = 0.104$	$w = 1/[\sigma^2(F_o^2) + (0.0582P)^2 + 0.1763P]$
$S = 1.14$	where $P = (F_o^2 + 2F_c^2)/3$
1473 reflections	$(\Delta/\sigma)_{\text{max}} = 0.009$
172 parameters	$\Delta\rho_{\text{max}} = 0.24 \text{ e } \text{\AA}^{-3}$
1 restraint	$\Delta\rho_{\text{min}} = -0.32 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.9665 (3)	0.7781 (5)	0.84935 (11)	0.0179 (5)
N1	0.7888 (3)	0.8052 (4)	0.79739 (10)	0.0185 (4)
H1	0.7443	0.9655	0.7857	0.022*
N2	0.0763 (3)	-0.1088 (4)	0.56535 (9)	0.0180 (4)
O1	0.7161 (3)	0.3675 (4)	0.77761 (9)	0.0227 (4)
O2	0.5362 (3)	0.6890 (3)	0.71426 (8)	0.0196 (4)
O3	-0.1087 (2)	-0.1712 (4)	0.58598 (9)	0.0248 (4)
O4	0.1657 (3)	-0.2175 (4)	0.51627 (8)	0.0231 (4)
C2	1.1431 (4)	0.9546 (5)	0.84631 (12)	0.0219 (5)
H2	1.1414	1.0883	0.8110	0.026*
C3	1.3226 (4)	0.9341 (6)	0.89534 (12)	0.0248 (5)
H3	1.4432	1.0546	0.8935	0.030*
C4	1.3255 (4)	0.7399 (6)	0.94631 (12)	0.0257 (6)
H4	1.4489	0.7249	0.9792	0.031*

C5	1.1480 (4)	0.5660 (6)	0.94961 (12)	0.0261 (5)
H5	1.1498	0.4330	0.9851	0.031*
C6	0.9670 (4)	0.5853 (6)	0.90111 (11)	0.0214 (5)
H6	0.8451	0.4669	0.9037	0.026*
C7	0.6852 (4)	0.5994 (5)	0.76518 (11)	0.0169 (4)
C8	0.4214 (4)	0.4908 (5)	0.67556 (11)	0.0177 (5)
C9	0.5166 (3)	0.3802 (5)	0.61711 (11)	0.0190 (5)
H9	0.6578	0.4381	0.6027	0.023*
C10	0.4012 (4)	0.1825 (5)	0.58006 (11)	0.0187 (5)
H10	0.4625	0.1017	0.5400	0.022*
C11	0.1954 (3)	0.1055 (5)	0.60271 (11)	0.0161 (4)
C12	0.0975 (4)	0.2213 (5)	0.65993 (11)	0.0189 (5)
H12	-0.0457	0.1672	0.6735	0.023*
C13	0.2135 (4)	0.4187 (5)	0.69708 (11)	0.0198 (5)
H13	0.1508	0.5024	0.7365	0.024*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0170 (10)	0.0182 (11)	0.0183 (9)	0.0038 (10)	-0.0015 (7)	-0.0028 (9)
N1	0.0191 (9)	0.0118 (9)	0.0241 (9)	0.0013 (8)	-0.0045 (7)	-0.0005 (8)
N2	0.0152 (9)	0.0161 (10)	0.0224 (8)	-0.0008 (8)	-0.0022 (7)	0.0029 (9)
O1	0.0238 (8)	0.0150 (9)	0.0286 (8)	0.0000 (7)	-0.0060 (6)	0.0001 (7)
O2	0.0188 (8)	0.0154 (8)	0.0240 (7)	-0.0009 (7)	-0.0058 (6)	-0.0014 (7)
O3	0.0153 (7)	0.0257 (10)	0.0334 (8)	-0.0076 (8)	0.0006 (6)	0.0016 (8)
O4	0.0207 (8)	0.0215 (9)	0.0269 (8)	0.0002 (8)	-0.0016 (6)	-0.0052 (8)
C2	0.0230 (11)	0.0208 (13)	0.0218 (10)	-0.0031 (10)	-0.0008 (8)	0.0009 (10)
C3	0.0205 (11)	0.0267 (14)	0.0269 (11)	-0.0036 (10)	-0.0020 (8)	-0.0045 (10)
C4	0.0218 (11)	0.0264 (14)	0.0280 (11)	0.0036 (11)	-0.0076 (9)	-0.0041 (11)
C5	0.0303 (13)	0.0235 (13)	0.0238 (10)	0.0022 (12)	-0.0061 (9)	0.0027 (11)
C6	0.0215 (11)	0.0204 (12)	0.0221 (10)	-0.0020 (11)	-0.0017 (8)	0.0002 (10)
C7	0.0163 (10)	0.0155 (11)	0.0190 (9)	0.0017 (9)	0.0008 (7)	-0.0003 (9)
C8	0.0188 (10)	0.0130 (11)	0.0209 (10)	-0.0012 (10)	-0.0049 (8)	0.0010 (9)
C9	0.0127 (9)	0.0196 (12)	0.0244 (10)	-0.0032 (10)	-0.0012 (8)	0.0019 (10)
C10	0.0151 (10)	0.0198 (11)	0.0212 (9)	-0.0010 (9)	0.0013 (8)	-0.0002 (9)
C11	0.0133 (10)	0.0146 (10)	0.0200 (9)	-0.0004 (9)	-0.0039 (7)	0.0013 (9)
C12	0.0151 (10)	0.0201 (13)	0.0215 (10)	0.0008 (9)	0.0004 (8)	0.0019 (9)
C13	0.0191 (10)	0.0201 (12)	0.0203 (9)	0.0011 (10)	0.0012 (8)	-0.0004 (9)

Geometric parameters (Å, °)

C1—C6	1.382 (3)	C4—C5	1.388 (4)
C1—C2	1.392 (4)	C4—H4	0.9500
C1—N1	1.426 (3)	C5—C6	1.396 (3)
N1—C7	1.346 (3)	C5—H5	0.9500
N1—H1	0.8800	C6—H6	0.9500
N2—O4	1.224 (3)	C8—C13	1.381 (3)
N2—O3	1.237 (2)	C8—C9	1.385 (3)

N2—C11	1.465 (3)	C9—C10	1.390 (3)
O1—C7	1.210 (3)	C9—H9	0.9500
O2—C7	1.364 (3)	C10—C11	1.384 (3)
O2—C8	1.405 (3)	C10—H10	0.9500
C2—C3	1.395 (3)	C11—C12	1.385 (3)
C2—H2	0.9500	C12—C13	1.391 (3)
C3—C4	1.376 (4)	C12—H12	0.9500
C3—H3	0.9500	C13—H13	0.9500
C6—C1—C2	120.4 (2)	C1—C6—H6	120.3
C6—C1—N1	122.2 (2)	C5—C6—H6	120.3
C2—C1—N1	117.4 (2)	O1—C7—N1	126.8 (2)
C7—N1—C1	123.7 (2)	O1—C7—O2	123.4 (2)
C7—N1—H1	118.1	N1—C7—O2	109.8 (2)
C1—N1—H1	118.1	C13—C8—C9	122.7 (2)
O4—N2—O3	123.8 (2)	C13—C8—O2	117.8 (2)
O4—N2—C11	118.45 (18)	C9—C8—O2	119.5 (2)
O3—N2—C11	117.76 (19)	C8—C9—C10	118.6 (2)
C7—O2—C8	114.97 (19)	C8—C9—H9	120.7
C3—C2—C1	119.7 (2)	C10—C9—H9	120.7
C3—C2—H2	120.2	C11—C10—C9	118.8 (2)
C1—C2—H2	120.2	C11—C10—H10	120.6
C4—C3—C2	120.2 (2)	C9—C10—H10	120.6
C4—C3—H3	119.9	C10—C11—C12	122.7 (2)
C2—C3—H3	119.9	C10—C11—N2	119.0 (2)
C3—C4—C5	120.0 (2)	C12—C11—N2	118.30 (19)
C3—C4—H4	120.0	C11—C12—C13	118.5 (2)
C5—C4—H4	120.0	C11—C12—H12	120.8
C4—C5—C6	120.4 (2)	C13—C12—H12	120.8
C4—C5—H5	119.8	C8—C13—C12	118.8 (2)
C6—C5—H5	119.8	C8—C13—H13	120.6
C1—C6—C5	119.4 (2)	C12—C13—H13	120.6
C6—C1—N1—C7	-40.3 (3)	C7—O2—C8—C9	-85.5 (3)
C2—C1—N1—C7	139.6 (2)	C13—C8—C9—C10	-2.2 (4)
C6—C1—C2—C3	0.8 (4)	O2—C8—C9—C10	179.3 (2)
N1—C1—C2—C3	-179.1 (2)	C8—C9—C10—C11	0.5 (3)
C1—C2—C3—C4	0.2 (4)	C9—C10—C11—C12	1.4 (4)
C2—C3—C4—C5	-0.9 (4)	C9—C10—C11—N2	-178.0 (2)
C3—C4—C5—C6	0.5 (4)	O4—N2—C11—C10	1.8 (3)
C2—C1—C6—C5	-1.1 (4)	O3—N2—C11—C10	-179.0 (2)
N1—C1—C6—C5	178.8 (2)	O4—N2—C11—C12	-177.6 (2)
C4—C5—C6—C1	0.5 (4)	O3—N2—C11—C12	1.6 (3)
C1—N1—C7—O1	4.5 (4)	C10—C11—C12—C13	-1.6 (4)
C1—N1—C7—O2	-174.95 (18)	N2—C11—C12—C13	177.8 (2)
C8—O2—C7—O1	-1.1 (3)	C9—C8—C13—C12	2.0 (4)
C8—O2—C7—N1	178.43 (18)	O2—C8—C13—C12	-179.5 (2)
C7—O2—C8—C13	95.9 (2)	C11—C12—C13—C8	-0.1 (3)

Hydrogen-bond 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—H1···O1 ⁱ	0.88	2.05	2.903 (3)	164

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