

Crystal structure of 2-oxo-2-phenylethyl diisopropylcarbamate

Viktor Martens,^a Helmar Görls^b and Wolfgang Imhof^{a*}

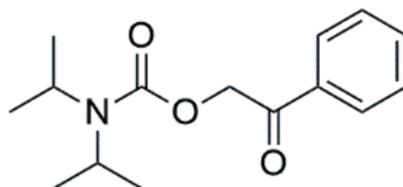
^aInstitute of Integrated Natural Sciences, University Koblenz - Landau, Universitätsstr. 1, 56070 Koblenz, Germany, and

^bInstitute of Inorganic and Analytical Chemistry, Friedrich-Schiller-University Jena, Humboldtstr. 8, 07743 Jena, Germany. *Correspondence e-mail: Imhof@uni-koblenz.de

In the molecular structure of the title compound, C₁₅H₂₁NO₃, the urethane function and the benzoyl group are almost perpendicular to each other [dihedral angle 88.97 (5)°]. In the crystal structure, infinite supramolecular layers in the *bc* plane are formed by weak C—H...O hydrogen bonds.

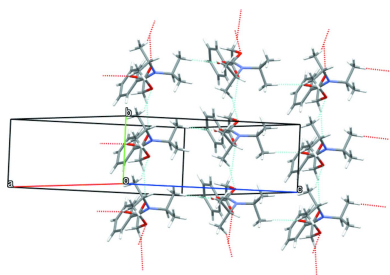
1. Chemical context

Phenacyl and desyl compounds have been a subject of interest for many years due to their use as photoremovable protecting groups (PPGs) (Givens *et al.*, 2012; Kammari *et al.*, 2007; Klán *et al.*, 2013; Sheehan & Umezawa, 1973). Carbamates are used for the protection of carboxylic acids and may also act as suitable protecting groups for amines (Speckmeier *et al.*, 2018). Speckmeier and co-workers synthesized several phenacyl urethanes, but the protection of diisopropylamine by a phenacyl group has not been reported so far. The title compound was synthesized according to reported routes (Speckmeier *et al.*, 2018).



2. Structural commentary

As expected, the carbamate functional moiety (N1/C3/O3/O2) is essentially planar (maximum deviation of 0.01 Å for C3). The same is true for the benzoyl group (C1/O1/C10–C15, maximum deviation of 0.05 Å for O1). These two planes subtend a dihedral angle of 88.97 (5)° and therefore an almost perpendicular arrangement (Fig. 1). Otherwise, the bond lengths and angles are of expected values with C3–N1 [1.348 (2) Å] and C3–O2 [1.368 (2) Å] being slightly shorter than a typical C–O or C–N single bond due to the partial double-bond character of the respective bonds in a carbamate.



3. Supramolecular features

The crystal structure of the title compound features weak hydrogen bonds (Desiraju & Steiner, 2001) of the C—H...O type, as shown in Table 1. The interaction C5—H5B...O3

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C2-H2B\cdots O1^i$	0.99	2.70	3.605 (2)	152
$C5-H5B\cdots O3^{ii}$	0.98	2.62	3.578 (2)	167
$C9-H9B\cdots O2^{iii}$	0.98	2.68	3.599 (2)	157

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

links molecules of the title compound into infinite chains parallel to the c -axis direction. Additional $C2-H2B\cdots O1$ and $C9-H9B\cdots O2$ interactions link these infinite chains to a supramolecular sheet parallel to the bc plane (Fig. 2). The latter interaction is accompanied by a short $C9-H9B\cdots C3$ contact, which makes the contact look like a non-classical hydrogen bond towards the π -system of a $C=O$ double bond, again showing the partial double-bond character of the respective bond.

4. Database survey

In the CSD (ConQuest Version 2020.3.0; Groom *et al.*, 2016), only one other carbamate with a $CH_2-C(O)-Ph$ group attached to the carbamate oxygen atom is reported (NIWQUI; Jiang *et al.*, 2019). The respective compound shows a diethylamino group and a p -chlorophenyl substituent instead of the diisopropylamino group and the non-substituted phenyl group in the title compound. In contrast to the title compound, the carbamate plane and the benzoyl plane are almost coplanar. The carbonyl oxygen atoms show numerous short contacts towards different $C-H$ groups of neighboring molecules, leading to a dense three-dimensional network.

5. Synthesis and crystallization

Diisopropylamine (0.05 mol, 5.05 g) and 1 equiv. of cesium carbonate (0.05 mol, 16.55 g) were placed in a Schlenk tube and dissolved in anhydrous DMSO (150 mL). The tube was sealed with a septum and two balloons filled with CO_2 were bubbled through the reaction mixture within one h while stirring. After the addition of CO_2 , 1.1 equiv. of 2-bromo-1-phenylethan-1-one (0.055 mol, 10.95 g) dissolved in a small

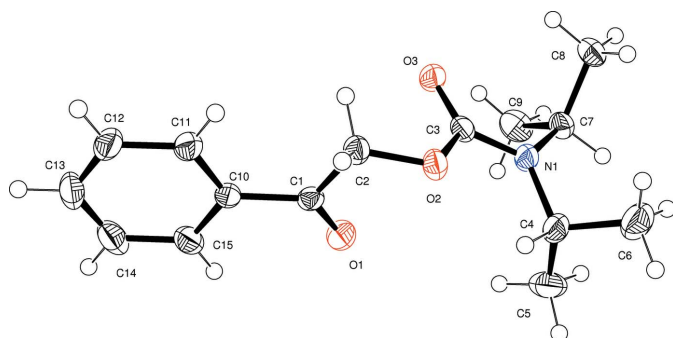


Figure 1
Molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{15}H_{21}NO_3$
M_r	263.33
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	133
a, b, c (Å)	18.4574 (8), 5.7020 (2), 14.8058 (6)
β (°)	113.468 (1)
V (Å ³)	1429.33 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.09
Crystal size (mm)	0.10 × 0.10 × 0.08
Data collection	
Diffractometer	Nonius KappaCCD
Absorption correction	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)
T_{min}, T_{max}	0.674, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13968, 3280, 2464
R_{int}	0.040
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.049, 0.113, 1.04
No. of reflections	3280
No. of parameters	177
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.27, -0.21

Computer programs: COLLECT (Nonius 1998), DENZO (Otwinowski & Minor, 1997), SHELXS97 (Sheldrick, 2008), SHELXL2018/3 (Sheldrick, 2015), ORTEP-3 (Farrugia, 2012) and Mercury (Macrae *et al.*, 2020).

amount of DMSO was added in one portion. The consumption of 2-bromo-1-phenylethan-1-one was monitored by TLC and after 30 min the reaction mixture was poured on ice to quench the reaction. After extraction with dichloromethane (3×), the combined organic phases were washed with brine, separated and dried over Na_2SO_4 . The solvent was removed *in vacuo* and the crude product was recrystallized from n -hexane/ethanol (4:1) to afford the title compound (12.90 g; 98%) as a colorless solid, m.p. 347.5°C. ¹H NMR (500 MHz, $CDCl_3$) [ppm]: δ = 7.90 (*dd*, 2H), 7.55 (*ddt*, 1H), 7.45 (*dd*, J = 8.4, 7.1 Hz, 2H), 5.33

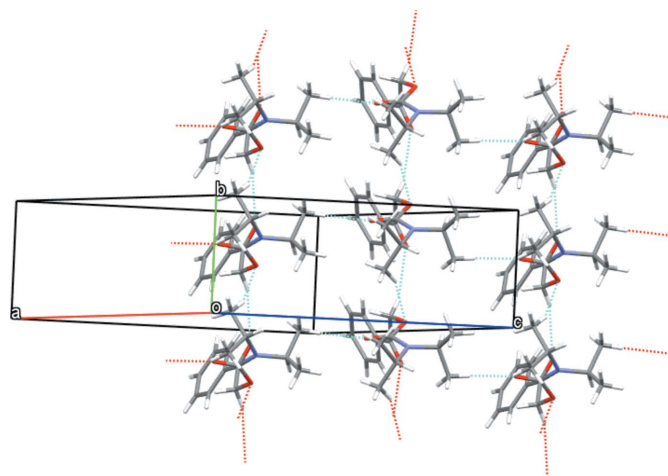


Figure 2
Crystal structure of the title compound showing layers of molecules along the bc plane that are built up by $C-H\cdots O$ hydrogen bonds.

(s, 2H), 3.97 (hept, 2H), 1.25 (d, 12H); ^{13}C NMR (126 MHz, CDCl_3) [ppm]: δ = 193.91 (C=O), 154.80 (NC=O), 134.69, 133.65, 128.84, 127.83 (C_{ar}), 66.36 (O=C–O), 46.32 [$(\text{H}_3\text{C})_2\text{CH}$ –], 20.99 [$(\text{H}_3\text{C})_2\text{CH}$ –].

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms were placed in idealized positions (C–H = 0.95–0.99 Å) and refined using a riding model with isotropic displacement parameters calculated as $U_{\text{iso}}(\text{H}) = 1.2 \times U_{\text{eq}}(\text{C})$ for methylene and hydrogen atoms of the phenyl group or $1.5 \times U_{\text{eq}}(\text{C})$ for methyl groups.

Acknowledgements

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supporting information

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Computing details

Data collection: *COLLECT* (Nonius 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015); molecular graphics: *ORTEP-3* (Farrugia, 2012); software used to prepare material for publication: *Mercury* (Macrae *et al.*, 2020).

2-oxo-2-phenylethyl diisopropylcarbamate

Crystal data

$C_{15}H_{21}NO_3$

$M_r = 263.33$

Monoclinic, $P2_1/c$

$a = 18.4574$ (8) Å

$b = 5.7020$ (2) Å

$c = 14.8058$ (6) Å

$\beta = 113.468$ (1)°

$V = 1429.33$ (10) Å³

$Z = 4$

$F(000) = 568$

$D_x = 1.224$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 13968 reflections

$\theta = 2.8$ – 27.5 °

$\mu = 0.09$ mm⁻¹

$T = 133$ K

Prism, colourless

$0.10 \times 0.10 \times 0.08$ mm

Data collection

Nonius KappaCCD

diffractometer

phi + ω – scans

Absorption correction: multi-scan

(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.674$, $T_{\max} = 0.746$

13968 measured reflections

3280 independent reflections

2464 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 2.8$ °

$h = -23$ → 23

$k = -5$ → 7

$l = -19$ → 18

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.113$

$S = 1.04$

3280 reflections

177 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2 + 0.6743P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.27$ e Å⁻³

$\Delta\rho_{\min} = -0.21$ e Å⁻³

Extinction correction: SHELXL2018/3 (Sheldrick 2015)

Extinction coefficient: 0.0093 (16)

Special details

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.38605 (6)	0.7949 (2)	0.38826 (9)	0.0338 (3)
O2	0.27936 (6)	0.4581 (2)	0.32610 (8)	0.0280 (3)
O3	0.24228 (6)	0.6202 (2)	0.17458 (8)	0.0285 (3)
N1	0.17054 (7)	0.6836 (3)	0.26709 (9)	0.0285 (3)
C1	0.41005 (8)	0.6137 (3)	0.36687 (11)	0.0234 (3)
C2	0.35448 (8)	0.4079 (3)	0.32488 (12)	0.0257 (3)
H2A	0.348514	0.377390	0.256450	0.031*
H2B	0.376866	0.265560	0.364461	0.031*
C3	0.23136 (8)	0.5945 (3)	0.24965 (11)	0.0249 (3)
C4	0.16762 (9)	0.6747 (4)	0.36534 (12)	0.0371 (4)
H4	0.211633	0.570586	0.407718	0.044*
C5	0.18152 (13)	0.9155 (5)	0.41331 (15)	0.0605 (7)
H5A	0.228794	0.985787	0.409862	0.091*
H5B	0.188987	0.899895	0.482386	0.091*
H5C	0.135734	1.015930	0.378631	0.091*
C6	0.09072 (11)	0.5665 (4)	0.36026 (15)	0.0452 (5)
H6A	0.046572	0.670305	0.322993	0.068*
H6B	0.093071	0.545940	0.427083	0.068*
H6C	0.083000	0.413759	0.327431	0.068*
C7	0.11069 (9)	0.8271 (3)	0.19039 (11)	0.0278 (4)
H7	0.074178	0.887235	0.220031	0.033*
C8	0.06055 (9)	0.6780 (3)	0.10240 (12)	0.0319 (4)
H8A	0.019602	0.775918	0.054376	0.048*
H8B	0.035643	0.551161	0.124422	0.048*
H8C	0.094128	0.610990	0.071729	0.048*
C9	0.14496 (11)	1.0413 (3)	0.16096 (14)	0.0405 (5)
H9A	0.176297	0.991762	0.124230	0.061*
H9B	0.178789	1.126741	0.220191	0.061*
H9C	0.101940	1.143637	0.119443	0.061*
C10	0.49370 (8)	0.5861 (3)	0.37810 (11)	0.0248 (3)
C11	0.51983 (9)	0.3863 (3)	0.34607 (12)	0.0315 (4)
H11	0.484354	0.260546	0.317232	0.038*
C12	0.59781 (10)	0.3710 (4)	0.35634 (13)	0.0420 (5)
H12	0.615586	0.234665	0.334388	0.050*
C13	0.64925 (10)	0.5519 (4)	0.39804 (13)	0.0478 (6)
H13	0.702529	0.540331	0.404875	0.057*
C14	0.62389 (10)	0.7512 (4)	0.43024 (13)	0.0437 (5)
H14	0.659736	0.876252	0.458872	0.052*
C15	0.54637 (9)	0.7686 (3)	0.42078 (12)	0.0327 (4)

H15 0.529143 0.904967 0.443406 0.039*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0316 (6)	0.0311 (6)	0.0386 (7)	0.0050 (5)	0.0140 (5)	-0.0076 (5)
O2	0.0204 (5)	0.0369 (6)	0.0260 (6)	0.0011 (5)	0.0087 (4)	0.0069 (5)
O3	0.0261 (5)	0.0375 (7)	0.0229 (6)	0.0009 (5)	0.0108 (4)	0.0031 (5)
N1	0.0201 (6)	0.0433 (8)	0.0219 (7)	0.0018 (6)	0.0081 (5)	0.0037 (6)
C1	0.0248 (7)	0.0269 (8)	0.0182 (7)	0.0041 (6)	0.0080 (6)	0.0014 (6)
C2	0.0227 (7)	0.0278 (8)	0.0264 (8)	0.0023 (6)	0.0095 (6)	0.0021 (6)
C3	0.0199 (7)	0.0310 (8)	0.0211 (7)	-0.0038 (6)	0.0055 (6)	0.0007 (6)
C4	0.0257 (8)	0.0627 (13)	0.0251 (8)	0.0034 (8)	0.0125 (7)	0.0044 (8)
C5	0.0611 (13)	0.0909 (18)	0.0325 (10)	-0.0377 (13)	0.0217 (10)	-0.0224 (11)
C6	0.0487 (11)	0.0512 (12)	0.0475 (11)	-0.0061 (9)	0.0314 (9)	0.0003 (9)
C7	0.0218 (7)	0.0317 (9)	0.0269 (8)	0.0026 (6)	0.0065 (6)	-0.0008 (7)
C8	0.0251 (7)	0.0352 (9)	0.0289 (8)	-0.0006 (7)	0.0041 (7)	-0.0019 (7)
C9	0.0418 (10)	0.0327 (10)	0.0417 (10)	-0.0035 (8)	0.0108 (8)	0.0002 (8)
C10	0.0227 (7)	0.0335 (9)	0.0174 (7)	0.0036 (6)	0.0069 (6)	0.0035 (6)
C11	0.0278 (8)	0.0404 (10)	0.0257 (8)	0.0066 (7)	0.0101 (7)	0.0001 (7)
C12	0.0323 (9)	0.0672 (13)	0.0276 (9)	0.0201 (9)	0.0133 (7)	0.0047 (9)
C13	0.0209 (8)	0.0923 (17)	0.0311 (10)	0.0091 (10)	0.0111 (7)	0.0159 (10)
C14	0.0265 (8)	0.0666 (14)	0.0318 (10)	-0.0123 (9)	0.0051 (7)	0.0068 (9)
C15	0.0288 (8)	0.0404 (10)	0.0252 (8)	-0.0038 (7)	0.0068 (7)	0.0003 (7)

Geometric parameters (Å, °)

O1—C1	1.2149 (19)	C7—C9	1.517 (2)
O2—C3	1.3684 (18)	C7—C8	1.522 (2)
O2—C2	1.4230 (17)	C7—H7	1.0000
O3—C3	1.2148 (18)	C8—H8A	0.9800
N1—C3	1.348 (2)	C8—H8B	0.9800
N1—C7	1.4764 (19)	C8—H8C	0.9800
N1—C4	1.478 (2)	C9—H9A	0.9800
C1—C10	1.494 (2)	C9—H9B	0.9800
C1—C2	1.519 (2)	C9—H9C	0.9800
C2—H2A	0.9900	C10—C15	1.392 (2)
C2—H2B	0.9900	C10—C11	1.392 (2)
C4—C5	1.520 (3)	C11—C12	1.389 (2)
C4—C6	1.522 (2)	C11—H11	0.9500
C4—H4	1.0000	C12—C13	1.371 (3)
C5—H5A	0.9800	C12—H12	0.9500
C5—H5B	0.9800	C13—C14	1.384 (3)
C5—H5C	0.9800	C13—H13	0.9500
C6—H6A	0.9800	C14—C15	1.385 (2)
C6—H6B	0.9800	C14—H14	0.9500
C6—H6C	0.9800	C15—H15	0.9500

C3—O2—C2	114.64 (12)	N1—C7—C8	111.27 (13)
C3—N1—C7	119.12 (13)	C9—C7—C8	112.63 (14)
C3—N1—C4	122.37 (13)	N1—C7—H7	106.3
C7—N1—C4	117.83 (13)	C9—C7—H7	106.3
O1—C1—C10	121.89 (14)	C8—C7—H7	106.3
O1—C1—C2	120.45 (14)	C7—C8—H8A	109.5
C10—C1—C2	117.64 (13)	C7—C8—H8B	109.5
O2—C2—C1	110.00 (13)	H8A—C8—H8B	109.5
O2—C2—H2A	109.7	C7—C8—H8C	109.5
C1—C2—H2A	109.7	H8A—C8—H8C	109.5
O2—C2—H2B	109.7	H8B—C8—H8C	109.5
C1—C2—H2B	109.7	C7—C9—H9A	109.5
H2A—C2—H2B	108.2	C7—C9—H9B	109.5
O3—C3—N1	125.75 (14)	H9A—C9—H9B	109.5
O3—C3—O2	122.46 (14)	C7—C9—H9C	109.5
N1—C3—O2	111.72 (13)	H9A—C9—H9C	109.5
N1—C4—C5	111.30 (16)	H9B—C9—H9C	109.5
N1—C4—C6	111.37 (14)	C15—C10—C11	119.50 (15)
C5—C4—C6	111.69 (16)	C15—C10—C1	118.42 (15)
N1—C4—H4	107.4	C11—C10—C1	122.07 (14)
C5—C4—H4	107.4	C12—C11—C10	119.92 (17)
C6—C4—H4	107.4	C12—C11—H11	120.0
C4—C5—H5A	109.5	C10—C11—H11	120.0
C4—C5—H5B	109.5	C13—C12—C11	120.25 (18)
H5A—C5—H5B	109.5	C13—C12—H12	119.9
C4—C5—H5C	109.5	C11—C12—H12	119.9
H5A—C5—H5C	109.5	C12—C13—C14	120.29 (16)
H5B—C5—H5C	109.5	C12—C13—H13	119.9
C4—C6—H6A	109.5	C14—C13—H13	119.9
C4—C6—H6B	109.5	C13—C14—C15	120.11 (18)
H6A—C6—H6B	109.5	C13—C14—H14	119.9
C4—C6—H6C	109.5	C15—C14—H14	119.9
H6A—C6—H6C	109.5	C14—C15—C10	119.93 (18)
H6B—C6—H6C	109.5	C14—C15—H15	120.0
N1—C7—C9	113.40 (13)	C10—C15—H15	120.0

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>
C2—H2B...O1 ⁱ	0.99	2.70	3.605 (2)	152
C5—H5B...O3 ⁱⁱ	0.98	2.62	3.578 (2)	167
C9—H9B...O2 ⁱⁱⁱ	0.98	2.68	3.599 (2)	157

Symmetry codes: (i) *x*, *y*-1, *z*; (ii) *x*, -*y*+3/2, *z*+1/2; (iii) *x*, *y*+1, *z*.