

## Structures of *tert*-Butyl *N*-Benzoyl-*N*-phenylcarbamate and *tert*-Butyl *N*-Acetyl-*N*-phenylcarbamate

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**Abstract.** (I):  $C_{18}H_{19}NO_3$ ,  $M_r = 297.35$ , orthorhombic,  $Pna2_1$ ,  $a = 18.506$  (4),  $b = 14.411$  (3),  $c = 6.258$  (1) Å,  $V = 1668.9$  (6) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.18$  (1) Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54178$  Å,  $\mu = 0.616$  mm<sup>-1</sup>,  $F(000) = 632$ ,  $T = 298$  K, melting point 371.5 (5) K. Final  $R = 0.041$  for 1174 unique observed reflections. (II):  $C_{13}H_{17}NO_3$ ,  $M_r = 235.23$ , monoclinic,  $P2_1$ ,  $a = 6.018$  (1),  $b = 8.188$  (1),  $c = 13.982$  (4) Å,  $\beta = 100.34$  (2)°,  $V = 677.8$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.15$  (1) Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54178$  Å,  $\mu = 0.634$  mm<sup>-1</sup>,  $F(000) = 252$ ,  $T = 298$  K, melting point 332.5 (5) K. Final  $R = 0.044$  for 1363 reflections. The amide bonds C1—N1 are unusually long. In (I) this distance is increased by 0.058 (8) Å compared to benzanilide and in (II) by 0.083 (6) Å compared to acetanilide. This fact partially elucidates the relatively mild reaction conditions sufficient for the aminolysis of these compounds. The carbamate C2—N1 bonds are also longer than usual.

**Introduction.** The aminolysis of the title compounds (I) and (II) takes place under exceptionally mild conditions (Grehn, Gunnarsson & Ragnarsson, 1985, 1986). The assumed mechanism of the reaction requires easy-leaving PhCO or CH<sub>3</sub>CO groups. Therefore, the corresponding amide bond lengths in compounds (I) and (II) are of principal interest to us.

**Experimental.** Both colorless samples were recrystallized by slow evaporation at room temperature, (I) from a toluene-methanol mixture, (II) from a toluene-methanol-water mixture. The density of the crystals was not determined. Oscillation and Weissenberg photographs were taken with Cu  $K\alpha$  radiation yielding Laue groups and preliminary cell dimensions. The possible space groups were determined from systematic absences on a Syntex  $P2_1$  diffractometer with graphite monochromator and Cu  $K\alpha$  radiation. Final cell dimensions were refined on 15 diffractometer reflections from a range

$12.0 < 2\theta < 63.0^\circ$ . For intensity data collection  $\theta$ - $2\theta$  scan was used. Crystal (I):  $0.2 \times 0.3 \times 0.4$  mm,  $hkl$  range  $0 \leq h \leq 20$ ,  $0 \leq k \leq 16$ ,  $0 \leq l \leq 7$ ,  $[(\sin \theta)/\lambda]_{\max} = 0.5617$  Å<sup>-1</sup>, 1370 unique reflections measured, 1174 of which were considered observed with  $I > 1.96\sigma_I$ . The standard reflections 400, 020 and 002 were monitored after each 47 reflections. They showed a 5% decrease during data collection. Crystal (II) did not withstand any suitable glue, therefore the crystal of size  $0.45 \times 0.45 \times 0.55$  mm was measured in a Lindemann-glass capillary,  $hkl$  range  $0 \leq h$

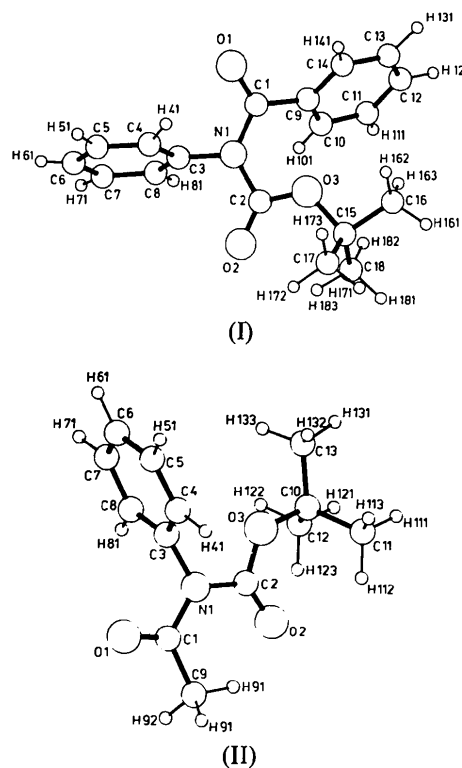


Fig. 1. The minimum-overlap views of molecules (I) and (II).

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and  $B_{eq}$  ( $\text{\AA}^2$ ) values with *e.s.d.*'s in parentheses
$$B_{eq} = \frac{1}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

(I) BocN(Ph)Bz	x	y	z	$B_{eq}$
N1	9248 (2)	2949 (2)	2110 (9)	4.3 (1)
C1	8585 (2)	3251 (3)	1276 (11)	4.5 (1)
O1	8576 (2)	3625 (3)	-477 (9)	6.4 (1)
C2	9326 (2)	2190 (3)	3509 (10)	4.4 (1)
O2	9882 (1)	2014 (2)	4397 (10)	6.2 (1)
O3	8720 (1)	1707 (2)	3609	5.2 (1)
C3	9904 (2)	3383 (3)	1344 (10)	4.2 (1)
C4	10177 (2)	3139 (3)	-647 (12)	5.1 (1)
C5	10801 (3)	3561 (4)	-1379 (12)	5.9 (2)
C6	11155 (2)	4203 (3)	-139 (13)	5.9 (2)
C7	10889 (2)	4434 (3)	1823 (13)	5.6 (2)
C8	10245 (2)	4026 (3)	2564 (11)	4.8 (1)
C9	7924 (2)	3204 (3)	2591 (9)	3.9 (1)
C10	7927 (2)	3506 (3)	4686 (11)	4.6 (1)
C11	7282 (3)	3567 (4)	5810 (12)	5.5 (2)
C12	6647 (3)	3311 (3)	4873 (12)	5.4 (1)
C13	6642 (2)	2981 (4)	2806 (12)	5.4 (1)
C14	7272 (2)	2937 (3)	1642 (12)	4.9 (1)
C15	8634 (2)	893 (3)	5042 (11)	5.4 (1)
C16	7835 (3)	659 (4)	4718 (17)	7.7 (2)
C17	9107 (3)	123 (3)	4228 (14)	7.4 (2)
C18	8798 (4)	1155 (5)	7333 (12)	8.2 (2)

(II) BocN(Ph)Ac	x	y	z	$B_{eq}$
N1	9199 (3)	1924 (4)	2382 (1)	4.3 (1)
C1	10694 (4)	3167 (4)	2196 (2)	4.5 (1)
O2	8362 (4)	687 (4)	1730 (2)	4.5 (1)
O1	11350 (3)	4148	2824 (1)	5.6 (1)
O3	8839 (4)	457 (4)	948 (1)	6.4 (1)
O4	6904 (4)	-139 (4)	2122 (1)	6.2 (1)
C3	8626 (4)	1919 (4)	3349 (1)	4.2 (1)
C4	6752 (4)	2752 (4)	3511 (2)	5.1 (1)
C5	6142 (5)	2671 (5)	4427 (3)	6.4 (1)
C6	7410 (7)	1735 (6)	5153 (2)	6.9 (1)
C7	9259 (6)	925 (6)	4982 (2)	6.9 (1)
C8	9925 (5)	1018 (5)	4073 (2)	5.6 (1)
C9	11441 (6)	3241 (6)	1227 (2)	6.8 (1)
C10	5934 (5)	-1747 (5)	1700 (2)	5.3 (1)
C11	4422 (6)	-1421 (6)	721 (3)	7.5 (1)
C12	7774 (7)	-2934 (6)	1587 (4)	8.3 (1)
C13	4580 (9)	-2271 (7)	2472 (4)	9.5 (2)

$\leq 8$ ,  $-11 \leq k \leq 11$ ,  $-18 \leq l \leq 18$ ,  $[(\sin \theta)/\lambda]_{\max} = 0.6095 \text{ \AA}^{-1}$ , 2730 reflections were measured. Standard reflections 400, 040, 004 were stable during data collection. 1363 averaged reflections gave  $R_{\text{int}} = 0.028$ . 1334 reflections were considered observed with  $I > 1.96\sigma_I$ . Relative absorption effects were assessed by  $\psi$  scan on ten selected reflections and considered negligible (less than 10%).

The measurements were reduced to the same scale with program *INTER* (Langer, 1973). Corrections were made for Lorentz and polarization factors, but not for absorption. The *E* statistics indicated acentricity. The structures were solved with the *MULTAN87* direct methods package (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987). Refinement of the alternative solutions in centrosymmetric space groups *Pnma* and *P2<sub>1</sub>/m* were unsuccessful. Least-squares refinement was performed on  $|F|$  by the full-matrix method with *SHELX76* (Sheldrick, 1976). The positional and isotropic displacement parameters of H atoms, within the phenyl ring of (I), were refined without constraints while positional parameters of methyl H

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) with *e.s.d.*'s in parentheses

(I) BocN(Ph)Bz			
N1—C1	1.403 (6)	N1—C2	1.408 (7)
N1—C3	1.447 (6)	C1—O1	1.222 (8)
C1—C9	1.476 (7)	C2—O2	1.197 (6)
C2—O3	1.321 (4)	O3—C15	1.485 (6)
C3—C4	1.390 (9)	C3—C8	1.356 (7)
C4—C5	1.383 (7)	C5—C6	1.374 (8)
C6—C7	1.364 (11)	C7—C8	1.408 (6)
C9—C10	1.381 (9)	C9—C14	1.399 (6)
C10—C11	1.388 (8)	C11—C12	1.364 (8)
C12—C13	1.378 (10)	C13—C14	1.376 (7)
C15—C16	1.530 (7)	C15—C17	1.502 (7)
C15—C18	1.513 (10)		
C2—N1—C3	117.1 (3)	C1—N1—C3	118.4 (4)
C1—N1—C2	124.2 (4)	N1—C1—C9	120.2 (4)
N1—C1—O1	118.9 (4)	O1—C1—C9	120.6 (4)
N1—C2—O3	110.6 (4)	N1—C2—O2	122.8 (4)
O2—C2—O3	126.6 (4)	C2—O3—C15	122.4 (4)
N1—C3—C8	119.9 (4)	N1—C3—C4	119.5 (4)
C4—C3—C8	120.6 (4)	C3—C4—C5	119.3 (5)
C4—C5—C6	120.5 (6)	C5—C6—C7	120.1 (4)
C6—C7—C8	120.0 (5)	C3—C8—C7	119.6 (5)
C1—C9—C14	119.4 (5)	C1—C9—C10	120.8 (4)
C10—C9—C14	119.5 (4)	C9—C10—C11	119.8 (5)
C10—C11—C12	120.4 (6)	C11—C12—C13	120.2 (5)
C12—C13—C14	120.5 (5)	C9—C14—C13	119.6 (5)
O3—C15—C18	110.7 (4)	O3—C15—C17	108.4 (4)
O3—C15—C16	101.4 (4)	C17—C15—C18	112.9 (5)
C16—C15—C18	112.0 (5)	C16—C15—C17	110.8 (4)

(II) BocN(Ph)Ac			
N1—C1	1.413 (4)	N1—C2	1.395 (4)
N1—C3	1.454 (2)	C1—O1	1.203 (3)
C1—C9	1.503 (4)	C2—O2	1.192 (3)
C2—O3	1.327 (4)	O3—C10	1.478 (5)
C3—C4	1.371 (4)	C3—C8	1.377 (4)
C4—C5	1.396 (5)	C5—C6	1.386 (5)
C6—C7	1.353 (6)	C7—C8	1.402 (4)
C10—C11	1.525 (5)	C10—C12	1.503 (6)
C10—C13	1.526 (7)		
C2—N1—C3	119.2 (2)	C1—N1—C3	116.0 (2)
C1—N1—C2	124.7 (2)	N1—C1—C9	119.9 (2)
N1—C1—O1	118.9 (2)	O1—C1—C9	121.2 (3)
N1—C2—O3	108.2 (2)	N1—C2—O2	126.0 (3)
O2—C2—O3	125.8 (3)	C2—O3—C10	123.0 (2)
N1—C3—C8	119.1 (2)	N1—C3—C4	119.2 (2)
C4—C3—C8	121.4 (2)	C3—C4—C5	119.2 (2)
C4—C5—C6	119.8 (3)	C5—C6—C7	120.2 (3)
C6—C7—C8	120.8 (3)	C3—C8—C7	118.6 (3)
O3—C10—C13	100.5 (3)	O3—C10—C12	110.7 (3)
O3—C10—C11	109.7 (3)	C12—C10—C13	112.9 (4)
C11—C10—C13	112.1 (3)	C11—C10—C12	110.6 (3)

atoms were constrained to keep the ideal geometry of methyl groups. Methyl H atoms of (II) were found to be disordered. No suitable model for their refinement was found. Also, the location of some phenyl H atoms oscillated during refinement. Therefore all H atoms of (II) were located in theoretical positions with fixed parameters.

Crystal (I): 256 parameters refined,  $(\Delta/\sigma)_{\max} = 0.163$ ,  $R = 0.0413$ ,  $wR = 0.0463$ ,  $S = 1.359$  for 1174 observed reflections,  $w = 1.0/(\sigma_F^2 + 0.0009F^2)$ ,  $\sigma_F$  from counting statistics,  $\Delta\rho_{\max}/\Delta\rho_{\min} = 0.16/-0.16 \text{ e \AA}^{-3}$ . Crystal (II): 154 parameters refined, an empirical correction for secondary extinction  $F_c^{\text{corr}} = F_c(1 - gF_c^2/\sin\theta)$  was included during the last cycles of refinement,  $g = 0.2(1) \times 10^{-6}$ ,  $(\Delta/\sigma)_{\max} = 0.054$ ,  $R = 0.0444$ ,  $wR = 0.0580$ ,  $S = 2.307$  for all 1363 reflections,  $w = 0.1481/(\sigma_F^2 + 0.0009F^2)$ ,  $\sigma_F$  from counting statistics,  $\Delta\rho = 0.19$  and  $-0.14 \text{ e \AA}^{-3}$ .

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The interactive graphics program *PMODEL* (Maloň, 1988) was used for molecular geometry inspection. Final geometrical calculations were performed with *PARST83* (Nardelli, 1983) and graphical projections with *PLUTO88* (Cambridge Structural Database, 1988).

**Discussion.** The minimum-overlap views of the molecules investigated are shown in Fig. 1. The fractional atomic coordinates and  $B_{eq}$  values are given in Table 1, selected bond lengths and angles in Table 2. The crystal packings are shown in Fig. 2.\*

The amide bond lengths C1—N1 are unusually long in these crystal structures: 1.403 (6) Å for (I) and 1.413 (4) Å for (II), *i.e.* 0.058 (8) Å and 0.083 (6) Å longer than in benzanilide and acetanilide, respectively (Kashino, Ito & Haisa, 1979; Brown & Corbridge, 1954). This finding conforms to the previous observation that this bond is cleaved by aminolysis and the reaction conditions are mild in comparison with other amides without the *tert*-butoxycarbonyl group (Boc). However, the carbamate bond lengths C2—N1 are also longer

\* Lists of structure factors, anisotropic thermal displacement parameters, H-atom coordinates and displacement parameters, and intermolecular contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52455 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

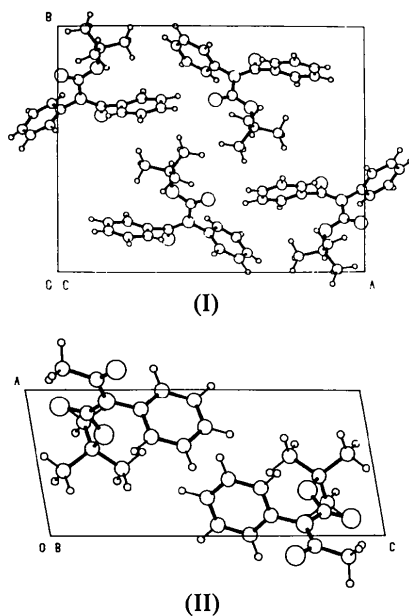


Fig. 2. The crystal packing projections of (I) and (II).

Table 3. *Twist and out-of-plane bending parameters* ( $^{\circ}$ ) *describing the amide groups of (I) and (II)*

Parameter definition and parameter values: (I) on upper line, (II) on lower.

$\omega_1[\text{C9—C1—N1—C2}]$	35.7 (7) 1.7 (4)	$\omega_2[\text{O1—C1—N1—C3}]$	23.5 (5) -1.7 (4)
$\omega_3[\text{O1—C1—N1—C2}]$	-150.5 (5) -178.1 (3)	$\omega_4[\text{C9—C1—N1—C3}]$	-150.3 (5) 178.1 (3)
$\tau' = \omega_1 + \omega_2$	59.2 (7) 0.0 (4)	$\chi_C = \omega_1 - \omega_3 + 180$	6.2 (7) -0.2 (4)
$\chi_N = \omega_2 - \omega_3 + 180$	-6.0 (7) -3.6 (4)	(mod 360)	

than usual although several similar cases have already been encountered (Wyss, Brisse & Hanessian, 1984; Albright & Moran, 1986; Cambridge Structural Database, 1988). In Boc-alanine and Boc-proline these bond lengths were found to be 1.344 (5) and 1.346 (4) Å, respectively (Benedetti, di Blasio, Pavone, Pedone, Toniolo & Bonora, 1981; Benedetti, Ciajolo & Maisto, 1974). There is also a significant difference in the bond angles C1—N1—C3 which are smaller than the corresponding angles within benzanilide and acetanilide [124.3 (5) and 129.1 (5) $^{\circ}$ ].

The *tert*-butoxycarbonyl group conformation is very similar in both molecules. The torsional angle O2—C2—O3—C15 of (I) is 5.4 (7) $^{\circ}$  and O2—C2—O3—C10 of (II) is 10.5 (5) $^{\circ}$ , *i.e.* the corresponding atoms occupy an eclipsed conformation. The *tert*-butyl group is in a staggered conformation in both (I) and (II). The amide groups of (I) and (II) consisting of the atoms C9, O1, C1, N1, C2 and C3 have been described using the twist and out-of-plane bending parameters (Warshel, Levitt & Lifson, 1970; Winkler & Dunitz, 1971) which are listed in Table 3. The amide group of (I) has a pronounced twist ( $\tau'$ ) around the amide bond C1—N1 and the out-of-plane bending at carbonyl C1 ( $\chi_C$ ) is unusually high. The amide group of (II) is essentially planar with a slight pyramidity at the N atom ( $\chi_N$ ). The phenyl ring of (I) occupies a *cis-cis* position with respect to the C1—O1 and C2—O2 carbonyl groups. In contrast, in molecule (II) it occupies a *cis-trans* position with respect to the corresponding carbonyl groups. Selected least-squares planes of molecules (I) and (II) are listed in Table 4. The  $\chi^2$  values of planes 1 and 4 indicate that the central part of molecule (I) is rather puckered in comparison with that of molecule (II). The interplanar angles are also listed in Table 4.

It is interesting to note that compound (II) was found in the form of a single enantiomorph in the crystal investigated, despite being racemic in solution. The pyramidal arrangement overturn at N is very easy. No attempt was made to determine the absolute configuration in crystal (II).

Table 4. Selected least-squares planes of molecules (I) and (II)

E.s.d.'s of the interplanar angles = 0.1°.  $\chi^2 = \sum(\Delta/\sigma)^2$ .

Molecule	Plane	Atoms included in plane	$\chi^2$	Interplanar angles				
				1	2	3	4	5
(I)	1	C9, C1, O1, N1, C3, C2, O2, O3	41591	1	0			
(I)	2	C3, C4, C5, C6, C7, C8	11	2	97.6			
(I)	3	C9, C10, C11, C12, C13, C14	99	3	107.1	26.9	0	
(II)	4	O1, C9, C1, N1, C3, C2, O2, O3, C10, C13	2730	4	—	—	—	0
(II)	5	C3, C4, C5, C6, C7, C8	22	5	—	—	—	88.8
								0

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## Topochemical Studies. XII.\* Structure of a Cinnamamide–Cinnamic Acid (1/1) Complex

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**Abstract.** C<sub>9</sub>H<sub>9</sub>NO.C<sub>9</sub>H<sub>8</sub>O<sub>2</sub>,  $M_r = 295.24$ , m.p. 377–379 K, monoclinic,  $P2_1/a$ ,  $a = 40.183$  (3),  $b = 9.5084$  (6),  $c = 4.0569$  (5) Å,  $\beta = 97.540$  (9)°,  $V = 1536.6$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.28$  (1),  $D_x = 1.277$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 0.72$  mm<sup>-1</sup>,  $F(000) = 624$ ,  $T = 295$  K,  $R = 0.058$  for 2454 unique reflections. The molecules of

cinnamamide (*A*) and cinnamic acid (*B*) are held together by two kinds of hydrogen bonds between the amide group and carboxyl group to form a dimer. The nearest C=C bonds are related by a *c* translation with a C...C distance of 4.057 (4) Å for both (*A*) and (*B*), the spacings between the planes through four C atoms involving the C=C bonds being 3.435 (4) Å for (*A*) and 3.394 (4) Å for (*B*). This fact suggests the possibility of the formation of  $\beta$ -type photodimers of (*A*) and (*B*) by topochemical reaction.

\* Part XI: Iwamoto, Kashino & Haisa (1989b).

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