Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cl1	0.52440 (11)	0.48225 (13)	0.2543 (2)	0.0467 (5)
Cl2	0.97357 (11)	0.20781 (12)	0.2345 (2)	0.0424 (5)
O1	1.3582 (3)	−0.4973 (4)	−0.0268 (5)	0.0462 (12)
O2	1.1601 (3)	0.7250 (4)	0.0620 (5)	0.0441 (11)
N1	1.1859 (4)	0.4765 (4)	0.0597 (6)	0.0349 (12)
N2	1.0638 (3)	0.4453 (4)	0.1592 (5)	0.0333 (11)
C1	1.1289 (3)	0.4065 (4)	0.1020 (5)	0.0247 (11)
N3	1.1368 (3)	0.2898 (4)	0.0893 (5)	0.0332 (12)
N4	1.2015 (3)	0.2478 (4)	0.0239 (5)	0.0313 (11)
C2	1.2024 (4)	0.1359 (5)	0.0043 (6)	0.0339 (14)
C3	1.2770 (4)	0.0934 (5)	−0.0588 (6)	0.0338 (13)
N5	1.2820 (3)	−0.0175 (4)	−0.0688 (5)	0.0311 (10)
N6	1.3508 (3)	−0.0613 (4)	−0.1241 (6)	0.0350 (12)
C4	1.3636 (4)	−0.1784 (5)	−0.1232 (6)	0.0337 (13)
N7	1.3128 (4)	−0.2482 (5)	−0.0684 (7)	0.0441 (14)
N8	1.4292 (4)	−0.2187 (4)	−0.1780 (7)	0.052 (2)
C5	1.1366 (3)	0.0501 (4)	0.0407 (5)	0.0378 (14)
C6	1.1669 (3)	0.0113 (4)	0.1905 (5)	0.070 (2)
C7	1.3399 (4)	0.1806 (6)	−0.1054 (8)	0.056 (2)

Table 2. *Selected geometric parameters (Å, °)*

N1—C1	1.308 (7)	C3—N5	1.274 (6)
N2—C1	1.314 (6)	C3—C7	1.515 (8)
C1—N3	1.346 (7)	N5—N6	1.370 (6)
N3—N4	1.372 (6)	N6—C4	1.350 (7)
N4—C2	1.292 (7)	C4—N7	1.305 (7)
C2—C3	1.485 (7)	C4—N8	1.313 (7)
C2—C5	1.493 (7)	C5—C6	1.47
N2—C1—N1	122.6 (5)	N5—C3—C7	125.3 (5)
N2—C1—N3	117.6 (5)	C2—C3—C7	119.8 (5)
N1—C1—N3	119.8 (5)	C3—N5—N6	117.2 (5)
C1—N3—N4	118.5 (4)	C4—N6—N5	118.6 (4)
C2—N4—N3	116.6 (4)	N7—C4—N8	121.6 (5)
N4—C2—C3	114.9 (5)	N7—C4—N6	120.7 (5)
N4—C2—C5	125.6 (5)	N8—C4—N6	117.7 (5)
C3—C2—C5	119.6 (4)	C6—C5—C2	112.1 (3)
N5—C3—C2	114.9 (5)		

The crystal for the X-ray measurements was mounted on a glass fibre using the oil-drop method (Kottke & Stalke, 1993). The distance C5—C6 was constrained to 1.47 Å in the refinement.

Data collection: *AFC-7S Software* (Molecular Structure Corporation, 1993*a*). Cell refinement: *AFC-7S Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993*b*). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1391). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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N-(*tert*-Butoxycarbonyl)-2-phenylglycine

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Abstract

In solution at room temperature *N*-(*tert*-butoxycarbonyl)-2-phenylglycine, $C_{13}H_{17}NO_4$, shows the presence of two confomers, *Z* and *E* in the ratio 1:3, as a result of restricted rotation about the N—CO bond. In the solid state, however, only the *Z* isomer was observed [HN—N—C2—O4 173.1 (4)°] with the N—CO bond showing considerable double-bond character [N—C2 1.357 (3) Å].

Comment

As a part of our research directed towards the synthesis of 3-aryl-4(3*H*)-isoquinolinone derivatives, we have

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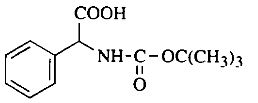
designed a synthetic route in which the initial substrate is the simple α-amino acid DL-2-phenylglycine. The protection of its primary amino group with *tert*-butoxycarbonyl gave the title compound, (1).



(1)

The ^{1}H-NMR spectrum of (1) in $CDCl_3$ indicates the presence of two conformers, *Z* and *E*, in the ratio 1:3. The stereochemical assignments were made on the basis of their HN proton chemical shifts: at 5.52 p.p.m. for the *Z* isomer *versus* 8.04 p.p.m. for the *E* isomer in which the downfield proton is deshielded by the anisotropy cone of the carbonyl group (Silverstein, Bassler & Morril, 1981). This type of conformational equilibrium in solution is similar to that observed for amides in which the rotation around the acyl-to-nitrogen bond is restricted because of the partial double-bond character (Lewin, Frucht, Chen, Benedetti & Di Blasio, 1975). Consequently, we conducted a crystallographic study of *N*-(*tert*-butoxycarbonyl)-2-phenylglycine, (1), to determine the nature of the carbamate bond.

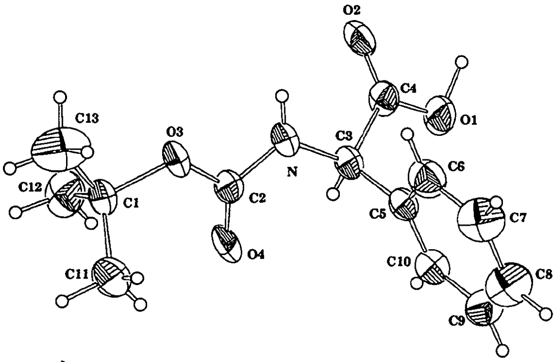


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (1) showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been assigned arbitrary radii.

In the solid-state, (1) only crystallized as the *Z* isomer with the carbonylic-O atom O4 eclipsed by the tertiary-C atom C3 [C3—N—C2—O4 −7 (5)°], and antiperiplanar to the NH atom [HN—N—C2—O4 −173.1 (4)°]. The N atom is sp^2 hybridized, as deduced from the sum of the valence angles [359.6°], and by it being coplanar with C2, C3 and HN [deviation −0.000 (2) Å]. The large difference in the two nitrogen–carboxylic-C atom bond distances [N—C3 1.447 (3) and N—C2 1.357 (3) Å] indicates a considerable double-bond character for the latter. By use of the standard single [C—N 1.47 Å] and double [C=N 1.125 Å] bond lengths in Pauling's equation relating bond character and length (Carpenter & Donohue, 1950), this was calculated to be 33%. A strong hydrogen bond involving two carboxyl groups [O1···O2^{i} 2.644 (4) Å; (i) = $-x$, $2-y$, $-z$] can be postulated from the observation of a broad band in the IR spectrum (KBr) at 3125–2800cm^{-1}, attributable to the associated stretching vibration of the OH bond. Nevertheless, there are no hydrogen bonds involving the NH H atom which is consistent with the sharp band in the IR at 3380 cm^{-1}, similar to the free NH stretching vibration of secondary amides (Silverstein, Bassler & Morril, 1981),

Experimental

The *N*-Boc α-amino acid, *N*-(*tert*-butoxycarbonyl)-2-phenylglycine, (1), was prepared by reaction of DL-2-phenylglycine and di-*tert*-butyl dicarbonate under basic conditions (Keller, Keller, van Look & Wersin, 1985), and was fully characterized by NMR and IR spectroscopy. Crystals suitable for X-ray analysis were obtained by recrystallization from hexane/ethyl acetate, 9.0:1.0.

Crystal data

$C_{13}H_{17}NO_4$
$M_r = 251.28$
Triclinic
$P\overline{1}$
$a = 5.309\ (5)$ Å
$b = 10.548\ (4)$ Å
$c = 12.514\ (4)$ Å
$\alpha = 104.550\ (3)°$
$\beta = 95.600\ (5)°$
$\gamma = 103.430\ (5)°$
$V = 650.6\ (7)$ Å^3
$Z = 2$
$D_x = 1.28$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 9–15°$
$\mu = 0.089$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.31 × 0.28 × 0.11 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
3833 measured reflections
3794 independent reflections
2307 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0804$
$\theta_{\rm max} = 29.98°$
$h = -7 \rightarrow 7$
$k = -14 \rightarrow 14$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: 4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0676$
$wR(F^2) = 0.3275$
$S = 1.054$
2924 reflections
169 parameters
Only H-atom *U*'s refined
$w = 1/[\sigma^2(F_o^2) + (0.1562P)^2 + 0.2235P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.047$

$\Delta\rho_{\rm max} = 0.562$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.313$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.10 (2)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.3148 (5)	1.0665 (2)	0.0832 (2)	0.0697 (7)
O2	0.0372 (4)	0.8621 (2)	0.0368 (2)	0.0669 (6)
O3	0.3641 (3)	0.58438 (15)	0.21396 (14)	0.0457 (4)
O4	0.7310 (3)	0.7407 (2)	0.2047 (2)	0.0564 (5)
N	0.3239 (4)	0.7724 (2)	0.1763 (2)	0.0434 (5)
C1	0.5016 (4)	0.4812 (2)	0.2289 (2)	0.0433 (5)
C2	0.4953 (4)	0.7014 (2)	0.1987 (2)	0.0388 (5)
C3	0.4271 (4)	0.9098 (2)	0.1708 (2)	0.0392 (5)
C4	0.2373 (4)	0.9439 (2)	0.0901 (2)	0.0401 (5)
C5	0.4894 (4)	1.0168 (2)	0.2833 (2)	0.0387 (5)
C6	0.3088 (5)	1.0165 (3)	0.3557 (2)	0.0509 (6)
C7	0.3702 (6)	1.1158 (3)	0.4586 (2)	0.0602 (7)
C8	0.6064 (6)	1.2119 (3)	0.4885 (2)	0.0618 (8)
C9	0.7835 (6)	1.2125 (3)	0.4162 (2)	0.0593 (7)
C10	0.7262 (5)	1.1155 (2)	0.3135 (2)	0.0490 (6)
C11	0.7219 (6)	0.5397 (3)	0.3288 (2)	0.0591 (7)
C12	0.5978 (6)	0.4251 (3)	0.1229 (2)	0.0635 (7)
C13	0.2858 (6)	0.3753 (3)	0.2512 (3)	0.0647 (8)

Table 2. *Selected geometric parameters (Å, °)*

O1—C4	1.290 (3)	N—C3	1.447 (3)
O2—C4	1.210 (3)	C1—C12	1.499 (4)
O3—C2	1.338 (3)	C1—C13	1.504 (3)
O3—C1	1.482 (2)	C1—C11	1.518 (3)
O4—C2	1.212 (3)	C3—C5	1.517 (3)
N—C2	1.357 (3)	C3—C4	1.522 (3)
C2—O3—C1	120.7 (2)	N—C3—C4	110.0 (2)
C2—N—C3	118.7 (2)	C5—C3—C4	109.8 (2)
O4—C2—O3	126.3 (2)	O2—C4—O1	124.2 (2)
O4—C2—N	124.1 (2)	O2—C4—C3	122.6 (2)
O3—C2—N	109.6 (2)	O1—C4—C3	113.2 (2)
N—C3—C5	114.2 (2)		

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CFEO* (Solans, 1978). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1093). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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o-Cyanophenol

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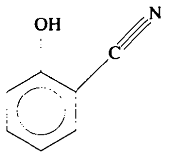
Abstract

O—H···N—C hydrogen bonds connect the two independent molecules of the title compound *o*-hydroxybenzonitrile, C_7H_5NO, into infinite chains. The effects of substituents on endocyclic bond angles are close to additivity.

Comment

The structure of the title compound, (I), was determined as part of a study of hydrogen bonding of donor–acceptor substituted aromatic compounds. There are two independent molecules in the asymmetric unit. The normal probability plot (Abrahams & Keve, 1971; *International Tables for X-ray Crystallography*, 1974) shows that the differences in their geometries are only statistical (the correlation coefficient is 0.98).



(I)

Hydrogen bonds (see Table 3) connect the molecules into *ABAB* chains along the [001] direction. Similar hydrogen-bonding patterns were observed in the structures of *p*-cyanophenol (Higashi & Osaki, 1977) and in 2,6-dibromo-4-cyanophenol (Baughman, Virant & Jacobson, 1981). In both independent molecules, the