C17	−0.3084 (5)	−0.0230 (2)	−0.20887 (14)	0.0524 (8)
O17	−0.3305 (4)	0.0101 (2)	−0.25857 (10)	0.0719 (7)
C18	−0.5715 (5)	−0.1271 (3)	−0.1660 (2)	0.0679 (10)
C19	−0.4161 (5)	−0.4413 (2)	−0.09522 (15)	0.0605 (9)

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

C1—C2	1.528 (4)	C9—C10	1.557 (4)
C1—C10	1.542 (4)	C10—C19	1.539 (5)
C2—C3	1.502 (5)	C11—C12	1.527 (4)
C3—O3	1.435 (4)	C12—C13	1.524 (4)
C3—C4	1.521 (4)	C13—C17	1.513 (4)
O3—C3′	1.406 (5)	C13—C14	1.530 (4)
C4—C5	1.529 (4)	C13—C18	1.539 (5)
C5—C6	1.522 (4)	C14—C15	1.524 (4)
C5—C10	1.541 (4)	C15—C16	1.549 (4)
C6—C7	1.526 (4)	C16—C16*A*	1.527 (5)
C7—C8	1.528 (4)	C16—C16*B*	1.529 (5)
C8—C14	1.518 (4)	C16—C17	1.538 (4)
C8—C9	1.550 (3)	C17—O17	1.213 (3)
C9—C11	1.532 (4)		
C2—C1—C10	113.5 (2)	C1—C10—C9	109.9 (2)
C3—C2—C1	111.5 (3)	C12—C11—C9	113.9 (2)
O3—C3—C2	107.7 (3)	C13—C12—C11	110.1 (2)
O3—C3—C4	112.0 (2)	C17—C13—C12	117.1 (2)
C2—C3—C4	110.7 (3)	C17—C13—C14	100.6 (2)
C3′—O3—C3	114.0 (3)	C12—C13—C14	109.2 (2)
C3—C4—C5	111.1 (2)	C17—C13—C18	105.6 (3)
C6—C5—C4	112.2 (2)	C12—C13—C18	110.1 (3)
C6—C5—C10	112.6 (3)	C14—C13—C18	114.1 (2)
C4—C5—C10	113.3 (3)	C8—C14—C15	121.1 (2)
C5—C6—C7	111.3 (2)	C8—C14—C13	113.4 (2)
C6—C7—C8	112.6 (3)	C15—C14—C13	103.8 (2)
C14—C8—C7	112.1 (2)	C14—C15—C16	104.6 (2)
C14—C8—C9	109.2 (2)	C16*A*—C16—C16*B*	108.6 (3)
C7—C8—C9	111.1 (2)	C16*A*—C16—C17	110.7 (3)
C11—C9—C8	112.7 (2)	C16*B*—C16—C17	108.8 (3)
C11—C9—C10	114.5 (2)	C16*A*—C16—C15	113.7 (3)
C8—C9—C10	111.8 (2)	C16*B*—C16—C15	111.6 (3)
C19—C10—C5	112.9 (2)	C17—C16—C15	103.2 (2)
C19—C10—C1	108.7 (3)	O17—C17—C13	126.2 (3)
C5—C10—C1	107.2 (2)	O17—C17—C16	124.2 (3)
C19—C10—C9	110.9 (3)	C13—C17—C16	109.5 (2)
C5—C10—C9	107.1 (2)		

Data collection: *DIF*4 (Stoe & Cie, 1989*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1989*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*92 (Sheldrick, 1992).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: KA1056). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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An Enantiomerically Pure 4-Oxo-α-amino Acid Derivative

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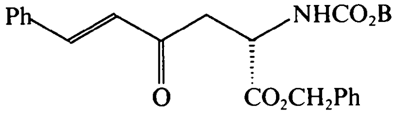
Abstract

In the molecule of benzyl 2(*S*)-[(*tert*-butoxycarbonyl)amino]-4-oxo-6-phenyl-5(*E*)-hexenoate, $C_{24}H_{27}NO_5$, the amine NH group does not form intramolecular hydrogen bonds with any of the three carbonyl groups present, even the most favourably positioned one, which would give a six-membered ring. Instead, weak intermolecular hydrogen-bonding interactions occur between the NH and CO groups of the amide units in adjacent molecules, linking them into a chain.

Comment

Enantiomerically pure α-amino acids can be prepared in various ways (Williams, 1989). Recent research into methods which do not involve the formation of one of the four bonds to the α centre and which instead retain the chirality already established at this centre, has been successful in producing a wide range of protected 4-oxo-α-amino acids and protected phenylalanine analogues from an organozinc intermediate (Jackson, Wishart, Wood, James & Wythes, 1992). The title compound, (I), is one of these 4-oxo-α-amino acid derivatives. Its structure has been determined in order to confirm the enantiomeric purity and to investigate the hydrogen bonding which may be expected to occur between the amino group and one of the three carbonyl groups within the molecule.



(I)

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Although enantiomeric purity is consistent with the polar space group, it is not thereby proved, since it is possible for crystals of both enantiomers to be present in the sample. For the crystal selected, the absolute structure could not be confirmed from the diffraction study because of an insufficiently strong anomalous-dispersion effect; the absolute structure (Fig. 1) was assumed from the synthesis.

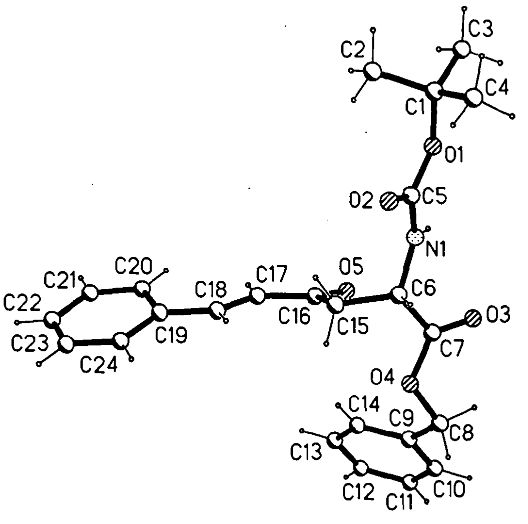

Fig. 1. The molecular structure and atom-labelling scheme.

Although intramolecular hydrogen bonding is likely in solution, it does not occur in the crystal structure. Instead, the N—H bond is directed towards the amide carbonyl O2 atom of the next molecule (related by translation along the *b* axis) to give an essentially linear N—H···O=C unit with an O···H distance (calculated with a constrained N—H bond) of 2.44 Å and with O···H—N and C=O···H angles of 179 and 173°, respectively. This represents only a weak hydrogen-bonding interaction, which links the molecules into chains running along the short crystallographic *b* axis. There are no other notable intermolecular interactions and the intramolecular geometry is unexceptional.

Experimental

The compound was prepared as described previously (Jackson, Wishart, Wood, James & Wythes, 1992). Single crystals were obtained by vapour diffusion of petrol (313-333 K boiling range) into an isopropyl acetate solution.

Crystal data

$C_{24}H_{27}NO_5$
$M_r = 409.47$
Monoclinic
$P2_1$
$a = 13.322\ (4)$ Å
$b = 5.367\ (2)$ Å
$c = 16.266\ (5)$ Å
$\beta = 112.88\ (2)°$
$V = 1071.5\ (6)$ Å^3
$Z = 2$
$D_x = 1.269$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 32 reflections
$\theta = 10.81-12.43°$
$\mu = 0.089$ mm^{-1}
$T = 160.0\ (10)$ K
Block
0.58 × 0.52 × 0.28 mm
Colourless

Data collection

Stoe Siemens diffractometer
ω/θ scans with on-line profile fitting (Clegg, 1981)
Absorption correction: none
4308 measured reflections
3144 independent reflections
2635 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0968$ (on F^2)
$\theta_{\rm max} = 24.99°$
$h = -15 \rightarrow 15$
$k = -6 \rightarrow 6$
$l = -19 \rightarrow 19$
5 standard reflections
frequency: 60 min
intensity variation: 15%

Refinement

Refinement on F^2
$R(F) = 0.0341$
$wR(F^2) = 0.0924$
$S = 1.062$
3142 reflections
275 parameters
Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.0383P)^2 + 0.2454P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.180$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.158$ e Å^{-3}
Extinction correction: *SHELXL* (Sheldrick, 1994)
Extinction coefficient: 0.0072 (20)
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)

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

	x	y	z	$U_{\rm eq}$
N1	0.65565 (14)	0.5655 (3)	0.20395 (12)	0.0254 (9)
O1	0.83285 (11)	0.5044 (3)	0.27247 (10)	0.0291 (7)
O2	0.71820 (12)	0.1694 (3)	0.23440 (11)	0.0328 (8)
O3	0.53130 (13)	0.8638 (3)	0.06874 (10)	0.0321 (8)
O4	0.37722 (12)	0.6704 (3)	0.06058 (10)	0.0315 (7)
O5	0.48975 (13)	0.8355 (3)	0.25825 (10)	0.0309 (9)
C1	0.9324 (2)	0.3510 (4)	0.31122 (15)	0.0277 (10)
C2	0.9310 (2)	0.2024 (5)	0.3901 (2)	0.0377 (12)
C3	1.0218 (2)	0.5447 (5)	0.3421 (2)	0.0499 (12)
C4	0.9446 (2)	0.1858 (5)	0.2395 (2)	0.0355 (12)
C5	0.7341 (2)	0.3925 (4)	0.23639 (13)	0.0239 (11)
C6	0.5427 (2)	0.4926 (4)	0.15545 (14)	0.0239 (10)
C7	0.4854 (2)	0.7010 (4)	0.09123 (13)	0.0243 (10)
C8	0.3116 (2)	0.8397 (5)	−0.0084 (2)	0.0382 (12)
C9	0.2409 (2)	1.0022 (5)	0.0224 (2)	0.0308 (10)
C10	0.1861 (2)	1.1974 (5)	−0.0323 (2)	0.0467 (15)
C11	0.1193 (3)	1.3547 (6)	−0.0084 (3)	0.063 (2)
C12	0.1078 (2)	1.3188 (6)	0.0713 (2)	0.056 (2)
C13	0.1618 (2)	1.1265 (6)	0.1262 (2)	0.0525 (14)
C14	0.2277 (2)	0.9668 (6)	0.1017 (2)	0.0428 (12)
C15	0.4853 (2)	0.4112 (4)	0.21600 (15)	0.0252 (11)
C16	0.4704 (2)	0.6209 (4)	0.27168 (15)	0.0244 (10)
C17	0.4305 (2)	0.5664 (4)	0.3427 (2)	0.0289 (11)
C18	0.3896 (2)	0.3492 (4)	0.35475 (15)	0.0281 (11)
C19	0.3448 (2)	0.2984 (4)	0.42244 (15)	0.0277 (10)
C20	0.3614 (2)	0.4580 (4)	0.4945 (2)	0.0313 (12)
C21	0.3154 (2)	0.4072 (5)	0.5559 (2)	0.0337 (12)
C22	0.2536 (2)	0.1940 (5)	0.5479 (2)	0.0362 (12)
C23	0.2379 (2)	0.0329 (5)	0.4777 (2)	0.0340 (11)
C24	0.2825 (2)	0.0828 (4)	0.4154 (2)	0.0311 (12)

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

N1—C5	1.343 (3)	C9—C10	1.384 (4)
N1—C6	1.455 (3)	C10—C11	1.388 (4)
O1—C5	1.354 (3)	C11—C12	1.376 (5)
O1—C1	1.477 (3)	C12—C13	1.371 (4)
O2—C5	1.214 (3)	C13—C14	1.391 (4)
O3—C7	1.202 (3)	C15—C16	1.506 (3)
O4—C7	1.339 (3)	C16—C17	1.476 (3)
O4—C8	1.444 (3)	C17—C18	1.333 (3)
O5—C16	1.218 (3)	C18—C19	1.468 (3)
C1—C3	1.512 (3)	C19—C20	1.399 (3)
C1—C2	1.517 (3)	C19—C24	1.402 (3)
C1—C4	1.524 (3)	C20—C21	1.386 (3)
C6—C7	1.518 (3)	C21—C22	1.386 (4)
C6—C15	1.526 (3)	C22—C23	1.382 (4)
C8—C9	1.505 (3)	C23—C24	1.385 (3)
C9—C14	1.382 (3)		
C5—N1—C6	120.7 (2)	C10—C9—C8	117.9 (2)
C5—O1—C1	119.8 (2)	C9—C10—C11	121.1 (3)
C7—O4—C8	116.8 (2)	C12—C11—C10	119.8 (3)
O1—C1—C3	102.7 (2)	C13—C12—C11	119.7 (3)
O1—C1—C2	110.5 (2)	C12—C13—C14	120.5 (3)
C3—C1—C2	110.3 (2)	C9—C14—C13	120.4 (3)
O1—C1—C4	110.1 (2)	C16—C15—C6	113.0 (2)
C3—C1—C4	110.5 (2)	O5—C16—C17	119.6 (2)
C2—C1—C4	112.4 (2)	O5—C16—C15	120.8 (2)
O2—C5—N1	124.7 (2)	C17—C16—C15	119.6 (2)
O2—C5—O1	125.4 (2)	C18—C17—C16	125.5 (2)
N1—C5—O1	109.9 (2)	C17—C18—C19	125.6 (2)
N1—C6—C7	108.2 (2)	C20—C19—C24	118.0 (2)
N1—C6—C15	113.5 (2)	C20—C19—C18	122.5 (2)
C7—C6—C15	114.3 (2)	C24—C19—C18	119.5 (2)
O3—C7—O4	125.2 (2)	C21—C20—C19	120.9 (2)
O3—C7—C6	124.5 (2)	C22—C21—C20	120.5 (2)
O4—C7—C6	110.2 (2)	C23—C22—C21	119.2 (2)
O4—C8—C9	112.0 (2)	C22—C23—C24	120.9 (2)
C14—C9—C10	118.5 (2)	C23—C24—C19	120.5 (2)
C14—C9—C8	123.6 (2)		

Isotropic H atoms were constrained to give N—H 0.90 and C—H 0.95–1.00 Å depending on position, H—C—H 109.5°, aromatic and olefinic H atoms on angle external bisectors and $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$. Data collection and cell refinement: *DIF*4 (Stoe & Cie, 1992). Data reduction: local programs. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL* (Sheldrick, 1994). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL* and local programs.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HA1079). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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p-Methyl-*N*-(pentafluorobenzylidene)-aniline (1), 1,2,3,4-Tetrafluoro-7-methoxy-acridine (2), 1,2,3,4,7-Pentafluoroacridine (3) and 3-(*p*-Methylanilino)-1,2,4-trifluoro-7-methylacridine (4): Four Molecules Representing Key Stages in the One-Pot Synthesis of 1,2,3,4-Tetrafluoroacridines by Treating Pentafluorobenzaldehyde with *para*-Substituted Anilines

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Abstract

All of the title compounds, $C_{14}H_8F_5N$, $C_{14}H_7F_4NO$, $C_{13}H_4F_5N$ and $C_{21}H_{15}F_3N_2$, display a characteristic stacking of their π systems in which adjacent members of the stack are related by crystallographic inversion centres. This leads to a particularly efficient mode of packing in which fluorinated rings overlap unfluorinated sections of the molecules at interplanar spacings ranging from 3.40 to 3.51 Å.

Comment

During the purification of a crude sample of the Schiff base $C_6F_5CH{=}NC_6H_4(OCH_3\text{-}4)$ [(1) with $R = OCH_3$] obtained by heating pentafluorobenzaldehyde with *p*-methoxyaniline in boiling *n*-butyl acetate, Flowers & DeFigueredo (1990) isolated a by-product which they concluded was 7,8,9,10-tetrafluoro-2-methoxyphenanthridine on the basis of the results of elemental, NMR and mass spectometric analyses. Their interest centred only on the preparation of Schiff bases of the type $C_6F_5CH{=}NAr$ for mass spectral studies. For our part we wished to compare the mechanism of this intramolecu-

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