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Key indicators

Single-crystal X-ray study
 $T = 160\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.026
 wR factor = 0.051
Data-to-parameter ratio = 20.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.*tert*-Butyl (2*R*)-2-(9*H*-Fluoren-9-ylmethoxy-
carbonylamino)-3-iodopropionate

The title compound, $\text{C}_{22}\text{H}_{24}\text{INO}_4$, is a chiral reagent developed and used for the synthesis of unnatural amino acids. It forms chains in its crystal structure, *via* weak $\text{N}-\text{H}\cdots\text{O}=\text{C}$ hydrogen bonds. The bulky iodo substituent lies *gauche* to the two substituents on the neighbouring C atom, about a C—C single bond, rather than *gauche* to one and *trans* to the other. This does not seem to be a consequence of any significant intermolecular interactions. The absolute configuration has been confirmed by this experiment and is as expected from the synthesis.

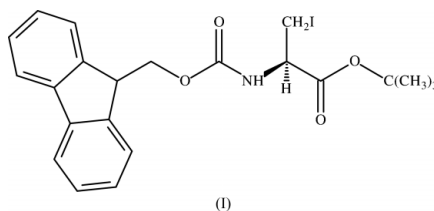
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Comment

The title compound, (I), more simply known as *N*-Fmoc 3-iodoalanine *tert*-butyl ester, is a useful starting material for the preparation of unnatural amino acids (Deboves *et al.*, 2001), *via* its conversion to zinc and copper derivatives.



The molecular structure of (I) is shown in Fig. 1, with selected torsion angles in Table 1. Bond lengths and angles are normal. The carbamate linkage (from C2 to C9, including O3) is approximately planar (r.m.s. deviation 0.115 Å) and the ester linkage (from C2 to C4, including O1) is almost perfectly planar (r.m.s. deviation 0.002 Å); the dihedral angle between these two groups is 33.68 (12)°. The fluorenyl group is also essentially planar (r.m.s. deviation 0.043 Å) and makes a dihedral angle of 62.93 (8)° with the carbamate group.

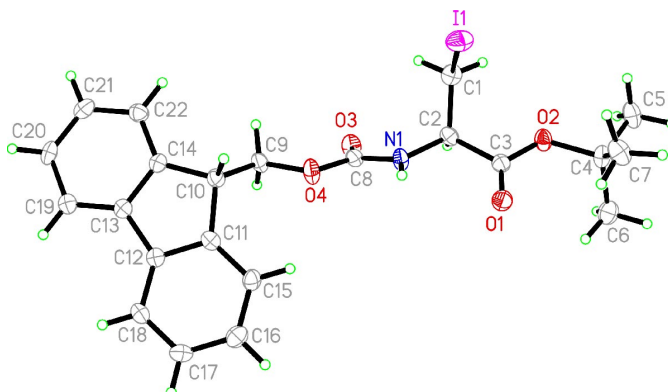


Figure 1

The molecular structure, with atom labels and 50% probability ellipsoids for non-H atoms.

The conformation about the C1–C2 bond is almost perfectly staggered, as shown by the torsion angles in Table 1. It is perhaps surprising that the bulky iodo substituent is *gauche* to both the amino group and the ester group, rather than lying *trans* to one of them.

Molecules are linked together by relatively weak N–H···O=C hydrogen bonds, as shown in Fig. 2 and Table 2, to form chains along the *a* axis. Any interaction between the iodine atom and the π -bonding system of the fluorenyl group in the next molecule is likely also to be weak, with I···C distances greater than 3.5 Å; the I atom lies almost directly over C16 in a projection perpendicular to the aromatic system, rather than over a bond or the centre of a ring.

The absolute configuration of the molecule, confirmed with the help of the significant anomalous scattering of iodine, is as expected from the synthesis, which begins with enantiomerically pure L-serine (Deboves *et al.*, 2001).

Experimental

The synthesis and spectroscopic characterization of the title compound have been fully described by Deboves *et al.* (2001). Crystals were obtained from hexane solution by slow cooling.

Crystal data

C ₂₂ H ₂₄ INO ₄	Mo K α radiation
<i>M_r</i> = 493.32	Cell parameters from 9823 reflections
Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁	θ = 2.4–28.6°
<i>a</i> = 9.2875 (7) Å	μ = 1.51 mm ^{−1}
<i>b</i> = 12.3181 (9) Å	<i>T</i> = 160 (2) K
<i>c</i> = 18.9028 (13) Å	Block, colourless
<i>V</i> = 2162.6 (3) Å ³	0.49 × 0.16 × 0.12 mm
<i>Z</i> = 4	
<i>D_x</i> = 1.515 Mg m ^{−3}	

Data collection

Bruker SMART 1K CCD diffractometer	5121 independent reflections
Thin-slice ω scans	4536 reflections with <i>I</i> > 2 σ (<i>I</i>)
Absorption correction: multi-scan (SADABS; Sheldrick, 2002)	<i>R</i> _{int} = 0.029
<i>T</i> _{min} = 0.667, <i>T</i> _{max} = 0.835	θ _{max} = 28.7°
13825 measured reflections	<i>h</i> = −11 → 12
	<i>k</i> = −15 → 14
	<i>l</i> = −17 → 25

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0241P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.051$	(Δ/σ) _{max} = 0.002
<i>S</i> = 0.98	$\Delta\rho$ _{max} = 0.53 e Å ^{−3}
5121 reflections	$\Delta\rho$ _{min} = −0.48 e Å ^{−3}
256 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	2159 Friedel pairs
	Flack parameter = −0.027 (12)

Table 1

Selected torsion angles (°).

I1–C1–C2–C3	−61.0 (2)	C3–C2–N1–C8	−154.7 (2)
I1–C1–C2–N1	65.1 (2)	C2–N1–C8–O3	11.7 (4)
C1–C2–C3–O1	128.3 (2)	C2–N1–C8–O4	−167.77 (19)
C1–C2–C3–O2	−51.1 (2)	N1–C8–O4–C9	170.05 (19)
N1–C2–C3–O1	0.6 (3)	O3–C8–O4–C9	−9.4 (3)
N1–C2–C3–O2	−178.76 (18)	C8–O4–C9–C10	−176.84 (19)
C1–C2–N1–C8	78.1 (3)		

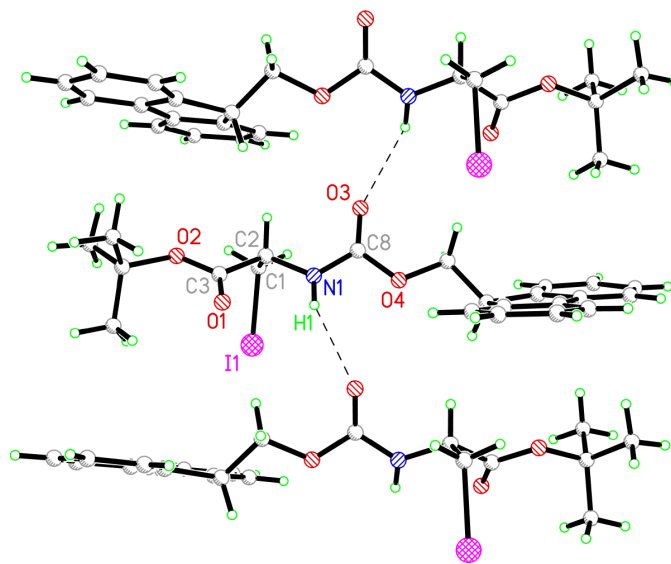


Figure 2

A view of three molecules, showing the chain formation through N–H···O=C hydrogen bonding and the staggered conformation about the C1–C2 bond, with the I atom *gauche* to both the adjacent carbamate and ester groups.

Table 2

Hydrogen-bonding 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···O3 ⁱ	0.88	2.49	3.309 (3)	155

Symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$.

H atoms were placed geometrically and refined with a riding model (including free rotation about C–C bonds), with C–H = 0.95–1.00 Å and N–H = 0.88 Å, and with *U*_{iso} constrained to be 1.2 (1.5 for methyl groups) times *U*_{eq} of the carrier atom.

Data collection: SMART (Bruker, 2001); cell refinement: local programs; data reduction: SAINT (Bruker, 2001); program(s) used to solve structure: SHELXTL (Sheldrick, 2001); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and local programs.

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