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Key indicators

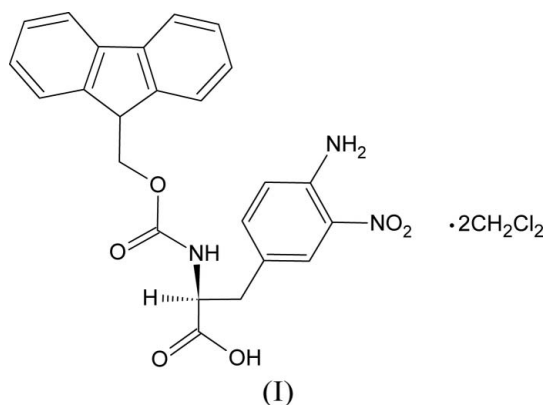
Single-crystal X-ray study
 $T = 100\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
Disorder in solvent or counterion
 R factor = 0.061
 wR factor = 0.112
Data-to-parameter ratio = 22.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**(2*S*)-3-(4-Amino-3-nitrophenyl)-2-(9*H*-fluoren-9-ylmethoxycarbonylamino)propanoic acid dichloromethane disolvate**

The title compound, $\text{C}_{24}\text{H}_{21}\text{N}_3\text{O}_6 \cdot 2\text{CH}_2\text{Cl}_2$, crystallizes with two independent molecules in the asymmetric unit, each with a different conformation. In the crystal structure, molecules form two-dimensional sheets in the *ab* plane due to a combination of $\text{O}-\text{H} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds. Only edge-to-face stacking interactions are observed between fluorenyl aromatic groups of adjacent sheets. Solvent molecules are located within the intermolecular voids along the *b* axis and fill the spaces between carbamate linkages or lie between the fluorenyl aromatic groups.

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Comment

The title compound, (I), known more simply as *N*-Fmoc 3-(4-amino-3-nitrophenyl)alanine dichloromethane disolvate, is a non-proteinaceous amino acid derived from *L*-phenylalanine and obtained by a four-step synthesis from enantiomerically pure (2*S*)-2-(acetylamino)-3-(4-nitrophenyl)propanoic acid. It forms part of our study of a series of model dipeptides containing various 3-(quinoxaline-6-yl)alanine analogues (Staszewska *et al.*, 2005).



We report here the molecular structure of (I), which crystallizes in the space group $P2_1$ with two independent molecules, *A* and *B*, in the asymmetric unit (Figs. 1 and 2), which differ in the orientations of their fluorenyl and aromatic groups (Table 1). Three ordered and one disordered CH_2Cl_2 solvent molecules complete the asymmetric unit.

The orientations of both amino and nitro groups within molecules *A* and *B* are determined by the intramolecular $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds (Table 2). All four N atoms are essentially coplanar with their attached benzene rings. However, the NO_2 group on atom $\text{N}2B$ is displaced slightly on steric grounds.

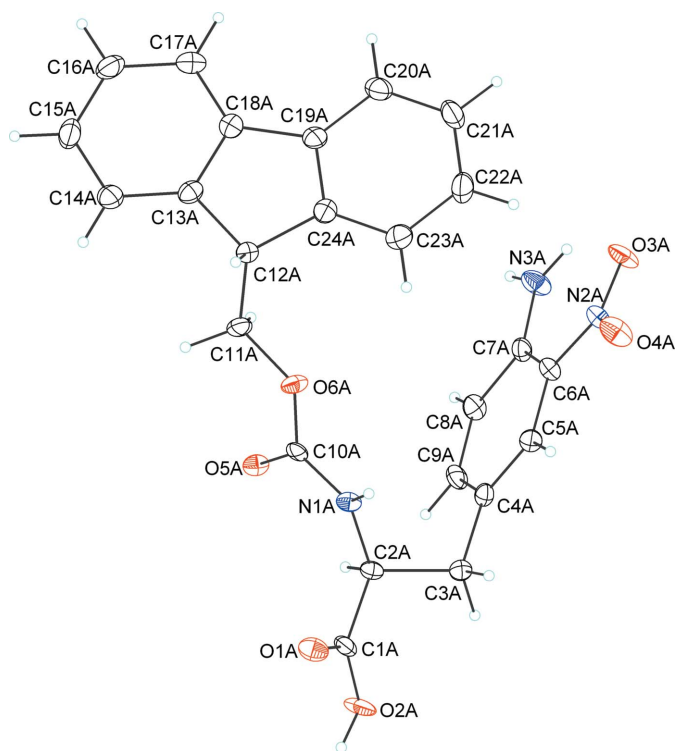


Figure 1
The structure of molecule *A* of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

The urethane amide groups adopt a *cis* conformation, with the $C2n-N1n-C10n-O5n$ ($n = A$ or B) torsion angles close to 0° . Such a urethane amide conformation in Fmoc-NH-groups is rare (Broda *et al.*, 2004). The $C2n-C3n-C4n-C9n$ (χ^{22}) and $C2n-C3n-C4n-C5n$ (χ^{21}) torsion angles (Table 2) differ from those observed in L-phenylalanine hydrochloride (Al-Karaghoulis & Koetzle, 1975) and L-phenylalanine L-phenylalaninium dihydrogenphosphate (Ravikumar *et al.*, 2002), due to rotation around the $C\beta-C\gamma$ bond.

Molecules of (I) are linked together by $N-H\cdots O$ and $O-H\cdots O$ hydrogen bonds (Table 2 and Fig. 3). In a two-centre hydrogen bond, atoms $N3A$ and $N3B$ in molecules *A* and *B* at (x, y, z) act as donors to atoms $O1A/O1B$ at $(x, y - 1, z)$. This motif generates by translation a $C(10)$ chain (Bernstein *et al.*, 1995) running parallel to the $[010]$ direction. Two $C(7)$ chains arise from $O2A\cdots O5A^i$ and $O2B\cdots O5B^{iii}$ hydrogen bonds [symmetry codes as in Table 2]. These adjacent chains are located alternately on the bc plane and are linked *via* four additional $N-H\cdots O$ hydrogen bonds, engaging NO_2 groups as acceptors. The combination of interactions between the $C(7)$ chain for molecule *A* and the $C(10)$ chain for molecule *B* (Table 2) results in the formation of four edge-fused rings comprising two $R_3^2(11)$ and two $R_2^2(15)$ rings. Similar motifs are present for the $C(7)$ chain for molecule *B* and the $C(10)$ chain for molecule *A*. The action of all these chain pairs results in a two-dimensional hydrogen-bond network in the bc plane (Fig. 3).

Two of the CH_2Cl_2 molecules are linked to the *A* molecules by weak $C-H\cdots O$ contacts involving the NO_2/CO_2 groups.

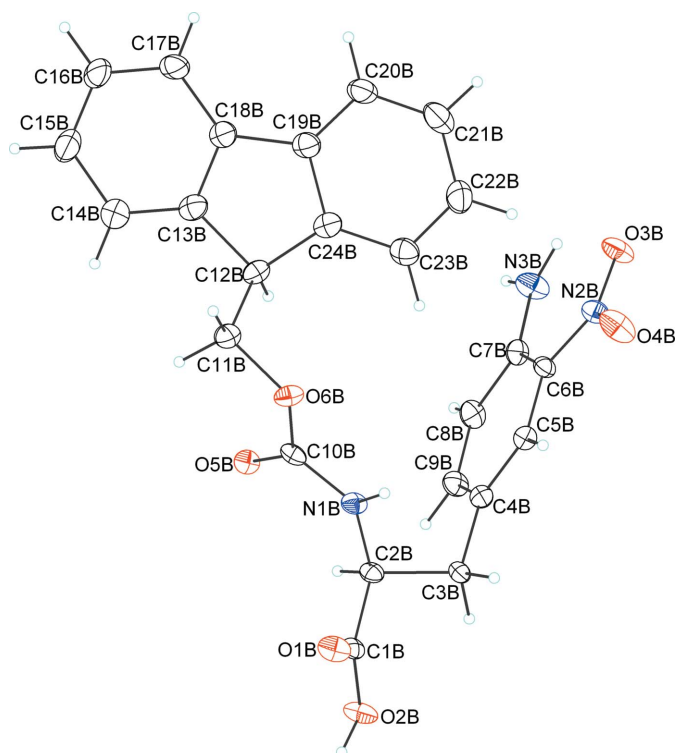


Figure 2
The structure of molecule *B* of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Other CH_2Cl_2 molecules do not form $C-H\cdots O$ interactions with *A* or *B* molecules but fill spaces within the intersheet channels running along the b axis. Each layer of the channel consists of chains of *A* and *B* molecules, located alternately on the ac plane (Fig. 4). Only $C-H\cdots \pi$ interactions (the geometries of which are not discussed here in detail) are engaged in edge-to-face stacking between the fluorenyl systems from alternating *A*-to-*B* sheets.

Experimental

The synthesis and NMR characterization of (I) have been fully described by Staszewska *et al.* (2005). Crystals for X-ray experiments were obtained from a CH_2Cl_2 solution of (I) by slow evaporation.

Crystal data

$C_{24}H_{21}N_3O_6 \cdot 2CH_2Cl_2$
 $M_r = 617.29$
 Monoclinic, $P2_1$
 $a = 12.362$ (3) Å
 $b = 10.489$ (3) Å
 $c = 22.958$ (4) Å
 $\beta = 103.17$ (3)°
 $V = 2898.6$ (12) Å³

$Z = 4$
 $D_x = 1.415$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.45$ mm⁻¹
 $T = 100$ (2) K
 Block, yellow
 $0.25 \times 0.2 \times 0.15$ mm

Data collection

Oxford Diffraction KM-4-CCD diffractometer
 ω scans
 Absorption correction: numerical (CrysAlis RED; Oxford Diffraction, 2003)
 $T_{min} = 0.913$, $T_{max} = 0.947$

44865 measured reflections
 15906 independent reflections
 9639 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.064$
 $\theta_{max} = 33.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.061$
 $wR(F^2) = 0.112$
 $S = 0.95$
 15906 reflections
 715 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0457P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.51 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.54 \text{ e } \text{Å}^{-3}$
 Absolute structure: Flack (1983),
 with 4474 Friedel pairs
 Flack parameter: 0.12 (4)

Table 1

Selected torsion angles ($^\circ$).

| | | | |
|--------------------|-----------|--------------------|-----------|
| O1A—C1A—C2A—N1A | −4.5 (4) | O1B—C1B—C2B—N1B | −7.3 (3) |
| C2A—C3A—C4A—C5A | 113.4 (3) | C2B—C3B—C4B—C5B | 103.9 (3) |
| C2A—C3A—C4A—C9A | −64.6 (3) | C2B—C3B—C4B—C9B | −74.3 (3) |
| C2A—N1A—C10A—O5A | 13.3 (4) | C2B—N1B—C10B—O5B | −0.1 (4) |
| O6A—C11A—C12A—C24A | 65.5 (3) | O6B—C11B—C12B—C24B | −62.4 (3) |

Table 2

Hydrogen-bond geometry (Å , $^\circ$).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|-------|-------------|-------------|---------------|
| O2A—H2O ^A ⋯O5A ⁱ | 0.84 | 1.80 | 2.631 (3) | 173 |
| N1A—H1A⋯O3B | 0.88 | 2.35 | 3.134 (3) | 148 |
| N3A—H3A1⋯O3A | 0.88 | 2.03 | 2.643 (3) | 126 |
| N3A—H3A1⋯O4B ⁱⁱ | 0.88 | 2.32 | 2.958 (3) | 129 |
| N3A—H3A2⋯O1A ⁱⁱ | 0.88 | 2.08 | 2.932 (3) | 163 |
| O2B—H2O ^B ⋯O5B ⁱⁱⁱ | 0.84 | 1.83 | 2.669 (3) | 178 |
| N1B—H1B⋯O3A ^{iv} | 0.88 | 2.37 | 3.186 (3) | 154 |
| N3B—H3B2⋯O3B | 0.88 | 2.01 | 2.630 (3) | 126 |
| N3B—H3B2⋯O4A | 0.88 | 2.39 | 2.942 (3) | 121 |
| N3B—H3B1⋯O1B ⁱⁱ | 0.88 | 2.13 | 2.977 (3) | 161 |
| C5B—H5B⋯O3A ^{iv} | 0.95 | 2.50 | 3.277 (3) | 139 |
| C8B—H8B⋯O5B ^v | 0.95 | 2.41 | 3.326 (3) | 162 |
| C30—H301⋯O1A ^{vi} | 0.99 | 2.49 | 3.170 (4) | 125 |
| C40—H401⋯O4A ⁱⁱⁱ | 0.99 | 2.35 | 3.239 (7) | 149 |

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

The absolute configuration of (I) was established by the anomalous scattering of solvent Cl atoms, and is in accord with the enantiomerically pure L-phenylalanine derivative.

H atoms bonded to N and O atoms were treated as riding, with $N-H = 0.88 \text{ Å}$ and $O-H = 0.84 \text{ Å}$, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N}, \text{O})$. H atoms bonded to C atoms were also treated as riding, with C—H distances in the range 0.95–1.00 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. One of the CH_2Cl_2 molecules is disordered over two positions and was refined with site occupancies of 0.764 (6) and 0.236 (6). This CH_2Cl_2 molecule was subject to geometrical and displacement parameter constraints and restraints.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL97*.

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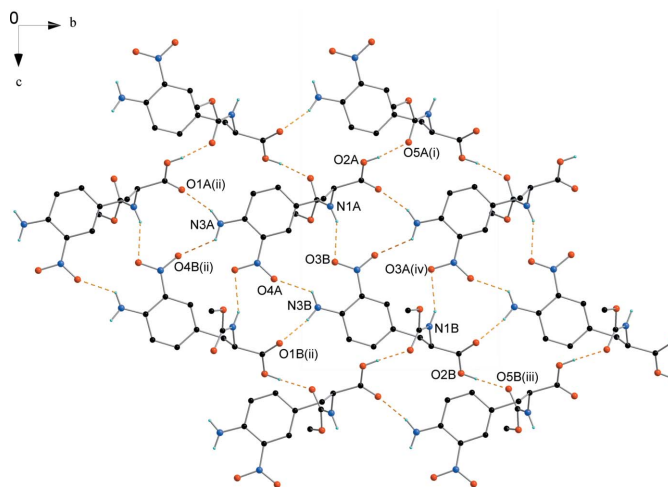


Figure 3

A view of the intermolecular hydrogen bonds (dashed lines) involving molecules A and B. For the sake of clarity, H atoms bonded to C atoms and fluorenyl groups have been omitted. (Symmetry codes as in Table 2.)

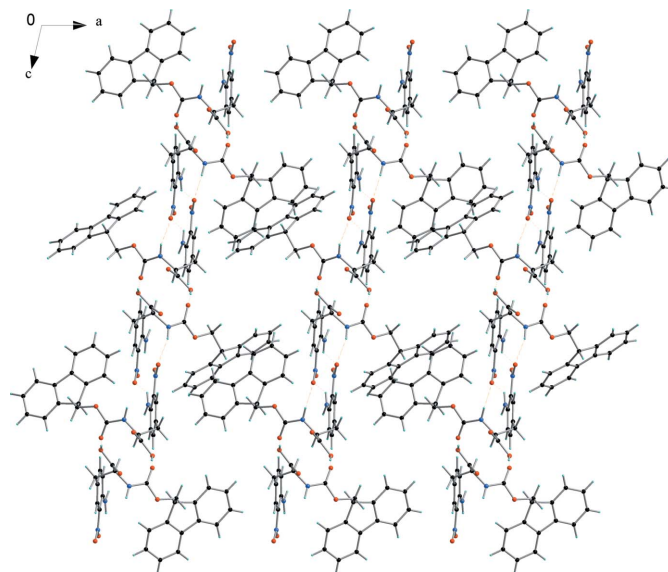


Figure 4

A view of the crystal packing in (I). Hydrogen bonds are indicated by dashed lines. Channels can be seen, where the solvent molecules reside.

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