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## Key indicators

Single-crystal X-ray study  
 $T = 100$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
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**

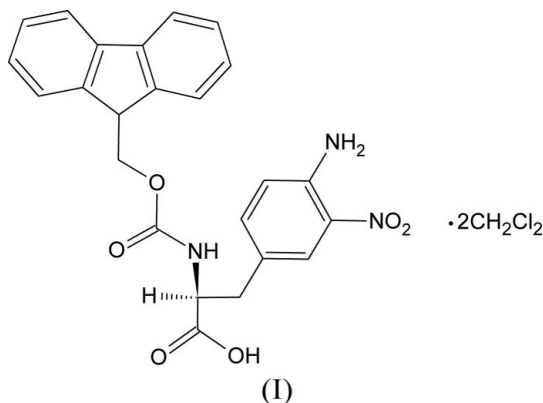
The title compound,  $\text{C}_{24}\text{H}_{21}\text{N}_3\text{O}_6 \cdot 2\text{CH}_2\text{Cl}_2$ , crystallizes with two independent molecules in the asymmetric unit, each with a different conformation. In the crystal structure, molecules form two-dimensional sheets in the  $ab$  plane due to a combination 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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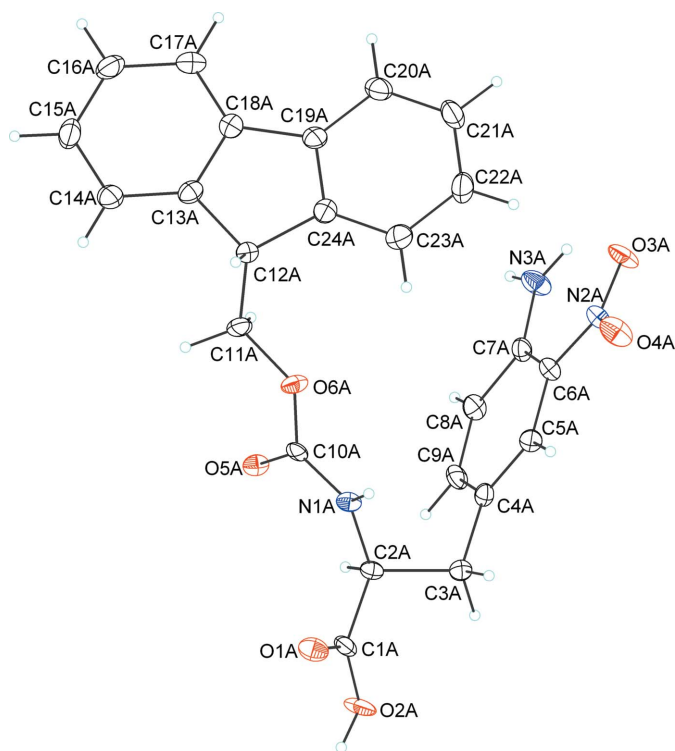
## Comment

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  $\text{CH}_2\text{Cl}_2$  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  $\text{NO}_2$  group on atom  $\text{N}2\text{B}$  is displaced slightly on steric grounds.

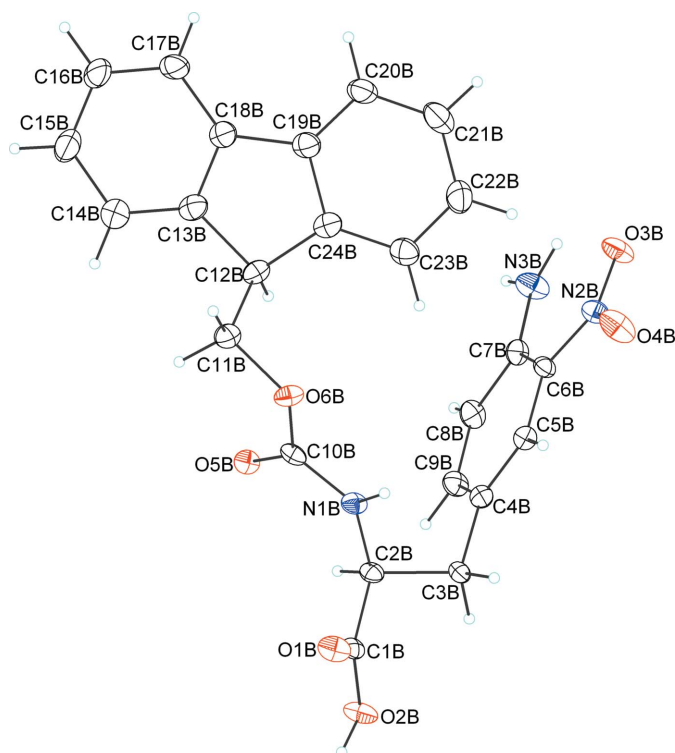


**Figure 1**  
The structure of molecule *A* of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

The urethane amide groups adopt a *cis* conformation, with the  $C2n-N1n-C10n-O5n$  ( $n = A$  or  $B$ ) torsion angles close to  $0^\circ$ . Such a urethane amide conformation in Fmoc-NH-groups is rare (Broda *et al.*, 2004). The  $C2n-C3n-C4n-C9n$  ( $\chi^{22}$ ) and  $C2n-C3n-C4n-C5n$  ( $\chi^{21}$ ) 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) Å<sup>3</sup>

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

### Data collection

Oxford Diffraction KM-4-CCD diffractometer  
 $\omega$  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  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.51 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.54 \text{ e } \text{\AA}^{-3}$   
 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 ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2A—H2O <sup>A</sup> ···O5A <sup>i</sup>	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 <sup>ii</sup>	0.88	2.32	2.958 (3)	129
N3A—H3A2···O1A <sup>ii</sup>	0.88	2.08	2.932 (3)	163
O2B—H2O <sup>B</sup> ···O5B <sup>iii</sup>	0.84	1.83	2.669 (3)	178
N1B—H1B···O3A <sup>iv</sup>	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 <sup>ii</sup>	0.88	2.13	2.977 (3)	161
C5B—H5B···O3A <sup>iv</sup>	0.95	2.50	3.277 (3)	139
C8B—H8B···O5B <sup>v</sup>	0.95	2.41	3.326 (3)	162
C30—H301···O1A <sup>vi</sup>	0.99	2.49	3.170 (4)	125
C40—H401···O4A <sup>iii</sup>	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  $N-H = 0.88 \text{ \AA}$  and  $O-H = 0.84 \text{ \AA}$ , 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  $0.95\text{--}1.00 \text{ \AA}$  and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . One of the  $\text{CH}_2\text{Cl}_2$  molecules is disordered over two positions and was refined with site occupancies of 0.764 (6) and 0.236 (6). This  $\text{CH}_2\text{Cl}_2$  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*.

## References

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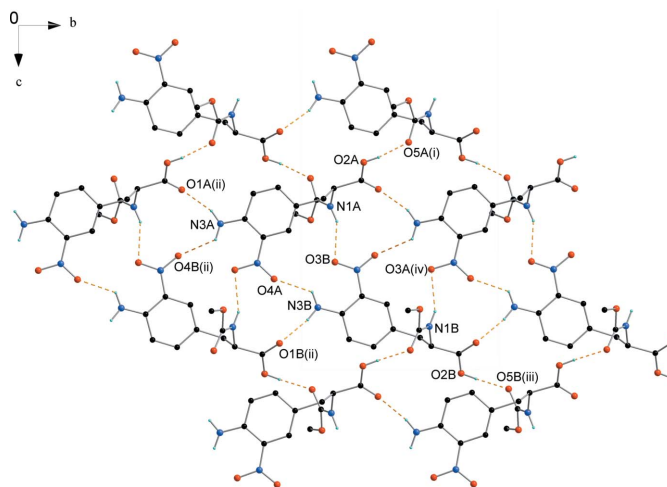


Figure 3

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.)

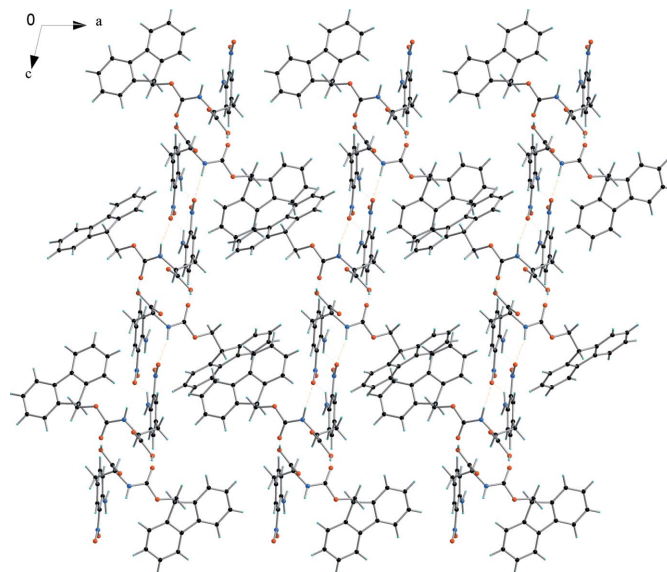


Figure 4

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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