

Table 1. Selected geometric parameters (Å, °)

O1—C3	1.256 (2)	C2—C3	1.513 (3)
O2—C7	1.222 (2)	C3—C4	1.438 (3)
O3—C7	1.299 (2)	C4—C14	1.387 (3)
O4—C14	1.331 (2)	C4—C5	1.493 (3)
C1—C6	1.490 (3)	C5—C6	1.345 (3)
C1—C7	1.508 (3)	C5—C8	1.477 (3)
C1—C2	1.542 (3)	C14—C15	1.480 (3)
C6—C1—C7	113.4 (2)	C6—C5—C8	120.9 (2)
C6—C1—C2	108.5 (2)	C6—C5—C4	117.6 (2)
C7—C1—C2	109.9 (2)	C8—C5—C4	121.2 (2)
C3—C2—C1	110.0 (2)	C5—C6—C1	121.5 (2)
O1—C3—C4	123.0 (2)	O2—C7—O3	123.4 (2)
O1—C3—C2	117.7 (2)	O2—C7—C1	122.6 (2)
C4—C3—C2	119.2 (2)	O3—C7—C1	114.1 (2)
C14—C4—C3	117.7 (2)	O4—C14—C4	121.3 (2)
C14—C4—C5	125.5 (2)	O4—C14—C15	112.4 (2)
C3—C4—C5	116.8 (2)	C4—C14—C15	126.3 (2)

All non-H atoms in the structure were found by direct methods, whereas all H atoms were located in subsequent $\Delta\rho$ maps.

Data collection: *DIF4* (Stoe & Cie, 1992a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1992b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1478). Services for accessing these data are described at the back of the journal.

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L-Phenylalanine L-Phenylalaninium Perchlorate

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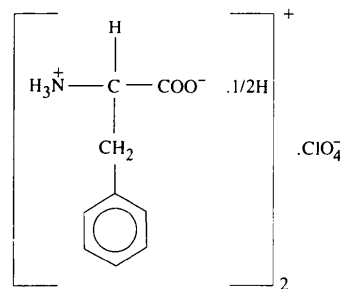
(Received 20 May 1996; accepted 13 January 1997)

Abstract

The crystal of the title compound, $C_9H_{11}NO_2 \cdot C_9H_{12}NO_2^+ \cdot ClO_4^-$, is made up of a twofold symmetric hydrogen-bonded dimer carrying a net positive charge and a negatively charged perchlorate ion. The crystal structure involving alternating polar and non-polar zones is stabilized by hydrogen bonds and van der Waals interactions.

Comment

The crystal structures of amino acids and their complexes have provided a wealth of interesting information pertaining to the patterns of their aggregation and the effect of other molecules and ions on their interactions and molecular properties (Vijayan, 1988; Prasad & Vijayan, 1993). The structure analysis of the title compound, (I), has been carried out as a contribution to this body of information.



(I)

The structure of L-phenylalanine L-phenylalaninium perchlorate, (I), contains two formula units of phenylalanine and one unit of perchlorate in the asymmetric unit (Fig. 1). The amino group in both molecules is protonated and positively charged. The phenylalanine molecules are related by a non-crystallographic pseudotwofold symmetry. The carboxyl groups share a proton in what appears to be a symmetric $O \cdots O$ hydrogen bond. The symmetric hydrogen-bonded dimer thus formed has a net positive charge which is neutralized by the negatively charged perchlorate ion.

Both phenylalanine molecules have a similar conformation. They have the sterically least favourable g+ con-

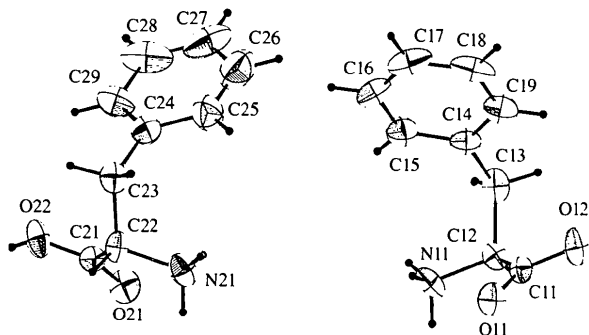


Fig. 1. ORTEP (Johnson, 1965) drawing of L-phenylalanine L-phenylalaninium perchlorate. Displacement ellipsoids are drawn at the 50% probability level. The disordered perchlorate anion has been omitted.

The polar core of each double layer, made up of amino and carboxyl groups and perchlorate ions, is flanked by the hydrophobic side chains of phenylalanine. Each double layer has a pseudo-twofold symmetry parallel to the *c* axis, which passes through the perchlorate ion and relates the two amino acid molecules in the hydrogen-bonded dimer. The double layers in the crystal are held together by non-polar interactions involving phenylalanine side chains. This arrangement is such that the crystal has polar and non-polar zones which alternate along the longest crystallographic axis.

Experimental

L-Phenylalanine L-phenylalaninium perchlorate crystals were grown from aqueous solutions of L-phenylalanine and perchloric acid in the stoichiometric ratio 2:1.

Crystal data

$C_9H_{11}NO_2 \cdot C_9H_{12}NO_2^+ \cdot ClO_4^-$
 $M_r = 430.83$
 Orthorhombic
 $P2_12_12_1$
 $a = 5.3907(11) \text{ \AA}$
 $b = 12.680(2) \text{ \AA}$
 $c = 29.152(5) \text{ \AA}$
 $V = 1992.7(6) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.436 \text{ Mg m}^{-3}$
 $D_m = 1.441 \text{ Mg m}^{-3}$
 D_m measured by flotation

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 2-25^\circ$
 $\mu = 0.241 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Transparent needle
 $0.4 \times 0.3 \times 0.2 \text{ mm}$
 Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\omega-2\theta$ scans
 Absorption correction: none
 2072 measured reflections
 2069 independent reflections
 1536 reflections with $I > 2\sigma(I)$

$R_{int} = 0.073$
 $\theta_{max} = 24.96^\circ$
 $h = 0 \rightarrow 6$
 $k = 0 \rightarrow 15$
 $l = 0 \rightarrow 34$
 3 standard reflections every 70 reflections
 intensity decay: 1.2%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.235$
 $S = 1.074$
 2032 reflections
 305 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 1.4484P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = -0.045$
 $\Delta\rho_{max} = 0.217 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.196 \text{ e \AA}^{-3}$

Extinction correction: SHELXL93 (Sheldrick, 1993)
 Extinction coefficient: 0.0021(7)
 Scattering factors from International Tables for Crystallography (Vol. C)
 Absolute configuration: Flack (1983)
 Flack parameter = 0.12(15)

formation, with χ^1 values of 68.3(5) and 64.8(5) (Benedetti, Morelli, Nemethy & Scheraga, 1983; Suresh, Prasad & Vijayan, 1994).

Interestingly, the present structure is strikingly similar to that of L-phenylalanine L-phenylalaninium formate (Gorbitz & Etter, 1992). The amino acid molecules have the *g*⁺ conformation and they also form hydrogen-bonded dimers in the formate. Furthermore, the aggregation of the molecules is remarkably similar in the two structures.

The arrangement of molecules in the crystal structure is illustrated in Fig. 2, while the parameters of the hydrogen bonds that stabilize the structure are given in Table 2. Each amino N atom is involved in hydrogen bonding with one carboxyl O atom and two perchlorate O atoms. Since the perchlorate is disordered, the hydrogen bonding for these O atoms has two possibilities.

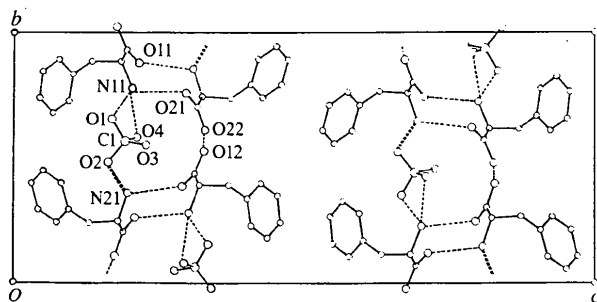


Fig. 2. A packing diagram of the molecule viewed down the *a* axis. The hydrogen bonds are shown by dotted lines. Only one disordered perchlorate group is shown.

The molecules aggregate into hydrogen-bonded double layers parallel to the longest crystallographic axis. In each layer in the double layer, the phenylalanine dimers and the perchlorate ions alternate along the axis of intermediate length. The two layers are held together by N—H...O hydrogen bonds.

Table 1. Selected geometric parameters (\AA , $^\circ$)

O11—C11	1.217 (5)	O22—C21	1.266 (5)
O12—C11	1.284 (5)	O21—C21	1.228 (5)
C11—C12	1.527 (6)	C21—C22	1.538 (6)
O11—C11—O12	126.2 (4)	O21—C21—O22	127.3 (4)
O11—C11—C12	121.6 (4)	O21—C21—C22	120.3 (4)
O12—C11—C12	112.2 (4)	O22—C21—C22	112.4 (4)
O11—C11—C12—N11	2.5 (5)	O21—C21—C22—N21	2.7 (5)
N11—C12—C13—C14	68.3 (5)	N21—C22—C23—C24	64.8 (5)
C12—C13—C14—C15	-83.8 (5)	C22—C23—C24—C25	-90.6 (5)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O22—HO22...O12 ⁱ	1.15 (7)	1.31 (7)	2.440 (4)	165 (6)
N11—H1N1...O21 ⁱⁱ	0.89	1.911	2.788 (4)	168
N11—H2N1...O1 ⁱⁱⁱ	0.89	2.075	2.954 (14)	169
N11—H2N1...O3* ⁱⁱⁱ	0.89	2.235	3.00 (2)	144
N11—H3N1...O3* ⁱⁱⁱ	0.89	2.186	3.070 (17)	172
N11—H3N1...O4 ⁱⁱⁱ	0.89	2.253	2.919 (14)	131
N21—H1N2...O2 ⁱⁱ	0.89	2.382	3.268 (13)	174
N21—H1N2...O2* ⁱⁱⁱ	0.89	2.178	2.956 (17)	146
N21—H2N2...O11 ⁱⁱⁱ	0.89	1.956	2.821 (5)	164
N21—H3N2...O1* ⁱⁱⁱ	0.89	2.132	2.906 (13)	145
N21—H3N2...O2 ⁱⁱⁱ	0.89	2.390	3.278 (14)	175

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

For H atoms, only the coordinates and isotropic displacement parameters of HO22 were refined. Perchlorate O atoms show disorder over two positions (occupancies of 0.58 and 0.42) corresponding to each atom.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

The authors acknowledge the use of the Bioinformatics Centre MKU in carrying out the computation.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1040). Services for accessing these data are described at the back of the journal.

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Unusual Substitution of $-\text{SCH}_3$ by $-\text{OH}$ in 9,10-Dihydrophenanthrene†

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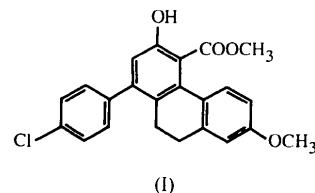
Abstract

The unusual nucleophilic substitution of methylthio by a hydroxyl group in the presence of alkali and dimethylformamide in the synthesis of methyl 1-(4-chlorophenyl)-3-hydroxy-7-methoxy-9,10-dihydrophenanthrene-4-carboxylate, $\text{C}_{23}\text{H}_{19}\text{ClO}_4$, has been confirmed by single-crystal X-ray structure determination.

Comment

Aromatic nuclei and their immediately attached atoms in isolated (*i.e.* not fused) polycyclic systems are generally coplanar and their intramolecular fusion results in inflexible ring skeletons. The electronic character of such systems mainly depends upon the nature of the substituents attached to the ring; these govern the conformation of the molecule (Ram & Goel, 1996), which is an essential factor in biological recognition.

Nucleophilic substitution of $-\text{SCH}_3$ by alkoxide is very common, while its displacement by hydroxyl is quite unusual in the presence of alkali in dry dimethylformamide at room temperature. The presence of the unexpected hydroxyl group and its conformation necessitated the X-ray crystallographic study of the title compound, (I).



The conformation of the title molecule and the atomic numbering scheme are shown in Fig. 1. The molecule contains one phenanthrene ring (fused-ring system A/B/C) to which a phenyl ring (D) has been

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