Table 2. *Intramolecular distances (Å) and angles (°) involving the non-H atoms*

Cu(1)—N(1)	2.007 (9)	Cu(1)—N(5)	1.961 (8)
Cu(1)—N(2)	2.095 (8)	O(1)—C(1)	1.22 (1)
Cu(1)—N(3)	1.981 (8)	N(5)—C(1)	1.11 (1)
Cu(1)—N(4)	2.111 (7)		
N(1)—Cu(1)—N(2)	79.5 (3)	N(2)—Cu(1)—N(4)	105.3 (3)
N(1)—Cu(1)—N(3)	173.7 (3)	N(2)—Cu(1)—N(5)	133.2 (3)
N(1)—Cu(1)—N(4)	99.3 (3)	N(3)—Cu(1)—N(4)	79.5 (3)
N(1)—Cu(1)—N(5)	93.5 (3)	N(3)—Cu(1)—N(5)	92.4 (3)
N(2)—Cu(1)—N(3)	94.8 (3)	N(4)—Cu(1)—N(5)	121.5 (3)

nates and vibrational parameters for non-H atoms are presented in Table 1 and selected bond lengths and angles in Table 2.* The title molecule, including atomic labelling, is displayed in Fig. 1.

Related literature. The square-pyramidal distorted trigonal bipyramidal geometry seen here is very similar to that in bis(2,2'-bipyridyl)thiocyanatocopper(II) tetrafluoroborate (Tyagi & Hathaway, 1981). The relatively short equatorial thiocyanate Cu—N bond is interpreted as resulting from an angular distortion away from a trigonal bipyramid rather than to the potentially π-bonding role of the thiocyanate ligand.

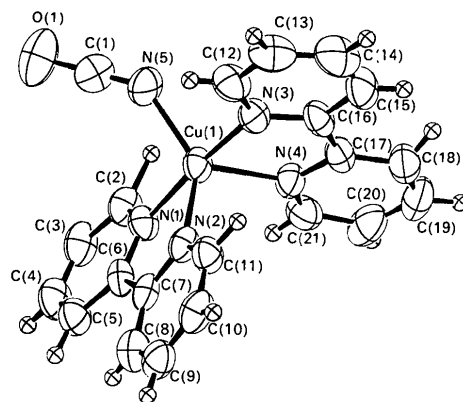We thank the Xunta de Galicia for a grant.

Fig. 1. The title molecule, drawn using *ORTEP*II (Johnson, 1976).

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Structure of L-Phenylalanine L-Phenylalaninium Formate

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Abstract. $C_9H_{11}NO_2.C_9H_{12}NO_2^+.CHO_2^-$, $M_r = 376.41$, monoclinic, $P2_1$, $a = 11.507$ (6), $b = 5.638$ (3), $c = 14.610$ (5) Å, $\beta = 100.65$ (4)°, $V = 932$ (1) Å^3, $Z = 2$, $D_x = 1.342$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 0.94$ cm^{-1}, $F(000) = 400$, $T = 295$ K, final $R = 0.047$ for 2693 observed reflections. The phenylalanine zwitterion and the phenylalanine cation form a Speakman-salt-type hydrogen bond [O···O = 2.496 (3) Å]. Aromatic side chains constitute a thick hydrophobic layer with edge-to-face interactions between the phenyl rings.

Introduction. Structural studies of peptides are often hampered by difficulties in obtaining crystals large enough for X-ray diffraction. Based on our success in controlling crystal morphology and size of small molecular crystals using cocrystallization techniques (Etter, 1988), we have now turned our attention to

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applying these methods to aid in the preparation of high-quality peptide crystals. As part of a systematic survey to define the chemical parameters needed for formation of peptide cocrystals, one of our approaches was to crystallize various amino acids with simple carboxylic acids.

Experimental. Colorless prisms were obtained by slow evaporation from a dilute formic acid solution of phenylalanine. Phenylalanine–formic acid 2:1 composition was established with ^{1}H NMR. A specimen with dimensions $0.55 \times 0.50 \times 0.30$ mm used for data collection, Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, cell constants obtained by least squares from 25 reflections in the range $17 < 2\theta < 40°$, ω–2θ scan mode, $2\theta_{max} = 51.9°$, 7268 reflections collected, 3644 unique, equivalent reflections merged, $R_{int} = 0.086$, $-14 \le h \le 14$, $0 \le k \le 6$, $0 \le l \le 18$, three test reflections, 9.5% decay, corrected with a linear correction factor, Lp and secondary-extinction (coefficient $= 0.572 \times 10^{-5}$) corrections applied, no absorption correction. Structure solved by direct methods using $MITHRIL$ (Gilmore, 1984) and $DIRDIF$ (Beurskens 1984), non-H atoms refined anisotropically, carboxyl H atom located from difference synthesis, carboxyl and ammonium H atoms refined isotropically, other H atoms included in idealized positions ($d_{C-H} = 0.95$ Å) with fixed isotropic $B = 1.2 \times B$ of bonded atom. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, $w = 4F_o^2[\sigma^2(F_o^2)]^{-1}$, final $R = 0.047$, $wR = 0.051$, $S = 1.047$ using 2693 observed reflections with $I > 2\sigma(I)$, 272 variables, max. shift/e.s.d. in final cycle $= 0.09$, max. residual height 0.23, min. -0.28 e Å^{-3}. All calculations performed using $TEXSAN$ (Molecular Structure Corporation, 1985) with atomic scattering factors from $International\ Tables\ for\ X\text{-}ray\ Crystallography$ (1974, Vol. IV). Final positional parameters for all refined atoms and equivalent isotropic temperature factors are listed in Table 1.*

Discussion. The asymmetric unit, which consists of one phenylalanine zwitterion (P), one phenylalanine cation (P^+) and a formate anion (Fo$^-$), is depicted in Fig. 1. The presence of P^+ and Fo$^-$ in the crystal was unexpected, given the pK_a values 1.83 and 3.75, respectively. There is a very short syn–syn carboxyl–carboxylate hydrogen bond between P^+ and P, similar to the interactions studied by Speakman in acid salts (Speakman, 1972) with normal range

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Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

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

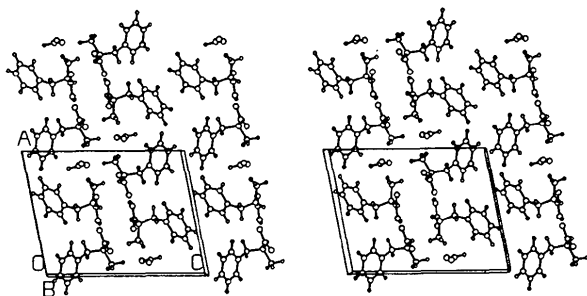|	x	y	z	B_{eq}
O1A	0.6405 (2)	0.1288	0.6171 (1)	3.33 (9)
O2A	0.8021 (2)	0.2787 (5)	0.5775 (1)	3.15 (9)
N1A	0.9127 (2)	−0.1300 (7)	0.5795 (2)	2.9 (1)
C1A	0.7998 (2)	−0.1313 (7)	0.6154 (2)	2.4 (1)
C2A	0.7441 (2)	0.1144 (6)	0.6021 (2)	2.3 (1)
C3A	0.8176 (2)	−0.2150 (7)	0.7172 (2)	2.9 (1)
C4A	0.8796 (2)	−0.0412 (7)	0.7874 (2)	2.8 (1)
C5A	0.8173 (3)	0.1318 (7)	0.8250 (2)	3.9 (1)
C6A	0.8742 (3)	0.2975 (8)	0.8877 (2)	4.6 (2)
C7A	0.9950 (3)	0.2871 (8)	0.9160 (2)	4.4 (2)
C8A	1.0576 (3)	0.1168 (8)	0.8806 (2)	4.6 (2)
C9A	1.0008 (3)	−0.0481 (7)	0.8166 (2)	3.6 (1)
O1B	0.3695 (2)	0.4101 (5)	0.6000 (1)	3.44 (9)
O2B	0.5561 (2)	0.5361 (5)	0.6196 (2)	3.9 (1)
N1B	0.2836 (2)	0.8542 (7)	0.6078 (2)	3.0 (1)
C1B	0.4138 (2)	0.8214 (6)	0.6320 (2)	2.8 (1)
C2B	0.4436 (2)	0.5644 (6)	0.6150 (2)	2.6 (1)
C3B	0.4604 (2)	0.8964 (7)	0.7334 (2)	3.0 (1)
C4B	0.4272 (2)	0.7325 (7)	0.8063 (2)	3.0 (1)
C5B	0.3233 (3)	0.7639 (8)	0.8387 (2)	4.1 (1)
C6B	0.2913 (4)	0.6137 (9)	0.9049 (2)	5.9 (2)
C7B	0.3628 (5)	0.4288 (9)	0.9384 (2)	6.1 (2)
C8B	0.4662 (5)	0.3935 (9)	0.9076 (3)	6.3 (2)
C9B	0.4993 (3)	0.5440 (8)	0.8415 (2)	4.8 (2)
O1C	0.1005 (2)	0.5736 (6)	0.6496 (2)	5.7 (1)
O2C	0.1115 (2)	0.1963 (6)	0.6148 (2)	4.9 (1)
C1C	0.1170 (4)	0.3680 (8)	0.6665 (2)	5.7 (2)
H1	0.955 (3)	−0.241 (8)	0.607 (2)	4.0 (8)
H2	0.899 (4)	−0.164 (11)	0.507 (3)	10 (1)
H3	0.946 (3)	0.032 (10)	0.583 (2)	6 (1)
H2B	0.582 (3)	0.386 (9)	0.611 (2)	4.8 (8)
H12	0.265 (3)	0.996 (8)	0.620 (2)	3.7 (8)
H13	0.257 (2)	0.839 (6)	0.545 (2)	2.5 (6)
H14	0.233 (4)	0.721 (10)	0.632 (3)	8 (1)
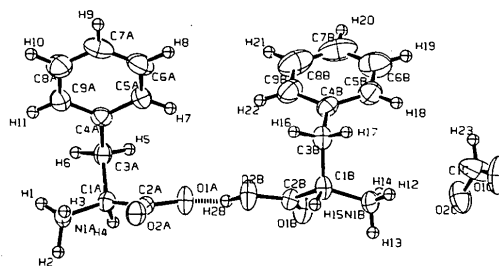
Fig. 1. $ORTEP$ (Johnson, 1976) drawing (thermal ellipsoids, 50% probability level and H atoms of arbitrary size) with numbering scheme indicated. The short carboxyl–carboxylate hydrogen bond has been dotted.

2.50–2.60 Å and minimum 2.40 Å. Apparently, the formation of a PP^+ dimer is preferred over a mixed P^+Fo$^-$ heterodimer because of the specific stability attributable to nearly symmetric short hydrogen bonds between chemically identical groups.

The molecular geometry is given in Table 2. All bond lengths and bond angles are close to expected values, except the two unusually short C—O bonds of Fo$^-$ (1.193 and 1.222 Å). These results may be anomalous, being affected by high thermal motion in the anion. The $gauche^+$ side-chain orientation found for P and P^+ (Table 2) is the least frequently observed conformation for Phe residues in peptides

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°)

O1A—C2A	1.254 (4)	C3B—C4B	1.512 (5)
O2A—C2A	1.234 (4)	C4B—C5B	1.376 (5)
N1A—C1A	1.488 (4)	C4B—C9B	1.387 (5)
C1A—C2A	1.523 (5)	C5B—C6B	1.385 (6)
C1A—C3A	1.537 (4)	C6B—C7B	1.362 (7)
C3A—C4A	1.501 (4)	C7B—C8B	1.362 (8)
C4A—C5A	1.383 (5)	C8B—C9B	1.391 (6)
C4A—C9A	1.381 (4)	O1C—C1C	1.193 (5)
C5A—C6A	1.386 (5)	O2C—C1C	1.222 (5)
C6A—C7A	1.377 (5)	N1A—H1	0.85 (5)
C7A—C8A	1.358 (6)	N1A—H2	1.06 (5)
C8A—C9A	1.393 (5)	N1A—H3	0.99 (5)
O1B—C2B	1.209 (4)	O2B—H2B	0.92 (6)
O2B—C2B	1.294 (3)	N1B—H12	0.85 (5)
N1B—C1B	1.486 (4)	N1B—H13	0.91 (5)
C1B—C2B	1.520 (5)	N1B—H14	1.05 (5)
C1B—C3B	1.538 (4)		

N1A—C1A—C2A	109.0 (3)	N1B—C1B—C3B	110.6 (2)
N1A—C1A—C3A	111.9 (2)	C2B—C1B—C3B	111.8 (2)
C2A—C1A—C3A	112.4 (2)	O1B—C2B—O2B	125.8 (3)
O1A—C2A—O2A	125.8 (3)	O1B—C2B—C1B	122.9 (3)
O1A—C2A—C1A	115.3 (3)	O2B—C2B—C1B	111.3 (3)
O2A—C2A—C1A	118.8 (3)	C1B—C3B—C4B	114.9 (3)
C1A—C3A—C4A	115.0 (3)	C3B—C4B—C5B	120.8 (3)
C3A—C4A—C5A	121.1 (3)	C3B—C4B—C9B	121.2 (3)
C3A—C4A—C9A	121.2 (3)	C5B—C4B—C9B	118.0 (3)
C5A—C4A—C9A	117.7 (3)	C4B—C5B—C6B	121.4 (4)
C4A—C5A—C6A	121.4 (3)	C5B—C6B—C7B	119.9 (4)
C5A—C6A—C7A	119.8 (4)	C6B—C7B—C8B	120.0 (4)
C6A—C7A—C8A	119.5 (3)	C7B—C8B—C9B	120.5 (5)
C7A—C8A—C9A	120.8 (3)	C4B—C9B—C8B	120.2 (4)
C4A—C9A—C8A	120.7 (3)	O1C—C1C—O2C	130.9 (3)
N1B—C1B—C2B	109.1 (3)		

O1A—C2A—C1A—N1A	170.2 (2)	O1B—C2B—C1B—N1B	-11.7 (4)
N1A—C1A—C3A—C4A	72.3 (4)	N1B—C2B—C3B—C4B	70.8 (4)
C1A—C3A—C4A—C5A	87.2 (4)	C1B—C3B—C4B—C5B	-88.6 (4)

Table 3. *Normalized hydrogen-bond distances* (Å), *angles* (°) *and torsion angles* (°)

O—H, N—H and C—H bond lengths were corrected to 1.015, 1.033 and 1.099 Å, respectively, to correspond to neutron diffraction distances (Taylor & Kennard, 1983; Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987).

D—H···O	H···O	D···O	D—H···O	C—O···H	O—C—O···H
O2B—H2B···O1A	1.50	2.496	167	117	-5
N1A—H1···O1C	1.81	2.773	155	130	75
N1A—H2···O2C^i	1.96	2.967	166	104	10
N1A—H3···O2C^{ii}	2.06	2.906	138	115	-89
N1B—H12···O2C^{iii}	1.96	2.780	134	114	118
N1B—H13···O2A^{iv}	1.71	2.737	173	108	-74
N1B—H14···O1C^v	1.82	2.791	157	112	-88
C1B—H15···O1A^{vi}	2.36	3.173	130	142	134

Symmetry code: (i) $2 - x$, $0.5 + y$, $1 - z$; (ii) x, $1 + y$, z; (iii) $x - 1$, $y + 2$, z; (iv) $1 - x$, $0.5 + y$, $1 - x$; (v) $x - 1$, $y + 1$, z; (vi) x, $1 - y$, z.
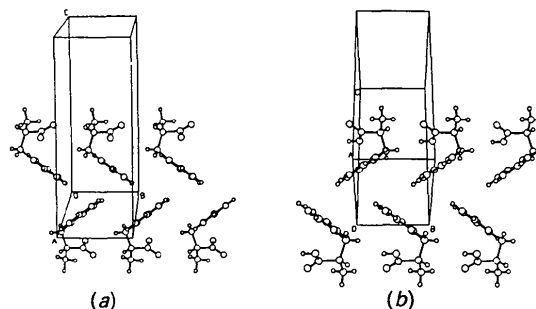

Fig. 3. 'Herringbone' patterns formed by stacking of (*a*) *P* phenyl groups and (*b*) P^+ phenyl groups. Both views are approximately along the *a* axis. Centroid separation and interplanar angle are 5.12 Å and 75.4° for *P* chains and 4.92 Å and 72.0° for P^+ chains. The nearest intermolecular distances are C7A···H9 (2.90 Å) and C7B···H21 (2.86 Å), respectively.

Fig. 2. Stereoscopic packing diagram viewed down the *b* axis of the unit cell.

(Benedetti, Morelli, Némethy & Scheraga, 1983) and proteins (Ponder & Richards, 1987), but occurs in the structure of L-phenylalanine hydrochloride (Al-Karaghauli & Koetzle, 1975). This rotamer may be favored in the PP^+ dimer by allowing a distinct segregation of hydrophilic and hydrophobic regions of the crystal, illustrated in Fig. 2.

The hydrophilic layers along the *a* axis comprise two parallel chains of PP^+ dimers with Fo⁻ linkers in 'sandwich-like' positions between —NH$_3^+$ groups. Only one of the five H atoms accepted by Fo⁻ is located near the usually preferred carboxylate plane (Görbitz & Etter, 1992), as reflected by O—C—O···H torsion angle values far from O (*syn* position) or 180° (*anti* position), Table 3. The *P* carboxylate takes

part in just two regular hydrogen bonds and a weak C^α—H···O interaction.

Energy calculations show that intramolecular and intermolecular edge-to-face interactions involving aromatic rings give a significant contribution to the overall interaction energy of the crystal (Burley, Wang, Votano & Rich, 1987; Burley & Petsko, 1986). Molecules with two phenyl groups studied by Burley, Wang, Votano & Rich (1987) displayed folded conformations (I) in all structures.

(I)
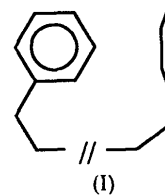
Such intramolecular contacts do not occur either within the PP^+ dimer or between neighboring dimers related by translation. There are instead intermolecular edge-to-face P—P and P^+—P^+ interactions due to the thick 'double-layer' build-up of the

hydrophobic sheets (Fig. 2), each leading to a typical 'herringbone' pattern as shown in Fig. 3. Molecular modelling experiments indicate that a dimer conformation with phenyl groups oriented as shown in (I) is possible only if the P^+ side chain is in the *trans* position. This also requires a close to perpendicular orientation of the P^+ carboxyl group relative to the P carboxylate (observed interplanar angle = 27.3°). Such conformations could not support the hydrogen-bond network observed in the crystal structure.

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cis-7-Oxo-8-oxabicyclo[4.3.0]non-2-ene-5-cis-carboxylic Acid

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Abstract. $C_9H_{10}O_4$, $M_r = 182.15$, orthorhombic, $P2_12_12_1$, $a = 6.589$ (4), $b = 7.003$ (4), $c = 18.436$ (12) Å, $V = 850.7$ Å^3, $Z = 4$, $D_x = 1.422$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.106$ mm^{-1}, $F(000) = 384$, $T = 293$ K, $R = 0.0517$ for 913 unique reflections with $F > 6.\sigma(F)$. The bond lengths and angles are all within the accepted ranges. The molecule resembles a hinge with the two rings lying at approximately 110° to one another with the carboxyl group on C5 equatorial and effectively coplanar with the cyclohexene. No intramolecular hydrogen bond is formed between O7 and O10/O11 but a network of intermolecular hydrogen bonding between carboxyl groups holds the molecules together in the *a*-axis direction. Other packing interactions are hydrophobic. The torsion angles determined by NMR are in good agreement with those determined from the crystal structure.

Experimental. The title compound was prepared by the Diels–Alder condensation of 1-hydroxypenta-2,4-diene with maleic anhydride and crystals were obtained by recrystallization from H_2O. Colourless prism, $0.4 \times 0.2 \times 0.2$ mm, mounted on Siemens–

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