Refinement

Refinement on F	$w = 1/\sigma^2(F)$
$R = 0.045$	$(\Delta/\sigma)_{max} = 0.13$
$wR = 0.058$	$\Delta\rho_{max} = 0.22$ e Å^{-3}
$S = 0.85$	$\Delta\rho_{min} = -0.25$ e Å^{-3}
2241 reflections	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
255 parameters	
All H-atom parameters refined	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

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

	x	y	z	U_{eq}
O(1)	0.3141 (1)	0.00280 (5)	0.2616 (3)	0.0422 (4)
O(2)	0.5321 (1)	0.07655 (5)	0.1683 (3)	0.0378 (4)
C(1)	−0.1605 (2)	0.2114 (1)	0.3101 (5)	0.0601 (9)
C(2)	−0.1188 (2)	0.1343 (1)	0.3540 (5)	0.0641 (9)
C(3)	0.0210 (2)	0.0897 (1)	0.2918 (4)	0.0507 (7)
C(4)	0.2670 (1)	0.07779 (7)	0.1185 (3)	0.0350 (5)
C(5)	0.3897 (1)	0.11777 (7)	0.2345 (3)	0.0343 (5)
C(6)	0.4301 (2)	0.22868 (7)	−0.0332 (4)	0.0401 (5)
C(7)	0.4780 (2)	0.3383 (1)	−0.2701 (5)	0.0595 (8)
C(8)	0.4317 (3)	0.4136 (1)	−0.3715 (7)	0.076 (1)
C(9)	0.2851 (3)	0.4586 (1)	−0.3578 (7)	0.073 (1)
C(10)	0.1881 (3)	0.42907 (9)	−0.2437 (6)	0.0594 (9)
C(11)	−0.0182 (2)	0.36009 (9)	0.0185 (5)	0.0539 (8)
C(12)	−0.1090 (2)	0.3273 (1)	0.1342 (5)	0.0569 (8)
C(13)	−0.0652 (2)	0.2476 (1)	0.2080 (4)	0.0490 (7)
C(14)	0.0802 (1)	0.20346 (8)	0.1650 (4)	0.0396 (6)
C(15)	0.1192 (1)	0.12352 (8)	0.2016 (3)	0.0393 (6)
C(16)	0.1814 (2)	0.24022 (7)	0.0716 (3)	0.0376 (5)
C(17)	0.3364 (1)	0.19708 (7)	0.0773 (3)	0.0353 (5)
C(18)	0.1314 (2)	0.31807 (8)	−0.0185 (4)	0.0434 (6)
C(19)	0.2310 (2)	0.35181 (8)	−0.1363 (4)	0.0461 (7)
C(20)	0.3797 (2)	0.30630 (8)	−0.1508 (4)	0.0448 (6)

Table 2. *Selected geometric parameters* (Å, °)

O(1)—C(4)	1.423 (2)	C(8)—C(9)	1.400 (4)
O(2)—C(5)	1.420 (2)	C(9)—C(10)	1.359 (4)
C(1)—C(2)	1.367 (3)	C(10)—C(19)	1.417 (2)
C(1)—C(13)	1.402 (3)	C(11)—C(12)	1.351 (3)
C(2)—C(3)	1.411 (3)	C(11)—C(18)	1.436 (2)
C(3)—C(15)	1.372 (2)	C(12)—C(13)	1.427 (3)
C(4)—C(5)	1.533 (2)	C(13)—C(14)	1.421 (2)
C(4)—C(15)	1.513 (2)	C(14)—C(15)	1.417 (2)
C(5)—C(17)	1.513 (2)	C(14)—C(16)	1.438 (2)
C(6)—C(17)	1.349 (2)	C(16)—C(17)	1.437 (2)
C(6)—C(20)	1.431 (2)	C(16)—C(18)	1.406 (2)
C(7)—C(8)	1.376 (3)	C(18)—C(19)	1.436 (2)
C(7)—C(20)	1.409 (2)	C(19)—C(20)	1.419 (2)
O(1)—C(4)—C(5)	111.3 (1)	O(2)—C(5)—C(4)	111.7 (1)
O(1)—C(4)—C(15)	110.6 (1)	O(2)—C(5)—C(17)	110.7 (1)
C(5)—C(4)—C(15)	109.2 (1)	C(4)—C(5)—C(17)	109.9 (1)
O(1)—C(4)—C(5)—O(2)	56.6 (1)		
O(1)—C(4)—C(5)—C(17)	179.8 (1)		
C(15)—C(4)—C(5)—O(2)	178.9 (1)		
C(15)—C(4)—C(5)—C(17)	−57.8 (1)		

D—H···A	D—H	H···A	D···A	D—H···A
O(1)—H···O(2^{i})	0.83 (2)	1.89 (2)	2.718 (1)	175 (2)
O(2)—H···O(1^{ii})	0.78 (3)	1.93 (3)	2.703 (1)	170 (3)

Symmetry codes: (i) $1-x, -y, -z$; (ii) $1-x, -y, 1-z$.

The structure was solved using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). For all other crystallographic calculations, in-house programs were used (Carrell, Shieh & Takusagawa, 1981). The structure refinement was carried out using a least-squares procedure. H atoms were located from difference Fourier maps and included in the final refinements.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, least-squares-planes data with r.m.s deviations, along with comparison of the molecular geometry of various benzo[*a*]pyrene moieties reported in the literature have been deposited with the IUCr (Reference: SZ1006). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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DL-Proline Monohydrate

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Abstract

In the crystal of the title compound, $C_5H_9NO_2.H_2O$, hydrogen-bonded centrosymmetric dimers of proline molecules stack along **a** to form columns stabilized by *S*1-type head-to-tail sequences. These columns are interconnected by water molecules to give rise to

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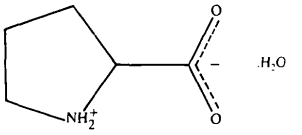
corrugated sheets which stack along **b**. The water molecules in the structure occur in infinite channels parallel to **a**.

Comment

DL-Proline is among the few amino acids for which crystal structures are not available. Our long term research programme on crystalline complexes involving amino acids and peptides (Vijayan, 1988; Prasad & Vijayan, 1993; Suresh, Prasad & Vijayan, 1994), aimed at elucidating the geometric features of biologically and evolutionarily important interactions, involves the comparison of the aggregation patterns of DL and L amino acids with those in their crystalline complexes. The crystal structure of DL-proline has been determined with this purpose in mind. An X-ray study of the title compound, (I), has been reported previously (Fox & Rosenstein, 1976), but no structural details were available.



(I)

The conformation of the pyrrolidine ring is intermediate between an envelope and half chair, and may be described as C_2—C^{γ}_{exo}—C^{δ}_{endo} or C_s—C^{γ}_{exo} or C_s—C^{δ}_{endo} (Ashida & Kakudo, 1974; Nair & Vijayan, 1981). In the crystal structure of (I) (Fig. 1), the proline molecules dimerize across inversion centres *via* N(1)···O(1) hydrogen bonds, as do many other amino acid racemates (Soman & Vijayan, 1989). In all other such amino acid structures, however, O(2) instead of O(1) is involved in the hydrogen bonds that stabilize the dimer. The dimers stack along **a** to form columns, each stabilized by an *S*1-type head-to-tail sequence involving an N(1)···O(1) hydrogen bond and its translation equivalents (Suresh & Vijayan, 1983). *c*-Glide-related water molecules in the structure occur in infinite channels along **a**, and serve to interconnect proline columns to form corrugated layers parallel to the *ac* plane. The layers then stack along **b** to form the crystal. Although there is an element of similarity between the structures of DL- and L-proline (Kayushina & Vainshtein, 1966), the similarity is not striking, unlike in the case of the DL and L isomers of most other hydrophobic amino acids (Soman & Vijayan, 1989).

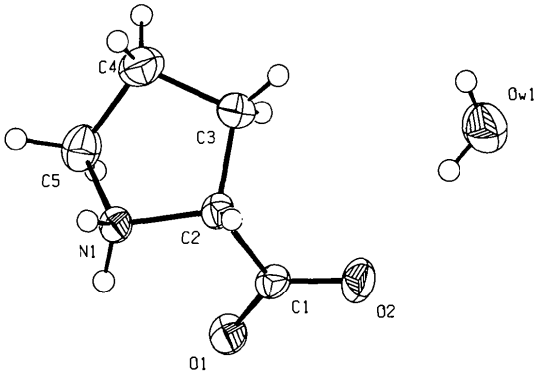


Fig. 1. *PLATON* (Spek, 1990) plot of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.

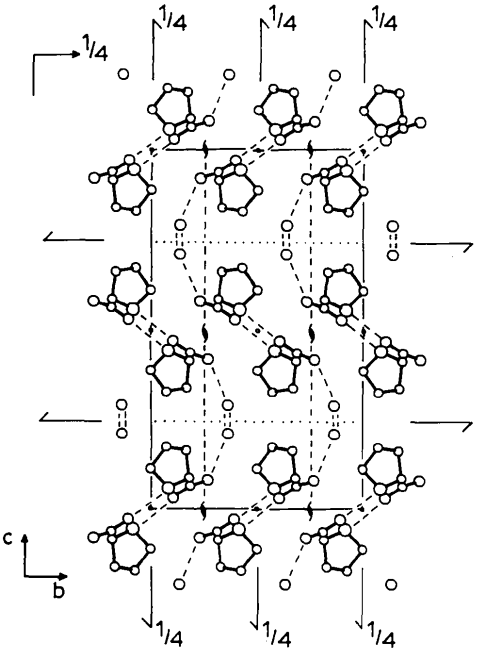


Fig. 2. Crystal structure as viewed along the *a* axis (*PLUTO*; Motherwell, 1982). C, O and N atoms are represented as spheres of increasing size.

Experimental

The compound was obtained from Sigma Chemical Co. The crystal density D_m was measured by flotation in a mixture of benzene and carbon tetrachloride.

Crystal data

$C_5H_9NO_2.H_2O$
M_r = 133.15
Orthorhombic
Pbca
a = 5.274 (1) Å
b = 12.087 (1) Å
c = 20.053 (2) Å
V = 1278.3 (3) Å^3
Z = 8
D_x = 1.384 Mg m^{-3}
D_m = 1.38 (2) Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 9.9–18.6°
μ = 0.114 mm^{-1}
T = 296 (2) K
Chunk
0.63 × 0.45 × 0.23 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
1391 measured reflections
1391 independent reflections
1195 observed reflections [$I > 2\sigma(I)$]
$\theta_{max} = 27°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 25$
3 standard reflections
frequency: 60 min
intensity decay: 3.85%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0391$
$wR(F^2) = 0.1066$
$S = 1.098$
1391 reflections
126 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0682P)^2 + 0.3024P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.119$
$\Delta\rho_{max} = 0.231$ e Å^{-3}
$\Delta\rho_{min} = -0.226$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
O1	0.2076 (2)	0.60536 (8)	0.02947 (5)	0.0335 (3)
O2	0.2496 (2)	0.76870 (9)	0.08009 (5)	0.0393 (3)
N1	−0.2827 (2)	0.58298 (9)	0.05647 (5)	0.0256 (3)
C1	0.1256 (2)	0.68583 (10)	0.06274 (6)	0.0256 (3)
C2	−0.1510 (2)	0.68180 (10)	0.08519 (6)	0.0250 (3)
C3	−0.1742 (3)	0.6678 (2)	0.16111 (7)	0.0433 (4)
C4	−0.3560 (3)	0.57210 (14)	0.17171 (7)	0.0428 (4)
C5	−0.3127 (3)	0.50003 (12)	0.11117 (8)	0.0405 (4)
OW1	0.1879 (3)	0.36355 (12)	0.20966 (8)	0.0529 (4)

Table 2. *Selcted torsion angles* (°)

O1—C1—C2—N1	−5.45 (15)	C3—C4—C5—N1	−39.6 (2)
O2—C1—C2—N1	175.42 (11)	C2—N1—C5—C4	34.71 (14)
N1—C2—C3—C4	−9.3 (2)	C5—N1—C2—C3	−15.75 (14)
C2—C3—C4—C5	30.4 (2)		

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···A	H···A	D···A	H—D···A	D—H···A
N1—H1N1···O1^{i}	2.19 (2)	2.883 (1)	34 (1)	133 (1)
N1—H2N1···O1^{ii}	1.91 (2)	2.755 (1)	13 (1)	161 (2)
OW1—H1W···O2^{iii}	2.05 (3)	2.859 (2)	1 (2)	179 (2)
OW1—H2W···OW1^{iv}	2.32 (3)	3.094 (2)	3 (2)	177 (3)

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

Data collection: Enraf–Nonius CAD-4 diffractometer software. Cell refinement: Enraf–Nonius CAD-4 diffractometer software. Data reduction: local program. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLATON* (Spek, 1990), *PLUTO* (Motherwell, 1982).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1113). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Ethyl 6,7-Bis(trifluoromethyl)isocoumarin-3-carboxylate: Formed by a Novel Diels–Alder Cycloaddition Involving Two Different α,β-Unsaturated Esters

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Abstract

In common with other isocoumarin-based molecules, the planar fused ring system [maximum deviation 0.05 (2) Å] in the title molecule, ethyl 1-oxo-6,7-bis(trifluoromethyl)-1*H*-2-benzopyran-3-carboxylate, $C_{14}H_8F_6O_4$, contains a non-delocalized double bond

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