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Crystal structure of L-tryptophanium phosphite, $(C_{11}H_{13}N_2O_2)[H_2PO_3]$

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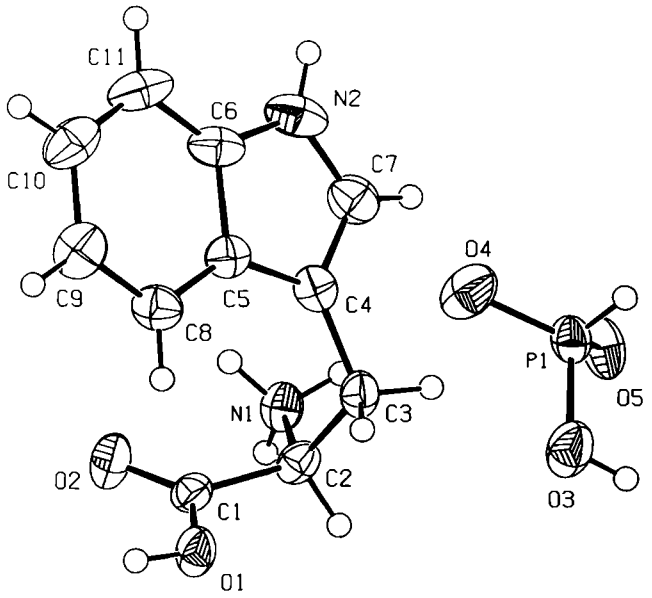

Abstract

$C_{11}H_{15}N_2O_5P$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 5.5442(6)$ Å, $b = 8.3603(4)$ Å, $c = 27.427(3)$ Å, $V = 1271.3$ Å^3, $Z = 4$, $R_{gt}(F) = 0.053$, $wR_{ref}(F^2) = 0.146$, $T = 293$ K.

Source of material

A few drops of phosphorous acid were added to a aqueous solution of L-tryptophan. Within few months transparent single crystals of prismatic shape grew from the solution. The single crystal used for the X-ray study was checked prior to data collection by Laue photographs.

Experimental details

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms using SHELXL-97 defaults [1]. Examination of the crystal structure with PLATON [2] showed that there are no solvent-accessible voids in the crystal lattice. Due to the lack of significant anomalous dispersion at the MoK_α wavelength, the well-known absolute configuration of the L-tryptophanium cations was chosen to fix the enantiomer. The Flack parameter was found to be 0.5(2).)

Discussion

L-Tryptophan is a naturally occurring amino acid, with a non-polar side chain and no net charge at physiological pH. Tryptophan fluorescence is widely used as a tool to monitor changes in proteins and to make inferences regarding conformation and dynamics [3,4]. The nonexponential fluorescence decay of tryptophan, in aqueous solutions, has been explained by the emission from non-interconverting rotamers which have different lifetimes due to different rates of intramolecular charge transfer [5]. Looking for compounds with optical properties and phase transitions, we have been synthesizing L-tryptophan salts, namely the title compound, L-tryptophanium phosphite. The non-centrosymmetric structure contains anions and positively charged amino acid molecules with the carboxyl and amino group protonated. The anion shows P—O bond lengths of 1.566(3) Å, 1.508(3) Å and 1.464(3) Å, for O3, O4 and O5 respectively, showing that one H atom was transferred to the amino acid. The O–P–O angles approximate the ideal tetrahedral angle of 109.47°. The amino acid, when viewed along the C2–C3 bond, shows a staggered conformation with C4 (C_γ) laying at *gauche* position relatively to both carboxyl and amino groups. The χ^1 torsion angle, N1–C2–C3–C4, is 52.2(4)° and χ^2, C2–C3–C4–C5, is 78.7(5)°. The carboxylic distances are d(O1—C1) = 1.295(5) Å and d(O2—C1) = 1.218(5) Å, showing that this group is neutral.

Only a very few L-tryptophan salts are found in Cambridge Structural Database, namely L-tryptophan hydrobromide [6], L-tryptophan hydrochloride [6] and L-tryptophan picric acid [7]. The halide salts of tryptophan show a conformation of the amino acid similar to that of the title compound. In the picric acid salt there are two independent tryptophan molecules with staggered conformations: one of them has the indole group *gauche* relatively to the amino and *anti* to the carboxyl group, the other has the indole group *gauche* relatively to the carboxyl and *anti* to the amino group. In addition to the electrostatic interaction between the ions, there are conventional hydrogen bonds re-enforcing the structure. These bonds exhaust the capacity of the ions as donors, with exception of N2, the in-ring nitrogen atom, that donates the hydrogen atom to the π system of a neighboring L-tryptophan. The most of the hydrogen bonds lie in the *a,b* plane with only N1–H1A···O5 2.797(4) Å linking two successive layers. Molecules pack in such a way that along the *a* axis there are two layers of non-polar indole rings and two charged layers, as seen previously in L-tryptophan hydrobromide and L-tryptophan hydrochloride [6]. The two charged layers are composed of anions and charged heads of the cations and are intra and interlinked by conventional hydrogen bonds. The double non-polar layers are interlinked by three weak intermolecular X–H···π interactions. Two of them correspond to a geometry where the shared H atom is above the centre of the ring but the X–H bond points towards a C atom of the ring. The third, with the phosphorous atom as the donor, corresponds to a classical T-shape geometry. An analysis of data collected in the Brookhaven Protein Data bank reveals that interactions between proline CH groups and aromatic rings of phenylalanine, tyrosine and tryptophan as acceptors are frequently observed in proteins [8]. A search for phase transitions in this compound is under way since we have recently found a reproducible peak in the DSC curve of a similar compound, L-tryptophan selenite.

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Table 1. Data collection and handling.

Crystal:	yellow prism, size 0.17 × 0.25 × 0.29 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.35 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$ (profile data)
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3366, 2892
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1801
$N(param)_{refined}$:	175
Programs:	SHELXL-97 [1], PLATON [2], SHELXS-97 [9], ORTEP-II [10]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(0)	4*a*	0.9362	0.8813	0.1390	0.040
H(3)	4*a*	0.6293	0.9128	0.1963	0.076
H(1A)	4*a*	0.7729	0.4253	0.2307	0.050
H(1B)	4*a*	0.8277	0.5032	0.1846	0.050
H(1C)	4*a*	0.8441	0.3302	0.1887	0.050
H(2)	4*a*	1.0844	0.3146	0.0306	0.059
H(1)	4*a*	0.1653	0.1169	0.1939	0.057
H(22)	4*a*	0.4118	0.4782	0.2028	0.037
H(3A)	4*a*	0.3126	0.4199	0.1202	0.039
H(3B)	4*a*	0.5064	0.5550	0.1250	0.039
H(7)	4*a*	0.9054	0.5141	0.0807	0.050
H(8)	4*a*	0.3185	0.0804	0.1043	0.046
H(9)	4*a*	0.3838	−0.1611	0.0661	0.055
H(10)	4*a*	0.7174	−0.2021	0.0170	0.060
H(11)	4*a*	0.9956	0.0005	0.0047	0.056

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	4*a*	0.9420(2)	0.8289(1)	0.17096(4)	0.0350(6)	0.0251(5)	0.0404(5)	−0.0072(5)	−0.0011(5)	0.0011(5)
O(3)	4*a*	0.6774(6)	0.8218(4)	0.1908(1)	0.036(2)	0.034(2)	0.083(2)	−0.000(2)	0.004(2)	0.002(2)
O(4)	4*a*	1.0179(6)	0.6632(4)	0.1629(1)	0.040(2)	0.035(2)	0.092(2)	−0.009(2)	0.011(2)	−0.019(2)
O(5)	4*a*	1.0964(6)	0.9313(3)	0.2037(1)	0.053(2)	0.029(2)	0.048(2)	−0.012(1)	−0.014(2)	0.004(1)
N(1)	4*a*	0.7636(6)	0.4167(4)	0.1984(1)	0.034(2)	0.027(2)	0.039(2)	−0.004(2)	−0.006(2)	−0.003(2)
N(2)	4*a*	0.9544(7)	0.2996(5)	0.0471(1)	0.033(2)	0.071(3)	0.041(2)	−0.008(2)	0.007(2)	0.003(2)
O(1)	4*a*	0.1968(5)	0.2116(3)	0.1895(1)	0.029(2)	0.025(2)	0.061(2)	−0.003(1)	0.000(1)	0.003(1)
O(2)	4*a*	0.5685(6)	0.1326(3)	0.2088(1)	0.036(2)	0.027(2)	0.062(2)	0.003(1)	−0.007(2)	0.001(1)
C(1)	4*a*	0.4257(8)	0.2347(4)	0.1957(1)	0.030(2)	0.027(2)	0.032(2)	0.002(2)	0.003(2)	−0.004(2)
C(2)	4*a*	0.5077(7)	0.4023(5)	0.1837(1)	0.022(2)	0.029(2)	0.041(2)	0.001(2)	−0.002(2)	−0.005(2)
C(3)	4*a*	0.4782(7)	0.4415(5)	0.1295(1)	0.028(2)	0.026(2)	0.045(2)	−0.001(2)	−0.001(2)	0.005(2)
C(4)	4*a*	0.6411(7)	0.3514(5)	0.0962(1)	0.027(2)	0.034(2)	0.035(2)	−0.004(2)	−0.006(2)	0.003(2)
C(5)	4*a*	0.6215(6)	0.1897(5)	0.0787(1)	0.027(2)	0.038(2)	0.028(2)	0.003(2)	−0.005(2)	0.000(2)
C(6)	4*a*	0.8258(8)	0.1594(6)	0.0482(1)	0.028(2)	0.058(3)	0.028(2)	−0.001(2)	0.000(2)	−0.002(2)
C(7)	4*a*	0.8470(8)	0.4112(6)	0.0757(1)	0.037(2)	0.047(3)	0.041(2)	−0.005(2)	−0.001(2)	0.003(2)
C(8)	4*a*	0.4543(8)	0.0657(5)	0.0849(1)	0.035(2)	0.041(2)	0.038(2)	−0.005(2)	0.001(2)	−0.003(2)
C(9)	4*a*	0.4939(8)	−0.0784(6)	0.0618(2)	0.043(3)	0.042(3)	0.052(2)	−0.004(2)	−0.010(2)	−0.011(2)
C(10)	4*a*	0.6959(9)	−0.1034(6)	0.0320(2)	0.052(3)	0.054(3)	0.044(2)	0.015(3)	−0.005(2)	−0.016(2)
C(11)	4*a*	0.8625(8)	0.0161(6)	0.0248(2)	0.032(2)	0.075(4)	0.032(2)	0.016(2)	−0.002(2)	−0.013(2)

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