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THE STRUCTURE OF L-TYROSINE

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Of the amino acids naturally occurring in proteins only a few have not been fully investigated by X-ray methods. One of these is L-tyrosine for which the difficulty of obtaining good single crystals seems to have been an obstacle for the structural characterization (1,2). A method of growing single crystals has been worked out and this procedure has been published elsewhere (3). The present paper describes the results of the structure determination of L-tyrosine by X-ray methods. The crystal data obtained were as follows: L-tyrosine, $C_9H_{11}O_3N$, orthorhombic, space group $\underline{P}\ 2_12_12_1$; cell dimensions: $\underline{a}$ = 6.913(0.007)Å; $\underline{b}$ = 21.116(0.004)Å; $\underline{c}$ = 5.829(0.006)Å. The figures in parentheses are estimated standard deviations. Density (measured): 1.41 $g.cm^{-3}$, density (calculated): 1.414 $g.cm^{-3}$; $\underline{Z}$ = 4. Intensity data were recorded on an automatic Picker diffractometer. 2259 unique reflections with intensities above the background level were recorded using the ω-2θ scanning mode. The structure was solved by three-dimensional direct methods and refined by Fourier and least-squares calculations to a conventional $\underline{R}$-factor of 0.046. The hydrogen atoms were localized and included in the refinements. Bond lengths and angles arrived at are given in Figure 1, which shows the molecule as seen along the $\underline{a}$-axis. Corrections for thermal effects have not been applied. Estimated standard deviations are 0.002Å for bond lenghts and 0.1-0.2° for bond angles.

The values are in good agreement with expected ones and compare well with those found in the 3-hydroxylated derivative L-DOPA (4). The zwitterionic nature of the amino acid is revealed by the localization of three hydrogen atoms attached to the nitrogen atom as well as by the nearly symmetric arrangement in the carboxyl group.

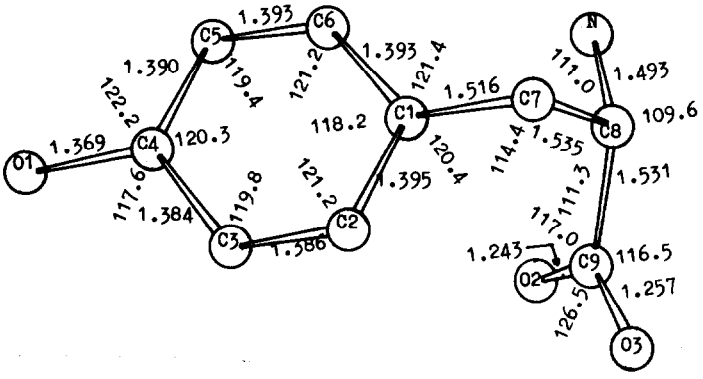

Figure 1. Bond lengths and angles in L-tyrosine.

The plane through C1-C7-C8 forms an angle of 85° with the plane of the phenyl ring. The conformation about the C7-C8 bond is staggered. In contrast to what was found in L-DOPA, however, the hydrogen atom at C8 is in trans position relative to C1. Both the amino and the carboxyl groups are thus gauche relative to the aromatic ring, the dihedral angles about the C7-C8 bond being 69° and 307°, respectively. A similar conformation is reported for L-phenylalanine (5).

The nitrogen atom is situated close to the plane of the carboxyl group. The dihedral angle O2-C9-C8-N is 14.4°. All hydrogen atoms linked to non-carbon atoms are engaged in inter-molecular hydrogen bonding. The phenolic oxygen atom is hydrogen donor to a carboxyl oxygen atom, the oxygen-oxygen separation being 2.67Å. There are three hydrogen bonds from the nitrogen atom to neighbouring molecules, one to a phenolic oxygen atom and two to carboxyl oxygen atoms; the hydrogen bond lengths are 2.88, 2.88 and 2.82Å, respectively. O3 is hydrogen acceptor in two hydrogen bonds, whereas O2 is engaged in only one. This may explain why the C9-O3 bond is slightly longer than the C9-O2 bond.

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