

03.3-8 CONFORMATION OF METHYLATED AMINO ACIDS: CRYSTAL AND MOLECULAR STRUCTURE OF AN ANALOG OF ALDOMET, 3,4-DIMETHOXY- α -METHYL-DL-PHENYLALANINE SESQUIHYDRATE*. K.K. Chacko[†], V. Ravichandran[†] and T. Srikrishnan[†], Center for Crystallographic Research[†], Roswell Park Memorial Institute, Buffalo, NY 14263 USA and Department of Physics[‡], University of Madras, Madras 600025, India.

Dihydroxyphenylalanine (DOPA) is an amino acid found in seedlings, pods and beans. Aldomet, the anti-hypertensive drug is an alpha methylated analog of DOPA. The crystal structure of the title compound, which is a 3,4-dimethoxy analog of Aldomet, was undertaken to study the conformation of methylated amino acids in the solid state.

Crystals of the title compound are triclinic, space group PT, with cell dimensions: $a = 5.872(1)$, $b = 11.437(2)$, $c = 20.434(1)$ Å, $\alpha = 95.74(1)^\circ$, $\beta = 96.91(1)$, $\gamma = 89.18(1)^\circ$, $V = 1355.5$ Å³, $Z = 4$ (two molecules per asymmetric unit) and $D_{\text{calc}} = 1.303$ g/c.c. The density was measured by flotation in bromoform and benzene at 1.29 g/c.c. The preliminary data was collected on a GEXRD-6 diffractometer and the complete three-dimensional data collected on a CAD-4 diffractometer. A total of 6313 reflections were collected, out of which 4006 were considered significant. The data was processed on a PDP 11/34 computer. The structure was obtained by a multi-solution technique, using the MULTAN program and refined by full-matrix least-squares method to a final R-value of 0.042 for the observed 4006 reflections ($I > 3\sigma$).

Both the molecules in the asymmetric unit exist as zwitterions in the solid state. Although both molecules have similar conformations, there are some essential differences. The C-0¹ is shorter than C-0² by 0.016 and 0.039 Å respectively in molecules A and B. C-0² of molecule B is considerably longer (0.013 Å) than C-0² of molecule A, because O² of molecule B is involved in three strong hydrogen bonds whereas O² of molecule A accepts only two. The torsion angles ψ_1 and ψ_2 are $+47.2^\circ$, $\mp 134.4^\circ$ in molecule A and $\pm 33.3^\circ$ and $\mp 147.3^\circ$ in molecule B respectively. Looking along C α -C β , the three substituents α -methyl group, NH₃⁺ and COO⁻ are at dihedral angles of $+67.2$, ± 66.8 ; ∓ 174.3 , $\mp 175.6^\circ$ and ∓ 59.2 and $\mp 59.5^\circ$ in molecules A and B respectively. Atom C β is coplanar with the benzene ring and the two methoxy groups lie on the phenyl plane. The amino groups each take part in three hydrogen bonds, to two water oxygen atoms and O¹ of the carboxyl groups. Two water molecules OW1 and OW2 donate two hydrogen bonds to the carboxyl oxygens and receive one each from the amino nitrogen atoms. The third water molecule OW3, on the contrary receives two hydrogen bonds from each of the amino nitrogen atoms of molecules A and B and donates two hydrogen bonds to the carboxyl oxygen O² of A and B. The hydrogen bonding environment of OW1 is trigonal nonplanar, OW2 is trigonal planar and OW3 is tetrahedral.

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03.3-9 CRYSTAL STRUCTURE OF AN AMIDE ALKALOID PIPERLONGUMINE. By T. Banerjee and S. Chaudhuri, Saha Institute of Nuclear Physics, Crystallography and Molecular Biology Division, Sector I, Block 'AF', Bidhannagar, Calcutta-700 064, India.

Piperlongumine {N-(3,4,5-trimethoxycinnamoyl)- Δ^3 -piperidin-2-one}, an alkaloid amide, was isolated from the root of Piper longum L., commonly known as 'Pipple', a climbing plant found in abundance in the tropical regions of India and used in the treatment of asthma and chronic bronchitis in Ayurvedic medicine (Chatterjee & Dutta, Tetrahedron (1967) 23, 1769; Kirtikar & Basu, Indian Medicinal Plants, Vol III, ed. Basu, Allahabad (1933) p.2128).

Crystal and experimental data: C₁₇H₁₉NO₅, $M_r = 317.34$, monoclinic, P2₁/n, $a = 15.793(3)$, $b = 4.089(4)$, $c = 24.649(5)$ Å, $\beta = 97.56(3)^\circ$, $V = 1578(2)$ Å³, $Z = 4$, $D_m = 1.341$, $D_x = 1.336$ Mg m⁻³, $F(000) = 672$, $\lambda = 1.5418$ Å, $\mu = 8.3$ cm⁻¹.

The structure was solved by direct methods. Full-matrix refinement led to a final R of 0.053 with 1863 'observed' reflections [$I > 3\sigma(I)$]. All hydrogen atoms were located in a difference Fourier synthesis and their parameters were refined.

The bond distances in the piperidone ring show that the double bond is between C(3) and C(4) instead of C(5) and C(6) as proposed originally (Chatterjee & Dutta (1967)). Other distances and angles in the molecule agree well with those reported in similar structures. The progressive decrease in the C-C-C angles along the chain from the trimethoxyphenyl ring to the piperidone ring has been attributed to steric interaction of the hydrogen atoms (Grynpsas & Lindley, Acta Cryst. (1975) B31, 2663). As in other molecules having the piperidylcarbonyl moiety, the C-N bond has appreciable double bond character (Herbstein, Schwotzer, Addae-Mensah, Torto & Woode, Acta Cryst. (1981), B37, 702). This, together with the observed planarity of the piperidyl nitrogen, indicates interaction between the nitrogen atom lone pair and the carbonyl group. The half chair conformation of the piperidone ring is evident from the endocyclic torsion angles. A pair of intramolecular C-H...O interactions involving the ethylenic hydrogen atoms stabilize the conformation of the molecule.

