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3-Iodo-L-tyrosine Methanol Solvate (1/1)

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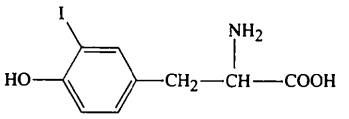
Abstract

In the title compound, $C_9H_{10}INO_3.CH_4O$, the carboxyl and amino groups are charged and folded back towards the phenol ring. The 3-iodo-L-tyrosine molecules are held together in the crystal by means of a hydrogen-bond network involving the carboxyl, amino and phenolic hydroxyl groups and I atoms of the amino acid molecule, and the methanol solvent.

Comment

The primary precursor for thyroid hormone is thyroglobulin, in which the first step is iodination at position 3 and then at position 5 of the tyrosine residue. Coupling of monoiodotyrosine and diiodotyrosine residues then occurs within the thyroglobulin molecule to form thyroid hormone. Such iodination of tyrosines and coupling of iodinated tyrosines takes place at the active site of the enzyme peroxidase (Nakamura & Ohtaki, 1990; Grodsky, 1983). For structural elucidation of the above thyroid hormone and the bio-synthetic processes induced in thyroglobulin by peroxidase, it is important to know the fine structure of the related compounds of the thyroid hormone. In this study, the crystal structure of 3-iodo-L-tyrosine, (I), has been determined. The crystal structure of 3,5-diiodo-L-tyrosine has been reported (Hamilton & Steinrauf, 1967).



(I)

The torsion angle C(1)—C(7)—C(8)—N(1), which has the greatest effect on the side-chain orientation, is 66.1 (5)°. This value is similar to one of the energy minima of the amino acid group: 60, 80 and −60° (Cody, 1980). The carboxyl and amino group are folded back towards the phenol ring, and the C(7)—C(8) bond is almost perpendicular to the phenol ring [C(6)—C(1)—C(7)—C(8) = −94.1 (6)°]. The molecules are held together by intermolecular hydrogen bonds: N(1)—H(1*A*)···O(4) ($\frac{1}{2}+x, \frac{3}{2}-y, -z$) 2.708 (6); N(1)—H(1*B*)···I(1) ($\frac{3}{2}-x, 2-y, -\frac{1}{2}+z$) 3.777 (5); N(1)—H(1*C*)···O(3) ($\frac{1}{2}+x, \frac{5}{2}-y, -z$) 2.801 (6); O(1)—H(1)···O(2) ($\frac{3}{2}-x, 2-y, -\frac{1}{2}+z$) 2.706 (5); O(4)—H(4)···O(3) ($-\frac{1}{2}+x, \frac{3}{2}-y, 1-z$) 2.726 (6) Å.

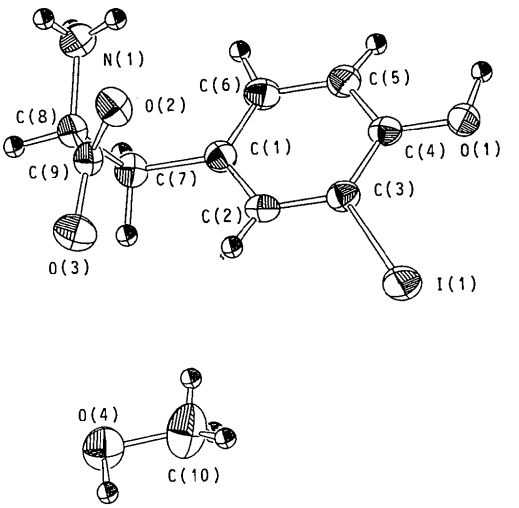


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound with the atomic numbering scheme. Ellipsoids for non-H atoms correspond to 50% probability. H atoms are shown as small circles of arbitrary radii.

Experimental

The title compound was crystallized from methanol solution. The crystal density D_m was measured by flotation in $CCl_4/C_2H_2Br_4$.

Crystal data

$C_9H_{10}INO_3.CH_4O$	Mo $K\alpha$ radiation
M_r = 339.13	λ = 0.71069 Å
Orthorhombic	Cell parameters from 25 reflections
$P2_12_12_1$	θ = 24.1–24.92°
a = 7.996 (3) Å	μ = 2.549 mm^{-1}
b = 20.077 (2) Å	T = 269 K
c = 7.733 (2) Å	Plate
V = 1241.3 (4) Å^3	0.40 × 0.10 × 0.10 mm
Z = 4	Colourless
D_x = 1.814 Mg m^{-3}	
D_m = 1.79 (2) Mg m^{-3}	

Data collection

Rigaku AFC-5*R* diffractometer	θ_{max} = 27.5°
$\omega/2\theta$ scans	$h = 0 \rightarrow 10$
Absorption correction: none	$k = 0 \rightarrow 25$
1678 measured reflections	$l = 0 \rightarrow 9$
1678 independent reflections	3 standard reflections monitored every 150 reflections
1470 observed reflections [$I > 2.0\sigma(I)$]	intensity decay: 2.4%

Refinement

Refinement on F	$(\Delta/\sigma)_{max}$ = 0.01
R = 0.027	$\Delta\rho_{max}$ = 0.73 e Å^{-3}
wR = 0.036	$\Delta\rho_{min}$ = −0.65 e Å^{-3}

$S = 1.49$
1470 reflections
145 parameters
H-atom parameters not refined
$w = 4F_o^2/\sigma^2(F_o^2)$

Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
I(1)	0.38538 (5)	0.98241 (2)	0.25723 (5)	3.49 (2)
O(1)	0.5386 (5)	0.9036 (2)	−0.0669 (5)	2.7 (2)
O(2)	0.9075 (5)	1.1609 (2)	0.1310 (5)	2.9 (2)
O(3)	0.6869 (5)	1.2254 (2)	0.1872 (5)	3.1 (2)
O(4)	0.3455 (6)	0.2508 (3)	0.5069 (6)	3.9 (2)
N(1)	0.9142 (5)	1.1873 (2)	−0.2040 (5)	2.6 (2)
C(1)	0.5853 (6)	1.1082 (3)	−0.1504 (6)	2.2 (2)
C(2)	0.5181 (6)	1.0826 (3)	0.0035 (6)	2.2 (2)
C(3)	0.5002 (6)	1.0150 (3)	0.0276 (6)	2.2 (2)
C(4)	0.5537 (6)	0.9696 (3)	−0.0970 (6)	2.2 (2)
C(5)	0.6169 (6)	0.9953 (2)	−0.2492 (8)	2.8 (2)
C(6)	0.6322 (6)	1.0642 (3)	−0.2766 (6)	2.6 (2)
C(7)	0.6036 (7)	1.1833 (3)	−0.1757 (6)	2.4 (2)
C(8)	0.7676 (6)	1.2130 (2)	−0.1043 (6)	2.1 (2)
C(9)	0.7899 (6)	1.1985 (2)	0.0889 (6)	2.1 (2)
C(10)	0.313 (1)	0.1826 (4)	0.4760 (9)	4.7 (3)

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

I(1)—C(3)	2.103 (5)	C(1)—C(7)	1.527 (7)
O(1)—C(4)	1.350 (6)	C(2)—C(3)	1.378 (7)
O(2)—C(9)	1.249 (6)	C(3)—C(4)	1.394 (7)
O(3)—C(9)	1.244 (6)	C(4)—C(5)	1.381 (7)
O(4)—C(10)	1.414 (9)	C(5)—C(6)	1.405 (7)
N(1)—C(8)	1.496 (7)	C(7)—C(8)	1.543 (7)
C(1)—C(2)	1.403 (7)	C(8)—C(9)	1.532 (7)
C(1)—C(6)	1.370 (7)		
C(2)—C(1)—C(6)	118.2 (5)	C(4)—C(5)—C(6)	121.9 (5)
C(2)—C(1)—C(7)	120.5 (5)	C(1)—C(6)—C(5)	120.3 (5)
C(6)—C(1)—C(7)	121.3 (4)	C(1)—C(7)—C(8)	114.7 (4)
C(1)—C(2)—C(3)	121.1 (5)	N(1)—C(8)—C(7)	110.3 (4)
I(1)—C(3)—C(2)	117.8 (4)	N(1)—C(8)—C(9)	110.2 (4)
I(1)—C(3)—C(4)	121.0 (4)	C(7)—C(8)—C(9)	112.0 (4)
C(2)—C(3)—C(4)	121.3 (5)	O(2)—C(9)—O(3)	127.0 (5)
O(1)—C(4)—C(3)	119.7 (5)	O(2)—C(9)—C(8)	117.2 (5)
O(1)—C(4)—C(5)	123.1 (4)	O(3)—C(9)—C(8)	115.8 (5)
C(3)—C(4)—C(5)	117.2 (5)		

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985) and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1168). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Beurskens, P. T. (1984). *DIRDIF. Direct Methods for Difference Structures – an Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors*. Technical Report 1984/1. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.
Cody, V. (1980). *Endocr. Rev.* **1**, 140–166.
Grodsky, G. M. (1983). *Harper's Review of Biochemistry*, 19th ed., pp. 486–493. Singapore: Marzen Asia.
Hamilton, J. A. & Steinrauf, L. K. (1967). *Acta Cryst.* **23**, 817–825.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Nakamura, M. & Ohtaki, S. (1990). *Protein Nucleic Acid Enzyme (Jpn)*, **35**, 814–824.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

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5-*tert*-Butyl-5-methyl-1,3,2-dioxathiane 2,2-Dioxide

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Abstract

The six-membered sulfate ring of the title compound, $C_8H_{16}O_4S$, has a chair form with the *tert*-butyl group in an equatorial position. Although most of the bond lengths and angles are as predicted, one C—C bond is considerably longer than the others. The structure determined confirms the interpretation of IR and NMR spectra.

Comment

The conformational analysis of cyclic sulfates using ^{13}C and ^{17}O NMR spectroscopy has been reported (Hellier & Liddy, 1988); all of these sulfates (which have five- and six-membered rings) have flexible conformations in solution, and ^1H NMR studies at ambient-to-low temperatures suggest that the barrier to pseudorotation or inversion is quite low. The title compound, (1), was studied initially by ^1H NMR spectroscopy (Hellier & Webb, 1977), which showed it to be exceptional