between N(7) and C(8) suggests predominantly double-bond character. O(10) is assigned as a carbonyl oxygen based on its bond length of 1·252 Å with C(2) and being capable of forming relatively strong intermolecular hydrogen bonds with one of the pair of water molecules. As shown in Fig. 2, the two water molecules are linked to each other and also to the neighboring pair of water molecules in the adjacent unit cell. Such a hydrogen-bond arrangement is only possible when *W*(2) shares its H atoms with *W*(1), since the latter shares its H atoms with the two symmetry-related carbonyl oxygen atoms. N(12) is presumably covalently bonded to two H atoms in order for it to be hydrogen bonded to N(7) and *W*(2) simultaneously. A double bond is designated between C(5) and C(6) owing to its bond length of 1·391 Å, which is almost equivalent to a benzene bond [1·395 (3) Å] (Sutton, 1965). The observed distance of 2·846 Å between N(3) and N(9) suggests that they are linked by a rather strong H-bond. As a result, (2*a*) and (3*a*) can be eliminated as possible tautomers. The structure (1*a*) appears to be the stable tautomer for 1-methylisoguanine dihydrate in the solid state.

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Structure and Conformation of L-Tyrosyl-L-tyrosine Dihydrate, $C_{18}H_{20}N_2O_5.2H_2O$

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Abstract. $M_r = 380·40$, orthorhombic, $C222_1$, $a = 12·118$ (2), $b = 12·800$ (2), $c = 24·523$ (3) Å, $V = 3803·8$ Å^3, $Z = 8$, $D_m = 1·34$, $D_x = 1·329$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 12·7$ cm^{-1}, $F(000) = 1616$, $T = 298$ K. Final $R = 0·037$ for 1568 independent observed reflections. The structure was solved using successively *MULTAN* and *DIRDIF* programs applied first to $C2$ space group, then extended to $C222_1$. The dipeptide exists in the crystal as a zwitterion and adopts a fully extended $\beta\beta$ conformation; χ_1 angles are close to −60 and 180° and χ_{2_1} to 60 and 120°, respectively, for the two residues. The crystallographic work was completed by a conformational analysis of the dipeptide using empirical calculations. Several stable conformations are found, the extended $\beta\beta$ being the most stable.

Introduction. The L-tyrosyl-L-tyrosine (L-Tyr-L-Tyr) dipeptide structure determination was undertaken in a general study of dipeptide structures with aromatic side chains. Unfortunately, we could not completely solve the structure, either by direct methods (*MULTAN*78, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), or through Patterson-function studies. We decided then to use our recent experience with *DIRDIF* (direct methods applied to difference structure factors,

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Beurskens *et al.*, 1982; Doesburg & Beurskens, 1983) to solve the structure.

Because of peptide flexibility, many conformations are possible for a given dipeptide. The crystal-structure conformation generally belongs to the preferred ones, but is not necessarily the most stable (Cotrait, Geoffre, Hospital & Précigoux, 1983). For this reason the crystallographic work was completed by conformational analysis using empirical calculations.

During the same time, the structure was solved independently by Subramanian, Lalitha & Bordner (1984, unpublished results) by direct methods, using *MULTAN*78, but as they emphasized, 'the structure solution presented considerable difficulties'. This paper makes some comparisons of the two sets of results.

Experimental. Title compound, supplied by Fluka, crystallized from methanol–water mixtures, 0·2 × 0·2 × 0·3 mm, D_m determined by flotation. Unit-cell dimensions determined by a least-squares procedure on 2θ values of 12 reflections with $\theta > 30°$, Cu $K\alpha$; intensity data collected on a Siemens four-circle diffractometer, in one octant of the Ewald sphere and $\sin\theta/\lambda \leq 0{\cdot}55$ Å^{-1} ($h \leq 13$, $k \leq 14$, $l \leq 27$) with an ω–2θ scan; 1568 independent reflections with $I > 3\sigma(I)$; reflections 080 and 0,0,22 monitored during data collection with fluctuations <1%; intensity data not corrected for absorption.

Attempts to solve the structure using the *MULTAN* procedure failed; only a fragment of the molecule (one third of all atoms) was found on the *E* map and no further improvement was possible. Only one tyrosyl side chain could be determined from the Patterson function. The model, obtained from the *MULTAN* map (10 atoms), was uses as input to the program *DIRDIF* for the application of direct methods to difference structure factors (Beurskens *et al.*, 1982). The orientation of the model was verified using the vector search program by Nordman & Schilling (1970). At first, *DIRDIF* led to chicken-wire patterns, showing the presence of a hexagonal frame in various fragments of the structure, in the same orientation. The structure was solved by the following steps:

–Expansion of the data to the triclinic space group $P1$.

–Application of *DIRDIF* in $P1$.

–Translation functions in *DIRDIF* ($P1$–Fourier space) (Doesburg & Beurskens, 1983), which only gave the position of the model with respect to the twofold axis along **a**.

–Expansion of the original data to monoclinic symmetry, space group $C2$, a axis unique.

–Successive application of *DIRDIF* in $C2$, carefully enlarging the model until the structure was solved.

–Finding the other symmetry elements and shifting the origin to the conventional position in space group $C222_1$.

The structure was refined by least squares using anisotropic parameters for C, N and O atoms, on a CII–Mini 6 computer. H atoms, except those of water molecules owing to their rather high thermal motion, were located from a difference Fourier synthesis. The refinement was resumed using isotropic temperature factors for the well positioned H atoms; $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 1$ when $|F_o| < p$ and $\sqrt{w} = p/F_o$ when $|F_o| > p$, where $p = [F_o^2(\max.)/10]^{1/2}$; $(\Delta/\sigma)_{\max} = 0{\cdot}3$; final ΔF excursions 0·3 and −0·2 e Å^{-3}; scattering factors from *International Tables for X-ray Crystallography* (1974); final $R = 0{\cdot}037$, $wR = 0{\cdot}043$, $S = 1{\cdot}025$; final $R = 0{\cdot}059$ in Subramanian's work for 1740 observed reflections, with $I > \sigma(I)$ and $\sin\theta/\lambda \leq 0{\cdot}59$ Å^{-1}.

Theoretical conformational analysis

The conformational analysis of the protected peptide Ac-Tyr-Tyr-MA (Ac: acetyl; MA: methylamide, *i.e.* acetamido) was performed through empirical calculations. The presence of Ac and MA groups prevents strong electrostatic interactions between charged groups, and allows us to simulate peptide fragments included in longer sequences. An approach combining the low-energy conformations for each residue has been used (Anderson & Scheraga, 1978).

All torsional angles (φ, ψ, χ_1 and χ_{2_1} for each residue), except ω_i, have been considered as variables. Molecular conformations have been generated and their energies calculated using the *ECEPP* program (*Quantum Chemistry Program Exchange,* 1976) with a dielectric constant $\varepsilon = 2$; energy minimizations were performed with the *SIMPLEX* program (Nelder & Mead, 1965).

Discussion. The final atomic parameters for C, N and O atoms are listed in Table 1.* Projection of the unit cell along x is shown in Fig. 1.

Bond lengths and angles of the dipeptide molecule are shown in Table 2. These values agree reasonably well with those found for other peptides having a tyrosyl residue (Stenkamp & Jensen, 1973; Cotrait, Barrans & Leroy, 1982), and especially well with Subramanian's L-tyrosyl-L-tyrosine structure: interatomic distances and angles do not differ by more than 0·016 Å and 2° respectively.

As expected, both phenol groups are planar; the H atoms of the phenolic OH groups deviate somewhat from these planes; also C_β atoms [here atoms C(3) and C(18)] deviate from the mean planes through the phenyl groups, as pointed out by Subramanian *et al.*; the carboxylic and peptide groups are perfectly planar.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and details of the hydrogen bonding have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39338 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The fact that the phenolic groups are nearly parallel is of no importance in our opinion because of the great distance between such groups, as has been emphasized by these authors.

Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters for the non-*H *atoms with e.s.d.'s in parentheses*

	x	y	z	B_{eq}*(Å^2)
N(1)	0·3676 (2)	0·3998 (2)	0·4369 (1)	2·4 (1)
C(2)	0·2824 (3)	0·4478 (2)	0·4010 (1)	2·4 (1)
C(3)	0·1682 (3)	0·4089 (2)	0·4174 (1)	3·3 (1)
C(4)	0·1531 (2)	0·2914 (2)	0·4139 (1)	2·8 (1)
C(5)	0·1614 (3)	0·2385 (3)	0·3651 (1)	3·2 (1)
C(6)	0·1408 (3)	0·1311 (3)	0·3621 (1)	3·1 (1)
C(7)	0·1109 (3)	0·0777 (2)	0·4087 (1)	2·8 (1)
O(8)	0·0852 (2)	−0·0274 (2)	0·4078 (1)	3·5 (1)
C(9)	0·1044 (3)	0·1292 (3)	0·4575 (1)	3·6 (2)
C(10)	0·1252 (3)	0·2357 (3)	0·4603 (1)	3·5 (2)
C(11)	0·2867 (2)	0·5660 (2)	0·4087 (1)	2·3 (1)
O(12)	0·3104 (2)	0·6042 (2)	0·4533 (1)	3·1 (1)
N(13)	0·2581 (2)	0·6215 (2)	0·3653 (1)	2·6 (1)
C(14)	0·2576 (3)	0·7360 (2)	0·3652 (1)	2·3 (1)
C(15)	0·1886 (3)	0·7759 (2)	0·3174 (1)	2·6 (1)
O(16)	0·1764 (2)	0·7194 (2)	0·2769 (1)	4·0 (1)
O(17)	0·1501 (2)	0·8676 (2)	0·3215 (1)	3·2 (1)
C(18)	0·3777 (3)	0·7738 (2)	0·3599 (1)	2·9 (1)
C(19)	0·3937 (2)	0·8901 (2)	0·3680 (1)	2·6 (1)
C(20)	0·4320 (3)	0·9527 (2)	0·3264 (1)	3·1 (1)
C(21)	0·4509 (3)	1·0589 (3)	0·3343 (1)	3·3 (1)
C(22)	0·4302 (3)	1·1024 (2)	0·3843 (1)	2·8 (1)
C(23)	0·3934 (3)	1·0414 (3)	0·4266 (1)	3·7 (2)
C(24)	0·3750 (3)	0·9359 (3)	0·4180 (1)	3·5 (2)
O(25)	0·4487 (2)	1·2075 (2)	0·3943 (1)	3·9 (1)
O(26)	0·4238 (2)	0·3242 (2)	0·3075 (1)	3·7 (1)
O(27)	0·2521 (3)	0·4966 (3)	0·2674 (1)	7·4 (2)

$$^* B_{eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s*

N(1)–C(2)	1·490 (4)	N(13)–C(14)	1·465 (4)
C(2)–C(3)	1·526 (4)	C(14)–C(15)	1·528 (4)
C(2)–C(11)	1·526 (4)	C(14)–C(18)	1·539 (4)
C(3)–C(4)	1·517 (4)	C(15)–O(16)	1·238 (4)
C(4)–C(5)	1·380 (5)	C(15)–O(17)	1·268 (4)
C(4)–C(10)	1·384 (5)	C(18)–C(19)	1·515 (4)
C(5)–C(6)	1·398 (5)	C(19)–C(20)	1·377 (4)
C(6)–C(7)	1·380 (5)	C(19)–C(24)	1·377 (4)
C(7)–C(8)	1·381 (4)	C(20)–C(21)	1·392 (5)
C(7)–C(9)	1·369 (5)	C(21)–C(22)	1·370 (5)
C(9)–C(10)	1·387 (5)	C(22)–O(25)	1·387 (4)
C(11)–O(12)	1·233 (4)	C(22)–C(23)	1·373 (5)
C(11)–N(13)	1·326 (4)	C(23)–C(24)	1·384 (5)

N(1)–C(2)–C(3)	109·7 (3)	N(13)–C(14)–C(15)	109·7 (3)
N(1)–C(2)–C(11)	108·2 (3)	N(13)–C(14)–C(18)	108·1 (3)
N(3)–C(2)–C(11)	108·8 (3)	C(15)–C(14)–C(18)	110·4 (4)
C(2)–C(3)–C(4)	114·6 (3)	C(14)–C(15)–O(16)	119·1 (3)
C(3)–C(4)–C(5)	121·9 (3)	C(14)–C(15)–O(17)	116·8 (3)
C(3)–C(4)–C(10)	119·6 (4)	O(16)–C(15)–O(17)	124·1 (3)
C(5)–C(4)–C(10)	118·5 (4)	C(14)–C(18)–C(19)	114·8 (4)
C(4)–C(5)–C(6)	121·0 (4)	C(18)–C(19)–C(20)	121·2 (4)
C(5)–C(6)–C(7)	119·4 (4)	C(18)–C(19)–C(24)	120·9 (4)
C(6)–C(7)–O(8)	122·0 (3)	C(20)–C(19)–C(24)	117·9 (4)
C(6)–C(7)–C(9)	120·0 (4)	C(19)–C(20)–C(21)	121·4 (5)
O(8)–C(7)–C(9)	118·1 (3)	C(20)–C(21)–C(22)	119·4 (5)
C(7)–C(9)–C(10)	120·4 (4)	C(21)–C(22)–C(23)	120·3 (5)
C(9)–C(10)–C(4)	120·7 (4)	C(21)–C(22)–O(25)	121·5 (4)
C(2)–C(11)–O(12)	120·8 (3)	C(23)–C(22)–O(25)	118·1 (4)
C(2)–C(11)–N(13)	115·0 (3)	C(22)–C(23)–C(24)	119·4 (5)
O(12)–C(11)–N(13)	124·2 (3)	C(23)–C(24)–C(19)	121·6 (5)
C(11)–N(13)–C(14)	122·5 (3)		

The *SNOOPY* drawing (Davies, 1983) of the molecule is shown in Fig. 2(*a*).

The torsion angles of the molecules, as shown in Fig. 2(*b*), are given in accordance with the IUPAC–IUB Commission of Biochemical Nomenclature (1970) as follows: tyrosyl: ψ[N(1)–C(2)–C(11)–N(13)] = 150·0, χ_1[N(1)–C(2)–C(3)–C(4)] = −59·7, χ_{2_1}[C(2)–C(3)–C(4)–C(10)] = −62·6, ω[C(2)–C(11)–N(13)–C(14)] = 180·1, τ[C(6)–C(7)–O(8)–H(108)] = 15·1°; tyrosine: φ[C(11)–N(13)–C(14)–C(15)] = −162·4, ψ[N(13)–C(14)–C(15)–O(17)] = 157·4, χ_1[N(13)–C(14)–C(18)–C(19)] = −170·9, χ_{2_1}[C(14)–C(18)–C(19)–C(24)] = 66·4, τ[C(21)–C(22)–O(25)–H(125)] = 24·3°. These values agree quite well with those given by Subramanian *et al.* The dipeptide main-chain conformation can be described as fully extended ($\beta\beta$ type); the side chains, defined by χ_1 and χ_{2_1} angles, have classical conformations:

−χ_1 values are close to two out of the three usual values: −60, 60 and 180°.

−χ_{2_1} values lie within the range 90 ± 30° (Cotrait & Bideau, 1974; Benedetti, Morelli, Nemethy & Scheraga, 1983).

The structure shows numerous hydrogen bonds, involving NH_3^+ and COO^- charged groups, NH, phenolic OH and C=O polar groups and both water molecules; these intermolecular bonds are listed in Table 3.* Water molecules form hydrogen bridges, namely between NH_3^+ and COO^- groups, which, surprisingly, are not facing each other. Each carboxylate O atom is engaged in two hydrogen bonds; the phenolic OH groups are involved in rather strong hydrogen bonds, as underlined by Subramanian *et al.*

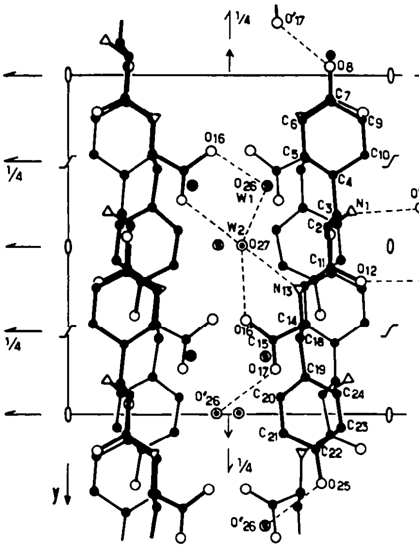

Fig. 1. Projection of the unit cell along x.

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* Deposited.

Such a complicated hydrogen-bond network has been found in zwitterionic peptide structures such as Tyr-Pro-Asn-Gly (Précigoux, Geoffre, Hospital & Leroy, 1982). In such structures, molecular conformation might be influenced a great deal by the environment. This is the reason we have undertaken the conformational study of the isolated Ac-Tyr-Tyr-MA dipeptide.

Conformational calculations

Starting conformations have been generated by combining the preferred conformations* related to an isolated tyrosyl residue (Lewis, Momany & Scheraga, 1973); the minimization of the energy takes place by optimization of torsion angles. Finally about two thirds of the 49 starting conformations are stable.*

Because polypeptide folding essentially depends on the main-chain conformation of its constitutive residues, forms differing only by one or more of their side-chain conformations (χ_1 and χ_{2_1} angles in the present case) have been considered as degenerate. The denominations used for standard residue main-chain conformations are as follows: β for stretched structure ($\varphi \sim -150$, $\psi \sim 150°$), β' for ($\varphi \sim -70$, $\psi \sim 150°$), α for the right-handed helix ($\varphi \sim -70$, $\psi \sim -50°$), γ for the C_7^{eq} form ($\varphi \sim -80$, $\psi \sim 80°$). The list of the most stable conformations, with the corresponding torsional angles and relative energy ΔE, is given in Table 4. The most stable form ($\Delta E = 0{\cdot}0$ kJ mol^{-1}) is a $\beta\beta$ fully stretched conformation, in complete agreement with the crystal structure but it must be kept in mind that many other conformations are possible within the 12·0 kJ mol^{-1} range.

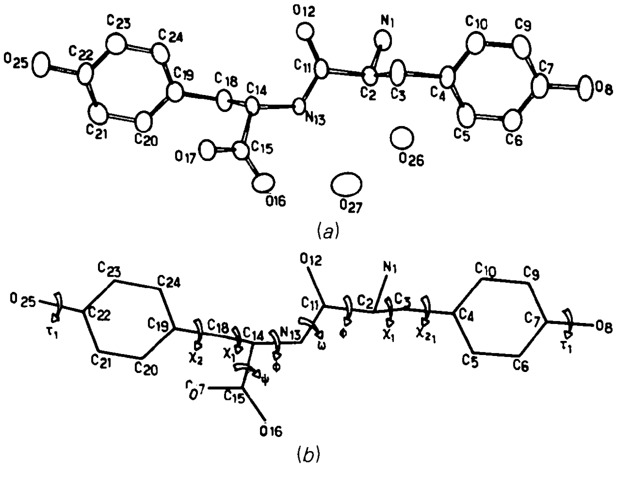

Fig. 2. (*a*) *SNOOPY* drawing and (*b*) torsion-angle notations of the dipeptide.

Table 4. *Non-degenerate stable conformations* ($\Delta E <$ 12·0 kJ mol^{-1}) *for Ac-Tyr-Tyr-MA*

Torsion angles are in °, $\bar{\sigma} = 1{\cdot}2°$.

		Tyr$_1$				Tyr$_2$				
No.	Type	φ	ψ	χ_1	χ_{2_1}	φ	ψ	χ_1	χ_{2_1}	ΔE (kJ mol^{-1})
(1)	$\beta\beta$	−158	152	178	78	−145	152	−60	100	0·0
(2)	$\beta'\beta$	−89	141	182	78	−146	148	−62	105	0·8
(3)	$\beta\gamma$	−155	149	176	75	−85	84	−61	108	2·5
(4)	$\beta\beta'$	−154	145	181	69	−79	136	183	84	4·6
(5)	$\alpha\gamma$	−68	−40	179	79	−88	76	−61	105	5·9
(6)	$\gamma\beta$	−86	82	−63	110	−145	149	−61	106	6·3
(7)	$\gamma\gamma$	−85	79	−61	109	−89	78	−57	112	7·5
(8)	$\alpha\beta$	−71	−40	177	72	−154	144	176	76	8·4
(9)	$\alpha\alpha$	−66	−41	174	72	−85	−36	−63	107	9·2
(10)	$\gamma\alpha$	−84	71	−59	107	−80	−40	−57	114	10·0
(11)	$\beta\alpha$	−153	147	60	94	−77	−41	182	80	11·7

The molecule exists in the crystal in its zwitterionic form and adopts a $\beta\beta$ stretched conformation; χ_1 angles are close to −60 to 180°, χ_{2_1} angles to −60 and 60°, respectively, for the first and second residues. The crystal cohesion results from numerous intermolecular hydrogen bonds involving water molecules as bridges.

The crystallographic results are in agreement with those obtained by Subramanian *et al.*

The conformational analysis study using empirical calculations shows that many conformations coexist in a rather limited energy range. Nevertheless the $\beta\beta$ stretched structure appears to be the most stable one.

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* Within a 12·0 kJ mol^{-1} range from the most stable conformation.

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rel-(1*S*,3a*R*,4*R*,7*S*,7a*R*)-5,6,7,7a-Tetrahydro-4,7-methano-1*H*-indene-1,3a(4*H*)-diol, $C_{10}H_{14}O_2$

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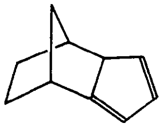
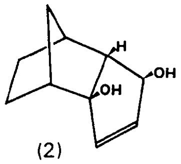
Abstract. $M_r = 166\cdot22$, monoclinic, $P2_1/c$, $a = 13\cdot657\,(3)$, $b = 6\cdot212\,(2)$, $c = 11\cdot069\,(3)$ Å, $\beta = 112\cdot42\,(3)°$, $V = 868\cdot0\,(4)$ Å^3, $Z = 4$, $D_x = 1\cdot272$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1\cdot54178$ Å, $\mu = 7\cdot09$ cm^{-1}, $F(000) = 360$, room temperature, $R = 0\cdot043$ for 1056 unique reflections with intensities greater than $3\sigma(I)$. A planar cyclopentene ring is *cis* fused to a norbornane moiety. The two hydroxyl groups lie on the same side of the five-membered ring and participate in the formation of two intermolecular hydrogen bonds. π-system distortion and a short C=C distance are observed as in other strained ring systems.

Introduction. The three isomers of isodicyclopentadiene and their cycloaddition reactions have been studied (Subramanyam, Bartlett, Iglesias, Watson & Galloy, 1982; Paquette, Williams, Carr, Charumilind & Blount, 1982; Bartlett & Wu, 1983). The diene isomer (1) rapidly absorbs oxygen from the air even at low temperatures (253 K). When molecular oxygen is bubbled into a dilute solution of (1) in CH_2Cl_2 at 273 K and in the dark, a low-molecular-weight copolymer of (1) and O_2 is obtained (Wu, 1983). The polyperoxide, $(C_{10}H_{12}O_2)_n$, has a (1) to O_2 ratio of 1:1, a measured molecular weight of 1220 ($n = 7\cdot4$), and is stable up to 405 K where it decomposes with gas evolution.

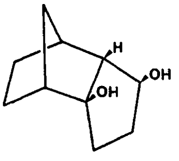
When the polymer is reduced with $LiAlH_4$ in ether, a mixture of the diols (2) and (3) is obtained. Because an unambiguous determination of relative stereochemistry is essential for the understanding of stereoelectronic effects in these molecules, the structure was determined by X-ray diffraction techniques. The structural data are needed also for the development of suitable molecular mechanics parameters for norbornene and sesquinorbornene strained ring systems.



(1)



(2)



(3)

Experimental. Crystal of dimensions 0·4 × 0·33 × 0·25 mm, Syntex $P2_1$ diffractometer, $\theta{:}2\theta$ scan, variable scan rate, $2\theta_{\max} = 120°$, graphite-monochromated Cu $K\alpha$ radiation; lattice parameters from least squares of 15 medium-angle reflections, space group $P2_1/c$ (systematic absences $l = 2n+1$ for $h0l$ and $k = 2n+1$ for $0k0$); a monitored reflection showed no significant change in intensity; 1188 independent reflections ($0 \le h \le 14$, $0 \le k \le 6$, $-11 \le l \le 11$), 1056 with $I > 3\sigma(I)$; Lorentz and polarization, no absorption corrections; direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) located all heavy atoms, H atoms located in difference Fourier map but only positional parameters refined; $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F_o)$, final $R = 0\cdot043$, $R_w = 0\cdot063$, $S = 0\cdot23$ (186 parameters), $(\Delta/\sigma)_{\rm av} = 0\cdot02$, $(\Delta/\sigma)_{\max} = 0\cdot09$, highest peak in final difference Fourier map $0\cdot24$ e Å^{-3}. Final calculations performed with *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Atomic scattering factors for C and O from Cromer & Mann (1968), those for H from Stewart, Davidson & Simpson (1965). Atomic positional parameters and $U_{\rm eq}$ values are listed in Table 1 while Table 2 gives bond lengths and valence angles.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39393 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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