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Structures of (1*R**,2*R**,3a*S**,5*S**,6*S**,7a*S**)- and (±)-(1*R**,2*S**,3a*S**,5*R**,6*S**,7a*S**)-Perhydro-1,2,5,6-indenetetrol, (I) and (II), $C_9H_{16}O_4$

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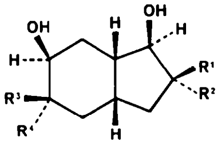
Abstract. (I): $M_r = 188{\cdot}2$, monoclinic, $P2_1$, $a = 6{\cdot}989\,(1)$, $b = 13{\cdot}107\,(2)$, $c = 5{\cdot}293\,(1)$ Å, $\beta = 100{\cdot}41\,(1)°$, $V = 476{\cdot}9\,(1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}31$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 0{\cdot}98$ mm^{-1}, $F(000) = 204$, $T = 295$ K, $R = 0{\cdot}031$ based on 853 reflections. (II): $M_r = 188{\cdot}2$, orthorhombic, $Pna2_1$, $a = 12{\cdot}254\,(1)$, $b = 5{\cdot}177\,(1)$, $c = 14{\cdot}275\,(1)$ Å, $V = 905{\cdot}6\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}38$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 1{\cdot}03$ mm^{-1}, $F(000) = 408$, $T = 295$ K, $R = 0{\cdot}025$ based on 779 reflections. Resolution of the racemic modification of (I) was spontaneously achieved by recrystallization from an ethanol solution. All the hydroxyl groups form intermolecular hydrogen bonds, but not intramolecular ones.

Introduction. Hydroxylation of (±)-(3a*S**,7a*S**)-3a,4,7,7a-tetrahydroindene with hydrogen peroxide and formic acid gives a *trans* tetrol (I) identified on the basis of ^{1}H- and ^{13}C-NMR spectral evidence (Matoba, Yamashita, Ogawa, Ishii & Ogawa, 1984). On the other hand, catalytic hydroxylation by OsO_4 with *N*-methylmorpholine *N*-oxide yields a *cis* tetrol (II) (Matoba, Ohnishi, Kagohashi, Ishii & Ogawa, 1983).



	R¹	R²	R³	R⁴
(I)	H	OH	H	OH
(II)	OH	H	OH	H

Four enantiomeric pairs of the diastereomers for each tetrol might be obtainable, but one of the pairs was exclusively isolated from the products of the respective hydroxylations. Thus, the structure determination of (I) and (II) was undertaken in order to elucidate their structures, and thereby establish the stereochemistry and the mechanism of the hydroxylations.

Crystals of (I) and (II) were obtained from solutions of the respective racemic modifications. In the case of (I), however, spontaneous resolution occurs.

Experimental. Columnar crystals of (I) (m.p. 470–471 K) and (II) (421–422 K) obtained from ethanol solutions, approximate dimensions $0{\cdot}3 \times 0{\cdot}3 \times 0{\cdot}3$ mm (I) and $0{\cdot}3 \times 0{\cdot}2 \times 0{\cdot}2$ mm (II); Rigaku AFC-5UD diffractometer, graphite monochromator; cell parameters determined by least squares from 2θ values for 20 reflections ($35 \le 2\theta \le 45°$); no corrections for absorption; $\sin\theta_{\max}/\lambda = 0{\cdot}6095$ Å^{-1}; $-8 \le h \le 8$, $0 \le k \le 15$, $0 \le l \le 6$ (I); $0 \le h \le 14$, $0 \le k \le 6$, $0 \le l \le 17$ (II); 3 reference reflections monitored every 100 reflections showed no significant variation; 934 (I) and 865 (II) unique reflections measured, 4 (I) and 9 (II) reflections unobserved [$I < \sigma(I)$]; structures solved using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); $\sum(w|\Delta F|^2)$ minimized in least-squares refinement; H atoms located on difference electron density map; positional parameters for all atoms and anisotropic thermal parameters for non-H atoms refined by block-diagonal least squares, temperature factor of H equal to $B_{\rm eq}$ of non-H atom attached; $R = 0{\cdot}031$ (I) (for 853 reflections with $w \ne 0$) and $0{\cdot}025$ (779), $wR = 0{\cdot}044$ (I) and $0{\cdot}034$ (II), $S = 1{\cdot}26$ (I) and $1{\cdot}20$ (II); $w = 1/\sigma^2(F_o)$ for observed reflections with $|F_c| \ge \sigma(F_o)$ and $|\Delta F| < 3\sigma(F_o)$, $w = 0$ otherwise, $\sigma(F_o) = [\sigma_1^2(F_o) + c^2|F_o|^2]^{1/2}$, $\sigma_1(F_o)$ due to counting errors, $c^2 = 0{\cdot}00138$ (I) and $0{\cdot}00081$ (II); final $\Delta < 0{\cdot}5\sigma$; max. $\Delta\rho$ excursions in final difference map $0{\cdot}2$ e Å^{-3}; atomic scattering factors calculated by $\sum[a_i\exp(-b_i\lambda^{-2}\sin^2\theta)] + c$ $(i = 1-4)$ (*International Tables for X-ray Crystallography*, 1974); calculation carried out on a FACOM M-150F computer at Shionogi Research Laboratories.†

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† Lists of anisotropic thermal parameters, structure factors, torsion angles necessary to describe the ring conformations and positional parameters of H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39100 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates* ($\times 10^4$) *and isotropic temperature factors* ($\text{Å}^2 \times 10^2$) *with e.s.d.'s in parentheses*

$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
(I)				
C(1)	6652 (2)	3202 (2)	7936 (3)	223 (3)
C(2)	8615 (2)	3757 (2)	8216 (3)	278 (3)
C(3)	10182 (2)	2966 (2)	9225 (4)	332 (4)
C(3a)	9111 (2)	1952	9523 (2)	227 (3)
C(4)	9016 (2)	1259 (2)	7172 (3)	245 (3)
C(5)	7579 (2)	382 (2)	7184 (3)	258 (3)
C(6)	5539 (2)	793 (2)	7161 (2)	226 (3)
C(7)	5514 (2)	1469 (2)	9511 (3)	241 (3)
C(7a)	7056 (2)	2311 (2)	9817 (2)	216 (3)
O(10)	5125 (2)	3823 (2)	8542 (2)	285 (3)
O(11)	8952 (2)	4137 (2)	5800 (3)	583 (5)
O(12)	7530 (2)	−255 (2)	4983 (2)	381 (3)
O(13)	4173 (2)	−19 (2)	7100 (2)	315 (3)
(II)				
C(1)	2857 (1)	1361 (3)	6909 (1)	234 (3)
C(2)	4032 (1)	2041 (3)	7242 (1)	261 (3)
C(3)	4747 (1)	−172 (4)	6883	294 (3)
C(3a)	4235 (1)	−843 (3)	5936 (1)	228 (3)
C(4)	4569 (1)	1044 (3)	5166 (1)	271 (3)
C(5)	3823 (1)	891 (3)	4309 (1)	267 (3)
C(6)	2659 (1)	1492 (3)	4613 (1)	256 (3)
C(7)	2242 (1)	−521 (3)	5310 (1)	254 (3)
C(7a)	2993 (1)	−760 (3)	6164 (1)	218 (3)
O(10)	2194 (1)	323 (3)	7646 (1)	336 (3)
O(11)	4133 (1)	2289 (3)	8232 (1)	364 (3)
O(12)	3842 (1)	−1645 (3)	3906 (1)	316 (3)
O(13)	1925 (1)	1519 (3)	3830 (1)	344 (3)

Table 2. *Bond lengths* (Å) *with e.s.d.'s in parentheses*

	(I)	(II)		(I)	(II)
C(1)—C(2)	1·536 (4)	1·557 (2)	C(3a)—C(7a)	1·546 (3)	1·557 (2)
C(1)—C(7a)	1·527 (4)	1·538 (2)	C(4)—C(5)	1·527 (4)	1·529 (2)
C(1)—O(10)	1·424 (4)	1·434 (2)	C(5)—C(6)	1·522 (4)	1·523 (2)
C(2)—C(3)	1·532 (4)	1·531 (3)	C(5)—O(12)	1·429 (4)	1·434 (2)
C(2)—O(11)	1·431 (4)	1·424 (2)	C(6)—C(7)	1·530 (4)	1·529 (2)
C(3)—C(3a)	1·547 (3)	1·530 (3)	C(6)—O(13)	1·426 (4)	1·435 (2)
C(3a)—C(4)	1·532 (3)	1·526 (2)	C(7)—C(7a)	1·531 (4)	1·532 (2)

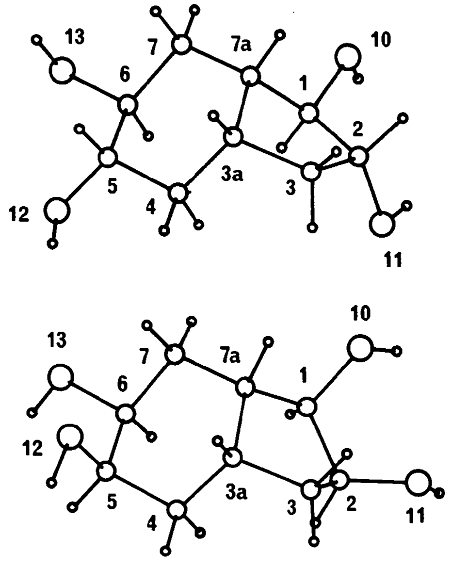

Fig. 1. Perspective views of the molecules of (I) (upper) and (II) (lower).

Table 3. *Bond angles* (°) *with e.s.d.'s in parentheses*

	(I)	(II)
C(2)—C(1)—C(7a)	104·0 (2)	105·8 (1)
C(2)—C(1)—O(10)	113·6 (2)	112·6 (1)
C(7a)—C(1)—O(10)	110·4 (2)	107·5 (1)
C(1)—C(2)—C(3)	106·4 (2)	104·9 (1)
C(1)—C(2)—O(11)	111·5 (2)	113·8 (1)
C(3)—C(2)—O(11)	108·9 (2)	110·5 (1)
C(2)—C(3)—C(3a)	106·8 (2)	103·4 (1)
C(3)—C(3a)—C(4)	112·2 (2)	112·4 (1)
C(3)—C(3a)—C(7a)	103·0 (2)	102·1 (1)
C(4)—C(3a)—C(7a)	110·9 (2)	113·3 (1)
C(3a)—C(4)—C(5)	112·0 (2)	112·5 (1)
C(4)—C(5)—C(6)	110·4 (2)	108·7 (1)
C(4)—C(5)—O(12)	110·8 (2)	111·0 (1)
C(6)—C(5)—O(12)	108·4 (2)	108·5 (1)
C(5)—C(6)—C(7)	110·3 (2)	111·1 (1)
C(5)—C(6)—O(13)	111·0 (2)	111·5 (1)
C(7)—C(6)—O(13)	110·2 (2)	107·7 (1)
C(6)—C(7)—C(7a)	113·1 (2)	111·8 (1)
C(1)—C(7a)—C(3a)	103·5 (2)	105·7 (1)
C(1)—C(7a)—C(7)	116·0 (2)	115·3 (1)
C(3a)—C(7a)—C(7)	114·8 (2)	115·0 (1)

Table 4. *Intermolecular hydrogen bonds* (Å)

(I)		
Equivalent positions	O(10)—H···O(12$^{\text{i}}$)	2·671 (4)
(i) $1-x, \frac{1}{2}+y, 1-z$	O(10)···H—O(13$^{\text{ii}}$)*	2·731 (4)
(ii) $1-x, \frac{1}{2}+y, 2-z$	O(11)···H—O(12$^{\text{iii}}$)*	2·687 (4)
(iii) $2-x, \frac{1}{2}+y, 1-z$	O(11)—H···O(13$^{\text{i}}$)	2·672 (4)
(II)		
Equivalent positions	O(10)—H···O(12$^{\text{i}}$)†	2·704 (2)
(i) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$	O(10)···H—O(13$^{\text{ii}}$)†	2·811 (2)
(ii) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}+z$	O(11)···H—O(12$^{\text{iii}}$)	2·682 (2)
(iii) $1-x, -y, \frac{1}{2}+z$	O(11)—H···O(13$^{\text{i}}$)†	2·684 (2)

* Formed in the layer parallel to the (101) plane.
† Formed in the layer parallel to the (100) plane.

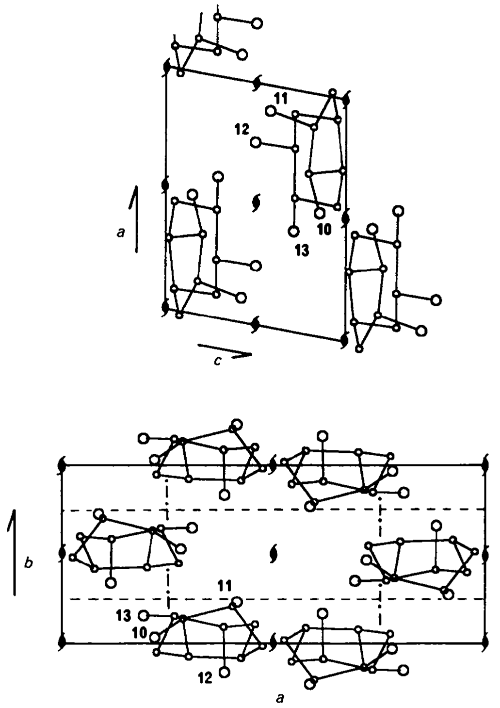

Fig. 2. Crystal structures of (I) (upper) and (II) (lower).

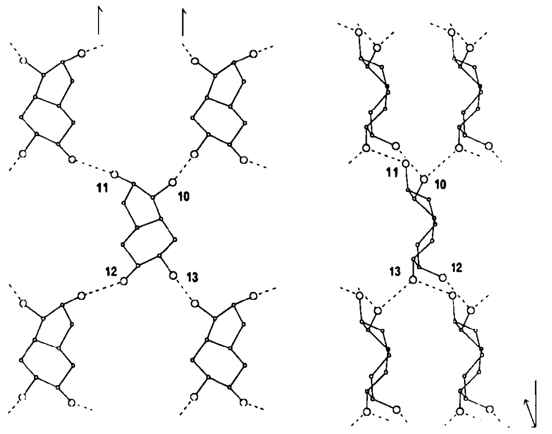

Fig. 3. Molecular arrangements in the layers in (I) (left) and (II) (right). Broken lines indicate intermolecular hydrogen bonds formed in the layer.

Discussion. Atomic coordinates and equivalent isotropic temperature factors are listed in Table 1. Perspective views of (I) and (II) with atom-numbering schemes are shown in Fig. 1. The relative configuration is $1R^*,2R^*,3aS^*,5S^*,6S^*,7aS^*$ for (I), and $1R^*,2S^*,3aS^*,5R^*,6S^*,7aS^*$ for (II). The cyclohexane rings are in a slightly distorted chair form. The cyclopentane ring of (I) adopts the envelope form, while that of (II) adopts the half-chair form. The hydroxyl groups of O(12) and O(13) in (I) occupy the equatorial positions, and those in (II) individually occupy the axial and equatorial positions. Bond lengths and angles respectively are given in Tables 2 and 3.

Crystal structures are shown in Fig. 2. The structures of (I) and (II) may be described as consisting of layers parallel to the (101) and (100) planes, respectively. The molecules lying in each layer of (I) and (II) are similarly arranged as seen in Fig. 3. The hydroxyl groups in (I) participate individually in two hydrogen bonds, one being formed in the layer and another formed between the layers (Table 4). In (II), the O(11)H and O(12)H groups form two hydrogen bonds as in (I), but the O(10)H and O(13)H groups form bonds within the layer. The symmetry elements lying between the layers are 2_1 axes for both the crystals. Those in the layer are 2_1 axes for (I) and *n*-glide plane for (II). Thus, the hydrogen-bonding network in the layer of (I) can be formed by the pure enantiomers.

Kuhn (1952) revealed by an IR spectral study that the hydroxyl groups of *cis*-cyclopentane-1,2-diol, *cis*-cyclohexane-1,2-diol and *trans*-cyclohexane-1,2-diol (only when both hydroxyl groups occupy the equatorial positions) form intramolecular hydrogen bonds in CCl_4 solutions. However, such intramolecular hydrogen bonds are not formed in the crystals of (I) and (II).

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Détermination Structurale à 213 K du Monomère Bis(phénylcarbamate) de Hexadiyne-2,4 Diyle-1,6, $C_{20}H_{16}N_2O_4$

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Abstract. $M_r = 348{\cdot}4$, monoclinic, $C2/c$, $a = 23{\cdot}54$ (2), $b = 7{\cdot}753$ (6), $c = 18{\cdot}66$ (1) Å, $\beta = 94{\cdot}48$ (4)°, $V = 3395$ (7) Å^3, $Z = 8$, $D_x = 1{\cdot}36$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 0{\cdot}80$ mm^{-1}, $F(000) = 1456$, $T = 213$ K, $R = 0{\cdot}077$ for 1513 *hkl* with $F_o \geq \sigma(F_o)$. The neighbouring diacetylene vectors are not all parallel but half the molecules cross at an angle of 35 (4)°. These molecules form, in the cell, parallel ribbons in which H bonds maintain intermolecular cohesion. The title compound is moderately active; the polymerizability criteria are discussed.

Introduction. Dans le cadre de l'étude de composés diacétyléniques R—C≡C—C≡C—R polymérisables à

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