Data collection

Siemens *R3m/V* diffractometer	$\theta_{max} = 22.5°$
	$h = 0 \rightarrow 9$
$\omega/2\theta$ scans	$k = 0 \rightarrow 11$
Absorption correction: none	$l = 0 \rightarrow 16$
	2 standard reflections
1187 measured reflections	monitored every 98
1169 independent reflections	reflections
968 observed reflections	intensity decay: $\leq 1\%$
$[I > 3\sigma(I)]$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} < 0.001$
$R = 0.039$	$\Delta\rho_{max} = 0.12$ e Å^{-3}
$wR = 0.045$	$\Delta\rho_{min} = -0.15$ e Å^{-3}
$S = 0.884$	Extinction correction: none
968 reflections	Atomic scattering factors
190 parameters	from *SHELXTL-Plus*
$w = 1/[\sigma^2(F) + 0.0029F^2]$	(Sheldrick, 1990)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.1243 (4)	0.3408 (3)	0.9304 (2)	0.060 (1)
O2	0.3264 (5)	0.2471 (3)	0.8864 (2)	0.091 (1)
O3	−0.0349 (4)	0.4661 (3)	0.9967 (2)	0.071 (1)
O4	−0.1278 (4)	0.7074 (4)	1.2510 (3)	0.099 (2)
C1	0.2646 (6)	0.3049 (4)	0.9427 (3)	0.057 (2)
C2	0.3208 (5)	0.3481 (4)	1.0303 (3)	0.046 (1)
C3	0.4462 (4)	0.4424 (4)	1.0201 (3)	0.049 (1)
C4	0.4958 (5)	0.4769 (4)	1.1129 (3)	0.053 (1)
C5	0.3719 (4)	0.5398 (4)	1.1654 (3)	0.042 (1)
C6	0.2315 (4)	0.5479 (3)	1.1046 (2)	0.038 (1)
C7	0.1918 (4)	0.4132 (3)	1.0729 (2)	0.039 (1)
C8	0.0801 (5)	0.4143 (4)	1.0011 (3)	0.048 (1)
C9	0.2807 (4)	0.6141 (3)	1.0197 (2)	0.040 (1)
C10	0.3858 (5)	0.5585 (4)	0.9774 (3)	0.047 (1)
C11	0.1000 (4)	0.6109 (4)	1.1503 (3)	0.046 (1)
C12	0.0009 (5)	0.5282 (4)	1.2048 (3)	0.053 (1)
C13	−0.1124 (5)	0.5940 (5)	1.2550 (3)	0.051 (1)
C14	−0.2110 (5)	0.5160 (5)	1.3100 (3)	0.068 (2)
C15	0.4193 (5)	0.6706 (4)	1.1928 (3)	0.055 (1)
C16	0.3445 (5)	0.4635 (4)	1.2511 (2)	0.054 (1)
C17	0.2136 (6)	0.7344 (4)	0.9887 (3)	0.061 (1)

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

C2—C3	1.548 (6)	C2—C7	1.526 (6)
C3—C4	1.529 (6)	C3—C10	1.514 (6)
C4—C5	1.552 (6)	C5—C6	1.596 (6)
C6—C7	1.571 (5)	C6—C9	1.544 (5)
C9—C10	1.310 (6)		
C3—C2—C7	109.0 (3)	C2—C3—C10	107.9 (3)
C2—C3—C4	106.9 (3)	C4—C3—C10	107.8 (3)
C3—C4—C5	111.1 (3)	C4—C5—C6	108.9 (3)
C5—C6—C9	105.8 (3)	C5—C6—C7	108.5 (3)
C7—C6—C9	103.7 (3)	C2—C7—C6	111.8 (3)
C6—C9—C10	114.7 (3)	C3—C10—C9	116.1 (4)

H atoms were located from difference Fourier maps; they were positioned geometrically and included as riding atoms with fixed isotropic temperature factors in the structure-factor calculations.

Data collection: *Siemens P3 Diffractometer Program* (Siemens, 1989). Cell refinement: *Siemens P3 Diffractometer Program*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990). Structure solution: *SHELXTL-Plus*. Structure refine-

ment: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Preparation of materials for publication: *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: VJ1007). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structural Studies of Intermediates in the Synthesis of Mifepristone (RU 486). II. Structure of a β-Epoxy Steroid

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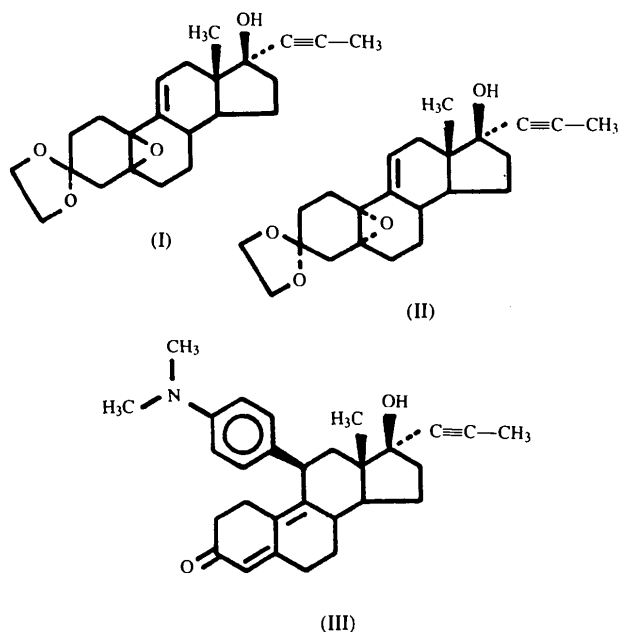*Bio-Organic Laboratory, Indian Institute of Chemical Technology, Hyderabad 500 007, India*

Abstract

Structure determination of the title compound, 5β,10-β-epoxy-3,3-ethylenedioxy-17β-hydroxy-17α-(1-propynyl)estra-9(11)-ene, $C_{23}H_{30}O_4$, establishes the configuration of the epoxy O atom as 5β,10β and locates the position of the double bond between C(9) and C(11). The strain caused by the presence of an epoxy O atom between C(5) and C(10) in the molecule is reflected in the distortion of bond angles around several tetrahedral

C atoms. The propynyl group is oriented perpendicular to the steroid skeleton. The molecules are hydrogen-bonded head-to-tail through hydroxyl groups.

Comment

The title $5\beta,10\beta$-epoxy steroid (I) is the stereoisomer of the key intermediate $5\alpha,10\alpha$-epoxy steroid (II) in the synthesis of mifepristone (RU 486) (III), the first steroidal antiprogesterone drug for non-surgical abortion in clinical use (Ulmann & Dubois, 1989; Heikinheimo, Ylikorkala & Lahteenmaki, 1990).

(I)

(II)

(III)

The antagonistic activity of RU 486 is due to the 11β-(dimethylamino)phenyl substitution (Benhamou et al., 1992). The most convenient method for introducing a substituent into the 11β-position of a 19-nor-steroid is the epoxidation of 5(10),9(11)-estradienes (Gasc & Nedelec, 1971), which mainly yields the desired $5\alpha,10\alpha$-epoxide along with a small amount of a mixture of $5\beta,10\beta$- and $9\alpha,11\alpha$-epoxide isomers. Recrystallization from methanol resulted in diffraction-quality crystals of the title compound.

Our X-ray analysis unequivocally establishes the molecular structure and the relative stereochemistry of the epoxy O atom as $5\beta,10\beta$, and locates the double bond between C(9) and C(11). A drawing of the molecule with the atomic numbering scheme is shown in Fig. 1. Bond lengths, bond angles and torsion angles of the non-H atoms are within the range of expected values (Griffin, Duax & Weeks, 1984). The strain caused by the presence of an epoxy O atom between C(5) and C(10) in the molecule is reflected in the distortion of bond angles around several tetra-

hedral C atoms involving C(5) and C(10). The interior angle C(17)—C(13)—C(14) [101.0 (4)°] of ring D is significantly smaller than the other endocyclic valency angles. Ring A adopts a 2β-sofa conformation [asymmetry parameter (Duax & Norton, 1975) $\Delta C_S[C(2)] = 11.67°$]. Ring B also adopts an 8β-sofa conformation [$\Delta C_S[C(8)] = 11.58°$]. Ring C has a $13\beta,14\alpha$-half-chair conformation [$\Delta C_2[C(13)—C(14)] = 7.97°$]. The five-membered ring D assumes the commonly found 13β-envelope conformation [$\Delta C_S[C(13)] = 3.03°$]. Both the C(18) methyl group and the O(4) hydroxyl group are prominently β-oriented. The perpendicular orientation of the propynyl group [defined by the torsion angle C(15)—C(16)—C(17)—C(19) of 94.6 (5)°] is similar to that in RU 486 [−93.8 (4)°; van Geerestein, Kanters, van der Sluis & Kroon, 1986] and that in ORG 761 [−103.3 (5)°; van Geerestein, Kanters & Kroon, 1987].

The packing of the molecules is shown in Fig. 2. Molecules are hydrogen-bonded head-to-tail through H[O(4)] and a screw-related $(-x + 1, y + 1/2, -z + 1)$ O(3) atom {O(4)···O(3) 2.910 (7), H[O(4)]··· O(3) 2.060 (7) Å and O(4)—H[O(4)]···O(3) 176.9 (6)°}.
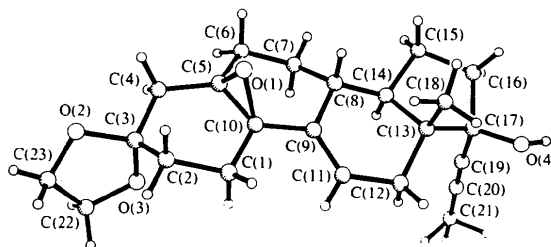
Fig. 1. Perspective view of the title molecule showing the labelling of the non-H atoms.

Fig. 2. Molecular packing in the unit cell viewed down the [100] axis.

Experimental

Crystal data

$C_{23}H_{30}O_4$
$M_r = 370.5$
Monoclinic
$P2_1$
$a = 8.877$ (2) Å
$b = 12.179$ (3) Å
$c = 9.734$ (2) Å
$\beta = 106.11$ (2)°
$V = 1011.0$ (4) Å^3
$Z = 2$
$D_x = 1.217$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 4–19°$
$\mu = 0.08$ mm^{-1}
$T = 294$ K
Needle
$0.19 \times 0.17 \times 0.15$ mm
Transparent

Data collection

Siemens $R3m/V$ diffractometer
ω–2θ scans
Absorption correction: none
1549 measured reflections
1404 independent reflections
1286 observed reflections
$[I \geq 3\sigma(I)]$

$R_{int} = 0.012$
$\theta_{max} = 22.5°$
$h = 0 \to 9$
$k = 0 \to 13$
$l = -10 \to 10$
2 standard reflections monitored every 98 reflections intensity decay: <1%

Refinement

Refinement on F
$R = 0.046$
$wR = 0.053$
$S = 0.952$
1286 reflections
243 parameters
H atoms refined as riding atoms

$w = 1/[\sigma^2(F) + 0.0063F^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1990)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O(1)	0.8402 (5)	0.4725	0.2295 (5)	0.072 (2)
O(2)	0.9724 (6)	0.2166 (3)	-0.0131 (4)	0.089 (3)
O(3)	0.8133 (5)	0.1439 (3)	0.1107 (5)	0.071 (2)
O(4)	0.2681 (5)	0.6067 (4)	0.6234 (5)	0.070 (2)
C(1)	0.6362 (6)	0.3449 (4)	0.0942 (6)	0.051 (3)
C(2)	0.7467 (7)	0.3191 (4)	0.0012 (6)	0.050 (3)
C(3)	0.8749 (7)	0.2457 (5)	0.0762 (7)	0.061 (3)
C(4)	0.9747 (6)	0.2981 (4)	0.2082 (6)	0.057 (3)
C(5)	0.8938 (6)	0.3664 (4)	0.2958 (6)	0.059 (3)
C(6)	0.9703 (6)	0.3753 (4)	0.4506 (6)	0.057 (4)
C(7)	0.8682 (6)	0.3898 (4)	0.5498 (6)	0.057 (3)
C(8)	0.7246 (6)	0.4661 (5)	0.4839 (6)	0.048 (2)
C(9)	0.6303 (6)	0.4207 (4)	0.3425 (6)	0.044 (6)
C(10)	0.7215 (6)	0.3893 (4)	0.2371 (6)	0.045 (2)
C(11)	0.4767 (6)	0.4089 (4)	0.3101 (6)	0.046 (2)
C(12)	0.3737 (6)	0.4418 (4)	0.4060 (6)	0.046 (2)
C(13)	0.4602 (6)	0.5232 (4)	0.5209 (6)	0.046 (2)
C(14)	0.6270 (6)	0.4785 (4)	0.5888 (6)	0.045 (2)
C(15)	0.6913 (6)	0.5501 (4)	0.7239 (6)	0.060 (3)
C(16)	0.5443 (6)	0.5849 (4)	0.7680 (6)	0.052 (3)
C(17)	0.4000 (6)	0.5366 (4)	0.6547 (6)	0.050 (2)
C(18)	0.4628 (6)	0.6360 (4)	0.4494 (6)	0.065 (3)
C(19)	0.3604 (6)	0.4297 (5)	0.7100 (6)	0.048 (2)
C(20)	0.3239 (6)	0.3473 (5)	0.7575 (6)	0.058 (3)
C(21)	0.2723 (6)	0.2449 (4)	0.8117 (7)	0.087 (4)
C(22)	0.8339 (9)	0.0636 (5)	0.0140 (8)	0.100 (5)
C(23)	0.9215 (10)	0.1150 (5)	-0.0769 (11)	0.096 (4)

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

O (1)—C(5)	1.464 (5)	O(1)—C(10)	1.479 (6)
O (2)—C(3)	1.430 (9)	O(2)—C(23)	1.402 (8)
O (3)—C(3)	1.432 (8)	O(3)—C(22)	1.404 (9)
O (4)—C(17)	1.412 (7)	C(1)—C(2)	1.540 (9)
C (1)—C(10)	1.488 (7)	C(2)—C(3)	1.472 (8)
C (3)—C(4)	1.487 (8)	C(4)—C(5)	1.508 (9)
C (5)—C(6)	1.475 (8)	C(5)—C(10)	1.503 (7)
C (6)—C(7)	1.507 (9)	C(7)—C(8)	1.565 (7)
C (8)—C(9)	1.504 (7)	C(8)—C(14)	1.518 (9)
C (9)—C(10)	1.521 (9)	C(9)—C(11)	1.320 (7)
C (11)—C(12)	1.530 (9)	C(12)—C(13)	1.531 (7)
C (13)—C(14)	1.544 (7)	C(13)—C(17)	1.548 (9)
C (13)—C(18)	1.544 (8)	C(14)—C(15)	1.549 (8)
C (15)—C(16)	1.542 (9)	C(16)—C(17)	1.556 (7)
C (17)—C(19)	1.488 (8)	C(19)—C(20)	1.187 (8)
C (20)—C(21)	1.475 (8)	C(22)—C(23)	1.470 (14)
C(5)—O(1)—C(10)	61.4 (3)	C(3)—O(2)—C(23)	108.2 (5)
C(3)—O(3)—C(22)	108.4 (5)	C(2)—C(1)—C(10)	112.4 (5)
C(1)—C(2)—C(3)	111.3 (5)	O(3)—C(3)—C(2)	110.4 (5)
O(2)—C(3)—C(2)	111.3 (5)	O(2)—C(3)—O(3)	105.2 (5)
C(2)—C(3)—C(4)	111.1 (5)	O(3)—C(3)—C(4)	110.1 (5)
O(2)—C(3)—C(4)	108.4 (5)	C(3)—C(4)—C(5)	117.5 (5)
O(1)—C(5)—C(4)	112.6 (4)	C(4)—C(5)—C(10)	118.8 (5)
C(4)—C(5)—C(6)	117.5 (5)	O(1)—C(5)—C(10)	59.8 (3)
O(1)—C(5)—C(6)	112.7 (4)	C(6)—C(5)—C(10)	120.5 (5)
C(5)—C(6)—C(7)	118.3 (5)	C(6)—C(7)—C(8)	111.9 (5)
C(7)—C(8)—C(14)	109.6 (5)	C(7)—C(8)—C(9)	109.8 (5)
C(9)—C(8)—C(14)	112.1 (5)	C(8)—C(9)—C(11)	122.3 (5)
C(8)—C(9)—C(10)	116.4 (5)	C(10)—C(9)—C(11)	121.3 (5)
C(5)—C(10)—C(9)	117.8 (5)	C(1)—C(10)—C(9)	119.6 (5)
C(1)—C(10)—C(5)	119.2 (5)	O(1)—C(10)—C(9)	112.4 (4)
O(1)—C(10)—C(5)	58.8 (3)	O(1)—C(10)—C(1)	112.7 (4)
C(9)—C(11)—C(12)	125.4 (5)	C(11)—C(12)—C(13)	110.6 (5)
C(12)—C(13)—C(18)	108.3 (5)	C(12)—C(13)—C(17)	117.6 (5)
C(12)—C(13)—C(14)	108.2 (4)	C(17)—C(13)—C(18)	109.7 (4)
C(14)—C(13)—C(18)	112.0 (5)	C(14)—C(13)—C(17)	101.0 (4)
C(8)—C(14)—C(13)	113.9 (5)	C(13)—C(14)—C(15)	104.4 (4)
C(8)—C(14)—C(15)	118.9 (5)	C(14)—C(15)—C(16)	104.5 (4)
C(15)—C(16)—C(17)	107.0 (4)	C(13)—C(17)—C(16)	103.2 (5)
O(4)—C(17)—C(16)	113.3 (4)	O(4)—C(17)—C(13)	110.0 (5)
C(16)—C(17)—C(19)	107.7 (5)	C(13)—C(17)—C(19)	112.5 (5)
O(4)—C(17)—C(19)	110.0 (5)	C(17)—C(19)—C(20)	176.5 (6)
C(19)—C(20)—C(21)	177.6 (6)	O(3)—C(22)—C(23)	107.2 (5)
O(2)—C(23)—C(22)	105.5 (6)		

C(10)—C(1)—C(2)—C(3)	54.1 (6)
C(1)—C(2)—C(3)—C(4)	-62.4 (6)
C(2)—C(3)—C(4)—C(5)	38.7 (7)
C(3)—C(4)—C(5)—C(10)	-7.4 (8)
C(9)—C(8)—C(14)—C(13)	-41.1 (6)
C(12)—C(13)—C(14)—C(8)	61.2 (6)
C(11)—C(12)—C(13)—C(14)	-47.1 (6)
C(14)—C(13)—C(17)—C(16)	41.3 (5)
C(17)—C(13)—C(14)—C(15)	-43.4 (5)
C(13)—C(14)—C(15)—C(16)	28.3 (5)
C(14)—C(15)—C(16)—C(17)	-2.1 (6)
C(15)—C(16)—C(17)—C(13)	-24.6 (6)
C(9)—C(11)—C(12)—C(13)	18.6 (8)
C(8)—C(9)—C(11)—C(12)	2.0 (9)
C(14)—C(8)—C(9)—C(11)	9.0 (8)
C(4)—C(5)—C(10)—C(1)	-0.5 (8)
C(2)—C(1)—C(10)—C(5)	-22.1 (7)
C(8)—C(9)—C(10)—C(5)	21.8 (7)
C(6)—C(5)—C(10)—C(9)	-0.5 (8)
C(10)—C(5)—C(6)—C(7)	9.7 (8)
C(5)—C(6)—C(7)—C(8)	-37.9 (7)
C(6)—C(7)—C(8)—C(9)	57.0 (6)
C(7)—C(8)—C(9)—C(10)	-49.3 (6)

A $\Delta\rho$ map showed the positions of all H atoms. H atoms were included in the refinement at calculated positions riding on their bonded atoms with fixed isotropic displacement parameters. The Siemens program system *SHELXTL-Plus* (Sheldrick, 1990) was used for data processing, structure solution and refinement. The *PARST* (Nardelli, 1983) program

was used for the final interpretation of molecular geometry and crystal packing. All calculations were performed on a VAX 3100 workstation.

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Ligands for Application in Coordination Chemistry: Three Dicarboxylic Acids

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Abstract

Three potential ligand molecules have been investigated. 6,6'-o-Phenylenedioxybis(2,2-dimethyl-4-oxahexanoic acid), $C_{20}H_{30}O_8$ (I), has twofold crystallographic symmetry and adopts a conformation in which the two pendant carboxylic arms minimize any potential molecular cavity between them; zigzag polymeric chains are formed as a result of C=O···H—O hydrogen bonding about inversion centers. 2,2,9,9-Tetramethyl-4,7-dioxadecanedioic acid, $C_{12}H_{22}O_6$ (II), also forms polymeric hydrogen-bonded chains involving the car-

boxylic acid moieties but differs from (I) in its molecular conformation. 2,2,6,6,10,10-Hexamethyl-4,8-dioxaundecanedioic acid, $C_{15}H_{28}O_6$ (III), forms discrete rectangular-shaped centrosymmetric dimers in which any potential molecular cavity is minimized as a result of the close proximity of two of the pendant etheral arms.

Comment

The structure determinations of the three polyether dicarboxylic acids (I), (II) and (III) were undertaken as part of a program directed towards the development of polyoxygenated ligands for use in the synthesis of transition metal complexes with O atoms in the coordination sphere. Such complexes, with several potentially labile metal–oxygen bonds which could facilitate the generation of free coordination sites for interaction with reactive molecules, might serve as soluble analogs of metal sites at transition-metal–oxide surfaces. The anticipated lability of metal–ether bonds in particular was expected to result in the formation of complexes with unusual structures and coordination geometries about metal atoms (Ferguson, McAlees, McCrindle, Restivo & Roberts, 1977; McAlees & McCrindle, 1981; McCrindle, Ferguson, McAlees & Roberts, 1981). We now report the structures of three dicarboxylic acids which may have potential application as chelating or bridging ligands in inorganic and organometallic coordination chemistry, and show that on their own in the solid state they associate by C=O···H—O hydrogen bonding about inversion centers forming both hydrogen-bonded polymers and dimers. In the structures of the Cu complexes $Cu_2(X)_2(L)_2$ [X = dicarboxylate of (II); L = H_2O, C_5H_5N and PPh_3], the O atoms of each carboxylate moiety bridge the two Cu atoms and both dicarboxylate ligands behave as macrocyclic chelates towards the Cu_2 unit (McCrindle, Ferguson, McAlees & Roberts, 1981).

(I)

(II)

(III)
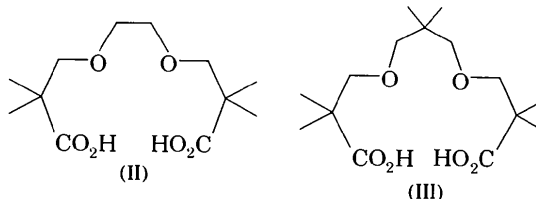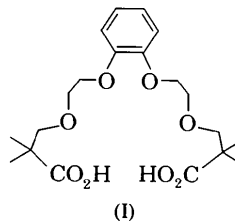
6,6'-o-Phenylenedioxybis(2,2-dimethyl-4-oxahexanoic acid), (I) (Fig. 1), which resides on a twofold axis passing through the aromatic ring, adopts a