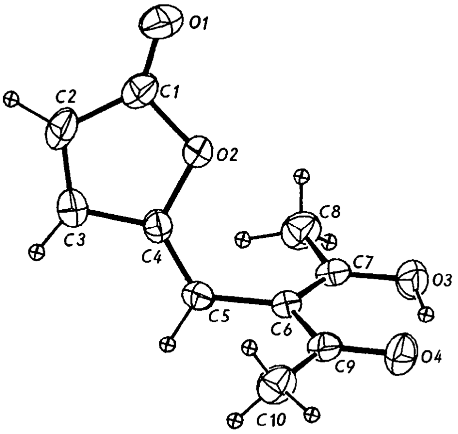

Fig. 1. A perspective view of molecule (II) showing the numbering of the atoms. The thermal ellipsoids are drawn at the 50% probability level.

out of the plane; on the other hand, the O(1) and C(5) atoms are displaced by 0.039 (2) and 0.063 (2) Å, respectively, on the same side of the five-atom plane.

On the other end of the molecule there is a strong intramolecular hydrogen bond between O(3)—H and O(4) (obviously, the main factor stabilizing the enol form), thus effectively forming a six-membered ring; the details of this H bond are: O(3)···O(4) = 2.422 (3), O(3)—H = 1.09 (3), H···O(4) = 1.41 (3) Å, O(3)—H···O(4) = 151 (3)°. The effects of the strong hydrogen bond are reflected in the overall geometry of the hydrogen-bonded ring, which exhibits a shortening and a lengthening of the formal single and double bonds, respectively; the ring is also planar to within ±0.014 (2) Å. Thus, the molecule can be regarded as consisting of two planar fragments, with a twist angle of 61.4 (2)° about the central C(5)—C(6) single bond.

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Structure of 2,3-Di-*tert*-butyl-5,6,7,8-*endo*-tetrakis(hydroxymethyl)bicyclo[2.2.2]oct-2-ene

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Abstract. $C_{20}H_{36}O_4$, $M_r = 340.50$, orthorhombic, $Pbca$, $a = 29.056\,(9)$, $b = 13.127\,(3)$, $c = 10.068\,(2)$ Å, $V = 3840\,(2)$ Å^3, $Z = 8$, $D_x = 1.178$, $D_m = 1.174$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0.71069$ Å, $\mu = 0.075$ mm^{-1}, $F(000) = 1504$, $T = 293.7$ K, $R = 0.083$ for 2435 observed reflections. Owing to the bulky *ortho* substituents, *tert*-butyl groups and *endo*-hydroxymethyl groups, large deviations from the torsion angles of an eclipsed conformation and large C—C—R (R = *tert*-butyl or hydroxymethyl) angles were observed. The crystal packing is constructed from double layered networks formed by O···O hydrogen bonds. These double layers are stacked along the *a* axis and interactions between double layers are of a van der Waals type involving *tert*-butyl groups.

Introduction. Two isomers were obtained from Diels–Alder reaction of 3,4-di-*tert*-butylthiophene 1,1-dioxide and maleic anhydride. The conformation of

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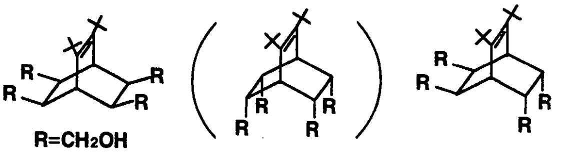
Table 1. *Positional parameters* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å^2) *for non*-H *atoms*

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

	x	y	z	B_{eq}
C(1)	1708 (1)	−661 (3)	2801 (3)	1.91 (9)
C(2)	1201 (1)	−355 (3)	2658 (3)	2.08 (9)
C(3)	1154 (1)	619 (3)	2225 (3)	2.06 (9)
C(4)	1618 (1)	1063 (3)	1762 (3)	1.80 (8)
C(5)	1981 (1)	1135 (3)	2895 (3)	1.91 (9)
C(6)	1959 (1)	130 (3)	3700 (4)	2.03 (9)
C(7)	1963 (1)	−642 (3)	1441 (3)	1.94 (9)
C(8)	1826 (1)	339 (3)	706 (3)	1.83 (9)
C(20)	840 (1)	−1176 (3)	3054 (4)	3.25 (11)
C(21)	705 (2)	−1096 (5)	4545 (5)	6.78 (20)
C(22)	418 (2)	−1181 (4)	2167 (7)	7.80 (22)
C(23)	1036 (2)	−2265 (4)	2930 (6)	5.92 (18)
C(30)	727 (1)	1344 (3)	2107 (4)	2.91 (11)
C(31)	876 (2)	2467 (4)	2005 (6)	5.74 (17)
C(32)	422 (2)	1284 (4)	3356 (5)	6.24 (19)
C(33)	441 (2)	1154 (4)	844 (5)	5.80 (18)
C(50)	1959 (1)	2121 (3)	3688 (4)	2.32 (9)
C(60)	1740 (1)	236 (3)	5065 (4)	2.52 (10)
C(70)	1909 (1)	−1611 (3)	635 (4)	2.59 (10)
C(80)	1507 (1)	230 (3)	−496 (4)	2.64 (10)
O(5)	2057 (1)	2982 (2)	2843 (3)	3.26 (8)
O(6)	1793 (1)	−696 (2)	5783 (2)	3.72 (8)
O(7)	2158 (1)	−2406 (2)	1289 (3)	3.24 (8)
O(8)	1764 (1)	50 (2)	−1696 (3)	3.48 (8)

the major product was suggested to be *endo*/*endo* (1) or *exo*/*exo* (2), while that of the minor product was *endo*/*exo* (3). An X-ray crystal structure analysis of the major product was carried out in order to determine the conformation of this compound and to study the steric effects of bulky *tert*-butyl and/or hydroxymethyl groups at *ortho* positions.



(1) *endo/endo* (2) *exo/exo* (3) *endo/exo*

Major Minor

Experimental. Colorless thin plates were crystallized from ethanol/hexane. Density was measured by flotation in aqueous KI solution. Crystals showed distinct cleavage perpendicular to the *a* axis. A crystal of dimensions 0.375 × 0.450 × 0.125 mm was used. Cell parameters were obtained from a least-squares refinement using 24 reflections ($23.4 < 2\theta < 35.1°$). Intensity data were collected using a Rigaku AFC-4 diffractometer with graphite monochromator; $2 \leq 2\theta < 55°$, h 0–37, k 0–17, l 0–13; 2θ–ω scan mode; scan range $\Delta\omega = (1.2 + 0.4\tan\theta)°$; scan speed 4° min^{-1}. Intensities of three standard reflections (10,0,0, 02$\bar{2}$, 022) monitored every 50 reflections showed a gradual decrease to 90%. Corrections were made for intensity variation. 4448 independent reflections were measured of which 2435 reflections were observed with $|F| \geq 3\sigma(F)$. No absorption correction was applied.

The structure was solved by the program *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Some H atoms were found from the difference maps. The positions of the remaining H atoms, most of which were those of *tert*-butyl groups, were located by the geometrical calculations. Block-diagonal least-squares refinement with anisotropic temperature factors for non-H atoms and isotropic temperature factors for H. $\sum w(|F_c| - k^{-1}|F_o|)^2$ was minimized with $w = 1/[\sigma^2(F) + 0.00037|F_o|^2]$. The final R value was 0.083 and wR was 0.077 for 362 parameters. $\Delta\rho_{max} = 0.35$ e Å^{-3}, $\Delta/\sigma_{max} = 0.09$, $S = 1.660$. The relatively high R value was due to the poor quality of the crystals (they were very thin because of distinct cleavage and gradual decomposition) and the large thermal motions of the bulky *tert*-butyl groups.

The final atomic parameters are given in Table 1.* Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All computations were performed on HITAC M260D and IBM ES/3090-180S computers of the Information Processing Center of the University of Electro-Communications with the programs *UNICS*III (Sakurai & Kobayashi, 1979), *MULTAN*78 and *ORTEP*II (Johnson, 1976).

Discussion. The molecular structure with the atomic numbering is shown in Fig. 1. Bond distances, bond angles, selected torsion angles and the geometry of the intermolecular hydrogen bonds are listed in Table 2.

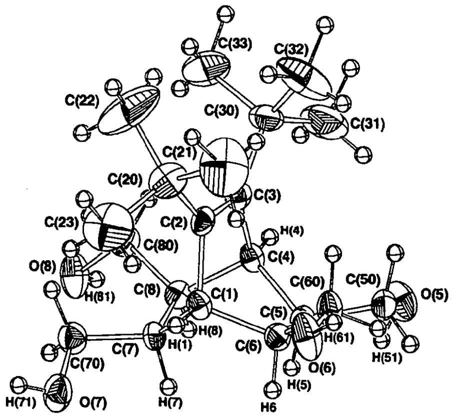


Fig. 1. The molecular structure with atomic numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability.

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* Lists of structure factors, anisotropic thermal parameters for non-H atoms, atomic parameters for H atoms, and bond lengths and angles for H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54814 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0535]

Table 2. *Bond lengths* (Å), *bond angles* (°), *selected torsion angles* (°) *of non*-H *atoms and intermolecular hydrogen-bond geometry* (Å, °)

C(1)—C(2)	1.533 (5)	C(7)—C(70)	1.517 (5)
C(1)—C(6)	1.559 (5)	C(8)—C(80)	1.530 (5)
C(1)—C(7)	1.558 (5)	C(20)—C(21)	1.555 (7)
C(2)—C(3)	1.357 (5)	C(20)—C(22)	1.516 (8)
C(2)—C(20)	1.556 (6)	C(20)—C(23)	1.543 (7)
C(3)—C(4)	1.541 (5)	C(30)—C(31)	1.539 (8)
C(3)—C(30)	1.570 (5)	C(30)—C(32)	1.540 (7)
C(4)—C(5)	1.555 (5)	C(30)—C(33)	1.540 (7)
C(4)—C(8)	1.549 (5)	C(50)—O(5)	1.442 (5)
C(5)—C(6)	1.550 (5)	C(60)—O(6)	1.429 (5)
C(5)—C(50)	1.523 (5)	C(70)—O(7)	1.430 (5)
C(6)—C(60)	1.521 (6)	C(80)—O(8)	1.439 (5)
C(7)—C(8)	1.538 (5)		

C(2)—C(1)—C(6)	109.3 (3)	C(8)—C(7)—C(70)	114.7 (3)
C(2)—C(1)—C(7)	111.8 (3)	C(4)—C(8)—C(7)	106.6 (3)
C(6)—C(1)—C(7)	106.1 (3)	C(4)—C(8)—C(80)	111.4 (3)
C(1)—C(2)—C(3)	111.9 (3)	C(7)—C(8)—C(80)	117.4 (3)
C(1)—C(2)—C(20)	116.2 (3)	C(2)—C(20)—C(21)	111.8 (4)
C(3)—C(2)—C(20)	131.9 (3)	C(2)—C(20)—C(22)	113.4 (4)
C(2)—C(3)—C(4)	111.5 (3)	C(2)—C(20)—C(23)	111.9 (4)
C(2)—C(3)—C(30)	132.4 (3)	C(21)—C(20)—C(22)	111.3 (4)
C(4)—C(3)—C(30)	116.1 (3)	C(21)—C(20)—C(23)	103.5 (4)
C(3)—C(4)—C(5)	113.2 (3)	C(22)—C(20)—C(23)	104.3 (4)
C(3)—C(4)—C(8)	108.3 (3)	C(3)—C(30)—C(31)	111.4 (4)
C(5)—C(4)—C(8)	106.1 (3)	C(3)—C(30)—C(32)	111.2 (4)
C(4)—C(5)—C(6)	107.8 (3)	C(3)—C(30)—C(33)	113.0 (4)
C(4)—C(5)—C(50)	114.0 (3)	C(31)—C(30)—C(32)	105.4 (4)
C(6)—C(5)—C(50)	116.6 (3)	C(31)—C(30)—C(33)	104.6 (4)
C(1)—C(6)—C(5)	106.4 (3)	C(32)—C(30)—C(33)	110.9 (4)
C(1)—C(6)—C(60)	112.9 (3)	C(5)—C(50)—O(5)	110.4 (3)
C(5)—C(6)—C(60)	114.3 (3)	C(6)—C(60)—O(6)	109.5 (3)
C(1)—C(7)—C(8)	108.2 (3)	C(7)—C(70)—O(7)	108.2 (3)
C(1)—C(7)—C(70)	114.0 (3)	C(8)—C(80)—O(8)	111.5 (3)

C(6)—C(1)—C(2)—C(3)	53.8 (3)	C(20)—C(2)—C(3)—C(30)	8.3 (5)
C(7)—C(1)—C(2)—C(3)	−63.3 (3)	C(50)—C(5)—C(6)—C(60)	22.4 (4)
C(2)—C(1)—C(6)—C(5)	−68.8 (3)	C(70)—C(7)—C(8)—C(80)	20.4 (4)
C(7)—C(1)—C(6)—C(5)	51.8 (3)	C(4)—C(5)—C(50)—O(5)	−62.7 (3)
C(2)—C(1)—C(7)—C(8)	44.4 (3)	C(6)—C(5)—C(50)—O(5)	170.6 (2)
C(1)—C(2)—C(3)—C(4)	10.4 (4)	C(5)—C(6)—C(60)—O(6)	−172.4 (2)
C(2)—C(3)—C(4)—C(5)	−62.8 (3)	C(1)—C(6)—C(60)—O(6)	65.8 (3)
C(2)—C(3)—C(4)—C(8)	54.6 (3)	C(1)—C(7)—C(70)—O(7)	−69.5 (3)
C(3)—C(4)—C(5)—C(6)	43.4 (3)	C(8)—C(7)—C(70)—O(7)	164.9 (2)
C(8)—C(4)—C(5)—C(6)	−75.3 (3)	C(4)—C(8)—C(80)—O(8)	149.3 (2)
C(3)—C(4)—C(8)—C(7)	−69.1 (3)	C(7)—C(8)—C(80)—O(8)	−87.4 (3)
C(5)—C(4)—C(8)—C(7)	52.7 (3)		
C(4)—C(5)—C(6)—C(1)	18.0 (3)	C(2)—C(1)···C(4)—C(3)	5.6 (2)
C(1)—C(7)—C(8)—C(4)	17.6 (3)	C(6)—C(1)···C(4)—C(5)	11.2 (2)
C(6)—C(1)—C(7)—C(8)	−74.6 (3)	C(7)—C(1)···C(4)—C(8)	10.8 (2)

A—H···*B*	*A*···*B*	H···*B*	*A*—H···*B*
O(6)—H(61)···O(8^{i})	2.722 (4)	2.04 (4)	140 (4)
O(7)—H(71)···O(6^{ii})	2.756 (4)	2.01 (3)	163 (3)
O(8)—H(81)···O(5^{iii})	2.760 (4)	2.02 (4)	173 (4)
O(5)—H(51)···O(7^{iv})	2.813 (4)	1.96 (5)	173 (4)

Symmetry code: (i) $x, y, z + 1.0$; (ii) $x, -y - 0.5, z - 0.5$; (iii) $x, 0.5 - y, z - 0.5$; (iv) $0.5 - x, 0.5 + y, z$.

The structure analysis revealed that the compound is an *endo*/*endo* isomer. The C(2)—C(3) bond is longer than the normal double-bond length. The mean value of the lengths of the C(1)—C(2) and C(3)—C(4) bonds, 1.537 Å, is slightly shorter than that of the other C—C bonds in the bicyclooctane ring, 1.552 Å. The two cyclohexene and one cyclohexane rings have distorted boat-type conformations. The dihedral angles between planes, (I) C(1), C(2), C(3) and C(4), (II) C(1), C(6), C(5) and C(4), (III) C(1), C(7), C(8) and C(4), are 123.2 (2), 121.6 (2) and 114.7 (2)° for (I)—(II), (I)—(III) and (II)—(III), respectively. In the bicyclo[2.2.2]oct-2-ene ring large distortions from the *cis* conformation are observed for C(1)—C(2)—C(3)—C(4), C(1)—C(6)—C(5)—C(4) and C(1)—C(7)—C(8)—C(4). The corresponding values are 3.0, 7.1 and −1.0° for tetramethyl bicyclo[2.2.2]oct-2-ene-5-*endo*,6-*exo*,7-*exo*,8-*endo*-tetracarboxylate (Brückner, Malpezzi & Grassi, 1983) and 2.0, 5.0, 7.3° for 6-chloro-1-methoxy-3-methylbicyclo[2.2.2]oct-2-ene-6-carbonitrile (Dykes & Davis, 1977). Cross-ring torsion angles around C(1)···C(4) (Table 2) are also larger than the corresponding angles in these related compounds. The C(1)···C(4) distance is 2.507 (5) Å. Large torsion angles between *ortho* substituents, C(20)—C(2)—C(3)—C(30), C(50)—C(5)—C(6)—C(60) and C(70)—C(7)—C(8)—C(80), and large bond angles at ^{t}BuC═C, C(3)—C(2)—C(20) and C(2)—C(3)—C(30), and at *R*—C—C(—*R*) (R = CH$_2$OH), C(6)—C(5)—C(50), C(5)—C(6)—C(60), C(8)—C(7)—C(70) and C(7)—C(8)—C(80), show the molecular distortion resulting from the bulky *ortho* substituents.

A stereoscopic drawing of the crystal structure is shown in Fig. 2. The crystal packing is constructed from a double-layered network formed by intermolecular hydrogen bonding. Part of the tetrakis(hydroxymethyl)cyclohexane plane of each molecule is surrounded by six planes of other molecules forming a two-dimensional molecular layer with O···O hydrogen bonds [O(6)···O(8^{i}), O(7)···O(6^{ii}) and O(8)···O(5^{iii})]. This molecular layer is also linked to the neighboring one by another hydrogen bond [O(5)···O(7^{iv})] to form a double-layered structure. Each O atom acts as a donor and an acceptor of the hydrogen bonding. The bridged di-*tert*-butylethylene groups are nearly perpendicular to these double-layered networks. The double layers are stacked along the *a* axis and the interactions between double

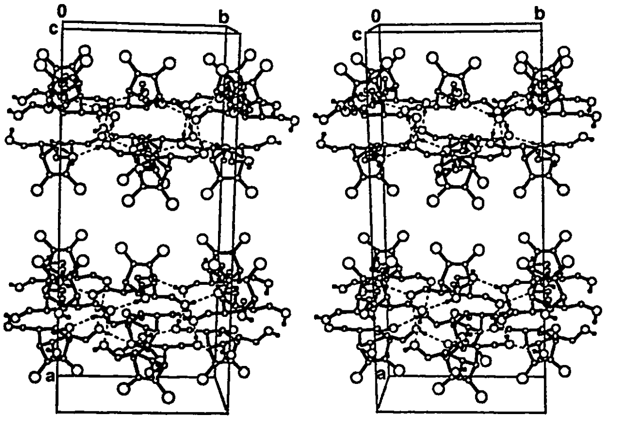

Fig. 2. Stereoscopic view of the crystal packing. Broken lines indicate hydrogen bonds. *tert*-Butyl groups are represented by large open circles for clarity.

layers are of a van der Waals type involving hydrophobic *tert*-butyl groups. The crystal cleavage perpendicular to the *a* axis is ascribed to this double-layered structure. In ten compounds having a bicyclooctane framework and hydroxyl groups found in a search of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) no such cleaved double-layered structure has been observed.

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Structure of an Anti-Arrhythmic and Hypotensive Agent: 1-{3-[4-(3-Chlorophenyl)-1-piperazinyl]-2-hydroxypropyl}pyrrolidin-2-one

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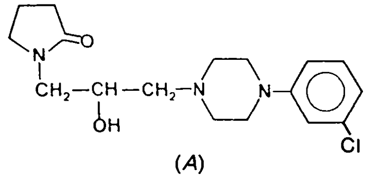
Abstract. $C_{17}H_{24}ClN_3O_2$, $M_r = 337.85$, monoclinic, $P2_1/c$ (C^5_{2h}), $a = 15.492$ (2), $b = 6.592$ (1), $c = 17.193$ (2) Å, $\beta = 99.96$ (1)°, $V = 1729.3$ (4) Å^3, $Z = 4$, $D_m = 1.29$ (1), $D_x = 1.298$ (1) Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.23$ mm^{-1}, $F(000) = 720$, $T = 295$ K, $R = 0.0478$ for 1899 unique observed reflections [$F_o \geq 2\sigma(F_o)$]. The geometry of the amino-alcohol chain of the molecule, believed to be a pharmacophore, is antiperiplanar with an O(7)—C(7)—C(8)—N(9) torsion angle of −171.7 (2)° and an O(7)···N(9) distance of 3.742 (2) Å. It is associated with a relatively strong intermolecular hydrogen bond O(7)—H(O7)···O(2) translated by **b**, with O(7)···O(2) = 2.720 (3) Å. The compound exhibits anti-arrhythmic and hypotensive activity, as has been shown by pharmacological tests.

Introduction. Following the structure determination of 1-[2-hydroxy-3-(4-phenyl-1-piperazinyl)propyl]-pyrrolidin-2-one, refered to hereafter as (*B*) (Stadnicka, Ciechanowicz-Rutkowska & Malawska, 1991), we undertook the analogous study of its chloro derivative, 1-{3-[4-(3-chlorophenyl)-1-piperazinyl]-2-hydroxypropyl}pyrrolidin-2-one, (*A*).



(*A*)

The compound was synthesized and studied by Malawska, Gorczyca, Cebo & Krupińska (1988). It has anti-arrhythmic and hypotensive activity, weaker, however, than propranolol and quinidine but comparable to that of compound (*B*) (Malawska, Gorczyca, Filipek, Cros, Liutkus & Serrano, 1990).

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