

C(7)–C(6) sont, comme N(1)–C(2), dissymétriques par rapport au cycle benzénique et, de plus, hors plan avec les distances suivantes à P1: Se(1) 0,0073 (4), C(7) 0,057 (4) et N(1) 0,037 (5) Å. Le plan moyen P2 de l'hétérocycle est caractérisé par un écart maximum égal à 0,014 (4) Å [atome C(7)]. L'angle dièdre P1–P2 vaut 1,2 (1)° [1,8 et 1,7 (1)° dans (II)]. Les atomes C(2), N(1), O(1) et O(2) sont coplanaires avec des distances au plan moyen P3 inférieures à 0,1 σ . Angle P1–P3 = 5,1 (1)° [(II): 3,4 (1) et 4,9 (1)°]. Quant au plan moyen P4 des atomes du cycle benzénique C(8) à C(13), il forme un angle dièdre égale à 13,2 (1)° avec P2. N(2) est distant de P4 de 0,053 (3) Å. Les interactions intermoléculaires correspondent à des liaisons du type van der Waals, moins courtes que dans (II), ce qui est conforme aux valeurs calculées des densités respectives. La Fig. 3 montre une vue (100) de la maille cristalline.

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Structure of the Monoclinic Form of 2,6-Di-*tert*-butyl-4-phenylphenol

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Abstract. C₂₀H₂₆O, $M_r = 282.4$, monoclinic, $P2_1/a$, $a = 23.277$ (8), $b = 8.197$ (2), $c = 9.033$ (4) Å, $\beta = 94.63$ (3)°, $V = 1718$ (2) Å³, $Z = 4$, $D_x = 1.092$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 4.28$ cm⁻¹, $F(000) = 616$, $T = 293$ K, final $R = 0.065$ for 2807 observed independent diffractometer-measured intensity data. The two *tert*-butyl groups have approximately the same orientation about the ring plane and the dihedral angle between the two ring planes has the value 37.7 (4)°. There are no hydrogen bonds as usually found in phenol molecules due to steric hindrance, but there is a weak intramolecular interaction C–H...O.

Introduction. This study was undertaken to discover the molecular conformation of this phenol with large substituents near the OH position. The steric hindrance at the *ortho* position of the OH group gives particular properties to the phenolic function: the H atom of the hydroxyl group is often out of the benzene ring plane (Rumpf & Lumbroso, 1950); the benzene ring is

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deformed (Demerseman, Reynaud, Lechartier, Pène, Chentin, Royer & Rumpf, 1966). In addition it is interesting to know the dihedral angle between the two benzene rings and to compare its value with the value in *p*-phenylphenol.

Experimental. Suitable crystals were grown by slow evaporation of a mixture of ethyl ether and hexane or ethyl ether and propanol at room temperature, or from chloroform at low temperature. Needle approximately 0.7 × 0.3 × 0.3 mm used for data collection; crystals seem to have different morphology in various solvents. Preliminary unit-cell parameters were obtained at room temperature from Weissenberg photographs; accurate values were determined by least squares from setting angles of 25 reflexions in the range 3.8 < θ < 44.4°, using a Nonius CAD-4 diffractometer, ω -2 θ scan technique used to collect intensities of 7425 independent reflexions with θ < 73° (range of hkl : h –28→28, k –10→10, l 0→11), 2807 of which considered as observed [$I > 3\sigma(I)$]. One standard reflexion

measured every 60 min to control the intensity and at intervals of 100 reflexions to control the orientation of the crystal. Lorentz and polarization corrections made. Structure determined by direct methods and refined on *F* by *SHELX76* (Sheldrick, 1976). 212 independent parameters; the *E* map showed all non-H atoms. H positions determined by a difference Fourier synthesis, and introduced into the refinement with C—H lengths fixed at 1.08 Å. Atoms refined first isotropically, then anisotropically; $(\Delta/\sigma)_{\max} = 1.796$ for *x* of C(24), $(\Delta/\sigma) = 0.368$; the Δ/σ values for the C atoms of the *tert*-butyl groups are large, as well as their U_{eq} factors, probably due to the high thermal motion or disorder of these atoms; residual electron density = 0.08 e Å⁻³; *S* = 1.2; final *R* = 0.065. Atomic scattering factors from *SHELX76*.

Discussion. Fig. 1 shows the molecule drawn by *PLUTO* (Motherwell & Clegg, 1978). Table 1 gives the final atomic coordinates with their e.s.d.'s and the equivalent isotropic thermal parameters.* The bond distances and angles are listed in Table 2. The aromatic C—C bond distances are normal and vary from 1.379 (5) to 1.413 (3) Å with a mean value of 1.392 (4) Å. In the benzene ring the internal angles at the substituted C atoms deviate from the mean value, 120°: less than 120° due to the σ -releasing character of the *tert*-butyl substituents at C(2) and C(6) and phenyl

* Lists of structure factors, anisotropic vibration parameters, H-atom coordinates, torsion angles and deviations of atoms from selected mean planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51275 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

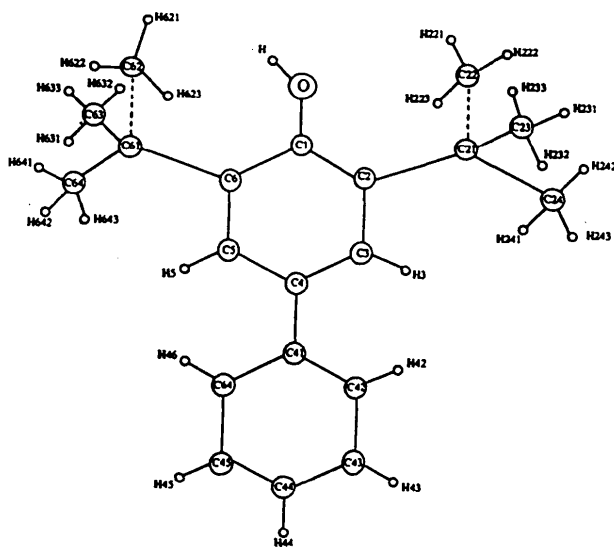


Fig. 1. Molecule viewed perpendicular to the C(6)—C(1)—C(2) plane and numbering scheme.

Table 1. Fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters for non-H atoms, with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (Å ²)
C(1)	1632 (1)	3928 (3)	10034 (3)	0.045 (1)
C(2)	1159 (1)	4738 (3)	9327 (3)	0.042 (1)
C(3)	946 (1)	6080 (3)	10047 (3)	0.041 (1)
C(4)	1198 (1)	6629 (3)	11414 (3)	0.042 (1)
C(5)	1659 (1)	5773 (3)	12079 (3)	0.046 (1)
C(6)	1892 (1)	4405 (3)	11435 (3)	0.045 (1)
C(41)	975 (1)	8110 (3)	12130 (3)	0.045 (1)
C(42)	785 (1)	9467 (4)	11298 (3)	0.052 (1)
C(43)	584 (1)	10853 (4)	11987 (4)	0.063 (1)
C(44)	571 (1)	10897 (4)	13518 (4)	0.067 (1)
C(45)	753 (1)	9559 (5)	14355 (4)	0.065 (1)
C(46)	954 (1)	8186 (4)	13682 (3)	0.057 (1)
C(21)	870 (1)	4158 (3)	7804 (3)	0.047 (1)
C(22)	644 (2)	2410 (4)	7928 (4)	0.065 (1)
C(23)	1306 (2)	4247 (5)	6604 (3)	0.063 (1)
C(24)	357 (2)	5224 (5)	7294 (5)	0.068 (1)
C(61)	2391 (1)	3434 (4)	12239 (3)	0.050 (1)
C(62)	2195 (2)	1678 (5)	12546 (5)	0.077 (1)
C(63)	2928 (1)	3428 (5)	11363 (4)	0.065 (1)
C(64)	2582 (2)	4220 (6)	13761 (4)	0.084 (2)
O	1847 (1)	2621 (3)	9286 (2)	0.065 (1)

Table 2. Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

C(1)—C(2)	1.395 (3)	C(41)—C(42)	1.394 (4)
C(2)—C(3)	1.389 (3)	C(42)—C(43)	1.394 (4)
C(3)—C(4)	1.397 (3)	C(43)—C(44)	1.387 (4)
C(4)—C(5)	1.378 (3)	C(44)—C(45)	1.379 (5)
C(5)—C(6)	1.394 (4)	C(45)—C(46)	1.380 (4)
C(6)—C(1)	1.413 (3)	C(46)—C(41)	1.407 (4)
C(2)—C(21)	1.557 (3)	C(41)—C(4)	1.489 (3)
C(21)—C(22)	1.534 (4)	C(61)—C(63)	1.533 (4)
C(21)—C(23)	1.544 (4)	C(61)—C(62)	1.542 (5)
C(21)—C(24)	1.522 (4)	C(61)—C(64)	1.551 (4)
C(6)—C(61)	1.540 (3)	C(1)—O	1.381 (3)
O—C(1)—C(2)	116.7 (2)	C(64)—C(61)—C(6)	110.8 (2)
O—C(1)—C(6)	120.5 (2)	C(46)—C(41)—C(42)	117.8 (3)
C(6)—C(1)—C(2)	122.9 (2)	C(41)—C(42)—C(43)	120.9 (3)
C(1)—C(2)—C(3)	117.5 (2)	C(42)—C(43)—C(44)	120.1 (3)
C(2)—C(3)—C(4)	121.9 (2)	C(43)—C(44)—C(45)	119.7 (3)
C(3)—C(4)—C(5)	118.5 (2)	C(44)—C(45)—C(46)	120.5 (3)
C(4)—C(5)—C(6)	122.9 (2)	C(45)—C(46)—C(41)	121.0 (3)
C(5)—C(6)—C(1)	116.3 (2)	C(42)—C(41)—C(4)	121.5 (2)
C(3)—C(4)—C(41)	120.7 (2)	C(46)—C(41)—C(4)	120.7 (2)
C(5)—C(4)—C(41)	120.8 (2)	C(21)—C(2)—C(1)	121.9 (2)
C(61)—C(6)—C(1)	122.1 (2)	C(21)—C(2)—C(3)	120.7 (2)
C(61)—C(6)—C(5)	121.6 (2)	C(22)—C(21)—C(2)	110.3 (2)
C(62)—C(61)—C(6)	110.2 (2)	C(22)—C(21)—C(23)	110.1 (3)
C(62)—C(61)—C(63)	110.8 (3)	C(22)—C(21)—C(24)	107.0 (3)
C(62)—C(61)—C(64)	107.2 (3)	C(23)—C(21)—C(24)	107.8 (3)
C(63)—C(61)—C(64)	105.7 (3)	C(23)—C(21)—C(2)	110.1 (2)
C(63)—C(61)—C(6)	111.9 (2)	C(24)—C(21)—C(2)	111.4 (2)

substituent at C(4); more than 120° at C(1) due to the OH group (Domenicano, Vaciago & Coulson, 1975). As in other phenols the external angles at C(1) have different values [C(2)—C(1)—O: 116.7 (2); C(6)—C(1)—O: 120.5 (2)°] the larger being on the side of the hydroxyl H. A weak intramolecular interaction is found between O and H(221) of the *tert*-butyl group: O...H(221) = 2.32 (3) Å. The C(4)—C(41) bond length [1.489 (3) Å] is in good agreement with the

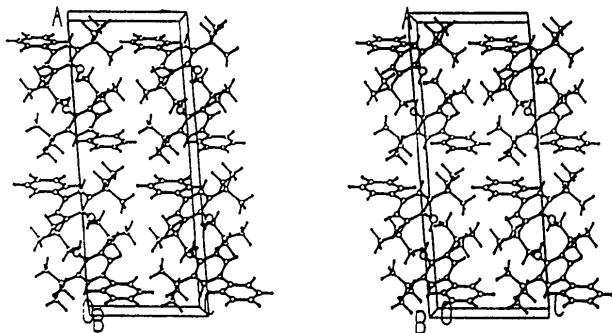


Fig. 2. Stereoscopic view of the structure seen along [010] drawn by *PLUTO*.

1.487 Å value calculated for a C(sp^2)—C(sp^2) bond by Dewar & Schmeisinger (1960). The phenyl ring is planar while the phenolic ring is distorted, probably due to the substituents, as found by Maze-Baudet (1973). The O atom is at 0.051 (2) Å from the ring plane and the H atom is at 0.43 (4) Å from that plane. Comparisons with other phenols with one or two *tert*-butyl groups at *ortho* positions will be made in a later paper. The dihedral angle between the two ring planes has the

value 37.7 (4)°; so the inter-ring torsion is large compared with the value of 2° found for 4-hydroxybiphenyl (Brock & Haller, 1984).

The packing is shown in Fig. 2. No close intermolecular contacts between the atoms were found in the crystal; so there are no hydrogen bonds because of the steric hindrance at *ortho* positions.

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Structure of Cholesterol *n*-Hexyl Carbonate

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Abstract. 5-Cholesten-3 β -ol-3-*n*-hexyl carbonate, C₃₄H₅₈O₃, $M_r = 514.6$, monoclinic, $P2_1$, $a = 12.728$ (2), $b = 9.184$ (1), $c = 13.991$ (2) Å, $\beta = 92.93$ (1)°, $V = 1633.3$ (6) Å³, $T = 298$ K, Mo $K\alpha$ graphite monochromator, $\lambda = 0.71073$ Å, $Z = 2$, $D_m = 1.05$, $D_x = 1.046$ g cm⁻³, $\mu = 0.34$ cm⁻¹, $F(000) = 572$, $R =$

0.126 for 1600 data having $I > 3\sigma(I)$. The bond lengths and valence angles in the structural unit of the cholesterol and carbonate groups are normal but the hexyl group has shortened bond lengths due to the high thermal vibration in this region, and the C(17) cholesterol side chain is almost fully extended. Adjacent