Table 1. *Atomic coordinates and isotropic temperature factors (Å²) of thiourea dioxide*

$$B_{eq} = \tfrac{8}{3}\pi^2 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}/B
S	0·45975 (1)	0·25	0·36497 (3)	3·02 (1)
C	0·11194 (3)	0·25	0·9019 (1)	2·57 (2)
N	0·16367 (2)	0·13639 (2)	0·8390 (1)	3·43 (1)
O	0·40051 (1)	0·12865 (2)	0·50769 (4)	3·48 (1)
H(1)	0·2533 (2)	0·1306 (2)	0·7437 (6)	6·4 (1)
H(2)	0·1206 (2)	0·0680 (2)	0·8816 (6)	3·2 (1)

bonds where the two crystallographically independent N···O distances are roughly equal (2·84 Å). The N—H(1)···O bond is believed to be stronger than N—H(2)···O from the closer value of the N—H(1)···O angle to 180° and the lengthening of the N—H(1) bond. A comparison between this work, the previous one and the structure of thiourea at 123 K (Mullen & Hellner, 1978) is given in Table 2. The C—S bond is obviously lengthened in the title compound which indicates single-bond character in the dioxide.

Table 2. *Comparison between thiourea dioxide and thiourea*

	Thiourea dioxide (Sullivan & Hargreaves, 1962)	Thiourea dioxide (This work)	Thiourea (123 K) (Mullen & Hellner, 1978)[*]
C–S	1·85 (2) Å	1·8615 (4) Å	1·716 (8) Å
			1·712 (8)
S–O	1·49 (8)	1·4890 (4)	
C–N	1·310 (8)	1·2972 (4)	1·332 (6)
			1·334 (8)
N–H(2)	1·27 (9)	0·846 (2)	0·80 (6)
			0·93 (6)
N–H(1)	1·09 (8)	1·027 (2)	1·00 (6)
			0·93 (5)
N···O	2·85 (2)	2·8392 (5)	
∠N–H(1)···O	166 (7)°	170·4 (2)°	
H(1)···O	1·8 (1) Å	1·821 (2) Å	
H(2)···O	1·6 (1)	2·060 (2)	
N···O	2·84 (2)	2·8429 (9)	
∠N–H(2)···O	161 (6)°	153·5 (1)°	

[*] Two independent molecules.

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Structure of the *tert*-Butyl-*ortho*-tolylcarbinol, 2,2,4,4-Tetramethyl-3-(2-methyl-4-methoxyphenyl)pentan-3-ol, C₁₇H₂₈O₂

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Abstract. $M_r = 264·41$, triclinic, $P\bar{1}$, $a = 8·259$ (3), $b = 7·888$ (3), $c = 13·493$ (3) Å, $\alpha = 102·2$ (3), $\beta = 96·8$ (3), $\gamma = 110·1$ (3)°, $V = 789·2$ (5) Å³, $Z = 2$, $D_x = 1·113$ (1), $D_m = 1·12$ (1) g cm⁻³, λ(Mo $K\alpha$) = 0·70926 Å, $\mu = 0·763$ cm⁻¹, $F(000) = 292$, room temperature. Final $R = 0·05$ for 1736 observed reflections. The geometry indicates severe overcrowding at the alcoholic C atom. The molecular geometry agrees quite well with that predicted by the molecular-mechanics method. The molecule has the synperiplanar conformation with the hydroxyl group rotated 11·6° out of the plane of the phenyl ring.

Introduction. Over the last few years much attention has been given to steric effects and, in particular, to their influence upon reactivity. One aspect of this work is concerned with highly congested molecules, containing usually one or more *tert*-butyl groups, which show interesting and often unexpected behaviour. Crystallographic studies of such compounds, though not

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* ($\text{Å}^2 \times 100$)

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}
C(1)	0·3436 (5)	0·7623 (6)	0·2195 (3)	3·3
C(2)	0·3825 (5)	0·7095 (6)	0·1216 (3)	3·3
C(3)	0·5271 (6)	0·8325 (6)	0·0944 (3)	3·8
C(4)	0·6342 (6)	1·0052 (6)	0·1594 (4)	4·1
C(5)	0·5964 (6)	1·0592 (6)	0·2533 (4)	4·4
C(6)	0·4572 (6)	0·9402 (6)	0·2825 (4)	4·1
C(7)	0·2811 (6)	0·5310 (7)	0·0359 (4)	4·6
O(8)	0·7777 (4)	1·1309 (4)	0·1365 (3)	4·7
C(9)	0·8274 (6)	1·0702 (7)	0·0416 (4)	5·0
C(10)	0·1930 (5)	0·6416 (6)	0·2627 (3)	3·1
O(11)	0·0831 (4)	0·4892 (4)	0·1768 (2)	3·5
C(12)	0·2749 (6)	0·5538 (7)	0·3429 (4)	4·6
C(13)	0·1347 (8)	0·4284 (8)	0·3880 (5)	7·5
C(14)	0·4214 (8)	0·6984 (9)	0·4333 (5)	7·2
C(15)	0·3606 (8)	0·4317 (8)	0·2827 (5)	7·4
C(16)	0·0680 (6)	0·7515 (6)	0·2993 (3)	4·0
C(17)	0·0449 (7)	0·8590 (8)	0·2197 (5)	6·4
C(18)	−0·1205 (7)	0·6137 (8)	0·2949 (5)	6·3
C(19)	0·1285 (8)	0·8872 (8)	0·4086 (4)	6·4

numerous, reveal spectacular deviations of bond angles and bond lengths from standard values. In this article we wish to report the crystal structure of a stable rotameric alcohol.

Lomas, Luong & Dubois (1977) found that addition of *ortho*-tolyllithium to di-*tert*-butyl ketone gives a rotameric pair of anti- and synperiplanar isomers of di-*tert*-butyl-*ortho*-tolylcarbinol, the latter (I), being the more stable. Although the structures could be assigned by IR and NMR spectroscopy, it was interesting to determine the structure of at least one rotamer crystallographically and to compare this with the known structures of related compounds, (II) and (III), from which the *ortho*-methyl group is absent. The 4-methoxy derivative of the synperiplanar alcohol proved to be suitable for this purpose.

(I)   (II)   (III)
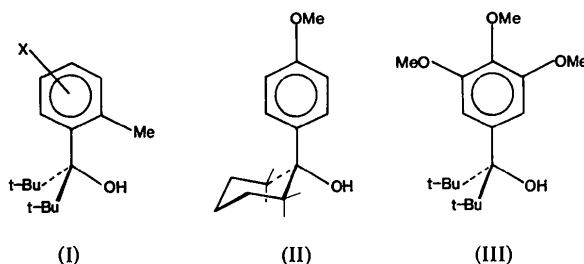
Experimental. Crystals of (I) (X = 4-methoxy) from crude oily reaction product, polycrystalline (*cf.* Cheng & Nyburg, 1978) but one roughly cubic fragment, sides *ca* 0·5 mm, was single crystal. Data for 2746 reflections, 1010 unobserved [$I < 3\sigma(I)$] on Syntex P1 at University of Oslo, graphite-monochromated Mo $K\alpha$ radiation, $2 \le \theta \le 25°$, Lp corrected, absorption ignored. Cell parameters by least squares from 15 reflections. 313, 116 and 321 used as intensity controls

but no decline during data collection. *hkl* ranges: 0 to 9, −9 to 8, −15 to 15, respectively. Density by flotation in KI solution. Structure solved by direct methods (*MULTAN*74, Main, Woolfson, Lessinger, Germain & Declercq, 1974), refined based on F using *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Scattering factors from Cromer & Mann (1968) for C and O and Stewart, Davidson & Simpson (1965) for H. All H's located in ΔF map. Final refinement, H's isotropic, C and O anisotropic to $R = 0·05$, $wR = 0·075$ using $1/\sigma(I)$ weights. $(\Delta/\sigma)_{av} = 0·02$, $(\Delta/\sigma)_{max} = 0·4$, max. residual electron density in final ΔF map $\pm 0·4$ e Å^{-3}. Calculations carried out on a CYBER 74 computer at the University of Oslo and a CYBER 171 MP at the University of Tromsø.

Discussion. Atomic coordinates and U_{eq} values for C and O are given in Table 1.*

The molecule is illustrated in Fig. 1 and the atomic numbering scheme and bond lengths and angles for the non-H atoms are shown in Fig. 2.

The most important result is that this study confirms that the alcohol in question has the synperiplanar conformation with an out-of-plane angle for the alcohol group of 11·6°, very similar to that in the phenyl derivative (III) (van Koningsveld & van Meurs, 1977) despite the presence of the *ortho*-methyl group. The orientation of the −OH group corresponds to the conformation to which was attributed the −OH stretching frequency at 3643 cm^{-1} (3650 cm^{-1} in the antiperiplanar isomer) (Lomas *et al.*, 1977), the other one (3612 cm^{-1} in the antiperiplanar isomer) being

* Lists of structure factors, anisotropic thermal parameters, hydrogen coordinates and bond lengths and angles from molecular-mechanics calculations have been deposited with the British Libary Lending Division as Supplementary Publication No. SUP 39493 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
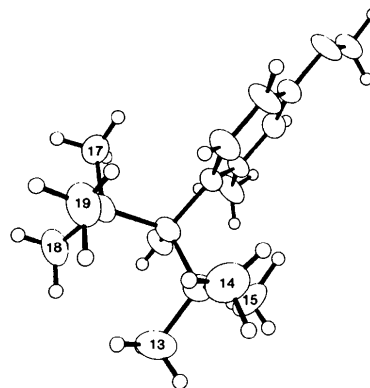

Fig. 1. The title molecule including the numbering scheme for the *tert*-butyl methyl groups. Thermal ellipsoids are drawn at 50% probability.

much weaker because of unfavourable interactions between the methyl and hydroxyl group H atoms. The relevant C(7)—O(11) distance is 2·611 (6) Å.

The largest deviation from planarity in the phenyl ring is 0·004 (3) Å [C(5)] and the methoxy group on C(4) is rotated 5·7° out of this plane. The mean aromatic C—C bond length is the normal 1·39 Å although the bonds to C(1) are slightly elongated and the C(5)—C(6) bond is short [1·357 (7) Å]. The C_{sp^3}—C_{sp^3} bonds within the tert-butyl groups are normal to within the accuracy of this determination, with a mean value of 1·54 Å.

The gem-di-tert-butyl system containing C(10), C(12) and C(16) shows evidence of severe overcrowding with C—C bond lengths of 1·604 (8) and 1·618 (7) Å and a C—C—C angle of 118·6 (4)°. Such distortion is normal in systems of this type, the geometry here being closely similar to that in (III) (van Koningsveld & van Meurs, 1977), in a di-tert-butylphenylmethane ligand described by van Meurs & van Koningsveld (1976) and in 1,1,3,3-tetra-tert-butylacetone (Lepicard, Berthou, Delettré, Laurent & Mornon, 1973).

In spite of the close non-bonded contact between O(11) and C(7) which was mentioned above, the

Table 2. Torsion angles (°) involving C(10)

	(a)	(b)	(c)
C(2)—C(1)—C(10)—O(11)	−12·2 (7)	−6·0	−7·9
C(6)—C(1)—C(10)—O(11)	169·4 (5)	174·1	172·6
C(2)—C(1)—C(10)—C(12)	102·0 (5)	105·4	103·7
C(2)—C(1)—C(10)—C(16)	−125·4 (5)	−119·4	−121·3
C(1)—C(10)—C(12)—C(13)	−178·7 (4)	−178·0	−177·0
C(1)—C(10)—C(12)—C(14)	57·0 (6)	57·4	58·4
C(1)—C(10)—C(12)—C(15)	−60·6 (4)	−60·6	−59·8
C(1)—C(10)—C(16)—C(17)	39·5 (4)	32·4	31·5
C(1)—C(10)—C(16)—C(18)	154·1 (4)	148·7	147·6
C(1)—C(10)—C(16)—C(19)	−83·8 (5)	−89·1	−90·8

(a) Results from this X-ray determination.
(b) Molecular-mechanics results for di-tert-butylphenylcarbinol.
(c) Molecular-mechanics results for di-tert-butyl-ortho-tolyl-carbinol.

C(1)—C(10)—O(11) angle of 105·6 (3)° is less than tetrahedral; it is, however, similar to the equivalent angle in (III) [104 (2)°]. That this is a consequence of overcrowding between the tert-butyl groups is supported by comparison with the less crowded tert-butylphenylcarbinol described by Baumgarten, McMahon, Elia, Gold, Day & Day (1976) where the angle is 109·5 (2)°.

All the protons in the tert-butyl groups are oriented in an approximately staggered way as is the whole C(12) tert-butyl group. It is noticeable that C(10)—C(12)—C(14) and C(10)—C(16)—C(19) are the largest of the angles at C(12) and C(16), reflecting the close approach of the C(14) and C(19) methyl groups. On the other hand, the C(10)—C(12)—C(15) and C(10)—C(12)—C(17) angles are less than tetrahedral, since the C(15) and C(17) methyl groups lie in a relatively uncrowded environment. Table 2 contains the torsion angles involving C(10) together with values calculated for di-tert-butylphenylcarbinol and di-tert-butyl-ortho-tolylcarbinol by the molecular-mechanics method using the MM2 program (Allinger, Chang, Glaser & Hönig, 1980) with Newton–Raphson minimization and using parameters for the benzene ring proposed by Beckhaus (1983). Bond lengths and angles from these calculations are deposited. In spite of certain systematic errors the molecular-mechanics calculations reproduce the experimental geometry quite satisfactorily. This is particularly so for the torsion angles around the C(1)—C(10), C(10)—C(12) and C(10)—C(16) bonds, the C(12) tert-butyl group being in a staggered conformation whereas the C(16) tert-butyl group is rotated approximately 24° out of the staggered position. Such a rotation is necessary to minimize repulsion between non-bonded H atoms across the space between the two tert-butyl groups, although it is normally distributed so that both tert-butyl groups are out of stagger but are (as here) non-parallel by some 25–30° (van Koningsveld & van Meurs, 1977; van Meurs & van Koningsveld, 1976).

There is also clear evidence of steric repulsion between O(11) and the C(7) methyl group with a C—O
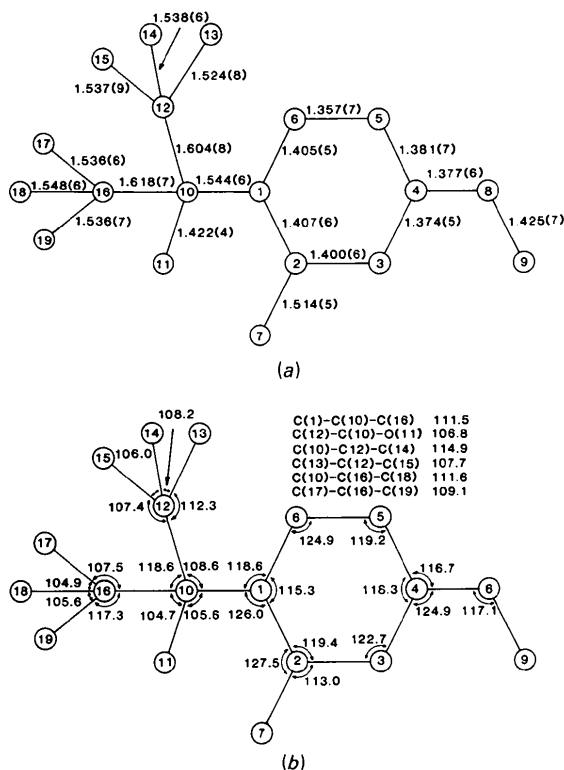

Fig. 2. Atomic-numbering scheme with (a) bond lengths in the molecule (Å) and (b) bond angles (°). E.s.d.'s of the angles are 0·4°.
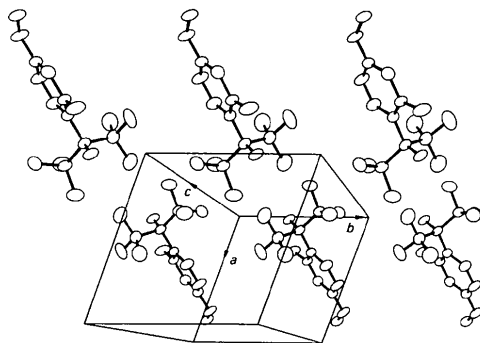
Fig. 3. The crystal structure.

contact distance of 2·611 (6) Å. This results in an opening of the C(10)—C(1)—C(2) and C(1)—C(2)—C(7) angles to 126·0 (3) and 127·5 (3)° respectively, closing of the endocyclic angle at C(1) to 115·3 (4)° and lengthening of the C(1)—C(10) bond. It is also noteworthy that the longer bond to *tert*-butyl, C(10)—C(16), is to the *tert*-butyl group which lies closer to the plane of the aromatic ring (see Table 2) and that this group makes the larger angle with the C(1)—C(10) bond.

The crystal structure, shown in Fig. 3, consists of sheets of molecules approximately parallel to the (100) planes in the crystal. Molecules within these sheets are stacked obliquely with the aromatic rings at approximately 45° to the sheets. All intramolecular contacts are of the van der Waals type.

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The Structure of Ethyl 5,6,7,8,9-Pentaacetoxy-2-amino-4-nitromethyl-D-*glycero*-D-*manno*-2-nonene-3-carboxylate, C$_{23}$H$_{34}$N$_2$O$_{14}$

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Abstract. $M_r = 562\cdot5$, orthorhombic, $P2_12_12_1$, $a = 17\cdot367$ (1), $b = 18\cdot176$ (1), $c = 9\cdot446$ (1) Å, $V = 2981\cdot7$ (3) Å^3, $Z = 4$, $D_m = 1\cdot26$, $D_x = 1\cdot25$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1\cdot5418$ Å, $\mu = 0\cdot95$ mm^{-1}, $F(000) = 1192$, $T = 300$ K, final $R = 0\cdot057$ for 2303 observed independent reflections. The configuration around the chiral centres C(8), C(7), C(6), C(5) and C(4) of the sugar chain is R, R, R, S and S, that is D-*glycero*-D-*manno*. The molecule has an intramolecular hydrogen bond between the N and O atoms of the amino and carbonyl groups, showing a chelate structure. Packing of the molecules is governed by normal van der Waals contacts.

Introduction. Crystals of the title compound were prepared by Gómez-Sánchez, Mancera, Rosado & Bellanato (1980). They reported an easy way to obtain 3-(pentaacetoxypentyl)pyrrole derivatives by a