compared with the corresponding projections for the BSX–DMF and BSX–DOX structures (Cobbledick & Small, 1973*b*,*c*). The difference in the three types of structure lies in the symmetry of packing of the units (2 BSX + 2 solvent), the determining factor being the difference in solvent-molecule profile involved. In the present structure the closest contacts between BSX and solvent are N(4)···O(14), 3·035 Å and N(6)···O(14), 2·844 Å compared with 2·891 and 2·969 Å in BSX–DMF and 3·116 and 3·199 Å in BSX–DOX.

Although many nitramine–solvent complexes have been reported to exist, only three other structure determinations have been reported. In the complex of hexahydro-1,3,5-trinitro-1,3,5-triazine and tetrahydrothiophene 1,1-dioxide (sulfolane) contacts between N (nitro) and O (sulfolane) of 3·02 and 3·13 Å are found (Haller, Brill & Rheingold, 1984). In the structures of the complexes of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane with *N*,*N*-dimethylformamide (Cobbledick & Small, 1975) and *N*-methyl-2-pyrrolidinone (Haller, Rheingold & Brill, 1985) no short contacts between solvent molecules and the nitramine are reported. In both of these structures the solvent molecules are disordered. Disorder is not uncommon in structures involving small solvent molecules; no ready explanation is offered for the disorder in the present structure.

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Structure of 4-*tert*-Butyl-2,2,6,6-tetramethylcyclohexanol

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Abstract. $C_{14}H_{28}O$, $M_r = 212{\cdot}38$, monoclinic, $P2_1/n$, $a = 6{\cdot}047\,(1)$, $b = 17{\cdot}224\,(2)$, $c = 26{\cdot}708\,(5)$ Å, $\beta = 91{\cdot}46\,(2)°$, $V = 2780{\cdot}8\,(8)$ Å^3, $Z = 8$, $D_x = 1{\cdot}014$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}06$ mm^{-1}, $F(000) = 952$, $T = 295$ K, $R = 0{\cdot}076$ for 902 observed diffractometer data. The structure has

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been solved by direct methods. The hydroxyl group is equatorial. The hydroxyl-group H atoms could not be located, presumably due to disorder as suggested by the results of molecular-mechanics calculations. The two independent molecules are in the chair conformation. They are linked into a polymeric chain by hydrogen bonding.

Introduction. In the framework of a research project on structural information provided by functional-group vibrations, the OH-stretching vibration has been extensively studied as it proves to be sensitive to slight structural variations in its environment (Lutz & van der Maas, 1985; Caballero Baza & van der Maas, 1985). The title compound is considered to be of particular interest since its hydroxyl group is heavily overcrowded by alkyl groups. This gives rise to considerable non-bonding intramolecular interactions and consequently to only limited intermolecular interactions.

Reduction of 4-*tert*-butyl-2,2,6,6-tetramethylcyclohexanone with $LiAlH_4$ in ether proved to be stereoselective as it yielded just one pure alcohol. The similarity between the ^{13}C chemical shifts of the alcohol and the corresponding ketone is evidence of the equatorial position of the hydroxyl group (Haines & Shandiz, 1981). The assignment of the hydroxyl-group position does not follow straightforwardly from the IR data as the equatorially as well as the axially positioned OH group is in the close vicinity of four β-methyl(ene) groups. Thus, we have determined the crystal structure of the title compound to establish its molecular conformation.

Experimental. Regularly grown needle-shaped crystals, dimensions $0{\cdot}2 \times 0{\cdot}2 \times 0{\cdot}8$ mm. Enraf–Nonius CAD-4 diffractometer; Mo $K\alpha$ radiation; cell measurements with setting angles of 23 reflections in θ range from 3 to 11°; $\omega/2\theta$ scan of width $(0{\cdot}80 + 0{\cdot}35\tan\theta)°$ and variable speed; $2\theta_{\max} = 40°$, $h = 0$ to 5, $k = 0$ to 16, $l = -25$ to 25; no systematic fluctuations in standard reflections $1\bar{1}2$ and $\bar{1}\bar{1}2$; 2712 independent reflections, 902 considered observed $[I > 2{\cdot}5\sigma(I)]$. Lp corrections, but no absorption correction.

The crystal was twinned by reticular pseudo-merohedry with coinciding zones for $h = 0$. From measurements of separated reflections it was established that the volume fraction of the larger twin was 0·698 (3). The intensities of the zeroth-layer reflections were rescaled accordingly. The geometrical relation $-a/(2c\cos\beta) = 4{\cdot}4$ indicates that zones for $h = 4$ and $h = 5$ contain partially coinciding non-equivalent reflections. As an approximation, this partial overlap was taken into account by the introduction of layer scale factors in the anisotropic refinement of F following the solution of the structure by direct methods (*SHELXS*84; Sheldrick, 1984).

A difference Fourier synthesis showed maxima at plausible positions for the aliphatic H atoms (methyl: 0·5, methylene: 0·45, methine: 0·35 e Å^{-3}). However, no information about the hydroxyl-group H atom was obtained. Refinement with unit weights was continued with methyl H atoms as rigid rotators and an overall isotropic temperature factor; remaining H atoms riding on their carrier atoms, also with a common isotropic thermal parameter. Convergence was reached at $R = 0{\cdot}076$, $wR = 0{\cdot}076$, $S = 2{\cdot}77$,* with 136 parameters; twinning apparently being responsible for the not so good quality of the data. Scaling layer factors with respect to $0kl$ reflections: 1·017, 1·018, 1·017, 1·048, 1·033 for $h = 1$, 2, 3, 4 and 5, respectively. $\Delta/\sigma = 0{\cdot}6$ (max.); final remaining electron densities within 0·12 e Å^{-3}. Scattering factors were taken from Cromer & Mann (1968) for C and O atoms and from Stewart, Davidson & Simpson (1965) for H atoms.

Calculations carried out on the CDC Cyber 855 computer of the University of Utrecht with programs *SHELX*76 (Sheldrick, 1976), *APOLLO* (data reduction and correction by A. L. Spek) and *EUCLID* [calculation of geometrical data and illustrations (Spek, 1982)].

Discussion. Positional and isotropic equivalent thermal parameters are given in Table 1. Perspective views of the independent molecules (H atoms omitted for reasons of clarity) are shown in Fig. 1 together with their atomic numbering schemes. Bond lengths and bond angles are shown in Table 2. The two independent molecules, both in the chair conformation with the OH groups in equatorial positions and their *tert*-butyl groups and methyl groups practically in the idealized staggered conformations, are very much alike.

The rather loose packing of the structure can be inferred from Fig. 2, which shows the projection along the *a* axis. It exhibits a lot of pseudosymmetry with pseudo-glide-plane symmetry in the **a** and **c** directions.

The two independent molecules form the asymmetric unit of a chain running parallel to the direction of the *a* axis and held together by hydrogen-bond interactions [O(1)···O(2): 3·12 (2); O(2)···O(1)(1+*x*, *y*, *z*): 3·18 (2) Å]. In principle, there are two opposite directions possible for the H bonding, which cannot be discriminated by the present crystal-structure analysis as the H atoms concerned could not be located. Therefore, molecular-mechanics calculations were performed, both on the isolated molecule and on two molecules with their crystal environment simulated

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43837 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

	x	y	z	U_{eq}*(Å^2)
Molecule I				
O(1)	0·682 (2)	0·3066 (5)	0·3671 (4)	0·065 (5)
C(1)	0·745 (3)	0·3844 (9)	0·3709 (6)	0·063 (8)
C(2)	0·704 (2)	0·4313 (8)	0·3222 (5)	0·046 (6)
C(3)	0·799 (2)	0·5141 (7)	0·3276 (5)	0·044 (6)
C(4)	0·731 (2)	0·5573 (6)	0·3744 (5)	0·041 (6)
C(5)	0·799 (2)	0·5086 (6)	0·4200 (5)	0·043 (6)
C(6)	0·701 (2)	0·4246 (7)	0·4205 (5)	0·047 (6)
C(7)	0·816 (3)	0·391 (1)	0·2783 (6)	0·076 (6)
C(8)	0·451 (2)	0·4347 (9)	0·3092 (6)	0·060 (6)
C(9)	0·821 (2)	0·6419 (7)	0·3761 (6)	0·050 (6)
C(10)	0·733 (3)	0·681 (1)	0·4235 (6)	0·080 (10)
C(11)	1·073 (2)	0·6459 (9)	0·3783 (7)	0·070 (8)
C(12)	0·726 (3)	0·688 (1)	0·3311 (6)	0·080 (8)
C(13)	0·819 (3)	0·3810 (9)	0·4631 (5)	0·064 (6)
C(14)	0·450 (2)	0·4271 (9)	0·4314 (6)	0·053 (6)
Molecule II				
O(2)	0·187 (2)	0·2554 (5)	0·3681 (4)	0·063 (4)
C(21)	0·270 (2)	0·1765 (7)	0·3712 (5)	0·033 (5)
C(22)	0·200 (2)	0·1395 (7)	0·4214 (5)	0·057 (6)
C(23)	0·304 (3)	0·0580 (7)	0·4232 (5)	0·061 (6)
C(24)	0·238 (2)	0·0081 (6)	0·3776 (5)	0·032 (5)
C(25)	0·311 (2)	0·0495 (7)	0·3300 (5)	0·053 (6)
C(26)	0·210 (2)	0·1308 (7)	0·3232 (5)	0·050 (6)
C(27)	0·310 (3)	0·1890 (10)	0·4637 (6)	0·077 (8)
C(28)	−0·053 (2)	0·1380 (10)	0·4286 (7)	0·063 (6)
C(29)	0·330 (2)	−0·0770 (7)	0·3815 (5)	0·047 (6)
C(30)	0·240 (3)	−0·1157 (9)	0·4288 (6)	0·067 (8)
C(31)	0·247 (3)	−0·1242 (9)	0·3357 (6)	0·070 (10)
C(32)	0·583 (2)	−0·0800 (10)	0·3842 (8)	0·073 (8)
C(33)	0·326 (3)	0·1730 (10)	0·2800 (5)	0·064 (6)
C(34)	−0·037 (2)	0·1260 (10)	0·3099 (7)	0·061 (8)

* $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

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

Molecule I		Molecule II	
O(1)–C(1)	1·40 (2)	O(2)–C(21)	1·45 (2)
C(1)–C(2)	1·55 (2)	C(21)–C(22)	1·55 (2)
C(1)–C(6)	1·52 (2)	C(21)–C(26)	1·54 (2)
C(2)–C(3)	1·54 (2)	C(22)–C(23)	1·54 (2)
C(2)–C(7)	1·53 (2)	C(22)–C(27)	1·55 (2)
C(2)–C(8)	1·56 (2)	C(22)–C(28)	1·55 (2)
C(3)–C(4)	1·52 (2)	C(23)–C(24)	1·54 (2)
C(4)–C(5)	1·53 (2)	C(24)–C(25)	1·53 (2)
C(4)–C(9)	1·56 (2)	C(24)–C(29)	1·57 (2)
C(5)–C(6)	1·56 (2)	C(25)–C(26)	1·54 (2)
C(6)–C(13)	1·53 (2)	C(26)–C(33)	1·55 (2)
C(6)–C(14)	1·55 (2)	C(26)–C(34)	1·53 (2)
C(9)–C(11)	1·53 (2)	C(29)–C(30)	1·54 (2)
C(9)–C(12)	1·54 (2)	C(29)–C(31)	1·54 (2)
C(9)–C(10)	1·54 (2)	C(29)–C(32)	1·53 (2)
O(1)–C(1)–C(2)	114 (1)	O(2)–C(21)–C(22)	109 (1)
O(1)–C(1)–C(6)	116 (1)	O(2)–C(21)–C(26)	111 (1)
C(2)–C(1)–C(6)	118 (1)	C(22)–C(21)–C(26)	116 (1)
C(1)–C(2)–C(3)	111 (1)	C(21)–C(22)–C(23)	106 (1)
C(1)–C(2)–C(7)	110 (1)	C(21)–C(22)–C(27)	106 (1)
C(1)–C(2)–C(8)	110 (1)	C(21)–C(22)–C(28)	114 (1)
C(3)–C(2)–C(7)	109 (1)	C(23)–C(22)–C(27)	108 (1)
C(3)–C(2)–C(8)	110 (1)	C(23)–C(22)–C(28)	113 (1)
C(7)–C(2)–C(8)	107 (1)	C(27)–C(22)–C(28)	109 (1)
C(2)–C(3)–C(4)	115 (1)	C(22)–C(23)–C(24)	113 (1)
C(3)–C(4)–C(5)	108·3 (9)	C(23)–C(24)–C(25)	109 (1)
C(3)–C(4)–C(9)	112 (1)	C(23)–C(24)–C(29)	113 (1)
C(5)–C(4)–C(9)	114 (1)	C(25)–C(24)–C(29)	112 (1)
C(4)–C(5)–C(6)	115 (1)	C(24)–C(25)–C(26)	114 (1)
C(1)–C(6)–C(5)	110 (1)	C(21)–C(26)–C(25)	106 (1)
C(1)–C(6)–C(13)	110 (1)	C(21)–C(26)–C(33)	106 (1)
C(1)–C(6)–C(14)	112 (1)	C(21)–C(26)–C(34)	115 (1)
C(5)–C(6)–C(13)	107 (1)	C(25)–C(26)–C(33)	109 (1)
C(5)–C(6)–C(14)	110 (1)	C(25)–C(26)–C(34)	111 (1)
C(13)–C(6)–C(14)	108 (1)	C(33)–C(26)–C(34)	108 (1)
C(4)–C(9)–C(10)	108 (1)	C(24)–C(29)–C(30)	109 (1)
C(4)–C(9)–C(11)	113 (1)	C(24)–C(29)–C(31)	109 (1)
C(4)–C(9)–C(12)	110 (1)	C(24)–C(29)–C(32)	113 (1)
C(10)–C(9)–C(11)	108 (1)	C(30)–C(29)–C(31)	108 (1)
C(10)–C(9)–C(12)	107 (1)	C(30)–C(29)–C(32)	109 (1)
C(11)–C(9)–C(12)	111 (1)	C(31)–C(29)–C(32)	109 (1)

using the program *MM2HB* (Kroon-Batenburg & Kanters, 1983). First the energy was calculated as a function of the hydroxyl-group conformation by using the driver option (Allinger & Yuh, 1980) and the result is shown in Fig. 3. Two equivalent global energy minima are found near the anticlinal conformation ($\varphi = 0°$ corresponds to an exact anticlinal conformation), while the synclinal conformation corresponds to a subsidiary minimum, being 3·3 kJ mol^{-1} higher. Noteworthy is the flattened course of the curve ranging from −40 to +40°. Thus, in view of the rather low barrier at 0° it is to be expected that, at least at room temperature, the H atom is oscillating between the two global minima.

In order to compare the two alternative H-bond schemes, molecular-mechanics calculations were also carried out on a part of the polymeric chain simulated

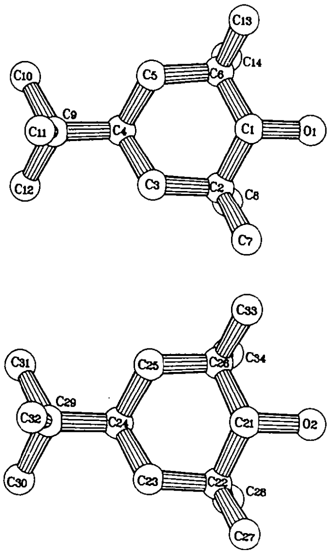

Fig. 1. *PLUTO* (*EUCLID* version) drawing of 4-*tert*-butyl-2,2,6,6-tetramethylcyclohexanol illustrating the molecular conformation and the adopted numbering scheme.

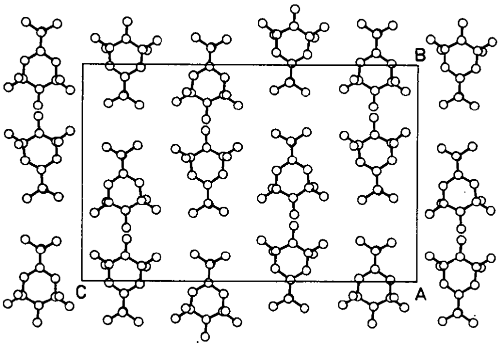

Fig. 2. Projection of the structure down [100].

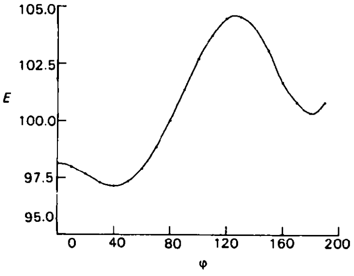

Fig. 3. The variation of the energy E (in kJ mol^{-1}) with the torsion angle φ (H—O—C—H) (°) as calculated by molecular mechanics.

by two independent molecules each connected with a water molecule that substitutes for a cyclohexanol molecule. The H-bond scheme in which the donor H atoms are anticlinal appears to be 5·0 kJ mol^{-1} lower in energy than that with the H atoms in the synclinal conformation. Therefore, also in view of the calculations on the isolated molecule it seems obvious that the failure to detect the hydroxyl-group H-atom positions is due to (dynamic) disorder.

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Stereochemical Studies. 122.* Structures of Two Crystal Modifications of 5,8-Methano-*cis-transoid-cis*-tetrahydro-4*H*-3,1-benzoxazine-2(1*H*)-thione

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Abstract. $C_9H_{11}NOS$, $M_r = 181{\cdot}26$. The title compound has two monoclinic modifications. Modification I: $P2_1/c$, $a = 7{\cdot}684\,(4)$, $b = 9{\cdot}488\,(2)$, $c = 12{\cdot}344\,(6)$ Å, $\beta = 101{\cdot}93\,(3)°$, $V = 880{\cdot}5\,(7)$ Å^3, $Z = 4$, $D_x = 1{\cdot}367$ Mg m^{-3}, m.p. 424–425 K, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}27$ mm^{-1}, $F(000) = 384$, $T = 293$ K, final $R = 0{\cdot}060$ for 931 observed reflections. Modification II: $P2_1/n$, $a = 12{\cdot}615\,(4)$, $b = 7{\cdot}296\,(2)$, $c = 10{\cdot}544\,(5)$ Å, $\beta = 112{\cdot}89\,(3)°$, $V = 894{\cdot}0\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}347$ Mg m^{-3}, m.p. 419–421 K, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 2{\cdot}67$ mm^{-1}, $F(000) = 384$, $T = 293$ K, final $R = 0{\cdot}071$ for 1238 observed reflections. The molecules in the two modifications have similar bond lengths and angles and form dimers connected through N—H···S hydrogen bonds with lengths H···S = 2·45, N···S = 3·391 (5) Å (I), H···S = 2·27, N···S = 3·317 (4) Å (II) and angles 145 (4) and 163 (4)°, respectively. The 3,1-benzoxazine ring adopts an E_4 envelope conformation in both modifications.

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* Part 121: Richter, Fülöp, Bernáth & Pflegel (1987).

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