Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{max} = 73°$
$\omega/2\theta$ scans	$h = 0 \rightarrow 9$
Absorption correction: none	$k = 0 \rightarrow 10$
2140 measured reflections	$l = 0 \rightarrow 35$
2140 independent reflections	3 standard reflections
2030 reflections with	every 100 reflections
$I > 2\sigma(I)$	intensity decay: <1%

Refinement

Refinement on F^2	Extinction correction:
$R[F^2 > 2\sigma(F^2)] = 0.059$	*SHELXL*93
$wR(F^2) = 0.176$	Extinction coefficient:
$S = 1.008$	0.0040 (12)
2137 reflections	Scattering factors from
215 parameters	*International Tables for*
H atoms: see below	*Crystallography* (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.0708P)^2]$	Absolute structure:
where $P = (F_o^2 + 2F_c^2)/3$	Flack (1983)
$(\Delta/\sigma)_{max} = 0.003$	Flack parameter = 0.1 (4)
$\Delta\rho_{max} = 0.357$ e Å^{-3}	
$\Delta\rho_{min} = -0.249$ e Å^{-3}	

Table 1. *Selected torsion angles (°)*

C1—O1—C0'—N1	175.6 (3)
O1—C0'—N1—C1A	−173.7 (3)
C0'—N1—C1A—C1'	−119.8 (3)
N1—C1A—C1B—C1G	−58.9 (4)
C1A—C1B—C1G—C1D2	−60.5 (6)
C1A—C1B—C1G—C1D1	174.4 (3)
N1—C1A—C1'—N2	0.9 (4)
C1A—C1'—N2—C2A	169.3 (3)
C1'—N2—C2A—C2'	−139.6 (3)
N2—C2A—C2B—O2G	73.2 (3)
N2—C2A—C2B—C2G	−51.5 (3)

Table 2. *Selected hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N1···O2G[i]	0.86	2.40	3.056 (3)	134
N3—H2N3···O1'[ii]	0.86	2.17	2.941 (4)	163
O2G···O2'[i]	—	—	2.750 (4)	—

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, -z$; (ii) $x - \frac{1}{2}, \frac{3}{2} - y, -z$.

All H-atom positions, except that of O2G, were geometrically fixed and allowed to ride on the corresponding non-H atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *SDP* (Frenz, 1978). Data reduction: *CAD-4 Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1997). Software used to prepare material for publication: *SHELXL* and *PARST* (Nardelli, 1995).

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Dineopentylprehnitene (1,2,3,4-tetramethyl-5,6-dineopentylbenzene) at 296 and 223 K

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Abstract

The title substance, $C_{20}H_{34}$, crystallized in the centrosymmetric space group $C2/c$ with a single molecule as the asymmetric unit. The molecule is quite crowded intramolecularly, and has a notably non-planar benzene ring. There is, however, virtually no intermolecular crowding.

Comment

Interest in dineopentylprehnitene, (I), is associated with its potential for substantial crowding in the crystalline state. It crystallized in the centrosymmetric space group

(I)
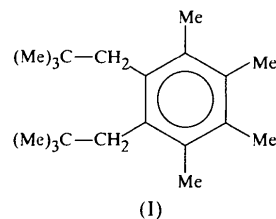
*C*2/*c* with a single molecule as the asymmetric unit. The refined molecules at 296 and 223 K are shown in Fig. 1 together with the numbering scheme. Not surprisingly, as can be seen in Fig. 1 and the packing diagram, Fig. 2, the neopentyl groups are oriented strongly out of the nominal benzene-ring plane, and in opposite directions. [Newman *et al.* (1964) were able to make a model of the molecule with both neopentyl groups on the same side of the benzene ring plane, though they conjectured that such an arrangement was much less likely to exist than the arrangement found here.]

With respect to intramolecular structure, the molecules are indeed crowded, as measured by H···H closest approaches. At 296 K, nine H···H distances
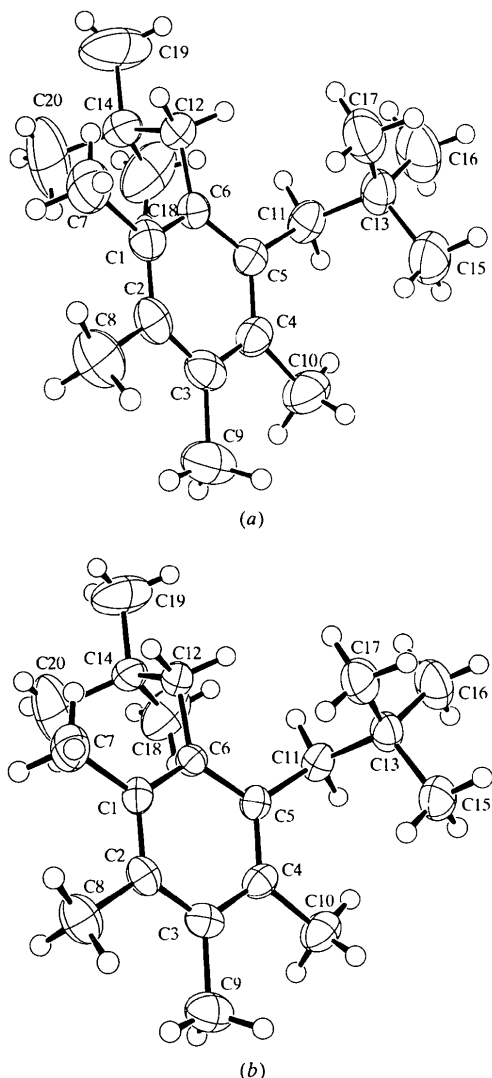

Fig. 2. *ORTEP*II (Johnson, 1976) stereo-packing diagram of the title substance at 223 K. Displacement ellipsoids are drawn for 50% probability. H atoms have been omitted for clarity.

(*a*)

(*b*)

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of dineopentylprehnitene: (*a*) at 296 K; (*b*) at 223 K, showing the numbering schemes. Displacement ellipsoids are drawn at 50% probability for non-H atoms; circles of arbitrary small radius depict H atoms.
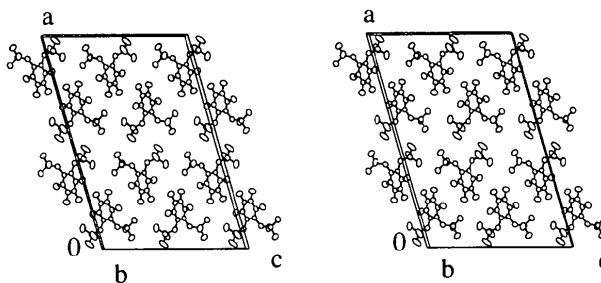
(for H atoms not bonded to the same C atom) fall short of the Bondi (1964) van der Waals radius sum by amounts greater than 0.15 Å, with four having deficits from 0.38 to 0.58 Å. Similarly, at 223 K there are six such H···H distances, with four having deficits from 0.47 to 0.57 Å. The four H···H pairs exhibiting the largest deficits are identical at the two temperatures. By type, and in decreasing order, they are H(ring methyl)···H(neopentyl), H(ring methyl)···H(neopentyl), H(neopentyl)···H(neopentyl) and H(ring methyl)···H(ring methyl) (H7*A*···H12*B*, H10*A*···H11*A*, H11*B*···H12*A*, and H8*C*···H9*A*, respectively). Moreover, very similar patterns of such H···H deficits are found when the H atoms are fully refined: at 296 K, there are then nine such deficits (which range from 0.16 to 0.45 Å), while at 223 K, there are then five such (which range from 0.26 to 0.53 Å). Another notable feature of the molecular disposition is the substantial rumpling of the benzene ring. The average deviation of the ring-C atoms from the best-fit plane describing them is 0.030 (15) Å at 296 K, and 0.029 (18) Å at 223 K, while the maximum deviations are 0.048 (3) and 0.046 (2) Å, respectively. These deviations are approximately ten times as large as the corresponding values for 'normal' benzene rings (see below, for example).

With respect to the crystalline packing (Fig. 2), however, this is one of the least crowded structures we have determined. At 296 K, only three intermolecular close approaches have distances less than the sum of the corresponding Bondi radii; the largest deficit is 0.08 Å [C2···H8*B*[i]; symmetry code: (i) $\frac{1}{2} - x$, $\frac{1}{2} - y$, $-z$]. At 223 K, there are only two such intermolecular close approaches; both have deficits of 0.12 Å (C2···H8*B*[i] and H8*B*···H8*B*[i]).

For structural comparisons, the somewhat similar hydrocarbon 1,4-bis-(α-ethylpropyl)benzene (Kravers *et al.*, 1979) appears appropriate. With respect to intramolecular features, its benzene ring is much more nearly planar, with the maximum deviation of a ring-C atom from the best-fit ring plane being 0.004 (4) Å. Also, there is much less intramolecular crowding than described above for the title molecule. Only two H···H

distances (as above) are less than the sum of Bondi radii, the largest deficit being 0.29 Å. The intermolecular close approaches, however, are quite comparable for the two substances. For the latter structure, only a single intermolecular approach is less than the corresponding Bondi radius sum. Its deficit is 0.12 Å, just matching the greatest deficit determined for the title structure.

Selected distances and angles in the title molecule at 296 and 223 K are given in Tables 1 and 2. All distances and angles fall within normal ranges. The close agreement between corresponding distances and angles at the two temperatures is exemplified by comparison of the two sets of 34 torsion angles involving four C atoms: the greatest difference is 1.4°, while the average difference is 0.6°.

Hindered rotation about the C_{Ar}—CH_2 bonds in dineopentylprehnitene in solution, as studied by NMR methods, is described by Dix et al. (1966).

Experimental

Dineopentylprehnitene was obtained from a sample in the chemical collection of Dr M. S. Newman. Its synthesis is described by Newman et al. (1964). Suitable crystals were cut to provide the room-temperature and low-temperature experimental samples.

Compound (I) at 296 K
Crystal data

$C_{20}H_{34}$	Mo $K\alpha$ radiation
$M_r = 274.49$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$C2/c$	reflections
$a = 30.559\,(3)$ Å	$\theta = 10.2–16.3°$
$b = 6.363\,(3)$ Å	$\mu = 0.051$ mm^{-1}
$c = 19.744\,(4)$ Å	$T = 296$ K
$\beta = 105.82\,(1)°$	Cut column
$V = 3693\,(2)$ Å^3	$0.42 \times 0.31 \times 0.27$ mm
$Z = 8$	Colorless
$D_x = 0.987$ Mg m^{-3}	
$D_m = 0.984\,(8)$ Mg m^{-3}	
D_m measured by pycnometry	

Data collection

AFC-5S diffractometer	$\theta_{max} = 27.56°$
ω scans	$h = 0 \rightarrow 39$
Absorption correction: none	$k = 0 \rightarrow 8$
4754 measured reflections	$l = -25 \rightarrow 24$
4282 independent reflections	6 standard reflections
1538 reflections with	every 150 reflections
$I > 2\sigma_I$	intensity decay: 30.6%
$R_{int} = 0.052$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = < 0.01$
$R(F) = 0.086$	$\Delta\rho_{max} = 0.48$ e Å^{-3}
$wR(F^2) = 0.112$	$\Delta\rho_{min} = -0.51$ e Å^{-3}
$S = 1.54$	Extinction correction: none

4282 reflections
181 parameters
H atoms fixed (see text)
$w = 1/\sigma^2(F^2)$

Scattering factors from Stewart et al. (1965) for H, Creagh & McAuley (1992) for C

Table 1. *Selected geometric parameters (Å, °) for (I) at 296 K*

C5—C11	1.520 (3)	C13—C16	1.534 (4)
C6—C12	1.528 (3)	C13—C17	1.511 (4)
C11—C13	1.552 (4)	C14—C18	1.507 (4)
C12—C14	1.562 (4)	C14—C19	1.505 (4)
C13—C15	1.535 (4)	C14—C20	1.504 (4)
C5—C11—C13	116.7 (2)	C11—C13—C17	112.3 (3)
C6—C12—C14	116.5 (2)	C12—C14—C18	111.9 (3)
C11—C13—C15	111.7 (3)	C12—C14—C19	108.1 (3)
C11—C13—C16	107.6 (3)	C12—C14—C20	112.8 (3)

Compound (I) at 223 K
Crystal data

$C_{20}H_{34}$	Mo $K\alpha$ radiation
$M_r = 274.49$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$C2/c$	reflections
$a = 30.439\,(2)$ Å	$\theta = 10.3–16.4°$
$b = 6.314\,(3)$ Å	$\mu = 0.055$ mm^{-1}
$c = 19.663\,(3)$ Å	$T = 223$ K
$\beta = 106.06\,(1)°$	Cut plate
$V = 3632\,(2)$ Å^3	$0.35 \times 0.35 \times 0.27$ mm
$Z = 8$	Colorless
$D_x = 1.004$ Mg m^{-3}	
D_m not measured	

Data collection

AFC-5S diffractometer	$\theta_{max} = 27.56°$
ω scans	$h = 0 \rightarrow 39$
Absorption correction: none	$k = 0 \rightarrow 8$
4818 measured reflections	$l = -25 \rightarrow 24$
4194 independent reflections	6 standard reflections
2064 reflections with	every 150 reflections
$I > 2\sigma_I$	intensity decay: 8.4%
$R_{int} = 0.080$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = < 0.01$
$R(F) = 0.072$	$\Delta\rho_{max} = 0.44$ e Å^{-3}
$wR(F^2) = 0.107$	$\Delta\rho_{min} = -0.43$ e Å^{-3}
$S = 1.80$	Extinction correction: none
4194 reflections	Scattering factors from
181 parameters	Stewart et al. (1965) for
H atoms fixed (see text)	H, Creagh & McAuley
$w = 1/\sigma^2(F^2)$	(1992) for C

Table 2. *Selected geometric parameters (Å, °) for (I) at 223 K*

C5—C11	1.528 (3)	C13—C16	1.530 (3)
C6—C12	1.530 (3)	C13 C17	1.523 (4)
C11—C13	1.562 (3)	C14—C18	1.516 (4)
C12—C14	1.563 (3)	C14—C19	1.504 (3)
C13—C15	1.527 (3)	C14—C20	1.520 (3)
C5—C11—C13	116.2 (2)	C11—C13—C17	111.8 (2)
C6—C12—C14	116.5 (2)	C12—C14—C18	111.8 (2)
C11—C13—C15	111.7 (2)	C12—C14—C19	108.2 (2)
C11—C13—C16	107.5 (2)	C12—C14—C20	112.1 (2)

The low temperature was obtained with an MSC low-temperature apparatus; the stated temperature, 223 K, is accurate to ± 2 K. Scan widths were $(1.60 + 0.35\tan\theta)°$ in ω, with background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. The intensity decays were treated as linear. As decay at 296 K was so large (very likely owing principally to sublimation), the 223 K study was performed. Ultimately, however, both structures proved to be fully satisfactory. The Laue group assignments, systematic absences and centrosymmetric intensity statistics indicated space group $C2/c$ (No. 15) for both sets of data; since the refinements proceeded well, it was adopted. Difference Fourier methods were used to locate the initial H-atom positons and the H atoms were then refined isotropically. Subsequently, the H atoms were made canonical, with C—H = 0.98 Å and U_{iso} = 1.2 × U_{eq} of the attached C atom. Extinction coefficients, which were predicted to be negative in the later least-squares cycles, were not included in the models. The maximum positive residual peaks are located ~0.8 and 1.2 Å, respectively, from C12; similarly, the maximum negative peaks are located ~1.1 and 1.4 Å from C14.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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6,6'-Dimethoxy-3,3',5,5'-tetramethyl-biphenyl-2,2'-dimethanol

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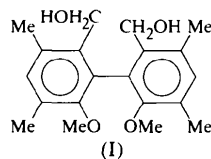
Abstract

The title compound, $C_{20}H_{26}O_4$, crystallized in the centrosymmetric space group $P2_1/c$ with a single molecule as the asymmetric unit. The two hydroxyl-H atoms are ordered and are involved in hydrogen bonds whose $O_D \cdots O_A$ distances are 2.807 (2) and 2.805 (2) Å; one of these bonds is intramolecular. The intramolecular dihedral angle between the ring planes (twist angle) is 87.3 (1)°.

Comment

This report on 6,6'-dimethoxy-3,3',5,5'-tetramethylbiphenyl-2,2'-dimethanol, (I), is one of a series on hydrogen bonding in substituted biphenyls which includes, most recently, 6,6'-dimethylbiphenyl-2,2'-dicarboxylic acid (Gerkin, 1998). The title compound crystallized in

(I)

the centrosymmetric space group $P2_1/c$ with a single molecule as the asymmetric unit. The refined molecule is shown in Fig. 1 together with the numbering scheme. Each of the hydroxyl-H atoms is ordered and is involved in a hydrogen bond. Geometric details of these two hydrogen bonds are given in Table 2. Hydrogen-bond graph-set analysis (Bernstein *et al.*, 1995) gives, in the order of Table 2, first-level graphs $C(9)$, a chain propagating in the c direction which links molecules of space group symmetry types 1 and 4 or 2 and 3, and $S(9)$, an intramolecular ring; the basic second-level set is $C_2^2(4)[S(9)]$, a chain of rings with the chain propagating in the c direction. These hydrogen bonds are shown in Fig. 2.

Since the O atoms of the methoxy groups (O3 and O4) are not involved with the hydroxyl-H atoms, significant C—H$\cdots$O interactions involving them may be expected. Three such interactions having H$\cdots O_A$ dis-