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Acta Cryst. (1990). C**46**, 919–922

Structures of Three Related Biphenyl Compounds: 4,4′-Biphenyldiol, 3,3′,5,5′-Tetra-*tert*-butyl-4,4′-biphenyldiol, and 3,3′,5,5′-Tetra-*tert*-butyl-1,1′-bicyclohexa-2,5-dienylidene-4,4′-dione

BY MARGO A. JACKISCH, FRANK R. FRONCZEK, C. CECIL GEIGER, PAUL S. HALE, WILLIAM H. DALY AND LESLIE G. BUTLER*

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, USA

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Abstract. 4,4′-Biphenyldiol (I), $C_{12}H_{10}O_2$, $M_r = 186{\cdot}2$, monoclinic, $P2_1/c$, $a = 10{\cdot}5512\,(9)$, $b = 5{\cdot}359\,(2)$, $c = 7{\cdot}9939\,(8)$ Å, $\beta = 95{\cdot}736\,(8)°$, $V = 449{\cdot}7\,(6)$ Å^3, $Z = 2$, $D_x = 1{\cdot}375$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54184$ Å, $\mu = 7{\cdot}13$ cm^{-1}, $F(000) = 196$, $T = 299\,(1)$ K, $R = 0{\cdot}037$ for 738 reflections with $I > 3\sigma(I)$ (919 unique observations). This is a redetermination; the original study was based on visually estimated film data, with $R = 0{\cdot}20$ for 240 observations [Akhmed, Farag & Amin (1971). *J. Struct. Chem.* (*USSR*), **12**, 676–677; *Zh. Strukt. Khim.* **12**, 738–739]. The molecule is centrosymmetric, and the biphenyl ring system is planar, with average deviation 0·002 (1) Å. The O atom lies 0·013 (1) Å out of this plane, and the hydroxy H atom lies 0·26 (2) Å out of the plane. The central C—C bond has length 1·4954 (11) Å, and the C—O bond 1·3845 (12) Å. Chains of hydrogen bonds along the *b* direction exist, with O···O 2·8940 (8) Å and a 167 (2)° angle at H. 3,3′,5,5′-Tetra-*tert*-butyl-4,4′-biphenyldiol (II), $C_{28}H_{42}O_2$, $M_r = 410{\cdot}6$, orthorhombic, $Fdd2$, $a = 20{\cdot}719\,(3)$, $b = 19{\cdot}905\,(3)$, $c = 12{\cdot}836\,(2)$ Å, $V = 5293{\cdot}7\,(14)$ Å^3, $Z = 8$, $D_x = 1{\cdot}030$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54184$ Å, $\mu = 4{\cdot}49$ cm^{-1}, $F(000) = 1808$, $T = 298\,(1)$ K, $R = 0{\cdot}032$ for 1031 reflections with $I > 3\sigma(I)$ (1457 unique observations). The long axis of the molecule lies along a twofold axis. The two phenyl rings are twisted slightly with respect to each other, forming a dihedral angle of 159·4 (2)°. One of the rings exhibits out-of-plane deviations of 0·010 (2) Å for its off-axis atoms, while these deviations are 0·001 (2) Å for the other ring. The central C—C bond of the molecule has length 1·486 (4) Å, with C—O bond lengths 1·385 (4) and 1·391 (3) Å. The C—C bonds of the *tert*-butyl groups are 1·527 (3)–1·545 (4) Å in length. Each of the hydroxy H atoms is disordered into two equally populated positions. 3,3′,5,5′-Tetra-*tert*-butyl-1,1′-bicyclohexa-2,5-dienylidene-4,4′-dione (III), $C_{28}H_{40}O_2$, $M_r = 408{\cdot}6$, triclinic, $P\bar{1}$, $a = 6{\cdot}1004\,(10)$, $b = 10{\cdot}4197\,(11)$, $c = 10{\cdot}5260\,(14)$ Å, $\alpha = 81{\cdot}490\,(8)$, $\beta = 75{\cdot}991\,(11)$, $\gamma = 81{\cdot}582\,(14)°$, $V = 637{\cdot}8\,(2)$ Å^3, $Z = 1$, $D_x = 1{\cdot}064$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54184$ Å, $\mu = 4{\cdot}65$ cm^{-1}, $F(000) = 224$, $T = 295\,(1)$ K, $R = 0{\cdot}045$ for 2199 reflections with $I > 3\sigma(I)$ (2628 unique observations). This determination confirms the recent determination of Khan, Osman & Tuck [*Acta Cryst.* (1986), **C42**, 1399–1402], which was based on 1131 observed data with Mo $K\alpha$ radiation. Although the present results represent a doubling of the precision, the agreement between the two determinations is excellent, with the largest single difference in a bond distance being only 0·008 Å (2σ).

Experimental. Intensity data for all three structures were obtained on a Enraf–Nonius CAD-4 diffractometer with a graphite incident-beam monochromator using Cu $K\alpha$ radiation. The ω–2θ scans were made at variable scan rates. Absorption corrections were based on ψ scans. All structures were solved by direct methods using *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The structures were refined by full-matrix least squares with Enraf–Nonius *SDP*

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* To whom correspondence should be addressed.

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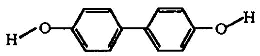
Table 1. *Experimental details* (I), (II), (III)

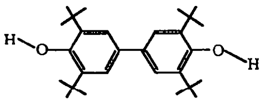
	(I)	(II)	(III)
Crystal	Colorless	Yellow	Yellowish-red transmitted; metallic purple reflected
Dimensions	0·05 × 0·24 × 0·53 mm	0·13 × 0·23 × 0·33 mm	0·10 × 0·30 × 0·55 mm
Unit cell	25 reflections $25 < \theta < 30°$	25 reflections $22 < \theta < 27°$	25 reflections $20 < \theta < 30°$
Standards	500, 040, 002	800, 220, 004	200, 020, 004
R_{int}	0·014	0·018	0·011
Corrections	Background, Lorentz–polarization Empirical absorption [0·8616–0·9963 on (I)]	Background, Lorentz–polarization Empirical absorption [0·9346–0·9941 on (I)]	Background, Lorentz–polarization Empirical absorption [0·8861–0·9978 on (I)] Linear decay [0·9825–1·0968 on (I)]
Scan rates (° min^{-1})	0·75–3·30	0·46–3·30	0·37–3·30
2θ range (°)	4–150 (full sphere)	4–150 (2 octants)	4–150 (full sphere)
hkl	$h = -13$ to 13 $k = -6$ to 6 $l = -10$ to 10	$h = 0$ to 24 $k = 0$ to 24 $l = -16$ to 16	$h = -7$ to 7 $k = -13$ to 13 $l = -13$ to 13
Reflections	3684 total 919 unique 738 with $I > 3\sigma(I)$	2912 total 1457 unique 1031 with $I > 3\sigma(I)$	5266 total 2628 unique 2199 with $I > 3\sigma(I)$
Parameters refined	85	139	217
R, wR, R (all)	0·037, 0·052, 0·044	0·035, 0·037, 0·055	0·045, 0·070, 0·051
Goodness of fit, S	2·373	1·531	3·641
Maximum shift/e.s.d.	0·03	0·01	0·02
$\Delta\rho$ (e Å^{-3})	0·16, −0·14	0·13, −0·10	0·24, −0·26
H atoms	Refined, iso.	Fixed contributions	Refined, iso.
Extinction	1·88 (9) × 10^{-5}	5·2 (2) × 10^{-5}	1·36 (4) × 10^{-5}

(Frenz, 1985), where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight, w, was defined as $4F_o^2\mathrm{Lp}^2/[S^2(C + R^2B) + (0{\cdot}020F_o^2)^2]$, S = scan rate, C = integrated count, R = scan time/background time, and B = background count. Atomic scattering factors, including those for anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974). C and O atoms were refined anisotropically. H atoms were located in difference maps and were refined isotropically for (I) and (III). They were placed in calculated positions for (II), with C—H distance 0·95 Å and $B = 1{\cdot}3\ B_{eq}$ for the bonded C atom. Each of the OH H atoms in (II) is disordered into two 50% occupied sites; these atoms were included as fixed contributions.

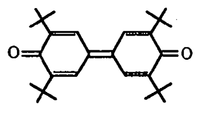
Compound (I) was purchased from Aldrich and recrystallized from ethanol/water (1/5). Details of the data collection and structural refinement are given in Table 1. Final positional and equivalent isotropic



(I)



(II)



(III)

Table 2. *Positional parameters and their e.s.d.'s* (I)

	x	y	z	B_{eq}(Å^2)*
O	0·44802 (7)	−0·0077 (2)	0·2479 (1)	4·00 (2)
C1	0·06798 (8)	−0·0001 (2)	0·0369 (1)	2·27 (2)
C2	0·11630 (9)	−0·1876 (2)	0·1461 (2)	2·90 (2)
C3	0·2425 (1)	−0·1878 (3)	0·2151 (2)	3·18 (2)
C4	0·32330 (9)	0·0001 (2)	0·1754 (1)	2·76 (2)
C5	0·2792 (1)	0·1881 (2)	0·0667 (2)	3·15 (2)
C6	0·1524 (1)	0·1865 (2)	−0·0009 (1)	2·99 (2)

* $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

Table 3. *Selected bond lengths* (Å), *bond angles* (°) (I)

O—C4	1·3845 (12)	C2—C3	1·389 (2)
O—H1OH	0·96 (2)	C3—C4	1·377 (2)
C1—C1′	1·4954 (11)	C4—C5	1·380 (2)
C1—C2	1·393 (2)	C5—C6	1·393 (2)
C1—C6	1·392 (2)		

C4—O—H1OH	105·3 (9)	O—C4—C3	117·78 (10)
C1′—C1—C2	121·60 (9)	O—C4—C5	122·12 (10)
C1′—C1—C6	121·53 (9)	C3—C4—C5	120·10 (9)
C2—C1—C6	116·87 (8)	C4—C5—C6	119·35 (11)
C1—C2—C3	121·71 (10)	C1—C6—C5	122·07 (10)
C2—C3—C4	119·91 (11)		

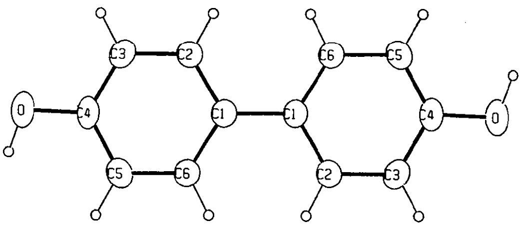


Fig. 1. 40% Ellipsoids of (I) (Johnson, 1965).

Table 4. *Positional parameters and their e.s.d.'s* (II)

	x	y	z	B_{eq}(Å^2)*
O1	0	0	0	6·08 (6)
O2	0	0	0·7661 (2)	6·82 (6)
C1	0	0	0·1084 (2)	3·96 (6)
C2	0·0353 (1)	−0·0496 (1)	0·1604 (2)	3·75 (4)
C3	0·0347 (1)	−0·0471 (1)	0·2685 (2)	3·78 (4)
C4	0	0	0·3253 (2)	3·37 (5)
C5	0	0	0·4411 (2)	3·55 (6)
C6	0·0162 (1)	−0·0572 (1)	0·4974 (2)	3·98 (4)
C7	0·0168 (1)	−0·0592 (1)	0·6059 (2)	4·12 (4)
C8	0	0	0·6582 (2)	4·55 (7)
C9	0·0739 (1)	−0·1048 (1)	0·1033 (2)	4·49 (5)
C10	0·1017 (2)	−0·1564 (1)	0·1795 (2)	7·23 (7)
C11	0·0299 (2)	−0·1453 (1)	0·0309 (2)	6·50 (7)
C12	0·1296 (2)	−0·0738 (2)	0·0423 (3)	7·75 (7)
C13	0·0357 (1)	−0·1242 (1)	0·6630 (2)	5·02 (5)
C14	0·0520 (2)	−0·1812 (1)	0·5873 (3)	6·82 (7)
C15	−0·0211 (1)	−0·1489 (1)	0·7310 (3)	7·26 (7)
C16	0·0964 (1)	−0·1125 (2)	0·7298 (2)	6·59 (7)

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

Table 5. *Selected bond lengths* (Å), *bond angles* (°) *and torsion angles* (°) (II)

O1—C1	1·391 (3)	C7—C8	1·400 (3)
O2—C8	1·385 (4)	C7—C13	1·539 (3)
C1—C2	1·399 (2)	C9—C10	1·531 (4)
C2—C3	1·389 (3)	C9—C11	1·531 (4)
C2—C9	1·543 (3)	C9—C12	1·527 (4)
C3—C4	1·389 (3)	C13—C14	1·531 (4)
C4—C5	1·486 (4)	C13—C15	1·545 (4)
C5—C6	1·389 (3)	C13—C16	1·541 (4)
C6—C7	1·394 (3)		
C2—C1—C2′	123·0 (2)	C7—C8—C7′	122·7 (2)
O1—C1—C2	118·5 (1)	C2—C9—C10	111·6 (2)
C1—C2—C3	116·5 (2)	C2—C9—C11	110·8 (2)
C1—C2—C9	123·2 (2)	C2—C9—C12	110·3 (2)
C3—C2—C9	120·3 (2)	C10—C9—C11	105·1 (2)
C2—C3—C4	123·6 (2)	C10—C9—C12	108·3 (2)
C3—C4—C5	121·7 (1)	C11—C9—C12	110·6 (2)
C4—C5—C6	121·3 (1)	C7—C13—C14	112·2 (2)
C5—C6—C7	123·0 (2)	C7—C13—C15	110·1 (2)
C6—C7—C8	117·0 (2)	C7—C13—C16	110·2 (2)
C6—C7—C13	120·1 (2)	C14—C13—C15	106·9 (2)
C8—C7—C13	122·9 (2)	C14—C13—C16	106·6 (2)
O2—C8—C7	118·7 (1)	C15—C13—C16	110·8 (2)
C3—C4—C3′	116·6 (2)	C6—C5—C6′	117·4 (2)
C1—C2—C9—C10	−174·0 (2)	C13—C7—C8—O2	−0·3 (2)
C1—C2—C9—C11	−57·2 (3)	C6—C7—C13—C14	−0·1 (3)
C1—C2—C9—C12	65·6 (3)	C6—C7—C13—C15	−119·0 (2)
C3—C2—C9—C10	6·4 (3)	C6—C7—C13—C16	118·5 (2)
C3—C2—C9—C11	123·1 (2)	C8—C7—C13—C14	−179·8 (2)
C3—C2—C9—C12	−114·0 (2)	C8—C7—C13—C15	61·2 (3)
C3—C4—C5—C6	−21·1 (1)	C8—C7—C13—C16	−61·3 (3)

thermal parameters are given in Table 2, and bond lengths and bond angles are listed in Table 3.* Fig. 1 shows the molecule and the atomic numbering scheme.

Compound (II) was prepared by reducing (III) with sodium hydrosulfite (Kharasch & Johi, 1957).

Table 6. *Positional parameters and their e.s.d.'s* (III)

	x	y	z	B_{eq}(Å^2)*
O1	0·5470 (2)	−0·35497 (9)	0·0812 (1)	6·40 (2)
C1	0·9319 (2)	−0·0508 (1)	0·0113 (1)	2·94 (2)
C2	0·9266 (2)	−0·1273 (1)	−0·0918 (1)	3·08 (2)
C3	0·7987 (2)	−0·2264 (1)	−0·0744 (1)	3·00 (2)
C4	0·6579 (2)	−0·2620 (1)	0·0593 (1)	3·61 (2)
C5	0·6560 (2)	−0·1834 (1)	0·1663 (1)	2·98 (2)
C6	0·7872 (2)	−0·0847 (1)	0·1394 (1)	3·10 (2)
C7	0·7923 (2)	−0·3035 (1)	−0·1862 (1)	3·31 (2)
C8	0·9429 (3)	−0·2510 (1)	−0·3171 (1)	4·75 (3)
C9	0·8802 (3)	−0·4479 (1)	−0·1551 (2)	4·72 (3)
C10	0·5487 (2)	−0·2923 (2)	−0·2056 (2)	4·82 (3)
C11	0·5049 (2)	−0·2173 (1)	0·3034 (1)	3·30 (2)
C12	0·5240 (3)	−0·1258 (1)	0·4003 (1)	4·78 (3)
C13	0·5774 (3)	−0·3566 (2)	0·3605 (2)	5·48 (4)
C14	0·2552 (3)	−0·2028 (2)	0·2937 (2)	5·24 (4)

* $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

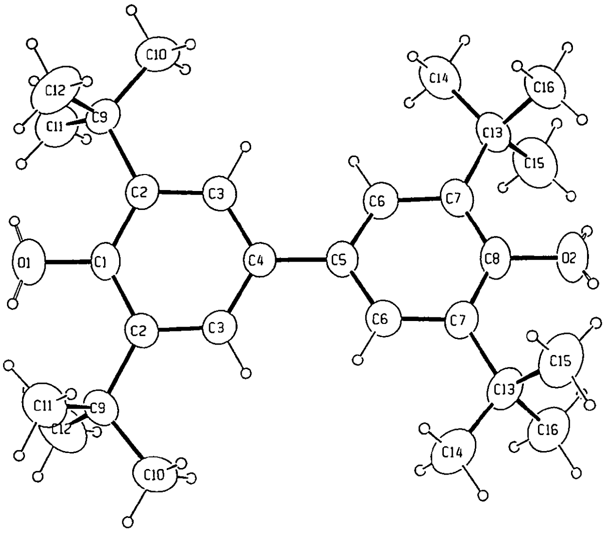


Fig. 2. 40% Ellipsoids of (II) (Johnson, 1965). The hydroxyl H-atom positions are half populated.

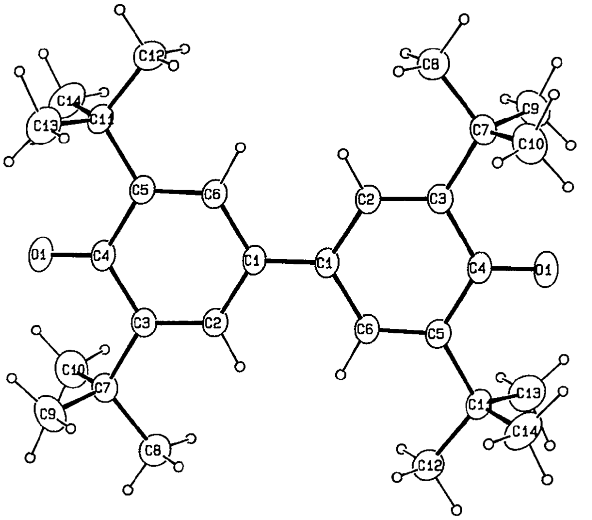


Fig. 3. 40% Ellipsoids of (III) (Johnson, 1965).

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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 52381 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Crystals were grown for X-ray analysis in diethyl ether. Details of the data collection and structural refinement are given in Table 1. Final positional and equivalent isotropic thermal parameters are given in Table 4, and both lengths, bond angles, and torsion angles, are listed in Table 5.* Fig. 2 shows the molecule and the atomic numbering scheme.

Compound (III) was prepared by passing oxygen through a vigorously stirred solution of 2,6-di-*tert*-butylphenol, CuCl and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine in 95% ethanol (Hay, 1969). Crystals were grown for X-ray analysis in ethyl acetate. Details of the data collection and structural refinement are given in Table 1. Final positional and equivalent isotropic thermal parameters are given in Table 6.* Fig. 3 shows the molecule and the atomic numbering scheme.

Related literature. Original crystal structure of (I): Akhmed, Farag & Amin (1971). The structure of hydroquinone: Maartmann-Moe (1966); structure of 2,6-di-*tert*-butyl-4-phenylphenol: Bekkouch, Perrin & Thozet (1988) related to our compounds (I) and (II); structure of *p*-benzoquinone: Trotter (1960). Original crystal structure of (III): Khan, Osman & Tuck (1986).

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* See deposition footnote

Acta Cryst. (1990). C**46**, 922–924

A Bichromophoric Difulvene from 1,5-Cyclooctadione

By Frank R. Fronczek, John M. Cronan Jr and Mark L. McLaughlin*

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803-1804, *USA*

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Abstract. 1,5-Bis(2,4-cyclopentadien-1-ylidene)cyclooctane, $C_{18}H_{20}$, $M_r = 236·4$, monoclinic, $P2_1/n$, $a = 7·498\,(2)$, $b = 11·415\,(3)$, $c = 16·555\,(3)$ Å, $\beta = 97·80\,(2)°$, $V = 1403·7\,(10)$ Å^3, $Z = 4$, $D_x = 1·118$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0·71073$ Å, $\mu = 0·58$ cm^{-1}, $F(000) = 512$, $T = 296$ K, $R = 0·050$ for 1550 observations with $I > 1\sigma(I)$ (of 2471 unique data). The eight-membered ring of the title molecule adopts a boat–chair conformation with considerable bond angle distortions observed for all the methylenes forming the eight-membered ring. These six bond angles range from 113·3 (2)–116·1 (2)°. The bond angles exocyclic to the cyclopentadienylidene ring are 116·7 (2) and 116·6 (2)°. The intramolecular distance, 2·957 (2) Å, between the carbons that are exocyclic to the cyclopentadienylidene ring is well within the sum of van der Waals radii. The title compound exhibits a molar absorptivity which is less than half that of a single fulvene chromophore. The cyclopentadienylidene rings are nearly planar, with maximum deviations of 0·008 (2) and 0·013 (2) Å, and they form a dihedral angle of 32·2 (1)°.

Experimental. The title compound was prepared by condensing 1,5-cyclooctadione and 1,3-cyclopentadiene with pyrrolidine as a catalyst in methanol (Stone & Little, 1985). Crystals grown by slow cooling of refluxing hexane, m.p. 396–397 K, were suitable; a yellow crystal 0·10 × 0·48 × 0·75 mm was mounted in a capillary on an Enraf–Nonius CAD-4 diffractometer with Mo $K\alpha$ radiation and a graphite monochromator. Cell dimensions were determined

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* Author to whom correspondence should be addressed.

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