

N(2)	1.00	-0.3051 (3)	0.2442 (2)	0.37760 (16)	4.34 (12)
N(3)	1.00	-0.2010 (3)	0.2166 (2)	0.57267 (16)	4.19 (12)
N(4)	1.00	0.1296 (3)	0.2999 (2)	0.58722 (16)	4.14 (12)
N(5)	1.00	0.6941 (3)	0.39217 (19)	0.00204 (16)	3.85 (12)
N(6)	1.00	0.3792 (2)	0.37867 (19)	0.04593 (16)	3.88 (12)
C(1)	1.00	0.1244 (5)	0.1981 (5)	0.2512 (3)	6.0 (2)
C(2)	1.00	0.0159 (3)	0.2005 (3)	0.3175 (2)	4.37 (15)
C(3)	1.00	-0.1553 (4)	0.1535 (3)	0.2565 (2)	4.56 (16)
C(4)	1.00	-0.2752 (4)	0.1274 (3)	0.3084 (2)	4.25 (15)
C(5)	1.00	-0.4281 (5)	0.0553 (4)	0.2327 (3)	6.3 (2)
C(6)	1.00	-0.4112 (4)	0.2322 (4)	0.4369 (3)	5.17 (19)
C(7)	1.00	-0.3544 (4)	0.1582 (3)	0.5021 (2)	5.09 (18)
C(8)	1.00	-0.1245 (4)	0.1403 (3)	0.6266 (2)	4.47 (16)
C(9)	1.00	-0.2280 (6)	0.1120 (5)	0.6876 (3)	6.7 (3)
C(10)	1.00	0.0388 (4)	0.2031 (3)	0.6907 (2)	4.84 (18)
C(11)	1.00	0.1671 (4)	0.2143 (3)	0.6397 (2)	4.54 (15)
C(12)	1.00	0.3309 (5)	0.2543 (5)	0.7133 (3)	6.9 (2)
C(13)	1.00	0.2375 (4)	0.3057 (4)	0.5275 (2)	4.85 (18)
C(14)	1.00	0.1771 (4)	0.3780 (3)	0.4616 (2)	4.98 (17)
C(15)	1.00	0.8121 (4)	0.1944 (3)	-0.0294 (3)	4.98 (19)
C(16)	1.00	0.6606 (3)	0.2563 (2)	-0.0365 (2)	3.62 (13)
C(18)	1.00	0.3818 (3)	0.2457 (2)	-0.0030 (2)	3.67 (13)
C(17)	1.00	0.5537 (3)	0.2153 (3)	0.0162 (2)	3.77 (14)
C(19)	1.00	0.2791 (4)	0.1679 (4)	0.0291 (3)	5.5 (2)
C(20)	1.00	0.7785 (3)	0.5795 (3)	-0.0241 (3)	4.60 (17)
C(21)	1.00	0.7667 (4)	0.4406 (3)	-0.0583 (3)	4.56 (18)

C(18)—N(6)—C(20')—C(21')	-167.8 (3)
N(5)—C(16)—C(17)—C(18)	68.7 (2)
C(16)—C(17)—C(18)—N(6)	-72.3 (2)
N(6')—C(20)—C(21)—N(5)	-70.8 (2)

Symmetry code: (i) 1 - x, 1 - y, -z.

H atoms were located using a difference Fourier method. All three water molecules and all H atoms attached to N atoms are disordered. All parameters were refined for ordered H atoms, but only *U* was refined for disordered H atoms. Program used: *NRCVAX* (Gabe, Le Page, White & Lee, 1987).

This work was supported by the National Science Council, ROC, under grants NSC84-2112-M007-019 and NSC84-2113-M007-021. The authors are also indebted to Ms Shu-Fang Tung for collecting the X-ray diffraction data.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, hydrogen-bond geometry, bond distances and angles involving H atoms, least-squares-planes data and torsion angles have been deposited with the IUCr (Reference: AS1126). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected geometric parameters (Å, °)

N(1)—C(2)	1.465 (4)	C(3)—C(4)	1.522 (4)
N(1)—C(14)	1.469 (4)	C(4)—C(5)	1.525 (5)
N(2)—C(4)	1.468 (4)	C(6)—C(7)	1.517 (5)
N(2)—C(6)	1.460 (4)	C(8)—C(9)	1.529 (5)
N(3)—C(7)	1.465 (4)	C(8)—C(10)	1.511 (5)
N(3)—C(8)	1.464 (4)	C(10)—C(11)	1.520 (5)
N(4)—C(11)	1.463 (3)	C(11)—C(12)	1.525 (5)
N(4)—C(13)	1.459 (4)	C(13)—C(14)	1.516 (4)
N(5)—C(16)	1.471 (3)	C(15)—C(16)	1.514 (4)
N(5)—C(21)	1.461 (4)	C(16)—C(17)	1.517 (4)
N(6)—C(18)	1.464 (3)	C(17)—C(18)	1.527 (4)
N(6)—C(20')	1.466 (3)	C(18)—C(19)	1.517 (4)
C(1)—C(2)	1.519 (4)	C(20)—N(6')	1.466 (3)
C(2)—C(3)	1.522 (4)	C(20)—C(21)	1.503 (4)
C(2)—N(1)—C(14)	116.4 (2)	C(9)—C(8)—C(10)	111.1 (3)
C(4)—N(2)—C(6)	115.6 (3)	C(8)—C(10)—C(11)	117.7 (3)
C(7)—N(3)—C(8)	114.0 (2)	N(4)—C(11)—C(10)	110.7 (2)
C(11)—N(4)—C(13)	114.2 (2)	N(4)—C(11)—C(12)	111.1 (3)
C(16)—N(5)—C(21)	113.8 (2)	C(10)—C(11)—C(12)	110.8 (3)
C(18)—N(6)—C(20')	114.2 (2)	N(4)—C(13)—C(14)	111.8 (3)
N(1)—C(2)—C(1)	112.1 (3)	N(1)—C(14)—C(13)	114.2 (3)
N(1)—C(2)—C(3)	109.7 (2)	N(5)—C(16)—C(15)	112.0 (2)
C(1)—C(2)—C(3)	110.5 (3)	N(5)—C(16)—C(17)	110.5 (2)
C(2)—C(3)—C(4)	117.7 (2)	C(15)—C(16)—C(17)	110.7 (2)
N(2)—C(4)—C(3)	109.8 (2)	C(16)—C(17)—C(18)	117.2 (2)
N(2)—C(4)—C(5)	112.0 (3)	N(6)—C(18)—C(17)	109.5 (2)
C(3)—C(4)—C(5)	109.8 (3)	N(6)—C(18)—C(19)	112.4 (3)
N(2)—C(6)—C(7)	115.0 (3)	C(17)—C(18)—C(19)	110.6 (2)
N(3)—C(7)—C(6)	110.7 (3)	N(6')—C(20)—C(21)	111.2 (2)
N(3)—C(8)—C(9)	111.4 (3)	N(5)—C(21)—C(20)	112.0 (3)
N(3)—C(8)—C(10)	110.2 (2)		
C(14)—N(1)—C(2)—C(3)	174.1 (3)		
C(2)—N(1)—C(14)—C(13)	-62.3 (2)		
C(6)—N(2)—C(4)—C(3)	-176.5 (3)		
C(4)—N(2)—C(6)—C(7)	60.0 (2)		
C(8)—N(3)—C(7)—C(6)	-169.9 (3)		
C(7)—N(3)—C(8)—C(10)	175.0 (3)		
C(13)—N(4)—C(11)—C(10)	-173.7 (3)		
C(11)—N(4)—C(13)—C(14)	170.2 (3)		
N(1)—C(2)—C(3)—C(4)	-66.7 (2)		
C(2)—C(3)—C(4)—N(2)	68.9 (2)		
N(2)—C(4)—C(3)—N(3)	60.8 (2)		
N(3)—C(8)—C(10)—C(11)	-68.1 (2)		
C(8)—C(10)—C(11)—N(4)	68.1 (2)		
N(4)—C(13)—C(14)—N(1)	-61.4 (2)		
C(21)—N(5)—C(16)—C(17)	-167.5 (2)		
C(16)—N(5)—C(21)—C(20)	172.3 (3)		
C(20')—N(6)—C(18)—C(17)	174.0 (2)		

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Two Conformational Isomers of 2-Bromo-2,3-dihydro-2,3-(bibenzyl-2,2'-diyl)methano-1,4-naphthoquinone

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Abstract

The crystal structures of the two conformational isomers of the title compound, spiro[5,6-dihydro-11*H*-dibenzo-

[*a,d*]cycloheptene-1,11'-1*a'*,2',7',7*a'*-tetrahydro-1*H'*-cyclopropa[*b*]naphthalene-2',7'-dione], C₂₅H₁₇BrO₂, have been determined by X-ray diffraction. Isomer (I) has a conformation in which the spirodibenzocycloheptane moiety is close to the Br atom with a distance of 2.96(3) Å between the Br atom and the H atom at the 4-position of the tricyclic system. Isomer (II), obtained on heating (I), has a conformation in which the cycloheptane ring is flipped over apart from the Br atom and is characterized by the significantly short bibenzyl ethylene bond [1.458(11) Å].

Comment

Cyclopropene-fused quinones, so-called homoquinones, are intriguing compounds, since their thermolysis (Oshima & Nagai, 1993) and photolysis (Moriwaki, Oshima & Nagai, 1994) exhibit a variety of reaction features associated with ring strain and the conjugated π system. Recently, we prepared the title spiro-linked homoquinone compound from dipolar addition of 5-diazo-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene and 2-bromonaphthoquinone, and found that the dibenzocycloheptane moiety undergoes a conformational inversion on heating (Oshima & Nagai, unpublished results). In this paper, we describe the conformational details of these two isomers, (I) and (II), as determined by X-ray crystallography in order to discover the driving force of the inversion.

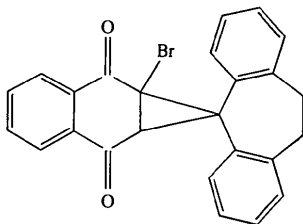


Fig. 1 shows the molecular structures of the two isomers with the atomic numbering scheme (ORTEP; Johnson, 1976). The two isomers differ from each other in conformation. The central cycloheptane ring of the tricyclic system has an appreciably twisted-boat form with a C(13)—C(14)—C(15)—C(16) torsion angle of $-28.3(7)^\circ$ for (I), while (II) adopts only a slightly twisted-boat form with a torsion angle of $4.3(13)^\circ$.

The corresponding values of the bond lengths and angles in the isomers agree fairly well with each other except for the C(14)—C(15) bond length. This bond length [1.458(11) Å] in (II) is apparently shorter than the corresponding bond [1.503(8) Å] in (I).

In (I), the intramolecular non-bonded contact [2.96(3) Å] between atoms Br(1) and H(17) is appreciably shorter than the sum (3.15 Å) of their van der Waals radii. The relatively small distance between them makes torsional vibration of the C(14)—C(15) bond difficult

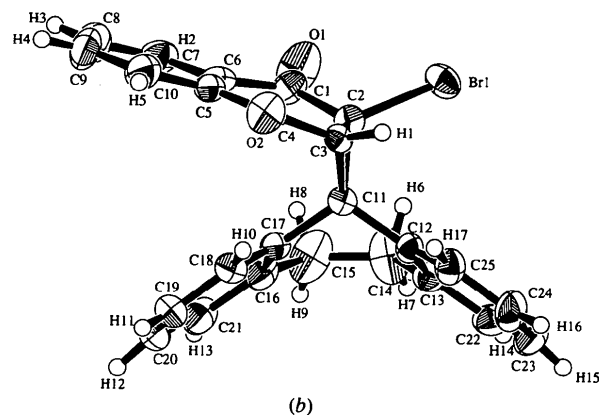
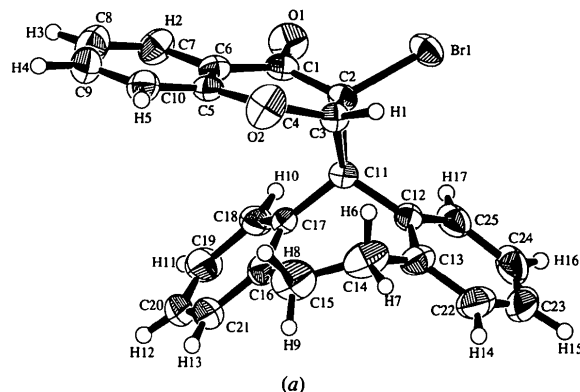


Fig. 1. Molecular structures of (a) isomer (I) and (b) isomer (II), with the atomic numbering scheme. Displacement ellipsoids are plotted at the 40% probability level. H atoms are drawn as spheres of arbitrary radii.

and the cycloheptane ring is twisted in order to reduce the steric repulsion between atoms Br(1) and H(17).

In isomers (I) and (II), the C(13)—C(14)—C(15)—C(16) torsion angles and the dihedral angles of the two benzene rings [105.5° for (I) and 111.1° for (II)] in the dibenzocycloheptane moieties are very small, compared with corresponding values of analogous compounds such as (a) (1*S*,4*R*)-3'-chloro-10',11'-dihydro-*N,N*-dimethylspiro(2-cyclohexene-1,5'-5*H*-dibenzo[*a,d*]cyclohepten)-4-amine (Wagner, 1980), (b) 5-*p-N,N*-dimethylaminophenyl-10,11-dihydro-5*H*-dibenzo[*b,f*]silepin (Corey, Corey & Glick, 1975), and (c) (*Z*)-9,10-dihydro-4*H*-benzocyclohepta[7,6-*b*]thiophen-4-ylideneacetic acid (Gutiérrez-Puebla & Monge, 1981) [(a) torsion angles $-83.6(11)$ and $-81.5(11)$, dihedral angles $139.1(9)$ and $143.3(5)^\circ$; (b) $90.7(3)$, $123.5(18)^\circ$; (c) $-64.8(3)$, 124.5°]. The reason is that in isomers (I) and (II), the spiro C(11) atom, which is the bow of a boat comprising the cycloheptane ring, is greatly raised out of the plane in order to reduce the steric repulsion between the bulky naphthoquinone and dibenzocycloheptane moieties facing each other. On the other hand, since the tricyclic derivatives (a), (b) and (c) with their

linear or planar spiro substituents have T-shaped geometries, the substituents are bonded to the tricyclic moieties without as great a raising of the atoms corresponding to C(11).

The differences between the isomers (I) and (II) in the C(14)—C(15) bond lengths, the torsion angles around the bond and the intramolecular H···Br non-bonded contacts show that the metastable isomer (I) is transformed into the stable isomer (II) on heating.

Experimental

Crystals of (I) and (II) were obtained by slow evaporation of benzene–hexane solutions at room temperature.

Isomer (I)

Crystal data

C₂₅H₁₇BrO₂

M_r = 429.31

Triclinic

P $\bar{1}$

a = 9.165 (1) Å

b = 13.155 (1) Å

c = 8.850 (1) Å

α = 101.58 (1)°

β = 116.59 (1)°

γ = 80.77 (1)°

V = 931.7 (2) Å³

Z = 2

D_x = 1.530 Mg m⁻³

D_m = 1.53 Mg m⁻³

D_m measured by flotation

Data collection

Rigaku AFC-5R diffractometer

$\theta/2\theta$ scans

Absorption correction: empirical, ψ scan

T_{min} = 0.817, *T_{max}* = 1.000

4271 measured reflections

3955 independent reflections

2401 observed reflections

$[|F_o| > 3\sigma(|F_o|)]$

Refinement

Refinement on *F*

R = 0.037

wR = 0.040

S = 1.48

2401 reflections

313 parameters

All H-atom parameters refined except H(8), H(9), which were not refined

Weighting scheme based on measured e.s.d.'s

Mo *K*α radiation

λ = 0.7107 Å

Cell parameters from 25 reflections

θ = 10.015–12.785°

μ = 2.20 mm⁻¹

T = 296 K

Prismatic

0.40 × 0.20 × 0.20 mm

Colorless

R_{int} = 0.021

θ_{max} = 30.07°

h = -10 → 0

k = -18 → 16

l = -11 → 12

3 standard reflections

monitored every 100 reflections

intensity decay: -1.66%

$(\Delta/\sigma)_{max}$ = 0.46

$\Delta\rho_{max}$ = 0.355 e Å⁻³

$\Delta\rho_{min}$ = -0.433 e Å⁻³

Extinction correction: none

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2A)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (I)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Br(1)	-0.19896 (5)	0.63672 (4)	0.02386 (6)	0.0549 (1)
O(1)	-0.1413 (3)	0.8371 (2)	-0.0528 (4)	0.0617 (9)
O(2)	0.4021 (3)	0.5830 (2)	0.1761 (4)	0.067 (1)
C(1)	-0.0123 (4)	0.7893 (3)	0.0228 (4)	0.041 (1)
C(2)	-0.0021 (4)	0.7075 (3)	0.1237 (4)	0.037 (1)
C(3)	0.1537 (4)	0.6386 (3)	0.1915 (4)	0.037 (1)
C(4)	0.2920 (4)	0.6516 (3)	0.1558 (5)	0.046 (1)
C(5)	0.2853 (4)	0.7459 (3)	0.0850 (4)	0.040 (1)
C(6)	0.1409 (4)	0.8095 (3)	0.0189 (4)	0.041 (1)
C(7)	0.1371 (7)	0.8915 (4)	-0.0606 (6)	0.058 (2)
C(8)	0.2742 (8)	0.9110 (4)	-0.0713 (7)	0.074 (2)
C(9)	0.4169 (7)	0.8484 (4)	-0.0050 (6)	0.069 (2)
C(10)	0.4219 (5)	0.7669 (4)	0.0723 (6)	0.054 (1)
C(11)	0.1046 (4)	0.7190 (3)	0.3160 (4)	0.036 (1)
C(12)	0.0632 (4)	0.6779 (3)	0.4369 (5)	0.039 (1)
C(13)	0.1893 (5)	0.6246 (3)	0.5604 (5)	0.051 (1)
C(14)	0.3554 (6)	0.6035 (5)	0.5620 (7)	0.071 (2)
C(15)	0.4459 (6)	0.6958 (5)	0.5875 (6)	0.083 (2)
C(16)	0.3589 (5)	0.7991 (3)	0.5335 (5)	0.050 (1)
C(17)	0.1990 (4)	0.8131 (3)	0.4064 (4)	0.038 (1)
C(18)	0.1279 (6)	0.9116 (3)	0.3794 (5)	0.053 (1)
C(19)	0.2114 (8)	0.9981 (4)	0.4674 (7)	0.074 (2)
C(20)	0.3702 (8)	0.9853 (5)	0.5850 (7)	0.081 (2)
C(21)	0.4420 (6)	0.8890 (5)	0.6188 (6)	0.069 (2)
C(22)	0.1572 (9)	0.5898 (4)	0.6798 (6)	0.074 (2)
C(23)	0.0078 (11)	0.6108 (5)	0.6808 (8)	0.092 (3)
C(24)	-0.1127 (9)	0.6667 (5)	0.5665 (9)	0.083 (2)
C(25)	-0.0858 (5)	0.7014 (4)	0.4429 (6)	0.057 (1)

Table 2. Selected geometric parameters (Å, °) for (I)

Br(1)—C(2)	1.920 (3)	C(3)—C(11)	1.536 (5)
O(1)—C(1)	1.210 (4)	C(4)—C(5)	1.479 (5)
O(2)—C(4)	1.215 (4)	C(11)—C(12)	1.498 (5)
C(1)—C(2)	1.497 (5)	C(11)—C(17)	1.500 (5)
C(1)—C(6)	1.487 (5)	C(13)—C(14)	1.498 (6)
C(2)—C(3)	1.503 (5)	C(14)—C(15)	1.503 (8)
C(2)—C(11)	1.526 (4)	C(15)—C(16)	1.511 (7)
C(3)—C(4)	1.478 (5)	C(16)—C(17)	1.403 (5)
O(1)—C(1)—C(2)	120.8 (3)	C(4)—C(5)—C(6)	121.5 (3)
O(1)—C(1)—C(6)	121.4 (3)	C(1)—C(6)—C(5)	122.0 (3)
C(2)—C(1)—C(6)	117.8 (3)	C(2)—C(11)—C(3)	58.8 (2)
Br(1)—C(2)—C(1)	112.0 (2)	C(2)—C(11)—C(12)	123.1 (3)
Br(1)—C(2)—C(3)	114.8 (2)	C(2)—C(11)—C(17)	120.2 (3)
Br(1)—C(2)—C(11)	120.6 (2)	C(3)—C(11)—C(12)	117.1 (3)
C(1)—C(2)—C(3)	118.7 (3)	C(3)—C(11)—C(17)	119.9 (3)
C(1)—C(2)—C(11)	120.5 (3)	C(12)—C(11)—C(17)	109.5 (3)
C(3)—C(2)—C(11)	60.9 (2)	C(11)—C(12)—C(13)	117.3 (3)
C(2)—C(3)—C(4)	119.8 (3)	C(12)—C(13)—C(14)	120.4 (4)
C(2)—C(3)—C(11)	60.3 (2)	C(13)—C(14)—C(15)	117.5 (4)
C(4)—C(3)—C(11)	121.8 (3)	C(14)—C(15)—C(16)	122.5 (4)
O(2)—C(4)—C(3)	119.7 (4)	C(15)—C(16)—C(17)	125.2 (4)
O(2)—C(4)—C(5)	122.1 (3)	C(11)—C(17)—C(16)	118.2 (3)
C(3)—C(4)—C(5)	118.1 (3)		

Isomer (II)

Crystal data

C₂₅H₁₇BrO₂

M_r = 429.31

Monoclinic

Cc

a = 15.037 (3) Å

b = 9.913 (1) Å

c = 12.547 (2) Å

β = 91.29 (1)°

Mo *K*α radiation

λ = 0.7107 Å

Cell parameters from 25 reflections

θ = 14.83–15.00°

μ = 2.19 mm⁻¹

T = 296 K

Prismatic

$V = 1869.7 (5) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.525 \text{ Mg m}^{-3}$
 $D_m = 1.53 \text{ Mg m}^{-3}$
 D_m measured by flotation

Data collection

Rigaku AFC-5R diffractometer
 $\theta/2\theta$ scans
 Absorption correction: empirical, ψ scan
 $T_{\min} = 0.812$, $T_{\max} = 1.000$
 3002 measured reflections
 2902 independent reflections
 1767 observed reflections
 $[|F_o| > 3\sigma(|F_o|)]$

Refinement

Refinement on F^2
 $R = 0.035$
 $wR = 0.035$
 $S = 1.35$
 1767 reflections
 304 parameters
 All H-atom parameters refined except H(6), H(7), H(8), H(9), which were not refined

$0.70 \times 0.40 \times 0.40 \text{ mm}$
 Colorless

$R_{\text{int}} = 0.063$
 $\theta_{\text{max}} = 30.064^\circ$
 $h = 0 \rightarrow 21$
 $k = 0 \rightarrow 14$
 $l = -18 \rightarrow 18$
 3 standard reflections monitored every 100 reflections
 intensity decay: -0.57%

Weighting scheme based on measured e.s.d.'s
 $(\Delta/\sigma)_{\text{max}} = 0.409$
 $\Delta\rho_{\text{max}} = 0.655 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.387 \text{ e \AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2A)

Table 4. Selected geometric parameters (\AA , $^\circ$) for (II)

Br(1)—C(2)	1.918 (5)	C(3)—C(11)	1.525 (7)
O(1)—C(1)	1.202 (6)	C(4)—C(5)	1.497 (7)
O(2)—C(4)	1.217 (6)	C(11)—C(12)	1.502 (7)
C(1)—C(2)	1.493 (7)	C(11)—C(17)	1.513 (7)
C(1)—C(6)	1.474 (8)	C(13)—C(14)	1.511 (10)
C(2)—C(3)	1.501 (7)	C(14)—C(15)	1.458 (11)
C(2)—C(11)	1.524 (7)	C(15)—C(16)	1.501 (9)
C(3)—C(4)	1.483 (7)		
O(1)—C(1)—C(2)	121.3 (6)	C(4)—C(5)—C(6)	121.2 (5)
O(1)—C(1)—C(6)	121.5 (5)	C(1)—C(6)—C(5)	122.5 (5)
C(2)—C(1)—C(6)	117.2 (5)	C(2)—C(11)—C(3)	59.0 (3)
Br(1)—C(2)—C(1)	112.6 (4)	C(2)—C(11)—C(12)	117.0 (4)
Br(1)—C(2)—C(3)	116.2 (4)	C(2)—C(11)—C(17)	122.0 (4)
Br(1)—C(2)—C(11)	119.9 (3)	C(3)—C(11)—C(12)	119.9 (4)
C(1)—C(2)—C(3)	120.4 (4)	C(3)—C(11)—C(17)	119.3 (4)
C(1)—C(2)—C(11)	118.1 (5)	C(12)—C(11)—C(17)	111.0 (4)
C(3)—C(2)—C(11)	60.5 (3)	C(11)—C(12)—C(13)	118.2 (5)
C(2)—C(3)—C(4)	118.2 (4)	C(12)—C(13)—C(14)	122.3 (5)
C(2)—C(3)—C(11)	60.5 (3)	C(13)—C(14)—C(15)	124.1 (6)
C(4)—C(3)—C(11)	123.7 (4)	C(14)—C(15)—C(16)	122.0 (5)
O(2)—C(4)—C(3)	120.1 (5)	C(15)—C(16)—C(17)	122.9 (5)
O(2)—C(4)—C(5)	121.4 (5)	C(11)—C(17)—C(16)	120.3 (5)
C(3)—C(4)—C(5)	118.5 (4)		

For (II), the systematic absences indicated the possible space groups $C2/c$ and Cc . The centrosymmetric space group $C2/c$ was, however, excluded by the symmetry of the molecule.

Most H atoms were located from difference Fourier maps (*DIRDIF*; Beurskens *et al.*, 1992) and refined isotropically. Some H atoms of the bibenzyl ethylene bonds were fixed at geometrically calculated positions. Calculations were carried out on an IRIS INDIGO workstation at the Faculty of Science, Osaka University.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *PROCESS TEXSAN* (Molecular Structure Corporation, 1992); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *LS TEXSAN*; software used to prepare material for publication: *FINISH TEXSAN*.

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (II)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^* \cdot \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Br(1)	0.0	0.01225 (6)	0.0	0.0509 (1)
O(1)	-0.0399 (4)	0.3089 (5)	-0.0416 (4)	0.088 (2)
O(2)	0.0668 (3)	0.2149 (4)	0.3616 (3)	0.057 (1)
C(1)	-0.0267 (4)	0.2888 (6)	0.0519 (4)	0.048 (2)
C(2)	-0.0339 (3)	0.1505 (5)	0.0980 (4)	0.038 (1)
C(3)	-0.0104 (3)	0.1258 (5)	0.2133 (4)	0.035 (1)
C(4)	0.0305 (3)	0.2376 (5)	0.2757 (4)	0.040 (1)
C(5)	0.0274 (4)	0.3768 (5)	0.2296 (4)	0.042 (1)
C(6)	-0.0039 (3)	0.3996 (6)	0.1260 (4)	0.043 (1)
C(7)	-0.0066 (4)	0.5325 (7)	0.0870 (6)	0.058 (2)
C(8)	0.0216 (6)	0.6358 (8)	0.1499 (7)	0.079 (3)
C(9)	0.0544 (6)	0.6123 (7)	0.2500 (7)	0.081 (3)
C(10)	0.0575 (5)	0.4842 (7)	0.2913 (6)	0.061 (2)
C(11)	-0.1077 (3)	0.1237 (5)	0.1765 (4)	0.035 (1)
C(12)	-0.1561 (4)	-0.0084 (5)	0.1660 (4)	0.037 (1)
C(13)	-0.2219 (4)	-0.0206 (6)	0.0862 (4)	0.049 (2)
C(14)	-0.2408 (6)	0.0897 (8)	0.0058 (6)	0.081 (3)
C(15)	-0.2508 (6)	0.2317 (7)	0.0331 (6)	0.083 (3)
C(16)	-0.2368 (4)	0.2823 (6)	0.1450 (5)	0.049 (2)
C(17)	-0.1694 (3)	0.2341 (5)	0.2130 (4)	0.037 (1)
C(18)	-0.1649 (4)	0.2779 (6)	0.3179 (4)	0.043 (1)
C(19)	-0.2230 (5)	0.3742 (6)	0.3535 (6)	0.059 (2)
C(20)	-0.2864 (5)	0.4280 (7)	0.2871 (7)	0.066 (2)
C(21)	-0.2939 (4)	0.3810 (6)	0.1849 (7)	0.064 (2)
C(22)	-0.2674 (4)	-0.1419 (8)	0.0787 (6)	0.061 (2)
C(23)	-0.2519 (6)	-0.2452 (8)	0.1455 (7)	0.073 (3)
C(24)	-0.1875 (6)	-0.2331 (6)	0.2249 (6)	0.067 (2)
C(25)	-0.1400 (4)	-0.1147 (6)	0.2359 (4)	0.049 (2)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1150). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tris(*n*-butyl)phosphine, Tris(*tert*-butyl)phosphine and Tris(trimethylsilyl)phosphine

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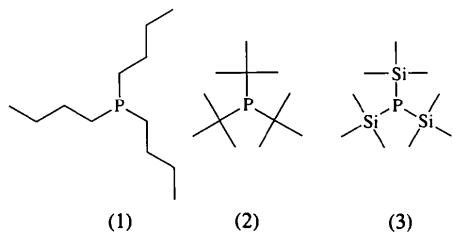
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Abstract

Single crystals of the title compounds, C₁₂H₂₇P (1), C₁₂H₂₇P (2), and C₉H₂₇PSi₃ (3), were grown in capillaries at low temperature using zone-melting techniques [Brodalla, Mootz, Boese & Osswald (1985). *J. Appl. Cryst.* **18**, 316–319]. The molecular and crystal structures of all three compounds were determined at 102 K. Compound (1) has a pseudo-mirror plane and C—P—C angles between 100.5 (1) and 102.7 (1)°. Compound (2) has a pseudosymmetric threefold rotation axis and C—P—C angles of 107.1 (1), 107.4 (1) and 107.8 (1)°. Isomorphous compound (3) has Si—P—Si angles between 105.8 (1) and 106.5 (1)°.

Comment

In our systematic investigation of phosphine ligands, we crystallized tris(*n*-butyl)phosphine [P(*n*-butyl)₃], (1). The C—P—C angles are between 100.5 (1) and 102.7 (1)° (Table 2, Fig. 1). These values are as expected for non-bulky and flexible ligands such as *n*-butyl. The C—C distances tend to lower values with increasing distance from the P atom (Table 2). The C atoms of each



n-butyl group compose a plane [torsion angles range from 177.3 (3) to 179.3 (3)°]. Plane 1 (C1, C2, C3, C4)

and plane 2 (C5, C6, C7, C8) are oriented nearly parallel to one another [the dihedral angle between 1 and 2 is 5 (1)°], and both are almost perpendicular to plane 3 (P, C9, C10, C11, C12) [the dihedral angles between 1 and 3, and 2 and 3 are 90 (1) and 95 (1)°, respectively]. Plane 3 is an approximate mirror. The cone angle θ (for a definition see Tolman, 1977; Bruckmann & Krüger, 1995) is determined as $159 \pm 2^\circ$. Tolman (1970) measured $130 \pm 4^\circ$ as the minimum cone angle, using CPK atomic models, by folding back the flexible substituents on the P atom, while maintaining threefold symmetry (Tolman, 1970, 1977).

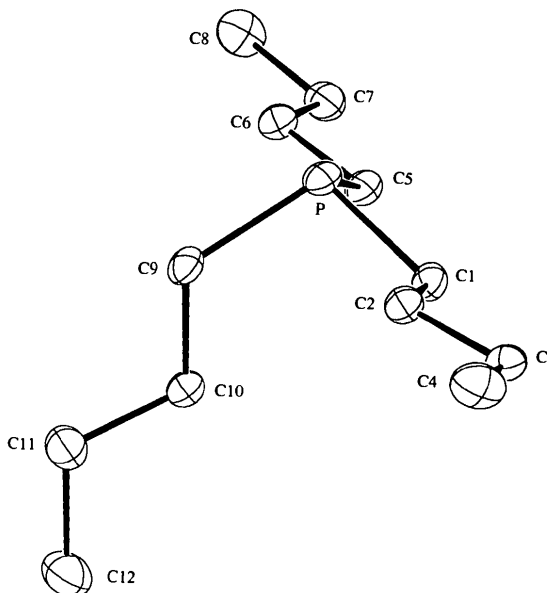


Fig. 1. An ORTEP (Johnson, 1976) view of P(*n*-butyl)₃ with displacement ellipsoids drawn at the 50% probability level.

The dimensions and general molecular structure of tris(*tert*-butyl)phosphine [P(*tert*-butyl)₃], (2), are as expected. Although the *tert*-butyl groups are crystallographically independent, they are arranged in a pseudosymmetric way generated by a threefold rotation axis passing through the P atom (Fig. 2). Corresponding angles show no significant differences, but five of the six tetrahedral angles at every tertiary C atom are significantly different. All C—C distances are within the same range (Table 4). H atoms were located and are in good agreement with the threefold pseudosymmetry. In (2), the C—P—C angles are widened to 107.1 (1), 107.4 (1) and 107.8 (1)° by steric effects. These effects are also evident from the large angles involving the P atom, the tertiary C atoms and atoms C4, C7 and C12 [118.0 (1), 117.8 (1) and 117.4 (1)°, respectively]. The values of all other P—C—C angles are about 10° smaller (Table 4). The P—C distances are more than 0.06 Å longer than in (1). This reflects the bulkiness of the *tert*-butyl groups. The cone angle θ is $176 \pm 2^\circ$ and differs slightly from the value of $182 \pm 2^\circ$ given by Tolman (1970).