Table 1. *Selected geometric parameters (Å, °)*

S1—C9	1.8872 (19)	S1—C10	1.798 (2)
C1′—C2′	1.423 (2)	C1′—C6′	1.400 (3)
C2′—C3′	1.405 (2)	C3′—C4′	1.369 (3)
C4′—C5′	1.361 (3)	C5′—C6′	1.367 (3)
C1···C10	3.273 (4)	C9a···C10′	3.145 (3)
C3′···H8*b*′	2.58	C9a···H10*c*′	2.35
C4a···H10*c*′	2.50		
C1′—C2′—C7′	130.98 (15)	C3′—C2′—C7′	113.63 (16)
C2′—C1′—C9	128.01 (16)	C6′—C1′—C9	114.94 (15)
C1′—C9—C8a	115.67 (14)	C1′—C9—C9a	121.83 (14)
S1—C9—C9a	101.70 (11)	S1—C9—C8a	99.44 (11)
C2′—C7′—C10′	115.52 (14)	C2′—C7′—C8′	109.26 (15)
C2′—C7′—C9′	109.93 (15)		
S1—C9—C9a—C4a	91.53 (15)		
C4b—C8a—C9—C1′	143.98 (15)		

The rotation of the methyl H atoms were refined by the circular difference electron density method available in *SHELXL*97 (Sheldrick, 1997). All H atoms are riding.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1997). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *LS* in *TEXSAN* and *SHELXL*97. Molecular graphics: *TEXSAN* and *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN*, *SHELXL*97 and *PLATON* (Spek, 1990).

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2,2′-Dibromobiphenyl

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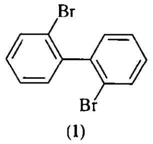
Abstract

The title compound, $C_{12}H_8Br_2$, crystallizes in the orthorhombic space group *Pbca*. The molecule displays non-planar behaviour and the dihedral angle between the two six-membered rings is 84.8 (2)°. The bond length between the two phenyl rings (C1—C1′) and the C—Br bond lengths (C2—Br1 and C2′—Br2) are 1.499 (9), 1.895 (8) and 1.915 (7) Å, respectively.

Comment

The biphenyl system has been extensively studied by X-ray crystallography. Of particular interest in relation to bonding theory is the length of the inter-ring C—C bond and the interplanar dihedral angle. Furthermore, the inter-ring torsion angle has been correlated to the toxicities of polychlorinated biphenyls (PCBs) (Miao *et al.*, 1996) and also crystal-packing effects (Brock & Minton, 1989). Most crystal structures in the literature have inter-ring angles in the rather limited range of 30–60° and only *ortho*-substituted biphenyls display larger angles. We report now the crystal structure of 2,2′-dibromobiphenyl, (I), to provide further structural data for biphenyls having larger inter-ring angles, and as part of our studies of *ortho*-substituted biphenyls.



(I)

The C—C bond distances within the phenyl rings in the title compound are normal and range from 1.365 (11) to 1.402 (9) Å with a mean of 1.378 Å. The corresponding bond angles range from 116.7 (7) to 122.9 (7)°. The phenyl rings are planar, but the Br1 and Br2 atoms deviate by 0.049 (9) and 0.037 (10) Å from planarity. Atoms C4, C1, C1′ and C4′ are almost collinear, the tilt angle being 2.0°. The C—Br bond lengths are 1.895 (8) and 1.915 (7) Å for C2—Br1 and C2′—Br2, respectively. The inter-ring C1—C1′ distance is 1.499 (9) Å, which compares well with values usually observed for halogenated biphenyls which range from 1.467 (14) Å for 2,2′,5,5′-tetrachlorobiphenyl (Miao *et al.*, 1996) to 1.55 (2) Å for 2,3,3′-trichlorobiphenyl (Moes & Lenstra, 1986). The dihedral angle between the two phenyl rings is 84.8 (2)° and the average of the four torsion angles around the central C1—C1′ bond is 85.4 (8)°. This large angle, due to intramolecular Br···Br and Br···H repulsive interactions, is only surpassed by 86.9 (5)° for decachlorobiphenyl (Pedersen, 1975) and 87.9° for 2,2′,4,4′,6,6′-hexachlorobiphenyl (Singh & McKinney, 1979). In comparison, the inter-ring angles for 2-fluorobiphenyl (Rajnikant *et al.*, 1995), 2,2′-dichlorobiphenyl (Rømming *et al.*, 1974) and 2,2′-dibromooctafluorobiphenyl (Hamor & Hamor, 1980) are considerably smaller, measuring 54.1 (3), 66.5 and 76.0 (5)°, respectively. Rømming *et al.* (1974) have previously compared inter-ring angles in 2,2′-dihalobiphenyls observed in the gas phase with calculated values. In general, the calculated values deviate significantly from those observed in the gas phase and solid state. However, the angle computed for the title compound is 82°, which is in close agreement with the X-ray experiment. Interestingly, the value observed in the gas phase is 75°, which is significantly lower than the value obtained in our experiment.

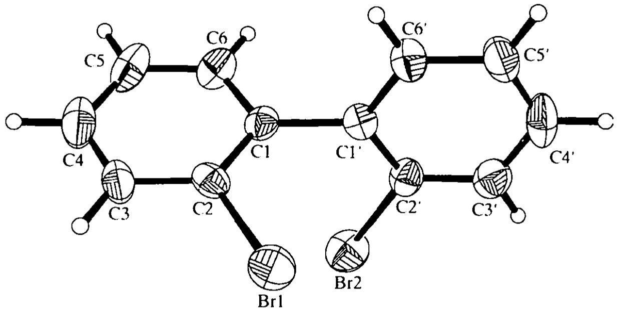


Fig. 1. The structure of (I) showing 30% probability displacement ellipsoids.

Experimental

2,2′-Dibromobiphenyl was prepared and purified according to literature procedures (Gilman & Gaj, 1957). The crude product was recrystallized from 95% ethanol and single crystals were obtained from 95% ethanol solutions at 270 K.

Crystal data

$C_{12}H_8Br_2$
$M_r = 312.00$
Orthorhombic
Pbca
$a = 14.0723\,(9)$ Å
$b = 7.462\,(2)$ Å
$c = 21.489\,(1)$ Å
$V = 2256.5\,(5)$ Å^3
$Z = 8$
$D_x = 1.837$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 21 reflections
$\theta = 35–39.4°$
$\mu = 8.751$ mm^{-1}
$T = 296\,(1)$ K
Needle
0.25 × 0.20 × 0.15 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.205$, $T_{\max} = 0.269$
1838 measured reflections
1838 independent reflections

835 reflections with $F > 4\sigma(F)$
$\theta_{\max} = 63.52°$
$h = -16 \rightarrow 0$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 24$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.033$
$wR(F^2) = 0.113$
$S = 1.032$
1837 reflections
129 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 2.5P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.364$ e Å^{-3}
$\Delta\rho_{\min} = -0.476$ e Å^{-3}
Extinction correction: empirical
Extinction coefficient: 0.00125 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)

The structure was solved by direct methods. H atoms were included in idealized positions and constrained to ride on the parent atom while a common $U_{\rm iso}$ was refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1994*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1062). Services for accessing these data are described at the back of the journal.

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(*E*)-Dimethyl 4-isopropyl-3-[tris(trimethylsilyl)silylmethylene]-1,1-cyclohexanedicarboxylate

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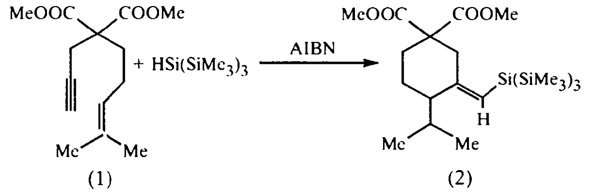
Abstract

The title isomer carbocyclic compound, $C_{23}H_{48}O_4Si_4$, was prepared by treatment of the 1,7-enyne system dimethyl (4-methylpent-3-enyl)propanodioate with tris(trimethylsilyl)silicon hydride in the presence of azobisisobutyronitrile. The C=C distance is 1.335 (4) Å, the C=C—Si bond angle is 132.6 (2)° and the C—C=C—Si torsion angle is 6.2 (5)°. The *E* configuration of the exocyclic double bond has been confirmed by the present X-ray study.

Comment

Tris(trimethylsilyl)silane (TTMS) has emerged as an alternative to the more common tri-*n*-butyltin hydride in free-radical chain processes (Curran, 1988; Chatgilialoglu, 1992, 1995). The hydrosilylating ability of TTMS with alkenes and alkynes (Chatgilialoglu *et al.*, 1992) has been used in particular for intramolecular addition of the corresponding alkyl (Kulicke *et al.*, 1992) or vinyl (Miura *et al.*, 1993) radicals generated on the other additional double bond. As a result of synthetic work in the free-radical cyclization of 1,6- and 1,7-enyne systems through silylation of the triple bond with TTMS, the six-membered cyclic compound, (*E*)-dimethyl 4-isopropyl-3-[tris(trimethylsilyl)silylmethylene]-1,1-cyclohexanedicarboxylate, (2), has been isolated in 51% yield as a colourless crystal with a melting point of 356 (1) K.



No other compounds in which the bulky 'supersilyl' $(Me_3Si)_3Si$ group is bonded to the methylene exocyclic double bond of the cyclohexane ring such as (2) are available in the literature. The enol system formed by 2,2-dimethyl-1-tris(trimethylsilyl)silylethanol (Frey *et al.*, 1994), compound (3), is however the most similar one to compare with some parameters of the title compound. Parameters of the title compound can also be compared with 1-tris(trimethylsilyl)silyl-3,4,5,6-tetrakis-(trimethylsilyl)cyclohex-1-ene (Puranik & Fink, 1994), compound (4), where the supersilyl group is bonded to an endocyclic double bond of the cyclohexene ring. The crystal-structure determination of compound (2) was undertaken to confirm the *E* configurations of the exocyclic double bond. The Si—Si and C—Si distances of the tris(trimethylsilyl)silane of the title compound are close to the distances reported for the 'supersilyl' $(Me_3Si)_3Si$ group (Frey *et al.*, 1994). The C1—C7 distance reveals the existence of a double bond. The C7—Si1 distance changes from 1.94 Å in compound (3) and 1.904 (3) Å in compound (4) to 1.888 (3) Å in the title compound. This difference suggests that compounds (3) and (4) have more steric strains due to the presence of large pendant groups in their structures. The C1—C7—Si1 angle is 133.2° in compound (3). This value is close to the value found in the present structure [132.6 (2)°]. This relatively large bond angle is likely to be due to the steric effects of the bulky groups in both compounds. A torsion angle of 6.2 (5)° for C6—C1—C7—Si1 shows the *E* configuration of compound (2). The cyclohexane backbone adopts a chair conformation with θ = 174 (1)° and φ = 85 (1)° (Cremer & Pople, 1975). The geminal carboethoxy groups bonded to C5 of the cyclohexane ring are oriented in such a way that the C=O groups maintain