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Bis(4-methoxyphenyl)methano[60]fullerene with a Methano Bridge at the 6–6-Ring Junction

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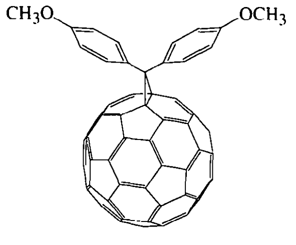
Abstract

In the title compound, $C_{75}H_{14}O_2$, a bis(4-methoxyphenyl)methylene group bridges a 6–6-ring junction of the C_{60} sphere, forming a slightly deformed cyclopropane ring. The C—C bond length involved in the cyclopropane ring fusion is 1.635 (4) Å, more than 0.2 Å longer than that at the 6–6-ring junction of C_{60}. The elongation of this C—C bond leads to a slight deformation of the C_{60} framework, especially a shortening of two C—C bonds in equatorial positions.

Comment

Since the discovery of the method for large-scale preparation of fullerenes, their chemical modifications have been investigated intensively for the purpose of functionalization. Addition of diazoalkanes or diazoacetates to C_{60}-fullerene developed by Wudl and co-workers (Suzuki, Li, Khemani, Wudl & Almarsson, 1991; Wudl, 1992) is a promising method for the preparation of the functionalized fullerenes. Single addition of diazo compounds to C_{60} gives a mixture of isomers with a methano-bridge at different positions, either at the 6–6-ring junction or the 5–6-ring junction of the C_{60} sphere as determined by ^1H and ^{13}C NMR spectroscopy (Isaacs, Wehrsig & Diederich, 1993). Recently, the 6–6-ring-bridged structure was confirmed by X-ray analysis for several methano-bridged fullerenes (Osterodt, Nieger & Vogtle, 1994; Anderson *et al.*, 1994; Paulus & Bingel, 1995). The X-ray structure is useful for the prediction of the reactivity of a C—C bond on the C_{60} sphere and the estimation of intermolecular interactions. We report here the X-ray structure analysis of the title compound, (I), and compare its structure with those of previously reported methano-bridged fullerenes.



(I)

Fig. 1 shows the molecular structure of (I). The molecule has a mirror plane containing atoms C(8), C(9), C(10), C(25) and C(26), since both 4-methoxyphenyl groups are arranged symmetrically. The phenyl ring is essentially planar and the methoxy group belongs to this plane [deviations of the atoms from the least-squares plane through atoms C(1) and O(1) and the phenyl ring are less than 0.006 Å]. The phenyl ring is almost perpendicular to the plane through atoms C(5), C(8) and C(5′) [symmetry code: (′) $x, \frac{1}{2}-y, z$; dihedral angle 88.3 (2)°]. The dihedral angle between the least-squares planes through the phenyl rings is 99.8 (3)°.

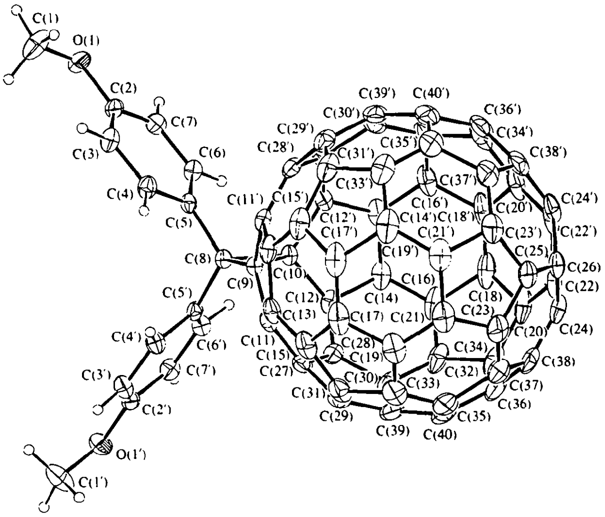


Fig. 1. An *ORTEP* view (Johnson, 1965) of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The C(9)—C(10) bond involved in the cyclopropane ring fusion is 1.635 (4) Å long, which is the longest among the reported methano-bridged fullerenes. It is 0.12 Å longer than a C—C bond in cyclopropane (1.52 Å), leading to a slight deformation of the cyclopropane ring [angles C(9)—C(8)—C(10), C(8)—C(9)—C(10) and C(8)—C(10)—C(9) are 65.3 (2), 57.4 (2) and 57.3 (2)°, respectively]. The C(9)—C(10) bond length is more than 0.2 Å longer than that at the 6–6-ring junction of C_{60} (1.40 Å) determined by NMR spectroscopy (Yannoni, Bernier, Bethune, Meijer & Salem, 1991). The elongation of a C—C bond leads to a slight deformation of the C_{60} framework. The most affected bonds are those at the 6–6-ring junction in equatorial positions, C(17)—C(17′) and C(18)—C(18′), which have lengths of 1.370 (5) and 1.374 (5) Å, respectively. They are the shortest two bonds on the C_{60} sphere and thus have the highest double-bond character. This supports the theory, as demonstrated by theoretical and experimental methods, that the position of highest reactivity towards nucleophiles is at the equatorial position of singly methano-bridged fullerenes (Hirsch, Lamparth & Karfunkel, 1994; Hirsch, Lamparth, Grösser & Karfunkel, 1994).

Fig. 2 shows the crystal packing of (I). The packing is characterized by a layer parallel to the *ac* plane. The closest packed layers cut the *b* axis at $y = \frac{1}{4}$ and $\frac{3}{4}$. The molecules are arranged in the same direction in a layer. A convenient molecular axis passing through atom C(8) and the midpoint of C(25)—C(26) forms an angle of 41.3 (1)° with the *a* axis. The adjacent layers are related by a twofold screw axis perpendicular to the *ac* plane. The shortest intermolecular distance between the phenyl ring and the C_{60} sphere is 3.359 (3) Å, between atom C(2) of one molecule and atom C(37′) of the next molecule in the same layer. This is close to the sum of the van der Waals radii, suggesting a weak interaction, as observed in (3,4-dimethoxyphenyl)phenylmethano[60]-fullerene (Osterodt, Nieger & Vogtle, 1994).

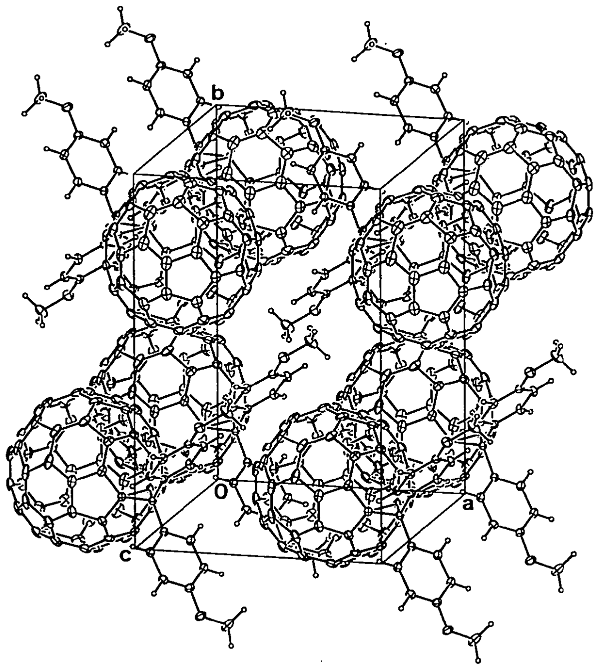


Fig. 2. A molecular packing diagram of (I) in the unit cell.

Experimental

The title compound, (I), was synthesized according to the literature method of Shi, Khemani, Li & Wudl (1992). A solution of 2 equiv. of bis(4-methoxyphenyl)diazomethane and one equiv. of C_{60} in toluene was stirred at room temperature for 12 h and then refluxed for 24 h. The products were separated by flash chromatography on neutral alumina using toluene/hexane (1:1 *v*/*v*) solution as eluent. One of the fractional solutions yielded black crystals without any cooling or concentration. The crystals were heated to 430 K under reduced pressure to remove traces of solvent. The density D_m was measured on a Berman density torsion balance.

Crystal data

$C_{75}H_{14}O_2$
$M_r = 946.9$
Monoclinic
$P2_1/m$
$a = 11.323$ (2) Å
$b = 17.602$ (4) Å
$c = 9.852$ (2) Å
$\beta = 101.94$ (2)°
$V = 1921.3$ (7) Å^3
$Z = 2$
$D_x = 1.63$ Mg m^{-3}
$D_m = 1.63$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 15$–17.5°
$\mu = 0.097$ mm^{-1}
$T = 298$ K
Prism
0.30 × 0.25 × 0.20 mm
Black

Data collection

Mac Science MXC18K diffractometer
$2\theta/\omega$ scans
Absorption correction: none
4980 measured reflections
4093 independent reflections
3003 observed reflections [$F > 3\sigma(F)$]

$R_{\rm int} = 0.03$
$\theta_{\rm max} = 27.5°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 12$
3 standard reflections monitored every 100 reflections
intensity decay: 3%

Refinement

Refinement on F
$R = 0.041$
$wR = 0.038$
$S = 0.756$
3003 reflections
383 parameters
H atoms refined isotropically
Unit weights applied

$(\Delta/\sigma)_{\rm max} = 0.430$
$\Delta\rho_{\rm max} = 0.17$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O(1)	0.5507 (1)	0.5009 (1)	0.8341 (2)	0.050 (1)
C(1)	0.6385 (3)	0.5341 (2)	0.7695 (4)	0.071 (2)
C(2)	0.4846 (2)	0.4420 (1)	0.7671 (2)	0.036 (1)
C(3)	0.4984 (2)	0.4125 (1)	0.6415 (2)	0.043 (1)
C(4)	0.4267 (2)	0.3522 (1)	0.5841 (2)	0.040 (1)
C(5)	0.3410 (2)	0.3210 (1)	0.6490 (2)	0.031 (1)
C(6)	0.3276 (2)	0.3518 (1)	0.7748 (2)	0.037 (1)
C(7)	0.3989 (2)	0.4115 (1)	0.8337 (2)	0.039 (1)
C(8)	0.2749 (2)	1/4	0.5914 (3)	0.031 (1)
C(9)	0.2125 (2)	1/4	0.4399 (3)	0.030 (1)
C(10)	0.1382 (2)	1/4	0.5656 (3)	0.030 (1)
C(11)	0.1906 (2)	0.1829 (1)	0.3467 (2)	0.035 (1)
C(12)	0.0597 (2)	0.1828 (1)	0.5675 (2)	0.036 (1)
C(13)	0.1829 (2)	0.2091 (1)	0.2063 (2)	0.044 (1)

C(14)	−0.0516 (2)	0.2092 (2)	0.6007 (2)	0.045 (1)
C(15)	0.1159 (2)	0.1696 (2)	0.0940 (2)	0.055 (1)
C(16)	−0.1593 (2)	0.1691 (2)	0.5565 (2)	0.056 (1)
C(17)	0.0452 (2)	0.2111 (2)	−0.0227 (2)	0.060 (1)
C(18)	−0.2709 (2)	0.2110 (2)	0.5099 (2)	0.064 (2)
C(19)	−0.0664 (2)	0.1690 (2)	−0.0690 (2)	0.061 (2)
C(20)	−0.3414 (2)	0.1692 (2)	0.3936 (3)	0.063 (2)
C(21)	−0.1735 (2)	0.2091 (2)	−0.1143 (2)	0.055 (1)
C(22)	−0.4097 (2)	0.2089 (2)	0.2829 (3)	0.059 (1)
C(23)	−0.2837 (2)	0.1836 (2)	−0.0749 (2)	0.050 (1)
C(24)	−0.4129 (2)	0.1835 (2)	0.1423 (2)	0.050 (1)
C(25)	−0.3519 (3)	1/4	−0.0511 (3)	0.046 (2)
C(26)	−0.4152 (3)	1/4	0.0564 (3)	0.047 (2)
C(27)	0.1246 (2)	0.1206 (1)	0.3710 (2)	0.040 (1)
C(28)	0.0579 (2)	0.1204 (1)	0.4835 (2)	0.040 (1)
C(29)	0.0527 (2)	0.0799 (1)	0.2540 (3)	0.050 (1)
C(30)	−0.0546 (2)	0.0797 (1)	0.4344 (3)	0.052 (1)
C(31)	0.0499 (2)	0.1033 (2)	0.1185 (3)	0.056 (2)
C(32)	−0.1600 (2)	0.1031 (2)	0.4725 (3)	0.058 (2)
C(33)	−0.0639 (2)	0.1029 (2)	0.0168 (3)	0.061 (2)
C(34)	−0.2739 (2)	0.1029 (2)	0.3697 (3)	0.061 (2)
C(35)	−0.1684 (2)	0.0787 (2)	0.0555 (3)	0.058 (2)
C(36)	−0.2755 (2)	0.0788 (2)	0.2359 (3)	0.059 (2)
C(37)	−0.2809 (2)	0.1201 (2)	0.0082 (3)	0.053 (1)
C(38)	−0.3469 (2)	0.1200 (2)	0.1198 (3)	0.053 (1)
C(39)	−0.0570 (2)	0.0546 (1)	0.2941 (3)	0.056 (2)
C(40)	−0.1654 (3)	0.0539 (2)	0.1964 (3)	0.060 (2)

Table 2. *Selected geometric parameters (Å, °)*

C(8)—C(9)	1.514 (4)	C(18)—C(18′)	1.374 (5)
C(8)—C(10)	1.516 (4)	C(21)—C(21′)	1.440 (5)
C(9)—C(10)	1.635 (4)	C(25)—C(26)	1.396 (5)
C(13)—C(13′)	1.438 (4)	C(39)—C(40)	1.395 (4)
C(17)—C(17′)	1.370 (5)		
C(5)—C(8)—C(5′)	112.1 (2)	C(8)—C(9)—C(10)	57.4 (2)
C(9)—C(8)—C(10)	65.3 (2)	C(8)—C(10)—C(9)	57.3 (2)
C(3)—C(4)—C(5)—C(8)	−173.1 (4)	C(8)—C(5)—C(6)—C(7)	172.5 (4)

Data collection: MAC Science MXC software. Cell refinement: MAC Science MXC software. Data reduction: MAC Science MXC software. Program(s) used to solve structure: *SIR* (Altomare *et al.*, 1994) in *CRYSTAN-GM* (Edwards, Gilmore, Mackay & Stewart, 1995). Program(s) used to refine structure: *LSQ* (Mallinson & Muir, 1985) in *CRYSTAN-GM*. Molecular graphics: *ORTEP* (Johnson, 1965) in *CRYSTAN-GM*. Software used to prepare material for publication: *CRYSTAN-GM*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1208). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-Cyano-1-[4-(1,3-dithian-2-yl)butyl]-1,4,5,6-tetrahydropyridine

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Abstract

The title nitrile {1-[4-(1,3-dithian-2-yl)butyl]-1,4,5,6-tetrahydropyridine-3-carbonitrile, $C_{14}H_{22}N_2S_2$} was prepared as part of our investigations into the conjugate addition reactions of unsaturated nitriles [Fleming & Pak (1995). *J. Org. Chem.* **60**, 4299–4301]. The tetrahydropyridine ring adopts a half-chair conformation and is appended by a four-carbon chain to the dithiane ring which adopts a chair conformation.

Comment

Conjugate addition to unsaturated nitriles is often problematic with conventional nucleophiles (Lipshutz, Wilhelm & Kozlowski, 1984; House & Umen, 1973). We sought to promote the conjugate addition reaction by tethering a nucleophilic dithiane anion to an unsaturated nitrile and therefore prepared the title compound, (I), as a suitable substrate for this reaction. (I) is readily prepared by coupling 3-cyanotetrahydropyridine (Kikugawa, Kuramoto, Saito & Yamada, 1973) with 2-(4-chlorobutyl)-1,3-dithiane (Seebach, Jones & Corey, 1968). Concentration of the crude reaction mix-

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