

Hexaphenylbenzene $C_6(C_6H_5)_6$

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Abstract

The structure of the title compound has been determined by single-crystal X-ray diffraction work. The crystals are orthorhombic, space group $Pna2_1$ with $a = 11.095(3)$, $b = 21.834(7)$, $c = 12.574(4)$ Å, and $R1 = 0.0667$. The average carbon bond length in aromaticity in the molecule is 1.386(1) Å and the average single bond length linking the central benzene ring and peripheral phenyl rings is 1.491(3) Å. The average dihedral angle between the central benzene ring and each of six peripheral phenyl rings is $67.1(1)^\circ$ and the average dihedral angle between neighboring two phenyl rings is $55.0(1)^\circ$. Thus the molecule adopts a quasi-propeller configuration with approximate six-fold rotation symmetry.

1. Introduction

In the process of the synthesis of the 1,4-bis((E)-2-(1-methyl-2,3,4,5-tetraphenyl-1H-silolilyl)vinyl)benzene good single crystals were obtained and so we collected its intensities of a hemisphere of reciprocal space with a resolution 0.75 Å and then solved the structure. Unexpectedly, however, the hexaphenylbenzene (I) was obtained. The synthetic mechanism of (I) is not clear, but the study of the mechanism is in progress in our group.

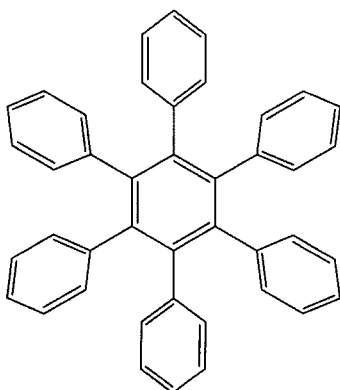
The structure of (I) was already elucidated by

Bart in 1968.¹⁾ Here we report a better structural result of (I) than previous one.¹⁾

2. Experimental section

2-1. Collection and reduction of X-ray diffraction data

Suitable crystal of $C_6(C_6H_5)_6$ was mounted in air on a glass fiber tip onto a goniometer head. Single-crystal X-ray diffraction data were collected on a Bruker SMART diffractometer²⁾ with 1 K CCD area detector using graphite-monochromated $MoK\alpha$ radiation ($\lambda = 0.71072$ Å) at room temperature (295(2)K). Unit cell parameters were initially obtained from the reflections taken from 60 frames collected in three different ω regions and eventually refined against about 3311 reflections. A hemisphere of reciprocal space was scanned by 0.3° ω steps, collecting 1800 frames each at 10 s exposure. Intensity decay was monitored by recollecting the initial 50 frames at the end of data collection and analyzing the duplicate reflections. The collected frames were processed for integration; an empirical absorption correction was made on the basis of the symmetry-equivalent reflection intensities.³⁾ The reflection conditions $0kl : k + l = 2n$ and $h0l : h = 2n$ indicated this compound could belong to either space group $Pna2_1(33)$ or



(I)

Pnam(62).

2-2. Structure solution and refinement

The structure was solved by direct methods and subsequent Fourier synthesis with the space group Pna2₁; it was refined by full-matrix least-squares on F^2 using reflections with $I > 2\sigma(I)$.⁴⁾ Scattering factors for neutral atoms and anomalous dispersion corrections were taken from the internal library of SHELX97. Weights were assigned to individual observations according to the formula $\omega = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $p = (F_o^2 + 2F_c^2)/3$; a and b were chosen to give a flat analysis of variance in terms of F_o^2 . Anisotropic displacement parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were placed in idealized position riding on their parent atom with an isotropic displacement parameter 1.2 times that of the pertinent carbon atom. Final difference electron density map showed no features of chemical significance, with highest peak 0.19 at 1.40 Å from C4 atom. The crystallographic data, final conventional agreement indexes and other structure

refinement parameters are listed in Table 1. The absolute structure parameter 9(10) means that the absolute structure can not be determined reliably because the molecule does not contain anomalous scatterer. Final atomic coordinates and the equivalent isotropic thermal parameters are given in Table 2.

3. Results and discussion

An ORTEP diagram of (I) with the atomic labeling scheme is shown in Fig. 1,⁵⁾ and the selected bond lengths and angles are presented in Table 3. A full list of I_{obs} and I_{cal} is available from authors.

As shown in Table 2, all atoms have quite normal thermal parameters except for the abnormally high thermal parameters of C(33), C(34), C(35). Reasonably enough the thermal parameters for the central benzene ring atoms are nearly isotropic and the atoms in the peripheral phenyl rings have gradually increasing values of the thermal parameters as their distances from the center of the molecule increase. The similar tendency occurred in the previous one.¹⁾

Table 1. Crystal data and structure refinement for (I)

Empirical formula	C42 H30	
Formula weight	534.66	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	orthorhombic, Pna2(1)	
Unit cell dimensions	a = 11.095(3) Å b = 21.834(7) Å c = 12.574(4) Å	alpha = 90 deg. beta = 90 deg. gamma = 90 deg.
Volume	3046.0(17) Å ³	
Z, Calculated density	4, 1.166 Mg/m ³	
Absorption coefficient	0.066 mm ⁻¹	
F(000)	1128	
Crystal size	0.26 × 0.20 × 0.09 mm	
Theta range for data collection	1.87 to 28.31 deg.	
Limiting indices	-12 ≤ h ≤ 14, -28 ≤ k ≤ 28, -16 ≤ l ≤ 13	
Reflections collected/unique	19374/6041 [R(int) = 0.0865]	
Completeness to theta = 28.31	99.6%	
Max. and min. transmission	0.9941 and 0.9828	
Refinement method	Full-matrix least-squares on F ²	
Data/restraints/parameters	6041/1/379	
Goodness-of-fit on F ²	1.004	
Final R indices [I > 2σ(I)]	R1 = 0.0667, wR2 = 0.1548	
R indices (all data)	R1 = 0.2052, wR2 = 0.2427	
Absolute structure parameter ⁶⁾	9(10)	
Largest diff. peak and hole	0.192 and -0.262 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (I). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
C(1)	7038(5)	1742(2)	6995(5)	58(2)
C(2)	6963(5)	1935(2)	5932(5)	58(1)
C(3)	7099(5)	1513(3)	5095(5)	56(1)
C(4)	7256(5)	886(2)	5324(5)	57(1)
C(5)	7359(5)	693(2)	6379(5)	57(1)
C(6)	7273(5)	1117(2)	7220(5)	56(1)
C(7)	6845(5)	2182(3)	7880(5)	60(2)
C(8)	7646(6)	2657(3)	8074(6)	75(2)
C(9)	7446(7)	3073(3)	8897(6)	84(2)
C(10)	6466(8)	3005(4)	9534(7)	91(2)
C(11)	5656(8)	2546(4)	9356(6)	92(2)
C(12)	5859(6)	2127(3)	8540(5)	75(2)
C(13)	6741(5)	2600(2)	5692(5)	61(2)
C(14)	7613(6)	2957(3)	5196(6)	72(2)
C(15)	7395(7)	3578(3)	4974(6)	83(2)
C(16)	6325(8)	3835(3)	5271(7)	89(2)
C(17)	5463(7)	3499(3)	5769(6)	83(2)
C(18)	5656(5)	2876(3)	5990(6)	71(2)
C(19)	7111(5)	1720(3)	3967(5)	60(2)
C(20)	8194(6)	1697(3)	3403(5)	71(2)
C(21)	8236(8)	1857(3)	2327(6)	88(2)
C(22)	7212(8)	2037(3)	1812(7)	94(2)
C(23)	6144(8)	2075(3)	2369(6)	89(2)
C(24)	6091(6)	1923(3)	3441(6)	77(2)
C(25)	7339(5)	433(2)	4445(5)	56(1)
C(26)	8372(5)	94(3)	4265(5)	69(2)
C(27)	8406(6)	-335(3)	3447(6)	74(2)
C(28)	7447(7)	-423(3)	2805(6)	79(2)
C(29)	6417(6)	-86(3)	2952(6)	77(2)
C(30)	6358(6)	343(3)	3755(5)	68(2)
C(31)	7541(6)	30(3)	6645(5)	64(2)
C(32)	8620(7)	-164(3)	7081(6)	85(2)
C(33)	8796(11)	-780(4)	7338(7)	123(4)
C(34)	7854(15)	-1184(5)	7160(9)	150(6)
C(35)	6814(12)	-1013(4)	6724(9)	133(4)
C(36)	6643(7)	-392(3)	6448(7)	90(2)
C(37)	7482(5)	930(2)	8339(5)	57(1)
C(38)	8520(5)	1116(3)	8871(5)	63(2)
C(39)	8740(6)	938(3)	9892(6)	76(2)
C(40)	7949(7)	565(3)	10441(6)	82(2)
C(41)	6919(7)	386(3)	9936(6)	81(2)
C(42)	6673(6)	557(3)	8893(6)	74(2)

The carbon bond lengths in aromaticity in the molecule range from 1.331(15) of C(35)-C(34) to 1.418(7) Å of C(2)-C(6) Å with a mean value of 1.386(1) Å and the C-C-C angles are from 117.5(6)°

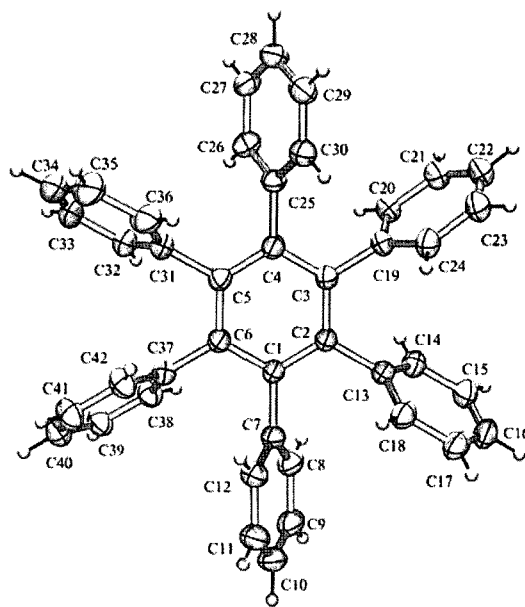


Fig. 1. The ORTEP drawing⁵⁾ of a molecule projected onto the least-square plane through the central benzene ring with 15% probability and the labeling of the atoms. H-atoms are represented as spheres of arbitrary radii.

to 123.1(6)° with a mean of 120.2(1)°.

The single bond length linking the central benzene ring and peripheral phenyl rings range from 1.484(9) to 1.504(8) Å with a mean value of 1.491(3) Å meaning clearly single bond length.

The central benzene ring, C1, C2, C3, C4, C5, C6, is planar within 0.025(4) Å, and its peripheral rings C7, C8, C9, C10, C11, C12 (A) within 0.011(5); C13, C14, C15, C16, C17, C18 (B) within 0.008(5); C19, C20, C21, C22, C23, C24, C25 (C) within 0.015(4); C25, C26, C27, C28, C29, C30 (D) within 0.012(4); C31, C32, C33, C34, C35, C36 (E) within 0.012(8); C37, C38, C39, C40, C41, C42 (F) within 0.007(5) Å (see Fig. 1).

The dihedral angles between the central benzene ring and each of its six peripheral phenyl rings A to F are 65.7(2), 66.2(2), 70.1(2), 62.2(2), 69.2(3), 69.3(2)°, respectively, and their average value is 67.1(1)°. The dihedral angles between two neighboring planes from A to F in sequence are 52.3(2), 57.9(3), 54.5(2), 55.1(2), 51.4(3), 58.9(2)°, respectively, with an average value 55.0(1)°. All average

Table 3. Bond lengths [\AA] and angles [deg] for (I)

C(1)-C(2)	1.404(8)	C(1)-C(6)	1.418(7)	C(1)-C(7)	1.486(8)
C(2)-C(3)	1.407(8)	C(2)-C(13)	1.504(8)	C(3)-C(4)	1.409(8)
C(3)-C(19)	1.488(8)	C(4)-C(5)	1.397(8)	C(4)-C(25)	1.486(8)
C(5)-C(6)	1.407(8)	C(5)-C(31)	1.500(7)	C(6)-C(37)	1.484(9)
C(7)-C(12)	1.378(9)	C(7)-C(8)	1.387(8)	C(8)-C(9)	1.395(10)
C(9)-C(10)	1.360(10)	C(10)-C(11)	1.365(10)	C(11)-C(12)	1.393(9)
C(13)-C(14)	1.390(8)	C(13)-C(18)	1.398(8)	C(14)-C(15)	1.404(9)
C(15)-C(16)	1.365(10)	C(16)-C(17)	1.359(10)	C(17)-C(18)	1.403(8)
C(19)-C(24)	1.384(8)	C(19)-C(20)	1.395(8)	C(20)-C(21)	1.398(9)
C(21)-C(22)	1.366(10)	C(22)-C(23)	1.379(10)	C(23)-C(24)	1.390(10)
C(25)-C(26)	1.383(8)	C(25)-C(30)	1.405(8)	C(26)-C(27)	1.392(9)
C(27)-C(28)	1.350(9)	C(28)-C(29)	1.371(9)	C(29)-C(30)	1.379(9)
C(31)-C(36)	1.380(8)	C(31)-C(32)	1.384(9)	C(32)-C(33)	1.397(10)
C(35)-C(34)	1.331(15)	C(35)-C(36)	1.412(11)	C(33)-C(34)	1.386(15)
C(37)-C(38)	1.392(8)	C(37)-C(42)	1.398(8)	C(38)-C(39)	1.363(9)
C(39)-C(40)	1.382(9)	C(40)-C(41)	1.365(9)	C(41)-C(42)	1.390(10)
C(2)-C(1)-C(6)	119.3(5)	C(2)-C(1)-C(7)	120.7(5)		
C(6)-C(1)-C(7)	120.0(6)	C(1)-C(2)-C(3)	120.7(5)		
C(1)-C(2)-C(13)	119.4(5)	C(3)-C(2)-C(13)	120.0(5)		
C(2)-C(3)-C(4)	119.8(5)	C(2)-C(3)-C(19)	121.0(5)		
C(4)-C(3)-C(19)	119.2(5)	C(5)-C(4)-C(3)	119.8(5)		
C(5)-C(4)-C(25)	120.0(5)	C(3)-C(4)-C(25)	120.1(5)		
C(4)-C(5)-C(6)	120.6(5)	C(4)-C(5)-C(31)	120.9(5)		
C(6)-C(5)-C(31)	118.4(5)	C(5)-C(6)-C(1)	119.7(6)		
C(5)-C(6)-C(37)	121.4(5)	C(1)-C(6)-C(37)	118.8(5)		
C(12)-C(7)-C(8)	117.9(6)	C(12)-C(7)-C(1)	120.6(5)		
C(8)-C(7)-C(1)	121.6(6)	C(7)-C(8)-C(9)	121.1(7)		
C(10)-C(9)-C(8)	119.5(7)	C(9)-C(10)-C(11)	120.7(8)		
C(10)-C(11)-C(12)	119.8(8)	C(7)-C(12)-C(11)	121.0(7)		
C(14)-C(13)-C(18)	118.6(5)	C(14)-C(13)-C(2)	121.2(5)		
C(18)-C(13)-C(2)	120.2(5)	C(13)-C(14)-C(15)	120.7(6)		
C(16)-C(15)-C(14)	119.5(7)	C(17)-C(16)-C(15)	121.0(7)		
C(16)-C(17)-C(18)	120.5(7)	C(13)-C(18)-C(17)	119.7(6)		
C(24)-C(19)-C(20)	118.2(6)	C(24)-C(19)-C(3)	123.1(6)		
C(20)-C(19)-C(3)	118.7(5)	C(19)-C(20)-C(21)	120.8(7)		
C(22)-C(21)-C(20)	120.2(8)	C(21)-C(22)-C(23)	119.4(8)		
C(22)-C(23)-C(24)	120.9(7)	C(19)-C(24)-C(23)	120.4(7)		
C(26)-C(25)-C(30)	117.8(6)	C(26)-C(25)-C(4)	121.9(5)		
C(30)-C(25)-C(4)	120.3(5)	C(25)-C(26)-C(27)	120.2(6)		
C(28)-C(27)-C(26)	121.1(6)	C(27)-C(28)-C(29)	120.0(7)		
C(28)-C(29)-C(30)	120.1(7)	C(29)-C(30)-C(25)	120.7(6)		
C(36)-C(31)-C(32)	119.4(6)	C(36)-C(31)-C(5)	120.5(6)		
C(32)-C(31)-C(5)	120.1(6)	C(31)-C(32)-C(33)	120.5(8)		
C(34)-C(35)-C(36)	119.1(11)	C(34)-C(35)-C(32)	118.0(10)		
C(35)-C(34)-C(33)	122.9(10)	C(31)-C(36)-C(35)	120.0(9)		
C(38)-C(37)-C(42)	117.5(6)	C(38)-C(37)-C(6)	120.3(5)		
C(42)-C(37)-C(6)	122.2(6)	C(39)-C(38)-C(37)	121.1(6)		
C(38)-C(39)-C(40)	121.7(7)	C(41)-C(40)-C(39)	117.9(7)		
C(40)-C(41)-C(42)	121.8(6)	C(41)-C(42)-C(37)	120.0(6)		

values are calculated by the Program ESD.⁷⁾

The unequal magnitudes of the above-mentioned bond distances, angles, and dihedral angles verify there can be only a pseudo six-fold rotation sym-

metry along the normal of the central benzene ring in a molecule, but the molecular configuration is certainly very similar to a propeller model whose pivot is the normal of the central benzene ring as

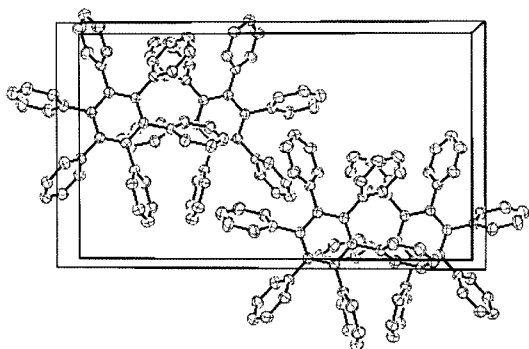


Fig. 2. The ORTEP drawing⁵⁾ of four molecules in a unit cell viewed along [100]. Hydrogen atoms are omitted for clarity. Origin, lower left; b-axis, horizontal; c-axis, vertical.

shown in Fig. 1.

The overall geometry of the molecule in this paper is similar to that elucidated by Bart.¹⁾ However the results elucidated with 6041 unique reflections in this paper are much better than those carried out with only 1405 reflections by Bart⁽¹⁾, let

alone the structural accuracy.

There is no intermolecular contact less than 2.031 Å. Fig. 2 shows a packing diagram viewed along [100] direction which demonstrates that the directions of the central benzene rings are parallel to that of the shortest a-axis.

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