Chem. Ber. **116**, 3359–3365 (1983)

An Improved Synthesis of Hexavinylbenzene and its Solid State Structure

Carl Krüger and *Mohamed Yalpani**

Max-Planck-Institut für Kohlenforschung,
Kaiser-Wilhelm-Platz 1, D-4330 Mülheim an der Ruhr

Received February 3, 1983

Hexavinylbenzene (**1**) has been synthesized from hexakis(1-bromoethyl)benzene in over 95% yield. Its solid state photopolymerisation is non-specific in accordance with its molecular packing in the crystals.

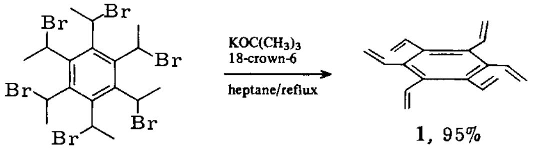
Eine verbesserte Synthese von Hexavinylbenzol und seine Struktur im Festzustand

Hexavinylbenzol (**1**) wurde aus Hexakis(1-bromethyl)benzol mit über 95% Ausbeute dargestellt. Die Photopolymerisation im festen Zustand ist nichtspezifisch in Übereinstimmung mit der Molekülpackung im Kristall.

Space filling molecular models of hexavinylbenzene indicate the alternately *anti*-arrangement of the vinyl groups would lead to the least crowded conformation **1** with a D_{3d} symmetry. This conformation is also found in the structurally similar hexaethylbenzene and its η^6-arene tricarbonyl complexes$^{1)}$ as well as in several other substituted hexamethylbenzenes$^{2)}$.

Provided molecules of **1** were stacked favourably in the crystal lattice, they would be a potential monomer for solid state polymerization to a poly[3.3′.3.3′.3.3′]cyclophane. We set out to explore this possibility.

The colourless per-olefinic benzene **1** had been prepared in 8% crude yield$^{3)}$. Repeating the procedure reported using a more concentrated alcoholic potassium hydroxide solution resulted in a 40% yield of **1**. The yield could be further improved to over 90% by the recently described procedure for dehydrohalogenation reactions$^{4)}$ using potassium *tert*-butoxide and a crown ether in a hydrocarbon solvent.



1, 95%

Crystals of **1** had been reported to turn yellow on exposure to light and even on extended standing in the dark with the resulting formation of insoluble materials$^{3)}$. We found that irradiation of solid hexavinylbenzene with a 125 watt medium pressure lamp in the form of a thin film of crystals deposited on the walls of the reaction vessel gave,

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after 24 h, a red-brown crystalline solid which was totally insoluble in all organic solvents tested, did not melt up to 300 °C, and had no vapor pressure in high vacuum (no mass spectrum). The infra-red spectrum showed residual vinyl, together with aliphatic C – H and C – C stretching and vibrational bands.

In view of the observed solid state decomposition the molecular geometry and packing of 1 deserves special attention. The molecular geometry is depicted in Fig. 1.

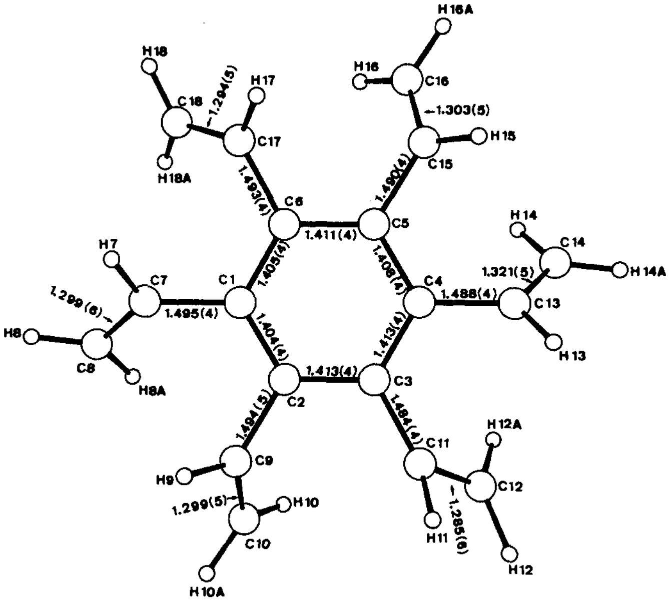

Fig. 1. Molecular geometry of hexavinylbenzene (**1**)

Contrary to the initial assumption of molecular symmetry D_{3d}, all vinyl groups point in one direction only, resulting in approximate molecular symmetry C_6. Whereas all central C – C bonds may be averaged within reasonable limits to yield the expected values ($C_{Ph} - C_{Ph}$ 1.409(4), $C_{Ph} - C_{sp^2}$ 1.491(4)), a larger discrepancy in the averaged bond lengths of the vinyl groups (1.30(1) Å) is observed. This may be attributed to a larger thermal motion of these groups. Correction for rigid body thermal motion does not improve the overall agreement significantly. It seems worthwhile mentioning that the angular arrangement of all vinyl groups at the benzene ring is not perpendicular to the ring plane, but rather shows torsional angles of about 135°. However, these differ substantially from each other (see Table 1). As seen in Fig. 2 this arrangement is brought about by close contacts between double bonds of one vinyl group and one of the terminal hydrogen atoms of a neighbouring vinyl group. In this way short contacts between hydrogen atoms themselves are avoided (cf. Table 2). All non-bonded distances between vinyl groups within one molecule are between 2.878 and 2.921 Å. The values indicate less overcrowding than found for hexamethylradialene(6). The benzene ring is planar within ± 0.007 Å. A summary of all intramolecular angles are given in Table 1, and bond lengths are summarized in Fig. 1.

Table 1. Bond and torsional angles (°)

C1-C2-C3	120.1(3)	C8-C7-C1	126.2(4)
C2-C3-C4	119.6(3)	C10-C9-C2	126.1(4)
C3-C4-C5	120.2(3)	C12-C11-C3	128.5(4)
C4-C5-C6	119.8(3)	C14-C13-C4	125.4(3)
C5-C6-C1	120.1(3)	C16-C15-C5	126.8(3)
C6-C1-C2	120.2(3)	C18-C17-C6	126.9(3)
C7-C1-C2	120.6(3)	C13-C4-C5	120.7(3)
C7-C1-C6	119.0(3)	C13-C4-C3	119.0(3)
C9-C2-C3	120.7(3)	C15-C5-C6	121.4(3)
C9-C2-C1	119.1(3)	C15-C5-C4	118.7(3)
C11-C3-C4	122.0(3)	C17-C6-C1	121.4(3)
C11-C3-C2	118.2(3)	C17-C6-C5	118.5(3)
C6-C1-C7-C8	134.76	C3-C4-C13-C14	130.19
C1-C2-C9-C10	128.39	C4-C5-C15-C16	135.61
C2-C3-C11-C12	138.21	C5-C6-C17-C18	133.87

Table 2. Short intramolecular distances between adjacent vinyl groups in **1**

C7–C9	2.892	C8–C10	3.700
C9–C11	2.878	C10–C12	3.840
C11–C13	2.921	C12–C14	3.811
C13–C15	2.885	C14–C16	3.801
C15–C17	2.898	C16–C18	3.773
C17–C7	2.908	C18–C8	3.804
averaged to 2.897(16)		averaged to 3.79(5)	

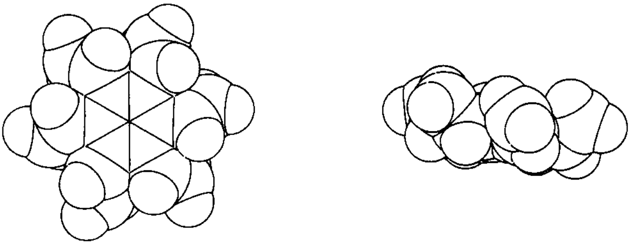

Fig. 2. Space filling model of **1**

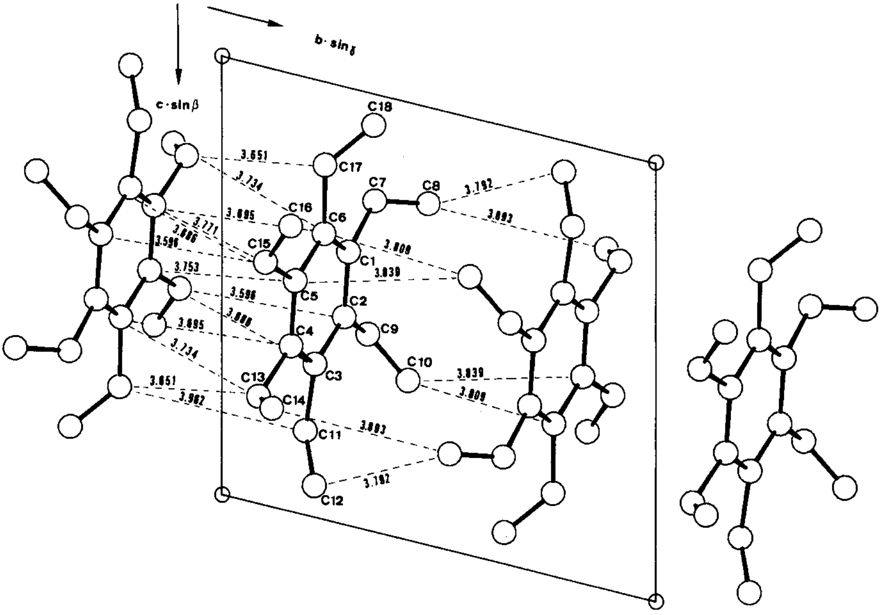

Fig. 3. Intermolecular distances of **1**

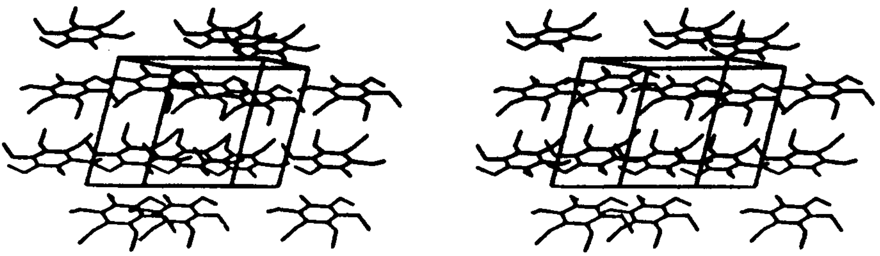

Fig. 4. Stereo view of molecules of **1** in the crystal

As seen in Fig. 3, two molecules of **1** are arranged in pairs across a centre of inversion such that aromatic rings are facing each other and all substituents point away from each other. These pairs of molecules form molecular columns as evident from Fig. 3. Intermolecular distances (Fig. 3) indicate that the contacts within the given molecular pairs are rather short (3.59 to 3.73 Å) and involve mainly atoms of the central benzene ring, but also some vinyl group contacts. Intramolecular contacts of vinyl groups, for comparison, range from 2.87 (inner sphere) to 3.80 Å (outer sphere). In contrast, close contacts to the adjacent pairs of molecules within one stack are made by vinyl groups only (3.7 to 3.8 Å). This arrangement of molecules yields an unfavourable low packing coefficient[5] of 0.61. This value may be compared to the rather normal values of hexaethylidenecyclohexane[6] (0.72), hexaethylbenzene[1] (0.71), and triisopropylidenecyclopropane[5] (0.70). All intermolecular distances to adjacent stacks of molecules range from 3.95 Å upwards. The arrangement of molecular columns is clearly shown in a stereo view, given in Fig. 4. It seems evident from the given intermolecular distances that, according to *Schmidt's*[7] rules of solid state photochemical reactions, a non-specific polymerization (α-type reaction) along one stack may occur upon irradiation[7]. Similar observations have been reported for triisopropylidenecyclopropane[8].

In agreement with this irradiation of the single crystal used for the above analysis with a medium pressure lamp resulted only in the progressive disappearance of the diffraction pattern without any significant changes in the crystal shape.

Experimental Part

Preparation of hexavinylbenzene (**1**): 5.5 g (7.6 mmol) of hexakis(1-bromoethyl)benzene, 5.65 g (50.3 mmol) of potassium *tert*-butoxide, and 0.18 g of 18-crown-6 in 150 ml of *n*-heptane under argon were stirred and refluxed for 2 h. After cooling the suspension was added to about 200 ml of ice water. The organic layer was separated and the aqueous layer after neutralization with dilute sulfuric acid was extracted with pentane. The combined organic phase was dried over Na_2SO_4. It gave 1.78 g of a light brown crystalline solid. Recrystallization from methanol afforded 1.55 g (88%) of a pale yellow solid, m.p. 77 – 78 °C (Lit.[3] 77 – 78.5 °C). From the mother liquor after filtration on silica-gel another 0.18 g of the substance was obtained. ^1H NMR ($CDCl_3$) is in agreement with that reported[3].

*Crystal structure determination**): Hexavinylbenzene (**1**) forms plate-like triclinic crystals which darken upon prolonged exposure to X-rays. Accurate values (Nonius CAD 4 diffractometer) of the cell dimensions [a = 8.7862(7), b = 9.233(1), c = 10.1838(5) Å, α = 76.037(6)°, β = 62.195(7)°, γ = 86.003(8)°, V = 708.311 Å^3, Z = 2, d_c = 1.0988 gcm^{-3}, $P\bar{1}$] were obtained by a least squares analysis of Bragg angles for 75 reflections.

Intensity data of the same crystal (dimensions 0.8 × 0.5 × 0.1 mm), which was sealed in a thin walled glass capillary under argon atmosphere and showed just satisfactory quality in preliminary scans, were collected to Θ = 74.6° (Ni-filtered Cu radiation, λ = 1.54179 Å). The ω-2Θ scan technique with the scans varying from 1.3 to 10.0° min^{-1}, depending on the standard deviation to intensity ratio of a preliminary fast scan, was used. A total of 2906 reflections were recorded ($\pm h$, $\pm k$, l), from which 777 were considered unobserved ($I \geq 2.0\sigma(I)$). A Ni-filter was inserted in front of the detector if the peak count was greater than 50000 counts s^{-1}. The intensity of three monitor reflections (4 3 3, 2 1 5, 3 4 0) were remeasured after every 90 min of X-ray exposure. From the variation of these intensities, a 10% isotropic decay of the crystal was detected and intensities were corrected accordingly. Intensities were also corrected for Lorentz- and Polarisation effects, but the effects of X-ray absorption were not taken into account (μ = 4.3 cm^{-1}). The structure was finally solved after several rescaling procedures by direct methods[9]. One E-map revealed all heavy atoms, yielding an initial R-value of 0.20. After anisotropic refinement of these atoms, all hydrogen atom positions were clearly evident. From a difference Fourier synthesis hydrogen atom parameters were included in the final refinement, which converged for 235 refined parameters at R = 0.082 (R_w = 0.10). As consequence of the rather poor crystal quality as well as of the observed decomposition of the crystal, no efforts were undertaken to continue the refinement any further. The function minimized in the full matrix least squares refinement was $\Sigma\omega (F_o - F_c)^2$[2]

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*) Further details and basic data concerning the X-ray analysis may be obtained from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen (W. Germany), by specifying registry number CSD 50376, author, and source.

with $\omega = 1/\sigma(F_0)$. A final difference Fourier synthesis was essentially featureless. Neutral scattering factors for carbon were those of *Cromer* and *Waber*[10], and those for hydrogen were taken from *Stewart, Davidson,* and *Simpson*[11]. Final atomic parameters are given in Table 3.

Table 3. Final atomic parameters of **1**

ATOM	X	Y	Z	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
C1	0.6579(3)	0.2911(3)	0.3757(2)	0.041	0.059	0.039	-0.004	-0.019	-0.006
C2	0.6261(3)	0.2813(3)	0.5261(2)	0.048	0.056	0.044	-0.004	-0.026	-0.009
C3	0.4698(3)	0.2137(3)	0.6504(2)	0.057	0.053	0.035	-0.006	-0.023	-0.009
C4	0.3444(3)	0.1587(2)	0.6223(2)	0.045	0.051	0.037	-0.004	-0.015	-0.011
C5	0.3767(3)	0.1685(3)	0.4713(2)	0.043	0.053	0.040	0.000	-0.019	-0.016
C6	0.5340(3)	0.2346(3)	0.3480(2)	0.042	0.060	0.034	0.002	-0.018	-0.014
C7	0.8281(3)	0.3514(4)	0.2436(3)	0.046	0.093	0.046	-0.010	-0.019	-0.010
C8	0.9084(5)	0.4753(5)	0.2202(4)	0.070	0.120	0.059	-0.044	-0.031	0.009
C9	0.7634(3)	0.3356(3)	0.5526(3)	0.052	0.082	0.054	-0.006	-0.029	-0.018
C10	0.7447(5)	0.4287(4)	0.6357(4)	0.080	0.090	0.068	-0.015	-0.037	-0.025
C11	0.4491(4)	0.1917(3)	0.8072(3)	0.091	0.073	0.039	-0.018	-0.034	-0.005
C12	0.3163(6)	0.2125(5)	0.9277(4)	0.112	0.122	0.046	-0.035	-0.029	-0.016
C13	0.1828(3)	0.0834(3)	0.7543(3)	0.057	0.071	0.042	-0.013	-0.015	-0.011
C14	0.0253(4)	0.1142(5)	0.7745(4)	0.055	0.108	0.054	-0.019	-0.014	-0.020
C15	0.2473(3)	0.0992(3)	0.4463(3)	0.051	0.067	0.049	-0.011	-0.019	-0.019
C16	0.1904(4)	0.1577(4)	0.3487(3)	0.052	0.107	0.055	-0.012	-0.027	-0.026
C17	0.5676(3)	0.2368(4)	0.1896(3)	0.046	0.084	0.040	0.001	-0.019	-0.022
C18	0.6269(4)	0.3492(5)	0.0722(3)	0.058	0.123	0.035	-0.014	-0.020	-0.008
H7	0.890(4)	0.298(4)	0.159(4)	0.076					
H8	1.026(5)	0.507(4)	0.120(4)	0.077					
H8A	0.829(5)	0.533(4)	0.308(5)	0.098					
H9	0.894(5)	0.305(4)	0.498(4)	0.088					
H10	0.628(5)	0.467(4)	0.681(4)	0.083					
H10A	0.853(5)	0.452(4)	0.645(4)	0.097					
H11	0.501(3)	0.135(3)	0.875(3)	0.046					
H12	0.331(4)	0.176(4)	1.038(4)	0.081					
H12A	0.213(6)	0.261(5)	0.904(5)	0.129					
H13	0.192(4)	0.001(4)	0.840(4)	0.070					
H14	0.020(5)	0.195(4)	0.688(4)	0.086					
H14A	-0.072(4)	0.053(4)	0.871(4)	0.072					
H15	0.197(4)	-0.001(4)	0.512(3)	0.066					
H16	0.230(4)	0.258(4)	0.280(4)	0.078					
H16A	0.110(5)	0.096(4)	0.338(4)	0.090					
H17	0.554(4)	0.141(4)	0.171(4)	0.080					
H18	0.648(4)	0.340(3)	-0.030(4)	0.066					
H18A	0.639(5)	0.436(4)	0.093(4)	0.084					

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