Synthesis and X-Ray Structure of 1,3,5-Tri(phenylethynyl)benzene
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Abstract

The chemistry which has been used for preparing 1,3,5-triiodobenzene (1) is based on the well established palladium catalyzed cross-coupling reaction of terminal acetylenes and aryl halides [10]. Treating a triethylamine solution of 1,3,5-triiodobenzene with 3 equivalents of phenylacetylene at room temperature in the presence of Pd(dba)2 and P3P resulted in the formation of white crystalline 1 with yields of 60 to 65%.

Especially catalyzed, 1,3,5-triiodobenzene reacts with excess PhC≡CH or PhC≡CYb1 to yield 3,5-I2C6H3(C≡CPh) + 3 HI

Crystals of 1 suitable for X-ray diffraction were obtained by crystallization from hexane. The most interesting feature of the molecular structure (Fig. 1) is the non planar conformation of the molecule indicating that there is no significant electron delocalization between the aromatic rings via the ethynyl bridges. While two phenyl groups are nearly coplanar with the central benzene ring, with torsion angles of 0.2(6) and 8.9(5)°, the third one is almost perpendicular to it (80.6(2)°). Furthermore, the significant differences in the C-C=C-C bond lengths of each bridging unit (1.455(11) / 1.161(10) Å) are proof of pronounced single and triple bond character.

Results and Discussion

The chemistry which has been used for preparing 1,3,5-tri(phenylethynyl)benzene (1) is based on the well established palladium catalyzed cross-coupling reaction of terminal acetylenes and aryl halides [10]. Treating a triethylamine solution of 1,3,5-triiodobenzene with 3 equivalents of phenylacetylene shows an unusual non planar molecular structure.

Introduction

One of the most exciting areas in chemical research which attracted interest in recent years is that of the acetylene chemistry. Thus, acetylenes are used as ideal rigid building blocks in the synthesis of dendrimers, π-conjugated polymers and new rigid rod materials [1 - 7]. Acyclic substituted ethynyl arenes are of crucial importance in designing and synthesizing novel organometallic molecules [8]. Recently polynuclear complexes with (phenylethynyl)benzenes coordinated to tricarbonylchromium units were prepared by coupling tricarbonyl[η^6-(phenylethynylbenzene)]-chromium(0) with triiodobenzene [9]. The most highly substituted complex of this type, μ3-[η^6-η^6-η^6-[1,3,5-benzenetriyltris(2,1-ethynyl)]tris-(benzene)]tris[tricarbonylchromium(0)] contains the ligand 1,3,5-tri(phenylethynyl)benzene, which, until now, has not been isolated in the free state. Since this ligand promises to be of great value in the synthesis of novel organometallic complexes, we describe its isolation and structure.

1,3,5-Tri(phenylethynyl)benzene 1 obtained by coupling triiodobenzene with phenylacetylene shows an unusual non planar molecular structure.
Fig. 1. ORTEP [11] plot of the molecule with the labelling scheme used. Thermal ellipsoids correspond to 50% probability. Hydrogen atoms are omitted for clarity.

Fig. 2. PLUTON [12] plot of the unit cell. The viewing direction is along the monoclinic axis $b$.

of the molecules is not perpendicular but diagonal to the stacking direction (see Fig. 5) allowing the perpendicular phenyl group to take part in the stacking as well. Since the molecule is not planar, least squares planes were calculated separately for each ring to approximate the distance between two adjacent molecules within a stack. The distances between successive and corresponding planes are 3.30 Å for the central ring and 3.41, 3.29, and 3.49 Å for the phenyl groups. These values are in the range of the graphite layer distance (3.35 Å).

Studies concerning the reactivity and coordination behaviour of 1 are in progress. Preliminary experiments indicate that 1 is very reactive towards sodium, naphthalene complexes of ytterbium, and dicyclopentadienyl vanadium.

Experimental

Preparation of 1,3,5-C$_6$H$_3$(C≡CPh)$_3$ (1)

A solution of 2.39 g (5.24 mmol) of 1,3,5-C$_6$H$_3$I$_3$ and 2 ml (18.21 mmol) of PhC≡CH in 30 ml Et$_3$N was added to a stirred mixture of 0.07 g (0.12 mmol) of Pd(db)$_2$ and 0.14 g (0.53 mmol) of PPh$_3$ in 20 ml of Et$_3$N at room temperature. The reaction mixture was stirred for 6 h. The resulting white salt was removed by filtration, and the solvent was evaporated under reduced pressure. The residue was purified by silica column chromatography. Elution with hexane gave white crystals of 1.

Yield: 1.25 g (63 %), m. p.: 145°C. $^1$H NMR (CDCl$_3$) $\delta$ (ppm) = 7.31 - 7.38 (m, 9H, m, p -C$_6$H$_5$), 7.48 - 7.55 (m, 6H, o -C$_6$H$_5$), 7.64 (s, 3H, C$_6$H$_3$). - IR (Nujol): 2200, 840, 750, 720, 650 cm$^{-1}$.

Crystal data for 1: C$_{30}$H$_{18}$, $M = 378.44$, monoclinic, space group C2/c (No. 15); $a = 35.739(13)$, $b = 4.8517(13)$, $c = 24.859(7)$ Å, $\beta = 98.51(3)^\circ$, $V = 4268(2)$ Å$^3$, $Z = 8$, $D_c = 1.178$ g cm$^{-3}$, $\mu = 0.067$ mm$^{-1}$, $F(000) =$
The structure was solved with direct methods using SHELXS 86 [13] and refined against $F^2$ using SHELXL 93 [14]. All carbon atoms were refined anisotropically. Hydrogen atoms were added, but not refined. $R(F) = 0.0765$, $R_w(F^2) = 0.1823$. Full details of the crystal structure determination have been deposited at the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen, Germany (E-Mail: crysdata@FIZ-Karlsruhe.de), under the depositary number CSD-408703.

Calcd C 95.20 H 4.80 %,  
Found C 94.52 H 4.47 %.

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