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Restricted Rotation in Hexaarylbenzenes[1]

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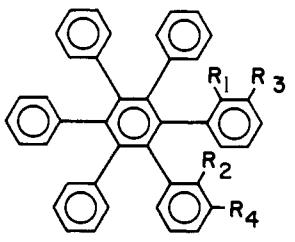
Abstract: Hexaarylbenzenes exist in a conformation in which the peripheral rings are perpendicular to the plane of the central ring on the nmr time scale. Hexaarylbenzenes substituted in ortho or meta positions of the peripheral rings display restricted rotation about the single bonds joining the central and peripheral rings, and complex stereoisomerism and stereoisomerization behavior results. The rotational barriers observed are relatively high (up to ~38 kcal/mol), and even rings bearing only a *m*-methyl substituent lead to barriers of ~16 kcal/mol.

Recent studies of torsional isomerism in triarylmethanes,[2] tetraarylethanes,[3] and related systems[2,4] suggested that suitably substituted hexaarylbenzenes might also demonstrate restricted rotation. If substituted hexaarylbenzenes having relatively high barriers to rotation about the bonds connecting the peripheral and central aromatic rings could be synthesized, a molecular system possessing a rich variety of interesting stereochemical features would result. Reported here are the results of an initial study demonstrating that this is indeed the case.

Synthesis and Properties of Substituted Hexaarylbenzenes. Previously synthesized hexaarylbenzenes have been unsubstituted, or have had substituents only in the para positions of some of the peripheral rings.[5] To investigate the possibility of restricted rotation in this class of compounds, molecules bearing substituents in the ortho or meta positions were desired. Hexaarylbenzene **1**, in which two adjacent phenyl rings each



1, $R_1 = OCH_3$; $R_2 = CH_3$; $R_3 = R_4 = H$

2, $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$

3, $R_1 = R_2 = H$; $R_3 = R_4 = CH_3$

bear an ortho substituent, was prepared using a series of well-known reactions (see Experimental Section). The synthesis of *trans*-2-methoxy-2′-methylstilbene was accomplished by means of the Wittig reaction. Using the procedure of Fieser,[5c] this material was brominated with pyridinium hydrobromide perbromide, and the resulting dibromide was dehydrohalogenated with potassium hydroxide to yield 2-methoxy-2′-methyldiphenylacetylene. Refluxing a mixture of the acetylene and tetraphenylcyclopentadienone in benzophenone gave **1** in 66% yield. Column chromatography of **1** (silica gel, carbon tetrachloride) yielded two different substances, **1a** and **1b**, in roughly equal amounts. These two substances gave similar, but not identical, ^1H NMR spectra. The spectrum of **1a** featured a single aromatic methyl singlet at δ 2.02 ppm, and a single methoxy group resonance at 3.40, as well as the expected aromatic proton resonances, whereas the spectrum of **1b** featured the aromatic methyl resonance at δ 2.02 and the methoxy resonance at 3.47. Each compound gave carbon and hydrogen analyses and mass spectra consistent with the proposed structure, and each melted at 358–359 °C with some sublimation before melting.

Upon heating in 1-bromonaphthalene solution at 215 °C for 30 min, **1a** was converted cleanly to a mixture containing 46% **1a** and 54% **1b**. Under the same conditions, **1b** gave an identical mixture. Further heating did not change these percentages. Kinetic studies of the interconversion (see Experimental Section) yielded[6] $\Delta G^{\ddagger}_{419} = 32.7$ kcal/mol for the conversion of **1a** into **1b**, and $\Delta G^{\ddagger}_{419} = 32.8$ kcal/mol for the reverse reaction. As is shown in the following sections, all of the above data are consistent with the conclusion that **1a** and **1b** are stereoisomers which are interconverted at elevated temperatures by rotation about the single bonds joining the central and peripheral aryl rings.

Conformation of Hexaarylbenzenes. A perusal of molecular models suggests that the six peripheral rings of a substituted hexaarylbenzene cannot lie in the plane of the central ring because of steric hindrance. An x-ray structure determination of hexaphenylbenzene itself[7] showed a propeller conformation in which the peripheral aryl rings make angles of ~65° with the plane of the central ring. An electron diffraction study[8] found that, in the gas phase, the peripheral rings were approximately perpendicular to this plane, with oscillations of about ±10°. These data suggest that, in the ground-state conformation, hexaarylbenzenes assume either a propeller-like geometry or a conformation in which the peripheral rings are approximately perpendicular to the plane of the central rings.

The results reported above for **1** shed some light on the solution conformation of hexaarylbenzenes. In the event of restricted rotation of the peripheral rings, the various possible

substitution patterns on the peripheral rings lead to a multitude of stereoisomers. The number and kinds of such isomers and their stereoisomerization modes may be determined mathematically using the methods developed by Hässelbarth and Ruch,[9] and such an analysis will be presented in a later report which discusses the isomerization mechanism in detail. For a simple substitution pattern such as occurs in **1**, the possibilities for isomerism may be readily determined by inspection.

If **1** assumed a propeller conformation, it should exist as four diastereomeric pairs of enantiomers, and each pair should give rise to a unique aromatic methyl resonance in the NMR spectrum and a unique methoxy resonance. On the other hand, if the molecule assumes a perpendicular conformation on the time scale of measurement, four stereoisomers may exist; a *dl* pair in which both substituents are on the same side of the plane of the central ring, and a *dl* pair in which the substituents are on opposite sides of this plane. In this case, each of these two *dl* pairs should give rise to a single methyl resonance and a single methoxy resonance. Since only two diastereomers were observed for **1**, and since each of these featured only a single methyl and a single methoxy resonance in the ^{1}H NMR spectrum, the evidence supports either a perpendicular conformation or a propeller conformation with rapid interconversion of propeller isomers through a perpendicular conformation. Results for all other hexaarylbenzenes studied to date, as described below, are also consistent with this interpretation. Therefore, in the discussion which follows, the stereochemistry of hexaarylbenzenes will be analyzed in terms of a conformation in which the six peripheral rings are essentially perpendicular to the central ring, with the understanding that this structure may in fact represent an effective time average conformation on the NMR time scale. The two stereoisomers **1a** and **1b** may thus be identified with the two *dl* pairs discussed above for this conformation, although assignment of a particular isomer to a particular pair cannot be made at present.

Isomerization of Hexaarylbenzenes. Interconversions of the stereoisomers of **1** will consist of diastereomerizations and enantiomerizations. Diastereomerization involves rotation by about π radians of only one of the rings bearing a substituent (methyl or methoxy group), whereas enantiomerization involves rotation by about π radians of both rings bearing substituents. The interconversion barriers measured for **1a** and **1b** necessarily represent diastereomerizations. There are two diastereomeric sets of enantiomeric diastereomerization pathways for the isomers of **1**. One set involves rotation of a ring bearing a methyl group, whereas the other involves rotation of a ring bearing a methoxy group. Interconversion by either set would bring about the observed kinetic behavior. Does the ring bearing the methyl group rotate in **1**, or does rotation of the ring bearing the methoxy group give rise to the observed interconversion?

Since a methyl group generally exerts a larger steric effect than a methoxy group, it seems reasonable to conclude that the isomerization involves rotation of the ring bearing the methoxy group. This conclusion is supported by studies of hexaarylbenzene **2**, which was prepared by heating a mixture of tetraphenylcyclopentadienone and di-*o*-tolylacetylene in the absence of solvent (see Experimental Section). This preparation yielded a mixture of two diastereomeric hexaarylbenzenes, **2a** and **2b**, whose ^{1}H NMR spectra featured single aromatic methyl resonances at δ 2.00 and 2.07 ppm, respectively. These diastereomers were partially separated by recrystallization from benzene, and the kinetics of interconversion in 1-bromonaphthalene solution at 217.5 °C yielded $\Delta G^{\ddagger}_{490.7}$ = 37.6 kcal/mol for conversion of **2a** into **2b**, and $\Delta G^{\ddagger}_{490.7}$ = 38.1 kcal/mol for the reverse reaction. At equilibrium, the ratio of **2a** to **2b** was 0.6 at 217.5 °C.

Compound **2** would be expected to exist in two diastereomeric forms. One of these is an achiral form in which both methyl substituents are on the same side of the plane of the central ring, and the other is a *dl* pair with the substituents on opposite sides of this plane. Each diastereomer would be expected to give rise to a single aromatic methyl resonance in the ^{1}H NMR spectrum, and this is indeed observed.

For diastereomerization to occur in **2**, one ring bearing a methyl group must rotate through the plane of the central ring. Since this requires about 38 kcal/mol for **2**, one might expect that the energy of activation for a similar process in **1** would be similar. Since the free energy of activation for isomerization of **1** is actually much lower than 38 kcal/mol, the assumption that the rotating ring in **1** bears a methoxy group, rather than a methyl group, is strongly supported.

Although enantiomerization cannot be detected in the experiments described above, enantiomerization barriers could be measured if **1a** or **1b** were resolved. Since enantiomerization necessarily involves rotation of the ring bearing the methyl group as well as the ring bearing the methoxy group, it is probable that enantiomerization requires more energy than diastereomerization.

The high barriers to stereoisomerization for **1** and **2** suggested that hexaarylbenzenes having substituents only in the meta positions might also demonstrate restricted rotation. Hexaarylbenzene **3** was prepared from diphenylacetylene and the appropriate substituted tetraphenylcyclopentadienone, which in turn was synthesized from dibenzyl ketone and 3,3′-dimethylbenzil by the method of Fieser[5c] (see Experimental Section).

Compound **3** is stereochemically correspondent[2,4a,c] to **2**, and the stereochemical analysis given for **2** applies equally well for **3**. Therefore, if the barriers to isomerization are sufficiently high, one would expect to see two aromatic methyl resonances for the compound in the ^{1}H NMR spectrum (one for each diastereomer). Indeed, at 0 °C the 100-MHz ^{1}H NMR spectrum of the methyl region of **3** showed two peaks of essentially equal intensity separated by 1.7 Hz. As the sample was warmed, these two peaks broadened and coalesced to a singlet at 21 °C. This coalescence yields[10] an energy of activation of $\Delta G^{\ddagger}_{294}$ = 16.4 kcal/mol for diastereomerization.

Inspection of molecular models suggests that, in **3**, most of the steric hindrance to rotation must come about through interactions involving the ortho hydrogens, and that *m*-methyl groups would be expected to have relatively little steric influence. In view of this fact, the diastereomerization barrier for **3**, although much lower than those for **1** and **2**, is still remarkably high. Buttressing effects involving unsubstituted phenyl groups may contribute to the magnitude of this barrier, but experimental data bearing on this point are not yet available.

The results discussed above shed only a little light on the mechanisms of the observed transformations. They provide data concerning the relative motions of the substituted rings, but reveal little concerning any possible effects of the four unsubstituted rings. The hexaarylbenzene system has a superficial resemblance to the systems studied by Schaefer and co-workers[11] and, indeed, to substituted biphenyl systems. However, the hexaarylbenzenes are much more stereochemically complex and may potentially display some very subtle isomerization phenomena. Structural and mechanistic studies involving more highly substituted hexaarylbenzenes should reveal any such behavior.

Experimental Section

Elemental analyses were performed by Midwest Microlab, Ltd., Indianapolis, Ind. Melting points were obtained with a Mel-Temp apparatus and are uncorrected. NMR spectra were obtained on a Varian XL-100 or T-60 spectrometer, and refer to ~20% solutions in $CDCl_3$ with tetramethylsilane as an internal reference unless

specified otherwise. Mass spectra were obtained on an Atlas CH-4B or SM-1B instrument.

***trans*-2-Methoxy-2′-methylstilbene.** A mixture of 18 g (97 mmol) of *o*-xylyl bromide and 26 g (97 mmol) of triphenylphosphine dissolved in 250 mL of xylene was heated at reflux for 3 h. The white precipitate of phosphonium salt (37.8 g, 87% yield) melted at 276.5–277.5 °C after recrystallization from an ~1:1 mixture of benzene and ethanol. The phosphonium salt (37 g, 83 mmol) was stirred under nitrogen with 314 mL of benzene, and 94 mmol of butyllithium as a 2.17 M solution in hexane was added dropwise. When addition was complete, stirring was continued for 2 h, and the red solution was then treated dropwise with a solution of *o*-anisaldehyde (13 g, 94 mmol) in 20 mL of benzene. The pale yellow solution was stirred for 3 h at room temperature and then refluxed 30 min, cooled, and filtered. The benzene was distilled from the filtrate at reduced pressure, and the residue was distilled at reduced pressure (0.15 Torr) to yield 16.7 g (90% yield) of a mixture of *cis*- and *trans*-2-methoxy-2′-methylstilbene (bp 95–145 °C). Redistillation yielded *trans*-2-methoxy-2′-methylstilbene (bp 140–145 °C at 0.15 Torr; mp 73.5–74.5 °C after recrystallization from methanol). The ^{1}H NMR spectrum featured resonances at δ 2.43 (3 H, s, CH_3), 3.87 (3 H, s, OCH_3), and ~6.8–7.8 (10 H, m, aromatic and vinylic H). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.58; H, 7.03.

2-Methoxy-2′-methyldiphenylacetylene. A solution of *trans*-2-methoxy-2′-methylstilbene (3.90 g, 17.5 mmol) in 25 mL of acetic acid was warmed on the steam bath, and pyridinium hydrobromide perbromide (6.3 g) was added. After heating for 10 min, the solution was allowed to cool, and white crystals of 2-methoxy-2′-methylstilbene dibromide were isolated by filtration, washed with methanol, and dried under vacuum (4.2 g, 62% yield). The dibromide (15.6 g, 40.6 mmol) and 15.3 g of potassium hydroxide pellets were dissolved in 60 mL of triethylene glycol and heated to 160 °C for 5 min. The resulting dark solution was cooled to room temperature and diluted with 200 mL of H_2O. The solution was extracted with 100 mL of benzene, and the benzene layer was separated, washed with 75 mL of water, dried over anhydrous $MgSO_4$, and filtered. Distillation at reduced pressure yielded 6.88 g (76% yield) of the desired acetylene (bp 127–130 °C at 0.18 Torr). The ^{1}H NMR spectrum featured resonances at δ 2.55 (3 H, s, CH_3), 3.88 (3 H, s, OCH_3), and 6.7–7.6 (8 H, m, aromatic H). The mass spectrum yielded *m/e* 222.1047 (calcd for $C_{16}H_{14}O$, 222.1045).

1-(2-Methoxyphenyl)-2-(2-methylphenyl)-3,4,5,6-tetraphenylbenzene (1). Tetraphenylcyclopentadienone (4.00 g, 10.4 mmol) and 2-methoxy-2′-methyldiphenylacetylene (3.00 g, 13.5 mmol) were added to a flask containing 20 g of molten benzophenone. The mixture was refluxed for 3 h. After the mixture cooled to room temperature, 20 mL of acetone was added. The white crystalline precipitate of **1** (6.0 g, 66% yield) was removed by filtration. This material was chromatographed on a silica gel column (CCl_4) to yield two fractions.

The first compound to elute, **1a,** melted at 358–359 °C with some sublimation at lower temperatures. The ^{1}H NMR spectrum of **1a** featured resonances at δ 2.02 (3 H, s, CH_3), 3.40 (3 H, s, OCH_3), and 6.2–7.2 (28 H, m, aromatic H). The mass spectrum was consistent with the proposed structure with the parent ion at *m/e* 578. Anal. Calcd for $C_{44}H_{34}O$: C, 91.31; H, 5.92. Found: C, 91.01, H, 5.80.

The second compound to elute, **1b,** also melted at 358–359 °C with sublimation. The ^{1}H NMR spectrum featured resonances at δ 2.02 (3 H, s, CH_3), 3.47 (3 H, s, OCH_3), and 6.2–7.2 (28 H, m, aromatic H). The mass spectrum was consistent with the proposed structure with the parent ion at *m/e* 578. Anal. Found: C, 90.95; H, 5.86.

Equilibration Studies on 1. Aliquots of a 2.4×10^{-3} M solution of **1b** in 1-bromonaphthalene were sealed in glass tubes and heated at 146 °C. Tubes were quenched at intervals, and the ratio of **1a:1b** was determined by high pressure liquid chromatographic analysis (silica gel, 5% chloroform in cyclohexane). Analysis[6] yielded $\Delta G^{\ddagger}_{419}$ = 32.5 kcal/mol for conversion of **1a** to **1b,** and 32.7 kcal/mol for the reverse reaction, with a correlation coefficient of 0.997 (10 points). The equilibrium ratio of **1a:1b** was 46:54. Similar studies on 7.3×10^{-3} M solutions of **1a** and **1b** in 1-bromonaphthalene gave similar results, with an average $\Delta G^{\ddagger}_{419}$ of 32.7 kcal/mol for conversion of **1a** to **1b** and $\Delta G^{\ddagger}_{419}$ = 32.8 kcal/mol for the reverse reaction.

1,2-Bis(2-methylphenyl)-3,4,5,6-tetraphenylbenzene (2). Tetraphenylcyclopentadienone (0.95 g, 2.5 mmol) and di-*o*-tolylacetylene[12] (0.64 g, 3.1 mmol) were heated in a test tube over an open flame until the deep red color disappeared and a white solid began to form. After cooling, 10 mL of acetone was added, and the solid was ground with a spatula. Filtration, followed by washing with acetone, yielded white plates of **2** (0.75 g, 54% yield), mp 374–376 °C with sublimation. Anal. Calcd for $C_{44}H_{34}$: C, 93.91; H, 6.09. Found: C, 93.84; H, 6.04.

Repeated recrystallization from benzene yielded a fraction enriched in **2a** (66% **2a**) and a fraction enriched in **2b** (70% **2b**). The ^{1}H NMR spectrum of **2a** featured resonances at δ 2.00 (6 H, s, CH_3) and 6.87 (28 H, m, aromatic H). The spectrum of **2b** featured resonances at δ 2.07 (6 H, s, CH_3) and 6.87 (28 H, m, aromatic H).

Equilibration studies were carried out at 217.5 °C as described above, with the exception that the experiment was carried out in an NMR tube, and ratios were determined from the ratios of the areas of the methyl resonances in the ^{1}H NMR spectrum. The results were $\Delta G^{\ddagger}_{490.7}$ = 37.6 kcal/mol for conversion of **2a** into **2b** and $\Delta G^{\ddagger}_{490.7}$ = 38.1 kcal/mol for the reverse reaction (6 points, correlation coefficient 0.997). The ratio of **2a:2b** at equilibrium was 0.6 at 217.5 °C.

2,5-Diphenyl-3,4-bis(3-methylphenyl)cyclopentadienone. A solution of dibenzyl ketone (2.1 g, 10 mmol) and 3,3′-dimethylbenzil[13] (2.4 g, 10 mmol) in 10 mL of triethylene glycol was heated to 100 °C, and 2 mL of a 40% solution of benzyltrimethylammonium hydroxide in methanol was added. A purple-red product formed rapidly. After the mixture cooled to room temperature, 10 mL of methanol was added, and the product was removed by filtration and recrystallized from triethylene glycol to yield the desired product as thin plates (1.2 g, 30% yield), mp 186.5–187 °C. The ^{1}H NMR spectrum featured resonances at δ 2.15 (6 H, s, CH_3) and 6.7–7.4 (18 H, m, aromatic H). Mass spectral analysis yielded *m/e* 412.1814 (calcd for $C_{31}H_{24}O$, 412.1827).

1,2-Bis(3-methylphenyl)-3,4,5,6-tetraphenylbenzene. The above substituted tetraphenylcyclopentadienone (0.53 g, 1.3 mmol) and diphenylacetylene (0.50 g, 2.8 mmol) were placed in a test tube and heated as described for **2.** After a workup similar to that described for **2, 3** was obtained in 79% yield (0.57 g, mp 390–391 °C). The ^{1}H NMR spectrum in benzene-d_6 featured resonances at δ 1.90 (6 H, s, CH_3) and 6.7–7.3 (28 H, m, aromatic H). Anal. Calcd for $C_{44}H_{34}$: C, 93.91; H, 6.09. Found: C, 93.67; H, 6.06.

When a solution of **3** in a 5:3 mixture of chloroform-*d* and carbon disulfide was placed in the Varian XL-100 NMR spectrometer and cooled to 0 °C, the methyl resonance was found to have split into two resonances of approximately equal intensity with $\Delta\nu$ = 1.7 Hz. These resonances coalesced to a singlet at 21 °C and sharpened with further heating. From this data, $\Delta G^{\ddagger}_{294}$ = 16.4 kcal/mol was calculated using the Gutowsky-Holm approximation[10] and the Eyring equation.

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