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Conformational Dynamics of Polyarylbenzenes. Buttressing Effects

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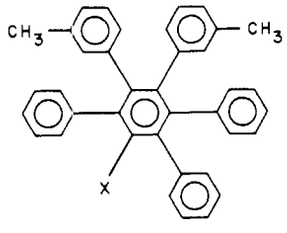
The free energies of activation for rotational stereoisomerization of a series of pentaarylbenzenes have been measured. The results reveal that substantial steric effects are transmitted around the circumference of the central aryl ring from sites remote from the rotating rings. The free energies of activation for compounds bearing various substituents on the central ring range from 15.5 to 18.7 kcal/mol and obey a linear relationship with respect to $-\Delta G°$ for the same substituents in the axial–equatorial cyclohexane equilibrium. This relationship permits the estimation of $-\Delta G°$ for additional substituents. The value for the 1-hydroxyethyl group was found to be 1.8 kcal/mol, whereas a lower limit of 5.6 kcal/mol was determined for the *tert*-butyl group.

Recent investigations[2,3] of the static and dynamic stereochemistry of hexaarylbenzenes have established that these molecules exist in a conformation in which the peripheral rings are perpendicular to the plane of the central ring on the NMR time scale. Hexaarylbenzenes suitably substituted in ortho or meta positions of the peripheral rings display restricted rotation about the single bonds joining the central and peripheral rings, and the resulting stereoisomerism and stereoisomerization behavior is readily observable by nuclear magnetic resonance methods. Kinetic studies[3] have shown that isomerization occurs via a mechanism wherein one peripheral ring at a time rotates by $\sim\pi$ rad.

Stereoisomerism resulting from restricted rotation has also been observed in a pentaarylbenzene, 1.[3] In the limit



1, X = H
2, X = C_6H_5
3, X = $CH(CH_3)_2$
4, X = CH_3
5, X = CH_2CH_3
6, X = $CH(OH)CH_3$
7, X = $C(CH_3)_3$

of slow rotation on the NMR time scale, 1 exists in the perpendicular conformation as two diastereomeric *dl* pairs. In one of these pairs, the meta methyl groups reside on the same side of the plane of the central ring, whereas in the other, these groups lie on opposite sides of this plane. The ^1H NMR spectrum of 1 at low temperatures features four resonances in the methyl region and is therefore consistent with the presence of two diastereomers. These resonances broaden and coalesce pairwise when the sample is warmed. The coalescence signifies diastereomerization, and line-shape analysis yielded a free energy of activation of $\Delta G^{\ddagger}_{288} = 15.5$ kcal/mol for this process.[3] In contrast, the barrier to aryl ring rotation measured for hexaarylbenzene **2**, in which the hydrogen has been replaced by a phenyl group, was nearly 2 kcal/mol higher.[3]

Although in principle this difference in free energies of activation could be due to any of a variety of steric or electronic influences, it was suggested that most of the difference was due to steric buttressing.[3] Reported below are the results of a more extensive study of the effects of groups meta or para to the substituted rings of pentaarylbenzenes which was undertaken to either confirm or refute the above suggestion and to yield a more complete picture of steric and electronic effects in these compounds.

Results

Pentaarylbenzene derivatives **3–7**, which bear substituents that differ greatly in steric requirements, were prepared by the Diels–Alder reaction of the appropriate alkyne with 3,4-bis(3-methylphenyl)-2,5-diphenylcyclopentadienone[2,4] (see Experimental Section).

At −9 °C, the 100-MHz ^1H NMR spectrum of the isopropyl derivative **3**, prepared in this manner, showed four resonances of essentially equal intensities in the aromatic

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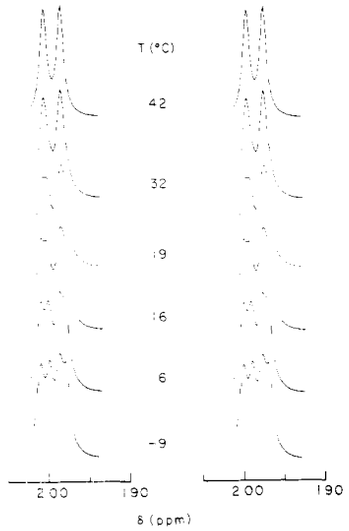

Figure 1. Experimental (left) and computer-simulated (right) ^1H NMR spectra of the aromatic methyl groups of pentaarylbenzene **3** at selected temperatures.

Table I. Free Energies of Activation for Aryl Rotation in Polyarylbenzenes

compd	substituent	$\Delta G^{\ddagger}_{293}$, kcal/mol	$-\Delta G^{\circ}$,[a] kcal/mol
1	H	15.5[b]	0
2	C_6H_5	17.3[b]	3.0
3	$CH(CH_3)_2$	16.8	2.15
4	CH_3	16.2	1.70
5	CH_2CH_3	16.1	1.75
6	$CH(OH)CH_3$	16.4	
7	$C(CH_3)_3$	18.7	

[a] *A* values taken from ref 6. [b] Based on data from ref 3 (see Experimental Section).

methyl region at δ 1.94, 1.96, 1.98, and 2.00 (Figure 1). Compound **3** is expected to exist in two diastereomeric forms similar to those observed for **1**. The NMR results at −9 °C are consistent with this expectation. Two of the four methyl resonances arise from the two constitutionally heterotopic methyl groups of one *dl* pair, whereas the other two resonances are due to the two aromatic methyl groups of the diastereomeric *dl* pair. The two isomers are present in approximately equal concentrations.

When the sample was warmed in the spectrometer, the resonances broadened and coalesced pairwise to two resonances at δ 1.95 and 1.99 which sharpened on further heating (Figure 1). This coalescence behavior reflects diastereomerization due to rotation of one of the aryl groups bearing a meta methyl substituent about its bond to the central ring. Line-shape analyses of the temperature-dependent spectra yielded rate constants for each temperature (see Experimental Section), and application of the Eyring equation gave $\Delta G^{\ddagger}_{293}$ = 16.8 kcal/mol for isomerization.

Pentaarylbenzenes **4**–**7** had ^1H NMR spectra which were similar to those obtained for **3**, and line-shape analyses were performed for these spectra (see Experimental Section). The resulting free energies of activation for rotation of a meta methyl bearing ring are listed in Table I.

Discussion

It is obvious from Table I that the sterically more demanding substituents on the central ring give rise to the higher barriers to rotation. Quantification of this relationship requires the use of an accepted measure of the steric requirements of the substituents. A commonly used

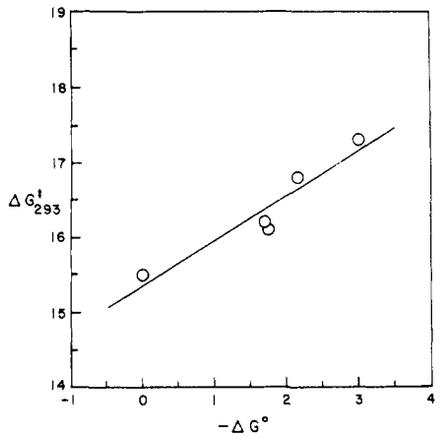

Figure 2. Plot of the free energy of activation for rotation of an aryl ring ($\Delta G^{\ddagger}_{293}$) against $-\Delta G^{\circ}$ for the axial–equatorial cyclohexane equilibrium for polyarylbenzenes **1**–**5**. The solid line is the linear least-squares best fit for the data shown (see text).

measure is the "*A* value" or $-\Delta G^{\circ}$ for the axial–equatorial equilibrium in cyclohexane derivatives.[5,6] Figure 2 shows a plot of the free energies of activation for rotation ($\Delta G^{\ddagger}_{293}$) for substituted pentaarylbenzenes **1**–**5** against the *A* value[6] of the substituent (Table I). A linear relationship is found, within the limits of error of both measurements. A least-squares fit yields $\Delta G^{\ddagger}_{293} = 0.599\ (-\Delta G^{\circ}) + 15.35$ with a standard deviation in $\Delta G^{\ddagger}_{293}$ of 0.19 kcal/mol.

This relationship supports the idea that the differences in free energy of activation seen for **1**–**5** are indeed of steric origin. The original suggestion[3] that these effects reflect changes in buttressing of the phenyl rings adjacent to the meta methyl bearing rings appears to be justified. Similar buttressing effects have long been known in biphenyl systems.[7,8]

Inspection of molecular models suggests that most of the steric hindrance to rotation of an aryl ring in a polyarylbenzene arises from interactions with the two adjacent rings. These interactions could be partially relieved by increasing the in-plane angle between adjacent bonds to the central ring. Such in-plane splaying interactions have recently been shown to be important in naphthalene derivatives.[9,10] However, the results presented above indicate that the significant steric interactions are not confined to rings adjacent to the rotating ring but are spread throughout the molecule. Thus, one reason for the relatively high barriers to stereoisomerization found in hexaarylbenzenes is that steric strain cannot be substantially relieved by splaying motions of the rings in the plane of the central ring. This is the case because the structure of the molecule is such that relief of steric repulsions by increasing the in-plane angle between any two adjacent rings necessarily results in a decrease in this angle between all other pairs of peripheral rings and a concomitant increase in strain in these regions of the molecule. Similar interactions in, for example, a 1,2-diarylbenzene would undoubtedly be very small. In this connection, these results suggest that rotational barriers for 1,2,3,4-tetraphenylbenzenes bearing substituents on rings 2 and 3[11] will

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be significantly smaller than those for their hexaarylbenzene analogues.[2,3]

The linear relationship between $\Delta G^{\ddagger}_{293}$ and $-\Delta G°$ reported above suggests not only that steric interactions are the major source of the variations in $\Delta G^{\ddagger}_{293}$ among the compounds studied but also that the steric interactions in the pentaarylbenzenes are similar in their general nature to those in cyclohexanes. That is, for the substituents in question, $\Delta G^{\ddagger}_{293}$ and $-\Delta G°$ reflect steric requirements in similar ways. It is well-known that other systems, such as hindered biphenyls, display steric interactions of a different sort and that results from these systems do not correlate well with $-\Delta G°$ for cyclohexanes.[5,12] Some qualitative reasons for the good correlation in this case are easily appreciated. The steric interactions between substituent X and the adjacent rings is mainly a "side-by-side" interaction such as is observed between 1,3-axial groups in cyclohexanes. In biphenyls, the interacting groups point toward one another.[5] In addition, the steric repulsions in pentaarylbenzenes will decrease as the C-X bond is lengthened. A similar situation occurs in cyclohexanes but not in biaryls.

A consequence of the correlation between $\Delta G^{\ddagger}_{293}$ for pentaarylbenzenes and $-\Delta G°$ for cyclohexanes is that the pentaarylbenzene system may be used to estimate *A* values. Thus, a measure of steric bulk which can be correlated with the well-known $-\Delta G°$ scale can in principle be obtained for many substituents which have not been studied in the cyclohexane system. For example, an *A* value for the 1-hydroxyethyl group is not reported in the usual compilations.[5,6] Table I gives $\Delta G^{\ddagger}_{293}$ for the appropriate pentaarylbenzene derivative (**6**) in chloroform-*d* solution, and use of the linear relationship detailed above yields an estimate of $-\Delta G°$ = 1.8 kcal/mol for this substituent. Thus, this substituent is intermediate in steric requirement between the ethyl and the isopropyl group. This appears to be a reasonable result in chloroform solution because the hydroxy group is intermediate in steric requirement between hydrogen and methyl.[5,6] However, it must be remembered that the $-\Delta G°$ value for the hydroxymethyl group has been found to be strongly solvent dependent.[13,14]

Perusal of Table I shows that $\Delta G^{\ddagger}_{293}$ = 18.7 kcal/mol for the *tert*-butyl group. It is tempting to employ the relationship shown in Figure 2 to calculate a value of $-\Delta G°$ = 5.6 kcal/mol for the *tert*-butyl group. However, this value is in fact only a lower limit for $-\Delta G°$. The reason for this is as follows. Examination of structure **1** reveals that diastereomerization may occur by rotation by $\sim\pi$ rad of either the methyl-bearing ring meta to the hydrogen atom on the central ring or the ring para to that hydrogen atom. For a pentaarylbenzene derivative whose substituent X is less sterically demanding than a phenyl group, it is reasonable to assume that an aryl group meta to X will experience less steric hindrance to rotation than will an aryl ring in the para position. Thus, the measured barrier to rotation will be that for the meta aryl ring. This will be the case for **1**, **3**, **4**, **5**, and **6**. In **2**, both methyl-bearing rings are equivalent or enantiotopic in all diastereomers, and rotation of either ring will be equally facile under the experimental conditions. However, if X is sterically more demanding than phenyl, as is the case for **7**, rotation of the aryl group para to X should become energetically most favorable, because the para ring is furthest from X and is thus insulated more completely from the effects of X than is the meta aryl group.

This change of mechanism for stereoisomerization renders the relationship in Figure 2 invalid for the *tert*-butyl group. The value of 5.6 kcal/mol is, however, an acceptable lower limit for $-\Delta G°$. Empirical force field calculations[15,16] have yielded values of 5.4 kcal/mol for the *tert*-butyl group, and an estimate of $-\Delta G°$ = 5.7 kcal/mol has been reported.[17] On the other hand, another recent empirical force field calculation yielded a value of 4.7 kcal/mol for this group.[18]

On the basis of the results for the relatively small sample of pentaarylbenzenes **1**–**7**, the relationship in Figure 2 appears to be useful for estimating the steric requirements of groups smaller than phenyl and for setting lower limits for the requirements of larger groups. This result should prove helpful in the study of steric effects in systems not readily amenable to more common methods of investigation.

Experimental Section

Elemental analyses were performed by Galbraith Laboratories. ^{1}H NMR spectra were obtained on a Bruker WH-90 or Varian XL-100 spectrometer and refer to ~20% solutions in chloroform-*d* with tetramethylsilane as an internal reference unless specified otherwise.

D NMR Studies. Variable-temperature NMR studies were carried out in chloroform-*d* solution on a Varian XL-100 continuous-wave spectrometer with a variable-temperature accessory. Temperature measurements were calibrated by using a methanol standard and the temperature–shift correlations of Van Geet.[19] Spectra were analyzed as described previously.[3] As discussed in the text, stereoisomerization of **1**–**7** could in principle occur by rotation of either of the meta methyl bearing rings. For **1** and **3**–**7**, the arguments presented above suggest that rotation of a particular substituted ring will be energetically much more favorable than rotation of the other, and therefore it is assumed that the free energies of activation for isomerization and for rotation about a particular aryl bond to the central ring are equivalent. For **2**, on the other hand, rotation of either ring is equally probable, and so the rate of rotation about a particular aryl bond to the central ring is half the rate of stereoisomerization. This fact has been taken into account in compiling the results in Table I.

1-Isopropyl-3,4-bis(3-methylphenyl)-2,5,6-triphenylbenzene (3). A solution of 3,4-bis(3-methylphenyl)-2,5-diphenylcyclopentadienone[2,4] (1.0 g, 2.4 mmol) and 3-methyl-1-phenyl-1-butyne[20] (0.5 g, 3.5 mmol) in 5 mL of triethylene glycol was refluxed under nitrogen for 9 h. After the solution had cooled, 3 mL of acetone was added and the product was collected by filtration and washed several times with acetone to yield white plates (0.6 g, 47% yield). A portion of the product (0.16 g) was sublimed under vacuum [230 °C (0.06 torr)] to yield white crystals, mp 309–311 °C. The ^{1}H NMR spectrum ($CDCl_3$) featured resonances at δ 0.88 (6 H, d, isopropyl CH_3), 1.95 (3 H, s, aromatic CH_3), 1.99 (3 H, s, aromatic CH_3), 3.16 (1 H, septet, isopropyl CH), and 6.40–7.30 (23 H, m, aromatic H). Anal. Calcd for $C_{41}H_{36}$: C, 93.14; H, 6.86. Found: C, 92.88; H, 6.75.

The ^{1}H NMR spectrum of the aromatic methyl region was temperature dependent as described in the text and shown in Figure 1. Line-shape analysis was performed as described previously and yielded the results in Table I.

1-Methyl-3,4-bis(3-methylphenyl)-2,5,6-triphenylbenzene

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(4) was prepared by heating 3,4-bis(3-methylphenyl)-2,5-diphenylcyclopentadienone (0.50 g, 1.2 mmol) and 1-phenyl-1-propyne (0.28 g, 2.4 mmol) under reflux until the purple color was discharged. The resulting brown liquid was cooled to room temperature and stirred with 10 mL of acetone. The white solid was removed by filtration, washed with acetone, and recrystallized from toluene–petroleum ether to yield white crystals of 4 (0.24 g, 39% yield, mp 217–219 °C). The ^{1}H NMR spectrum featured resonances at δ 1.90 (3 H, s, CH_3), 1.95 (3 H, s, CH_3), 1.98 (3 H, s, CH_3), and 6.5–7.3 (23 H, m, aromatic H). Anal. Calcd for $C_{39}H_{32}$: C, 93.56; H, 6.44. Found: C, 93.46; H, 6.73.

At −10 °C the aromatic methyl region of the NMR spectrum consisted of four resonances of essentially equal intensity at δ 1.94, 1.96, 1.97, and 1.99. The two central resonances were not resolved. The resonances broadened when the sample was warmed and coalesced pairwise as was observed for 3. Line-shape analysis yielded the results reported in Table I.

1-Ethyl-3,4-bis(3-methylphenyl)-2,5,6-triphenylbenzene (5). A solution of 3,4-bis(3-methylphenyl)-2,5-diphenylcyclopentadienone (1.0 g, 2.4 mmol) and a large excess of 1-phenyl-1-butyne in 5 mL of triglyme was refluxed for 2 h. After the solution had cooled, 40 mL of water and 10 mL of ethyl ether were added and the resulting precipitate was collected by filtration. Vacuum sublimation yielded white crystals (0.3 g, 22% yield, mp 248–250 °C). The ^{1}H NMR spectrum ($CDCl_3$) featured resonances at δ 0.72 (3 H, t, CH_2CH_3), 1.92 (3 H, s, CH_3), 1.96 (3 H, s, CH_3), 2.36 (2H, q, CH_2CH_3), and 6.5–7.3 (23 H, m, aromatic H). Anal. Calcd for $C_{40}H_{34}$: C, 93.34; H, 6.66. Found: C, 93.08; H, 6.68.

At −5 °C the ^{1}H NMR spectrum of the aromatic methyl region featured four resonances of approximately equal intensity at δ 1.91, 1.93, 1.95, and 1.97. Coalescence similar to that observed for 3 occurred when the sample was warmed. Line-shape analysis gave the results shown in Table I.

1-(1-Hydroxyethyl)-3,4-bis(3-methylphenyl)-2,5,6-triphenylbenzene (6) was prepared from 3,4-bis(3-methylphenyl)-2,5-diphenylcyclopentadienone (0.50 g, 2.4 mmol) and 4-phenyl-3-butyn-2-ol (0.50 g, 3.4 mmol) by the procedures described above for 4. The resulting product was chromatographed (silica gel, toluene) to yield 0.32 g of 6 (25% yield, mp 257–259 °C). The ^{1}H NMR spectrum showed resonances at δ 1.20 (3 H, d, $CHOHCH_3$), 1.95 (3 H, s, aromatic CH_3), 1.99 (3 H, s, aromatic CH_3), 4.87 (1 H, q, $CH(OH)CH_3$), and 6.5–7.4 (23 H, m, aromatic H). Anal. Calcd for $C_{40}H_{34}O$: C, 90.53; H, 6.46. Found: C, 90.51; H, 6.57.

At −20 °C the ^{1}H NMR spectrum of the aromatic methyl region featured four resonances of approximately equal intensity at δ 1.94, 1.96, 1.98, and 2.00 which coalesced at higher temperatures to two resonances. Line-shape analysis yielded the results reported in the text. Although 6 contains a chiral center, no additional resonances were observed in the aromatic methyl region of the ^{1}H NMR spectrum at low temperatures.

1,2-Bis(3-methylphenyl)-3,5,6-triphenyl-4-*tert*-butylbenzene (7). A mixture of 3,4-bis(3-methylphenyl)-2,5-diphenylcyclopentadienone (1.0 g, 2.4 mmol) and 3,3-dimethyl-1-phenyl-1-butyne[21] (0.8 g, 5.4 mmol) was refluxed for a total of 56 h. The excess alkyne was removed by allowing it to condense on a cool stirring rod. After the mixture had cooled, 3 mL of acetone was added and the resulting crystals were separated by filtration and washed with acetone several times to yield very small brown crystals (0.4 g, 31% yield). A portion of the product was recrystallized from hexane–toluene (2:1) and then sublimed under vacuum [230 °C (0.1 torr)] twice to yield white crystals, mp 297–299 °C. The ^{1}H NMR spectrum featured resonances at δ 1.06 (9 H, s, C_4H_9), 1.96 (6 H, multiple resonances, aromatic CH_3), and 6.4–7.4 (23 H, m, aromatic H). Anal. Calcd for $C_{42}H_{38}$: C, 92.94; H, 7.06. Found: C, 92.60; H, 6.95.

At 40 °C the ^{1}H NMR spectrum in the aromatic methyl region featured four poorly resolved resonances at δ 1.95, 1.96, 1.97, and 1.99. Warming the sample caused pairwise coalescence of the resonances, and at 80 °C two sharp resonances were observed. Although line-shape analysis proved somewhat more difficult for this compound than for those mentioned above due to the extensive overlap of resonances in the low-temperature spectrum, a satisfactory analysis was performed and yielded $\Delta G^{\ddagger}_{293} = 18.7$ kcal/mol for isomerization.

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Registry No. 1, 68977-55-9; 2, 69010-11-3; 3, 71885-65-9; 4, 71885-66-0; 5, 71885-67-1; 6, 71885-68-2; 7, 71885-69-3; 3,4-bis(3-methylphenyl)-2,5-diphenylcyclopentadienone, 64897-54-7; 3-methyl-1-phenyl-1-butyne, 1612-03-9; 1-phenyl-1-propyne, 673-32-5; 1-phenyl-1-butyne, 622-76-4; 4-phenyl-3-butyn-2-ol, 5876-76-6; 3,3-dimethyl-1-phenyl-1-butyne, 4250-82-2.

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Stereochemistry of the Cyclobutane Dimers of *trans*-Cycloheptenones

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Irradiation of the three isomeric benzocycloheptadienones **10**, **14**, and **15** produces in each case a trans intermediate which can be trapped by furan. In the absence of a trapping agent, cyclobutane dimers are formed whose stereochemistry, established mainly by X-ray diffraction on crystals, differs for each of the three substrates (**10** → **12**; **14** → **18**, **19**; **15** → **22**, **23**, **24**, **25**). The formation of head-to-tail dimers **23** and **25** is novel and argues against a diradical mechanism. Dimer stereochemistry corresponds to a $_\pi2_s + _\pi2_a$ ground state cycloaddition between two trans species for **10**, a trans + cis species for **14**, and both types for **15**. A rationale in terms of the most strained trans intermediate being the least selective for its reaction partner is proposed to explain the results.

trans-2-Cycloheptenone is formed when the cis isomer is irradiated.[1] It reacts rapidly with dienes[1] and with nucleophiles,[2] but in the absence of trapping agents such as these, it forms cyclobutane dimers. The detailed structure of these dimers, and the mechanism by which they are formed, is still not known. For example, do they result from the combination of two trans isomers or from the combination of a trans and a cis isomer?

The situation is similar with *trans*-2-cyclooctenone,[2b,3] although the structures of dimers obtained from certain

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