Dynamic Stereochemistry of Hexaarylbenzenes[1]

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Abstract: Rotational isomerism in hexaarylbenzenes has been analyzed mathematically and studied experimentally. The mathematical analysis demonstrates that 13 rearrangement modes are possible for such molecules. The isomerization pathway actually followed is revealed by experimental studies of highly substituted hexa- and pentaarylbenzenes, one of which gives rise to 16 rotational stereoisomers. Kinetic studies using both NMR and classical methods strongly support a mechanism wherein one peripheral aryl ring at a time rotates by $\sim\pi$ radians. Measured free energies of activation for isomerization vary from about 33 kcal/mol for rotations of rings bearing an ortho methoxy group to about 17 kcal/mol for rotations of rings bearing meta substituents.

Hexaarylbenzenes assume conformations in which the six peripheral aryl rings are approximately perpendicular to the central ring on the NMR time scale. Properly substituted hexaarylbenzenes have been found to demonstrate restricted rotation about the single bonds joining the central and peripheral aryl groups.[2] The free energies of activation for rotations about these bonds are quite high (up to 38 kcal/mol in the compounds studied). The present report describes the results of investigations into the mechanism of isomerization of these hexaarylbenzenes. The possible rearrangements are enumerated mathematically, and the results of new experimental studies of stereoisomerization in these compounds are presented in the light of the theoretical description.

Group-Theoretical Analysis of Rearrangement Modes

The simplest hexaarylbenzene, hexaphenylbenzene, has $\mathbf{D_{6h}}$ symmetry in the perpendicular conformation wherein the planes of the six peripheral rings are at right angles to that of the central ring. Rotational isomerism may arise when two or more of the peripheral rings bear substituents, and one or more of the substituted rings lack local C_2 axes coincident with the bonds joining them to the central rings due to ortho and/or meta substitution. The number of isomers depends upon the particular substitution pattern. Structure **1** depicts a geometric

1
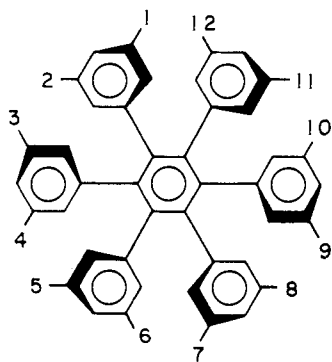
model for such a substituted hexaarylbenzene. The peripheral rings are taken to be perpendicular to the plane of the central ring, and substitution is represented by numerical labeling of the 12 meta positions. It is clear that in the limit of slow rotation about all six single bonds to the central ring, diversely substituted hexaarylbenzenes will give rise to complex stereoisomerism and stereoisomerization behavior.

This behavior is readily analyzed using group-theoretical methods such as those described by Hässelbarth and Ruch,[3] where isomers and isomerizations are treated in terms of permutations of ligands in sites on a rigid skeleton. Structure **1**
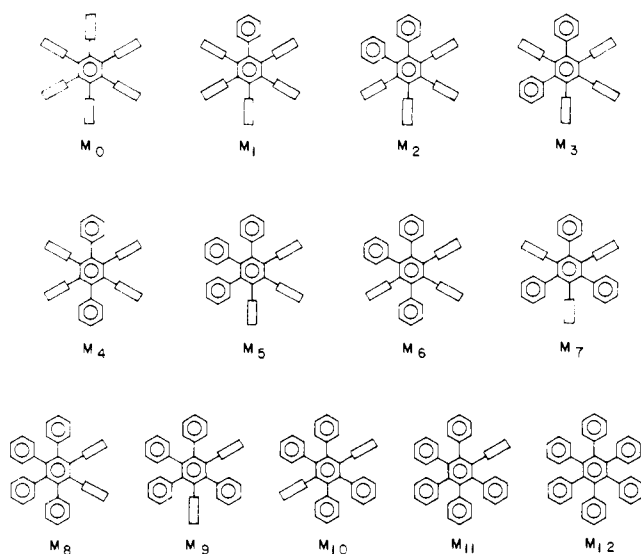
represents such a skeleton. If a different ligand is placed in each of the 12 meta sites, one isomer of a maximally substituted hexaarylbenzene (in terms of stereoisomerism) is produced. The results of an isomerization of this hexaarylbenzene may be represented mathematically by a permutation. For example, the permutation (1,2) signifies a pairwise interchange of the ligands in sites one and two. An isomerization corresponding to this permutation (rotation of an aryl ring in the present case) would give rise to a new isomer. In the case of **1**, all conceivable permutations among the 12 sites are contained in the symmetric group $\mathbf{S_{12}}$ of order 12! (= 479 001 600). Since we are concerned only with rotational isomerism in the present study, a more manageable feasible permutation group may be employed.[4] This group, a subgroup of $\mathbf{S_{12}}$, is the semidirect product $(\mathbf{S_2})^6 \wedge \mathbf{D_6}$, of order 768. The permutations corresponding to the torsional group describing internal rotations of the aryl rings $((\mathbf{S_2})^6)$, the point group of the molecular skeleton ($\mathbf{D_{6h}} \simeq \mathbf{D_6} \times \mathbf{C_2}$), and the rotational subgroup of the point group ($\mathbf{D_6}$) are in turn subgroups of the feasible permutation group. The total number of rotational isomers possible for a hexaarylbenzene with six uniquely substituted peripheral rings which lack local C_2 axes is given by the index of $\mathbf{D_6}$ in $(\mathbf{S_2})^6 \wedge \mathbf{D_6}$ and equals 64.

Similarly, there are 64 rearrangements (classes of rotationally equivalent permutations[3]) possible for a given rotational isomer, which (with the exception of the identity rearrangement) lead to new rotational isomers. These may be derived[3] by decomposing the feasible permutation group into right cosets with respect to the rotational subgroup $\mathbf{D_6}$. These 64 rearrangements may in turn be grouped into 13 rearrangement modes[3,5] using the double coset formulations of Hässelbarth and Ruch.[3,6] These modes are listed in Table I. Each rearrangement is denoted by one representative permutation. The permutations are given as cycles, and the "replaced by" convention is employed.

The physical significance of these rearrangements is that each corresponds to a different rotational isomerization for a given hexaarylbenzene. Rearrangement modes are sets of symmetry-related rearrangements, all of which represent isomerizations which may occur by the same rotational "mechanism", as the term is classically used in organic chemistry.[7] Figure 1 shows schematic representations of the idealized transition states for each of these mechanisms. Hexagons represent aryl rings in the plane of the central ring, whereas rectangles denote rings perpendicular to this plane. The peripheral aryl rings shown as hexagons are those which undergo rotation by π radians during the interconversion in question. The substituents in the two meta positions of a ring are interchanged by such a rotation, as are any ortho substituents. For example, $\mathbf{M_0}$ is the identity rearrangement, and no net isomerization occurs by this mode. $\mathbf{M_{12}}$ results in pairwise interchange of all ortho and all meta substituents, and signifies

Table I. Rearrangement Modes for Hexaarylbenzenes

M_0	M_1	M_2	M_3
E (identity)	(1,2)	(1,2)(3,4)	(1,2)(5,6)
	(3,4)	(1,2)(11,12)	(1,2)(9,10)
	(5,6)	(3,4)(5,6)	(3,4)(7,8)
	(7,8)	(5,6)(7,8)	(3,4)(11,12)
	(9,10)	(7,8)(9,10)	(5,6)(9,10)
	(11,12)	(9,10)(11,12)	(7,8)(11,12)

M_4	M_5	M_6	M_7
(1,2)(7,8)	(1,2)(3,4)(5,6)	(1,2)(3,4)(7,8)	(1,2)(5,6)(9,10)
(3,4)(9,10)	(1,2)(3,4)(11,12)	(1,2)(5,6)(7,8)	(3,4)(7,8)(11,12)
(5,6)(11,12)	(1,2)(9,10)(11,12)	(1,2)(5,6)(11,12)	
	(3,4)(5,6)(7,8)	(1,2)(3,4)(9,10)	
	(5,6)(7,8)(9,10)	(1,2)(7,8)(9,10)	
	(7,8)(9,10)(11,12)	(1,2)(7,8)(11,12)	
		(3,4)(5,6)(9,10)	
		(3,4)(5,6)(11,12)	
		(3,4)(7,8)(9,10)	
		(3,4)(9,10)(11,12)	
		(5,6)(7,8)(11,12)	
		(5,6)(9,10)(11,12)	

M_8	M_9	M_{10}	M_{11}
(1,2)(3,4)(5,6)(7,8)	(1,2)(3,4)(5,6)(9,10)	(1,2)(3,4)(7,8)(9,10)	(1,2)(3,4)(5,6)(7,8)(9,10)
(1,2)(3,4)(5,6)(11,12)	(1,2)(3,4)(7,8)(11,12)	(1,2)(5,6)(7,8)(11,12)	(1,2)(3,4)(5,6)(7,8)(11,12)
(1,2)(3,4)(9,10)(11,12)	(1,2)(5,6)(7,8)(9,10)	(3,4)(5,6)(9,10)(11,12)	(1,2)(3,4)(5,6)(9,10)(11,12)
(1,2)(7,8)(9,10)(11,12)	(1,2)(5,6)(9,10)(11,12)		(1,2)(3,4)(7,8)(9,10)(11,12)
(3,4)(5,6)(7,8)(9,10)	(3,4)(5,6)(7,8)(11,12)		(1,2)(5,6)(7,8)(9,10)(11,12)
(5,6)(7,8)(9,10)(11,12)	(3,4)(7,8)(9,10)(11,12)		(3,4)(5,6)(7,8)(9,10)(11,12)

M_{12}
(1,2)(3,4)(5,6)(7,8)(9,10)(11,12)

Figure 1. Idealized transition states for rotational mechanisms corresponding to the 13 rearrangement modes of hexaarylbenzenes.

enantiomerization in the case of a molecule represented by **1** when no secondary chirality due to chiral substituents, etc., is present. The derivation of rearrangement modes may be more easily grasped qualitatively if it is noted that there exists a formal mapping of the modes represented in Figure 1 onto the set of all possible isomeric chlorobenzenes. For example, M_3 may be mapped onto 1,3-dichlorobenzene, etc.

Experimental Studies of Rotational Mechanisms

Isomerizations by rotational mechanisms corresponding to any of the 13 modes are in principle possible for a given substituted hexaarylbenzene. By studying the isomerizations of suitably substituted molecules, it is possible to derive information concerning the isomerization modes which actually

occur. Reported below are the results of studies of this type which, when considered together, reveal the preferred isomerization pathway.

Hexaarylbenzenes with Two Substituents. It was previously reported[2] that hexaarylbenzenes **2** and **3** are separable into diastereomers at normal laboratory temperatures. The free energies of activation for diastereomerization of the isomers of **2** are ~33 kcal/mol, whereas those for **3** are ~38 kcal/mol.
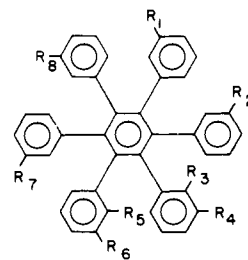
2, $R_3 = OCH_3$; $R_5 = CH_3$, $R_1 = R_2 = R_4 = R_6 = R_7 = R_8 = H$

3, $R_3 = R_5 = CH_3$; $R_1 = R_2 = R_4 = R_6 = R_7 = R_8 = H$

4, $R_4 = R_6 = CH_3$; $R_1 = R_2 = R_3 = R_5 = R_7 = R_8 = H$

5, $R_4 = R_6 = OCH_3$; $R_1 = R_2 = R_3 = R_5 = R_7 = R_8 = H$

6, $R_2 = R_5 = R_7 = CH_3$; $R_3 = OCH_3$; $R_1 = R_4 = R_6 = R_8 = H$

7, $R_1 = R_8 = OCH_3$; $R_4 = R_6 = CH_3$; $R_2 = R_3 = R_5 = R_7 = H$

In each of these molecules, only two diastereomers are possible, and little mechanistic information can be obtained. The observed isomerizations are consistent with any of the modes other than M_0 and M_{12}. In addition, rotations belonging to either of these two modes could theoretically be occurring, but would not be detected under the experimental conditions.

Hexaarylbenzenes with only meta substituents also display restricted rotation. Hexaarylbenzene **4** was previously shown to exist in two diastereomeric forms (a C_s conformation and a *dl* pair with C_2 symmetry) at 0 °C on the NMR time scale.

This fact was revealed by the observation of two methyl resonances separated by 1.7 Hz in the 100-MHz ^{1}H NMR spectrum.[2] As the sample was warmed and diastereomerization became more rapid, these resonances coalesced to a singlet. A complete line-shape analysis of the spectra yields a free energy of activation of $\Delta G^{\ddagger}_{294} = 17.0$ kcal/mol for this process.[8,10] This molecule is stereochemically correspondent[12] to **3**, and yields no additional information concerning the rearrangement mode.

Hexaarylbenzene **5** was synthesized using methods similar to those described previously[2] (see Experimental Section). At 10 °C, the 100-MHz ^{1}H NMR spectrum of the methoxy region of a solution of **5** in 5:3 chloroform-*d*–carbon disulfide showed two peaks of equal intensity separated by 1.1 Hz. At 21 °C these peaks coalesced to a singlet which sharpened with further heating. This behavior indicates diastereomerization (interconversion of the C_s and C_2 isomers). Line-shape analysis[8] yields $\Delta G^{\ddagger}_{294} = 17.1$ kcal/mol for this process.

Hexaarylbenzene **5** is stereochemically correspondent to **3** and **4**, and the NMR results for **5** do not exclude any additional modes as explanations for the observed coalescence. However, the results for **5** do shed some light on the energetics of the interconversion process. The rotational barriers for **2** are about 5 kcal/mol lower than those for **3**. This difference derives from the effect of the smaller steric bulk of the methoxy group relative to a methyl group, since electronic effects are expected to be small in these systems. (For example, in hindered biphenyls, replacement of a para hydrogen by a methoxy group changes the rotational barrier by less than 1 kcal/mol.[13]) The barriers for **4** and **5**, on the other hand, are identical within experimental error, even though the substituents are methyl in one case and methoxy in the other. This finding supports our previous suggestion[2] that methyl and methoxy groups in meta positions have relatively little steric influence, and that the observed barriers for these compounds reflect interactions involving mainly the aryl rings themselves and the attached hydrogen atoms. These results also confirm that any electronic effects on the rotational barriers are essentially identical for meta methyl and meta methoxy groups.

Hexaarylbenzenes with Four Substituents. The results mentioned above exclude only two of the 13 modes as pathways for the observed isomerizations in hexaarylbenzenes. More information can be obtained from studies of molecules such as **6** which bear four substituents. Hexaarylbenzene **6** was prepared by refluxing a mixture of 2,5-bis(3-methylphenyl)-3,4-diphenylcyclopentadienone and 2-methoxy-2'-methyldiphenylacetylene in benzophenone solution for 2.5 h (see Experimental Section). Chromatography of the resulting crystalline product on a silica gel column yielded two isomeric hexaarylbenzenes, **6a** and **6b**. Each of these two substances had elemental analyses consistent with the proposed structure **6**. At 30 °C, the 100-MHz ^{1}H NMR spectrum of the methyl region of **6a** in benzene-d_6 featured a broad singlet at δ 3.16 ppm, a broad singlet at 2.30 ppm, and a broad multiplet at 1.93 ppm. Heating the sample to 75 °C in the NMR spectrometer sharpened all three of these resonances to narrow singlets. The resonance at 3.16 ppm arises from the methoxy group of **6a**, whereas that at 2.30 ppm can be ascribed to the ortho methyl group (by comparison with the spectrum of **2** in the same solvent). The resonances at 1.93 ppm may be assigned to the two meta methyl groups (by comparison with the spectrum of **4**).[2] The two meta methyl resonances are accidentally isochronous at 75 °C. Isomer **6b** has a similar ^{1}H NMR spectrum at 30 °C with peaks in the methyl region at δ 3.21, 2.21, 1.95, and 1.91 (all broad singlets). These resonances also sharpen on heating.

The broadness of the resonances of **6a** and **6b** at 30 °C suggests that incomplete averaging of chemical shifts due to slow rotation on the NMR time scale is occurring. Such a
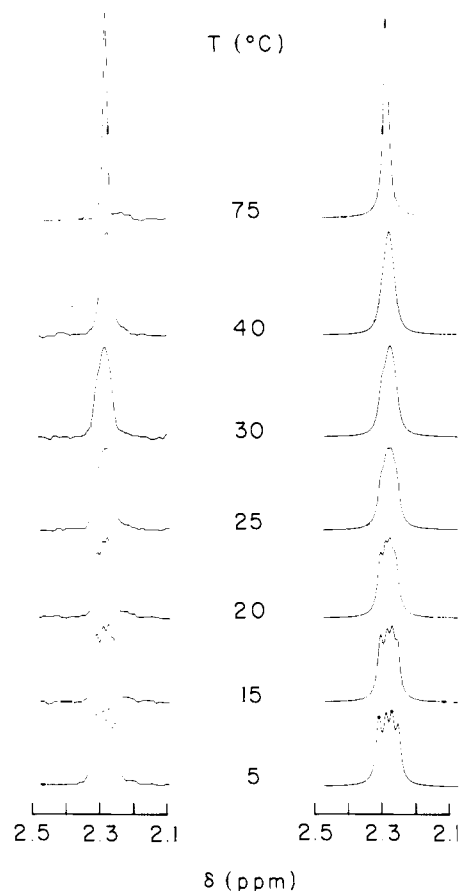

Figure 2. The 100-MHz ^{1}H NMR spectrum (ortho methyl region) of **6a** at various temperatures (left) and the corresponding calculated spectra based upon an M_1 rearrangement (right).

suggestion is in accord with previous observations on the related compounds **4** and **5**. Indeed, at 5 °C the broad resonances in the methyl region of **6a** have split into multiple resonances. This is shown most clearly by the resonance at 2.30 ppm which corresponds to the ortho methyl group (Figure 2). At 5 °C, this resonance has split into four closely spaced resonances. As shown in Figure 2, these four resonances broaden with heating and eventually coalesce to a sharp singlet. Analogous behavior was observed for **6b**.

It was also found that if a solution of either **6a** or **6b** is heated to about 140 °C or higher, clean interconversion of these isomers is observed, and an equilibrium mixture containing 46% **6a** and 54% **6b** is obtained. Kinetic studies of this interconversion process (see Experimental Section) yielded $\Delta G^{\ddagger}_{419} = 32.6$ kcal/mol for the conversion of **6a** into **6b**, and $\Delta G^{\ddagger}_{419} = 32.7$ kcal/mol for the reverse process. The rate of interconversion was found to be concentration independent over a 20-fold concentration range. Kinetic studies over a temperature range of 135–166 °C yielded $\Delta H^{\ddagger} = 31.4$ kcal/mol and $\Delta S^{\ddagger} = -2.7$ eu for the conversion of **6a** to **6b**. These findings are in accord with an intramolecular rotational process as an explanation for the observed interconversion. Thus, **6** undergoes at least two distinct classes of rotational processes: a high-temperature class which is rapid at about 150 °C on the laboratory time scale, and a low-temperature class which becomes rapid on the NMR time scale at about 30 °C.

The behavior reported above for **6a** and **6b** reflects rotational isomerization processes of some kind. In order to understand these processes, the stereochemistry of **6** must be examined in detail. Hexaarylbenzene **6** would be expected to exist in 16 stereoisomeric forms (eight *dl* pairs). Eight of these isomers (one from each *dl* pair) are shown schematically in Figure 3.
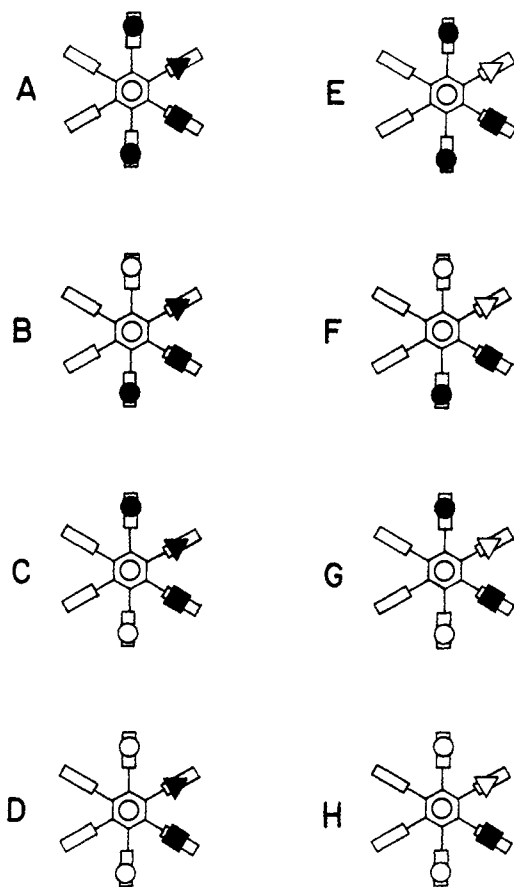
Figure 3. Schematic representation of eight of the 16 stereoisomers of **6** (one from each *dl* pair). Circles represent meta methyl groups, squares represent ortho methyl groups, and triangles represent ortho methoxy groups. Solid symbols denote substituents above the plane of the central ring, whereas hollow symbols signify substituents below this plane.

Figure 4. Graph for the stereoisomerizations of the isomers of **6** by M_1. Vertices represent isomers (see Figure 3) and edges represent stereoisomerizations.

Four of the *dl* pairs (A, B, C, D and their enantiomers $\overline{A}$, $\overline{B}$, $\overline{C}$, $\overline{D}$) have the ortho methyl group and the ortho methoxy group on the same side of the plane of the central ring, whereas the other four (E, F, G, H and $\overline{E}$, $\overline{F}$, $\overline{G}$, $\overline{H}$) have the ortho groups on opposite sides of this plane.

The above analysis suggests that eight diastereomeric forms of **6** should be experimentally observable in the low-temperature limit. This is indeed the case, as illustrated by the ortho methyl resonances in the ^{1}H NMR spectra. Compound **6a** shows four such resonances at 5 °C (one for each of four diastereomers), and **6b** features resonances for four additional *dl* pairs. Thus, a mixture of **6a** and **6b** would show eight ortho methyl resonances which would correspond to the eight diastereomeric *dl* pairs of enantiomers. It is not possible to assign each resonance to a particular *dl* pair at this time.

Upon warming, interconversion of these diastereomers is observed. By analogy with the results for **2**, **3**, **4**, and **5**, the low-temperature isomerizations must involve rotations of only the aryl rings bearing no substituents or meta substituents, whereas the high-temperature processes which interconvert **6a** and **6b** must involve rotation of ortho-substituted rings. If this is indeed the case, then the analysis of isomerization modes summarized in Figure 1 reveals that only four modes are consistent with the low-temperature process. These are M_1, M_2, M_3, and M_5. Interconversion by any of the other modes either would not achieve the observed coalescence or would also involve rotation of one of the rings bearing an ortho substituent.

The results of interconversions by a rearrangement mode are conveniently represented graphically. Figure 4 depicts the interconversions of the rotational isomers of **6** by mechanisms
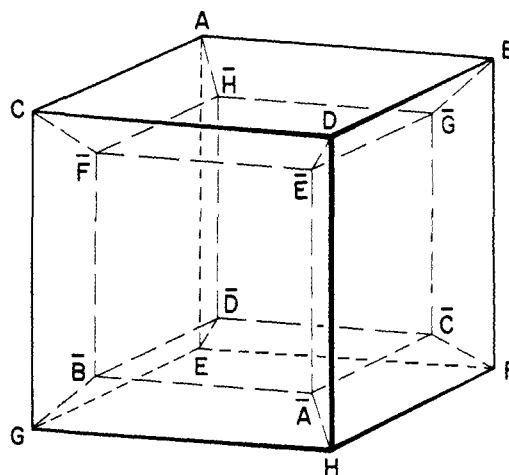
belonging to M_1. By employing this graph the isomerizations mentioned above may be readily visualized. The graph has the form of two cubes whose vertices are pairwise interconnected.[14] The vertices of the outer cube represent the isomers A, B, C, D, E, F, G, and H, and those of the inner cube represent the enantiomers, as shown. The M_1 rearrangements are denoted by the edges of the graph. The top and bottom edges of the cubes (A $\rightleftarrows$ B, A $\rightleftarrows$ C, B $\rightleftarrows$ D, C $\rightleftarrows$ D, etc.) represent isomerizations involving rotations of the rings bearing meta substituents. All vertical edges of the graph signify isomerizations in which the ortho methoxy group rotates. The dashed lines interconnecting the two cubes represent rotations of the ortho methyl group.

The isomerization behavior observed for **6** may be readily interpreted by reference to this graph. Below 5 °C all rotations by $\sim\pi$ radians are slow and eight diastereomeric *dl* pairs are observed as eight ortho methyl resonances in the ^{1}H NMR spectra of **6a** and **6b**. When these samples are warmed to about 30 °C rotation of the groups bearing meta methyl substituents becomes rapid on the NMR time scale. On the graph, these low-temperature processes are represented by rapid isomerizations along the top and bottom edges of the cubes. Thus, A, B, C, and D form a set of rapidly interconverting isomers, as do E, F, G, and H, and the corresponding sets of enantiomers (inner cube). The coalescence depicted for **6a** in Figure 2 reflects interconversions among the members of one of these sets of four isomers and among the members of the enantiomeric set, whereas the corresponding behavior for **6b** reflects the corresponding interconversions of the members of the diastereomeric set, and of their enantiomers.

At about 150 °C the class of high-temperature isomerizations becomes rapid. These isomerizations involve rotations of the rings bearing ortho methoxy groups by analogy with the results reported previously for **2** and **3**,[2] and are represented on the graph by the eight vertical edges. It should be noted that only one of the four diastereomeric sets of enantiomeric diastereomerization pathways need be traversed in order to achieve interconversion of all eight isomers within a cube. At 150 °C, **6** exists as a simple *dl* pair on the time scale of measurement.

In addition to the two aforementioned classes of diastereomerizations for **6**, a third isomerization process can in principle be observed: enantiomerization. In order to achieve enantiomerization by a mechanism belonging to M_1, rotation of not only the rings bearing meta methyl groups and ortho methoxy groups, but also the rings bearing ortho methyl groups, must occur. In terms of the graph (Figure 4), enan-

tiomerization requires that at least one edge joining the two cubes be traversed. This process has not as yet been observed experimentally, but would be expected to require significantly more energy of activation than was needed for the high-temperature diastereomerization processes, which necessitate rotation of rings bearing at most an ortho methoxy group.[2]

The above analysis of isomerization in **6** has been couched in terms of mechanisms belonging to M_1, wherein only one aryl ring at a time rotates $\sim\pi$ radians. As mentioned above, isomerizations belonging to modes M_2, M_3, and M_5 would also explain the results, and a similar graphical analysis could be presented for these modes. However, the isomerizations of mode M_1 are the simplest and most intuitively reasonable ones for **6** and other hexaarylbenzenes. Consequently it is postulated that the observed isomerizations of hexaarylbenzenes actually occur by mechanisms belonging to M_1. As will be shown in the next section, there is additional experimental evidence which supports this assignment.

A computer line-shape analysis of the exchange broadened NMR spectra of **6a** based on an M_1 mechanism (see Experimental Section) provides a satisfactory fit of the experimental data (Figure 2). Calculated free energies of activation for all isomerizations of the rotamers of **6a** were within ±0.1 kcal/mol of $\Delta G^{\neq}_{294} = 17.7$ kcal/mol. A similar analysis also yields $\Delta G^{\neq}_{294} = 17.7$ kcal/mol for the analogous processes in **6b**. As expected, these energies of activation are very close to those observed for isomerizations of other hexaarylbenzenes which involve the rotation of rings bearing meta substituents. The small increase in $\Delta G^{\neq}$ relative to the values for **4** and **5** may probably be attributed to the increased steric bulk of the rings bearing ortho substituents in **6**.

Pentaarylbenzenes. Differentiation among rotational mechanisms belonging to modes M_1, M_2, M_3, and M_5 is not possible in **6** because this molecule contains no probe groups for the detection of rotations of the rings bearing R_1 and R_8. Hexaarylbenzene **7** was prepared in order to study the rotations of these rings. Unfortunately, accidental isochronies precluded useful NMR studies. As a result, a different approach was taken: restricted rotation in two pentaarylbenzenes was investigated. The results for these compounds throw additional light on the rotational behavior of the hexaarylbenzenes.

Pentaarylbenzene **8** was prepared from phenylacetylene and the necessary substituted tetraphenylcyclopentadienone by a method analogous to that employed for the hexaarylbenzenes (see Experimental Section).[15] In the limit of slow rotation on

$$8 , R_1 = R_2 = H ; R_3 = R_4 = CH_3$$

$$9 , R_1 = R_3 = CH_3 ; R_2 = OCH_3 ; R_4 = H$$
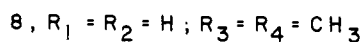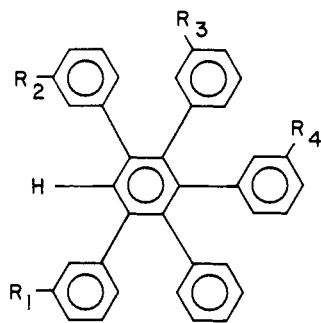
the NMR time scale, this molecule will exist in the perpendicular conformation as two diastereomeric *dl* pairs. In one of these pairs, the meta methyl groups reside on the same side of the plane of the central ring, whereas in the diastereomeric pair, these groups reside on opposite sides of this plane. Each

pair should give rise to two methyl resonances in the ^{1}H NMR spectrum.

At -20 °C, the spectrum of **8** features resonances in the methyl region at δ 2.02, 2.00, and 1.97 ppm in the ratio 1.0: 2.1:1.1. The resonance at 2.00 ppm is equal in area to the sum of the other two resonances and represents an accidental superposition of two methyl resonances (see below). Thus, the spectrum is in accord with that expected for this molecule in a perpendicular conformation. When the sample is warmed to -5 °C the four resonances begin to broaden, and at 10 °C they coalesce to two resonances at 2.01 and 1.98 ppm. These resonances sharpen upon further heating. This behavior represents diastereomerization. Line-shape analysis[8] yields $\Delta G^{\neq}_{288} = 15.5$ kcal/mol for the diastereomerization of either diastereomer, because they are present in nearly equal amounts. Since the free energy of activation for the diastereomerization is similar to those measured for **4**, **5**, and **6** (low-temperature isomerizations), it seems reasonable to postulate that isomerization in all of these molecules occurs by similar mechanisms. Granted this assumption isomerization in **8** must take place by a pathway similar to a mode M_1, M_2, M_3, or M_5 mechanism.

The diastereomerization behavior of pentaarylbenzene **9** differs sharply from that of **8** and related molecules. This pentaarylbenzene was prepared from *m*-methoxyphenylacetylene and 2,5-bis(3-methylphenyl)-3,4-diphenylcyclopentadienone (see Experimental Section). Restricted rotation in this molecule would result in the appearance of four diastereomeric *dl* pairs of isomers, and the ^{1}H NMR spectrum should feature four methoxy proton resonances and eight aromatic methyl resonances.

At ambient temperatures, the 90-MHz ^{1}H NMR spectrum of **9** in chloroform-*d* showed one methoxy resonance at δ 3.54 ppm and two aromatic methyl resonances at 2.20 and 2.01 ppm. This spectrum is consistent with that expected for **9** if diastereomerization is rapid on the NMR time scale. Cooling the sample to -65 °C did not cause any of these resonances to split into multiple peaks, and therefore gave no evidence for slow rotation. Similar studies in 4:1 chloroform-*d*--carbon disulfide (-65 °C, 100 MHz), acetone-d_6 (-16 °C, 90 MHz), and toluene-d_8 (-85 °C, 100 MHz) likewise yielded no evidence for slow rotation on the NMR time scale.

The failure to observe multiple NMR resonances for any of the three types of methyl hydrogen atoms of **9** even at very low temperatures means that either diastereomerization is still rapid at these temperatures, or all four expected resonances for each of the three methyl groups are accidentally isochronous. This last alternative seems unlikely, because studies in a variety of solvents all yielded the same result. In addition, the structural features of **9** are not very different from those of the hexa- and pentaarylbenzenes studied above where accidental isochrony did not occur. It appears, then, that rapid diastereomerization even at low temperatures is the most likely explanation for the failure to observe diastereomers in the NMR spectrum.

An examination of the structure of **9** reveals that in order to observe diastereomers, rotation of at least one aryl ring adjacent to the hydrogen on the central ring must be slow. Since no diastereomers are observed, rotation of these rings must be rapid even at the lowest temperatures studied. This is a reasonable result, since a hydrogen atom would be expected to exert much less steric influence than an aryl group in the same position. In the biphenyl series, for example, 2,2'-dimethylbiphenyl exhibits a barrier to rotation of $\Delta G^{\neq}_{238} = 17.4$ kcal/mol.[16] In this molecule, both rings bear an ortho substituent. If one ring bore only a meta substituent, the barrier would certainly be much lower. Indeed, even in the highly sterically hindered 1,8-diarylnaphthalenes and related molecules, the barriers to rotation of a ring bearing a meta sub-

stituent are only ~15–16 kcal/mol.[17] In-plane splaying of the peri groups accounts in part for this relatively low barrier.[17b]

The results for **9** suggest that for pentaarylbenzenes in general, rotation of an aryl ring adjacent to a hydrogen will be much more facile than rotation of a ring flanked by two other aryl groups. If we now consider pentaarylbenzene **8** again, it can be seen that if isomerization of the diastereomers of **8** were to occur by a mechanism similar to a mode M_2 mechanism, then one such isomerization would involve rotation of a phenyl ring adjacent to the hydrogen on the central ring. From the above argument, such an isomerization should be much more facile than isomerization by a similar mechanism where this hydrogen was replaced by a phenyl group. Thus, the free energy of activation for diastereomerization of **8** by an M_2 type mechanism should be much lower than that for a similar M_2 isomerization in **4** and related compounds. However, the barriers for **4** and **8** are actually quite similar. Isomerization of these molecules by an M_2 type mechanism is therefore very unlikely. Inspection of Table I or Figure 1 reveals that similar arguments may be made against M_3 and M_5 type mechanisms for the isomerization of penta- and hexaarylbenzenes. Mechanisms of type M_1 are the only ones consistent with the arguments outlined above. Small differences in energies of activation such as that seen for **4** ($\Delta G^{\pm}_{294} = 17.0$ kcal/mol) and **8** ($\Delta G^{\pm}_{288} = 15.5$ kcal/mol) can be attributed to second-order buttressing effects rather than direct interaction between a rotating ring and a hydrogen on the central ring.

Conclusions

The experimental results reported above suggest that diastereomerizations of all hexaarylbenzenes studied to date occur by mechanisms belonging to mode M_1. Results for pentaarylbenzenes are consistent with a similar mechanism. The most reasonable mechanism belonging to M_1 is a simple rotation by ~π radians of a single aryl ring, as suggested by the idealized transition state in Figure 1.

It should be noted that the NMR evidence discussed here of necessity only pertains to the initial and final states in the isomerization process. The actual rotation is not observed. Thus, the transition state diagrammed in Figure 1 is highly idealized, and considerable motion and distortion can and no doubt does occur in parts of the molecule other than the rotating ring. The fact of importance here is that only one ring at a time rotates by ~π radians. In addition, the experiments described here do not reveal the direction of rotation of a ring, since rotation by ~π radians in either direction will yield the same overall result. Presumably, the direction of rotation is such that steric interactions among substituents are minimized.

Experimental Section

Elemental analyses were performed by Midwest Microlab, Ltd., Indianapolis Ind., or Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points were obtained with a Mel-Temp or Thomas-Hoover apparatus, and sample tubes were sealed when necessary to avoid oxidation or sublimation. NMR spectra were obtained on a Bruker WH-90, Varian XL-100, or Varian 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 SM-1B instrument.

3,4-Bis(3-methoxyphenyl)-2,5-diphenylcyclopentadienone. A solution of dibenzyl ketone (2.1 g, 10 mmol) and 3,3′-dimethoxybenzil[18] (2.7 g, 10 mmol) in 10 mL of triethylene glycol was heated to 100 °C and 1 mL of a 35% solution of benzyltrimethylammonium hydroxide in methanol was added. A reddish color appeared, and a dark oil formed rapidly. After the mixture cooled to room temperature, 10 mL of methanol was added, and the crystalline product was removed by filtration and recrystallized from a mixture of benzene and methanol to yield the desired product (3.15 g, 71% yield, mp 190–191.5 °C). The ¹H NMR spectrum featured resonances at δ 3.50 (6 H, s, OCH_3)

and 6.4–7.4 (18 H, m, aromatic H). Anal. Calcd for $C_{31}H_{24}O_3$: C, 83.78; H, 5.41. Found: C, 83.72; H, 5.61.

1,2-Bis(3-methoxyphenyl)-3,4,5,6-tetraphenylbenzene (5). A mixture of 3,4-bis(3-methoxyphenyl)-2,5-diphenylcyclopentadienone (0.58 g, 1.3 mmol) and diphenylacetylene (0.50 g, 2.8 mmol) in a test tube was heated with a flame until the purple color disappeared and frothing ceased. The refluxing excess diphenylacetylene was removed by allowing it to condense on a glass rod inserted into the test tube. The remaining light brown liquid was allowed to cool to ambient temperature, and the resulting solid mass was triturated in 10 mL of acetone to a white powder, which was recrystallized from a mixture of benzene and methanol to yield **5** (0.56 g, 73% yield, mp 307–308.5 °C). The ¹H NMR spectrum in 5:3 $CDCl_3$-CS_2 showed resonances at δ 3.44 (6 H, s, OCH_3) and 6.3–7.4 (28 H, m, aromatic H). Anal. Calcd for $C_{44}H_{34}O_2$: C, 88.89; H, 5.72. Found: C, 88.78; H, 5.81.

2,5-Bis(3-methylphenyl)-3,4-diphenylcyclopentadienone. A solution of 1,3-di-*m*-tolylpropan-2-one[19] (2.38 g, 10 mmol) and benzil (2.10 g, 10 mmol) in 10 mL of triethylene glycol was heated to 110 °C and 2 mL of 40% benzyltrimethylammonium hydroxide in methanol was added. The resulting dark solution was allowed to cool to room temperature, 10 mL of methanol was added, and the crystalline product was removed by filtration, washed with methanol, and recrystallized from a mixture of benzene and methanol to yield the desired product as dark flakes (2.63 g, 64% yield, mp 169–170 °C). The ¹H NMR spectrum included resonances at δ 2.27 (6 H, s, CH_3) and 6.8–7.4 (18 H, m, aromatic H). The mass spectrum yielded *m/e* 412.1775 (calcd for $C_{31}H_{24}O$, 412.1827).

1-(2-Methoxyphenyl)-2-(2-methylphenyl)-3,6-bis(3-methylphenyl)-4,5-diphenylbenzene (6). A solution of 2-methoxy-2′-methyldiphenylacetylene[2] (1.50 g, 6.8 mmol) and 2,5-bis(3-methylphenyl)-3,4-diphenylcyclopentadienone (2.32 g, 5.6 mmol) in 10 mL of benzophenone was refluxed for 2.5 h using an air-cooled condenser. The solution was cooled, and 10 mL of acetone was added. The crystalline product was removed by filtration, and consisted of a mixture of diastereomers **6a** and **6b** (2.33 g, 68% yield). The diastereomers were separated by column chromatography on silica gel (CCl_4).

The first diastereomer to elute, **6a**, melted at 338–340 °C with some sublimation at lower temperatures. The ¹H NMR spectrum in benzene-d_6 at 30 °C consisted of resonances at δ 1.93 (6 H, m, meta CH_3), 2.30 (3 H, br s, ortho CH_3), 3.16 (3 H, br s, OCH_3), and 6.1–7.4 (26 H, m, aromatic H). The spectrum was temperature dependent, as discussed below and in the text. Anal. Calcd for $C_{46}H_{38}O$: C, 91.05; H, 6.31. Found: C, 90.75; H, 6.44.

The second diastereomer to elute, **6b**, showed identical melting behavior with **6a**. The ¹H NMR spectrum in benzene-d_6 at 30 °C featured resonances at δ 1.91 (3 H, br s, meta CH_3), 1.95 (3 H, br s, meta CH_3), 2.21 (3 H, br s, ortho CH_3), 3.21 (3 H, br s, OCH_3), and 6.1–7.6 (26 H, m, aromatic H). The spectrum of this material was also temperature dependent. Anal. Found: C, 90.79; H, 6.39.

Equilibration Studies on 6. Upon heating, solutions of **6a** or **6b** were found to isomerize to an equilibrium mixture containing 46% **6a** and 54% **6b**. Kinetic studies on a 4.12×10^{-4} M solution of **6a** in 1-bromonaphthalene were carried out in the manner described previously for **2**.[2] At 146 °C, these studies yielded $\Delta G^{\pm}_{419} = 32.6$ kcal/mol for the conversion of **6a** into **6b** and $\Delta G^{\pm}_{419} = 32.7$ kcal/mol for the reverse reaction, with a correlation coefficient of 0.998 (12 data points). Similar studies on an 8.24×10^{-3} M solution of **6a** gave identical results, within experimental error, as did a study using an 8.24×10^{-3} M solution of **6b** at the same temperature. Kinetic studies were also carried out with solutions of **6a** at 135.2, 156.0, and 166.2 °C. The data for four temperatures yielded $\Delta H^{\pm} = 31.4$ kcal/mol and $\Delta S^{\pm} = -2.7$ eu for the conversion of **6a** to **6b** and $\Delta H^{\pm} = 31.7$ kcal/mol and $\Delta S^{\pm} = -2.4$ eu for the reverse process.

Dynamic Nuclear Magnetic Resonance Studies of 6a and 6b. ¹H NMR spectra were determined on a Varian XL-100 spectrometer equipped with a variable temperature accessory. Temperature measurements were based on the chemical shift difference of the protons of methanol and utilized the temperature-shift correlation of Van Geet.[20]

At 5 °C the ¹H NMR spectrum of **6a** was characteristic of four diastereomers with slow exchange on the NMR time scale, as discussed in the text. In particular, the ortho methyl resonance had split into four resonances (Figure 2) at δ 2.25, 2.27, 2.29, and 2.31 ppm, with relative areas of 1.00:1.12:1.07:1.26 (from line-shape analysis). Upon heating, these resonances coalesced to a singlet. In order to extract energies of activation for diastereomerization from these spectra, a line-shape analysis is necessary. There are two major

problems associated with such an analysis for **6a**: assignment of resonances and estimation of relative exchange rates for protons in the four sites. In order to assign resonances, it is first necessary to decide whether **6a** is made up of structures A, B, C, D and their enantiomers or E, F, G, H and the corresponding enantiomers (Figure 3). Since the experimental data do not yield this information, **6a** was arbitrarily assigned structures A, B, C, D, and their enantiomers for purposes of analysis only. The four resonances observed at 5 °C must now be assigned to the four diastereomers. Again, the data do not permit an unambiguous assignment. An assignment which is consistent with the experimental results is $A\overline{A}$ (2.25), $B\overline{B}$ (2.27), $C\overline{C}$ (2.31), and $D\overline{D}$ (2.29).

In order to estimate exchange rates for protons in the various sites, it is necessary to postulate a rearrangement mode. As a first attempt at analysis, mode M_1 was selected. Given this mode, it is seen from Figure 4 that for the low-temperature diastereomerization process, protons in an A site may exchange with those in a B or C site, protons in a B site may exchange with those in an A or D site, etc. Since each diastereomer (and its corresponding enantiomer) may be converted to two other isomers, there are a total of eight rate constants to be considered in the analysis of **6a**. Since these rotational processes are structurally all very similar, it was assumed that all rate constants were identical, and the values for these rate constants were then varied only as necessary to account for the slight population differences. A lineshape analysis[8] using these assumptions was carried out for **6a**, and the results are shown in Figure 2. From the figure, it may be seen that the calculated spectra are good matches for the experimental spectra, and that the assumptions discussed above are consistent with the experiment. The energies of activation for the eight processes extracted from the analysis using data for five temperatures were essentially identical, and yield the values reported in the text. It must be stressed that, although the solution presented here is consistent with the experimental results, it is not unique. In particular, other assignments of NMR resonances to isomers shown in Figure 3 yield the same calculated results.

The ^1H NMR spectra of **6b** showed temperature-dependent behavior similar to that observed for **6a**. At −20 °C, a solution of **6b** in 4:1 benzene-d_6–carbon disulfide also featured four ortho methyl resonances of nearly equal intensities which coalesced to a singlet upon warming. A line-shape analysis similar to that described for **6a** yielded the results reported in the text.

1,2-Bis(3-methoxyphenyl)-4,5-bis(3-methylphenyl)-3,6-diphenylbenzene (7). A mixture of 3,4-bis(3-methoxyphenyl)-2,5-diphenylcyclopentadienone (0.58 g, 1.3 mmol) and 3,3'-dimethyldiphenylacetylene[21] (0.41 g, 2.0 mmol) in a test tube was heated as described for **5** to yield a dark solid with an oily appearance. This material was chromatographed on silica gel (CHCl$_3$) to yield a white solid which was recrystallized from acetone to yield **7** (0.175 g, 22% yield, mp 298–299 °C). The ^1H NMR spectrum in 3:2 chloroform-*d*–carbon disulfide consisted of resonances at δ 1.99 (6 H, s, aromatic CH$_3$), 3.44 (6 H, s, OCH$_3$), and 6.3–7.0 (26 H, m, aromatic H). Upon cooling, multiple peaks appeared in the methyl and methoxy region, but accidental isochronies precluded studies which would yield new mechanistic information. Anal. Calcd for C$_{46}$H$_{38}$O$_2$: C, 88.75; H, 6.11. Found: C, 88.69; H, 6.30.

1,2-Bis(3-methylphenyl)-3,4,6-triphenylbenzene (8). A mixture of 3,4-bis(3-methylphenyl)-2,5-diphenylcyclopentadienone[2] (1.0 g, 2.4 mmol) and phenylacetylene (0.5 g, 4.8 mmol) was heated in a test tube over an open flame until the purple color disappeared. After cooling, 10 mL of acetone was added, and the yellow glass was broken up with

a spatula. The resulting powder was removed by filtration, washed with acetone, and recrystallized from a mixture of toluene and hexane to yield white crystals of **8** (0.38 g, 33% yield, mp 216–217 °C). The ^1H NMR spectrum featured resonances at δ 1.98 (3 H, s, CH$_3$), 2.01 (3 H, s, CH$_3$), and 6.6–7.6 (24 H, m, aromatic H). Anal. Calcd. for C$_{38}$H$_{30}$: C, 93.79; H, 6.21. Found: C, 94.06; H, 6.30.

1-(3-Methoxyphenyl)-2,5-bis(3-methylphenyl)-3,4-diphenylbenzene (9). A mixture of 2,5-bis(3-methylphenyl)-3,4-diphenylcyclopentadienone (1.0 g, 2.4 mmol) and 3-methoxyphenylacetylene[22] (0.40 g, 3.0 mmol) was heated in a test tube over an open flame until the purple color was discharged. The mixture was allowed to cool and stirred with 10 mL of acetone. Slow evaporation of the solvent resulted in the deposition of white crystals which were removed by filtration and chromatographed on a silica gel column (toluene) to yield a colorless oil, which crystallized from cyclohexane. The yield of **9** was 0.841 g (67%) of material of mp 158–160 °C with softening at ∼152 °C. The ^1H NMR spectrum was consistent with the proposed structure with resonances at δ 2.03 (3 H, s, aromatic CH$_3$), 2.22 (3 H, s, aromatic CH$_3$), 3.55 (3 H, s, OCH$_3$), and 6.3–7.4 (23 H, m, aromatic H). Anal. Calcd for C$_{39}$H$_{32}$O: C, 90.70; H, 6.20. Found: C, 91.01; H, 6.48.

References and Notes

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(2) D. Gust, *J. Am. Chem. Soc.*, **99**, 6980–6982 (1977).
(3) W. Hässelbarth and E. Ruch, *Theor. Chim. Acta*, **29**, 259–267 (1973).
(4) C. M. Woodman, *Mol. Phys.*, **19**, 753–780 (1970).
(5) J. I. Musher, *J. Am. Chem. Soc.*, **94**, 5662–5665 (1972).
(6) The group-theoretical manipulations discussed here are best performed on a group the size of $(S_2)^6 \wedge D_6$ by means of a simple computer program written for the purpose.
(7) For another recent application of this type of analysis to organic chemistry, see P. Finocchiaro, D. Gust, W. D. Hounshell, J. P. Hummel, P. Maravigna, and K. Mislow, *J. Am. Chem. Soc.*, **98**, 4945–4952 (1976); P. Finocchiaro, W. D. Hounshell, and K. Mislow, *ibid.*, **98**, 4952–4963 (1976).
(8) The computer program used for line-shape analysis is based on one originated by M. Saunders.[9] We thank Mr. George Underwood for developing this program.
(9) M. Saunders in "Magnetic Resonance in Biological Systems", A. Ehrenberg, B. C. Malmström, and T. Vänngård, Ed., Pergamon Press, Elmsford, N.Y., 1967, p 85.
(10) The free energy of activation for this isomerization was previously estimated at $\Delta G^{\ddagger}_{294}$ = 16.4 kcal/mol using the Gutowsky–Holm approximation.[11] The line-shape analysis provides a more precise value for this quantity.
(11) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228–1234 (1956).
(12) D. Gust and K. Mislow, *J. Am. Chem. Soc.*, **95**, 1535–1547 (1973); D. Gust, P. Finocchiaro, and K. Mislow, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 3445–3449 (1973); K. Mislow, *Acc. Chem. Res.*, **9**, 26–33 (1976).
(13) M. Oki and G. Yamamoto, *Bull. Chem. Soc. Jpn.*, **44**, 266–270 (1971).
(14) This type of graph has also been used to represent isomerizations of Ar$_3$Z systems and trischelates (see K. Mislow, D. Gust, P. Finocchiaro, and R. J. Boettcher, *Top. Curr. Chem.*, **47**, 1–28 (1974)).
(15) Pentaarylbenzene derivatives have been known for many years (W. Dilthey, W. Schommer, and O. Trösken, *Chem. Ber.*, **66**, 1627–1628 (1933); C. F. H. Allen and L. J. Sheps, *Can. J. Res.*, **11**, 171–179 (1934)).
(16) W. Theilacker and H. Böhm, *Angew. Chem., Int. Ed. Engl.*, **6**, 251 (1967).
(17) (a) H. O. House, W. J. Campbell, and M. Gall, *J. Org. Chem.*, **35**, 1815–1819 (1970); (b) R. L. Clough and J. D. Roberts, *ibid.*, **43**, 1328–1331 (1978).
(18) A. Schönberg and W. Malchow, *Chem. Ber.*, **55B**, 3746–3752 (1922).
(19) E. C. S. Jones and J. Kenner, *J. Chem. Soc.*, 1842–1857 (1931).
(20) A. L. Van Geet, *Anal. Chem.*, **42**, 679–680 (1970).
(21) G. H. Coleman, W. H. Holst, and R. D. Maxwell, *J. Am. Chem. Soc.*, **58**, 2310–2312 (1936).
(22) W. S. Johnson, D. K. Banerjee, W. P. Schneider, C. D. Gutsche, W. E. Shelberg, and L. J. Chinn, *J. Am. Chem. Soc.*, **74**, 2832–2849 (1952).