

pair is expected for a maximally labeled derivative. It may be safely anticipated that such conditions will be attainable only at elevated temperatures, given the magnitude (30.1 kcal mol<sup>-1</sup>) of the calculated gear-slippage barrier. By the same token, under ordinary laboratory conditions only gearing remains rapid ( $G_{12}$ ), and three residual DL pairs are anticipated for a maximally labeled structure.<sup>69</sup> Finally, in the event that both processes are frozen out, there should be 18 DL pairs for a maximally labeled structure; given the magnitude of the calculated barrier (0.19 kcal mol<sup>-1</sup>), however, this is unlikely to be observed in the absence of a major perturbation of the PE hypersurface.<sup>61</sup>

**Minimal Labeling.** The minimum degree of labeling necessary to distinguish between different rearrangement modes can be derived from Table X by considering that a distinction between two modes is possible if a given labeling pattern shows different numbers of isomers, depending on which rearrangement mode is operational. Thus, for **3**,  $G_{12}$  (gearing) and  $G_{36}$  (gearing and gear slippage) both lead to one meso species if we label only one Tp group (e.g.,  $L_6$ ). When both Tp groups are substituted equivalently ( $L_4$ ), the mode  $G_{36}$  leads to one meso species but  $G_{12}$  leads to a meso isomer plus a DL pair. In principle, these may be distinguished spectroscopically. Though similar results are obtained for more complicated substitution patterns, the pattern  $L_4$  is the simplest one that can still distinguish between  $G_{12}$  (gearing) and

$G_{36}$  (gearing and gear slippage).

### Summary

Group theory has been used to enumerate all isometric structures of molecules **1**, **2**,<sup>16</sup> and **3**, as well as all rearrangement modes. Each such mode interconverts some or all of the isometric structures; i.e., it partitions them into sets (or isomers) such that interconversion occurs between isometric structures within but not among sets. In order to distinguish different sets, we find that the molecule under investigation must be labeled in such a manner that different sets (or isomers) have different physical properties. Some labeling patterns lead to different numbers of isomers, depending on the effective rearrangement or interconversion mode, and can therefore be used to distinguish among different modes. With the help of EFF calculations, some of the rearrangement modes have been associated with detailed mechanisms, i.e., with detailed changes in geometry and energy occurring during the interconversion. Specifically, our analyses and calculations lead to the prediction that of the three compounds studied, only **3** is capable of existing in suitably derivatized isomeric forms at ambient temperature, i.e., under ordinary laboratory conditions. A test of this prediction is described in the following paper.<sup>70</sup>

**Acknowledgment.** We thank the National Science Foundation (CHE-8009670) for support of this work. H.B.B. thanks the chemistry faculty at Princeton University for their hospitality during his stay in the spring term of 1981.

Registry No. **1**, 74-98-6; **2**, 1070-87-7; **3**, 73611-46-8.

(68) Experimental support has been adduced from a scatter plot of torsional coordinates ( $\phi$ ,  $\phi'$ ) for the two CC<sub>3</sub> rotors in structural fragments of the type C<sub>3</sub>C-C-CC<sub>3</sub>: Nachbar, R. B., Jr.; Johnson, C. A.; Mislow, K. J. *Org. Chem.* **1982**, *47*, 4829.

(69) For a  $C_3(2/1)$  ground state,<sup>53</sup> the double coset representing gearing generates the same group  $G_{12}$  and therefore the same isomer table ( $G_{12b}$  in ref 4).

(70) Guenzi, A.; Johnson, C. A.; Cozzi, F.; Mislow, K. J. *Am. Chem. Soc.*, following paper in this issue.

## Dynamic Gearing and Residual Stereoisomerism in Labeled Bis(9-triptycyl)methane and Related Molecules. Synthesis and Stereochemistry of Bis(2,3-dimethyl-9-triptycyl)methane, Bis(2,3-dimethyl-9-triptycyl)carbinol, and Bis(1,4-dimethyl-9-triptycyl)methane<sup>1</sup>

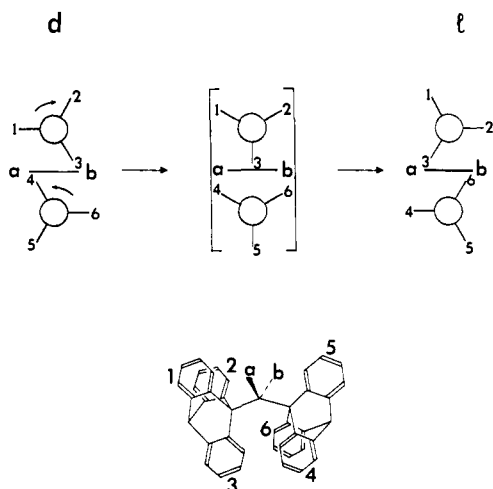
Alberto Guenzi, Constance A. Johnson, Franco Cozzi, and Kurt Mislow\*

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08544. Received May 10, 1982

**Abstract:** The substitution patterns of bis(9-triptycyl)methane (**1**) and -carbinol (**2**), two molecular bevel gear systems, have been classified according to the number of residual stereoisomers remaining under the full operation of the gearing mode and in the presence or absence of gear-slippage constraints. Substitution patterns have been identified in which enantiomeric conformations are interconverted by gearing through exclusively chiral pathways. Bis(2,3-dimethyl-9-triptycyl)methane (**3**) and -carbinol (**4**) have each been separated into residual meso and DL isomers, and the isomers have been unambiguously identified by NMR spectroscopy. *meso-3* (**3a**) and DL-**3** (**3b**) are interconverted at elevated temperatures by a gear-slippage mechanism; the diastereomerization barrier ( $\Delta G^\ddagger$ ) is 34 kcal mol<sup>-1</sup> at 145–165 °C. The racemization barrier of **3b**, which also involves gear slippage, is found to be >22 kcal mol<sup>-1</sup>. These findings are in accord with an empirical force field (EFF) prediction of 30 kcal mol<sup>-1</sup> for the gear-slippage barrier in **1**. The methyl groups in the 1- and 1'-positions of *meso*-bis(1,4-dimethyl-9-triptycyl)methane (**5a**) restrict cogwheeling of the 9-triptycyl groups, and a gearing barrier is therefore measurable by dynamic NMR. The measured  $\Delta G^\ddagger$  of 14 kcal mol<sup>-1</sup> is comparable to a barrier of 17 kcal mol<sup>-1</sup> calculated (EFF) for the conformational interconversion by the gearing mechanism. The gear-slippage barrier, as measured by conversion of **5a** to the DL isomer (**5b**), is 39 kcal mol<sup>-1</sup> at 215 °C. The present work describes the first measurement of stereoisomerization barriers resulting from restricted gearing and gear slippage.

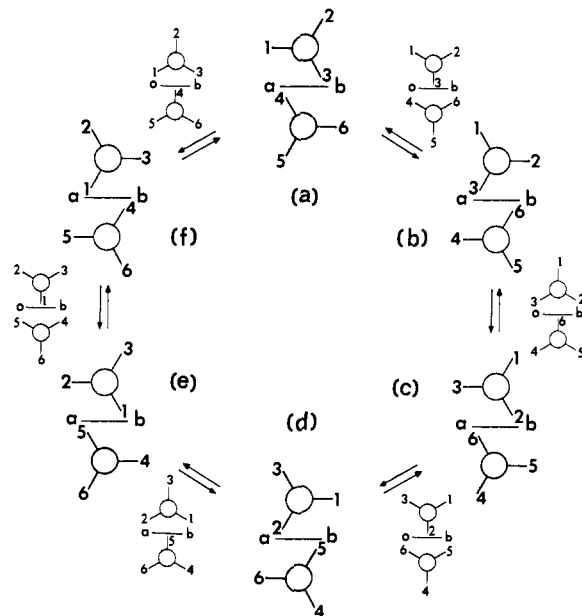
Empirical force field (EFF) calculations reported in the preceding paper<sup>2</sup> have shown that the 9-triptycyl (Tp) moieties in

bis(9-triptycyl)methane<sup>3</sup> (**1**) undergo virtually unhindered correlated disrotation (dynamic gearing). The molecule has a  $C_2$



**Figure 1.** Schematic representation of the basic gearing mechanism in bis(9-triptycyl)methane (**1**). Labeled benzene rings (1–6) and methylene hydrogens (a and b) are shown in the structural formula. In the bracketed projection, which corresponds to the formula, the view is along the bisector of the H–C–H angle, symbolized by a—b. The circles represent C9 and C9' of the 9- and 9'-triptycyl moieties in **1**, and the three lines radiating from each circle represent the three aryl blades of each triptycyl group. A  $C_2$  ground-state conformation, designated *d*, undergoes internal disrotation (curved arrows), through a  $C_2(2/1)$  transition state (bracketed), to the enantiomeric *l* form.

ground state, and enantiomerization occurs by gearing of the Tp groups through a  $C_2$  transition state  $0.19 \text{ kcal mol}^{-1}$  higher in energy.<sup>6</sup> Let us arbitrarily designate enantiomers that are so interconvertible as *d* and *l* isomers (Figure 1).<sup>7</sup> By a cyclic permutation of the three benzene-ring labels in each Tp moiety of *d*- and *l*-**1**, it is possible to generate a total of 18 isomeric<sup>9</sup>  $C_2$

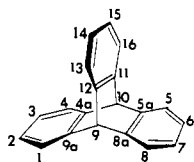


**Figure 2.** Conformational gearing circuit for bis(9-triptycyl)methane (**1**,  $a = b = \text{H}$ ) and bis(9-triptycyl)carbinol (**2**,  $a = \text{H}$ ;  $b = \text{OH}$ ). The schematic projections around the perimeter, six of which are lettered, follow the convention in Figure 1. Transition-state structures are shown as smaller projections near the arrows.

(1) Portions of this work were reported in preliminary communications: (a) Hounshell, W. D.; Johnson, C. A.; Guenzi, A.; Cozzi, F.; Mislow, K. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6961. (b) Cozzi, F.; Guenzi, A.; Johnson, C. A.; Mislow, K.; Hounshell, W. D.; Blount, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 957. (c) Johnson, C. A.; Guenzi, A.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6240.

(2) Bürgi, H.-B.; Hounshell, W. D.; Nachbar, R. B., Jr.; Mislow, K. *J. Am. Chem. Soc.*, preceding paper in this issue.

(3) Throughout this, as in our previous papers,<sup>1,2</sup> we adopt the IUPAC<sup>4</sup> and *Chemical Abstracts* numbering for triptycene (9,10-dihydro-9,10-*o*-benzenoanthracene) shown. This supersedes the old system in which triptycene was regarded as a derivative of bicyclo[2.2.2]octane.<sup>5</sup>



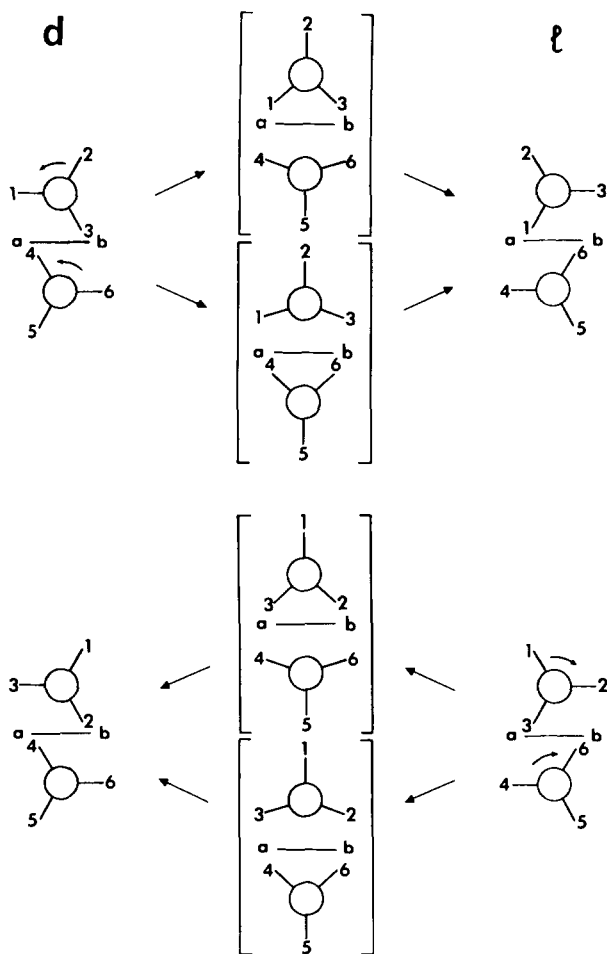
(4) In "Nomenclature of Organic Chemistry"; IUPAC (Organic Chemistry Division), Commission of Nomenclature of Organic Chemistry, prepared by J. Rigaudy and S. P. Klesney, Pergamon Press: Oxford, 1979; Rule A-34.1, p 35.

(5) Bartlett, P. D.; Ryan, M. J.; Cohen, S. G. *J. Am. Chem. Soc.* **1942**, *64*, 2649.

(6) (a) The force field used in these calculations was taken from the MM2 program (Allinger, N. L.; Yuh, Y. H. *QCPE* **1981**, *13*, 395) with two modifications designed for  $C_{ar}-C_{ar}$  bonds ( $l^0 = 1.3937 \text{ \AA}$  and  $k_r = 8.0667 \text{ mdyne \AA}^{-1}$ ). The optimization was performed by use of the program BIGSTRN-3.<sup>2</sup> (b) Preliminary calculations,<sup>1a</sup> using a different force field and optimization program, had indicated a  $C_2$  ground state for **1** and a  $C_2$  gearing transition state  $1.0 \text{ kcal mol}^{-1}$  higher in energy. However, this switch in ground- and transition-state symmetries has no effect on any observable quantities (i.e., number and kinds of residual stereoisomers, NMR signals, etc.).

(7) Since the gearing barrier is only ca.  $0.2 \text{ kcal mol}^{-1}$ , i.e., considerably less than *RT* at room temperature, the designation of enantiomeric ground-state structures in **1** as "isomers" might be called into question.<sup>8</sup>

(8) Eliel, E. L. *Isr. J. Chem.* **1976/1977**, *15*, 7.



**Figure 3.** Schematic representation of the gear-slippage mechanism in bis(9-triptycyl)methane (**1**). Projections follow the convention in Figure 1. Curved arrows indicate direction of net conrotation. Note that the  $C_2(2/2)$  transition states (bracketed) are of the gear-clashed variety, as contrasted to the gear-meshed transition state in Figure 1: (top) gear slippage of the *d* isomer in Figure 1 (left to right); (bottom) gear slippage of the *l* isomer in Figure 1 (right to left).

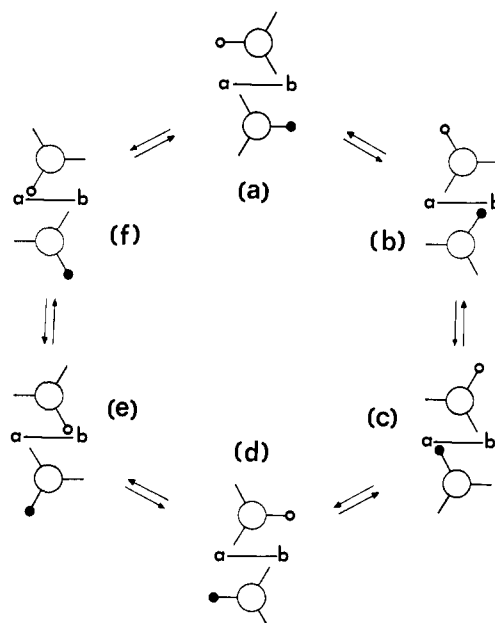
structures that differ in label distribution and that are partitioned, under the operation of the gearing mode, into three disjoint sets of six structures (three *d* and three *l* isomers) each. One such set is shown in the gearing circuit of Figure 2. Each of the three sets consists of an ensemble of six rapidly interconverting isomers that constitute a residual meso (or achiral) isomer,<sup>13,16</sup> for a total of three residual meso isomers. Since these differ only in label distribution, it is appropriate to call them *label isomers*.

None of the six structures in a set that constitutes a given label isomer can be converted, by gearing, into a structure that belongs to another set. Thus, there can be no interconversion of label isomers by gearing. Such interconversion becomes possible, however, by a second mechanism for the enantiomerization of *d*- and *l*-1, i.e., gear slippage. According to our calculations,<sup>2</sup> this process entails net conrotation of the Tp moieties through a  $C_s$ -( $2/2$ ) transition state 30.1 kcal mol<sup>-1</sup> above the ground state (Figure 3). Thus, gear slippage of the *d* isomer in Figure 1, which belongs to the set in Figure 2, yields an *l* isomer (Figure 3, top) that is a member of a second set. Similarly, gear slippage of the *l* isomer in Figure 1, which also belongs to the set in Figure 2, yields a *d* isomer (Figure 3, bottom) that is a member of the third set. Under the operation of the gearing mode, the two new isomers in Figure 3 generate two sets of six isometric structures that differ in label distribution from the set in Figure 2 and from each other. These three sets constitute the three label isomers.

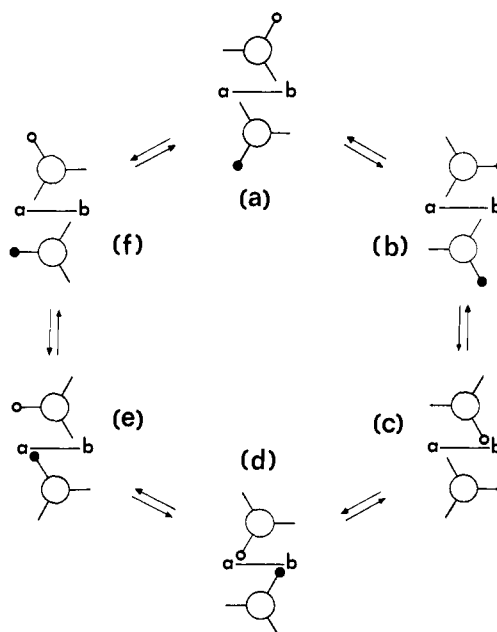
The existence of three label isomers of 1 and the calculated high-energy barrier for interconversion among them led to the prediction<sup>1a,2</sup> that suitably substituted derivatives of 1 should exist in isomeric forms that should be separable at ambient temperatures and interconvertible at elevated temperatures. The present paper describes experimental verification of this prediction. Such a verification requires conversion of the chemically indistinguishable *label isomers* into residual *chemical isomers*. In discussing the experimental design, it is therefore appropriate to begin by considering the relation of substitution patterns to the number and types of associated residual stereoisomers. The choice of the substitution pattern will then be dictated by its suitability to the purpose at hand.

#### Isomers and Isomerizations in Substituted Derivatives of Bis(9-triptycyl)methane

**Classification of Substitution Patterns.** It has been shown<sup>1a</sup> that there are only 20 substitution patterns for  $Tp_2X$  systems with *achiral* substituents. The central X may have either local  $C_{2v}$  [e.g., X = O, CH<sub>2</sub>, CO (a = b, Figure 1)] or local  $C_s$  [e.g., X = CHOH (a ≠ b, Figure 1)] symmetry, and the substituents may be distributed among the six benzene rings. We ignore, for the moment, the particular placement of the substituents among the four possible locations on a given benzene ring. As part of the experimental design, it is convenient to partition these 20 substitution patterns into four classes (Table I). The characteristic property



**Figure 4.** Conformational gearing circuit for residual meso derivatives of 1 with substitution patterns 9, 10, and 12 (Table I). Schematic projections around the perimeter follow the convention in Figure 1 (benzene-ring labels omitted). The small filled and open circles denote substituted benzene rings. For pattern 9, a = b and ● = ○; for pattern 10, a = b and ● ≠ ○; for pattern 12, a ≠ b and ● = ○.



**Figure 5.** Same as Figure 4 but for the residual D or L isomer. The structures in the circuit of the other residual enantiomer are the mirror images of the ones shown in this figure.

(9) Two objects are isometric if they are properly or improperly congruent. Accordingly, there are two types of isometric molecular structures: homomers,<sup>10,11</sup> which are properly congruent and which may be chiral or achiral, and enantiomers, which are necessarily chiral and only improperly congruent. All other structures are anisometric.<sup>10</sup>

(10) Mislow, K. *Bull. Soc. Chim. Belg.* 1977, 86, 595.

(11) The interconversion of homomers (a mechanistic process) is most appropriately termed "homomerization", in analogy to "isomerization", "enantiomerization", etc. This term should be differentiated from "topomerization", which additionally implies site exchange of ligands.<sup>12</sup>

(12) Binsch, G.; Eliel, E. L.; Kessler, H. *Angew. Chem., Int. Ed. Engl.* 1971, 10, 570.

(13) Residual stereoisomerism results whenever closed subsets of appropriately substituted interconverting isomers are generated from the full set of isomers at a particular time scale of observation and under the operation of a given stereoisomerization mode.<sup>14</sup> Note that stereoisomers should be described according to symmetry properties that are appropriate to the time scale of observation.<sup>15</sup> Where there is only one residual isomer, it is preferable to speak of a "residual species".<sup>8</sup>

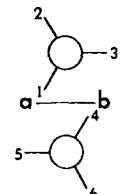
(14) Mislow, K. *Acc. Chem. Res.* 1976, 9, 26.

(15) Mislow, K.; Bickart, P. *Isr. J. Chem.* 1976/1977, 15, 1.

(16) The definition of residual meso (or achiral) isomer or species also encompasses systems where all or some of the components are themselves achiral by virtue of possession of an improper axis of rotation ( $S_n$ , including  $\sigma$  ( $n = 1$ ) and  $i$  ( $n = 2$ )). Such would be the case, for example, if ground- and transition-state symmetries in 1 were reversed.<sup>6b</sup>

of each class is the isomer count under two conditions: disallowed (i.e., frozen) and allowed (i.e., rapid) gear slippage. These conditions correspond to the full operation of two rearrangement modes: gearing, for which the appropriate molecular symmetry subgroup ( $G_i^2$  ( $P^{1a}$ )) is  $G_{12}^2$  ( $G_{12b}^{1a}$ ), and gearing combined with gear slippage, for which it is  $G_{36}^2$  ( $G_{36}^{1a}$ ).

The eight patterns that constitute classes I and II are unsuitable for our purposes since the isomer count is the same whether gear slippage takes place or not. Compounds in class I consist of single residual meso (achiral) species, as exemplified by 1 (pattern 1) or by bis(9-triptycyl)carbinol (2) (pattern 4). Residual stereoisomerism in class II is exclusively associated with the presence of one or more chiral centers.<sup>17</sup> Compounds in this class form

Table I. Classes of Residual Stereoisomers for All Substitution Patterns of Tp<sub>2</sub>Cab under the Full Operation of the Gearing Mode


residual isomer or species class	isomer count <sup>a</sup>		substitution pattern <sup>b</sup>	pattern no.
	gear slippage disallowed	gear slippage allowed		
I	1/0	1/0	a = b, 1 = 2 = 3 = 4 = 5 = 6	1
	1/0	1/0	a = b, 1 = 2 = 3 ≠ 4 = 5 = 6	2
	1/0	1/0	a = b, 1 = 2 = 3; 4 = 5 ≠ 6	3
	1/0	1/0	a ≠ b, 1 = 2 = 3 = 4 = 5 = 6	4
II	0/1	0/1	a = b, 1 = 2 = 3; 4 ≠ 5 ≠ 6	5
	0/1	0/1	a ≠ b, 1 = 2 = 3 ≠ 4 = 5 = 6	6
	0/1	0/1	a ≠ b, 1 = 2 = 3; 4 = 5 ≠ 6	7
	0/2	0/2	a ≠ b, 1 = 2 = 3; 4 ≠ 5 ≠ 6	8
III	1/1	1/0	a = b, 1 = 2 = 4 = 5 ≠ 3 = 6	9
	1/1	1/0	a = b, 1 = 2 ≠ 3; 4 = 5 ≠ 6	10
	1/1	1/0	a = b, 1 = 4 ≠ 2 = 5 ≠ 3 = 6	11
	1/1	1/0	a ≠ b, 1 = 2 = 4 = 5 ≠ 3 = 6	12
	2/2	2/0	a ≠ b, 1 = 4 ≠ 2 = 5 ≠ 3 = 6	13
	IV	0/3	0/1	a = b, 1 = 2 ≠ 3; 4 ≠ 5 ≠ 6
0/3		0/1	a = b, 1 = 4 ≠ 2 = 6 ≠ 3 = 5	15
0/3		0/1	a ≠ b, 1 = 2 ≠ 3; 4 = 5 ≠ 6	16
0/3		0/1	a ≠ b, 1 = 4 ≠ 2 = 6 ≠ 3 = 5	17
0/6		0/2	a = b, 1 ≠ 2 ≠ 3; 4 ≠ 5 ≠ 6	18
0/6		0/2	a ≠ b, 1 = 2 ≠ 3; 4 ≠ 5 ≠ 6	19
0/12		0/4	a ≠ b, 1 ≠ 2 ≠ 3; 4 ≠ 5 ≠ 6	20

<sup>a</sup> For each entry (x/y), x = number of meso (achiral) isomers and y = number of racemic pairs. The isomer count refers to achiral ensembles observed under achiral conditions. <sup>b</sup> Achiral substituents only. A semicolon between sets {1, 2, 3} and {4, 5, 6} signifies that the two sets may share some, but not all, of their elements.

conventional pairs of residual enantiomers or diastereomers, and no stereomutation is possible by gear slippage.

The 12 patterns that constitute classes III and IV are, however, suitable for the experimental demonstration. Class III is characterized by systems that consist of *n* residual meso species and *n* residual racemic pairs in the absence of gear slippage, and that reduce to *n* residual meso species under the full operation of gear slippage. Class IV contains systems in which 3*n* racemic pairs similarly reduce to *n* racemic pairs. Since separation of residual stereoisomers was required as part of the proposed experimental test, our choice narrowed down to the systems with the fewest such isomers, i.e., those with substitution patterns 9–12 (class III). Figures 4–7 depict the conformational gearing circuits for the residual isomers in this class.

The residual meso isomer in each case consists of a mixture of three interconverting *dl* pairs. For patterns 9 and 10 (Figure 4), these pairs are (a)/(d), (b)/(c), and (f)/(e); the last two are homomeric in pattern 9 since (b)/(f) and (c)/(e) are homomeric pairs. For pattern 12 (Figure 4), the *dl* pairs are (a)/(d), (b)/(e), and (c)/(f). For patterns 11 and 13 (Figure 6), the three *dl* pairs are (a)/(d), (b)/(e), and (c)/(f).

The two residual enantiomers that constitute the residual racemic pairs will be denoted by D and L. Each consists of a mixture of chiral diastereomers that undergo interconversion under the operation of the gearing mode. However, gearing does not result

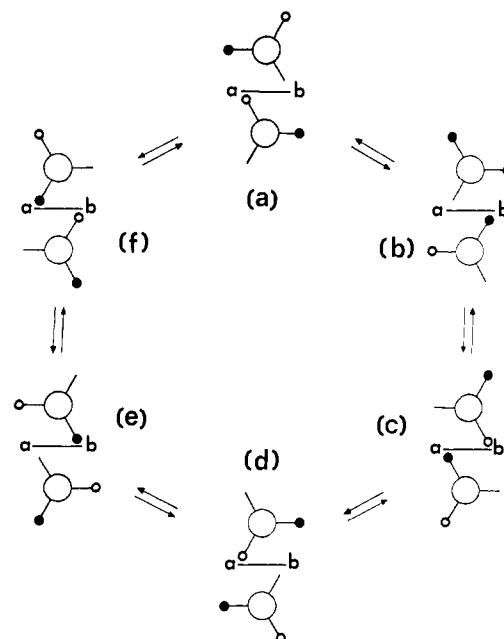


Figure 6. Conformational gearing circuit for residual meso derivatives of **1** with substitution patterns 11 and 13 (Table I). Schematic projections around the perimeter follow the convention in Figure 1 (benzene ring labels omitted). The small filled and open circles denote substituted benzene rings that are different from each other. For pattern 11, a = b; for pattern 13, a ≠ b.

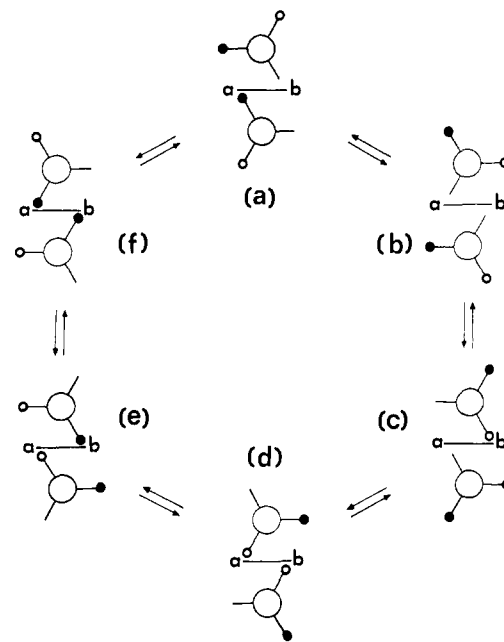


Figure 7. Same as Figure 6 but for the residual D or L isomer. The structures in the circuit of the other residual enantiomer are the mirror images of the ones shown in this figure.

in enantiomerization, and the ensemble therefore retains its residual chirality. That is, the D and L forms are not interconverted in the absence of gear slippage. For pattern 9, there are four diastereomers (Figure 5): (a), (b) or (f), (c) or (e), and (d), since (b)/(f) and (c)/(e) are homomeric pairs. There are six diastereomers for patterns 10 and 12 (Figure 5) as well as for patterns 11 and 13 (Figure 7).

Systems with patterns 11 and 13 are distinguished from the others in the same class by the presence of chiral centers. Under conditions of rapid gear slippage, the stereochemistry of such systems is as conventional as that of systems in classes II and IV. All of the systems in class IV possess one or more chiral centers,<sup>17</sup> and accordingly one obtains, under conditions of rapid gear

(17) There are five loci for such centers in derivatives of **1**, i.e., the central methylene carbon and the four bridgehead carbons in the Tp groups. However, because the configurations at C10 and C10' are determined by those at C9 and C9', there are only three independent stereogenic centers.

slippage, one (patterns 14–17), two (patterns 18 and 19), or four (pattern 20) residual *RS* pairs. The same is true of systems with patterns 11 and 13 where, however, residual meso forms are obtained under the same conditions. In the case of pattern 13, the two meso isomers form a "pseudosymmetric pair" because the central carbon atom serves as a stereogenic center.<sup>18</sup>

**Enantiomerization through Chiral Pathways.** Residual meso isomers (or species) with substitution patterns 4 and 11–13 form achiral ensembles of chiral molecules (Figures 2, 4, and 6) that enantiomerize through *exclusively* chiral pathways so long as gear slippage is disallowed. Because situations of this kind are rarely encountered, a brief discussion is in order.

Enantiomerization of chiral tetraatomic molecules by unimolecular processes unavoidably requires the intermediacy of achiral structures, as, for example, in the racemization of  $N^1H^2H^3H$  or of  $H_2O_2$ . In more complex systems, however, enantiomerization may proceed through *either* achiral or chiral pathways.<sup>19</sup> In a few instances, it has been established that molecules enantiomerize *exclusively* through chiral pathways, as, for example, in the five-step enantiomerization of phosphoranes by the Berry pseudorotation mechanism<sup>20</sup> and in the three-step enantiomerization of maximally labeled triaryl amines by the two-ring flip mechanism.<sup>14,21,22</sup> The prototype of this class of compounds is 4-[(*R*)-*sec*-butyl]-4'-[(*S*)-*sec*-butyl]-2,2',6,6'-tetramethylbiphenyl.<sup>23,24a,25</sup> The gear systems under discussion provide the latest example.

Enantiomers related in this way are said to be *chirally connected*.<sup>26</sup> Any of the *dl* pairs in Figures 2 (pattern 4 only), 4 (pattern 12 only), and 6 are so connected and by the same token cannot properly be placed into heterochiral classes.<sup>26</sup> The point is that in the course of any imagined continuous deformation (e.g., torsion) along the *d* → *l* interconversion coordinate, there is no unique point (i.e., an *achiral zero*) that defines the boundary between heterochiral sets of conformations, i.e., between enantiomers. The associated observables (chirality phenomena) must therefore pass through a *chiral zero*.<sup>26</sup> The restriction to chiral connectedness is relaxed if gear slippage is allowed, since the corresponding transition states can now be achiral.

### Synthesis of Appropriately Substituted Derivatives of Bis(9-triptycyl)methane

**Synthetic Strategy.** The choice among the four viable substitution patterns 9–12 can be narrowed to two by applying the additional criterion of ready synthetic availability. Triptycene derivatives are most conveniently prepared by the Wittig procedure,<sup>27</sup> i.e., by addition of a benzyne to anthracene; the presence of two triptycene moieties in the target molecules therefore calls for the addition of two benzyne to two anthracenes, with substituents appropriately distributed among these fragments. In systems with patterns 9, 11, and 12, the two benzyne and the

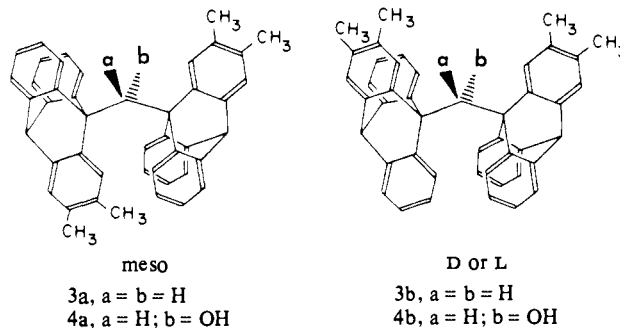
two anthracenes have the same constitution, but a nonstereospecific synthesis of systems with pattern 11 will also yield pattern 15 (because of the presence of chiral centers at C9(C10) and C9'(C10')) and will therefore result in a mixture of five residual diastereomers (one meso and four *DL*). In systems with pattern 10, two constitutionally different benzenes and/or two constitutionally different anthracenes are required. It follows that systems with patterns 9 and 12 offer the fewest synthetic complications and are therefore the systems of choice.

The most straightforward synthetic approach to such systems, and the one chosen in the present work, is the single-step addition of two appropriately substituted benzyne to a molecule containing two 9-anthryl groups. There is ample precedent for such a procedure: bis(9-triptycyl),<sup>28</sup> 1,2-bis(9-triptycyl)- and 1,2-bis(1,4-dimethyl-9-triptycyl)ethane, -ethene, and -ethyne<sup>29</sup> have all been prepared by single-step addition of two benzyne or dimethylbenzyne to the corresponding bis(9-anthryl) precursors. Indeed, **1** (pattern 1)<sup>30</sup> and **2** (pattern 4),<sup>1a</sup> which differ in the same way as systems with patterns 9 and 12, were recently prepared by single-step addition of two benzyne to bis(9-anthryl)methane<sup>31</sup> and bis(9-anthryl)carbinol,<sup>32</sup> respectively.

In both target molecules, one benzene ring in each Tp moiety is substituted by a chemical label so that the two moieties have the same constitution. We now turn to a consideration of the criteria for selection of this label.

A prime requirement<sup>2</sup> is that the label does not significantly modify the torsional potential energy (PE) hypersurface of **1**. Whether this requirement is met depends on the nature of the substituent and on its position in the ring. An isotopic label would be ideal, but one might expect that the residual isomers would then be very difficult to separate. We therefore selected methyl, the smallest nonpolar, nonisotopic group, as the chemical label. Its placement in the sterically unencumbered 2-, 3-, or 4-positions on the ring, far from the hub near the 9-position, would presumably perturb the PE hypersurface to only a minor extent. In contradistinction, placement in the 1-position, i.e., in the crowded, central region of the molecule, should interfere with the gearing motion and should therefore substantially alter the PE hypersurface. These views are supported by the results of EFF calculations (see below).

Ready synthetic availability once again entered as the decisive factor in choosing a placement of labels among the three unencumbered positions. Single-step addition of two monosubstituted benzyne (e.g., 4-methylbenzyne) to bis(9-anthryl)methane yields a mixture of three constitutional isomers (e.g., the 2,2'-, 2,3'-, and 3,3'-dimethyl derivatives of **1**), whereas single-step addition of two disubstituted benzyne with twofold rotational symmetry (i.e., 4,5- or 3,6-dimethylbenzyne) results in a single product. The latter is thus the preferred synthetic route and 4,5-dimethylbenzyne the reagent of choice, since addition to bis(9-anthryl)methane and -carbinol would yield bis(2,3-dimethyl-9-triptycyl)methane (**3**)



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and bis(2,3-dimethyl-9-triptycyl)carbinol (4), compounds with the desired labeling patterns 9 and 12, respectively, and with chemical labels (methyl groups) placed in relatively unencumbered positions. On the other hand, addition of 3,6-dimethylbenzynes to bis(9-anthryl)methane would yield bis(1,4-dimethyl-9-triptycyl)methane (5), a compound with label pattern 9 but with methyl groups located in the 1- and 1'-positions, where they could act as internal brakes on cogwheeling.

**Synthetic Procedures.** Preliminary experiments were designed to ascertain beyond any doubt that the methyl groups in the two dimethylbenzynes were in fact located in the assigned positions. The benzynes were generated by the method of Friedman and Logullo.<sup>33</sup> The benzyne precursors were 2-amino-3,6-dimethylbenzoic acid<sup>34</sup> for 3,6-dimethylbenzyne and 2-amino-4,5-dimethylbenzoic acid, prepared by two independent routes from different starting materials,<sup>35,36</sup> for 4,5-dimethylbenzyne. Addition of 3,6-dimethylbenzyne to anthracene gave 1,4-dimethyltriptycene (6), whose physical<sup>37</sup> and spectroscopic<sup>38</sup> properties were in agreement with those of the product of benzyne addition to 1,4-dimethylanthracene. Addition of 4,5-dimethylbenzyne to anthracene gave a product (7) whose melting point (240–242 °C) differed significantly from that (302 °C) reported<sup>39</sup> for the product of benzyne addition to 2,3-dimethylanthracene. However, the physical and spectroscopic properties of 7 (Experimental Section) left no doubt of its identity as 2,3-dimethyltriptycene. We are unable to account for the discrepancy between our observed and previously reported melting points.

The title compounds (3, 4, and 5) were prepared by single-step addition of the thus authenticated dimethylbenzynes to bis(9-anthryl)methane and bis(9-anthryl)carbinol.

#### Empirical Force Field Calculations

A key assumption, for which we have thus far offered no supporting evidence, is that substitution of methyl groups in the 2,2',3,3'-positions of 1 (to give 3) and of 2 (to give 4) has a negligible effect on the PE hypersurface, whereas substitution of methyl groups in the 1,1',4,4'-positions of 1 (to give 5) strongly interferes with gearing. Inspection of molecular models, though often useful in the assessment of conformational ground-state properties, can be grossly misleading when extended to the dynamics of conformational interconversion.<sup>40</sup> It may even fail as a reliable gauge of ground-state properties. A relevant case in point is the central bond angle in 1 (129.3°)<sup>41</sup> and 2 (129.0°).<sup>1b</sup> We are not aware of any molecular models that would have predicted this extraordinary angle expansion.<sup>42</sup> In contrast, the EFF method, which has proven its worth in these systems,<sup>1,2,41</sup> remains the best means for assessing the adequacy of the model.

All calculations were performed as described for 1,<sup>2</sup> by using the MM2 force field in conjunction with the BIGSTRN-3 program.<sup>6a</sup>

**Bis(2,3-dimethyl-9-triptycyl)methane (3).** Salient results of our calculations on this molecule are summarized in Table II. Inspection of comparable structural parameters shows that in the conversion of 1 to 3, the central C–CH<sub>2</sub>–C bond angle ( $\theta$ ) remains virtually unchanged, as do the central C–C bond lengths ( $r$  and  $r'$ ). Even the torsion angles of the Tp rotors ( $\phi$  and  $\phi'$ ), which are highly sensitive to small perturbations, suffer only minor

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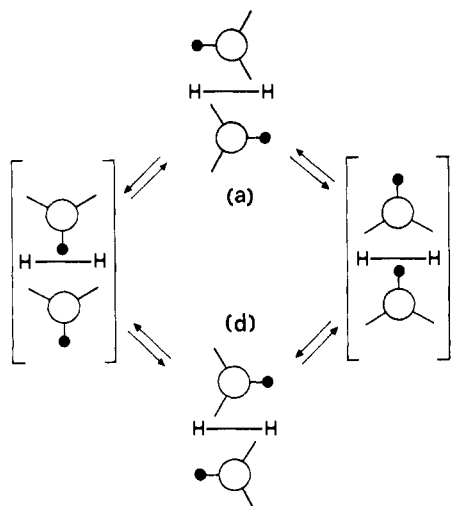
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(42) This inadequacy of molecular models is traceable to the circumstance that "commercially available model sets are in fact collections of atomic models".<sup>24b</sup>

Table II. Selected Structural Parameters Calculated for Gearing Conformations of Bis(2,3-dimethyl-9-triptycyl)methane (3)

parameter <sup>e</sup>	anisometric conformations with C <sub>2</sub> -1 skeletons <sup>b,c</sup>						anisometric conformations with C <sub>s</sub> -1 skeletons <sup>c,d</sup>					
	DL-3			DL-3			DL-3			DL-3		
	1 <sup>a</sup>	meso-3	1 <sup>a</sup>	DL-3	DL-3	DL-3	meso-3	DL-3	DL-3	DL-3	DL-3	
$r$	1.554	1.554	1.556	1.556	1.556	1.555	1.543	1.542	1.543	1.542	1.544	1.554
$r'$	1.554	1.554	1.553	1.553	1.553	1.555	1.566	1.566	1.566	1.566	1.567	1.565
$\theta$	130.2	130.3	130.1	130.1	130.1	129.9	129.3	129.4	129.3	129.4	129.1	129.3
$\phi$	32.1	32.4	28.7	30.0	33.0	33.0	57.1	58.1	59.9	58.1	55.5	53.4
$\phi'$	32.1	32.4	35.6	34.3	30.9	30.9	4.1	2.4	0.1	2.4	-5.9	8.7

<sup>a</sup> Calculated values from Tables VII and VIII of ref 2. <sup>b</sup> Each conformation in Figures 4 and 5 (pattern 9) is isometric to one of the structures shown. <sup>c</sup> Deviations from exact symmetry, particularly in the torsion angles, are due to incomplete optimization of the structure. <sup>d</sup> Each conformation with this skeleton that is encountered along the gearing circuit of *meso*- and DL-3 is isometric to one of the structures shown. <sup>e</sup> Values for central C–C bond lengths  $r$  and  $r'$  refer to triptycyl rotors with torsion angles  $\phi$  and  $\phi'$ , respectively. Bond lengths in angstroms, central C–CH<sub>2</sub>–C bond angle ( $\theta$ ) and torsion angles in degrees.

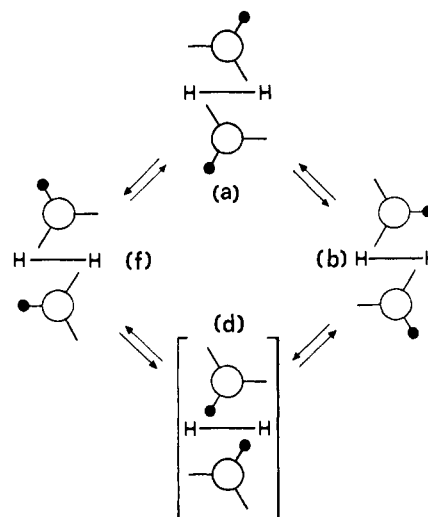


**Figure 8.** Conformational gearing circuit for *meso*-bis(1,4-dimethyl-9-triptycyl)methane. Schematic projections around the perimeter follow the convention in Figure 1 (benzene-ring labels omitted). Symbols for (a) and (d) correspond to those in Figure 4, with  $a = b = \text{H}$  and  $\bullet = \text{O}$ . Transition-state structures are bracketed.

changes. The implication that the introduction of methyl groups in the 2,2',3,3'-positions of **1** has no significant effect on the PE hypersurface is borne out by an examination of this surface along the gearing trajectory: for *meso*-**3**, the largest energy difference between any two of the four anisometric conformations (Table II) is 0.9 kcal mol<sup>-1</sup>, and for the DL isomer, the largest difference between any two of the seven anisometric conformations (Table II) is 1.8 kcal mol<sup>-1</sup>. The largest difference between any two of all 11 anisometric structures is also 1.8 kcal mol<sup>-1</sup>.

These numerical findings provide strong evidence in support of the assumption that the chemical labels in **3** do not significantly modify the PE hypersurface of **1** along the gearing trajectory.<sup>43</sup> Nor do the chemical labels appear to have a significant effect on the transition state to gear-slippage, as will be discussed in further detail below. Additionally, we have assumed that the hydroxy group on the central carbon atom of **4** also represents a negligible perturbation.

**Bis(1,4-dimethyl-9-triptycyl)methane (5).** The presence of methyl groups in the 1- and 1'-positions of the Tp moieties results in drastic alteration of the PE hypersurface of **1**. In the course of the gearing motion, a benzene ring bearing a 1-methyl group is forced into the notch between the two aryl rings in the other rotor. Accommodation of this group in an already overcrowded space (to judge by the observed<sup>16,41</sup> central bond-angle and bond-length deformations in **1**, **2**, and bis(9-triptycyl) ketone (**8**)) substantially increases the steric strain of the molecule and profoundly affects the gearing behavior. Thus, of the three *dl* pairs in the circuit of the *meso* isomer (Figure 4, pattern 9), only the (a)/(d) pair (molecular symmetry C<sub>2</sub>) remains, separated by two homomeric transition states with C<sub>s</sub> symmetry (Figure 8). The strain of forcing a 1-methyl group into a sterically congested environment is reflected in the energy of the transition state, which lies 17.0 kcal mol<sup>-1</sup> above the ground state.<sup>44,45</sup> This strain is also reflected in the geometry of the transition state, notably in a stretched central C-C bond length ( $r = 1.543 \text{ \AA}$ ,  $r' = 1.583 \text{ \AA}$ ) and an expanded central C-CH<sub>2</sub>-C bond angle ( $\theta = 139.0^\circ$ ). By contrast, structural parameters in the C<sub>2</sub> ground state ( $r = r' =$



**Figure 9.** Conformational gearing circuit for D- or L-bis(1,4-dimethyl-9-triptycyl)methane. Schematic projections around the perimeter follow the convention in Figure 1 (benzene-ring labels omitted). Symbols for (a), (b), (d), and (f) correspond to those in Figure 5, with  $a = b = \text{H}$  and  $\bullet = \text{O}$ . The structures in the circuit of the other residual enantiomer are the mirror images of the ones shown in this figure. The transition-state structure (d) is bracketed.

**Table III.** <sup>1</sup>H and <sup>13</sup>C NMR Signal Counts for Bis(9-triptycyl)methane and Derivatives on the Time Scale of Rapid Conformational Interconversion by Gearing

type	compd no.	number of signals <sup>a</sup>					
		aromatic region				methyl region	
		substituted ring		unsubstituted ring		<sup>1</sup> H or <sup>13</sup> C	<sup>13</sup> C
		<sup>1</sup> H (AB) <sup>b</sup>	<sup>13</sup> C {H}	<sup>1</sup> H (ABCD) <sup>b</sup>	<sup>13</sup> C {H}	{ <sup>1</sup> H}	{ <sup>13</sup> C}
I	1, 2, 8			1	6		
II	3a, 5a	1	6	1	6		2
III	3b, 4a, 5b	1	6	2	12		2
IV	4b	2	12	4	24		4

<sup>a</sup> See Tables IV and V for chemical shifts and coupling constants. <sup>b</sup> Number of AB or ABCD spin systems.

1.555 Å,  $\theta = 131.2^\circ$ ) differ little from those in C<sub>2</sub>-**1** (Table II).

For the gearing circuit of D- or L-**5**, our calculations indicate the presence of at least seven local minima: four of these correspond to homomeric pairs (b)/(f) and (c)/(e) in Figure 5 (pattern 9), one corresponds to structure (a), and the remaining two to structures intermediate between (a) and (b)/(f). Structure (d) is found to be a transition state. All minima except the one corresponding to the ground state are quite shallow, and the circuit is therefore well approximated by the simplified scheme in Figure 9. The ground-state homomers (b) and (f) are asymmetric (C<sub>1</sub>) and interconvert via two structures with C<sub>2</sub> symmetry, (a) and (d), the former a shallow minimum and the latter a transition state, which lie 1.7 and 21.0 kcal mol<sup>-1</sup> above the ground state, respectively.<sup>44</sup> The relative magnitudes of the two barriers reflect the location of the 1- and 1'-methyl groups in the molecule: in the low-energy intermediate, both groups are well away from the crowded central region of the molecule, whereas in (d), both are forced into this congested environment. This strain is also reflected in the bonding parameters of (d) ( $r = r' = 1.572 \text{ \AA}$ ,  $\theta = 140.4^\circ$ ), as contrasted with the structural parameters of the ground-state molecule ( $r = 1.558$ ,  $r' = 1.556 \text{ \AA}$ ,  $\theta = 132.5^\circ$ ) and the low-energy intermediate ( $r = r' = 1.563 \text{ \AA}$ ;  $\theta = 131.9^\circ$ ).

#### Separation, Identification, and Interconversion of Residual Stereoisomers

The residual *meso* and DL isomers of **3** and **4** were separated by column chromatography on silica Woelm (particle size 32–63 μm). In both cases the *meso* isomers (**3a**, **4a**) were eluted first,

(43) In further support of this conclusion, no line broadening is observed in *meso*-**3** (**3a**) down to  $-50^\circ\text{C}$ .

(44) Preliminary calculations<sup>16</sup> of gearing transition-state energies, using a different force field and optimization program, had yielded values of 16.5 kcal mol<sup>-1</sup> for *meso*-**5**, and 3.5 and 22.8 kcal mol<sup>-1</sup> for the D and L isomers.

(45) As shown in pioneering studies by Ōki and co-workers,<sup>46</sup> bulky substituents in the 1-position are capable of slowing torsional processes at the 9-position of triptycene.

(46) Ōki, M. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 87 and references therein. See also: Yamamoto, G.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 473, 481.

Table IV. <sup>1</sup>H NMR Data for Triptycene Derivatives<sup>d</sup>

compd	-CH <sub>3</sub>	>CH <sub>2</sub>	>CHOH	>CHOH	>CH	aromatic region <sup>d</sup>
1 <sup>b</sup>		4.86 (s, 2 H)			5.48 (s, 2 H)	6.68-7.08 and 7.41-7.61 (1 ABCD m, 24 H)
2 <sup>b</sup>			7.96 <sup>e</sup> (d, 1 H)	2.88 <sup>e</sup> (d, 1 H)	5.37 (s, 2 H)	6.62-7.00 and 7.36-7.90 (1 ABCD m, 24 H)
3a <sup>b</sup>	1.75, 2.12 (2 s, 12 H)	4.82 (s, 2 H)			5.41 (s, 2 H)	6.71-7.08 and 7.39-7.68 (1 ABCD m, 16 H) 7.22 (1 AB s, 4 H)
3b <sup>b</sup>	1.97, 2.18 (2 s, 12 H)	4.81 (s, 2 H)			5.41 (s, 2 H)	6.51-7.07 and 7.34-7.67 (2 ABCD m, 16 H) 7.26-7.31 (1 AB d, 4 H)
4a <sup>b</sup>	1.66, 2.02 (2 s, 12 H)		7.85 <sup>f</sup> (d, 1 H)	2.84 <sup>f</sup> (d, 1 H)	5.23 (s, 2 H)	6.61-7.04 and 7.33-8.04 (2 ABCD m, 16 H) 7.11-7.13 (1 AB d, 4 H)
4b <sup>b</sup>	1.70, 1.87, 2.04, 2.08 (4 s, 12 H)		7.78 <sup>g</sup> (d, 1 H)	2.84 <sup>g</sup> (d, 1 H)	5.23 (s, 2 H)	6.48-8.01 (4 ABCD m, 16 H and 2 AB d, 4 H)
5a <sup>c</sup>	2.10, 2.48 (2 s, 12 H)	5.21 (s, 2 H)			5.63 (s, 2 H)	6.56-6.98 and 7.29-7.61 (1 ABCD m, 16 H) 6.39-6.71 (1 AB q, 4 H)
6 <sup>b</sup>	2.46 (s, 6 H)				5.63 (s, 2 H)	6.92-7.01 and 7.32-7.41 (1 AA'BB' m, 8 H) 6.70 (1 A <sub>2</sub> s, 2 H)
7 <sup>b</sup>	2.13 (s, 6 H)				5.33 (s, 2 H)	6.89-6.98 and 7.29-7.38 (1 AA'BB' m, 8 H) 7.16 (1 A <sub>2</sub> s, 2 H)
8 <sup>b</sup>					5.43 (s, 2 H)	6.66-7.09 and 7.40-7.63 (1 ABCD m, 24 H)

<sup>a</sup> All chemical shifts are in ppm downfield from tetramethylsilane as internal reference. <sup>b</sup> Trichloro[<sup>2</sup>H]methane, 89.55 MHz, ambient temperature. <sup>c</sup> Tetrachloro[1,2-<sup>2</sup>H<sub>2</sub>]ethane, 100.1 MHz, 90 °C. <sup>d</sup> <sup>3</sup>J<sub>HH</sub> = 7.0-7.8 Hz, <sup>4</sup>J<sub>HH</sub> = 0.9-1.9 Hz, <sup>5</sup>J<sub>HH</sub> = 0-0.7 Hz. <sup>e</sup> <sup>3</sup>J<sub>HH</sub> = 2.75 Hz. <sup>f</sup> <sup>3</sup>J<sub>HH</sub> = 2.5 Hz. <sup>g</sup> <sup>3</sup>J<sub>HH</sub> = 2.4 Hz.

followed by the DL isomers (3b, 4b). In the case of 5, the only product isolated proved to be the meso isomer (5a). The isomers were unambiguously identified by the number of signals in the <sup>1</sup>H and <sup>13</sup>C NMR spectra.

**Identification of Isomers by NMR.** We have classified the signal counts observed in this and related work into four types (Table III), of which the simplest is type I, exemplified by 1, 2, and 8. Since structures (a)-(f) in Figure 2 are isometric, all six benzene rings (1-6) become equivalent on the time scale of rapid gearing, and only one such ring is therefore observed (Tables IV and V).<sup>47</sup>

To facilitate the analysis for the residual stereoisomers of 3 and 4, let us number the benzene rings in conformations (a)-(f) in Figures 4 and 5 according to the scheme in Figure 2. For the residual meso isomer of 3 (3a, Figure 4, pattern 9), rings 1/6, 2/5, and 3/4 in conformations (a) and (d) are pairwise equivalent by symmetry (C<sub>2</sub>). Furthermore, the two 2,3-dimethyl-9-triptycyl moieties, and therefore rings 1/6, 2/4, and 3/5, are pairwise enantiotopic by external comparison between (a) and (d). On the time scale of rapid gearing, two sets of equivalent rings, 1/6 and 2/3/4/5, are therefore produced, corresponding to a NMR signal count of type II. For the residual D or L isomer of 3 (3b, Figure 5, pattern 9), rings 1/6, 2/5, and 3/4 in conformations (a) and (d) are also pairwise equivalent by symmetry (C<sub>2</sub>). The same pairs of rings are homotopic by external comparison between (b) and (f) and between (c) and (e). Accordingly, three sets of equivalent rings are produced under conditions of rapid gearing, corresponding to the more complex NMR signal count of type III. The two residual stereoisomers of 3 are therefore easily differentiated and identified (Tables IV and V).

In the residual meso isomer of 4 (4a, Figure 4, pattern 12), the two 2,3-dimethyl-9-triptycyl moieties, and therefore rings 1/2, 2/4, and 3/5, are pairwise enantiotopic by external comparison between (a) and (d), (b) and (e), and (c) and (f). Accordingly, three sets of pairwise equivalent rings are produced under conditions of rapid gearing, corresponding to a signal count of type III; note that the enantiomerizations take place through exclusively chiral pathways (see above). However, in the residual D or L isomers (4b, Figure 5, pattern 12), all six conformations are anisometric. It follows that the six rings remain nonequivalent under conditions of rapid gearing, corresponding to an even more complex signal count, type IV. The two residual stereoisomers of 4 are therefore easily differentiated and identified (Tables IV and V).

The residual meso and DL isomers of 5, 5a and 5b have the same substitution pattern (9) as 3a and 3b. The NMR signal counts therefore belong to types II and III, respectively, making for

straightforward differentiation and identification (Tables IV and V).

**Interconversion of Residual Stereoisomers.** Interconversion of such isomers in the systems under discussion can only take place through gear slippage. Operationally, two distinct processes can be envisaged, involving chemically labeled derivatives of 1 such as 3, 4, or 5: interconversion of residual D and L forms (enantiomerization) and interconversion of residual meso and D (or L) forms (diastereomerization). These two processes differ in one important respect: in diastereomerization, one of the two labeled (i.e., substituted) benzene rings is placed into the crowded central region of the transition state, whereas in enantiomerization this is not the case. This is easily seen by inspection of the gear-slippage mechanism depicted in the top of Figure 3: only when the substituted rings are the ones labeled 2 and 5 is slippage possible without placing one such ring into the central region. The result is enantiomerization (D ⇌ L). The same conformation can be reached by gearing of conformations in which the rings labeled 1 and 4, or 3 and 6, are the ones that carry the methyl substituents, since all three are members of the same gearing circuit (Figure 5). All other arrangements lead to diastereomerization (meso ⇌ D, meso ⇌ L).

Thus, enantiomerization might appear to involve a transition state of lower energy than diastereomerization. However, further analysis shows that this is not the case. As seen by inspection of Figure 5 in ref 2, replacement of hydrogen atoms by methyl groups in the 2,2',3,3'-positions of the transition state for gear slippage does not lead to marked overcrowding, particularly if it is remembered that such substitution breaks the C<sub>s</sub> symmetry and that the transition state can thus relax to accommodate the additional substituent atoms. EFF calculations support this view. Consider the transformations shown in the top half of Figure 3, and let a = b, 1 = 3 = 5 = 6 ≠ 2 = 4 (pattern 9). The d and l structures then represent meso-3 (Figure 4c) and D- or L-3 (Figure 5b), respectively. Our calculations show that diastereomerization by either one of the two bracketed transition states requires only ca. 31 kcal mol<sup>-1</sup>, a barrier barely higher than the one calculated for homomerization of 1. Accordingly, enantiomerization and diastereomerization serve equally well as experimental tests of the predicted gear-slippage barrier.

In principle, enantiomerization is observable by dynamic NMR. In 3b and 5b, gear slippage by enantiomerization equivalences the two unsubstituted rings in each rotor, and the NMR signal count for these rings (Table III) should therefore be halved; in 4b, gear slippage by the same mechanism equivalences the two rotors, and the NMR signal count for all resonances (Table III) should therefore be halved. However, no change was observed in the aromatic region of the <sup>1</sup>H NMR spectrum of 3b in tetrachloro[1,2-<sup>2</sup>H<sub>2</sub>]ethane at temperatures up to 145 °C. The lower limit of the enantiomerization barrier estimated from this ob-

(47) No line broadening is observed in 1 and bis(9-triptycyl) ether (to -94 °C),<sup>30</sup> 2 (to -80 °C),<sup>1b</sup> and 8 (to -90 °C).<sup>41</sup>



Table V.  $^{13}\text{C}\{^1\text{H}\}$  NMR Data for Triptycene Derivatives<sup>a,b</sup>

compd	$-\text{CH}_3$	$>\text{CH}_2$	$>\text{CHOH}$ or $>\text{C}=\text{O}$	$>\text{CH}$	$>\text{C}<$	aromatic protonated carbons	aromatic quaternary carbons
1 <sup>c</sup>		25.8		55.3		123.5, 124.4, 124.9, 125.2	146.2, 146.2
2 <sup>c</sup>				56.0	62.6	123.5, 124.3, 125.2, 127.0	145.2, 146.6
3a <sup>d</sup>	19.2, 19.4	25.7	72.6 <sup>f</sup>	54.8	54.7	123.2, 124.2, 124.6, 124.7, 125.0, 126.8	131.7, 132.6, 143.7, 144.3, 146.4, 147.2
3b <sup>d</sup>	19.3, 19.7	25.7		54.8	54.7	123.1, 123.2, 124.0, 124.3, 124.7, 124.9, 125.0, 125.6, 125.7	132.0, 132.9, 144.3, 144.8, 146.1, 146.5, 146.5, 146.5, 147.3
4a <sup>c</sup>	19.0, 19.3		72.8 <sup>f</sup>	55.5	62.3	123.2, 123.5, 124.1, 124.5, 124.7, 124.8, 125.4, 126.1, 127.4, 128.9	131.8, 132.8, 142.2, 144.4, 145.5, 146.3, 146.3, 147.3
4b <sup>c</sup>	19.1, 19.1, 19.4, 19.6		72.8 <sup>f</sup>	55.5	62.3	123.4, 123.4, 123.5, 123.5, 124.0, 124.2, 124.2, 124.4, 124.9, 124.9, 125.1, 125.1, 125.1, 125.4, 126.1, 126.7, 126.7, 127.4, 128.4, 129.4	131.8, 132.0, 132.9, 133.1, 142.9, 142.9, 144.3, 144.3, 145.2, 146.0, 146.6, 146.6, 147.3, 147.3, 147.3, 147.3
5a <sup>e</sup>	19.5, 26.0	29.3		52.3	58.5	123.2, 124.2, 125.4, 125.8, 127.3, 130.7	129.8, 132.3, 145.9, 146.5, 147.0, 147.0
6 <sup>c</sup>	18.3			50.6		123.6, 125.0, 126.2	129.3, 143.3, 145.5
7 <sup>c</sup>	19.4			53.7		123.4, 125.0, 125.0	132.8, 142.9, 145.6
8 <sup>c</sup>			210.4 <sup>g</sup>	52.2	70.6	123.6, 124.5, 125.6, 126.5	143.7, 146.0

<sup>a</sup> All chemical shifts are in ppm downfield from tetramethylsilane as internal reference. <sup>b</sup> The multiplicity of the carbons was determined either from off-resonance or gated decoupling experiments. <sup>c</sup> Trichloro[ $^2\text{H}$ ]methane, 22.5 MHz, ambient temperature. <sup>d</sup> Trichloro[ $^2\text{H}$ ]methane, 25.2 MHz, ambient temperature. <sup>e</sup> Tetrachloro[1,2- $^2\text{H}_2$ ]ethane, 25.2 MHz, 100 °C. <sup>f</sup> Carbonyl carbon. <sup>g</sup> Carbonyl carbon.

Table VI. Kinetic Parameters for the Interconversion of 3a and 3b in Nitro[ $^2\text{H}_5$ ]benzene

temp- erature, °C	starting isomer	$K$ (3b/3a) <sup>a</sup>	$k \times 10^5, \text{s}^{-1}$		$\Delta G^\ddagger,$ kcal mol <sup>-1</sup>	
			3a → 3b	3b → 3a	3a → 3b	3b → 3a
145.8	3a	1.8	2.17	1.19	33.74	34.24
145.8	3b	1.9	2.78	1.47	33.53	34.06
155.8	3a	1.8	6.67	3.61	33.61	34.13
155.8	3b	1.8	7.22	4.44	33.54	33.95
165.0	3a	1.8	11.94	6.62	33.84	34.35
165.0	3b	1.9	20.00	10.83	33.39	33.92

<sup>a</sup> Equilibrium constant.

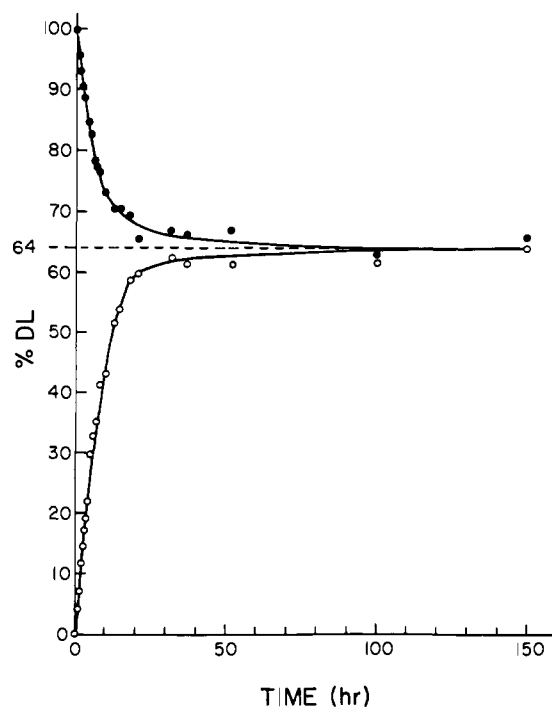


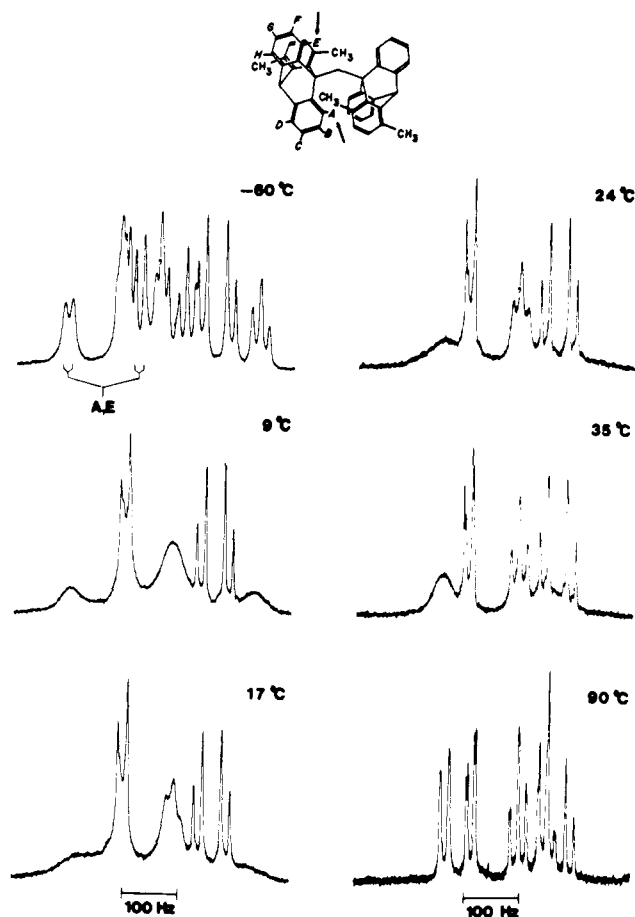
Figure 10. Interconversion of the residual diastereomers of 3 in nitro- $^2\text{H}_5$ benzene at 145.8 °C as a function of time: (open circles) *meso*-3 (3a); (filled circles) DL-3 (3b); (dashed line) equilibrium composition.

servation, 22 kcal mol<sup>-1</sup>, is consistent with the barrier of 30.1 kcal mol<sup>-1</sup> predicted for 1. A direct determination thus requires resolution and racemization of a DL pair. However, attempts to resolve 4b by column chromatography on microcrystalline cellulose triacetate<sup>48</sup> or by HPLC on a chiral stationary phase<sup>49</sup> proved unsuccessful. We therefore resorted to a determination of the diastereomerization barrier. The interconversion of the residual diastereomers 3a and 3b in nitro[ $^2\text{H}_5$ ]benzene solvent was studied at 145.8, 155.8, and 165.0 °C and monitored by integration of the two upfield methyl signals in the  $^1\text{H}$  NMR spectrum.<sup>50</sup> The results are summarized in Table VI, and a plot of the kinetic experiment at 145.8 °C is shown in Figure 10. The equilibrium constant,  $K(3\text{b}/3\text{a}) = 1.8 \pm 0.1$  at 155.8 °C, corresponds to an almost statistical ratio of DL and *meso* isomers. This result is in accord with the configurational assignments and provides experimental support for the conclusion, on the basis of EFF calculations, that introduction of methyl groups in the 2,2',3,3'-positions of 1 has a negligible effect on the relative ground-state energies of the residual diastereomers. The diastereomerization barrier ( $\Delta G^\ddagger$ ) of ca. 34 kcal mol<sup>-1</sup> is somewhat higher than the calculated gear-slippage barrier. The enantiomerization barrier

(48) Hayes, K. S.; Nagumo, M.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1980**, *102*, 2773 and references therein.

(49) Pirkle, W. H., private communication.

(50) The two NMR signals for the 2- and 3-methyl protons appear at  $\delta$  1.77 and 2.07 in 3a and  $\delta$  1.93 and 2.07 in 3b (nitrobenzene solvent).



**Figure 11.** Variable-temperature  $^1\text{H}$  NMR spectrum of *meso*-bis(1,4-dimethyl-9-triptycyl)methane (**5a**) (aromatic region) in dichloro[ $^2\text{H}_2$ ]-methane ( $-60$  to  $35$  °C) and tetrachloro[ $1,2\text{-}^2\text{H}_2$ ]ethane ( $90$  °C). For clarity, the protons on the diastereotopic benzene rings are labeled ABCD and EFGH. The downfield doublet at  $-60$  °C is due to A split by B or to E split by F, and the downfield doublet at  $90$  °C to the time-averaged signal.

of D- and L-**3b** (and presumably of D- and L-**4b**) is therefore judged to be  $22 < \Delta G^*_{\text{rac}} \approx 34$  kcal mol $^{-1}$ .

These observations complete the experimental verification of our original predictions:<sup>2</sup> residual stereoisomers resulting from chemical labeling of **1** were separated and interconverted at elevated temperatures.<sup>51,52</sup> The barrier estimate is also consistent with the predicted value. We now turn to a consideration of **5**, a system of a type that, as discussed above, is in a different category from that of **1-4** and **8**.

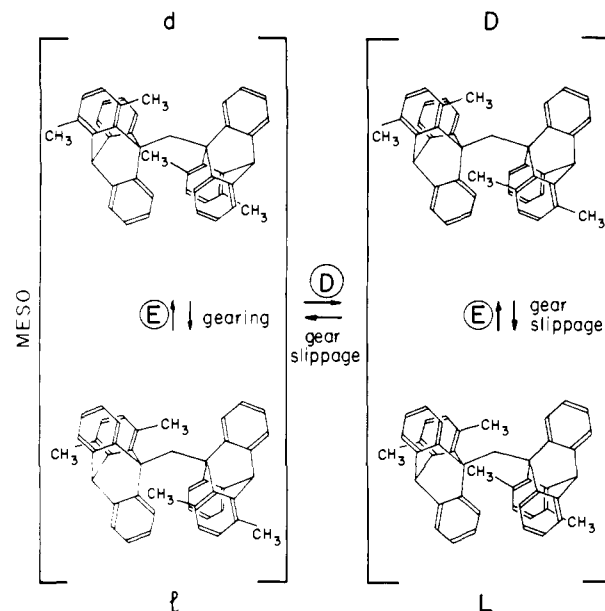
As in the case of **3**, gear slippage in **5** becomes observable only at elevated temperatures. In nitro[ $^2\text{H}_5$ ]benzene at  $215$  °C, **5a** is slowly converted to a mixture containing the residual DL isomer (**5b**). The diastereomerization was monitored by integration of the two upfield methyl signals in the  $^1\text{H}$  NMR spectrum.<sup>53,54</sup> The equilibrium constant,  $K(\mathbf{5b}/\mathbf{5a}) = 1.0 \pm 0.1$  at  $215$  °C, which is half the statistical ratio, and the diastereomerization barrier,  $\Delta G^* = 39.4 \pm 0.5$  kcal mol $^{-1}$  at  $215$  °C, which is substantially higher than the barrier for diastereomerization in **3**, are clear manifes-

(51) Residual stereoisomerism in conformational systems was first demonstrated for molecular propellers under the operation of the two-ring flip mechanism.<sup>14,22</sup>

(52) Similar conclusions were independently obtained in work on bis(3-chloro-9-triptycyl) ether: Kawada, Y.; Iwamura, H. *J. Am. Chem. Soc.* **1981**, *103*, 958; *Tetrahedron Lett.* **1981**, 22, 1533.

(53) The two NMR signals for the 1- and 4-methyl protons appear at  $\delta$  2.33 and 2.55 in **5a** and  $\delta$  2.95 and 2.55 in **5b** (nitrobenzene solvent).

(54) The accidental isochrony of one set of signals (presumably ascribable to the diastereotopic methyl groups in the 4-position) at  $\delta$  2.55<sup>53</sup> parallels the similar accidental isochrony of the methyl NMR signals at  $\delta$  2.07 in **3a** and **3b**.<sup>50</sup> The relative chemical shifts of the other two signals are consistent with our assignments.



**Figure 12.** Representative conformations of stereoisomers of bis(1,4-dimethyl-9-triptycyl)methane (**5**). Enantiomers are paired in brackets. The mechanism of stereomutation is indicated next to the circled E (enantiomerization) and D (diastereomerization).

tations of the steric effect of the 1- and 1'-methyl groups in the ground and transition states of **5**.

**Stereochemical Consequences of Restricted Gearing.** Figuratively speaking, the 1- and 1'-methyl groups act as molecular monkey wrenches in the Tp cogwheel system: as indicated by the EFF calculations, forcing the methyl group on one Tp rotor into the notch between the teeth of the other increases the strain energy by 17 kcal mol $^{-1}$ . The calculations thus lead to the prediction that enantiomerization of the *dl* pair (a)/(d) (Figure 8), which constitutes the residual meso isomer **5a**, should be observable on the NMR time scale.

These computational predictions are borne out by the NMR behavior of **5a**: the  $^{13}\text{C}\{^1\text{H}\}$  NMR signal count, which is of type II at  $100$  °C (Table V), changes to one of type III at  $-50$  °C.<sup>55</sup> An experimental estimate of the enantiomerization barrier was obtained from the variable-temperature  $^1\text{H}$  NMR spectrum of **5a** (Figure 11), most conveniently from the coalescence of the downfield doublets that originate in the proximal peri (A and E) protons of the diastereotopic benzene rings.<sup>56</sup> Application of the Gutowsky-Holm equation yielded  $\Delta G^* = 14.2 \pm 0.5$  kcal mol $^{-1}$  at  $17$ – $20$  °C, in fair agreement with the  $17.0$  kcal mol $^{-1}$  estimated by EFF calculations.<sup>57</sup>

(55)  $^{13}\text{C}\{^1\text{H}\}$  NMR (25.2 MHz) in dichloro[ $^2\text{H}_2$ ]methane ( $-50$  °C);  $\delta$  148.1, 146.8, 145.8, 145.1, 144.4, 143.4, 131.5, 130.1, 130.0, 127.4, 126.7, 125.3, 124.8, 124.6, 123.5, 122.7, 122.5, 122.3 (aromatic carbons), 57.1 (quaternary carbon), 50.8 (methine carbon), 28.0 (methylene carbon), 25.6, 19.4 (methyl carbons). The 300-MHz  $^1\text{H}$  NMR spectrum in trichloro[ $^2\text{H}$ ]-methane ( $-21$  °C) shows two ABCD multiplets in the aromatic region. We thank Mary Baum for this measurement.

(56) Assignments are based on an analysis of  $^1\text{H}$  chemical shifts for a set of related bis(9-triptycyl)methane derivatives. In every case, the proximal peri protons in the unsubstituted rings are shifted downfield relative to the other aromatic protons. For trichloro[ $^2\text{H}$ ]methane solutions of **3a**, **1**, **2**, **8**, and **5a** at ambient temperature,  $\delta(\text{H}_A, \text{H}_B, \text{H}_C, \text{H}_D) = (7.64, 6.81, 6.99, 7.44)$ ,  $(7.57, 6.78, 6.99, 7.46)$ ,  $(7.85, 6.71, 6.91, 7.41)$ ,  $(7.58, 6.75, 6.99, 7.50)$ , and  $(7.68, 6.70, 6.99, 7.44)$ , respectively. For triptycene itself,  $\delta(\text{H}_{A/D}, \text{H}_{B/C}) = (7.29, 6.88)$ . In further support of this assignment, we note that the signals of the downfield diastereotopic protons are separated by a much larger chemical shift [ $\Delta\delta(\text{A}, \text{E}) = 0.63$ ] than the comparable pair of diastereotopic protons in the distal peri positions [ $\Delta\delta(\text{D}, \text{H}) = 0.17$ ].

(57) The observed site exchange phenomenon corresponds to a process in which two diastereotopic benzene rings become enantiotopic (and hence isochronous) on the NMR time scale at the fast exchange limit and can only be accounted for by one of two enantiomerization mechanisms. The first of these, enantiomerization of the *DL* pair by gear slippage, is ruled out because this process would require a substantially higher barrier than observed. It follows that the observed site exchange results from enantiomerization of the *dl* pair by gearing.

Our findings are summarized in Figure 12. At elevated temperatures, i.e., on the time scale of rapid gearing and gear slippage, **5** is a single, achiral species. As the temperature is lowered and gear slippage—but not gearing—is frozen out, enantiomerization of the D or L forms and diastereomerization of the meso and DL forms is slowed, and three stereoisomers (meso, D, and L) are formed. Finally, as the temperature is lowered further and gearing is also frozen out, the meso isomer is partitioned into a pair of enantiomers (*dl*). Thus, on the time scale of slow gearing and gear slippage there are four stereoisomers: *d*, *l*, D and L. Under these conditions, the *d* and *l* conformers are virtually immobilized, but homomerization<sup>11</sup> of the D and L isomers still takes place quite rapidly through the low-energy intermediate (Figure 9a).

### Experimental Section

The elemental analysis and osmometric molecular weight determination were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY. NMR spectra were recorded either on a Varian XL-100 spectrometer equipped with variable-temperature accessories or on a JEOL FX-90Q spectrometer, both operating in the Fourier transform mode. Chemical shifts are in ppm downfield from tetramethylsilane as internal reference and are reported in Tables IV and V. Mass spectra were measured on an AEI MS-9 high-resolution mass spectrometer, with an ionizing voltage of 70 eV. Melting points were measured in a Mel-Temp or a Thomas-Hoover apparatus in sealed capillary tubes and are corrected.

**2,3-Dimethyltriptycene (7).** 2-Amino-4,5-dimethylbenzoic acid (1.73 g, 10.5 mmol), mp 209–210 °C dec (lit.<sup>36</sup> mp 213–214 °C), in 20 mL of diglyme was added dropwise to a gently refluxing solution of anthracene (1.78 g, 10.0 mmol) and isoamyl nitrite (1.32 g, 10.9 mmol) in 30 mL of 1,2-dichloroethane. After 1 h of reflux, the solvents boiling below 150 °C were removed by distillation, and maleic anhydride (0.72 g, 7.3 mmol) was added. After a few minutes of reflux, a solution of potassium hydroxide (2.85 g, 51.0 mmol) in 35 mL of 2:1 methanol/water was added to the cooled (10 °C) mixture. The mixture was filtered, and the residue was washed with 4:1 methanol/water until the washings were colorless. The light tan solid (1.50 g) was chromatographed on silica gel, petroleum ether 30–60 °C as eluant, to give 1.02 g (37%) of white crystals: mp 240–242 °C (lit.<sup>39</sup> mp 302 °C); MS, *m/e* (rel intensity) 282 (81), 267 (100), 252 (41), 141 (25), 133 (41); MS (high resolution), *m/e* 282.1398 ± 0.0014 (282.1409 calcd for C<sub>22</sub>H<sub>18</sub>); molecular weight determination (osmometry in methyl ethyl ketone) 302. Anal. Calcd for C<sub>22</sub>H<sub>18</sub>: C, 93.57; H, 6.43. Found: C, 93.35; H, 6.47.

**Bis(2,3-dimethyl-9-triptycyl)methane (3).** 2-Amino-4,5-dimethylbenzoic acid (6.00 g, 36.4 mmol) in 100 mL of diglyme and isoamyl nitrite (5.84 g, 49.9 mmol) in 25 mL of 1,2-dichloroethane were added dropwise and simultaneously to a refluxing suspension of bis(9-anthryl)methane (3.35 g, 9.1 mmol), mp 308–310 °C (lit.<sup>31</sup> mp 313–315 °C), in 250 mL of 1,2-dichloroethane. After 2 h of reflux, the solvents were removed by distillation and the dark residue was washed several times with 4:1 methanol/water. The brown residue was chromatographed on silica gel, 98:2 pentane/ethyl ether as eluant. The fraction containing the title compound was chromatographed on silica Woelm 32–63 μm, 98:2 pentane/ethyl ether as eluant. **3a** (mp 324–327 °C) was eluted first, followed, after some mixed fractions, by pure **3b** (mp 382–385 °C).

**3a:** MS, *m/e* (rel intensity) 576 (71), 561 (4), 293 (26), 280 (100), 266 (76); MS (high resolution), *m/e* 576.2814 ± 0.0148 (576.2819 calcd for C<sub>45</sub>H<sub>36</sub>).

**3b:** MS, *m/e* (rel intensity) 576 (85), 561 (4), 293 (12), 281 (100), 266 (29); MS (high resolution), *m/e* 576.2784 ± 0.0100 (576.2819 calcd for C<sub>45</sub>H<sub>36</sub>).

**Bis(2,3-dimethyl-9-triptycyl)carbinol (4).** 2-Amino-4,5-dimethylbenzoic acid (3.45 g, 21.0 mmol) in 25 mL of diglyme and isoamyl nitrite (2.79 g, 23.9 mmol) in 25 mL of 1,2-dichloroethane were added dropwise and simultaneously to a refluxing solution of bis(9-anthryl)carbinol (1.34 g, 3.5 mmol), mp 196–198 °C (lit.<sup>32</sup> mp 209–211 °C), in 100 mL of 1,2-dichloroethane. After 3 h of reflux, the solvents were removed under reduced pressure, and the residue was stirred with 200 mL of 4:1 methanol/water for 2 h. The suspension was filtered to give a tan solid, which was chromatographed on silica gel, 7:3 pentane/ethyl ether as eluant. The fraction containing the title compound was chromatographed on silica Woelm 32–63 μm, 9:1 pentane/ethyl ether as eluant. **4a** was eluted first, followed, after some mixed fractions, by pure **4b**. Neither com-

pound had a well-defined melting point; both turned to a glass at ca. 200 °C and decomposed at ca. 300 °C.

**4a:** MS, *m/e* (rel intensity) 592 (100), 574 (25), 309 (59), 282 (76), 281 (78), 267 (55), 266 (61); MS (high resolution), *m/e* 592.2777 ± 0.0058 (592.2766 calcd for C<sub>45</sub>H<sub>36</sub>O).

**4b:** MS, *m/e* (rel intensity) 592 (47), 574 (17), 309 (51), 282 (90), 281 (100), 267 (74); MS (high resolution), *m/e* 592.2771 ± 0.0029 (592.2766 calcd for C<sub>45</sub>H<sub>36</sub>O).

**Bis(1,4-dimethyl-9-triptycyl)methane (5).** 2-Amino-3,6-dimethylbenzoic acid (1.50 g, 9.0 mmol), mp 120–121 °C (lit.<sup>34</sup> 122–123 °C), in 30 mL of diglyme and isoamyl nitrite (3.49 g, 29.8 mmol) in 10 mL of diglyme were added dropwise and simultaneously to a refluxing solution of bis(9-anthryl)methane (0.55 g, 1.5 mmol) in 100 mL of 1,2-dichloroethane. After 4 h of reflux, the solvents boiling below 150 °C were removed by distillation, and maleic anhydride (0.30 g, 3.0 mmol) was added. After a few minutes of reflux, a solution of potassium hydroxide (1.43 g, 25.5 mmol) in 18 mL of 2:1 methanol/water was added to the cooled (10 °C) mixture. The mixture was filtered, and the residue was chromatographed on silica gel, 99:1 petroleum ether 30–60 °C/ethyl ether as eluant. A yellow oil was isolated, which was rinsed with ethyl ether to give **5a** as a colorless solid: mp 351–354 °C; MS, *m/e* (rel intensity) 576 (41), 561 (18), 368 (100), 281 (27); MS (high resolution), *m/e* 576.2831 ± 0.0029 (576.2819 calcd for C<sub>45</sub>H<sub>36</sub>).

**Diastereomerization Kinetics.** Solutions of **3a** and **3b** in nitro[<sup>2</sup>H<sub>5</sub>]benzene were placed in thin-walled NMR tubes. For each kinetic run, a tube containing a solution of **3a** and a tube containing a solution of **3b** were immersed in a constant-(±0.3 °C) temperature bath maintained at 145.8, 155.8, and 165.0 °C. After a measured amount of time, the two tubes were removed from the bath and immediately cooled in ice-water. At each time interval, the <sup>1</sup>H NMR spectra of the methyl region were recorded at 89.55 MHz,<sup>50</sup> and the relative integrated area of the peaks was used to calculate the percent composition of the sample.<sup>58</sup> The values of the rate constants *k*(**3a** → **3b**) and *k*(**3b** → **3a**) for the equilibration of the diastereomers at the three temperatures were calculated by using a previously described expression for reversible first-order reactions.<sup>22</sup> In order to determine the equilibrium constant *K*, the tubes were heated at 145.8, 155.8, and 165.0 °C for 150, 47, and 28.5 h, respectively. The value of *K*(**3b**/**3a**) was found to be the same, within experimental error, starting from either **3a** or **3b**. A value of *K*(**3b**/**3a**) = 1.8 ± 0.1 was found at 155.8 °C. A least-squares treatment of ln([**3a**]*K* - [**3b**]) vs. *t* and the value of *K*, together with the Eyring equation,<sup>59</sup> gave the values of Δ*G*<sup>‡</sup> for **3** reported in Table VI. A solution of **5a** in nitro[<sup>2</sup>H<sub>5</sub>]benzene was placed in a thin-walled NMR tube, which was sealed under argon by using three freeze-pump-thaw cycles. The tube was placed in a thermostated aluminum block maintained at 215 °C. After a measured amount of time, the tube was removed from the bath and immediately cooled in ice-water. At each time interval, the <sup>1</sup>H NMR spectrum of the methyl region was recorded at 89.55 MHz,<sup>53</sup> and the relative integrated area of the peaks was used to calculate the percent composition of the sample.<sup>60</sup> The tube was heated at 215 °C for 125 h in order to determine the equilibrium constant *K*; *K*(**5b**/**5a**) was found to be 1.0 ± 0.1 at 215 °C. A kinetic treatment of the data as described above gave a value of Δ*G*<sup>‡</sup> = 39.4 ± 0.5 kcal mol<sup>-1</sup>.

**Variable-Temperature NMR Measurements.** All variable-temperature <sup>1</sup>H NMR spectra were recorded at 100.1 MHz in the Fourier transform mode on a Varian XL-100 spectrometer. NMR samples in dichloro[<sup>2</sup>H<sub>2</sub>]methane or tetrachloro[1,2-<sup>2</sup>H<sub>2</sub>]ethane were placed in 5-mm o.d. tubes. Temperature measurements were made with a Wilmad T-811 NMR probe thermometer and are estimated to be accurate to ±1 °C.

**Acknowledgment.** We thank the National Science Foundation (CHE-8009670) for support of this work, the Consiglio Nazionale delle Ricerche for a fellowship to F.C., and Dr. Robert B. Nachbar, Jr., for helpful discussions.

**Registry No.** 1, 73611-46-8; 2, 76913-32-1; *meso-3a*, 76913-31-0; DL-**3b**, 76946-58-2; *meso-4a*, 84109-37-5; DL-**4b**, 84170-85-4; *meso-5a*, 84170-86-5; 6, 17417-17-3; 7, 27884-45-3; 8, 82510-94-9.

(58) The integral was fine-tuned until level base lines were obtained and until the area of the peak at δ 2.07 was equal to the sum of the areas of the peaks at δ 1.77 and 1.93.

(59) The transmission coefficient was taken to be unity.

(60) The integral was fine-tuned until level base lines were obtained and until the area of the peak at δ 2.55 was equal to the sum of the areas of the peaks at δ 2.33 and 2.95.