Application of Empirical Force Field Calculations to Internal Dynamics in 9-Benzyltriptycenes

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Conformational maps for internal rotation in 9-benzyltriptycene (1), 9-(2,6-dimethylbenzyl)triptycene (2), and 1-methyl-9-(2,6-dimethylbenzyl)triptycene (6) have been calculated by the empirical force field (EFF) method and the results compared with variable-temperature NMR data for 9-(2,4,6-trimethylbenzyl)triptycene (3) and 1,4-dimethyl-9-(2,4,6-trimethylbenzyl)triptycene (7). It is found that gearing (correlated disrotation) is the dominant mode of conformational interconversion in 2, 3, 6, and 7 and that this motion may be further facilitated in (9-anthryl)(9-triptycyl)methane, relative to 3, because of the flexibility of the anthracene ring. The results also indicate that the MM2 force field somewhat overestimates the barrier to gearing in these compounds.

Correlated rotation has been demonstrated for propeller-shaped molecules in which two or three aromatic rings (blades) are attached to a common atomic center.[2] Given a suitable substitution pattern for the aromatic rings, correlated rotation leads to residual stereoisomerism, as has been demonstrated for di- and triarylmethanes and for analogous compounds.[3]

The highest local symmetry (C_{2v}) of a blade corresponds to that of a twofold rotor. The question of whether correlated rotation might be observable in systems with n-fold rotors of higher local symmetry was recently addressed by Yamamoto and Ōki in a dynamic NMR (DNMR) study of 9-(3,5-dimethylbenzyl)triptycene and 9-(2-methylbenzyl)triptycene derivatives.[4] The 9-triptycyl group represents, to a close approximation, a rigid array of local C_{3v} symmetry, and the parent compound, 9-benzyltriptycene (1), may be viewed as a system composed of a twofold (phenyl ≡ Ph) and a threefold (9-triptycyl ≡ Tp) rotor attached to a common frame (CH_2). The notches between the rings in the Tp moiety easily accommodate the Ph blade in the benzyl moiety, and the resulting intermeshing of the two rotors may lead to correlated disrotation in 1 or in suitably substituted derivatives. The one-step (primitive) rearrangement for this motion is illustrated for 1 in Figure 1. The assumed[4] bisected ground-state conformation (A and C) has C_s symmetry, with the threefold axis of Tp in the plane of the Ph ring. In the C_s transition state (B), the plane of this ring is perpendicular to the one in A and C. In the course of the rearrangement A → C, the Ph ring undergoes edge interchange[2] concomitant with a rotation by π about the Ph–CH_2 bond axis, while the Tp group rotates by $2\pi/3$ in the opposite direction about the Tp–CH_2 bond axis.[5]

Although residual stereoisomerism is precluded for this class of compounds,[7] Yamamoto and Ōki were able to make a strong case for correlated disrotation in certain of their compounds.[9] More recently we provided a detailed analysis of internal motions in bis(9-triptycyl)methane using empirical force field (EFF) calculations to describe the torsional portion of the potential energy (PE) hypersurface for gearing and gear slippage,[10] and it seemed desirable to extend these computational studies to 1 and to some of its derivatives. Our purpose was to furnish an overview of the minimum-energy trajectories which connect the energy minima in the torsional space of such molecules and to provide a critical comparison of computed with experimentally observed transition-state energies. Such a study would also serve to evaluate further the utility of EFF calculations in predicting geometries and energies for conformational processes in systems of tightly coupled rotors containing aromatic rings.

Force Field Calculations. Initial geometries of appropriate conformations were based on standard bond lengths and bond angles. These structures were then optimized[11] by the program BIGSTRN-3[12] using the MM2 force field.[13] Final structures were characterized as minima,

(1) (a) Molecular Design, Ltd., Hayward, CA. (b) On leave from Chalmers University of Technology and University of Göteborg, Sweden.

(2) Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26 and references therein. Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 1535 and references therein.

(3) Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 3198 and references therein. Glaser, R.; Blount, J. F.; Mislow, K. *Ibid.* **1980**, *102*, 2777.

(4) Yamamoto, G.; Ōki, M. *Chem. Lett.* **1979**, 1251, 1255; *Bull. Chem. Soc. Jpn.* **1981**, *54*, 473, 481.

(5) It has been pointed out[6] that a stereochemical correspondence exists between 1 and the cluster compound $Co_3(CO)_9CCH_2^+$. In the latter, a twofold rotor (CH_2–C) and a threefold rotor ($Co_3(CO)_9$–C) undergo a gear motion analogous to that shown in Figure 1. The chief difference between the two systems is the coupling mechanism: the forces governing the concerted torsions in the cluster are under orbital symmetry control, whereas those in 1 originate from nonbonded interactions.

(6) Edidin, R. T.; Norton, J. R.; Mislow, K. *Organometallics* **1982**, *1*, 561.

(7) Kawada, Y.; Iwamura, H. *Tetrahedron Lett.* **1981**, *22*, 1533. In a system of two coupled chemical rotors, residual stereoisomerism for certain labeled derivatives becomes possible only if the greatest common divisor (N) of the periodicities exceeds unity, as it does in two-bladed molecular propellers ($N = 2$)[2] and in molecular gear systems of the type Tp_2X ($N = 3$).[8] In contradistinction, $N = 1$ for 1. A moment's reflection shows that no residual stereoisomerism is possible for *any* labeling pattern of 1 under gear motion.

(8) (a) Cozzi, F.; Guenzi, A.; Johnson, C. A.; Mislow, K.; Hounshell, W. D.; Blount, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 957. (b) Kawada, Y.; Iwamura, H. *Ibid.* **1981**, *103*, 958.

(9) For example, it was found[4] that the barrier (10.0 kcal mol^{-1}) for site exchange of 3- and 5-methyl protons in 9-(3,5-dimethylbenzyl)-2-methoxytriptycene is very similar to the barriers (10.8, 11.0 kcal mol^{-1}) for interconversion of the *ap* and *sc* conformers. The barrier for site exchange of 3- and 5-methyl protons in 9-(3,5-dimethylbenzyl)triptycene was found[4] to be 10.2 kcal mol^{-1}.

(10) Bürgi, H.-B.; Hounshell, W. D.; Nachbar, R. B., Jr.; Mislow, K. *J. Am. Chem. Soc.*, in press.

(11) Geometry optimizations were routinely begun with the steepest descent (S-D) method and concluded with the full-matrix Newton–Raphson (N-R) method; analytical derivatives were used at both stages. For some partial maxima, it was necessary to minimize the gradient norm (i.e., forces) during the S-D stage in order to keep the structure in the neighborhood of the partial maximum. The final convergence criteria for the N-R stage were as follows: rms gradient less than 10^{-6} kcal mol^{-1} Å^{-1} and rms atom movement less than 10^{-6} Å.

(12) Nachbar, R. B., Jr.; Mislow, K., to be submitted to QCPE. A listing is available from the authors upon request.

(13) Allinger, N. L.; Yuh, Y. H. *QCPE* **1981**, *13*, 395. Two modifications for C_{ar}–C_{ar} bonds were l^0 = 1.3937 Å and k_s = 8.0667 mdyn Å^{-1}. See also: Ōsawa, E.; Onuki, Y.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 7475.

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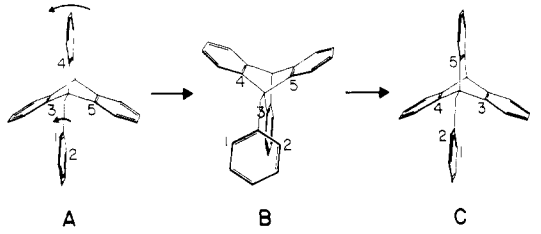

Figure 1. Primitive rearrangement for correlated disrotation in 9-benzyltriptycene (1). Numbers are used to label the ortho carbons on the two edges of the phenyl ring (Ph) and the three carbons attached to C(9) in the 9-triptycyl group (Tp). Viewed along the Ph–CH_2 bond axis toward CH_2, the torsion of Ph is counterclockwise; viewed along the Tp–CH_2 bond axis toward CH_2, the torsion of Tp is clockwise (curved arrows).

transition states, or partial maxima by the number of negative eigenvalues of the matrix of analytical second derivatives. Primitive, minimum-energy pathways were determined by descent[14] from each transition-state structure to the adjacent minima. The transition-state structures were distorted along the transition vector,[15] and were then reoptimized by the variable metric method.[16]

Torsional coordinates[18] used to describe the torsion of the two rotors are

$$\phi(\text{Ph}) = (\omega_1 + \omega_2 - \pi)/2$$

$$\phi(\text{Tp}) = (\omega_3 + \omega_4 + \omega_5 - 2\pi)/3$$

where ω_1 and ω_2 are the torsion angles centered at the Ph–CH_2 bond, and ω_3, ω_4, and ω_5 are torsion angles centered at the Tp–CH_2 bond. With reference to Figures 2–4

$$\omega_1 = \text{C(1)–C}(\alpha)\text{–C}(\beta)\text{–C}(\gamma)$$

$$\omega_2 = \text{C(2)–C}(\alpha)\text{–C}(\beta)\text{–C}(\gamma)$$

$$\omega_3 = \text{C(3)–C}(\gamma)\text{–C}(\beta)\text{–C}(\alpha)$$

$$\omega_4 = \text{C(4)–C}(\gamma)\text{–C}(\beta)\text{–C}(\alpha)$$

$$\omega_5 = \text{C(5)–C}(\gamma)\text{–C}(\beta)\text{–C}(\alpha)$$

The values of ϕ(Ph) and ϕ(Tp) for the various conformations were used to construct the conformational maps in Figures 2–4.

Results and Discussion

In Figure 2, the stationary points and minimum-energy trajectories for internal rotation in 1 are mapped onto the ϕ(Ph),ϕ(Tp) torsional subspace. The symmetry of the hypersurface is isomorphic to the subgroup modulo 2π of the plane group $p2$.[19] The unit cell, of dimensions π by $2\pi/3$, contains four stationary points: an energy minimum, corresponding to the bisected C_s conformation, two anisometric C_s transition states, and one C_s double partial maximum, of relative energies 0.0, 11.4, 14.0, and 40.0 kcal mol^{-1}, respectively. Inspection of Figure 2 reveals two competing primitive pathways for the homomerization of 1. One of these (a ⇄ [b] ⇄ c) is an uncorrelated motion, in which Ph undergoes edge interchange while Tp merely librates about its equilibrium position. This is the motion referred to by Yamamoto and Ōki as "isolated [phenyl] rotation". The other pathway (a ⇄ [d] ⇄ e) corresponds to correlated disrotation ("gear motion"). No minimum-energy pathway was observed for isolated Tp rotation.

According to our calculations, isolated phenyl rotation is preferred over correlated disrotation (i.e., [d] exceeds [b] by ca. 2.6 kcal mol^{-1}).[20] The opposite conclusion had been drawn on the basis of DNMR studies.[4,9] However, there is reason to believe that the calculated barrier for gear motion in 1 is almost certainly overestimated; we shall return to this point in our discussion of 6, below.

To dispel any ambiguity as to the preferred pathway, we modified 1, so as to increase the barrier to isolated Ph rotation and decrease the barrier to gear motion, by substitution of both *o*-hydrogens in Ph by methyl groups.[21] In the resulting compound, 9-(2,6-dimethylbenzyl)-triptycene (2), the *o*-methyls not only increase the strain in the transition state to isolated Ph rotation but also increase the strain in the ground state[22] with a concomitant decrease in the barrier to gear motion.

Stationary points and minimum-energy trajectories for internal rotation in 2 are shown in Figure 3. Methyl substitution does not reduce the symmetry of the hypersurface, which remains $p2$, with a unit cell of dimensions π by $2\pi/3$. The ground state has approximate C_s symmetry; the 2,6-dimethylphenyl (Ph′) and Tp torsion angles differ from those in an ideally bisected conformation by ±6.6° and ∓2.8°, respectively. The structure with exact C_s symmetry [ϕ(Ph′) = 0, ϕ(Tp) = π] is barely higher in energy (0.02 kcal mol^{-1}), and the region encompassing these structures represents a broad, shallow minimum. In addition, the unit cell contains four other stationary points: a local energy minimum, 4.7 kcal mol^{-1} above the ground state; a transition state, 4.9 kcal mol^{-1} above the ground state and connecting the two anisometric energy minima; a second transition state, 14.1 kcal mol^{-1} above the ground state and connecting two local minima; a double partial maximum, 49.8 kcal mol^{-1} above the ground state.

As is evident from the above description and from a comparison of Figures 2 and 3, the topographies of the hypersurfaces for 1 and 2 differ significantly. Clearly, gearing in 2 is the dominant conformational rearrangement (a ⇄ b ⇄ c). The widening of the central C–CH_2–C bond angle in the ground state, from 119.6° calculated for 1 to 128.4° calculated for 2, is clear evidence for the expected increase in ground-state strain;[23] the same conclusion de-

(14) Müller, K. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1.
(15) Stanton, R. E.; McIver, J. W., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 3632. Ermer, O. *Ibid.* **1976**, *98*, 3964.
(16) Because conformational reaction pathways have relatively small gradients, the S-D optimization is excruciatingly slow. On the other hand, N-R optimization of the initial, distorted structure often returned to the transition state. In those instances where the descending pathway was followed, the N-R method was inefficient due to the repeated need for new inverse second derivative matrices. The variable metric method[17] proved to be the ideal solution to these problems: first, it is much more efficient than the S-D method (because it has available second derivative information) and, second, it cannot return uphill to the transition state.
(17) Walsh, G. R. "Methods of Optimization"; Wiley: New York, 1975; Chapter 4.
(18) Murray-Rust, P.; Bürgi, H.-B.; Dunitz, J. D. *Acta Crystallogr., Sect. A* **1979**, *A35*, 703.
(19) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I, p 58.
(20) The ordering of the energies does not appear to be force field dependent. Thus, the relative energies of the four stationary points, in the order listed above, are 0.0, 10.8, 14.9, and 33.5 kcal mol^{-1} according to calculations employing the force field described by Andose and Mislow [Andose, J. D.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 2168] in conjunction with BIGSTRN-3.[11,12]
(21) Our calculations indicate that substitution of both meta (3,5) hydrogens by methyl groups[4] does not significantly perturb the PE hypersurface of 1: corresponding stationary points have virtually identical geometries and differ in steric energy by less than 1 kcal mol^{-1}.
(22) In the ground state, one of the methyl groups is forced into the notch between two aryl rings in the Tp moiety. This interaction is similar to the one encountered in the transition state for gearing in *meso*-bis-(1,4-dimethyl-9-triptycyl)methane. See: Johnson, C. A.; Guenzi, A.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6240. Guenzi, A.; Johnson, C. A.; Cozzi, F.; Mislow, K. *J. Am. Chem. Soc.*, in press.
(23) This angle expansion is comparable to that found for the central C–C–C bond angles in bis(9-triptycyl)methane,[24a] bis(9-triptycyl)-carbinol,[8a] bis(9-triptycyl)ketone,[24a] and 1,1,1,3,3,3-hexaphenylpropane.[24b]

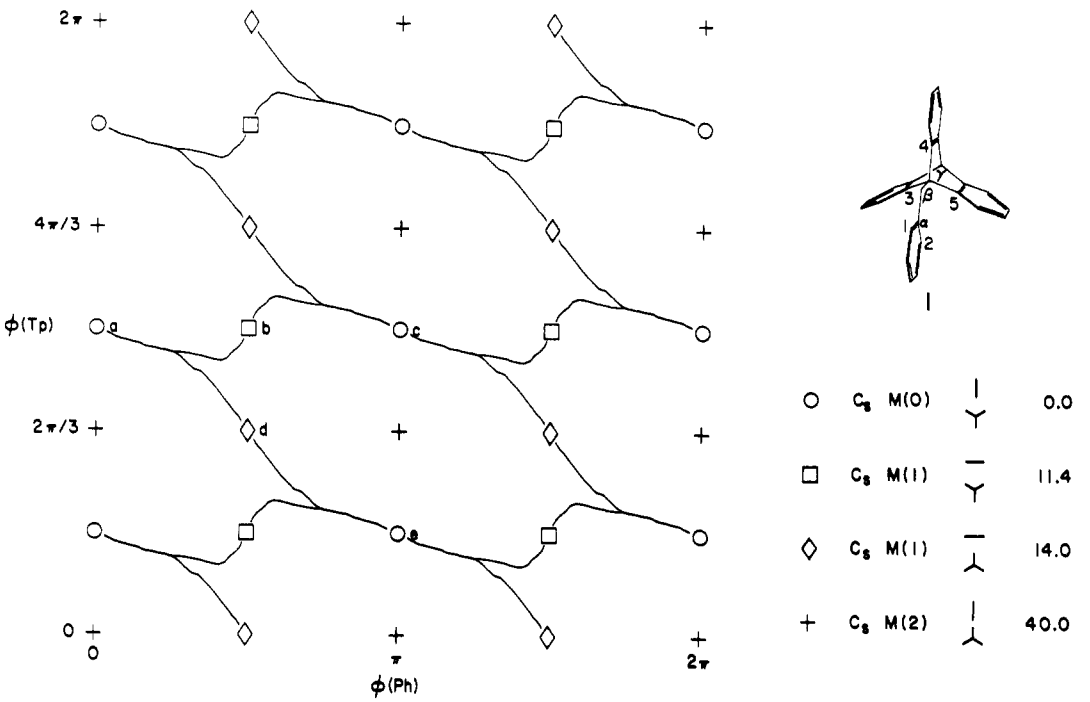

Figure 2. Conformational map of the ϕ(Ph), ϕ(Tp) torsional subspace for 9-benzyltriptycene (1), showing stationary points and minimum-energy pathways interconnecting minima via transition states. Upper right: perspective view of 1; carbon atoms are labeled to correspond to the indices in Figure 1; Ph ipso, CH_2, and Tp C(9) carbons are labeled α, β, and γ, respectively. Lower right: key showing mapping symbol, symmetry, order of the point [M(0) = minimum, M(1) = transition state, M(2) = double partial maximum], a schematic sketch of the conformation with lines representing rotor blades, and the relative steric energies (in kilocalories per mole) for the various stationary points.

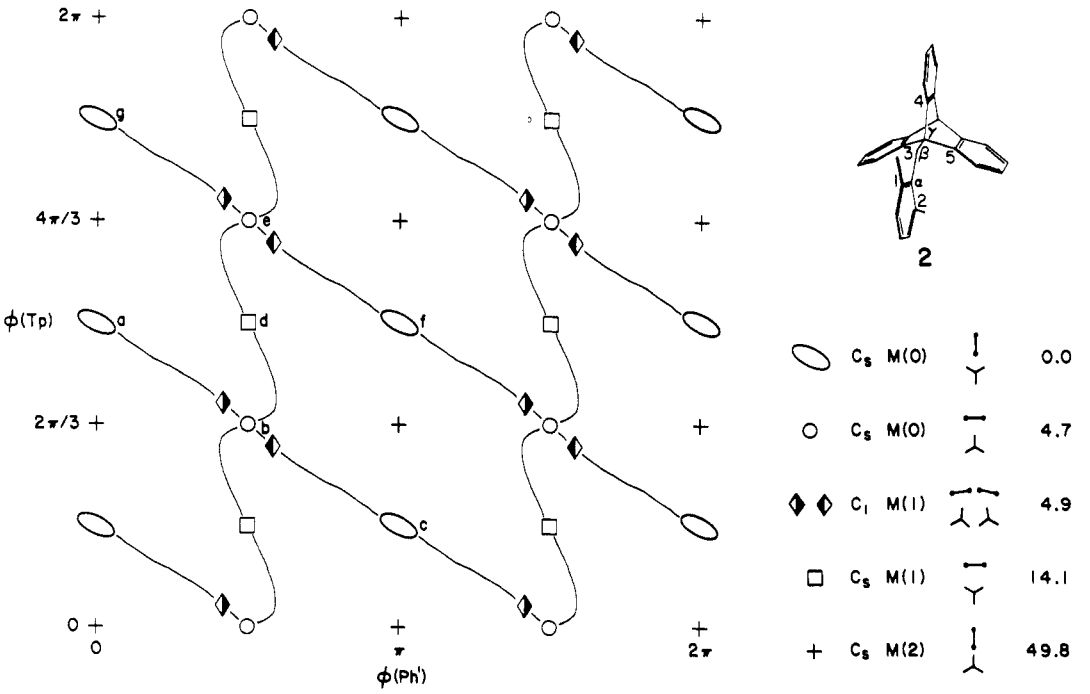

Figure 3. Conformational map of the ϕ(Ph'),ϕ(Tp) torsional subspace for 9-(2,6-dimethylbenzyl)triptycene (2). The labeling and key are as in Figure 2. The filled circles at the ends of the rotor blades represent methyl groups.

rives from a comparison of steric energies for the ground states of 9-(3,5-dimethylbenzyl)triptycene (9.0 kcal mol^{-1})[21] and of 2 (19.5 kcal mol^{-1}). The gearing transition state in 1 has now become a reaction intermediate (local minimum b) in 2, which can be reached by traversing a barrier of only 4.9 kcal mol^{-1} or less.[25] That the low barrier to gearing in 2 can be ascribed primarily to an increase in ground-state energy follows from a comparison of the virtually identical steric energies in the gearing transition state of 9-(3,5-dimethylbenzyl)triptycene (23.0 kcal mol^{-1}) and in the gearing intermediate of 2 (24.2 kcal mol^{-1}). Experi-

(24) (a) Johnson, C. A.; Guenzi, A.; Nachbar, R. B., Jr.; Blount, J. F.; Wennerström, O.; Mislow, K. *J. Am. Chem. Soc.* **1982**, *104*, 5163. (b) Blount, J. F.; Gutiérrez, A.; Mislow, K. *J. Org. Chem.* **1982**, *47*, 4359.

(25) As we have noted elsewhere in the text, the energy for a conformation such as that of the intermediate b is likely to be overestimated by this force field. This argument carriers over to the transition state which is close to the intermediate in geometry.

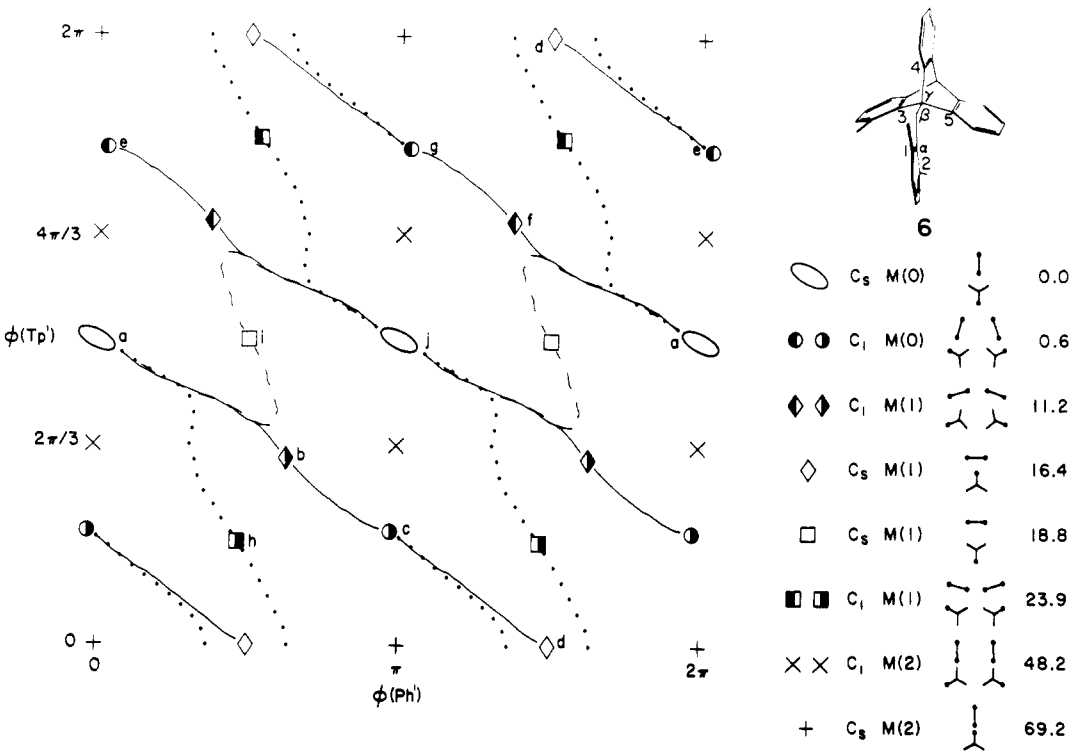

Figure 4. Conformational map of the ϕ(Ph'),ϕ(Tp') torsional subspace for 1-methyl-9-(2,6-dimethylbenzyl)triptycene (6). The labeling and key are as in Figure 2. The filled circles at the ends of the rotor blades represent methyl groups.

mental support for the calculated low barrier comes from the absence of significant broadening of the *o*-methyl singlet in the 100-MHz ^{1}H NMR spectrum of 9-(2,4,6-trimethylbenzyl)triptycene (**3**)[26] at low temperature (to −81 °C, in CD_2Cl_2).

Another feature in which the two systems differ is isolated Tp rotation in **2** (b ⇄ [d] ⇄ e), which replaces isolated Ph rotation in **1** as a primitive process. Note that isolated rotation of Ph′ as a primitive process (i.e., a ⇄ [d] ⇄ f) is precluded by the presence of the bulky *o*-methyl groups. Isolated Tp rotation requires 9.4 kcal mol^{-1} from local minimum to local minimum; the conformation of the transition state (d) is the same as that for isolated Ph rotation in **1** (b in Figure 2). This pathway can be combined with gearing in three different ways: a ⇄ b ⇄ [d] ⇄ e ⇄ g, a ⇄ b ⇄ [d] ⇄ e ⇄ f, and c ⇄ b ⇄ [d] ⇄ e ⇄ g. The first of these composite pathways corresponds to homomerization of **2** with *net* isolated Tp rotation, the second to homomerization with *net* isolated Ph′ rotation, and the third to homomerization with *net* gearing. Higher order composite (multistep) pathways are easily envisaged. All of these processes require exactly the same energy, 14.1 kcal mol^{-1}.

Replacement of Ph′ in **3** by a 9-anthryl group leads to similar results. Both (9-anthryl)(9-triptycyl)methane (**4**) and its synthetic precursor, (9-anthryl)(10-bromotriptyc-9-yl)methane (**5**),[27] have simple ^{1}H and ^{13}C NMR spectra at room temperature (Experimental Section), consistent with the assumption of rapid gearing, and no significant line broadening was observed in the 100-MHz ^{1}H NMR spectra at low temperatures (to −85 °C, in CD_2Cl_2). The gearing barrier in these compounds is likely to be even lower than in **3**, because of increased flexibility in the anthracene ring [by folding of the anthracene plane about the C(9)–C(10) line] in the gearing transition state.[29]

In the course of their study,[4] Yamamoto and Ōki also investigated the effect of substituents in the peri positions of Tp on the barrier to internal rotation. We decided to study this effect computationally on 1-methyl-9-(2,6-dimethylbenzyl)triptycene (**6**), and to compare the results with a DNMR study of 1,4-dimethyl-9-(2,4,6-trimethylbenzyl)triptycene (**7**),[26] as a test of the computational model.

Stationary points and minimum-energy trajectories for internal rotation in **6** are shown in Figure 4. Following precedent,[4] one may designate conformational isomers of **6** as antiperiplanar (*ap*) or synclinal (±*sc*). The ground state of *ap*-**6** resembles that of **2** insofar as it possesses approximate C_s symmetry, with Ph′ and 1-methyl-9-triptycyl (Tp′) torsion angles differing from those in an ideally bisected conformation by ±9.3° and ∓4.2°, respectively. Again as in **2**, the structure with exact C_s symmetry [ϕ(Ph′) = 0, ϕ(Tp′) = π] is barely higher in energy (0.08 kcal mol^{-1}), and the region encompassing these structures represents a broad, shallow minimum. The Ph′ and Tp′ torsion angles in *sc*-**6** also differ only slightly (±3.5° and ∓7.1°, respectively) from those in an ideally bisected conformation, but the minimum is much narrower than in the *ap* isomer. The calculations indicate a slight energy difference (0.6 kcal mol^{-1}) between the isomers (*ap*

(26) This compound was prepared by the general procedure given[4] for the synthesis of substituted 9-benzyltriptycenes (Experimental Section).

(27) (9-Anthryl)(9-triptycyl)methane could be obtained in poor yield from addition of copper(I) iodide to 9-triptycyllithium[28] in ether at −35 °C, followed by addition of 9-(chloromethyl)anthracene in dry benzene. Significantly higher yields were obtained from addition of copper(I) iodide to 10-bromo-9-triptycyllithium, followed by addition of 9-(chloromethyl)anthracene and debromination of the resulting (9-anthryl)(10-bromotriptyc-9-yl)methane (Experimental Section).

(28) Wittig, G.; Tochtermann, W. *Justus Liebigs Ann. Chem.* **1962**, *660*, 23.

(29) Consistent with the greater flexibility of the 9-anthracyl moiety in the transition state is the observation[30b] that the transition state for ring flipping of the *m*-phenylene ring in (9,10)-anthraceno[2.2]metacyclophane is 2.6 kcal mol^{-1} lower in energy than the corresponding transition state in [2.2]metaparacyclophane.

(30) (a) Hefelfinger, D. T.; Cram, D. J. *J. Am. Chem. Soc.* **1971**, *93*, 4767. (b) Sherrod, S. A.; da Costa, R. L.; Barnes, R. A.; Boekelheide, V. *Ibid.* **1974**, *96*, 1565.

below ±*sc*), which is decreased even more if the entropy factor (RT ln 2) is taken into account.

Inspection of Figure 4 shows that there are two distinct, minimum-energy pathways, which interconnect the ±*sc* and *ap* ground states by "single gearing" (SG, solid line) and "double gearing" (DG, dotted line) modes. In addition, a third pathway interconverts homomeric *ap* conformations by an "isolated Ph′ rotation" (IR, dashed line) mode.[31] The symmetry of the PE hypersurface remains isomorphic to *p*2, but, due to the reduced symmetry of the Tp′ rotor, the unit cell dimensions are now π by 2π.

Two primitive rearrangements generate the SG mode: a ⇄ [b] ⇄ c, corresponding to ap ⇄ +sc (or −sc), and c ⇄ [d] ⇄ e, corresponding to +sc ⇄ −sc. These two steps involve gearing motions over a *peri*-hydrogen and a *peri*-methyl in Tp′, respectively; the former requires 11.2 (*ap* → +*sc* (or −*sc*)) or 10.6 kcal mol^{-1} (+*sc* (or −*sc*) → *ap*) and the latter 15.8 kcal mol^{-1}. An alternative pathway for the interconversion of +*sc*- and −*sc*-**6** involves the intermediacy of *ap*-**6**, e.g., c ⇄ [b] ⇄ a ⇄ [f] ⇄ g, and is obviously preferred energetically (10.6 kcal mol^{-1}). The striking increase in the calculated barrier for gearing over the *peri*-hydrogen, from ca. 5 kcal mol^{-1} in **2** to ca. 11 kcal mol^{-1} in **6**, originates primarily in repulsive, nonbonded interactions among the *peri*-methyl, the leading *o*-methyl, and the methylene groups in the transition state.

The DG rearrangement involves a motion in which the Ph′ group hurdles over two Tp′ peri positions in a single step. Where one of the two peri positions is occupied by a methyl group, this rearrangement interconverts *ap* and +*sc* or *ap* and −*sc* isomers (dotted line); otherwise +*sc* and −*sc* isomers are interconverted. Our calculations indicate that the former (*ap* ⇄ ±*sc*, e.g., a ⇄ [h] ⇄ g in Figure 4), with an activation energy of 23.9 (23.3) kcal mol^{-1}, corresponds to a minimum energy pathway, while the latter (+*sc* ⇄ −*sc*, e.g., e ⇄ [i] ⇄ c) corresponds to a trajectory which is substantially lower in energy (18.2 kcal mol^{-1}) and whose transition state is also the transition state for the IR rearrangement (e.g., a ⇄ [i] ⇄ j).[32]

The low-temperature ^{1}H NMR spectrum of **7** is consistent with the presence of only the *sc* conformer; a conservative estimate of the *sc*/*ap* ratio is 10:1 at −100 °C, corresponding to ΔG = 0.8 kcal mol^{-1}. The discrepancy with our calculated energy difference is thus ≥1.4 kcal mol^{-1}. Variable-temperature studies reveal two processes for interconversion of *sc* isomers. The barrier ($\Delta G^{\ddagger}$) for the lower energy process, monitored by coalescence of the methylene AB spin system, is 8.5 ± 0.5 kcal mol^{-1} at 180 K. The barrier ($\Delta G^{\ddagger}$) for the higher energy process, monitored by coalescence of the two *o*-methyl proton signals, is 15.4 ± 0.1 kcal mol^{-1} at 314 K.

To determine the mechanism of these two processes, we made use of our analysis of **6**. If we limit ourselves to one- or two-step mechanisms, it is easily shown that the observed site exchanges entail enantiomerizations of *sc* conformers. For the one-step mechanism (±*sc* ⇄ ∓*sc*) two rearrangement modes can be envisaged, SG and DG, with calculated barriers of 15.8 and 18.2 kcal mol^{-1}, respectively. For the two-step mechanism (±*sc* ⇄ *ap* ⇄ ∓*sc*) the same two rearrangement modes require calculated barriers of 10.6 and 23.3 kcal mol^{-1}, respectively. The observed high-energy process in **7** implicates the one-step SG mechanism, though the possibility of a DG mechanism cannot be rigorously excluded. The barrier of 8.5 kcal mol^{-1} observed for the low-energy process is consistent only with the two-step mechanism (because of the absence of *o*-methyl site exchange), which therefore corresponds to the calculated barrier of 10.6 kcal mol^{-1}. It follows that the force field overestimates the magnitude of the gearing barrier in **6** and, presumably, in **1** and **2** as well.[33] This permits the further inference that the barriers to gearing and isolated rotation in **1** are comparable in magnitude and that the gearing barriers in **2** and **4** are well below the level of detection by currently available DNMR techniques.

Experimental Section

Unless otherwise noted, NMR spectra were recorded on a JEOL FX-90Q spectrometer, with tetramethylsilane as an internal reference. 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 Thomas-Hoover or a Mel-Temp apparatus in capillary tubes and are corrected. Dry ethyl ether (Mallinckrodt) was used without further purification. Pyridine was dried over and distilled from KOH prior to use. Benzene was dried by distillation from calcium hydride.

9-(2,4,6-Trimethylbenzyl)-9,10-dihydro-9-anthrol. Anthrone (2.91 g, 15 mmol) was added portionwise to the Grignard reagent prepared from 2,4,6-trimethyl-1-(chloromethyl)benzene (5.06 g, 30 mmol) and magnesium (0.70 g, 30 mmol) in 100 mL of dry ether. After being stirred 1 h at ambient temperature, the mixture was refluxed for 1 h. The reaction mixture was poured onto 150 mL of saturated ammonium chloride solution, and the phases were separated. After being dried ($MgSO_4$), the ethereal solution was concentrated to 20 mL and filtered to yield 0.55 g of unreacted anthrone. Addition of methanol to the solution precipitated 0.61 g of 1,2-dimesitylethane, mp 112–113 °C (lit.[35] mp 117–118 °C). Concentration of the solution yielded 0.68 g of a mixture containing anthrone and 1,2-dimesitylethane. The solution was evaporated to dryness to give a yellow oil (3.62 g) which was chromatographed on silica gel (eluent dichloromethane). There was thus obtained 2.20 g of the title compound: mp 137–140 °C (71% based on reacted anthrone); ^{1}H NMR (89.55 MHz, trichloro[^{2}H]methane) δ 1.73 (s, 6 H, *o*-CH_3), 2.22 (s with shoulder, 4 H, *p*-CH_3 and OH), 3.12 (s, 2 H, CH_2), 3.79 (AB q, 2 H), 6.70 (s, 2 H, mesitylene protons), 7.24–7.66 (m, 8 H); ^{13}C NMR (22.5 MHz, trichloro[^{2}H]methane) δ 143.1, 139.0, 135.6, 134.5, 129.7 (quaternary aromatic carbons), 128.7, 127.1, 127.0, 126.5, 125.2 (protonated aromatic carbons), 75.4 (C-OH), 41.8, 35.0 (secondary aliphatic carbons), 20.8 (*p*-CH_3), 19.8 (*o*-CH_3); mass spectrum, *m*/*e* (relative intensity) 310 (3), 195 (100), 165 (13), 134 (24), 133 (18); mass spectrum (high resolution) *m*/*e* 310.1718 ± 0.0030 (310.1722 calcd for $C_{24}H_{22}$, the product of dehydration).

9-(2,4,6-Trimethylbenzyl)anthracene. Dry pyridine (6 mL) and thionyl chloride (3 mL) were added to a solution of 9-(2,4,6-trimethylbenzyl)-9,10-dihydro-9-anthrol (1.96 g, 6 mmol) in 50 mL of dry benzene. After the mixture was stirred for 1 h at 50 °C, water was added, and the phases were separated. The solution was dried ($MgSO_4$) and evaporated to give a yellow-brown

(31) In the *sc* isomer this mode is rendered energetically unfavorable by severe nonbonded interaction between *o*-methyl and *peri*-methyl groups in the hypothetical IR transition-state structure.

(32) Although we found no one-step, minimum-energy pathway for a DG rearrangement in **2**, such a process (e.g., c ⇄ [d] ⇄ g in Figure 3), were it to occur, would require the same activation energy (14.1 kcal mol^{-1}) as the composite, minimum-energy pathway c ⇄ b ⇄ [d] ⇄ e ⇄ g.

(33) An extreme example of this overestimation is furnished by a calculation of the energy barrier to *m*-phenylene ring flipping in [2.2]-metaparacyclophane. The transition state, in which a hydrogen atom on this ring protrudes into the center of the face of the *p*-phenylene ring, bears some resemblance to the transition state for gearing in **1**, where H(1) of the Tp group protrudes into the center of Ph. However, the calculated distance between the protruding hydrogen and the benzene ring center in the transition state for ring flipping (1.66 Å) is considerably shorter than in the transition state for gearing (2.44 Å), implying substantially greater nonbonded repulsive interactions for which the MM2 force field is not parametrized. Indeed, our calculations grossly overestimate the barrier: 29.1 kcal mol^{-1}, as compared to an experimental value ($\Delta H^{\ddagger}$) of 17–18 kcal mol^{-1}.[30,34]

(34) Ring flipping in [2.2]metaparacyclophane is handled more satisfactorily by a specially developed combined π-SCF-LCAO-MO force field method: Lindner, H. J. *Tetrahedron* **1976**, *32*, 753.

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solid, which was chromatographed on silica gel (eluent dichloromethane). The title compound (1.46 g, 79%) thus obtained had the following: mp 125–127 °C; ^{1}H NMR (89.55 MHz, trichloro[^{2}H]methane) δ 2.03 (s, 6 H, o-CH_3), 2.29 (s, 3 H, p-CH_3), 5.00 (s, 2 H, CH_2), 6.84 (s, 2 H, mesitylene protons), 7.32–7.53 (m, 4 H), 7.97–8.25 (m, 4 H), 8.39 (s, 1 H, 10-H); ^{13}C NMR (22.5 MHz, trichloro[^{2}H]methane) δ 136.4, 135.6, 135.1, 133.7, 131.5, 130.6 (quaternary aromatic carbons), 129.8, 129.2, 126.3, 125.4, 124.7, 124.7 (protonated aromatic carbons), 30.1 (CH_2), 21.4 (o-CH_3), 20.7 (p-CH_3); mass spectrum, m/e (relative intensity) 310 (100), 295 (15), 279 (14), 266 (14), 191 (15), 178 (42), 133 (84); mass spectrum (high resolution) m/e 310.1721 ± 0.0030 (310.1722 calcd for $C_{24}H_{22}$).

9-(2,4,6-Trimethylbenzyl)triptycene (3). A solution of anthranilic acid (0.55 g, 4.0 mmol) in 10 mL of diglyme was added dropwise to a gently refluxing solution of 9-(2,4,6-trimethylbenzyl)anthracene (0.62 g, 2.0 mmol) and isoamyl nitrite (0.53 g, 4.5 mmol) in 10 mL of 1,2-dichloroethane. An additional 0.53 g of isoamyl nitrite was added, and the dark solution was heated under reflux for 1 h. The solvents were distilled under reduced pressure, and the brown, oily residue was chromatographed on silica gel [eluent 19:1 petroleum ether (bp 30–60 °C)/ethyl ether]. A yellow oil was isolated, which was rinsed with methanol to give 3 (0.18 g, 23%) as a colorless, crystalline solid: mp 233–235 °C; ^{1}H NMR (89.55 MHz, trichloro[^{2}H]methane, ambient temperature) δ 2.09 (s, 6 H, o-CH_3), 2.32 (s, 3 H, p-CH_3), 4.32 (s, 2 H, CH_2), 5.41 (s, 1 H, CH), 6.93 (s, 2 H, mesitylene protons), 6.86–7.08 (m, 6 H), 7.32–7.44 (m, 6 H); ^{13}C NMR (22.5 MHz, trichloro[^{2}H]-methane, ambient temperature) δ 147.4, 145.9, 137.4, 135.1, 131.6 (quaternary aromatic carbons), 130.7, 125.1, 124.8, 123.3, 122.5 (protonated aromatic carbons), 54.4 (CH), 53.0 (quaternary carbon), 32.7 (CH_2), 23.5 (o-CH_3), 20.6 (p-CH_3); mass spectrum, m/e (relative intensity) 386 (41), 371 (5), 266 (40), 253 (100), 133 (20); mass spectrum (high resolution) m/e 386.2032 ± 0.0038 (386.2035 calcd for $C_{30}H_{26}$).

(9-Anthryl)(10-bromotriptyc-9-yl)methane (5). A 2.4 M solution of n-butyllithium in hexane (15 mL, 36 mmol) was added, under a dry nitrogen atmosphere, to a solution of 9,10-dibromotriptycene[36] (7.83 g, 19 mmol) in 50 mL of dry benzene. After 2 h of stirring, 50 mL of dry ethyl ether was added, and the solvent was decanted. The precipitate was washed twice with 10-mL portions of dry ethyl ether and then suspended in 30 mL of dry ethyl ether. Dry cuprous iodide (4.0 g, 21 mmol) was added, and the mixture was stirred for 2 h. A solution of 9-(chloromethyl)anthracene (4.31 g, 19 mmol) in 50 mL of dry benzene was added, and the mixture was stirred overnight. The mixture was filtered, and the solvent was removed under reduced pressure. The residue was recrystallized from dichloromethane/methanol to give 6.40 g (64%) of light yellow solid: mp 331–335 °C dec; ^{1}H NMR (89.55 MHz, trichloro[^{2}H]methane) δ 5.44 (s, 2 H, CH_2), 6.81–7.49 (m, 13 H), 7.89–8.10 (m, 7 H), 8.51 (s, 1 H); ^{13}C NMR (22.5 MHz, trichloro[^{2}H]methane) δ 145.6, 145.0, 131.9, 130.4 (quaternary aromatic carbons), 129.4, 128.5, 126.9, 126.0, 125.4, 125.0, 124.6, 123.6, 122.8 (protonated aromatic carbons), 53.4 (quaternary carbon), 34.0 (CH_2). We were unable to detect the remaining two lines. Mass spectrum, m/e (relative intensity) 524 (50), 522 (48), 265 (22), 252 (71), 191 (100); mass spectrum (high resolution), m/e 522.0973 ± 0.0050 (522.0984 calcd for $C_{35}H_{23}{}^{79}Br$).

(9-Anthryl)(9-triptycyl)methane (4). Addition of an excess of a 2.4 M solution of n-butyllithium in hexane to a solution of (9-anthryl)(10-bromotriptyc-9-yl)methane in dry ethyl ether, followed, after 1 h of stirring, by quenching with methanol gave, after the usual workup, a quantitative yield of a slightly yellow compound: mp 250–260 °C dec; ^{1}H NMR (89.55 MHz, trichloro[^{2}H]methane) δ 5.44 (s, 2 H, CH_2), 5.53 (s, 1 H, CH), 6.76–7.52 (m, 16 H), 7.99–8.20 (m, 4 H), 8.52 (s, 1 H); ^{13}C NMR (22.5 MHz, trichloro[^{2}H]methane) δ 147.2, 146.1, 131.9, 130.5, 129.0 (quaternary aromatic carbons), 129.3, 128.1, 127.1, 125.2, 124.8, 124.5, 123.4, 123.3 (protonated aromatic carbons), 54.6 (CH), 54.3 (quaternary carbon), 33.6 (CH_2); mass spectrum, m/e (relative intensity) 444 (100), 265 (20), 254 (24), 253 (97), 252 (49), 192 (39), 191 (93), 189 (23); mass spectrum (high resolution), m/e 444.1869 ± 0.0044 (444.1878 calcd for $C_{35}H_{24}$).

1,4-Dimethyl-9-(2,4,6-trimethylbenzyl)triptycene (7). A solution of 2-amino-3,6-dimethylbenzoic acid[37] (0.66 g, 4.0 mmol) in 10 mL of diglyme was added dropwise to a gently refluxing solution of 9-(2,4,6-trimethylbenzyl)anthracene (0.62 g, 2.0 mmol) and isoamyl nitrite (0.53 g, 4.5 mmol) in 10 mL of 1,2-dichloroethane. An additional 0.53 g of isoamyl nitrite was added, and the dark solution was heated under reflux for 1 h. The solvents boiling below 160 °C were distilled, 4:1 methanol/water was added, and the mixture was cooled. The filtered solid was dissolved in dichloromethane, and the solution was dried ($MgSO_4$) and evaporated. The brown residue was chromatographed on silica gel [eluent 19:1 petroleum ether (bp 30–60 °C)/ethyl ether]. The fraction containing the title compound was chromatographed on silica gel 60 (40–63 μm, E. Merck, Darmstadt, eluent tetrachloromethane) to give 7 (0.16 g, 19%) as a white solid: mp 235–237 °C; ^{1}H NMR (89.55 MHz, trichloro[^{2}H]methane, ambient temperature) δ 1.74 (br s, 3 H, o-CH_3), 2.33 (s, 3 H, p-CH_3), 2.37 (s, 3 H, CH_3), 2.47 (br s, 3 H, o-CH_3), 2.56 (s, 3 H, CH_3), 4.47 (s, 2 H, CH_2), 5.67 (s, 1 H, CH), 6.59–6.84 (AB q, 2 H, H(2) and H(3)), 6.84–7.10 (m, 6 H), 7.35–7.49 (m, 4 H); ^{13}C NMR (22.5 MHz, trichloro[^{2}H]methane, ambient temperature) δ 148.7, 146.1, 144.5, 144.4, 137.5, 137.5, 134.7, 134.1, 132.0, 129.0 (quaternary aromatic carbons), 131.4–129.9 (C(3,5) of mesitylene), 129.2, 126.8, 124.9, 124.8, 123.0, 122.4 (protonated aromatic carbons), 54.8 (quaternary carbon), 50.8 (CH), 36.4 (CH_2), 22.9 (o-CH_3), 20.5 (p-CH_3), 21.3, 19.0 (1,4-CH_3); mass spectrum, m/e (relative intensity) 414 (35), 399 (3), 294 (11), 281 (100), 266 (25), 133 (18); mass spectrum (high resolution) m/e 414.2360 ± 0.0040 (414.2348 calcd for $C_{32}H_{30}$).

Variable-Temperature NMR Measurements. High-temperature ^{1}H NMR spectra of 7 were recorded at 100.1 MHz on a Varian XL-100 spectrometer operating in the Fourier Transform mode, with tetrachloro[1,2-$^2H_2$]ethane as the solvent. Temperatures were measured with a copper–constantan thermocouple and are considered accurate to ±2 °C. When the sample was heated, the two singlets for the o-methyl protons broadened and coalesced and on further heating reappeared as a sharp singlet. The barrier was calculated from the Gutowsky–Holm equation to be ΔG^* 15.4 ± 0.1 kcal mol^{-1} at 314 K.

Low-temperature ^{1}H NMR spectra of 7 were recorded on a Bruker WH 270 instrument with dichloro[$^2H_2$]methane as the solvent. The temperatures were uncorrected. When the sample was cooled, the singlet for the methylene protons broadened and decoalesced to give an AB quartet. The five singlets for the methyl protons broadened and resharpened to give singlets, indicative of an intermediate conformation with higher energy. The low-temperature spectrum is consistent with the presence of only one conformer. The low-temperature barrier was calculated from the equation for a coupled AB system with equal spin populations[38] ($\Delta\nu$ = 74 Hz, ^2J = 18 Hz) to yield ΔG^* 8.5 ± 0.5 kcal mol^{-1} at 180 K.

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Registry No. 1, 83692-86-8; 2, 83692-87-9; 3, 83692-88-0; 4, 83692-89-1; 5, 83692-90-4; 6, 83692-91-5; 7, 83692-92-6; anthrone, 90-44-8; 2,4,6-trimethyl-1-(chloromethyl)benzene, 1585-16-6; 9-(2,4,6-trimethylbenzyl)-9,10-dihydro-9-anthrol, 83692-93-7; 9-(2,4,6-trimethylbenzyl)anthracene, 83704-17-0.

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