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Restricted Rotation Involving the Tetrahedral Carbon. XLVII. The "Positive" and the "Negative" Buttressing Effects on the Rotational Barriers in 9-(1,1-Dimethyl-2-phenylethyl)-1-halotriptycenes[1)]

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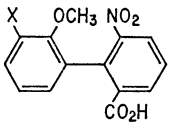
9-(1,1-Dimethyl-2-phenylethyl)-1,2,3,4-tetrahalotriptycenes (halogen=F, Cl, and Br) were synthesized and the kinetic studies of the rotational isomerization were made. The obtained data were compared with those for the corresponding 1-halo derivatives. The equilibrium constants (±*sc*/*ap*) for the tetrahalo compounds are smaller than those for the respective monohalo counterparts. The tetrafluoro compound isomerizes twice slower than the monofluoro one at 240 °C, showing the "positive" buttressing effect. Contrarily, the tetrachloro and the tetrabromo compounds isomerize 13 and 100 times, respectively, faster than the corresponding monohalo compounds at 175 °C, exhibiting the "negative" buttressing effect. These intriguing phenomena are discussed in terms of the molecular deformation in these congested compounds, which affects both the ground state and the transition state for rotation.

In 1934, Chien and Adams found that the presence of a substituent in 3′-position considerably reduces the rate of racemization of the optically active 2-carboxy-2′-methoxy-6-nitrobiphenyl (**1**),[2)] the degree of retardation being dependent on the 3′-substituent. The origin of the effect was not fully understood at that time. Later, Rieger and Westheimer found that 2,2′-diiodo-5,5′-dicarboxybiphenyl (**2a**) racemizes 30,000 times faster than 2,2′,3,3′-tetraiodo-5,5′-dicarboxybiphenyl (**2b**),



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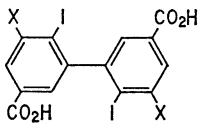


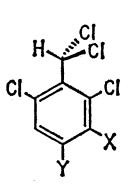
2a: X=H
2b: X=I

the enthalpies of activation being 21.0 and 27.3 kcal mol^{-1} (1 cal=4.18 J), respectively.[3)] These enthalpy values were satisfactorily reproduced by calculation in their pioneering works on molecular mechanics. The calculation revealed the origin of the retarding effects of the *m*-substituents, which is now recognized as the buttressing effect. In the planar transition state for racemization, the ortho groups bend away from each other to relieve the steric strain. Presence of a group in the neighboring meta position prevents the bending to some extent by "buttressing" the *o*-substituent, thus raising the transition state energy. The ground state in these compounds is considered almost free of strain, and the buttressing by the *m*-substituents does not appreciably affect the ground state energy. Therefore, the buttressing effect operates to increase the energy barrier to racemization, which we refer to as the "positive" buttressing effect.

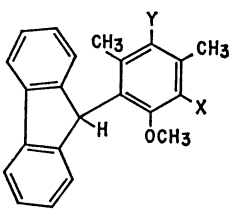
The buttressing effect on the energy barrier to internal rotation about an sp^2-sp^2 single bond is generally positive, because the ground state of the molecule is not much affected by the introduction of a buttressing substituent. However, when internal rotation about an sp^2-sp^3 or sp^3-sp^3 bond is concerned, the situation is somewhat different because the ground state usually suffers from some congestion.

If a substituent is introduced into the neighborhood of a congested site, it would increase the congestion and would raise the ground state energy. Since an energy barrier to rotation is a difference in energies between the ground and the transition states, if the change in the ground state energy is not negligible, it is possible that the buttressing effect either raises or lowers the barrier. The transition state is naturally more congested than the ground state and hence the buttressing effect should operate more effectively in the transition state than in the ground state: this results in the "positive" buttressing effect on the energy barrier, as is commonly observed.

Some examples of the buttressing effect on the energy barrier to rotation about an sp^2-sp^3 bond are known. The buttressed compound **3b** showed a higher barrier to rotation of the dichloromethyl group than **3a** ($\Delta G^{\ddagger}_{298}$: 15.4 *vs.* 14.9 kcal mol^{-1}).[4)] We observed the positive buttressing effect in 9-arylfluorenes (**4**) as



3a: X=H, Y=Cl
3b: X=Cl, Y=H



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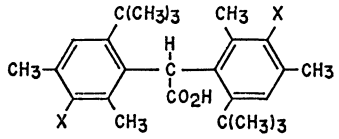
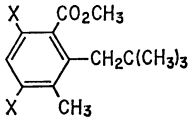
well. Free energies of activation for rotation at 329 K are 25.0 kcal mol^{-1} if X=Y=H, 25.9 kcal mol^{-1} if X=H and Y=Br, 26.5 kcal mol^{-1} if X=Br and Y=H, and 27.2 kcal mol^{-1} if X=Y=Br.[5)]

Though not definite, there are a few examples of the "negative" buttressing effect, namely, the lowering of the barrier by the presence of a buttressing substituents, in the literature. The barrier to racemization of optically active **5** decreases by the introduction of methyl groups in *m*-positions ($\Delta G^{\ddagger}_{298}$: 22.8 *vs.* 22.1 kcal mol^{-1}).[6)] Since there are two C–C$_{ar}$ bonds about which internal rotation is restricted, the observed barriers may not be mechanistically simple, although the authors attributed the retardation to the increase in the ground state energy.[6)] In compounds **6**, the

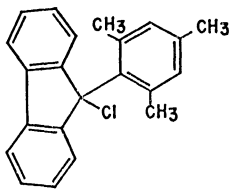


5: X=H or CH_3



6: X=H or CH_3

rotational barrier of the neopentyl group is reduced by the presence of buttressing methyl groups ($\Delta G^{\ddagger}_{298}$: 14.6 *vs.* 13.8 kcal mol^{-1}).[7] In this case, the barrier reduction was ascribed to the change in conformation of the ester group because the ester moiety can no longer be coplanar with the benzene ring in the presence of the neighboring methyl group. The barrier to exchange of the diastereotopic *o*-methyl groups was suggested to be higher in compound **7** than in **8**.[8]



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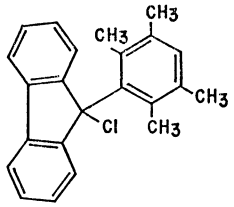

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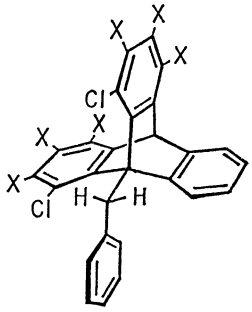
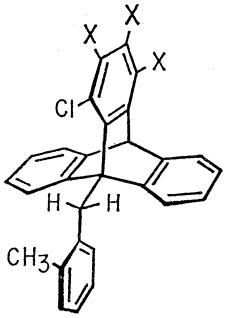
This fact was interpreted by the original authors in terms of sterically accelerated ionization followed by ion-pair return.[8] This conclusion was questioned from the results in solvent effect studies: the barriers showed no appreciable solvent dependence.[9] Thus one of the remaining possibilities is the restricted rotation about the C_9–C_{ar} bond which is subjected to the "negative" buttressing effect.

Several examples of the buttressing effect in sp^3-sp^3 systems have been found during the course of our studies on rotational barriers in 9-substituted triptycene derivatives. Dynamic NMR studies revealed that the barrier to the $+sc \rightleftarrows -sc$ interconversion in **9b** is 2.0



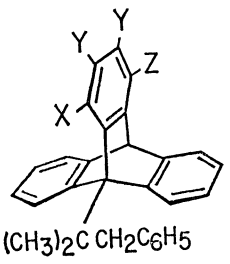
9a: X=H
9b: X=Cl



10: X=H or Cl

kcal mol^{-1} higher than in **9a** ($\Delta G^{\ddagger}_{c}$: 18.1 kcal mol^{-1} at 100 °C *vs.* 16.1 kcal mol^{-1} at 60 °C).[10] This suggests that the buttressing effect destabilizes the transition state to a greater extent than the ground state. A similar but less remarkable trend was also observed in the stereodynamics of compounds **10**.[11]

Recently we found an interesting dependence of the energy barrier to rotation upon the *peri*-substituent in 9-*t*-alkyltriptycenes.[12,13] In a series of 9-(1,1-dimethyl-2-phenylethyl)triptycene derivatives (**11**—**17**), the



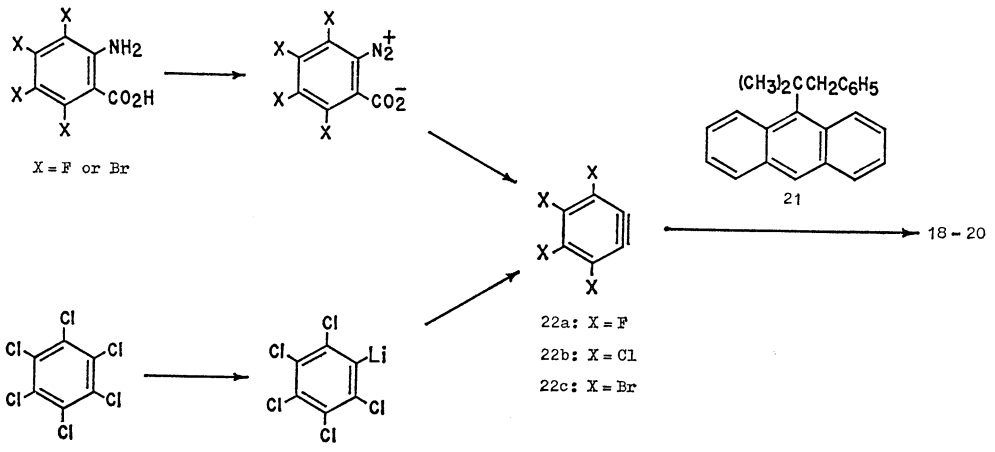
	X	Y	Z
11	H	Cl	H
12	F	H	H
13	Cl	H	H
14	Br	H	H
15	OCH_3	H	OCH_3
16	CH_3	H	CH_3
17	CF_3	H	H
18	F	F	F
19	Cl	Cl	Cl
20	Br	Br	Br

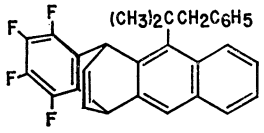
compounds with small *peri*-substituents, **12** and **15**, show higher barriers ($\Delta G^{\ddagger}_{500}$: 43.2 and 42.5 kcal mol^{-1}, respectively) than the *peri*-unsubstituted derivative **11** ($\Delta G^{\ddagger}_{500}$: 40.4 kcal mol^{-1}), but the *peri*-chloro compound **13** has almost the same barrier ($\Delta G^{\ddagger}_{500}$: 40.4 kcal mol^{-1}) as **11** and those with the even bulkier *peri*-substituent, **14**, **16**, and **17**, have lower barriers than **11**, the barrier height decreasing in this order ($\Delta G^{\ddagger}_{500}$: 39.2, 38.4, and 33.8 kcal mol^{-1}, respectively).[13] This implies that the presence of a bulky *peri*-substituent destabilizes the transition state to a lesser extent than the ground state.

It seemed interesting to investigate how the buttressing effect affects the energy barrier in these circumstances. We report in this paper the kinetic studies on the rotational barriers in 9-(1,1-dimethyl-2-phenylethyl)-1,2,3,4-tetrahalotriptycenes (**18**—**20**) to provide clear examples of the "negative" buttressing effect, comparing the data with those for the 1-halo counterparts **12**—**14** reported before.[13] The "positive" and the "negative" buttressing effects observed are discussed in terms of the molecular deformation in this highly congested system.[14]

Results

Syntheses. The tetrahalotriptycenes **18**—**20** were synthesized by reactions of 9-(1,1-dimethyl-2-phenylethyl)anthracene (**21**) with tetrahalobenzynes **22a**—**22c**. Tetrafluoro- and tetrabromobenzynes were generated by pyrolysis of the corresponding tetrahalo-2-diazoniobenzoates prepared from the respective anthranilic acids, while tetrachlorobenzyne was generated by pyrolysis of pentachlorophenyllithium prepared from hexachlorobenzene and butyllithium.[15] Reaction of either **22b** or **22c** with **21** afforded the *ap* atropisomer of the respective triptycene as a sole product.[17] Tetrafluorobenzyne (**22a**) reacted with **21** to give two products in a 3:2 ratio. The major product was the desired triptycene *ap*-**18**, and the minor one was assigned to a 1,4-adduct **23** by the ^{1}H NMR spectrum. As the chromatographic separation of **23** from *ap*-**18** seemed tedious, isolation of *ap*-**18** was performed by oxidative degradation of **23** with potassium permanganate followed by chromatography. The $\pm sc$ rotamers of **18**—**20** were isolated in pure forms from the equilibrated mixture of the rotamers by column chromatography. In each case, the $\pm sc$ rotamer eluted faster than the corresponding *ap* rotamer, in sharp contrast with the behavior exhibited by the 1-halo derivatives **12**—**14**, where the *ap* rotamers eluted faster.[13]





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Kinetics. Kinetic measurements of rotamer isomerization were performed in 1-chloronaphthalene solutions according to the procedure described before.[13] Equilibrium and rate constants at several temperatures and the free energies of activation therefrom are compiled in Table 3. Allowance for the degeneracy of the $\pm sc$ rotamers is made in the calculations of the van't Hoff and the Eyring parameters, which are given in Table 1. Table 2 shows a comparison of the data with those of the 1-halo counterparts. Comparison is made at 240 °C for the fluoro pair and at 175 °C for the chloro and the bromo pairs. The reference temperatures are chosen because they are nearly the midpoints of the temperature range in which the kinetic measurements were made for each pair.

Discussion

Buttressing Effect on the Ground State Properties. A 9-*t*-alkyltriptycene is a highly congested molecule with some of the atoms in 9-*t*-alkyl group locating within the sum of the van der Waals radii from the triptycyl skeleton. Substitution at a *peri*-position increases the congestion so that the C_9–C_{alkyl} bond is forced to bend away from the *peri*-substituent. This feature was actually observed in the X-ray structure of 9-*t*-butyl-1,2,3,4-tetrachlorotriptycene.[18] It deserves to mention here that the 1,2,3,4-tetrachlorobenzo group is almost planar including the chloro groups. It would not have been possible to discuss the buttressing effect if the chloro groups deviated seriously from coplanarity. We assume the compounds in question take the similar structure. Then 9-(1,1-dimethyl-2-phenylethyl)-1,2,3,4-tetrahalotriptycenes (**18**—**20**) are supposed to be more crowded than the corresponding 1-halo compounds (**12**—**14**) in the vicinity of the axis bond.

A long-range spin-spin coupling is observed between the 1-fluorine and protons in the $\pm sc$-methyl group in any of the fluorine-containing atropisomers.[19] The coupling constant is larger in a tetrafluoro rotamer (9.2 Hz in *ap*-**18**, and 8.3 Hz in $\pm sc$-**18**) than in the corresponding monofluoro one (8.4 Hz in *ap*-**12** and 7.9 Hz in $\pm sc$-**12**), which may be the consequence of the closer proximity between the methyl group and the 1-fluorine in the tetrafluoro rotamers than in the monofluoro counterparts.

The buttressing effect in the ground state is manifested in the rotamer equilibrium. Table 2 shows that the equilibrium constants ($\pm sc/ap$) for the tetrahalo compounds are slightly smaller than those for the monohalo counterparts regardless of the kind of halogen. Increase in congestion by the presence of the buttressing halogens should cause a greater destabilization of the $\pm sc$ rotamer than the *ap* because the former has the bulkier benzyl group in the $\pm sc$ site. Thermodynamic data on **11**—**17** show that the equilibrium constant monotonously decreases as the bulkiness of the *peri*-substituent becomes larger. In this context, the buttressing effect in the ground state is understood as the increase in the effective bulkiness of the *peri*-halogen substituent in the tetrahalo compounds relative to the respective monohalo ones.

Buttressing Effect on the Rotational Barriers. Phenomenological Aspects: Plotting the barriers to rotation in 1-substituted 9-(1,1-dimethyl-2-phenylethyl)triptycenes **11**—**17** against the bulkiness (van der Waals radius) of the 1-substituent, we find a maximum at the 1-fluoro compound **12** and a gradually descending curve as the bulkiness increases.[13] This will imply that in compounds with a *peri*-substituent bulkier than fluorine, the presence of a buttressing substituent should lower the barrier, exhibiting the negative buttressing effect.

The tetrachloro compound **19** isomerizes 13 times faster than the monochloro counterpart **13** at 175 °C with the barrier drop of 2.3 kcal mol^{-1}, manifesting the negative buttressing effect. Even more conspicuous negative effect is found in the tetrabromo compound **20**, which isomerizes 100 times faster than the monobromo one **14** at 175 °C, the drop in the free energy of activation being 4.1 kcal mol^{-1}. Appearance of the negative effect in these compounds are in line with the expectation discussed above. A greater magnitude of the effect in the tetrabromo compound **20** than in the tetrachloro one **19** is also reasonable on the ground

Table 1. Thermodynamic and kinetic parameters for 9-(1,1-dimethyl-2-phenylethyl)-1,2,3,4-tetrahalotriptycenes[a)]

Compound	ΔH° / kcal mol^{-1}	ΔS° [b)] / eu	ΔH^* / kcal mol^{-1}	ΔS^* [b)] / eu
18	0.29±0.43	−0.2±0.8	41.1±0.3	−5.7±0.6
19	1.45±0.02	0.2±0.1	32.6±0.5	−11.5±1.2
20	1.70±0.10	0.4±0.3	30.7±0.1	−8.8±0.3

a) Obtained from the data shown in Table 3. b) Degeneracy of $\pm sc$ rotamers is taken into account.

Table 2. Comparison between the tetrahalo and the monohalo compounds

Compound	Temp / °C	K	k_1 / s^{-1}	ΔG^* / kcal mol^{-1}	$\Delta\Delta G^*$ / kcal mol^{-1}	$k_1(X_4)/k_1(X)$
18	240	1.35	1.9×10^{-6}	44.0	0.7	0.5
12[a)]	240	1.53	3.8×10^{-6}	43.3		
19	175	0.44	3.6×10^{-6}	37.8	−2.3	13
13[a)]	175	0.52	2.8×10^{-7}	40.0		
20	175	0.37	1.1×10^{-4}	34.7	−4.1	100
14[a)]	175	0.43	1.1×10^{-6}	38.8		

a) Ref. 13.

Table 3. Thermodynamic and kinetic data

$$ap \underset{k_{-1}}{\overset{2k_1}{\rightleftharpoons}} \pm sc \quad K=2k_1/k_{-1}$$

Compound	Temp / °C	K	k_1 / s^{-1}	ΔG^* / kcal mol^{-1}	Bath liquid
18	258	1.35	7.40×10^{-6}	44.1_6	Diphenyl ether
	246	1.35	2.88×10^{-6}	44.1_2	Diethylene glycol
	238	1.36	1.55×10^{-6}	44.0_4	Quinoline
	226.5	1.33	5.99×10^{-7}	43.9_8	Hexylbenzene
19	208	0.49	4.80×10^{-5}	38.1_2	Nitrobenzene
	196	0.47	2.01×10^{-5}	37.9_6	1,2-Ethanediol
	184.5	0.45	7.62×10^{-6}	37.8_9	1,2-Propanediol
	162	0.42	1.20×10^{-6}	37.5_8	Mesitylene
20	202[a)]	0.40			Silicone oil
	175	0.37	1.12×10^{-4}	34.6_9	Decane
	166	0.35	5.47×10^{-5}	34.6_0	Mesitylene
	157	0.33	2.49×10^{-5}	34.5_4	Bromobenzene
	133	0.30	2.87×10^{-6}	34.3_2	Chlorobenzene

a) Only the equilibrium constant is obtained.

mentioned above, because both the buttressing and the buttressed halogens are bulkier in **20** than in **19**.

As for the tetrafluoro compound **18**, it is difficult to predict *a priori* the sign of the buttressing effect, since the 1-fluoro compound **12** gives a maximal barrier in the series of compounds **11**—**17**: the introduction of a buttressing substituent could lower the barrier, if a phantom substituent smaller than fluorine gives a real maximum in the series, and the reverse could occur if a phantom substituent a little bulkier than fluorine gives a maximum. In practice, the tetrafluoro compound **18** isomerizes twice slower than the monofluoro one **12** at 240 °C, exhibiting a small positive buttressing effect. This fact is an indication that a compound with a *peri*-substituent slightly bulkier than fluorine, if existed, should give a maximal barrier in a series of 1-substituted 9-(1,1-dimethyl-2-phenylethyl)triptycenes.

Analysis of the Barrier: Although the simple explanation in terms of the increase in the effective bulkiness of the *peri*-halogen substituent is possible for the observed buttressing effect, it turns out to be too rough in some cases. For example, the equilibrium constant for the tetrachloro compound **19** (0.44 at 175 °C) is almost identical with that for the monobromo compound **14** (0.43), and hence we can say that the 1-chlorine in **19** has almost the same effective bulkiness as the 1-bromine in **14**. However, the rotational barrier in **19** is lower than that in **14** by 1.0 kcal mol^{-1}. This implies that the buttressing effect on the energy barrier operates somewhat differently from that on the ground state and thus we must consider the effect on the transition state in some detail.

We have developed a hypothesis which uses a rigid rotor model to explain the observed dependence of the barrier on the bulkiness of the 1-substituent; that is, the lowering of the barrier with the increasing bulkiness of the *peri*-substituent should at least partly ascribed to lowering of the transition state energy.[13] The hypothesis states that a bulky *peri*-substituent in-

duces the deformation of the molecule typically manifested in the tilting of the axis bond of the 9-substituent away from the *peri*-substituent. If this feature is retained during the rotation about the axis bond, the maximal eclipsing interactions between the β-groups of the 9-substituent and the *peri*-substituent or hydrogens do not occur simultaneously at the three sites but sequentially with some time lags. Therefore, the transition state is not destabilized to such an extent that would be expected from the bulkiness of the *peri*-substituent, causing the decrease in the barrier. As the *peri*-substituent becomes bulkier, these time lags should become larger and hence the barrier should become lower, which was actually observed.

However this hypothesis still fails to explain the differential behavior observed in compounds **14** and **19**. The fact that **19** has a lower barrier to rotation than **14** suggests that the transition state for rotation in **19** is more "stabilized" than that in **14** relative to the respective ground state. A possible rationalization may be as follows. In order to relieve a large congestion in the transition state, 9- and *peri*-substituents further bend away from each other. While the 1-bromo group in **14** is prone to easy in-plane bending away from the 9-substituent, the bending of the 1-chloro group in **19** is restricted because of the buttressing effect. Hence the axis bond of the 9-substituent in **19** suffers a greater additional tilting than that in **14** on going from the ground to the transition state. This results in the larger time lags between the maximal eclipsing interactions in the transition state and thus the lower barrier in **19** than in **14**.

Thus we have to admit that the molecule is subjected to further deformation in the course of internal rotation for the better understanding of the buttressing effect. We conclude that the negative buttressing effect is originated from the fact that the transition state for rotation is less destabilized than the ground state upon introduction of a buttressing substituent.

Experimental

Melting points are not corrected. ^{1}H NMR spectra were obtained on a Hitachi R-20B (60 MHz) or a Varian EM-390 (90 MHz) spectrometer with tetramethylsilane as an internal reference. ^{19}F NMR spectra were recorded on a Varian EM-390 at 84.67 MHz with hexafluorobenzene as an internal reference, and the chemical shifts are given in ppm downfield from C_6F_6.

ap-*9-(1,1-Dimethyl-2-phenylethyl)-1,2,3,4-tetrafluorotriptycene* (ap-**18**). A solution of 1.05 g (5 mmol) of 1,2,3,4-tetrafluoroanthranilic acid[20] in 15 mL of dry acetone was added dropwise to a boiling solution of 764 mg (2.46 mmol) of 9-(1,1-dimethyl-2-phenylethyl)anthracene (**21**)[21] and 1 mL of isopentyl nitrite in 20 mL of dichloromethane during the course of 1 h. The mixture was heated under reflux for 1 h and evaporated. The residue was chromatographed through an alumina column. The desired triptycene *ap*-**18** and a by-product, which was assigned to the 1,4-adduct (**23**) by its ^{1}H NMR [($CDCl_3$, δ): 1.80 (3H, s), 1.86 (3H, s), 3.33 and 3.67 (2H, AB-q, J=13.2 Hz), 5.42 (1H, td J=1.7 and 6.0 Hz), 5.99 (1H, br d, J=6.2 Hz), 6.34 (1H, ddd, J=1.6, 6.2, and 7.2 Hz)], eluted together, which weighed 519 mg (47%). The mixture was dissolved in 20 mL of acetone and chilled to 0 °C, to which a solution of 190 mg of potassium permanganate in 15 mL of water was added dropwise. The mixture was stirred at 0 °C for 2 h and evaporated. The residue was extracted with dichloromethane and chromatographed through an alumina column with hexane as eluent affording 208 mg (19% based on **21**) of *ap*-**18** as colorless crystals, mp 192—194 °C (from benzene–hexane). Found: C, 78.76; H, 5.08%. Calcd for $C_{30}H_{22}F_4$: C, 78.59; H, 4.84%. ^{1}H NMR ($CDCl_3$, δ): 2.04 (6H, d, J=9.2 Hz), 3.87 (2H, s), 5.74 (1H, br d, J=1.6 Hz), 6.9—7.7 (11H, m), 8.08 (2H, m). ^{19}F NMR ($CDCl_3$): 2.96 (t, J=19.5 Hz, 2-F), 3.59 (ddd, J=22.0, 19.4, and 5.3 Hz, 3-F), 12.80 (dd, J=22.0 and 13.7 Hz, 4-F), 38.05 (br, 1-F).

±sc-*9-(1,1-Dimethyl-2-phenylethyl)-1,2,3,4-tetrafluorotriptycene* (±sc-**18**). The equilibrated mixture of the rotamers was chromatographed on alumina with hexane as eluent. The ±*sc* rotamer eluted faster than the *ap*, and was recrystallized from tetrahydrofuran–hexane, mp 203—204 °C. Found: C, 78.88; H, 4.66%. Calcd for $C_{30}H_{22}F_4$: C, 78.59; H, 4.84%. ^{1}H NMR ($CDCl_3$, δ): 1.95 (3H, d, J=8.3 Hz), 2.09 (3H, s), 2.61 (1H, d, J=14.1 Hz), 3.97 (1H, dd, J=14.1 and 2.4 Hz), 5.70 (1H, br d, J=1.6 Hz), 6.9—7.7 (12H, m), 7.81 (1H, m). ^{19}F NMR ($CDCl_3$): 3.24 (t, J=19.8 Hz, 2-F), 4.03 (ddd, J=22.9, 19.8, and 6.1 Hz, 3-F), 12.79 (dd, J=22.9 and 13.4 Hz, 4-F), 40.40 (br, 1-F).

ap-*1,2,3,4-Tetrachloro-9-(1,1-dimethyl-2-phenylethyl)triptycene* (ap-**19**). To a suspension of 3.68 g (12.9 mmol) of hexachlorobenzene in 200 mL of diethyl ether was added dropwise a solution of 13 mmol of butyllithium in hexane at −78 °C. The mixture was stirred at −78 °C until the solid had disappeared, to which an ethereal solution of 1.5 g (4.84 mmol) of **21** was added dropwise. The mixture was allowed to slowly warm up to room temperature, and then heated under reflux for 2 h. Column chromatography on alumina with hexane–benzene as eluent gave a mixture of *ap*-**19** and unidentified by-products, presumably polychlorobiphenyls. Repeated chromatographies and recrystallizations from tetrahydrofuran–methanol afforded a pure sample of *ap*-**19**, mp 283—285 °C. Found: C, 68.73; H, 4.25; Cl, 26.79%. Calcd for $C_{30}H_{22}Cl_4$: C, 68.72; H, 4.23; Cl, 27.05%. ^{1}H NMR ($CDCl_3$, δ): 2.36 (6H, s), 3.81 (2H, s), 6.12 (1H, s), 7.0—7.6 (11H, m), 8.08 (2H, m).

±sc-*1,2,3,4-Tetrachloro-9-(1,1-dimethyl-2-phenylethyl)triptycene* (±sc-**19**). The equilibrated mixture of the rotamers was chromatographed on alumina with benzene–hexane as eluent. ±*sc*-**19** eluted faster than *ap*-**19**. Recrystallization from tetrahydrofuran–hexane afforded pure ±*sc*-**19**, mp 231—232 °C. Found: C, 68.71; H, 4.17; Cl, 26.64%. Calcd for $C_{30}H_{22}Cl_4$: C, 68.72; H, 4.23; Cl, 27.05%. ^{1}H NMR ($CDCl_3$, δ): 2.12 (3H, s), 2.37 (3H, s), 4.13 and 4.37 (2H, AB-q, J=15.2 Hz), 6.11 (1H, s), 6.9—7.7 (11H, m), 7.92 (1H, m), 8.16 (1H, m).

ap-*1,2,3,4-Tetrabromo-9-(1,1-dimethyl-2-phenylethyl)triptycene* (ap-**20**). A solution of 2.7 g (6 mmol) of tetrabromoanthranilic acid[22] in 10 mL of 1,2-dimethoxyethane (DME) was added dropwise to a boiling solution of 486 mg (1.56 mmol) of **21** and 1 mL of isopentyl nitrite in 20 mL of DME during the course of 2.5 h. The mixture was heated under reflux for 1 h, evaporated and chromatographed on alumina with dichloromethane–hexane as eluent, affording 194 mg (18%) of *ap*-**20**, mp 291—293 °C (from tetrahydrofuran–hexane). Found: C, 51.30; H, 2.88%. Calcd for $C_{30}H_{22}Br_4$: C, 51.32; H, 3.16%. ^{1}H NMR ($CDCl_3$, δ): 2.51 (6H, s), 3.75 (2H, s), 6.24 (1H, s), 7.0—7.6 (11H, m), 8.10 (2H, m).

±sc-*1,2,3,4-Tetrabromo-9-(1,1-dimethyl-2-phenylethyl)triptycene*

*(±sc-**20**).* Addition of hexane to the equilibrated mixture of rotamers of **20** in 1-chloronaphthalene caused selective crystallization of *ap*-**20**, leaving the ±*sc*-enriched mixture in the mother liquor, which was chromatographed on alumina with hexane as eluent. The ±*sc* rotamer eluted slightly faster than the *ap*. The fractions containing almost pure ±*sc*-**20** was evaporated and recrystallized from tetrahydrofuran–hexane, affording a pure sample of ±*sc*-**20**, mp 223—225 °C. Found: C, 51.57; H, 3.28; Br, 45.55%. Calcd for $C_{30}H_{22}Br_4$: C, 51.32; H, 3.16; Br, 45.52%. ^{1}H NMR ($CDCl_3$, δ): 2.01 (3H, s), 2.57 (3H, s), 4.08 and 4.67 (2H, AB-q, J=15.5 Hz), 6.23 (1H, s), 6.9—7.7 (11H, m), 7.95 (1H, m), 8.15 (1H, m).

Kinetic Measurements. The experimental procedures described before[13] were followed. Relative populations of the rotamers were obtained by integrating the 1-fluorine signals for **18** and the *gem*-dimethyl signals for **19** and **20**. The liquids used for the boiling bath were shown in Table 3. The equilibrium constant for **20** at 202 °C was obtained in a conventional silicone oil bath.

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