atropisomers and of the *E* and *Z* isomers (Figure 4b). In fact the atropisomers equilibrated much more rapidly than isomerization occurs around the imino bond. When a sample of **2** in $[^{2}\mathrm{H}_8]$toluene solution was warmed to ca. 90 °C, the signals of the atropisomers ZA and ZB broadened and coalesced owing to the onset of fast rotation of the 1-naphthyl group on the NMR time scale. Application of the graphical procedure of Jaeschke et al.[11] to the coalescing NCH*Me* doublets ($\Delta\nu$ = 1.8 Hz, line width in the absence of exchange = 0.65 Hz) gave k = 3.2 s^{-1} and $\Delta G^{\ddagger}$ = 20.5 kcal mol^{-1} at the coalescence temperature of 89 °C. The barrier is similar to that measured previously ($\Delta G^{\ddagger}$ = 20.4 kcal mol^{-1}) for 1-naphthyl rotation in a related imine derived from 1-acetylnaphthalene using a prochiral *N*-isopropyl substituent to monitor the process.[12] The atropisomerization probably also accounts for a very rapid initial decrease in optical rotation of imine **2** observed in the first few minutes after dissolution in CD_3OD. This preceded the much slower *E–Z* isomerization process depicted in Figure 1 and corresponds to a half-life in the region of 1 min at 28 °C and a $\Delta G^{\ddagger}$ value of ca. 20 kcal mol^{-1}. This estimate is in good agreement with the naphthyl rotation barrier determined in $[^{2}\mathrm{H}_8]$toluene solution by dynamic NMR.

Experimental Section

Mutarotation studies were carried out by using a Perkin-Elmer Model 241 automatic polarimeter equipped with a thermostatically controlled (±0.5 °C) cell and a chart recorder. NMR spectra were obtained on a Bruker WH-90, Bruker WM-250, or a Varian XL-100 spectrometer.

The imines were obtained by condensation of the appropriate ketone with optically pure 1-phenylethylamine using either a Dean–Stark trap and refluxing xylene containing a trace of *p*-toluenesulfonic acid,[6] or the $TiCl_4$ catalyzed method.[12]

N-[1-Phenylethylidene]-1-phenylethylamine (**1**) prepared from (*S*)-(−)-1-phenylethylamine had bp 110–115 °C (0.005 mm) [lit.[6] bp 123 °C (1.0 mm)] and $[\alpha]_D$ +74° ($CHCl_3$).

N-[1-(1′-Naphthyl)ethylidene]-1-phenylethylamine (**2**) prepared from (*R*)-(+)-1-phenylethylamine had bp 120–125 °C (0.01 mm), mp 85–86 °C, and $[\alpha]_D$ +95° ($CHCl_3$). Anal. Calcd for $C_{20}H_{19}N$: C, 87.9; H, 7.0; N, 5.1. Found: C, 88.0; H, 7.2; N, 5.15.

N-(1-Phenyl-2-methylpropylidene)-1-phenylethylamine (**3**) prepared from (*S*)-(−)-1-phenylethylamine had bp 114–115 °C (0.01 mm) [lit.[6] bp 121 °C (0.4 mm)] and $[\alpha]_D$ −130° ($CHCl_3$).

^{1}H and ^{13}C NMR data for imines **1**–**3** are given in Table I.

Registry No. (*E*)-**1**, 100483-17-8; (*Z*)-**1**, 100483-18-9; (*E*)-**2**, 100430-66-8; (*Z*)-**2**, 100430-65-7; (*Z*)-**3**, 100483-19-0; $PhCOCH_3$, 98-86-2; $PhCOCH(CH_3)_2$, 611-70-1; (*S*)-1-phenylethylamine, 2627-86-3; (*R*)-1-phenylethylamine, 3886-69-9; 1-acetylnaphthalene, 941-98-0.

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[11] Jaeschke, A.; Muensch, H.; Schmid, H. G.; Friebolin, H.; Mannschreck, A. *J. Mol. Spectrosc.* **1969**, *31*, 14.

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2,2′-Dicarbomethoxy-9,9′-bitriptycyl. Synthesis, Conformational Stability, and Separation and Identification of the Conformers[1]

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Received August 20, 1985

The synthesis of 2,2′-dicarboxy-9,9′-bianthryl (**6d**) was achieved in four steps from 2-chloroanthrone (**7**). Resolution with quinidine yielded optically pure **6d**, which was converted to the corresponding dimethyl ester (**6c**) with CH_2N_2. Optically pure **6c** was converted to 2,2′-dicarbomethoxy-9,9′-bitriptycyl (**5c**) with excess anthranilic acid and *n*-butyl nitrite. Compound **5c** was shown to be conformationally stable. The anti (**5c′**) and gauche (**5c″**, **5c‴**) conformers were separated and identified. A precise value of the rotational barrier of **5c** could not be measured, but a minimum value of 55 kcal/mol was established. The gauche conformer was shown to be only 30% optically pure. This is taken to indicate that the rate of addition of the second benzyne, in the conversion of **6c** to **5c**, and the rate of rotation about the central bond in the monoadduct, 2-carbomethoxy-9-(2′-carbomethoxy-9′-anthracyl)triptycene (**9**), are of comparable magnitudes.

Restricted rotation between sp^3 hybridized carbon atoms has been the subject of considerable activity over the past 20 years. Many attempts have been made to devise systems with high rotational barriers, to separate conformers, and to examine the factors which influence rotational barriers, both experimentally and theoretically.[2] Generally, larger interfering substituents result in larger barriers. However, Ōki and co-workers have shown that rotational barriers can decrease as the interfering groups become larger. This effect has been attributed to ground-state strain and molecular distortion, which leads to sequential rather than simultaneous passage of groups past each other.[2b,3] Most of the reported examples of conformationally stable substituted ethanes contain a 1-substituted bicyclo[2.2.2]octatriene backbone (**1**), e.g., **2**,[4] **3**,[5] and **4**,[6] which insures that three of the six interfering substituents are directed toward the other three.

Early on, we chose to study the 9,9′-bitriptycyl system **5**.[7] In contrast to compounds of the type illustrated by

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[1] This work was supported in part by grants from the National Science Foundation (GP 3511, GP 6404), the City University of New York, and the City College Faculty Senate Committee on Research and Publication.

[2] Many publications are worthy of mention. The following review articles contain pertinent references. (a) Long, D. A. *J. Mol. Struct.* **1985**, *126*, 9. (b) Ōki, M. In "Topics in Stereochemistry"; Allinger, N. L., Eliel, E. L., Wilen, S. H., Eds.; John Wiley and Sons: New York, 1983; Vol. 14.

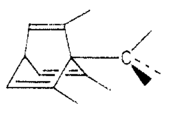
[3] (a) Yamamoto, G.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2219. (b) Yamamoto, G.; Tanaka, A.; Suzuki, M.; Morita, Y.; Ōki, M. *Ibid.* **1984**, *57*, 891. (c) Yamamoto, G.; Ōki, M. *Ibid.* **1983**, *56*, 2082. (d) Yamamoto, G.; Suzuki, M.; Ōki, M. *Ibid.* **1983**, *56*, 809. (e) Yamamoto, G.; Suzuki, M.; Ōki, M. *Ibid.* **1983**, *56*, 306.

[4] Iwamura, H. *J. Chem. Soc., Chem. Commun.* **1973**, 232.

[5] Yamamoto, G.; Ōki, M. *J. Chem. Soc., Chem. Commun.* **1974**, 713.

[6] Ōki, M.; Yamamoto, G. *Chem. Lett.* **1972**, 45.

[7] Koukotas, C.; Mehlman, S. P.; Schwartz, L. H. *J. Org. Chem.* **1966**, *31*, 1970.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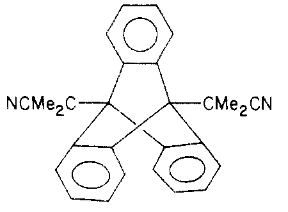
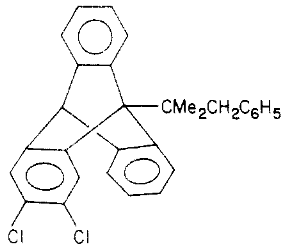
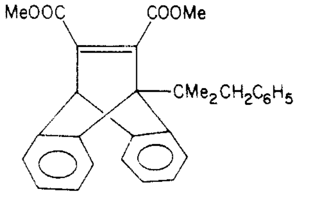


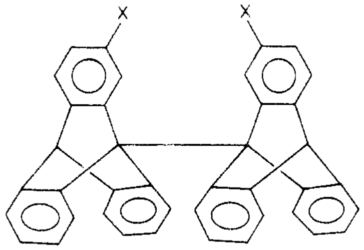
2 (E_a = 37.7 kcal/mol)



3 (E_a = 33.6 kcal/mol)



4 (E_a = 33.2 kcal/mol)



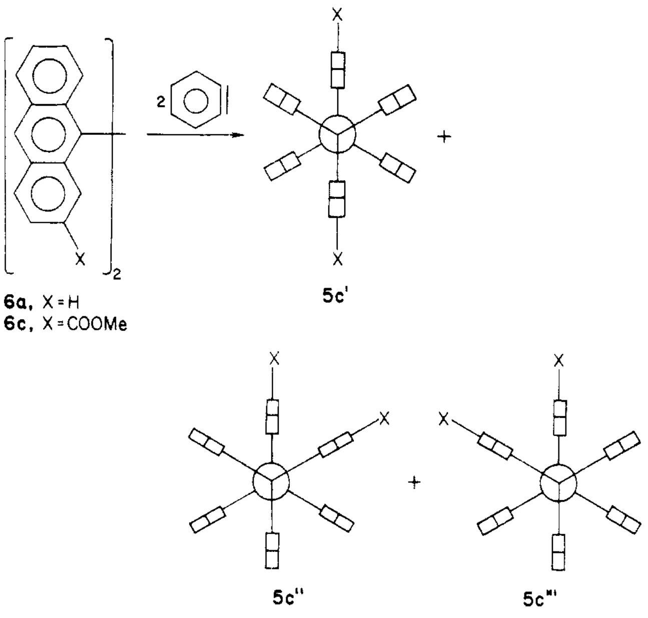
5a, X=H
5b, X=CH_3
5c, X=COOMe
5d, X=COOH

2, 3, and 4, both sets of interfering substituents in 9,9′-bitriptycyls are directed toward each other. In addition, the interfering groups are small hydrogen atoms. This minimizes ground-state strain. The combination of a high rotational transition state energy with an uncongested ground state is most favorable for a large rotational barrier.[2b] As anticipated, 2,2′-dimethyl-9,9′-bitriptycyl (**5b**) was found to have an enormous rotational barrier, a minimum of 54 kcal/mol, which represents the largest barrier reported to date.[8] However, we were not able to get a precise value for the rotational barrier because of decomposition at the high temperature employed. We also were not able to separate the conformers. We now direct attention toward 2,2′-dicarbomethoxy-9,9′-bitriptycyl (**5c**). The increased polarity of the carbomethoxy groups of **5c** compared to the methyl groups of **5b** would be expected to aid in the chromatographic separation of the conformers. If the thermal decomposition observed in the measurement of the rotational barrier of **5b** was initiated by hydrogen abstraction, due to the presence of traces of oxygen or other radical-forming species, **5c** might possibly be more stable. Finally, hydrolysis of the carbomethoxy groups to carboxyl groups would result in a handle for optical resolution. This would be one way to distinguish the chiral gauche conformer from the achiral anti conformer. In this paper we report on the synthesis, the identification of the separated conformers, and on our attempts to measure the rotational barrier of **5c**.

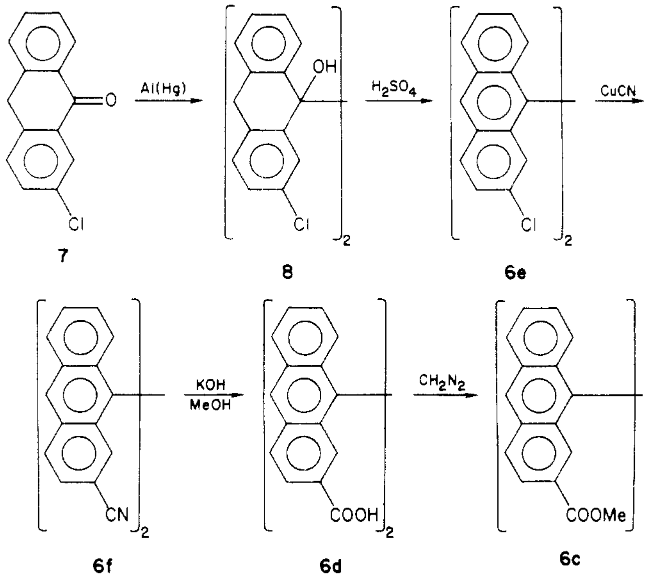
Results and Discussion

The synthesis of **5c** was achieved by the addition of benzyne to 2,2′-dicarbomethoxy-9,9′-bianthryl (**6c**) (Scheme I). In principle, **5c** could be formed in three conformations, anti (**5c′**) and two enantiomeric gauche (**5c″**, **5c‴**). 9,9′-Bianthryls **6** are appreciably less reactive toward dienophiles than is anthracene. Thus, whereas anthracene reacts readily with *p*-benzoquinone,[9] 9,9′-bianthryl (**6a**) fails to give the corresponding diadduct.[10] We have found that 9,9′-bianthryls react sluggishly and in poor yields with benzyne, while the corresponding anthracenes react readily and in relatively good yields.[11] The steric effect of one anthracene ring toward the approach of benzyne to the second anthracene ring can account for these results. Steric effects have been suggested in the addition of benzyne to 9,10-diphenylanthracene[12] and in the stereospecific syntheses of conformers of 9-substituted triptycenes.[2b] Our best results were achieved with an 8–10-fold excess of anthranilic acid and *n*-butyl nitrite as the benzyne generating reagents. Other benzyne precursors, such as 1,1-dioxo-1,2,3-benzothiadiazole, *o*-bromo-

Scheme I



Scheme II



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[8] Schwartz, L. H.; Koukotas, C.; Yu, C. S. *J. Am. Chem. Soc.* **1977**, *99*, 7710.

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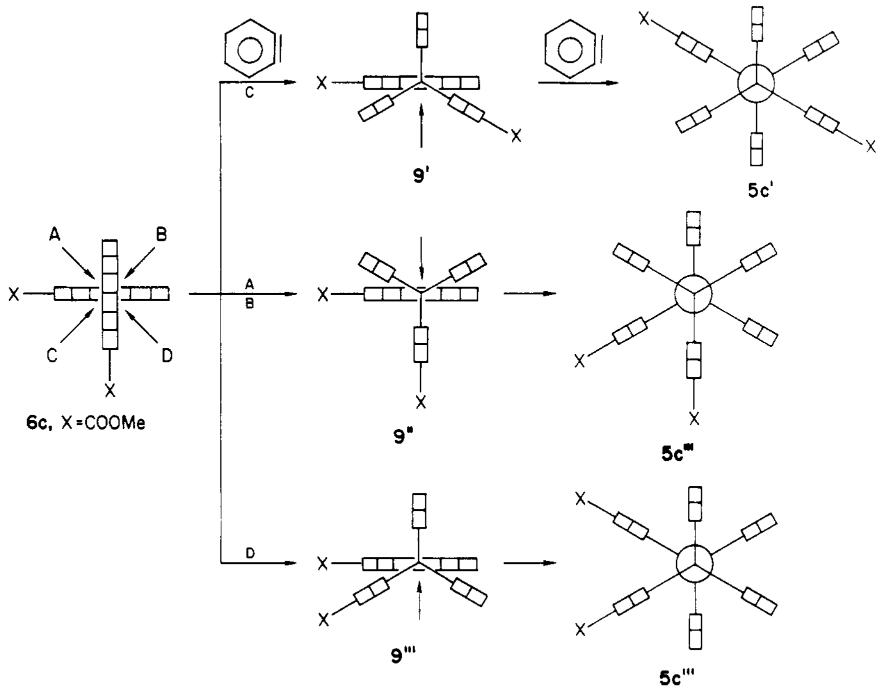
[11] Unpublished results of Koukotas, C. and Yu, C. S.

[12] Klanderman, B. H.; Criswell, T. R. *J. Org. Chem.* **1969**, *34*, 3426.

Scheme III



fluorobenzene, and *o*-diphenyliodonium carboxylate, proved to be less satisfactory in that lower yields and less pure products were generally obtained.[11]

The synthesis of **6c** is outlined in Scheme II. Details are presented in the Experimental Section.

The method we chose in order to demonstrate conformational stability in **5c** and to distinguish between the conformers, involves the reaction of benzyne with one of the enantiomers of **6c**. If the entire product, **5c**, were to exhibit optical activity, conformational stability would be confirmed.[13] The arguments and assumptions used to reach this conclusion are presented, below. This approach has an additional advantage in that the eventual establishment of the absolute configuration of **6c** would also establish the absolute configurations of **5c″** and **5c‴**. In the event that optical activity is observed, the separation of the conformers would allow the chiral gauche and achiral anti conformers to be identified.

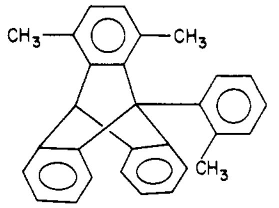
Consider the stepwise addition of two benzynes to one of the enantiomers of **6c** (Scheme III). The first benzyne is pictured as approaching the two faces of the front ring from one of four directions, A, B, C, and D. These directions minimize steric effects toward the incoming benzyne and lead to relatively strain-free conformers of the product, 2-carbomethoxy-9-(2′-carbomethoxy-9′-anthracyl)triptycene (**9**) (monoadduct). Initial addition to the rear ring would give identical results. Statistically, the ratio **9′**:**9″**:**9‴** would be 1:2:1.

The carbomethoxy groups could conceivably exert an influence on the direction of addition. Opposing effects can be envisioned. If coordination with the incoming benzyne occurs, direction C would be favored. If the carbomethoxy groups sterically impede the benzyne, direction C would be disfavored. We are not able to assess the relative magnitudes of these effects, which would alter the ratio of monoadducts formed from the statistical ratio. However, our approach for demonstrating conformational stability in **5c** would still be valid.[14]

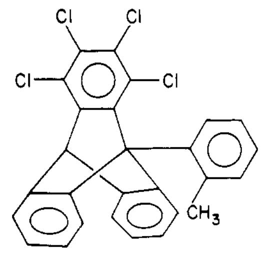
If bond rotations in monoadducts **9′**, **9″**, and **9‴** are appreciably slower than the addition of the second benzyne, we arrive at the results shown at the right of Scheme III. The additions are each pictured to occur along the direction which minimizes steric effects toward the incoming benzyne and each yields a stable, staggered conformer.[2b] Additions from other directions would lead to higher energy forms of **5c**. From one enantiomer of **6c**, a mixture of one of the enantiomeric gauche conformers (**5c‴** in the example shown in Scheme III) and the inactive anti conformer, **5c′**, would be obtained. If the effect of the carbomethoxy groups is negligible, and if the addition follows the directions shown, a mixture of three parts **5c‴** and one part **5c′** would result. This mixture would be capable of exhibiting optical activity if the rotational barrier in the 9,9′-bitriptycyl system were sufficiently large.

However, if bond rotation in the monoadduct is rapid compared to the addition of the second benzyne, **9′**, **9″**, and **9‴** will interconvert and racemize. The end result would be the formation of **5c′** and equal amounts of **5c″** and **5c‴**, i.e., the final product would be optically inactive.

Nakamura and Ōki have reported the rotational energy barriers in a variety of 9-aryltriptycenes.[15] Although the barriers in most cases were found to be substantial, between 13 and 15 kcal/mol, e.g., **10** and **11**, they were unexpectedly low based on the anticipated steric interactions in the transition states. Ground-state strain was offered as the cause. A comparison of the molecular



10 ($\Delta G^{\ddagger}$ 13.4 kcal/mol)



11 ($\Delta G^{\ddagger}$ 14.6 kcal/mol)

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[13] This approach does not require the separation of conformers.

[14] Except if direction C is the exclusive pathway. In this case, only 5c′ would form, and the product would be optically inactive, even if rotation in the 9,9′-bitriptycyl system were highly hindered.

[15] Nakamura, M.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2106.

models of **9**, **10**, and **11** suggested to us similar steric interactions in the ground states and rotational-transition states of these species. We, therefore, expected a rotational barrier in the neighborhood of 13–15 kcal/mol for **9**. We anticipated that a barrier of this magnitude would be significantly higher than the barrier for the addition of benzyne to **6c**, a necessary requirement for our approach to be successful.[16]

2,2′-Dicarboxy-9,9′-bianthryl (**6d**) was resolved with quinidine. Its specific rotation at optical purity was established by the formation of diastereomeric amides using dextrorotatory and levorotatory samples with (+)-α-phenylethylamine. Optically pure (−)-**6d** was converted to **6c** with CH_2N_2 (Scheme II). The latter was treated with an excess of anthranilic acid and *n*-butyl nitrite (Scheme I). The crude product was initially separated by column chromatography into a series of fractions which were each further purified by a combination of digestions, column chromatography, preparative TLC, and crystallizations. The entire process was monitored by NMR analysis. Two white solids, mp 483–485 °C and mp 340–361 °C, were obtained, which exhibited almost identical IR, NMR, UV, and mass spectra, each completely consistent with structure **5c**.

The higher melting solid was obtained from the early chromatographic fractions. Its optical rotation could not be determined directly because of very poor solubility in common organic solvents. Hydrolysis gave the diacid, **5d**, which could be dissolved to the extent of 1.2% in 48% aqueous dimethyl sulfoxide containing 5.5% tetramethylammonium hydroxide. The resulting solution showed no optical rotation at selected wavelengths between 589 nm and 365 nm. On this basis, the higher melting solid is assigned as the anti conformer, **5c′**.

Because of its greater solubility, the optical rotation of the lower melting solid could be determined directly. It showed $[\alpha]^{23}{}_D$ −14.7° (*c* 0.375, $CHCl_3$). This material is, therefore, the chiral gauche conformer (**5c″** and/or **5c‴**). These assignments are consistent with the more symmetrical anti conformer having the higher mp and lower solubility. The isolation of separate conformers of **5c** and the optical activity of one of them establishes the conformational stability of **5c**.

The obtain information concerning the relative rates of rotation in the monoadduct **9** and addition of benzyne to **9**, we determined the enantiomeric purity of the gauche conformer (**5c″**, **5c‴**). An NMR analysis using the chiral shift reagent tris[3-[(heptafluoropropyl)hydroxymethylene]-*d*-camphorato]europium(III) (Eu(hfc)$_3$) was carried out. Addition of Eu(hfc)$_3$ caused the OCH_3 peak to split into two closely spaced singlets ($\Delta\delta$ 0.12) of unequal intensities. The low field singlet corresponded to approximately 65% of the total absorption and is assigned to the levorotatory gauche conformer on the basis of the overall negative optical rotation of the mixture of gauche conformers obtained. The optical purity of this mixture, obtained from optically pure **6c**,[17] is, therefore, 30%. This low value suggests that rotation about the central bond in the monoadduct is competitive with the addition of the second benzyne.

Our attempts to obtain a precise value for the rotational barrier of **5c** were not successful. Samples of the anti and gauche conformers of **5c** were heated in naphthalene solution under a N_2 atmosphere at 300 °C in a sealed tube. Decomposition was indicated by the darkening of the solution. Within 24 h, the solution was brown. Heating was continued for a maximum of 170 h. The NMR spectra of the recovered samples indicated no interconversion of conformers. It is estimated that a conversion of the one part in 180 could be detected. Assuming an Arrhenius preexponential value of 10^{13},[2b] the minimum rotational barrier is calculated to be 55 kcal/mol. This is within 1 kcal/mol of that previously found for **5b**.

The calculated minimum barrier is rather insensitive to small changes in the experimental conditions. In light of the observed thermal decomposition, a change to even harsher conditions did not appear to be worthwhile. For example, an extension of the heating period by 24 h increases the minimum barrier by 0.15 kcal/mol. An increase in temperature to 325 °C increases the minimum barrier by 2.4 kcal/mol.

Experimental Section

IR spectra were recorded on Beckman IR-20A and Perkin-Elmer 137 spectrometers. NMR spectra were recorded on Joelco JNM-MH-100 and IBM WP-200SY spectrometers. UV spectra were measured on a Cary 15 spectrometer. Optical rotations were determined on a Perkin-Elmer 141 polarimeter. Mass spectra were determined on a Varian CH5 instrument with linear mass scan. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points were determined in open capillary tubes and are corrected.

2,2′-Dichloro-9,9′-anthrapinacol (8). Aluminum amalgam was prepared by heating a well-stirred mixture of 6 g of aluminum powder (20 mesh and finer), 2 g of $HgCl_2$, and 80 mL of tetrahydrofuran for 30 min at reflux. After cooling, the THF solution was decanted, and the metallic residue was washed once with 30 mL of THF and once with 30 mL of benzene. The aluminum amalgam was used immediately.

A mixture of 10 g of 2-chloroanthrone (**7**), 300 mL of benzene, and the amalgam was heated at reflux with stirring for 30 min. The heat source was removed, and 60 mL of absolute ethanol were carefully added with stirring. After the exothermic reaction had subsided, the heat source was replaced, and the mixture was heated at reflux with stirring for an additional 6 h. During this heating period the mixture became extremely viscous. After cooling, 75 mL of 2.4 M HCl was cautiously added with good stirring and the mixture was stirred vigorously for 15 min. The organic layer was washed with water, dried, and evaporated to yield crude product. Purification was effected by digestion with refluxing hexane or cyclohexane. The product at this stage (average yield 60–70%) was sufficiently pure for conversion to **6e**. Crystallization of a sample from benzene–cyclohexane (1:1) gave **8** as white crystals: mp 182–184 °C; IR (KBr) 3520 cm^{-1}; mass spectrum, *m/e* (relative intensity) 444 (10), 442 (43), 440 (60), 426 (5), 424 (21), 422 (37), 231 (34), 230 (53), 229 (100), 228 (99). Anal. Calcd for $C_{28}H_{20}O_2Cl_2$: C, 73.21; H, 4.39; Cl, 15.44. Found: C, 73.03; H, 4.31; Cl, 15.44.

2,2′-Dichloro-9,9′-bianthryl (6e). A mixture of 3 g of **8**, 30 mL of HOAc, and 30 mL of 70% aqueous H_2SO_4 was heated with stirring for 5 h at 98 °C, cooled, diluted with 200 mL of H_2O, and filtered. The resulting solid was thoroughly washed with water, digested with 150 mL of hot 95% aqueous EtOH, and finally washed several times with cold EtOH to yield 2.1 g of **6e**, sufficiently pure for conversion to **6f** [mp 280–282 °C; IR (KBr) identical with that of a purified sample]. This tan product could be further purified by crystallization from EtOH–C_6H_6 (2.5:1): mp 296–298 °C (lit[18] mp 289 °C); mass spectrum, *m/e* (relative intensity) 426 (15), 424 (63), 422 (100), 389 (2), 387 (7.5), 385 (10.5), 352 (10.5), 351 (26), 350 (28).

2,2′-Dicyano-9,9′-bianthryl (6f). A mixture of 20 g of **6e**, 48 g of CuCN, and 450 mL of *N*-methyl-2-pyrrolidinone was heated at reflux with stirring for 72 h and cooled. A solution of 250 g

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[16] The use of molecular models for the quantitative prediction of steric effects is very risky. In our case, we had a backup method for demonstrating conformational stability in **5c**. A successful separation of the anti (**5c′**) and gauche (**5c″**, **5c‴**) conformers would also prove the point.

[17] It is assumed that conversion of optically pure **6d** to **6c** with CH_2N_2 proceeded with complete retention.

[18] Bergmann, E. D.; Hirschfield, A. *Tetrahedron Lett.* **1965**, 4129.

of $FeCl_3 \cdot 6H_2O$ in 65 mL of HCl and 400 mL of H_2O was added. The resulting mixture was heated at 75–80 °C for 1.5 h and diluted with 2 L of H_2O to yield a black solid, which was thoroughly washed with H_2O, followed by a few portions of warm 95% EtOH. The crude product was extracted into $CHCl_3$ and decolorized with activated carbon. Crystallization from $CHCl_3$–95% EtOH (1:2) yielded yellow crystals [mp 341–346 °C]. Mass spectral analysis indicated the presence of 2-chloro-2′-cyano-9,9′-bianthryl. Further purification was achieved by chromatography on silica gel by using C_6H_6–$CHCl_3$ (1:1) as eluent, followed by crystallization from C_6H_6 to give greenish yellow crystals (28%): mp 342.5–345.5 °C; IR (KBr) 2250 cm^{-1}; mass spectrum, m/e (relative intensity) 404 (100), 378 (13), 377 (15). Anal. A solution of 250 g of $FeCl_3 \cdot 6H_2O$ in 65 mL of HCl and 400 mL of H_2O was added. Calcd for $C_{30}H_{16}N_2$: C, 89.08; H, 3.99; N, 6.93. Found: C, 89.38; H, 3.94; N, 7.04.

2,2′-Dicarboxy-9,9′-bianthryl (6d). A suspension of 3 g of **6f** in a solution containing 94 g of KOH in 100 mL of H_2O and 375 mL of MeOH was heated at reflux for 28 h. Dilution with water, filtration, and acidification yielded crude **6d**. Crystallization from HOAc gave yellow crystals (78%): mp 412–417 °C; IR (KBr) 3300–2500, 1700 cm^{-1}; mass spectrum, m/e (relative intensity) 442 (100), 398 (32), 350 (28). Anal. Calcd for $C_{30}H_{18}O_4$: C, 81.45; H, 4.10. Found: C, 81.32; H, 4.53.

Resolution of 6d. A suspension of 9.52 g of **6d** in 750 mL of hot acetone was slowly added to a boiling solution of 16.4 g of quinidine·2.5 H_2O in 1.1 L of acetone. After distillaton of aproximately 75 mL of solvent, precipitation began. The mixture was allowed to crystallize slowly. Yellow crystals (12 g) were obtained [mp 236–237 °C; $[\alpha]^{23}_D$ +35° (c 0.58, acetone)]. Further recrystallization improved the rotation only slightly and resulted in a considerable loss of material. The mother liquor was concentrated to 150 mL, cooled, and filtered, and the filtrate was evaporated to dryness to yield 10.3 g of yellow solid. This solid was dissolved in 65 mL of EtOH, cooled to 0 °C, and treated with 50 mL of concentrated HCl, followed by 70 mL of H_2O. The resulting yellow solid was washed with EtOH–HCl (1:1) and water and dried [yield = 3.7 g; $[\alpha]^{23}_D$ +101° (c 0.65, acetone)].

The dextrorotatory quinidine salt was decomposed in a similar manner to yield 4.5 g of yellow solid [$[\alpha]^{23}_D$ – 114° (c 0.65, acetone)]. It was found that crystallization of (–)-**6d** from HOAc increased the specific rotation by approximately 1° and resulted in the loss of considerable material.

Determination of the Specific Rotation of 6d at Optical Purity.[19] Samples of **6d**, of various optical rotations, were heated at reflux in benzene suspension with a 100–200 molar excess of oxalyl chloride for 65–70 h. After evaporation, the residue was dissolved in benzene and treated with a 5 molar excess of (+)-α-phenylethylamine at 5 °C. This mixture was stirred at room temperature for 3–5 h, diluted with benzene, washed with dilute HCl, H_2O, 10% $NaHCO_3$, and saturated saline solution, dried, and evaporated to give the diamide in 95–105% yield. The diastereomeric compositions were obtained by HPLC using a 12 in. × $^1/_4$ in. microporisil column at 1500 PSI with 3% EtOAc–CH_2Cl_2 as eluent. The specific rotation of optically pure **6d** was calculated to be [$[\alpha]^{23}_D$ 115° ± 2° (c 0.30, acetone)].

(–)-2,2′-Dicarbomethoxy-9,9′-bianthryl (6c). A solution of 7.28 g of **6d** [$[\alpha]^{23}_D$ –115° (c 0.30, acetone)] in 1.3 L of dioxane was treated with a solution of CH_2N_2 in ether, generated from 0.1 mol of "Diazald" (Aldrich Chemical Co. Milwaukee, WI). Concentration and dilution with H_2O yielded a yellow solid, which was purified by chromatography on silica gel by using $CHCl_3$–C_6H_6 (1:1) as eluent, followed by crystallization from $CHCl_3$–MeOH to give a yellow solid (87%): mp 232–233 °C; $[\alpha]^{23}_D$ –159° (c 0.30, $CHCl_3$); IR (KBr) 1715 cm^{-1}; mass spectrum, m/e (relative intensity) 470 (100), 439 (18), 350 (20). Anal. Calcd for $C_{32}H_{22}O_4$: C, 81.68; H, 4.71. Found: C, 81.48; H, 4.69.

Reaction of Optically Active 6c with Benzyne. To a solution of 1.0 g (2.1 mmol) of optically pure (–)-**6c** and a few drops of n-butyl nitrite in 60 mL of 2-butanone at 60 °C were added simultaneously solutions of anthranilic acid (2.90 g, 21.2 mmol) and n-butyl nitrite (2.40 g, 23.3 mmol), each in 60 mL of 2-butanone, at a constant rate, over a period of 4.5 h. The reaction mixture was maintained at 60 °C for an additional 0.5 h, cooled, and evaporated under reduced pressure to give a dark-brown semisolid. Addition of 200 mL of $CHCl_3$ and filtration removed a small amount of insoluble material (acridone, by IR). The $CHCl_3$ solutions of three similar reactions were combined and evaporated to yield a semisolid.

This semisolid was separated into seven arbitrary fractions by dry-column chromatography by using C_6H_6/$CHCl_3$ (1:1.5) as eluent. Those fractions rich in the starting material, **6c**, were combined and subjected to a further reaction with benzyne, followed by dry-column chromatography, as above. Each of the chromatographic fractions was subjected to a series of digestions by using MeOH, $CHCl_3$, and acetone, in order to remove an insoluble white solid (**5c′**), followed by one or more column chromatographies, preparative TLC separations, and crystallizations. The entire process was monitored by NMR analysis. The desired product, **5c**, exhibits a distinctive singlet at δ 5.66 for the bridgehead H. An attempt was made to work as quantitatively as possible in order to decrease the error in the determination of the optical purity of the gauche conformer to be made later.

Two white solids were isolated: **5c′**: not very soluble in common organic solvents; 97 mg; mp 483–485 °C; IR (KBr) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.51 (s, OCH_3), 5.66 (s, CH), 6.4–8.0 (m, Ar H); UV ($CHCl_3$) λ_{max} (log E) 292.1 (3.48), 264.8 (4.18), 239.3 (4.59); mass spectrum, m/e (relative intensity) 622 (100). Anal. Calcd for $C_{44}H_{30}O_4$: C, 84.87; H, 4.86. Found: C, 84.72; H, 4.93. **5c″**, **5c‴**: appreciably more soluble in common organic solvents than **5c′**; 175 mg; mp 340–361 °C; IR (KBr) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.48 (s, OCH_3), 5.66 (s, CH), 6.4–8.0 (m, Ar H); UV ($CHCl_3$) λ_{max} (log E) 293.6 (3.51), 263.1 (4.16), 238.8 (4.55); mass spectrum, m/e (relative intensity) 622 (100); $[\alpha]^{23}_D$ –14.7° (c 0.375, $CHCl_3$). Anal. Calcd for $C_{44}H_{30}O_4$: C, 84.87; H, 4.86. Found: C, 84.70; H, 4.84.

The optical purity of **5c″**, **5c‴** was determined by NMR analysis by using a chiral shift reagent (see text).

Because of its insolubility, the optical rotation of **5c′** could not be determined directly. It was, therefore, hydrolyzed to the corresponding diacid, **5d**, using a mixture of 10 g of KOH in 40 mL of diethylene glycol and 5 mL of H_2O at 70 °C. A 1.2% solution of **5d** in 48% aqueous dimethyl sulfoxide containing 5.5% tetramethylammonium hydroxide showed no rotation at 589, 578, 546, 436, and 365 nm using a 10-cm cell.

Determination of the Rotational Barrier of 5c. Samples (0.5 mg) of the anti conformer (**5c′**) and the gauche conformer (**5c″**, **5c‴**) were each dissolved in 1 mL of dried and distilled $CHCl_3$. Sublimed naphthalene (100 mg) was added, and the resulting solutions were transferred to ampoules and evaporated. The mixtures were degassed by using the freeze–pump–melt technique and sealed under a N_2 (oxygen free) atmosphere. The ampoules were immersed in a silicone oil bath at 300 ± 1 °C for 170 h. After 24 h the samples were brown. The samples were sublimed to remove the naphthalene. $CDCl_3$ (100%, 1 mL) was added to each residue. Neither material completely dissolved. Each mixture containing a dark insoluble solid. The mixtures were filtered into NMR tubes, and expanded ^1H NMR spectra of the resulting light brown solutions were run (200 MHz, 500 accumulations) in the neighborhood of the OCH_3 absorption. The spectrum of the heated anti conformer was identical with that of an unheated sample, i.e., a single absorption at δ 3.51 was present. At δ 3.48, 1 part in 180 of the gauche conformer would have been detected. The spectrum of the heated gauche conformer contained a singlet at δ 3.48, no absorption at δ 3.51, which indicated the absence of the anti conformer and an impurity peak (5–10% of the δ 3.48 peak) at δ 3.50.

Registry No. **5c** (anti isomer), 100206-84-6; **5c** (gauche isomer), 100296-05-7; **5d**, 100206-85-7; **6c**, 26440-87-9; **6d**, 100206-82-4; **6d** (isomer 1), 26440-88-0; **6d** (isomer 2), 26440-89-1; **6d**·quinidine, 100206-83-5; **6e**, 100206-80-2; **6f**, 100206-81-3; **7**, 4887-99-4; **8**, 100206-79-9; Al, 7429-90-5; $HgCl_2$, 7487-94-7; aluminum amalgam, 11146-30-8; quinidine, 56-54-2; anthranilic acid, 118-92-3.

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[19] We thank Dr. R. Gupta for this determination.