mol) of methyl iodide at such a rate that gentle refluxing was observed. A small amount of the quaternary salt separated during the addition and the remainder was precipitated upon dilution with 50 ml of ethyl acetate and cooling. After being collected and dried at room temperature, the product, mp 229–230° (lit.[24] mp 231–232°), amounted to 11.75 g (94%).

***1,1,4,4,4-d_5*-1-Butene** (1).—A solution of 3.72 g (0.015 mol) of the deuterium-labeled quaternary ammonium iodide in 35 ml of deuterium oxide and 5 ml of methanol-*O-d* was stirred for 1 hr with freshly precipitated silver oxide. The mixture was rapidly filtered through Celite and lyophilized. The solid material was dissolved in 25 ml of deuterium oxide and the lyophilization procedure was repeated. The viscous, colorless residue was dissolved in 40 ml of deuterium oxide and pyrolyzed according to a known procedure.[24] The olefin was condensed in a trap immersed in liquid nitrogen during the pyrolysis and later allowed to distil into a constricted 5-mm nmr tube containing hexamethyldisilane (HMDS) and immersed in a Dry Ice–acetone slush. The nmr tube was subsequently degassed and sealed at atmospheric pressure at −68°. From a typical run it was possible to obtain two samples of 1 suitable for analysis by nmr spectroscopy.

The isotopic purity of 1 prepared in this manner was 97% in the methyl group and 93% at C-1 as determined by nmr. When the pyrolysis was conducted in water *ca.* 15% of the terminal olefinic deuteriums were exchanged.

The silver oxide used in the above synthesis was prepared by treatment of a hot (85°) solution of 5.1 g (0.03 mol) of silver nitrate in 51 ml of water with an equally warm solution of 1.2 g of sodium hydroxide in 12 ml of water. The precipitated material was washed by decantation with five 20-ml portions of hot deuterium oxide.

Nmr Spectral Determinations.—All spectra were recorded on a Varian A-60 spectrometer equipped with an NMR Specialities HD-60A heteronuclear spin decoupler, a V-6058A homonuclear decoupler, and a V-6040 temperature controller. Conditions of deuterium decoupling were maintained on phase lock mode of the homonuclear decoupler for all spectral determinations. Spectra were calibrated by interpolation between audio-modulation sidebands of internal hexamethyldisilane (HMDS) produced using a Hewlett-Packard Model 3300A function generator monitored by a Hewlett-Packard Model 3734A frequency counter.

The probe temperatures were measured before and after each experiment by means of a copper–constantan thermocouple inserted into an empty stationary nmr tube positioned in the probe. The temperatures generally agreed within 0.5°. The average of the two temperatures was used as the temperature of the experiment and is believed to be accurate to ±1°. For each experiment, the probe and sample were allowed to thermally equilibrate 4–5 hr before commencing spectral determinations.

Spectra were determined using neat samples containing *ca.* 15% v/v) HMDS as internal standard and prepared as described above. In general, 24 HMDS side-band calibrated spectra were recorded for the allylic protons at each temperature by alternately sweeping up-field and downfield. A FORTRAN IV computer program was written and used to facilitate data refinement. The program calculated the frequency of each observed transition of each spectrum from the center at half-height using the frequencies of the sidebands and the corresponding calibration factor. The calculated frequencies for a given transition were averaged over all spectra and those frequencies whose deviations were greater than or equal to twice the standard deviation were discarded. The calculation was repeated for each transition in the spectrum until all deviations from the average were less than twice the corresponding standard deviations. This procedure led to an average of 18 spectra at each temperature and afforded standard deviations of the transition frequencies of less than 0.06 Hz with the majority in the range 0.02–0.04 Hz.

The deuterium-decoupled nmr spectrum of neat 1 consists of a triplet and a doublet for the vinyl (A) and allylic (X_2) protons, respectively. The frequency difference between transitions composing the doublet was taken as J_{AX} and the chemical shift, ν_x, of the allylic protons was taken as the mean frequency of the doublet transitions. All transitions at each temperature had widths at half-height comparable to that of HMDS (0.3–0.6 Hz).

Phase lock instability at the audiofrequencies necessary to calibrate spectra between 340 and 380 Hz by interpolation resulted in intolerably large (0.08–0.12 Hz) standard deviations in the transition frequencies of the triplet. In normal mode of operation, field fluctuations precluded obtaining optimum deuterium decoupling. Other spectrum calibrated techniques[9] led to an improvement in precision, but not to the degree that the standard deviations in ν_A were less than the change of ν_A over the temperature range adopted. Consequently, ν_A could not be used in the conformational analysis of 1.

Registry No.—1, 36789-12-5; diethyl-*3,3,3-d_3*-propane-1,1-dicarboxylate, 36789-13-6; *4,4,4-d_3*-butyric acid, 36789-14-7; *N,N*-dimethyl-*4,4,4-d_3*-butyramide, 36789-15-8.

Acknowledgment.—The authors are grateful for National Science Foundation Grant No. GP-3815, which provided support for this work.

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[24] P. A. S. Smith and S. Frank, *J. Amer. Chem. Soc.*, **74**, 509 (1952).

Conformational Inversion of 9,10-Dihydro-9,10-*o*-xylyleneanthracenes[1a]

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2,7-Dimethyl-9,10-dihydro-9,10-*o*-xylyleneanthracene (2), synthesized from the reaction of 2,7-dimethylanthracene with *o*-xylylene, was used for a variable-temperature nmr study of the conformational inversion proposed earlier for the parent hydrocarbon (1). The signal for the six methyl hydrogens of 2 remained a sharp singlet in a variety of solvents down to −120°, the lowest attainable temperature. The Diels–Alder adduct (8) from 2,7-dimethylanthracene and benzocyclobutadiene, prepared as a model of 2 "locked" in its preferred conformation, showed two sharp singlets separated by 13.5 Hz for the two methyl groups. Use of this value as a minimum $\Delta\nu_{\max}$ for 2 and −120° as a maximum temperature of coalescence of the methyl signals in 2 leads to a $\Delta G_{\max}{}^*$ of 7.7 kcal/mol for conformational inversion in 2. This value is compared with values reported for related systems.

Several years ago, Sisido and coworkers[2-4] reported the preparation of 9,10-dihydro-9,10-*o*-xylyleneanthracene (1) from the reaction of anthracene with *o*-xylylene. They noted that molecular models of the symmetrical conformer 1b can only be constructed with substantial expansion of the tetrahedral angles about the methylene carbon atoms whereas conformers 1a and 1a′, although being fully eclipsed, are devoid of angle distortion. This, along with the observation that in the room temperature nmr spectrum of 1

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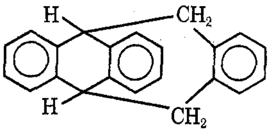
[1] (a) Support in part by NASA Grant No. Ns(T)-21 is gratefully acknowledged. (b) Abstracted from the Ph.D. Thesis of D. M. Wieland, West Virginia University, 1970; NASA Trainee, 1965–1968.

[2] K. Sisido, Y. Udo, and H. Nozaki, *J. Org. Chem.*, **26**, 584 (1961).

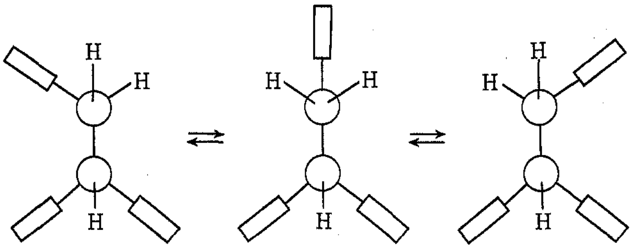
[3] K. Sisido, R. Noyori, and H. Nozaki, *J. Amer. Chem. Soc.*, **84**, 3562 (1962).

[4] K. Sisido, R. Noyori, N. Kozaki, and H. Nozaki, *Tetrahedron*, **19**, 1185 (1963).

the methine hydrogens appeared as a simple triplet from coupling with two adjacent and equivalent methylene hydrogens, led them to conclude that **1** is not frozen as **1a** or **1a′** but is rapidly interconverting between these two conformers *via* **1b**. They further speculated that conformer **1a** (or **1a′**) may be as much as 10 kcal/mol more stable than **1b**.[3]



1



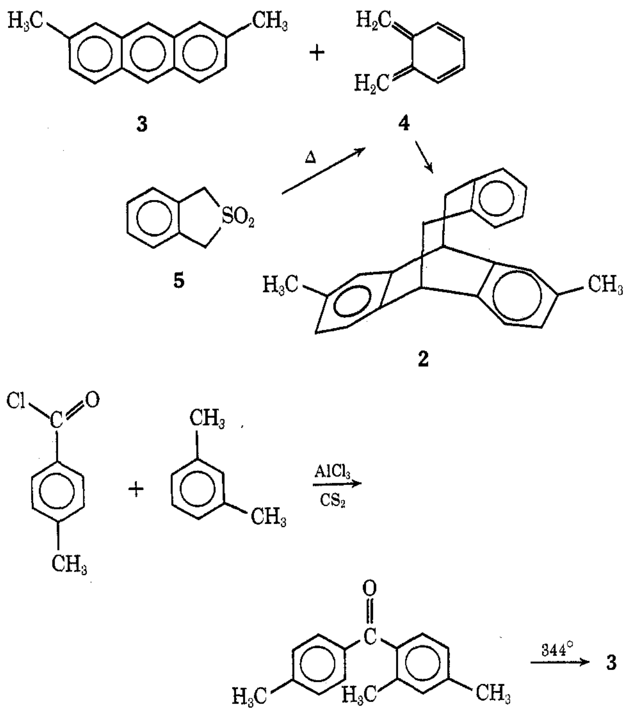
1a **1b** **1a′**

We felt that, if this is indeed an accurate description of the conformational dynamics of this molecule, then the rate of such an inversion might be amenable to a variable-temperature nmr study. However, the anticipated complexity of the nmr pattern for the methylene and methine hydrogens in **1** at low temperatures prompted us to consider the use of the 2,7-dimethyl derivative (**2**) as a model for **1**. In the 2 and 7 positions the methyl groups should be remote enough not to interact sterically with the *o*-xylylene moiety and yet close enough to lie within the shielding region of its benzene ring. A Dreiding model of **2** shows the closest approach of the *o*-xylylene group to the methyl substituent to be about 5 Å, or 1.3 Å greater than the sum of the van der Waals radii of the benzene ring (1.70 Å) and the methyl group (2.0 Å).[5]

Use of the Johnson–Bovey[6] tables of isoshielding values for the benzene ring suggests that when "flipping" in **2** is sufficiently slow (below the coalescence temperature), the two methyl groups should have resonances separated by approximately 15.6 Hz, a chemical shift difference large enough to permit facile analysis at low temperatures. Assuredly this value may be subject to some error, not the least of which could be introduced by a perturbation of the shielding effect of the *o*-xylyl ring by virtue of its face-to-face encounter with the anthranyl ring. The crux of concern is whether this encounter would cause a sizable reduction of the shielding effect, consequently resulting in a diminution in the chemical shift difference between the two methyl groups. It has been found, however, that compounds with a similar, but somewhat closer, positioning of benzene rings (*viz.*, 1,8-diphenylnaphthalene,[7] 1,2-diphenylcyclopropane,[8] and janusene[9]) exhibit a strong mutual shielding of their aromatic protons.

Results and Discussion

The synthesis of **2** was in direct analogy with that of the parent compound (**1**)[2] as shown by the following sequence.



3 **4** **5** **2** **6**

The work of Morgan and Coulson[10] provided an unambiguous synthesis of **3** *via* the ketone **6** which was itself synthesized from the Friedel–Crafts reaction of *m*-xylene with *p*-toluoyl chloride. When subjected to the conditions of the Elbs reaction,[11] **6** provided **3** in modest yield.

The room temperature nmr spectrum of **2** in CS$_2$ is consistent with the proposed structure. The six methyl hydrogens appear as a single sharp peak at δ 2.18, consistent with the idea of rapid conformational interconversion. The methylene protons show a sharp doublet (J = 7.0 Hz) centered at δ 3.08 and further downfield near δ 4.0 are the two methine hydrogens appearing as two triplets (J = 7.0 Hz) separated by 2.2 Hz. The two pair of methylene hydrogens, although not chemically equivalent, are seemingly too far removed from the source of asymmetry to suffer an observable chemical shift difference. Correct integral ratios were obtained for all peaks including the aromatic multiplet centered at δ 6.8. The ultraviolet spectrum of **2** correlates well with that reported for **1**,[4] a small bathochromic shift (4–5 nm) being noted for **2**.

No real change in the room temperature nmr spectrum of **2** was noted down to −65° in CDCl$_3$, to −90° in CS$_2$, and to −50° in chlorobenzene (chosen because of the ability of aromatic solvents to accentuate some-

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(5) L. D. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1963, p 214.

(6) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(7) H. O. House, R. W. Magin, and H. W. Thompson, *J. Org. Chem.*, **28**, 2403 (1963).

(8) C. G. Overberger and J. P. Anselme, *Chem. Ind.* (*London*), 280 (1964).

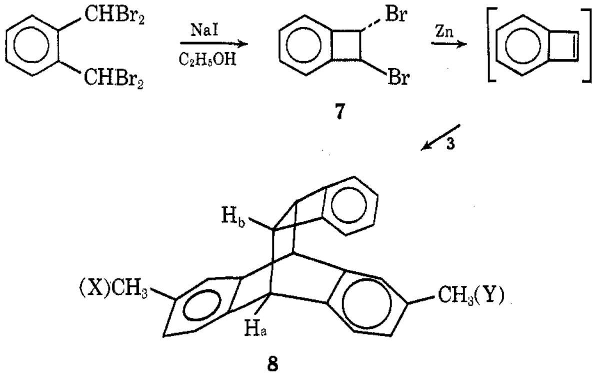
(9) S. J. Cristol and D. C. Lewis, *J. Amer. Chem. Soc.*, **89**, 1476 (1967).

(10) G. T. Morgan and E. A. Coulson, *J. Chem. Soc.*, 2203 (1929).

(11) L. F. Fieser, *Org. React.*, **1**, 129 (1942).

times a chemical shift difference[12]). Attainment of lower temperatures was thwarted by either the freezing of the solvent or by insufficient solubility of the compound. The halocarbon $CHFCl_2$ was found to lend sufficient solubility to **2** for spectra down to −120°. However, even at −120°, **2** still displayed a single, sharp methyl hydrogen peak (no real broadening when compared to the change in half-height width of TMS over the same temperature interval). Resolution of the methine peaks was insufficient at temperatures below −90° to observe any change, and the methylene resonance remained a poorly resolved doublet down to −120°. Solubility and technical difficulties prevented the attainment of spectra in $CHFCl_2$ at temperatures below −120°.

These results provoked efforts to show irrevocably that the two methyl groups in **2** will have an observable chemical shift difference if the conformational inversion can be sufficiently retarded. Ideally what is needed is a means of "locking" **2** into its supposed preferred conformation to prevent conformational exchange and, in doing so, not introduce any factor that would modify the hopefully already inherent chemical shift difference of the two methyl substituents. The model compound which approximates this ideal is **8**, conveniently synthesized by Diels–Alder addition of benzocyclobutadiene to 2,7-dimethylanthracene (**3**) as shown in the following scheme.



7

8

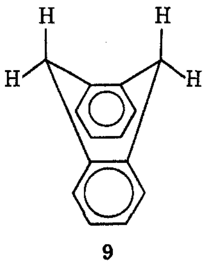
Dreiding models show the methyl group (Y) in **8** to be 0.4 Å further from the center of o-xylyl benzene ring than the respective methyl group in **2**. The calculated chemical shift difference for the two methyl groups in **8** (using the Johnson–Bovey tables) is 13.5 Hz. The observed nmr spectrum of **8** in $CDCl_3$ displays a sharply defined aromatic multiplet centered at δ 6.90, two narrow multiplets of equal intensity at δ 4.45 and 3.70 for the H_a and H_b methine protons, respectively, and, of utmost concern, two sharp methyl peaks of equal intensity at δ 2.24 and 2.10. It would be reasonable to assume that the methyl group (Y) is the peak at higher field (δ 2.10). The chemical shift difference between the two methyl peaks in $CHFCl_2$ is 13.4 Hz, and spectra in this solvent taken at temperatures down to −120° showed this chemical shift difference to be essentially independent of temperature.

Whether 13.4 Hz represents a valid figure for the expected maximum separation ($\Delta\nu_{max}$) of the methyl groups in **2** depends of course on the validity of assuming **8** as the model for the slow exchange or preferred conformation of **2**. The nmr spectrum of equimolar amounts of **2** and **8** in $CHFCl_2$ shows the lone methyl peak of **2** almost exactly midway between the two methyl peaks of **8**. This observation indicates that introduction of the methylene cross link has not, to any appreciable extent, unsymmetrically altered the magnetic environments of the two methyl groups—an observation not wholly unexpected in view of the small anisotropic effect of the C–C single bond in cyclobutane.[13]

The remarkably close agreement between the calculated (13.5 Hz) and the observed (13.4 Hz) values for **8** might encourage one to predict the actual experimental value for **2** to be near the calculated figure of 15.6 Hz. However, the safest prediction is that the experimental $\Delta\nu_{max}$ for **2** will have a minimum value of 13.4 Hz. Inspection of eq 1[14] reveals that, as $\Delta\nu_{max}$ increases, the value for ΔG^* decreases. By using 13.4 Hz as a reasonable minimum value for $\Delta\nu_{max}$ and −120° as the maximum temperature of coalescence (T_c) a ΔG_{max}^* value of 7.7 kcal/mol is obtained for the free energy of activation associated with the conformational inversion in **2**. Since the methyl substituents are not expected to raise the ground-state energy of **2** relative to **1**, this maximum of 7.7 kcal/mol is also applicable to the parent compound **1**.

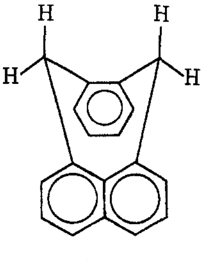
$$\Delta G^* = 4.57T_c[9.97 + \log (T_c/\Delta\nu_{max})] \qquad (1)$$

It is interesting to compare the ΔG_{max}^* value for "flipping" in **1** and **2** with the values obtained for ring inversion in related systems. Lansbury,[15] in a recent review article, gives perspective to the present case by comparing conformational inversion in 9,10-dihydroanthracene (**9**), 7,10-dihydropleiadene (**10**), and 1,8-(1′,8′-naphthyldimethyl)naphthalene (**11**). The ΔG^* values for inversions in these compounds are given below the structures.



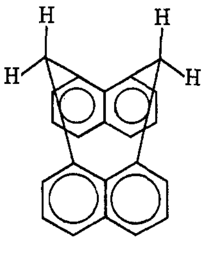
9

ΔG^* = <5 kcal/mol



10

13.5 kcal/mol



11

<23 kcal/mol

An examination of molecular models suggests that **1** has much in common with **10**. In each molecule the o-xylene moiety bridges a distance of ~2.8 Å, and both molecules are folded to the same extent (~109°). Yet the ΔG^* value for **10** is a minimum of 5.8 kcal/mol higher than that of **1**. The reason for this ΔG^* variance is no doubt manifold, but an important contributing factor could be the difference in the pathways for relief of angle strain in the respective transition states of the two compounds. The bond angle strain about the methylene carbon atoms

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[12] (a) D. L. Harris and K. M. Wellman, *Tetrahedron Lett.*, 5225 (1968); (b) D. J. Bertelli and J. T. Gerig, *ibid.*, 2481 (1967).

[13] J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **86**, 1870 (1964).

[14] J. E. Anderson and J. M. Lehn, *Tetrahedron*, **24**, 123 (1968).

[15] P. T. Lansbury, *Accounts Chem. Res.*, **2**, 210 (1969).

in the transition state of **1** (or **2**) is readily eased by a downward flexing of the central boat of the anthranyl moiety. Such relief should not be possible in **10** because of the planar and rigid aromatic rings to which the *o*-xylylene group is directly attached.

Generalizations on **9**, **10**, and **11**[15] were made possible because the hinge carbons similarly connect aromatic rings. The inability to extend these generalizations to **1** demonstrates that not only the degree of folding of the molecule but also the nature and flexibility of the substituent to which the *o*-xylyl group is bound are important factors affecting the ΔG^* for conformational exchange in *o*-xylyl systems.

Experimental Section

General.—All nmr spectra were obtained by Mr. Robert Smith and D. M. W. on a Varian Model HA-60-EL spectrometer equipped with a V-4340 variable-temperature probe. Signal positions are reported in parts per million with respect to tetramethylsilane (δ = 0.0) used as an internal standard. Samples were run as 10% w/v solutions or as saturated solutions if not soluble to the extent of 10%. All variable-temperature samples were run in Wilmad 507-PP Imperial tubes sealed with Teflon caps, except for samples run in $CHFCl_2$ in which case the sample tubes were precision sealed. Sample temperature was measured with a Leeds & Northrup Model 8686 precision potentiometer and a calibrated copper-constantan thermocouple mounted in a dummy sample tube containing acetone or carbon disulfide. Cooling was achieved by controlled vaporization of liquid N_2 in a 25-l. dewar flask connected *via* a vacuum-jacketed tube to a dewar insert in the probe. Temperature readings were reproducible to within ±0.50° down to −60° and to within ±1.0° on down to −120°.

Microanalytical work was performed by Galbraith Laboratories, Inc., Knoxville, Tenn. All melting points were taken on a Mel-Temp apparatus and are uncorrected. Ultraviolet spectra were obtained on a Bausch and Lomb Spectronic 505 spectrophotometer. In some of the synthesis reported here no attempt was made to optimize yields since only small quantities of pure compounds were needed for subsequent spectral studies.

2,4,4′-Trimethylbenzophenone (6) was prepared according to the procedure of Morgan and Coulson.[10] Equimolar amounts (0.33 mol) of *p*-toluoyl chloride (50.0 g) and *m*-xylene (34.4 g), mixed in carbon disulfide and combined with 50.0 g of aluminum chloride, afforded 54 g (74%) of the clear, oily ketone, bp 69–71° (4.0 mm) [lit.[10] bp 69° (4.0 mm)].

2,7-Dimethylanthracene (3) was formed in low yield when the 54 g of ketone from the preceding procedure was boiled (344°) beneath an air reflux for 6 hr and then cooled. The crude dimethylanthracene which separated upon cooling was removed by filtration. Recrystallization from acetic acid followed by a second recrystallization from toluene produced 2.25 g of yellow-green fluorescent plates, mp 240–241° (lit.[10] mp 241°). The nmr spectrum was in agreement with the proposed structure.

Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.10; H, 6.80.

1,3-Dihydroisothianaphthene 2,2-Dioxide (5).—The method of Cava and Deana[16] was used with minor modification. Equal volumes (55 ml) of acetic acid and acetic anhydride were mixed in a flask with 53 ml of 30% hydrogen peroxide. The addition of 13 g of 1,3-dihydroisothianaphthalene[16] was made over a 3-hr period while the reaction mixture was being stirred and cooled. The mixture was then stirred at room temperature for 120 hr. Addition of 50 ml of cold water and filtration of the precipitated sulfone gave 14.5 g (90%) of white needles, mp 147–148°. Recrystallization from methylene chloride-petroleum ether yielded white needles, mp 147–148° [lit.[16] mp 150–152°].

2,7-Dimethyl-9,10-dihydro-9,10-*o*-xylyleneanthracene (2).—A finely ground mixture of **5** (1.0 g, 0.006 mol) and **3** (1.27 g, 0.006 mol) was heated at 245–265° for 15 min in a Wood's Metal bath. After an additional 15 min at 295–305°, the mixture was cooled and dissolved in warm petroleum ether (bp 65°). Elution with petroleum ether-benzene on a column of neutral alumina afforded 0.43 g (25%) of white, fluffy needles, mp 187–189°. Recrystallization from ethanol followed by a second recrystallization from petroleum ether gave white needles: mp 190.5–191°; nmr (CS_2) δ 2.18 (s, 6, methyl), 3.08 (d, 4, J = 7.0 Hz, methylene), 4.01 (t, 1, J = 7.0 Hz, methine), 4.07 (t, 1, J = 7.0 Hz, methine), 6.18 (m, 10, aromatic); uv (95% ethanol) λ_{max}, nm (log ϵ), 263 (3.47), 269 (3.64), 275 (3.62), 278 (3.55).

Anal. Calcd for $C_{24}H_{22}$: C, 92.90; H, 7.10. Found: C, 92.82; H, 7.25.

***trans*-1,2-Dibromobenzocyclobutane (7).**—The procedure of Cava and Napier[17] was adopted using 50 g of $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene (Aldrich Chemical Co.), 75 g of sodium iodide, and 275 ml of absolute ethanol. This mixture was heated under reflux with stirring for 46 hr. Some ethanol (125 ml) was then removed by distillation. Water (100 ml) was added, and more ethanol (100 ml) was removed. Sulfur dioxide was bubbled through the reaction mixture to reduce the iodine which had been liberated during the reaction. After 30 min of vigorous stirring at 0°, the aqueous layer was decanted from the gray precipitate. The precipitate was collected by filtration, washed with cold water, and then dissolved in Skellysolve C and dried over magnesium sulfate. The solution was concentrated to 40 ml and passed through a column of neutral alumina with Skellysolve C as eluent. The first fraction (130 ml) produced 20 ml of a pink oil which, upon distillation, bp 80–86° (0.2 mm) [lit.[17] bp 95–100° (0.6 mm)], double recrystallization from petroleum ether (bp 65°) and a third from methanol gave 4.17 g of white crystals, mp 42–43°. This material was used without further purification for the subsequent reaction.

Diels-Alder Adduct of 2,7-Dimethylanthracene and Benzocyclobutadiene (8).—To a near boiling solution of 1.43 g (0.007 mol) of **3** and 30 ml of dimethylformamide containing 1.50 g of suspended zinc dust (preactivated with 5% hydrochloric acid) was added dropwise 2.62 g (0.010 mol) of **7** in 10 ml of dimethylformamide. The reaction mixture was heated under reflux with stirring for 1.5 hr and cooled; then 100 ml of *m*-xylene and 1.5 g of maleic anhydride were added to the solution. After 5 hr under reflux, the solvent was evaporated and the solid residue triturated with warm, concentrated aqueous sodium hydroxide to dissolve the maleic anhydride adduct. The base-insoluble solid was dissolved in benzene and passed through a short column of neutral alumina to yield a yellow solid. This solid was sublimed (100°, 0.2 mm) and recrystallized from methanol to give 40 mg of white needles: mp 155–156°; nmr ($CDCl_3$) δ 6.90 (m, 10, aromatic), 4.45 (m, 2, anthranyl methine), 3.70 (m, 2, cyclobutyl methine), 2.24 (s, 3, methyl), 2.10 (s, 3, methyl).

Anal. Calcd for $C_{24}H_{20}$: C, 93.51; H, 6.49. Found: C, 93.28; H, 6.58.

Registry No.—**2**, 36803-32-4; **3**, 782-23-0; **7**, 14420-75-8; **8**, 36803-34-6.

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[16] M. P. Cava and A. A. Deana, *J. Amer. Chem. Soc.*, **81**, 4266 (1959).

[17] M. P. Cava and D. R. Napier, *ibid.*, **79**, 1701 (1957).