a solution of 4 (2.10 g, 10 mmol) in dry DMF (100 mL) and a solution of 8 (crude, 3.77 g, 5 mmol) in dry DMF (100 mL). The addition lasted 4 h, and stirring was continued for 18 h. The reaction mixture was decomposed and worked up in the usual manner (vide infra). The crude product was chromatographed on a silica gel column (100 g) using C_6H_6 as eluent. PLC chromatography of the eluted product on silica PLC plates using hexane–benzene (7:1) afforded **1a** (R_f 0.28) as a pale yellow solid, identical [UV, IR, NMR (270 MHz), TLC] with a sample of **1a** prepared by method A. The yield was 0.3% (0.008 g).

Acknowledgment. We are grateful to our colleague Professor H. J. G. Hayman of The Hebrew University of Jerusalem for stereoscopic drawings of **1a** and **1b**. We also would like to thank The Weizmann Institute of Science, Rehovot, Israel, for use of a Brüker WH-270 NMR spectrometer.

Registry No.—**1a**, 69551-53-7; **1b**, 69609-72-9; **2a**, 37445-17-3; **2b**, 37402-37-2; **2c**, 37445-16-2; **4**, 1210-05-5; **6**, 4371-26-0; **7**, 69551-54-8; **8**, 69551-55-9; **9**, 69551-56-0; **11**, 61358-43-8; pyrene, 129-00-0; phenanthrene, 85-01-8; triethyl phosphite, 122-52-1; 2,2′-bis(bromomethyl)biphenyl, 38274-14-5.

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Dynamic Stereochemistry in Overcrowded Ethylenes. Conformational Behavior of Bianthrones[1a]

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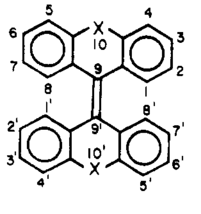
The ground-state conformation of bianthrone derivatives in solution was investigated by ^1H NMR spectroscopic techniques. The experimental data are consistent with a folded structure. The existence of geometrical isomers in this series is established, and their chromatographic separation at low temperatures is described. A DNMR study of 2,2′-disubstituted bianthrones (**2**) and their benzannelated analogues (**5** and **6**) revealed low values of the free energy of activation ($\Delta G^{\ddagger}_c$) for thermal E,Z isomerization. $\Delta G^{\ddagger}_c$ values were not lowered by benzannelation of the parent system. The low $\Delta G^{\ddagger}_c$ values are ascribed predominantly to the high-energy content of the folded ground-state conformations of these systems. An isomerization pathway implying a double-minimum free-energy profile and a nonorthogonal, partly twisted and folded highest energy transition state is discussed in terms of steric and electronic effects in the ground state and in the transition state.

The bistricyclic ethylene (**1**) enigma has fascinated chemists since thermochromism in bianthrone (**2a**)[1b] was revealed by Meyer at the beginning of the century.[2] While the majority of the extensive studies of bianthrones have been devoted to the origins of the photochromic, thermochromic, and piezochromic properties of these systems,[3] their dynamic stereochemistry has hardly been considered. The study of the mechanisms of uncatalyzed thermal E,Z isomerizations around carbon–carbon double bonds has been focused mainly on polarized ethylenes and on electronic effects, whereas the data on the conformational behavior of symmetrical overcrowded ethylenes are scarce.[4–7]



1

2a X = C=O

3 X = N–CH_3

4 X = O

Bianthrone (**2a**) is the leading member of the bistricyclic ethylenes series (**1**). These systems are attractive substrates for the study of the conformational behavior of symmetrical overcrowded ethylenes. Steric effects become most influential in determining their ground-state conformations as well as their dynamic stereochemistry. An idealized coplanar bistricyclic ethylene would maintain very short nonbonded carbon–carbon and hydrogen–hydrogen distances in the vicinity of the central double bond ("pinch"). The associated repulsive

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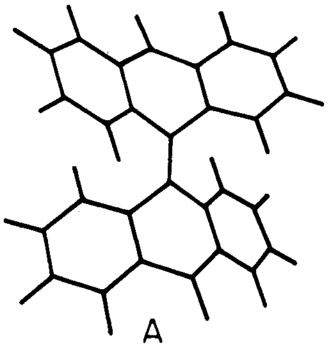


Figure 1. A form of bianthrone (**2a**).

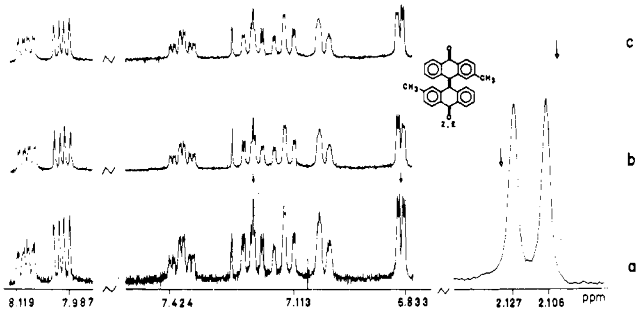
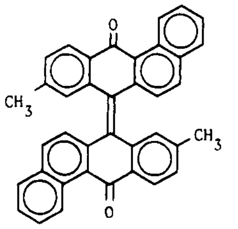


Figure 2. ^{1}H NMR spectra (300 MHz) of **2b** in $CDBr_3$ at 25 °C: (a) nondecoupled spectrum; (b) irradion at the low-field Me signal; (c) irradiation at the high-field Me signal.

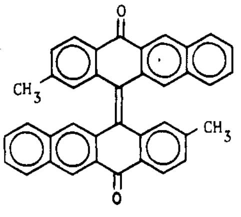
interactions could be relieved by deviations from coplanarity, e.g., by torsion around the double bond or folding in opposite directions at the olefinic termini.[3,7] Indeed, an early X-ray crystallographic investigation of the crystal and molecular structure of bianthrone (**2a**)[8] indicated that the molecule adopts in the ground-state a folded centrosymmetric geometry (the A form); the central rings are boat shaped and the tricyclic halves are folded in opposite directions at the olefinic termini (Figure 1). On the other hand, the colored species (the B form) of **2** was postulated to exist in a twisted conformation about the "pinch" with a calculated torsional angle of 57°.[9] In the past, the existence of *E,Z* isomers and thermal isomerizations in the **2** series had hardly been noticed.[1,6] The "void" of geometrical isomerism served as a basis of a rationale for the thermochromic properties of the bianthrones.[3]

The objective of our investigation was to reveal the dynamic stereochemistry of **1** in solution. We have previously reported on the ground-state structure and conformational behavior of the *N,N'*-dimethylbiacridan (**3**) and dixanthylene (**4**) systems.[1a,10] The present article is devoted to the bianthrones. In addition to the role of steric effects in the conformational behavior of the **2a** system, special emphasis is drawn to the effects of *benzannelation* on the transition states as well as on the ground state. There is a recent renewed activity in the field of overcrowded ethylenes, including static[11] and dynamic[12] aspects.

Ground-State Conformation in Solution. The substrates of the present investigation were 2,2'-disubstituted bianthrones (**2**) and their linearly and angularly benzannelated analogues **5** and **6**, as well as other substituted bianthrones.

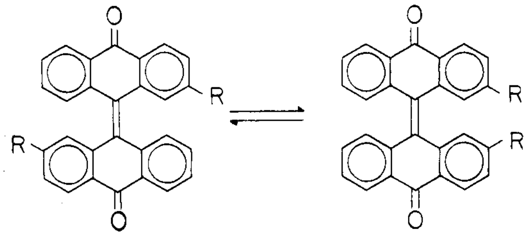


5 (E,Z)



6 (E,Z)

The introduction of tag substituents at the 2 and 2' positions permits the determination of possible *Z,E* isomerism and thermal isomerization without altering substantially the steric interactions around the "pinch" (in the ground state) relative to the parent compound. Tag substituents at the 3 and 3' or 4 and 4' positions proved to be too far away from the other half of the molecule and therefore unsuitable probes for detection of inequivalent magnetic environment in the two geometrical isomers by conventional NMR techniques. Only by resorting to high-field ^{1}H NMR or the lanthanide-induced shift (LSI) techniques could the separation of the isomeric CH_3 signals of 3,3'-dimethylbianthrone be realized. The absence of geometrical isomerism in this derivative had previously been claimed.[13a] The introduction of bulky substituents (bulkier than fluorine) at the 1 and 1' positions leads to the exclusive formation of *E* isomers due to enhanced steric repulsions in the corresponding *Z* isomers. The benzannelated bianthrone analogues **5** and **6** proved to be superior in differentiation between the *E* and *Z* ^{1}H NMR signals due to the efficient aromatic ring current affecting the substituent opposite to the naphthalene rings. In **2c**, the larger chemical shift of fluorine as compared with hydrogen was reflected also in a better separation of ^{19}F NMR signals of the two geometrical forms.



(E) - 2 (Z) - 2

2a R = H
2b R = CH_3
2c R = CF_3
2d 2,2',3,3'-tetramethyl-6,6'-dibromo

Consider the *folded* (e.g., A type) centrosymmetric geometry of **2** in solution. The *E* isomer has a center of symmetry element while the *Z* isomer has a C_2 symmetry axis; hence, symmetry causes both substituents in each geometrical isomer to be isochronous. The same conclusion holds true in the case of the alternative *twisted* geometry, in which both the *E* isomer and the *Z* isomer have a C_2 symmetry axis. Symmetry considerations show also that the two anthrone halves in each isomer would have identical aromatic spectra.

The ^{1}H NMR spectra of all of the bianthrone derivatives which do not carry substituents at the 1 and 1' positions show the presence of the two forms, *E* and *Z*. The existence of *E,Z* isomers in 1,1'-difluoro-6,6'-diisopropylbianthrone has previously been reported.[14] The *E,Z* isomerism is manifested in the ^{1}H NMR signals of the substituents at the appropriate region and also in the high-field ^{1}H NMR signals of the aromatic protons. The pattern of the aromatic absorptions is more complex than that expected from one isomer. A 300-MHz ^{1}H NMR spectrum of **2b** in $CDBr_3$ is shown in Figure 2a. The two methyl singlets at high field represent the two geometrical forms. The aromatic region shows doubled signals [e.g., doubled H(1) and H(1') doublets at $\delta \sim 6.84$, identified

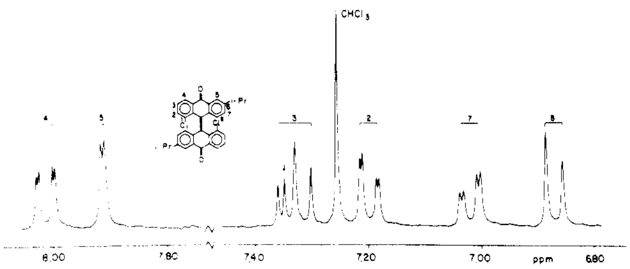


Figure 3. Aromatic region of the ^{1}H NMR spectrum (270 MHz) of 7 in CDCl$_3$ at 25 °C. The arrow marks an impurity.

by their pattern of meta coupling to H(3) and H(3′) and high-field shift (vide infra)], indicating the presence of a mixture of the two isomers. Additional support for this conclusion came from the following decoupling experiment: irradiation of the 2- and 2′-Me signals affected the absorptions of the neighboring H(1) and H(1′) (at δ ~6.84) and H(3) and H(3′) (at δ ~7.25) (these aromatic absorptions are marked in Figure 2 by arrows). Irradiation at the low-field Me signal affected only one of the two doublets at δ ~6.84 (Figure 2b), while irradiation at the high-field Me signal affected only the other doublet (Figure 2c). This behavior indicates that the aromatic spectrum is a superposition due to two different species.

On the other hand, the aromatic region of the 270-MHz ^{1}H NMR spectrum of 1,1′-dichloro-6,6′-diisopropylbianthrone (7) is simple, permitting the assignment of the signals to the various hydrogens of only one isomeric form (Figure 3). The assignment shown in Figure 3 is based on the pattern expected from each proton, on the coupling constants of the various protons, and on the relative position of each signal, taking into account a shielding effect of the *i*-Pr group, a deshielding effect of the Cl group, and the effects of the carbonyl and the other half of the molecule on the ^{1}H NMR absorptions (vide infra). These findings support the contention that the introduction of bulky substituents (bulkier than fluorine) at the 1 and 1′ positions of the **2a** system leads to the exclusive formation of *E* isomers. This is apparently due to the enhanced steric repulsions in the corresponding *Z* isomers. Consistently, early X-ray studies of 1,1′-dimethylbianthrone and 1,1′-dibromobianthrone showed that these 1,1′-disubstituted derivatives of **2a** are present in the solid state in only the *E* forms.[13]

In order to verify whether the bianthrone system adopts a nonplanar (e.g., folded) geometry also in solution, the isopropyl prochiral[15,16] substituent was employed. In a nonplanar molecule, the two methyl groups of the isopropyl prochiral center become diastereotopic and may show chemical shift nonequivalence. The methyl region of the 270-MHz ^{1}H NMR spectrum of 7 is given in Figure 4. It shows the exclusive presence of the *E* isomer. The "isopropyl" methyl groups of (*E*)-7 appear as a double doublet, indicating the lack of a plane of symmetry in the molecule. This conclusion was strengthened by the 250-MHz ^{1}H NMR studies of various 2,2′- and 3,3′-dimethylbianthrones and their benzannelated analogues in the presence of a chiral lanthanide shift reagent (LSR).[17] In all cases, doubling of the isomeric ^{1}H NMR methyl signals was observed in the presence of the chiral LSR, indicating the lack of a plane of symmetry in these substituted bianthrones. The chirality of the folded *Z* isomers and the enantiotopicity of the substituents in the folded *E* isomers are thus established.

A decision between the two alternative nonplanar geometries (twisted and folded) could be made on the basis of the ^{1}H NMR absorptions in the aromatic region. The spectrum of the parent compound (**2a**) may be divided into three aromatic regions: one at a relatively high field (δ ~7.00–7.10), one at a relatively low field (δ ~8), and the other at a normal aromatic field (δ ~7.10–7.43). A similar pattern is observed in substituted bianthrones. The downfield absorptions are ascribed to the protons ortho to the carbonyl bridges [H(4), H(5), H(4′), H(5′)]; these protons are deshielded by the carbonyl anisotropy. The upfield absorptions are ascribed to the protons ortho to the "pinch" [H(1), H(8), H(1′), H(8′)]. These protons are shifted to a high field by the ring current of the opposing benzene rings. This shielding effect is indicative of the proximity of these protons to the sixfold axes of the opposite benzene rings, in accordance with the folded form. The same picture is retained also in the benzannelated analogues. By contrast, the shielding of the protons ortho to the "pinch" would be inconsistent with a twisted geometry. Indeed, a downfield shift of these protons is characteristic of the twisted $\Delta^{9,9'}$-bisfluorenylidenes. The remaining protons [H(2), H(3), H(6), H(7), H(2′), H(3′), H(6′), H(7′)] of **2a** absorb, as expected, at the normal aromatic region. The appearance of high-field ^{1}H NMR aromatic absorptions in the benzannelated analogues indicates that the folded geometry is not interrupted by benzannelation.

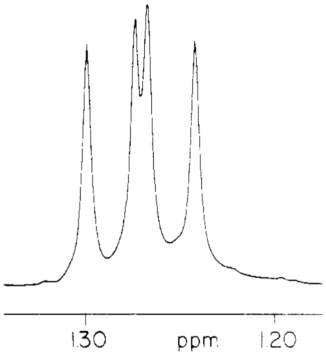


Figure 4. Methyl region of the ^{1}H NMR spectrum (270 MHz) of 7 in CDCl$_3$ at 25 °C.

The *Z*/*E* isomeric ratio in **2b–d** is 1; the ratio differs slightly from 1 only in **5** and **6**. This is consistent with a folded ground-state conformation that prevents additional steric interactions between the 2, 2′, 7, and 7′ positions. This equality in population of the two isomers is retained also in the bulkier CF$_3$-substituted derivative (**2c**). By contrast, in the **3** and **4** series the *E*/*Z* isomeric ratio proved to be more sensitive to the bulkiness of the 2 and 2′ substituents. This difference points toward a smaller interaction between the 2, 2′, 7, and 7′ positions in the bianthrone series (**2**) than in the related **3** and **4** systems.

Dynamic Behavior. The thermal *E*,*Z* isomerization of the 2,2′-disubstituted bianthrone derivatives **2b–d** and the benzannelated analogues **5** and **6** was investigated by the DNMR[6,18,19] method. Table I summarizes the ^{1}H DNMR results. The data were calculated by the usual coalescence approximation[6,18,19] or by the graphic method approximation[20] applying Eyring's formula. It is now generally accepted that these methods give good approximations of the free energy of activation at the coalescence temperature, $\Delta G^{\ddagger}_{c}$. The dependence of $\Delta\nu$ on the temperature found in a few derivatives was taken into account by a linear plot of $\Delta\nu$ vs. T and extrapolating to T_c (coalescence temperature). The data of $\Delta G^{\ddagger}_{c}$ in Table I are the "formal" free energy of activation values for the process $E \rightarrow Z$. They were calculated from the rate constants at the coalescence temperature, assuming a value of unity for the transmission coefficient κ in Eyring's formula.

The dynamic kinetic nature of the line shape changes observed upon heating the solutions of the **2**-type derivatives was

Table I. ^{19}F and ^{1}H NMR and Activation Data for the $E \rightarrow Z$ Isomerization Process in 2

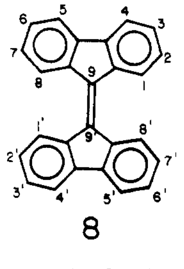
compd	signal followed	solvent	$\Delta\nu_c$, Hz	T_c, K	$\Delta G^{\ddagger}_c$, kcal/mol	$\Delta G°$, kcal/mol
2b	CH_3	bromoform	1.9 ± 0.1^a	357 ± 3	20.0 ± 0.5	0
2d	2,2′-CH_3	bromoform	4.6 ± 0.1^a	374 ± 3	20.3 ± 0.3	0
2c	CF_3	bromoform	16 ± 1^b	414 ± 3	21.5 ± 0.3	0
6	CH_3	bromoform	34.6 ± 0.3^a	423 ± 5	21.6 ± 0.3	0.18 ± 0.02
		hexachloropropene	35.6 ± 0.3^a	420 ± 5	21.6 ± 0.3	0.27 ± 0.03
5	CH_3	bromoform	9.8 ± 0.2^c	425 ± 3	22.7 ± 0.3	0.14 ± 0.02

[a] At 100 MHz. [b] At 84.66 MHz. [c] At 80 MHz.

confirmed by the following independent decoupling experiment (at 250 MHz). Irradiation of the low-field (2.140 ppm) CH_3 singlet of **6** (associated with one isomer) at 120 °C caused a lowering of the intensity of the high-field (1.800 ppm) CH_3 singlet associated with the other isomer. No influence on the high-field signal by decoupling at the low-field singlet was observed at 80 °C and at room temperature; at these lower temperatures, the *E,Z* isomerization process was slowed down.

The fundamental result indicated in Table I is the low values of $\Delta G^{\ddagger}_c$ for the thermal *E,Z* isomerizations of the bianthrone derivatives studied, $\Delta G^{\ddagger}_c$ 20–23 kcal/mol. These exceptionally low rotational energy barriers for an ethylenic system are attributed *predominantly* to the high-energy contents of the folded ground-state conformations. In an idealized planar model of bianthrone, the substantial overlaps of the van der Waals radii at the 1, 1′, 8, and 8′ positions result in strong primary steric interactions. In order to relieve these repulsive interactions, the molecule deviates from coplanarity and adopts the folded geometry in the ground state. The folded ground-state conformation tends to prevent additional steric interactions between R(2) and H(7′). The fast rates of *E,Z* isomerization of the **2**-type derivatives indicate that the folded conformations are of relatively high energy due to the transmission of primary steric interactions into π- and σ-electronic strain. *Ground-state destabilization* is thus the major contributor to the fast thermal *E,Z* isomerizations of these systems.

A careful analysis of the results depicted in Table I leads to the following observations. (i) The $\Delta G^{\ddagger}_c$ values are increased when the 2 and 2′ positions of **2a** are substituted by a bulkier group [$\Delta G^{\ddagger}_c$(**2b**) vs. $\Delta G^{\ddagger}_c$(**2c**)]. (This trend was systematically revealed in the **3** and **4** series.) It is contrary to the traditional decrease in $\Delta G^{\ddagger}_c$ values in substituted ground-state twisted ethylenes upon increasing the "size"[21] of the substituents.[4-7,12,22,23] (ii) The variation of the $\Delta G^{\ddagger}_c$ values depends only on the 2 and 2′ substituents and is insensitive to substituents located further away from the pinch [$\Delta G^{\ddagger}_c$(**2b**) vs. $\Delta G^{\ddagger}_c$(**2d**)]. (iii) Contrary to the behavior of the $\Delta^{9,9'}$-bisfluorenylidene system (**8**),[24] benzannelation of the bianthrone system does not lead to lower $\Delta G^{\ddagger}_c$ values. In the benzannelated analogues **5** and **6**, the $\Delta G^{\ddagger}_c$ values are even higher than those in **2b** and **2d.** (iv) The $\Delta G^{\ddagger}_c$ value of the angularly benzannelated bianthrone **5** is higher than the corresponding value of the linearly benzannelated bianthrone **6**.



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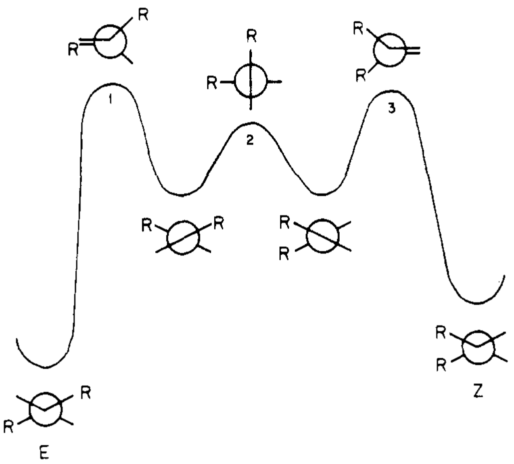


Figure 5. Proposed free-energy profile and isomerization pathway of *E,Z* isomerization in **2**.

We have previously concluded from the dynamic behavior of the 2,2′-disubstituted *N,N*′-dimethylbiacridans[10a,b] and dixanthylenes[10c] that the pure π-electronic barrier in these bistricyclic overcrowded ethylenes is lower in energy than the barrier associated with the highest free-energy transition state (HTS) for the *E,Z* isomerization process. The proposed isomerization scheme for the thermal *E,Z* isomerization of **2** and its free-energy profile are given in Figure 5. This scheme implies a double minimum potential.[10c] It takes into account only one-way rotations that prevent the somewhat higher energy R(2)–R(2′) type steric interactions. The first folded–twisted transition state (F–T TS) suggested for the process exhibits only one primary H(1)–H(8′) type and one secondary R(2)–H(7′) type steric interaction. The secondary R(2)–H(7′) type steric interactions in the HTS may be influenced by an increase in the size of the substituents at positions 2 and 2′ and are responsible for the increase in $\Delta G^{\ddagger}_c$ values on going to a bulkier substituent. The other transition states, TS-2 and TS-3, are expected to be insensitive to the size of the 2 and 2′ substituents; in these transition states, interactions with the 2 and 2′ positions are avoided. The traditional $\pi/2$ twisted ethylene appears along the isomerization pathway only as a transition state between two partially twisted intermediates, but not as the HTS.

Our present results strengthened this picutre of the *E,Z* isomerization pathway. Benzannelation of the bianthrone system (compounds **5** and **6**) offers an advantageous opportunity of a favorable biradical stabilization by the more extensive conjugation in each of the benzanthronyl units. Consider the traditional $\pi/2$ twisted biradical transition state of the *E,Z* isomerization process. According to this scheme, isomerization becomes faster the more stable the corresponding biradical of the olefin is.[5] Therefore, a decrease in $\Delta G^{\ddagger}_c$ values would be expected upon benzannelation. This prediction was substantiated in the case of the twisted $\Delta^{9,9'}$-bisfluorenylidenes (**8**). Lower energy barriers for *E,Z*

Table II. R_f Values in TLC Separations of *E* and *Z* Isomers of Bianthrone Derivatives[a]

bianthrone derivative	R_f at 23 °C	R_f at −15 °C
2,2′-CH_3	0.30	0.41 0.26
2,2′-CF_3	0.80	0.59 0.44
3,3′-CH_3	0.65	0.44 0.29

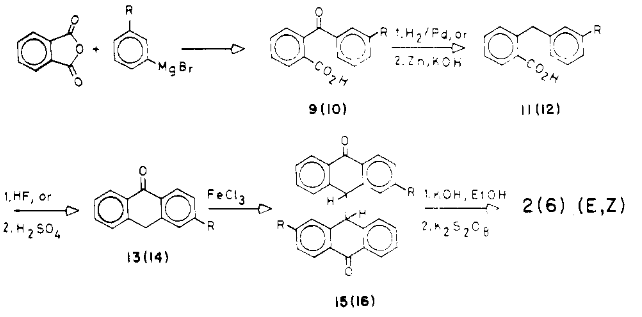
[a] On alumina TLC plates in a 1:1 mixture of dichloromethane and petroleum ether (40–60 °C).

isomerization were realised in $\Delta^{11,11'}$-bis(11*H*-benzo[*b*]fluorenylidene)[24] relative, e.g., to 2,2′-difluorobisfluorenylidene.[25] This benzannelation effect was attributed to the effective delocalization of the unpaired electrons in the biradical transition state due to the favorable extensive conjugation in each of the two orthogonally accommodated aromatic benzo[*b*]fluorenyl units. However, in the case of the bianthrones, the experimental findings point toward a contradictory behavior, providing corroborative evidence in favor of the *E,Z* isomerization scheme presented in Figure 5. The observed increase in $\Delta G^{\ddagger}_c$ values upon benzannelation of the bianthrone system may be rationalized by an enhanced ground-state stabilization (relative to the parent system) due to the more extensive π conjugation exhibited in compounds **5** and **6**. This conjugation effect plays only a minor role in the stabilization of the F–T TS. The free energy of the latter is determined mainly by steric interactions (primary and secondary) around the "pinch". It is obvious that the pattern of the *E,Z* isomerizations of ground-state folded bistricyclic ethylenes is more complex than that encountered in *E,Z* isomerizations of ground-state twisted ethylenes. The barrier associated with the proposed folded–twisted HTS is determined by a combination of the *main* (primary and secondary) steric interactions [H(1)–H(8′) and R(2)–H(7′) type] and the partial loss of π-electronic overlap by twisting about the "pinch". The possibility of stabilizing the biradical $\pi/2$ twisted structure by delocalization in the four phenyl substituents renders its energy lower than the energy of the proposed HTS. The proposed HTS of the *E,Z* isomerization in the bianthrone series is consistent with the calculated dependence of the strain energy on torsion around the "pinch" in bianthrone. The calculations suggested that the structure of the highest energy is not the orthogonal $\pi/2$ twisted ethylene, but an ~40° twisted form.[9]

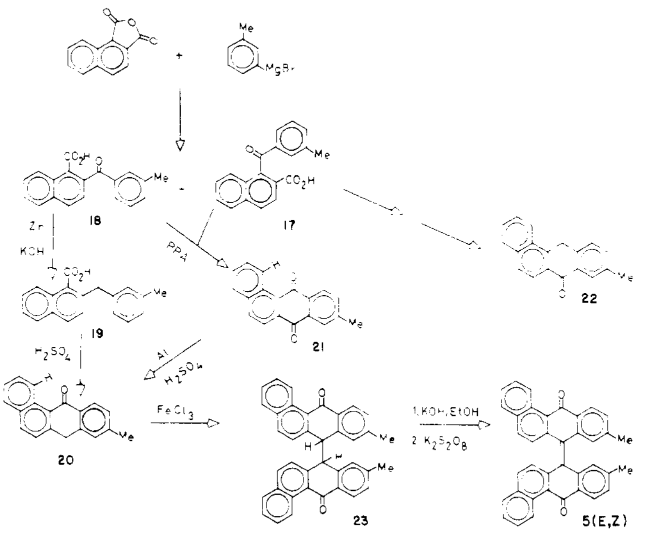
Finally, the difference between $\Delta G^{\ddagger}_c(5)$ and $\Delta G^{\ddagger}_c(6)$ should be considered. The higher value of $\Delta G^{\ddagger}_c(5)$ may be explained by a higher extent of ground-state stabilization in **5** as compared with **6**. In the linearly benzannelated derivative **6**, additional steric interactions between the naphthalene rings and the bucking substituents contribute to the deviation from coplanarity. This destabilizing effect is absent in the angularly benzannelated derivative **5**. By inference, a more extensive π-electronic conjugation is expected in **5**. Its ground-state energy should therefore be lower, leading to higher barriers for *E,Z* isomerization.

Contrary to the low barriers to *E,Z* isomerization in **2**, **5**, and **6**, the free energy of activation of the molecular inversion of **7** is high. In this compound, the ^1H NMR chemical shifts representing the isopropyl methyl groups are strongly temperature dependent. However, the variations of the line shape were not characteristic of a dynamic process. At 270 MHz and 145 °C, two sharp double doublets of these protons were still evident ($\Delta\nu$ = 4.70 Hz). Hence, $\Delta G^{\ddagger}_c$ of the molecular inversion of **7** exceeds 22.8 kcal/mol. The chlorine substituents at the 1 and 1′ positions in **7** increase the energy of the folded–twisted HTS and inhibit a fast molecular inversion. The corresponding molecular inversion process in the related 2,2′-diisopropyldixanthylene system was significantly lower, $\Delta G^{\ddagger}_c$ = 17.7 kcal/mol; the transition state for this process is probably the folded–twisted HTS-1 (Figure 5).

Scheme I. Synthesis of 2-Type Derivatives



Scheme II. Synthesis of 5



The low $\Delta G^{\ddagger}$ values for *E,Z* isomerization in the **2a** series account for the failure of various attempts to separate between *E* and *Z* isomers of **2a** derivatives by chromatography at room temperature.[14] Previous efforts to resolve optical isomers of bianthrone-3-carboxylic acid were also futile,[26] probably because of the fast dynamic conformational processes in this series. These experiments might be successful when carried out at sufficiently low temperatures, in order to ensure a slowdown of the dynamic processes. Indeed, TLC separations between *E* and *Z* isomers of few bianthrone derivatives were achieved at −15 °C. At room temperature the mixture of *E* and *Z* isomers was running in the TLC experiment as a single spot, which at −15 °C was separated into two spots. The experimental data are given in Table II.

Synthetic Approach. The synthesis of the model 2,2′-disubstituted bianthrones and the benzannelated analogues **5** and **6** is outlined in Schemes I and II. The synthetic schemes were based on known reactions; however, the application to new derivatives required several modifications of the known methods (see Experimental Section). The route outlined in Scheme I was followed in the preparation of compounds **2b**, **2c**, and **6**. The meta-substituted *o*-benzoylbenzoic acids (**9**) and 3-(3-methylbenzoyl)-2-naphthoic acid (**10**) were obtained by a Grignard reaction[27–29] between phthalic anhydride, or the symmetrical naphthalene-2,3-dicarboxylic anhydride, and meta-substituted phenylmagnesium bromides. This route permitted the introduction of the tag substituent in a meta position relative to the carbonyl. Reduction of **9** with hydrogen on Pd or with zinc dust in an alkaline medium[30,31] gave the acids **11** and **12**, which were cyclized by HF or H_2SO_4[32,33] to the 3-substituted anthrones **13** [or 2,3-benzo-6-methylanthrone (**14**)]. These cyclizations were found to attack preferentially the para rather than the ortho positions (relative to the substituent on the benzene ring). The direction of the cyclization was established by the ^{1}H NMR spectra of **13** and **14**. These spectra showed two downfield signals due to the deshielded protons ortho to the carbonyl group, while no recognized effect on the absorption of the substituent was observed upon cyclization. The anthrone derivatives **13** and **14** were converted to the bianthronyls **15** and **16** by a bimolecular oxidative coupling with $FeCl_3$.[32-34] The resulting bianthronyl derivatives are expected to be a mixture of meso and (±) modiciations as two new asymmetric centers are formed in the coupling reaction. This expectation[35] has recently been realized.[36] Likewise, most ^{1}H NMR spectra of the present bianthronyl derivatives showed doubled signals due to the methine protons, due to the substituents, and due to some of the aromatic protons, resulting from a superposition of the meso and (±) ^{1}H NMR signals. The bianthronyl derivatives **15** and **16** were enolized (KOH in EtOH) and dehydrogenated ($K_2S_2O_8$) to yield a mixture of *E* and *Z* isomers of the bianthrone derivatives **2** and **6**.[32-34]

The synthetic approach to **5** is outlined in Scheme II. A Gringnard reaction of naphthalene-1,2-dicarboxylic anhydride with *m*-tolylmagnesium bromide gave a mixture of 1-(3-methylbenzoyl)-2-naphthoic acid (**17**) and 2-(3-methylbenzoyl)-1-naphthoic acid (**18**). Fieser[29] has shown that the reaction of this unsymmetrical anhydride with *o*-tolylmagnesium bromide gave preferentially 2-(2-methylbenzoyl)-1-naphthoic acid. Thus, the Grignard reagent favors a nucleophilic attack on the carbonyl at position 2 of the naphthalene-1,2-dicarboxylic anhydride. The mixture of the acids **17** and **18** was separated by several recrystallizations (from benzene or ethanol) into two fractions, a major one with mp 184–185 °C and a minor one with mp 216–218 °C, which were not changed upon further recrystallizations. Comparison of several known derivatives of 1-benzoyl-2-naphthoic and 2-benzoyl-1-naphthoic acids substituted at the benzoyl ring by the same substituents showed that the 1-naphthoic acid always has the lower melting point.[37] This fact, along with Fieser's results,[29] tentatively assigned the major fraction (with the lower melting point) to 2-(3-methylbenzoyl)-1-naphthoic acid (**18**). This assignment was ultimately proved by the identification of the benzanthrone formed from this acid by two independent routes. Route i used the method of reduction of the acid **18** by zinc dust to 2-(3-methylbenzyl)-1-naphthoic acid (**19**) followed by cyclization (H_2SO_4) of the latter to 1,2-benzo-6-methyl-9-anthrone (**20**). (Unequivocal cyclization to the para position relative to the methyl substituent was established as above.)

In route ii a mixture of the acids **17** and **18** was cyclized by polyphosphoric acid to 1,2-benzo-6-methyl-9,10-anthraquinone (**21**). The cyclization goes unequivocally to the position para relative to the methyl. The quinone **21** was reduced by Al/H_2SO_4 to **20**. This method of reduction was shown to affect selectively the 10-carbonyl of the parent 1,2-benzo-9,10-anthraquinone.[34,38] A final verification of the structure of **20** and its naphthoic acid precursors came from the ^{1}H NMR spectra. The spectra of **20** and **21** contain a low-field doublet absorption at δ 9.5~9.9 due to one hydrogen. This low-field absorption is characteristic of the angular hydrogen in proximity to the carbonyl group (which is strongly deshielded by it). For comparison, the corresponding absorption in the model compound 1,2,3,4-tetrahydro-4-oxophenanthrene appeared at δ 9.42.[39] The isomeric benzanthrone (**22**) expected from the acid **17** or from reduction of the 9-carbonyl of **21** would not display such a low-field absorption. For comparison, the corresponding absorption in the model compound 1,2,3,4-tetrahydro-1-oxophenanthrene appeared at δ 8.10.[39] The characteristic low-field absorption of the angular hydrogen in proximity of a carbonyl group establishes the structure of the benzanthrone (**20**) derived from the acid **18**. Consequently, the structure of **18** is identified as 2-(3-methylbenzyl)-1-naphthoic acid. The presence of this low-field absorption in the product of the Al/H_2SO_4 reduction of the benzanthraquinone **21** confirms also the selectivity of this method of reduction, which prefers an attack at the 10 position of **21**. The synthesis of the *E,Z* mixture of **5** from **20** was completed by adopting the classical route applied to the other bianthrone derivatives.

Experimental Section

General. The ^{1}H NMR spectra were obtained using Varian HA-100, Brüker WH-270, Cameca 250-MHz, or Varian 300-MHz spectrometers equipped with a variable temperature unit. The DNMR changes proved to be reversible and characteristic of a dynamic exchange. Temperatures were measured with ethylene glycol using the substitution technique and the Varian or Cameca correlation charts and are considered to be accurate within ±2 °C. ^{1}H NMR spectra were obtained using internal locking, and the data are reported in parts per million, usually downfield from Me_4Si as internal reference (δ units). IR spectra were recorded on a Perkin-Elmer 457 spectrometer. Electronic spectra were recorded on a Unicam SP-800 spectrometer. Mass spectra were recorded on Varian MAT 311 spectrometer. Melting points were measured on a Fischer-Jones capillary melting point apparatus and are uncorrected. Samples were dried over P_2O_5 under vacuum (~1 mm), usually at 100 °C before analysis. No attempts were made to optimize yields.

3-(3-Methylbenzoyl)-2-naphthoic Acid (10). *m*-Tolylmagnesium bromide, prepared by the usual procedure from *m*-bromotoluene (27.4 g, 0.16 mol) and magnesium turnings (4.2 g, 0.17 mol) in dry ether (100 mL), was added dropwise at ~95 °C (under anhydrous conditions) into a well-stirred suspension of naphthalene-2,3-dicarboxylic anhydride[40] (27.7 g, 0.14 mol) in dry benzene (140 mL) and di-*n*-butyl ether (140 mL). The reaction mixture was refluxed for 2 h, and the reaction was terminated by pouring its contents on an ice–HCl mixture. The solvents were removed by steam distillation, and the residue was collected and treated with an aqueous solution of Na_2CO_3 and dichloromethane (~50 mL). The combined aqueous fractions were acidified (HCl), and the precipitating acid was filtered off and washed with water. The acid **10** was purified by trituration with ethanol. It was obtained as a colorless powder: yield 70%; mp 185–188 °C; IR (Nujol) 1680 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3 H), 7.20–7.95 (m, 9 H), 8.59 (s, 1 H); UV λ_{max} (EtOH) nm (log ϵ) 231 (4.75), 327 s (3.20), 337 (3.28); MS *m/e* 290 (M^+, 57), 119 (100). Anal. ($C_{19}H_{14}O_3$) C, H.

The dichloromethane fraction contained some 1,1-di-*m*-tolylnaphthalide (identified by IR and mass spectra) formed by the reaction of two molecules of the Grignard reagent with one molecule of the anhydride.

2-(3-Methylbenzoyl)benzoic acid (9a) was prepared from *m*-tolylmagnesium bromide and phthalic anhydride by a similar procedure to that described above for **10** in 37% yield. In this preparation, the Grignard reagent, prepared from *m*-bromotoluene (8.5 g, 0.05 mol) in dry ether (30 mL), was added dropwise at 0 °C (under anhydrous conditions) to a well-stirred suspension of phthalic anhydride (7.3 g, 0.049 mol) in dry ether (20 mL) and benzene (60 mL). The reaction mixture was then refluxed (at ~70 °C) for 4 h. Following the workup, the crude acid **9a** was obtained as a colorless powder: mp 164–168 °C (lit.[41] mp 159.2–159.6 °C); IR (Nujol) 1675 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3 H), 7.30–7.70 (m, 7 H), 8.05 (dd, J_1 = 2.5 Hz, J_2 = 7 Hz, 1 H), 9.95 (s, 1 H); UV λ_{max} (EtOH) nm (log ϵ) 217 (4.15), 253 (4.07), 280 s (3.45); MS *m/e* 240 (M^+, 30), 119 (100).

2-[3-(Trifluoromethyl)benzoyl]benzoic acid (9b) was prepared from *m*-(trifluoromethyl)phenylmagnesium bromide[42] and phthalic anhydride by the procedure described above for **9a** in 58% yield. The crude acid **9b** was obtained as a colorless powder: mp 167–169 °C (lit.[43] mp 166–168 °C); IR (Nujol) 1678 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 7.20–8.20 (m, 8 H), 8.73 (s, 1 H); UV λ_{max} (EtOH) nm (log ϵ) 239 (4.16), 280 s (3.36), 330 s (2.08); MS *m/e* 294 (M^+, 18), 149 (100). Anal. ($C_{15}H_9F_3O_3$) C, H, F.

1-(3-Methylbenzoyl)-2-naphthoic Acid (17) and 2-(3-Methylbenzoyl)-1-naphthoic Acid (18). *m*-Tolylmagnesium bromide, prepared from *m*-bromotoluene (36.6 g, 0.22 mol) and magnesium turnings (6.1 g, 0.25 mol) in dry ether (120 mL), was added in one portion to a well-stirred solution of naphthalene-1,2-dicarboxylic anhydride[44,45] in dry benzene (800 mL) at ~50 °C. The reaction temperature was then raised to ~100 °C, and the reaction mixture was refluxed for 2 h. After the workup as described for **10**, a mixture of the acids **17** and **18** was obtained in 56% yield. Recrystallization of the mixture of **17** and **18** from benzene or ethanol followed by slow precipitation without cooling yielded the acid **18**, mp 184–185 °C. This melting point was not changed by additional recrystallizations. Acid **18** was obtained as colorless crystals in 29% overall yield: IR (Nujol) 1723 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 3 H), 7.15–8.10 (m, 9 H), 8.86 (d, J = 12 Hz, 1 H); UV λ_{max} (EtOH) nm (log ϵ) 240 (4.30), 285 s (3.73), 301 (3.80), 325 s (3.49); MS *m/e* 290 (M$^+$, 100). Anal. ($C_{19}H_{14}O_3$) C, H.

Concentration of the mother liquors from the above recrystallizations and further recrystallization from benzene or ethanol with cooling (~0 °C) yielded a crop of the acid **17**, mp 216–218 °C (not changed by additional recrystallizations). Acid **17** was obtained as colorless crystals in 5% overall yield: IR (Nujol) 1680 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.33 (s, 3 H), 7.18–8.11 (m, 10 H); UV λ_{max} (EtOH) nm (log ϵ) 233 (4.71), 283 (3.88), 294 (3.79), 322 (3.20), 335 (3.24); MS *m/e* 290 (M$^+$, 92), 119 (100). Anal. ($C_{19}H_{14}O_3$) C, H.

3-(3-Methylbenzyl)-2-naphthoic Acid (12). A magnetically stirred suspension of zinc dust (30 g), $CuSO_4$ (0.3 g), aqueous ammonia solution (25%, 50 mL), and water (150 mL) was boiled for ~15 min to activate the zinc. The acid **10** (10 g) and KOH (10 g) were then added, and the reaction mixture was refluxed (at ~110 °C) for ~48 h. An aqueous ammonia solution (25%, 50 mL) was added to the reaction mixture after ~24 h. The reaction mixture was filtered off, the residue was washed well with aqueous ammonia solution, and the combined filtrate was acidified (HCl). The precipitating acid **12** was collected, washed with water, and recrystallized from methanol. Acid **12** was obtained as colorless crystals: yield 97%; mp 194.5–196 °C; IR (Nujol) 1690 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.27 (s, 3 H), 4.52 (s, 2 H), 6.95–7.94 (m, 9 H), 8.60 (s, 1 H); UV λ_{max} (EtOH) nm (log ϵ) 232 (4.82), 267 (3.78), 280 (3.78), 330 s (3.04), 338 (3.05); MS *m/e* 276 (M$^+$, 25), 258 [(M – H_2O)$^+$, 100]. Anal. ($C_{19}H_{16}O_2$) C, H.

2-(3-Methylbenzyl)benzoic Acid (11a). The acid **9a** (crude, 2.5 g) was dissolved in absolute methanol (30 mL), 10% Pd on carbon was added (~0.2 g), and the solution was hydrogenated on a Parr hydrogenation apparatus at a hydrogen pressure of ~50 psi while heating with a 150-W lamp for about 5 h. After the solvent was evaporated to dryness, the acid **11a** was recrystallized from hexane–petroleum ether (40–60 °C) to yield colorless crystals: yield 99%; mp 106–107 °C; IR (Nujol) 1683 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 3 H), 4.50 (s, 2 H), 7.00–7.60 (m, 7 H), 8.06 (dd, J_1 = 7 Hz, J_2 = 2 Hz, 1 H), 10.0 (s, 1 H); UV λ_{max} (EtOH) nm (log ϵ) 279 (3.18); MS *m/e* 226 (M$^+$, 24), 208 [(M – H_2O)$^+$, 100]. Anal. ($C_{15}H_{14}O_2$) C, H.

2-[3-(Trifluoromethyl)benzyl]benzoic acid (11b) was prepared from **9b** by the procedure described above for **11a** in quantitative yield. It was obtained as colorless crystals: mp 111 °C (from hexane); IR (Nujol) 1695 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 4.48 (s, 2 H), 7.15–7.55 (m, 7 H), 8.09 (dd, J_1 = 8 Hz, J_2 = 2 Hz, 1 H), 8.77 (s, 1 H); UV λ_{max} (EtOH) nm (log ϵ) 216 (4.17), 262 s (3.11), 273 (3.20), 275 (3.24); MS *m/e* 280 (M$^+$, 20), 263 [(M – H_2O)$^+$, 100]. Anal. ($C_{15}H_{11}F_3O_2$) C, H. F.

2-(3-Methylbenzyl)-1-naphthoic acid (19) was prepared from **18** by the procedure described above for **12** in 92% yield. It was obtained as a colorless hemihydrate from the aqueous solution, mp 97–100 °C (the compound changed into a viscous oil at about 75 °C before melting). Repeated trials to obtain the anhydrous acid by azeotropic distillation with benzene yielded an oily product: IR (Nujol) 1690 cm^{-1} (C=O); ^{1}H NMR ($CDBr_3$) δ 2.24 (s, 3 H), 4.18 (s, 2 H), 6.90–8.00 (m, 10 H), 8.60 (s, 2 H, OH + 0.5 H_2O); UV λ_{max} (EtOH) nm (log ϵ) 235 (4.23), 275 (3.65), 321 (2.50); MS *m/e* 276 (M$^+$, 43), 258 [(M – H_2O)$^+$, 100]. Anal. ($C_{19}H_{16}O_2 \cdot 0.5H_2O$) C, H.

2,3-Benzo-6-methyl-9-anthrone (14). Anhydrous HF (~50 mL) was transferred directly through copper tubing into a Teflon-made flask, cooled by an ice–salt cooling bath. **12** (5 g) was introduced, the flask was stoppered, and the reaction mixture was held at ~0 °C for 1 h while occasionally mixing. The flask was then opened, and the HF was allowed to evaporate. The residue was neutralized with aqueous ammonia solution, and the product was filtered off or extracted with dichloromethane. Recrystallization from ethyl acetate gave pale yellowish crystals of **14**: yield 86%; mp 202–203 °C; IR (Nujol) 1660 cm^{-1} (C=O); ^{1}H NMR ($CDBr_3$) δ 2.38 (s, 3 H), 4.33 (s, 2 H), 7.10–8.05 (m, 7 H), 8.17 (d, J = 8 Hz, 1 H), 8.80 (s, 1 H); UV λ_{max} (EtOH) nm (log ϵ) 223 (4.68), 261 (4.40), 304 s (4.11), 315 (4.19), 360 (3.34); MS *m/e* 258 (M$^+$, 100). Anal. ($C_{19}H_{14}O$) C, H.

3-Methyl-9-anthrone (13a) was prepared from **11a** by the procedure described above for **14** in 94% yield. It was obtained as pale yellowish crystals: mp 98–99 °C (lit.[46] mp 101 °C) (from methanol); IR (Nujol) 1658 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3 H), 4.26 (s, 2 H), 7.15–7.60 (m, 5 H), 8.20–8.50 (m, 2 H); UV λ_{max} (EtOH) nm (log ϵ) 274 (4.23); MS *m/e* 208 (M$^+$, 100). Anal. ($C_{15}H_{12}O$) C, H.

3-(Trifluoromethyl)-9-anthrone (13b) was prepared from **11b** by the procedure described above for **14** in 94% yield. It was obtained as pale yellowish crystals: mp 144–145 °C (from petroleum ether, 120 °C); IR (Nujol) 1665 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 4.41 (s, 2 H), 7.40–7.65 (m, 4 H), 7.71 (s, 1 H), 8.26–8.46 (m, 2 H); UV λ_{max} (CH_2Cl_2) nm (log ϵ) 265 (4.22), 302 s (3.62), 310 s (3.58), 350 s (2.04); MS *m/e* 262 (M$^+$, 100). Anal. ($C_{15}H_9F_3O$) C, H, F.

1,2-Benzo-6-methyl-9,10-anthraquinone (21). A mixture of the acids **17** and **18** (3 g) was added under anhydrous conditions to a well-stirred (mechanically) polyphosphoric acid (Fluka, ~83% P_2O_5) solution at 100 °C. After 3 h, the reaction mixture was poured on vigorously stirred water (~500 mL). The green product was filtered off and washed with aqueous $NaHCO_3$ and water. Recrystallization from methanol gave **21** as greenish crystals: yield 85%; mp 124–130 °C; IR (Nujol) 1670 cm^{-1} (C=O); ^{1}H NMR ($CDBr_3$) δ 2.53 (s, 3 H), 7.40–8.30 (m, 8 H), 9.55 (dd, J_1 = 7 Hz, J_2 = 2 Hz, 1 H); UV λ_{max} (CH_2Cl_2) nm (log ϵ) 255 (4.22), 286 (4.58), 344 (3.59), 394 s (3.34); MS *m/e* 272 (M$^+$, 100). Anal. ($C_{19}H_{12}O_2$) C, H.

1,2-Benzo-6-methyl-9-anthrone (20). Procedure A. 19 (3.1 g) was added under anhydrous conditions to concentrated H_2SO_4 (50 mL) at 0 °C, and the mixture was kept at this temperature for 3.5 h with magnetic stirring. After an additional hour at room temperature, the reaction mixture was poured on ice water and the product was extracted with dichloromethane. The organic fraction was evaporated under vacuum incompletely, and the oily residue was triturated with petroleum ether (40–60 °C) to give the product as a brown powder in 45% yield. Attempted recrystallizations resulted in oily products, so the crude product was used for the next steps.

Procedure B. 21 (0.5 g) was dissolved under anhydrous conditions in concentrated H_2SO_4 (6 mL) at 0 °C, and Al powder (0.12 g) was added portionwise. The reaction mixture was magnetically stirred for 3 h at 0 °C and for an additional 3 h at room temperature until its dark color became orange. The reaction was terminated by pouring the solution into ice water and worked up as in procedure A to give **20.** The products of procedures A and B had the same spectral characteristics: IR (Nujol) 1660 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3 H), 4.32 (s, 2 H), 7.17–8.26 (m, 8 H), 9.85 (d, J = 8 Hz, 1 H); UV λ_{max} (CH_2Cl_2) nm (log ϵ) 257 (4.24), 274 s (4.18), 284 (4.26), 292 (4.25), 325 (3.89), 392 s (3.05); MS *m/e* 258 (M$^+$, 100).

7,7′-Dimethyl-2,3:2′,3′-dibenzobianthronyl (16). A gently boiled (145 °C), magnetically stirred solution of **14** (6.4 g) in glacial AcOH (40 mL) was treated dropwise with a solution of $FeCl_3 \cdot 6H_2O$ (12.8 g) and AcONa (~0.3 g) in water (13 mL). The reaction mixture was then refluxed for 1 h; the colorless product started to precipitate within ~15 min. After being cooled, the reaction mixture was diluted with methanol (~20 mL) and the product was filtered off. Recrystallization of the product from ethyl acetate gave **16** in 92% yield as colorless crystals: mp 249–250 °C; IR (Nujol) 1666 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.12 (s, 3 H), 2.22 (s, 3 H), 4.55 (s, 1 H), 4.59 (s, 1 H), 6.24 (s, 1 H), 6.48 (s, 1 H), 6.90–7.90 (m, 14 H), 8.28 (s, 1 H), 8.31 (s, 1 H); UV λ_{max} (CH_2Cl_2) nm (log ϵ) 234 (4.83), 265 (4.73), 317 (4.41), 360 (3.79); MS *m/e* 514 (M$^+$, 0.3), 257 [(M/2)$^+$, 100]. Anal. ($C_{38}H_{26}O_2$) C, H.

2,2′-Dimethylbianthronyl (15a) was prepared from **13a** by the procedure described above for **16** in 88% yield. It was obtained as colorless crystals, mp 234–239 °C dec (lit.[47] mp 239 °C dec), from benzene: IR (Nujol) 1660 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.14 (s, 3 H), 2.29 (s, 3 H), 4.54 (s, 2 H), 6.26 (s, 1 H), 6.50 (s, 1 H), 6.70–8.00 (m, 12 H); UV λ_{max} (EtOH) nm (log ϵ) 275 (4.30), 315 s (4.00); MS *m/e* 414 (M$^+$, seen only on the scope of the instrument, very unstable peak), 208 [(M/2 + 1)$^+$, 100]. Anal. ($C_{30}H_{22}O_2$) C, H.

2,2′-Bis(trifluoromethyl)bianthronyl (15b) was prepared from **13b** by the procedure described above for **16** in 90% yield. It was obtained as colorless crystals, mp 235–238 °C, directly from the reaction mixture: IR (Nujol) 1670 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 4.79 (s, 2 H), 6.51–8.05 (m, 14 H); UV λ_{max} (EtOH) nm (log ϵ) 262 (4.38), 312 s (3.85); MS *m/e* 522 (M$^+$, 0.4), 233 (100). Anal. ($C_{30}H_{16}F_6O_2$) C, H, F.

2,2′-Dimethyl-5,5′,6,6′-dibenzobianthronyl (23) was prepared from **20** by the procedure described above for **16** in 90% yield. It was obtained as colorless crystals: mp 260–262 °C (from chloroform); IR (Nujol) 1660 cm^{-1} (C=O); ^{1}H NMR ($CDBr_3$) δ 1.83 (s, 6 H), 4.75 (s, 2 H), 5.56 (s, 2 H), 7.00–8.20 (m, 14 H), 9.47 (d, J = 9 Hz, 2 H); UV λ_{max} (CH_2Cl_2) nm (log ϵ) 236 (4.62), 260 s (4.45), 295 (4.21), 338 (4.23); MS *m/e* 514 (M^+, 0.3), 258 [$(M/2 + 1)^+$, 100]. Anal. ($C_{38}H_{26}O_2$) C, H.

7,7′-Dimethyl-2,3:2′,3′-dibenzobianthrone (6). Compound **16** (3.3 g) was added to a magnetically stirred solution of KOH (14 g) in absolute EtOH (100 mL) in an argon atmosphere, and the mixture was refluxed for ~0.5 h. The dark blue solution was filtered into a well-stirred solution of $K_2S_2O_8$ (4 g) in water (400 mL). After 2 h, the greenish-yellow product was filtered off, washed with water, and dried. **6** was obtained as yellowish tiny crystals: yield 93%; mp >300 °C (from ethyl acetate); IR (Nujol) 1660 cm^{-1} (C=O); ^{1}H NMR ($CDBr_3$, 100 MHz) δ 1.81, 2.16 (2s, 1:1.25, 6 H), 6.60–8.10 (m, 16 H), 8.58 (s, 2 H), $\nu_E - \nu_Z$ (Me signals) = 34.6 Hz; UV λ_{max} (CH_2Cl_2) nm (log ϵ) 248 (4.93), 277 s (4.66), 298 s (4.59), 350 s (4.05), 420 (4.05); MS *m/e* 512 (M^+, 100). Anal. ($C_{38}H_{24}O_2$) C, H.

2,2′-Dimethylbianthrone (2b) was prepared from **15a** by the procedure described above for **6** in 96% yield. It was obtained as yellowish crystals, mp >300 °C, by column chromatography on alumina (neutral, deactivated with 5% ethyl acetate) with 2:1 benzene–petroleum ether (40–60 °C) as eluent: IR (Nujol) 1670 cm^{-1} (C=O); ^{1}H NMR ($CDBr_3$, 100 MHz) δ 2.07, 2.09 (2s, 1:1, 6H), 6.70–7.40 (m, 10 H), 7.80–8.05 (m, 4 H), $\nu_E - \nu_Z$ (Me signals) = 1.9 Hz; UV λ_{max} (CH_2Cl_2) nm (log ϵ) 268 (4.50), 290 (4.29), 392 (4.21); MS *m/e* 412 (M^+, 100). Anal. ($C_{30}H_{20}O_2$) C, H.

2,2′-Bis(trifluoromethyl)bianthrone (2c) was prepared from **15b** by the procedure described above for **6** in 90% yield. It was obtained as yellowish crystals: mp >300 °C (from xylene); IR (Nujol) 1670 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 6.85–8.36 (m, 14 H); ^{19}F NMR ($CHBr_3$, 84.66 MHz) δ ($CFCl_3$, 84.66 MHz) 63.28, 63.53 (2s, 1:1), $\nu_E - \nu_Z$ (CF_3 signals) = 21.0 Hz; UV λ_{max} (CH_2Cl_2) nm (log ϵ) 234 (4.79), 260 s (4.42), 285 s (4.18), 304 s (4.09), 398 (4.19); MS *m/e* 520 (M^+, 100). Anal. ($C_{30}H_{14}F_6O_2$) C, H, F.

2,2′-Dimethyl-5,6:5′,6′-dibenzobianthrone (5) was prepared from **23** by the procedure described above for **6** in 96% yield. It was obtained as yellowish crystals: mp 290–294 °C dec (from xylene); IR (Nujol) 1664 cm^{-1} (C=O); ^{1}H NMR ($CDBr_3$, 80 MHz) δ 1.99, 2.11 (2s, 1:1.18, 6 H), 6.70–7.92 (m, 16 H), 9.24 (d, J = 9 Hz, 2 H), $\nu_E - \nu_Z$ (Me signals) = 9.8 Hz; UV λ_{max} (CH_2Cl_2) nm (log ϵ) 250 (4.53), 265 s (4.48), 300 (4.34), 325 s (4.15), 406 (4.24); MS *m/e* 512 (M^+, 100). Anal. ($C_{38}H_{24}O_2$) C, H.

2,2′,3,3′-Tetramethyl-6,6′-dibromobianthrone (2d):[33] ^{1}H NMR ($CDBr_3$, 100 MHz) δ 1.97, 2.02 (2s, 1:1, 6 H), 2.26 (s, 6 H), 6.70–7.30 (m, 6 H), 7.34 (s, 2 H), 8.08 (d, J = 2 Hz, 2 H), $\nu_E - \nu_Z$ (Me signals) = 4.6 Hz.

1,1′-Dichloro-6,6′-diisopropylbianthrone (7): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.262, 1.295 (2d, 1:1, J = 7.05 Hz, 12 H), 2.964 (h, J = 7.05 Hz, 2 H), 6.875 (d, J = 8.0 Hz, 2 H), 7.025 (dd, J_1 = 8.0 Hz, J_2 = 1.7 Hz, 2 H), 7.203 (dd, J_1 = 7.8 Hz, J_2 = 1.3 Hz, 2 H), 7.335 (2d, central lines overlap, J_1 = 8.0 Hz, J_2 = 7.8 Hz, 2 H), 7.918 (d, J = 1.7 Hz, 2 H), 8.017 (dd, J_1 = 8.0 Hz, J_2 = 1.3 Hz, 2 H).

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Registry No.—(*E*)-**2b,** 58821-85-5; (*Z*)-**2b,** 58821-82-2; (*E*)-**2c,** 58821-84-4; (*Z*)-**2c,** 58821-83-3; (*E*)-**2d,** 69611-32-1; (*Z*)-**2d,** 69611-33-2; (*E*)-**5,** 69611-40-1; (*Z*)-**5,** 69611-41-2; (*E*)-**6,** 69653-06-1; (*Z*)-**6,** 69653-07-2; **7,** 69653-08-3; **9a,** 2159-37-7; **9b,** 13450-38-9; **10,** 69653-09-4; **11a,** 69653-10-7; **11b,** 58821-80-0; **12,** 69653-11-8; **13a,** 69653-12-9; **13b,** 69653-13-0; **14,** 69653-14-1; (±)-**15a,** 69653-15-2; *meso*-**15a,** 69653-16-3; (±)-**15b,** 69653-17-4; *meso*-**15b,** 69653-18-5; (±)-**16,** 69668-78-6; *meso*-**16,** 69653-19-6; **17,** 69653-20-9; **18,** 69653-21-0; **19,** 69653-22-1; **20,** 69653-23-2; **21,** 59953-97-8; **23,** 69653-24-3; *m*-bromotoluene, 591-17-3; naphthalene-2,3-dicarboxylic anhydride, 716-39-2; phthalic anhydride, 85-44-9; *m*-trifluoromethylphenyl bromide, 401-78-5; naphthalene-1,2-dicarboxylic anhydride, 5343-99-7.

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