Bridged [18]Annulenes. A Study of the Synthesis and Properties of 12c,12d,12e,12f-Tetrahydrobenzo[*g,h,i*]perylene and Its Analogues

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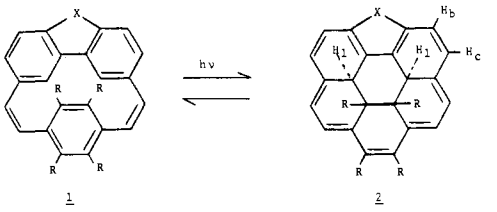
Abstract: A synthesis of [2.2](3,3′)biphenyloparacyclophane-1,9-diene (**1a**) and its five analogues (**1b, 1c, 1d, 1e,** and **1f**) is described. These cyclophanedienes are converted on irradiation to 12c,12d,12e,12f-benzo[*g,h,i*]perylene (**2a**) and its analogues, **2b, 2c, 2d, 2e,** and **2f,** respectively. All of the 12c,12d,12e,12f-benzo[*g,h,i*]perylene derivatives show the NMR spectral characteristics to be expected for bridged [18]annulenes having a strong diamagnetic ring current. The effect of different bridging groups upon the magnitude of the ring current is discussed. For those bridged [18]annulene derivatives (**2d** and **2f**) having internal methyl groups, dehydrogenation or oxidation leads to the corresponding phenanthreno- or dibenzothiopheno[18]annulenes, **16d** and **16f.**

In the accompanying paper,[1] the desirability of having higher membered annulenes with rigid, planar perimeters as test molecules for the predictions that annulenes become polyenic in their properties with larger ring size is discussed. At present the bridged annulenes appear to be one of the more likely types of structure to provide a clear answer to the question of what ring size is the limiting one for aromatic character. In our previous studies we developed synthetic methods for providing variously substituted dihydropyrenes, as examples of bridged [14]annulenes.[2] We now report the extension of these methods for the synthesis of higher membered analogues.

The best examples of the dihydropyrenes, as representatives of bridged [14]annulenes, are the *trans*-15,16-dialkyldihydropyrenes. To prepare higher membered annulenes with internal alkyl groups appears to be a very formidable task. However, *trans*-15,16-dihydropyrene can be prepared in solution by irradiation of [2.2]metacyclophane-1,9-diene.[3] Although *trans*-15,16-dihydropyrene is readily oxidized to pyrene on contact with oxygen and attempts to isolate it in a pure crystalline state under an inert atmosphere have been unsuccessful, degassed solutions of *trans*-15,16-dihydropyrene are relatively stable and quite satisfactory for measuring NMR and electronic spectra.[3] The lack of pure crystalline material prevents x-ray crystallographic analysis, and the obtaining of certain other data. However, if one is willing to accept this limitation of only being able to examine the properties of a molecule in solution, the task of preparing highe r members of the bridged annulenes is made very much easier. This approach depends then on preparing appropriate, stable cyclophanedienes which on irradiation, give solutions containing the corresponding bridged annulenes.

The simplest extension of this method, and the one to which we have addressed ourselves in this study, is the synthesis of rigid, bridged [18]annulenes. As illustrated below, the photocyclization of a [2.2](3.3′)biphenyloparacyclophane-1,9-diene (**1**) would be expected to yield the corresponding bridged [18]annulene, a 12c,12d,12e,12f-tetrahydrobenzo[*g,h,i*]perylene (**2**).

The overall approach taken for the syntheses of the six cyclophane dienes, **1af,** was the same in each case and this is summarized in Scheme I. A coupling reaction between a 3,3′-disubstituted biphenyl **3** and a *p*-xylylene derivative **4** provided a dithiacyclophane **5.** This was subjected to a Stevens rearrangement to give the corresponding ring-contracted cyclophane **6.** Subjection of **6** to the Hofmann exhaustive

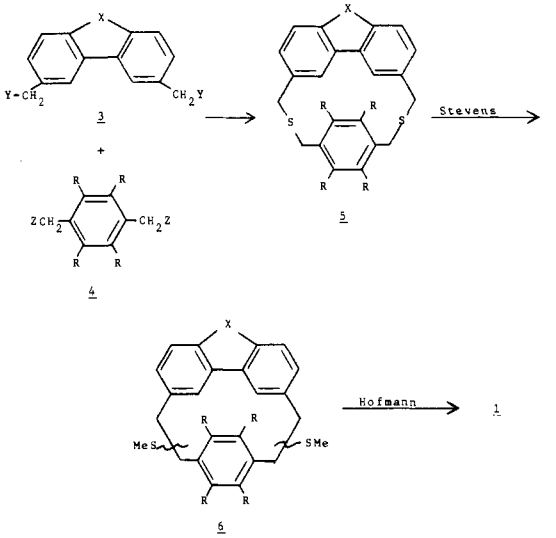


a, X= -H,-H,R= -H
b, X= $-CH_2CH_2-$,R= -H
c, X= -CH=CH-,R= -H
d, X= -CH=CH-,R= $-CH_3$
e, X= -S-,R= -H
f, X= -S-,R= $-CH_3$

methylation procedure then gave the desired cyclophanediene **1.** In almost all cases the coupling reactions to form the dithiacyclophanes **5** proceeded in high yield (~85%). The yields in the Stevens rearrangement step were poor to average, and the yields in the Hofmann elimination step were generally poor.

For the preparation of **1a,** it was necessary to obtain 3,3′-bis(mercaptomethyl)biphenyl (**3,** X = -H, -H; Y = -SH), and this was prepared most conveniently by the bromination of commercial 3,3′-dimethylbiphenyl with *N*-bromosuccinimide followed by reaction of the product with thiourea and hydrolysis.

Scheme I



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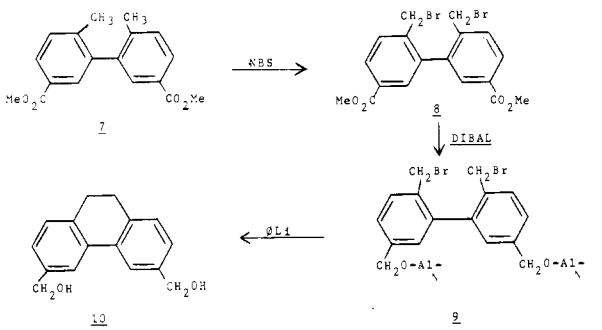
For the preparations of **1c** and **1d,** a suitable 3,6-disubstituted phenanthrene was needed. Oxidative photocyclization of *trans*-4,4′-bis(carboethoxy)stilbene readily gave 3,6-bis(carboethoxy)phenanthrene (**3,** X = -CH=CH-; Y = $-CO_2Et$). This, on reduction with lithium aluminum hydride to the diol followed by reaction with hydrobromic acid, readily gave the desired 3,6-bis(bromomethyl)phenanthrene (**3,** X = -CH=CH-; Y = -Br).

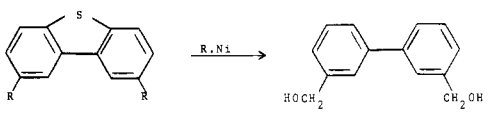
It had been hoped that either chemical or electrochemical reduction of one of the available 3,6-disubstituted phenanthrene derivatives from the previous synthesis would readily give the needed corresponding 3,6-disubstituted 9,10-dihydrophenanthrene, but all such attempts were unsuccessful. For the preparation of **1b,** then, we turned to 2,2′-dimethyl-5,5′-bis(carbomethoxy)biphenyl (**7**), formed by the Ullmann reaction of methyl 3-iodo-4-methylbenzoate. Treatment of **7** with *N*-bromosuccinimide gave a mixture of isomers, from which the desired dibromide **8** could be separated in poor yield by a rather tedious recrystallization. Various methods of effecting the cyclization of **8** to the corresponding 9,10-dihydrophenanthrene were tried without success. However, it was found that the reduction of **8** with diisobutylaluminum hydride (DIBAL) occurred smoothly without destruction of the carbon–bromine bonds. However, workup of the reaction mixture without hydrolysis of the bromomethyl group as well as providing suitable protecting groups for the hydroxyls proved to be a problem. Fortunately, both of these difficulties could be by-passed very nicely by treating the intermediate **9,** from the



DIBAL reduction, directly with a solution of phenyllithium. The overall conversion of **8** to **10** in this manner was accomplished in 65% yield. Treatment of **10** with phosphorus tribromide then gave the desired 3,6-bis(bromomethyl)-9,10-dihydrophenanthrene (**3,** X = $-CH_2CH_2-$; Y = Br) in 97% yield.

For the syntheses of **1e** and **1f,** a 2,8-disubstituted dibenzothiophene was needed. Neumoyer and Amstutz had reported that the bromination of dibenzothiophene gave 2,8-dibromobenzothiophene (**11**),[4] and we were able to repeat their procedure in a much improved yield. The von Braun replacement of bromine with cyanide gave **12** in 64% yield, and the subsequent reduction of **12** with DIBAL produced the dialdehyde **13** in 50% yield. Alternatively, treatment of 2,3-dibromodibenzothiophene (**11**) with *n*-butyllithium followed by addition of dimethylformamide gave the dialdehyde **13** directly in 68% overall yield. Reduction of dialdehyde **13** with sodium borohydride gave the diol **14** in 98% yield. At this point the question of whether the bromination of dibenzothiophene had in fact given the 2,8-dibromo derivative **11** was settled. Treatment of the diol **14** with Raney nickel catalyst effected removal of the sulfur and gave 3,3′-bis(hydroxymethyl)biphenyl, identical in all respects with a sample of **3** (X = -H, -H; Y = -OH) prepared previously. Finally, the reaction of the diol **14** with hydrobromic acid gave the bis(bromomethyl) derivative **15** in 93% yield.

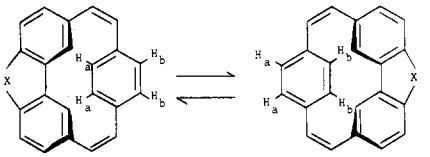
From these synthetic efforts the six cyclophanedienes **1af** were available. Before considering their possible cyclizations



11, R= -Br
12, R= -CN
13, R= -CH=O
14, R= $-CH_2OH$
15, R= $-CH_2Br$

to **2,** we should describe their probable geometry. In the case of the biphenyl derivative **1a,** the two benzene rings of the biphenyl moiety are probably twisted out of the plane with respect to each other and the whole of the biphenyl moiety undergoes conformational flipping across the face of the para-bridged benzene ring. The protons of the para-bridged ring of **1a** appear as a singlet at τ 2.72 and this spectrum is unchanged by cooling to below −100 °C. Thus, **1a** shows easy conformational mobility providing a single time-averaged environment for the protons of the para-bridged benzene ring.

For the other cyclophanedienes **1b–f,** the biphenyl moiety is held rigidly planar by a bridging atom or atoms. The only conformational flipping possible in these cases is that of the planar biphenyl moiety across the face of the para-bridged rings. As is illustrated below, the one conformer of **1b, 1c,** and **1e** has the H_a protons under the face of the biphenyl moiety, whereas in the other conformer it is the H_b protons that are under the face of the biphenyl moiety. The protons under the face of the biphenyl moiety will be shifted sharply upfield owing to the ring current of the biphenyl moiety and, if the rate of conformational flipping is slow on the NMR time scale, the para-bridged aromatic protons will appear as two separate signals. However, if the rate of conformational flipping is fast, the four para-bridged aromatic protons will appear as a singlet.[5] For **1b** and **1c** the rate of conformational flipping is fast



Conformational Flipping of 1b, 1c, and 1e

and their NMR spectra, showing the four para-bridged aromatic protons as a singlet, is unchanged on cooling to the lowest temperature (−100 °C) experimentally feasible.

However, the NMR spectrum of **1e** is temperature dependent and the signal for the four para-bridged aromatic protons, which appears as a broad singlet at τ 3.3 at room temperature, is split into two singlets at τ 2.62 and 4.09 at −65 °C. The coalescence temperature is −10 °C which makes possible an estimation of 12 kcal/mol for the energy of activation of the conformational flipping process.[6] Apparently, the bond angles for the dibenzothiophene moiety differ enough from those of the other biphenyl moieties to provide a measurable energy barrier to conformational flipping.

The durene derivatives **1d** and **1f** behave quite analogously to their *p*-xylylene counterparts. The NMR spectrum of **1d** shows no temperature dependence in the temperature range feasible for measurement. On the other hand, the NMR spectrum of **1f** is also temperature dependent and the signal for the methyl groups on the para-bridged aromatic ring, which appear at τ 8.36 at room temperature, is split into two signals at τ 7.53 and 9.27 at −60 °C. The coalescence temperature occurs at −33 °C, corresponding to an energy of activation of 11 kcal/mol. The fact that the conformational flipping process is slightly easier for the durene derivative **1f** as compared with the parent hydrogen example **1e** is probably due to the fact that

the steric interaction between the methyl groups and the dibenzothiophene moiety raises the energy of the extreme conformational ground states slightly, but has little or no effect on the energy of the transition state for the flipping process.

Examination of molecular models strongly suggests that, regardless of the conformational mobility of the cyclophanedienes **1a–f**, the cyclization process, either thermally or photochemically, can lead to only one possible stereoisomer for the bridged [18]annulene, that shown by structure **2**. It is interesting that the concerted thermal cyclization of **1** → **2**, a type of Diels–Alder reaction, is an allowed process by the Woodward–Hoffmann rules of conservation of orbital symmetry.[7] Furthermore, the mass spectra of **1a, 1b, 1c,** and **1e** show formation of the expected molecular ion with subsequent successive losses of four hydrogens, corresponding to cyclization and aromatization to the benzo[*g,h,i*]perylene moiety. Whether the cyclization of these cyclophanedienes is induced thermally or by electron impact is not clear. However, all attempts to effect a Diels–Alder-type cyclization of the cyclophanedienes **1a–f** under ordinary thermal conditions were unsuccessful, possibly due to an unfavorable energy relationship in the Diels–Alder equilibrium.

The photocyclization of **1** → **2** must proceed by two successive, *cis*-stilbene-type, ring closures. In the event, irradiation of solutions of each of the cyclophanedienes **1a–f** in perdeuteriotetrahydrofuran caused a change in color to deep orange or reddish orange, and the NMR spectra of the irradiated solutions showed new signals at both higher and lower field than those of the starting cyclophane dienes. The course of the photocyclization could readily be followed by NMR monitoring and, with the exception of the two examples (**1d** and **1f**) having internal methyl groups, the photostationary state corresponded to complete, or nearly complete, conversion to the bridged [18]annulenes. In the case of **1d,** the photostationary state corresponded to about a 40% conversion to **2d,** whereas with **1f** the conversion to **2f** was only ~20%.

The NMR chemical shifts for the internal protons of the various bridged [18]annulenes are summarized in Table I. Examples **2a, 2b, 2c,** and **2d**, where R = -H, show the four internal protons as an AA′BB′ multiplet broadened a bit by long-range coupling with the peripheral aromatic protons. The spectral pattern is somewhat complicated and the actual chemical shift values listed in Table I were derived from computer simulation experiments. The question of which proton is the upfield proton can be decided from theoretical calculations, as discussed in the accompanying paper.[1] The same assignment can also be deduced from a comparison of the NMR spectra of **2e** and **2f,** which differ only by substitution of methyl groups for two of the internal hydrogens. The downfield internal protons of **2e** remain unchanged in **2f,** whereas the upfield internal protons of **2e** are replaced by a new signal for the internal methyl protons.

The signals for the internal protons of **2a, 2b,** and **2c** are at high field and in accord with an aromatic molecule having a strong diamagnetic ring current. However, as discussed,[1] the chemical shifts for the internal protons of **2a, 2b,** and **2c** are not at as high a field as would be predicted and are drastically lower than the chemical shifts for the internal protons of 12b,-12c,12d,12e,12f,12g-hexahydrocoronene. The reasons for this are not obvious. Examination of Dreiding molecular models of **2a, 2b,** and **2c** suggest that each has a rigid, planar annulene perimeter. The replacement of the 1 and 12 hydrogens of **2a** by a bridging $-CH_2CH_2-$, as in **2b**, does not appear to affect the geometry of the molecule, and this is supported by the fact that the chemical-shift patterns for the internal protons for **2a** and **2b** are exactly the same.

In the accompanying paper,[1] it is suggested that a possible explanation for the lowered ring currents in **2a** and **2b** is the nonequivalence of the two Kekule structures contributing to the resonance hybrid in each case. Coupling constants of adjacent ortho hydrogens are a sensitive indicator of π-bond order and the differences in the coupling constants observed for **2a** provide evidence for some bond fixation. Thus, for **2a,** $J_{HX,Hb}$ = 8.9 Hz, whereas $J_{Hb,Hc}$ = 6.7 Hz. For **2b,** $J_{Hb,c}$ is likewise 6.7 Hz. However, for the phenanthrene derivative **2c,** $J_{Hb,Hc}$ = 9.0 Hz, an apparent reversal of the preferred Kekulé structure in going from **2a** or **2b** to **2c.** One of the puzzles of the chemical shift data in Table I is why **2c,** which contains a localized benzene ring, should exhibit an annulene ring current of greater magnitude than the simple bridged [18]annulenes, as in **2a** and **2b.** A possible explanation might be that the dampening effect on the annulene ring current due to the localized benzene ring is offset by the fact that the two Kekulé structures for **2c** are more nearly equivalent in energy than is the case for **2a** and **2b.**

Table I. Chemical-Shift Values for the Internal Protons of the Bridged [18]Annulenes

	Chemical shifts, τ[a]		
		R	
Compd	H_I	-H	$-CH_3$
2a	12.53	12.88	
2b	12.53	12.88	
2c	12.74	13.02	
2d	11.20		11.94
2e	14.94	15.66	
2f	14.96		13.74
16d			10.00
16f			8.88

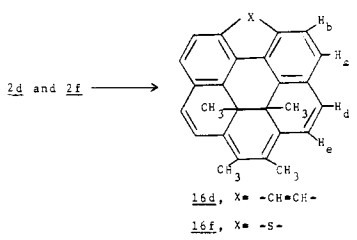
[a] Data are for perdeuteriotetrahydrofuran solutions measured at room temperature.

The sulfur derivatives **2e** and **2f** clearly show appreciably larger ring currents than do any of the other compounds in Table I. Yet, on inspection of molecular models their geometry appears no more favorable. The possibility that there is something inherent in having a heteroatom such as sulfur in the annulene perimeter that causes an increase in ring current would be rather surprising. In **2e** and **2f**, the coupling constant for $J_{Hb,Hc}$ is 8.6 Hz. The explanation for the greater ring current in **2e** and **2f** then may be simply that the two Kekulé structures for these molecules are more nearly equivalent in energy than is true for the other examples.

Whereas the irradiation of compounds **2a, 2b, 2c** and **2e** could be done at room temperature or lower, the photocyclization of **1d** and **1e** to provide a measurable quantity of **2d** or **2f** required that the irradiation be done at low temperature (−80 °C). From the work of Blattmann and Schmidt in the dihydropyrene series, it is known that the quantum yield for the photocyclization of [2.2]metacyclophane-1,9-dienes is ~1 and is essentially independent of both temperature and the presence of substituents.[8] However, the reverse photoreaction of dihydropyrene going to 12.2]metacyclophane-1,9-diene has a much smaller quantum yield and is strikingly dependent on both temperature and the presence of substituents. Thus, reasoning by analogy, one can interpret the need for low temperatures during the irradiation of **1d** and **1f** as being due to the fact that the photostationary state for these compounds at room temperature does not have a measurable concentration of the bridged [18]annulenes **2d** and **2f.** However, at −80 °C, where the quantum yield of the reverse photoreaction is much lower, the concentration of **2d** and **2f** builds up to the observed values of 40 and 20% in the photostationary state.

In general, the irradiated solutions containing the bridged [18]annulenes are stable at room temperature and can be stored indefinitely in the dark without change. When the solution containing **2f,** formed by irradiating **1f** at −80 °C, was brought to room temperature, the NMR signals for the pho-

toproduct **2f** slowly disappeared. The rate of disappearance of **2f** at 55 °C very nicely followed first-order kinetics with a half-life of 90 s and a calculated activation energy of 22.5 kcal/mol. At first it was thought that the first-order thermal reaction was simply a reversal of the cyclization to give back **1f**. When a solution of **1f** was carried through several cycles of low temperature irradiation followed by warming to 55 °C, though, its NMR spectrum showed signals indicating the formation of a new compound, **16f**. As summarized in Table I, **16f** shows a complete loss of signal for the internal H_1 protons and the signal for its internal methyl protons appears at τ 8.82 compared with the value of 13.74 for **2f**. Similarly, the signal for the protons of the external methyl groups, which appear at τ 6.65 in **2f**, now appear at 7.77. The chemical shift values



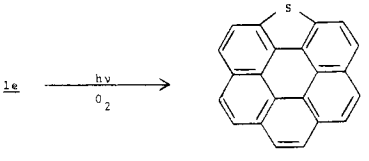
found for **16f** are in good accord with what one would have predicted based on the analogy of **16f** to the simple [18]annulene incorporating a phenanthrene moiety studied by Staab.[9]

The thermal reaction whereby **2f** is transformed into **16f** appears to be a concerted elimination of the two bowsprit hydrogens (H_1) with concomitant formation of the dibenzothiophene moiety. The concerted thermal elimination of the bowsprit hydrogens of 1,4-cyclohexadiene to give benzene is a well-studied reaction, occurring in the temperature range of 314–360 °C with a $\Delta G^{\ddagger}$ value of 42.69 kcal/mol.[10] The ease with which **2f** loses a molecule of hydrogen to form **16f** is surprising, but it may relate not only to the driving force to form the dibenzothiophene moiety but also to a substantial relief of steric strain.

When an attempt was made to form **16f** on a preparative scale by irradiating **1f** at 55 °C, there was no measurable reaction. To form **16f** the irradiation of **1f** must be carried out at low temperatures and then the solution can be warmed in the dark. This supports our earlier speculation that the photostationary state for the irradiation of **1f** at room temperature or above must contain only a minute concentration of **2f**.

An investigation of the irradiated solutions of **1d** showed that the photoproduct **2d** is appreciably more stable than **16f**, being unaffected by warming to 80 °C. However, when the solution containing **2d** was exposed to oxygen, there occurred a rapid dehydrogenation to give **16d**. The signal for the internal methyl protons of **16d** appears at τ 10.00, whereas the signal for the protons of the external methyl protons appears at τ 7.46. The fact that both **16d** and **16f** can be formed by air oxidation of the corresponding photoproducts **2d** and **2f** illustrates the greater stability conferred on the bridged annulenes by the presence of internal alkyl groups.

In the case of the other bridged [18]annulenes having only internal hydrogen atoms, exposure to oxygen leads to rapid aromatization giving the corresponding benzo[*g,h,i*]perylene derivative. This was carefully followed with **1e**. Irradiation of



a solution of **1e** in the presence of oxygen quickly led to a quantitative conversion to thiacoronene.

Probably the most significant impression to be gained from these studies is that rather subtle changes of structure within a series, such as the tetrahydrobenzo[*g,h,i*]perylenes, can cause surprisingly large changes in ring current and chemical shift values. Thus, considerable caution must be exercised in making any general statements about trends toward bond alternation or a limiting size for aromaticity based on experimental observations for a single compound or even a group of compounds. One must be certain that the best possible model structures have been employed before a firm conclusion can be drawn.

Experimental Section[11]

3,3′-Bis(mercaptomethyl)biphenyl (3, X = -H, -H; Y = -SH). A. From 3,3′-Bis(carbomethoxy)biphenyl. To a solution of 14.2 g of 3,3′-bis(carbomethoxy)biphenyl[12] in 200 mL of tetrahydrofuran was added in small portions with stirring 4.0 g of lithium aluminum hydride. The mixture was stirred at room temperature for 15 min, and then it was hydrolyzed by successive additions of 4 mL of water and 4 mL of 15% aqueous sodium hydroxide solution. After removal of the precipitate by filtration and concentration of the filtrate, the residual solid was recrystallized from dichloromethane to give 7.0 g (62%) of 3,3-bis(hydroxymethyl)biphenyl (**3**, X = -H, -H; Y = -OH) as white needles, mp 116.5–117.0 °C. Anal. ($C_{14}H_{14}O_2$) C, H.

A solution of 6.7 g of **3**, (X = -H, -H; Y = -OH) and 5.0 g of thiourea in 60 mL of a solution of 48% aqueous hydrobromic acid was boiled under reflux for 11 h. It was cooled, made basic, and stirred an additional 15 min. It was then brought to neutrality by careful addition of a 2 N aqueous solution of hydrochloric acid, and extracted with 200 mL of dichloromethane. The dichloromethane extract was dried and concentrated to give 6.9 g (90%) of 3,3′-bis(mercaptomethyl)biphenyl (**3**, X = -H, -H; Y = -SH) as fine white crystals, mp 61.0–61.5 °C. Anal. ($C_{14}H_{14}S_2$) C, H.

B. From 3,3′-Bis(bromomethyl)biphenyl (3, X = -H, -H; Y = -Br). A solution of 33.8 g of 3,3′-bis(bromomethyl)biphenyl[13] (**3**, X = -H, -H; Y = -Br) and 15.0 g of thiourea in 150 mL of dimethyl sulfoxide was stirred at room temperature for 14 h. It was then poured onto an ice slurry containing 45 g of sodium hydroxide in 450 mL of water. After the resulting mixture had been stirred for 15 min, it was extracted with dichloromethane. The extract was dried and concentrated. The residue was chromatographed over a short column of silica gel using dichloromethane for elution. The main eluate fraction gave 21.8 g (90%) of fine white crystals, mp 61.0–61.5 °C, identical in all respects with the sample of **3** (X = -H, -H; Y = -SH) prepared in A.

2,11-Dithia[3.3](3,3′)biphenyloparacyclophane (5, X = -H, -H, R = -H). A solution of 21.8 g of **3** (X = -H, -H; Y = -SH) and 23.2 g of 1,4-bis(bromomethyl)benzene (**4**, R = -H; Z = -Br) in 700 mL of benzene was added dropwise from a Hershberg funnel with stirring to a solution of 7.5 g of sodium hydroxide in 1,2 L of absolute ethanol. When the addition was complete (2 days), the mixture was concentrated and the residue extracted with 400 mL of dichloromethane. The dichloromethane extract was concentrated and the residue chromatographed over a short silica gel column using dichloromethane for elution. The main fraction of eluate gave 16.0 g (52%) of white needles: mp 215–216 °C; NMR multiplet at τ 2.6–3.1 (10 H, ArH), singlet at 3.52 (2 H, ArH), and singlets at 6.13 and 6.26 (4 H each, $-CH_2S-$). Anal. ($C_{22}H_{20}S_2$) C, H.

Stevens Rearrangement of 5 (X = -H, -H; R = -H). A mixture of 7.0 g of **5** (X = -H, H; R = -H) and 8.1 g of dimethoxycarbonium fluoroborate[14] in 100 mL of dichloromethane was stirred at room temperature for 14 h and then was diluted with methyl formate. The crystalline precipitate of the bissulfonium fluoroborate was collected by filtration and dried to give 11.1 g (100%) of crystals. To a solution of 2.0 g of the bissulfonium fluoroborate salt in 50 mL of dry tetrahydrofuran was added 1.2 g of potassium *tert*-butoxide. After the mixture had been stirred at room temperature for 30 min, it was diluted with 100 mL of dichloromethane and washed successively with dilute aqueous acid and water. The organic layer was dried and concentrated. Chromatography of the residual oil over silica gel using a 10:1 mixture of carbon tetrachloride and dichloromethane gave a mixture of stereoisomers corresponding to **6** (X = -H, -H; R = -H) as 300 mg (22%) of a colorless oil. One of the stereoisomers could be separated by fractional crystallization from a dichloromethane-pe-

troleum ether (30-60 °C) mixture as white needles, mp 131-132 °C. Anal. ($C_{24}H_{24}S_2$) C, H.

Hofmann Elimination to give 1a. A mixture of 2.70 g of **6** (X = -H, -H; R = -H) and 2.9 g of dimethoxycarbonium fluoroborate in 50 mL of dichloromethane was stirred at room temperature for 12 h and then diluted with methyl formate. The crystalline precipitate was collected by filtration and dried to give the bissulfonium fluoroborate of **6** (X = -H, -H; R = -H) as 3.05 g (70%) of crystals. A mixture of 2.96 g of the bissulfonium fluoroborate of **6** (X = -H, -H; R = -H) and 1.6 g of potassium *tert*-butoxide in 100 mL of tetrahydrofuran was stirred at room temperature for 10 min. It was then diluted with 100 mL of dichloromethane and washed successively with aqueous acid and water. After the organic layer had been dried and concentrated, the residual oil was chromatographed over silica gel using carbon tetrachloride for elution to give 190 mg (13%) of white plates: mp 150-151 °C; NMR multiplet at τ 2.6-3.0 (10 H, ArH), doublet at 2.90 (2 H, J = 12 Hz), doublet at 3.37 (2 H, J = 12 Hz), and singlet at 3.26 (2 H, ArH); mass spectrum (70 eV) *m/e* (rel intensity), 282 (34), 281 (28), 280 (100), 279 (50), 278 (36), 277 (62), and 276 (65). Anal. ($C_{22}H_{16}$) C, H.

Dimethyl 2,2'-Bis(bromomethyl)biphenyl-5,5'-dicarboxylate (8). A mixture of 4.4 g of dimethyl 2,2'-dimethylbiphenyl-5,5'-dicarboxylate (**7**),[15] 5.25 g of *N*-bromosuccinimide, and 30 mg of benzoyl peroxide in 60 mL of carbon tetrachloride was boiled under reflux for 5 h. After removal of succinimide by filtration, the filtrate was concentrated and the residue was chromatographed over silica gel using chloroform for elution. From the eluate a mixture of mono-, di-, and tribromides separated, from which, by fractional crystallization from a dichloromethane-hexane mixture, there was isolated 2.0 g (30%) of the dibromide **8** as white plates: mp 131.5-133.5 °C; NMR doublet of doublets at τ 1.88 (2 H, $J_{a,b}$ = 8 Hz, ArH), doublet at 2.05 (2 H, J = 2 Hz, ArH), doublet at 2.5 (2 H, J = 2 Hz, ArH), quartet at 5.74 (4 H, $-CH_2Br$), and singlet at 6.09 (6 H, CH_3O-); mass spectrum (70 eV) *m/e* 454, 456, and 458. Anal. ($C_{18}H_{16}O_4Br_2$) C, H, Br.

3,6-Bis(hydroxymethyl)-9,10-dihydrophenanthrene (10). To a solution of 1.45 g of dimethyl 2,2'-bis(bromomethyl)biphenyl-5,5'-dicarboxylate (**8**) in 75 mL of dry ether under nitrogen at 0 °C there was added dropwise with stirring 11.0 mL of a 1.18 M solution of diisobutylaluminum hydride in benzene. After the solution had been stirred at room temperature for 10 h, it was cooled to 0 °C and 13 mL of a 1.16 M solution of phenyllithium in ether was added. The mixture was warmed to room temperature and stirred an additional 1.5 h. The ether solution was then washed successively with water, dilute aqueous acid, and water. The ether solution was then dried and concentrated. Chromatography of the residue over silica gel using dichloromethane for elution yielded 497 mg (65%) of a white solid which, after recrystallization from dichloromethane, gave white needles: mp 95-97 °C; NMR singlet at τ 2.19 (2 H, ArH), multiplet at 2.74 (4 H, ArH), doublet at 5.24 (4 H, $-CH_2OH$), singlet at 7.13 (4 H, $ArCH_2-$), and triplet at 8.28 (2 H, -OH); mass spectrum *m/e* 240. Anal. ($C_{16}H_{16}O_2$) C, H.

3,6-Bis(bromomethyl)-9,10-dihydrophenanthrene (X = $-CH_2-CH_2-$; Y = -Br). To a solution of 3,6-bis(hydroxymethyl)-9,10-dihydrophenanthrene (**10**) in 40 mL of dry ether under nitrogen at 0 °C there was added dropwise with stirring a solution of 1.38 g of phosphorus tribromide in 5 mL of ether. The solution was then brought to room temperature and stirred for 13 h. After the solution had been washed with water, it was dried and concentrated. Recrystallization of the solid residue from a dichloromethane-hexane mixture gave 1.21 g (97%) of fine white needles: mp 157-160 °C; NMR doublet at τ 2.24 (2 H, J = 2 Hz, ArH), doublet of doublets at 2.72 (2 H, J = 8 Hz, ArH), doublet at 2.84 (2 H, J = 8 Hz, ArH), singlet at 5.46 (4 H, $-CH_2Ar$), and a singlet at 7.20-(4 H, $-CH_2Br$); mass spectrum (70 eV) *m/e* 364, 366, and 368. Anal. ($C_{16}H_{16}Br_2$) C, H.

2,11-Dithia[3.3](3',6')-9,10-dihydrophenanthroparacyclophane (5, X = $-CH_2CH_2-$; R = -H). A solution containing 1.2 g (3.29 mmol) of 3,6-bis(bromomethyl)-9,10-dihydrophenanthrene (**3**, X = $-CH_2CH_2-$; Y = -Br) and 560 mg (3.29 mmol) of 1,4-bis(mercaptomethyl)benzene (**4**, R = -H; Z = -SH) in 95 mL of benzene was added dropwise from a Hershberg funnel with stirring under nitrogen to a solution of 478 mg (7.24 mmol) of potassium hydroxide (85%) in 750 mL of absolute ethanol. After the addition was complete (24 h), the solution was stirred at room temperature for another 7 h. The solution was then concentrated and the residue was chromatographed over silica gel using a 1:1 benzene-hexane mixture for elution. The crystals isolated from the eluate were recrystallized from ethyl acetate to give 1.06 g (86%) of long white needles: mp 224-226 °C; NMR singlet at τ 2.66 (4 H, ArH), doublet at 2.93 (2 H, ArH), doublet of doublets at 3.03 (2 H, ArH), broad singlet at 3.39 (2 H, ArH), two singlets at 6.10 and 6.20 (8 H, $-CH_2S-$), and a singlet at 7.25 (4 H, $ArCH_2-$); mass spectrum (70 eV) *m/e* 374. Anal. ($C_{24}H_{22}S_2$) C, H.

Stevens Rearrangement of 5 (X = $-CH_2CH_2-$; R = -H). A mixture of 940 mg (2.51 mmol) of **5** (X = $-CH_2CH_2-$; R = -H) and 1.63 g (10.0 mmol) of dimethoxycarbonium fluoroborate in 50 mL of dichloromethane was stirred at −20 °C for 20 min and warmed to room temperature and stirred an additional 6 h before adding 50 mL of methyl formate. The crystalline solid, which separated, was collected and dried, giving 1.43 g (99%) of the bissulfonium fluoroborate. This was dissolved in 40 mL of dry dimethyl sulfoxide containing 555 mg of sublimed potassium *tert*-butoxide and was stirred at room temperature for 0.5 h. After addition of 100 mL of dichloromethane, the solution was washed with water, dried, and concentrated. The resulting yellow solid was chromatographed over silica gel using a 70:30 benzene-hexane mixture as eluent. Concentration of the main eluate fraction gave 160 mg (21%) of a mixture of stereoisomers of **6** (X = $-CH_2CH_2-$; R = -H) as a viscous oil: NMR multiplet at τ 2.1 -3.1 (6 H, ArH), multiplet at 3.2-4.1 (4 H, ArH), multiplet at 5.6-7.1 (6 H, ArH), multiplet at 7.1-7.3 (4 H, $-CH_2Ar$), and multiplet at 7.7-8.0 (6 H, $-SCH_3$); mol wt calcd for $C_{26}H_{26}S_2$, 402.148; mol wt found (high resolution mass spectrum), 402.147.

Hofmann Elimination of 6 (X = $-CH_2-CH_2-$; R = -H) to Give 1b. A mixture of 280 mg (1.77 mmol) of dimethoxycarbonium fluoroborate and 188 mg (0.44 mmol) of **6** (X = $-CH_2CH_2-$; R = -H) in 10 mL of dichloromethane was stirred at room temperature for 8 h. Then the solution was concentrated and 10 mL of methyl formate was added. The precipitate of the bissulfonium fluoroborate of **6** (X = $-CH_2CH_2-$; R = -H) was collected and dried, giving 139 mg (52%) of yellow crystals. To a suspension of the bissulfonium fluoroborate in 10 mL of tetrahydrofuran was added 78 mg (0.692 mmol) of sublimed potassium *tert*-butoxide. After the mixture was stirred at room temperature for 1.5 h, it was diluted by addition of 20 mL of dichloromethane, washed with water, dried, and concentrated. The residual yellow oil was purified by preparative thin layer chromatography over silica gel using a 1:1 mixture of benzene-hexane for elution. This gave 1 mg (3%) of white crystals: mp 208-210 °C; NMR broad singlet at τ 2.81 (4 H, ArH), doublet at 3.03 (2 H, J = 11.5 Hz, $-CH{=}CH-$), multiplet at 3.11 (4 H, ArH), broad singlet at 3.21 (H, ArH), doublet at 3.47 (2 H, J = 11.5 Hz, $-CH{=}CH-$), and singlet at 7.20 (4 H, $-CH_2CH_2-$); mass spectrum (70 eV) *m/e* 306, 305, 304, 303, 302, 301, 300, and 150 (M^{2+}); mol wt calcd for $C_{24}H_{18}$, 306.141; mol wt found (high resolution mass spectrum), 306.144.

Diethyl 3,6-Phenanthrenedicarboxylate. A solution of 9.27 g of diethyl 4,4'-stilbenedicarboxylate[16] in 3000 mL of benzene containing 400 mg of iodine was irradiated for 5 days using a medium-pressure mercury lamp (200-W Hanovia 654A36) in a quartz well while air was slowly bubbled through the reaction mixture. After removal of the solvent under reduced pressure, the residue was taken up in chloroform and passed over a short column of silica gel. Concentration of the eluate followed by addition of methanol precipitated a white solid which, on recrystallization from a dichloromethane-methanol mixture, gave 5.1 g (53%) of white prisms: mp 164-166 °C; NMR ($CDCl_3$) multiplet at τ 1.50-1.92 (6 H, ArH), singlet at 2.09 (2 H, ArH), quartet at 5.45 (4 H, $-OCH_2-$), and triplet at 8.52 (6 H, $-CH_2CH_3$). Anal. ($C_{20}H_{18}O_4$) C, H.

3,6-Bis(hydroxymethyl)phenanthrene (3, X = -CH=CH-; Y = -OH). To a solution of 8.3 g of diethyl 3,6-phenanthrenedicarboxylate in 150 mL of dry tetrahydrofuran was added 2.0 g of lithium aluminum hydride in portions over a 20-min interval. The mixture was decomposed by addition of water and the resulting precipitate was collected by filtration. Extraction of the precipitate with boiling chloroform, followed by evaporation of the solvent and recrystallization of the residue from chloroform, gave 4.1 g (66%) of white needles: mp 159-160 °C; NMR (pyridine-d_5) singlet at τ 1.0 (2 H, ArH), AB multiplet at 2.2 (4 H, ArH), broad singlet at 2.82 (2 H, ArH), and singlet at 4.86 (4 H, $-OCH_2-$).

3,6-Bis(bromomethyl)phenanthrene (3, X = -CH=CH-; Y = -Br). To a suspension of 4.0 g of 3,6-bis(hydroxymethyl)phenanthrene in 20 mL of glacial acetic acid was added 20 mL of a 32% solution of hydrogen bromide in acetic acid, and the mixture was warmed on a steam bath for 20 min. The resulting precipitate was collected and recrystallized from a dichloromethane-hexane mixture to give 5.77

g (94%) of white prisms: mp 173–175 °C; NMR broad singlet at τ 1.27 (2 H, ArH), multiplet from 2.01 to 2.40 (6 H, ArH), and singlet at 5.24 (4 H, $-CH_2Br$). Anal. ($C_{16}H_{12}Br_2$) C, H.

2,11-Dithia-5,6,8,9-tetramethyl[3.3](3′,6′)phenanthroparacyclophane (5, X = -CH=CH-; R = $-CH_3$). To a boiling solution of 1 L of ethanol in a Morton flask there was added dropwise simultaneously, but separately, a solution of 3.0 g of 3,6-bis(bromomethyl)phenanthrene in 500 mL of benzene from one Herschberg funnel and 1.86 g of 1,4-bis(mercaptomethyl)-2,3,5,6-tetramethylbenzene[17] in 500 mL of ethanol containing 1.0 g of sodium hydroxide and 5 mL of water from a second Herschberg funnel. The addition required 3 h while the reaction mixture was vigorously stirred. After removal of the solvent, the residue was taken up in dichloromethane and chromatographed over silica gel to give 2.24 g (62%) of white crystals: mp 220–225 °C; NMR multiplet centered at τ 2.25 (8 H, ArH), two close singlets at 5.95 and 6.05 (8 H, $ArCH_2-$), and singlet at 8.18 (12 H, $ArCH_3$). Anal. ($C_{28}H_{28}S_2$) C, H.

2,11-Dithia[3.3](3′,6′)phenanthroparacyclophane (5, X = -CH=CH-; R = -H). The coupling of 4.18 g of 3,6-bis(bromomethyl)phenanthrene and 2.05 g of 1,4-bis(mercaptomethyl)benzene (**4**, R = -H; Z = -SH) was carried out as described for the preparation of **5** (X = $-CH_2-CH_2-$; R = -H). From the chromatography over silica gel using dichloromethane for elution there was isolated 3.60 g (86%) of white crystals: mp 247–252 °C; NMR multiplet centered at τ 2.25 (4 H, ArH), singlet at 2.50 (2 H, ArH), singlet at 2.68 (2 H, ArH), sharp singlet at 2.72 (4 H, $-C_6H_4-$), singlet at 5.91 (4 H, $-CH_2S-$), and singlet at 6.22 (4 H, $-CH_2S-$); mass spectrum (70 eV) *m/e* (rel intensity) 372 (100), 235 (65), 206 (70), 205 (100), and 202 (70). Anal. ($C_{24}H_{20}S_2$) C, H.

4,5,7,8-Tetramethyl[2.2](3′,6′)phenanthroparacyclophane-1,9-diene (1d). A. Stevens Rearrangement of 5 (X = -CH=CH-; R = $-CH_3$). The methylation of **5** (X = -CH=CH-; R = $-CH_3$) and the Stevens rearrangement of the resulting bissulfonium salt was carried out as described earlier for the Stevens rearrangement of **5** (X = $-CH_2CH_2-$; R = -H). From the chromatography over silica gel using a 1:1 mixture of dichloromethane–petroleum ether for elution, the main fraction of eluate gave **6** (X = -CH=CH-; R = $-CH_3$) as a mixture of stereoisomers in 51% yield. The product was a pale yellow oil: NMR multiplet at τ 2.01–2.25 (4 H, ArH), broad singlet at 2.75 (2 H, ArH), singlet at 4.77 (2 H, ArH), multiplet from 6.5 to 7.8 (6 H, ArCH-), a singlet at 7.92 (12 H, $-SCH_3$ and $ArCH_3$), and singlet at 8.58 (6 H, $ArCH_3$ under the phenanthrene ring); mass spectrum (70 eV) *m/e* (rel intensity) 458 (10), 457 (17), 456 (35), 455 (20), 443 (15), 431 (33), 409 (14), 381 (40), 331 (45), and 296 (100). Anal. ($C_{30}H_{32}S_2$) C, H.

B. Hofmann Elimination to Give 1d. This was carried out as described previously for the preparation of **1a.** From the chromatography over silica gel using carbon tetrachloride, **1d** was isolated as a crystalline solid in 3% yield. Recrystallization of the solid from a hexane–carbon tetrachloride mixture gave white prisms: mp 248–250 °C; NMR doublet at τ 2.32 (2 H, J = 8 Hz, ArH), singlet at 2.41 (2 H, ArH), doublet at 2.49 (2 H, J = 2 Hz, ArH), doublet of doublets at 2.65 (2 H, J = 8 Hz, J' = 2 Hz, ArH), AB doublet at 2.92 (2 H, $J_{A,B}$ = 12 Hz, -C*H*=CH-), AB doublet at 3.12 (2 H, $J_{A,B}$ = 12 Hz, -CH=CH-), and singlet at 8.06 (12 H, $-CH_3$); a mass spectrum (70 eV) *m/e* (rel intensity) 360 (100), 343 (50), and 328 (48). Anal. ($C_{28}H_{24}$) C, H.

[2.2](3′,6′)Phenanthroparacyclophane-1,9-diene (1c). A. Benzyne-Stevens Rearrangement of 5 (X = -CH=CH-; R = -H). The general procedure for this experiment was patterned after that described by Otsubo and Boekelheide.[18] To a gently boiling solution of 181 mg of 2,11-dithia[3.3](3′,6′)phenanthroparacyclophane (**5**, X = -CH=CH-; R = -H) and 400 mg of isoamyl nitrite in 25 mL of 1,2-dichloroethane, there was added dropwise over 25 min a solution of 167 mg of anthranilic acid in 8 mL of tetrahydrofuran. After the solution had boiled under reflux an additional 20 min, it was concentrated to give an orange solid. This was preadsorbed and chromatographed over a silica gel column using benzene for elution. From the main fraction of eluate, the benzyne-Stevens rearrangement product, a mixture of stereoisomers, was obtained as 197 mg (77%) of a yellow wax: NMR multiplet at τ 1.8–3.0 (18 H, ArH), multiplet at 3.1–4.5 (4 H, ArH), two multiplets at 5.0–5.25 and 5.5–6.1 (2 H, -C*H*SPh), and multiplet at 6.4–7.5 (4 H, $ArCH_2-$); high resolution mass spectrum 524.160 (calcd for $C_{26}H_{28}S_2$, 524.163).

Hofmann Elimination to give 1c. The benzyne-Stevens rearrangement product from the previous experiment was subjected to the Hofmann elimination procedure as described previously for the preparation of **1a.** From the chromatography over silica gel using a 3:7 mixture of benzene–hexane as eluent, the desired diene **1c** was isolated in 2% yield as white crystals: NMR doublet at τ 2.38 (2 H, J = 8 Hz, ArH), singlet at 2.43 (2 H, ArH), broad singlet at 2.67 (2 H, ArH), doublet of doublets at 2.71 (2 H, J = 8 Hz, J' = 2 Hz, ArH), doublet at 2.89 (2 H, J = 11.5 Hz, -C*H*=CH-), singlet at 2.91 (4 H, ArH), and doublet at 3.20 (2 H, J = 11.5 Hz, -CH=CH-); UV (cyclohexane) λ_{max} 280 nm (ϵ 30 240) and 333 (9073); mass spectrum (70 eV) *m/e* at 304, 303, 302, 301, 300, and 150 (M^{2+}); mol wt calcd for $C_{24}H_{16}$, 304.125, mol wt found (high resolution mass spectrum), 304.126.

2,8-Dicyanodibenzothiophene (12). A solution of 70 g of 2,8-dibromodibenzothiophene, prepared in 75% yield by the method of Neumoyer and Amstutz,[19] and 67.0 g of cuprous cyanide in 200 ml of *N*-methylpyrrolidone was boiled under reflux for 5 h. Then it was poured into a cold solution of 150 g of ferric chloride in 200 mL of concentrated hydrochloric acid. This caused the solution to heat to boiling and boiling under reflux was continued an additional hour by external heating. To the cold solution was added 200 g of ice and the resulting precipitate was collected by filtration. After the solid had been washed on the filter with water and ethanol, it was placed in a Soxhlet and extracted continuously with chloroform for 14 h. Concentration of the chloroform extract followed by sublimation of the residue gave 27.0 g (6) of white crystals: mp 340 °C dec; NMR AB doublet at τ 1.56 (2 H, $J_{A,B}$ = 2 Hz, ArH), doublet at 1.99 (2 H, J = 8 Hz, ArH), and doublet of doublets at 2.23 (2 H, J = 8 Hz, J' = 2 Hz, ArH); mass spectrum (70 eV) *m/e* (rel intensity) 236 (3.3), 235 (19), and 234 (100). Anal. ($C_{14}H_{16}N_2S$) C, H, N.

2,8-Bis(formyl)dibenzothiophene (13). A. From 2,8-Dicyanodibenzothiophene (12). To a solution of 26.5 g of 2,8-dicyanodibenzothiophane (**8**) in 200 mL of benzene under nitrogen was added 170 g of a 20% solution of diisobutylaluminum hydride in benzene. After the mixture had been stirred overnight at room temperature, it was decomposed by the cautious dropwise addition of 100 mL of concentrated hydrochloric acid. The organic layer was extracted with three 400-mL portions of dichloromethane. The combined extracts were dried and concentrated to give a solid residue which, after recrystallization from dichloromethane, provided 13.6 g (50%) of pale orange needles: mp 233–234 °C dec; NMR singlet at τ 0.11 (2 H, -CH=O), AB doublet at 1.06 (2 H, $J_{A,B}$ = 2 Hz, ArH), doublet at 1.82 (2 H, J = 8 Hz, ArH), and doublet of doublets at 2.02 (2 H, J = 8 Hz, J' = 2 Hz, ArH); mass spectrum (70 eV) *m/e* (rel intensity) 242 (7), 241 (20), 240 (100), and 239 (64). Anal. ($C_{14}H_8O_2S$) C, H.

B. From 2,8-Dibromodibenzothiophene (11). To a well-stirred suspension of 99.8 g of 2,8-dibromodibenzothiophene (**11**) in 1200 mL of dry ether under a nitrogen atmosphere at 0 °C was added 375 mL of a 1.6 M solution of *n*-butyllithium in hexane. The resulting suspension was stirred for 20 min before adding 47 g of dimethylformamide. The mixture was allowed to warm to room temperature and was then stirred for 8 h. After addition of 190 mL of a 10% aqueous hydrochloric acid solution, the precipitated solid was collected by filtration. The organic layer from the filtrate was separated, washed with water, dried, and concentrated. The resulting solid residue was combined with the solid collected in the filtration and sublimed to give 47.3 g (68%) of white crystals, mp 233–234 °C dec, identical in all respects with the product from A.

2,8-Bis(hydroxymethyl)dibenzothiophene (14). To a solution of 13.5 g of 2,8-bis(formyl)dibenzothiophene (**13**) in 100 mL of absolute ethanol was added 9.5 g of sodium borohydride with stirring. After an additional 5 min, the solution was neutralized by addition of dilute aqueous acid. The white precipitate was collected and recrystallized from dichloromethane to give 13.4 g (98%) of white needles: mp 159.5–160.0 °C; NMR doublet at τ 1.72 (2 H, ArH), doublet at 2.11 (2 H, ArH), doublet of doublets at 2.49 (2 H, ArH), doublet at 5.15 (4 H, $-CH_2OH$), and triplet at 5.58 (2 H, -OH); mass spectrum (70 eV) *m/e* (rel intensity) 246 (7), 245 (18), 244 (10), 243 (10), and 242 (7). Anal. ($C_{14}H_{12}O_2S_2$) C,.H.

Raney Nickel Desulfurization of 14. To a solution of 1.0 g of 2,8-bis(hydroxymethyl)dibenzothiophene (**14**) in 50 mL of absolute ethanol was added 5 mL of an alcoholic slurry of W-7 Raney nickel catalyst.[20] The mixture was boiled under reflux for 4 h. After removal of the catalyst and solvent, the residue was chromatographed over silica gel using a 3:1 mixture of chloroform–acetone for elution. The solid from the main eluate fraction was recrystallized from a dichloromethane–petroleum ether (30–60 °C) mixture to give 650 mg (74%)

of white needles: mp 116.5–117.0 °C; identical in all respects with the sample of 3,3′-bis(hydroxymethyl)biphenyl (**3**, X = -H, -H; Y = -OH) described previously.

2,8-Bis(bromomethyl)dibenzothiophene (15). To a warm, stirred mixture of 19.35 g of 2,8-bis(hydroxymethyl)dibenzothiophene (**14**) in 400 mL of glacial acetic acid was added in one portion 200 mL of a 32% solution of hydrogen bromide in acetic acid. The resulting mixture was boiled under reflux for 2 h and then stirred at room temperature for 11 **h**. It was then cooled to 0 °C and the precipitate was collected by filtration. The solid was then dissolved in chloroform, washed with water, dried, and concentrated. Recrystallization of the solid residue from benzene gave 27.4 g (93%) of white needles: mp 217.5–218 °C; NMR doublet at τ 1.87 (2 H, J = 2 Hz, ArH), doublet at 2.22 (2 H, J = 8 Hz, ArH), doublet of doublets at 2.53 (2 H, J = 8 Hz, J' = 2 Hz, ArH), and singlet at 5.33 (4 H, $-CH_2Br$); mass spectrum (70 eV) *m/e* (rel intensity) 372 (5), 370 (10), 368 (5), 291 (60), 289 (60), 210 (100), 209 (30), and 208 (45). Anal. ($C_{14}H_{10}Br_2S$) C, H.

2,11-Dithia[3.3](2′,8′)dibenzothiophenoparacyclophane (5, X = -S-; R = -H). The coupling of 8.5 g of 2,8-bis(bromomethyl)dibenzothiophene (**15**) and 4.1 g of 1,4-bis(mercaptomethyl)benzene (**4**, R = -H; Z = -SH) was carried out as described for the preparation of **5** (X = -H, -H; R = -H). The product from the chromatography over silica gel using benzene for elution was recrystallized from dichloromethane–petroleum ehter (30–60 °C) mixture to give 8.97 g (88%) of white needles: mp 260–261 °C; NMR doublet at τ 2.36 (2 H, ArH), singlet at 2.60 (4 H, ArH), doublet of doublets at 2.77 (2 H, J = 8 Hz, J' = 2 Hz, ArH), doublet at 3.03 (2 H, J = 2 Hz, ArH), and pair of singlets at 5.88 and 6.02 (8 H, $-CH_2S-$); mass spectrum (70 eV) *m/e* (rel intensity) 386 (7), 379 (11), 378 (42), 241 (13), and 211 (100). Anal. ($C_{22}H_{18}S_3$) C, H.

[3.3](2′,8′)Dibenzothiophenoparacyclophane-1,9-diene (1e). A. Stevens Rearrangement of 5 (X = -S-; R = -H). The methylation of **5** (X = -S-; R = -H) and the Stevens rearrangement of the resulting bissulfonium salt was carried out as described earlier for the Stevens rearrangement of **5** (X = $-CH_2CH_2-$; R = -H). From the chromatography over silica gel using a 1:1 mixture of benzene–petroleum ether (30–60 °C), the main fraction of eluate gave **6** (X = -S-; R = -H) as a mixture of diastereoisomers in 22% yield. The product was a pale yellow glass: NMR multiplet at τ 2.2–4.0 (8 H, ArH), multiplet at 4.6–5.0 (2 H, ArH), multiplet at 5.5–7.5 (6 H, $-CH_2CHS-$), and multiplet at 7.8–7.82 (6 H, $-SCH_3$); mass spectrum (70 eV) *m/e* (rel intensity) 408 (16), 407 (22), 406 (77), 392 (39), 359 (67), 345 (57), and 256 (100).

B. Hofmann Elimination to Give 1e. This was carried out as described previously for the preparation of **1a**. The chromatography over silica gel using carbon tetrachloride for elution gave a crystalline solid in 19% yield. This, after recrystallization from a dichloromethane–petroleum ether (30–60 °C) mixture yielded white needles: mp 220–221 °C; NMR doublet at τ 2.51 (2 H, J = 8 Hz, ArH), doublet of doublets at 2.92 (2 H, J = 8 Hz, J' = 2 Hz, ArH), doublet at 3.06 (2 H, J = 11.5 Hz, $-CH{=}CH-$), doublet at 3.18 (2 H, J = 2 Hz, ArH), doublet at 3.18 (2 H, J = 11.5 Hz, $-CH{=}CH-$), and singlet at 3.35 (4 H, ArH); mass spectrum (70 eV) *m/e* (rel intensity) 312 (11.5), 311 (25), 310 (100), 309 (63), 308 (33), 307 (47), 306 (58), and 282 (28). Anal. ($C_{22}H_{14}S$) C, H.

5,6,8,9-Tetramethyl-2,11-dithia[3.3](2′,8′)dibenzothiophenoparacyclophane (5, X = -S-; R = $-CH_3$). The coupling of 4.92 g of 2,8-bis(bromomethyl)dibenzothiophene (**15**) and 3.0 g of 1,4-bis(mercaptomethyl)-2,3,5,6-tetramethylbenzene (**4**, R = $-CH_3$)[17] was carried out as described for the preparation of **5** (X = -H, -H, R = -H). The product from chromatography over silica gel, using a 7:3 mixture of benzene–petroleum ether (30–60 °C) for elution was recrystallized from a benzene–hexane mixture to give 2.4 g (42%) of white prisms: mp 223–225 °C; NMR doublet at τ 2.40 (2 H, J = 8 Hz, ArH), broad singlet at 2.72 (2 H, ArH), doublet of doublets at 2.83 (2 H, J = 8 Hz, J' = 2 Hz), two singlets at 5.88 and 5.97 (8 H, $ArCH_2-$), and singlet at 7.97 (12 H, $-CH_3$); mass spectrum (70 eV) *m/e* 434. Anal. ($C_{26}H_{26}S_3$) C, H.

5,6,8,9-Tetramethyl[3.3](2′,8′)dibenzothiophenoparacyclophane-1,9-diene (1f). A. Stevens Rearrangement of 5 (X = -S-; R = $-CH_3$). The methylation of **5** (X = -S-; R = $=CH_3$) and the subsequent Stevens rearrangement of its bissulfonium salt was carried out as described previously for the Stevens rearrangement of **5** (X = $-CH_2CH_2-$; R = -H). From the chromatography over silica gel using benzene as eluent, the major fraction of eluate gave **6** (X = -S-; R = $-CH_3$) as a mixture of diastereoisomers in 23% yield. The product was a pale yellow glass: NMR multiplet at τ 1.9–3.8 (6 H, ArH), multiplet at 5.5–7.3 (6 H, $ArCH_2CHS-$), three singlets at 7.34, 7.55, and 7.74 (12 H, $ArCH_3$), and two singlets at 7.89 and 8.00 (6 H, $-SCH_3$); mass spectrum (70 eV) *m/e* 462, 447, 415, and 368.

B. Hofmann Elimination to Give 1f. A mixture of 1.38 g of **6** (X = -S-; R = $-CH_3$) and 1.36 g of methyl fluorosulfonate ("Magic Methyl") in 40 mL of dichloromethane was stirred at 0 °C for 1 h and then at room temperature for 17 h. The crystalline precipitate was collected, washed with cold dichloromethane, and dried to give the bissulfonium salt as 2.03 g (98%) of a white powder. A mixture of 200 mg of this bissulfonium salt and 196 mg of potassium *tert*-butoxide was ground together well in a mortar and then placed in a gradient sublimator. When the sublimator was evacuated to 0.001 mm and heated to 200 °C, the desired diene sublimed out as a pure white solid. This was recrystallized from cyclohexane to give 43 mg (40%) of white prisms: NMR doublet at τ 2.40 (2 H, J = 8 Hz, ArH), doublet of doublets at 2.90 (2 H, J = 8 Hz, J' = 2 Hz, ArH), broad singlet at 3.10 (4 H, $-CH{=}CH-$), doublet at 3.20 (2 H, J = 2 Hz, ArH), and singlet at 8.36 (12 H, $ArCH_3$); mass spectrum (70 eV) *m/e* 366, 351, 336, 321, and 306. Anal. ($C_{26}H_{22}S$) C, H.

Irradiation of Cyclophanedienes 1a–f. In each case a sample (0.5 to 5.0 mg in weight) of the cyclophanediene was placed in a quartz NMR tube and sealed to a vacuum line. After the NMR tube had been evacuated to 10^{-6} mm, perdeuteriotetrahydrofuran was introduced from a reservoir where it was stored over a sodium–potassium alloy. The solution was then carefully degassed by three cycles of freeze–pump–thaw before being sealed and removed from the vacuum line. The sample solutions were then irradiated at −80 °C with a 2537-Å Ultraviolet Products Lamp and the formation of the bridged [18]annulenes **2a–f** was monitored by Fourier transform NMR. The NMR spectral data for each case are as follows (spectra measured at room temperature). **2a:** a doublet at τ 0.90 (2 H, J_{H_X,H_b} = 8.9 Hz, H_X-), a multiplet at 2.06 (4 H, ArH), a doublet at 2.14 (2 H, J_{H_b,H_c} = 6.7 Hz, H_c-), a singlet at 2.32 (2 H, ArH), a doublet of doublets at 2.53 (2 H, J_{H_X,H_b} = 8.9 Hz, J'_{H_b,H_c} = 6.7 Hz, H_b-), and AA′BB′ multiplet at 12.53 (2 H, H_1) and 12.88 (2 H, internal R = -H]. **2b:** a broad singlet at τ 2.14 (4 H, ArH), a double at 2.25 (2 H, J_{H_b,H_c} = 6.7 Hz), a singlet at 2.42 (2 H, ArH), a doublet at 2.79 (2 H, J_{H_b,H_c} = 6.7 Hz, H_b), a multiplet at 7.26 (4 H, $-CH_2CH_2-$], and an AA′BB′ multiplet at 12.53 (2 H, H_1-) and 12.88 (2 H, internal R = -H). **2c:** a singlet at τ 1.64 (2 H, ArH), a singlet at 1.69 (2 H, ArH), a doublet at 1.73 (2 H, J_{H_b,H_c} = 9.0 Hz, $-H_b$), a doublet at 1.81 (2 H, J_{H_b,H_c} = 9.0 Hz, $-H_c$), a broad singlet at 1.92 (4 H, ArH), and an AA′BB′ multiplet at 12.74 (2 H, $-H_1$) and 13.02 (2 H, internal R = -H). **2d:** a singlet at τ 2.10 (2 H, ArH), a doublet at 2.20 (2 H, J_{H_b,H_c} = 9.0 Hz, $-H_b$), a doublet at 2.38 (2 H, J_{H_b,H_c} = 9.0 Hz, $-H_c$), a broad singlet at 2.42 (4 H, ArH), a singlet at 7.16 (6 H, $ArCH_3$), a broad singlet at 11.20 (2 H, $-H_1$), and a singlet at 11.94 (6 H, internal R = $-CH_3$). **2e:** a singlet at τ 1.09 (2 H, ArH), a doublet at 1.11 (2 H, J_{H_b,H_c} = 8.6 Hz, $-H_b$), a broad singlet at 1.16 (4 H, ArH), a doublet at 1.30 (2 H, J_{H_b,H_c} = 8.6 Hz, $-H_c$), and an AA′BB′ multiplet at 14.94 (2 H, $-H_1$) and 15.66 (2 H, internal R = -H). **2f:** a doublet at τ 1.10 (2 H, J_{H_b,H_c} = 8.6 Hz, $-H_b$), a singlet at 1.15 (4 H, ArH), a doublet at 1.27 (2 H, J_{H_b,H_c} = 8.6 Hz, $-H_c$), a singlet at 6.65 (6 H, external R = $-CH_3$), a broad singlet at 14.96 (2 H, $-H_1$), and a singlet at 13.74 (6 H, internal R = $-CH_3$).

Thermal Conversion of 2f to 16f. A quartz NMR tube containing a sample of **1f** in perdeuteriotetrahydrofuran was irradiated at −80 °C until NMR monitoring indicated a photostationary state (**1f** ⇄ **2f**) was achieved. The sample tube was then brought to 55.0 ± 0.1 °C in the dark and the height of the peak signal at τ 13.74 was followed with time. The data are summarized below.

ϵ, s	Peak height, cm
0	20
135	7.1
204	5.1
278	3.3
356	1.6

After complete thermal conversion, the NMR spectrum of **16f** showed a doublet at τ 2.19 (2 H, J_{H_b,H_c} = 8.0 Hz, $-H_b$), a doublet at

2.59 (2 H, J_{H_b,H_c} = 8.0 Hz, -H_c), a doublet at 2.86 (2 H, J_{H_d,H_e} = 10.0 Hz, -H_d), a doublet at 3.12 (2 H, J_{H_d,H_e} = 10.0 Hz, -H_e), and singlets at 7.77 (6 H, external -CH_3) and 8.88 (6 H, internal -CH_3).

Oxidation of 2d to 16d. A sample of **2d** in perdeuteriotetrahydrofuran was irradiated at −80 °C until the deep orange color of the photostationary state was achieved. When the NMR tube was allowed to warm to 80 °C in the dark, no change in the NMR spectrum occurred. However, when the NMR tube was opened to the air at room temperature, photoproduct **2f** was rapidly converted to **16f**. The NMR spectrum of **16f** showed a singlet at τ 1.75 (2 H, ArH), a doublet at 1.83 (2 H, J_{H_b,H_c} = 8.0 Hz, -H_b), a doublet at 2.07 (2 H, J_{H_b,H_c} = 8.0 Hz, -H_c), a doublet at 2.23 (2 H, J_{H_d,H_e} = 10.0 Hz, -H_d), a doublet at 2.42 (2 H, J_{H_d,H_e} = 10.0 Hz, -H_e), a singlet at 7.46 (6 H, external -CH_3), and a singlet at 10.00 (6 H, internal -CH_3).

Irradiation of 1e in the Presence of Oxygen to Give Thiacoronene. A solution of 5.0 mg of **2e** in perdeuteriotetrahydrofuran was irradiated at room temperature in the presence of oxygen. NMR monitoring showed the rapid disappearance of signals for **1e** and **2e** and the development of the aromatic multiplet from τ 1.20 to 1.45 of thiacoronene. After removal of the solvent, the residue was purified by preparative thin layer chromatography over silica gel using chloroform for elution. This gave a pale yellow solid which, after recrystallization from a benzene-hexane mixture, gave 4.9 mg (100%) of tiny, yellow crystals: mp >350 °C; mol wt calcd for $C_{22}H_{10}S$, 306.050; mol wt found (high resolution mass spectrum), 306.050.

Comparison of the ultraviolet and visible spectrum of this product showed it to be identical with that of an authentic specimen of thiacoronene.[21]

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Synthesis, Structure, and Acetolysis of Some Fused Cyclobutane Derivatives

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Abstract: Syntheses of *exo*- and *endo*-7-hydroxy-6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene (*exo*- and *endo*-**5a**) are described. Several sulfonate esters were prepared from these alcohols. X-ray crystal structure anslyses were carried out on the exo carboxylic acid (*exo*-**5c**) and the endo methanesulfonate (*endo*-**5f**), which both crystallize in the monoclinic system, space group $P2_1/c$, with $Z = 4$ in unit cells of dimensions a = 8.63 (1), b = 20.21 (3), c = 7.35 (1) Å, β = 120.16 (10)°, for *exo*-**5c**, and a = 20.41 (1), b = 5.95 (1), c = 10.88 (1) Å, β = 98.50 (5)°, for *endo*-**5f**. The crystal structures were solved by direct phase-determining procedures and atomic parameters refined to R = 0.123 (1719 reflections from photographic data) for *exo*-**5c** and R = 0.051 (1761 reflections from diffractometer data) for *endo*-**5f**. Kinetic studies of the acetolysis of the exo trifluoromethanesulfonate (*exo*-**5i**) and the exo and endo methanesulfonates (**5f**) showed these to be among the least reactive cyclobutyl derivatives known. The acetates from the exo sulfonate esters were identified as the unrearranged acetate (*exo*-**5e**) and the epimeric, ring-opened *cis*- and *trans*-1-acetoxy-2-vinylacenaphthenes (*cis*- and *trans*-**14b**). The acetate obtained from the endo mesylate was identified as 7-acetoxy-7,8-dihydrocyclohept[*d*,*e*]naphthalene (**18a**). These results are compared with those reported for related cis-fused cyclobutane derivatives, and possible solvolysis pathways are proposed.

Introduction

Carbonium ion reactions of cyclobutane derivatives have been of interest for some time.[1] Those derivatives in which the cyclobutane ring is joined to another ring have attracted particular attention, since in these molecules the four-membered ring is more constrained than in simple cyclobutanes. A variety of compounds with fusion[2-4,5c] and bridging[5] of a four-membered ring to rings of varying sizes has been studied. The conformation of a cyclobutane is of major importance in determining the activity of its derivatives,[2a] since the preferred

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