Bridged [18]Annulenes. 12b,12c,12d,12e,12f,12g-Hexahydrocoronene and Its Mono- and Dibenzo Analogues. Ring-Current Contribution to Chemical Shifts as a Measure of Degree of Aromaticity

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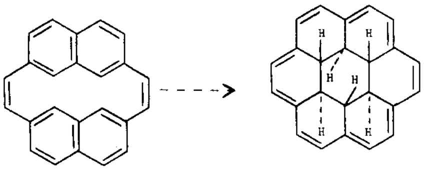
Abstract: Irradiation of [2.2.2]paracyclophane-1,9,17-triene (**7**) gives 12b,12c,12d,12e,12f,12g-hexahydrocoronene (**8**), a bridged [18]annulene. The corresponding benzo and dibenzo analogues, **28** and **33**, have been prepared and these, on irradiation, are similarly converted to 12b,12c,12d,12e,12f,12g-hexahydrobenzo[*a*]coronene (**30a** and **30b**) and 12b,12c,12d,12e,12f,12g-hexahydrodibenzo[*a,j*]coronene (**34a** and **34b**), respectively. The chemical shifts for the internal protons of **8** are in the range of τ 16.5–18.0, whereas those of the mixture of **30a** and **30b** are in the range of τ 11.0–12.6 and those of the mixture of **34a** and **34b** are in the range of τ 13.5–15.3. The fact that the dibenzo analogues, **34a** and **34b**, show a larger ring-current contribution to chemical shift than does the monobenzo analogue illustrates the important role of symmetry in ring-current contributions to chemical shift. A quantitative analysis of the ring currents present in 12b,12c,12d,12e,12f,12g-hexahydrocoronene (**8**) and in 1,2,12d,12e,12f,12g-hexahydrocoronene (**17**) has been made following Haddon's procedure. The large value of 0.87 found for the fraction of maximum calculated ring current for **8** is strong evidence that there is no significant trend toward bond alternation at the ring size of an [18]annulene.

One of the continuing questions in the concept of aromaticity is the effect of ring size. Various theoretical predictions have suggested that in the upper range of ring size, which has been variously estimated to be anywhere from 18 to 30 members, the special properties associated with aromatic rings will disappear and these larger molecules will behave simply as polyenes.[1-4] Although the brilliant work of Sondheimer and his colleagues has provided annulenes in the range of this ring size,[5] the conformational mobility of these simple large annulenes makes it very difficult to evaluate their properties in terms of polyene vs. aromatic character.[6] The dehydroannulenes, containing acetylene and/or acetylene–cumulene bonds, are much less conformationally mobile and the elegant studies of Nakagawa and his colleagues have made numerous examples of these larger annulenes available.[7] However, assessing the question of polyene vs. aromatic character in this series is again difficult because of the unknown acetylene–cumulene anisotropy effects as well as the unknown effect of having shortened fixed bonds in the annulene perimeter.

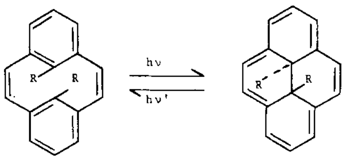
The ideal molecules for evaluating a trend toward bond alternation are those having rigid, planar annulene perimeters in which all of the annulene bonds are equivalent. As discussed by Haddon,[8] these criteria are presently best met in the bridged annulenes, such as the dihydropyrenes,[9] the 1,6-methano[10]annulenes,[10a] and the 1,6:8,13-propanediylidene[14]annulenes.[10b] In view of this it seemed desirable to examine whether the synthetic methods we have previously developed could be extended to provide examples of higher bridged annulenes. The present paper and its companion[11] describe syntheses of a series of bridged [18]annulenes and a calculation of the ring currents for several key compounds in the series.

Of the various possible bridged [18]annulenes, the structure having the greatest symmetry and the one for which molecular models show the most planar perimeter is the hexahydrocoronene defined by formula **2**. In our maiden attempts to prepare **2**, [2,2](2,7)naphthalenophane-1,11-diene (**1**) was prepared and subjected to various conditions predicated on the hope of effecting the necessary reductive cyclization to give **2**.[12] When these attempts proved to be of no avail, this scheme was abandoned and our attention turned to other possible bridged [18]annulenes.[13]



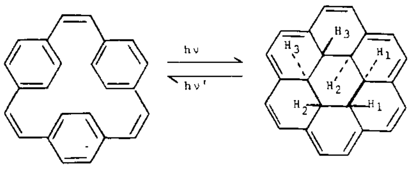
1 2

In the course of our studies on the dihydropyrenes,[14] it was found that 8,16-dialkyl[2.2]metacyclophane-1,9-dienes (**4**) spontaneously cyclize to give the corresponding *trans*-15,16-dialkyldihydropyrenes (**6**), whereas [2.2]metacyclophane-1,9-diene (**3**) itself is stable and does not undergo spontaneous thermal cyclization. However, all of the [2.2]-metacyclophane-1,9-dienes undergo photocyclization and this reaction, as well as the reverse photoinduced valence tautomerization, has been studied in detail by Blattmann and Schmidt.[15] As discussed in the accompanying paper,[11] the generalization of the photocyclization of cyclophanedienes (**3** → **5**) has provided access to a number of bridged [18]annulenes in the tetrahydrobenzo[*g,h,i*]perylene series.[16]



3, R= -H
4, R= -alkyl
5, R= -H
6, R= -alkyl

In these studies of the bridged [18]annulenes of the tetrahydrobenzo[*g,h,i*]perylene series, it became important to do a comparison with bridged [18]annulenes having a different contour of the annulene perimeter. An obvious choice was 12b,12c,12d,12e,12f,12g-hexahydrocoronene (**8**).[17] Actually, this was not a novel idea. In 1959, Cram and Dewhirst had attempted the synthesis of **8** by the photocyclization of



7 8a

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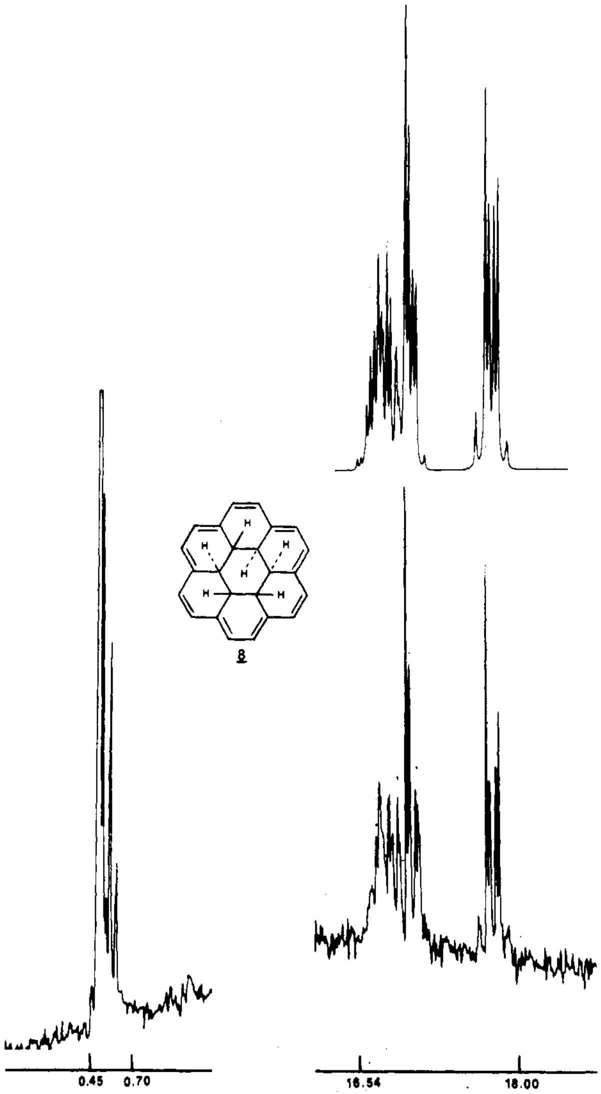


Figure 1. ^{1}H NMR spectrum of 12b,12c,12d,12e,12f,12g-hexahydrocoronene (**8**). Spectrum taken in perdeuteriotetrahydrofuran at −97 °C. Just above the τ 16.54–18.0 region of the spectrum is presented a computer simulation for the signal multiplet of the internal protons. For the computer simulation the coupling constant for the trans-vicinal protons is 17.0 Hz and that for the cis-vicinal protons is 14.0 Hz.

[2.2.2]paracyclophane-1,9,17-triene (**7**), but were unsuccessful.[18] However, in the studies by Blattmann and Schmidt,[15] as well as in our studies of the tetrahydrobenzo[*g,h,i*]perylenes,[11] it had become clear that irradiation of cyclophanedienes leads to a photostationary state and to gain an appreciable concentration of the photocyclized product requires meeting certain conditions. Thus, the quantum yield for the photocyclization (**4** → **6**) is ~1 and is essentially both substituent and temperature independent, whereas the quantum yield for the reverse photoinduced valence tautomerization (**6** → **4**) is much smaller and is both substituent and temperature dependent.[19] Measurements of quantum yields and their dependence on temperature and substituents have not been made in the current studies on the bridged [18]annulenes, but it would appear that their behavior is qualitatively similar. Thus, even though the attempts by Cram and Dewhirst to effect the photocyclization of **7** to **8** at room temperature had been unsuccessful, we were hopeful that irradiation of **7** at low temperature, where the quantum yield of the reverse reaction would be expected to be quite small, might provide **8** in measurable concentrations.

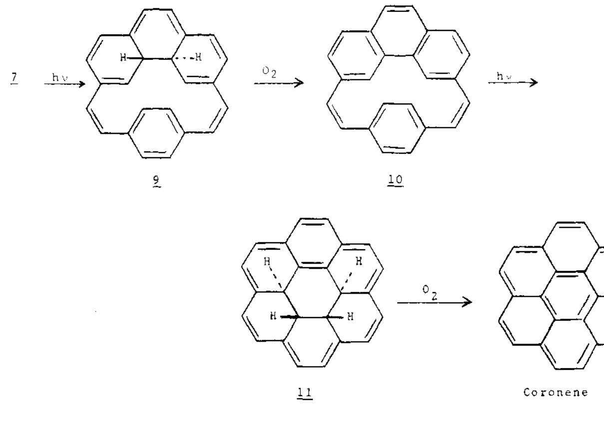
The synthesis of [2.2.2]paracyclophane-1,9,17-triene (**7**) proceeded smoothly following the procedure described by Cram and Dewhirst.[18] Irradiation of a degassed perdeuteriotetrahydrofuran solution of **7** in a quartz NMR tube at −60 °C led to an immediate deep red coloration which, when the irradiation was prolonged overnight at −60 °C, appeared to reach a constant intensity. The NMR spectrum of the irradiated solution showed the development of new signals at high and low fields, quite separate from the signals due to the triene **7** and the solvent. As shown in Figure 1, the ^{1}H NMR spectrum of this photoproduct, when measured at −97 °C, exhibits a multiplet (12 H) in the region of τ 0.45–0.70, with a singlet at 0.52, for the peripheral aromatic protons and an AA′BB′XX′ pattern (6 H) in the region of τ 16.54–17.96 for the internal protons.[21] Thus, the ^{1}H NMR spectrum of the photoproduct is fully in accord with a stereoisomer of hexahydrocoronene having C_2 symmetry as depicted by structure **8**. Examination of molecular models also suggests that the only feasible pathway for the photocyclization of **7** is that leading to **8**. Furthermore, the splitting pattern of the upfield signals for the photoproduct can be duplicated very nicely by a computer simulation (see Figure 1).[21] A comparison of the integrated areas of the signals for **7**, before and after irradiation, provides an estimate that the photostationary state at −60 °C corresponds to about a 20% conversion of **7** to **8**.

The visible spectrum of the colored photoproduct **8** is well defined showing absorption bands at 604, 617, 635 (sh), 655, 672, 685, 712, 723 (sh), 733, 758, and 785 nm in close similarity to the visible spectrum reported for [18]annulene by Blattmann, Heilbronner, and Wagniere.[22,23]

Attempts to obtain a pure sample of the hexahydrocoronene **8** have thus far been unsuccessful, despite efforts to effect the isolation and chromatography of **8** under an inert atmosphere. On the other hand, samples of the irradiated solutions containing hexahydrocoronene can be brought to room temperature in the absence of light and stored indefinitely without change. In common with *trans*-15,16-dihydropyrene (**13**),[14] hexahydrocoronene **8** reacts readily with oxygen, giving coronene in quantitative yield. This oxidation also provides additional proof of structure.

Actually, the irradiation of the triene **7** in the presence of oxygen gives an insight into the probable mechanism of the photocyclization. Thus, as shown in Scheme I, when the perdeuteriotetrahydrofuran solution of **7** is irradiated in the presence of oxygen, the first new ^{1}H NMR signals to be seen correspond exactly to those of the known phenanthrene **10**.[11] After a brief period of time the signals for **10** decrease and a new set of signals appear which correspond to those of the known tetrahydrodibenzo[*g,h,i*]perylene **11**.[11] Finally, these signals disappear, and the ^{1}H NMR spectrum of the solution becomes simply that of coronene. Presumably, the first step in the irradiation of **7** is the formation of **9**. In the absence of oxygen, **9** is converted by further irradiation to the hexahydrocoronene **8**. However, in the presence of oxygen, **9** readily

Scheme I



undergoes dehydrogenation to give **10** which, in turn, via **11** goes on to coronene.

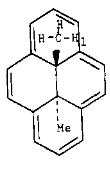
Although the strong upfield chemical shift values for the internal protons of 12b,12c,12d,12e,12f,12g-hexahydrocoronene (**8**) are good qualitative evidence of a diamagnetic current, and so **8** can be described as aromatic and diatropic,[5] it seemed important to us to try to assess the questions of aromaticity and bond alternation in a more quantitative fashion. Quantitative assessment is a common difficulty encountered in synthetic work designed to produce compounds for testing theories of aromaticity. At the conclusion of the synthetic effort the samples of compounds made available are normally inadequate for the standard criteria, such as measurements of heats of hydrogenation or combustion. Also, as in the present case, pure crystalline samples suitable for an x-ray analysis may not be available. However, even when other criteria are lacking, in almost all cases NMR spectra of the key products will be available.

In 1972, Haddon proposed that quantitative assessment of chemical shift data could be made, if the degree of aromaticity is defined as the ratio of the observed ring current to the maximum calculated value for the ring current.[8] In his studies Haddon restricted himself to annulenes whose molecular geometry was known from x-ray crystallographic studies. We have been intrigued by the possibility of applying Haddon's approach in a more general fashion and have found that, when x-ray data is unavailable, a reasonably satisfactory approximation of the molecular geometry of a molecule can often be obtained from shadowgrams using Dreiding molecular models.

We have applied this technique to 12b,12c,12d,12e,12f,12g-hexahydrocronene (**8**) and the results of our calculation are summarized in Table I, together with additional data from Haddon's table on compounds **13–16**, selected for comparative interest. The general method of calculation employed need not be discussed, since it is presented in detail by Haddon and we have simply followed his approach.[24] As did Haddon, we have used *trans*-15,16-dimethyldihydropyrene (**12**) as our standard reference compound. Our calculated value for the ring current of *trans*-15,16-dimethyldihydropyrene is slightly higher than that reported by Haddon and results in our calculated comparative values, such as the ratio of the observed ring current to the maximum calculated ring current, are slightly smaller than those reported by Haddon.[25] This is exemplified by the two calculations (ours and Haddon's) for *trans*-15,16-dihydropyrene (**13**) listed in Table I. Our value for the ratio of the observed ring current to the maximum calculated value (degree of aromaticity) for **13** is 0.95, whereas Haddon's value is 0.98.

At first glance the fact that *trans*-15,16-dihydropyrene (**13**) shows a smaller ring current than *trans*-15,16-dimethyldihydropyrene (**12**) may seem surprising, and Haddon questioned whether the difference was significant. However, ESR studies of the radical anion of **13** provide strong evidence that there is an exceptionally large hyperconjugative effect associated with the internal hydrogens of **13**.[26] It is our opinion that the calculated difference in ring current between **12** and **13** is real and is due to this hyperconjugative effect.

Included in Table I are Haddon's calculated data for 1,6-methanol[10]annulene (**14**), 1,6:8,13-propanediylidene-[14]annulene (**15**), and [18]annulene (**16**). Although **14** and **15** are clearly aromatic, their calculated ring currents are low. The fraction of maximum calculated ring current for **14** is 0.62 and that of **15** is 0.83. This decrease in ring current is undoubtedly due to the lack of planarity of the annulene perimeters in these molecules, and points up the sensitivity of calculated ring-current values to small deviations from planarity. When the current loops are not positioned directly above and below the carbocycle (as they are for a planar perimeter), it is difficult to calculate the ring-current geometric factor (RCGF). X-ray crystallographic studies show an appreciably greater deviation from planarity for **14** than **15**,[27,28] and this is in accord with the relative calculated values of the ring current for these molecules.



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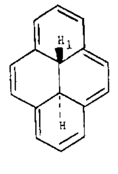

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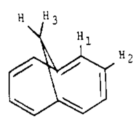

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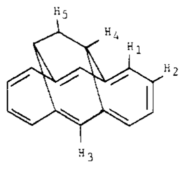

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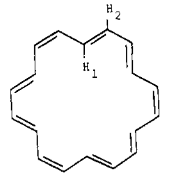

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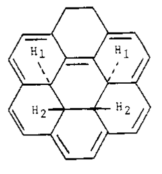
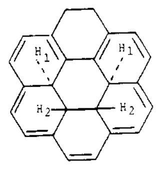
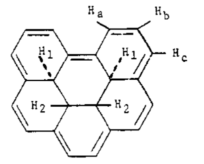


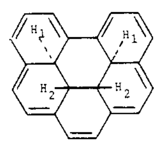
17a



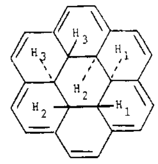
17b



18a



18b



8b

Although [18]annulene (**16**) has a planar perimeter in the crystalline state,[29] temperature-dependent NMR studies show that it has great conformational mobility in solution.[6] In Table I, the value of the fraction of maximum calculated ring current for **16** is only 0.56, quite a low value.

The values of the bond alternation parameter (β_1/β_2), given in Table I, have either been taken from Haddon or have been calculated according to Salem's method.[30] Values of the bond alteration parameter should be useful in detecting trends and the low value of 0.83 calculated for [18]annulene by Haddon suggested a fair degree of bond alternation. Based on this background, Dewar, Haddon, and Student did a MINDO/3 study of [18]annulene and concluded that their results "strongly reinforce the growing body of evidence that the bonds in [18]annulene do alternate in length".[4]

In view of this conclusion it seemed important to provide a quantitative assessment of the ring current exhibited by 12b,12c,12d,12e,12f,12g-hexahydrocoronene (**8**). Inherent in the use of Dreiding models for determining molecular geometry is the fact that canonical Kekulé structures constructed with these models may not have exactly the same geometry. Therefore, in using shadowgrams based on Dreiding models, one needs to make the calculations for each Kekulé structure separately to see how significant these differences are. The calculations for the two Kekulé structures, **8a** and **8b**, for 12b,12c,12d,12e,12f,12g-hexahydrocoronene are given in Table I and are in very good agreement with each other. There are three internal protons (H_1, H_2, and H_3) in structures **8a** and **8b** and the separate values of the ring currents calculated from the observed chemical shifts for each of these protons are exceedingly close, showing good internal consistency for the method. Also, the correct assignment of which internal protons have what chemical-shift value is made clear by these calculations. In turn this reinforces the assignment of stereochemistry given by structure **8**, as deduced earlier both from mechanistic considerations and the computer simulation of the splitting pattern given in Figure 1.

From the average ring currents found for **8a** and **8b**, one can calculate what the predicted individual chemical shifts would

Table I. Calculated Degree of Aromatic Character

Compound	H	Chemical Shift (τ)			RCGF[a]	Ring Current	Fraction Max Calc RC	B_1/b_2	Predicted Chemical Shift	RC Std. Deviations
		Obs.	Model Ref.	RC Contribution						
trans-15,16-dimethyldihydropyrene (12)	H_1	14.25	9.03[b]	5.22	-3.2267	-1.6178	1.00	1.00	-----	------
trans-15,16-dihydropyrene (13)	H_1	15.49	7.14[c]	8.35	-5.4094	-1.5436	0.95	0.93		
trans-15,16-dihydropyrene (13)[d]	H_1	15.49	7.14[c]	8.35	-5.4492	-1.5128	0.98	0.97		
1,6-methano[10]annulene (14)[d]	H_1	2.73	3.87	-1.14	1.1845	-0.7622	0.62	0.76		
	H_2	3.05	3.87	-0.82	1.2725					
	H_3	10.52	7.76	2.76	-3.6538					
1,6:8,13-Propanedylidene [14]annulene (15)[d]	H_1	2.26	3.87	-1.61	1.3342	-1.1402	0.83	0.89		
	H_2	2.45	3.87	-1.42	1.3304					
	H_3	2.12	3.87	-1.75	1.4378					
	H_4	11.16	7.14	4.02	-3.5903					
	H_5	10.61	8.22	2.39	-2.0476					
[18] annulene (16)[d]	H_1	12.26	3.87	8.39	-7.0984	-1.2043	0.56	0.83		
	H_2	0.97	3.87	-1.97	1.9178					
Hexahydrocoronene- (17a)	H_1	12.69[f]	7.14	5.55	-5.0662	-1.0955			12.69	0
or	H_2	13.04	7.75[e]	5.29	-4.8237	-1.0967			13.04	
Tetrahydrobenzoperylene (18a)					Ave.	-1.0961	0.59	0.83		
Hexahydrocoronene- (17b)	H_1	12.69	7.14	5.55	-5.3909	-1.0295			13.06	0.0471
or	H_2	13.04	7.75	5.29	-4.5311	-1.1675			12.73	
Tetrahydrobenzoperylene (18b)					Ave.	-1.0985	0.59	0.83		
Hexahydrocoronene- (8a)	H_1	17.96	7.75	10.21	-5.1692	-1.9752			17.78	0.0170
	H_2	16.54	7.75	8.79	-4.5277	-1.9414			16.54	
	H_3	16.92	7.75	9.17	-4.8127	-1.9054			17.09	
					Ave.	-1.9407	0.88	0.91		
Hexahydrocoronene- (8b)	H_1	17.96	7.75	10.21	-5.1859	-1.9688			17.81	0.0228
	H_2	16.54	7.75	8.79	-4.4683	-1.9672			16.42	
	H_3	16.92	7.75	9.17	-4.8648	-1.8850			17.19	
					Ave.	-1.9403	0.88	0.91		

[a] Ring-current geometric factor (for definition, see ref 8). [b] *trans*-15,16-Dimethyl-2,7,15,16-tetrahydropyrene.[36] [c] *trans*-9,10-Dihydronaphthalene.[37] [d] Data taken from the tables from Haddon.[8] [e] *cis*-1,2,3,4,4a,8a-hexahydronaphthalene.[38] [f] Spectrum measured at −100 °C.

be and, from this, ring-current standard deviations can be deduced as another measure of the precision of the data. The ring-current standard deviations for both **8a** and **8b** are very good.

In view of the high value of 0.88 for the fraction of maximum calculated ring current for **8** and its low degree of bond alternation (β_1/β_2 0.91) one can conclude that 12b,12c,12d,12e,12f,12g-hexahydrocoronene (**8**) is highly aromatic and, in going from a bridged [14]annulene to a bridged [18]annulene, no significant trend toward bond alternation is apparent. The MINDO/3 calculations of Dewar, Haddon, and Student must overestimate the importance of bond alternation.

As a future extension of this work, it would be highly desirable to synthesize rigid, bridged [22]- and [26]annulenes to see whether they exhibit the predicted trend toward bond alternation.

In the accompanying paper,[11] a synthesis of 1,2,12d,12e,12f,12g-hexahydrocoronene (**17**) is described. This hexahydrocoronene is also a bridged [18]annulene but one in which the annulene loop does not follow the outer perimeter of the molecule. Calculations relevant to **17** are included in Table I. Since the magnitude of the ring current is proportional to the area enclosed by the annulene loop, it would be expected that **17**, having a smaller enclosed area, would show a smaller ring current than **8**. In fact, the signals for the internal protons of **17** are shifted drastically to lower field, coming in the region of τ 12.7–13.0 as compared to τ 16.5–18.0 for **8.** Examinations of Dreiding molecular models of the Kekulé structures **17a** and **17b** show the annulene perimeter to be quite planar and do not provide any ready explanation for this sharp decrease in the ring current calculated for **17.** From Table I, it is apparent that with Kekulé structure **17a** there is a remarkable consistency for the H_1 and H_2 values, whereas with Kekulé structure **17b** the internal agreement between H_1 and H_2 is not nearly so good. This raises the question of whether it is possible that Kekulé structure **17a** is of lower energy and so of greater importance to the resonance hybrid than **17b.** Such a tendency toward bond fixation would be in agreement with the low value of 0.58 for the fraction of maximum calculated ring current for **17** and for its calculated bond alternation value of 0.83.

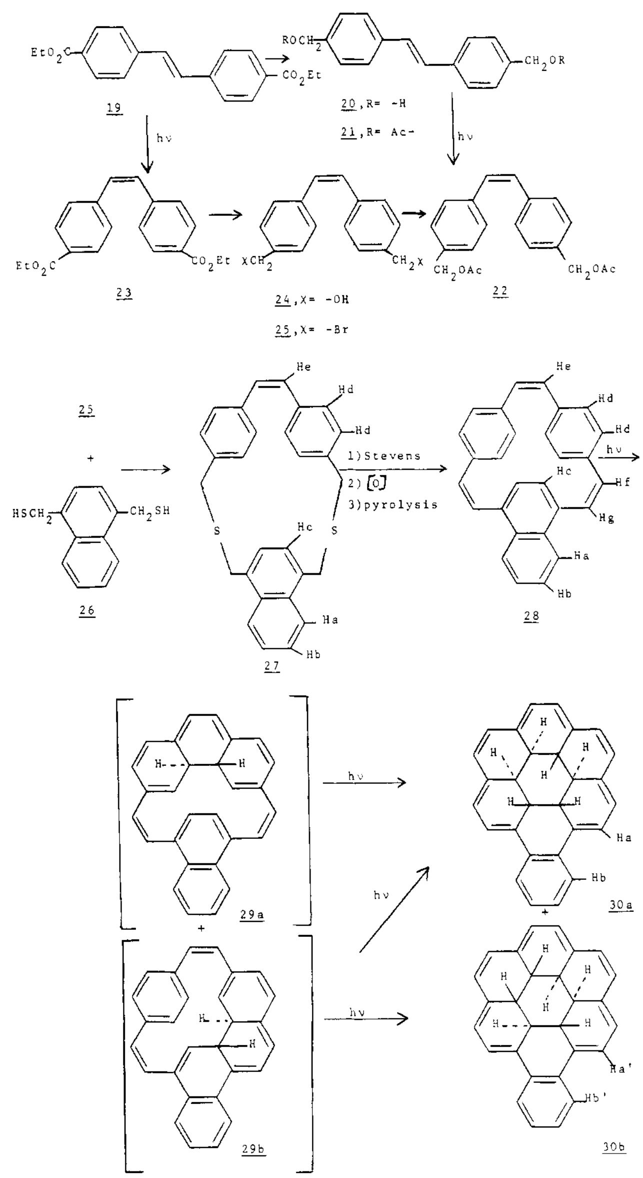
Also, in the accompanying paper is a description of the synthesis of 12c,12d,12e,12f-tetrahydrobenzo[*g,h,i*]perylene (**18**).[11] It is noteworthy that the observed chemical shifts for the internal protons of **18** are the same as those for **17.** Thus, substituting the hydrogen atoms at the 1 and 12 positions of 12c,12d,12e,12f-benzo[*g,h,i*]perylene by a bridging $-CH_2CH_2-$ moiety apparently has no effect on the geometry of the molecule nor the annulene ring current. This is also borne out by an examination of the Dreiding models for these molecules. A comparison of the shadowgrams of **17a** and **18a** shows no differences in the overall geometry of the molecule nor in the relative positions of the internal protons. Similarly, a comparison of the shadowgrams of the alternate Kekulé structures **17b** and **18b** shows no difference. Therefore, each pair of Kekulé structures **17a** and **18a,** as well as **17b** and **18b,** is given only one entry in Table I.

A sensitive indicator of π-bond differences in an aromatic perimeter is the comparative value of ortho coupling constants for adjacent protons. In the case of compound **18,** the coupling constants are $J_{\mathrm{Ha,Hb}}$ = 8.9 Hz and $J_{\mathrm{Hb,Hc}}$ = 6.7 Hz. This difference is even greater than the differences found for the ortho coupling constants of naphthalene or phenanthrene, two notable examples of this effect where an appreciable degree of bond fixation is accepted.[31] Thus, there is supportive evidence that, for **17** and **18,** the Kekulé structures do not contribute equally and that the Kekulé structures represented by **17a** and **18a** are favored in each case.

The data in Table I illustrate in a striking fashion the importance of having the best possible model if one is to draw any conclusions about trends in bond alternation in the larger annulenes. Relatively small changes in planarity or in other factors may well have large effects on the ring current and the chemical shifts being measured.

Another factor affecting ring currents and chemical shift values is benzoannellation. Since the method of synthesis employed for preparing **8** seemed adaptable for making benzo analogues, we undertook the synthesis of 12b,12c,12d,12e,12f,12g-hexahydrobenzo[a]coronene (**30a** and **30b**). This was accomplished successfully following the steps outlined in Scheme II.

Scheme II

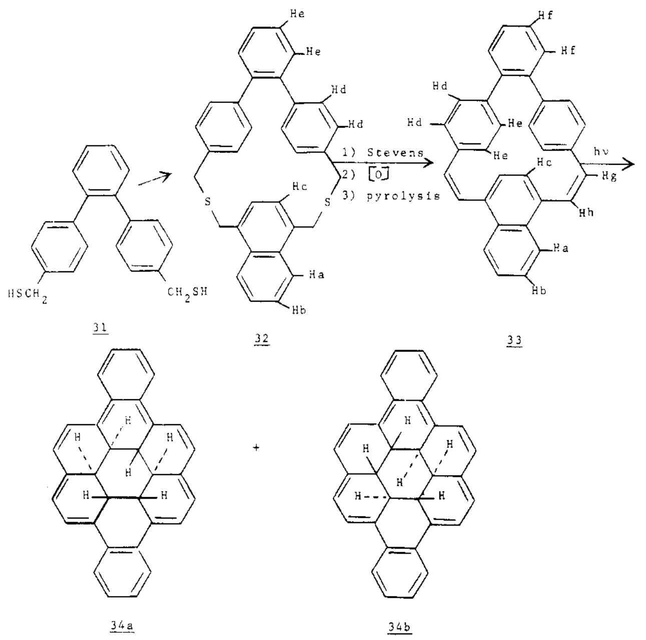


Critical to the synthesis of **30** was easy access to an appropriate *cis*-stilbene derivative. Toland, Wilkes, and Brutschy observed that *p*-toluic acid is converted conveniently to *trans*-4,4′-stilbenedicarboxylic acid,[32] and so this acid and its corresponding ester **19** were readily available starting materials. After irradiation of a solution of **19** in benzene for 16 h, NMR spectral analysis indicated a photostationary state containing approximately a 1:1 mixture of the cis and trans esters, **19** and **23.** When separation of the esters proved difficult, the crude mixture was reduced with lithium aluminum hydride and the cis diol **24** was separated by thin layer chromatography, but in poor yield. Because of these difficulties the alternate pathway was taken of reducing the trans diester **19** to the trans diol **20** and then irradiating the corresponding trans diacetate **21.** Again, the photostationary state was about a 1:1 mixture of the cis to trans isomers (**22**:**21**). However, differences in solubility readily allowed the separation of the cis diacetate **22** and it was readily converted to the pure cis diol **24.**

The cis dibromide **25,** prepared from **24** using phosphorus tribromide, underwent coupling with 1,4-bis(mercaptomethyl)naphthalene (**26**) to give the dithiacyclophane **27** in 62% yield. Although attempts to effect the benzyne modification[33] of the Stevens rearrangement failed, the normal Stevens rearrangement[14] proceeded to give the desired, ring-contracted cyclophane in 26% yield. This was oxidized to the bissulfoxide and pyrolyzed directly to give the desired cyclophanetriene **28** in 16% yield.

From our earlier discussion of the probable stepwise mechanism for the photocyclization of **7** to **8,** it would be expected that the initial step in the photocyclization of **28** would have about an equal probability of giving either **29a** or **29b.** Examination of molecular models indicates that the subsequent photocycylization of **29a** can lead only to **30a,** whereas photocyclization of **29b** seems equally likely to give either **30a** or **30b.** In the event, irradiation of a solution of **28** in perdeuteriotetrahydrofuran at −70 °C gave a deep red solution whose ^1H NMR spectrum indicated that **28** had been converted in high yield to a mixture of **30a** and **30b,** of which **30a** seemed

Scheme III



predominant. The signals for the internal protons of the photoprduct appear as a complicated multiplet in the region of τ 11.0-12.6 with major peaks at 11.36 and 12.00. The signals for the peripheral aromatic protons appear as a multiplet between τ 1.10 and 2.62. The signals at τ 1.52 and 1.66 we assign to the H_a protons of **30b** and **30a,** respectively, and the ratios of their integrated areas is 1:2.

Although it would be expected that the effect of benzoannellation would lead to a decrease in the ring current of the annulene perimeter, the extent to which the signals for the internal protons of **30a-b** had moved downfield compared with those of **8** was large. We thought it worthwhile, therefore, to examine the properties of the dibenzo analogues, **34a** and **34b,** for comparison. The steps in our successful synthesis of the 12b,12c,12d,12e,12f,12g-hexahydrodibenzo[*a,j*]coronenes (**34a** and **34b**) are outlined in Scheme III.

The coupling of 1,2-bis(4′-mercaptomethylphenyl)benzene (**31**) with 1,4-bis(bromomethyl)naphthalene proceeded smoothly in 85% yield to give the dithiacyclophane **32.** Subjection of the dithiacyclophane **32** to the usual conditions of the Stevens rearrangement gave the ring-contracted cyclophane in 69% yield. This, on oxidation to the bissulfoxide followed by pyrolysis, led to the desired cyclophanediene **33** in 8% yield.

Irradiation of a solution of **33** in perdeuteriotetrahydrofuran at −70 °C immediately led to a deep green color and the separation of a green solid. Because of the low solubility of the photoproduct it was necessary to use Fourier transform to obtain its ^{1}H NMR spectrum. Again, it would be expected that the photoproduct should be a mixture of the two stereoisomers **34a** and **34b.** The ^{1}H NMR spectrum of the photoproduct, **34a-b,** showed a broad multiplet for the internal protons in the region of τ 13.5-15.3 and a multiplet for the aromatic peripheral protons between τ 0.50 and 1.50.

The fact that the dibenzo analogue **34a-b** shows a greater ring current and a higher field chemical shift for its internal protons than does the monobenzo analogue **30a-b** illustrates the important role of symmetry with regard to the magnitude of the ring current. For either **34a** or **34b,** both the structure drawn and its canonical Kekulé partner will have essentially the same energy. However, for either **30a** or **30b,** one canonical structure has a localized benzene ring and its canonical Kekulé partner has an ortho-quinoid moiety. The appreciable difference in energy between these two principal contributing structures to the resonance hybrid promotes bond alternation. Thus, comparisons of annulenes, where benzoannelation is present, must take into account how such substitution affects the relative energies of the contributing structures to the resonance hybrid.[34] Iyoda, Morigaki, and Nakagawa reached the same conclusion in their earlier studies with regard to the naphthoannellation of 1,8-didehydro[14]annulenes.[35]

Experimental Section[39]

Irradiation of [2.2.2]Paracyclophane-1,9,17-triene (7). The preparation of [2.2.2]paracyclophane was carried out following the procedure of Tabushi et al.,[20] and was converted to the triene **7** just as described by Cram and Dewhirst.[18] Our sample of [2.2.2]paracyclophane-1,9,17-triene (**7**) melted at 130-132 °C, and its ^{1}H NMR spectrum showed two singlets at τ 3.16 (6 H, -C*H*═C*H*-) and at 3.25 (12 H, ArH).

A 5.0-mg sample was placed in a quartz NMR tube and by vacuum-line technique perdeuteriotetrahydrofuran, predried over a Na-K alloy, was transferred to the NMR tube. The solution was carefully degassed before sealing the NMR tube. The solution was then cooled to −60 °C and irradiated using a low pressure mercury lamp (2537 Å). After a short time the solution had become a deep red and the course of the reaction was monitored by periodically taking its NMR spectrum. After irradiation overnight, the solution no longer seemed to change on further irradiation. From the change in the integrated areas of the signals for the starting material, the conversion of **7** to **8** was estimated to be 20%. Since the NMR signals for the photoproduct **8** come at either higher or lower field than the starting material and solvent, its spectrum can be measured quite readily. In Figure 1, the ^{1}H NMR spectrum of **8** taken at −97 °C is presented. The NMR spectrum of **8** shows a small temperature dependence, so that the signals for the internal protons, which appear in the range of τ 16.54-17.96 at −97 °C (see Figure 1), shift to the range of τ 16.44-17.88 at −80 °C, 16.34-17.74 at −60 °C, 16.18-17.58 at −10 °C, and 16.06-17.42 at 35 °C.

Irradiation of a solution of 10 mg of [2.2.2]paracyclophane-1,9,17-triene (**7**) in 0.4 mL of perdeuteriotetrahydrofuran saturated with oxygen was followed by NMR monitoring. After a short period of time new signals appeared at τ 2.38, 2.43, 2.67, 2.71, 2.89, 2.91, and 3.20, corresponding exactly to those of the known cyclophanediene **10.**[11] Upon further irradiation, these signals began to disappear and new signals arose at τ 1.64, 1.69, 1.73, 1.81, 1.92, 12.74, and 13.02, corresponding very nicely to the previously observed spectrum for the bridged annulene **11.**[11] After still further irradiation, the NMR spectrum changed to that of coronene and, on workup, a crystalline product, identical with coronene in all respects, was isolated in essentially quantitative yield.

4,4′-Bis(acetoxymethyl)-*trans*-stilbene (21). A solution of 16.0 g of diethyl *trans*-stilbene-4,4′-dicarboxylate (**19**)[11] in 250 mL of tetrahydrofurn (THF) was added dropwise with stirring to a solution of 5 g of lithium aluminum hydride in 300 mL of dry THF held at room temperature under a nitrogen atmosphere. When the addition was complete, the mixture was boiled under reflux for 1 h and then decomposed by successive additions of ethyl acetate, ice-water, and dilute hydrochloric acid. After addition of solid sodium chloride to help separate the aqueous and organic layers, the THF layer was separated, dried, and concentrated to give 12.9 g (100%) of 4,4′-bis(hydroxymethyl)-*trans*-stilbene (**20**) as a white powder, mp 157-159 °C.[11] This was taken up directly in 200 mL of acetic anhydride and heated with stirring at 120 °C for 4 h. After concentration under reduced pressure, the residue was chromatographed over silica gel using benzene as eluent. The crystalline solid from the main fraction of eluate was recrystallized from benzene to give 11.8 g (74%) of colorless crystals: mp 140-142 °C; NMR doublets at τ 2.46 (4 H, J = 8 Hz, ArH) and 2.64 (4 H, J = 8 Hz, ArH), singlet at 2.88 (2 H, -CH═CH-), singlet at 4.87 (4 H, ArCH$_2$-), and singlet at 7.88 (6 H, -C(═O)CH$_3$). Anal. ($C_{20}H_{20}O_4$) C, H.

4,4′-Bis(hydroxymethyl)-*cis*-stilbene (24). A solution of 9.8 g of 4,4′-bis(acetoxymethyl)-*trans*-stilbene (**21**) in 2.5 L of benzene through which nitrogen was being bubbled was irradiated at room temperature using a medium pressure mercury lamp. NMR monitoring indicated that a 1:1 cis:trans photostationary state was reached after 3 h. After removal of the solvent, the semisolid residue was treated with a small amount of chloroform, which dissolved the cis isomer **22** but left the pure trans isomer **21** as a crystalline solid. After removal of **21** by filtration, the filtrate was concentrated to give 5.4 g (55%) of **22** as white crystals: NMR singlet at τ 2.77 (8 H, ArH), singlet at 3.40 (2 H, -CH=CH-), singlet at 4.92 (4 H, $ArCH_2$-), and singlet at 7.91 (6 H, -C(=O)CH_3). This was dissolved in 110 mL of a 50% aqueous ethanol solution containing 5.5 g of potassium hydroxide and allowed to stand at room temperature overnight. The solution was then neutralized with dilute aqueous hydrochloric acid and extracted with chloroform. After the chloroform extract had been dried, it was concentrated to give 3.4 g (84%) of white crystals: mp 110-113 °C; NMR singlet at τ 2.76 (8 H, ArH), singlet at 3.40 (2 H, -CH=CH-), singlet at 5.34 (4 H, $ArCH_2$-), and broad singlet at 8.16 (2 H, -OH). Anal. ($C_{16}H_{14}O_2$) C, H.

When a solution of diethyl *trans*-stilbene-4,4′-dicarboxylate (**19**)[11] in benzene was irradiated as described above, NMR monitoring indicated that a 1:1 cis:trans photostationary state was reached after 16 h. After removal of the solvent, attempts to separate the pure cis isomer **23** from the oily residue were unsuccessful. Therefore, the residue was taken up in ether and reduced with lithium aluminum hydride. The product obtained on workup was subjected to thin layer chromatography over silica using a 1:4 ethyl acetate-chloroform mixture as eluent. This gave a pure sample of **24**, but only in 8% yield.

4,4′-Bis(bromomethyl)-*cis*-stilbene (25). To a solution of 3.4 g of 4,4′-bis(hydroxymethyl)-*cis*-stilbene (**24**) in 100 mL of chloroform there was added dropwise with stirring 11.3 g of phosphorus tribromide. After addition of ice, the chloroform layer was separated, washed with water, dried, and concentrated. The solid residue was recrystallized from hexane to give 3.40 g (65%) of colorless plates: mp 69.0-69.5 °C; NMR singlet at τ 2.78 (8 H, ArH), singlet at 3.43 (2 H, -CH=CH-), and singlet at 5.56 (4 H, $ArCH_2$-). Anal. ($C_{16}H_{14}Br_2$) C, H.

Dithiacyclophane 27. For the preparation of 1,4-bis(mercaptomethyl)naphthalene (**26**), bromination of 1,4-dimethylnaphthalene was carried out as described by Ried and Boden,[40] and the resulting 1,4-bis(bromomethyl)naphthalene was converted via the corresponding thiuronium salt to **26** as described by the Henkel patent.[41] A solution of 600 mg of 4,4′-bis(bromomethyl)-*cis*-stilbene (**25**) and 360 mg of 1,4-bis(mercaptomethyl)naphthalene (**26**) in 200 mL of benzene was added dropwise from a Hershberg funnel with stirring to 1 L of ethanol (95%) containing 290 mg of potassium hydroxide (85%) boiling under reflux under a nitrogen atmosphere. When the addition was complete (3 days), the solution was taken up in benzene and chromatographed over silica gel using benzene as eluent. The crystals from the main fraction of eluate were recrystallized from a benzene-carbon tetrachloride mixture to give 435 mg (62%) of colorless plates: mp 187-188 °C; NMR doublet of doublets at τ 2.01 (2 H, J = 6 Hz, J' = 3 Hz, H_a), doublet of doublets at 2.47 (2 H, J = 6 Hz, J' = 3 Hz, H_b), singlet at 2.98 (2 H, H_c), singlet at 3.19 (2 H, H_d), singlet at 3.40 (2 H, H_e), singlet at 5.82 (4 H, -SCH_2-), and singlet at 6.12 (4 H, -CH_2S-); high resolution mass spectrum 424.133 (calcd for $C_{28}H_{24}S_2$, 424.132).

4,5-Benzo[2.2.2]paracyclophane-1,9,17-triene (28). A mixture of 210 mg of **27** and 156 mg of methyl fluorosulfonate ("Magic Methyl") in 20 mL of dry dichloromethane was stirred at room temperature under a nitrogen atmosphere for 1 day. The crystals, which separated, were collected by filtration, washed with dichloromethane, and dried to give 320 mg (94%) of the bissulfonium salt of **27**. To a suspension of the bissulfonium salt of **27** in 15 mL of dry THF there was added with stirring 320 mg of potassium *tert*-butoxide in one lot. After the resulting mixture had been stirred at room temperature under a nitrogen atmosphere for 2 h, 20 mL of dichloromethane was added. The solution was washed successively with dilute aqueous hydrochloric acid and water, dried, and concentrated. The residual oil was chromatographed over silica gel using a 1:1 benzene-hexane mixture as eluent. The first fraction of eluate gave the mixture of stereoisomers, corresponding to the Stevens rearrangement product, as 58 mg (62%) of a pale yellow oil: NMR multiplet at τ 1.95 (2 H, ArH), multiplet at 2.45 (2 H, ArH), multiplet at 2.7-3.8 (12 H, ArH), multiplet at 5.7-7.3 (6 H, -SCH< and -CH_2-), and singlet at 7.98 (6 H, -SCH_3); mass spectrum (70 eV) 452 (calcd for $C_{30}H_{28}S_2$, 452).

A mixture of 58 mg of the Stevens rearrangement product and 52 mg of *m*-chloroperbenzoic acid (85%) in 20 mL of chloroform was stirred at room temperature for 1 day under a nitrogen atmosphere. The solution was washed successively with aqueous sodium bicarbonate and water, dried, and concentrated. This gave the corresponding bissulfoxide as 64 mg of a pale yellow oil: NMR multiplet at τ 1.90 (2 H, ArH), multiplet at 2.40 (2 H, ArH), multiplet at 2.7-3.9 (12 H, ArH), multiplet at 5.4-7.0 (6 H, -S($\rightarrow$O)CH< and -CH_2-), and multiplet at 7.0-7.9 (6 H, -S($\rightarrow$O)CH_3). The bissulfoxide was placed in a gradient sublimator and heated at 300 °C at 5×10^{-3} mm pressure. The product was collected and chromatographed over silica gel using carbon tetrachloride as eluent. The crystals from the main fraction of eluate were recrystallized from hexane to give 7.5 mg (16%) of pale yellow plates: mp 134-135 °C; NMR doublet of doublets at τ 2.00 (2 H, J = 6 Hz, J' = 3 Hz, H_a), doublet of doublets at 2.50 (2 H, J = 6 Hz, H_b), AB doublet at 2.71 (2 H, J_{AB} = 12 Hz, H_g), AB doublet at 2.93 (2 H, J_{AB} = 12 Hz, H_f), singlet at 3.20 (4 H, H_c and H_e), and broad singlet at 3.39 (8 H, H_d); high resolution mass spectrum 356.157 (calcd for $C_{28}H_{20}$, 356.156).

Irradiation of 4,5-Benzo[2.2.2]paracyclophane-1,9,17-triene (28). As described for the irradiation of **7**, a carefully degassed solution of 5 mg of **28** in perdeuteriotetrahydrofuran in a sealed, quartz NMR tube was irradiated at −70 °C using a low pressure mercury lamp (2537 Å). The solution turned a deep red; based on NMR monitoring, the photostationary state was reached after 21 h, with a high conversion of **28** to a mixture of **30a** and **30b**. The H_a and $H_{a'}$ protons of **30a** and **30b** appear in the NMR spectrum as an A_2B_2 double doublet centered at τ 1.10 and the H_b and $H_{b'}$ appear separately at τ 1.66 and 1.52, respectively, with a ratio of integrated areas of ~2:1. The rest of the peripheral protons appear as a broad multiplet between τ 2.0 and 3.0. The internal protons of the mixture of **30a** and **30b** appear as a complicated multiplet between τ 11.0 and 12.6.

When the NMR tube containing the irradiated solution was opened and oxygen was bubbled through, the solution became colorless and its NMR spectrum showed a complete disappearance of the signals for both **28** as well as **30a** and **30b**. The new signals, which appeared, were in in the range of τ 0.4-1.4, having a pattern consistent with that to be expected for benzo[*a*]coronene. Unfortunately, no authentic spectra or samples of benzo[*a*]coronene are available to us for comparison.

Dithiacyclophane 32. A solution of 1.240 g of 1,4-bis(bromomethyl)naphthalene[40] and 1.278 g of 1,2-bis(4′-mercaptomethylphenyl)benzene (**32**)[42] in 300 mL of benzene was added dropwise with stirring under a nitrogen atmosphere to a boiling solution of 1 L of ethanol (95%) containing 725 mg of potassium hydroxide (85%). After the addition was complete (1.5 days), the solution was concentrated and the residual solid was chromatographed over silica gel using chloroform as eluent. From the first fraction of eluate a crystalline solid was obtained which, on recrystallization from benzene, gave 1.39 g (85%) of colorless prisms: mp 214-215 °C; NMR doublet of doublets at τ 1.98 (2 H, J = 6 Hz, J' = 3 Hz, H_a), doublet of doublets at 2.48 (2 H, J = 6 Hz, J' = 3 Hz, H_b), broad singlet at 2.71 (4 H, H_e), singlet at 2.85 (2 H, H_c), singlet at 3.17 (8 H, H_d), singlet at 5.80 (4 H, -SCH_2-), and singlet at 6.12 (4 H, -SCH_2-); high resolution mass spectrum 474.149 (calcd for $C_{32}H_{26}S_2$, 474.148).

Cyclophanediene 33. A mixture of 237 mg of dithiacyclophane **32** and 270 mg of methyl fluorosulfonate ("Magic Methyl") in 25 mL of dichloromethane was stirred overnight at room temperature under a nitrogen atmosphere. The white solid, which separated, was collected by filtration, washed with dichloromethane, and dried to give 341 mg (97%) of the corresponding bissulfonium salt. This was suspended in 20 mL of dry THF and 340 mg of potassium *tert*-butoxide was added in one lot. After the mixture had been stirred at room temperature under nitrogen for 2 h, 30 mL of dichloromethane was added. The mixture was washed successively with dilute aqueous hydrochloric acid and water, dried, and concentrated. The residual oil was chromatographed over silica gel using a 1:1 benzene-hexane mixture as eluent to provide the mixture of stereoisomers of the Stevens rearrangement product as 167 mg (69%) of a colorless oil: NMR multiplet at τ 1.8-2.0 (2 H, ArH), multiplet at 2.0-4.4 (26 H, ArH), multiplet at 5.5-7.3 (6 H, -SCH< and -CH_2-), and multiplet at 7.3-8.3 (6 H, -SCH_3); high resolution mass spectrum 502.176 (calcd for $C_{34}H_{30}S_2$, 502.179).

A mixture of 167 mg of the Stevens rearrangement product and 134 mg of *m*-chloroperbenzoic acid (85%) in 25 mL of chloroform was stirred at room temperature for 1 day. The mixture was then washed successively with aqueous sodium bicarbonate and water, dried, and concentrated to give the corresponding bissulfoxide as 180 mg (100%) of a colorless oil.

The bissulfoxide was heated in a gradient sublimator at 300 °C and

10^{-4}-mm pressure. The solid that collected was recrystallized from a hexane–carbon tetrachloride mixture to give **33** as 11 mg (8%) of fine, colorless crystals: mp 184–185 °C; NMR doublet of doublets at τ 2.01 (2 H, $J = 6$ Hz, $J' - 3$ Hz, $\mathrm{H_a}$), doublet of doublets at 2.51 (2 H, $J = 6$ Hz, $J' = 3$ Hz, $\mathrm{H_b}$), singlet at 2.66 (4 H, $\mathrm{H_f}$), doublet at 2.68 (2 H $J = 12$ Hz, $\mathrm{H_h}$), doublet at 2.90 (2 H, $J = 12$ Hz, $\mathrm{H_g}$), singlet at 3.11 (2 H, $\mathrm{H_c}$), and multiplet at 2.8–3.8 (8 H, $\mathrm{H_d}$ and $\mathrm{H_e}$); high resolution mass spectrum 406.170 (calcd for $C_{32}H_{22}$, 406.172).

Irradiation of Cyclophanediene 33. The irradiation of a solution of **33** in perdeuteriotetrahydrofuran was carried out at −70 °C in the same manner as described for the irradiation of **7.** The solution quickly turned a deep green and a green solid separated. Because of the low solubility of the photoproduct, Fourier transform was necessary to obtain its NMR spectrum. The NMR spectrum of the photoproduct, **34a** and **34b,** measured at −12 °C showed the peripheral protons as a cluster of complicated multiplets at τ 0.5–1.15 and 1.50. The internal protons appear as a broad multiplet in the range of τ 13.5–15.3.

As in the other examples, opening of the sealed NMR tube to allow contact of oxygen with the green irradiated solution quickly led to the disappearance of color. Attempts to isolate and purify the solid green photoproduct were unsuccessful.

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(23) Because of the uncertainty regarding the exact concentration of **8** in the irradiation solution, the extinction coefficients for these absorption bands are not given.

(24) We thank Professor C. E. Klopfenstein and Mr. M. Drabicky for help in the design and writing of the computer program used for these calculations. The program is stored in the University of Oregon Computer Library as MAGFLD-F-4.

(25) This slight discrepancy undoubtedly arises out of differing assumptions and choices made. For example we felt that the internal protons of **12,** which show large ring contributions to chemical shift, were a more reliable reference than the peripheral protons, and so we have used only the internal protons of **12** and have not averaged in the data from the peripheral protons. Similarly, the ring-current geometric factor (RCGF) for **12** was found using an average of 12 points in space for H_1, whereas the number of points used by Haddon is not given.

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