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Syntheses of Dihydropyrene–Cyclophanediene Negative Photochromes Containing Internal Alkenyl and Alkynyl Groups and Comparison of Their Photochemical and Thermochemical Properties

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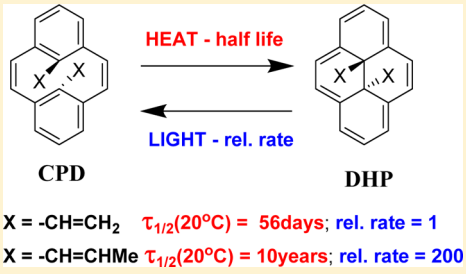
Supporting Information

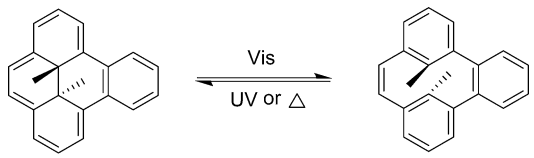
ABSTRACT: Synthesis of a variety of 8,16-disubstituted-*anti*-[2.2]-metacyclophanedienes (CPD) with alkenyl and alkynyl internal (8,16) groups is described together with their analogous dihydropyrenes (DHP). Eyring and Arrhenius parameters were determined for the thermal closing reaction, CPD to DHP, and half-lives at 20 °C were found to range from 11 days (X = CHO) to 36 years (X = CN), with alkenyl functions being from 56 days to 10 years. The visible light opening reaction, DHP to CPD, showed relative rates of 1 (X = CN) to 240 (X = CH═CMe$_2$).



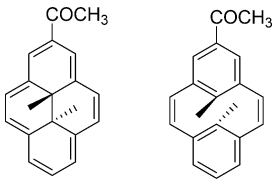
INTRODUCTION

Negative photochromes (−) are not as well-known as their positive (+) counterparts[1] but are interesting because the thermally stable isomer is the more colored one (positive ones have the colorless form, the more stable). The colored form bleaches on exposure to visible (longer wavelength) light and returns to the colored isomer on exposure to UV (shorter wavelength) light or in some cases thermally (T). Dihydropyrenes (DHPs), such as **1**, are thus negative-thermal [(−)T] photochromes because the deep red-purple **1** opens completely to the colorless cyclophanediene (CPD) form **2** when irradiated with visible light (λ > 400 nm). The latter completely reverts to DHP **1** on irradiation with UV light (λ < 350 nm) and also slowly thermally ($t_{1/2}$ = 7.3 days at 20 °C, 5.75 h at 46 °C) (Scheme 1).[2]

Scheme 1



Application of photoswitches for use in memory devices requires consideration of their thermal stability, fatigue resistance, overlap of the absorption spectra of the open and closed forms, quantum yield of the interconversions, and ability to nondestructively read the open and closed forms. Our more recent research focus has concentrated on two of these, namely design of more thermally stable dihydropyrene-based photoswitches with high quantum yields of interconversion, particularly for the photoopening reaction of dihydropyrenes with visible light.[3,4] Although the latter objective is easily addressed by incorporating carbonyl functionality at the 2 and/or 7 positions of the DHP as in **3**, it is at the cost of thermal stability of the CPD **4**.[5]



Since DFT calculations on the transition state of the CPD to DHP interconversion suggested radical character with spin density at the internal 8,16 positions,[6] we concentrated on influencing this by first changing the internal group. These calculations suggested that the cyano cyclophanediene **5** should have a high activation barrier for thermal cyclization to the dihydropyrene **6**. Indeed, it did, with an estimated half-life at room temperature of about 30 years![3] However, a new problem arose in that the corresponding dihydropyrene **6** suffered from an unexpectedly easy (half-life at 50 °C = 8.3 h) sigmatropic shift of the cyano groups over the π skeleton of the dihydropyrene to form **7**, then **8**, and finally **9** by elimination of HCN.

Again we were guided by calculations and subsequently were able to report[4] that isobutenyl groups at the internal position not only slow down the thermal return of cyclophanediene **10** to dihydropyrene **11** but also resist the sigmatropic shift of the internal groups over the π system of the dihydropyrene, which result in destruction of the photochrome. In addition, it turned out that the quantum yield of the opening reaction (**11** to **10**)[Φ = 0.12] was three times higher than that of **1** [Φ = 0.039].[4] In that paper,[4] we reported calculations for a variety of internal groups.

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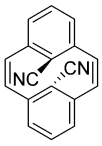

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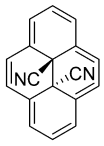

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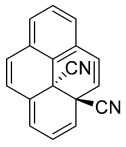

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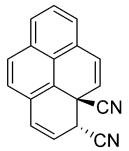

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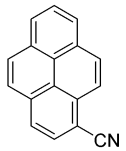

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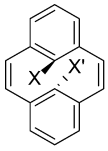
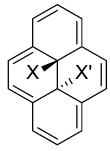
We now have been able to synthesize several of these, and so this paper reports the synthesis of these molecules and our experimental findings on the photochemical and thermal interconversion reactions.

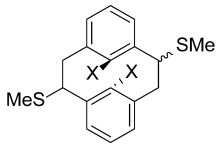




10	X=X'= -CH=CMe$_2$	11
12	X=X'= -CH=CH$_2$	13
14	X=X' = (*Z*)-CH=CHMe	15
16	X = (*Z*)-CH=CHMe	17
	X' = (*E*)-CH=CHMe	
18	X=X' = (*E*)-CH=CHMe	19
20	X=X' = (*Z*)-CH=CHPh	21
22	X = (*Z*)-CH=CHPh	23
	X' = (*E*)-CH=CHPh	
24	X=X' = (*E*)-CH=CHPh	25

RESULTS AND DISCUSSION

Synthesis. Our first targets were the vinyl- (**12**), propenyl- (**14**, **16**, **18**) and styryl-substituted (**20**, **22**, **24**) CPDs and their corresponding DHPs. The route used[4] was similar to that for the isobutenyl derivative **10**, in which conversion of the



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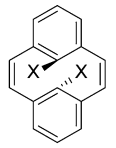

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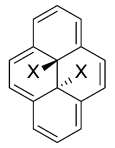

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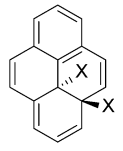

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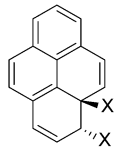

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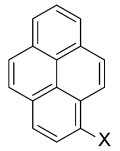


31

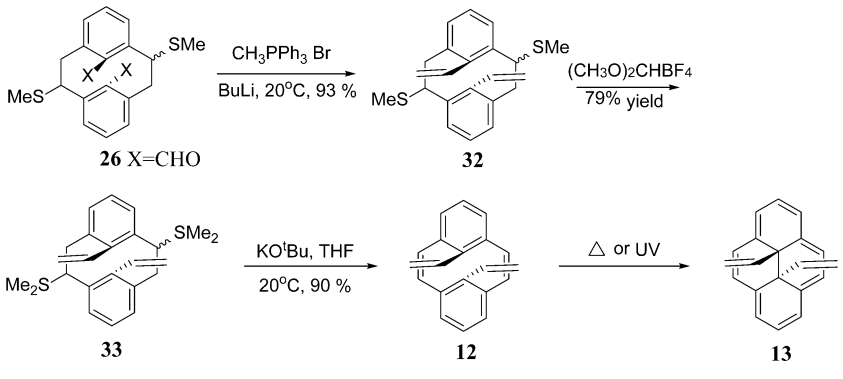
26-31 X = CHO

aldehyde groups of **26** was carried out early in the sequence because of the fragility of the dialdehyde **28**. Like DHP **6**, DHP **28** easily cascaded through a sequence to **31**, presumably via **29** and **30**.

Thus, Wittig reaction of mixed −SMe isomers of bis-aldehyde **26**[4] with a preformed ylide derived from methyltriphenylphosphonium bromide and BuLi for 1 h at 20 °C yielded 93% of the desired bis-vinyl derivative **32** (Scheme 2) as a mixture of isomers. For characterization, a single isomer of **32**, in which both −SMe groups are pseudoequatorial, was isolated, mp 228−229 °C. Full characterization for all new compounds is given in the Experimental Section. For synthetic purposes, the mixed isomers of **32** with dimethoxycarbonium tetrafluoroborate[10] gave 79% of the bis-sulfonium salts **33**, which on Hoffmann elimination gave the colorless cyclophanediene **12** in 90% yield. In the ^{1}H NMR spectrum of **12**, the protons of the internal vinyl substituent appeared clearly as three doublets of doublets at δ 6.32, 5.47, and 4.84.

Quantitative isomerization of **12** to **13** could easily be obtained either thermally or by irradiation with UV light; however for larger sized samples, it was most easily accomplished thermally. Heating a solution of **12** at 100 °C in toluene under argon for about 1 h was determined to be the optimum time and was easily monitored by following the changes in the ^{1}H NMR spectrum. In **13**, the DHP external protons appearing at δ 8.79 (s), 8.65 (d), and 8.08 (t) are significantly deshielded from the analogous ones of **12** by 2.41, 2.05, and 1.01 ppm, respectively. The internal vinyl protons at δ 2.67, 2.06, and 0.50 (all as doublets of doublets) are highly shielded by 2.17, 3.41, and 5.82 ppm, respectively, caused by the strong DHP ring current from those quoted above for **12**.

Scheme 2



26 X=CHO 32 33 12 13

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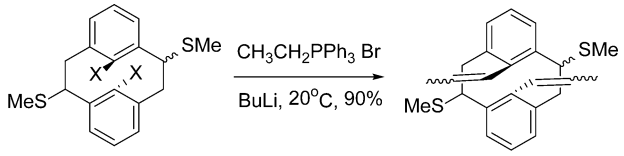
Wittig reaction of the bis-aldehyde **26** with the ylide derived from ethyltriphenylphosphosphonium bromide and BuLi, at 20 °C for 1 h, gave a good yield of **34** as a complex mixture of cyclophane−SMe and double bond (*ZZ*)-, (*ZE*)-, and (*EE*)-isomers (Scheme 3), and so the mixture was directly converted by Hoffmann elimination as for **12** to a 6:1 mixture of **14** (*ZZ*) and **16** (*ZE*). Existence of the third isomer **18** (*EE*) in this mixture was not confirmed.

Scheme 3



26 X=CHO **34**

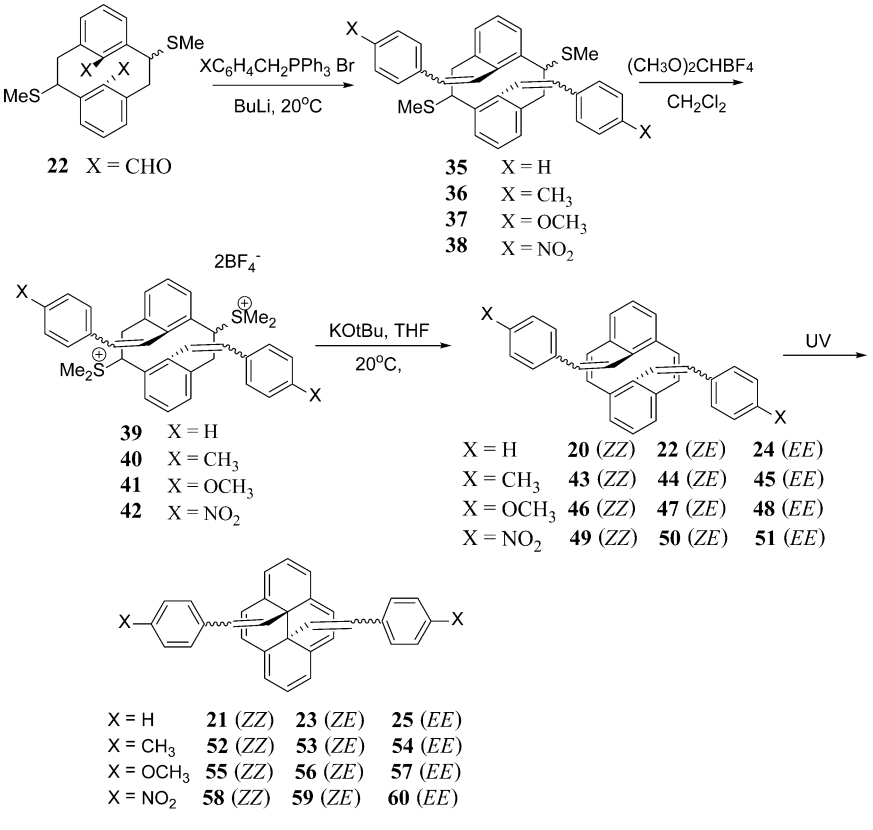
The (*ZZ*)- or *cis*−*cis*-isomer **14** was expected (nonstabilized ylide) to predominate, and did, and in its ^{1}H NMR spectrum, the *cis* orientation of the double bond was established by a coupling constant of 12.0 Hz between the olefinic protons and by an IR band at 711 cm^{-1}. All protons and carbons in the major isomer **14** could easily be accounted for but in the minor isomer **16**, the *cis*-propenyl protons and carbons were obscured by overlap with peaks from the major isomer. The *trans*-propenyl internal group in **16** was characterized by a coupling constant of 15.4 Hz for the alkene proton at δ 5.94 and by an IR band at 962 cm $^{-1}$. DHPs **15** and **17** were obtained preparatively by thermal isomerization of **14** and **16**, as above, or by irradiation with UV light (λ_{max} < 300 nm). The characteristic ^{1}H NMR peaks for the dihydropyrene skeleton were found in the region of δ 8−9, while the internal olefinic (δ 3.21 and 0.09) and methyl protons (δ 0.33(**15**) and 0.32 and 0.17 (**17**)) were quite shielded, being in the center of the ring current.

The styryl-substituted CPDs were obtained analogously (see Scheme 4) as a mixture of **20** (*ZZ*, 44%) **22** (*EZ*, 38%), and **24** (*EE*, 18%) that were easily separated by column chromatography. The styryl olefinic and aromatic protons were quite distinct for the (*Z*)- and (*E*)-isomers. The olefinic protons of the (*Z*)-styryl group in **20** appeared at δ 5.96 and 5.80 whereas in the (*E*)-styryl fragment in **24** these protons appeared accidentally as a singlet at δ 6.86.

Thermal isomerization of the (*ZZ*)-styryl CPD **20** (as described above) gave (*ZZ*)-styryl DHP **21** as orange crystals from cyclohexane, mp 152−154 °C. The olefinic protons in **21** appeared shielded at δ 0.28 and 4.21 as doublets (J = 12.6 Hz). The *ortho* protons of the styryl aromatic rings are also shielded to a small extent by the DHP ring current. The (*EE*)-styryl DHP **25** was obtained as dark green crystals, mp 232−234 °C. A significant difference in λ_{max} is observed between **21** and **25**. The absorption wavelength in the visible region for **25** is observed at 466 and 597 nm whereas the corresponding bands for **21** are observed at 487 and 624 nm. The olefinic protons in **25** appeared at δ 0.87 and 3.21.

To explore the electronic effect of substituents on the thermal behavior of cyclophanedienes, functionalized styryl substituents were also introduced. We synthesized the −OCH_3, −NO_2, and −CH_3 substituted styryl CPDs **43**−**51** as representative examples of electron -donor, -acceptor, and -neutral (hyperconjugation) substituents. A general synthesis of these cyclophanedienes and then conversion into dihydropyrenes is shown in Scheme 4; however, details of the syntheses, yields,

Scheme 4



22 X = CHO

35 X = H
36 X = CH_3
37 X = OCH_3
38 X = NO_2

39 X = H
40 X = CH_3
41 X = OCH_3
42 X = NO_2

X = H	**20** (*ZZ*)	**22** (*ZE*)	**24** (*EE*)
X = CH_3	**43** (*ZZ*)	**44** (*ZE*)	**45** (*EE*)
X = OCH_3	**46** (*ZZ*)	**47** (*ZE*)	**48** (*EE*)
X = NO_2	**49** (*ZZ*)	**50** (*ZE*)	**51** (*EE*)

X = H	**21** (*ZZ*)	**23** (*ZE*)	**25** (*EE*)
X = CH_3	**52** (*ZZ*)	**53** (*ZE*)	**54** (*EE*)
X = OCH_3	**55** (*ZZ*)	**56** (*ZE*)	**57** (*EE*)
X = NO_2	**58** (*ZZ*)	**59** (*ZE*)	**60** (*EE*)

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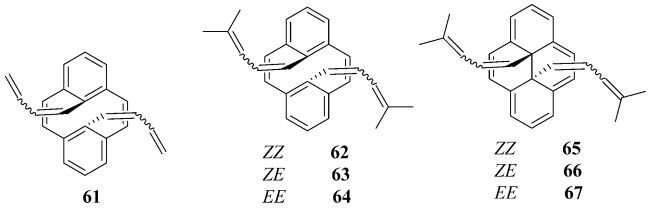
ratios of isomers, and characterizations are given in the Experimental Section.

As examples with extended linear conjugation, cyclophanediene **61** represents a simple example; however, all attempts to synthesize this compound resulted in a nonseparable mixture of isomers. On the other hand, the methyl-substituted analogues **62**–**64** could be easily synthesized as a mixture of (*ZZ*):(*ZE*):(*EE*) isomers which could be separated by column chromatography. Syntheses of compounds **62**–**67** were analogous to those of **20**–**25** above and are described in detail in the Experimental Section.



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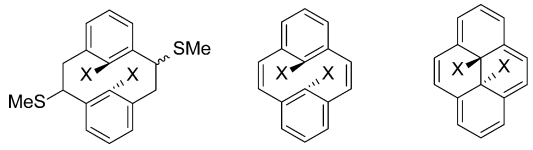
In order to investigate an acetylene-substituted CPD, the Wittig reaction of bis-aldehyde cyclophane **22** with the ylide derived from bromomethyltriphenylphosphonium bromide and KOtBu at 20 °C for 1 h with subsequent in situ elimination of HBr yielded the bis-acetylene cyclophane **68** as a mixture of isomers which was directly subjected to a sequence of S-methylation with $(CH_3O)_2CHBF_4$ and Hoffmann elimination as previously described to give the bis-acetylene CPD **69** as colorless solid. The alkyne was characterized by an IR ≡C−H stretch at 3293 cm^{-1}. Bis-acetylene DHP **70** was obtained by irradiation of cyclophanediene **69** with UV light as dark green crystals, with the internal alkyne protons appearing at δ −0.09, and the IR ≡C−H stretch at 3274 cm^{-1}. Note that neither **69** or **70** showed a clear C≡C stretch.

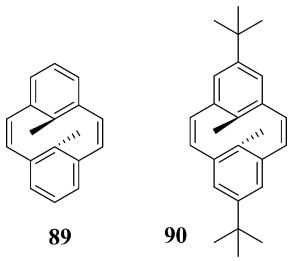


68 **69** **70**

68-70 X = ≡

For comparison purposes, the unsymmetrical cyclophanedienes **77** and **84** were also synthesized, starting from **71**[11] or **79** with **72**,[12] as shown in Scheme 5, with details in the Experimental Section. Dibromide **79** required for the synthesis of **84** was synthesized in the three-step process[13] shown in Scheme 6 from commercially available 2,6-dimethylaniline **86**.

Thermochemical Results. The objective of our work was to produce cyclophanedienes which have relatively slow thermal return reactions to the corresponding dihydropyrenes. Following the thermal return reaction is relatively straightforward using either UV/vis spectroscopy[5b] or by ^{1}H NMR spectrometry[3,5c] since the CPDs show very different spectra from the DHPs. Then use of Arrhenius plots leads to E_{act} and ln *A* data, while Eyring plots yield $\Delta H^{‡}$ and $\Delta S^{‡}$ data. However, understanding the thermal cyclization of CPDs to DHPs just by looking at the thermochemical data proves to be more difficult than one might imagine;[7] for example, direct comparison of energies of activation (E_{act}) tends to be somewhat misleading for this reaction because there appears to be a large variation in the pre-exponential factor (ln *A*) from system to system.[3] We have thus found that comparison of thermal conversion half-lives ($t_{1/2}$) at two or three temperatures to be more useful. While the full Eyring and Arrhenius data are given in the Supporting Information, Table 1 gives the half-life data determined for the compounds in this study.



89 **90**

The observed half-life values follow surprisingly well the calculated activation barriers:[4] for example, both $\Delta H^{‡}$ and $\tau_{1/2}$ (20 °C) follow the order **10** > **14** > **20**. The (*ZZ*)-internal alkenes thermally convert more slowly than the (*ZE*)-isomers, which are slower than the (*EE*)-isomers, e.g., for $\tau_{1/2}$ (20 °C) **20** > **22** > **24**. *Para*-substituents on the phenyl ring of **20** seem to have a larger effect on the (*ZZ*)-isomer than on the others. The mixed internal group compound **77** appears to have a barrier approximately midway between **5** and **89**. It is worth noting that our initial choice for target,[4] the bis-isobutenyl compound **10**, was a good one, as all of the compounds that follow have faster thermal conversions, though all are much slower and thus are better than the parents **89** or **90** .

Photo-opening Ractions. Visible light induced relative opening rate studies were performed using a 500 W tungsten lamp with an orange plastic ∼490 nm cutoff filter (see the Supporting Information for spectrum) using ^{1}H NMR studies in toluene-d_8, side by side with the standard, as we have described previously.[5c] Because the compounds tested in this study are slower opening than benzo-DHP **1**, first the styryl compound **52** was measured against **1** and then **52** was used to calibrate the others that are given in Table 2. Our initial target, the isobutenyl DHP **11**, still proved to open fastest, at about 25% of the rate of **1**, but the (ZZ)-isomers of the styryl, *p*-Me, and *p*-OMe styryl compounds (**21**, **52**, and **55**) all showed very similar and acceptable rates and all opened completely. Some of the compounds (indicated in Table 2 by the *) formed photostationary states. Surprisingly, the (*EE*)-styryl compounds **25**, **54**, **57**, and **60**, the (*EE*)-butadienyl compound **67**, and the phenylethynyl compound **85** did not result in any measurable open (CPD) form under these conditions, though it is possible that the CPD tail extended far enough into the visible to permit any "open" form to close again (the quantum yield of the photoclosing reaction is close to 1, much higher than that of the photoopening reaction[9]). Certainly when the *trans*–*trans*-styryl CPD **24** was irradiated under the same conditions, it closed to the DHP **25**. However, use of a 590 nm red plastic filter also failed to open it. The (*ZZ*)- and (*ZE*)-butadienyl compounds **65** and **66** only isomerized to the (*EE*)-isomer **67**. The vinyl compound **13** did not open appreciably, but decomposed. Robb[8] has shown that the photoopening reaction of the parent **91** occurs through a conical intersection between a biradical excited state and the ground one. However, the former is not the lowest energy excited state, and moreover excitation to it is symmetry forbidden. Stabilization of this state relative to the highly populated zwitterionic excited state should accelerate the photoopening reaction. However, it is not obvious whether this would be a dominating factor or not and how substituents affect this. Compound **15** with *cis*-propenyl groups completely

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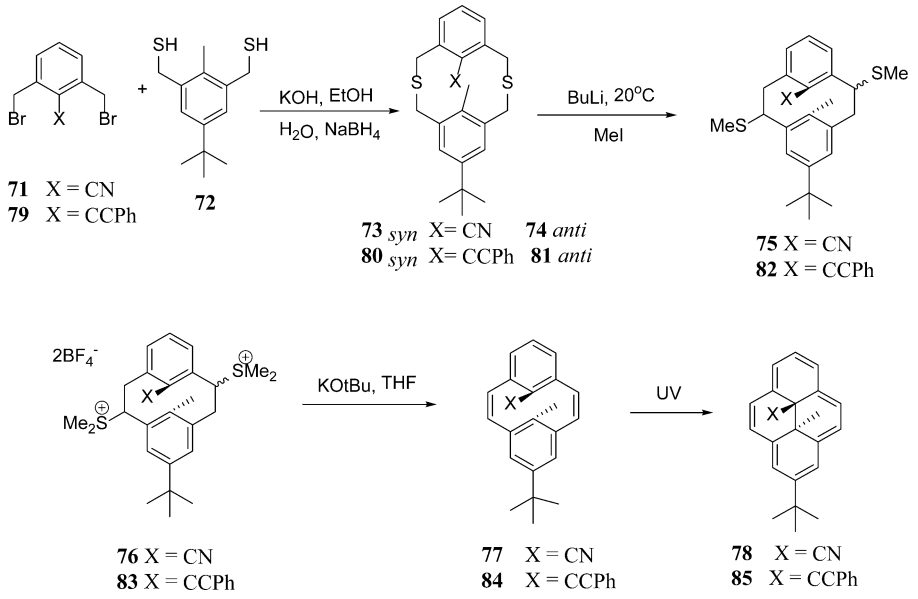
Scheme 5



71 X = CN
79 X = CCPh

72

73 *syn* X= CN **74** *anti*
80 *syn* X= CCPh **81** *anti*

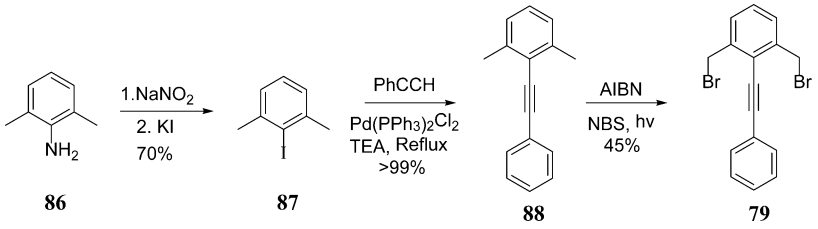
75 X = CN
82 X = CCPh

76 X = CN
83 X = CCPh

77 X = CN
84 X = CCPh

78 X = CN
85 X = CCPh

Scheme 6



86

87

88

79

Table 1. Thermal Half-Lives for the CPD to DHP Conversion Determined at Three Different Temperatures

compd	internal group(s)	$\tau_{1/2}$ (20 °C)[a]	$\tau_{1/2}$ (50 °C)[a]	$\tau_{1/2}$ (100 °C)[a]	$\Delta G^{\ddagger}$(calc) refs 4 and 6
5 (ref 4)	−CN	~36 y	110 d	5.0 h	25.2
10 (ref 4)	−CH═CMe_2	16 y	65 d	4.5 h	27.5
14	(*ZZ*) −CH═CHMe	10 y	33 d	94 m	26.6
69	−C≡CH	8.0 y	49 d	2.1 h	24.3
46	(*ZZ*) −CH═CHPh-OMe-*p*	6.0 y	28 d	2.2 h	26.5
43	(*ZZ*) −CH═CHPh-Me-*p*	5.0 y	25 d	2.2 h	
62	(*ZZ*) −CH═CH-CH═CMe_2	4.5 y	23 d	1.9 h	
20	(*ZZ*) −CH═CHPh	4.3 y	20 d	91 m	27.0
63	(*ZE*) −CH═CH-CH═CMe_2	4.0 y	18 d	82 m	
47	(*ZE*) −CH═CPh-OMe-*p*H	3.1 y	16 d	92 m	
22	(*ZE*) −CH═CHPh	2.8 y	14 d	73 m	24.7
44	(*ZE*) −CH═CHPh-Me-*p*	2.5 y	14 d	87 m	
48	(*EE*) −CH═CHPh-OMe-*p*	2.0 y	11 d	64 m	
49	(*ZZ*) −CH═CHPh-NO_2-*p*	1.9 y	11 d	77 m	26.5
50	(*ZE*) −CH═CHPh-NO_2-*p*	1.8 y	9.8 d	59 m	
45	(*EE*) −CH═CHPh-Me-*p*	1.7 y	10 d	63 m	
51	(*EE*) −CH═CHPh-NO_2-*p*	1.7 y	9.2 d	55 m	
64	(*EE*) −CH═CH-CH═CMe_2	1.6 y	8.5 d	45 m	
24	(*EE*) −CH═CHPh	1.2 y	6.3 d	40 m	23.6
12	−CH═CH_2	56 d	24 h	7.7 m	23.2
84	−Me; −C≡CPh	30 d	15 h		
77 (PhH)($CDCl_3$)	−Me; −CN	12 d; 9.5 d	6.7 h 5.2 h		22.3
27	−CHO	11 d	4.2 h		21.6
89 (ref 3)	−Me	42 h	69 m		20.4
90 (ref 3)	−Me (5,13-di-*t*-Bu)	54 h	2.0 h		20.6

[a]h = hours; d = days; m = minutes. Errors estimated are <5%.

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Table 2. Visible Light Opening Rates for the Dihydropyrenes to the Cyclophanedienes, Measured Relative to that of 1 = 1000 with Calculated Rates Relative to Parent 91

compd (int group)	calcd[b] relative rates vs DHP **91** = 1000	relative rates[c] vs benzo DHP **1** = 1000	CPD:DHP[d]
6[a] −CN	∼6	∼1	60:40
70[a] −C≡CH	65	4	60:40
15 (*ZZ*) −CH=CHMe	180	11	
58[a] (*ZE*) −CH=CHPh-NO_2-*p*	200	12	20:80
23[a] (*ZE*) −CH=CHPh	740	45	80:20
53[a] (*ZE*) −CH=CHPh-Me-*p*	980	60	50:50
56[a] (*ZE*) −CH=CHPh-OMe-*p*	1130	69	60:40
21 (*ZZ*) −CH=CHPh	2500	150	
55 (*ZZ*) −CH=CHPh-OMe-*p*	2900	180	
52 (*ZZ*) −CH=CHPh-Me-*p*	2900	180	
11 −CH=CMe_2	3900	240	

[a]P = photostationary state. [b]Approximately 16.25× rate for **1**.[5c] [c]Error estimates are less than 5%. [d]Estimated by ^{1}H NMR.

opened, while **17**, with one *trans*-group did not open at all! For the styryl compounds, the (*ZE*)-compounds do open, though more slowly than the (*ZZ*)-isomers. A qualitative explanation can be made on examination of the UV−vis spectra of the styryl-CPDs shown in Figure 1 (equimolar concentrations).

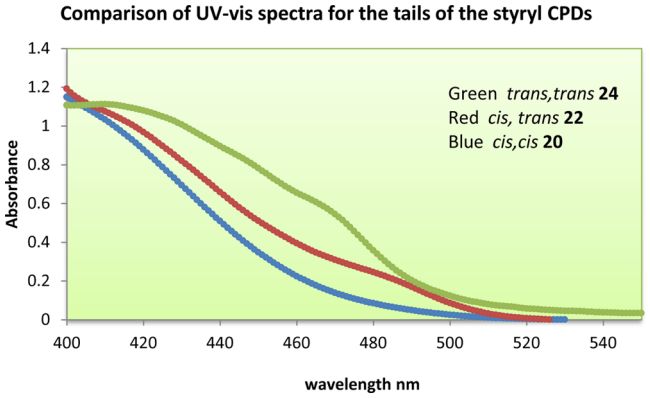
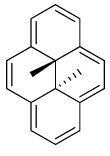


Figure 1. Comparison of the UV−vis spectra tails for the styryl CPDs **20**, **22**, and **24**.

For *cis,cis*-**20** (blue, Figure 1), the tail has reached baseline before 510 nm. For *cis,trans*-**22** and *trans,trans*-**24** the tails show increasingly significant tails above 500 nm, providing a qualitative explanation for DHP, *cis,cis*-**21** having the fastest opening rate, while for the *trans* compounds the photoclosing reaction increasingly competes.

For the *para*-substituted *cis,cis*-styryl CPDs shown in Figure 2 (equimolar concentrations), again examination of the CPD tails



91

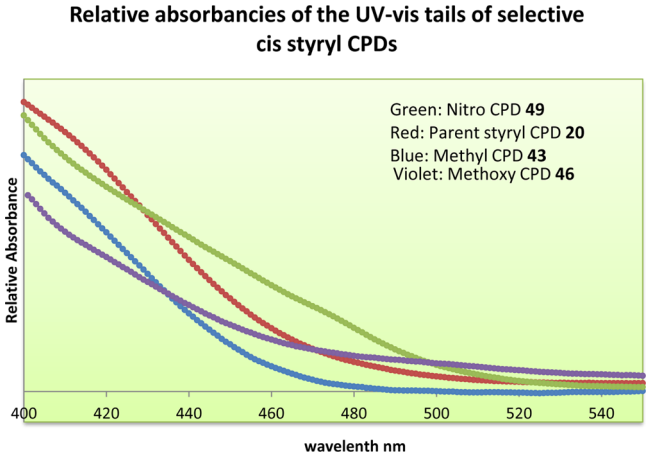


Figure 2. Comparison of the UV−vis spectra tails for the para-substituted *cis,cis*-styryl CPDs **20**, **43**, **46**, and **49**.

is consistent with the *p*-nitro DHP **58** showing the slowest rate of opening with considerable CPD content of the photostationary state, while the *p*-Me DHPs **52** shows the fastest rate and complete conversion.

Sigmatropic Rearrangement. The remaining objective that we have not yet discussed is the sigmatropic rearrangement that occurs >50 °C for the dicyano DHP **6** which ultimately led to **9**.[3] Happily, for the bis-isobutenyl DHP **11**, the rearrangement is suppressed and is not observed at all at 100 °C. With the exception of the diformyl DHP **28** which isomerized to **29** (E_{act} estimated to be <20 kcal/mol) and then on to **31** even more easily than for **6**, the other DHPs prepared in this study all showed no evidence of rearrangement at 100 °C.

CONCLUSIONS

In this paper, the synthesis of a number of cyclophanedienes with a variety of different internal alkenyl and alkynyl groups and their corresponding dihydropyrenes is described. The thermal conversions of the CPDs to DHPs and the photochemical conversions of the DHPs to CPDs are measured and compared. CPDs with *cis*-alkenyl internal groups showed the slowest thermal conversion to DHPs, with half-lives of several years at 20 °C, which is much better than that observed for benzo CPD **2**, but not as good as for isobutenyl CPD **10**. The photoopening reaction rate for the corresponding *cis*-alkenyl DHPs was similar to that of DHP **11**. As well, for the compounds studied, the sigmatropic rearrangement was suppressed. Of the compounds studied here, the CPD/DHP pairs **20**/**21**, **43**/**52**, and **46**/**55** show the most promising properties as photochromic switches. The relative observed thermal closing rates, CPD to DHP, agree reasonably well with previous[4] calculations.

EXPERIMENTAL SECTION

The general conditions and the numbering system used for NMR assignments are given in the Supporting Information.

General Thermolysis Procedure Used for Converting CPDs into DHPs. The cyclophanediene (25 mg) in toluene-d_8 (2 mL) was sealed in an NMR tube under argon, which was then heated at 100 °C until ^{1}H NMR indicated conversion to the dihydropyrene was complete (∼1−2 h). Evaporation yielded the DHP as colored crystals.

*2,10-Bis(methylthio)-8,16-diethenyl-anti-[2.2]metacyclophane (**32**).* BuLi (5.3 mL, 2.5 M in hexanes, 13 mmol) was added dropwise to a stirred suspension of methyltriphenylphosphonium bromide (3.6 g, 10.1 mmol) under argon in THF (40 mL) at 0 °C. After 20 min,

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diformylmethylthiocyclophane **26**[4] (1.5 g, 4.21 mmol) was added to this clear orange-red solution, and stirring was continued at 20 °C for 1.5 h. Water was then added followed by dichloromethane. The organic extract was washed, dried, and evaporated. The crude product was chromatographed over silica gel using hexanes/dichloromethane (7:3) as eluent and gave 1.38 g (93%) of divinylmethylthiocyclophane **32** as a mixture of isomers: EIMS *m*/*z* 352 (M^+); ^{1}H NMR δ 7.98 (d, *J* = 7.6 Hz), 7.80 (d, *J* = 7.7 Hz), 7.67−7.62 (m), 7.53−7.51 (m), 7.45−7.42 (m), 7.20−7.16 (m), 7.08−7.05 (m), 6.94 (t, *J* = 7.4 Hz), 4.80−4.60 (m), 4.52−4.40 (m), 4.28−4.25 (m), 4.11−4.08 (m), 3.08−3.04 (m), 2.87 (t, *J* = 12.0 Hz), 2.66 (t, *J* = 12.1 Hz), 2.12, 2.08 (s). For synthetic purposes, these were used directly in the next step. For characterization purposes, a single isomer of **32**, in which the 1,9-methylthio groups are pseudoequatorial was obtained by rechromatography as colorless crystals: mp 228−229 °C; ^{1}H NMR δ 7.81 (dd, *J* = 7.6, 1.1 Hz, 2H, H-6,14), 7.18 (dd, *J* = 7.5, 1.0 Hz, 2H, H-4,12), 7.07 (t, *J* = 7.5 Hz, 2H, H-5,13), 4.80−4.75 and 4.48−4.42 (m, 6H, H-19,20,17,18), 4.27 (dd, *J* = 11.6, 4.2 Hz, 2H, H-1,9), 3.06 (dd, *J* = 12.6, 4.2 Hz, 2H, H-2_{eq},10_{eq}), 2.66 (dd, *J* = 12.1, 11.9 Hz, 2H, H-2_{ax},10_{ax}), 2.13 (s, 3H, SMe); ^{13}C NMR δ 147.0 (C-8,16), 135.7 (C-7,15), 135.2 (C-3,11), 135.0 (C-17, 19), 128.9(C-4,12), 126.6 (C-5,13), 125.4 (C-6,14), 120.6(C-18,20), 53.2 (C-1,9), 43.3 (C-2,10), 15.3 (C-21,22); IR ν (KBr) 3078, 2960, 2909, 1438, 1397, 994, 930, 771, 748 cm^{-1}; UV−vis (cyclohexane) λ_{max} nm (ε_{max}) 227 (17300), 288 (3986); EIMS *m*/*z* 352 (M^+); HRMS calcd for $C_{22}H_{24}S_2$ 352.1319, found 352.1319. Anal. Calcd: C, 74.95; H, 6.86. Found: C, 74.48; H, 6.91.

*1,10-Bis(methylthio)-8,16-divinyl-anti-[2.2]metacyclophane Bis-sulfonium Salt (**33**).* The mixed isomers of **32** (360 mg, 1 mmol) in dry CH_2Cl_2 (20 mL) were added slowly to $(MeO)_2CHBF_4$ (Borch reagent)[10] (80% oil, 580 mg, 2.86 mmol) in CH_2Cl_2 (14 mL) at −78 °C with stirring under nitrogen. The mixture was then stirred at 20 °C for 3 h. The CH_2Cl_2 was then decanted from the oil, ethyl acetate (40 mL) was added, and stirring was continued for another 3 h (this was repeated if a nonsticky white powder was not obtained). The white precipitate was collected and dried to give 440 mg (79%) of the sulfonium salt **33**: ^{1}H NMR (DMSO-d_6) δ 7.72 (d, *J* = 7.8 Hz), 7.58 (d, *J* = 7.4 Hz), 7.54 (d, *J* = 7.3 Hz), 7.41 (d, *J* = 7.6 Hz), 7.28 (t, *J* = 7.6 Hz), 7.13 (t, *J* = 7.4 Hz), 5.2−4.6 (m), 3.46−3.05 (m), 2.90, 2.87(s). This was used directly in the next step.

*8,16-Divinyl-anti-[2.2]metacyclophane-1,9-diene (**12**).* *t*-BuOK (250 mg, 2.23 mmol) was added to a stirred suspension of the bis-sulfonium salt **33** (440 mg, 0.791 mmol) in THF (20 mL) under argon at 20 °C in a vessel wrapped in aluminum foil to exclude light. After the mixture was stirred for 30 min, water and CH_2Cl_2 were added. The organic extract was washed, dried, and evaporated (all with protection from light). The product was chromatographed over silica gel using hexanes as eluent gave 182 mg (90%) of **12** as colorless crystals from cyclohexane: ^{1}H NMR δ 7.07 (t, *J* = 7.4 Hz, 2H, H-5,13), 6.60 (d, *J* = 7.4 Hz, 4H, H-4,6,12,14), 6.38 (s, 4H, H-1,2,9,10), 6.32 (dd, *J* = 17.4, 11.0 Hz, 2H, H-17,19) 5.47 (dd, *J* = 17.4, 1.8 Hz, 2H, H-18,20b), 4.84 (dd, *J* = 11.0, 1.8 Hz, 2H, H-18,20a); ^{13}C NMR δ 146.4 (C-8,16), 135.8 (3,7,11,15), 135.2 (C-17,19), 133.2 (C-1,2,9,10), 129.5 (C-5,13), 126.7 (C-4,6,12,14), 118.9 (C-18,20); IR ν (KBr) 3077, 3049, 3004, 1618, 1436, 1397, 993, 903, 861, 807, 764, 605 cm^{-1}; UV−vis (cyclohexane) λ_{max} nm (ε_{max}) 202 (51700), 242 (33170), 279 (12370), 339 (11000), 377 (5710), 390 sh (2100); EIMS *m*/*z* 256 (M^+); HRMS calcd for $C_{20}H_{16}$ 256.1252, found 256.1255. Anal Calcd: C, 93.70; H, 6.30. Found: C, 93.51; H, 6.41. Attempted mp determination isomerized **12** into DHP **13.**

*10b,10c-Divinyl-trans-10b,10c-dihydropyrene (**13**). (a) Thermolysis (Best for Preparative Samples).* Cyclophanediene **12** (25 mg) in toluene-d_8 (2 mL) was sealed in an NMR tube under argon, which was then heated at 100 °C until ^{1}H NMR indicated conversion to dihydropyrene **13** was complete (∼1−2 h). Evaporation yielded 25 mg (100%) of **13** as dark green crystals from cyclohexane: mp 163−165 °C; ^{1}H NMR δ 8.79 (s, 4H, H-4,5,9,10), 8.65 (d, *J* = 7.6 Hz, 4H, H-1,3,6,8), 8.08 (t, *J* = 7.6 Hz, 2H, H-2,7), 2.67 (dd, *J* = 10.3, 1.4 Hz, 2H, H-12,14b), 2.06 (dd, *J* = 17.0, 1.5 Hz, 2H, H-12,14a), 0.50 (dd, *J* = 17.0, 10.3 Hz, 2H, H-11,13); ^{13}C NMR δ 133.8 (3a,5a,10a,10d), 128.6 (C-11,13), 125.5 (C-4,5,9,10), 124.4 (C-1,3,6,8), 123.8 (C-2,7), 109.8 (C-12,14), 36.1 (C-10b,10c); IR ν (KBr) 3032, 3007, 1621, 1399, 1295, 912, 841 cm^{-1}; UV−vis (cyclohexane) λ_{max} nm (ε_{max}) 339 (71300), 377 (30000), 462 (5600), 608 (100); EIMS *m*/*z* 256 (M^+); HRMS calcd for $C_{20}H_{16}$ 256.1252, found 256.1251. Anal. Calcd: C, 93.70; H, 6.30. Found: C, 93.92; H, 6.57.

(b) UV Irradiation (Only Used for Small Samples To Indicate That the Reaction Proceeds) . The cylophanediene **12** (2 mg) was dissolved in sufficient cyclohexane or dichloromethane to fill a quartz UV cuvette, which was then irradiated with 254 nm light from a hand-held TLC lamp. The irradiation was monitored at 15 s intervals until complete conversion to dihydropyrene **13** was observed (the bands at 462 and 608 nm maximize). This required 45−75 s. The UV−vis spectrum observed was the same as that obtained for thermolysis, method a.

***8,16**-Bis(prop-1-enyl)-anti-[2.2]metacyclophane-1,9-dienes (**14**) and (**16**).* Using the same procedure as for the sequence **26**−**32**−**33**−**12** above, except that ethyltriphenylphosphonium bromide was used, followed by the same methylation/Hoffmann elimination sequence, yielded after chromatography 202 mg (90%) of the two isomers **14** and **16** in approximately a ratio of 6:1. By further chromatography, these could be partially separated. One fraction was enriched in the major isomer, (*ZZ*)-**14**: ^{1}H NMR δ 6.94 (t, *J* = 7.4 Hz, 2H, H-5,13), 6.46 (d, *J* = 7.4 Hz, 4H, H-4,6,12,14), 6.12 (qd, *J* = 12.0, 1.8 Hz, 2H, H-17,19), 6.09 (s, 4H, H-1,2,9,10), 5.23 (qd, *J* = 12.0, 7.2 Hz, 2H, H-18,20), 1.55 (dd, *J* = 7.3, 1.8 Hz, 6H, H-21,22); ^{13}C NMR δ 142.3 (C-8,16), 136.9 (C-3,7,11,15), 132.0 (C-1,2,9,10), 129.4 (C-17,19), 128.2 (C-5,13), 126.0 (C-18,20), 125.5 (C-4,6,12,14), 15.4 (C-21,22); IR ν (thin film) 3036, 3001, 2930, 2848, 1599, 1561, 1434, 962, 929, 858, 842, 771, 711, 665 cm^{-1}; UV−vis (cyclohexane) λ_{max} nm (ε_{max}) 215 (25000), 243 (26200), 277 (11500), 340 (∼ 2500); EIMS *m*/*z* 284 (M^+); HRMS calcd for $C_{22}H_{20}$ 284.1565, found 284.1562.

The second fraction was enriched in the minor isomer, (*ZE*)-**16**: ^{1}H NMR δ 6.98 (t, *J* = 7.4 Hz, 1H, H-13), 6.86 (t, *J* = 7.4 Hz, 1H, H-5), 6.44 (d, *J* = 7.4 Hz, 2H, H-12,14), 6.42 (d, *J* = 7.4 Hz, 2H, H-4,6), 6.10−6.14 (AB*, 4H, H-1,2,9,10), 5.94 (dq, *J* = 15.4, 6.7 Hz, H-20), 1.57 (dd, *J* = 1.9 Hz, *J* = 6.6 Hz, 3H, H-21), 1.52 (dd, *J* = 6.6, 1.6 Hz, 3H, H-22) H-17−19*; ^{13}C NMR δ 145.9 (C-8), 141.3 (C-16), 137.4 (C-11,15), 135.1 (C-3,7), 132.6 (C-2,9), 131.8 (C-17), 130.8 (C-19), 129.8 (C-20), 128.5 (C-13), 127.8 (C-5), 126.2 (C-4,6), 125.4 (C-12,14), 18.2 (C-22), 15.3 (C-21), C-1,10,18*. *Indicates when peaks are not distinct (overlapped by the major isomer).

*10b,10c-Bis(prop-1-enyl)-trans-10b,10c-dihydropyrenes (**15**) and (**17**).* Using the same thermolysis procedure used for **12** above, CPD **15** (25 mg) was converted to (*ZZ*)-DHP **15** (25 mg, 100%): ^{1}H NMR δ 8.64 (d, *J* = 7.6 Hz, 4H, H-1,3,6,8), 8.63 (s, 4H, H-4,5,9,10), 8.05 (t, *J* = 7.6 Hz, 2H, H-2,7), 3.21 (qd, *J* = 12.4, 7.3 Hz, 2H, H-12, 14), 0.33 (dd, *J* = 7.3, 1.8 Hz, 6H, H-15,16), 0.09 (qd, *J* = 12.4, 1.8 Hz, 2H, H-11,13); ^{13}C NMR δ 135.3 (C-3a,5a,10a,10d), 126.1 (C-4,5,9,10), 125.4 (C-1,3,6,8), 123.61 (C-12,14), 123.59 (C-2,7), 121.9 (C-11,13), 11.5 (C-15,16); EIMS *m*/*z* 284 (M^+); HRMS calcd for $C_{22}H_{20}$ 284.1565, found 284.1557.

Thermolysis of the mostly (*ZE*)-isomer **16** gave 100% of (*ZE*)-DHP **17**: ^{1}H NMR δ 8.71 (d, *J* = 7.7 Hz, 2H, H-4,10), 8.67 (d, *J* = 7.6 Hz, 2H, H-6,8), 8.66 (d, *J* = 7.6 Hz, 2H, H-5,9), 8.58 (d, *J* = 7.7 Hz, 2H, H-1,3), 8.07 (t, *J* = 7.8 Hz, 1H, H-7), 8.02 (t, *J* = 7.7 Hz, 1H, H-2), 3.14 (qd, *J* = 12.4, 7.3 Hz, 1H, H-14), 2.36 (qd, *J* = 15.1, 6.5 Hz, 1H, H-12), 0.32 (dd, *J* = 7.2, 1.8 Hz, 3H, H-15), 0.17 (dd, *J* = 6.7, 1.5 Hz, 3H, H-16), 0.15 (m, 2H, H-11,13); ^{13}C NMR δ 135.2 (C-5a,10d), 134.8 (C-10a,3a), 126.1 (C-5,9), 125.2 (C-4,10), 125.1 (C-6,8), 124.2 (C-1,3), 123.44 (C-2), 123.39 (C-7), 123.0 (C-13), 122.8 (C-14), 120.6 (C-11), 120.3 (C-12), 16.4 (C-15), 11.1 (C-16); IR ν (KBr) 3018, 2923, 2852, 1365, 836, 797, 692 cm^{-1}; UV−vis (cyclohexane) λ_{max} nm (ε_{max}) 346 nm (46600), 369 (12700), 390 (21100), 482 (4500), 626 (120). Anal. Calcd: C, 92.91; H, 7.09. Found: C, 92.91; H, 7.10.

*8,16-Bis(2-phenylethenyl)-1,9-bis(methylthio)-anti-[2.2]-metacyclophane (**35**).* Using the same procedure as for **22** to **32** above, diformylmethylthiocyclophane **22** (1.40 g, 3.93 mmol) with the ylide prepared by reaction of *t*-BuOK (4.0 g, 36 mmol) and benzyl triphenylphosphonium bromide (5.0 g, 11.5 mmol) in THF (30 mL)

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followed by column chromatography using hexanes/dichloromethane (7:3) gave 400 mg (20%) of mixed isomers of distyrylmethylthiocyclophane **35**: ^{1}H NMR δ 7.98 (d, J = 7.7 Hz), 7.96 (d, J = 8.0 Hz), 7.91 (d, J = 7.6 Hz), 7.84 (d, J = 7.6 Hz), 7.38−6.90 (m), 6.34−6.27 (m), 5.93 (d, J = 12.4 Hz), 5.88 (d, J = 12.4 Hz), 5.73 (d, J = 16.4 Hz), 5.22 (d, J = 16.4 Hz), 5.16 (d, J = 16.4 Hz) 4.42−4.00 (m), 3.16−2.95 (m), 2.73−2.53 (m), 2.19, 2.18 (s), 1.61, 1.38, 1.37 (3 singlets); EIMS m/z 504 (M+); HRMS calcd for $C_{34}H_{32}S_2$ 504.1945, found 504.1938. These were used directly in the next step.

*8,16-Bis(2-phenylethenyl)-1,9-bis(methylthio)-anti-[2.2]-metacyclophane Bis-sulfonium Salt (**39**).* Using the same procedure as for **33** above, from the mixed isomers of **35** (600 mg, 1.19 mmol) with Borch reagent (80% oil, 1g, 5 mmol) in CH_2Cl_2 (10 mL) gave 700 mg (83%) of bis-sulfonium salt **39**: ^{1}H NMR (DMSO-d_6) δ 7.75−7.18 (m), 7.08−6.96 (m), 6.37−5.91 (m), 5.33 (d, J = 16.4 Hz), 4.61−4.51 (m), 4.28−3.95 (m), 3.48−3.37 (m), 3.29−3.15 (singlets) 2.98−2.80 (singlets), 2.27, 2.29 (s), 2.14, 1.96 (s), which were used directly in the next step.

*8,16-Bis(2-phenylethenyl)-anti-[2.2]metacyclophane-1,9-dienes (**20**), (**22**), and (**24**).* Using the same procedure as for **12** above, the bis-sulfonium salt **39** (650 mg, 0.93 mmol) and *t*-BuOK (500 mg, 4.5 mmol) in THF (10 mL) gave a mixture of cyclophanedienes which was purified by column chromatography using hexanes-dichloromethane 85: 15 as eluent. Elued first was the ***cis*−*cis*** or **bis-(1*Z*)-isomer 20**, 152 mg (41%), as pale yellow crystals from cyclohexane. ^{1}H NMR (CD_2Cl_2) δ 7.18 (t, J = 7.4 Hz, 2H, H-5,13), 7.09−7.02 (m, 6H, H-27−32), 6.81−6.77 (m, 4H, 23−26), 6.59 (d, J = 7.4 Hz, 4H, H-4,6,12,14), 5.96 (d, J = 12.4 Hz, 2H, H-19,20), 5.84 (s, 4H, 1,2,9,10), 5.80 (d, J = 12.4 Hz, 2H, H-17,18); ^{13}C NMR (CD_2Cl_2) δ 141.9 (C-8,16), 139.1 (C-21,22), 138.6 (3,7,11,15), 132.7 (C-1,2,9,10), 131.6 (C-19,20), 130.2 (C-5,13), 123.0 (C-17,18), 128.8 (C-23−26), 128.2 (C-31,32), 126.8 (C-27−30), 126.6 (C-4,6,12,14); IR ν (KBr) 3077, 3050, 3005, 1596, 1492, 1448, 1432, 961, 795, 769, 736, 702, 696, 646, 597 cm^{-1}; UV−vis (cyclohexane) λ_{max} nm (ε_{max}) 257 (28900), 280 (23900), 389 (3700); EIMS m/z 408 (M^+); HRMS calcd for $C_{32}H_{24}$ 408.1878, found 408.1884. On attempted melting point determination CPD **20** converted into DHP **21.**

Eluted second was the ***cis*−*trans*** or **8-(1*E*),16-(1*Z*)** isomer **22** as 132 mg (35.4%) of pale yellow crystals from cyclohexane: ^{1}H NMR δ 7.24−7.00 (m, 8H, 23,24, 27−32), 7.13 (t, J = 7.4 Hz, 1H, H-13), 6.83−6.80 (m, 2H, H-25,26), 7.00 (t, J = 7.4 Hz, 1H, H-5), 6.81 and 6.73 (AB, J = 16.3 Hz, H-17,19), 6.72 (d, J = 7.4 Hz, 2H, H-12,14), 6.45 (d, J = 7.4 Hz, 2H, H-4,6), 6.33 (d, J = 11.4 Hz, H-1,10), 6.06 (d, J = 12.5 Hz, 1H, H-20), 5.97 (d, J = 11.4 Hz, 2H, H-2,9), 5.92 (d, J = 12.5 Hz, 1H, H-18); ^{13}C NMR δ 146.1 (C-16), 140.1 (C-8), 138.8 (C-22), 138.6 (C-3,7), 138.1 (C-21), 136.2 (C-11,15), 133.3 (C-19), 133.0 (C-1,10), 132.7 (C-2,9), 131.5 (C-20), 130.3 (C-5), 129.5 (C-18), 128.82 (C-13), 128.75 (C-17), 128.6 (25,26), 126.8 (C-12,14), 126.3 (C-4,6); IR ν (thin film) 3020, 1597, 1574, 1493, 1448, 960, 793, 763, 737, 691 cm^{-1}; UV−vis (cyclohexane) λ_{max} nm (ε_{max}) 252 (29300), 282 (26500), 408 (1600); EIMS m/z 408 (M^+); HRMS calcd for $C_{32}H_{24}$ 408.1878, found 408.1884. On attempted melting point determination CPD **22** converted into DHP **23.**

Eluted third was 67 mg (18%) of the ***trans*−*trans*** or **bis-(1*E*)** isomer **24**: ^{1}H NMR δ 7.22−7.02 (m, 10H, H-23−32), 7.0 (t, J = 7.4 Hz, 2H, H-5,13), 6.86 (s, 4H, H-17−20), 6.62 (d, J = 7.4 Hz, 4H, H-4,6,12,14), 6.48 (s, 4H, H-1,2,9,10); ^{13}C NMR δ 144.6 (C-8,16), 138.2 (C-21,22), 136.7 (C-3,7,11,15), 133.6 (C-19,20), 133.3 (C-1,2,9,10), 129.3 (C-5,13), 128.8 (C-17,18), 127.4 (C-31,32), 127.0 (C-4,6,12,14), 126.8 (C-27,28,29,30), 126.5 (C-23,24,25,26); IR ν (KBr) 3026, 1598, 1492, 1447, 959, 838, 774, 763, 736, 690 cm^{-1}; UV−vis (cyclohexane) λ_{max} nm (ε_{max}) 258 (33000), 284 (33400), 308 (30300), 411 sh (1900). On attempted melting point determination CPD **24** converts into DHP **25**.

*10b,10c-Bis((1Z)-2-phenylvinyl)-trans-10b,10c-dihydropyrene (**21**).* Thermolysis of *cis,cis*- styryl CPD **20**, exactly as described for 12 above, gave 100% yield of the *cis,cis*-DHP **21** as orange crystals from cyclohexane: mp 152−154 °C; ^{1}H NMR (CD_2Cl_2) δ 8.26 (s, 4H, H-4,5,9,10), 8.21 (d, J = 7.5 Hz, 4H, H-1,3,6,8), 7.78 (t, J = 7.5 Hz, 2H, H-2,7), 7.15 (tt, J = 6.5, 1.1 Hz, 2H, H-25,26), 7.07−7.02 (m, 4H, H-21−24), 6.03−6.01 (m, 4H, H-17−20), 4.21 (d, J = 12.6 Hz, 2H, 13,14), 0.28 (d, J = 12.6 Hz, 2H, H-11,12); ^{13}C NMR (CD_2Cl_2) δ 136.8 (C-15,16), 134.2 (C-3a,5a,10a,10d), 128.8 (C-17−20), 127.5 (C-13,14), 126.9 (C-4,5,9,10), 126.4 (C-21−26), 125.7 (C-1,3,6,8), 124.1 (C-2,7), 122.5 (C-11,12), 36.7 (C-10b,10c); IR ν (KBr) 3024, 844, 830, 694, 609 cm^{-1}; UV−vis (cyclohexane) λ_{max} nm (ε_{max}) 351 nm (56400), 369 (15300), 395 (25700), 487 (5100), 624 (95); EIMS m/z 408 (M^+); HRMS calcd for $C_{32}H_{24}$ 408.1878, found 408.1887. Anal. Calcd: C, 94.08; H, 5.92. Found: C, 93.90; H, 6.02.

*10b-((1E)-2-Phenylvinyl)-10c-((1Z)-2-phenylvinyl)-trans-10b,10c-dihydropyrene (**23**).* Using the same procedure for *cis,trans*-styryl CPD **22** gave (∼100%) *cis,trans*-styryl DHP **23** as an oily film, which could not be crystallized: ^{1}H NMR δ 8.72 (d, J = 7.7 Hz, 2H, H-4,10), 8.64 (d, J = 7.7 Hz, 2H, H-1,3), 8.41 (d, J = 7.7 Hz, 2H, H-5,9), 8.27 (d, J = 7.7 Hz, 2H, H-6,8), 8.08 (t, J = 7.6 Hz, 1H, H-2), 7.81 (t, J = 7.7 Hz, 1H, H-7), 7.18 (tt, J = 7.4, 1.0 Hz, 1H, H-25), 7.09 (dd, J = 7.6, 7.4 Hz, 2H, H-21,22), 6.78−6.68 (m, 3H, H-23,24,26), 6.11 (dd, J = 7.8, 0.9 Hz, 2H, H-17,18), 5.99 (dd, J = 7.8, 1.4 Hz, 2H, H-19,20), 4.31 (d, J = 12.9 Hz, 1H, H-13), 3.22 (d, J = 15.8 Hz, 1H, H-14), 0.83 (d, J = 15.9 Hz, H-12), 0.41 (d, J = 12.9 Hz, 1H, H-11); ^{13}C NMR δ 136.5 (C-15), 136.3 (C-16), 134.0 (C-3a,10a), 133.7 (C-5a,10d), 128.6 (C-17,18), 127.8 (C-23,24), 127.2 (C-13), 126.9 (C-5,9), 126.6 (C-26), 126.1 (C-21,22,25), 125.8 (C-6,8), 125.6 (C-19,20), 125.3 (C-4,10), 124.8 (C-14), 124.2 (C-1,3), 124.0 (C-7), 123.7 (C-2), 122.6 (C-11), 120.2 (C-12), 37.3 (C-10b), 15.0(C-10c); IR ν (thin film) 3028, 1733, 1597, 1490, 1441, 1355, 1070, 958, 836, 738, 693, 599 cm^{-1}; UV−vis (dichloromethane) λ_{max} nm (ε_{max}) 256 nm (20000), 348 (54800), 389 (25300), 478 (5780), 609 (106).

*10b,10c-Bis((1E)-2-phenylvinyl)-trans-10b,10c-dihydropyrene (**25**).* From the *trans*−*trans*-styryl CPD **24** using the same thermolysis procedure gave 100% of the *trans,trans*-styryl DHP **25** as dark green crystals from cyclohexane: mp 232−234 °C; ^{1}H NMR δ 8.85 (s, 4H, H-4,5,9,10), 8.67 (d, J = 7.7 Hz, 4H, H-1,3,6,8), 8.08 (t, J = 7.7 Hz, 2H, H-2,7), 6.76−6.69 (m, 6H, H-21−26), 6.03 (dd, J = 8.0, 2.5 Hz, 4H, H-17−20), 3.22 (d, J = 15.8 Hz, 2H, H-13,14), 0.87 (d, J = 15.8 Hz, 2H, H-11,12); ^{13}C NMR δ 136.3 (C-15,16), 133.9 (C-3a,5a,10a,10d), 127.9 (C-21−24), 126.6 (C-25,26), 125.7 (C-17,20), 125.6 (C-4,5,9,10), 124.6 (C-1,3,6,8), 124.6 (C-13,14), 124.0 (C-2,7), 120.8 (C-11,12), 35.9 (C-10b,10c); IR ν (KBr) 3027, 1654, 1636, 1492, 1447, 959, 838, 774, 735, 717, 690 cm^{-1}; UV−vis (cyclohexane) λ_{max} nm (ε_{max}) 257 nm (47900), 342 (58000), 380 (26400), 466 (5770), 597 (165).

*8,16-Bis(2-(4-nitrophenyl)ethenyl)-1,9-bis(methylthio)-anti-[2.2]-metacyclophane (**38**).* To a suspension of 4-nitrobenzyltriphenylphosphonium bromide (4.0 g, 8.4 mmol, commercial supplier) in toluene (50 mL) was added potassium *tert*-butoxide (1.3g, 12 mmol), the mixture was heated at 50 °C for 1 h, and then 8,16-diformyl-(methylthio)cyclophane **22** (1.0 g, 2.81 mmol) was added. The mixture was heated to reflux over a period of 6 h and stirred overnight. The toluene was then evaporated, and the crude was extracted with water and dichloromethane. The organic layer was dried and evaporated. The residue was chromatographed over silica gel using dichloromethane−hexane (55:45) as eluent and gave 0.90 g (54%) **38** as a yellow orange mixture of isomers: ^{1}H NMR δ 8.14 (d, J = 8.7 Hz), 7.99−7.96 (m), 7.94 (d, J = 8.6 Hz), 7.90−7.76 (m), 7.42−7.05 (m), 6.51−6.31 (m), 6.02−5.90 (m), 5.42−5.20 (m), 4.43−4.23 (m), 3.96−3.85 (m), 3.17−3.05 (m), 2.98 (dd, J = 12.5, 3.9 Hz), 2.87 (t, J = 12.2 Hz), 2.68 (t, J = 12.5 Hz), 2.55−2.45 (m), 2.17, 2.11 (4s), 1.63 (s), 1.62 (s), 1.52 (s), 1.47 (s), 1.46 (s); HRMS calcd for $C_{34}H_{30}N_2O_4S_2$ 594.1647, found 594.1657. These mixed isomers were used directly in the next step.

*8,16-Bis(2-(4-nitrophenyl)ethenyl)-1,9-bis(methylthio)-anti-[2.2]-metacyclophane Bis-sulfonium Salt (**42**).* Using the same procedure as for **33**, the mixed isomers of **38** (900 mg, 1.50 mmol) on reaction with Borch reagent ((80% oil, 0.9 g, 4.4 mmol) in CH_2Cl_2 (22 mL) gave 1.20 g (quantitative) of bis-sulfonium salt **42**: ^{1}H NMR (DMSO-d_6) δ 8.22 (m), 7.89−7.39 (m), 6.61−6.19 (m), 4.60−4.54 (m), 4.32 (d, J = 12.6 Hz), 4.18 (d, J = 12.4 Hz), 3.44−3.32 (m), 3.26 (s), 3.25 (s), 3.23 (s), 3.20 (s), 2.95 (s), 2.94 (s), 2.92 (s), 2.87 (s), 2.81 (s). These were used in the next step.

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*Bis-2-(4-nitrophenyl)vinyl)-anti-[2.2]metacyclophane-1,9-dienes (**49**–**51**).* Using the same procedure as for **12**, reaction of bis-sulfonium salt **42** (1.20 g, 1.5 mmol) and *t*-BuOK (600 mg, 5.4 mmol) in THF (10 mL) gave 350 mg (90%) of a mixture of cyclophanedienes **49**–**51**. The residue was chromatographed over silica gel using hexanes/CH_2Cl_2 (60:40) as eluent. Eluted first was mostly the (*ZZ*)-isomer **49** (~75% pure). Washing the crystals with CH_2Cl_2 yielded 88 mg (23%) of pure (*ZZ*)-isomer as orange crystals: ^{1}H NMR δ 7.94 (d, J = 8.8 Hz, 4H, H-23,25,29,31), 7.23 (t, J = 7.4 Hz, 2H, H-5,13), 6.91 (d, J = 8.8 Hz, 4H, H-22,26,28,32), 6.60 (d, J = 7.4 Hz, 4H, H-4,6,12,14), 6.00 (s, 4H, H-17–20), 5.84 (s, 4H, H-1,2,9,10); ^{13}C NMR δ 146.2 (C-24,30), 145.8 (C-21,27), 140.8 (C-8,16), 138.2 (C-3,7,11,15), 132.6 (C-18,20), 132.5 (C-1,2,9,10), 130.9 (C-5,13), 129.4 (C-17,19), 129.2 (C-22,26,28,32), 126.6 (C-4,6,12,14), 123.3 (C-23,25,29,31); IR ν (KBr) 3045, 3008, 1592, 1512, 1339, 1106, 884, 855, 797, 772, 712 cm^{-1}; UV–vis (dichloromethane) λ_{max} nm (ε_{max}) 254 (14900), 342 (16400), 423 sh (5800); EIMS m/z 498 (M^+); HRMS calcd for $C_{32}H_{22}N_2O_4$ 498.1579, found 498.1593; attempted melting point determination converted CPD **49** into DHP **58**.

Eluted second was 175 mg (45%) of the (*ZE*)-isomer **50** as orange red crystals from dichloromethane: ^{1}H NMR δ 8.13 (d, J = 8.8 Hz, 2H, H-29,31), 7.96 (d, J = 8.8 Hz, 2H, H-23,25), 7.30 (d, J = 8.8 Hz, 2H, H-28,32), 7.20 (t, J = 7.4 Hz, 1H, H-5), 6.98 (t, J = 7.4 Hz, 1H, H-13), 6.96 (d, J = 8.8 Hz, 2H, H-22,26), 6.95 (d, J = 16.2 Hz, 1H, H-19), 6.86 (d, J = 16.2 Hz, 1H, H-20), 6.76 (d, J = 7.4 Hz, 2H, H-4,6), 6.45 (d, J = 7.4 Hz, 2H, H-12,14), 6.38 (d, J = 11.4 Hz, 2H, H-2,9), 6.10 (s, 2H, H-17,18), 6.00 (d, J = 11.4 Hz, 2H, H-1,10); ^{13}C NMR δ 146.7 (C-30), 146.3 (C-24), 145.8 (C-21), 144.8 (C-8), 144.3 (C-27), 139.6 (C-16), 138.6 (C-11,15), 136.9 (C-3,7), 133.3 (C-2,9), 133.08 (C-1,10), 132.7 (C-18), 132.3 (C-19), 130.9 (C-13), 130.7 (C-20), 130.1 (C-5), 129.6 (C-17), 129.2 (C-22,26), 127.1 (C-4,6), 126.9 (C-28,32), 126.6 (C-12,14), 124.1 (C-29,31), 123.4 (C-23,25); IR ν (KBr) 3007, 1592, 1512, 1339, 1108, 855, 795, 772, 711 cm^{-1}; UV–vis (dichloromethane) λ_{max} nm (ε_{max}) 258 (32100), 340 (25000), 435 sh (9300). Attempted melting point determination converted CPD **50** into DHP **59**.

Eluted third was 86 mg (22%) of the (*EE*)-isomer **51** as red crystals: ^{1}H NMR δ 8.17 (d, J = 8.8 Hz, 4H, H-23,25,29,31), 7.35 (d, J = 8.8 Hz, 4H, H-22,26,28,32), 7.05 (d, J = 16.2 Hz, 2H, H-17,19), 7.00 (t, J = 7.4 Hz, 2H, H-5,13), 6.96 (d, J = 16.2 Hz, 2H, H-18,20), 6.63 (d, J = 7.4 Hz, 4H, H-4,6,12,14), 6.55 (s, 4H, H-1,2,9,10); ^{13}C NMR δ 146.8 (C-24,30), 144.4 (C-21,27), 143.7 (C-8,16), 137.0 (C-3,7,11,15), 133.8 (C-1,2,9,10), 132.5 (C-17,19), 131.1 (C-18,20), 130.3 (C-5,13), 127.3 (C-4,6,12,14), 127.0 (C-22,26,28,32), 124.1 (C-23,25,29,31); IR ν (KBr) 3046, 1588, 1507, 1335, 1108, 965, 863, 817, 761, 745, 688 cm^{-1}; UV–vis (dichloromethane) λ_{max} nm (ε_{max}) 240 (27000), 258 (25400), 285 sh (18100), 369 (28800), 444 sh (13400). Attempted melting point determination converted CPD **51** into DHP **60**.

*10b,10c-Bis((1Z)-2-(4-nitrophenyl)vinyl)-trans-10b,10c-dihydropyrene (**58**).* Using the general thermolysis procedure above, (*ZZ*)-CPD **49** gave (*ZZ*)-DHP **58** quantitatively as orange crystals from dichloromethan: mp 243–244 °C; ^{1}H NMR δ 8.28 (s, 4H, H-4,5,9,10), 8.25 (d, J = 7.5 Hz, 4H, H-1,3,6,8), 7.94 (d, J = 8.6 Hz, 4H, H-21–24), 7.86 (t, J = 7.6 Hz, 2H, H-2,7), 6.20 (dd, J = 8.7, 0.8 Hz, 4H, H-17–20), 4.18 (d, J = 13.2 Hz, 2H, H-13,14), 0.38 (d, J = 13.2 Hz, 2H, H-11,12); ^{13}C NMR δ 146.6 (C-25,26), 143.8 (C-15,16), 133.4 (C-3a,5a,10a,10d), 129.2 (C-17–20), 126.9 (C-4,5,9,10), 125.9 (C-1,3,6,8), 125.2 (C-13,14), 124.3 (C-2,7), 123.4 (C-11,12), 121.4 (C-21–24), 36.1 (C-10b,10c); IR ν (KBr) 3074, 3036, 1598, 1515, 1341, 1107, 854, 842 cm^{-1}; UV–vis (dichloromethane) λ_{max} nm (ε_{max}) 281 (19500), 348 (46700), 397 (19500), 484 (5160); EIMS m/z 498 (M^+); HRMS calcd for $C_{32}H_{22}N_2O_4$ 498.1580, found 498.1586.

*10b-((1E)-2-(4-Nitrophenyl)vinyl)-10c-((1Z)-2-(4-nitrophenyl)-vinyl)-trans-10b,10c-dihydropyrene (**59**).* Using the general thermolysis procedure above, (*ZE*)-CPD **50** (25 mg) gave (*ZE*)-DHP **59** (25 mg, 100%) as olive green crystals from dichloromethane: mp 214–216 °C; ^{1}H NMR δ 8.75 (d, J = 7.8 Hz, 2H, H-4,10), 8.68 (d, J = 7.7 Hz, 2H, H-1,3), 8.40 (d, J = 7.8 Hz, 2H, H-5,9), 8.29 (d, J = 7.7 Hz, 2H, H-6,8), 8.12 (t, J = 7.7 Hz, 1H, H-2), 7.97 (d, J = 8.6 Hz, 2H, H-21,22), 7.88 (t, J = 7.7 Hz, 1H, H-7), 7.56 (d, J = 9.0 Hz, 2H, H-23,24), 6.26 (d, J = 8.7 Hz, 2H, H-17,18), 6.08 (d, J = 9.0 Hz, 2H, H-19,20), 4.23 (d, J = 13.1 Hz, 1H, H-13), 3.25 (d, J = 15.8 Hz, 1H, H-14), 0.96 (d, J = 15.8 Hz, 1H, H-12), 0.46 (d, J = 13.1 Hz, 1H, H-11); ^{13}C NMR δ 146.7 (C-25), 146.2 (C-26), 143.8 (C-15), 142.7 (C-16), 133.5 (C-3a,10a), 133.1 (C-5a,10d), 129.2 (C-17,18), 127.2 (C-5,9), 126.09 (C-19,20), 126.06 (C-6,8), 125.6 (C-4,10), 125.1 (C-12), 125.0 (C-13), 124.8 (C-1,3), 124.4 (C-2), 124.3 (C-7), 123.9 (C-11), 123.6 (C-14), 123.3 (C-23,24), 121.4 (C-21,22), 37.4 (C-10b), 34.8 (C-10c); IR ν (KBr) 3031, 1595, 1512, 1341, 846 cm^{-1}; UV–vis (dichloromethane) λ_{max} nm (ε_{max}) 228 (32100), 344 (65800), 387 (25800), 481 (6860), 606 (125).

*10b,10c-Bis((1E)-2-(4-nitrophenylvinyl)-trans-10b,10c-dihydropyrene (**60**).* Using the general thermolysis procedure above, (*EE*)-CPD **51** (25 mg) gave (*EE*)-DHP **60** (25 mg, 100%) as dark green crystals from cyclohexane: mp 275–276 °C; ^{1}H NMR δ 8.88 (s, 4H, H-4,5,9,10), 8.71 (d, J = 7.6 Hz, 4H, H-1,3,6,8), 8.13 (t, J = 7.6 Hz, 2H, H-2,7), 7.60 (d, J = 8.8 Hz, 4H, H-21–24), 6.12 (d, J = 8.9 Hz, 4H, H-17–20), 3.28 (d, J = 15.7 Hz, 2H, H-13,14), 1.05 (d, J = 15.8 Hz, 2H, H-11,12); The compound was too insoluble to give a satisfactory ^{13}C NMR spectrum. IR ν (KBr) 3032, 1513, 1340, 1109, 850 cm^{-1}; UV–vis (dichloromethane) λ_{max} nm (ε_{max}) 228 (16700), 340 (45900), 375 (16300), 473 (4800).

*8,16-Bis((2-(4-methoxyphenyl)ethenyl)-1,9-bis(methylthio)-anti-[2.2]metacyclophane (**37**).* Using the same procedure as for the synthesis of the *p*-nitro series (**49**) except that the reaction was heated to 80 °C overnight from 4-methoxybenzyltriphenylphosphonium bromide (3.89g, 8.4 mmol), potassium *tert*-butoxide (1.3g, 11.6 mmol), and diformylcyclophane (1.0g 2.81 mmol), in toluene (50 mL), there was obtained the cyclophanes **37** (795 mg, 1.4 mmol, 50%) as a mixture of isomers. Column chromatography over silica gel using dichloromethane–hexane 4:6 eluted the mixed isomers as a pale yellow solid: ^{1}H NMR 7.95–7.80 (m), 7.29–7.20 (m), 7.04–6.98 (m), 6.85–6.80 (m), 6.47–6.43 (m), 6.23 (d, J = 8.8 Hz), 6.18 (d, J = 9.0 Hz), 5.85–5.62 (m), 5.09–5.0 (m), 4.36 (dd), 4.09–3.93 (m), 3.801 (s), 3.800 (s), 3.798 (s), 3.66 (s), 3.65 (s), 3.63 (s), 3.62 (s), 3.12–3.00 (m), 2.91 (t), 2.72 (AB, J = 12 Hz), 2.59–2.50 (m), 2.17, 2.16, 2.10, 2.09, 1.64, 1.63, 1.52, 1.45, 1.44 (9 s)); EIMS m/z 564 (M^+); HRMS calcd for $C_{36}H_{36}O_2S_2$ 564.2157, found 564.2169.

*8,16-Bis((2-(4-methoxyphenyl)ethenyl)-1,9-bis(methylthio)-anti-[2.2]metacyclophane Bis-sulfonium Salt (**41**).* Using the same procedure as for **33**, mixed isomers **37** (200 mg, 0.35 mmol) on reaction with Borch reagent (80% oil, 0.5 g, 2.4 mmol) in CH_2Cl_2 (5 mL) gave 275 mg (quantitative) of bis-sulfonium salt **41**: ^{1}H NMR (DMSO-d_6) 7.84–7.34 (m), 7.25–7.17 (m), 6.99–6.91 (m), 6.63–6.55 (m), 6.28–5.88 (m), 4.62–4.52 (m), 3.77, 3.62 (2 s), 3.48–3.20 (6 s), 2.97, 2.94, 2.92 (3 s), 2.36, 2.34, 2.24, 2.23, 1.99 (5 s), which were used directly in the next step.

*Bis-2-(4-methoxyphenyl)vinyl)-anti-[2.2]metacyclophane-1,9-dienes (**46**–**48**).* Using the same procedure as for **12**, reaction of bis-sulfonium salt **41** (200 mg, 0.26 mmol) and *t*-BuOK (250 mg, 2.2 mmol) in THF (10 mL) gave a mixture of cyclophanedienes **46**–**48**. The residue was chromatographed over silica gel using hexanes/DCM 60:40. Eluted first was 19 mg (16%) of the (*ZZ*) isomer **46** as colorless crystals: ^{1}H NMR δ 7.15 (t, J = 7.3 Hz, 2H, H-5,13), 6.74 (d, J = 8.7 Hz, 4H, H-22,26,28,32), 6.61 (d, J = 8.7 Hz, 4H, H-23,25,29,31), 6.57 (d, J = 7.3 Hz, 4H, H-4,6,12,14), 5.91 (d, J = 12.4 Hz, 2H, H-18,20), 5.86 (s, 4H, H-1,2,9,10), 5.73 (d, J = 12.4 Hz, 2H, H-17,19), 3.74 (s, 6H, H-33,34); ^{13}C NMR δ 158.3 (C-24,30), 141.9 (C-8,16), 138.2 (C-3,7,11,15), 132.4 (C-1,2,9,10), 131.4 (C-21,27), 130.9 (C-18,20), 129.7 (C-22,26,28,32), 129.6 (C-5,13), 128.3 (C-17,19), 126.2 (C-4,6,12,14), 113.3 (C-23,25,29,31), 55.3 (C-33,34); IR ν (KBr) 3003, 2835, 1605, 1509, 1458, 1303, 1252, 1178, 1032, 832, 812, 784, 739, 517 cm^{-1}; UV–vis (dichloromethane) λ_{max} nm (ε_{max}) 228 (46400), 257 (46100), 372 sh (4160); EIMS m/z 468 (M^+); HRMS calcd for $C_{34}H_{28}O_2$ 468.2089, found 468.2095. Attempted melting point determination converted CPD **46** into DHP **55**.

Eluted second was 57 mg (47%) of the (*ZE*) isomer **47** as a pale yellow solid: ^{1}H NMR δ 7.17 (d, J = 8.8 Hz, 2H, H-22,26), 7.09 (t, J = 7.4 Hz, 1H, H-13), 7.02 (t, J = 7.3 Hz, 1H, H-5), 6.82 (d, J = 8.8 Hz, 2H, H-23,25), 6.78 (d, J = 8.7 Hz, 2H, H-28,32), 6.69 (d, J = 7.4 Hz,

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2H, H-12,14), 6.68 (AB hidden, 2H, H-17,18), 6.65 (d, J = 8.6 Hz, 2H, H-29,31), 6.46 (d, J = 7.4 Hz, 2H, H-4,6), 6.32 (d, J = 11.3 Hz, 2H, H-1,10), 6.00 (d, J = 11.3 Hz, 2H, H-2,9), 5.98 (d, J = 12.3 Hz, 1H, H-20), 5.79 (d, J = 12.3 Hz, 1H, H-19), 3.82 (s, 3H, H-33), 3.75 (s, 3H, H-34); ^{13}C NMR δ 159.2 (C-24), 158.3 (C-30), 146.5 (C-16), 140.3 (C-8), 138.6 (C-3,7), 135.9 (C-11,15), 133.1 (C-2,9), 132.8 (C-18), 132.5 (C-2,9), 131.3 (C-27), 131.1 (C-21), 131.0 (C-17), 130.1 (C-5), 129.8 (C-28,32), 128.28 (C-19), 128.24 (C-13), 128.0 (C-22,26), 126.7 (C-12,14), 126.3 (C-4,6), 114.0 (C-23,25), 113.3 (C-29,31), 55.5 (C-33), 55.3 (C-34); IR ν (KBr) 3031, 3001, 2834, 1604, 1509, 1465, 1250, 1175, 1033, 832, 812, 783 cm^{-1}; UV−vis (dichloromethane) λ_{max} nm (ε_{max}) 227 (44600), 257 (50000), 283 (36300), 417 sh (4900). Attempted melting point determination converted CPD **47** into DHP **56**.

Eluted third was 27 mg (22%) of the (*EE*) isomer **48** as pale yellow crystals: ^{1}H NMR δ 7.20 (d, J = 8.8 Hz, 4H, H-22,26,28,32), 6.98 (t, J = 7.4 Hz, 2H, H-5,13), 6.84 (d, J = 8.8 Hz, 4H, H-23,25,29,31), 6.76 (AB, hidden, 4H, H-17−20), 6.60 (d, J = 7.4 Hz, 4H, H-4,6,12,14), 6.45 (s, 4H, H-1,2,9,10), 3.83 (s, 6H, OMe); ^{13}C NMR δ 159.2 (C-24,30), 144.8 (C-8,16), 136.4 (C-3,7,11,15), 133.14 (C-18,20), 133.11 (C-1,2,910), 131.2 (C-21,27), 128.9 (C-23,25,29,31), 128.3 (C-5,13), 128.0 (C-22,26,28,32), 127.0 (C-17,19), 126.9 (C-4,6,12,14), 55.5 (C-33,34); IR ν (KBr) 3031, 3001, 2833, 1604, 1509, 1465, 1438, 1250, 1174, 1034, 966, 810, 770, 753 cm^{-1}; UV−vis (dichloromethane) λ_{max} nm (ε_{max}) 228 (50600), 263 (45700), 417 sh (6200). Attempted melting point determination converted CPD **48** into DHP **57**.

*10b,10c-Bis((1Z)-2-(4-methoxyphenyl)vinyl)-trans-10b,10c-dihydropyrene (**55**).* Using the general thermolysis procedure above, (*ZZ*)-CPD **48** (25 mg) gave (*ZZ*)-*p*-methoxystyryl DHP **55** (25 mg, 100%) as orange crystals from dichloromethane: ^{1}H NMR δ 8.28 (s, 4H, H-4,5,9,10), 8.24 (d, J = 7.6 Hz, 4H, H-1,3,6,8), 7.79 (t, J = 7.6 Hz, 2H, H-2,7), 6.59 (d, J = 8.6 Hz, 4H, H-21−24), 5.92 (d, J = 8.6 Hz, 4H, H-17−20), 4.12 (d, J = 12.8 Hz, 2H, H-13,14), 3.83 (OMe), 0.25 (d, J = 12.8 Hz, 2H, H-11,12); ^{13}C NMR (CD_2Cl_2) δ 158.6 (C-25,26), 134.3 (3a,5a,10a,10d), 129.8 (C-17−20), 129.1 (C-15,16), 127.3 (C-13,14), 126.8 (C-4,5,9,10), 125.7 (C-1,3,6,8), 124.0 (C-2,7), 122.9 (C-11,12), 111.8 (C-21,24), 55.7 (OMe), 36.8 (10b,10c); IR ν (thin film) 3030, 2834, 1605, 1574, 1507, 1463, 1243, 1174, 1034, 960, 860, 814, 737, 704 cm^{-1}; UVvis (dichloromethane) λ_{max} nm (ε_{max}) 228 (34600), 351 (47100), 394 (25200), 486 (5500), 619 (140); EIMS m/z 468 (M$^+$); HRMS calcd for $C_{34}H_{28}O_2$ 468.2089, found 468.2094.

*10b-((1E)-2-(4-Methoxyphenyl)vinyl)-10c-((1Z)-2-(4-methoxyphenyl)-vinyl)-trans-10b,10c-dihydropyrene (**56**).* Using the general thermolysis procedure above, CPD **47** (25 mg), gave mostly (*ZE*)-*p*-methoxystyryl DHP **56** as an olive green solid containing a little of the (*EE*)-isomer (total 25 mg): ^{1}H NMR (CD_2Cl_2) δ 8.72 (d, J = 7.7 Hz, 2H, H-4,10), 8.64 (d, J = 7.7 Hz, 2H, 1,3), 8.44 (d, J = 7.7 Hz, 2H, H-5,9), 8.31 (d, J = 7.7 Hz, 2H, H-6,8), 8.06 (t, J = 7.7 Hz, 1H, H- 2), 7.83 (t, J = 7.7 Hz, 1H, H-7), 6.62 (d, J = 8.5 Hz, 2H, H-21,22), 6.25 (d, J = 8.8 Hz, 2H, H-23,24), 5.98 (d, J = 8.4 Hz, 2H, H-17,18), 5.89 (d, J = 8.8 Hz, 2H, H-19,20), 4.20 (d, J = 12.8 Hz, 1H, H-13), 3.84 (s, 3H, H-33), 3.48 (s, 3H, H-34), 3.15 (d, J = 15.8 Hz, 1H, H-14), 0.65 (d, J = 15.8 Hz, 1H, H-12), 0.33 (d, J = 12.8 Hz, 1H, H-11); ^{13}C NMR (CD_2Cl_2) δ 159.0 (C-26), 158.6 (C-25), 134.4 (C-3a,10a), 134.1 (C-5a,10d), 129.8 (C-17,18), 127.2 (C-5,9), 127.1 (C-13), 126.8 (C-19,20), 126.0 (C-6,8), 125.7 (C-4,10), 124.4 (C-1,3), 124.3 (C-14), 124.2 (C-7), 123.9 (C-2), 123.4 (C-11), 118.3 (C-12), 113.6 (C-23,24), 111.9 (C-21,22), 55.7 (C-33), 55.5 (C-34), 37.7 (C-10b), 35.6 (C-10c); IR ν (thin film) 3030, 2834, 1606, 1509, 1464, 1440, 1244, 1174, 1034, 959, 842, 815, 736, 704 cm^{-1}; UV−vis (dichloromethane) λ_{max} nm (ε_{max}) 225 (24300), 264 (32300), 346 (42100), 387 (21200), 472 (5400), 607 (120).

*10b,10c-Bis((1E)-2-(4-methoxyphenylvinyl)-trans-10b,10c-dihydropyrene (**57**).* Using the general thermolysis procedure above, CPD **48** (25 mg) gave *p*-methoxystyryl DHP **57** (25 mg, 100%) was obtained as a dark green oily solid, which would not crystallize: ^{1}H NMR (CD_2Cl_2) δ 8.88 (s, 4H, H-4,5,9,10), 8.70 (d, J = 7.7 Hz, 4H, 1,3,6,8), 8.10 (t, J = 7.7 Hz, 2H, H-2,7), 6.28 (d, J = 8.8 Hz, 4H, H-21−24), 5.95 (d, J = 8.8 Hz, 4H, H-17−20), 3.51 (OMe), 3.17 (d, J = 15.8 Hz, 2H, H-13,14), 0.70 (d, J = 15.8 Hz, 2H, H-11,12); ^{13}C NMR (CD_2Cl_2) δ 159.0 (C-25,26), 134.5 (C-3a,5a,10a,10d), 129.8 (C-15,16), 126.8 (C-17−20), 126.0 (C-4,5,9,10), 124.8 (C1,3,6,8), 124.21 (C-13,14), 124.17 (C-2,7), 119.0 (C-11,12), 113.6 (C-21−24), 55.5 (OMe), 36.4 (C-10b,10c); IR ν (thin film) 3030, 2834, 1606, 1509, 1464, 1440, 1244, 1174, 1034, 959, 842, 815, 736, 704 cm^{-1}; UV−vis (dichloromethane) λ_{max} nm (ε_{max}) 225 (31000), 265 (40200), 343 (46800), 382 (22400), 470 (6400), 606 (130).

*8,16-Bis(2-(4-methylphenyl)ethenyl)-1,9-bis(methylthio)-anti-[2.2]metacyclophane (**36**).* Using the same procedure as for **12**, reaction of diformylmethylthiocyclophane **22** (0.80 g, 2.25 mmol) with an ylide prepared by reaction of *t*-BuOK (1.7 g, 15 mmol) and 4-methylbenzyl triphenylphosphonium bromide (4.5 g, 10 mmol, commercial supplier) in THF (45 mL), followed by column chromatography using hexanes:dichloromethane (7:3) eluted 685 mg (57%) of **36** as a mixture of isomers: ^{1}H NMR δ 7.88 (d, J = 7.6 Hz), 7.84 (d, J = 7.7 Hz), 7.83−7.80 (m), 7.44−6.94 (m), 6.76−6.69 (m), 6.24 (d, J = 8.2 Hz), 6.20 (d, J = 8.2 Hz), 6.16 (d, J = 8.6 Hz), 6.14 (d, J = 8.3 Hz), 6.10 (d, J = 8.2 Hz), 5.92 (d, J = 12.3 Hz), 5.87 (d, J = 12.4 Hz), 5.82 (d, J = 12.4 Hz), 5.68 (d, J = 16.3 Hz), 5.23 (d, J = 16.3 Hz), 5.10 (d, J = 16.3 Hz), 4.35 (dd, J = 11.5, 4.0 Hz), 4.15−3.95 (m), 3.14−2.87 (m), 2.75−2.51 (m), 2.36, 2.32, 2.28, 2.26 (4s), 2.17, 2.16, 2.15, 2.12, 2.11, 2.10, 2.03 (7s), 1.61, 1.60, 1.42, 1.40 (s)); EIMS m/z 532 (M$^+$); HRMS calcd for $C_{36}H_{36}S_2$ 532.2258, found 532.2253. These were used directly in the next step.

*8,16-Bis(2-(4-methylphenyl)ethenyl)-1,9-bis(methylthio)-anti-[2.2]metacyclophane Bis- sulfonium salt (**40**).* Using the same procedure as for **33**, mixed isomers **36** (650 mg, 1.21 mmol) on reaction with Borch reagent (80% oil, 1.0 g, 4.8 mmol) in CH_2Cl_2 (7 mL) gave 510 mg (57%) of bis-sulfonium salt **40**: ^{1}H NMR (DMSO-d_6) δ 7.83 (d, J = 7.7 Hz), 7.75 (d, J = 7.6 Hz), 7.71−7.50 (m), 7.47 (t, J = 7.6 Hz), 7.20−7.10 (m), 6.86−6.76 (m), 6.24−6.05 (m), 6.00−5.87 (m), 5.46 (d, J = 16.4 Hz), 5.30 (d, J = 16.6 Hz), 4.53 (br d), 4.26−3.97 (m), 3.30, 3.22, 3.21, 3.20, 3.18 (s), 2.98−2.78 (m), 2.30, 2.28 (3 s), 2.18, 2.10, 1.96 (4 s). These were used in the next step.

*Bis-2-(4-methylphenyl)vinyl)-anti-[2.2]metacyclophane-1,9-dienes (**43**−**45**).* Using the same procedure as for **12**, reaction of bis-sulfonium salt **40** (470 mg, 0.63 mmol) and *t*-BuOK (200 mg, 1.8 mmol) in THF (8 mL) gave a mixture of cyclophanedienes **43**−**45**. The residue was chromatographed over silica gel using hexanes:dichloromethane (90:10). Eluted first was 116 mg (42%) (*ZZ*)-CPD **43** as colorless crystals: ^{1}H NMR δ 7.16 (t, J = 7.3 Hz, 2H, H-5,13), 6.88 (d, J = 8.0 Hz, 4H, H-23,25,29,31), 6.70 (d, J = 8.0 Hz, 4H, H-22,26,28,32), 6.57 (d, J = 7.3 Hz, 4H, H-4,6,12,14), 5.94 (d, J = 12.4 Hz, 2H, H-18,20), 5.85 (s, 4H, H-1,2,9,10), 5.78 (d, J = 12.4 Hz, 2H, H-17.19), 2.25 (s, 6H, Me); ^{13}C NMR δ 141.8 (C-8,16), 138.2 (C-3,7,11,15), 136.0 (C-24,30). 135.8 (C-21,27), 132.4 (C-1,2,9,10), 131.3 (C-18,20), 129.6 (C-5,13), 128.9 (C-17,19), 128.6 (C-23,25,29,31), 128.4 (C-22,26,28,32), 126.1 (C-4,6,12,14), 21.4 (C-33,34); IR ν (KBr) 3041, 3015, 3003, 1560, 1508, 1370, 1405, 1151, 859, 817, 782, 749, 737, 594 cm^{-1}; UV−vis (cyclohexane) λ_{max} nm (ε_{max}) 257 (30100), 277 (24000), 392 (3300); EIMS m/z 436 (M$^+$); HRMS calcd for $C_{34}H_{28}$ 436.2191, found 436.2205. Attempted melting point determination converted CPD **43** into DHP **52**.

Eluted second was 105 mg (38%) of the (*ZE*)-isomer **44** as pale yellow crystals from cyclohexane: ^{1}H NMR δ 7.12 (d, J = 8.3 Hz, 2H, H-22,26), 7.10 (t, J = 7.5 Hz, 1H, H-13), 7.08 (d, J = 8.4 Hz, 2H, H-23,25), 7.01 (t, J = 7.4 Hz, 1H, H-5), 6.90 (d, J = 8.0 Hz, 2H, H-29,31), 6.86−6.73 (m, 4H, H-17,18,28,32), 6.71 (d, J = 7.4 Hz, 2H, H-12,14), 6.47 (d, J = 7.4 Hz, 2H, H-4,6), 6.33 (d, J = 11.3 Hz, 2H, H-1,10), 6.02 (d, J = 12.3 Hz, H-20), 6.00 (d, J = 11.4 Hz, 2H, H-2,9), 5.83 (d, J = 12.3 Hz, 1H, H-19). 2.34 (s, 3H, H-33), 2.26 (s, 3H, H-34); ^{13}C NMR δ 146.3 (C-16), 140.2 (C-8), 137.2 (C-24), 138.6 (C-3,7), 136.09 (C-30), 136.07 (C-11,15), 135.8 (C-27), 133.2 (C-18), 133.0 (C-1,10), 132.6 (C-2,9), 131.5 (C-20), 130.2 (C-5), 129.2 (C-13), 128.9 (C-19), 128.6 (C-29,31), 128.5 (C-28,32), 127.8 (C-17), 126.8 (C-12,14), 126.7 (C-22,26), 126.3 (C-4,6), 21.5 (C-33), 21.4 (C-34) IR ν (thin film) 3045, 3019, 3005, 1510, 1436, 1265, 963, 868, 816, 805, 786, 777, 746, 702, 647 cm^{-1}; UV−vis (cyclohexane)

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λ_{max} nm (ε_{max}) 252 (60000), 280 (48400), 413 sh (6600). Attempted melting point determination converted CPD **44** into DHP **53**.

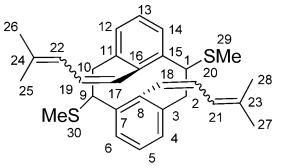
Eluted third was 30 mg (11%) of the (*EE*)-isomer **45** as pale yellow crystals: ^{1}H NMR δ 7.16 (AB, J = 8.1 Hz, 4H, H-22,26,28,32), 7.10 (AB, J = 8.1 Hz, 4H, H-23,25,29,31), 6.98 (t, J = 7.3 Hz, 2H, H-5,13), 6.86 and 6.84 (AB, J = 16.2, 4H, H-17−20), 6.60 (d, J = 7.3 Hz, 4H, H-4,6,12,14), 6.46 (s, 4H, H-1,2,9,10) 2.34 (s, 6H, Me); ^{13}C NMR δ 144.7 (C-8,16), 137.2 (C-24,30), 136.5 (C-3,7,11,15), 135.5 (C-21,27), 133.5 (C-18,20), 133.2 (C-1,2,9,10), 129.2 (C-23,25,29,31), 129.1 (C-5,13), 127.9 (C-17,19), 126.9 (C-4,6,12,14), 126.7 (C-22,26,28,32). 21.5 (C-33,34, Me) ; IR ν (KBr) 3045, 3022, 3003, 1560, 1513, 1458, 1429, 960, 797, 755, 653, 631 cm^{-1}; UV−vis (cyclohexane) λ_{max} nm (ε_{max}) 257 (53500), 285 (53000), 313 (48700), 410 sh (6100). Attempted melting point determination converted CPD **45** into DHP **54**.

*10b,10c-Bis((1Z)-2-(4-methylphenyl)vinyl)-trans-10b,10c-dihydropyrene (**52**).* Using the general thermolysis procedure above, (*ZZ*)-CPD **43** (25 mg) gave (*ZZ*)-*p*-methylstyryl DHP **52** (25 mg, 100%) as orange crystals from cyclohexane: ^{1}H NMR (CD_2Cl_2) δ 8.25 (s, 4H, H-4,5,9,10), 8.22 (d, J = 7.5 Hz, 4H, H-1,3,6,8), 7.78 (t, J = 7.5 Hz, 2H, H-2,7), 6.84 (d, J = 7.6 Hz, 4H, H-21−24), 5.89 (d, J = 7.5 Hz, 4H, H-17−20), 4.17 (d, J = 12.9 Hz, 2H, H-13,14), 2.34 (s, 6H, Me) 0.25 (d, J = 12.9 Hz, 2H, H-11,12); ^{13}C NMR (CD_2Cl_2) δ 135.8 (C-25,26), 134.2 (C-3a,5a,10a,10d), 133.7 (C-15,16), 128.6 (17−20), 127.5 (C-13,14), 127.0 (C-21−24), 126.9 (C-4,5,9,10), 125.7 (C-1,3,6,8), 124.0 (C-2,7), 122.5 (C-11,12), 36.7 (C-10b,10c), 21.5 (Me); IR ν (KBr) 3038, 3019, 1507, 1345, 860, 836, 607 cm^{-1}; UV−vis (cyclohexane) λ_{max} nm (ε_{max}) 227 (37500), 353 (68800), 396 (33300), 490 (6300), 624 (130); EIMS m/z 436 (M$^+$); HRMS calcd for $C_{34}H_{28}$ 436.2191, found 436.2197.

*10b-((1E)-2-(4-Methylphenyl)vinyl)-10c-((1Z)-2-(4-methylphenyl)-vinyl)-trans-10b,10c-dihydropyrene (**53**).* Using the general thermolysis procedure above, (*ZE*)-CPD **44** (25 mg) gave (*ZE*)-*p*-methylstyryl DHP **53** (25 mg, 100%) as an olive green oily film which could not be crystallized: ^{1}H NMR (CD_2Cl_2) δ 8.72 (d, J = 7.7 Hz, 2H, H-4,10), 8.63 (d, J = 7.7 Hz, 2H, H-1,3), 8.41 (d, J = 7.7 Hz, 2H, H-5,9), 8.28 (d, J = 7.7 Hz, 2H, H-6,8), 8.06 (t, J = 7.7 Hz, 1H, H-2), 7.82 (t, J = 7.7 Hz, 1H, H-7), 6.89 (d, J = 7.7 Hz, 2H, H-21,22), 6.51 (d, J = 8.1, 2H, H-23,24), 5.95 (d, J = 7.4 Hz, 2H, H-17,18), 5.84 (d, J = 8.3 Hz, 2H, H-19,20), 4.22 (d, J = 12.8 Hz, 1H, H-13), 3.17 (d, J = 15.9 Hz, 1H, H-14), 2.36 (s, 3H, H-33), 1.96 (s, 3H, H-34), 0.73 (d, J = 15.9 Hz, 1H, H-12), 0.32 (d, J = 12.9 Hz, 1H, H-11); ^{13}C NMR (CD_2Cl_2) δ 136.9 (C-26), 135.9 (C-25), 134.4 (C-3a,10a), 134.1 (C-5a,10d), 133.7 (C-15), 133.6 (C-16), 128.9 (C-23,24), 128.7 (C-17,18), 127.4 (C-13), 127.3 (C-5,9), 127.1 (C-21,22), 126.1 (C-6,8), 125.5 (C-19,20), 124.9 (C-14), 124.4 (C-1,3), 124.3 (C-7), 123.9 (C-2), 122.9 (C-11), 119.6 (C-12), 37.7 (C-10b), 35.5 (C-10c), 21.5 (C-33), 21.0 (C-34); IR ν (thin film) 3025, 2921, 2851, 1637, 1512, 1458, 1123, 962, 840, 801, 711 cm^{-1}; UV−vis (dichloromethane) λ_{max} nm (ε_{max}) 227 (24500), 257 (28900), 347 (42900), 387 (19100), 478 (4300), 607 (100).

*10b,10c-Bis((1E)-2-(4-methylphenylvinyl)-trans-10b,10c-dihydropyrene (**54**).* Using the general thermolysis procedure above, (*EE*)-CPD **45** (25 mg) gave (*EE*)-*p*-methylstyryl DHP **54** (25 mg, 100%) as a dark green oily solid which could not be crystallized: ^{1}H NMR (CD_2Cl_2) δ 8.88 (s, 4H, H-4,5,9,10), 8.69 (d, J = 7.6 Hz, 4H, H-1,3,6,8), 8.10 (t, J = 7.6 Hz, 2H, H-2,7), 6.55 (d, J = 8.2 Hz, 4H, H-21−24), 5.89 (d, J = 8.2 Hz, 4H, H-17−20), 3.19 (d, J = 15.8 Hz, 2H, H-13,14), 1.99 (s, Me), 0.79 (d, J = 15.8 Hz, 2H, H-11,12); ^{13}C NMR (CD_2Cl_2) δ 137.0 (C-25,26), 134.4 (C-3a,5a,10a,10d), 133.5 (C-15,16), 128.9 (C-21−24), 126.0 (C-4,5,9,10), 125.6 (C-17−20), 124.9 (C-1,3,6,8), 124.7 (C-13,14), 124.3 (C-2,7), 120.1 (C-11,12), 36.3 (C-10b,10c) 21.0 (Me); IR ν (KBr) 3025, 2921, 2851, 1637, 1512, 1458, 962, 840, 801, 711 cm^{-1}; UV−vis (dichloromethane) λ_{max} nm (ε_{max}) 227 (19100), 259 (33700), 343 (40300), 380 (21000), 468 (5400), 593 (170).

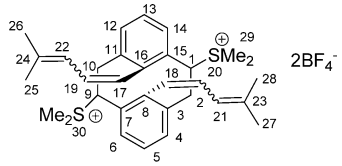
*8,16-Bis(4-methylpenta-1,3-dienyl)-1,9-bis(methylthio)-anti-[2.2]metacyclophane (**92**).*



92

Using the same procedure as for **12**, reaction of diformylmethylthiocyclophane **22** (680 mg, 1.91 mmol) with an ylide prepared by reaction of *t*-BuOK (1.60 g, 14.3 mmol) and 3-methylbut-2-enyltriphenylphosphonium bromide (4.2 g, 10.2 mmol) in THF (40 mL), followed by column chromatography using hexanes/dichloromethane (75:25) gave 590 mg (67%) of **92** as a mixture of isomers: ^{1}H NMR δ 7.88−7.78 (m), 7.24−6.89 (m), 5.86−5.56 (m), 5.50−5.40 (m), 5.15−4.91 (m), 4.70−4.56 (m), 4.40−4.32 (m), 4.10−3.95 (m), 3.10−3.00 (m), 2.91−2.83 (m), 2.70−2.50 (m), 2.28 (t, J = 11.4 Hz), 2.19, 2.18 (s), 2.13, 2.09 (3 s), 2.06, 2.04, 2.03 (3 s), 1.74, 1.61, 1.60 (br s), 1.53, 1.51 (br s)); EIMS m/z 460 (M$^+$); HRMS calcd for $C_{30}H_{36}S_2$ 460.2258, found 460.2257. These were used directly in the next step

*8,16-Bis(4-methylpenta-1,3-dienyl)-1,9-bis(methylthio)-anti-[2.2]metacyclophane Bis-sulfonium Salt (**93**).*



93

Using the same procedure as for **33**, mixed isomers of **92** (0.55 g, 1.2 mmol) on reaction with Borch reagent ((80% oil, 0.9 g, 4.4 mmol) in CH_2Cl_2 (8 mL) gave 320 mg (41%) of bis-sulfonium salt **93**: ^{1}H NMR (DMSO-d_6) 7.77−7.32 (m), 7.26 (t, J = 7.6 Hz), 7.10 (t, J = 7.5 Hz), 6.08−5.92 (m), 5.82−5.71(m), 5.06 (t, J = 12.2 Hz), 4.93−4.74 (m), 4.63−4.42 (m), 4.18 (d, J = 11.2 Hz), 4.12 (d, J = 11.7 Hz) 4.04 and 4.02 (AB, J = 14.2, 7.0 Hz), 3.9 (d, J = 11.2 Hz), 3.52−3.10 (m), 3.32−3.29 (overlapping singlets), 2.91−2.76 (6 s), 1.75, 1.64, 1.62, 1.57, 1.55, 1.52 (br s). These were used in the next step.

*8,16-Bis(4-methylpenta-1,3-dienyl)-anti-[2.2]metacyclophane-1,9-dienes (**62**−**64**).* Using the same procedure as for **12**, reaction of bis-sulfonium salt **93** (300 mg, 1.05 mmol) and *t*-BuOK (400 mg, 3.6 mmol) in THF (20 mL) gave a mixture of cyclophanedienes (325 mg, 85%, approximately 1:1:1 isomer mixture), which was chromatographed over silica gel using hexanes/dichloromethane (19:1). Eluted first from column was a mixture of (*EE*)-isomer **64** and (*ZE*)-**63** and then last **63** and the (*ZZ*)-isomer **62**. Although the isomers could not be obtained completely free of each other, their spectral properties could be obtained:

*(EE)-Isomer **64**:* ^{1}H NMR (CD_2Cl_2) δ 6.98 (t, J = 7.4 Hz, 2H, H-5,13), 6.80 (dd, J = 15.3, 11.0 Hz, 2H, H-19,20), 6.53 (d, J = 7.4 Hz, 4H, H-4,6,12,14), 6.38 (s, 4H, H-1,2,9,10), 6.09 (d, J = 15.4 Hz, 2H, H-17,18), 5.60 (dm, J = 10.8 Hz, 2H, H-21,22), 1.78 (s, 6H, H-25,28), 1.72 (s, 6H, H-26,27); ^{13}C NMR (CD_2Cl_2) δ 146.0 (C-8,16), 136.4 (C-3,7,11,15), 136.3 (C-23,24), 133.5 (C-1,2,9,10), 130.9 (C-19,20), 129.8 (C-17,18), 129.0 (C-5,13), 127.1 (C-21,22), 126.9 (C-4,6,12,14), 26.5 (C-25,28), 18.7 (C-26,27); EIMS m/z 364 (M$^+$); HRMS calcd for $C_{28}H_{28}$ 364.2191, found 364.2195.

*(EZ)-Isomer **63**:* ^{1}H NMR (CD_2Cl_2) δ 7.09 (t, J = 7.4 Hz, 1H, H-13), 6.99 (t, J = 7.4 Hz, 1H, H-5), 6.75 (dd, J = 15.2, 11.0 Hz, 1H, H-20), 6.58 (d, J = 7.4 Hz, 2H, H-12,14), 6.57 (d, J = 7.4 Hz, 2H, H-4,6), 6.33 and 6.31 (AB, J = 11.4 Hz, 4H, H-1,2,9,10), 6.04 (d, J = 15.4 Hz, 1H, H-18), 6.00−5.95 (m, 1H, H-21), 5.83 (dd, J = 12.4, 11.8 Hz, 1H, H-19), 5.79 (d, J = 12.4 Hz, 1H, H-17), 5.60 (dm, J = 12.5 Hz, 1H, H-22), 1.78 (s, 3H, H-28), 1.74 (s, 3H, H-25), 1.72 (s, 3H, H-27), 1.71 (s, 3H, H-26); ^{13}C NMR (CD_2Cl_2) δ 147.1 (C-8), 142.4 (C-16), 138.2 (C-11,15), 137.4 (C-23), 136.5 (C-24), 136.2 (C-3,7), 133.1 (C-2,9), 133.0 (C-1,10), 130.9 (C-20), 129.8 (C-13), 129.6 (C-18),

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128.4 (C-5), 127.1 (C-22), 126.89 (C-4,6), 126.87 (C-17), 126.42 (C-19), 126.40 (C-12,14), 123.4 (C-21), 26.6 (C-25), 26.5 (C-28), 18.7 (C-27), 18.6 (C-26).

(ZZ)-Isomer ***62***. ^{1}H NMR (CD_2Cl_2) δ 7.10 (t, J = 7.4 Hz, 2H, H-5,13), 6.63 (d, J = 7.4 Hz, 4H, H-4,6,12,14), 6.24 (s, 4H, H-1,2,9,10), 6.00−5.97 (m, 2H, H-21,22), 5.76 (br s, 4H, H-17−20), 1.74 (s, 6H, H-25,28), 1.71 (s, 6H, H-26,27); ^{13}C NMR (CD_2Cl_2) δ 143.4 (C-8,16), 137.9 (C-3,7,11,15), 137.6 (C-23,24), 132.6 (C-1,2,9,10), 129.2 (C-5,13), 126.6, 126.5 (C-17−20), 126.3 (C-4,6,12,14), 26.6 (C-25,28), 18.6 (C-26,27); IR (mix) ν (KBr) 3041, 3002, 2965, 2910, 1636, 1560, 426, 1375, 952, 786, 777, 750 cm^{-1}; UV−vis (cyclohexane) λ_{max} (ε_{max}) 246 (27900), 284 (32600), 390 (5000), 406 sh (4800).

*10b,10c-Bis(4-methylpenta-1,3-dienyl)-trans-10b,10c-dihydropyrene Dihydropyrenes (**65**−**67**).* A mixture of cyclophanedienes **62**−**64** (45 mg) in toluene-d_8 (6 mL) was sealed in a glass tube under argon and heated at 110 °C for 2 h, which converted it into a mixture of dihydropyrenes **65**−**67** (45 mg, approximately 1:1:1). The mixture was chromatographed over silica gel using hexanes-dichloromethane (9:1) as eluent. Eluted first was the (*EE*)-isomer **67**, dark green colored crystals: mp 188−190 °C; ^{1}H NMR δ 8.76 (s, 4H, H-4,5,9,10), 8.63 (d, J = 7.8 Hz, 4H, H-1,3,6,8), 8.06 (t, J = 7.7 Hz, 2H, H-2,7), 4.04 (dm, J = 10.9 Hz, 2H, H-15,16), 2.95 (dd, J = 15.0, 10.8 Hz, 2H, H-13,14), 1.15, 1.10 (s, 12H, Me), 0.22 (d, J = 15.0 Hz, 2H, H-11,12); ^{13}C NMR δ 134.4 (C-3a,5a,10a,10d), 133.5 (C-17,18), 125.3 (C-4,5,9,10), 124.2 (C-1,3,6,8), 123.8 (C-15,16), 123.7 (C-2,7), 121.8 (C-11,12), 121.4 (C-13,14), 35.8 (C-10b,10c), 25.5, 18.0 (C19−22); IR ν (KBr) 3053, 3029, 3003, 1654, 1648, 1441, 1376, 956, 843, 710 cm^{-1} ; UV−vis (cyclohexane) λ_{max} nm (ε_{max}) 247 (76200), 338 (78300), 380 (27900), 469 (7900), 609 (135) EIMS m/z 364 (M$^+$); HRMS calcd for $C_{28}H_{28}$ 364.2191, found 364.2195.

Eluted second was mostly the (*ZE*)-isomer **66**: ^{1}H NMR δ 8.72 and 8.69 (AB, J = 7.7 Hz, 4H, H-4,5,9,10), 8.69 (d, J = 7.6 Hz, 2H, H-6,8), 8.60 (d, J = 7.8 Hz, 2H, H-1,3), 8.08 (t, J = 7.7 Hz, 1H, H-7), 8.04 (t, J = 7.8 Hz, 1H, H-2), 4.50 (dm, J = 12, 1.3 Hz, 1H, H-15), 4.06 (dm, J = 10.8 Hz 1H, H-16), 3.84 (t, J = 12.3 Hz, 1H, H-13), 3.03 (dd, J = 15.0, 10.8 Hz, 1H, H-14), 1.52, 1.00 (br s, 6H, H-19,20), 1.16. 1.11 (2s, 6H, H-21,22), 0.23 (d, J = 15.0 Hz, 1H, H-12), 0.01 (d, J = 12.4 Hz, 1H, H-11); ^{13}C NMR 135.9 (C-17,18), 135.3 (C-5a,10d), 134.8 (3a,10a), 126.3 (C-5,9), 125.4 (C-4,10), 125.1 (C-6,8), 124.4 (C-1,3), 123.84 (C-16), 123.78 (C-2), 123.2 (C-7), 122.7 (C-13), 121.9 (C-14), 120.8 (C-12), 120.0 (C-11), 119.4 (C-15), 37.8 (C-10b), 34.8 (C-10c), 26.5, 17.1 (C-19,20), 25.5, 18.0 (C-21,22); IR ν (KBr) 3030, 3003, 2926, 2853, 1654, 1438, 1374, 955, 843, 838, 714, 645 cm^{-1}; UV−vis (cyclohexane) λ_{max} nm (ε_{max}) 250 nm (54800), 344 (56400), 389 (30400), 475 (6058), 614 (120).

Eluted third was mostly the (*ZZ*)-isomer **65**: ^{1}H NMR δ 8.65 (d, J = 7.7 Hz, 4H, H-1,3,6,8), 8.62 (s, 4H, H-4,5,9,10), 8.08 (2H, H-2,7), 4.53 (dm, J = 12.2, 1.4 Hz, 2H, H-15,16), 3.90 (dd, J = 12.2 Hz, 2H, H-13,14), 1.52, 1.01 (s, 12H, Me), −0.02 (d, J = 12.5 Hz, 2H, H-11,12); ^{13}C NMR δ 136.1 (C-17,18), 135.9 (C-3a,5a,10a,10d), 126.3 (C-4,5,9,10), 125.4 (C-1,3,6,8), 123.5 (C-2,7), 123.3 (C-13,14), 119.4 (C-15,16), 119.0 (C-11,12), 36.6 (C-10b,10c), 26.6, 17.1 (C-19−22); IR ν (KBr) 3023, 2965, 1647, 1654, 1438, 1374, 836, 729 cm^{-1}; UV (cyclohexane) λ_{max} nm (ε_{max}) 251 (42900), 347 (38200), 392 (20100), 486 (5000), 627 (137).

*8,16-Diethynyl-anti-[2.2]metacyclophane-1,9-diene (**69**).* Using the procedure above for **32**, from the ylide prepared by reaction of *t*-BuOK (3.0 g, 27 mmol) and bromomethyl triphenylphosphonium bromide (2.76 g, 6.3 mmol) in THF (25 mL) and diformylmethylthiocyclophane **22** (1.0 g, 2.81 mmol) and column chromatography using hexanes: dichloromethane (7:3) there was obtained 600 mg (see below for yield) of a mixture of isomers containing **68**: ^{1}H NMR δ 7.86 (d, J = 7.6 Hz), 7.84 (d, J = 7.7 Hz), 7.67−7.62 (m), 7.55−7.52 (m), 7.47−7.41 (m), 7.30−7.25 (m), 7.19 (t, J = 7.5 Hz), 7.06 (t, J = 7.3 Hz), 5.83−5.73 (m), 4.58 (d, J = 7.8 Hz), 4.54 (d, J = 7.6 Hz), 3.89 (dd, J = 11.5, 4.0 Hz), 3.80 (dd, J = 711.5, 3.9 Hz), 3.17−3.13 (m), 2.55 (t, J = 12.5 Hz), 2.44 (t, J = 12.1 Hz), 2.17, 2.15, 2.12, 2.10 (4 s); ^{13}C NMR δ 144.4, 143.0, 141.7, 141.2, 136.1, 135.90, 135.87, 134.9, 133.2, 132.7, 132.3, 132.14, 132.12, 132.0, 131.4, 130.2, 129.8, 129.6, 129.2, 128.9, 128.8, 128.7, 128.5, 128.4, 128.0, 127.9, 127.6, 127.5, 127.3, 127.1, 126.3, 125.9, 125.2, 124.9, 123.5, 110.2, 109.5, 109.3, 109.04, 108.96, 87.2, 54.0, 53.5, 53.3, 53.0, 50.7, 46.2, 44.12, 44.05, 43.6, 29.9, 28.4, 22.9, 21.1, 17.6, 17.0, 16.9, 15.9, 15.6, 14.3. This material was used directly in the next step using the same procedure used to prepare **33**. From these mixed isomers (600 mg) on reaction with Borch reagent (80% oil, 1.0 g, 4.84 mmol) in CH_2Cl_2 (7 mL) there was obtained 600 mg of the bis-sulfonium salt of **68**: ^{1}H NMR (DMSO-d_6) δ 7.81 (d, J = 7.8 Hz), 7.69 (d, J = 7.5 Hz), 7.62 (d, J = 7.6 Hz), 7.52 (d, J = 7.6 Hz), 7.41 (t, J = 7.6 Hz), 7.27 (t, J = 7.2 Hz), 6.41 (d, J = 7.6 Hz), 6.36 (d, J = 7.8 Hz), 6.25 (d, J = 8.0 Hz), 5.08 (d, J = 7.7 Hz), 4.74 (d, J = 7.8 Hz), 4.57 (dd, J = 11.2, 3.3 Hz), 4.48−4.42 (m), 3.55−3.50 (m), 3.33, 3.32 (2s), 2.86, 2.84 (s), 2.93−2.74 (m). These were then suspended in THF (20 mL) and *t*-BuOK (600 mg, 5.35 mmol) was added and the mixture stirred at 20 °C for 2h. Water and CH_2Cl_2 were added and the organic extract was washed, dried and evaporated. Chromatography over silica gel using hexane−CH_2Cl_2 90:10 gave the colorless diethynyl CPD **69** (100 mg, ∼14% overall). However, the yield was variable from run to run: ^{1}H NMR δ 7.19 (t, J = 7.5 Hz, 2H, H-5,13), 6.75 (d, J = 7.5 Hz, 4H, H-4,6,12,14), 6.49 (s, 4H, H-1,2,9,10), 2.84 (H-18,20); ^{13}C NMR δ 141.1 (C-3,7,11,15), 133.9 (C-1,2,9,10), 131.4 (C-5,13), 129.8 (C-8,16), 126.5 (C-4,6,12,14), 834 (C-18,20), 81.8 (C-17,19); IR ν (KBr) 3293, 3050, 3005, 1727, 1427, 1262, 857, 805, 755, 655 cm^{-1}; UV−vis (dichloromethane) λ_{max} nm (ε_{max}) 235 (35800), 281 (12900); EIMS m/z 252 (M$^+$, 100%); HRMS calcd for $C_{20}H_{12}$ 252.0939, found 252.0923. On attempted melting point determination, diethynyl CPD **69** isomerized to diethynyl DHP **70**.

*10b,10c-Diethynyl-trans-10b,10c-dihydropyrene (**70**).* Using the general thermolysis procedure above, diethynyl CPD **69** (25 mg) gave diethynyl DHP **70** (25 mg, 100%) as dark green crystals from CH_2Cl_2: mp 245−250 °C dec; ^{1}H NMR δ 8.88 (s, 4H, H-4,5,9,10), 8.74 (d, J = 7.6 Hz, 4H, H-1,3,6,8), 8.27 (t, J = 7.7 Hz, 2H, H-2,7), −0.09 (s, 2H, H-12,14); ^{13}C NMR δ 132.9 (C-3a,5a,10a,10d), 125.5 (C-4,5,9,10), 124.6 (C-2,7), 123.8 (C-1,3,6,8), 75.4 (C-11,13), 65.0 (C-12,14), 30.0 (C-10b, 10c); IR ν (KBr) 3264, 3042, 1654, 1353, 845, 756, 662 cm^{-1}; UV−vis (dichloromethane) λ_{max} nm (ε_{max}) 223 (2900), 229 (7900), 336 (9700), 372 (42700), 399 (4400), 452 (7200), 535 (100), 596 (130), 639 (210); EIMS m/z 252 (M$^+$); HRMS calcd for $C_{20}H_{12}$ 252.0939, found 252.0923.

*6-tert-Butyl-18-cyano-9-methyl-2,11-dithia[3.3]metacyclophanes (**73**) and (**74**).* A solution of 2,6-bis(bromomethyl)benzonitrile[11] **79** (4.40 g, 15.2 mmol) and 2,6 bis(mercaptomethyl)-4-*tert*-butyltoluene[12] **72** (3.80 g, 15.2 mmol) in deaerated benzene (700 mL) was added dropwise under nitrogen to an ethanolic KOH solution, prepared by adding KOH (4.83 g) to deaerated water (230 mL) and ethanol (2090 mL) followed by addition of sodium borohydride (0.9 g). The drop rate was crucial (∼1 every 3−4 s), and the addition took 44 h. The solvent was then evaporated and the residue was dissolved in dichloromethane and was washed with water, dried, and evaporated. The residue was chromatographed on silica gel using CH_2Cl_2−hexanes (35:65) as eluent. Eluted first was 1.90 g (34%) of *anti*-thiacyclophane **74** as colorless crystals from cyclohexane: mp 147−148 °C; ^{1}H NMR δ 7.42−7.45 (m, 3H, H-14,15,16), 7.43 (s, 2H, H-5,7), 3.92 and 3.72 (AB, J = 14.4 Hz, 4H, H-1,12), 3.82 and 3.74 (AB, J = 14.0 Hz, 4H, H-3,10), 1.43 (s, 3H, Me), 1.39 (s, 9H, C(CH_3)$_3$); ^{13}C NMR δ 149.3 (C-6), 141.5 (C-13,17), 136.6 (C-9), 133.5 (C-4,8), 131.9 (C-15), 129.6 (C-14,16), 128.2 (C-5,7), 115.4 (CN), 115.1 (C-18), 34.6 (C(CH_3)$_3$), 33.0 (C-3,10), 31.6 (C-1,12), 31.3 (C(CH_3)$_3$), 15.4 (C-20); IR ν (KBr) 3027, 2954, 2217, 1588, 1483, 1464, 1417, 1236, 877, 804, 794, 755 cm^{-1}; UV (cyclohexane) λ_{max} nm (ε_{max}) 297 (1410), 307 (1390); EIMS m/z 367 (100); HRMS calcd for $C_{22}H_{25}NS_2$ 367.1428, found 367.1413. Anal. Calcd: C, 71.89; H, 6.86; N, 3.81. Found: C, 71.52; H, 6.87; N, 3.69.

Eluted second using CH_2Cl_2−hexanes (45:55) was 1.80 g (32%) of the *syn*-thiacyclophane **73** as colorless crystals from cyclohexane: mp 166−167 °C; ^{1}H NMR δ 7.07 (br s, 3H, H-14−16), 6.96 (s, 2H, H-5,7), 4.36 and 3.75 (AB, J = 15.1 Hz, 4H, H-1,12), 4.36 and 3.67(AB, J = 15 Hz, 4H, H-3,10), 2.56 (s, 3H, Me), 1.18 (s, 9H, C(CH_3)$_3$); ^{13}C NMR δ 147.4 (C-6), 142.5 (C-13,17), 135.9 (C-4,8),

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132.9 (C-15), 132.2 (C-9), 128.7 (C-14,16), 126.3 (C-5,7), 117.7 (CN), 111.7 (C-18), 35.8 (C-1,12), 34.9 (C-3,10), 34.3 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$), 17.0 (C-20); IR ν (KBr) 3040, 2962, 2214, 1592, 1478, 1225, 1185, 871, 746 cm^{-1}; UV (cyclohexane) λ_{max} nm (ε_{max}) 292 (2320), 311 (1210); EIMS m/z 367 (M^+); HRMS calcd for $C_{22}H_{25}NS_2$ 367.1428, found 367.1419. Anal. Calcd: C, 71.89; H, 6.86; N, 3.81. Found: C, 71.56; H, 6.52; N, 3.70.

For synthetic purposes, both isomers could be used together in the next step.

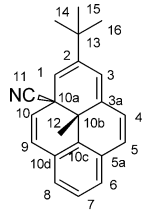
*1,10-Bis(methylthio)-5-tert-butyl-16-cyano-8-methyl-anti-[2,2]-metacyclophane (**75**).* BuLi (2.5 mmol, 1 mL, 2.5 M in hexanes) was added dropwise to a solution of either the *syn*- thiacyclophane **73** or *anti*-**74** or a mixture of both (250 mg, 0.68 mmol) in dry THF (30 mL) at 0 °C. The solution was allowed to warm to room temperature over 10 min. Excess MeI (0.4 mL) was then added and the mixture allowed to stir for another 10 min, when it was quenched using water and then extracted with dichloromethane. The organic extracts were dried and evaporated. The residue was chromatographed over silica gel using CH_2Cl_2–hexanes (12:88) as eluent to afford 242 mg (90%) of **75** as a mixture of isomers, which could be used in the next synthetic step. For characterization purposes, rechromatography yielded a single isomer of **75** in which the 1,10-methylthio groups are pseudoequatorial: mp 139–140 °C; ^{1}H NMR δ 7.97 (d, J = 7.7, 2H, H-12,14), 7.39 (t, J = 7.7, 1H, H-13), 7.28 (s, 2H, H-4,6), 4.09 (dd, J = 11.2, 4.2 Hz, 2H, H-1,10), 2.67 (dd, J = 12.6, 4.2, 2H, H-2_{eq}, 9_{eq}), 2.67 (dd, J = 11.4, 12.6 Hz, 2H, H-2_{ax},9_{ax}), 2.13 (s, 6H, S-Me), 1.33 (s, 9H, C(CH_3)$_3$), 0.54 (s, 3H, Me); ^{13}C NMR δ 150.2 (C-5), 140.9 (C-8), 140.3 (C-11,15), 134.9 (C-3,7), 130.8 (C-13), 126.6 (C-12,14), 126.4 (C-4,6), 119.6 (C-16), 114.4 (CN), 54.8 (C-1,10), 42.8 (C-2,9), 34.2 ($C(CH_3)_3$, 31.3 (C(CH_3)$_3$), 15.5 (S-Me), 14.5 (C-17); IR ν (KBr) 3049, 2951, 2864, 2216, 1598, 1479, 1455, 866, 792, 743, 578 cm^{-1}; UV (cyclohexane) λ_{max} nm (ε_{max}) 274 (3040), 295 (3530); EIMS m/z 395(M^+); HRMS calcd for $C_{24}H_{29}NS_2$ 395.1741, found 395.1747. Anal. Calcd: C, 72.86; H, 7.39; N, 3.54. Found: C, 72.41; H, 7.02; N, 3.50.

*Bis-sulfonium salt **76**.* Using the same procedure as for **33** mixed isomers of cyclophane **75** (2.8 g, 7.0 mmol) and Borch reagent (4.5 g, 22 mmol) in dichloromethane (25 mL) gave 3.24 g (77%) of the air sensitive bis-sulfonium salt **76**: ^{1}H NMR (DMSO-d_6) δ 8.02 (d, J = 7.9 Hz), 7.91–7.85 (m), 7.75–7.62 (m), 7.49, 7.50 (singlets), 7.35–7.27 (m), 7.22–7.12 (m), 7.08 (t, J = 6.5 Hz), 6.63, 6.60 (s), 5.84–5.54 (m), 4.85–4.74 (m), 4.73–4.67 (m), 3.45–3.30 (m), 3.10–2.92 (m), 1.34–1.30 (singlets), 1.11, 1.04, 0.97, 0.69, 0.63, 0.56 (s). These were used directly in the next step.

*5-tert-Butyl-16-cyano-8-methyl-anti-[2.2]metacyclophane-1,9-diene (**77**).* Using the same procedure as for **12**, reaction of *t*-BuOK (0.87 g 7.7 mmol) and bis-sulfonium salt **76** (2.0 g, 3.35 mmol) in THF (35 mL) followed by column chromatography using CH_2Cl_2–hexanes (4:6) as eluent gave 710 mg (70%) of **77** as colorless crystals from cyclohexane: ^{1}H NMR δ 7.28 (t, J = 7.5 Hz, 1H, H-13), 6.85 (d, J = 7.5 Hz, 2H, H-12,14), 6.79 (s, 2H, H-4,6), 6.62 (d, J = 11.3 Hz, 2H, H-2,9), 6.30 (d, J = 11.3 Hz, 2H, H-1,10), 1.57 (s, 3H, Me), 1.31 (s, 9H, –C(CH_3)$_3$); ^{13}C NMR δ 154.0 (C-5), 141.5 (C-8), 141.0 (C-11,15), 137.7 (C-2,9), 136.2 (C-3,7), 133.3 (C-13), 123.0 (C-1,10), 126.6 (C-12,14), 124.6 (C-4,6), 120.0 (C-16), 115.9 (CN), 34.5 (–$C(CH_3)_3$), 31.5 (–C(CH_3)$_3$), 19.8 (C-18); IR ν (KBr) 3048, 3009, 2964, 2904, 2867, 2215, 1571, 1476, 1443, 1217, 1154, 873, 843, 808, 768, 679, 660, 583, 556, 490 cm^{-1}; UV (cyclohexane) λ_{max} nm (ε_{max}) 225 (31100), 287 (12440), 337 (14970), 375 (6800); EIMS m/z 299 (M^+); HRMS calcd for $C_{22}H_{21}N$ 299.1674, found 299.1669. Attempted mp determination converted CPD **77** into DHP **78** and the migration product **94**.

*2-tert-Butyl-10c-cyano-10b-methyl-trans-10b,10c-dihydropyrene (**78**).* Irradiation of an NMR sample of cyclophanediene 77 (10 mg) in benzene-d_6 with a UV source with output 254 nm quickly converts **77** in to **78** in ~75% yield (~7.5 mg) as a dark green solid: ^{1}H NMR δ 8.56 (s, 2H, H-1,3), 8.44 and 8.41 (AB, J = 7.9 Hz, 4H, H-4,5,9,10), 8.30 (d, J = 7.8 Hz, 2H, H-6,8), 7.75 (t, J = 7.8 Hz, H-7), 1.49 (s, 9H, –C(CH_3)$_3$, *t*-Bu), –3.97 (s, 3H, Me); ^{13}C NMR δ 150.0 (C-2), 140.0 (C-10a,3a), 126.3 (C-5,9), 125.7 (C-5a,10d), 124.7 (C-6,8), 124.5 (C-4,10), 122.8 (C-7), 122.5 (C-1,3), 112.7 (CN), 36.6 (–$C(CH_3)_3$), 33.2 (C-10c), 32.0 (–C(CH_3)$_3$), 30.2 (C-10b), 12.0 (C-12); IR ν (thin film) 3040, 2964, 2867, 2217, 1601, 1576, 1478, 1463, 1231, 965, 878, 843, 825, 757, 736, 716 cm^{-1}; UV–vis (cyclohexane) λ_{max} nm (ε_{max}) 203 (50300), 274 (7500), 339 (43600), 377 (5600), 463 (3340), 533 (40), 575 (105), 600 (50). Attempted mp determination converted DHP **78** into the migration product **94**.

*2-tert-Butyl-10a-cyano-10b-methyl-trans-10a,10b-dihydropyrene (**94**).*



94

Cyclophanediene **77** (10 mg) was sealed in a glass tube under argon and heated at 70 °C for 3 h (or until completely colorless), which quantitatively converted it into colorless **94**. Evaporation gave crystals: mp 82–84 °C; ^{1}H NMR δ 7.18 (dd, J = 7.6, 1H, H-7), 7.07–7.03 (m, 2H, H-6,8), 6.72 (d, J = 9.1, 1H, H-9), 6.50 and 6.34 (AB, J = 9.5, 1H, H-4,5), 6.13 (s, 1H, H-3), 5.99 (d, J = 9.1 Hz, 1H, H-10), 5.53 (s, 1H, H-1), 1.157 (s, 3H, Me), 1.153 (s, 9H, –C(CH_3)$_3$); ^{13}C NMR δ 150.6 (C-2), 143.2 (C-3a), 136.2 (C-10c), 131.7 (C-5a), 130.9 (C-10d), 129.0 (C-5), 127.8 (C-7), 127.4 (C-6), 126.8 (C-8), 126.6 (C-4), 125.7 (C-10), 121.52 (CN), 121.48 (C-3), 113.7 (C-1), 43.2 (C-10b), 40.8 (C-10a), 34.7 (-$C(CH_3)_3$), 28.9 (-C(CH_3)$_3$), 17.4 (C-12); IR ν (KBr) 3038, 2961, 2904, 2867, 2217, 1625, 1577, 1477, 1465, 1367, 1210, 966, 865, 825, 813, 756, 746, 661 cm^{-1}; UV (dichloromethane) λ_{max} nm (ε_{max}) 259 nm (12200), 273 (8870), 289 (4380), 301 (4520), 315 (3870), 339 (3660), 353 (3750); EIMS m/z 299 (M^+) HRMS calcd for $C_{22}H_{21}N$ 299.1674, found 299.1674.

*6-tert-Butyl-9-methyl-18-phenylethynyl-2,11-dithia[3.3]-metacyclophanes (**80**) and (**81**).* A solution of bis-bromomethyl-2-phenylethynylbenzene[13] **79** (3.90 g, 10.7 mmol) and 2,6 bis-mercaptomethyl-4-*tert*-butyltoluene[12] **72** (2.57 g, 10.7 mmol) in deaerated benzene (500 mL) was added dropwise to an ethanolic KOH solution, prepared by adding KOH (3.4 g) to deaerated water (160 mL) and ethanol (1470 mL) followed by addition of sodium borohydride (0.64 g). The drop rate was very crucial, and there was a drop every 5–6 s, such that the addition took ~56 h. The solvent was then evaporated, and the residue was dissolved in dichloromethane, washed with water, dried, and evaporated. The residue was chromatographed on silica gel using CH_2Cl_2-hexanes (15:85) as eluent. Eluted first was 700 mg (15%) of *anti* **81** as colorless crystals from cyclohexane: mp 148–149 °C; ^{1}H NMR δ 7.44–7.39 (m, 2H, H-22, 26), 7.40 (d, J = 7.6 Hz, 2H, H-14,16), 7.33–7.31 (m, 3H, H-23,24,25), 7.27 (s, 2H, H-5,7), 7.22 (t, J = 7.6 Hz, 1H, H-15), 4.16 and 3.72 (AB, J = 14.1 Hz, 4H, H-1, 12), 3.80–3.70 (m, 4H, H-3,10), 1.42 (s, 3H, Me), 0.98 (s, 9H, –C(CH_3)$_3$.); ^{13}C NMR δ 148.3 (C-6), 139.3 (C-13,17), 135.9 (C-9), 134.1 (C-4,8), 131.6 (C-22,26), 129.1 (C-14,16), 128.51 (C-23,25), 128.45 (C-24), 127.8 (C-15), 127.3 (C-5,7), 125.7 (C-18), 124.0 (C-21), 100.2 (C-20), 86.2 (C-19), 34.1 (-$C(CH_3)_3$), 32.4 (C-3,10), 32.1 (C-1,12), 31.1(-C(CH_3)$_3$), 15.3 (C-27); IR ν (KBr) 3057, 2959, 2904, 2862, 1594, 1477, 1488,1440, 756. 7477, 691 cm^{-1}; UV (cyclohexane) λ_{max} nm (ε_{max}) 288 (10100) 303 (11700), 318 (11900); EIMS m/z 442 (M^+); HRMS calcd for $C_{29}H_{30}S_2$ 442.1788, found 442.1779.

Eluted second was 2.20 g (47%) of *syn*-**80** as colorless crystals from cyclohexane: mp 170–171 °C; ^{1}H NMR δ 7.62 (dd, J = 7.8, 1.8 Hz, 2H, H-22,26), 7.40–7.44 (m, 3H, H-23,24,25), 7.02 (d, J = 7.6, 2H, H-14,16), 7.01 (s, 2H, H-5,7), 6.86 (t, J = 7.6 Hz, 1H, H-15), 4.65 and 3.67 (AB, J = 14.8 Hz, 4H, H-1,12), 4.41 and 3.62 (AB, J = 14.8 Hz, 4H, H-3,10), 2.54 (s, 3H, Me) 1.22 (s, 9H, –C(CH_3)$_3$); ^{13}C NMR δ 147.2 (C-6), 140.4 (C-13,17), 136.0 (C-4,8), 132.2 (C-9), 131.4 (C-22,26), 129.0 (C-15), 128.84 (C-23,25), 128.75 (C-24), 128.0 (C-14,16), 126.0 (C-5,7), 123.6 (C-21), 121.7 (C-18), 99.2 (C-20), 87.8 (C-19), 35.8 (C-1,12), 34.7 (C-3,10), 34.3 (-$C(CH_3)_3$), 31.3

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(-C(CH_3)$_3$), 17.2 (C-27); IR ν (thin film, KBr) 3057, 2961, 2906, 2864, 1596, 1489, 1478, 1461, 1361, 1261, 872, 792, 755, 748, 691 cm^{-1}; UV (cyclohexane) λ_{max} nm (ε_{max}) 258 (16100), 297 (13600), 319 (11000); EIMS m/z 442 (M$^+$); HRMS calcd for $C_{29}H_{30}S_2$ 442.1788, found 442.1786.

There was no need to separate **80**and **81** for synthetic purposes.

*1,10-Bis(methylthio)-5-tert-butyl-8-methyl-16-phenylethynyl-anti-[2,2]metacyclophane (**82**).* BuLi (2.5 mmol, 1 mL, 2.5 M in hexanes) was added dropwise to a solution of mixed thiacyclophanes **80**/**81** (300 mg, 0.68 mmol) in dry THF (30 mL) at 0 °C. The solution was allowed to warm up to room temperature over 10 min when the dark solution had turned pale yellow. Excess MeI (0.4 mL) was added and was allowed to stir for another 10 min. The reaction was quenched with water (5 mL) and then was extracted with dichloromethane. The organic extracts were dried and evaporated. The residue was chromatographed over silica gel using CH_2Cl_2-hexanes (12:88) as eluent and gave 290 mg (80%) of mixed isomers of **82**. For characterization purposes, rechromatography yielded 150 mg of a single isomer of **82** in which the 1,10 methylthio groups are pseudo-equatorial: mp 203−204 °C; ^{1}H NMR δ 7.86 (d, J = 7.6 Hz, 2H, H-12,14), 7.28 (tt, J = 6.4, 1.5 Hz, 1H, H-22), 7.27−7.17 (m, 4H, H-20,21,23,24), 7.21 (t, J = 7.6 Hz, 1H, H-13), 7.14 (s, 2H, H-4,6), 4.45 (dd, J = 11.4, 4.1 Hz, 2H, H-1$_{ax}$,10$_{ax}$), 3.24 (dd, J = 12.4, 4.1 Hz, 2H, H-2$_{eq}$,9$_{eq}$), 2.74 (dd, J = 12.2, 11.6 Hz, 2H, H-2$_{ax}$,9$_{ax}$), 2.18 (s, 6H, S-Me), 0.91 (s, 9H, −C(CH_3)$_3$), 0.63 (s, 3H, Me); ^{13}C NMR δ 148.4 (C-5), 140.0 (C-8), 138.8 (C-11,15), 135.2 (C-3,7), 131.7 (C-13), 130.2 (C-16), 128.3 (C-22), 127.3, 128.5 (C-20,21,23,24), 125.8 (C-12,14), 125.2 (C-4,6), 123.6 (C-19), 92.8 (C-18), 86.2 (C-17), 54.6 (C-1,10), 43.5 (C-2,9), 34.1 (-C(CH$_3$)$_3$), 31.3 (-C(CH_3)$_3$), 15.9 (C-30,31), 14.9 (C-25); IR (thin film, KBr) 3044, 2952, 2913, 1596, 1490, 1425, 754, 745, 690 cm^{-1}; UV (cyclohexane) λ_{max} nm (ε_{max}) 280 (13000), 293 (13500), 320 (12600); EIMS m/z 470 (M$^+$); HRMS calcd for $C_{31}H_{34}S_2$ 470.2102, found 470.2104. Anal. Calcd: C, 79.09; H, 7.28. Found: C, 79.35; H, 7.01

*1, 10-Bis(methylthio)-8-methyl-16-phenylethynyl-anti-[2.2]-metacyclophane Bis-sulfonium Salt (**83**).* Using the same procedure as for **33**, the pure 1,10-diequatorial-methylthio isomer of **83** (1.0 g, 2.1 mmol) on reaction with Borch reagent (1.0 g, 4.8 mmol) in CH_2Cl_2 (7 mL) gave 1.4 g (quant.) of **83** as a single isomer: ^{1}H NMR (DMSO-d_6) δ 7.87 (d, J = 7.8 Hz, 2H, H-12,14), 7.58 (dd J = 7.8, 2.3 Hz, 2H, H-20,24), 7.47 (t, J = 7.76 Hz, 1H, H-13), 7.41 (m, 3H, H-21−23), 7.35 (s, 2H, H-4,6), 4.66 (dd, J = 12.0, 4.2 Hz, 2H, H-1$_{ax}$,10$_{ax}$), 3.60 (dd, J = 12, 4.2 Hz, 2H, H-2$_{eq}$,9$_{eq}$), 3.46 (s, 6H, S-Me$_2$), 3.17 (triplet, J = 12 Hz, 2H, H-2$_{ax}$,9$_{ax}$), 3.04 (s, 6H, S-Me$_2$), 0.89 (s, 9H, −C(CH_3)$_3$), 0.75 (s, 3H, Me). When mixed isomers were used the following NMR data was obtained: ^{1}H NMR (DMSO-d_6) δ 7.88−7.34 (m), 7.0−6.8 (m), 6.6 (br s), 5.83−5.55 (m), 4.8−4.6 (m), 4.04−3.00 (m), 2.26, 1.98 (s), 1.18, 0.78 (9 singlets). These were used in the next step.

*5-tert-Butyl-8-methyl-16-phenylethynyl-anti-[2.2]metacyclophane-1,9-diene (**84**).* Using the same procedure as for **12**, reaction of bis-sulfonium salt **83** (300 mg, 0.45 mmol) and *t*-BuOK (120 mg, 1.1 mmol) in THF (10 mL) followed by chromatography over silica gel in a foil wrapped column using hexanes/CH_2Cl_2 (80:20) as eluent gave 147 mg (90%) of CPD **84** as colorless crystals: ^{1}H NMR δ 7.25−7.23 (m, 5H), 7.12 (t, J = 7.4 Hz, 1H), 6.77 (d, J = 7.4 Hz, 2H), 6.58 (s, 2H), 6.49 (d, J = 11.3 Hz, 2H), 6.36 (d J = 11.3 Hz, 2H), 1.65 (s, 3H, Me), 0.80 (s, 9H, C(CH_3)$_3$, ^{t}Bu); ^{13}C NMR δ 150.6, 141.7, 137.4, 131.3, 130.2, 129.4, 128.3, 127.8, 125.9, 124.6, 123.1, 95.1, and 90.0 (C≡C), 33.0 (C-26), 30.7 (-C(CH_3)$_3$) 20.2 (Me). ^{1}H NMR (C_6D_6) δ 7.28 (dd, J = 7.1, 1.5 Hz, 2H, H-20,24), 6.92−6.98 (m, 3H, H-21−23), 6.86 (t, J = 7.4 Hz, 1H, H-13), 6.73 (s, 2H, H-4,6), 6.54 (d J = 7.4 Hz, 2H, H-12,14), 6.42 and 6.23 (AB, J = 11.3 Hz, 2H, H-1,2,9,10), 1.83 (s, 3H, Me), 0.93 (s, 9H, −C(CH_3)$_3$); ^{13}C NMR (C_6D_6) δ 150.9 (C-5), 142.5 (C-8), 141.2 (C-11,15), 138.1 (C-3,7), 135.4 (C-2,9), 132.3 (C-20,24), 132.0 (C-1,10), 131.1 (C-16), 129.8 (C-13), 128.7 (C-21,23), 128.1 (C-22), 126.3 (C-12,14), 125.5 (C-19), 123.7 (C-4,6), 95.9 (C-18), 91.0 (C-17), 34.2 (-C(CH$_3$)$_3$), 31.7 (-C(CH$_3$)$_3$), 20.8 (C-25); IR ν (thin film) 3041, 3004, 2867, 2962, 1597, 1491, 1442, 871, 772, 757, 737, 690, 673 cm^{-1}; UV (cyclohexane) λ_{max} nm (ε_{max}) 288 nm (13500), 339 (15000), 377 (6700); EIMS 374 (M$^+$). Attempted mp determination converted CPD **84** into DHP **85**.

*2-tert-Butyl-10b-methyl-10c-phenylethynyl-trans-10b,10c-dihydropyrene (**85**).* *t*-BuOK (140 mg, 1.2 mmol) was added to a stirred suspension of mixed isomers of bis-sulfonium salt **83** (350 mg, 0.52 mmol), in THF (10 mL) under argon at 20 °C. After refluxing for 6 h, water was added and then dichloromethane (90 mL). The extract was washed, dried, and evaporated. The residue was chromatographed over silica gel using hexanes/CH_2Cl_2 (85:15) as eluent to give 160 mg (85%) of the dihydropyrene **85** as green crystals from methanol: mp 112−113 °C; ^{1}H NMR δ 8.72 and 8.65 (AB, J = 7.8 Hz, 2H, H-4,5,9,10), 8.69 (s, 2H, H-1,3), 8.62 (d, J = 7.8 Hz, 2H, H-6,8), 8.07 (t, J = 7.8 Hz, 1H, H-7), 6.83 (tt, J = 7.8, 1.8 Hz, 1H, H-16), 6.72 (dd, J = 7.8, 7.5 Hz, 2H, H-15,17), 6.04 (dd, J = 7.4, 1.8 Hz, 2H, H-14,18), 1.74 (s, 9H, −C(CH_3)$_3$), −4.00 (3H, s, Me); ^{13}C NMR δ 148.2 (C-2), 140.0 (C-3a,10a), 131.1 (C-14,18), 130.1 (C-5a,10d), 127.4 (C-15,17), 127.0 (C-16), 125.1 (C-5,9), 123.5 (C-4,10), 123.3 (C-6,8), 122.5 (C-13), 122.0 (C-7), 121.3 (C-1,3), 84.6 (C-12) 75.4 (C-11), 36.4 (-C(CH$_3$)$_3$), 32.1 (-C(CH_3)$_3$), 31.2 (C-10b), 30.5 (C-10c), 12.9 (C-19); IR ν (thin film) 3036, 2963, 1597, 1489, 1478, 1442, 1230, 874, 822, 755, 737, 691, 682, 628 cm^{-1}; UV−vis (cyclohexane) λ_{max} nm (ε_{max}) 250 (41200), 339 (1.64 × 10^5), 377 (73200), 467 (14900), 577 (380), 639 (300); EIMS 374 (M$^+$); HRMS calcd for $C_{29}H_{26}$ 374.2034, found 374.2036.

*8,16-Diformyl-anti-[2.2]metacyclophane-1,9-diene (**27**).* DIBAL (2.5 mmol, 2.5 mL of 1 M solution in cyclohexane) was added dropwise to a solution of dicyano CPD[3] **5** (250 mg, 1 mmol) in dry dichloromethane (12 mL) at room temperature, over a period of 6 min. It was stirred for 5 h at 20 °C, after which it was slowly added to methanol (5 mL) and stirred for 30 min. Then HCl (10 mL, 1M) was added carefully and the resulting solution was extracted with dichloromethane . The organic layer was dried, evaporated, and column chromatographed over silica using ethyl acetate:dichloromethane (1:9) as eluent to yield 146 mg (56%) of the diformyl-CPD **27** as colorless crystals from methanol: ^{1}H NMR δ 9.35 (s, 2H, H-17,18), 7.39 (t, J = 7.4 Hz, 2H, H-5,13), 6.85 (d, J = 7.4 Hz, 4H, H-4,6,12,14), 6.73 (s, 4H, H-1,2,9,10); ^{13}C NMR) δ 185.8 (C-17,18), 145.4(C-8,16), 140.0 (C-3,7,11,15), 135.4 (C-1,2,9,10), 135.3 (C-5,13), 128.8 (C-4,6,12,14); IR ν (KBr) 3056, 3011, 2924, 2869, 2768, 1712, 1683, 1559, 1445, 1222, 1181, 816, 761, 628 cm^{-1}; UV−vis (dichloromethane), λ_{max} nm (ε_{max}) 245 nm (8500), 274 (8600), 338 (4150), 345 (4130), 395 sh (1500); EIMS m/z 260 (M$^+$). Attempted mp determination converted CPD **27** into migration product **30**.

*1,10a-Diformyl-trans-1,10a-dihydropyrene (**30**).* Diformyl-CPD **27** (10 mg) in $CDCl_3$ (1 mL) was sealed in a glass tube under argon and heated at 70 °C for 1 h, which converted it into **30**. Evaporation gave colorless solid (10 mg, 100%) which decomposed on attempted chromatography but was pure enough to obtain the following data: ^{1}H NMR δ 9.71 (d, J = 3.4 Hz, 1H, H-18), 9.34 (s, 1H, H-17), 7.69 (d, J = 8.3 Hz, 1H, H-5), 7.61 (d, J = 8.4 Hz, 1H, H-6), 7.32 (dd, J = 6.9, 8.4 Hz, 1H, H-7), 7.28 (d, J = 8.3 Hz, 1H, H-4), 7.11 (d, J = 6.8 Hz, 1H, H-8), 6.9 (d, J = 9.6 Hz, 1H, H-9), 6.7 (d, J = 9.9 Hz, 1H, H-3), 5.91 (dd, J = 9.6, 6.2 Hz, 1H, H-2), 5.68 (d, J = 9.6 Hz, 1H, H-10), 3.76 (dd, J = 6.3, 3.5 Hz, 1H, H-1); ^{13}C NMR δ 198.7 (C-18), 191.0(C-17), 133.5 (C-5a), 132.9 (C-9), 131.3 (C-3), 131.2 (C-3a), 130.5 (C-10d), 128.6 (C-6), 128.41 (C-10c), 128.2 (C-5), 127.1 (C-7), 126.1 (C-4), 125.6 (C-10b), 125.3 (C-8), 122.7 (C-10), 122.0 (C-2), 55.9 (C-10a), 51.1 (C-1); IR ν (thin film) 3048, 2927, 2820, 2721, 1719, 1685, 1590, 1569, 1502, 1174, 842, 770, 734 cm^{-1}; UV−vis (dichloromethane) λ_{max} nm (ε_{max}) 208 (850), 243 (13500), 274 (24600), 322 (3600), 322 (3600), 338 (4100), 402 (2130), 470 *sh* (460); EIMS m/z 260 (M$^+$)

Attempted chromatography of **30** led to formation of 1-formylpyrene **31**.

■ ASSOCIATED CONTENT

Supporting Information

Table S1: Thermodynamic parameters for the thermal back reaction: cyclophanediene to dihydropyrene. UV−vis spectrum of the orange plastic cutoff filter used for the photo-opening

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experiments. General synthetic experimental conditions. The numbering system used for NMR assignments. ^{1}H and ^{13}C NMR spectra for all new compounds. Thermal closing data with Arrhenius and Eyring plots for the thermal closing reaction for the compounds studied. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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