Synthesis and Photochromic Properties of Molecules Containing [e]-Annelated Dihydropyrenes. Two and Three Way π-Switches Based on the Dimethyldihydropyrene−Metacyclophanediene Valence Isomerization

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Abstract: The syntheses of several new simple negative, a simple positive, and multiple negative photochromes containing the dihydropyrene−cyclophanediene photochromic system are described. The photo-openings of the negative photochromes, the [e]-annelated benzo (**7**), naphtho (**9**), anthro (**11**), furano (**19**), and triphenyleno (**15**) derivatives of the parent 2,7-di-*tert*-butyl-*trans*-10b,10c-dimethyl-dihydropyrene (**5**), as well as its 4,5-dibromo derivative (**13**), are described to give the corresponding cyclophanedienes, as well as their photoclosures and thermal closures back to the dihydropyrenes. These are compared to the results obtained for the positive photochrome dibenzo[e,l]dihydropyrene (**21**) and to the bis-(dihydropyreno)chrysene (**44**) and the (dihydropyrenobenzo)(benzo)metacyclophanediene (**47**) photochromes, which have more than one photochromic switch present and thus have more than a simple "on−off" state. Thermodynamic data are obtained for the thermal closing reactions. The anthrodihydropyrene (**12**) has the fastest thermal closing ($\tau_{1/2}$ = 20 min), while the furanodihydropyrene (**19′**) has the slowest ($\tau_{1/2}$ = 63 h) at 46 °C. An electrochemical readout of the state of the switch is demonstrated for the benzodihydropyrene (**7**).

Introduction

A recent issue of *Chemical Reviews* is devoted to the topic "Photochromism: Memories and Switches"[1] and indicates the considerable current interest in such molecules, which include diarylethenes, fulgides, and spiropyrans. Much less investigation of dihydropyrenes has been made, even though they are also photochromic[2] and are thus potential photoswitches[3] which may have some future application. The dihydropyrene (DHP)−cyclophanediene (CPD) system is however especially interesting because it is an example of the less common negative photochromes,[4] in which the thermally stable form is colored and which on irradiation becomes colorless.

The green dimethyldihydropyrene **1** has a rigidly planar extended π-system and has absorptions out to 600 nm. The colorless cyclophanediene form **2** is a stepped molecule which is also rigid but has the olefinic bridges almost at right angles

to the benzene rings and thus only shows benzenoid absorption with an extended tail.[5] The effective size of the π-system thus
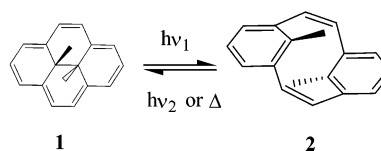
changes from 14π in **1** to 6π in **2**. Irradiation of the parent green dihydropyrene form **1** with visible light from an ordinary tungsten household lightbulb partially converts it to the colorless cyclophanediene form **2**. Unfortunately, the reverse reaction occurs not only photochemically with UV light but also thermally. This is surprising, since the photochemical processes involve *allowed* conrotatory opening and closing of the central bond and are examples of the more general *cis*-stilbene dihydrophenanthrene interconversion.[6] The thermal back reac-

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(1) Irie, M. (Guest Editor) *Chem. Rev.* **2000**, *100*, 1683−1890.
(2) Mitchell, R. H. *Eur. J. Org. Chem.* **1999**, 2695−2703.
(3) Marsella, M. J.; Wang, Z. Q.; Mitchell, R. H. *Org. Lett.* **2000**, *2*, 2979−2982.
(4) Bouas-Laurent, H.; Dürr, H. *Pure Appl. Chem.* **2001**, *73*, 639−665.

(5) Blattmann, H. R.; Meuche, D.; Heilbronner, E.; Molyneux, R. J.; Boekelheide, V. *J. Am. Chem. Soc.* **1965**, *87*, 130−131. Blattmann, H. R.; Schmidt, W. *Tetrahedron* **1970**, *26*, 5885−5899.
(6) Muszkat, K. A.; Gegiou, D.; Fischer, E. *Chem. Commun.* **1965**, 447−448. Muszkat, K. A.; Eisenstein, M.; Fischer, E.; Wagner, A.; Ittah, Y.; Luttke, W. *J. Am. Chem. Soc.* **1997**, *119*, 9351−9360.

tion of **2** to **1** on the other hand, since it gives the same product as the photochemical reaction, must break Woodward−Hoffmann rules if it is a concerted process.[7] The thermal reaction has an E_{act} of about 23 kcal/mol, and so to achieve high conversions of **1** to **2**, the reaction mixture first needs to be cooled to <0°C. Second, the quantum yield of the back reaction, **2** to **1**, is approximately 50 times greater than that for the forward reaction, and so for the best conversion of **1** to **2**, irradiation into the tail of **2** must be avoided; thus, a filter is required to restrict the wavelength of the light used to >500 nm.[2]

When benzenoid systems are fused to dihydropyrenes, the extended π-system continues to be approximately planar, and the principle absorptions are red shifted. In their open CPD forms however, the staircase geometry interrupts the π-system, and benzenoid absorption persists. Benzenoid annelation of dihydropyrenes thus modifies the properties of the switch but does not change its nature.[8]

This paper examines the changes in photochromic properties that occur when various benzenoid systems are annelated onto **1** and the properties of switches with *three* states which are formed when two dihydropyrene systems are fused onto a benzenoid.[9]
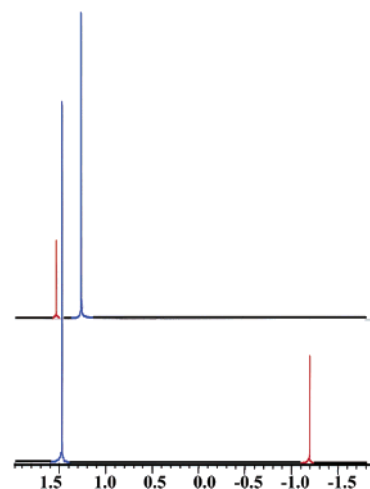
Results and Discussion

The disadvantages of the parent system mentioned previously are much reduced in the benzo[*e*]annelated system **3** to **4**. First, E_{act} for the thermal return reaction **4** to **3** is higher by 2 kcal/mol (25 kcal/mol), and so, the half-life of **4** is extended to about a week at room temperature.[10]
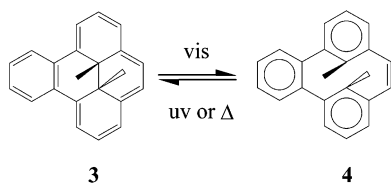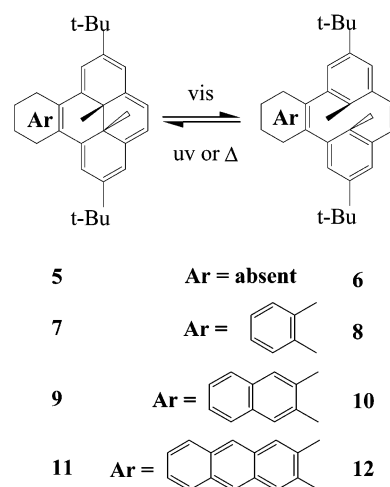
Second the quantum yield for the conversion of **3** to **4** appears to be much better than that for **1** to **2**. Simply holding a solution of **DHP 3** in front of an ordinary tungsten bulb causes complete bleaching to the colorless **CPD 4**. As noted previously, during the photochromic conversion, there is a large change in the effective π-system: Red **3** has 18 interacting p-orbitals, while colorless **4** has only isolated 6π-systems, because of the orthogonality of the orbitals in the CPD form.

Simple Arene [*e*]-Annelated Derivatives. Although we first reported **3** some two decades ago,[10] its lengthy multistep synthesis from benzene precursors prevented a full exploration of its properties. Discovery of a route[11a] to a series of [*a*]-annelated dihydropyrenes from a common dihydropyrene "aryne" reactive intermediate opened up syntheses in this area. Coupling this discovery with using the more easily synthesized

(7) Schmidt, W. *Helv. Chim. Acta* **1971**, *54*, 862−868. Schmidt, W. *Tetrahedron Lett.* **1972**, *13*, 581−584.
(8) Mitchell, R. H.; Iyer, V. S.; Mahadevan, R.; Venugopalan, S.; Zhou, P. *J. Org. Chem.* **1996**, *61*, 5116−5120.
(9) Mitchell, R. H.; Ward, T. R.; Wang, Y.; Dibble, P. W. *J. Am. Chem. Soc.* **1999**, *121*, 2601−2602.
(10) Mitchell, R. H.; Yan, J. S. H.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2551−2559.
(11) (a) Mitchell, R. H.; Iyer, V. S.; Khalifa, N.; Mahadevan, R.; Venugopalan, S.; Weerawarna, S. A.; Zhou, P. *J. Am. Chem. Soc.* **1995**, *117*, 1514−1532. (b) Mitchell, R. H.; Ward, T. R. *Tetrahedron*, **2001**, *57*, 3689−3695.

Figure 1. Partial ^{1}H NMR spectrum of CPD **8** (top) after irradiation (see text) of the DHP **7** (bottom). The *tert*-butyl signals are the larger signals in each spectrum.

starting material, the 2,7-di-*tert*-butyl derivative of **1** (= **5**) (the Supporting Information gives a large scale preparation of **5**) has led[11b] to a variety of [*e*]-annelated dihydropyrenes suitable for photochemical study.

Photochemistry of 5−12. The reported[12] quantum yield for the conversion of the di-*t*-Bu substituted **5** to **6** was 0.002, an order of magnitude smaller than that for conversion of the unsubstituted parent **1** to **2**, so we were unsure as to whether **7** would be as good at switching as was **3**. In the event, **7** is readily bleached with visible light. Placing a reddish-purple solution of **7** in cyclohexane on the surface of an ordinary overhead transparency projector bleaches it in a couple of minutes, at a rate not noticeably different from that of the parent **3**. The conversion of colored **7** to colorless **8** was essentially quantitative by NMR. When an NMR sample was held about 8 cm from a 250 W tungsten lamp with ice cooling (Pyrex glass), no peaks of the starting isomer **7** were observable after a few minutes of irradiation. This can be seen clearly in Figure 1. This is important, because many photochromic systems give photo stationary states and complete conversion from one isomer to the other is not possible.[1] It is not possible to achieve this on the parent **5**, unless a 500 nm cutoff filter is used with ice

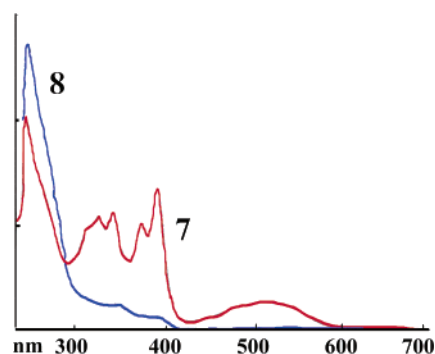(12) Murakam, S.; Tsutsui, T.; Saito, S.; Yamato, T.; Tashiro, M. *Nippon Kagaku Kaishi* **1988**, 221−229.

Figure 2. UV−vis spectrum of CPD **8** and DHP **7** in cyclohexane.

Table 1. Half-Lives ($\tau_{1/2}$, h, 46 °C), Energies of Activation (E_{act}, kcal/mol), and AM1 Calculated Differences in Heats of Formation (ΔH_f(DHP−CPD), kcal/mol) for the Thermal Reactions Shown

reaction	$\tau_{1/2}$	E_{act}	ΔH_f
6 → 5	1.88	23.0	2.27
8 → 7	5.75	24.5	1.47
10 → 9	1.15	22.1	1.12
12 → 11	0.33	19.1	0.96

cooling. Holding a hand-held UV chromatography lamp in front of the NMR tube containing bleached sample **8** quickly and quantitatively converted it back to **7**.

The corresponding UV−visible spectra using cyclohexane as solvent are shown in Figure 2. The long wavelength absorptions of purple **7** are removed on visible irradiation, as colorless **8** forms. Almost identical spectra are obtained in the solid state, if the DHP **7** is dissolved in polystyrene−dichloromethane (20: 80) (1% **7** by weight of the polystyrene) and spin coated onto a film on glass. Photoisomerization also takes place in the crystal state. Small crystals bleach in color on exposure to visible light and return to purple on exposure to UV light.

The naphtho analogue **9** bleached to **10** even faster than did **7** to **8**; however, bleaching of the anthro analogue **11** was slower than that of **7**. The major differences between these three analogues was in the thermal return reactions.

Thermal Return Reactions. Previously, we have observed[8] that when ΔH_f(DHP−CPD) (AM1) is large, the thermal return of the CPD to the DHP form is fast. For the [*e*]-annelated compounds here however, the ΔH_f values are all small. The thermal return of **12** to **11** is approximately 3 to 4 times faster than that of **10** to **9**, which is 4 times faster than that of **8** to **7**, which is 3 times slower than the parent **6** to **5**. Table 1 shows the relevant data.

Thus, for a practical application, although under the same irradiation conditions, the naphtho derivative **9** photochemically opens and closes faster than the benzo derivative **7**, a slow thermal return reaction (CPD to DHP) is important, and so the benzannelated derivative **8/7** is the best.

Why the thermal return of **8** to **7** is slowest is not immediately obvious. Since this reaction is "Woodward−Hoffmann forbidden", perhaps the transition state has radical or ionic character, which the anthro and naphtho rings would certainly stabilize better, lowering E_{act}. This would not explain why E_{act} for **6** to **5** is not higher than that for **8** to **7**. A number of factors may contribute, one of which may be the change in length of the bridge bond during the photoreaction. In the cyclophanediene **6**, the bridge bond is a pure double bond, 1.34 D. In the annulene **5**, all bonds are equal at 1.40 D. During the transition, this bond

length has to undergo considerable change. For the annelated derivatives, this change would be smaller, because the annelated rings cause partial bond fixation in each other. This might reduce E_{act} for the thermal reactions of **8/10/12** relative to **6**. Another factor is strain. In the planar annelated DHP derivatives **7/9/11**, there are "phenanthrene bay type" steric interactions between the periprotons of the annelating ring and the protons of the DHP ring (protons 1/12 and 8/9 in **7** for example). These are absent in the twisted CPD isomers. Thus the thermal reaction **8 → 7** has to overcome this strain, while the parent **6 → 5** does not. This should raise E_{act} for the former relative to the latter. The summation of these effects, the stabilization of the "intermediate", the change in bridge bond length, and the change in strain may then produce the observed order, in which the benzo system **8** to **7** has the greatest value for E_{act} (slowest thermal return).

Two additional data points were easily accessible making use of the dibromide pair **13/14** and the triphenylene annelated pair **15/16**.
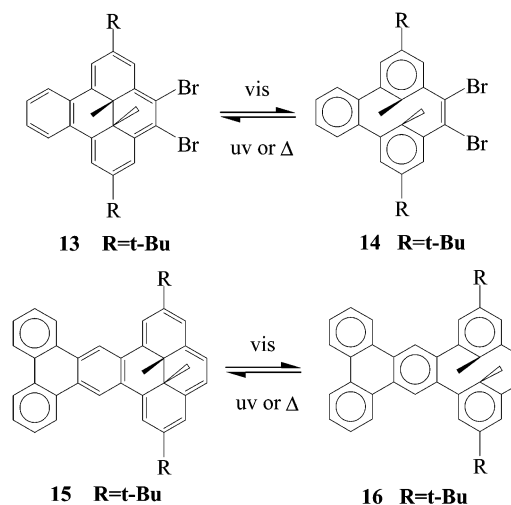
Bromination of **7** with NBS/DMF/CH$_2$Cl$_2$[13] at 20 °C gave a 48% yield of dibromide **13**. The $\tau_{1/2}$ value found at 46 °C for the thermal return reaction **14** to **13** was 9.50 h, almost double that of **8** to **7**, with E_{act} increasing to 25.8 kcal/mol. Indeed, PCMODEL[14] calculations indicate an additional 1 kcal/mol difference in strain energies between the DHP pair (**7/13**) and the CPD pair (**8/14**). In the dibromide, the DHP ring hydrogens sterically interact with the bromine atoms in the planar DHP form more than they do in the twisted CPD form (see **2**). This is suggestive that increasing strain in the DHP form relative to the CPD form slows the thermal reaction. However, Lai[15] has shown that too much strain destabilizes the DHP form too much and then prevents full equilibration between the photoisomers; for example, **17** and **18** will not fully interconvert. Bromine may also introduce an electronic effect.

Reaction of the furan **19**[11b] with 9-bromophenanthrene and NaNH$_2$/*t*-BuOK in THF gave an 85% yield of adduct **20**, which on deoxygenation with Fe$_2$(CO)$_9$ in refluxing benzene gave an 86% yield of the triphenylene **15**, as a stable purple compound,

(13) Mitchell, R. H.; Lai, Y. H.; Williams, R. V. *J. Org. Chem.* **1979**, *44*, 4733−4735. Mitchell, R. H.; Chen, Y.; Zhang, J. *Org. Prep. Proced. Int.* **1997**, *29*, 715−719.
(14) *PCMODEL*, version 7.0; Serena Software: Bloomington, IN 47402-3076.
(15) Lai, Y. H.; Chen, P.; Peck, T. G. *Pure Appl. Chem.* **1993**, *65*, 81−87.

mp 188−193 °C (dec). The $\tau_{1/2}$ value found at 46 °C for **16** to **15** was 3.6 h (E_{act} = 23.4 kcal/mol), 1.6 times faster than that for **8** to 7.
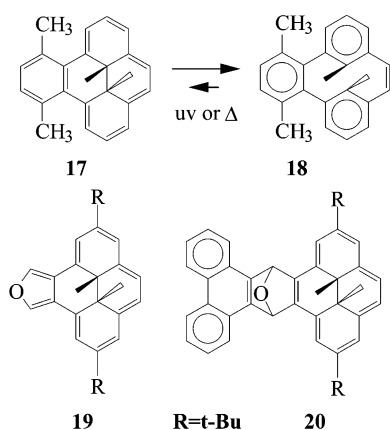

Calculations[14] suggest there is little change in the steric interactions (<0.2 kcal/mol) between the DHP ring hydrogens with the adjacent aromatic hydrogens on going from **7** to **15**. However, a charged or radical intermediate would be expected to be additionally stabilized, and thus, the thermal reaction of **16** to **15** might be expected to be faster than that of **8** to **7**.

Both pairs, **13/14** and **15/16**, photochemically opened and closed easily; however, of the simple [*e*]-annelated dihydropyrenes, the benzo compound **7** appears to be the best photoswitch so far, offering a reasonable compromise among ease of synthesis, efficiency or ease of the photoconversions, and relatively slow thermal return reaction.

In principle, the corresponding arene[*a*]annelated derivatives should also photoswitch. Laser flash studies, similar to that of the parent,[16] suggest they do, but the thermal return reactions are extremely fast, which does not make them very convenient to study. AM1 calculations show they have much larger values of ΔH_f(DHP−CPD) with the DHP being the more stable isomer.[8]

Diarene Annelated Derivatives. The situation for the diarene annelated derivative **21/22** is quite different from that of either the [*a*]- or the [*e*]-annelated derivatives. In this case, the CPD **21** is calculated to be the thermally stable isomer, ΔH_f(CPD−DHP) (AM1)[17] = 18.4 kcal/mol (18.2 kcal/mol when R═H), and so, we would expect the DHP form **22** to revert thermally quite rapidly to CPD **21** when the latter is irradiated with UV light.
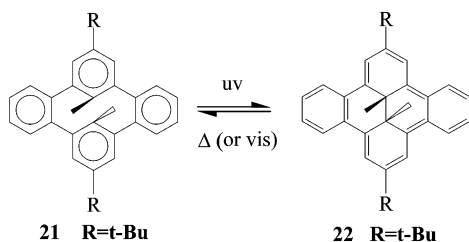
Syntheses. Despite considerable effort, synthesis of the dibenzannulene **22** was not achieved until almost 20 years after our synthesis of **3**![18] Coupling the bis-Grignard reagent **23** with

o-dibromobenzene failed to provide any cyclophane **21** (R═H). Bis-alkylation of the dianion of the sulfone **24** with either *o*-bis-(bromomethyl)benzene or *o*-phthalaldehyde, followed by SO$_2$ expulsion, was also fruitless.
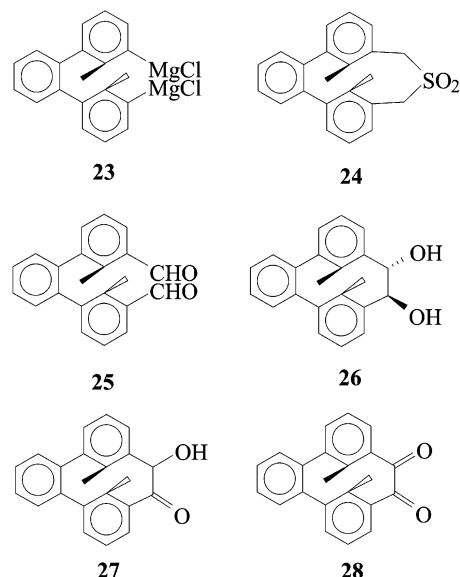
Our first[19] successful synthesis of the *o*−*m*−*o*−*m*-cyclophane system of **21** utilized the dialdehyde **25**.[20] McMurry coupling[21] of **25** using Zn/Cu and TiCl$_3$ in refluxing dimethoxyethane yielded 75−85% yields of the pinacol **26**, mp 215−218 °C. Swern oxidation[22] of diol **26** using oxalyl chloride−DMSO gave 75−80% yields of the hydroxyketone **27**, which on repeat treatment gave 75−90% yields of yellow diketone **28**, mp 186−187 °C. Direct oxidation of **26** to **28** gave a lower yield (20%). The internal methyl proton chemical shifts for the three cyclophanes, **26** (δ 0.61), **27** (δ 0.56 and 0.84), and **28** (δ 0.89), were all shielded as expected. Attempted Wittig reaction on the diketone **28**, or reaction with vinyl or ethynyl Grignard reagents, caused cleavage of the cyclophane ring, as evidenced by the loss of these upfield methyl protons. However, a derivative of our target **21** could be obtained by reaction of **28** with *o*-phenylenediamine which gave 55−60% of cyclophane **29**, as yellow crystals, mp 211−213 °C. These showed the characteristic upfield cyclophane internal methyl protons at δ 1.20 and gave a correct mass spectrum molecular ion at *m/z* 384 and elemental analysis. Likewise, from dialdehyde **30**,[19] the dione **31** gave the cyclophane **32**.

Irradiation of benzene or THF solutions of **29** or **32** at 254 nm rapidly produces unstable reddish-purple solutions. We believe these contain the dihydropyrenes **33**, just as we observed for the monoannelated cyclophanedienes **8** and **10**. However, such symmetrically annelated annulenes have the possibility of biradicaloid structures contributing to the resonance hybrid (see structure **33**) which reduces the bond fixation in the strongly aromatic annelating arenes. This has been demonstrated in [*a,h*]-fused dihydropyrenes.[23] Such radical contributors prevent an unchallengeable structure proof from being obtained.[19] Unam-

(16) Murphy, R. S.; Chen, Y. S.; Ward, T. R.; Mitchell, R. H.; Bohne, C. *Chem. Commun.* **1999**, 2097−2098.
(17) *Spartan 02 for Windows*, version 1.0; Wavefunction, Inc.: Irvine, CA 92612.
(18) (a) Mitchell, R. H.; Yan, J. S. *Can. J. Chem.* **1977**, *55*, 3347−3348. (b) Mitchell, R. H.; Chen, Y. *Tetrahedron. Lett.* **1996**, *37*, 5239−5242.
(19) Mitchell, R. H.; Weerawarna, S. A. *Tetrahedron. Lett.* **1986**, *27*, 453−456.
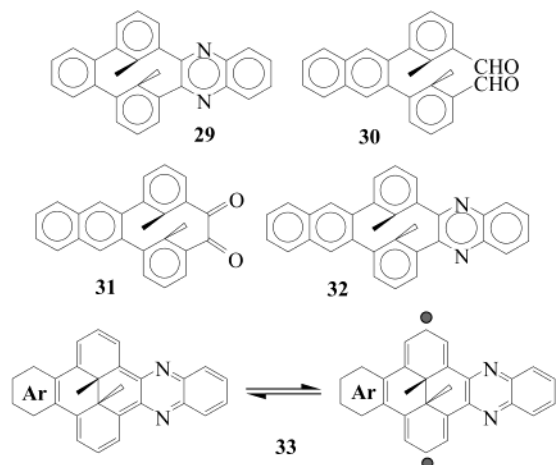(20) Mitchell, R. H.; Yan, J. S. H. *Can. J. Chem.* **1980**, *58*, 2584−2587.
(21) McMurry, J. E.; Kees, K. L. *J. Org. Chem.* **1977**, *42*, 2655−2656.
(22) Mancuso, A. J.; Huang, S. L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480−2482.
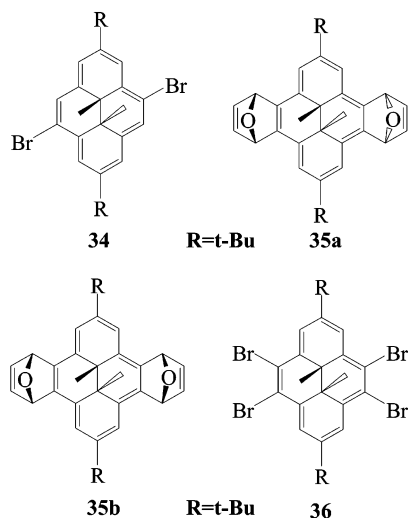
biguous formation of [*e*]-position dibenzannelated dihydropy-renes had to await the discovery of the "aryne route".[24]

Initially[18b] we utilized dibromide **34** with NaNH$_2$/*t*-BuOK in furan−THF to yield the adducts **35a,b** (1:1 mixture of isomers) in 60% yield. Subsequently, we found that use of the tetra-bromide **36** with *n*-BuLi as base in furan/THF improved the yield of **35** to 85%.

The *anti* isomer **35a**, with the two oxygens anti to each other, was less soluble, mp 236−238 °C, and showed only one internal methyl proton peak at δ −3.99, while the more soluble *syn* isomer **35b** showed two peaks at δ −3.70 and −4.30. Deoxygenation of the mixed isomers **35** with Fe$_2$(CO)$_9$ in refluxing benzene yielded 68% of the colorless cyclophane **21**, mp 231−232 °C. The internal methyl protons of **21** appeared at δ 1.07, and the UV spectrum was typical of that of a cyclophane rather than that of the highly colored dihydropyrenes.[11]

Photochemistry of 21. Irradiation of **21** with UV light (254 or 300 nm) at room temperature produced no apparent change; to prove that the valence isomerization does take place but the thermal return reaction is rapid, the irradiation was carried out at low temperature. Indeed, when a sample of **21** in d_8-THF in an NMR tube was cooled to about −90 °C (pentane−N$_{2(l)}$ bath),

(23) Mitchell, R. H.; Dingle, T. W.; West, P. R.; Williams, R. V.; Thompson, R. C. *J. Org. Chem.* **1982**, *47*, 5210−5214.
(24) Mitchell, R. H.; Zhou, P. *Tetrahedron. Lett.* **1990**, *31*, 5277−5280.

removed from the bath, and placed in front of a 300 nm source for one minute, the sample turned green. As the sample warmed, the green color was lost. This process could be repeated many times. If the cold green sample was wiped free of frost and quickly transferred to an NMR spectrometer at −50 °C, the spectrum of the green dihydropyrene **22** could easily be seen, with the internal methyl protons highly shielded at δ −3.41. Integration suggested a 35:65 ratio of **22/21**; warming the solution resulted in complete reversion to cyclophane **21**. The thermal return reaction, **22** to **21**, is essentially stopped, so long as the green solution is held at −50 °C or below. Irradiation of this green solution with visible light from an ordinary tungsten lamp quickly (<1 min) converts **22** to **21**. The photoreaction thus does proceed in both directions.

Thermal Reaction of 22 to 21. As we anticipated, thermal conversion of **22** to **21** is fast at room temperature. Using NMR integrations, E_{act} for the thermal reaction was estimated (see later) at 20 kcal/mol, giving DHP **22** a half-life of 400 min at −40 °C but only 1−2 s at 20 °C.

We thought that this thermal reaction might be slowed in the solid state. Evaporation of a dichloromethane solution of polystyrene mixed with CPD **21** on a glass plate gave a film, which when irradiated with 300 nm light at room temperature became green. When the plate was removed from the light, the green color faded after 2−3 s. The process could be repeated at least 15 times, even after storing the sample for a year. The photoisomerization was also observed when silica gel or alumina was used instead of polystyrene; however, the sample suffers some decomposition on these supports. Clearly the thermal reaction is slowed somewhat in the solid state.

Dinaphtho Annelated Derivative 38. Reaction of the dibromide **34** with isobenzofuran (generated in situ from 1-methoxyphthalan) and NaNH$_2$ gave 33% of the mixed isomers of **37** which when deoxygenated with Fe$_2$(CO)$_9$ as previously yielded 95% of colorless cyclophane **38**, mp 340−342 °C. Its internal methyl protons appeared at δ 1.06, similar to those of **21** (δ 1.07). However, irradiation of CPD **38** with 300 nm light at −90 °C produced no colored species. We suspect, based on the behavior of **10** relative to **8**, that the thermal reaction is just too fast to see any buildup of the DHP derived from CPD **38**.
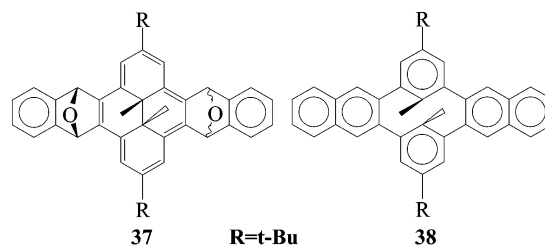
Synthesis of the elusive dibenzo annelated pair **21/22** has finally been achieved. Photoswitching between **21** and **22** is possible, but the very fast thermal return reaction has to be taken into account in any switching applications.

Molecules Containing More Than One Switch. Because of the stepped nature of the CPDs (see **2**), the π-orbitals of the benzenoid rings in **8** are prevented from overlapping to make a contiguous π-system, as is present in the DHP **7**. Thus, when **7** switches to **8**, an 18π-system switches to what is essentially a 6π-system. This is a rather dramatic change of the π-system and leads to the very different properties of **8** versus **7**. Multiple
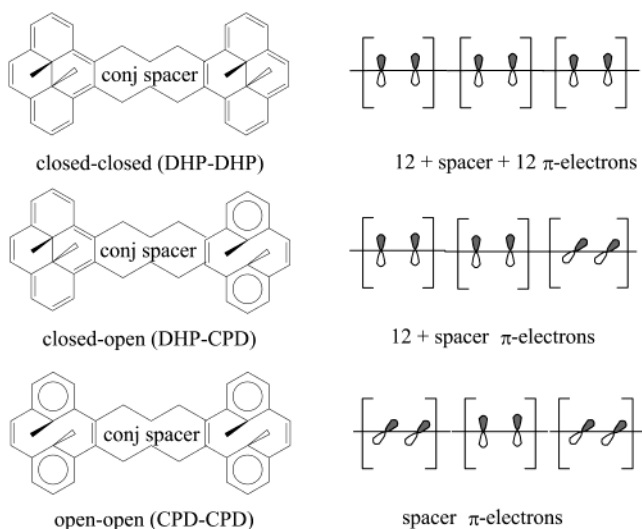
Figure 3.

state switches can in principle be obtained, by linking two or more dihydropyrenes together via conjugated spacers as in Figure 3.

In the closed—closed state, the π-system has $12 + \text{spacer} + 12 = 24 + s$ ($s =$ number of spacer π-electrons) contiguous planar p-orbitals; in the closed—open state, it has $12 + s$ planar p-orbitals; and in the open—open state, s p-orbitals. In the latter case, if s is less than 6, then the cyclophane benzene rings would dominate. Thus, if $s = 6$, that is, the spacer is a benzene ring, the switch goes from a 30π to essentially an 18π to a 6π-system as it changes its states. Such dramatic changes should lead to significantly different properties.

Our first[7] test of this idea utilizes chrysene as the spacer. The main reason for this choice was synthetic. The bis-furan **39** is accessible[25] easily from its precursor **40** and reacts with 2.7 equiv of bromide **41** in the presence of NaNH$_2$/t-BuOK in THF at room temperature to generate aryne **42**, which reacts twice in situ with the bis-furan to give a surprisingly good yield, 81%, of the adduct **43**, as mainly an equal mixture of two sets of two isomers (oxygen's *syn/anti*, methyl's *syn/anti* of *trans*).
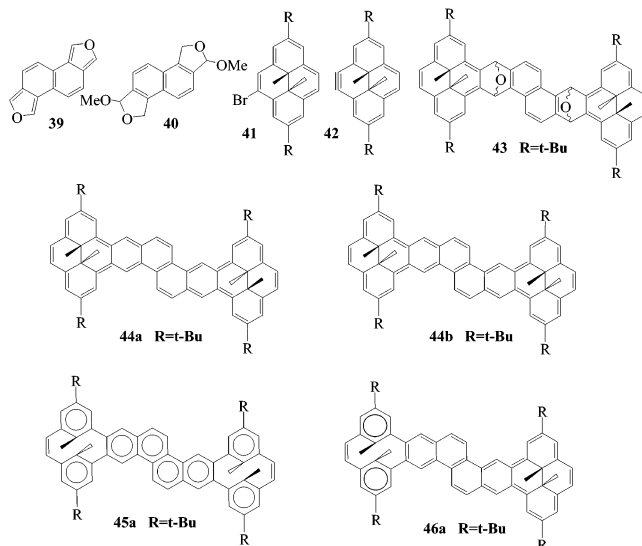
This mixture gave a correct mass spectrum at m/z 893 for MH$^+$ and showed the internal methyl protons at the characteristic shift

for dihydropyrenes, between δ -3 and -4. This mixture of isomers was directly deoxygenated with Fe$_2$(CO)$_9$ as previously to yield 82% of the bis(dihydropyreno)chrysene **44a,b**. These two isomers did not separate on TLC or column chromatography. In CDCl$_3$, the internal methyl protons appear together as a somewhat broadened singlet at δ -0.73, while the t-Bu protons appear in two sets at δ 1.57 and 1.52. In C$_6$D$_6$, the methyl protons separate into two peaks at δ -0.28 and -0.29 in an approximate 1:3 ratio, probably derived from two methyl signals from **44a** and one from **44b**. The two t-Bu signals remain at δ 1.45 and 1.44. The bay protons were also unresolved slightly broadened singlets.

The DHP—DHP **44** was intense red, with the most intense UV—vis band at 427 nm (ϵ = 132 000 dm^3 mol^{-1} cm^{-1}), strongly red shifted from that of **1** (338 nm).[26] The DHP **44** also shows longer wavelength bands at 527 and 576 nm ($\epsilon \approx$ 10 000) and a tail to 700 nm. Irradiation of a 5 mg sample of **44** with a light of a wavelength > 600 nm (from a 250W tungsten filament bulb and a 600 nm cutoff filter) in an ice—water chilled d_8-toluene solution enabled the photoswitching to be followed conveniently by NMR, Figure 4.

Conversion of DHP—DHP **44** (Figure 4, left, top) to CPD—CPD **45** (Figure 4, left, bottom) was complete after about 75 min of irradiation. No evidence by NMR (or UV, see later) could be found for CPD—DHP **46** (Figure 4, right) at intermediate irradiation times. As can be seen from Figure 4, the internal methyl protons of **44** at δ -0.22 are replaced by those of **45** (two isomers) at δ 1.71−1.75, and likewise, the *tert*-butyl signals become less deshielded, moving from $\sim\delta$ 1.6 to 1.45. The other isomer, CPD—DHP **46**, could however be observed in both the thermal and UV induced reverse reactions. It showed a new NMR signal for the internal methyl protons at δ -0.27 (those of **44** were at δ -0.22 in d_8-toluene) and a new t-Bu signal at δ 1.62 (those of **44** were at δ 1.66 and 1.64). Likewise, when a cyclohexane solution of **44** was similarly irradiated, the 427 nm absorption of **44** disappeared into the baseline and only the chrysene absorption at 313 nm remained.[27] The presence of an isosbestic point suggested also that **46** was not involved. In cyclohexane, on UV ($\sim$350 nm) irradiation, new peaks first appeared at 392 and 413 nm, which then reduced and were replaced by those of **44** at 406 and 427 nm.[27]

Thus, although the closed—closed and open—open states of the switch could be attained fairly easily, the intermediate position, open—closed (isomer **46**), could not be obtained as a single species, only mixed with **45** early in the return reaction or with **44** late in the reaction. Clearly, future work on switches with DHPs at both ends needs to find a way of distinguishing one end from the other, so that the intermediate switch position can be more clearly attained.

Relatively few systems appear to have been reported where several photochromes are linked, and as far as we know, none, where a rigid conjugated spacer is used. Interestingly, in the most closely connected analogues, the dithienylethylenes of Irie and Branda, four papers[28] report dithienylcyclopentenes linked by conjugated but not rigid spacers, and in all of these papers, it appears that both photochromes do not close. It is not obvious to us why the dihydropyrenes do.

(25) Yu, D. W.; Preuss, K. E.; Cassis, P. R.; Dejikhangsar, T. D.; Dibble, P. W. *Tetrahedron Lett.* **1996**, *37*, 8845−8848.
(26) Boekelheide, V.; Phillips, J. B. *J. Am. Chem. Soc.* **1967**, *89*, 1695−1704.
(27) See Figure 2 in ref 6.
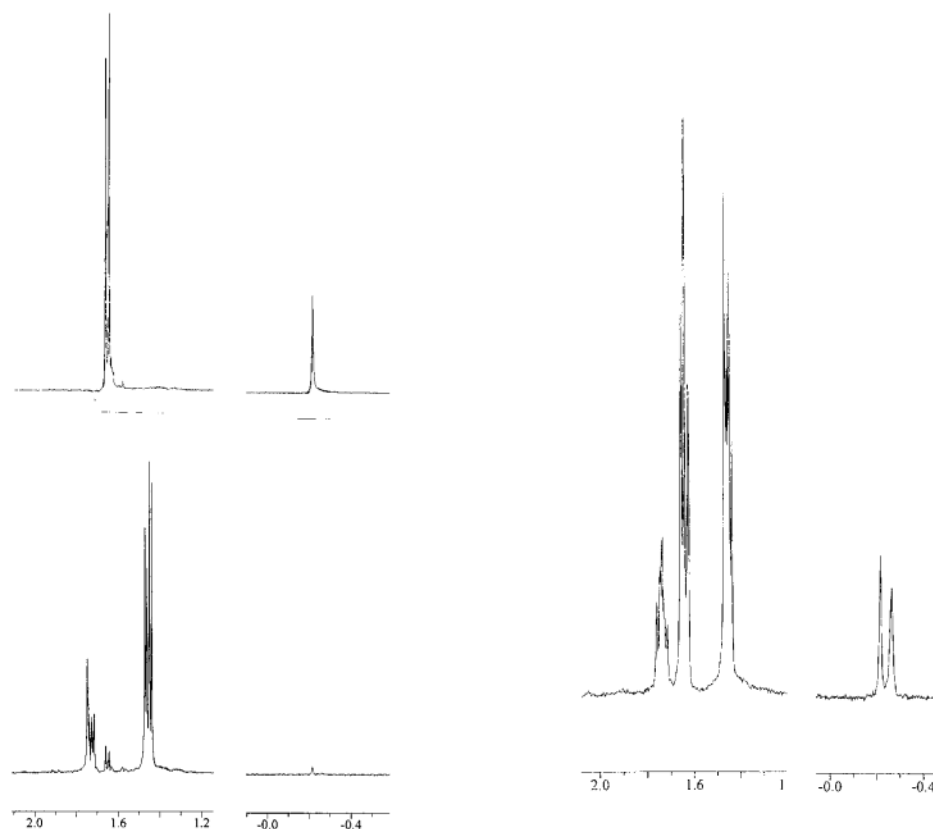
Figure 4. Partial ^{1}H NMR spectrum of DHP−DHP **44** (top left) before irradiation with visible light and after irradiation to form CPD−CPD **45** (bottom left) and then (right) after thermal or UV closing to form some CPD−DHP **46** and then DHP−DHP **44**.

A Clear Three Position Photoswitch. One method of distinguishing one DHP from the other is to dibenzannelate one. As we observed previously, a DHP with a benzene fused at both [*e*]-positions has a thermal state that is open, that is, **21**. Having only one benzene [*e*]-fusion gives a thermal state that is closed, that is, **7**. Thus, compound **47** should be the thermally stable state of the three way switch **48/47/49**, which on irradiation with UV should close to **48** or on irradiation with visible light should open to **49**. Isomers **48** and **49** should both thermally return to **47** or by irradiation with visible or UV light, respectively.
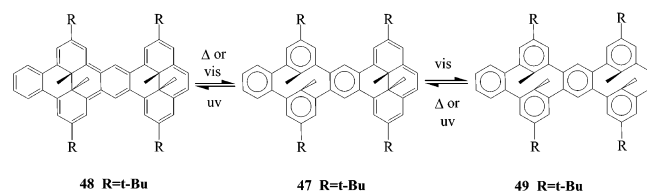
Synthesis and Structure of 47. Reaction of dibromobenzopyrene **13** with excess isofuran **19** in toluene at −40 °C with *n*-butyllithium for just 15 min gave about 12% of a 1:1 mixture of the adducts **50a** and **50b**. Despite much experimentation, this yield could not be improved. This mixture showed the expected eight internal methyl proton signals in its ^{1}H NMR spectrum and was used in the next step directly. However, chromatography yielded one isomer pure, mp 222−225 °C, which showed

(28) Peters, A.; Branda, N. R. *Adv. Mater. Opt. Electron.* **2000**, *10*, 245. Kawai, T.; Sasaki, T.; Irie, M. *Chem. Commun.* **2001**, 711−712. Osuka, A.; Fujikane, D.; Shinmori, H.; Kobatake, S.; Irie, M. *J. Org. Chem.* **2001**, *66*, 3913−3923. Kaieda, T.; Kobatake, S.; Miyasaka, H.; Murakami, M.; Iwai, N.; Nagat, Y.; Irie, M. *J. Am. Chem. Soc.* **2002**, *124*, 2015−2025.

four distinct internal methyl proton signals at δ −4.18, −3.60 (DHP) and −1.99, and −1.04 (benzo-DHP), as well as four distinct *tert*-butyl signals. Mass spectroscopy (LSIMS and exact mass) confirmed the overall structure.
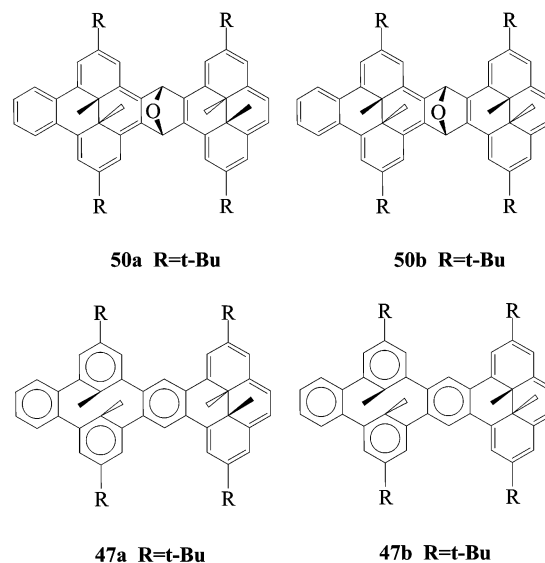
Deoxygenation of the mixed isomers with Fe$_2$(CO)$_9$ gave about 60% yield of two isomers of **47**, namely **47a** and **47b**, while deoxygenation of the chromatographed single isomer of **50** gave a single isomer of **47**, in which the DHP internal methyl protons appeared at δ −1.37 (DHP). From the spectra of the mixed isomers, the corresponding signals for the methyl protons of the other isomer were at δ −1.67. The CPD methyl protons

were at δ 1.18 in both isomers. The overall structure was confirmed again by mass spectroscopy (EI and exact mass), but in the absence of an X-ray structure, it is difficult to be certain which isomer is which. We have previously prepared[29] the furans **51a** and **51b**, and by analysis of their ^{1}H NMR spectra and AM1 calculated structures, we suggested that **51b** was the less distorted and had the most shielded internal methyl DHP protons (δ −1.66) and most deshielded aromatic proton (H-4, δ 9.10); isomer **51a** signals were at δ −1.37 and 8.95, respectively. Since the isomer we separated had internal methyl DHP protons at δ −1.37 and the most deshielded proton at δ 8.94 (the other isomer was δ −1.67 and 9.09), this is strongly suggestive that the single isomer of **47** that we were able to obtain pure was **47a**.

51a R=t-Bu   **51b** R=t-Bu   **52** R=t-Bu
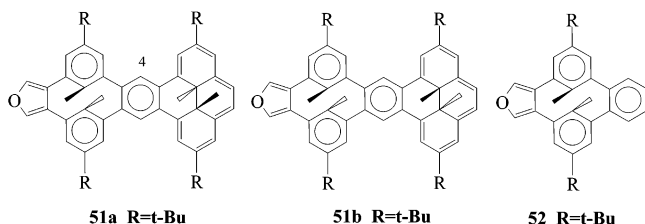
In an attempt to improve the yield, we also tried an alternate method of adduct formation, namely a reaction of furan **52**[29] with aryne **42** derived from bromide **41**. However, despite several tries, no product could be isolated. The more condensed adducts **50** decompose slowly on standing in solution, need protection from air and light, and are substantially less robust than the simple adducts such as **35** which lead to the simple benzo-derivatives. As well, the more condensed dihydropyrenes such as **47** are also more sensitive to air and light than their simpler counterparts, and for example, NMR solutions on standing give spectra with broader lines.

Photochemistry of 47. Despite these longer term stability problems, the DHP unit in **47** easily opens on irradiation either with broad band (household tungsten lamp) white light or with a 598 nm cut off filter to give the colorless bis-CPD **49**. The intense red of **47** thus bleaches with visible light, the main λ_{max} of **49** at 268 nm,[2] but can be returned on irradiation at 300 nm or thermally (see later). The photoswitching of **47/49** can also be followed by ^{1}H NMR but, because of stability problems, not in a halogenated solvent. In d_8-toluene, the internal methyl protons of the single isomer **47a** were found at δ −1.01 (DHP) and 1.64 (CPD). On photoswitching, this solution gave peaks at δ 1.78 and 1.58 corresponding to the bis-CPD **49**. Again, this reversed with 300 nm light. There were similar changes in the other protons; for example, the most deshielded bay protons of **47** at δ 9.7 and 8.9 disappear on irradiation and reform thermally, while the olefinic protons of **49** at δ 6.6 form on irradiation and then disappear thermally.

Accessing the other photoisomer **48** was expected to be more difficult, because of the extremely easy thermal return (see **21**). Laser flash photolysis of **47** at 355 nm (10 ns pulse) in deaerated cyclohexane solution produced a transient with a new λ_{max} at 486 nm, corresponding to the larger π-system of **48**, while that due to **47** at 406 nm decreased in intensity.

Thermal Reaction of 48. In the thermal reaction, the peak at 486 nm decreased, and the peak at 406 nm reformed, with a

(29) Mitchell, R. H.; Ward, T. R.; Wang, Y. *Heterocycles* **2001**, *54*, 249−257.

Table 2. Thermal Return Reaction (CPD to DHP) Reaction Rates (min^{-1} at 46 °C), Half-Lives ($\tau_{1/2}$, H, 46 °C), and Energies of Activation (E_{act}, kcal/mol) for the Thermal Reactions Shown[a]

reaction	k	$\tau_{1/2}$	E_{act}
12 → 11	0.0344(9)	0.33	19.1
10 → 9	0.0101(3)	1.15	22.1
6 → 5	0.006 10(12)	1.88	24.0
45 → 44	0.0057(2)	2.0	24
16 → 15	0.003 07(7)	3.76	23.9
49 → 47	0.002 24(6)	5.16	24.1
8 → 7	0.002 00(5)	5.75	24.5
14 → 13	0.001 24(3)	9.50	25.8
19′ → 19	0.000 183(6)	63.3	26.1

[a] Note: Since **45** to **44** has intermediate **46**, the value for E_{act} is the overall reaction apparent value. **19′** is the CPD form of **19**. Values in parentheses after the rates are 3σ errors, based on integration error estimates.

half-life of about 0.1 s at 20 °C. Based on an E_{act} of about 20 kcal/mol, the parent system **22** has a half-life of about 2 s at 20 °C. There are more steric interactions present in **48** than in **22**, and so, the former would be expected to revert thermally to **47** faster than **22** does to **21**, consistent with our observations. Even after hundreds of laser flashes, in the absence of oxygen and in cyclohexane, the UV spectrum of **47** was returned unchanged at the end of the experiment.

Thus, it is possible to prepare a three way switch where the other two states (**48, 49**) of the switch thermally revert to the central position (**47**) and where different signals (vis, UV) do the switching.

Thermal Return of CPDs to DHPs. Because the thermal return reactions have E_{act} values around 24 kcal/mol, the reactions can conveniently be followed by ^{1}H NMR spectroscopy, using the sharp methyl or *tert*-butyl signal integrations to estimate the amounts of CPD and DHP present. The thermal return reactions follow first-order kinetics,[4] and so for comparison, the reaction rates, and more conveniently for discussion, the half-lives at 46 °C arranged in increasing value order, and E_{act} values are shown in Table 2.

Not surprisingly, the three way switch **49** has similar values as the benzo system **8** and the chrysene containing switch **45** behaves between the naphtho switch **10** and the benzo switch **8**.

Because of the thermal return reaction, dihydropyrenes are both T and P types.[4] If the thermal return reaction could be shut down, they would then be pure P-type. Clearly converting the benzo ring of **7/8** into a different arene increases the thermal return rate. The exception is the furan **19**. In the dithienylethenes of Irie,[30] replacement of the benzene rings of *cis*-stibene with less aromatic thiophene rings results in less of a loss of aromatic stabilization energy of the closed versus the open form. However, in the dihydropyrene **7**, it is the ethene bridge of stilbene (metacyclophanediene) that has been annelated. In our cases, if the forbidden thermal reaction involves some intermediate with partial ionic character, then the annelating aromatic with the largest resonance energy should stabilize the charge better, and so in our cases, we would expect the thermal rates to be in the order anthracene > naphthalene > benzene > furan, which indeed (Table 2) is exactly the order found. Unfortunately, the furan **19**, despite its nice slow thermal return rate, is too unstable to use as a photoswitch. Although it opens readily and cleanly with visible light, photoclosing with UV causes some

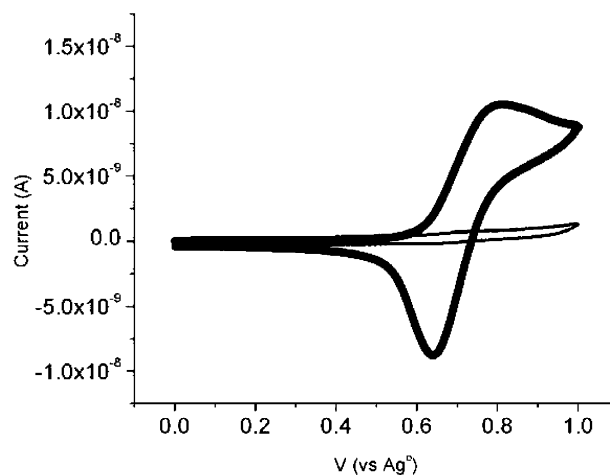(30) Irie, M. *Chem. Rev.* **2000**, *100*, 1685−1716.

decomposition, and as well, it is somewhat air sensitive. It does suggest that it would be worth investigating other heteroarenes, for example, the thiophene fused species in the future. The fact that steric bulk at the 4,5-positions of **7/8**, as in the dibromide **13/14**, also slows the thermal return reaction suggests that, instead of switches with fused arene spacers (as in **44** and **48**), perhaps sterically bulky substituted spacers might be worth pursuing. We shall report on such attempts in the future.

Best Switch So Far, the Benzo Switch 7/8. The best "switch" in the dihydropyrene series is the benzo switch **7/8**. It has a reasonably slow thermal return yet relatively good photo-opening and -closing. We need to examine in detail though how substituents change the quantum yields and the thermal return rate.

It would be helpful if such an investigation could be guided by calculations. We have noted previously that AM1 type calculations give quite reasonable results for ΔH_f calculations, but they fail miserably however at predicting reliable bond lengths and at predicting the $S_0 - S_1$ transition (the band gap E_g). DFT calculations give reliable bond length data for these annulenes[31] but do not solve the band gap problem; for example, simple estimation of E_g for benzo-DHP **7** by subtracting E_{HOMO} from E_{LUMO} yields the highly overestimated values of 1117 and 1127 nm for AM1 and DFT calculations, respectively, while the experimental value is 584 nm. We were pleased to find that time dependent (TD-DFT) calculations[32] yielded a value for **7** of 580 nm and likewise for **8** a value of 380 nm (experimental, 404 nm).

Electrochemical Readout of the Benzo Switch. We have noted previously that the CPD isomers of the photochromic compounds discussed in this paper are essentially isolated 6π-systems, while the DHP isomers have contiguous large π-systems. In the case of **7**, there are 18 contiguous π-orbitals. The change in the π-system, $\Delta\pi$, on photoswitching, is thus rather dramatic. Electrochemically, the 6π-system, benzene, is relatively inert. The 18π-system, **7**, should be relatively easy to oxidize electrochemically. Electrochemical readout of the two states of the photochrome **7/8** should thus be relatively easy and clear. Indeed, when a solution of benzopyrene **7** in dry degassed dichloromethane containing TBA PF$_6$ was placed in a quartz cell using Pt button electrodes and a Ag^0 reference electrode, using a scan rate of 100 mV/sec over a potential window from 0 to 1.00 V (ferrocene $E_{p,a} = 0.55$ V), the peak anodic current ($E_{p,a}$) was centered at 0.75 V. The cell was then irradiated with a 500 W household tungsten lamp affixed with a 400 nm cutoff filter for a few seconds, which completely opened **7** to CPD **8**, and then across the same potential window, this state was redox silent. The cyclic voltammogram is shown in Figure 5. Switching the light source to a 4 W 365 nm ultraviolet light rapidly promoted the back reaction and gave the same redox features as before. The results appeared to be stable over several cycles, though no quantitative degradation studies were made at this time. The cyclic voltammogram clearly demonstrates that the electrochemical readout of each state is unequivocally discernible.

(31) Mitchell, R. H.; Chen, Y.; Iyer, V. S.; Lau, D. Y.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 2907−2911. Williams, R. V.; Armantrout, J. R.; Twamley, B.; Mitchell, R. H.; Ward, T. R.; Bandyopadhyay, S. *J. Am. Chem. Soc.* **2002**, *124*, 13495−13505.
(32) For example, see: Houk, K. N.; Lee, P. S. Nendel, M. J. *J. Org. Chem.* **2001**, *66*, 5517−5521. Performed using Gaussian 98W (revision A.9), Gaussian, Inc, Pittsburgh, PA, 1998.

Figure 5. Cyclic voltammogram of DHP **7** (bold line, redox active) and CPD **8** (fine line, redox silent).

Clearly, study of future photochromic systems using electrochemistry will also be worthwhile.

Summary and Conlusions

Simple arene [*e*]-fused dihydropyrenes are negative photochromes, where the thermally stable form is colored. We conclude that the benzo compound **7/8** is the best photochrome in this series and has the best combination of desirable properties, namely 100% switching, reasonably high quantum yield, good stability, and slow thermal return. We have also prepared the positive photochrome, the dibenzo derivative **21/22**, in which the colorless form is the thermally stable one. This can also be photochemically switched but has a very fast thermal return reaction. By fusing two dihydropyrenes onto a common chrysene spacer, **44**, a switch was obtained with more than two states. Although the fully open **45** and fully closed **44** states of the switch were easily accessible, it was not possible to access the third position, **46**, completely. The three way switch **47/48/49**, which contains both mono- and dibenzannelated dihydropyrenes, has a cleanly accessible middle switch position but difficult to obtain fully closed position, **48**. Switches containing dihydropyrenes joined by fused conjugated spacers also have limited stability. Overall this suggests that future efforts should be made by joining benzo systems with nonfused arene spacers, to improve stability and give optimal switching properties. Bulky substituents at the 4,5-positions may also serve to slow the thermal return reaction. Electrochemical readout of the state of the switch is demonstrated for the benzo system as a potential useful alternative to optical readouts.

Experimental Section

Melting points were determined on a Reichert 7905 melting point apparatus integrated to an Omega Engineering model 199 chromel−alumel thermocouple. Infrared spectra, calibrated with polystyrene, were recorded as KBr disks on a Bruker IFS25 FTIR spectrometer and only the major fingerprint bands are reported. UV−visible spectra were recorded on a Cary 5 UV−vis−NIR spectrometer using cyclohexane as solvent unless otherwise stated. Proton NMR spectra were recorded, unless otherwise specified, on a Bruker AMX 360 spectrometer at 360 MHz in CDCl$_3$, using the solvent residual peak for calibration (7.240 ppm for CHCl$_3$). Where stated, 250 MHz spectra were recorded on a Bruker WM 250. Carbon NMR spectra were recorded at 90.6 MHz (or where stated 62.9 MHz), using the solvent (CDCl$_3$) peak at 77.0 ppm for calibration. Where peaks within the same sample are very close

in chemical shift, a third decimal place is given. Mass spectra were recorded on a Finnigan 3300 gas chromatography–mass spectroscopy system using methane as a carrier gas for chemical ionization. Exact mass measurements were obtained on a Kratos Concept-H instrument using perfluorokerosene as the standard. Elemental analyses were performed by Canadian Microanalytical Services Ltd., Vancouver, B. C. All evaporations were carried out under reduced pressure on a rotary evaporator or by using an oil pump and dry ice condenser. SiGel refers to Merck silica gel, 60–200 mesh. Alumina refers to Aldrich aluminum oxide, activated, neutral, Brockmann I, standard grade, ~150 mesh. Solutions of oxygen sensitive compounds for NMR spectroscopy were prepared by dissolving the compound in the minimum amount of deuterated solvent, filtration through alumina deactivated with 5% water, rinsing the alumina with sufficient deuterated solvent to make up the correct volume for the spectrometer, and bubbling argon through the filtrate in the NMR tube for 5–10 min. The tubes were then carefully capped under argon, and the spectra obtained. NMR spectra of photoisomerizable compounds were obtained using 5 mm amber NMR tubes. Where NMR assignments are made, these were on the basis of 2D COSY/NOESY experiments for ^{1}H and HETCORR/HMQCB experiments for ^{13}C. H-1,2 means H-1 and H-2; H-1/2 means H-1 or H-2. Expanded data sets were used to obtain coupling constant data.

To clarify the NMR assignments, numbering of the relevant parent structures is shown here in the order they appear in the experiment (compound numbers in parentheses):
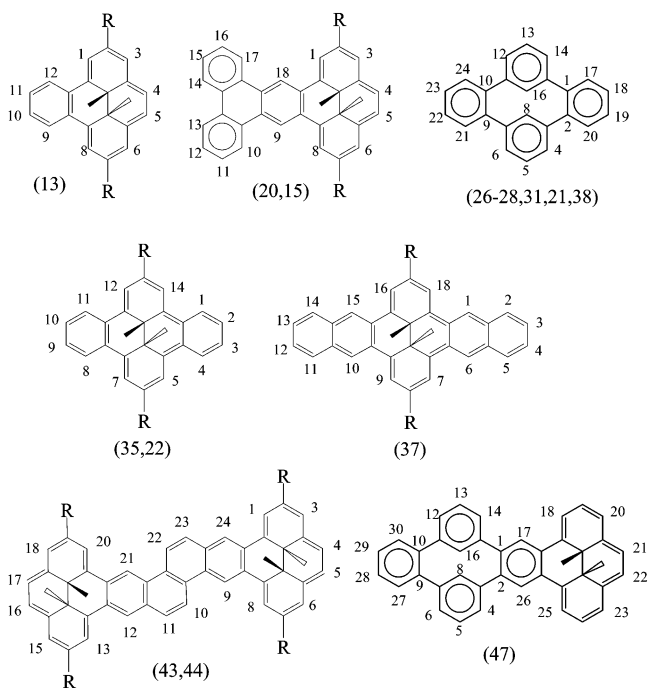
4,5-Dibromo-2,7-di-*tert*-butyl-*trans*-12c,12d-dihydro-12c,12d-dimethylbenzo[*e*]pyrene 13. A solution of vacuum-dried benzopyrene **7**[11b] (285 mg, 0.721 mmol) in dry CH$_2$Cl$_2$ (200 mL) was prepared under argon in the dark and cooled in an ice bath. NBS (vacuum-dried, 257 mg, 1.44 mmol) in dry DMF (40 mL) was then added slowly with stirring. After the addition, the reaction mixture was allowed to warm to room temperature and let stir for 2 h. The reaction mixture was then poured into hexanes (280 mL) and was washed with water (8 × 200 mL). The organic phase was separated, dried, and evaporated. The residue was purified by repeated (4×) chromatography (to remove fluorescent close moving compounds) on SiGel (deactivated with 5% water), using hexanes/CH$_2$Cl$_2$ (9:1) as eluant and yielded 191 mg (48%) of purple crystals of the dibromide **13**, which on recrystallization from cyclohexane had mp (dec) 187–189 °C; ^{1}H NMR δ 8.69–8.64 (AA′XX′, 2H, H-9,12), 8.21 (d, *J* = 1.3 Hz, 2H, H-1,8), 7.73 (d, *J* =

1.3 Hz, 2H, H-3,6), 7.65–7.60 (AA′XX′, 2H, H-10,11), 1.49 (s, 18H, C(CH$_3$)$_3$), −1.30 (s, 6H, CH$_3$); ^{13}C NMR δ 148.67, 136.16, 135.71, 129.15, 126.67 (C-10,11), 124.69 (C-9,12), 120.15 (C-3,6), 117.51 (C-1,8), 117.04, 39.13, 35.87, 30.37 (C(*C*H$_3$)$_3$), 17.34 (C-12c,d); IR 1616, 1602, 1475, 1445, 1367, 1361, 1318, 1255, 1201, 1121, 1000, 959, 913, 866, 800, 754, 637, 610 cm^{-1}; CIMS *m/z* 551, 553, 555 (MH$^+$) (Br$_2$ pattern). Anal. Calcd for C$_{30}$H$_{32}$ Br$_2$: C, 65.23; H, 5.84. Found: C, 65.33; H, 5.89.

2,7-Di-*tert*-butyl-9,18-epoxy-18c,18d-dimethyl-9,18,18c,18d-tetrahydrotetrabenzo[de,j,l,qr]naphtacene 20. NaNH$_2$ (570 mg, 14.6 mmol) and *t*-BuOK (2 mg) were added to a stirred solution of the isofuran **19**[11b] (84 mg, 0.22 mmol) and 9-bromophenanthrene (282 mg, 1.10 mmol) in dried THF (25 mL) under argon. The mixture was stirred overnight, and then methanol (5 mL) and hexanes (25 mL) were added. The organic phase was washed, dried, and evaporated. The solid was chromatographed over deactivated SiGel using benzene/hexanes (1:1) as eluant. The green band was collected and gave 104 mg (85%) of the adduct, which on recrystallization from toluene gave dark green crystals: mp 221–222 °C; ^{1}H NMR δ 8.59 (d, *J* = 8.3 Hz, 2H, H-13,14) 8.43, 8.40 (d, *J* ≈ 1.2 Hz, 1H each, H-1/8), 8.41, 8.27 (dd, *J* = 8.1 Hz, 1.1 Hz, 1H each, H-10/17), 8.13, 8.10 (d, *J* = 1.2 Hz, 1H each, H-3/6), 8.07 (s, 2H, H-4,5), 7.63, 7.61 (s, 1H each, H-9/18), 7.72–7.64, 7.59–7.52 (m, 2H each, H-11,16/12,15), 1.66, 1.63 (s, 9H each, C(CH$_3$)$_3$), −3.14, −4.12 (s, 3H each, CH$_3$); ^{13}C NMR δ 145.52, 145.30, 145.01, 144.66, 137.28, 136.22, 136.18, 135.76, 129.61, 129.47, 127.81, 127.22, 126.78 and 126.75 (C-11,16), 126.67, 126.62, 126.04 and 125.97 (C-12,15), 124.47 and 124.36(C-4,5), 124.23 and 124.03 (C-10,17), 123.57 (C-13,14), 121.23 (C-3,6), 115.47 and 114.70 (C-1,8), 81.72 and 81.14 (C-9,18), 35.74, 35.69, 34.21, 33.32, 31.54 and 31.51 (C(*C*H$_3$)$_3$), 16.50 and 14.25 (C-18c,d); IR (KBr) 1616, 1448, 1363, 1343, 1260, 883, 865, 777, 755, 745, 721, 716, 671, 632 cm^{-1}; CIMS *m/z* 561 (MH$^+$). Anal. Calcd for C$_{42}$H$_{40}$O: C, 89.96; H, 7.19. Found: C, 89.66; H, 7.34.

2,7-Di-*tert*-butyl-*trans*-18c,18d-dimethyl-18c,18d-dihydrotetrabenzo-[de,j,l,qr]naphtacene 15. A mixture of the epoxide **20** (88 mg, 0.16 mmol) and Fe$_2$(CO)$_9$ (88 mg, 0.24 mmol) in benzene (30 mL) was refluxed under argon in the dark for 5 h. After the mixture was cooled to room temperature, it was filtered through a short column (5 cm) of deactivated SiGel using benzene as eluant. The solvent was then removed, and the dark purple solid product was carefully washed with pentane until the initial brownish color disappeared and gave 73 mg (86%) of the product **15**. Slow evaporation from hexanes/CH$_2$Cl$_2$ yielded dark purple crystals: mp (dec) 188–193 °C; ^{1}H NMR δ 9.92 (s, 2H, H-9,18), 8.92 (dd, *J* = 8.2 Hz, 1.3 Hz, 2H, H-10,17), 8.67 (dd, *J* = 8.2 Hz, 1.2 Hz, 2H, H-13,14), 8.40 (d, *J* = 1.3 Hz, 2H, H-1,8), 7.78–7.74 (m, 2H, H-11,16), 7.71–7.67 (m, 2H, H-12,15), 7.23 (d, *J* = 1.2 Hz, 2H, H-3,6), 6.99 (s, 2H, H-4,5), 1.55 (s, 18H, C(CH$_3$)$_3$), −1.07 (s, 6H, CH$_3$); ^{13}C NMR δ 144.51, 138.81, 135.19, 130.15, 130.06, 128.59, 127.54, 127.46 (C-11,16), 127.37 (C-12,15), 123.53 (C-13,14), 123.33 (C-10,17), 121.26 (C-4,5), 120.15 (C-3,6), 118.57 (C8,19), 117.43 (C-1,8), 36.47, 35.39, 30.63 (C(*C*H$_3$)$_3$), 18.31 (C-18c,d); UV (CHCl$_3$) λ$_{max}$ (ε$_{max}$) nm 284 (43 200), 337 (38 600), 374 sh (22 200), 392 (46 200), 412 (72 400), 529 (5700), 644(600); IR (KBr) 1627, 1605, 1490, 1434, 1360, 1227, 886, 872, 754, 719, 673 cm^{-1}; CIMS *m/z* 545 (MH$^+$). Anal. Calcd for C$_{42}$H$_{40}$: C, 92.60; H, 7.40. Found: C, 92.58; H, 7.64.

***anti*-8,16-Dimethyl-9,10-benzo[2.2]metacyclophane-*trans*-1,2-diol 26.** Zn–Cu couple[33] (13.6 g, 202 mmol) was added to TiCl$_3$ (15.7 g, 102 mmol) in dry 1,2-dimethoxyethane (400 mL) under N$_2$, and the solution was stirred vigorously under reflux for 15 h, which yielded a black slurry. The dialdehyde **25**[20] (1.46 g, 4.46 mmol) in dimethoxyethane (1500 mL) was then added slowly to the refluxing slurry over 85 h. After the mixture was cooled in ice, saturated aq K$_2$CO$_3$ (300 mL) was added over 1 h. The reaction mixture was then filtered through

(33) Gribble, G. W.; Leese, R. M. *Synthesis* **1977**, 172–176.

a short pad of florisil, dried, and evaporated. The crude product was then chromatographed over florisil (15 cm × 1.5 cm) using hexanes/ THF (1:4) as eluant to yield 1.1 g (78%) of white crystals of diol **26**: mp 215−218 °C; ^{1}H NMR (250 MHz, d_8-THF) δ 7.71−7.65 (m, 4H), 7.44−7.41 (m, 2H), 7.07−7.04 (m, 4H), 4.98 (bs, 2H, −OH), 4.24 (s, 2H, H-1,2), 0.61 (s, 6H, CH$_3$); ^{13}C NMR (62.9 MHz, d_8-THF) δ 143.06, 139.27, 138.66, 138.02, 130.73, 129.45, 129.04, 125.65, 124.91, 81.29, 17.22; IR 3510, 3365, 1446, 1418, 1050, 1032, 1012, 752, 738, 714 cm^{-1}; EIMS at m/z 316 (M$^+$). Anal. Calcd for C$_{22}$H$_{20}$O$_2$: C, 83.51; H, 6.37. Found: C, 83.48; H, 6.32.

anti-8,16-Dimethyl-9,10-benzo[2.2]metacyclophan-1-ol-2-one 27. Dry DMSO (2 mL, 26 mmol) was added to oxalyl chloride (l mL, 11 mmol) in dichloromethane (25 mL) maintained at −30 °C under nitrogen. The mixture was stirred for 2 min, and then the diol **26** (0.46 g, 1.45 mmol) in THF (5 mL) was added within 5 min. The reaction mixture was then stirred for 1 h at −30 °C, and then triethylamine (7 mL, 50 mmol) was added; the mixture was stirred again for 30 min. The reaction mixture was then allowed to warm to ambient temperature and extracted with diethyl ether (150 mL). The ether layer was washed with water (100 mL) and 10% aq HCl (100 mL). Each aq layer was re-extracted with diethyl ether (150 mL), and organic layers were combined. These were then washed with water, 5% aq Na$_2$CO$_3$, and water and then were dried and evaporated. The crude product obtained was chromatographed on a column of florisil (15 cm × 1.5 cm) using pentane/dichloromethane (1:9) as eluant to give the product, which was recrystallized from chloroform/hexane to give 0.41 g (90%) of **27** as white crystals: mp 205−208 °C; ^{1}H NMR (250 MHz, d_8-THF) δ 7.77− 7.70 (m, 2H), 7.52−7.44 (m, 3H), 7.23−7.05 (m, 5H), 5.26 (d, $J = 4$ Hz, 1H), 5.11 (d, $J = 4$ Hz, 1H, −OH), 0.84 and 0.56 (s, 3H each, −CH$_3$); ^{13}C NMR (62.9 MHz, d_8-THF) δ 203.70, 142.01, 141.75, 140.19, 138.52 (×2), 138.01, 134.07, 133.73, 132.81, 131.57, 129.86, 129.69, 129.57, 129.46, 126.72, 126.49, 125.20, 124.37, 82.97, 17.19, 17.10; IR 3462, 1702, 1447, 1410, 1132, 1112, 1052, 940, 789, 759, 748, 732 cm^{-1}; EIMS m/z 314 (M$^+$). Anal. Calcd for C$_{22}$H$_{18}$0$_2$: C, 84.05; H, 5.77. Found: C, 84.06; H, 5.75.

anti-8,16-Dimethyl-9,10-benzo[2.2]metacyclophane-1,2-dione 28. Dry DMSO (2 mL, 26 mmol) was added to a stirred solution of oxalyl chloride (1 mL, 11 mmol) in dichloromethane (25 mL) maintained at −30 °C under nitrogen. After 2 min, the hydroxyketone **27** (0.52 g, 1.7 mmol) in dichloromethane (5 mL) was added over 5 min, and the mixture was then stirred for 1 h at −30 °C. Triethylamine (7 mL. 50 mmol) was then added, and the mixture was stirred for a further 30 min at −30 °C. The reaction mixture was then allowed to warm to ambient temperature and was extracted with dichloromethane (150 mL) and washed with water and 10% aq HCl. The aq layers were re-extracted with dichloromethane (150 mL), and the combined organic layers were then washed with water, 5% aq Na$_2$CO$_3$, and water and then were dried and evaporated. The crude product was chromatographed on a column of florisil (10 cm × 1.5 cm) using pentane/ dichloromethane (1:9) as eluant to give the diketone product, which on recrystallization from ether/hexanes gave 0.46 g (89%) of **28** as yellow crystals: mp 178−180 °C; ^{1}H NMR (250 MHz, CD$_2$Cl$_2$) δ 7.80−7.74 (AA′XX′, 2H), 7.58−7.51 (AA′XX′, 2H), 7.49−7.16 (m, 6H), 0.89 (s, 6H); ^{13}C NMR (62.9 MHz, CD$_2$Cl$_2$) δ 191.84, 140.37, 139.34, 139.29, 134.77, 134.28, 129.86, 129.63, 128.08, 127.73, 18.45; IR 1680, 1551, 1403, 1368, 1214, 913, 795, 775, 745, 710 cm^{-1}; UV (CH$_2$Cl$_2$) λ_{max} (ϵ_{max}) nm 249 (49 500), 323 (3260); EIMS m/z 312 (M$^+$). Anal. Calcd for C$_{22}$H$_{16}$0$_2$: C, 84.59; H, 5.16. Found: C, 84.45; H, 5.44.

Direct Oxidation of Diol 26 to Diketone 28. Sulfur trioxide/pyridine complex (2.00 g, 12.6 mmol) in DMSO (10 mL) at 20 °C under nitrogen was added to the diol **26** (0.75 g, 2.4 mmol) in DMSO (10 mL) and triethylamine (6.12 g, 8.4 mL, 60 mmol) at −20 °C. The reaction mixture was stirred under nitrogen for 3 h and then was acidified with 10% aq HCl. The product was precipitated by adding water. The precipitate was collected and then was extracted with dichloromethane

(25 mL), dried, and evaporated. The residue was chromatographed on florisil (12 cm × 1.5 cm) using dichloromethane/pentane (9:1) as eluant and gave 0.15 g (20%) of the diketone **28**, identical to the previous sample.

Benzoquinoxalinocyclophane 29. The diketone **28** (0.25 g, 0.80 mmol) and *o*-phenylenediamine (0.09 g, 0.83 mmol) were refluxed in methanol (25 mL) under nitrogen for 2 h with stirring. The reaction mixture was then cooled to room temperature, and the yellow deposit of **29** was filtered. A second crop of **29** was obtained by dropwise addition of water to the filtrate. The combined crops were recrystallized from benzene/methanol to give 0.19 g (56%) of colorless cyclophane **29**: mp 211−213 °C; ^{1}H NMR (250 MHz) δ 8.19−8.12 (m, 2H), 7.78− 7.69 (m, 4H), 7.47−7.39 (m, 2H), 7.36−7.21 (m, 4H), 7.14−7.09 (m, 2H), 1.20 (s, 6H, −CH$_3$); ^{13}C NMR (62.9 MHz) δ 156.43, 142.06, 141.54, 140.68, 139.81, 136.49, 132.98, 132.14, 129.70, 129.22, 128.85, 128.79, 127.63, 19.23; IR 1410, 1302, 1213, 1016, 795, 750, 723 cm^{-1}; UV (CH$_2$Cl$_2$) λ_{max} (ϵ_{max}) nm 256 (117 000), 291 (21 000), 347 (20 800); EIMS m/z 384 (M$^+$). Anal. Calcd for C$_{28}$H$_{20}$N$_2$: C, 87.47; H, 5.24. Found: C, 87.93; H, 5.36.

Irradiation. When the colorless d_8-THF NMR solution of **29** was irradiated with 254 nm light, it turned reddish-purple and showed new broad absorptions at 350 and 525 nm. The ^{1}H NMR spectrum however only gave very broad featureless signals, possibly due to **33** (see text).

anti-8,16-Dimethyl-9,10-(2′,3′-naphtho)[2.2]metacyclophane-1,2-dione 31. From TiCl$_3$ (14.5 g, 94 mmol) and Zn−Cu couple (12.8 g, 190 mmol) in dimethoxyethane (400 mL) and dialdehyde **30**[11a] (1.2 g, 3.3 mmol) in dimethoxyethane (1200 mL), exactly as described for **26**, there was obtained 0.98 g (82%) of *anti*-8,16-dimethyl-9,10-(2′,3′-naphtho)[2.2]metacyclophane-*trans*-1,2-diol as white crystals: mp 244− 246 °C; ^{1}H NMR (250 MHz, d_8-THF) δ 8.20 (s, 2H), 7.97−7.90 (m, 2H), 7.72−7.69 (m, 2H), 7.52−7.46 (m, 2H), 7.21−7.18 (m, 2H), 7.11− 7.05 (m, 2H), 4.95 (s, 2H, −OH), 4.26 (s, 2H), 0.64 (s, 6H); ^{13}C NMR (62.9 MHz, d_8-THF) δ 141.77, 139.13, 137.98, 134.68, 131.86, 128.95, 128.56, 128.19, 126.86, 125.53, 125.02, 81.20, 17.19; IR 3492, 3380, 1418, 1210, 1098, 1025, 1010, 988, 785, 718 cm^{-1}; CIMS m/z 367 (MH$^+$). Anal. Calcd for C$_{26}$H$_{22}$O$_2$: C, 85.21; H, 6.05. Found: C, 85.26; H, 6.17.

From this diol (0.52 g, 1.4 mmol) in THF (5 mL) and DMSO (1.7 mL, 22 mmol) and oxalyl chloride (1 mL, 11 mmol) in dichloromethane (25 mL) and then triethylamine (7 mL), exactly as described above for hydroxyketone **27**, there was obtained 0.48 g (86%) of *anti*-8,16-dimethyl-9,10-(2′,3′-naphtho)[2.2]metacyclophan-1-ol-2-one as white crystals: mp 225−228 °C; ^{1}H NMR (250 MHz, d_8-THF) δ 8.27 (s, 1H), 8.25 (s, 1H), 8.00−7.94 (m, 2H), 7.55−7.50 (m, 3H), 7.42−7.38 (m, 1H), 7.27−7.08 (m, 4H), 5.30 (d, $J = 4$ Hz, 1H), 5.11 (d, $J = 4$ Hz, 1H, −OH), 0.88 and 0.60 (3, 3H each, −CH$_3$); ^{13}C NMR (62.9 MHz, d_8-THF) δ 203.79, 140.46, 140.31, 140.10, 139.17, 138.63, 138.42, 134.84, 134.69, 134.04, 133.75, 133.93, 132.69, 128.76, 128.67 (×2), 128.58, 127.28, 127.22, 126.58, 126.34, 125.25, 124.53, 82.79, 17.18, 17.09; IR 3490, 1710, 1442, 1418, 1378, 1115, 1090, 940, 774, 743, 715 cm^{-1}; EIMS m/z 364 (M$^+$). Anal. Calcd for C$_{26}$H$_{20}$O$_2$: C, 85.69; H, 5.53. Found: C, 85.57; H, 5.52.

From this hydroxyketone (0.55 g, 1.55 mmol) in dry CH$_2$Cl$_2$ (5 mL) and dry DMSO (1.7 mL, 22 mmol), oxalyl chloride (1 mL, 11 mmol), CH$_2$Cl$_2$ (25 mL), and triethylamine (7 mL, 50 mmol), exactly as described for dione **28**, there was obtained 0.48 g (88%) of diketone **31**, as yellow crystals: mp 186−187 °C; ^{1}H NMR (250 MHz, CD$_2$-Cl$_2$) δ 8.26 (s, 2H), 8.02−7.96 (AA′XX′, 2H), 7.62−7.54 (AA′XX′, 2H), 7.49 (dd, $J = 7.2$, 1.8 Hz, 2H), 7.35 (t, $J = 7.2$ Hz, 2H), 7.29 (dd, $J = 7.2$, 1.8 Hz, 2H), 0.91 (s, 6H, −CH$_3$); ^{13}C NMR (62.9 MHz, CD$_2$-Cl$_2$) δ 191.76, 139.88, 139.18, 138.78, 135.82, 134.27 (×2), 128.73, 128.32, 128.22, 127.53, 127.32, 18.44; IR 1695, 1220, 782, 738, 719; UV (CH$_2$Cl$_2$) λ_{max} (ϵ_{max}) nm 250 (42 000), 320 (3730); EIMS m/z 362 (M$^+$). Anal. Calcd for C$_{26}$H$_{18}$O$_2$: C, 86.16; H, 5.01. Found: C, 86.03; H, 5.25.

Naphthoquinoxalinocyclophane 32. From the diketone **31** (0.23 g, 0.63 mmol), *o*-phenylenediamine (70 mg, 0.64 mmol), and MeOH (25 mL), exactly as described for cyclophane **29**, there was obtained 0.19 g (63%) of cyclophane **32**, as colorless crystals from chloroform/THF: mp 247−250 °C; ^{1}H NMR (250 MHz, d_8-THF) δ 8.27 (s, 2H), 8.16−8.09 (m, 2H), 7.98−7.94 (m, 2H), 7.81−7.75 (m, 2H), 7.55−7.50 (m, 2H), 7.38−7.25 (m, 6H), 1.21 (s, 6H, −CH$_3$); ^{13}C NMR (62.9 MHz, d_8-THF) δ 156.89, 142.70, 141.60, 141.09, 140.73, 137.84, 134.88, 134.66, 133.21, 130.32, 130.08, 128.62, 128.52, 128.00, 127.20, 19.35; IR 1300, 1210, 788, 742, 720 cm^{-1}; UV (CH$_2$Cl$_2$) λ_{max} (ϵ_{max}) nm 253 (120 000), 280 (86 300), 342 (26 500), 368 (21 100); EIMS m/z 434 (M$^+$). Anal. Calcd for C$_{32}$H$_{22}$N$_2$: C, 88.45; H, 5.10. Found: C, 88.39; H, 5.03.

6,13-Di-*tert*-butyl-1,4:8,11-diepoxy-*trans*-14b,14c-dimethyl-1,4,8,11,14b,14c-hexahydrodibenzo[*fg,op*]naphthacene 35. *n*-BuLi (0.92 mL, 2.3 mmol, 2.5 M in hexane) in hexane (15 mL) was added dropwise over 30 min to a stirred solution of the tetrabromide **36**[34] (0.684 g, 1.04 mmol) in furan (50 mL) and THF (5 mL) at −78 °C under Ar. The cooling bath was then removed, and the mixture was stirred for a further 2 h at room temperature. Methanol (2 mL) was added to quench the mixture, and then ether (100 mL) and ice−water (100 g) were added. A simple filtration at this stage yielded 0.16 g of bright green crystals, pure isomer **35a**. The filtrate was extracted with ether (2 × 100 mL). The ether extracts were then washed, dried, and evaporated to yield a further 0.26 g (total yield, 85%) of the product, about 20% of isomer **35a** and 80% of isomer **35b**. For preparative purposes, these isomers could be combined and used in the next step or sufficient ether can be added initially to dissolve all the material.

For characterization purposes, isomer **35a** could be fractionally crystallized from hexanes: mp 236−238 °C; ^{1}H NMR δ 8.34 and 8.31 (bs, 2H each, H-5,7,12,14), 7.29 and 7.19 (dd, J = 5.5 and 1.9 Hz, 2H each, H-2,3,9,10), 6.674−6.667 and 6.651−6.646 (m, 2H each, H-1,4,8,11), 1.67 (s, 18H, *t*-Bu), −3.99 (s, 6H, −CH$_3$); ^{13}C NMR δ 145.07, 141.70 (×2), 139.18, 138.87, 128.41, 128.37, 115.79, 115.21, 82.01, 81.69, 35.97, 31.94, 31.32, 14.19; UV (CHCl$_3$) λ_{max} (ϵ_{max}) nm 284 (5100), 377 (53 000), 391 (36 100), 446 (6900), 665 (800); IR 1467, 1254, 1090, 1027, 864, 802 cm^{-1}; CIMS m/z 477 (MH$^+$). Anal. Calcd for C$_{34}$H$_{36}$O$_2$: C, 85.94; H, 7.60. Found: C, 85.67; H, 7.61.

The main difference in the ^{1}H NMR spectrum of the more soluble isomer **35b**, was in the chemical shift of the internal methyl protons at δ −3.70 and −4.30 (**35a** δ −3.99).

When NaNH$_2$ (400 mg, 10 mmol) and *t*-BuOK (2 mg) were added to a stirred solution of dibromide **34** (see later) (430 mg, 0.86 mmol) in dried furan (5 mL) and THF (0.5 mL), and then the mixture was stirred at 55 °C for 4 days before addition of MeOH as previously. The residue after extraction was chromatographed over silica gel using hexanes/ethyl acetate (9:1) as eluant. Eluted first was a small amount of monoadduct (∼20 mg, 5%), followed by the bis-adducts **35**, 241 mg (59%), as a 1:1 mixture of the two isomers **35a** and **35b**, identical to those previously mentioned.

***anti*-[1,2;9,10]-Dibenzo-5,13-di-*tert*-butyl-8,16-dimethyl[2.2]meta-cyclophane 21.** The mixture of adducts **35** (100 mg, 0.21 mmol) and Fe$_2$(CO)$_9$ (190 mg, 0.53 mmol) in benzene (10 mL) was stirred under Ar at reflux for 6 h. The mixture was cooled and preabsorbed onto SiGel (2 g) and then was chromatographed over SiGel using hexanes to give 40 mg (68%) of cyclophane **21**, as colorless crystals from hexanes: mp 231−232 °C; ^{1}H NMR (d_8-THF) δ 7.71−7.66 (AA′XX′, 4H, H-17,20,21,24), 7.41−7.36 (AA′XX′, 4H, H-18,19,22,23), 6.95 (s, 4H, H-4,6,12,14), 1.29 (s, 18H, *t*-Bu), 1.07 (s, 6H, −CH$_3$); ^{13}C NMR (d_8-THF) δ 150.88, 144.57, 140.64, 138.94, 129.37, 129.23, 128.97, 34.75, 31.62, 18.70; UV (cyclohexane) λ_{max} (ϵ_{max}) nm 288 (12 000), tail to 400 nm; IR 1467, 1417, 1354, 1254, 1228, 877, 730, 638, 588 cm^{-1}; CIMS m/z 445 (MH$^+$). Anal. Calcd for C$_{34}$H$_{36}$: C, 91.84; H, 8.16. Found: C, 91.24; H, 8.36.

(34) Tashiro, M.; Yamato, T. *J. Am. Chem. Soc.* **1982**, *104*, 3701−3707.

UV Irradiation of Cyclophane 21; Valence Isomerization to Dibenzodihydropyrene 22. (A) By NMR. An NMR tube containing the cyclophane **21** (2.9 mg in 0.5 mL of d_8-THF) was first cooled to about −80 °C in a cooling bath of pentane, which was cooled by liquid nitrogen outside. Then the NMR tube in a small pentane cooling bath was transferred immediately into a photochemical reactor and irradiated at 300 nm for ∼1 min. A very heavy frost forms quickly on the cooling bath and on the NMR tube which is removed by methanol on a tissue. Then, the NMR tube was transferred into the NMR instrument which was already set at the desired temperature, and the NMR spectrum was immediately recorded at the desired temperature. ^{1}H NMR (d_8-THF, −80 °C) δ 9.45 (s, 4H, H-5,7,12,14), 9.38−9.35 (AA′XX′, 4H, H-1,4,8,11), 7.62−7.59 (AA′XX′, 4H, H-2,3,9,10), 1.79 (s, 18H, *t*-Bu), −3.41 (s, 6H, internal −CH$_3$). For reference, the peaks of the unchanged cyclophane **21** at this temperature were δ 7.74−7.70, 7.47−7.43, 6.98, 1.28, and 1.07, and the ratio **22/21** was about 35:65.

(B) By UV. A solution of cyclophane **21** (1.1 mg in 200 mL of THF) was cooled to about − 50 °C in a UV cell directly and then was irradiated with the light of wavelength 300 nm for about 15 s. Then, the cell was transferred into the UV−vis instrument, and the scanning started immediately. The green solution containing **22** showed new peaks (relative intensity) at 327 (0.52), 340 (0.51), 407 (0.44), 431 (1.00), 630 (0.25), 680 (0.25), and 730 (0.23) nm. If conversion were 100%, ϵ_{431} = 54 000 mol^{-1} cm^{-1}. Irradiation with visible light or warming returned cyclophane **21**.

Thermal Isomerization Studies of 22 to 21. The irradiated NMR solutions previously mentioned were held in the instrument at the desired temperature, and the ^{1}H NMR spectra were recorded at 10 min intervals at −40 °C to 70 min, 6 min intervals at −30 °C to 60 min, ∼1 min intervals at −20 °C to 20 min, and ∼1 min intervals at −10 °C to 12 min. Integrations of both the internal methyl protons and the aromatic protons were used to obtain the ratio r = **[22]**/**[21]**. Then, if the initial concentration of **22** is C_0, then as the thermal reaction proceeds, $C = C_0[r/(1 + r)]$ and hence $-\ln r/(1 + r) = kt +$ constant, from which the rate constant (k) at temperature T is easily determined. Then, using the standard $-\ln k$ versus $1/T$ plot, we are able to obtain the activation energy E_{act} for the process. The values of k (s^{-1}) and half-lives $\tau_{1/2}$ (min) found were as follows: 233 K, (2.86 ± 0.19) × 10^{-5}, 400; 243 K, (2.16 ± 0.12) × 10^{-4}, 54; 253 K, (9.45 ± 0.11) × 10^{-4}, 12; 263 K, (4.26 ± 0.08) × 10^{-3}, 2.7; E_{act} = 20.1 ± 0.7 kcal/mol.

At the end of all thermal isomerizations, only pure cyclophane **21** remained.

4,9-Dibromo-2,7-di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b,10c-di-hydropyrene 34. A precooled (−7 °C) solution of NBS (1.10 g, 6.17 mmol) in dry DMF (100 mL) was added slowly over 1 h to a precooled (−7 °C) solution of dihydropyrene **5**[34] (see also Supporting Information) (1.01 g, 2.94 mmol) in dry DMF/CCl$_4$ (350 mL/50 mL) at 0 °C, and then the reaction was stirred without cooling for 2 h. Hexanes (200 mL) were added, and then the mixture was poured into ice−water. The hexanes extract was washed well with water, dried, and evaporated. The residue was chromatographed over SiGel using hexanes and gave 1.3 g (88%), from which the less soluble **34** was easily separated from a small amount of the more soluble 4,10-isomer by fractional recrystallization from hexanes, as dark green crystals: mp 220−222 °C; ^{1}H NMR δ 8.81 (d, J = 1.1 Hz, 2H), 8.64 (s, 2H), 8.48 (bs, 2H), 1.68 (s, 18H, *t*-Bu), −3.83 (s, 6H, −CH$_3$); ^{13}C NMR δ 148.17, 137.22, 132.42, 126.93, 121.94, 121.54, 116.48, 36.32, 32.15, 31.85 (C(CH$_3$)$_3$), 14.26; IR 1329, 1241, 1115, 877, 777, 676 cm^{-1}; UV λ_{max} (ϵ_{max}) nm 350 (77 000), 389 (40 000), 486 (7000), 654 (1400). CIMS m/z 501 (MH$^+$, correct isotope pattern). HRMS (EI) Calcd (^{79}Br$_2$): 500.0714. Found: 500.0715. Anal. Calcd for C$_{26}$H$_{30}$Br$_2$: C, 62.17; H, 6.02. Found: C, 62.06, H, 6.01.

If NBS (3.53 g, 19.8 mmol) in CHCl$_3$ (150 mL) is added to the pyrene **5** (3.1 g, 9.01 mmol) in CHCl$_3$ at 20 °C and the mixture stirred overnight, 4.5 g (100%) of a 3:2 mixture of the 4,9-dibromo and 4,10-dibromo isomers is obtained. This mixture is suitable for use in the

Diels−Alder additions. The spectra of the 4,10-isomer could easily be obtained by subtraction: ^{1}H NMR δ 9.00 (d, $J = 1.3$ Hz, 2H), 8.96 (d, $J = 1.3$ Hz, 2H), 8.84 (d, $J = 1.3$ Hz, 2H), 1.70 (s, 9H, *t*-Bu), 1.67 (s, 9H, *t*-Bu), −3.69 (s, 3H, −CH₃), −3.71 (s, 3H, −CH₃); ^{13}C NMR δ 149.49, 137.86, 133.67, 133.52, 132.95, 127.45, 124.56, 124.10, 122.90, 122.05, 117.13, 36.60, 36.34, 34.50, 32.13, 31.76, 26.89, 14.60, 13.93.

Bis-isobenzofuran Adduct 37. LDA (15 mL, 1.5 M in cyclohexane, 22.5 mmol) was added to a solution of 1-methoxyphthalan (3.0 g, 20 mmol) in THF (35 mL) under Ar at room temperature. After 5 min, the dibromide **34** (or mixture of isomers) (1.0 g, 2.0 mmol) and sodium amide (400 mg, 10 mmol) were added, and stirring continued for 4 days. Methanol (2 mL) was then added, and the total mixture was preabsorbed onto SiGel and chromatographed using first hexanes as eluant (which gave some dihydropyrene **5** and bromo-**5**) and then hexanes−ether (20:1) which eluted some monoadduct and then was eluted a 1:1 mixture of bis-adduct isomers **37** (0.38 g, 33%). Recrystallization and chromatography failed to separate these two isomers completely, though they yielded a mixture enriched in the *syn*-isomer of **37** corresponding to **35b**, which enabled assignment of their proton spectra. ^{1}H NMR (*d*₈-THF) **37a** (*anti*-O) δ 8.65 (bs, 4, H-1,3,10,12), 7.48−7.45 and 7.40−7.37 (m, 2 each set, H-5,8,14,17), 7.03 (s, 4, H-4,9,13,18), 6.86−6.84 (m, 4, H-6,7,15,16), 1.73 (s, 18, *t*-Bu), −4.39 (s, 6, −CH₃). **37b** (*syn*-O) 8.61 (bs, 4, H-1,3,10,12), 7.41−7.39 and 7.32−7.30 (m, 2 each set, H-5,8,14,17), 7.02 (s, 4, H-4,9,13,18), 6.78−6.75 (m, 4, H-6,7,15,16), 1.750 and 1.746 (s, 9 each, *t*-Bu), −3.66 and −5.17 (s, 3 each, −CH₃). ^{13}C NMR (mixture of **37a** and **37b**) δ 149.96, 149.68, 146.40, 146.06, 145.72, 141.47, 141.07, 140.90, 140.78, 129.03, 128.79, 128.49, 128.39, 125.97, 125.90, 125.84, 125.78, 120.37, 120.16, 120.09, 119.91, 117.46, 116.55, 116.49, 83.10, 83.04, 82.65, 82.57, 36.71, 35.02, 32.76, 32.23, 30.88, 16.37, 14.29, 12.11. LSIMS (Matrix, mNBA) calcd: 577.3 (MH⁺). Found: 577.3. Anal. Calcd for C₄₂H₄₀O₂: C, 87.45; H, 6.99. Found: C, 86.19; H, 6.95. HRMS (EI) calcd: 576.3028. Found: 576.3029.

***anti*-5,13-Di-*tert*-butyl-8,16-dimethyl[1,2-b;9,10-b]dinaphtho[2.2]-metacyclophane 38.** The mixture of adducts **37** (68 mg, 0.12 mmol) and Fe₂(CO)₉ (130 mg, 0.35 mmol) in benzene (30 mL) was stirred under Ar at reflux for 8 h. The mixture was preabsorbed onto SiGel and chromatographed over SiGel using hexanes as eluant, which yielded 38 mg (59%) of colorless **38** as needles from cyclohexane: mp 340−341 °C (sublimes); ^{1}H NMR (*d*₈-THF) δ 8.22 (s, 4H, H-17,22,23,28), 7.97−7.94 (AA′XX′, 4H, H-18,21,24,27), 7.51−7.48 (AA′XX′, 4H, H-19,20,25,26), 7.14 (s, 4H, H-4,6,12,14), 1.31 (s, 18H, *t*-Bu), 1.06 (s, 6H, CH₃-8,16); ^{13}C NMR (*d*₈-THF) δ 150.65, 143.14, 140.32, 138.44, 134.75, 130.54, 128.54, 127.96, 126.84, 34.83, 31.66, 18.56; UV (THF) $\lambda_{\max}$ nm ($\epsilon_{\max}$) 261 (55 000), 287 (47 000), tail to 380 nm; IR 890, 870, 750, 740 cm⁻¹; CIMS *m/z* 545 (MH⁺). Anal. Calcd for C₄₂H₄₀: C, 92.59; H, 7.40. Found: C, 92.12; H, 7.60.

Eluted next was unchanged **37**, 25 mg (37%).

9,24;12,21-Diepoxy-2,7,14,19-tetra-*tert*-butyl-*trans*-20b,20c-*trans*-24c,24d-tetramethyl-9,12,20b,20c,21,24,24c,24d-octahydro-di-(4,5-pyreno)[b,k]chrysene 43. The bis-furan **39** was generated from **40** as described in the literature:[25] bis-acetal **40** (62 mg, 0.23 mmol) was added to LDA (2 mmol) in THF (20 mL) at −78 °C and then was allowed to warm to 0 °C for 10 min. The mixture was recooled to −78 °C and was then quenched with methanol (0.5 mL). Solvents were removed under vacuum at no more than 7 °C. The product was then taken up in hexane/ethyl acetate (8:2, 10 mL) and was filtered through a 4 cm column of alumina deactivated with 5% water, using the same mixed solvent (90 mL) to elute the colorless product. Solvents were removed under vacuum at 7 °C, and the product furan **39** was dried for an additional hour under vacuum at room temperature, to give 35 mg (74%) of colorless crystalline leaflets. To this was added dry THF (10 mL), bromopyrene **41** (192 mg, 0.455 mmol), sodium amide (240 mg), and potassium *tert*-butoxide (5 mg), and the mixture was stirred under argon for 24 h. The reaction was then cooled in an ice bath and quenched by slowly adding saturated aq ammonium chloride (5 mL). Ether was

added, and the organic layers were separated, washed with aq NH₄Cl, brine, dried and evaporated. The aqueous layers were further extracted with ether, dried and evaporated. The combined products were rinsed with hexanes (4 × 4 mL) and dried to yield 122 mg (81%) of adducts **43** as a green crystalline mixture of approximately equal amounts of two isomers, mp (dec) 205−210 °C; ^{1}H NMR (C₆D₆, 300 MHz) δ 8.6−7.5 (m, 16H), 7.4−7.2 (m, 2H), 6.95−6.8 (m, 2H), 1.7−1.6 (at least 4 overlapping s, 36H), −2.89, −2.95, −3.79, −3.92 (s, 12H total, internal CH₃); LSIMS *m/z* 893.4 (MH⁺); HR MS calcd for C₆₆H₆₉O₂ (MH⁺): 893.5297. Found: 893.5294

This mixture of isomers was used directly in the next step.

2,7,14,19-Tetra-*tert*-butyl-*trans*-20b,20c-*trans*-24c,24d-tetramethyl-20b,20c,24c,24d-tetrahydro-di-(4,5-pyreno)[b,k]chrysene 44. The mixed isomers of **43** (38 mg, 0.043 mmol) and Fe₂(CO)₉ (140 mg, 0.4 mmol) were stirred under reflux in benzene (15 mL) under argon in the dark for 2 h. After cooling, the mixture was filtered through deactivated SiGel, using an additional 100 mL of CHCl₃ to elute the brown product. The eluate was evaporated, and the residue was purified by further chromatography on deactivated SiGel under argon using hexanes/CH₂Cl₂ (6:1) as eluant. The reddish-brown product band was collected and evaporated to yield 30 mg (82%) of mixed isomers of **44**: mp (dec) >345 °C; ^{1}H NMR (C₆D₆ {values in CDCl₃}) δ 10.35{10.09} (s, 2H, H-9,21), 9.39{9.24} (s, 2H, H-12,24), 9.18{9.06} (d, $J = 9.0$ Hz, 2H, H-10,22), 8.54{8.39} (bs, 2H, H-8,20), 8.41{8.36} (bs, 2H, H-1,13), 8.17{8.36} (d, $J = 9.0$ Hz, 2H, H-11,23), 7.23{7.11}, 7.22{7.09} (bs, 4H, H-3,6,15,18), 6.90{6.84} (bs, 4H, H-4,5,16,17), 1.453{1.57} (s, 18H), 1.442{1.52} (s, 18H), −0.284 and −0.295{−0.73} (bs, 12H total (~1:3 ratio), −CH₃; ^{13}C NMR (C₆D₆, not all peaks visible, compound too unstable in CDCl₃) δ 144.76, 139.59, 139.36, 136.57, 136.04, 131.05, [129−127 peaks obscured by benzene], 124.37, 122.04, 121.96, 121.77, 120.92, 120.88, 119.31, 118.21, 118.21, 37.96, 35.30, 30.50 and 30.44 (C(CH₃)₃), 19.28 (C-20b,c;24c,d); UV (cyclohexane) $\lambda_{\max}$ ($\epsilon_{\max}$) nm 290 (51 600), 345 (43 400), 406 (70 900), 427 (132 000), 527 (10 000); LSIMS *m/z* 860.5 (M⁺); HRMS Calcd for C₆₆H₆₈: 860.5321. Found: 860.5323. Note: The peaks in the NMR spectrum broaden on standing despite the precautions taken described in the previous general section.

Epoxytetrabenzohexacene 50. *n*-BuLi (0.64 mmol) in hexane (1.6 mL) was added slowly via syringe to a stirred solution of isofuran **19**[11b] (720 mg, 1.87 mmol) and dibromide **13** (298 mg, 0.54 mmol) in dry toluene (15 mL) at −40 °C under argon in the dark. After 16 min, methanol (3 mL) was added. Then, solvents were removed under vacuum at ~10 °C. The residue was chromatographed over neutral alumina (deactivated with 5% water) using hexanes/benzene (2:1) as eluant and gave 50 mg (12%) of the adduct **50** as a golden solid as an equal mixture of two isomers. This mixture could be used directly in the next step. However, further chromatography and recrystallization from benzene yielded a single isomer (probably **50A**; see text) as dark golden crystals: mp 222−225 °C; ^{1}H NMR (*d*₈-THF) δ 8.82 (d, $J = 1.3$ Hz, 1H), 8.70 (d, $J = 1.2$ Hz, 1H), 8.66−8.62 (m, 2H), 8.45 (bs, 1H), 8.41 (bs, 1H), 8.32 and 8.29 (AB, $J = 8.3$ Hz, 2H), 8.16 (d, $J = 1.3$ Hz, 1H), 8.13 (d, 1H, $J = 1.3$ Hz), 7.92 (d, $J = 1.2$, 1H), 7.69 (d, $J = 1.3$, 1H), 7.50 (d, $J = 0.6$ Hz, 1H), 7.47 (bs, 1H), 7.48−7.43 (m, 2H), 1.76, 1.71, 1.60, 1.53 (s, 9H each, C(CH₃)₃), −1.04, −1.99, −3.60, −4.18 (s, 3H each, internal CH₃); ^{13}C NMR (*d*₈-THF) δ 146.23, 146.14, 145.34, 145.14, 138.48, 137.80, 137.68, 137.60, 136.65, 136.59, 136.35, 136.16, 130.55, 130.40, 128.46, 127.94, 127.61, 127.21, 126.80, 126.78, 125.88, 125.31, 125.19, 125.01, 124.78, 122.07, 121.85, 117.57, 117.43, 117.12, 116.53, 116.16, 80.47, 80.27, 39.87, 36.90, 36.66, 36.61, 36.16, 36.06, 33.40, 32.16, 31.08, 30.87, 30.77, 30.71, 19.52, 17.53, 15.76, 14.62; IR 1261, 888, 865, 754, 673, 651, 645 cm⁻¹; LSIMS *m/z* 776.4 (M⁺); HRMS calcd for C₅₈H₆₄O: 776.4957. Found: 776.4977. Note in C₆D₆ the mixed isomers showed internal methyl protons (300 MHz) at δ −0.63, −0.64, −1.67, −1.70, −3.17, −3.21, −3.87, −3.95.

5,13-Di-*tert*-butyl-8,16-dimethyl-1,2-[10,11-(2,7-di-*tert*-butyl-*trans*-12c,12d-dihydro-12c,12d-dimethylbenzo[*e*]pyreno)]-9,10-benzo[2.2]-

metacyclophane 47. (A) From the Single Isomer of 50A. A mixture of the single isomer **50A** from previously (40 mg, 0.052 mmol) and $Fe_2(CO)_9$ (70 mg, 0.2 mmol) was stirred under reflux in benzene (30 mL) under argon in the dark for 2 h. After the mixture was cooled, the mixture was filtered under argon through deactivated SiGel using benzene (50 mL) as eluant. The solvent was removed under argon in the dark. The residue was then chromatographed on deactivated SiGel under argon using hexanes/CH_2Cl_2 (6:1) as eluant. The first ∼70% of the red product band was collected. Evaporation of the solvent gave 24 mg (60%) of **47A** as an intense red solid, which on recrystallization from cyclohexane gave mp (dec) 170−175 °C; ^1H NMR δ 8.94 (bs, 2H, H-17,26), 8.32 (bs, 2H, H-18,25), 7.79−7.74 (AA′XX′, 2H, H-27,30), 7.48−7.43 (AA′XX′, 2H, H-28,29), 7.38 (bs, 2H, H-20,23), 7.15 (bs, 2H, H-21,22), 7.08 (d, $J = 2.1$ Hz, 2H, H-4,14), 7.00 (d, $J = 2.2$ Hz, 2H, H-6,12), 1.50 (s, 18H, 19,24-C(CH$_3$)$_3$), 1.31 (s, 18H, 5,13-C(CH$_3$)$_3$), 1.18 (s, 6H, 8,16-CH$_3$), −1.37 (s, 6H, 25b,c-CH$_3$) (note spectrum broadens on standing); ^{13}C NMR (not satisfactory because of decomposition); UV (deaerated cyclohexane) λ_{max} (ϵ_{max}) nm 250 (56 800), 280 (52 300), 354 (19 900), 390 (29 400), 408 (40 500), 520 (4900), 640 (650); LSIMS m/z 760.5 (M$^+$); HRMS calcd for $C_{58}H_{64}$: 760.5008. Found: 760.5004.

(B) From the Mixed Isomers 50. When the mixture of isomers was used, almost identical material was obtained. The ^1H NMR spectrum of the second isomer **47B** could be obtained by subtraction of the spectrum of **47A** from the spectrum of the mixture of isomers: ^1H NMR of **47B** (CDCl$_3$, 300 MHz) δ 9.09 (bs, 2H), 8.52 (bs, 2H), 7.80−7.74 (AA′XX′, 2H), 7.49−7.43 (AA′XX′, 2H), 7.52 (bs, 2H), 7.31 (bs, 2H), 7.09 (d, $J = 2$ Hz, 2H), 7.01 (d, $J = 2$ Hz, 2H), 1.54 (s, 18 H), 1.32 (s, 18 H), 1.18 (s, 6H), −1.67(s, 6H) (see **47A** for assignments). Note: The spectrum broadens on standing despite the precautions taken described in the previous general section.

Visible Light Irradiations of Dihydropyrenes to Form Cyclophanedienes. A solution of the dihydropyrene (5 mg) in degassed d_8-toluene in an NMR tube, cooled by a small cold water bath, was irradiated with a 250 W tungsten household lamp (the type used to light a room during painting) with a square of yellow plastic (absorbs light <400 nm) between the lamp and the sample, until the sample solution was colorless (usually a few minutes). The sample was held at 0 °C while being transferred to the NMR spectrometer (300 MHz), where the ^1H (unless otherwise specified) NMR spectra of the cyclophanediene form were recorded.

Parent-DHP-5: δ 8.77 (s, H-1,3,6,8), 8.64 (s, H-4,5,9,10), 1.78 (s, C(CH$_3$)$_3$), −3.61 (s, CH$_3$).

Parent-CPD-6: δ 6.87 (s, Ar−H), 6.44 (s, vinyl-H), 1.82 (s, CH$_3$), 1.40 (s, C(CH$_3$)$_3$).

Benzo-DHP-7: δ 9.01−8.94 (m, H-9,12), 8.56 (d, $J = 1$ Hz, H-1,8), 7.70−7.63 (m, H-10,11), 7.59 (d, $J = 1$ Hz, H-3,6), 1.62 (s, C(CH$_3$)$_3$)), −1.11 (s, CH$_3$).

Benzo-CPD-8: δ 7.88−7.80 (m, H-17,20), 7.41−7.33 (m, H-18,19), 7.13 (d, $J = 2$ Hz, H-4,14), 6.99 (d, $J = 2$ Hz, H-6,12), 6.50 (s, H-9,10), 1.62 (s, CH$_3$), 1.40 (s, C(CH$_3$)$_3$).

Naphtho-DHP-9: δ 9.21(s, H-9,14), 8.28 (d, $J = 1$ Hz, H-1,8), 7.97−7.91 (m, H-10,13), 7.47−7.41 (m, H-11,12), 7.08 (d, $J = 1$ Hz, H-3,6), 6.79 (s, H-4,5), 1.50 (s, C(CH$_3$)$_3$)), −0.06 (CH$_3$).

Naphtho-CPD-10: δ 8.31 (s, H-17,22), 7.86−7.79 (m, H-18,21), 7.47−7.40 (m, H-19,20), 7.25 (d, $J = 2$ Hz, H-4,14), 7.07 (d, $J = 2$ Hz, H-6,12), 6.60 (s, H-9,10), 1.66 (s, CH$_3$), 1.45 (s, C(CH$_3$)$_3$)).

Anthro-DHP-11: δ 9.30 (s, H-9,16), 8.47 (s, H-10,15), 8.21 (d, $J = 1$ Hz, H-1,8), 8.08−8.03 (m, H-11,14), 7.48−7.42 (m, H-12,13), 6.95 (d, $J = 1$ Hz, H-3,6), 6.62 (s, H-4,5), 1.56 (s, C(CH$_3$)$_3$)), 0.50 (s, CH$_3$).

Anthro-CPD-12: δ 8.47 (s, H-17,24), 8.30 (s, H-18,23), 7.99−7.94 (m, H-19,22), 7.45−7.40 (m, H-20,21), 7.37 (d, $J = 2$ Hz, H-4,14), 7.12 (d, $J = 2$ Hz, H-6,12), 6.62 (s, H-9,10), 1.63 (s, CH$_3$), 1.45 (s, C(CH$_3$)$_3$)).

Dibromobenzo-DHP-13: δ 8.80−8.74 (m), 8.42 (d), 8.20 (d), 7.62−7.56 (m) 1.56 (s), −1.03 (s) (for assignments, see **13**).

Dibromobenzo-CPD-14: δ 7.77 (d, $J = 2$ Hz, H-6,12), 7.76−7.69 (m, H-17,20), 7.36−7.29 (m, H-18,19), 7.10 (d, H-4,14), 1.62 (s, CH$_3$), 1.43 (s, C(CH$_3$)$_3$)).

Phenyleno-DHP-15: δ (CDCl$_3$, insufficiently soluble in d_8-toluene) 9.92 (s), 8.92 (dd), 8.67 (dd), 8.40 (d), 7.78−7.74 (m), 7.71−7.67 (m), 7.23 (d), 6.99 (s), 1.55 (s), −1.07 (s) (for assignments, see preparation from previous text).

Phenyleno-CPD-16: δ (CDCl$_3$) 8.89 (s, H-18,20), 8.76−8.66 (m, H-15,16), 7.72−7.64 (m, H-14,17), 6.98 (d, $J = 2$ Hz, H-6,12), 6.88 (d, $J = 2$ Hz, H-4,14), 6.51 (s), 1.51 (s, CH$_3$-8,16), 1.30 (s, t-Bu-5,13).

Furano-DHP-19: δ 7.98 (s, H-9,11), 7.18 (d, $J = 1$ Hz, H-1,8), 6.68 (d, $J = 1$ Hz, H-3,6), 6.39 (s, H-4,5), 1.40 (s, C(CH$_3$)$_3$)), 0.61 (s, CH$_3$).

Furano-CPD-19′: δ 7.60 (s, H-17,18), 7.10 (d, $J = 2$ Hz, H-4,14), 7.04 (d, $J = 2$ Hz, H-6,12), 6.55 (s, H-9,10), 1.45 (s, CH$_3$), 1.42 (s, C(CH$_3$)$_3$)).

Chryseno-bis-DHP-44: δ (see preparation from previous text for aryl signals) 1.657, 1.640 (s, t-Bu) and −0.22 (s, internal-CH$_3$)

Chryseno-bis-CPD-45 (TWO ISOMERS): δ 9.36, 9.35 (s), 8.84, 8.80 (d, $J = 9$ Hz), 8.50, 8.47 (s), 8.01, 7.96 (d, $J = 9$ Hz), 7.40−7.10 (m), 6.63 (s), 1.748, 1.740, 1.729, 1.716 (s, internal-CH$_3$), 1.472, 1.461, 1.451, 1.440 (s, t-Bu).

Cyclophano-DHP-47: δ 9.73 (s), 8.86 (s), 7.98−7.92 (m), 7.62 (d), 7.61 (d), 7.48−7.42 (m), 7.32 (s), 7.27 (s), 1.638 (s, CH$_3$), 1.630 (s, C(CH$_3$)$_3$)), 1.37 (s, C(CH$_3$)$_3$)), −1.01 (s, CH$_3$) (for assignments, see preparation from previous text).

Cyclophano-CPD-49: δ 8.65 (s, H-17,26), 7.94−7.88 (m, H-27,30), 7.47 (d, H-4,14), 7.46−7.40 (m, H-28,29), 7.40 (d, H-18,25), 7.25 (d, H-6,12), 7.03 (d, H-20,23), 6.56 (s, H-21,22), 1.78 (s, CH$_3$), 1.58 (s, CH$_3$), 1.34 (s, C(CH$_3$)$_3$)), 1.32 (s, C(CH$_3$)$_3$)) [J values ≈ 2 Hz].

Thermal Return Reactions. The NMR solutions previously mentioned were held in the probe of the NMR spectrometer at the appropriate temperatures, and the reaction followed by integration of the methyl or *tert*-butyl (or where appropriate sharp aromatic) signals, such that $-\ln[MCD/(MCD + DHP)]$ could be plotted against time to obtain the first-order rate constants, as described for **22** to **21** (data available in Supporting Information). The first-order rate constants were then used in an Arrhenius plot ($\ln(k)$ vs $1/T$) to obtain E_{act} and an Eyring plot ($\ln(k/T)$ vs $1/T$ to obtain $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in the normal way.

	k (min^{-1}) (3σ errors based on 10 integrations)		
compd	319 K	333 K	343 K
12	0.0344(9)	0.178(5)	0.270(7)
10	0.0101(3)	0.042(1)	0.117(3)
6	0.006 10(15)	0.0300(8)	0.086(2)
45	0.0057(2)	0.0297(8)	0.090(2)
16	0.003 07(7)	0.0149(8)	0.0431(8)
49	0.002 24(6)	0.0134(3)	0.0356(9)
8	0.001 98(5)	0.0095(2)	0.0299(8)
14	0.001 24(3)	0.0063(2)	0.0212(5)
19′	0.000 183(5)	0.001 08(3)	0.003 22(8)

	E_{act}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
compd	kcal/mol	kcal/mol	cal/deg mol
12	19.1	18.4	−7.4
10	22.1	21.4	−0.7
6	24.0	23.3	4.3
45	24.3	22.6	5.1
16	23.9	23.3	2.7
49	24.1	23.4	2.9
8	24.5	23.9	3.8
14	25.8	25.0	6.2
19′	26.1	26.3	4.4
	(±0.5−0.8)	(±0.5−0.8)	(±1)

Laser Flash Studies of 47. A sample of **47** was dissolved in cyclohexane and adjusted to an absorbance of ∼0.1 at 408 nm using 7 mm fluorescence cells. The sample was deaerated for 10 min with N$_2$

and capped and was held at 20 ± 1 °C. Laser flash photolysis was conducted using a YAG laser (Spectra Physics GCR-12) at 355 nm with pulse energies of ∼40 mJ/pulse, with a repetition rate of 1 Hz. Transient spectra were obtained using a xenon lamp (150 W, Oriel housing model 66057, PTI power supply, model LPS-220) connected to a pulser synchronized with the laser pulses. A photomultiplier (Hamamatsu R446) coupled with a monochromator (CVI Digikrom 240) and a baseline compensation unit was used to monitor the transient absorption spectra. The operating system is described in detail in ref 34. The transient spectrum showed bleaching of the 406 nm band of **47** and a large increase in absorption at 486 nm for a transient species, which appears very rapidly, about 10 ns after the laser pulse. The transient spectra are shown in the Supporting Information). The decay pattern of the transient was monitored at 486 nm, and it appeared to be first order, with a half-life of about 0.10 s at 20 °C. The transient showed an absorbance change of +0.23 at 486 nm, while the 406 nm band of **47** changed by −0.055. There was no change to the UV− visible spectrum obtained at the end of the laser flash study, even after hundreds of flashes.

Supporting Information Available: An improved large scale preparation of the dihydropyrene **5**, the first-order decay plots for the thermal isomerizations of the cyclophanedienes, and the laser flash transient spectra of **47**. This material is available free of charge via the Internet at http://pubs.acs.org.

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