JOC Article

Suppressing the Thermal Metacyclophanediene to Dihydropyrene Isomerization: Synthesis and Rearrangement of 8,16-Dicyano[2.2]metacyclophane-1,9-diene and Evidence Supporting the Proposed Biradicaloid Mechanism

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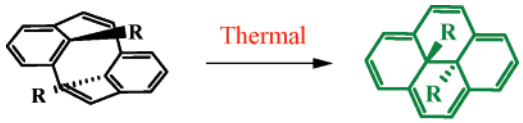

$R = CH_3$ $\tau_{1/2}$ (20 °C) = 42 hours

$R = CN$ $\tau_{1/2}$ (20 °C) = >30 years

Synthesis of 8,16-dicyano-*anti*-[2.2]metacyclophane-1,9-diene, **1b**, was achieved in five steps from 1,3-bis(bromomethyl)benzonitrile. Unlike most metacyclophanedienes which easily thermally isomerize ($\tau_{1/2}$ = minutes to days at 20 °C) to dihydropyrenes **2**, dinitrile **1b** shows no tendency to convert thermally to **2b** at room temperature ($\tau_{1/2}$ > 30 years), consistent with predictions based on calculation of activation barriers. Irradiation of cyclophanediene **1b** with UV light readily forms the dinitriledihydropyrene **2b**, which unexpectedly shows a much more facile (50 °C) 1,5-sigmatropic rearrangement of the internal nitrile groups to give dihydropyrenes **9b** and then **10b** than is the case for internal methyl substituents, **2a**, which forms **9a** at temperatures above 190 °C. Synthesis of the 2-formyl derivative **1c** and the 2-naphthoyl derivative **1d** are also described. These substituents were predicted to lower the activation barrier for the thermal closing reaction to the corresponding dihydropyrenes, and experimental evidence supports these calculations.

Introduction

The thermal electrocyclization of metacyclophanedienes (CPDs) **1** to the dihydropyrenes (DHPs) **2** is a Woodward−Hoffmann (W−H) forbidden reaction, but the geometry-enforced conrotatory closure renders the W−H path the only accessible one.[1,2] Over the decades,[3] a large number of substituted metacyclophanedienes and dihydropyrenes have been prepared, many by us, yet we have not been able to discern any particular trend in the ease of this thermal reaction. Williams[4] has recently shown by DFT calculations that the transition state (**TS**) in this rearrangement has biradical character, with much of the spin density at the internal 8,16 positions. Williams[4] calculated relative energies for **1**/**TS**/**2** for a series of substituents and found that the dinitrile **1b**/**TS**/**2b** had the highest calculated activation barriers for the thermal reversion (cyclization) of the CPD to DHP of all the substituents studied, with $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ (298) being about 25−27 kcal/mol. This prediction was initially perplexing as intuitively the radical stabilizing nitrile groups were anticipated to *lower* the activation

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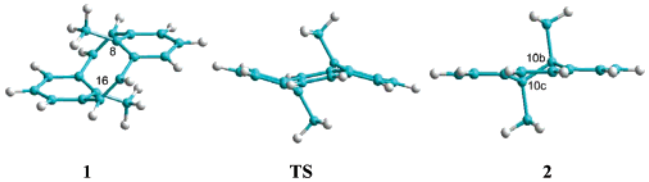
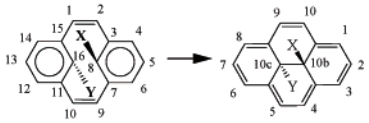
barrier. The major contributing factor appears to be that compared with the energies of the internal methyl species **1a**/**TS**/**2a**, the internal cyanometacyclophanediene **1b** is strongly stabilized by conjugation of the aryl rings with the nitrile groups, relative to **TS/2b**, *which then results in a high predicted barrier for the thermal closing of* ***1b*** *to* ***2b***. Since the next highest position of spin density was calculated to be at the 5,13-positions of **1**, some effect of substituents would also be expected here. Very recent CASSCF and CASPT2 calculations on the ground- and excited-state surfaces of **1a**/**2a** interconversion are in good agreement with our DFT results for this system.[5]

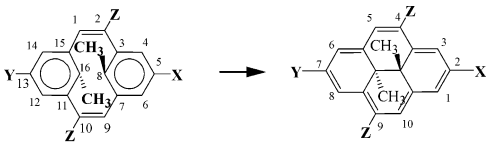




1a X=Y=CH_3 **2a**
1b X=Y=CN **2b**

Indeed, Blattman's[6] early data showed that 5-formyl-**1a** and 5-benzoyl-**1a** had smaller barriers for the thermal closing reaction, which is consistent with Williams' calculations.

In this paper, we report the synthesis and comparison of the thermal closing barriers for the dinitrile **1b** (calculated to close more slowly than **1a**) and the formyl compound **1c** and the naphthoyl compound **1d** (which are expected to close more rapidly than **1a**) and thus would be a further test of these calculations.

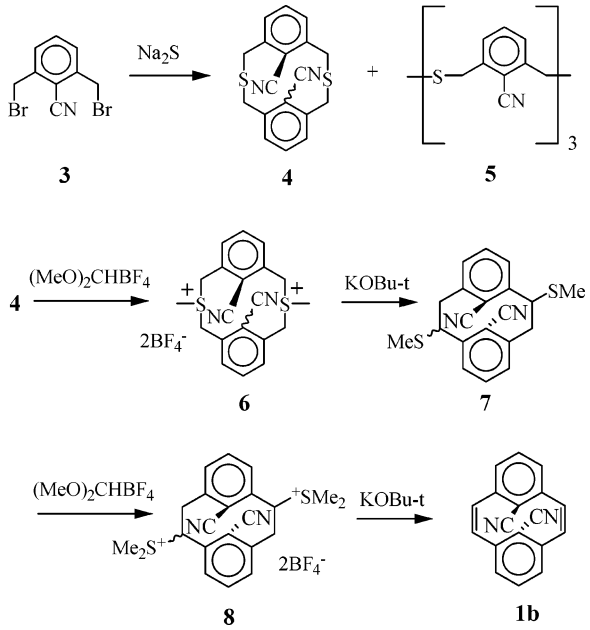


1c	**X=CHO, Y=*t*-Bu, Z=H**	**2c**
1d	**X=1-Naphthoyl, Y=*t*-Bu, Z=Br**	**2d**
1e	**X=Y= *t*-Bu, Z=H**	**2e**
1f	**X=CHO, Y=H, Z=H**	**2f**
1g	**X=COPh, Y=H, Z=H**	**2g**
1h	**X=Y=H, Z=CHO, H**	**2h**
1i	**X=Y= *t*-Bu, Z=CHO, H**	**2i**
1j	**X=Y= *t*-Bu, Z=COPh, H**	**2j**
1k	**X=Y= *t*-Bu, Z=Br**	**2k**

Results and Discussion

Syntheses. The dinitrile **1b** was synthesized as shown in Scheme 1. Normally, to prepare dithiacyclophanes, we prefer

SCHEME 1



our bis-thiol−bis-bromide coupling.[7] However, on attempted reaction of the bis-bromide **3** with thiourea, only a very poor yield of the corresponding bis-thiol was obtained, and so the direct, although usually lower yielding, coupling with sodium sulfide had to be used. Thus, reaction of the bis(bromomethyl)-nitrile[8] **3** and sodium sulfide by slow addition from two dropping funnels in ethanol−water−benzene over 20 h, gave a 50% yield of the dithiacyclophane **4**, as a 1:1 mixture of *anti*- and *syn*-isomers, as well as 18% of the cyclic trimer **5**. Vögtle[9] reported a 4% yield of **4** by this coupling method in 1971, but little experimental detail was given, and he may have obtained one or a mixture of the isomers. We were able to separate the two isomers of **4** by chromatography and they could be distinguished by their ^{1}H NMR spectra. The *anti*-isomer (which elutes from silica gel first) shows deshielded aromatic protons at δ 7.6 and closely spaced AB systems for the methylene bridge protons at δ 3.94 and 3.88, while the *syn*-isomer shows more shielded aromatic protons at δ 7.2 and 7.1 and more widely spaced AB systems at δ 4.55 and 3.81.

An X-ray structure was obtained for each isomer (Supporting Information). For preparative purposes, it was not necessary to separate the isomers of **4**, since during the ring contraction reaction, *syn*-isomers of **6** converted to *anti*-isomers of **7**, which ultimately led to the *anti*-cyclophanediene **1b**. The thiacyclophanes **4** were converted to the cyclophanediene **1b** via our Stevens rearrangement−Hoffmann elimination route[10] shown in Scheme 1, in about 70% overall yield. The cyclophanediene **1b** had the expected HRMS at *m*/*z* 254.0833 (calcd 254.0843), and the bridge alkene protons were observed as a shielded singlet at δ 6.65, consistent with related *anti*- dienes.[11] Although colorless when pure, diene **1b** rapidly becomes pale green because of photochemical closure to the dihydropyrene **2b**. Irradiation of a solution of **1b** with UV light in dichloromethane

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TABLE 1. Thermal Conversion Half-lives ($\tau_{1/2}$) at 20 and 50 °C for 1 Thermally Converting to 2, with Energies of Activation (E_{act}) and Pre-exponential Factors *A* Listed in Order of Increasing $\tau_{1/2}$ at 20 °C (Data Calculated from References Given or This Work)[a]

entry	compd	$\tau_{1/2}$ (20 °C)	$\tau_{1/2}$ (50 °C)	E_{act} (kcal mol^{-1})	A (s^{-1})	ref
1	**1f** [= 5-CHO-**1a**]	42 min	95 s	20.5	5.3×10^{11}	6
2	**1c**	51 min	120 s	20.4	3.0×10^{11}	
3	**1g** [= 5-benzoyl-**1a**]	90 min	200 s	20.8	4.2×10^{11}	6
4	**1d**	3.4 h	5.7 min	22.6	5.1×10^{12}	
5	**1i** [= 2-CHO-**1e**]	30 h	83 min	19.4	1.9×10^{9}	3g
6	**1a**	42 h	69 min	23.0	6.6×10^{11}	6
7	**1j** [= 2-benzoyl-**1e**]	45 h	84 min	21.8	7.6×10^{10}	3g
8	**1h** [= 2-CHO-**1a**]	49 h	114 min	21.6	5.3×10^{10}	
9	**1e** [= 5,13-di-*t*-Bu-**1a**]	54 h	126 min (122 min[3g])	20.4, 21.7[3g]	8.1×10^{9} (5.2×10^{10})[3g]	
10	1,2-benzo-**1e**	7.3 day	5.2 h	24.5	1.6×10^{12}	3f
11	**1b**	~36 years	107 days	30.3	4.2×10^{13}	

[a] For our data, errors are estimated as follows: E_{act} ±0.6 kcal/mol; $\tau_{1/2}$ ± 5%; A ± 10%.

quickly converts it to dark green dihydropyrene **2b**. The latter now shows its aromatic protons at δ 8.99−8.38, consistent with the strong diatropic ring current of the [14]annulene. The *trans* orientation of the nitrile groups was shown by an X-ray structure (Supporting Information).

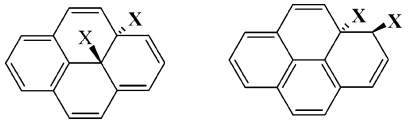
The aldehyde **2c** was obtained as a byproduct in 2% yield in a formylation reaction of **2e** using $SnCl_4$ and CH_3OCHCl_2 in dichloromethane at 20 °C, in which *ipso*-formylation-de-*tert*-butylation occurred as well as normal formylation[3g,12] (50% yield, see below). Aldehyde **2c** was obtained as reddish purple crystals, mp 116−117 °C. The formyl proton appeared at δ 10.53, and only one *tert*-butyl signal was observed at δ 1.68. The naphthoyl compound **2d** was likewise obtained from bromide **2k**[3f] using $AlCl_3$ and naphthoyl chloride in dichloromethane at 20 °C for 24 h, in about 30% yield as purple crystals, mp 211−212 °C. As expected, the dihydropyrene protons of **2d** (δ 9.38−8.53) were more deshielded than the naphthyl protons at δ 8.19−7.47; again, only one *tert*-butyl signal at δ 1.69 was observed. Full characterization of all of these compounds is provided in the Experimental Section.

These de-*tert*-butylation reactions in this system do not appear to have been reported before. Tashiro[12] obtained the normal 4-formyl and 4-acetyl products of **2e** using essentially the same conditions as us. Loss of the internal methyl groups during halogenation has been reported before,[13] as well as chlorine addition, but not replacement of the *tert*-butyl groups. Potentially, this de-*tert*-butylation reaction could be really useful in the synthesis of dihydropyrenes, since the parent di-*tert*-butyl compound **1e** is available on the 10 g scale, and replacement of one *tert*-butyl group in the sterically nonhindered 2-position has much potential which we intend to explore.

Thermal Ring Closure. Most cyclophanedienes **1** (which are colorless) convert to the highly colored dihydropyrenes **2** on warming in solution. Typical half-lives for conversion at 20 °C and 50 °C are shown in Table 1 (along with energies of activation and pre-exponential factors).

Energies of activation can be somewhat misleading in this series, since it appears that the pre-exponential factor shows considerable variation from 10^9 to 10^{13} and generally seem to be smaller for the lower E_{act} values, and thus, the half-lives shown give a more useful comparison. One can see that addition of 5,13-*tert*-butyl groups to **1a** (compare entries 9 and 6) actually decreases E_{act}, but this is compensated for by a reduction in A, such that the overall effect on $\tau_{1/2}$ is increased only slightly. However, addition of a carbonyl-containing group at the 5-position (entries 1−4), a position which has higher calculated spin density in the TS, dramatically shortens the half-lives and increase the rates of conversion, consistent with Williams' calculations. For cases 1−3, E_{act} is lowered from that of **1a** without much change in A. Substitution at the 2-position (entries 5, 7, and 8), where calculated spin density is low, has little or no effect. Again, addition of a *tert*-butyl group only has a small effect. However, exchange of the internal methyl groups for internal nitrile groups, compound **1b** (entry 11), has a very significant effect. The rate at the temperatures relevant for all the other cyclophanedienes measured is very slow. At 50 °C, no closure of CPD **1b** to DHP **2b** can be observed (consistent with the extrapolated value for $\tau_{1/2}$ given in Table 1), which is again consistent with Williams' calculations. Previously, the benzo derivative[3f] (entry 10) had the best thermal stability, but this is easily surpassed by the dinitrile **1b**, where E_{act} is approximately 30.3 kcal/mol. The pre-exponential factor, A, has also increased, but not enough to offset the large change in E_{act}. However, heating **1b** at 100 °C does not lead to isolable dihydropyrene **2b**, but instead a rearrangement product is observed.

The Perversity of Nature! The good thermal stability of dinitrile **1b** should make it an excellent candidate as a photoswitch; however, that requires that both photoproducts **1** and **2** are stable. Introduction of the internal nitrile substituents certainly has made the cyclophanediene **1b** stable, but unfortunately, a new twist now occurs. The dihydropyrene form **2b** is now thermally unstable and rearranges first to **9b** and then to **10b**.



9 **a** X=Me **10**
b X=CN

Rearrangement of the parent **2a** in to **9a** has been known since 1969,[14] but in this case the rearrangement does not occur until **2a** is heated to 190−210 °C. When the internal substituents are X = Et or Pr, then the rearrangement proceeds at lower temperature, about 80 °C.[15] Boekelheide et al. concluded that these rearrangements proceed through 1,5-sigmatropy.[14,15] In-

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terestingly, for the dinitrile **2b**, the rate for conversion in to **9b** in chloroform [$\tau_{1/2}$(50 °C) = 8.3 h; E_{act} = 23.4 kcal/mol, A = 1.3 × 10^{11} s^{-1}] is faster than in benzene [$\tau_{1/2}$ = 66 h, E_{act} = 28.5 kcal/mol, A = 5.2 × 10^{13} s^{-1}] or in the solid state [$\tau_{1/2}$ = 13 h, E_{act} = 28.5 kcal/mol, A = 2.0 × 10^{14} s^{-1}]. Using the B3LYP/6-31G* method as instituted in Gaussian 98,[16] we optimized the transition structures for **2/TS/9** for a range of substituted DHPs and herein report the results for **2a** and **2b**. Normal Mode visualization of the single imaginary frequencies of these TSs confirm that the displacements correspond with the anticipated 1,5-sigmatropic rearrangement. The calculated activation barriers ($\Delta H^{\ddagger}$ = 31.11, $\Delta G^{\ddagger}$ = 29.39 (298) kcal/mol) for the 1,5-sigmatropic shift (**2b**/**9b**) are about 7 kcal/mol less than those calculated for the migration of the internal methyl groups of **2a**. We calculate that rearranged product **9a** is about 3 kcal/mol lower in energy than dihydropyrene **2a**, but fortunately this reaction has high activation barriers ($\Delta H^{\ddagger}$ = 38.4, $\Delta G^{\ddagger}$ = 36.49 (298) kcal/mol) − (experimentally, E_{act} is probably less than this), which accounts for the fact that **2a** rearranges at a much higher temperature than for the nitrile **2b**. Carbonyl-containing groups are predicted to have lower barriers for rearrangement (**2** to **9**), e.g., ∼17 kcal/mol for X = COMe. Our calculated and experimental activation barriers for these 1,5-sigmatropic rearrangements (**2**−**9**) are in line with previously determined migratory aptitudes.[17] We will be attempting syntheses of these and compounds with related substituents to see if these calculations can be verified and also to find a substituent which like nitrile **1b** has a low thermal closure rate, but as well a low 1,5-rearrangement rate.

Conclusions

Calculations suggested the dinitrile **1b** should not thermally convert to the dihydropyrene **2b** at room temperatures. This turned out to be correct; E_{act} >30 kcal/mol and $\tau_{1/2}$ at 20 °C is calculated to be >30 years! Unexpectedly, however, the dihydropyrene **2b** obtained on UV closing of **1b**, underwent a relatively easy 1,5-sigmatropic rearrangement resulting in loss of the [14]annulene perimeter. Calculations verified that rearrangement of internal nitrile groups should be faster than the methyl groups of **2a**. Synthesis of **1c** and **1d**, which have radical-stabilizing carbonyl groups at the 2-position, led as predicted from calculations to increased thermal conversion rates to the dihydropyrenes, relative to parent **1a**.

Experimental Section

General conditions are given in the Supporting Information.

9,18-Dicyano-2,11-dithia[3.3]metacyclophane 4. The bis(bromomethyl)nitrile **3**[8] (4.00 g, 13.8 mmol) in deaerated benzene (400 mL) in one dropping funnel was added at the same drop rate (∼1 every 2−3 s) as $Na_2S{\cdot}9H_2O$ (3.32 g, 13.8 mmol) in deaerated water (400 mL) in a second funnel to a mixture of vigorously stirred ethanol (95%, 1400 mL) and water (200 mL) under nitrogen. The addition took about 20 h. The solvent was then evaporated, and the residue was dissolved in CH_2Cl_2 and water. The organic layer was washed, dried, and evaporated, and the residue was chromatographed on silica gel using CH_2Cl_2−hexanes (6:4) as eluant. Eluted first was 527 mg (24%) of *anti*-**4** as colorless crystals from dichloromethane: mp ∼220 °C dec; ^{1}H NMR δ 7.66−7.60 (m, 6H, ArH), 3.94 and 3.88 (AB, J = 14.4 Hz, 8H, $-CH_2-$); ^{13}C NMR δ 140.8 (C-4,8,13,17), 134.4 (C-6,15), 130.7(C-5,7,14,16), 115.4 (CN), 114.5 (C-9,18), 32.2 (C-1,3,10,12); IR ν (KBr) 2216, 1588, 1464, 1445, 1408, 1237, 810, 801, 752 cm^{-1}; UV (CH_2Cl_2) λ_{max} (ϵ_{max}) 305 nm (3400); EI MS m/z 322 (M^+). X-ray structure: see the Supporting Information. Eluted second was 553 mg (25%) of *syn*-**4** as colorless crystals from dichloromethane: mp ∼215 °C dec; ^{1}H NMR δ 7.15 (2d, J = ∼7.3 Hz, 4H, H-5,7,14,16), 7.07 (2d, J = ∼7.3 Hz, 2H, H-6,15), 4.55 and 3.81 (AB, J = 15.5 Hz, 8H, $-CH_2-$); ^{13}C NMR δ 142.0 (C-4,8,13,17), 133.0 (C-6,15), 129.5 (C-5,7,14,16), 116.7 (CN), 113.1 (C-9,18), 35.9 (C-1,3,10,-12); IR ν (KBr) 2212, 1590, 1466, 1452, 1414, 794, 751 cm^{-1}; UV (CH_2Cl_2) λ_{max} (ϵ_{max}) 298 nm (5800); EI MS m/z 322 (M^+). X-ray structure: see the Supporting Information. Eluted third was 400 mg (18%) of the cyclic trimer **5** as colorless crystals from dichloromethane: mp ∼220 °C dec; ^{1}H NMR δ 7.46−7.39 (m, 9H, ArH), 3.79 (s, 12H, -CH_2-); ^{13}C NMR δ 141.8 (C-4,8), 132.7 (C-6,15), 128.6 (C-5,7), 115.2 (CN), 114.1 (C-9), 33.8 (C-1,3); IR (KBr) ν 2213, 1590, 1466, 795, 754 cm^{-1}; UV (CH_2Cl_2) λ_{max} (ϵ_{max}) 295 nm (4700); EI MS m/z 483 (M^+).

For preparative purposes, *anti*- and *syn*-**4** need not be separated. Vogtle has reported **4** previously,[9] but in low yield and without separate characterization of each isomer.

Bis-sulfonium Salt 6. Mixed isomers of **4** (400 mg, 1.24 mmol) in dry CH_2Cl_2 (15 mL) were added slowly to $(MeO)_2CHBF_4$[18] (80% oil, 550 mg, 2.7 mmol) at −78 °C with stirring under nitrogen. The mixture was then stirred at 20 °C for 3 h. The CH_2Cl_2 was decanted, ethyl acetate (40 mL) was added, and stirring (trituration) was continued for a further 3 h. The white precipitate was then collected and dried to give 650 mg (quant) of bis-sulfonium salt **6**. This was used directly in the next step. If pure *anti*-**4** was used, the resultant salt showed ^{1}H NMR (DMSO-d_6) δ 8.14−8.12 (m, 2H), 7.98−7.97 (m, 4H), 5.14 and 4.27 (AB, J = 14.7 Hz, 4H, $-CH_2-$), 5.01 and 4.92 (AB, J = 14.1 Hz, 4H, $-CH_2-$), 3.46 (s, 6H, $-CH_3$). If pure *syn*-**4** was used, the salt showed a more complicated ^{1}H NMR spectrum, suggesting more than one conformer formed, with the aromatic protons at δ 8.0−7.2, the methylene protons at δ 5.5−4.0 and the methyl protons at δ 3.4 and 3.3.

[2.2]Cyclophane 7. *t*-BuOK (330 mg, 2.94 mmol) was added to a stirred suspension of mixed isomers of salt **6** (600 mg, 1.15 mmol) in THF (25 mL) under argon at 20 °C. After the mixture was stirred for 3 h, water was added followed by dichloromethane (120 mL). The extract was washed, dried, and evaporated. The residue was chromatographed over silica gel using CH_2Cl_2−hexane (6:4) as eluant to give 190 mg (48%) of product **7** as a mixture of isomers: EI MS m/z 350 (M^+, 100%). These could be used directly in the next step. For characterization, rechromatography yielded a single isomer of **7**, in which the 1,9-SMe groups are pseudoequatorial:[10] mp ∼215 °C dec; ^{1}H NMR δ 8.05−8.03 (m, 2H, H-6,14), 7.58−7.56 (m, 4H, H-4,5,12,13), 4.17 (dd, J = 11.5, 3.6 Hz, 2H, H-1,9), 3.53 (dd, J = 12.8, 3.6 Hz, 2H, H-2_{eq},10_{eq}), 2.87 (dd, J = 12.8, 11.5 Hz, 2H, H-2_{ax},10_{ax}), 2.17 (s, 6H, −SMe); ^{13}C NMR δ 141.0 (C-3,11), 140.3 (C-7,15), 134.6 (C-5,13), 130.8 (C-4,12), 127.3 (C-6,14), 119.8 (C-8,16), 114.9 (CN), 54.5 (C-1,9), 44.6 (C-2,10), 15.8 (CH_3); IR (KBr) ν 2215, 1579, 1460, 1440, 1431, 806, 766, 743, 580, 497 cm^{-1}; UV (CH_2Cl_2) λ_{max} (ϵ_{max}) 303 nm (1270); EI MS m/z 350 (M^+); HR MS calcd for $C_{20}H_{18}N_2S_2$ 350.0911, found 350.0902.

Bis-sulfonium Salt 8. Mixed isomers of **7** (350 mg, 1.00 mmol) in dry CH_2Cl_2 (20 mL) were added slowly to $(MeO)_2CHBF_4$[18] (80% oil, 600 mg, 3 mmol) at −78 °C with stirring under nitrogen. The mixture was then stirred at 20 °C for 3 h. The CH_2Cl_2 was decanted, ethyl acetate (20 mL) was added, and stirring (trituration) was continued for a further 3 h. The white precipitate was then collected and dried to give 550 mg (quant) of bis-sulfonium salt **8**. This was

(16) Gaussian 98, Revision A.9, Frisch, M. J. et al. Gaussian, Inc., Pittsburgh, PA, 1988. (The complete reference is given in the Supporting Information).

(17) For example, see: Battye, P. J.; Jones, D. W. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1479 and references cited therein.

(18) Borch, R. F. *J. Org. Chem.* **1969**, *34*, 627.

used directly in the next step. When the pure 1,9-diequatorial-SMe isomer of **7** was used, the product was a single isomer: ^{1}H NMR δ 8.18−7.81 (m, 6H, ArH), 4.92 (dd, J = 11.5, 3.6 Hz, 2H, H-1,9), 4.01 (dd, J = 12.8, 3.6 Hz, 2H, H-2_{eq},10_{eq}) and 3.19 (∼t, J = ∼12 Hz, 2H, H-2_{ax},10_{ax}), 3.46 and 3.07 (s, 6H, −SMe_2).

8,16-Dicyano-*anti*-[2.2]metacyclophane-1,9-diene 1b. (Note: To avoid photochemical conversion of **1b** to **2b**, these operations should be carried out under minimal light.) *t*-BuOK (250 mg, 2.23 mmol) was added to a stirred suspension of mixed isomers of bis-sulfonium salt **8** (550 mg, 0.980 mmol) in THF (25 mL) under argon at 20 °C. After the mixture was stirred for 30 min, water was added followed by dichloromethane (120 mL). The extract was washed, dried, and evaporated. The residue was chromatographed over silica gel using CH_2Cl_2 as eluant to give as the major product, 187 mg (75%) of **1b** as colorless crystals, which on attempted mp determination converts into DHP and migration product: ^{1}H NMR δ 7.54 (t, J = 7.6 Hz, 2H, H-5,13), 7.01 (d, J = 7.6 Hz, 4H, H-1,3,6,8), 6.63 (s, 4H, H-1,2,9,10); ^{13}C NMR δ 140.7 (C-3,7,-11,15), 135.9 (C-5,13), 134.8 (C-1,2,9,10), 128.5 (C-4,6,12,14), 120.1 (C-8,16), 115.8 (CN); IR (KBr) ν 2215, 1560, 1442, 859, 810, 757, 570 cm^{-1}; UV (CH_2Cl_2) λ_{max} (ϵ_{max}) 225 nm (30,000), 282 (9800), 330 (4800), 367 (1600); EI MS m/z 254 (M^+); HR MS calcd for $C_{18}H_{10}N_2$ 254.0843, found 254.0833. This compound on exposure to room light, and in particular UV, partially converts to the dihydropyrene **2b**.

***trans*-10b,10c-Dicyano-10b,10c-dihydropyrene 2b.** Irradiation of a solution of cyclophanediene **2a** in dichloromethane (concentration is not critical, 5 mg/mL is convenient) with a UV source with output 254 nm quickly converts **2a** in to **2b** quantitatively; however, **2b** slowly converts thermally into **3b**, even at room temperature (see below), and so irradiation should not be continued unnecessarily. Careful evaporation of the dichloromethane yields green crystals of product **2b**. On attempted mp determination, these turn colorless (from ∼70 °C up, depending upon the rate of heating, and finally melt at 143−144 °C, corresponding to **9b**). Slow evaporation (in the dark) from dichloromethane yielded X-ray-suitable crystals of **2b** (see the Supporting Information): ^{1}H NMR δ 8.97 (s, 4H, H-4,5,9,10), 8.83 (d, J = 7.8 Hz, 4H, H-1,3,6,8), 8.37 (t, J = 7.8 Hz, 2H, H-2,7); ^{13}C NMR δ 127.5 (C-3a,5a,10a,-10d), 126.7 (C-4,5,9,10), 126.3 (C-2,7), 125.5 (C-1,3,6,8), 108.6 (CN), 30.8 (C-10b,10c); IR (KBr) ν 2227, 1351, 1254, 974, 930, 855, 767, 620 cm^{-1}; UV (CH_2Cl_2) λ_{max} (ϵ_{max}) 640 (770), 599 (130), 528 (80), 442 (6400), 367 (34,300), 331 (87,300); EI MS m/z 254 (M^+); HR MS calcd for $C_{18}H_{10}N_2$ 254.0843, found 254.0832.

10a,10b-Dicyano-10a,10b-dihydropyrene 9b. Dihydropyrene **2b** (10 mg) in $CDCl_3$ (0.8 mL) was sealed in a glass tube under argon and heated at 70 °C for 30 min (or until completely colorless), which quantitatively converted it into colorless **9b**; evaporation gave crystals: mp 143−145 °C; ^{1}H NMR δ 7.35 (t, J = 7.7 Hz, 1H, H-7), 7.16 (dd, J = 7.7, 1.1 Hz, 1H, H-8), 7.13 (dd, J = 7.7, 1.0 Hz, 1H, H-6), 6.91 (d, J = 9.2 Hz, 1H, H-9), 6.60−6.57 (m, 2H, H-2,5), 6.43 (d, J = 9.7 Hz, 1H, H-4), 6.30 (dd, J = 5.7, 0.6 Hz, 1H, H-3), 6.17 (d, J = 9.2 Hz, 1H, H-10), 6.09 (d, J = 9.2 Hz, 1H, H-1); ^{13}C NMR δ 132.7 (C-3a,9), 132.1 (C-5a), 131.8 (C-10a), 130.81 (C-2), 130.75 (C-7), 129.7 (C-5), 128.6 (C-6), 127.7 (C-8), 125.5 (C-4), 125.1 (C-10), 124.4 (C-10c), 124.3 (C-3), 124.1 (C-1), 116.7 (10b-CN), 116.2 (10c-CN), 42.7 (C-10b), 40.6 (C-10a); IR (KBr) ν 2227, 1578, 1467, 974, 909, 882, 828, 801, 757, 731, 708 cm^{-1}; UV (CH_2Cl_2) λ_{max} (ϵ_{max}) 405 (2800), 385 (4100), 368 (3500), 348 (4300), 333 (5100), 311 (5400), 298 (5400), 257 (22000); EI MS m/z 254 (M^+); HR MS calcd for $C_{18}H_{10}N_2$ 254.0843, found 254.0834.

1,10a-Dicyano-1,10a-dihydropyrene 10b. Dihydropyrene **2b** (10 mg) in $CDCl_3$ (0.8 mL) was sealed in a glass tube under argon and heated at 70 °C for 4 days, which converted it into **10b**. Evaporation gave colorless solid which decomposed on attempted chromatography but was pure enough to obtain the following data: ^{1}H NMR δ 7.86 (d, J = 8.4 Hz, 1H, H-5), 7.74 (dd, J = 8.3 Hz, 1.0 Hz, 1H, H-6), 7.45 (dd, J = 8.4, 7.0 Hz, 1H, H-7), 7.41 (d, J = 8.3 Hz, 1H, H-4), 7.32 (dd, J = 6.9, 0.8 Hz, 1H, H-8), 7.08 (d, J = 9.5 Hz, 1H, H-9), 7.05 (d, J = 9.4 Hz, 1H, H-3), 6.11 (dd, J = 9.4, 6.2 Hz, 1H, H-2), 6.04 (d, J = 9.5 Hz, 1H, H-10), 3.92 (dd, J = 6.2, 0.6 Hz, 1H, H-1); ^{13}C NMR δ 133.4 (C-5a), 133.1 (C-9), 132.9 (C-3), 129.91 (C-3a), 129.87 (C-5), 129.4 (C-6), 128.4 (C-10d), 127.5 (C-7), 127.0 (C-8), 126.6 (C-10c), 126.2 (C-4), 121.6 (C-10b), 120.8 (C-10), 117.9 (10a-CN), 117.6 (C-2), 114.5 (1-CN), 34.9 (C-10a), 29.9 (C-1); IR (KBr) ν 2224, 1590, 1503, 924, 905, 841, 789, 766, 690, 656 cm^{-1}; EI MS m/z 254 (M^+); HR MS calcd for $C_{18}H_{10}N_2$ 254.0843, found 254.0829.

7-*tert*-Butyl-2-formyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene 2c. Tin tetrachloride (12.00 mL, 100.0 mmol) was added under nitrogen to a solution of DHP **1e**[3f] (7.54 g, 21.9 mmol) and α,α-dichloromethyl methyl ether (2.40 mL, 28.0 mmol) in dichloromethane (650 mL) at 0 °C. The resulting red-brown solution was then stirred at room temperature for 5 h, after which it was slowly added to ice−water (700 mL) and the resulting solution was extracted with dichloromethane (500 mL). The combined organic extracts were washed with water (3 × 600 mL), dried with anhydrous $MgSO_4$, and evaporated to yield a brown solid, which was chromatographed over silica gel. Hexane eluted first unchanged DHP **1e** and 4-chloro-**1e** (3:1 ratio, 3.2 g). Hexane/dichloromethane (2:1) then eluted aldehyde **2i** (4.2 g, 11.3 mmol, 52% based on the used DHP, 88% based on the consumed DHP) as a brown powder[12] and then 140 mg (2%) of purplish red aldehyde **2c**: mp 116−117 °C; ^{1}H NMR δ 10.53 (s, 1H, CHO), 8.95 (s, 2H, H-1, 3), 8.74 (d, J = 7.8 Hz, 2H, H-4, 10), 8.56 (s, 2H, H-6,8), 8.48 (d, J = 7.8 Hz, 2H, H-5,9), 1.68 (s, 9H, 7-C$(CH_3)_3$), −3.82 (s, 3H, 10b-CH_3), −3.84 (s, 3H, 10c-CH_3); ^{13}C NMR δ 193.6 (CO), 151.4 (C-7), 142.4 (C-5a,8a), 134.9 (C-3a,10a), 129.3 (C-4,10), 128.5 (C-2), 125.13 (C-1,3), 123.7 (C-5,9), 122.0 (C-6,8), 36.7 (7-*C*$(CH_3)_3$), 31.9 (7-C(*C*$H_3)_3$), 31.5 (C-10b), 31.3 (C-10c), 16.5 (10c-CH_3), 14.7 (10b-CH_3); IR (thin film on NaCl plate) ν 2961, 1675, 1552, 1134, 885 cm^{-1}; UV (cyclohexane) λ_{max} (ϵ_{max}) nm 212 (14,500), 240 (11,-600), 256 (9,880), 330 (35,600), 347 (73,300), 378 (15400), 402 (29000), 515 (1180), 596 (889), 661 (264); EI MS m/z 316 (M^+); HRMS calcd for $C_{23}H_{24}O$ 316.1827, found 316.1823.

Cyclophanediene Form 1c. Reddish-purple aldehyde **2c** (5−10 mg) in $CDCl_3$ (0.8 mL) in an NMR tube was irradiated with visible light from a 250W household tungsten bulb with a >490 nm cut off filter (using air cooling from a fan) for a few minutes to form a colorless solution of the open form **1c**: ^{1}H NMR (360 MHz) δ 9.79 (s, 1 H, CHO), 7.20 (s, 2H, H-1,3), 6.68 (s, 2H, H-6,8), 6.36 (AB, J = 11.3 Hz, 2H, H-4,10), 6.40 (AB, J = 11.3 Hz, 2H, H-5,9), 1.56 and 1.48 (s, 3H each, CH_3), 1.24 (s, 9H, -C$(CH_3)_3$); ^{13}C NMR (90.6 MHz) δ 192.0, 154.5, 153.0, 138.3, 138.1, 133.4, 131.5, 122.8, 34.3, 31.4, 20.8, 19.5.

4,9-Dibromo-2-naphthoyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene 2d. Aluminum chloride (200 mg, 1.5 mmol) was added to a solution of the dibromide **2k**[3f] (545 mg, 1.08 mmol) and naphthoyl chloride (490 mg, 2.6 mmol) in dichloromethane (35 mL), and the green solution was stirred for 24 h at 22 °C. Water (2 mL) was then added, turning the solution purple from aquamarine. The solution was then poured into hexanes and washed with NaOH (2 M) and water (2×). The organic layer was dried ($MgSO_4$) and evaporated. The residue was chromatographed over alumina (deactivated with 5% water) using hexanes/dichloromethane (2:1) as eluant. Eluted first was green unreacted starting material (180 mg, 0.36 mmol), eluted second was the normal 5-naphthoyl product (68 mg, 0.10 mmol), then a brown bromonaphthoyl product (131 mg, 0.23 mmol), and fourth, 195 mg (30%) of the desired purple product **2d**, which gave crystals from acetonitrile: mp 211−212 °C; ^{1}H NMR δ 9.38 (s, 1H, H-3), 8.87 (s, 1H, H-1), 8.86 (s, 1H, H-8), 8.79 (s, 1H, H-10), 8.71 (s, 1H, H-5), 8.53 (s, 1H, H-6), 8.19 (d, J = 8.6 Hz, H-20), 8.10 (d, J = 8.3 Hz, H-15), 7.99 (d, J = 7.8 Hz, H-17), 7.79 (dd, J = 7.0, 0.9 Hz, 1H, H-13), 7.63−7.61 (m, 1H, H-14), 7.57−7.54 (m, 1H, H-18), 7.50−7.47 (m, 1H, H-19), 1.69 (s, 9 H, H-25), −3.57 (s, 3H, H-23), −3.62 (s, 3H, H-22); ^{13}C NMR δ 198.5 (C-11), 153.3 (C-7), 141.9 (C-5a), 137.6 (C-12),

137.3 (C-10d), 135.5 (C-10a), 134.1 (C-16), 132.6 (C-10), 131.7 (C-2), 131.6 (C-21), 131.5 (C-3a), 131.4 (C-15), 128.7 (C-17), 128.1 (C-13), 128.0 (C-5), 127.4 (C-19), 127.0 (C-1), 126.7 (C-18), 126.6 (C-3), 126.2 (C-20), 124.7 (C-14), 123.0 (C-8), 123.0 (C-4), 122.6 (C-6), 117.0 (C-9), 37.0 (C-24), 33.5 (C-10c), 33.2 (C-10b), 31.9 (C-25), 16.1 (C-22), 14.812 (C-23); IR (KBr) ν 1643, 1548, 1507, 1461, 1335, 1276, 1189, 1132, 1108, 901, 783, 738 cm^{-1}; UV (cyclohexane) λ_{max} (ϵ_{max}) nm 220sh (68200), 360 (76800), 388 (23800), 412 (39600), 527 (13300), 604 (1440), 670 (325); EI MS *m/z* 600 (M^+); HRMS calcd for $C_{33}H_{28}Br_2O$ 598.0507, found 598.0501.

Cyclophanediene Form 1d. Purple ketone **2d** (5-10 mg) in $CDCl_3$ (0.8 mL) in an NMR tube was irradiated with visible light from a 250 W household tungsten bulb with a >490 nm cut-off filter (using air cooling from a fan) for a few minutes to form a colorless solution of the open form **1d**: ^{1}H NMR δ 8.11 (d, J = 7.2 Hz, 1H), 8.02 (d, J = 7.4 Hz, 1H), 7.95−7.93 (m, 1H), 7.87 (s, 1H), 7.58−7.50 (m, 4H), 7.24 (s, 1H), 7.21 (s, 1H), 6.87 (s, 1H), 6.80 (s, 1H), 6.75 (s, 1H), 1.58 (s, 3H), 1.56 (s, 3H), 1.28 (s, 9H); ^{13}C NMR δ 196.1, 153.1, 150.2, 138.4, 138.1, 137.8, 137.53, 137.49, 136.0, 135.4, 134.0, 133.9, 131.7, 131.0, 130.0, 128.9, 128.7, 127.8, 127.6, 126.9, 126.7, 125.7, 125.2, 124.5, 124.10, 124.06, 34.7, 31.3, 20.5, 19.8; UV−vis ($CHCl_3$) λ_{max} (ϵ_{max}) nm, 261 sh (30200), 303 (20100).

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Supporting Information Available: General synthetic experimental conditions, thermal closing data for **1b**−**e**; ^{1}H and ^{13}C NMR spectra for *anti*- and *syn*-**4**, **5**, **6** (^{1}H), **7**, **8** (^{1}H), **1b**, **2b**, **9b**, **10b**, **2c**, **1c**, **2d**, and **1d**; X-ray structures for *anti*-**4**, *syn*-**4**, and **2b**; tables of Cartesian coordinates and energies for all optimized structures and complete ref 16. This material is available free of charge via the Internet at http://pubs.acs.org.

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