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Calculation Driven Synthesis of an Excellent Dihydropyrene Negative Photochrome and its Photochemical Properties

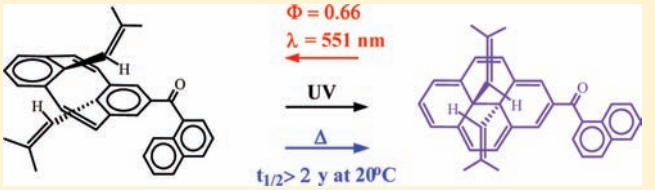
Khurshid Ayub,[†,§] Rui Li,[†] Cornelia Bohne,[†] Richard Vaughan Williams,[‡] and Reginald H. Mitchell*[,†]

[†]Department of Chemistry, University of Victoria, P.O. Box 3065, Victoria, BC, Canada V8W 3V6

[‡]Department of Chemistry, University of Idaho, P.O. Box 442343, Moscow, Idaho 83844-2343, United States

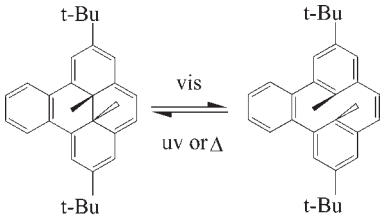
Supporting Information

ABSTRACT: The photochromic properties of dihydropyrenes have been substantially improved by making use of density functional theory (DFT) activation barrier calculations, which suggested that the di-isobutenylcyclophanediene **15′** should have a significant barrier to thermal isomerization to the dihydropyrene (DHP) **15**, which itself should resist isomerization involving migration of the internal groups to the rearranged dihydropyrene **9** (X = −CH═C(Me)$_2$). As a result of these calculations, the synthesis of the colorless cyclophanediene (CPD) **15′** was undertaken and achieved from the dinitrile **28** in four steps in 37% overall yield %. The cyclophanediene **15′** thermally isomerized to the dihydropyrene **15** at 100 °C with $t_{1/2}$ = 4.5 h, giving an extrapolated 20 °C $t_{1/2}$ of ∼16 y, consistent with the DFT calculations. No evidence for [1,5]-sigmatropic rearrangement in to **9** (X = −CH═C(Me)$_2$) was observed on heating to 130 °C. The ring-opening isomerization quantum yields (ϕ_{open}) for DHP **15** in to CPD **15′** were determined in cyclohexane to be 0.12 ± 0.01, which is three times greater than for the benzoDHP **1**. Friedel−Crafts naphthoylation of **15** gave 70% of purple **32**, which in toluene showed the largest photochemical ring-opening isomerization quantum yields (ϕ_{open}) of 0.66 ± 0.02 for any known dihydropyrene, ∼nine times greater than **1** in toluene. The thermal closing of **32′** to **32**, although faster than for **15′**, gave a useful extrapolated $t_{1/2}$ of ∼2 y at 20 °C.



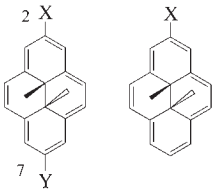
INTRODUCTION

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



1 DHP **1′** CPD

However, the quantum yield of the opening reaction, **1** to **1′**, is not so impressive (Φ = 0.042 in cyclohexane),[3a] and thus the objective of this work was to design a DHP photochrome which showed both a much improved quantum yield and a much lower rate of thermal return. This latter objective is important because we already knew[4] that addition of carbonyl or nitro groups, especially at the 2 and 7 positions of a DHP (**2**), for example as in **3**−**6**:



2

3 X=CHO
4 X=COMe
5 X=CONaphthyl
6 X=NO_2

(where Y = H), had a pronounced improvement in the photo-opening reaction rate but at a cost of a dramatically increased thermal rate of return of the CPD forms to the DHP isomers. We were hopeful that density functional theory (DFT) activation barrier calculations could lead us in the correct direction to design an improved DHP photochrome with also a very slow thermal return reaction. Our previous studies,[4c] in which calculations guided synthesis, gave us a thermally stable cyclophanediene, the

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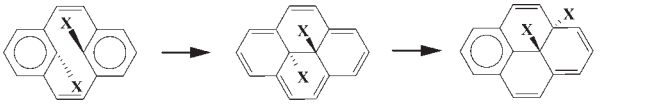
Table 1. Barriers (kcal/mol) to the Thermal Reversions of the CPDs to DHPs

	DHP/TS		CPD/TS		
compound[a] (symmetry)	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	R
8 (C_{2h})[b]	36.11	36.45	25.15	25.31	CN
10 (C_i)	36.05	36.13	21.55	21.29	CHO
11 (C_i)	33.91	34.53	20.87	20.45	$COCH_3$
12 (C_i)	32.96	33.47	22.96	22.60	CO_2H
13 (C_i)	35.99	36.82	23.15	22.98	$CH{=}CH_2$
13 (C_i)	35.99	36.82	23.15	22.98	$CH{=}CH_2$
14 (C_i)	30.95	31.09	26.55	27.01	*cis*-$CH{=}CHCH_3$
15 (C_i)	30.16	29.95	27.46	28.04	$CH{=}C(CH_3)_2$
16 (C_i)	29.27	30.01	26.96	26.53	*cis*-CH=CHPh
17 (C_1)	30.03	32.03	24.67	25.12	*cis/trans*-CH=CHPh
18 (C_1)	33.49	34.18	23.58	23.67	*trans*-CH=CHPh
19 (C_{2h})	34.67	35.14	24.34	24.48	C≡CH
20 (C_s)	39.73	40.41	22.25	21.79	CH_3; CN
21 (C_{2h})	34.51	35.32	34.98	35.38	NH_2
22 (C_{2h})	43.70	44.15	29.25	29.32	F
22 (C_i)	43.70	44.15	29.26	29.30	F
23 (C_i)	29.42	29.66	26.50	26.74	*cis*-CH=CH*p*MeOPh
24 (C_i)	29.05	29.97	26.46	26.38	*cis*-CH=CH*p*NO_2Ph

[a] The number (N) of the DHP is given; the CPD has number N′. [b] Results (from Gaussian 98 calculation) reported in ref 6.

dinitrile **8′**. Thus whereas $t_{1/2}$ (20 °C) for CPD **7′** thermally closing to DHP **7** was about 42 h, that for the dinitrile CPD **8′** forming DHP **8** was >30 y!! Nature can be a bit perverse at times though, since although DHP **7** is thermally stable[5] below ~200 °C, the dinitrile DHP **8** readily undergoes [1,5] sigmatropic rearrangement to the DHP **9b** at 50 °C.[4c]

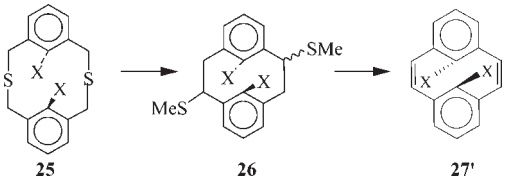


Thus the goal of this project was to use calculations to not only suggest suitable internal substituents that would retain the slow thermal reversion of **8′** to **8** but also would avoid the rearrangement of **8** to **9b** and also would yield derivatives with better quantum yields than compound **1**.

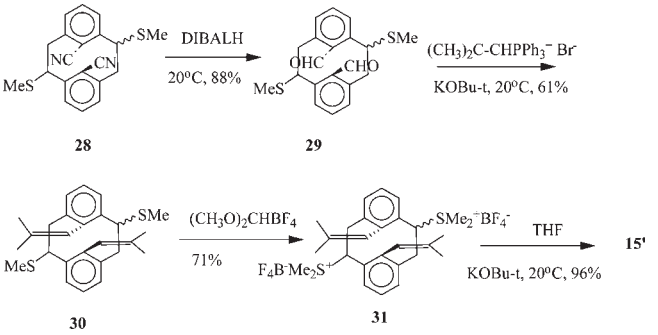
CALCULATIONS

Previously,[6] using B3LYP/6-31G* DFT calculations, we obtained structures and energies of 21 pairs of CPD's and DHP's along with their corresponding transition states (TSs). We found that the dinitrile **8′** has the highest calculated activation barrier for **8′**/**TS**/**8** of those studied. Indeed, when synthesized,[4c] **8′** showed a very long thermal half-life for conversion in to **8**: $t_{1/2}$ (exp) 5 h (100 °C), with extrapolated $t_{1/2}$ values of 107 days (50 °C), >30 y (20 °C). When we found that **8** easily isomerized to **9b**, we likewise calculated the barriers for **8**/**TS**/**9b** and **7**/**TS**/**9a** and indeed found that the calculated barrier for **8** to **9b** ($\Delta H^{\ddagger}$ = 31.1, $\Delta G^{\ddagger}$ = 29.4 (298) kcal/mol) was about 7 kcal/mol less than for **7** into **9a**, consistent with experiment. Thus for this project, we would need substituents that yield high barriers for both CPD to DHP and DHP to **9**.

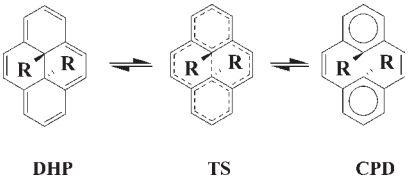
Scheme 1. The Synthetic Route Used to Most Cyclophanedienes[3b,4c]



Scheme 2. The Synthetic Route Used to Prepare 15′



From our earlier calculations,[6] we concluded that internal substituents capable of conjugating with the "benzene" rings of the CPDs lowered the energy of the CPDs and consequently stabilized them to orbital symmetry forbidden electrocyclizations to the DHPs. We were therefore motivated to examine a series of DHPs/TS/CPDs with conjugating internal substituents **10**−**24** in an effort to discover further long-lived CPDs (Table 1). The geometries for all compounds in this study were optimized using the B3LYP/6-31G* method as implemented in the Gaussian 03 suite of programs.[7] All optimized structures were confirmed to be minima (zero imaginary frequencies) or transition structures (one imaginary frequency) through their calculated energy second derivatives. All transition structures were further characterized by visualization of the imaginary normal mode.



Considering the barriers for thermal cyclo-reversion (CPD to DHP) and using $\Delta H^{\ddagger}$ for the dinitrile **8′** (25.3 kcal/mol) as a reference, the di-isobutenyl derivative **15′** at 28.0 kcal/mol, the diamino derivative **21′** at 35.4 kcal/mol, and the difluoro derivative **22′** at 29.3 kcal/mol are predicted to be the most thermally stable CPDs. The anti-difluoro CPD **22′** is known[8,9] and does not thermally or photochemically close to the DHP **22**. The analogous syn compound does close thermally at 35 °C to the *cis*-DHP, but the latter undergoes easy rearrangement to isomeric DHPs, finally giving substituted pyrenes.[8] Unsubstituted[10] amino DHPs are not known, probably because of the excessively electron-rich character of the aromatic ring which

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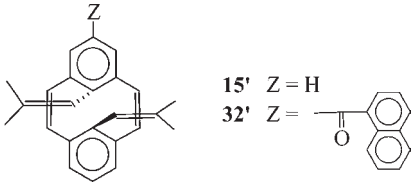
causes easy decomposition. All our attempts to prepare them have failed. Thus the most promising candidate from the above list is the isobutenyl derivative **15′**, providing sigmatropy from DHP **15** to **9c** is not facile. We were delighted to find that the B3LYP/6-31G* barriers ($\Delta H^{\ddagger}$ = 35.6, $\Delta G^{\ddagger}$ = 35.9 (298) kcal/mol) for **15**/**TS**/**9c** are approximately 5 kcal/mol higher than those for dinitrile **8**. Thus encouraged, we undertook the synthesis of **15′** and **15**. The syntheses and properties and the detailed calculational results of the other compounds in Table 1 will be reported elsewhere.

Synthesis of Isobutenyl Derivative 15′.



The dinitrile **8′** should serve as a suitable precursor to **15′** by functional group transformation of the CN groups into CH═$C(CH_3)_2$ groups, for example, by reduction of the nitrile groups to aldehydes and then Wittig reaction of these in to isobutenyl groups. In principle this conversion could be carried out on any of the normal intermediates (**25**−**27′**) used for the synthesis of cyclophanedienes,[3b,4c] shown in Scheme 1. However, given the calculated easy thermal closure of dialdehyde **10′** into **10** (Table 1), this particular sequence might be best carried out on the precursors **25** or **26**, where **X** = **CN**. In the event, the best yields were obtained by doing this functional group interconversion on the Wittig rearrangement product **26** (**X** = **CN**), as shown in Scheme 2.

Reduction of mixed isomers of **28**[4c] with DIBALH in dichloromethane at 20 °C gave 88% of mixed isomers of aldehyde **29**, which could be used directly in the next step. For characterization purposes, use of the pure diequatorial isomer of **28** gave a single isomer of **29** in which the two −SMe groups are pseudoequatorial. In this isomer, the CHO protons and carbons appeared as one singlet each at δ 8.95 and δ 188.7, respectively. In the mixed isomers, CHO protons could be seen at δ 9.04, 8.95, 8.91, and 8.75. Full characterization, including HRMS and elemental analysis, is given in the Experimental Section. Reaction of the dialdehyde **29** in THF with the preformed ylide from isopropyl triphenylphosphonium bromide and *t*-BuOK for 1 h at 20 °C yielded 61% of the bis-isobutenyl derivatives **30**, which were then methylated[4c] with $(MeO)_2CH^+BF_4^-$ in 71% yield to give mixed isomers of **31**, which were then subjected to the Hoffmann elimination using *t*-BuOK in THF at 20 °C for 1 h (reaction and work up in minimal light) and yielded 96% of the colorless CPD **15′**, with correct high-resolution mass spectrometry (HRMS) and elemental analysis and with fully assignable proton and carbon NMR spectra (see Experimental Section).

Does Isobutenyl CPD 15′ Resist Thermal Closure? Yes! Rates of thermal closing were determined at 100, 110, 120, and 130 °C, and the half-life at 100 °C was found to be 4.5 h (compare dinitrile **8′** at 6 h and parent **7′** at a few seconds). The extrapolated half-life at 20 °C is then ∼16 y for **15′**, which certainly makes it very satisfactory in potential applications as a photoswitch. Comparison data of **8′**[4c] and **15′** derived using Arrhenius and Eyring data (see Experimental Section) are given in Table 2.

Table 2. Comparison of Experimental (exp) and Extrapolated (ext) Thermal Data for the Thermal Electrocyclization of Dinitrile CPD 8′[4c] **and Bis-Isobutenyl CPD 15′ to the Corresponding DHPs**

	8′	15′
E_{act} (kcal/mol)	30 (±1)	28.2 (±0.5)
ln A	30 (±1)	28.0 (±0.6)
$\Delta H^{\ddagger}$ (kcal/mol)	29 (±1)	27.5 (±0.5)
ΔS (cal/mol/K)	−1 (±3)	−5 (±1)
$\tau_{1/2}$ (20 °C) (ext)	∼36y[a]	∼16 y
$\tau_{1/2}$ (50 °C) (ext)	107d[a]	65 d
$\tau_{1/2}$ (100 °C) (exp)	5.8 h	4.5 h
$\tau_{1/2}$ (110 °C) (exp)	1.6 h	1.8 h
$\tau_{1/2}$ (120 °C) (exp)	36 min	39 min
$\tau_{1/2}$ (130 °C) (exp)	14 min	16 min

[a] Extrapolated using 15 029 as value for E_{act}/R.

The question then arises: Is there any evidence for sigmatropic rearrangement of the internal groups of the DHP? When dinitrile **8′** thermally isomerizes to DHP **8** at >100 °C, the sigmatropic rearrangement to **9b** is sufficiently fast that this is the observed product.[4c] However, pleasingly, in the above studies of **15′**, no rearrangement products from the DHP **15** were observed. Fortunately, in this respect, isobutenyl groups appear to behave more like methyl groups.[5] Indeed, the calculated barriers to [1,5] sigmatropy for the isobutenyl DHP **15** are much closer to those for parent **7** than those for dinitrile **8**.

Naphthoylated CPD 32′ Data. We anticipated that introduction of a naphthoyl group in the two position of **15** would be necessary to improve its photochromic properties, but we required that the effects on the thermal properties on both the CPD and DHP also not be increased.[4] Naphthoylation of DHP **15** using naphthoyl chloride and $AlCl_3$ in dichloromethane is rapid, and so the reaction must be quenched within 4 s of addition of the $AlCl_3$ to obtain after purification ∼70% of DHP **32** as purple crystals, mp 179−180 °C. Longer reaction times produced multiple decomposition products.

Irradiation of a toluene solution of **32** in an NMR tube for a few minutes with >490 nm light (see Experimental Section) quantitatively converted it to the CPD form **32′**, on which the thermal closure studies were conducted. Experimentally, $t_{1/2}$ for the thermal conversion of **32′** to **32** was found to be 8.5 days at 50 °C and extrapolated to be 2 years at 20 °C. These values would permit **32′** to be a useful photochrome.

Photo-Opening/Photoclosing Reactions of 15 and 32. Qualitative photo-opening studies on **15** and **32** in dichloromethane are shown in Figure 1.

Since the same light flux conditions were used (8000 lm bulb at 15 cm), immediately obvious is that whereas **15** opens slowly, the naphthoyl derivative **32** opens extremely rapidly such that at UV−vis type concentrations, after three 1 s irradiation flash periods were used, the sample was essentially completely open.

Using ^{1}H NMR concentrations, the conversion at a given light intensity was of course slower, and then it was possible to quantify the amount of opening by NMR in a *d*-8 toluene solution on irradiation with visible light from a standard tungsten bulb and an orange filter to block light of λ < ∼490 nm. Then using equal NMR concentrations, with the same light source, **15** opens approximately four times more efficiently than the parent **7**, but ∼four times less efficiently than benzo-DHP **1**, while **32**

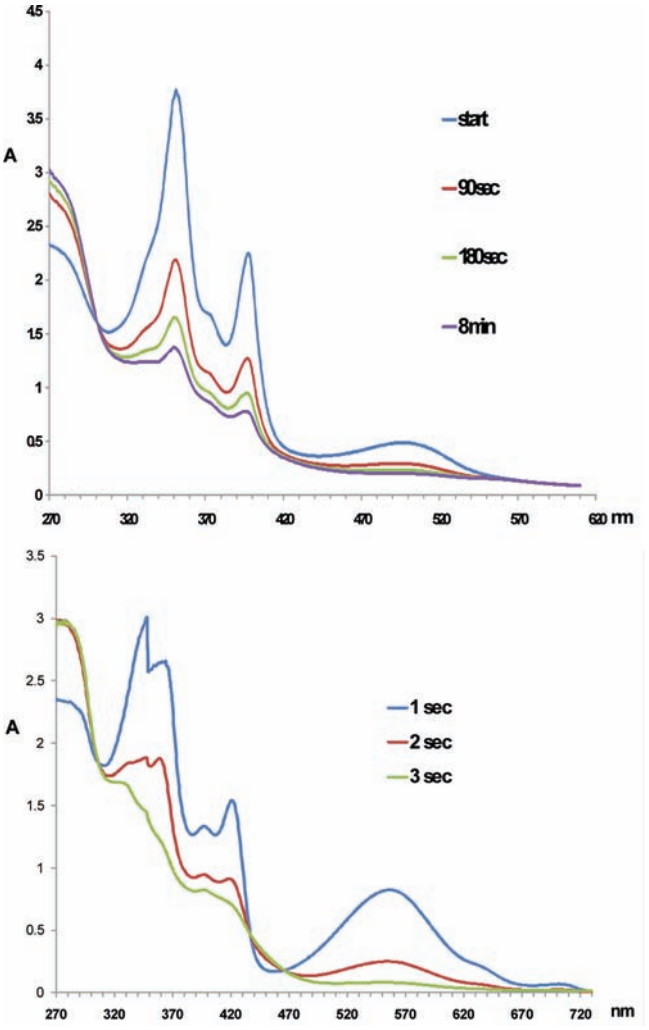


Figure 1. Visible light opening of DHP **15** (top) and naphthoyl-DHP **32** (bottom) in dichloromethane.

opens ~25 times more efficiently than benzo-DHP **1** and ~100 times more efficiently than **15**. This was confirmation of our expectation that introduction of the naphthoyl group in to **15** would considerably increase the efficiency of the photo-opening reaction of DHP to CPD. Most cyclophanedienes studied close easily with UV light into the corresponding DHPs.[3a,b] Experimentally **32** closes with essentially the same efficiency as benzo-DHP **1**.

Quantum Yields. Ring-opening isomerization quantum yields (ϕ_{open}) of DHP to CPD for compounds **1**, **15**, and **32** were determined using a potassium ferrioxalate actinometer[11] as the primary standard and benzo-DHP **1** as the secondary standard. The full experimental method is described in the Supporting Information. The quantum yield for benzo-DHP **1** was redetermined in cyclohexane as 0.039 ± 0.002 compared to 0.042 ± 0.002 in the original study[3a,b] to ensure consistency. The quantum yield for compound **15** was measured in cyclohexane relative to both ferrioxalate and benzo-DHP **1**, which agreed within experimental error, and ϕ_{open} was found to be 0.12 ± 0.01, approximately 3 times higher than that for **1**.

Since naphthoyl-DHP **32** showed poor solubility in cyclohexane, toluene was chosen as solvent, and so first ϕ_{open} for benzo-DHP **1** was determined in toluene and rather surprisingly was found to be 0.074 ± 0.004, which is twice the value in cyclohexane. This result indicates that the ring-opening quantum yield is solvent dependent, probably due to subtle changes to the relevant energies of the excited states and the reactive intermediates proposed to be involved in the ring-opening process.[12] The switch in solvent was dictated by the solubility of **32**, and studies on the solvent effect were beyond the scope of the present work. The quantum yield for naphthoyl-DHP **32** was measured in toluene relative to benzo-DHP **1** in toluene, and for **32**, ϕ_{open} = 0.66 ± 0.02, some 9 times greater than **1** in toluene and 16 times greater than **1** in cyclohexane. This is the largest quantum yield of opening for any DHP so far recorded and compares favorably with any other photochrome.[13]

CONCLUSIONS

DFT calculations were used to design targets for DHPs with slower (improved) thermal reversal reactions (CPD to DHP) and with no sigmatropic rearrangement (DHP to isomeric DHPs). This led to laboratory syntheses of two excellent negative photochromes (**15** and **32**) with relatively slow thermal reversal reactions. Specifically synthesis of the bis-*iso*-butenyl-DHP **15** was achieved from **28**[4c] in 5 steps in 37% overall yield. The thermal return reaction of **15′** to **15** had a extrapolated half-life of ~16 y at 20 °C, a huge improvement over the 7 days for that of our reference standard benzo-DHP, **1′** to **1**.

Importantly, the quantum yield in cyclohexane for the visible opening reaction, **15** to **15′**, was 0.12, approximately 3 times greater than that for the standard **1** to **1′**. As well, unlike the case of the dinitrile **8**, no thermal sigmatropic rearrangement of **15** was observed. Naphthoylation of **15** to **32** was achieved in 70% yield. The quantum yield of opening in toluene for **32** to **32′** was determined to be 0.66, the highest value yet obtained for a DHP and is some 9 times that of **1** to **1′** in toluene, 16 times greater than that in cyclohexane. The thermal closing reaction, **32′** to **32**, showed a extrapolated half-life at 20 °C of ~2 y, faster than for **15′** (~16 y), but much slower than for **1′**(~7 d). Calculational directed synthesis of **15** and **32** has shown that DHPs can be very respectable photochromes.

EXPERIMENTAL SECTION

For general information and structure numbering for the spectral assignments, see the Supporting Information.

2,10-Bis(thiomethyl)-8,16-diformyl-*anti*-[2.2]metacyclophane (29). DIBALH (20 mL of 1 M solution in hexane, 20 mmol) was added dropwise over 3 min to a solution of the dicyano-*anti*-thiomethylcyclophane **28**[4c] (2.30 g, 6.55 mmol, mixed isomers) in dichloromethane (60 mL) at room temperature under argon. The reaction mixture was allowed to stir for 2.5 h and then cooled to 0 °C, treated with excess methanol and stirred for 30 min. Then 0.35 M HCl (100 mL) was added and stirred for 1 h. The resulting solution was extracted between dichloromethane and water. The organic layer was dried over K_2CO_3 and evaporated. Column chromatography over silica gel using hexanes−dichloromethane (2:8) gave 2.05 g (88%) of **29** as a mixture of isomers. ^{1}H NMR ($CDCl_3$) δ 9.04, 8.94, 8.91, 8.75 (4s), 8.04 (d, J = 7.8 Hz), 7.98 (d, J = 7.3 Hz), 7.5−7.2 (m), 5.14 (dd, J = 11.4, 5.0 Hz), 4.83 (dd, J = 11.4, 4.8 Hz), 4.63 (dd, J = 3.37−3.33 (m), 3.20 (t), 2.19−2.18 (3 s, S−Me); EI MS m/z 356 (M^+). These could be used directly in the next step.

For characterization purposes, a single isomer of **29**, in which the 1,9-thiomethyl groups are pseudoequatorial was purified by more careful column chromatography over silica-gel and gave colorless crystals mp

187−192 °C. ^{1}H NMR ($CDCl_3$) δ 8.95 (s, 2H, H-17,18), 8.00 (dd, J = 7.6, 1.0 Hz, 2H, H-6,14), 7.36 (t, J = 7.6 Hz, 2H, H-5,13), 7.27 (dd, J = 7.5 Hz, 1.0 Hz, 2H, H-4,12), 5.15 (dd, J = 11.4, 5.0 Hz, 2H, H-1_{ax},9_{ax}), 3.36 (dd, J = 12.8, 5.0 Hz, 2H, H-2_{eq},10_{eq}), 3.21 (dd, J = 12.8, 11.4 Hz, 2H, H-2_{ax},10_{ax}), 2.19 (s, 6H, -SMe); ^{13}C NMR ($CDCl_3$) δ 188.74 (CHO), 143.49 (C-7,15), 142.94 (C-3,11), 141.15 (C-8,16), 133.28 (C-5,13), 131.24 (C-4,12), 127.04 (C-6,14), 50.89 (C-1,9), 42.23 (C-2,10), 15.82 (SMe); IR ν (KBr) 2890, 2889, 2786, 1682, 1580, 1445, 1208, 880, 789, 738, 707 cm^{-1}; UV (cyclohexane) λ_{max} nm (ε_{max}) 227 (5100), 259 (3500), 297 (800); EI MS m/z 356 (M^+); HR MS Calcd for $C_{20}H_{20}O_2S_2$, 356.0904; Found, 356.0902. Anal. Calcd: C, 67.38; H, 5.65. Found: C, 67.41; H, 5.57.

8,16-Bis(2′-methyl-1′-propenyl)-2,10-bis(thiomethyl)-*anti*-[2.2]-cyclophane (30). To a suspension of isopropyl triphenylphosphonium bromide (2.75 g, 7.14 mmol) in THF (25 mL), *t*-BuOK (2.00 g, 18.6 mmol) was added under argon at 20 °C, and the solution was stirred for 20 min when a clear dark orange-red solution was obtained. To this solution, the mixed isomers of the diformylthiomethylcyclophane **29** (1.00 g, 2.81 mmol) from above were added, and the reaction mixture was allowed to stir for 1 h before quenching with water. The resulting solution was extracted with CH_2Cl_2, washed, dried ($MgSO_4$), and evaporated. The crude mixture was chromatographed over silica gel using hexanes−dichloromethane (7:3) as eluant and gave 700 mg (61%) of mixed (−SMe) isomers the diisobutenylthiomethylcyclophane **30**. ^{1}H NMR ($CDCl_3$) δ 7.75 (d, J = 7.6 Hz), 7.735 (d, J = 7.6 Hz), 7.733 (d, J = 7.6 Hz), 7.24−7.17 (m), 7.06 (t, J = 7.5 Hz), 6.94 (t, J = 7.4 Hz), 4.04 (br s), 3.98 (dd, J = 11.4, 4.0 Hz), 3.92 (dd, J = 11.5, 4.0 Hz), 3.80 (br s), 3.69 (br s), 3.03 (dd, J = 12.1, 4.0 Hz), 2.59 (t, J = 11.8 Hz), 2.51 (t, J = 11.8 Hz), 2.12 (s), 2.07 (s), 1.43, 1.40, 1.39, 1.07, 0.97, 0.88 (6 singlets); ^{13}C NMR ($CDCl_3$) δ 145.77, 144.66, 143.68, 137.45, 137.37, 136.36, 136.21, 136.10, 135.81, 134.86, 134.49, 134.39, 134.36, 134.21, 128.57, 128.04, 128.43, 128.18, 126.05, 125.93, 125.77, 125.36, 125.32, 124.70, 122.48, 122.19, 122.08, 121.997, 53.30, 53.12, 43.87, 43.47, 32.15, 29.92, 29.58, 25.47, 25.27, 25.14, 22.91, 18.70, 18.57, 18.20, 16.11, 15.62, 14.33; IR ν (KBr) 3047, 2962, 2923, 2853, 1654, 1437, 1376, 833, 777, 731, 720 cm^{-1}; UV (cyclohexane) λ_{max} nm (ε_{max}) 230 nm sh (33 400); EI MS m/z 408 (M^+); HR MS Calcd, 408.1945; Found: 408.1950. These could be used directly in the next step.

8,16-Bis(2′-methyl-1′-propenyl)-1,9-bis(thiomethyl)-*anti*-[2.2]metacyclophane Sulfonium Salt (31). Mixed isomers of **30** (700 mg, 1.72 mmol) in dry CH_2Cl_2 (15 mL) were added slowly to $(MeO)_2CHBF_4$[4c] (80% oil, 1.50 g, 7.4 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, and ethyl acetate (40 mL) was added and stirring (trituration) was continued for a further 3 h. Decantation, followed by more ethyl acetate and stirring, was used if required. The white precipitate was then collected and dried to give the 71% of the mixed (−SMe) isomers of bis-sulfonium salt **31**. ^{1}H NMR (DMSO-*d6*) δ 7.71 (d, J = 7.8 Hz), 7.61 (d, J = 7.3 Hz), 7.50 (d, J = 7.2 Hz), 7.46−7.41 (m), 7.29 (t, J = 7.6 Hz), 7.14 (t, J = 7.4 Hz), 4.56 (dd, J = 11.6, 3.8 Hz), 4.41 (dd, J = 11.6, 4.0 Hz), 4.22 (s), 3.92 (br s), 3.54 (br s), 3.45 (dd, J = 12.1, 3.9 Hz), 3.38 (dd, J = 12.1, 3.9 Hz), 3.32 (s, SMe), 2.92−2.55 (m), 2.83 (s), 2.82 (s), 1.52, 1.49, 1.47, 1.13, 1.03, 0.86 (6 broad singlets). These was used directly in the next step.

8,16-Bis(2′-methylprop-1′-enyl)-*anti*-[2.2]metacyclophane-1,9-diene (15′). [Note: to avoid photochemical conversion of the cyclophanediene product to the DHP, these operations should be carried out under minimal light]. To a stirred suspension of mixed isomers of the bis-sulfonium salt **31** (640 mg, 1.05 mmol) in THF (25 mL), *t*-BuOK (400 mg, 3.57 mmol) was added under argon at 20 °C. After stirring for 30 min, water was added and then dichloromethane. The extract was washed, dried, and evaporated. The residue was chromatographed over silica gel using hexanes as eluant and gave 315 mg (96%) of cyclophanediene **15′** as colorless crystals from cyclohexane. ^{1}H NMR ($CDCl_3$) δ 7.04 (t, J = 7.4 Hz, 2H, H-5, 13), 6.60 (d, J = 7.4 Hz, 4H, H-4, 6, 12, 14), 6.26 (s, 4H, H-1, 2, 9, 10), 5.72−5.69 (m, 2H, H-17, 19), 1.57 (∼t, J = 1.6 Hz, 12H, Me); ^{13}C NMR ($CDCl_3$) δ 142.80 (C-8, 16), 137.45 (C-3, 7, 11, 15), 135.17 (C-18, 20), 132.14 (C-1, 2, 9, 10), 127.71 (C-5, 13), 125.71 (C-4, 6, 12, 14), 125.47 (C-17, 19), 20.64, 26.81 (C-21, 22, 23, 24); IR ν (KBr) 3045, 3011, 2956, 2892, 1637, 1444, 1434, 1052, 827, 763, 656, 637 cm^{-1}; UV (cyclohexane) λ_{max} nm (ε_{max}) 229 nm (46 000), 254 sh (16 900), 299 sh (2400), 355 (2800) EI MS m/z 312 (M+); HR MS Calcd for $C_{24}H_{24}$, 312.1878; Found, 312.1876. Anal. Calcd: C, 92.26; H, 7.74. Found: C, 92.00; H, 7.83. Attempted mp determination isomerizes these into DHP **15**.

10b,10c-Bis(2′-methylprop-1′-enyl)-*trans*-10b,10c-dihydropyrene (15). Cyclophanediene **15′** (100 mg) in toluene (20 mL) was heated under argon at 100 °C until it completely isomerized to the DHP **15** (about 24−36 h). Evaporation gave orange crystals, mp ∼142−143 °C with decomposition. Continued heating of the sample gave a final mp of 175−177 °C; ^{1}H NMR ($CDCl_3$) δ 8.55 (d, J = 7.5 Hz, 4H, H-1,3,6,8), 8.51 (s, 4H, H-4,5,9,10), 7.93 (t, J = 7.5 Hz, 2H, H-2, 7), 0.17 (d, J = 1.1 Hz, 6H, H-15,17), 0.14 (d, J = 1.3 Hz, 6H, H-16, 18), −0.15 to −0.18 (m, 2H, H-11,12); ^{13}C NMR ($CDCl_3$) δ 135.75 (C-3a, 5a, 10a, 10d), 130.73 (C-13, 14), 125.89 (C-4, 5 ,9, 10), 125.34 (C-1, 3, 6, 8), 123.10 (C-2, 7), 116.18 (C-11, 12), 36.22 (C-10b, 10c), 28.24 (C-15, 18), 16.16 (C-16, 17); IR ν (KBr) 3020, 2967, 2920, 1654, 1648, 1637, 838, 826, 764 cm^{-1}; UV−vis (cyclohexane) λ_{max} nm (ε_{max}) 205 (32 300), 243 (12 000), 349 (44 400), 371 (14 500), 395 (27 000), 494 (4200), 644 (130); EI MS m/z 312 (M^+); HR MS Calcd for $C_{24}H_{24}$: 312.1878; Found: 312.1876. Anal. Calcd: C, 92.26; H, 7.74. Found: C, 85.88; H, 7.21.

10b,10c-Bis(2′-methyl-1′-propenyl)-2-(1′′-naphthoyl)-*trans*-10b,10c-dihydropyrene (32). To avoid photo isomerization of the product, this reaction was carried out under minimal light. Dihydropyrene **15** (73 mg, 0.234 mmol) and naphthoyl chloride (300 mg, 1.57 mmol) were stirred in dichloromethane (10 mL) for 15 min. $AlCl_3$ (160 mg, 1.20 mmol) was added, and the reaction mixture was stirred for 4 s and then immediately quenched with water. The resulting solution was extracted with more dichloromethane, which was then washed, dried ($MgSO_4$), and evaporated. The residue was chromatographed over silica gel to give 76 mg (70%) of the naphthoylated product **32** as dark maroon solid from dichloromethane, mp 179−180 °C; ^{1}H NMR (CD_2Cl_2) δ 9.04 (s, 2H, H-1, 3), 8.63 (AB, J = 7.8 Hz, 2H, H- 4, 10), 8.52 (d, J = 7.8 Hz, 2H, H- 6, 8), 8.45 (AB, J = 7.8 Hz, H-5, 9), 8.14−8.02 (m, 4H, H-7, 23, 25, 28), 7.79 (dd, J = 7.0, 1.2 Hz, 1H, H-21), 7.65 (dd, J = 7.0 Hz, 1H, H-22), 7.55 (td, J = 6.8, 1.2 Hz, 1H, H-26), 7.44 (td, J = 6.7, 1.3 Hz, 1H, H-27), 0.30−0.29 (m, ∼3H), 0.29−0.28 (m, ∼6H) and 0.22−0.20(m, ∼3H)(H-15,16,17,18), 0.21 (septet, J = 1.2 Hz, 1H, H-12), 0.15 (septet, J = 1.2 Hz, H-11); ^{13}C NMR (CD_2Cl_2) δ 198.30 (C-19), 140.39 (C2, C-5a, 10d), 138.85 (C-20), 134.87 (C-3a, 10a), 134.43 (C-24), 132.40 (C-14), 132.27 (C-13), 131.72 (C-29), 131.60 (C-4, 10), 131.00 (C-23), 129.03 (C-25), 127.71 (C-1, 3), 127.64 (C-21), 127.40 (C-7), 126.96 (C-26), 126.79 (C-5, 9), 126.51 (C-27), 126.32 (C-6, 8), 125.30 (C-22), 117.19 (C-12), 115.63 (C-11), 37.85 (C-10c), 37.19 (C-10b), 28.37, 28.05, 16.44, 16.54 (C-15, 16, 17, 18); IR ν (thin film) 3046, 2963, 2924, 2853, 1637,1591, 1507, 1461, 1304, 1235, 1185, 1136, 1057, 1028, 883, 829, 785, 736 702, 631 cm^{-1}; UV−vis (dichloromethane) λ_{max} nm (ε_{max}) 228 (20 400), 361 (16 800), 397 (5590), 421 (6480), 557 (3320), 631 (284); EI MS m/z 466 (M+); HR MS Calcd for $C_{35}H_{30}O$: 466.2297; Found: 466.2294. Anal. Calcd: C, 90.09; H, 6.48. Found: C, 88.49; H, 6.55.

8,16-Bis(2′-methylprop-1′-enyl)-5-(1′′-naphthoyl)-*anti*-[2.2]metacyclophane-1,9-diene (32′). Dihydropyrene **32** (3 mg) in toluene (1 mL) was irradiated with light from a 500W household tungsten bulb (8500 lm) using a filter to allow λ > 490 nm through (see Supporting Information for diagram of setup) for about 1 min until the solution was colorless when conversion into **32′** was complete. ^{1}H NMR (CD_2Cl_2) δ 8.02−7.98 (m, 2H, H-31, 34), 7.94 (dd, J = 7.0, 1.3 Hz, 1H, H-29), 7.57−7.47 (m, 4H, H-27, 28, 32, 33), 7.18 (s, 2H, H-4, 6), 7.10

(t, J = 7.4 Hz, 1H, H-13), 6.62 (d, J = 7.4 Hz, H-12, 14), 6.25 and 6.32 (AB, J = 11.4 Hz, 4H, H-1 ,2, 9, 10), 5.83 (septet, J = 1.4 Hz, H-17), 5.82 (septet J = 1.4 Hz, 1H, H-19), 1.63 (d, J = 1.4 Hz, 3H, H-24), 1.62 (d, J = 1.4 Hz, 3H, H-23), 1.61 (d, J = 1.4 Hz, 3H, H-21), 1.55 (d, J = 1.4 Hz, 3H, H- 22); ^{13}C NMR (CD_2Cl_2) δ 197.43 (CO), 150.56 (C-8), 142.06 (C-16), 139.92 (C-20), 138.93 (C-11, 15), 138.61 (C-3, 7), 138.60 (C-26), 138.52 (C-5), 135.06 (C-30), 133.52 (C-1,10), 132.69 (C-2, 9), 132.12 (C-35), 131.60 (C-31/C-34), 129.86 (C-13), 129.58 (C-29), 129.10 (C-4, 6), 128.17, 127.62, 125.69 (C-27, 28, 32, 33) 126.86 (C-31/34), 126.86 (C-12, 14), 126.18 (C-17, 19), 28.08, 27.90 (C-21, 24), 21.95 (C-23), 21.60 (C-22).

Evaporation of the toluene under vacuum at 0 °C produced pale colored crystals, which on attempted melting point determination thermally converted them back to the DHP **32**. These crystals gave IR ν (thin film) 3048, 2971, 2927, 1652, 1591, 1507, 1461, 1292, 1234, 1186, 1127, 1056, 1028, 1008, 966, 853, 782, 736 cm^{-1}; UV (dichloromethane) λ_{max} nm (ε_{max}) 231 (24 000), 247 (23 300), 281 (14 500), 325 (6900), 396 sh (3200); EI MS m/z 466 (M^+); HR MS Calcd for $C_{35}H_{30}O$: 466.2297, Found: 466.2294.

Thermal Isomerization of CPDs 15′ and 32′ to DHPs 15 and 32. Crystals of **15′** (or **32′**) (5 mg) were dissolved in toluene-*d*8 in an NMR tube (shielded from ambient light by Al foil), and the tube was placed in a bath at the appropriate temperature for the desired time interval. The tube was removed, the thermal reaction quenched in an ice-bath, and then the ^{1}H NMR spectrum was obtained as quickly as possible. The tube was then returned to the bath for the next time interval, and the process repeated. Integration of appropriate corresponding NMR signals of the CPD and DHP forms was averaged to yield mole fractions of CPD present at each time interval, m_{CPD} = CPD/(CPD + DHP) integration ratio so that a $\ln(m_{CPD})$ vs time plot yielded the rate constant, k, at that temperature. From these using a $\ln(k)$ vs $1/T$ plot (Arrhenius), E_a and $\ln(A)$ were obtained from the slope and intercept, and likewise from a $\ln(k/T)$ vs $1/T$ plot (Eyring), $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained. The plots are shown in the Supporting Information Section.

Photo-Opening Relative Rate and Quantum Yield Measurements. These are described fully in the Supporting Information Section.

■ ASSOCIATED CONTENT

Supporting Information. General experimental conditions; numbering system for proton and carbon NMR spectra and copies of experimental spectra; thermal closing reaction plots for **15′** to **15** and **32′** to **32**; visible light photo-opening studies of **15** and **32** relative to **1**; determination of the photo-opening quantum yields for **1**, **15**, and **32**; optimized energies and coordinates − B3LYP/6-31G* for each of **15**/**TS**/**15′** and **15**/**TS**/**9c**, and complete ref 7. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
regmitch@uvic.ca

Present Addresses
[§]CIIT, Abbottabad, Pakistan, 22060.

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