Multistate π Switches: Synthesis and Photochemistry of a Molecule Containing Three Switchable Annelated Dihydropyrene Units

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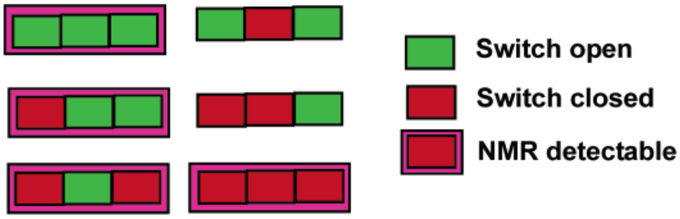
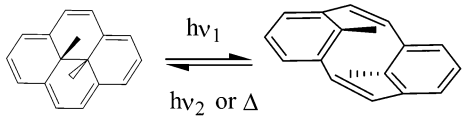


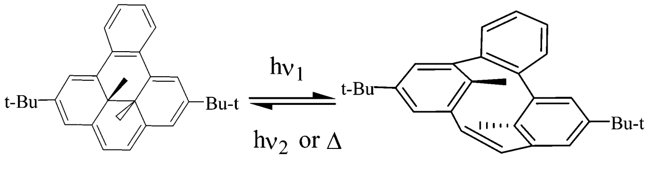
The synthesis of the multistate photochromic switch **3** is described. This switch contains three dihydropyrene (DHP) units in the most conjugated fully closed form **3-c,c,c**. The thermally stable form has the central DHP unit open and is **3-c,o,c**. NMR and laser flash photolysis experiments were used to characterize the multiple states in the photoswitching of **3** by visible and UV light. Three of the possible five isomeric states of **3-c,o,c** were observed. Irradiation of **3-c,o,c** by visible light led to the formation of **3-o,o,o** via the isomer **3-c,o,o** as an intermediate, which were observed by NMR. Irradiation by UV light led to the formation of **3-c,c,c**, which decays with a lifetime of 7.5 ms.

Introduction

Photochromic molecules have become of intense interest recently because of potential applications to memories and switches.[1] The dimethyldihydropyrene-dimethylmetacyclophanediene photochrome **1-c/1-o** (c=closed; o=open) belongs in the diarylethene class of photochromes. They have been much less studied than the dithienylcyclopentenes of Irie[2] and more recently Branda and others,[3] which attract much attention because of their thermal bistability and fatigue resistance. The dithienylcyclopentenes are positive photochromes, where the colorless form on irradiation becomes colored. The dihydropyrenes such as **1-c/1-o** and **2-c/2-o** are negative photochromes where now the thermally stable forms **1-c** and **2-c** are colored,[4−6] but more importantly, when annelated as in the benzo-derivative **2-c/2-o**, show a clean 100% conversion[6] between the two photostates, **2-c** and **2-o**, unlike the dithienylcyclopentene cousins, which generally tend to form photostationary mixtures (e.g. 80/20 and 70/30 in refs 3(a) and 3(b)). The dihydropyrenes do however, have a disadvantage that the thermal back reaction, although Woodward-Hofmann forbidden, does occur. In the case of the thermal reversion, **2-o** to **2-c**, E_{act} = 25 kcal/mol, and so the open form **2-o** has a half-life, $\tau_{1/2}$, of about one week at room temperature in solution.[6] An alternative viewpoint, especially in examples with lower E_{act} values, means that these molecules are also thermochromic![7]



1-c **1-o**



2-c **2-o**

If more than one photochrome is joined together, then multistate switches are possible, for example with two, the closed−closed, closed−open, and open−open states might exist.

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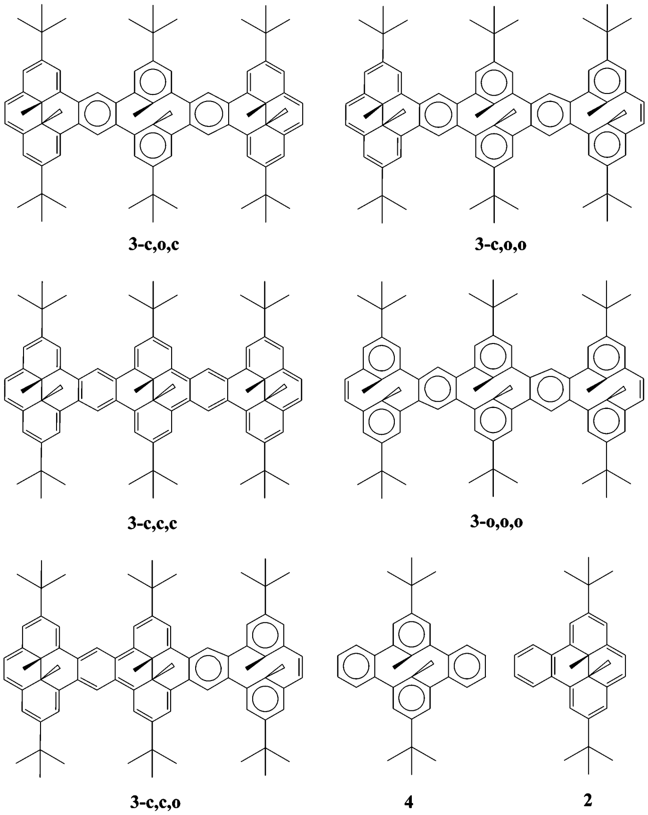
(1) Irie, M. *Chem. Rev.* **2000**, *100*, 1683−1890.

(2) Irie published 22 papers on dithienylethenes in 2004 alone. Recent examples: Murakami, M.; Miyasaka, H.; Okada, T.; Kobatake, S.; Irie, M. *J. Am. Chem. Soc.* **2004**, *126*, 14764−14772; Fukaminato, T.; Sasaki, T.; Kawai, T.; Tamai, N.; Irie, M. *J. Am. Chem. Soc.* **2004**, *126*, 14843−14849; Matsuda, K.; Irie, M. *J. Photochem. Photobiol., C* **2004**, *5*, 169−182.

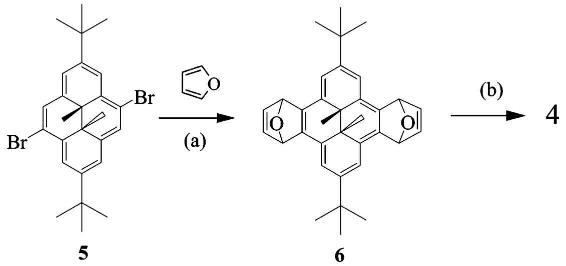
10.1021/jo052153g CCC: $33.50

SCHEME 1. Five Possible States of 3 (Only One Diastereomer of Each State is Shown)



We were the first to report[8] fused photochromes where both photochromes open and close. Dihydropyrenes seem of value here, since all of the fused or linked ones made so far[6,9] have opened and closed, while in the case of the dithienylethenes, most have not.[10] As more switchable moieties are added in one molecule, the possibility for more states exists. This paper reports the synthesis and photochemical study of the "tris-switch" **3**, containing three dihydropyrene units, which in principle could show 5 distinct states (ignoring diastereomers of the internal methyl groups, which are always trans within each dihydropyrene unit), as shown in Scheme 1. The closed−open−closed isomer **3-c,o,c** should be the thermally stable isomer based on the known preference for a dihydropyrene flanked by two benzene rings to be open, **4**, or flanked with one benzene ring to be closed, **2**.[6] The all-open isomer, **3-o,o,o** should be accessible by irradiation of **3-c,o,c** with visible light until both closed rings open, while irradiation of **3-c,o,c** with UV light should yield the all closed isomer **3-c,c,c**,[6] though this isomer may very rapidly thermally convert back, as does **4**. The isomer **3-c,o,o** might be accessible by part-way opening of **3-c,o,c** or part-way closing of **3-o,o,o**; however the remaining isomer **3-o,c,o** would not be expected to be thermally stable and thus if formed should have a short lifetime decaying to **3-o,o,o**.

SCHEME 2 [a]



[a] Conditions:[11] (a) $NaNH_2$/cat. *t*-BuOK/THF/55 °C; (b) $Fe_2(CO)_9$/benzene/80 °C.

Results and Discussion

Syntheses. To prepare the dibenz-annelated compound **4**, the dibromide **5** was reacted with sodium amide and catalytic *t*-BuOK in THF, conditions[6] which generate arynes, which were trapped with excess furan to give the bis Diels−Alder adduct **6**. The latter was deoxygenated with $Fe_2(CO)_9$ to give **4**.

We anticipated that **3** could be prepared from **5** via the analogous adduct **7** derived from addition of iso-furan **8**.[12] However, material obtained in this way was very difficult to purify.

It proved superior to first react adduct **6** with 1 equiv of 3,6-di(2′-pyridyl)-1,2,4,5-tetrazine[13] (**9**) to yield isofuran **10** and subsequently react this under aryne generating conditions with bromide **11** to yield adduct **12**, which then was subjected again to tetrazine **9** to yield **13** and again with the aryne from **11** to yield adduct **7**. This adduct showed poor solubility and so was directly deoxygenated by refluxing in benzene with $Fe_2(CO)_9$ to give the tris-DHP product **3**. This was then purified by chromatography and recrystallization from toluene and gave red crystals, mp 176−181 °C, in 7% overall yield from bis-adduct **6**.

Although this yield was not as great as the direct reaction of Scheme 3, the product could be obtained pure, which was essential for the photochemistry studies. The overall structure was confirmed by mass spectrometry, since MH^+ ($C_{82}H_{93}$) calculated was 1077.728 and found was 1077.726, and a satisfactory elemental analysis was obtained as well. In theory, three diastereomers of **3-c,o,c** should be obtained, represented graphically by **3a, 3b,** and **3c** in Figure 1, though not necessarily in equal amounts. The stability of the bis-adducts **7** should control which isomers of **3** are formed. However, PCMODEL calculations[14] on all of the possible isomers of **7** reveal that

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(3) Recent examples: Gorodetsky, B.; Samachetty, H. D.; Donkers, R. L.; Workentin, M. S.; Branda, N. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 2812−2815; Wigglesworth, T. J.; Branda, N. R. *Adv. Mater.* **2004**, *16*, 123−125; Myles, A. J.; Wigglesworth, T. J.; Branda, N. R. *Adv. Mater.* **2003**, *15*, 745−748; Mulder, A.; Jukovic, A.; Luca, L. N.; van, E. J.; Feringa, B. L.; Huskens, J.; Reinhoudt, D. N. *Chem. Commun.* **2002**, 2734−2735; Utsumi, H.; Nagahama, D.; Nakano, H.; Shirota, Y. *J. Mater. Chem.* **2002**, *12*, 2612−2619.

(4) Sheepwash, M. A.; Mitchell, R. H.; Bohne, C. *J. Am. Chem. Soc.* **2002**, *124*, 4693−4700.

(5) Sheepwash, M. A. L.; Ward, T. R.; Wang, Y.; Bandyopadhyay, S.; Mitchell, R. H.; Bohne, C. *Photochem. Photobiol. Sci.* **2003**, *2*, 104−112.

(6) Mitchell, R. H.; Ward, T. R.; Chen, Y. Wang, Y.; Weerawarna, S. A.; Dibble, P. W.; Marsella, M. J.; Almutairi, A.; Wang, Z. Q. *J. Am. Chem. Soc.* **2003**, *125*, 2974−2988.

(7) Mitchell, R. H.; Brkic, Z.; Sauro, V. A.; Berg, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 7581−7585.

(8) Mitchell, R. H.; Ward, T. R.; Wang, Y.; Dibble, P. W. *J. Am. Chem. Soc.* **1999**, *121*, 2601−2602.

(9) Mitchell, R. H. *Eur J. Org. Chem.* **1999**, *2695*, 5−2703. Mitchell, R. H.; Bandyopadhyay, S. *Org. Lett.* **2004**, *6*, 1729−1732.

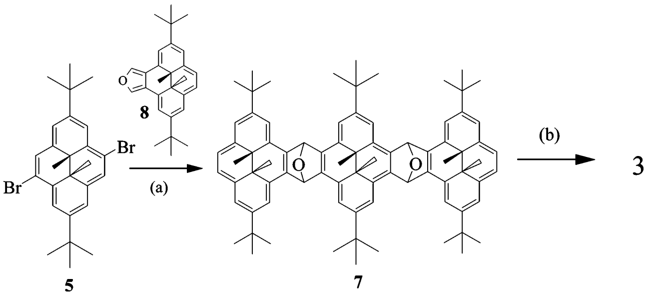
(10) Peters, A.; Branda, N. R. *Adv. Mater. Opt. Electron.* **2000**, 245−249. Kaieda, T.; Kobatake, S.; Miyasaka, H.; Murakami, M.; Iwai, N.; Nagata, Y.; Itaya, A.; Irie, M. *J. Am. Chem. Soc.* **2002**, *124*, 2015−2024; but see Kobatake, S.; Irie, M. *Tetrahedron* **2003**, *59*, 8359−141 for one that does.

(11) Mitchell, R. H.; Chen, Y. *Tetrahedron. Lett.* **1996**, *37*, 5239−5242.

(12) Mitchell, R. H.; Ward, T. R. *Tetrahedron* **2001**, *57*, 3689−3695.

(13) Geldard, J. F.; Lions, F. *J. Org. Chem.* **1965**, *30*, 318−319.

SCHEME 3 [a]



[a] Conditions: (a) NaNH$_2$/cat. *t*-BuOK/THF/55 °C; Fe$_2$(CO)$_9$/benzene/80 °C.

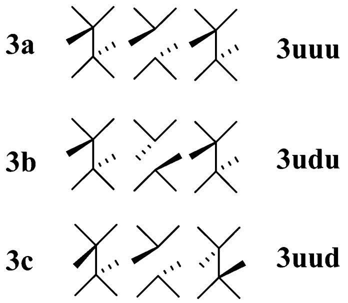


FIGURE 1. Graphical representation of the diastereomers of 3 (u = up or d = down refers to the orientation of each of the top internal methyl groups).

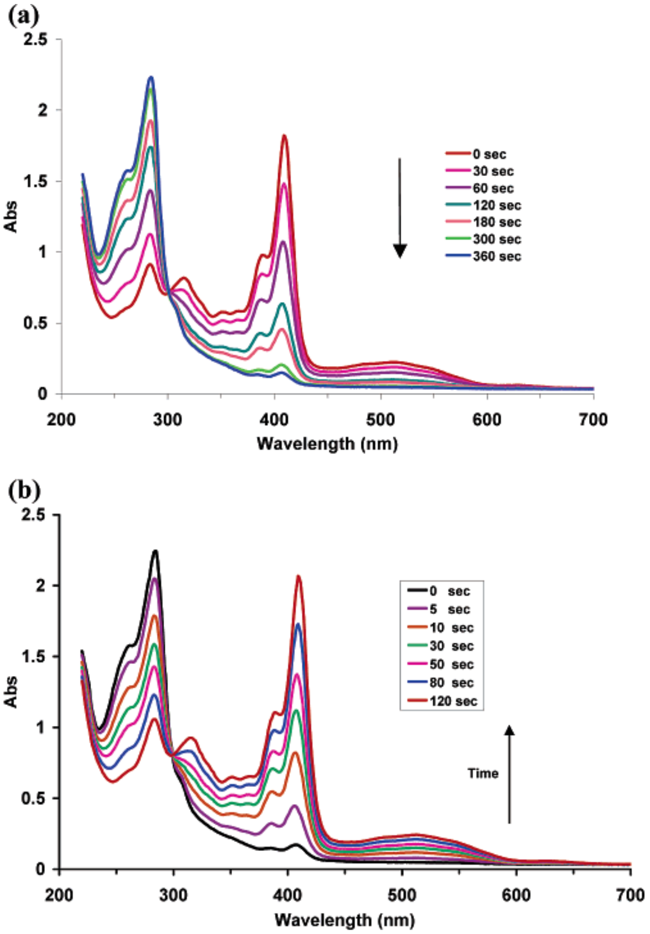


FIGURE 2. (a) Sequential UV−vis spectra of **3-c,o,c** on irradiation with visible light ($\lambda > 550$ nm) and (b) sequential UV−vis spectra of **3-o,o,o** on irradiation with UV ($\lambda = 350$ nm).

while the syn adducts (both oxygen atoms on the same side) are about 1 kcal/mol lower in energy than the trans adducts, within each set there is $<$0.5 kcal/mol difference in energy between the various u−d isomers of the methyl groups. Diastereomers **3a** = **3uuu** and **3b** = **3udu** have C_{2h} symmetry, and so the DHP internal methyl protons of each isomer should be a single peak, while in **3c** = **3uud**, there should be two. Indeed, four NMR signals are seen for the mixture of isomers at δ −1.360, −1.364, −1.622, and −1.626 (initially the ratio of the −1.3:−1.6 peaks was ∼1:1, but chromatography and recrystallization led to fractions richer in the −1.3 peaks). Given the closeness in energy of the precursors **7**, we are unable to assign which peaks belong to which isomer on these data, though one might expect that the less symmetrical isomer **3c (3uud)** would have one peak from each group, i.e., at $\sim\delta$ −1.36 and −1.63. The internal methyl protons of the cyclophane rings all appear as a broad signal at δ 1.28, and the *t*-Bu methyl signals appear at δ 1.53 and 1.56 for the DHP rings and 1.360 and 1.365 for the cyclophane rings and are not as well differentiated as the internal methyl protons. The ^{13}C NMR signals for the internal methyl carbons of **3** appeared at 18.8, 18.0, and 17.5 ppm, with the peak at δ 18.8 being more intense than the other two and so also do not permit assignment. It should be noted that chloroform solutions of **3** readily form small amounts of cation radicals that broaden the proton spectra; so solutions for NMR were filtered through alumina immediately prior to obtaining the spectra. Fortunately, as with other dihydropyrenes,[6] the diastereomers (**3a,b,c**) of **3-o,o,o** formed by irradiation with visible light also thermally close to return the starting isomers (**3-c,o,c**) but at slightly different rates. Careful examination using proton NMR of the growth of the various peaks of the DHPs formed in this thermal reversal reaction suggests that the internal methyl proton peaks at δ −1.364 and −1.622 belong to the same isomer, which must then be **3c (3uud)**. The peaks at δ −1.360 and −1.626 thus belong one to each of the other two isomers.

Simple Photochemistry: Continuous Irradiation. Irradiation with broadband light sources ($\lambda > 500$ nm) of the thermally stable isomer, **3-c,o,c**, is expected[6] to give the fully open isomer, **3-o,o,o**. Indeed, irradiation with light above 550 nm led to the disappearance of the visible bands with an increase in absorption in the UV, as expected (Figure 2a). It is important to note that a single isosbestic point was not observed at 300 nm (see SI Figure S1 for an expansion around 300 nm) but rather one point for the early spectra and one point for the late spectra, suggesting that **3-c,o,c** opens first to **3-o,o,c** which further opens to **3,o,o,o**. Likewise irradiation of **3-o,o,o** with 350-nm light led to the return of the absorption for **3-c,o,c** (Figure 2b), again with the observation (SI Figure S2) of an early and a late isosbestic point suggesting sequential closing.

That the fully open compound, **3-o,o,o**, is formed, is not in doubt, since when sequential NMR spectra (Figure 3a) are obtained (irradiation using >613 nm light in CDCl$_3$), all the dihydropyrene internal methyl signals disappear with irradiation of the sample with visible light. The same internal methyl NMR signals reappear (Figure 3b) when this opened sample is irradiated at 350 nm. All diastereomers of **3-c,o,c** must thus open to **3-o,o,o** and close back to **3-c,o,c**, because no residual NMR peaks corresponding to either **3-c,o,c** (in the opening) or

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(14) *PCMODEL*, V8.5; Serena Software: Bloomington, IN, 47402-3076.

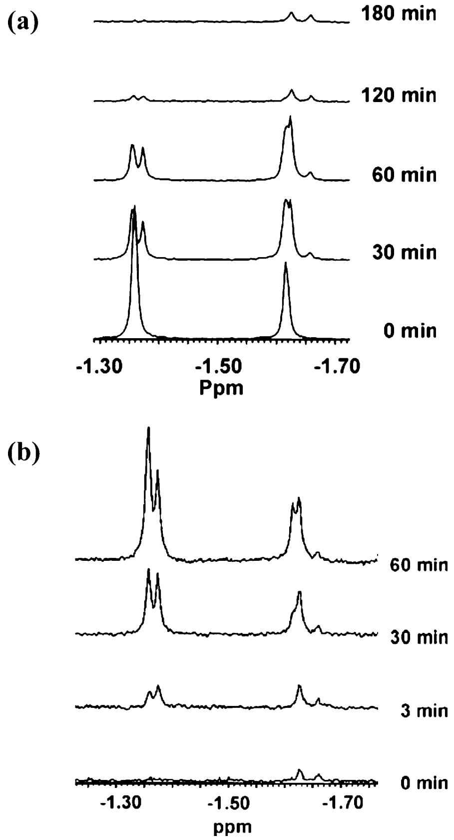

FIGURE 3. Sequential NMR spectra in the (a) visible light ($\lambda > 613$ nm) opening of **3-c,o,c** and (b) UV light ($\lambda = 350$ nm) closing of **3-o,o,o**.

3-o,o,o (in the closing) were observed, after the irradiation drove each reaction to completion.

On both opening and closing, new methyl proton signals appear (slightly shielded from those of **3-c,o,c**) which disappear again as irradiation is continued. It is important to note that the chemical shifts observed for the internal methyl peaks of the transient isomer are the same when **3-c,o,c** is opened by irradiation with visible light and when **3-o,o,o** is closed by irradiation at 350 nm. Therefore the same isomer is formed in both irradiations. The only two species that can be formed in the visible irradiation of **3-c,o,c** are **3-c,o,o** and **3-o,o,o**, because the excited states of the open moieties (which might lead to **3-c,c,c** or **3-c,c,o**) cannot be populated with irradiation above 550 nm. Therefore, the transient species observed was assigned to the **3-c,o,o** isomer, which is equivalent to **3-o,o,c**. Unfortunately, we were not able to separate and purify this isomer. To obtain clearer evidence, we thought that if we could differentiate the two DHP sides of **3**, such that one of the DHPs opened much faster than the other, the structure of the intermediate isomer equivalent to **3-c,o,o**, would be easier to observe and verify.

Our previous work[4,5] has shown that substituents can substantially alter the opening rate of DHPs with visible light. Unfortunately, **3** immediately turns black under acidic conditions, e.g., $BF_3{\cdot}Et_2O$, and so acetylation, for example, was not successful. Eventually we were able to synthesize the 4-phenyl-substituted derivative of **3**. The full synthesis is described in the Supporting Information but is shown briefly in Scheme 5.

Now, **18-c,o,o** is no longer identical to **18-o,o,c** and thus since one DHP is substituted and the other is not, one might expect[4,5] one DHP to open at a different rate to the other, and so form one isomer preferentially in the opening reaction. As can be seen in Scheme 5, the phenyl-substituted parent **15** was an intermediate, and the phenyl-substituted benzoDHP **19** was easily obtained, so that both could act as model compounds in our interpretation of the behavior of **18**. In fact, the phenyl substituted benzoDHP **19** opens with visible light about four times faster than benzoDHP **2**, and this, on the basis of observed chemical shifts, turns out to be true also for **18**, such that the spectra for **18-c,o,o** are more readily observed, than for unsubstituted **3-c,o,o**. Lai[15] has shown that introduction of an aryl substituent on to a DHP slightly reduces the ring current in the DHP by resonance conjugation, and thus the internal methyl protons are slightly deshielded with respect to the unsubstituted example. Thus in **15** and **19**, the internal methyl protons are at δ −3.84/−3.85 and −1.453/−1.456, respectively, slightly deshielded from those of the two parents 2,7-di-*t*-Bu-**1-c** and **2-c** at δ −4.06 and −1.58, respectively.[12] In **3-c,o,c**, the internal methyl protons appear at δ −1.37 and −1.63, while in **18-c,o,c**, there are two sets of each proton type at δ −1.23/−1.37 and δ −1.49/−1.62. The peaks at δ −1.23 and −1.49 thus belong to the phenyl-substituted side. These more deshielded peaks disappear first on irradiation with visible light (>590 nm in toluene, Figure 4). In fact the internal methyl proton chemical shifts of the newly formed isomer, **18-c,o,o**, are not exactly the same as for the unsubstituted DHP side of **18-c,o,c**, and so the more shielded pair actually become two close peaks each, where the peaks due to the original shifts are replaced by those at the new shifts, i.e., in d_8-toluene, δ −1.161 and −1.354 become δ −1.175 and −1.367; in this solvent the peaks at δ −1.030 and −1.228 have mostly gone in ~35 min, while complete disappearance (i.e., conversion to **18-o,o,o**) requires more than 90 min of irradiation. This leaves no doubt that during visible light irradiation the sequence **18-c,o,c** to **18-c,o,o** to **18-o,o,o** is followed. Sequential UV−visible opening and closing spectra for **18** are given in the Supporting Information (Figures S3 and S4) as well as sequential 1H NMR spectra in the UV closing of **18-o,o,o** to **18-c,o,c** (Figure S5).

Photochemistry: Transient Studies. Studies with model compounds were first performed in order to understand the photochemistry of switch **3**. The outside DHP moieties behave as and thus can be modeled by the benzo-DHP **2-c**. The cyclophanediene (CPD) isomer, **2-o**, formed when benzo-DHP is irradiated with visible light, is known to have a very long half-life ($t_{1/2} \geq 5$ h, 46 °C).[6] In the laser flash photolysis experiments, the benzo-CPD isomer (**2-o**) was longer lived than the longest lifetime that we can measure with the laser flash photolysis system. The system was reconfigured to measure lifetimes in the millisecond time domain (see SI for details), and the upper limit for lifetime measurements is determined by how fast the transient diffuses from the volume irradiated by the laser into the adjacent nonirradiated solution. Excitation of benzo-DHP **2-c** at 532 nm led to bleaching of the visible absorption bands due to the formation of the CPD isomer **2-o**. This signal was used to determine the time it takes for transients to diffuse out of the irradiation volume (τ ca. 4−6 s). No other transients were observed on shorter time scales.

The central moiety of **3** corresponds to the disubstituted benzo compound **4**, for which the CPD isomer is the thermodynamically stable isomer.[6] Compound **4** absorbs strongly in the UV

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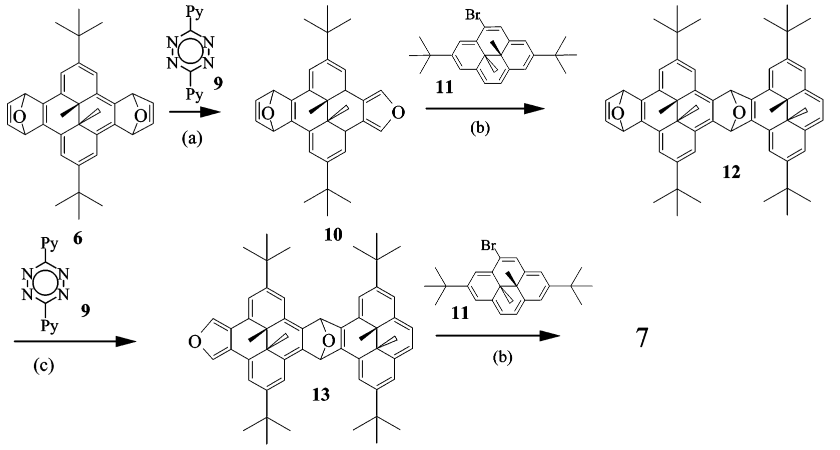
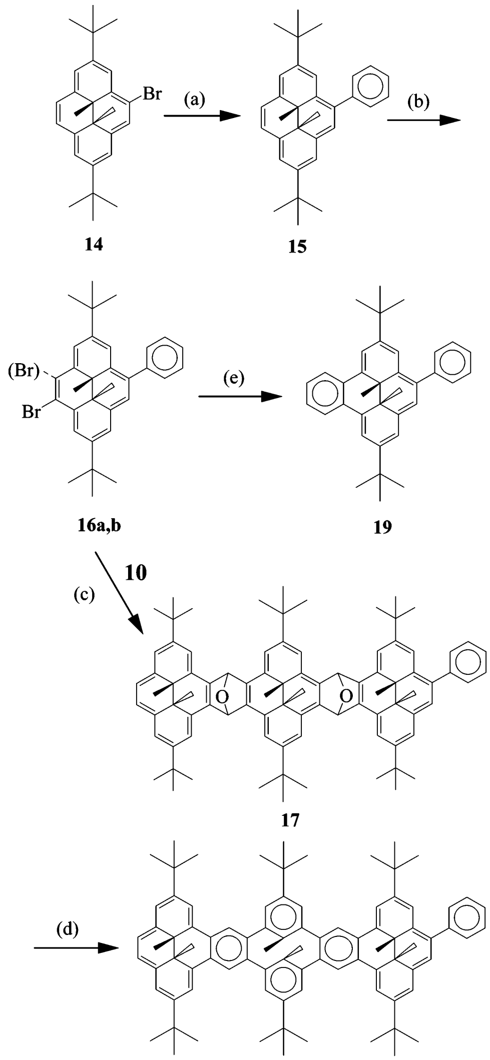
[15] Lai, Y. H.; Chen, P.; Dingle, T. W. *J. Org. Chem.* **1997**, *62*, 916−924. Lai, Y. H.; Jiang, J. P. *J. Org. Chem.* **1997**, *62*, 4412−4417.

SCHEME 4[a]



[a] Conditions: (a) 0 °C/THF/3 h; (b) $NaNH_2$/cat. *t*-BuOK/THF/20 °C/5 h; (c) 20 °C/THF/1 h.

SCHEME 5[a]



[a] Conditions: (a) $PhB(OH)_2/Pd(PPh_3)_2Cl_2$/THF/2 M Na_2CO_3, reflux 2 h; (b) NBS/CH_2Cl_2-DMF/−78 °C; (c) $NaNH_2$/KOBu-*t*/THF, RT 2−3 h; (d) $Fe_2(CO)_9$/PhH, reflux 1 h; (e) Furan/$NaNH_2$/KOBu-*t*/THF, RT 5 h.

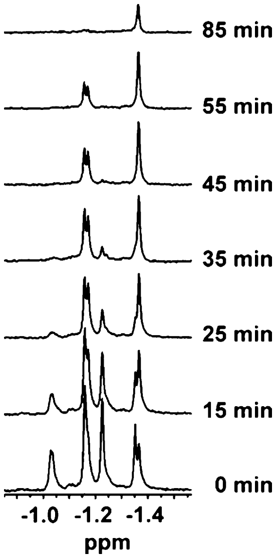


FIGURE 4. Sequential internal methyl proton NMR spectra of visible light (λ >590 nm) opening of **18-c,o,c**.

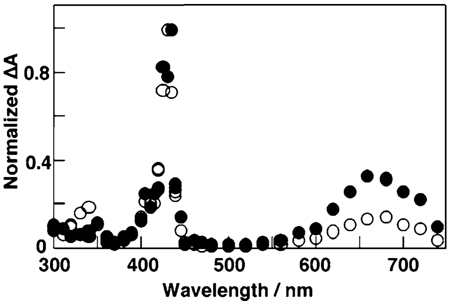


FIGURE 5. Normalized transient absorption spectra for the irradiation of 4 with 266 nm obtained with delays after the laser pulse of 27 ms (○, normalized at 430 nm; $\Delta A = 0.43$) and 370 ms (●, normalized at 435 nm; $\Delta A = 0.056$).

region of the spectrum, with a weak shoulder observed between 300 and 350 nm. Irradiation at 266 nm of cyclohexane solutions of **4** in the laser flash photolysis experiment led to long-lived transients (Figure 5). The spectrum at long delays was similar to that observed at short delays, but the absorption at 340 nm disappeared, while the ratio between the absorption in the 430-nm region and the absorption in the 650-nm region decreased. The spectra observed are consistent with the formation of a more

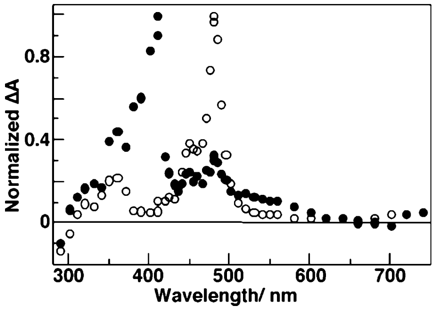
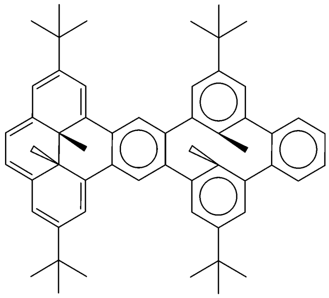


FIGURE 6. Normalized transient absorption spectra for the irradiation of **20** with 266 nm obtained with a delay after the laser pulse of 6.8 ms (○, normalized at 480 nm; $\Delta A = 0.20$) and 440 ms (●, normalized at 410 nm; $\Delta A = 0.016$).

conjugated system than the CPD isomer, as expected for the formation of the DHP isomer. The changes in the transient spectra with time indicate that more than one transient with similar absorption properties were present.

The transient kinetics of **4** in cyclohexane were measured at 430 and 660 nm. No decay of the absorptions was observed in the nano- and microsecond time domains. The kinetics at longer times did not follow a monoexponential decay. The decays were fitted to the sum of two exponentials, and the same two lifetimes (0.29 ± 0.07 s and 0.9 ± 0.3 s) were recovered from the fits at 430 and 600 nm. The longest lifetime value is shorter than the diffusional lifetime of transients out of the irradiation volume (ca. 6 s) but could have been shortened somewhat because of the diffusional effect. The nonexponential decays were observed in solvents of different polarity (cyclohexane vs acetonitrile), at various concentrations of **4** (varied by a factor of 5) and at various energies for the laser pulses. In addition, the same lifetimes were observed for two independently synthesized samples of **4**. These control experiments suggest that the nonexponential decay is not due to the presence of an impurity or due to the aggregation of **4**. The transients were not quenched by oxygen, since the same lifetimes were observed in aerated solutions and solutions bubbled with nitrogen.

Compound **20**[6] was the second model compound studied. The thermodynamically stable isomer which is shown, has a DHP moiety, which corresponds to benzo-DHP **2** and a CPD moiety, which corresponds to compound **4** and thus is actually **20-c,o**. Excitation at 530−532 nm should lead to the excitation of the DHP moiety, whereas the photons corresponding to 266 nm have enough energy to excite the CPD moiety of **20**.



20

Excitation of **20** in cyclohexane at 266 nm led to a transient with an absorption maximum at 480 nm, which decayed into a new transient with an absorption maximum at 410 nm (Figure 6). At 480 nm, the decay kinetics showed two components,

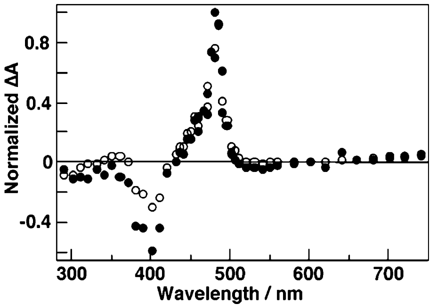


FIGURE 7. Normalized transient absorption spectra for the irradiation of **20** with 532 nm obtained with a delay after the laser pulse of 12 ms (○, normalized at 480 nm; $\Delta A = 0.35$) and 220 ms (●, normalized at 480 nm; $\Delta A = 0.055$).

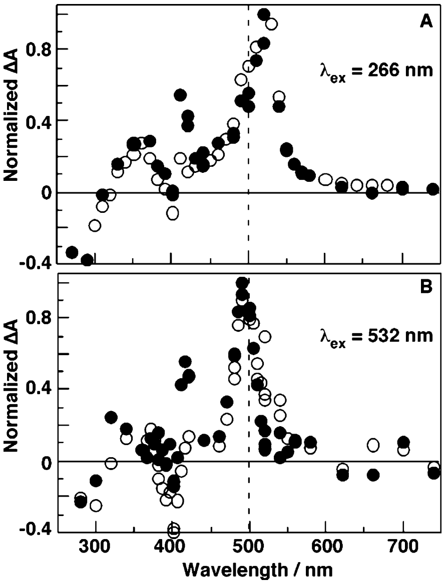


FIGURE 8. Normalized transient absorption spectra for **3** when excited at 266 nm (A, delays of 14 μs (○) and 3.6 ms (●), normalized at 520 nm) and when excited at 530 nm (B, delays 1.2 ms (○) and 33 ms (●), normalized at 490 nm). The dashed line at 500 nm was included to facilitate the comparison of both spectra.

whereas at 410 nm a growth was followed by a decay (see Figure 6 in SI). The lifetime for the fast component at both wavelengths was 100 ± 8 ms. The long-lived species decayed with a time constant similar to the diffusion of transients out of the irradiation volume, and for this reason, the formation of the long-lived transient is “permanent” ($\tau \geq 1$ s) on the time scales accessible by laser flash photolysis. The transients were not quenched by oxygen.

Excitation of **20** at 532 nm led to the formation of a transient with maximum absorption at 480 nm (Figure 7).

In the 400-nm region, a bleaching was observed. The same kinetics was observed at all monitored wavelengths, where the decays were mono exponential with a lifetime of 110 ± 10 ms. This transient was not quenched by oxygen. At all wavelengths above 400 nm, a “permanent” bleaching was observed after the decay of the transient (see Figure S7 in SI).

The transient absorption spectra for excitation of **3** at 266 nm initially showed a peak at 350 and 520 nm (Figure 8). An additional absorption grew in at 410 nm at longer delays. The ratio between the absorptions at 350 and 520 nm did not change with the delay after the laser pulse. Excitation of **3** at 532 nm

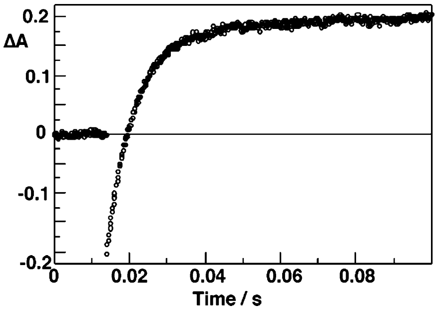


FIGURE 9. Transient kinetics at 410 nm for the irradiation at 266 nm of **3** in cyclohexane.

led to an increased absorption at 490 nm. This absorption is blue shifted when compared to the transient absorption observed for the excitation of **3** at 266 nm. At longer delays an increased absorption was observed at 410−415 nm. No increase in absorption was observed at 350 nm.

The transient absorption signal when **3** was excited at 532 nm did not follow a monoexponential function (see Figure S8 in SI). The decays were fitted to the sum of two exponentials, and the recovered lifetimes were 28 ± 5 ms and 250 ± 30 ms. The short lifetime corresponds to the formation of the transient with enhanced absorption at 410 nm. None of the transients were quenched by oxygen.

The kinetics for the excitation of **3** at 266 nm were also biphasic, where at 520 nm only a decay was observed, whereas at 410 nm a growth (Figure 9) was followed by a decay. The lifetime for the fast component was 7.5 ± 0.5 ms, whereas the second component decayed with the time constant for the diffusion out of the irradiation volume ($\tau \geq$ 1s). None of the transients were quenched by oxygen.

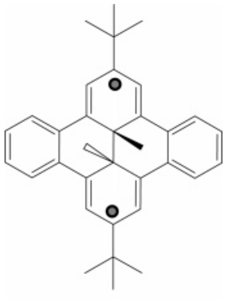
Discussion

NMR experiments provide valuable information for the assignment of the transients observed in the laser flash photolysis experiments. The longest lifetime of an isomer that we can measure by laser flash photolysis is ca. 1 s. For this reason, any species that is observable by NMR will appear as a "permanent" species in the laser flash photolysis experiments.

The most stable isomers of the multichromophoric compounds **3** and **20** contain DHP and CPD moieties within the same structure. Excitation at 530−540 nm corresponds to energies significantly lower than required to excite the S_1 state of the CPD chromophore, and for this reason, we assumed that only the DHP moiety was excited when **3** and **20** were irradiated at 530−540 nm. At 266 nm, the energy of the photons is high enough to excite the CPD moiety, and at this wavelength, the molar absorption coefficient is higher for CPD than DHP.[4] For this reason, we assumed that irradiation at 266 nm led mainly to the excitation of the CPD moieties. This rationale assumes that the DHP and CPD chromophores can be treated as independent. This is warranted because molecules containing at least one CPD unit are not planar and extended conjugation throughout the whole molecule is hindered. However, a small degree of extended conjugation has been previously observed in the fluorescence of arene [*e*]-annelated CPDs.[5] A further assumption made is that transients are formed from precursors that absorb one photon. Sequential absorption of photons is unlikely to lead to the transient phenomena observed because the transient spectra and lifetimes did not change by varying the energy of the laser pulses. Finally, we assumed that the absorption of one photon led to the breakage/formation of one bond for the switching between the DHP/CPD systems.

Excitation of **3**, **4**, and **20** with 266-nm light led to the closure of the CPD moiety. In the case of **4**, the DHP isomer of **4** was previously detected by NMR at low temperatures, but its lifetime at room temperature is short (estimated ca. 1−2 s)[6] because of the fast thermal return to **4**. Excitation of **4** at 266 nm led to a transient spectrum with enhanced absorption in the regions expected for a DHP isomer. The transient absorption above 600 nm with respect to the absorption in the 400 nm region is higher than that observed in the absorption spectra of stable DHPs. This difference can be explained by the fact that the transient spectra correspond to difference spectra between the absorption of the transient and the absorption of the precursor.

Two transients were observed for **4**, which have very similar absorption spectra. This result suggests that the transients have a chromophore similar to the conjugated aromatic systems of the DHP. One of the transients is the DHP isomer of **4**, and this isomer has either a lifetime of 0.3 or 0.9 s. The identity of the second transient is unclear at this point. The second transient cannot be a triplet excited state or a radical because both of these intermediates should have been quenched by oxygen. Although cis isomers of dihydropyrenes are known,[16] *no* conversion between the cis series and the trans series has ever been observed. One possibility is that the biradical **4-DHP−BR** is the second transient. This intermediate is still planar, and calculations have indicated that radicals of this type could have low energy[17] and for this reason would be much less reactive toward oxygen. However, we do not have any Supporting Information for this assignment. In addition, we cannot determine if the two transients were formed concomitantly within the laser pulse or if they are formed sequentially. The latter can only be concluded if a growth of a transient is observed, but the absence of growth kinetics does not eliminate the possibility of the sequential formation of the two transients.



4-DHP-BR

The thermodynamically stable isomer of **20** corresponds to the **20-c,o** isomer. It was previously shown[6] that irradiation of **20-c,o** with visible light above 590 nm led to the formation of

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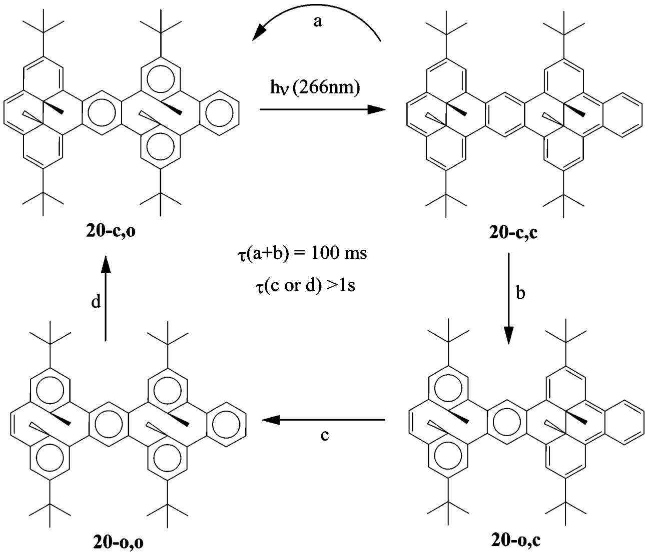
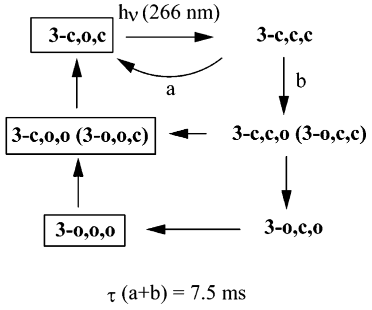
[16] Mitchell, R. H.; Boekelheide, V. *J. Chem. Soc., Chem. Commun.* **1970**, 1555−1557. Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1974**, *96*, 1547−1557. Kamp, D.; Boekelheide, V. *J. Org. Chem.* **1978**, *43*, 3475−3477. Mitchell, R. H.; Chaudhary, M.; Kamada, T.; Slowey, P. D.; Williams, R. V. *Tetrahedron* **1986**, *42*, 1741−1744. Mitchell, R. H.; Bodwell, G. J.; Vinod, T. K.; Weerawarna, K. S. *Tetrahedron. Lett.* **1988**, *29*, 3287−3290. Lai, Y. H.; Chew, P. *J. Org. Chem.* **1989**, *54*, 4586−4590. Lai, Y. H.; Zhou, Z. L. *J. Org. Chem.* **1994**, *59*, 8275−827. 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. Bodwell, G. J.; Bridson, J. N.; Chen, S. L.; Li, J. *Eur. J. Org. Chem.* **2002**, 243−249.

SCHEME 6. Possible Decay Pathways for 20-c,o When Excited at 266 nm.



SCHEME 7. Possible Decay Pathways for 3-c,o,c When Excited at 266 nm (Isomers Detected by NMR Are Shown in Squares)



20-o,o. This isomer was detected by NMR and had a half-life of 5 h at 46 °C or several days at room temperature. Formation of **20-o,o** led to an increase in the absorption in the UV region of the spectrum when compared to the absorption of **20-c,o**. Preliminary laser flash photolysis experiments were performed previously where **20** was irradiated at 355 nm.[9a] The transient absorption spectrum recorded was similar to the one observed in this work when **20** was excited at 266 nm. The growth of the transient at 410 nm was not observed in the earlier study because of the limited time range for those laser flash photolysis experiments.

The excitation of **20** at 266 nm led to a transient with a lifetime of 100 ms followed by an isomer that had a lifetime longer than 1 s. In contrast to the kinetics for **4,** a growth was observed at 410 nm, which was followed by a decay. This result suggests that the transients are sequentially formed. The excitation of **20-c,o** isomer at 266 nm leads to the formation of the **20-c,c** transient. The maximum of the transient at 485 nm indicates that this transient is more conjugated than the precursor, as expected for the formation of **20-c,c**. This transient decays with a 100-ms lifetime, but it forms an isomer different from the precursor (**20-c,o**) because a second transient with increased absorption at 410 nm was formed. The **20-c,c** isomer can decay either by (pathway a, Scheme 6) breaking the bond for the dibenzo-DHP moiety forming **20-c,o** (precursor) or by (pathway b, Scheme 6) breaking the bond of the benzo-DHP forming the **20-o,c** isomer. From the kinetic data available, it is not possible to determine the partition between the formation of **20-c,o** and **20-o,c** from **20-c,c**. The **20-o,c** isomer has to form the **20-o,o** isomer (pathway c, Scheme 6) before regenerating the precursor **20-c,o** (pathway d, Scheme 6). The transient with absorption at 410 nm has a lifetime longer than measurable with the laser flash photolysis system, and it could be either the **20-o,c** or the **20-o,o** isomer. The transient with the absorption at 410 nm is assigned to the **20-o,c** isomer, because the **20-o,o** formed when **20** is excited at 532 nm does not have an absorption at 410 nm. The lifetime of **20-o,c** has to be longer than 1 s but short enough for this transient not to be observed in the NMR experiment.

Excitation of **20-c,o** at 532 nm should lead to the formation of **20-o,o**, which was detected by NMR. The permanent bleaching observed at all wavelengths above 400 nm is consistent with the formation of the **20-o,o** isomer, since the extended conjugation is lost in this isomer. The assignment for the transient with absorption at 480 nm is not evident. This transient is not a triplet excited state or a radical because it is not quenched by oxygen. The transient is also not the **14-c,c** isomer formed by the absorption of two 532 nm photons, because the transient spectrum obtained is different from that measured when **20** was excited at 266 nm, and the formation of the 410 nm transient (**20-c,o**) was not observed. For this reason the equal lifetime (100 ms) measured for the transients when **20** is excited at 266 or 532 nm must be coincidental.

The isomers of **3** that can be detected by NMR are the **3-c,o,c** (stable isomer), **3-o,o,o** (fully open isomer), and **3-o,o,c** (equivalent to **3-c,o,o**) isomers. Therefore, the possible isomers with short lifetimes are the **3-c,c,c**, **3-c,c,o** (equivalent to **3-o,c,c**), and **3-o,c,o** isomers. The transient spectra for the irradiation of **3** at 266 nm are consistent with the formation of a more conjugated isomer, which can only be the **3-c,c,c** isomer. If this transient decayed only to the starting compound monoexponential kinetics would have been observed, with a decay back to the baseline at all wavelengths. Since this is not the case, the isomer **3-c,c,o** also has to be formed in the decay of **3-c,c,c**. The lifetime of the **3-c,c,c** isomer is 7.5 ms. This lifetime is shorter by a factor of 13 than the lifetime for the fully closed form of **20**. A slight decrease (ca. 2×) of the lifetime would have been expected from statistical considerations, because there are two flanking DHP moieties in **3** when compared to **20**. However, the decrease by an order of magnitude of the lifetime indicates that a larger degree of conjugation enhances the rate constant either for the ring opening of the flanking DHPs or the ring opening of the central dibenzo-DHP moiety.

The growth of the signal at 410−415 nm indicates the formation of isomers from **3-c,c,c** that are different from the stable precursor (**3-c,o,c**). This new transient has a lifetime longer than 1 s. The decay of **3-c,c,c** will lead to the formation of **3-c,c,o**, which can further decay to **3-c,o,o** and **3-o,c,o**. The latter will decay to **3-o,o,o**. One of the possible isomers absorbing at 410−415 nm is **3-c,c,o**, but the absorption could also be due to the isomers **3-c,o,o** and **3-o,o,o**, which are detectable by NMR.

Excitation of **3-c,o,c** with 532-nm light could lead to **3-c,o,o** (which is equivalent to **3-o,o,c**). This isomer is stable enough to be detected by NMR, and for this reason is responsible for

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(17) Mitchell, R. H.; Dingle, T. W.; West, P. R.; Williams, R. V.; Thompson, R. C. *J. Org. Chem.* **1982**, *47*, 5210−5214. Mitchell, R. H.; Williams, R. V.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2560−2571.

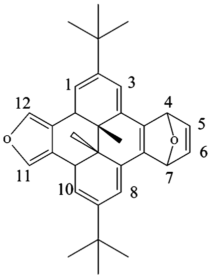
the "permanent" spectral changes observed in the laser flash photolysis experiments. The identity of the transients with 28- and 250-ms lifetimes is not known. The same arguments as outlined for **20** are also applicable here. The interesting point is that two fast-decaying transients are observed for **3** whereas only one is observed for **20**.

Conclusions

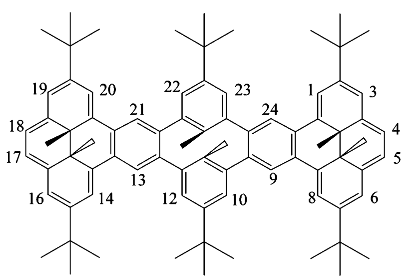
One of the challenges in designing multichromophoric photoswitches is to string together several photochromic units and to be able to address each one of them individually. The objective of this work was to establish in a molecule with three units if each one of them could be switched and if more than one isomer could be formed. In addition, the molecule chosen had a mixture of open and closed units in its thermodynamically stable form (**3-c,o,c**). The fully closed (**3-c,c,c**) and fully open forms (**3-o,o,o**) can be formed by UV and visible irradiation, respectively. In addition, the transient formation of **3-c,o,o** was observed by NMR and the formation of **3-c,c,o** was inferred from laser flash photolysis studies. Despite the fact that several of the lifetimes of the isomers are short, we established that the units in multichromophoric switches based on dihydropyrenes can be individually switched. The next challenge will be to tune the absorption properties of each moiety to be able to address specifically each unit.

Experimental Section

General conditions and spectral assignment methods are given in the Supporting Information. The proton numbering scheme for compounds **10** and **3** is shown below.



10



3

Isofuran Adduct 10. Tetrazine[13] **9** (51.3 mg, 0.217 mmol) was added to a cooled (0 °C) solution of the bis adduct[6] **6** (103.4 mg, 0.217 mmol) in dry THF (50 mL) under N_2 and was stirred for 3 h. The solvent was evaporated, and the residue was chromatographed on alumina using hexanes/benzene (1:1) as eluant and gave 28.3 mg (29%) of the product **10** as a red-orange solid, mp (dec) 182−183 °C; ^{1}H NMR δ 8.0183 and 8.0177 (d each, $J = 1.7$ Hz, 2H, H-11,12), 6.836 and 6.830 (d each, $J = 1.4$ Hz, 2H, H-1,10), 6.675 and 6.569 (dd each, $J = 5.6$, 1.8 Hz, 2H, H-5,6), 6.409 and 6.381 (d each, $J = 1.4$ Hz, 2H, H-3,8), 5.737 and 5.701 (dd each, $J = 1.8$, 1.4 Hz, 2H, H-4,7), 1.241 and 1.239 (s each, 9H, $C(CH_3)_3$), 0.37 and 0.14 (s each, 3H, CH_3); ^{13}C NMR δ 144.56, 144.28, 137.01 and 136.99 (C-11,12), 136.69 and 135.45 (C-5,6), 132.12, 131.67, 131.10, 131.04, 128.75, 128.60, 120.72, 120.61, 116.79 and 116.74 (C-1,10), 113.76 and 113.71 (C-3,8), 78.83 and 78.81 (C-4,7), 42.37, 41.64, 34.67, 34.65, 29.56 ($C(CH_3)_3$), 22.04, 19.76; CI MS *m*/*z*, 451 (MH^+); HRMS. Calcd for $C_{32}H_{34}O_2$: 450.2559. Found: 450.2559.

Bis-Adduct 12. $NaNH_2$ (400 mg, 10 mmol) and KO^{t}Bu (2 mg) were added to a solution of the isofuran adduct **10** (45.9 mg, 0.102 mmol) and the bromide[12] **11** (56.1 mg, 0.133 mmol) in dry THF (40 mL) under N_2, and the mixture was stirred at ∼20 °C for 5 h. The solvent was evaporated, and the residue was filtered through alumina using hexanes/benzene (1:1) as eluant and gave 58 mg (72%) of the product **12** as a green solid as a mixture of four isomers, LSIMS *m*/*z* 793.6 (MH^+); HRMS. Calcd for $C_{58}H_{64}O_2$ (MH^+): 793.4985. Found: 793.4987. These four isomers on further chromatography over aluminum oxide using hexanes/benzene (1:1) as eluant were separated into two portions which were oxygen bridge syn and anti isomers, each containing two isomers.

Eluted first were anti isomers (I and II in a ∼1:2 ratio): mp (dec) 183−188 °C; ^{1}H NMR isomer I: δ 8.85 (d, $J = 1.3$ Hz, 1H), 8.67 (d, $J = 1.3$ Hz, 1H), 8.66 (d, $J = 1.2$ Hz, 1H), 8.57 (d, $J = 1.3$ Hz, 1H), 8.22−8.21 (m, 2H), 8.16−8.15 (m, 2H), 8.084 (s, 2H), 7.97 (d, $J = 0.7$ Hz, 1H), 7.88 (d, $J = 0.7$ Hz, 1H), 7.22 & 7.09 (dd, $J = 5.5$, 1.7 Hz, 1H each), 6.57−6.56 (m, 1H), 6.53−6.52 (m, 1H), 1.75, 1.72, 1.71, 1.69, 1.68, 1.67, 1.63 (s from both isomers I and II, ratios: 2:1:1:2:2:2:2, $C(CH_3)_3$), −3.28, −3.77, −4.23, −4.41 (s, 3H each, CH_3). Isomer II: δ 8.79 (d, $J = 1.2$ Hz, 1H), 8.70 (d, $J = 1.2$ Hz, 1H), 8.65 (d, $J = 1.2$ Hz, 1H), 8.53 (d, $J = 1.4$ Hz, 1H), 8.25 (d, $J = 1.0$ Hz, 1H), 8.20 (d, $J = 1.3$ Hz, 1H), 8.17 (d, $J = 1.2$ Hz, 1H), 8.13 (d, $J = 1.2$ Hz, 1H), 8.080 (s, 2H), 7.93 (d, $J = 0.7$ Hz, 1H), 7.90 (d, $J = 0.7$ Hz, 1H), 7.21 & 7.08 (dd, $J = 5.5$, 1.7 Hz, 1H each), 6.57−6.56 (m, 1H), 6.53−6.52 (m, 1H), 1.75, 1.72, 1.71, 1.69, 1.68, 1.67, 1.63 (s from both isomers I and II, ratios: 2:1:1:2:2:2:2, $C(CH_3)_3$), −3.25, −3.77, −4.24, −4.43 (s, 3H each, CH_3). ^{13}C NMR Both isomers: δ 145.50, 145.41, 145.21, 144.98, 141.04, 140.95, 140.68, 140.41, 140.27, 137.92, 137.76, 137.35, 137.23, 137.08, 136.98, 136.91, 136.67, 128.56, 128.24, 128.10, 127.88, 127.59, 127.46, 127.20, 126.88, 124.29, 124.26, 121.34, 121.20, 121.08, 117.63, 117.31, 116.53, 116.40, 115.72, 115.30, 115.15, 115.02, 114.83, 81.90, 81.70, 81.62, 81.52, 81.38, 81.19, 35.98, 35.89, 35.83, 35.77, 33.06, 32.91, 32.81, 32.71, 32.28, 32.15, 31.94, 31.91, 31.65, 31.62, 31.25, 31.07, 30.32, 16.39, 16.29, 15.07, 15.00, 14.44, 14.28, 14.14.

Eluted second were the syn isomers III and IV (in about a 2:3 ratio): mp (dec) 179−182° C; ^{1}H NMR of isomer III: δ 8.84 (d, $J = 1.2$ Hz, 1H), 8.69−8.68 (m, 1H), 8.66−8.65 (m, 1H), 8.55 (d, $J = 1.3$ Hz, 1H), 8.21 (d, $J = 1.2$ Hz, 2H), 8.14 (d, $J = 1.3$ Hz, 1H), 8.13 (d, $J = 1.3$ Hz, 1H), 8.07 and 8.06 (AB, $J = 8.5$ Hz, 2H), 7.97 (d, $J = 0.6$ Hz, 1H), 7.89 (d, $J = 0.5$ Hz, 1H), 7.07 (dd, $J = 5.5$, 1.9 Hz, 1H), 6.93 (dd, $J = 5.5$, 1.8 Hz, 1H), 6.58 (dd, $J = 1.8$, 0.7 Hz, 1H), 6.56 (dd, $J = 1.8$, 0.8 Hz, 1H), 1.76, 1.722, 1.719, 1.685, 1.677, 1.65, 1.61 (s from both isomers III and IV, $C(CH_3)_3$), −3.29, −3.47, −4.32, −4.70 (s, 3H each, CH_3). Isomer IV: δ 8.82 (d, $J = 1.1$ Hz, 1H), 8.69−8.68 (m, 1H), 8.66−8.65 (m, 1H), 8.51 (d, $J = 1.2$ Hz, 1H), 8.27 (d, $J = 1.1$ Hz, 1H), 8.20 (d, $J = 1.1$ Hz, 1H), 8.16 (d, $J = 1.1$ Hz, 1H), 8.11 (d, $J = 1.2$ Hz, 1H), 8.06 (s, 2H), 7.93 (d, $J = 0.5$ Hz, 1H), 7.90 (d, $J = 0.6$ Hz, 1H), 7.09 (dd, $J = 5.5$, 1.8 Hz, 1H), 6.94 (dd, $J = 5.5$, 1.8 Hz, 1H), 6.53 (dd, $J = 1.9$, 0.8 Hz, 2H), 1.76, 1.722, 1.719, 1.685, 1.677, 1.65, 1.61 (s from both isomers III and IV, $C(CH_3)_3$), −3.26, −3.48, −4.31, −4.73 (s, 3H each, CH_3). ^{13}C NMR both isomers: δ 145.47, 145.44, 145.39, 145.32, 145.23, 145.00, 144.82, 141.05, 140.92, 140.84, 140.74, 140.52, 140.45, 140.27, 137.72, 137.62, 137.59, 137.46, 137.13, 137.08, 136.95, 136.88, 136.79, 128.75, 128.16, 127.99, 127.87, 127.83, 127.71, 127.63, 127.43, 127.21, 127.07, 126.76, 124.25, 124.21, 121.32, 121.28, 121.16, 121.07, 117.66, 117.31, 116.57, 116.46, 115.77, 115.32, 115.08, 114.85, 114.77, 114.65, 81.92, 81.69, 81.62, 81.50, 81.39, 81.24, 35.98, 35.91, 35.82, 35.79, 35.74, 34.66, 33.84, 33.77, 33.03, 32.89, 31.96, 31.91, 31.65, 31.60, 31.41, 31.26, 31.21, 31.01, 16.58, 16.45, 16.40, 16.28, 14.22, 14.11, 12.86.

Adduct 13. Tetrazine[13] **9** (18.3 mg, 0.078 mmol) was added to a solution of the bis-adduct **12** (56 mg, 0.071 mmol) in dry THF (20 mL) under N_2 and was stirred at 20 °C for 1 h. The solvent was evaporated, and the residual was filtered through alumina using hexanes/benzene (1:1) as eluant and gave 51 mg (93%) of the product **13** (suitable for use in the next step) as a reddish-brown solid as a mixture of unequal amounts of two isomers (I and II in a ratio of about 3:2), mp (dec) 190 °C, LSIMS *m*/*z* 767.5 (MH^+); HRMS. Calcd for $C_{56}H_{62}O_2$ (M^+): 766.4750. Found: 766.4737. Isomer I showed ^1H NMR (300 MHz) δ 8.54 (s, 1H), 8.43 (s, 1H), 8.40 (s, 1H), 8.36 (s, 1H), 8.324 (s, 1H), 8.316 (s, 1H), 7.98 (s, 1H), 7.97 (s, 1H), 7.07 (s, 1H), 7.05 (s, 1H), 7.00 (d, $J = 1.6$ Hz, 1H), 6.84 (d, $J = 1.6$ Hz, 1H), 6.81 (d, $J = 1.6$ Hz, 1H), 6.76 (d, $J = 1.6$ Hz, 1H), 1.69, 1.66, 1.35, 1.28 (s, 9H each), 0.45, −0.54, −3.68, −4.02 (s, 3H each); Isomer II δ 8.58 (s, 1H), 8.48 (s, 1H), 8.40 (2H), 8.33 (2H), 7.96−7.99 (2H), 7.09 (s, 1H), 7.06 (s, 1H), 6.95 (1H), 6.88 (1H), 6.83 (d, 1H), 6.81 (1H), 1.69, 1.68, 1.33, 1.31 (s, 9H each), 0.45, −0.52, −3.72, −4.04 (s, 3H each). NOTE: isomer II decomposed on chromatography much faster than isomer I, and hence peaks for each isomer were assigned after much of isomer II had decomposed.

Trisdihydropyrene-dioxide 7. $NaNH_2$ (400 mg, 10 mmol) and *t*-BuOK (2 mg) were added to a solution of the adduct **13** (as soon as possible after it was prepared above) (20 mg, 0.026 mmol) and the bromide[12] **11** (18 mg, 0.043 mmol) in dry THF (15 mL) under N_2, and the mixture was stirred at ∼20 °C for 5 h and then was filtered through a short alumina column (2 cm). For preparative purposes, the solvent was evaporated and the residual was used directly in the next reaction step below. The product **7** had poor solubility and was not very stable in solution, and so purification tried at this step was not very successful. The crude product which contained 6 isomers gave ^1H NMR (300 MHz) with peaks in the following regions: δ 8.86−8.44, 8.08−7.87 (ring protons), 1.87−1.76 (*t*-Bu on the middle ring), 1.64−1.55 (*t*-Bu on the side rings), −3.36, −3.37, −3.39, −3.50, −4.54, −4.57, −4.58, −4.62, −5.25, −5.28, −5.30 (internal methyls).

This product could also be obtained by reaction of isofuran[12] **8** (3 equiv) with dibromide **5** (1 equiv) and $NaNH_2$/*t*-BuOK (10 equiv) at 55 °C in THF; however, the product was much more difficult to purify than using the sequence described above.

Switch 3. Trisdihydropyrene **7** (crude from above) (21 mg, 0.019 mmol) and $Fe_2(CO)_9$ (10 mg, 0.027 mmol) were refluxed in benzene under argon for 1 h, and then the mixture was cooled to ∼20 °C when the solvent was evaporated. The residue was chromatographed on deactivated SiGel using hexanes/benzene (6:1) as eluant and gave 9 mg (44%) of the product **3-c,o,c** as a mixture of three diastereomers. Recrystallization from toluene gave dark-red crystals, mp (dec) 176−181 °C, which had increased amount of one of the symmetrical isomers, **3a** or **3b**, which gave ^1H NMR δ 9.00 (s, 4H, H-9,13,22,26), 8.37 (br. s, 4H, H-1,8,14,21), 7.40 (d, $J = 0.9$ Hz, 4H, H-3,6,16,19), 7.17 (s, 8H, H-4,5,17,18,10,12,23,25), 1.53 (s, 36H, $C(CH_3)_3$ from DHPs), 1.36, 1.35 (s, 36H total, $C(CH_3)_3$ from cyclophane), 1.28 (br. s, 6H, CH_3 from cyclophane), −1.360 (see text) (s, 12H, CH_3 from DHPs). The spectra of the other isomers were determined by subtraction: δ 9.142 and 9.136 (s, 4H, H-9,13,22,26), 8.55 (br. s, 4H, H-1,8,14,21), 7.52 (br. s, 4H, H-3,6,16,19), 7.31 (s, 4H, H-4,5,17,18), 7.17 (s, 4H, H-10,12,23,-25), 1.56 (s, 36H, $C(CH_3)_3$ from DHPs), 1.36, 1.35 (s, 36H total, $C(CH_3)_3$ from cyclophane), 1.28 (br. s, 6H, CH_3 from cyclophane), −1.364 and −1.622 (see text, isomer **3c**), and −1.626 (s, 12H total, CH_3 from DHPs). Mixed isomers: ^{13}C NMR δ 150.28, 144.74, 144.50, 141.93, 141.49, 140.10, 139.95, 138.63, 138.48, 137.93, 134.92, 134.48, 129.46, 129.25, 129.07, 124.38, 123.42, 121.25, 120.99, 119.87, 117.35, 116.77, 35.62, 35.56, 35.49, 34.99, 34.37, 31.53, 30.91, 30.76, 30.46, 29.71, 18.84, 17.96, 17.46; UV (chloroform) λ_{max} (ϵ_{max}) nm 287 (53 400), 310 (47 700), 394 (43 600), 413 (74 200), 513 (9 600), 628 (1 100); EI MS *m*/*z*, 1078 (MH^+); HRMS. Calcd for $C_{82}H_{93}$ (MH^+): 1077.7277. Found: 1077.7256. Anal. Calcd for $C_{82}H_{92}$: C, 91.39; H, 8.61. Found: C, 91.13; H, 8.87.

The syntheses of compounds **14**−**19** (Scheme 5) are given in the Supporting Information.

Photochemical Experiments. (a) Continuous Irradiation: Opening of 3-c,o,c to 3-o,o,o. A solution of dihydropyrene **3-c,o,c** (5 mg) in argon-degassed $CDCl_3$ (which had been filtered through basic alumina before use) was again filtered through alumina into an NMR tube, which was then chilled with running cold water while being irradiated by a 500-W tungsten household lamp (available in hardware stores to light a room during painting), with a ∼550-nm cutoff filter between the lamp and the sample. After about 3 h of irradiation, NMR monitoring indicated opening was mostly complete and that the sample solution was almost colorless. The ^1H NMR spectrum (300 MHz) of **3-o,o,o** (as mixed isomers 3a,b,c) then showed δ 8.04 (s), 7.98 (s), 7.96 (s), 7.19−7.00 (m), 6.96 (s), 6.86 (s), 6.49 (s), 1.42 (s), 1.31 (s), 1.30(s) as major peaks. When this sample was irradiated with 350-nm light (TLC lamp), the original spectrum was restored after about 1 h irradiation.

(b) Transient Studies. Samples for the laser flash photolysis experiments were prepared with spectrograde solvents. All experiments were performed at 20 °C. The concentrations were such that the absorptions at the excitation wavelengths were between 0.1 and 0.7 ($l = 7$ mm). Samples were placed in 7 × 7 mm^2 Suprasil cells. Unless otherwise stated, samples were purged with N_2 for at least 15 min.

The laser flash photolysis system previously described[18] was modified for measurements in the millisecond time range (see Supporting Information for details). Samples were excited using either a Nd:YAG laser at 266 (≤20 mJ/pulse) or 532 nm (≤50 mJ/pulse) or by using a tunable Coherent Infinity/OPO system for excitation at variable wavelengths. Transient decays were recorded at fixed wavelengths using a Xe-arc lamp. The signal from the photomultiplier tube was fed into an oscilloscope terminated externally at 1 kW. Decay traces were measured for samples either in static or flow cells, whereas transient spectra were collected using flow cells. The use of flow cells ensures that a fresh sample is irradiated at each laser pulse. This is important when transients are formed that have lifetimes longer than seconds and do not decay back to the precursor between two subsequent laser shots. Static cells were employed for lifetime measurements to avoid the diffusion of the transient out of the monitoring volume. When static cells were used, frequent measurements of the ground-state absorption of the sample ensured that the conversion of the precursor was low. The diffusion rate of the transient out of the excitation volume into the bulk solution determines the longest transient kinetics that can be measured. The diffusion time varies slightly for different experiments. For this reason, the diffusion time was measured by following the absorption of transients known to have known lifetimes longer than 10 s. For excitation at 266 nm, the formation of quinone methide from *o*-hydroxybenzhydrol in acetonitrile:water 9:1 ($t > 20$ s)[19] was used to determine the diffusion time. The diffusion time for excitation at 532 nm was determined by the irradiation of benzo-DHP **2-c**. The cyclophanediene isomer, **2-o**, formed from this compound has a half-life longer than 5 h at room temperature.[6]

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Supporting Information Available: Synthesis of compounds in Scheme 5, expansion of Figures 2a and 2b, sequential UV−vis spectra in photo-opening of **18-c,o,c** and sequential UV closing of **18-o,o,o**, ^1H NMR spectra (internal methyl region) of **18-c,o,c** and in UV closing of **18-o,o,o**, relative rate data for visible light opening of **3-c,o,c** and **18-c,o,c** with respect to **2-c**; changes to the lasher flash system, transient kinetics at 410 nm for irradiation at 266 nm of **20**, transient kinetics at different monitoring wavelengths for **14**, Transient kinetics at 490 nm for irradiation of **3** at 532 nm (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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