

Pi-Switches: Synthesis of Three-Way Molecular Switches Based on the Dimethyldihydropyrene–Metacyclophanediene Valence Isomerization

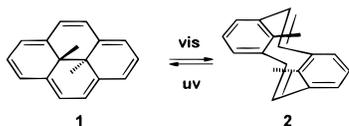
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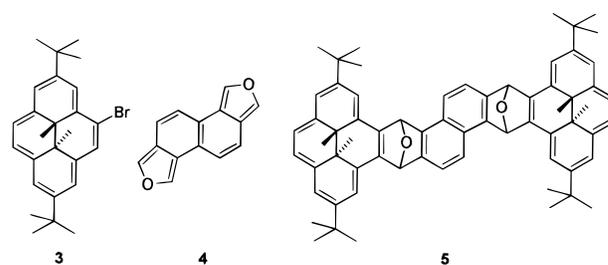
Three three-way switches have been prepared, where different photochemically interconvertible pi-systems correspond to the states of the switch. Molecular switches are currently popular synthetic targets.¹ Such switches usually have two stable states, corresponding to on/off. In principle, it should be possible to synthesize *pi-switches* which have more than two stable states, although we know of no examples. In particular, if the switching process breaks the conjugation of the pi-system by, for example, removing part of it out of the plane of the remainder, then inclusion of more than one such switch into the pi-system would lead to switches having more than a simple on/off state. This is illustrated in Figure 1.

The dimethyldihydropyrene–cyclophanediene (DHP–CPD) valence isomerization, **1** ↔ **2**, is particularly suited to this application, since **1**, a [14]annulene, has an extended pi-system with absorptions to 600 nm, whereas **2**, the cyclophane, has the olefinic



bridges almost at right angles to the benzene rings, and thus shows benzenoid absorption with an extended tail.² We have combined two DHP–CPD switches with a conjugated spacer to make a three-way switch, where the “red state” in Figure 1 corresponds to DHP–spacer–DHP, molecule **6**, the “blue state” to DHP–spacer–CPD, **7**, and the “green state” to CPD–spacer–CPD, **8**.

Reaction of the bromo-DHP³ **3** with NaNH₂ in THF to generate the intermediate aryne,⁴ in the presence of the bis-furan⁵ **4**, gave 58% of the bis-adduct **5** as a mixture of isomers⁶ which were directly de-oxygenated⁷ with Fe₂(CO)₉ in refluxing benzene for 2 h to give 85% of the reddish-brown colored bis-dihydropyrenochrysene **6**, as a mixture of the two anti stereoisomers.⁸ The ¹H



NMR spectrum did not resolve these and showed in CDCl₃ a single somewhat broadened internal methyl proton peak at δ –0.73, but two singlets in C₆D₆ at δ –0.284 and –0.295. Figure 2 shows the UV/visible spectra of the switching behavior: irradiation of **6** (main λ_{max} 427 nm) with visible light (tungsten garden floodlamps, 400–800 nm) opens both DHP units together to give the colorless bis-CPD **8** (the green state in Figure 1). This shows no long wavelength bands, only typical absorption for a substituted chrysene around 313 nm with a tail (chrysene or aryl-CPD) to 360 nm. Irradiation with UV light, (~350 nm) first closes one CPD to give mostly **7**, (main λ_{max} 414 nm) and then with extended irradiation (or thermal heating) closes both CPDs to return **6**. These changes could also be followed by ¹H NMR (C₆D₆), where **8** shows all of the internal methyl protons at δ ~1.7 (CPD), while **7** shows peaks at δ ~1.6 (CPD) and ~–0.3 (DHP). Other spacers between the DHPs can be used, for example benzene, although this requires a somewhat different synthetic approach: reacting the aryne from **3** with furan yielded 85% of adduct **9**; direct conversion⁹ of these with dipyrindyl-tetrazine¹⁰ at room temperature in THF for 1 h gave in 95% yield the iso-furan **10**.¹¹ This was re-trapped with the aryne from **3**, and the adduct was deoxygenated as above and gave about 20% of the bis-dihydropyrenobenzene **11**, with internal methyl protons at δ –1.07. This underwent similar switching behavior to **6**. Both **6** and **11** are examples of a switch where the thermal stable state is DHP–spacer–DHP, which can be changed to the CPD-containing states by visible light. This is consistent with the results from AM1 calculations^{2b} which indicate that **6** and **11** should be the thermally stable isomers. Interestingly though, the calculated ΔH_f values between **6**, **7**, and **8** (0.75, 0.60 kcal/mol) are somewhat smaller than for **11** and its mono- and bis-CPD isomers (1.06 and 1.36 kcal/mol). We thus will in future work explore how this difference affects the equilibria for these and other spacers.

When an additional benzene ring is fused to the side of **11**, the thermodynamics change. AM1 calculations indicate that the thermally stable isomer¹² should be the one which has one DHP and one CPD. Indeed reaction of the iso-furan **10** with the aryne derived from **12** gave ~60% of the adducts, which were directly

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(1) See for example: Ward, M. D. *Chem. Ind. (London)* **1997**, 640–645; Tsvigoulis, G. M.; Lehn, J. M. *Chem. Eur. J.* **1996**, *2*, 1399–1406; Spreitzer, H.; Daub, J. *Chem. Eur. J.* **1996**, *2*, 1150–1158; Archut, A.; Vogtle, F.; De Cola, L.; Azzellini, G. C.; Balzani, V.; Ramanujam, P. S.; Berg, R. H. *Chem. Eur. J.* **1998**, *4*, 699–706; Takeshita, M.; Irie, M. *Tetrahedron. Lett.* **1998**, *39*, 613–616; Irie, M.; Uchida, K. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 985–996; Pina, F.; Melo, M. J.; Maestri, M.; Ballardini, R.; Balzani, V. *J. Am. Chem. Soc.* **1997**, *119*, 5556–5561; Pina, F.; Roque, A.; Melo, M. J.; Maestri, M.; Ballardini, L.; Balzani, V. *Chem. Eur. J.* **1998**, *4*, 1184–1191.

(2) (a) Blattmann, H. R.; Meuche, D.; Heilbronner, E.; Molyneux, R. J.; Boekelheide, V. *J. Am. Chem. Soc.* **1965**, *87*, 130–131; Blattmann, H. R.; Schmidt, W. *Tetrahedron* **1970**, *26*, 5885–5899. (b) Mitchell, R. H.; Iyer, V. S.; Mahadevan, R.; Venugopalan, S.; Zhou, P. *J. Org. Chem.* **1996**, *61*, 5116–5120.

(3) Mitchell, R. H.; Chen, Y.; Zhang, J. *Org. Prep. Proc. Int.* **1997**, *29*, 715–719.

(4) 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; Mitchell, R. H.; Zhou, P. *Tetrahedron Lett.* **1990**, *37*, 5277–5280.

(5) Yu, D. W.; Preuss, K. E.; Cassis, P. R.; Deijkhangsar, T. D.; Dibble, P. W. *Tetrahedron. Lett.* **1996**, *37*, 8845–8848.

(6) The adduct **5** was obtained as green crystals, a mixture of isomers: ¹H NMR (300 MHz, C₆D₆) δ 8.5–7.5 (m, 16), 7.36–7.28 and 6.90–6.88 (m, 4, –OCH–), 1.67–1.63(4s, 36, *t*-Bu–), –2.89 and –3.79 and –2.95 and –3.92 (4s, total 12, –Me). LSIMS HRMS, C₆₆H₆₀O₂ requires: 893.5298. Found: 893.5311.

(7) Best, W. M.; Collins, P. A.; McCulloch, R. K.; Wege, D. *Aust. J. Chem.* **1982**, *35*, 843–848.

(8) The red crystals do not melt up to 345 °C. The two anti isomers are not sufficiently different to be distinguished by ¹H NMR (360 MHz, C₆D₆) δ 10.35 (s, 1), 9.39 (s, 1), 9.18 (d, *J* = 9.0 Hz, 1), 8.54 (s, 1), 8.41 (s, 1), 8.17 (d, *J* = 9.0 Hz, 1), 7.22 (s, 2), 6.90 (s, 2), 1.453 (s, 9), 1.442 (s, 9), –0.284 (s, 3), –0.295 (s, 3); HRMS, C₆₆H₅₆ requires: 860.5321. Found: 860.5323.

(9) Warrenner, R. N. *J. Am. Chem. Soc.* **1971**, *93*, 2346–2348; Russell, R. A.; Marsden, D. E.; Sterns, M.; Warrenner, R. N. *Aust. J. Chem.* **1981**, *34*, 1223–1234; Moursounidinis, J.; Wege, D. *Aust. J. Chem.* **1988**, *41*, 235–249; Mitchell, R. H.; Zhou, P. *Tetrahedron. Lett.* **1992**, *32*, 6319–6322.

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

(11) This was stable enough to be chromatographed at room temperature. ¹H NMR (300 MHz, CDCl₃) δ 8.32 (s, 2), 7.13 (s, 2), 6.47 (s, 2), 6.22 (s, 2), 1.29 (s, 18), 0.18 (s, 6).

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

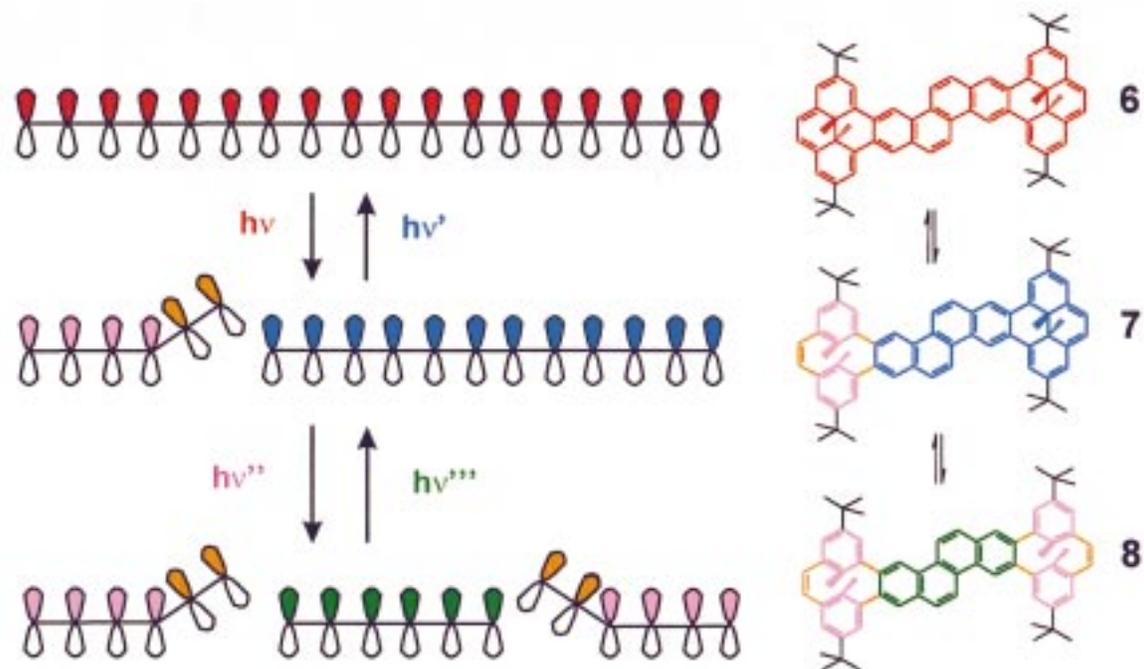


Figure 1. An illustration of a three-way pi-switch and the corresponding molecules 6–8.

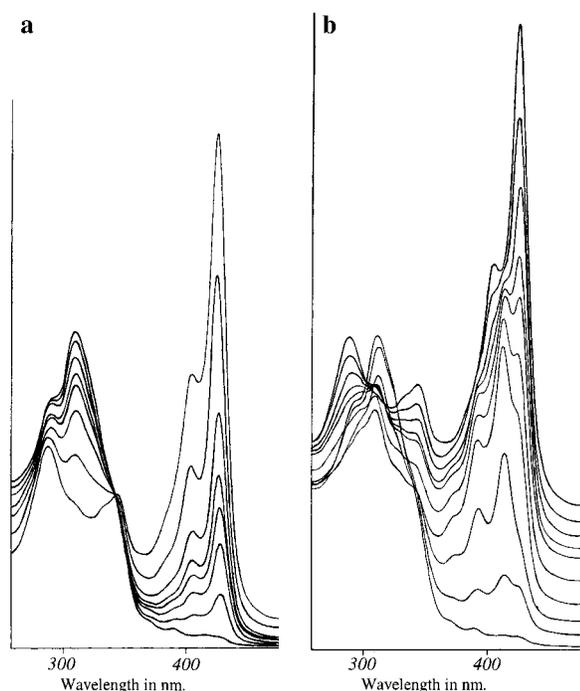
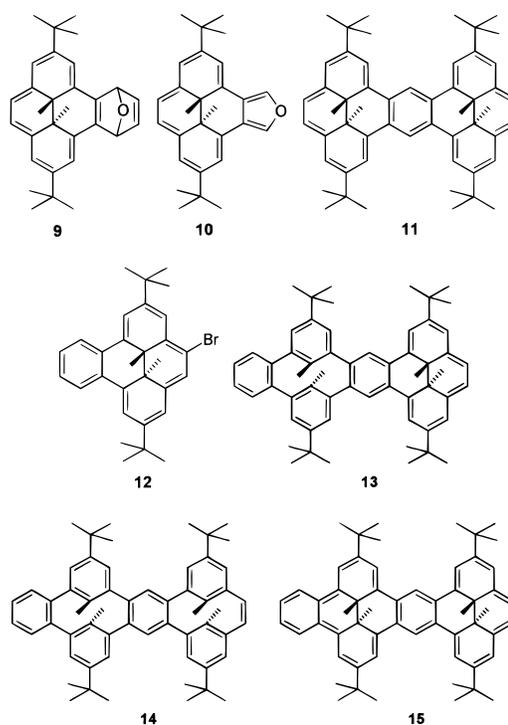


Figure 2. (a) Absorption spectra obtained when **6** ($\lambda = 427$ nm in cyclohexane) was irradiated with a Tungsten lamp using a 598-nm cutoff filter for (top to bottom) 0, 1, 2, 5, 7, 9, 13, 30 min; peak growing in at $\lambda = 313$ nm corresponds to **8**. (b) Absorption spectra obtained when **8** ($\lambda = 313$ nm in cyclohexane, bottom spectrum) was irradiated with UV light ($\lambda \sim 350$ nm) for ~ 2 s intervals (spectra offset upward) to first give formation of **7** ($\lambda = 392$ and 413 nm) which then forms **6** ($\lambda = 406$ and 427 nm).

deoxygenated to yield 85% of strawberry colored **13** (main λ_{max} 406 nm, $\delta(\text{Me}) +1.19, -1.35, \text{ and } -1.65$).¹³ Irradiation of **13** with visible light completely gave the colorless bis-CPD **14**, (λ_{max} 268 nm), which on UV irradiation, or slowly thermally, returned **13**. Laser flash (355 nm) irradiation of **13**, gave the bis-DHP **15** (main λ_{max} 486 nm), which thermally very rapidly returned to

(13) ¹H NMR (300 MHz, CDCl₃) δ 9.09–6.97 (m, 16), 1.544, 1.509, 1.322, 1.317 (4s, 9 each, *t*-Bu), 1.185 (s, 6, -CH₃), -1.367 and -1.662 (s, 3 each, -CH₃); HRMS, C₅₈H₆₄ requires: 760.5007. Found: 760.5004.



13. This process could be repeated 80 times without any apparent decomposition! Unlike **6**, where it is not yet possible to obtain the third state, **7**, of the switch pure, **13** is clearly a three-way switch which is driven from its thermal state by either UV or visible irradiation.

Clearly we have demonstrated that multiple pi-switches are possible. We are now investigating the more detailed switching behavior with selected wavelengths of light, and the possibility of modifying the switch behavior by substituents and changing the spacer.

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