The Metacyclophanediene-Dihydropyrene Photochromic π Switch

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This Microreview highlights the chemistry of the metacyclophanediene-dihydropyrene system, which is a reversible photochromic π switch. Although most studies have been carried out on systems with a single dihydropyrene, recently multiple dihydropyrenes have been fused to conjugated spacers to give multi-state switches.

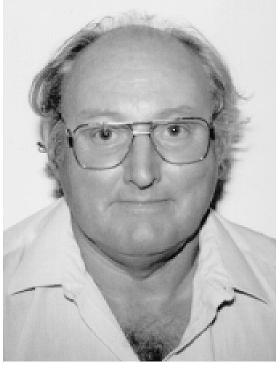
Background

Photochromic molecules are of considerable current interest, and involve molecules such as stilbenes, azobenzenes, spiropyrans, thioindigos, and fulgides.[1] In this review however, we concentrate on derivatives of stilbene. Probably the first report of the formation of an unstable yellow intermediate during the low temperature ultraviolet (UV) irradiation of *cis*-stilbene (**1**), Scheme 1, was that of Lewis and co-workers[2] in 1940, however, not until 1963 was the structure of the yellow product assigned as the dihydrophenanthrene **2** by Moore et al.[3] Muszkat and Fischer[4] published a detailed investigation of this system in 1967, studies that continue to the present. The reaction is complicated somewhat by isomerization of *cis*- to *trans*-stilbene (**3**), and loss of hydrogen from the product to give phenanthrene (**4**). The loss of hydrogen problem was avoided by Muszkat[5] in 1965 by substitution of methyl groups, as in **5** and **6**. Interestingly however, in January of that same year, Boekelheide et al.[6] had reported that the dimethyldihydropyrene **7** could be converted by visible light in to its photoisomer **8**, the metacyclophanediene, which thermally reverted back to **7** in the dark, Scheme 2. This *cis*-stilbene derivative could not isomerize to a *trans*-derivative, nor did it have internal hydrogens to lose. Moreover, the nonbenzenoid product **7**, a deep green dihydropyrene, was the thermally more stable isomer, unlike the case of all the stilbenes. This discovery thus initiated studies in to a very interesting photochromic system which we describe in detail below.

The Dihydropyrene-Metacyclophanediene Interconversion

Blattmann and Schmidt[7] made extensive studies on the reversible **7** to **8** interconversion, for **7** and many of its simple substituted derivatives. In general, irradiation of **7** and its derivatives with light of wavelength >365 nm ($h\nu_1$) converts it to **8**, while irradiation of **8** with light of wavelength <313 nm ($h\nu_2$) converts **8** back to **7**. The more surprising reaction was the Woodward−Hoffmann-forbidden thermal reaction of **8** to **7**. Schmidt[8] has extensively discussed the concertedness of this reaction.

Of more importance to this paper, is the fact that the dihydropyrenes are the thermally stable isomers (by about



Reg Mitchell was born and raised in London, England. He received his bachelor of arts degree in natural sciences from Cambridge University, England, in 1965. He remained at Cambridge to study with Franz Sondheimer and obtained his Ph. D. in 1968 on the synthesis and properties of several benzo and naphtho-annelated annulenes. He then moved to Eugene, Oregon for a two year post-doctoral fellowship with Virgil Boekelheide, where he was introduced to the dihydropyrene molecule. In 1970 he returned to the UK to work in the plastics industry with Formica International for two years and then in 1972 joined the University of Victoria on the west coast of Canada, where he has been able to indulge in his "love" of the dihydropyrene molecule for the past 27 years. His research interests involve aromaticity, strained molecules, cyclophanes, annulenes, organic synthesis, metal complexed aromatic compounds and photochromic molecules.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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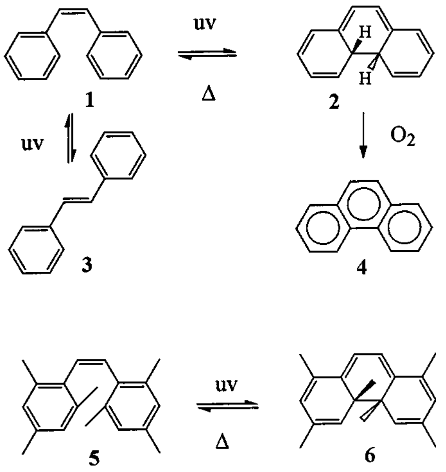
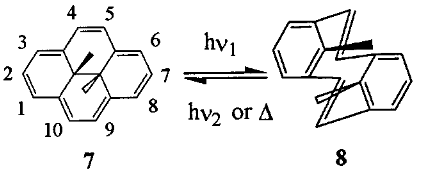


Scheme 1



Scheme 2

3 kcal/mol) that usually result from synthesis. These can be irradiated in hexane for example with visible light from regular tungsten lamps, though use of a long-wavelength filter, e.g. one that restricts λ to > 500 nm, gives more complete conversion (>95%) to the cyclophanediene form. Irradiation with shorter wavelength light, λ ≈ 300 nm, switches the cyclophanediene back to the dihydropyrene. Interestingly, the quantum yield for this reaction, **8** to **7**, is close to one, while that of the bleaching reaction, **7** to **8** is much less, about 0.02, though is greater (0.3−0.4) for the 2-formyl and 2-nitro derivatives.[7] The difference in enthalpy between the dihydropyrenes and the metacyclophanedienes is about 3 kcal/mol regardless of substituent. However, the activation barrier, and hence the rate of the thermal reaction, **8** to **7**, is affected by substituents (Table 1).

Table 1. Rate data (k) and activation energies (E_a) for the thermal reaction of **8** to **7** and substituted derivatives[7][9]

Compound	k(30°C) [min^{-1}]	E_a [kcal mol^{-1}]
dhp-**7**	0.0010	23.0
2-formyl-**7**	0.052	20.5
2-nitro-**7**	0.069	19.7
4-carboxy-**7**	0.00053	22.5
4-bromo-**7**	0.00058	25.2
1,3,6,8-tetramethyl-**7**	0.00095	24.5
2,7-di-*tert*-butyl-**7**	0.0019 (40°C)	21.8
4-nitro-2,7-di-*tert*-butyl-**7**	0.0018 (40°C)	23.7

It appears that an electron-withdrawing group at the 2-position speeds up the thermal return, while methyl groups slow it down. Tashiro et al.[9] have shown that when *tert*-butyl groups are in the 2,7-positions, other substituents do not affect the rate much. In general, the activation barrier for **8** going to **7** is about 20−24 kcal/mol, which puts the rate in a convenient region to study by UV or NMR techniques. Changing the internal substituent from methyl does make quite a difference. For the unsubstituted compound, the cyclophanediene form, **9**, is stable enough to be isolated at room temperature, and converts to the dihydropyrene **10** on irradiation with 254 nm light, but the reaction is not

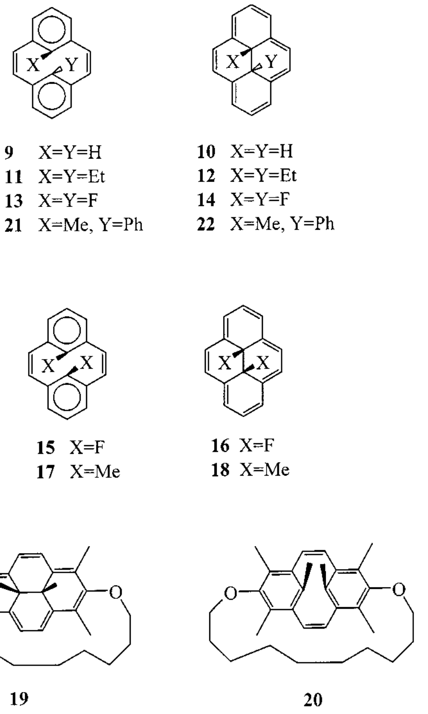
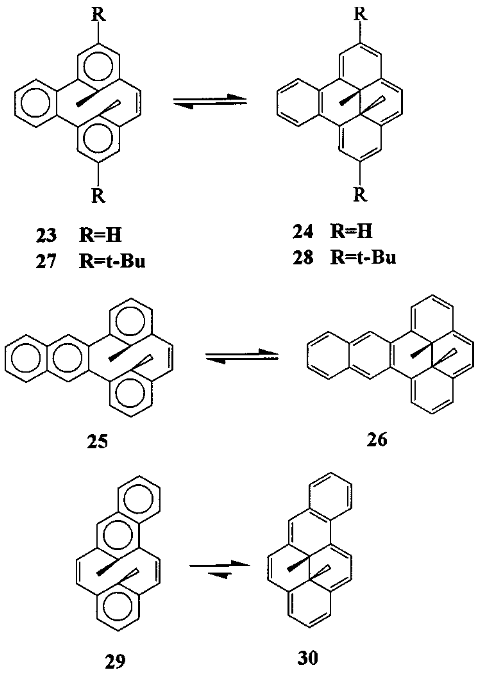
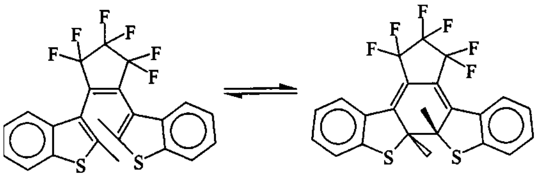


Figure 1. Structures of molecules **9** to **22**



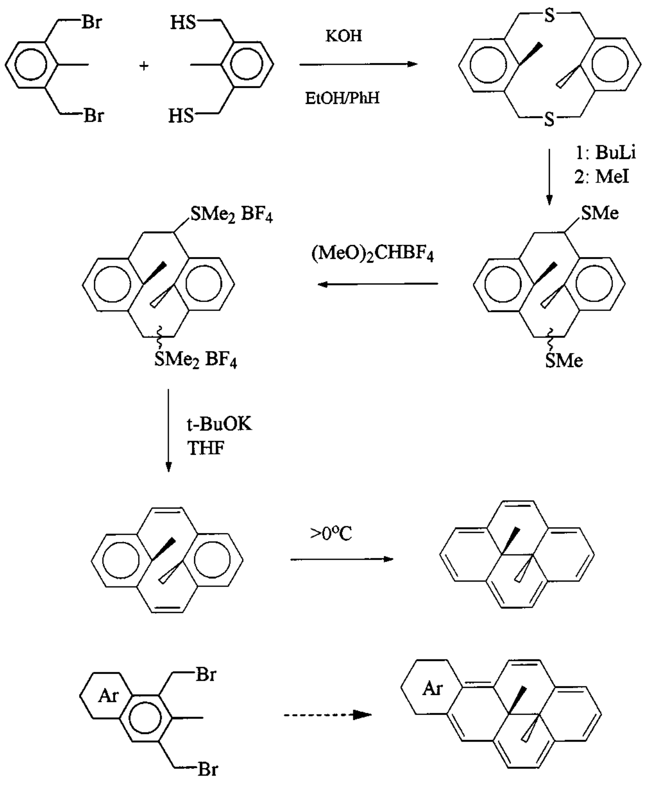
Scheme 3

reversible and is complicated by the easy loss of hydrogen to form pyrene.[10] Changing the internal methyl groups to ethyl groups, **11/12**, increases the rate of the thermal reaction about six times.[7] The case of the difluoro compound **13** is more complex. When first made, the compound obtained was not *syn* as thought[11] but was *anti*[12] and on irradiation gave fluoropyrene derivatives, with no isolated dihydropyrene **14**. We obtained the *syn* compound **15** in 1986[13] and thermally it converts to the *cis*-dihydropyrene **16**, which unfortunately is not very stable. Likewise the *syn*-dimethyl compound **17** thermally converts to the *cis*-dihydropyrene **18**,[10] but neither reaction appears to be reversible. Bodwell[14] has recently obtained a tethered *cis*-dihydropyrene **19**, which exists in equilibrium with the *syn*-cyclophanediene **20**, but it remains to be seen how reversible this isomerization is. In 1981[15] we made the diene **21**. This rapidly converts to the dihydropyrene **22**, but we were unable to reverse the reaction. So far, **22** has the bulkiest internal group – our attempts at introducing *tert*-butyl groups failed,[16] though Lai[17] has made examples with very long alkyl groups. Clearly, from a reversibility point of view, the *anti*/*trans* series with internal methyl groups seems best.



31 **32**

Scheme 4



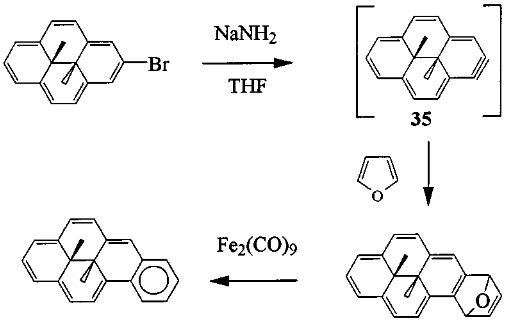
33 **34**

Scheme 5

Annelation of the Dihydropyrene

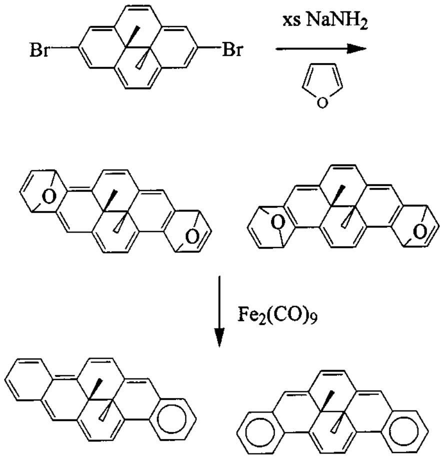
Benzannelation of the dihydropyrene has a rather dramatic effect on the equilibrium, Scheme 3.

Fusion in the [e] position of pyrene gives **24** which very readily quantitatively forms diene **23** with projector lamp light. Irradiation with UV light quantitatively returns **24**. Thermally, diene **23** also returns to dihydropyrene (dhp) **24**. E_{act} for this thermal reaction is 25 kcal/mol[18] compared to the 23 kcal/mol found for the parent **8**. This difference is sufficient to change the thermal rate constant at 30 °C from 10×10^{-4} min^{-1} to $<4 \times 10^{-4}$ min^{-1}. Benzannelation in the [e] position has thus slowed the thermal return reaction, something that is desirable in a photochemical switch.[19] The naphtho[e] isomer **25**[20][21] thermally returns to dhp **26** even more slowly. We have very recently made the *tert*-butyl-substituted compounds **27** and **28** such that comparison data with the parent can be made under the same conditions.

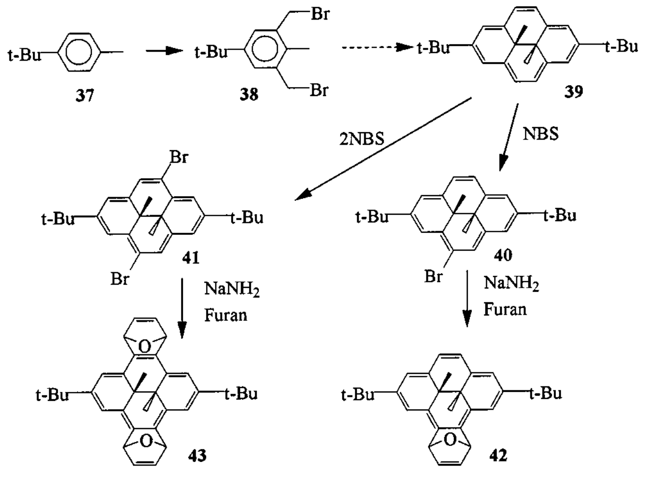


30 **36**

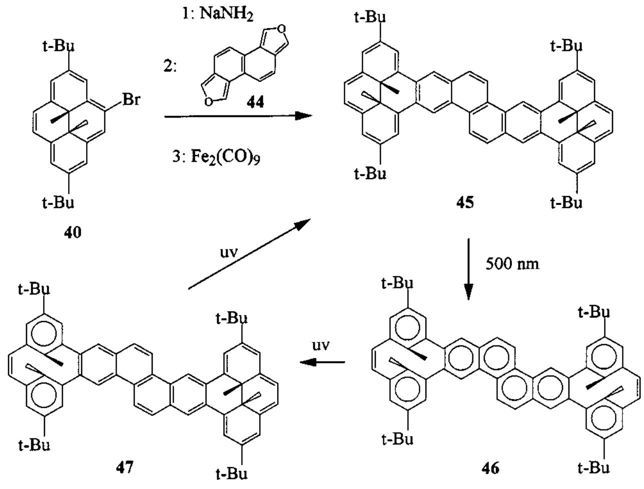
Scheme 6



Scheme 7



Scheme 8



Scheme 9

Fusion in the [a] position of pyrene gives very different results: The thermal reaction of **29** to dhp **30** is very rapid, such that visible light irradiation of **30** under ambient conditions permits no buildup of the diene **29**. Initial laser flash studies, suggest that diene **29** does form, but rapidly reverts to **30**. We intend to establish the kinetics of this reaction by low-temperature work in the future. Indeed, none of the [a] fused benzannulenes that we have made[20][21] allow useful amounts of the diene isomer to be observed. This is consistent with some of our calculations: While AM1 calculations (without CI) do not do a good job on calculating dhp **7** to be bond equal,[22] they do calculate reasonable heats of formation, H_f.[21] The difference in H_f (diene-**8** − dhp-**7**), ΔH_f, is calculated to be 3.4 kcal/mol in good agreement with the experimental value of 3 kcal/mol. For the benzo[e]pair **23/24** ΔH_f = 1.1 kcal/mol but for the benzo[a]pair **29/30**, ΔH_f is 10.6 kcal/mol. Clearly energy wise, **29** has more to gain on converting to **30**, than in the [e] series for **23** to **24**. The difference for the naphtho isomers, **29/30** is even less, 0.7 kcal/mol. It would thus seem on simple analysis, to slow the thermal return reaction, the heats of formation of the two isomers should be approximately the same. Irie et al.[19] have come to the same conclusion, but have tackled the problem in a different manner. They calculated the relative ground state energy differences between the open and closed forms of *cis*-1,2-diphenylethylene (**1** and **2**) (27.3 kcal/mol), 1,2-di(3-pyrrolyl)ethylene (15.5 kcal/mol), 1,2-di(3-furyl)ethylene (9.2 kcal/mol) and 1,2-di(3-thienyl)ethylene (−3.3 kcal/mol). Clearly the thienyl compounds are closest in energy, and appear to make the best

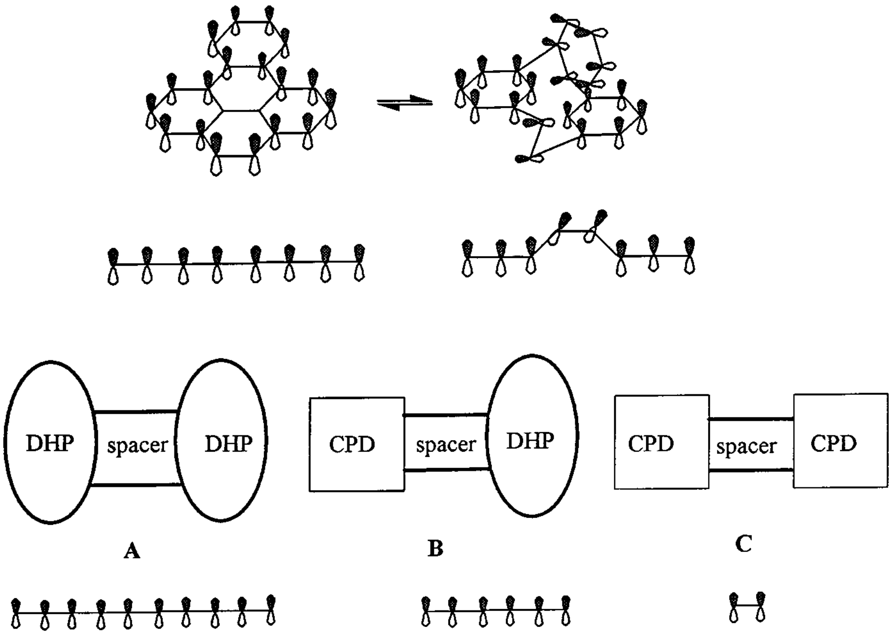
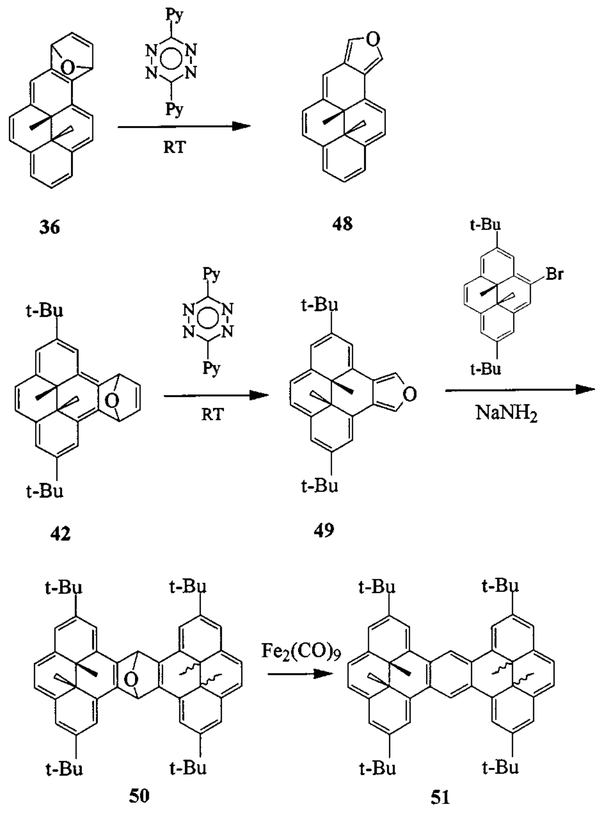
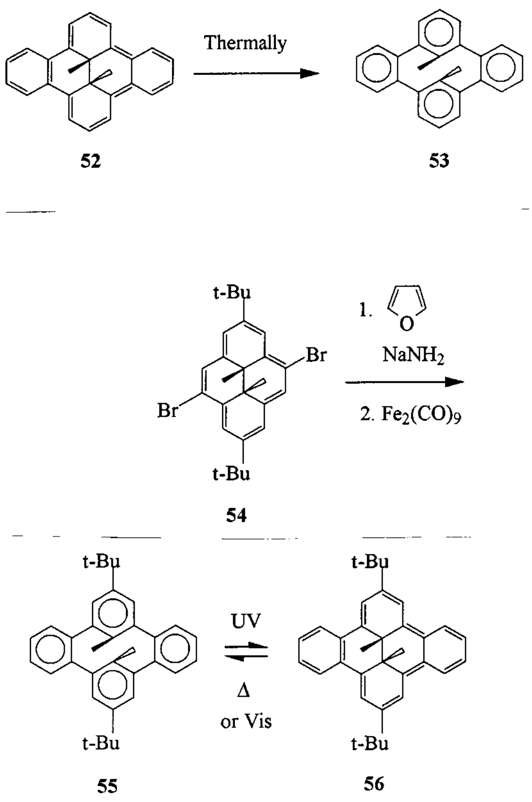


Figure 2. A diagram to (top) indicate the change in π orbital overlap when a dihydropyrene converts to a cyclophanediene because of the near orthogonality of the orbitals on the cyclophane bridges, and (bottom) to indicate the shortening of the π system that results when molecule A converts one DHP to a CPD, and then again when the second DHP converts to a CPD



Scheme 10



Scheme 11

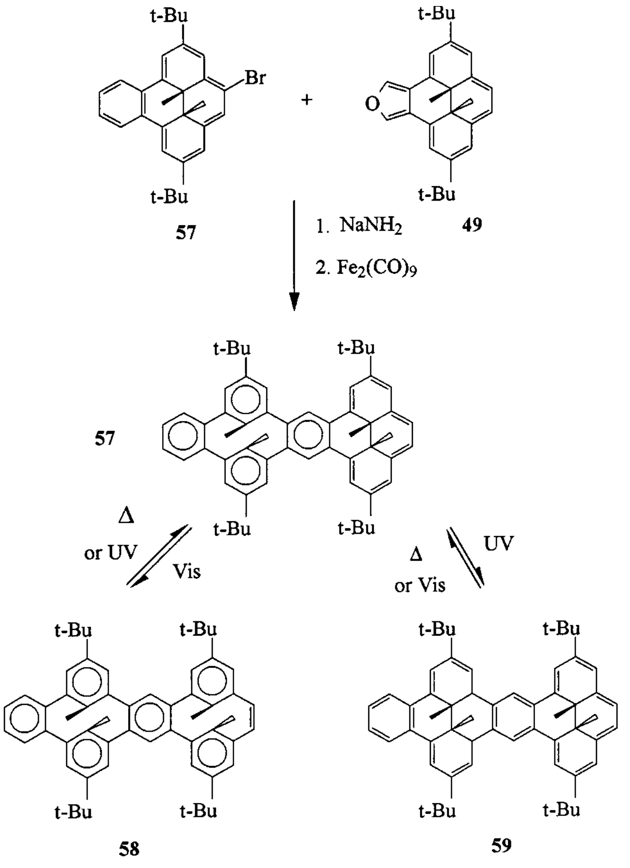
switches. They have overcome the *cis*/*trans*-stilbene isomerization by incorporating the alkene into a five-membered ring. An example is shown in Scheme 4.

In such systems the aromatic stabilization energy of the di-″aryl″-ethylene is decreased to make the open and closed forms of similar energy. In our system, we have annelated the ethylene and left the ″aryl″ groups alone to achieve the same change in energy. Compounds such as **32** seem quite robust, and have been put through >10^4 photochemical cycles.[19] By incorporating phenolic substituted thiophenes, Lehn et al.[23] have integrated electrochromic and photochromic systems to achieve a lockable photochromic switch. Such systems can be written photochemically, locked electrochemically, which allows the reading of the photochromic system without disturbing the equilibrium, and then when desired, unlocking electrochemically and erasing photochemically. Our systems are not so advanced!

Syntheses

We have been interested for some time to see if by inclusion of several dihydropyrenes in to a molecule, we could obtain a multi-state switch. For almost a quarter of a century, the difficulty in synthesis of the dhp framework thwarted our efforts. The last few years have seen this change!

The original syntheses[24][25] of the dihydropyrene system by Boekelheide and Phillips in the early sixties yielded only



Scheme 12

a few mg of dhp **7**. When I had the good fortune to be a post-doc with Virgil in 1968, we discovered[10] the thiacyclophane route to the dihydropyrenes, Scheme 5. This enabled, with some experience, about 2 g of the parent dihydropyrene **7** to be prepared within a few months. Moreover by starting with annelated 1,3-bis(bromomethyl)-2-methylbenzenes, (**33**), many new benzannelated dihydropyrenes, (**34**), could be accessed.[18,26,27] Still however, using the dhp now as the starting material for another long sequence was a daunting prospect for many new students! The breakthrough was made in 1990, Scheme 6, when my graduate student Pengzu Zhou discovered[28] we could make the aryne **35** of dhp as a reactive intermediate, which could be trapped by furan to give the adduct **36**. The latter was easily deoxygenated with $Fe_2(CO)_9$ to give the benzannulene **30**. Now a fused annulene could be made from the parent, without the necessity of a long synthesis of a new bromide **33**. By trapping the aryne **35** with other annelated furans, a variety of annelated dihydropyrenes could be made.[28] In 1995, we published[20] full details of the comparison of the older and newer methods. Interestingly and importantly, the method also works[29] for incorporating two annelations at once (Scheme 7). However mild bromination[30] of dhp **7** only yields the 2- and 2,7-bromo derivatives. To access photoswitchable dhp′s fused in the [e] position, would require the 4-bromo derivative. My student Yongsheng Chen had the bright idea to use Tashiro′s dhp **39**,[31] in which the bulky *tert*-butyl groups would direct incoming bromine to the 4-position. NBS can also be used in $CHCl_3$ or CH_2Cl_2 and with **39** can be controlled[32] to yield either the mono- (**40**) or dibromide (**41**, Scheme 8). Reaction of **40** with $NaNH_2$/furan proceeds via the aryne to adduct **42**, which as previously can be deoxygenated to give the benzannulene **28**, which like its counterpart **24** readily photoisomerizes with visible light to give **27**. Also of importance, was the improvement in the synthesis of bromide **38** from commercial *tert*-butyltoluene (**37**) by use of trioxane with $ZnBr_2$ and 30% HBr in glacial acetic acid at 80−85°C; put together with the new annelation method, this meant that the photoswitches **23/24** and **27/28** were now accessible in gram quantities such that more complex systems could be explored.

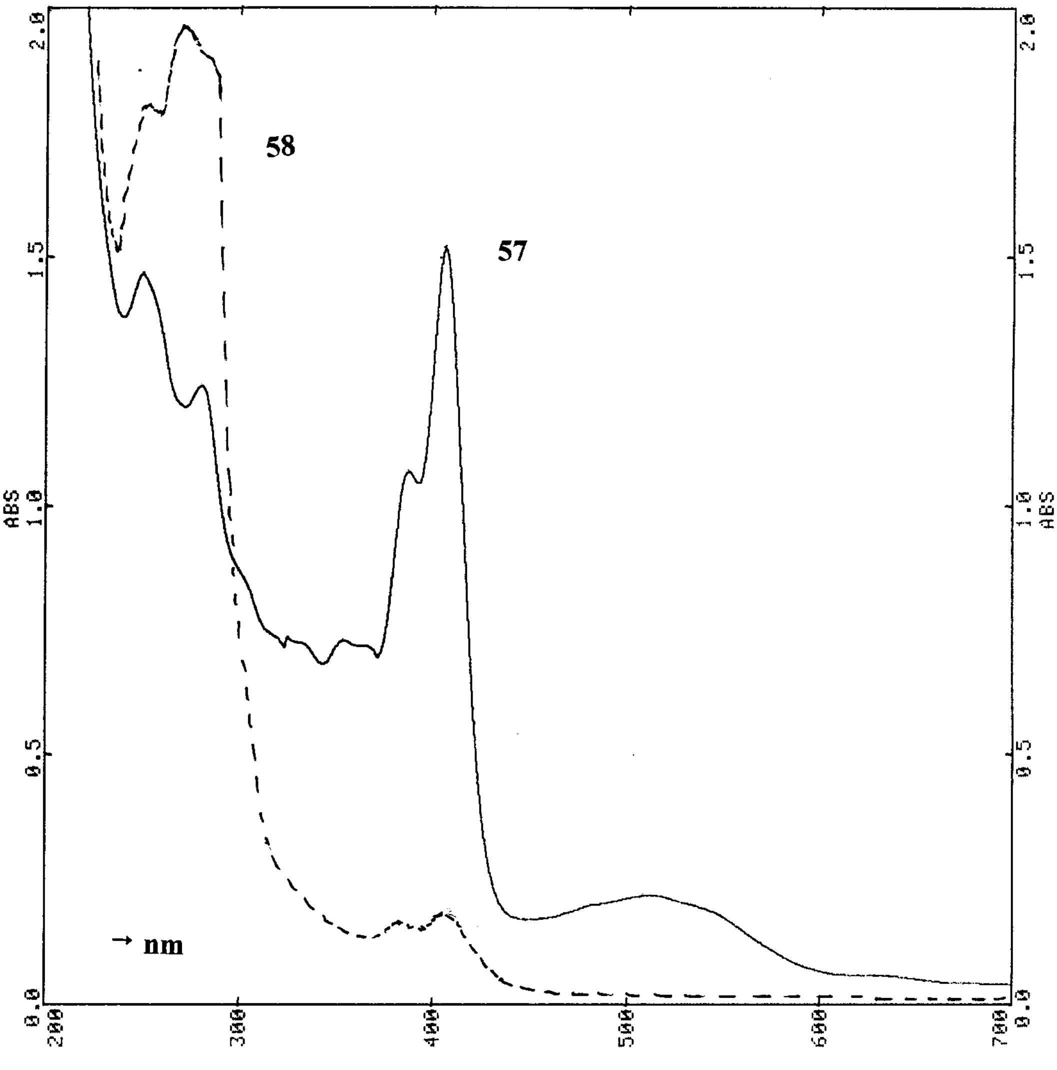


Figure 3. The absorption spectra of **57** (solid line) before and after irradiation with 598 nm light to give **58** (dashed line)

Multistate π Switches

The dihydropyrenes are almost planar[22] and simple annelation does not change this, though it should be mentioned that Lai[34] has shown that introduction of methyl groups at position 9 (on the benzene ring adjacent to the dihydropyrene ring) of **24** considerably reduces the stability of the dihydropyrene relative to the cyclophanediene form, presumably because of steric interaction. The cyclophanedienes are stepped. Thus in an annelated dhp, all of the π orbitals of the total system overlap, whereas in the corresponding cyclophanediene, because of the step, the bridging orbitals do not overlap well with the remainder – this is shown schematically in Figure 2. Use can be made of this if two or more dhp's are thus joined by conjugated spacers. In the bis-closed state of the switch, **A**, the two dhp's form a single conjugated π system; when one switch is opened to a cpd, **B**, the π system is shortened to that of the dhp-spacer, and then when both switches are open, **C**, the resulting conjugation is just that of the spacer. Student Tim Ward put this idea in to practice using Dibble's[35] bis-furan **44** (Scheme 9), which with excess of the aryne derived from **40**, followed by deoxygenation of the mixed isomers of adduct yielded the chrysene derivative **45**.[36] Visible light from garden flood lamps opened both dhp's quickly and gave the bis-cpd **46** (**C**). Irradiation of this with UV light (350 nm) gave first **47** (**B**) and then returned to **45** (**A**). We thus had a three way switch in one direction but two-way in the other. It remains to be seen as to whether selective long wavelength irradiation can open only one of the dhp's in **45**.

A very important synthetic reaction first discovered by Warrener in 1971[37] enabled us to take the next synthetic step. Reaction of the furan adducts **36** or **42** with 3,6-dipyridyltetrazine[38] yields the isofurans **48** and **49**, which are sufficiently stable to purify and chromatograph.[20][39] These can then be reacted with the dhp arynes to yield systems containing more than one dhp, for example **50**, shown in Scheme 10. Student Yunxia Wang found that although this could be deoxygenated as before, the product **51** readily over reacts with the iron carbonyl used. Molecules such as **45** and **51**, while having more than one photochromic switch present, need the ends to be different to make true three way switches. Reaction chemistry on one end of **45** or **51** may achieve this goal, providing they are sufficiently robust to undergo the chemistry involved. We intend to investigate this.

A True Three State Photochromic Switch

A somewhat modified approach enabled us to prepare a true three way switch. Calculations[21] indicated that the stable form of the dibenzannulene **52** would be the cyclophane **53** (Scheme 11). Student Yongsheng Chen made this a reality[40] by synthesis of **55** from the dibromide **54** using

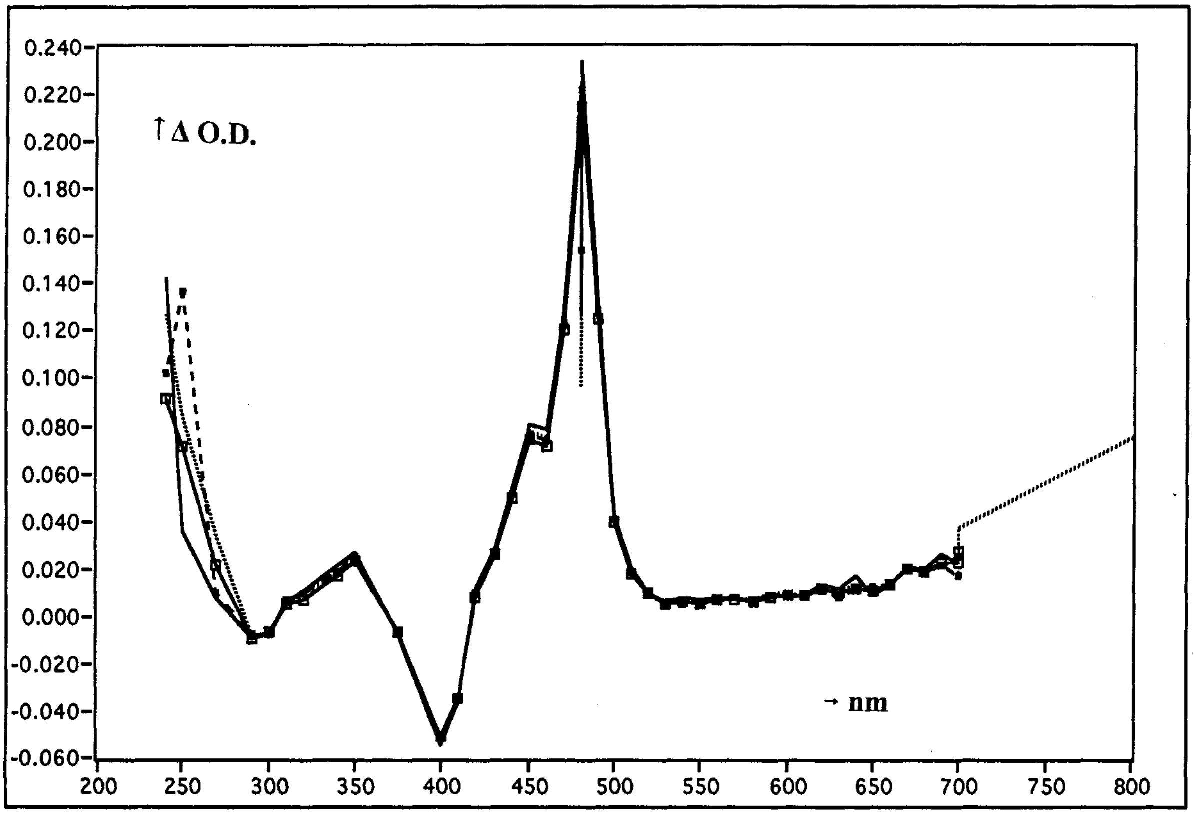
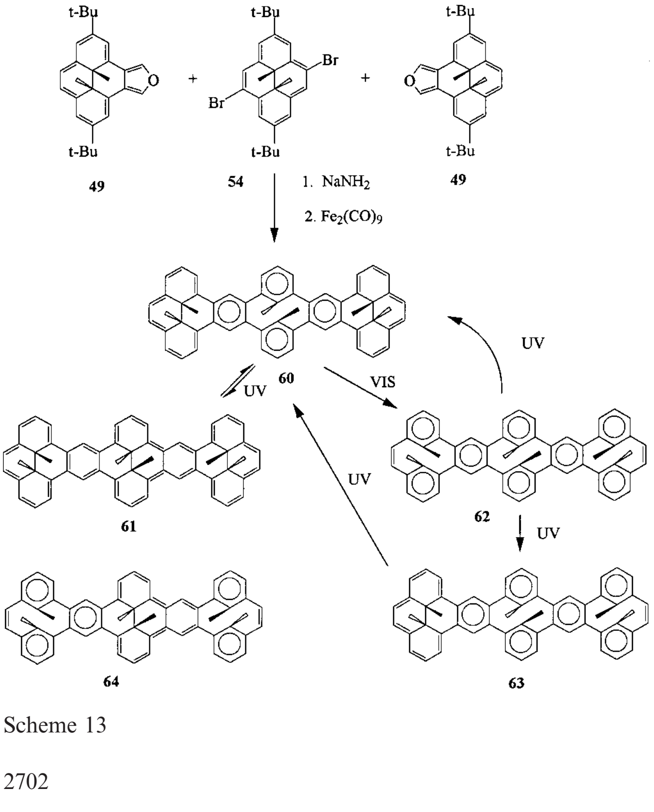


Figure 4. The difference in absorption spectra of **57** and **59** on laser flashing **57** with 355 nm light. Note: the absorption of **57** is at 406 nm which decreases, while the absorption of **59** is at 486 nm, which increases

excess $NaNH_2$ and furan, followed by deoxygenation with $Fe_2(CO)_9$ as before. The cyclophane was a colourless, very stable solid. Irradiation with 300 nm light at $-90\,°C$ gave the green dihydropyrene **56**, which on irradiation with visible light or on warming to room temperature, rapidly isomerized back to the cyclophane. Student Tim Ward then made use of this to synthesize[36] the first true three way photochromic photoswitch (Scheme 12): reaction of bromide **57** with isofuran **49** followed by deoxygenation of the mixture of adducts with $Fe_2(CO)_9$ gave the strawberry-coloured **57** (main λ_{max} 406 nm). Irradiation with >598 nm light opened the dhp and gave the colourless (main λ_{max} 268 nm) bis-cyclophane **58**, Figure 3, which on 300 nm irradiation or slowly thermally returned **57**. While irradiation of **57** at 355 nm using a laser flash system gave the bis-dhp **59**, Figure 4. This very rapidly thermally returned to **57**. Flashing **57** with UV light more than 100 times, resulted in no detectable decomposition.

Clearly multi-state switches are possible. How far can we go? Student Yunxia Wang has obtained three dihydropyrenes fused, as shown in Scheme 13. In principle this is a four-way switch, cpd-cpd-cpd (**62**); dhp-cpd-cpd (**63**); dhp-cpd-dhp (**60**); dhp-dhp-dhp (**61**), (the cpd-dhp-cpd form **64** is not likely to be accessible), possibly more if the ends can be differentiated chemically, however that remains to be verified. Each state of the switch has a different π system, and thus in principle is possible to address separately. Again in reality, that remains to be verified. If systems like **60** can be successfully brominated to give higher analogues of **54**, then the process may continue to 5, 7, 9, or ? fused dihydropyrenes.



Scheme 13

Concluding Remarks

Work on the dhp-cpd switch is not as far advanced as on the dithienylcyclopentenes,[19] and we have not even tackled the write-lock-read problem discussed by Lehn,[23] though we may be able to make similar use of the phenol-dienone interconversion that he does. Though other multi-state switches do exist,[41] we are not aware of multi-state ones that are purely photochemically interconverted, nor are we of systems that have several photoswitchable units fused in the same molecule. Recent improvements in the synthesis of dihydropyrenes and reactions to fuse them together, now permit a greater exploration of such systems, and that will be our goal.

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