Annelated Dimethyldihydropyrenes. Electrophilic Substitution and Valence Isomerization to Metacyclophanedienes

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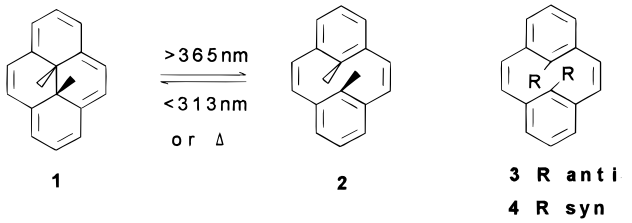
The reversible valence isomerization of cyclophanedienes to dihydropyrenes is discussed for a number of [a]- and [e]-annelated examples, **5** → **6** and **7** → **8**, and is related to AM1 and MM2+Pi calculations. Only in [e]-fused systems is the isomerization easily seen to be reversible. Electrophilic substitution of dihydropyrenes is discussed. Nitration of the highly annelated **20** gives a mixture of 8- and 7-nitro derivatives, while NBS/DMF bromination of the benzo[*a*]dihydropyrene **3** gives mostly 12-bromo derivative.

Introduction

Dimethyldihydropyrene (DHP) **1** is a fully delocalized bridged [14]annulene,[1] and since it is a Hückel aromatic compound would be expected to undergo electrophilic substitution. It does, provided relatively mild conditions are used,[2] and for example can be nitrated and acylated. In addition, one of the more interesting aspects of the chemistry of the green **1** is its reversible photoisomerization to the colorless cyclophanediene (CPD) **2**. Irradiation of DHP **1** with visible light partially converts it to CPD **2**, while allowing **2** to stand in the dark at room temperature, heating, or irradiation with UV light converts it back to **1**. The photochemical processes involve



a conrotatory opening and closing of the central bond and are examples of the more general *cis*-stilbene−dihydrophenanthrene interconversion. The more surprising reaction is the thermal conversion of **2** to **1**, giving the same product as the photochemical reaction, i.e., breaking Woodward−Hoffman rules if a concerted process. This aspect of the process has been discussed in detail[3] for **1**. The reversible valence isomerization between **1** and **2** has been observed and studied in several dozen simple substituted derivatives,[4] where the internal alkyl groups are methyl or ethyl and are *anti* to each other. Generally the dihydropyrene is the thermodynamically more stable isomer (by about 3 kcal/mol in the case of **1**), and the isomerization is fast, E_{act} is about 23 kcal/mol. This is different from *cis*-stilbene, which is the thermodynamically more stable isomer.

The thermal conversion of the CPD to the DHP has been particularly useful synthetically, since it has allowed access to a whole variety of dihydropyrenes (bridged [14]annulenes) from the more easily obtained cyclophanedienes.[1,5] It seems to be fairly general, proceeding normally spontaneously for a variety of internal groups, **3**, where the internal R groups are *anti* (giving the *trans*-dialkyl product) or **4**, where the groups are *syn* (giving the *cis*-dialkyl product). In the case of internal hydrogen substituents, **3** (R = H), care is required, since the product dihydropyrene easily rearranges and/or oxidizes to give pyrene.[5] The reversible photoisomerization has not been demonstrated in this case or for *syn*-dimethyldihydropyrenes.

Recently we have published the details of synthesis of a number of benzo and higher annelated derivatives of **1**,[6] some of which were available in sufficiently large amount to study further the electrophilic substitution and valence isomerization in such systems. This paper describes the results of these investigations.

Valence Isomerization Results

In all the annelated cyclophanedienes that we have prepared,[6−8] with either *anti* or *syn* internal methyl groups, the cyclophanediene isomers **5** (Ar = benzo, 1,2-naphtho, 2,3-naphtho, 6,7-phenaleno, 2,3-phenanthro) and **7** (Ar = benzo, 2,3-naphtho, 2,3-quinoxalino) spontaneously thermally (room temperature) convert into their corresponding dihydropyrene isomers **6** and **8**. The photochemical reaction is more complicated. In the benzannelated derivatives, on irradiation with visible light from a projector bulb, the benzo[*e*]-derivative **12** quantitatively forms diene **11.** The latter reverts to **12**, *both* thermally or on irradiation with UV light.

However irradiation of the [a]-isomer **10** under the same conditions leads to no detectable (<4%) diene **9**. We now report that *none* of the [a]-fused dihydropyrenes thus far prepared form any detectable amounts of their cyclophanediene isomers when placed in a slide projector

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(1) Mitchell, R. H. *Adv. Theoret. Interesting Mol.* **1989**, *1*, 135−199.
(2) Phillips, J. B.; Molyneux, R. J.; Sturm, E.; Boekelheide, V. *J. Am. Chem. Soc.* **1967**, *89*, 1704−1709.
(3) Schmidt, W. *Helv. Chim. Acta* **1971**, *54*, 862−868. Schmidt, W. *Tetrahedron Lett.* **1972**, *12*, 581−584.
(4) 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.
(5) Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1974**, *96*, 1547−1557.
(6) 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.
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(8) Mitchell, R. H.; Yan, J. S. H.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2551−2559.

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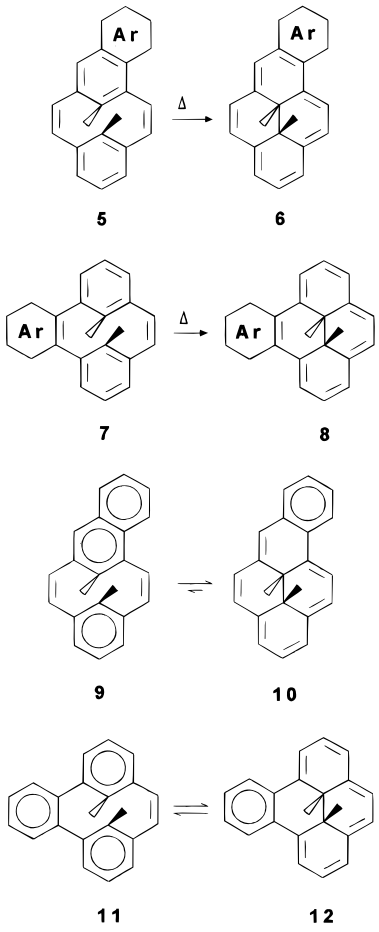
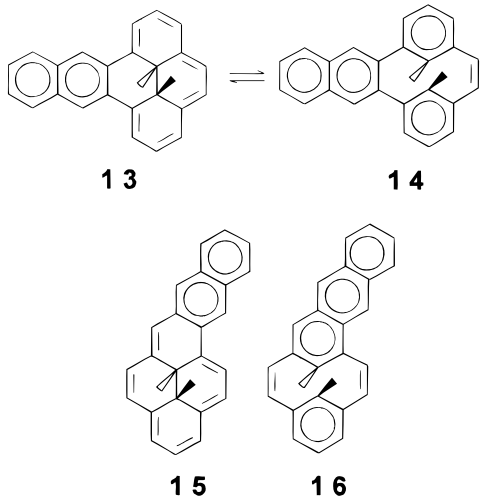


light beam, whereas *all* of the [e]-fused derivatives do. Thus violet solutions of the naphtho[*e*]dihydropyrene **13** bleach completely after a few seconds in a slide projector beam at room temperature, forming cyclophanediene **14**, which then reverts to **13** slowly enough thermally to be followed by NMR, or quickly on 254 nm irradiation. However, unlike the case of **1**, which undergoes hundreds of cycles without decomposition, repeated cycling of **13** ↔ **14** causes extensive decomposition. Irradiation of **13** itself with 254 nm light, even in the presence of O_2, does not seem to decompose the molecule, so possibly the decomposition occurs thermally. The product however is not known at this time.



The enthalpy changes that occur during a valence isomerization of a cyclophanediene to a dihydropyrene deserve some comment, especially in regard to annelated examples. During the isomerization of a diene to a dihydropyrene, a new sp^3-sp^3 bond is formed, a π-bond is lost, strain is reduced, and delocalization energy changes as 6π-systems are lost and 14π-systems are formed. The energy changes accompanying the isomerization of **9** to **10** and of **11** to **12** are thus not obvious, nor indeed are they equal, even though **9** and **11** are isomeric dienes and **10** and **12** are isomeric dihydropyrenes. We first attempted a partial analysis of this system by performing π-SCF/MM2-type calculations[9] of H_f for the five cyclophanedienes **2**, **9**, **11**, **14**, and **16** and their corresponding five dihydropyrenes **1**, **10**, **12**, **13**, and **15**. However, care is required since such calculations are not necessarily reliable. For example, the H_f values calculated for **1** (101.7 kcal/mol) and **2** (88.7 kcal/mol) must be wrong since the resulting ΔH_f of 13 kcal/mol would appear to favor **2**, whereas **1** is the thermodynamically preferred isomer. We have noticed that such calculations often underestimate through space $\pi-\pi$ interactions and underestimate the contribution of delocalized annulene π-bonds to the heat of formation. The net sum of these two factors is to move **2** and **1** closer together in energy. However, comparison of **9** with its isomer **11**, and of **10** with its isomer **12**, should be somewhat more reliable, and thus Table 1 gives the results for the comparison of the [a] with the [e] series.

Table 1. π-SCF/MM2 Values[9] of ΔH_f, ΔSE (strain energy), and $\Delta\pi$E (Pople π-energy) for the [a]- and [e]-Fused Cyclophanedienes (CPDs) and Dihydropyrenes (DHPs)

series	compd	ΔH_f (kcal/mol)	ΔSE (kcal/mol)	$\Delta\pi$E (kcal/mol)
	DHPs			
Δbenzo{[*e*] − [*a*]}	**12**−**10**	+5.34	+3.93	+1.81
Δnaphtho{[*e*] − [*a*]}	**13**−**15**	+4.11	+3.57	+0.56
	CPDs			
Δbenzo{[*e*] − [*a*]}	**11**−**9**	−8.94	−-0.19	−9.21
Δnaphtho{[*e*] − [*a*]}	**14**−**16**	−12.42	−0.25	−13.09

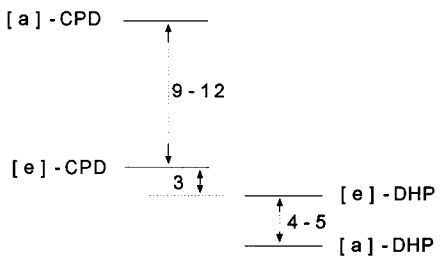


Figure 1. Schematic to show the relative energies of the DHPs and CPDs.

From the sign of ΔH_f, it can be seen that in the dihydropyrenes the [a] series is *more* stable than the [e] series by 4−5 kcal/mol, whereas in the cyclophanedienes the [a] series is *less* stable than the [e] series by 9−12 kcal/mol. This is represented schematically in Figure 1 using the *experimental* value of 3 kcal/mol as the difference between [*e*]-CPD and [*e*]-DHP.

From Table 1, most of the difference between the [*a*]- and the [*e*]-DHPs is a difference in strain energy, where the [e] series is more strained, presumably because of the increased H-interactions between two sets of "bay" hydrogens in the [e] series, but only one set in the [a] series. In the CPDs, on the other hand, there is almost

(9) PCMODEL 386, V4.0, from Serena Software, Box 3076, Bloomington, IN 47402-3076, was used.

Table 2. AM1[11] calculations of H_f and ΔH_f (CPD−DHP) (kcal/mol)

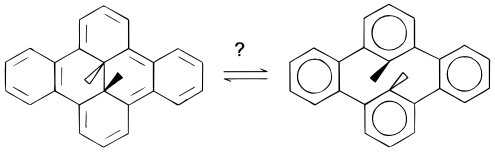
compd		H_f(CPD)		H_f(DHP)	ΔH_f(CPD−DHP)
parent	**2**	107.8	**1**	104.4	3.4
benzo[*e*]	**11**	119.5	**12**	118.4	1.1
naphtho[*e*]	**14**	137.9	**13**	137.2	0.7
benzo[*a*]	**9**	127.3	**10**	116.7	10.6
naphtho[*a*]	**16**	149.5	**15**	135.5	13.5

no difference in strain energy between the [a]- and [e]-fused series, the main difference being the different resonance energies (π-energies) between three benzene rings in **11** and one benzene and one naphthalene in **9**. Recently, Hernando-Huelmo and Rioseras-Garcia in a series of papers[10] have carried out AM1 calculations on the analogous compounds to **1** and **2** and **9**−**12** with internal hydrogen atoms rather than methyl groups. In all cases, the DHP shows a smaller H_f than the CPD, consistent with the direction of the thermal reaction (CPD → DHP). We therefore thought it worthwhile to carry out the AM1 calculations[11] on our series of compounds, with the internal methyl groups, which *substantially* change the strain energy of these compounds. These results are shown in Table 2.

Clearly the [e]-fused DHPs and CPDs have very similar H_f values, and the difference seems to reduce with annelation. On the contrary, the [a]-fused DHPs and CPDs have quite different H_f values, and the difference increases as the annelating ring gets larger. The schematic shown in Figure 1 thus need not be modified much if the AM1 results are used: the difference between the [*a*]- and [*e*]-DHPs is then 1−2 kcal/mol and the difference between [*a*]- and [*e*]-CPDs is then 8−11 kcal/mol. The ΔH_f value calculated for **2** − **1** of 3.4 kcal/mol is of the correct sign and agrees well (unlike the MM2+Pi case) with the experimental value of about 3 kcal/mol. We were surprised that the AM1 calculations gave a correct result, since we have observed that while AM1 calculations give good bond lengths for benzenoids (e.g., in cyclophanes), they do not do such a good job for annulenes. For example, they do *not* predict dihydropyrene **1** to be bond equal but rather bond alternating. In fact **1** is bond equal,[6] a result not easily obtained by high-level calculations.[12] Whether this wrong prediction of bond lengths and hence bond orders affects the value of H_f calculated for **1** must await an experimental determination, which we are attempting.

We have previously measured[8] E_{act} for the thermal reaction of **11** to **12** to be 25 kcal/mol, and we have now measured **14** to **13** also to be 25 kcal/mol, both very similar to the 23 kcal/mol measured[4] for **2** to **1**. Since from Table 2, ΔH_f (CPD−DHP) → 0 for the [e]-annelated derivatives, we can take 25 kcal/mol to be a reasonable estimate for the barrier to conversion of an [*e*]-CPD to an [e]-DHP. Since the [*a*]-CPDs are some 10−14 kcal/mol higher in energy than the [*a*]-DHPs, the barrier for conversion might reasonably be expected to be less than 25 kcal/mol and the transition state more reactant like. Indeed in the case of **9** compared to **11**, the already present bond fixation of the 1−2 naphthalene bond in **9** should make the transition state easier to obtain than the bond equal benzene ring of **11**. If E_{act} for **9** → **10** is substantially less than that for **11** → **12**, then the rate of the thermal return of **9** to **10** will be much faster than the rate for **11** to **12**, and thus no appreciable quantity of **9** may accumulate when **10** is irradiated at room temperature with visible light. We attempted the irradiation of **10** at −78 °C in the hope of slowing the thermal return sufficiently, but were not successful using low-temperature ^{1}H NMR as the method of detection. Since the first excited state of either **10** or **12** should have ample energy to overcome the reverse barrier to obtain **9** and **11**, there is no obvious reason why the photochemical opening to the dienes should not occur, and we thus believe the fast thermal return in the [a] series is why we cannot observe diene buildup. We hope to be able to test this hypothesis in the future by laser flash photolysis of **10**.

However, given that the AM1 calculations above have well predicted the thermodynamically favored isomer, e.g., dihydropyrene **1** is favored over cyclophanediene **2**, given the better understanding of the isomerization in the [e] series gained by the above analysis, it is interesting to predict what will occur for the dibenzannelated case **17** ↔ **18**, the synthesis of which has eluded us for a number of years.[13]



17 **18**

AM1 calculations indicate H_f values for **17** of 149.3 kcal/mol and for **18** of 131.2 kcal/mol and thus predict that in this case the cyclophanediene is the more stable and that **17** should spontaneously revert to **18**.

Electrophilic Substitution Reactions

Providing mild conditions are used, electrophilic substitution reactions can be carried out both on the parent **1**[14] and on its *cis*-dimethyl isomer.[15] In the case of **1,** substitution mostly occurs at the 2-position.[16] This is consistent with our AM1 calculations[11] of the relative stability order of the intermediate cations, e.g., shown as **19** for the 2-nitro intermediate, where the H_f values of these intermediates for 1-, 2- and 4-nitro substitution are 276.3, 268.5, and 272.4 kcal/mol, respectively. For the *cis*-isomer of **1**, acetylation gives a 2:1 mixture of 2- and 1-derivatives.[15] We have previously reported[8] nitration and acetylation of the benzo[*e*]annulene **12** in the 2-position, with introduction of two or more groups easy, if conditions are not carefully controlled. The annulene ring in such a species retains sufficient aromaticity to undergo substitution, and this occurs preferentially in

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(11) Calculated using Hyperchem, Version 2.

(12) Jay Siegel (University of California at San Diego) announced at ISNA-8 (July 31, 1995, Braunschweig, Germany) that a bond equal calculation for **1** can be obtained using density functional theory (MP2) at considerable computer resource expense.

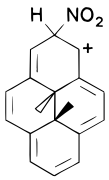
(13) Mitchell, R. H.; Weerawarna, S. A. *Tetrahedron Lett.* **1986**, *27*, 453−456.

(14) Phillips, J. B.; Molyneux, R. J.; Sturm, E.; Boekelheide, V. *J. Am. Chem. Soc.* **1967**, *89*, 1704−1709.

(15) Kamp, D.; Boekelheide, V. *J. Org. Chem.* **1978**, *43*, 3475−3477.

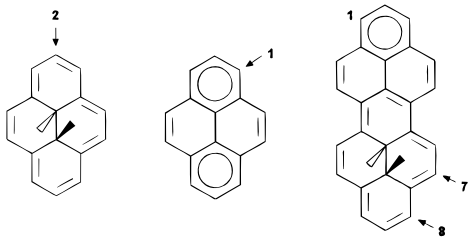
(16) For formylation of **1**, about 20% of the 1-aldehyde is also obtained. This has been misassigned as the 4-aldehyde in the literature.[17] Details of this are submitted to *Org. Prep. Proced. Int.*

(17) Boekelheide, V.; Sturm, E. *J. Am. Chem. Soc.* **1969**, *91*, 902−908.



19

the annulene rather than the benzene ring. We pointed out at that time that the preference for 2-substitution was consistent with a simple Hückel localization energy calculation. PCMODEL calculation of H_f (as above for **19**) for nitration of **12** indicates a substitution preference order of 2 > 3, 4 > 9, 10 > 1. AM1 calculations (rather time consuming for these larger π-systems) refine the order as 2 > 4 > 3 (H_f = 280.2, 286.2, 293.3 kcal/mol, respectively). Compound **20**, which has an even larger π-system, and was available in reasonable quantities, seemed to us an interesting example to examine further. It can be considered as a pseudo-pyrene, in which one of the benzene rings of pyrene, **21**, has been replaced by the dihydropyrene **1**. Whereas dihydropyrene **1** substitutes in the 2-position, pyrene **21** readily substitutes in the 1-position, and thus the position of substitution for **20** is not obvious. In fact nitration of **20** using cupric nitrate in acetic anhydride at 0 °C gave mostly the 8-nitro and 7-nitro derivatives of **20**, where substitution had taken place in the dihydropyrene ring, but to the greater extent at the unusual position (8, 1 of **1**). The structures of the two nitroderivatives of **20** were assigned by 2D-^{1}H NMR, using COSY and NOESY spectra. This substitution pattern is consistent with the calculated stabilities of the probable intermediates, the cationic σ-complexes, using PCMODEL's π-SCF-MM2 calculation.[9] These are shown in Table 3.



1 **21** **20**

As can be seen, the 7- and 8-nitro intermediates do indeed have the lowest H_f values, consistent with these being the products observed. It is interesting that the greater strain energy in these must be compensated by a lower π-energy for the cations. Since the AM1 calculations for **12** took about 30 h each, we did not attempt them for **20**.

Bromination of dihydropyrenes using bromine proceeds very rapidly and gives polybrominated products.[14] However reaction of **1** with NBS in DMF can be controlled to give mono- or dibromo derivatives.[6] It was thus of interest whether this method could be used for benzannelated derivatives of **1**. Indeed reaction of the benzo[*a*]dihydropyrene **10**, with NBS/DMF at 0 °C, gave mostly 12-bromo-**10**, with traces of other isomers. Thus with care, the dihydropyrene ring of benzannelated dihydropyrenes can be electrophilically substituted.

Conclusions

Fusion of one or more benzenoid rings in the [a] position of dimethyldihydropyrene appears to inhibit observation of the reversible valence isomerization to the cyclophanediene in contrast to fusion at the [e] position. In all cases thermal conversion of cyclophanediene to dihydropyrene readily occurs. These results are consistent with AM1 calculations of H_f, but only loosely with MM2+Pi difference calculations within the respective series. It further indicates that if reversible photochromic systems are desired, then [e]-fused rather than [a]-fused dihydropyrenes should be studied. Electrophilic substitution of benzannelated dihydropyrenes can be controlled provided mild conditions are used and the substitution patterns observed are consistent with the relative stabilities of the cationic σ-complexes.

Table 3. Calculated[9] Heats of Formation, H_f, and Strain Energies, SE, for the Cationic Intermediates of Type 19 Derived from 20

NO_2 position	H_f (kcal/mol)	SE (kcal/mol)
2	317.4	73.7
3	283.3	72.1
4	286.4	69.4
5	294.5	67.3
6	297.9	81.9
7	281.1	81.5
8	280.7	82.0
9	289.1	78.0

Experimental Section

Melting points were determined on a Reichert 7905 melting point apparatus integrated to a chrome−alumel thermocouple. Ultraviolet−visible spectra were recorded in cyclohexane. Proton and carbon NMR spectra were recorded in $CDCl_3$ as solvent. Mass spectra were recorded either using methane gas for chemical ionization (CI) or using electron impact (EI) at 70 eV. Exact mass measurements used perfluorokerosene as calibrant. Elemental analyses were carried out by Canadian Microanalytical Services Ltd., Vancouver, BC. All evaporations were carried out under reduced pressure on a rotary evaporator, and all organic extracts were washed with water and dried over anhydrous $MgSO_4$. SiGel refers to Merck silica gel, 70−230 mesh. PE refers to distilled petroleum ether, bp 30−60 °C.

Photoconversion of Naphtho[*e*]dihydropyrene 13 to Cyclophanediene 14 and Thermal Reversion of 14 to 13. When a *reddish purple solution* of **13** in cyclohexane (UV[7] 399 nm (66 800)) was irradiated by an ordinary tungsten projector bulb, the solution became colorless and formed **14**: UV 219 nm (69 100), 235sh (58 100), 267 (67 200). On warming, this returned to the purple spectrum of **13**. The kinetics of the thermal reversion were followed by bleaching a solution of **13** that had been equilibrated to the desired temperature and then following the absorption maximum at 399 nm, which grew as **14** re-formed **13**. Rate constants ($k \times 10^6$ s^{-1}) of 8.45, 32.3, 211, and 747 were obtained at the temperatures (K) 298, 308, 323, and 333, respectively. From an Arrhenius plot, E_a = 105 (±1) kJ mol^{-1} (25.1 kcal/mol).

Visible Light Irradiation of Benzo[*a*]dimethyldihydropyrene (10). A solution of **10**[7] (10 mg) in $CDCl_3$, CD_3CN, or THF-d_8 (1 mL) was irradiated in a projector beam at 20 °C, 0 °C, and about −70 °C for 30 min using cold dry nitrogen to maintain sample temperature, under conditions which readily convert **12** to **11**. The sample was then immediately transferred to a 360 MHz probe at the appropriate temperature, and the intensities of the internal methyl protons were studied. No peaks around δ +1 could be observed for those expected for **9**, nor did the intensity of those around δ −2 for **10** decrease from their original (non-irradiated) values or any other new peaks appear.

Nitration of Dihydropyrene 20. Powdered $Cu(NO_3)_2 \cdot 3H_2O$ (54 mg, 0.22 mmol) was added to a solution of **20**[6] (72 mg, 0.20 mmol) in acetic anhydride (50 mL) at 0 °C. After 2 h of stirring, the solution was poured into ice−water. This was then extracted well with benzene (4 × 100 mL). The

extracts were washed with water, an aqueous $NaHCO_3$ solution, and water and were dried and evaporated. The bluish-red residue was chromatographed over SiGel using first PE to elute unchanged **20** (26 mg, 50%) and then PE−dichloromethane (8:2) to elute a mixture containing about 5 mg each of two nitro derivatives of **20**. These were separated by preparative HPLC on a Varian Model 5000 liquid chromatograph using a silica-10 column, 50 cm × 8 mm and dichloromethane−hexane (35:65).

Eluted first was 8-nitro-**20**, as dark reddish-black crystals from cyclohexane: mp 222−224 °C; ^{1}H NMR (360 MHz) δ 9.91 and 9.89 (AB, J = 8.54Hz, H-6 and H-7), 9.79 and 8.94 (AB, J = 7.86 Hz, H-12 and H-11), 9.53 and 8.44 (AB, J = 9.33 Hz, H-5 and H-4), 9.51 and 8.43 (AB, J = 9.41 Hz, H-13 and H-14), 9.07 and 8.74 (AB, J = 8.59 Hz, H-9 and H-10), 8.34 (d, J = 7.6 Hz, H-1,3), 8.11 (t, J = 7.6 Hz, H-2), −4.01 and −4.05 (s, CH_3-12b,12c); COSY couplings were observed between H-1,3/2, H-4/5, H-6/7, H-9/10, H-11/12, H-13/14; NOESY interactions between H-3/4, H-5/6, H-10/11, H-12/13, H-14/1; UV (cyclohexane) λ_{max} (ϵ_{max}) nm 254 (10 800), 298 (6300), 373sh (7800), 442 (48 000), 514 (9500), 557 (9700), 695 (1000), 782 (750); CI MS m/z 402 (MH^+ for $C_{28}H_{19}NO_2$); HRMS calcd for $C_{28}H_{19}NO_2$ 401.1416, found 401.1420.

Eluted next was 7-nitro-**20**, as dark red crystals from cyclohexane: mp 228−230 °C; ^{1}H NMR (360 MHz) δ 10.51 (s, H-6), 9.85 (d, $J_{8,9}$ = 8.3 Hz, H-8), 9.83 and 8.94 (AB, J = 8.0 Hz, H-12 and H-11), 9.62 and 8.51 (AB, J = 9.3 Hz, H-5 and H-4), 9.47 and 8.38 (AB, J = 9.3 Hz, H-13 and H-14), 8.81 (d, $J_{10,9}$ = 7.7 Hz, H-10), 8.55 (t, H-9), 8.38 (d, $J_{3,2}$ = 9.3 Hz, H-3), 8.32 (d, $J_{1,2}$ = 7.9 Hz, H-1), 8.11 (t, H-2); COSY couplings were observed between H-1,3/2, H-4/5, H-8/9, H-10/9, H-11/12, H-13/14; NOESY interactions between H-3/4, H-5/6, H-12/13; UV (cyclohexane) λ_{max} (ϵ_{max}) nm 254 (6900), 315 (5200), 428sh (30 400), 440 (32 900), 470sh (12 300), 508 (7700), 571sh (3700), 774 (1100); CI MS m/z 402 (MH^+ for $C_{28}H_{19}NO_2$).

Bromination of 10. A solution of NBS (146 mg, 0.82 mmol) in dry DMF (25 mL) was added slowly to a stirred solution of **10**[6] (232 mg, 0.82 mmol) in dry DMF (25 mL) cooled by an ice bath. After the addition was complete, the solution was poured into ice−water, and ether (100 mL) was added. The ether layer was washed with water three times, dried, and evaporated. The residue was chromatographed on SiGel using PE as eluant to give 12-bromo-**10**, 291 mg (98%), as a green solid. A sample was recrystallized from heptane: mp 44−46 °C; ^{1}H NMR (250 MHz) δ 8.69−8.66 (m, H-10), 8.16 (s, H-11), 7.98−7.94 (m, H-7), 7.86 (s, H-6), 7.76 and 7.57 (AB, J = 9.0 Hz, H-4,5), 7.74−7.66 (m, H-1,8,9), 7.33 (d, J = 6.5 Hz, H-3), 7.24 (dd, J = 6.5, 8.8 Hz, H-2); ^{13}C NMR (62.9 MHz) δ 139.2, 137.0, 135.3, 134.6, 130.7, 128.6, 128.0, 127.3, 126.8, 126.4, 125.7, 124.1, 123.8, 122.3, 121.5, 114.4, 39.2, 35.9, 17.3, 17.2; CI MS m/z 361, 363 (MH^+). Anal. Calcd for $C_{22}H_{17}Br$: C, 73.14; H, 4.74. Found: C, 73.02; H, 4.92.

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