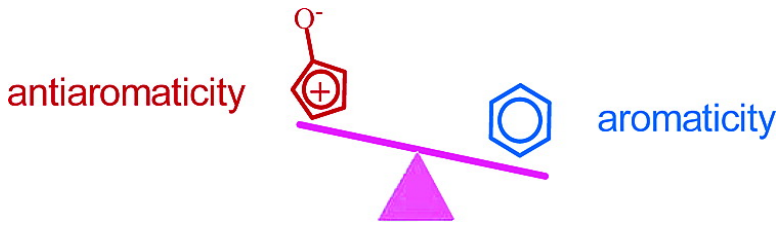
Article

# Measuring Antiaromaticity by an Analysis of Ring Current and Coupling Constant changes in a Cyclopentadienone-Fused Dihydropyrene

Reginald H. Mitchell, Rui Zhang, Wei Fan, and David J. Berg

*J. Am. Chem. Soc.*, **2005**, 127 (46), 16251-16254• DOI: 10.1021/ja055356v • Publication Date (Web): 01 November 2005






## More About This Article

J|A|C|S
ARTICLES
Published on Web 11/01/2005

# Measuring Antiaromaticity by an Analysis of Ring Current and Coupling Constant changes in a Cyclopentadienone-Fused Dihydropyrene

Reginald H. Mitchell,* Rui Zhang, Wei Fan, and David J. Berg

*Contribution from the Department of Chemistry, University of Victoria, Post Office Box 3065, Victoria, British Columbia, Canada V8W 3V6*

Received August 5, 2005; E-mail: regmitch@uvic.ca

***Abstract:*** The synthesis of the chloro- and parent cyclopentadienone-fused dihydropyrenes **10** and **7** are reported. Analysis of coupling constants, and chemical shift changes between these and the nonconjugated dihydro derivatives **11** and **8**, and between the benzannulene **4** and the parent annulene **12**, indicates without doubt that cyclopentadienone is behaving as an antiaromatic $4n$-$\pi$ system and that in its effect on the ring current of **12**, cyclopentanedienone has about 80% of the effect of benzene. This is the first time that a suitable probe has been used to estimate the relative ability of a $4n$-$\pi$ system to bond localize the probe in comparison to the $(4n + 2)$-$\pi$ system benzene.

## Introduction

Aromaticity continues to fascinate,[1] and considerable strides have been made to define the concept[2] and even attempt to measure it.[3,4] Thus far nobody has suggested an experimental method to estimate relative *antiaromaticities*, though Mills and co-workers[5] are attempting to relate both anti- and aromaticity to the highest occupied−lowest unoccupied molecular orbital (HOMO−LUMO) gap, Nucleus Independant Chemical Shift (NICS) values, and $^1$H NMR shifts[5a−c] and most recently to redox potentials.[5d−f] Given our successes in using ring current changes of our dihydropyrene probe to estimate *aromaticity* in a wide variety of systems,[3] which include charged species and organometallics, we thought we might be able to apply this method to antiaromatic species. In this paper, we use an analysis of ring current and coupling constant changes of dihydropyrene on annelation to estimate the relative antiaromaticity of cyclopentadienone.

Our method[3] of estimating relative aromaticity is effective because of several important points: (a) fusion of two aromatic systems along a common bond reduces the delocalization in each system proportional to the bond localization energy of each, which has a profound effect on $^3J_{H,H}$ coupling constants; (b) the geometry of the probe molecule is not affected much by the fusion, such that then the ring current flowing around the probe molecule is affected only by, and is proportional to, the new delocalization; (c) the $^1$H NMR probes used (the internal methyl protons or distant external protons) to estimate the ring current and hence the degree of delocalization in the probe ring are affected very little by other through space anisotropy effects; and (d) the measurement is made relative to that of a relevant system, benzene, and not to some arbitrary model. Thus the ring current flowing in the probe (dihydropyrene) ring of the fused system **1**, as estimated from the internal methyl proton

(1) See for example the special issue *Chem. Rev.* **2001**, *101* (5), 1115−1566. A search of current journals using ISI's Web of Science gave 102 articles from 2004 till July 2005 having aromaticity in the title, and both it and SciFinder Scholar found more than 500 in the text, of which 80 were in *J. Am. Chem. Soc.*!

(2) For example: (a) King, R. B. *Chem. Rev.* **2001**, *101*, 1119−1152. (b) Buhl, M.; Hirsch, A. *Chem. Rev.* **2001**, *101*, 1153−1183. (c) Santos, J. C.; Andres, J.; Aizman, A.; Fuentealba, P. *J. Chem. Theor. Comput.* **2005**, *1*, 84−87. (d) Van Droogenbroeck, J.; Van Alsenoy, C.; Blockhuys, F. *J. Phys. Chem. A* **2005**, *109*, 4847−4851. (e) Zhai, H. J.; Kuznetsov, A. E.; Boldyrev, A. I.; Wang, L. S. *ChemPhysChem* **2004**, *5*, 1885−1891. (f) Kovacevic, B.; Baric, D.; Maksic, Z. B.; Muller, T. *ChemPhysChem* **2004**, *5*, 1352−1364. (g) Rassat, A. *Phys. Chem. Chem. Phys.* **2004**, *6*, 232−237. (h) Randic, M. *Chem Rev.* **2003**, *103*, 3449−3605. (i) Tarko, L.; Filip, P. *Rev. Roum. Chim.* **2003**, *48*, 745−758. (j) Fowler, P. W.; Soncini, A. *Chem. Phys. Lett.* **2004**, *383*, 507−511. (k) Sakai, S. *J. Phys. Chem. A* **2003**, *107*, 9422−9427. (l) Corminboeuf, C.; Heine, T.; Weber, J. *Phys. Chem. Chem. Phys.* **2003**, *5*, 246−251. (m) Poater, J.; Fradera, X.; Duran, M.; Sola, M. *Chem. Eur. J.* **2003**, *9*, 400−406. (n) Sakai, S. *J. Phys. Chem. A* **2003**, *107*, 9422−9427.

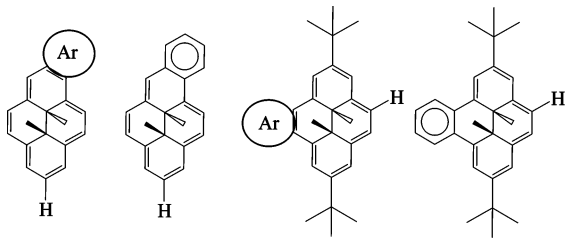
(3) (a) Mitchell, R. H. *Chem. Rev.* **2001**, *101*, 1301−1315. (b) Mitchell, R. H.; Ward, T. R. *Tetrahedron* **2001**, *57*, 3689−3695. (c) Mitchell, R. H.; Brkic, Z.; Berg, D. J.; Barclay, T. M. *J. Am. Chem. Soc.* **2002**, *124*, 11983−11988. (d) Williams, R. V.; Armantrout, J. R.; Twamley, B.; Mitchell, R. H.; Ward, T. R.; Bandyopadhyay, S. *J. Am. Chem. Soc.* **2002**, *124*, 13495−13505. (e) Kimball, D. B.; Haley, M. M.; Mitchell, R. H.; Ward, T. R.; Bandyopadhyay, S.; Williams, R. V.; Armantrout, J. R. *J. Org. Chem.* **2002**, *67*, 8798−8811.

(4) For example: (a) Gomes, J. A.; Mallion, R. B. *Chem. Rev.* **2001**, *101*, 1349−1383. (b) Katritzky, A. R.; Jug, K.; Oniciu, D. C. *Chem. Rev.* **2001**, *101*, 1421−1449. (c) Laskowski, M.; Steffen, W.; Smith, M. D.; Bunz, U. H. *Chem. Commun.* **2001**, 691−692. (d) De Proft, F.; Fowler, P. W.; Havenith, R. W. A.; Schleyer, P. V. R.; Van Lier, G.; Geerlings, P. *Chem. Eur. J.* **2004**, *10*, 940−950. (e) De Proft, F.; Geerlings, P. *Phys. Chem. Chem. Phys.* **2004**, *6*, 242−248. (f) Wannere, C. S.; Corminboeuf, C.; Allen, W. D.; Schaefer, H. F.; Schleyer, P. V. R. *Org. Lett.* **2005**, *7*, 1457−1460.

(5) (a) Mills, N. S.; Benish, M. A.; Ybarra, C. *J. Org. Chem.* **2002**, *67*, 2003−2012. (b) Levy, A.; Rakowitz, A.; Mills, N. S. *J. Org. Chem.* **2003**, *68*, 3990−3998. (c) Mills, N. S.; Levy, A.; Plummer, B. F. *J. Org. Chem.* **2004**, *69*, 6623−6633. (d) Tirla, C.; Mills, N. S.; Rakowitz, A.; Bria, A. L. M.; Hurd, C. M. M. Dications of tetrabenzo[5.5]fulvalenes. The relationship between oxidation potentials and antiaromaticity of 2,7 and 3,6-substituted tetrabenzo[5.5]fulvalenes. Abstracts of Papers, 229th ACS National Meeting, San Diego, CA, March 13−17, 2005; paper ORGN-889. (e) Cheng, F.; Baylan, J.; Mills, N. S. Synthesis of p-substituted 3-phenyltribenzo[5.7]fulvalenes and the evaluation of the antiaromaticity of their dications. Abstracts of Papers, 229th ACS National Meeting, San Diego, CA, March 13−17, 2005; paper CHED-540. (f) Hoang, T.; Mills, N. S.; Hooten, K. Syntheses of 3-substituted indenylidene fluorene: Study of antiaromaticity indenyl and fluorenyl systems. Abstracts of Papers, 229th ACS National Meeting, San Diego, CA, March 13−17, 2005; paper CHED-506.

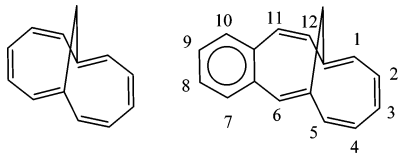
10.1021/ja055356v CCC: $30.25 

shifts or the distant protons shown, is compared to that flowing in **2**, the benzannelated system, which permits a direct experimental comparison of the relative bond localization energies of the aromatic in **1** to that of benzene in 2.[3]



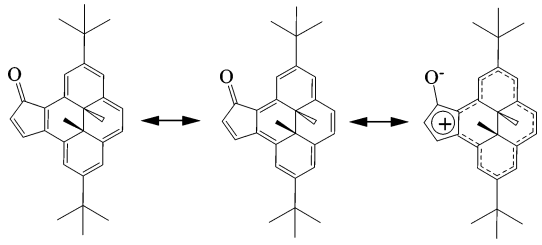

**1** **2** **3** **4**

It does not matter whether the [*a*]-fused dihydropyrenes **1**/**2** or the [*e*]-fused dihydropyrenes **3**/**4** are used, as good results are obtained with either series. Thus far, however, we have annelated only aromatic $(4n + 2)$-$\pi$ systems such as Ar = naphthalene, anthracene, cyclopentadienide anion, biphenylene, and organometallics such as a ruthenocene. In principle, our method should also work when Ar is a $4n$-$\pi$ species. Scott et al.[6] were the first to show unambiguously that fusion of a $4n$-$\pi$ system to a $(4n + 2)$-$\pi$ system also results in a reduction of ring current in each. Thus the bridge protons of **6** are 1.6 ppm less deshielded than those of **5** because of the reduction in the paratropic ring current of the $12\pi$ ring of **6** on benzannelation.




**5** **6**

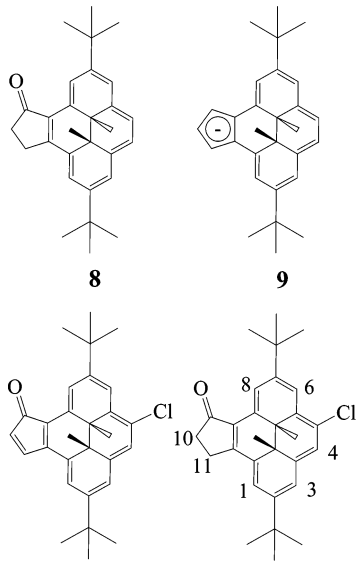
Likewise, the outside olefinic signals of the [12]-ring (H-1,2,3,4) of **6** ($\delta$ 5.6−6.2) are less shielded than those in **5** ($\delta$ 5.1−5.8). As well, the benzene ring diatropicity is reduced; its protons appear shielded at $\delta$ 6.78−7.14, with the two protons H-7,10 being most shielded. Scott estimated that benzannelation of **5**, reduced its paratropic ring current by about 40−50%. Estimating the magnitude of the change in ring current caused by the [12]$\pi$-ring on the benzene ring is more difficult. To quantify these results so that a comparison of the relative bond-localizing abilities of benzene and the $4n$-$\pi$ system (which we will loosely translate to aromaticity and antiaromaticity) may be made, then a common probe must be used. Dihydropyrene is in our view the best such probe, and so we synthesize here **7**, where Ar of **3** equals cyclopentadienone (which has the $4n$-$\pi$ resonance contributor shown in **7c**), and compare it to the analogous benzannelated system **4**.




**7a** **7b** **7c**

## Results

The cyclopentanone-fused dihydropyrene **8** was an intermediate in our synthesis[7] of the cyclopentadienide-fused dihydropyrene **9**, so in principle all that is required to synthesize **7** is to introduce the additional double bond into **8**. However, dihydropyrenes are very reactive to electrophiles and oxidizing reagents, and thus the reagents chosen need to be selective to avoid that ring, and so the mild conditions used by Sharpless et al.[8a] and Reich et al.,[8b] in which PhSeCl is used to introduce the −SePh moiety α to the carbonyl group, which then can subsequently be oxidatively eliminated to the enone, seemed attractive. Direct use[8a] of PhSeCl on **8**, however, did not yield useful product, though preformation of the enolate[8b] with lithium diisopropylamide, followed by PhSeCl in tetrahydrofuran (THF) and then by $H_2O_2$, did give the desired product **7**, but only in 28% yield. We thus tried an alternative procedure of Engman[9] in which $PhSeCl_3$ is used followed by mild base, avoiding the oxidation step above. Reaction of **8** with $PhSeCl_3$ in ether at 0 °C for 1 h, followed by treatment with aqueous $NaHCO_3$ at 20 °C for 4 h, yielded at least six products, however, 23% 5-chlorocyclopentadienone **10**, 26% 5-chlorocyclopentanone **11**, 5% cyclopentadienone **7**, and ∼4% starting **8** could be isolated by chromatography. On the surface, this might appear worse; however, in practice the stability of the chloro-substituted product **10** was much better than the original product **7**, and thus is much easier to fully characterize, and as well the desired model compound **11**, without the conjugated 5-ring, is obtained at the same time! The structure of the cyclopentanone **11** was




**8** **9**

**10** **11**

indicated by electron ionization mass spectrometry (EI MS) at *m*/*z* 432 and 434 in a 3:1 ratio, indicating the presence of chlorine, and high-resolution mass spectrometry (HRMS) at 432.2227 (calcd for $C_{29}H_{33}ClO$ = 432.2220). Only five dihydropyrene ring protons could now be seen, indicating that this

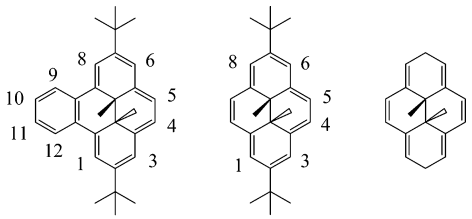
(6) Scott, L. T.; Kirms, M. A.; Günther, H.; Puttkamer, H. *J. Am. Chem. Soc.* **1983**, *105*, 1372−1373.
(7) Mitchell, R. H.; Fan, W.; Lau, D. Y.; Berg, D. J. *J. Org. Chem.* **2004**, *69*, 549−554.
(8) (a) Sharpless, K. B.; Lauer, R. F.; Teranishi, A. Y. *J. Am. Chem. Soc.* **1973**, *95*, 6137−6139. (b) Reich, H. J.; Reich, I. L.; Renga, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 5813−5815.
(9) Engman, L. *J. Org. Chem.* **1988**, *53*, 4031−4037.

***Table 1.*** NMR Data for Comparison of Ring Currents

| | 10 | 11 | 7 | 8 | 4 | 12 |
|---|---|---|---|---|---|---|
| $\delta$ internal C$H_3$ | −1.86 | −3.50 | −1.91 | −3.74 | −1.58 | −4.06 |
| | −1.83 | −3.50 | −1.87 | −3.71 | −1.58 | −4.06 |
| $\Delta\delta$ | 1.64 | | 1.83 | | 2.48 | |
| | 1.67 | | 1.84 | | | |
| $\delta$ internal *C*$H_3$ | 21.03 | 15.40 | | | 17.3 | 14.3 |
| | 20.40 | 14.77 | | | | |
| $\Delta\delta$ | 5.63 | | | | 3.0 | |
| | 5.63 | | | | | |
| $\delta$ (H-4/5) | | | 7.65 | 8.30 | 7.13 | 8.46 |
| $\Delta\delta$ | | | 0.65 | | 1.33 | |
| $J_{4,5}$ (Hz) | | | 8.7 | 7.26 | 6.9[a] | 7.3[a] |

[a] Determined from nonconjugated nonsymmetric derivatives.

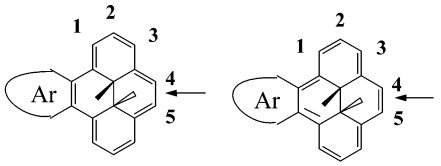
chlorine was on the dihydropyrene ring. Two-dimensional NMR proved that **11** was the 5-chloro isomer, and in fact it was the only isomer obtained. Fully assigned spectral data are given in the Experimental Section. The structure of **10** was again indicated by EI MS M and M + 2 signals in a 3:1 ratio at two mass units less than for **11**, with the HRMS at 430.2066 (calcd for $C_{29}H_{31}{}^{35}ClO$ = 430.2063). New alkene signals were found at $\delta$ 8.09 and 6.21, which were coupled with $J$ = 5.8 Hz, corresponding to protons H-11 and H-10, respectively. As well, the $^{13}C$ NMR showed loss of the two -$CH_2$- carbons of **8** but two new =CH carbons corresponding to C-10,11. As well, one =CH DHP carbon was replaced by a C−Cl carbon. The structure of the nonchlorinated **7** was indicated by a $^1H$ NMR spectrum almost identical to that of **10** and a correct HRMS; however, its lack of stability inhibited full spectral data collection.




**4** **12** **13**

**Relative Antiaromaticity.** The relevant data for comparison are collected in Table 1. For dihydropyrenes, we have found that $^1H$ data give more reliable analyses than $^{13}C$, which, however, should show the same general trends. Immediately evident from Table 1 is that the chlorine atom in both **10** and **11** (compare to **7** and **8**, respectively) have minimal effect on the internal methyl protons, consistent with our previous statements about substituents,[3,10] while introduction of the conjugating double bond into the five-membered ring has a huge effect. The magnitude of the ring currents flowing in the dihydropyrene rings can be taken as proportional to the chemical shift difference between the internal methyl protons for the annulene selected and a nonconjugated model, for example, **13**, where the internal methyl protons appear at $\delta$ +0.97[10a] (the *tert*-butyl groups are not expected to affect this shift significantly). However, because the cyclopentanone-fused annulenes **11** and **8** do not have *exactly* the same chemical shift as the parent **12**, then **10** must be compared to **11**, and **7** to **8**, rather than everything to **12**. The effects of the cyclopentadienones in **10** and **7** on the ring currents of the cyclopentanone-fused dihydropyrenes **11** and **8** can then be calculated, for example, for the internal methyl protons of **10** as $\Delta\delta$ (**10** − **11**)/$\Delta\delta$ (**13** − **11**) = 1.655/4.47 = 37%, and for **7** as $\Delta\delta$ (**7** − **8**)/$\Delta\delta$ (**13** − **8**) = 1.835/4.70 = 39%. Likewise in **4**, benzene reduces the ring current in **12** by $\Delta\delta$ (**4** − **12**)/$\Delta\delta$ (**13** − **12**) = 2.48/5.03 = 49%. Thus cyclopentadienone has about 80% (=38/49) of the ability (effect) of benzene on reducing the ring current of dihydropyrene and, on the basis of our previous studies,[3,10] thus approximately 80% of the bond delocalization energy ("resonance energy") of benzene. While carbon shifts and external proton shifts in charged species[11] do not give such reliable indicators, it can be seen from Table 1 that the trend is in the same direction: the carbons of both **10** and **4** are less shielded than those of **11** and **12**. As well, the external protons H-4/5 of both **7** and **5** are less deshielded than those of **8** and **12**.

**How Do We Know That the Cyclopentadienone Ring Is Displaying a Paratropic Ring Current?** Fortunately Günther and co-workers[12] have unambiguously shown that when two (4$n$ + 2)-$\pi$ systems are fused (**A**), the C2−C3 bond is shorter (the bond order is greater) than the C1−C2 bond (the total bond localization is as shown, with the ring junction being formally double, for resonance structure **7a**), while when a 4$n$-$\pi$ system is fused to a (4$n$ + 2)-$\pi$ system (**B**), the reverse is true (note the ring junction is formally single, resonance structure **7b**).




**(4n+2)π-fusion, A** **(4n)π-fusion, B**

This has the effect that the C4−C5 bonds (arrowed) are also different. In **A** (equivalent to the benz-fused system **4**) C4−C5 should be longer (lower bond order), and thus the coupling constant (Table 1) should be less than the parent **12**, which it is (6.9 versus 7.3 Hz), while in **B** (equivalent to the cyclopentadienone fused system **7**) C4−C5 should be shorter (the bond order greater), and thus the coupling constant should be larger than in parent **8** or **12**), which it is (8.7 vs 7.26 Hz). In our view, this leaves little doubt that the cyclopentadienone ring in **7** (and **10**) is behaving as an antiaromatic system. Günther and co-workers[12] have shown that their alterance parameter, $Q$, which equals the ratio of the bond orders of the benzene 9−10 and the 10−11 bonds, is <1.04 for antiaromatic systems, between 1.02 and 1.10 for nonaromatic systems, and >1.10 for aromatic systems. Unfortunately in **4** and **7** there is only one $^3J$ coupling in the probe (14$\pi$) ring, and so $Q$ cannot be determined. However, in benzocycloheptatrienyl anion, a benzo-8$\pi$ system, $Q$ = 0.889 = antiaromatic according to his classification. In this case, the $^3J$ values involved were 7.84 and 7.10 Hz. The coupling constants in our cases, 8.7 and 6.9 Hz, are clearly different enough that little doubt remains that the aromaticity

(10) (a) Mitchell, R. H.; Williams, R. V.; Mahadevan, R.; Lai, Y. H.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2571−2578. (b) 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. (c) Mitchell, R. H.; Chen, Y.; Khalifa, N.; Zhou, P. *J. Am. Chem. Soc*. **1998**, *120*, 1785−1794.

(11) Mitchell, R. H.; Khalifa, N. A.; Dingle, T. W. *J. Am. Chem. Soc*. **1991**, *113*, 6696−6697.

(12) (a) Cremer, D.; Günther, H. *Liebigs. Ann. Chem*. **1972**, *763*, 87−108. (b) Günther, H.; Shyoukh, A.; Cremer, D.; Frisch, K. H. *Liebigs. Ann. Chem.* **1978**, 150−164.

of the two $\pi$-systems of the cyclopentadienone and benzene annelating rings is quite different! If we could obtain bond length data for **10**, we might be able to comment further. Thus far we have not been able to obtain X-ray quality crystals, but we will continue to try. A referee pointed out that resonance structure **7c** could also be viewed as a [17]annulenone, which would have the same coupling constant consequences and IR data as we describe. That is true, but *if* the periphery conjugation was indeed the principal pathway, that is, really a [17]annulenone, then the total system is a $4n$-$\pi$ aromatic, and as such the internal methyl protons should be deshielded from those in the acyclic model **13**, that is, they should be at $\delta > 1$. We have shown this to be the case for other dihydropyrenes that are in total $4n$-$\pi$ species.[13] We therefore believe that **7** is best represented by **7c**, a fused cyclopentadienone−dihydropyrene system.

## Conclusions

The cyclopentadienone ring in **7** displays antiaromatic character resulting in bond localization in the annulene ring consistent with a $4n$-$\pi$ fused system. The ring current of the dihydropyrene fragment is reduced by fusion of the antiaromatic by about 80% of that caused by benzene.

## Experimental Section

For general information see ref 7.

**2,7-Di-*t*-butyl-5-Chloro-*trans*-11c,11d-dimethyl-11c,11d-dihydro-9-oxo-9*H*-cyclopenta[*e*]pyrene (10) and 10,11-Dihydroderivative 11.** A solution of cyclopentanone[7] 8 (100 mg, 0.25 mmol) in dry ether (5 mL) was added dropwise under argon to a stirred suspension of $PhSeCl_3$ (65.6 mg, 0.25 mmol) in dry ether (5 mL) at 0 °C. After the reaction mixture was stirred for 1 h at 0 °C, the solvent was removed under vacuum and replaced with dichloromethane (7 mL), followed by water (5 mL) containing $NaHCO_3$ (84 mg, 1 mmol). Stirring was continued for 4 h, and then hexane (15 mL) was added. The dark green organic layer was separated, washed, dried ($Na_2SO_4$), and evaporated. The residue was chromatographed on silica gel with hexane/ethyl acetate (10:1) as eluant. Eluted first and second were small amounts (a few milligrams) of products, which may ($^1$H NMR) be 10-chloro derivatives of 7 and 8. Eluted third was about 5 mg (5%) of product 7 (see below for characterization). Eluted fourth was 26 mg (23%) of product 10 as dark green crystals, mp ∼210 °C (decomp): $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.97 (d, $J$ = 1.2 Hz, 1H, H-8), 8.12 (d, $J$ = 1.2 Hz, 1H, H-6), 8.09 (d, $J$ = 5.8 Hz, 1H, H-11), 7.81 (s, 1H, H-4), 7.75 (d, $J$ = 1.2 Hz, 1H, H-1), 7.66 (br s, 1H, H-3), 6.21 (d, $J$ = 5.8 Hz, 1H, H-10), 1.53 [s, 9H, 7-C($CH_3$)$_3$], 1.48 [s, 9H, 2-C($CH_3$)$_3$], −1.83 (s, 3H, 11c-$CH_3$), −1.86 (s, 3H, 11d-$CH_3$); $^{13}$C NMR (125.7 MHz, $CDCl_3$) $\delta$ 197.13 (C-9), 154.53 (C-7), 149.36 (C-2), 145.00 (C-11), 142.11 (C-11e), 138.76 (C-11b/e), 137.33 (C-3f), 132.77 (C-11e/b), 132.37 (C-10), 132.09 (C-11a), 128.95 (C-5), 127.07 (C-4), 123.88 (C-3), 121.77 (C-11f), 121.40 (C-6), 117.15 (C-8), 115.47 (C-1), 38.33 (C-11d), 36.69 [2-*C*($CH_3$)$_3$], 36.35 (C-11c), 35.98 [7-*C*($CH_3$)$_3$], 31.00 & 30.92 [2,7-C(*C*$H_3$)$_3$], 21.03 (11d-$CH_3$), 20.40 (11c-$CH_3$); IR (KBr) $\nu$ 1667, 1607, 1556, 1260, 1173, 1134, 1070, 954, 892, 860, 820, 734, 668 cm$^{-1}$; UV−vis (cyclohexane) $\lambda_{max}$ ($\epsilon_{max}$) nm 235 (19 000), 316 (38 000), 399 (32 000), 475sh (11 000), 569 (1000), 625 (1300), 690 (1700); EI MS $m/z$ 430 ($M^+$) and 432 (M + 2) 3:1 (Cl); HRMS calcd for $C_{29}H_{31}{}^{35}$ClO 430.2063, found 430.2066. Eluted fifth was ∼4 mg (4%) of unchanged starting material 8. Eluted sixth was 29 mg (26%) of dark brownish-green crystals of the chlorocyclopentanone 11, mp 214−216 °C: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 9.81 (d, $J$ = 1.0 Hz, 1H, H-8), 8.69 (d, $J$ = 1.3 Hz, 1H, H-6), 8.67 (d, $J$ = 1.3 Hz, 1H, H-1), 8.40 (s, 1H, H-3), 8.29 (s, 1H, H-4), 3.92 & 3.83 (∼dt, $J_{11,11'}$ = 17.4 Hz, $J_{11,10}$ = 5.7 Hz, 2H total, H-11), 3.09 (∼t, $J$ = 5.7 Hz, 6.5 Hz, 2H, H-10), 1.68 [s, 9H, 7-C($CH_3$)$_3$], 1.65 [s, 9H, 2-C($CH_3$)$_3$], −3.50 (s, 6H, 11c,d-$CH_3$); $^{13}$C NMR (125.7 MHz, $CDCl_3$) $\delta$ 208.92 (C-9), 151.60 (C-7), 150.52 (C-11a), 146.39 (C-2), 136.82 and 132.91 (C-3a/11e), 132.72 (C-5a), 131.81 (C-11b), 126.91 (C-11f), 125.55 (C-4), 124.63 (C-5), 123.59 (C-3), 121.57 (C-1), 119.98 (C-8), 117.90 (C-6), 37.63 (C-10), 37.00 [7-*C*($CH_3$)$_3$], 36.25 [2-*C*($CH_3$)$_3$], 33.66 (C-11d), 31.98 [2-C(*C*$H_3$)$_3$], 31.91 [7-C(*C*$H_3$)$_3$], 31.20 (C-11c), 24.79 (C-11), 15.57 and 15.35 (11c,d-$CH_3$); IR (KBr) $\nu$ 1694, 1464, 1362, 1303, 1253, 1132, 1088, 957, 947, 891, 668 cm$^{-1}$; UV−vis (cyclohexane) $\lambda_{max}$ ($\epsilon_{max}$) nm 238 (12 000), 288 (6100), 345 (32 000), 363 (33 000), 378 (27 000), 402 (39 000), 509 (6100), 606 (1000), 678 (3600); EI MS $m/z$ 432 ($M^+$) and 434 (M + 2) 3:1 (Cl); HRMS calcd for $C_{29}H_{33}{}^{35}$ClO 432.2220, found 432.2227.

**2,7-Di-*t*-butyl-*trans*-11c,11d-dimethyl-11c,11d-dihydro-9-oxo-9H-cyclopenta[e]pyrene (7).** A solution of *i*-$Pr_2$NLi (0.13 mmol in 0.26 mL of hexane) was added at −78 °C to a stirred solution of ketone **8** (50 mg, 0.125 mmol, vacuum-dried) in dry THF (20 mL) under argon. The red solution was stirred for 5 min and then PhSeCl (24.9 mg, 0.13 mmol) in dry THF (5 mL) was added dropwise. The cooling bath was removed and the solution was stirred for 30 min. Water (1 mL) was then added, followed by 30% $H_2O_2$ (1 mL, 11.6 mmol), and then stirring was continued for 1 h. The mixture was then extracted with hexane (15 mL), and the organic phase was washed, dried ($Na_2SO_4$), and evaporated. The dark green residue was chromatographed on silica gel with hexane/ether (4:1) as eluant. Eluted first was 14 mg (28%) of the product **7** as a green solid, mp ∼210 °C (decomp, green to reddish-brown): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.91 (s, 1H, H-8), 8.08 (d, $J$ = 5.6 Hz, 1H, H-11), 7.74 (s, 1H, H-1), 7.69 & 7.68 (s, 1H each, H-3/6), 7.67 and 7.63 (AB, $J$ = 8.7 Hz, 1H each, H-4/5), 6.19 (d, $J$ = 5.6 Hz, 1H, H-10), 1.51 and 1.49 [s, 9H each, −C($CH_3$)$_3$], −1.87 and −1.91 (s, 3H each, −11c,d-$CH_3$); IR (KBr) $\nu$ 1661, 1556, 1463, 1263, 1193, 1193, 886, 820, 737 cm$^{-1}$; EI MS $m/z$ 396 ($M^+$); HRMS calcd for $C_{29}H_{32}O$ 396.2453, found 396.2452. This compound decomposes on standing. Eluted next was 22 mg (44%) of unchanged **8**.

**Acknowledgment.** We thank Science and Engineering Research Canada (formerly NSERC) and the University of Victoria for financial support.

JA055356V

(13) (a) Mitchell, R. H.; Boekelheide, V. *J. Chem. Soc., Chem. Commun.* **1970**, 1557−1558. (b) Mitchell, R. H.; Klopfenstein, C. E.; Boekelheide, V. *J. Am. Chem. Soc.* **1969**, *91*, 4931−4932. (c) Mitchell, R. H.; Zhou, P. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1013−1015.