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Measuring Aromaticity with the Dimethyldihydropyrene Ring Current Probe. Experimental and Computational Studies of the Fulvenes and the Strongly Antiaromatic Cyclopentadienone Reveal Large Mills−Nixon-Type Bond Localization Effects. Synthesis of Fulvene-Fused Dihydropyrenes

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Abstract: The synthesis of the methylfulvene- and phenylfulvene-annelated dihydropyrenes **10** and **22** from the cyclopentadiene-fused dihydropyrene **7** in 68% and 80% yields, respectively, are reported. However, the attempted formation of the parent fulvene-fused dihydropyrene **18** failed, both from the cyclopentadiene **7** with formaldehyde and from the cyclopentadienone **5** in Wittig-type reactions. Chemical shift data for the methylfulvene (**35**) and phenylfulvene (**36**)-fused dihydropyrenes **10** and **22** were used to estimate the reduction in the dihydropyrene nucleus aromaticity (DHPN) (relative to benzene fusion) in **10** and **22** (12−16% and 22−25% respectively). Calculations revealed that this reduction in diatropicity, contrary to the situation with benzene fusion, is not due to any aromaticity of the annelating fulvenes but instead is caused by Mills−Nixon-type effects. We conclude that methyl- and phenylfulvene are nonaromatic. An improved synthetic route to the cyclopentadienone **5** was found in an unprecedented cyclization of the *trans*-cinnamic acid analogue **29** in 80% yield. This enabled an X-ray structure of **5** to be obtained, for comparison to that of the saturated ketone **4**. Even though crystals of **5** and **4** show diastereomeric disorder, when the average bond length data of cyclopentadienone **5** is compared with those of cyclopentenone **4** and the parent and benzo dihydropyrenes **6** and **33**, it is clearly evident that **5** has the opposite bond-alternation pattern, consistent with a [4*n*] fused annulene. From the bond length data, cyclopentadienone has ∼87% of the effect of a benzene ring on bond alternation, which is in reasonable agreement with the previously found NMR value (78%). Structure and nucleus-independent chemical shift calculations support these results.

Introduction

We have spent several decades developing the dimethyldihydropyrene probe as an experimental method of measuring aromaticity relative to that of benzene for a variety of π systems,[1] including charged systems such as cyclopentadienide,[2] organometallics,[3] and most recently, antiaromatic species such as cyclopentadienone (**1**).[4] Our method[1−4] of estimating relative aromaticity depends upon the fact that when two aromatic systems are fused along a common bond, the delocalization in each system is proportional to the bond localization energy in that system. To be successful, the method requires (i) that the geometry of the probe molecule (the dihydropyrene) not be affected much by the fusion, so that the ring current flowing around the probe molecule is affected only by (and is proportional to) the new delocalization, and (ii) that the chemical shifts of the ^{1}H probes (usually the internal methyl protons), which are used to estimate the ring current and hence the amount of delocalization in the probe ring, are affected very little by through-space anisotropy effects. We have found this to be generally true, and the only failure to date[5] has been the dehydro[14]annulene-fused dihydropyrene **2** ($\delta_{Me} = -3.91$), where the change in chemical shift (0.14 ppm) from the model compound **3** ($\delta_{Me} = -3.77$) was too small to be differentiated from the through-space anisotropy effects. Nucleus-independent chemical shift (NICS) calculations, however, indicated that the dehydro[14]annulene ring of **2** did show some aromaticity, but

† University of Victoria.
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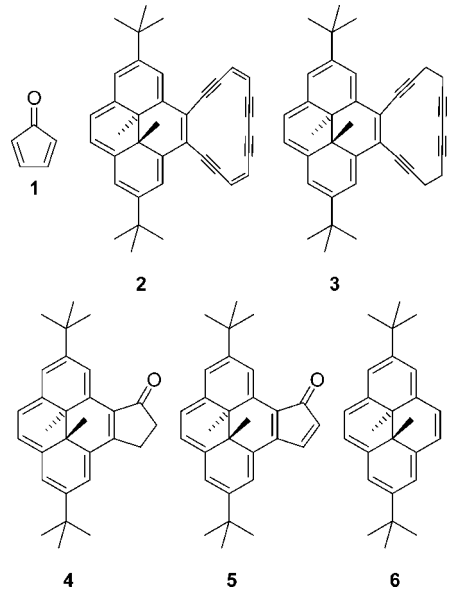
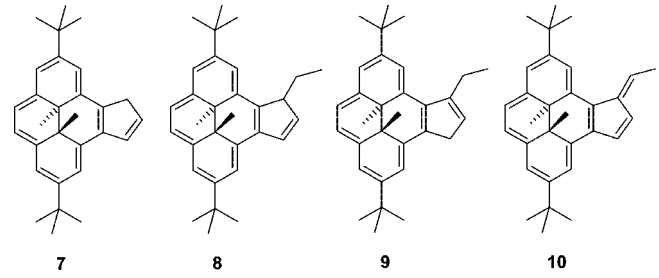
(1) (a) Mitchell, R. H. *Chem. Rev.* **2001**, *101*, 1301–1315. (b) Mitchell, R. H.; Ward, T. R. *Tetrahedron* **2001**, *57*, 3689–3695. (c) Williams, R. V.; Armantrout, J. R.; Twamley, B.; Mitchell, R. H.; Ward, T. R.; Bandyopadhyay, S. *J. Am. Chem. Soc.* **2002**, *124*, 13495–13505. (d) Mitchell, R. H.; Iyer, V. S.; Khalifa, N.; Mahadevan, R.; Venugopalan, S.; Weerawarna, S. A.; Zhou, P. *J. Am. Chem. Soc.* **1995**, *117*, 1514–1532.
(2) (a) Mitchell, R. H.; Khalifa, N. A.; Dingle, T. W. *J. Am. Chem. Soc.* **1991**, *113*, 6696–6697. (b) Mitchell, R. H.; Fan, W.; Lau, D. Y. K.; Berg, D. *J. Org. Chem.* **2004**, *69*, 549–554.
(3) (a) Mitchell, R. H.; Chen, Y.; Khalifa, N.; Zhou, P. *J. Am. Chem. Soc.* **1998**, *120*, 1785–1794. (b) Mitchell, R. H.; Brkic, Z.; Berg, D. J.; Barclay, T. M. *J. Am. Chem. Soc.* **2002**, *124*, 11983–11988.
(4) Mitchell, R. H.; Zhang, R.; Fan, W.; Berg, D. J. *J. Am. Chem. Soc.* **2005**, *127*, 16251–16254.
(5) 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.

evidently, ring-current effects in these compounds are masked by anisotropy effects. Perhaps this occurs because acetylenes have their shielding cones along the axis of the triple bond, unlike alkenes and aromatics (the previously studied examples), where the cone is perpendicular to the plane of the π system.[6] Thus, in the case of alkynes, the shielding along the axis of the alkyne could extend to the internal methyl groups and counteract any deshielding caused by bond fixation due to annulene fusion, resulting in an overall very small change. Obviously, when the fused system has a "large" aromaticity, the change in ring current is large; in this case, the chemical shift change for the internal methyl protons is also large, and other effects are not so important. To satisfactorily estimate the relative aromaticity of an annelating moiety, it is important to choose an appropriate "nonaromatic" model that accounts for effects other than aromaticity (e.g., anisotropy and Mills−Nixon effects) that may influence the chemical shifts. For example, in estimating the antiaromaticity of cyclopentadienone **1**, we[4] used **4** as the model for **5** rather than the parent **6**, to minimize any anisotropy effects of the carbonyl group. Reexamination of our NMR data for the

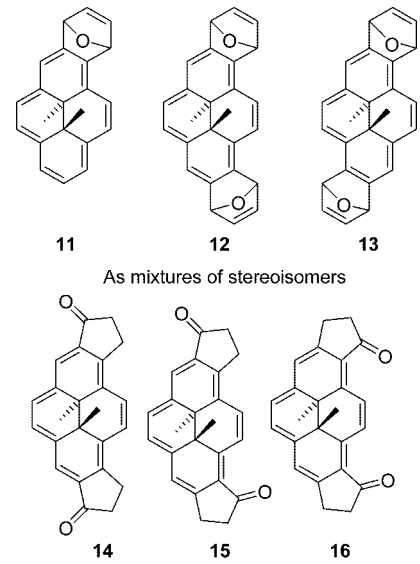


cyclopentadiene-fused dihydropyrene **7**[2b] indicated that even **4** does not fully account for all of the perturbations other than the antiaromaticity of the fusing cyclopentadienone, and our calculations support using **7** as the nonaromatic model rather than **4** (see below). In the current study, which was designed to measure any potential aromaticity or Mills−Nixon effects exhibited by fulvenes, it seemed appropriate to use compounds **8** and **9** as models for **10**, since they lack the full conjugation of **10** yet contain more or less the same substituents. They certainly should be better than the parent **6**. Nevertheless, given the potentially small value expected for fulvene aromaticity, care is needed in order to establish whether any resultant effect is due to aromaticity or other factors.

We have also used the dimethyldihydropyrene probe to gain experimental evidence for the Mills−Nixon effect (bond localization induced in an aromatic system upon small-ring annelation). Fusion of one or two cyclobutane[7] or cyclopentane[8] rings onto dimethyldihydropyrene gives no indication of a



Mills−Nixon effect; there is no bond localization in the dimethyldihydropyrene ring. Consistent with the generally accepted bond localization induced by bicyclic annelation,[9] the dimethyldihydropyrene probe indicates significant localization of the [14]annulene periphery in **11** and **12** but not, as expected, in **13**, where the effects cancel each other.[8] Surprisingly, a similar localization is observed in the cyclopentanone-annelated derivatives **14**−**16**.[10]



In recognition of the failure of the dimethyldihydropyrene probe to discern the weak aromaticity of the dehydro[14]annulene in **2** and its potential to identify Mills−Nixon-type localization not only in bicyclic systems but also in cyclopentanone-fused dihydropyrenes, it was of particular interest to investigate fulvene-annelated dimethyldihydropyrenes. Fulvenes continue to fascinate chemists,[11] despite the century that has passed since the first synthesis of their derivatives by Thiele[12] and the six decades since their first molecular-orbital descriptions.[13] In part this is because fulvene (**17**) can be written with the resonance structures **17a**−**c**, in which the cyclopentadienide character may impart some aromaticity. However, it is the extent of the

(6) For example, see: Abraham, R. J.; Fisher, J.; Loftus, P. In *Introduction to NMR Spectroscopy*; John Wiley & Sons: New York, 1988; p 23.

(7) Mitchell, R. H.; Slowey, P. D.; Kamada, T.; Williams, R. V.; Garratt, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 2431–2432.

(8) Mitchell, R. H.; Chen, Y.; Iyer, V. S.; Lau, D. Y. K.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 2907–2911.

(9) See ref 8 and references therein.

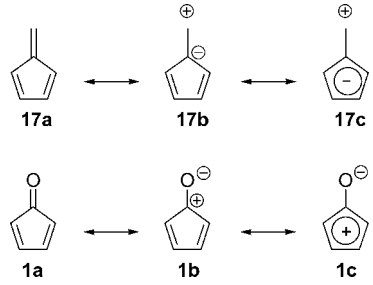
(10) Mitchell, R. H.; Lau, D. Y. K. *Tetrahedron Lett.* **1995**, *36*, 9281–9284.

(11) Using SciFinder Scholar, we found almost 3000 papers on fulvene(s), with 482 of them published between 2000 and November 2007.

(12) Thiele, J.; Buhner, A. *Justus Liebigs Ann. Chem.* **1906**, *347*, 249–274.

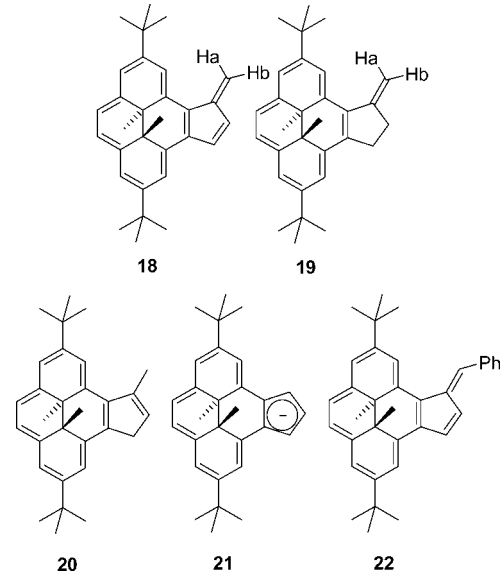
(13) (a) Coulson, C. A.; Craig, D. P.; Maccoll, A. *Proc. Phys. Soc. (London)* **1948**, *61*, 22–25. (b) Pullman, A.; Pullman, B.; Rumpf, P. *Bull. Soc. Chim. Fr.* **1948**, 280–284.

aromaticity present in fulvene that has created much discussion.[14] Some attempts to measure this have been made,[15] but aromaticity does not come neatly packaged with an "aromaticity meter"! In a similar manner, cyclopentadienone **1** could be expected to display "antiaromatic" properties.[16] In the current study, we have synthesized fulvene-fused dihydropyrenes and used NMR comparisons to estimate the effect of the fulvenes on the dihydropyrene nucleus aromaticity (DHPN). Also, through the calculation of optimized structures and NICS values, we have determined the causative factors in the reduction of DHPN.



Results

1. Syntheses. Of the methods listed in Bergmann's review[17] of fulvene syntheses, we first tried the Wittig reaction of our recently made[4] cyclopentadienone **5** with $Ph_3P{=}CH_2$. However, this approach failed to yield any **18**, despite the fact that in the model system, reaction of that ylide with the cyclopentenyl ketone **4**[2b] gave the fulvane **19** in 70% yield! In **19**, the two new exomethylene protons appeared at δ 6.46 and 5.69, with H_a more deshielded by its proximity to the dihydropyrene ring current. However, fulvane **19** was not very stable and both decomposed and rearranged to cyclopentadiene **20**, which was always present to a small extent in samples of **19**. Both the Tebbe olefination reaction[18] (using $Cp_2TiCH_2AlClMe_2$/THF) and the Peterson olefination reaction[19] [using $(CH_3)_3SiCH_2Li$/THF] also failed when tried on ketone **5**. These failures suggested that the reverse approach first used by Thiele,[12] in which the anion **21** derived from cyclopentadiene **7** is reacted with an aldehyde, might be more fruitful. In fact, Ottosson's procedure,[20] in which the pure anion **21** is isolated and reacted with aldehyde in the absence of base, and Shimizu's procedure,[21] in which **7** in aqueous THF is reacted with aldehyde in the presence of base and a phase-transfer reagent, both worked. With acetaldehyde, methylfulvene **10** was obtained in 68 and 30% yield, respectively, while with benzaldehyde, phenylfulvene **22** was obtained in 80 and 74% yield, respectively. Both of the fulvenes **10** and **22** form brown crystals, which have melting points of 124−125 and 132−133 °C, respectively. However, the methylfulvene is considerably less stable than the phenylfulvene, especially in chlorinated solvents (decomposing into an unknown insoluble material). Even in column chromatography using hexane under nitrogen, extensive decomposition of **10** occurred. Nevertheless, the structures of **10** and **22** followed from their proton and carbon NMR spectra and high-resolution mass spectrometry (HRMS) data (full assignments are given in the Experimental Section). In methylfulvene **10**, the exomethylene proton appeared at δ 7.40 and was split by the adjacent methyl group in to a quartet, while the corresponding methyl signal was at δ 2.14 and split into a doublet; in phenylfulvene **22**, the exomethylene proton was a singlet at δ 8.07. The dihydropyrene shifts are discussed below.



With these successes, we reattempted the synthesis of fulvene **18**. Reaction[21] of **7** with formaldehyde and NaOH in aqueous THF in the presence of cetyltrimethylammonium bromide gave alcohol **23** in 37% yield, for which the O−H stretch was at 3440 cm^{-1} in the IR spectrum and the $-OCH_2-$ protons at δ 4.6 in the ^1H NMR spectrum. Evidently, the alcohol is slow to eliminate water under these conditions and/or the product **18** decomposes rapidly. Alcohol **23** was reacted with TsCl in pyridine/dichloromethane to generate **24**, which was then treated with base but failed to yield any **18**, giving only products of decomposition.

Interestingly, the condensation reactions of **21** with acetone and benzophenone failed to yield any dimethylfulvene and diphenylfulvene, respectively. Severe steric interaction between the dihydropyrene ring and any group in the H_a position of **18**

(14) For example, see: (a) Möllerstedt, H.; Piqueras, M. C.; Crespo, R.; Ottosson, H. *J. Am. Chem. Soc.* **2004**, *126*, 13938–13939. (b) Najafian, K.; Schleyer, P. v. R.; Tidwell, T. T. *Org. Biomol. Chem.* **2003**, *1*, 3410–3417. (c) Stepien, B. T.; Krygowski, T. M.; Cyranski, M. K. *J. Org. Chem.* **2002**, *67*, 5987–5992. (d) Stepien, B. T.; Cyranski, M. K.; Krygowski, T. M. *Chem. Phys. Lett.* **2001**, *350*, 537–542. (e) Krygowski, T. M.; Cyranski, M. *Tetrahedron* **1996**, *52*, 1713–1722. (f) McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1992**, *114*, 5362–5368, and references therein. (g) Stahl, F.; Moran, D.; Schleyer, P. v. R.; Prall, M.; Schreiner, P. R. *J. Org. Chem.* **2002**, *67*, 1453–1461.

(15) (a) Baron, P. A.; Brown, R. D.; Burden, F. R.; Domaille, P. J.; Kent, J. E. *J. Mol. Spectrosc.* **1972**, *43*, 401–410. (b) Repogle, E. S.; Trucks, G. W.; Stanley, S. W. *J. Phys. Chem.* **1991**, *95*, 6908–6912. (c) Havenith, R. W. A.; Fowler, P. W.; Steiner, E. *J. Chem. Soc., Perkin Trans. 2* **2002**, 502–507. (d) Hosmane, R. S.; Liebman, J. F. *Tetrahedron Lett.* **1992**, *33*, 2303–2306. (e) Heffernan, M. L.; Jones, A. J. *Aust. J. Chem.* **1966**, *19*, 1813–1820.

(16) For example, see: Garbish, E. W.; Sprecher, R. F. *J. Am. Chem. Soc.* **1969**, *91*, 6785–6800.

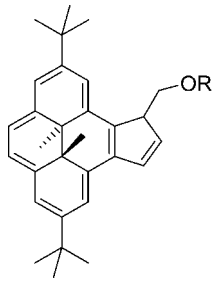
(17) Bergmann, E. D. *Chem. Rev.* **1968**, *68*, 41–84.

(18) (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611–3613. (b) Pine, S. H.; Shen, G. S.; Hoang, H. *Synthesis* **1991**, 165–167.

(19) (a) Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780–784. (b) Ager, D. J. *Synthesis* **1984**, 384–398. (c) Ager, D. J. *Org. React. (NY)* **1990**, *38*, 1–223.

(20) Chajara, K.; Ottosson, H. *Tetrahedron Lett.* **2004**, *45*, 6741–6744.

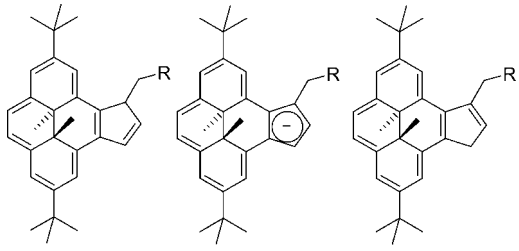
(21) (a) Shimizu, S.; Shirakawa, S.; Suzuki, T.; Sasaki, Y. *Tetrahedron* **2001**, *57*, 6169–6173. Also see: (b) Alper, H.; Laycock, D. E. *Synthesis* **1980**, 799–800.



23 R=H
24 R=Ts

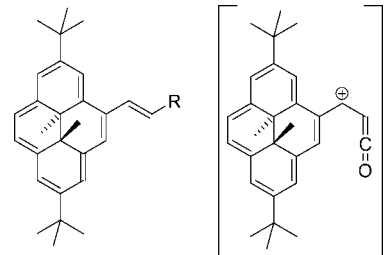
would be expected, and that is presumably the reason why only one isomer each is found for **10** and **22**.

Since the aromaticities of **10** and **22** were expected to be small, anisotropy and other effects of the substituent groups needed to be accounted for. The cyclopentenes **8** and **25** were thus prepared as chemical shift models. Reaction of the anion **21** with ethyl bromide and benzyl bromide yielded **8** and **25**, respectively, each as two diastereomers. Interestingly, formation of the anions **26** and **27** with base followed by quenching with water yielded single isomers each of **9** and **28**. No attempt was made to optimize these reactions, since only chemical shift data was needed.



8 R=Me
25 R=Ph
26 R=Me
27 R=Ph
9 R=Me
28 R=Ph

In order to carry out the reactions described above on the cyclopentadienone **5**, larger quantities of **5** than were easily generated by our original synthesis[4] were required. Student R.Z. decided to try the Friedel−Crafts cyclization of the *trans*-acid **29**, despite R.H.M.'s observation that ring closure of a *trans*-cinnamic acid under such conditions is totally without precedent in the literature,[22] especially given the large literature on the synthesis of indenones.[23] Acid **29** is, however, easily generated from ester **30**, an intermediate in our original synthesis of **5**,[2b] and in the event, conversion to the acid chloride **31** using excess oxalyl chloride and then direct cyclization with $BF_3 \cdot OEt_2$ yielded cyclopentadienone **5** in 80% yield!!

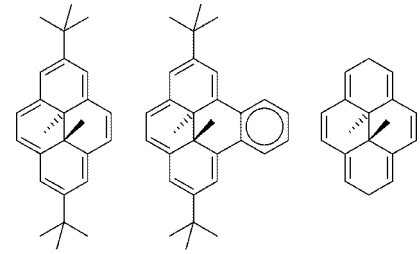


29 R=COOH
30 R=COOEt
31 R=COCl
32

While we have no proof, we speculate that if the ketene cation **32** is formed on reaction of acid chloride **31** with the Lewis acid BF_3, the *trans* bond in **31** would then be removed, allowing rotation and hence cyclization to give cyclopentadienone **5**. Formation of **32** would certainly be helped by the electron-rich dihydropyrene, which could stabilize the positive charge around the large ring. The larger quantities of **5** now available enabled us to obtain crystals suitable for an X-ray structure determination (see below).

2. Bond Localization from the ^{1}H NMR Data. The relevant proton data for the fulvenes of this study are presented in Table 1. Benzene was used as the solvent, rather than chloroform (as in most of our studies), because of better stability of the compounds.

The ring current[1c] in parent **6** is proportional to $\Delta\delta_{Me}$(**34** − **6**) = [0.97 − (−3.67)] = 4.64. The change in ring current in **10** is proportional to $\Delta\delta_{Me}$(**10** − **8**)/4.64 = 8.4% or $\Delta\delta_{Me}$(**10** − **9**)/4.64 = 6.7%. The change in ring current in **33** is proportional to $\Delta\delta_{Me}$(**33** − **6**)/4.64 = 53%. The effect of the fulvene relative to benzene is thus 6.7/53 to 8.4/53 = 13−16%.



6 **33** **34**

Thus, on the basis of our NMR results, methylfulvene reduces the DHPN of **6** *by about 13−16% relative to the corresponding effect of benzene.* Similarly, on the basis of data for **22** and **25** (or **28**), the relative effect of phenylfulvene is 22−25% of that of benzene. Examination of the effect of solvent change was possible for compounds **22** ($CDCl_3$, δ_{Me} −3.29 and −3.32) and **25** ($CDCl_3$, δ_{Me} −3.89, −3.94, and −3.95), since these were stable enough in $CDCl_3$ to obtain shifts. The data (in $CDCl_3$) for **6** (δ_{Me} −4.06) and **33** (δ_{Me} −1.58) yielded 25% as the DHPN reduction of phenylfulvene relative to that of benzene, which is identical with the C_6D_6 result. Also, the distant external protons (H-4,5 or H-3,6) can be used to assess bond localization, and for **22/25**, $\Delta\delta_H$ = 0.23 ppm for either set of protons, leading to a relative reduction of DHPN for phenylfulvene of 17−19%. For **10/8**, $\Delta\delta_H$ = 0.16 ppm for either set of protons, leading to a relative reduction of DHPN for methylfulvene of 12−13%. Generally, through-space anisotropy effects across the ring are very small for the distant protons (note that $\Delta\delta_{H\text{-}4,5}$ and $\Delta\delta_{H\text{-}3,6}$ are the same), so even though the shifts are small, the results are usually reliable unless some large "through-bond" effect is

(22) Conversion of *trans*-cinnamic acids to indenones appears to be unknown, while conversion of *cis*-cinnamic acid derivatives and some tri- and tetrasubstituted acids is known. For example, see: (a) Kohler, E. P.; Heritage, G. L.; Burnley, M. C. *Am. Chem. J.* **1910**, *44*, 60–76. (b) Floyd, M. B.; Allen, G. R. *J. Org. Chem.* **1970**, *35*, 2647–2653. (c) Galatsis, P.; Manwell, J. J.; Blackwell, J. M. *Can. J. Chem.* **1994**, *72*, 1656–1659. (d) Jabbar, S.; Banerjee, S. *Asian J. Chem.* **2002**, *14*, 1651–1654 (CAN 138:38911). (e) Mahmoud, M. R. *Indian J. Chem.* **1994**, *33B*, 1028–1032. (f) Enayat, E. I.; Abdel-Hamid, H. A.; Mahmoud, M. R. *Indian J. Chem.* **1990**, *B29*, 331–334. (g) Detty, M. R. *Organometallics* **1988**, *7*, 2188–2197. (h) El-Newaihy, M. F.; Salem, M. R.; Enayat, E. I.; El-Bassiouny, F. A. *J. Prakt. Chem.* **1982**, *324*, 379–384. (i) Hamrick, P. J.; Hauser, C. R. *J. Am. Chem. Soc.* **1960**, *82*, 1957–1959.

(23) Using Sci Finder Scholar, we found 297 references to "indenone preparation".

Table 1. ^{1}H NMR Data (δ) for the Internal Methyl Protons of Selected Dihydropyrenes in C_6D_6

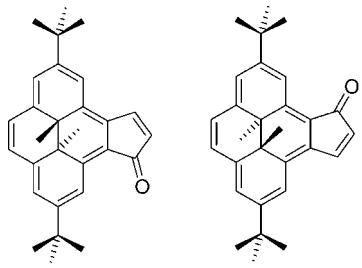
	10	**8**[a]	**9**	**22**	**25**[a]	**28**	**6**	**7**	**33**
δ_{Me}	−3.10	−3.46, −3.51	−3.42	−2.90	−3.53, −3.54	−3.48	−3.67	−3.48	−1.22
	−3.13	−3.53, −3.54	−3.43	−2.94	−3.54, −3.57	−3.48	−3.67	−3.51	−1.22
δ_{Me} (average)[b]	−3.12	−3.51	−3.43	−2.92	−3.55	−3.48	−3.67	−3.50	−1.22

[a] As a mixture of diastereomers. [b] This average value is used in calculating localization effects.

present, which is unlikely in these cases.[1d] Nevertheless, the chemical shift changes observed for the fulvene-fused systems **10** and **22** are much smaller than those found for the cyclopentadienone-fused system **5**, where $\Delta\delta_{Me}$ was 1.6−1.8 ppm, or ∼80% of that of benzene.[4]

What is very clear from these results is that conversion of the C═O of cyclopentadienone **1** (in compound **5**) to C═CHMe or C═CHPh (in compounds **10** or **22**) has a very dramatic effect on the delocalization, and hence the ring current, present in the dihydropyrene part of the molecules. In **22**, the dihydropyrene retains some 92−93% of its initial ring current, while with the strongly antiaromatic cyclopentadienone in **5**, the dihydropyrene only retains 61% of its ring current.[4] On the basis of our NMR results, the fulvenes in **10** and **22** have about 12−16 and 22−25%, respectively, of the effect of benzene, while the cyclopentadienone in **5** has 80% of the effect of benzene!

3. Crystal Structures of Cyclopentadienone 5 and Model 4. It would have been nice to support the chemical shift data given above for **5** with structural data at the time of our original publication.[4] However, with the improved synthesis of **5** used in this work, we were now able to obtain crystals of **5** suitable for X-ray structure determination. Full structure data for **5** and **4** are given in the Experimental Section and in Tables S3−S12 and the crystallographic information file (CIF) in the Supporting Information. Unfortunately, the crystals of both **5** and **4** are disordered. For **5**, the disorder is on the central bridge atoms and the site of the ketone. The structure could be refined, however, using a 69:31 occupancy of the bridges and a 91:9 occupancy of the ketone, resulting in the two diastereomers **5a** and **5b** being the major contributors. It should be noted that these diastereomers exist in the crystal because of the fixed orientations of the *tert*-butyl group shown. It is also notable that neither structure restricts the delocalization pattern within the dihydropyrene ring (only one Kekulé structure is shown for each) and that in both isomers, the fusion bond can be long. A similar pair exists for **4**, with 80:20 and 91:9 occupancies.



5a major **5b** minor

Of relevance here is the fact that in both **5** and **4**, the 17 carbon atoms of the dihydropyrene and cyclopentane ring framework form almost a perfect plane (the maximum deviations are only 0.08 Å for **5** and 0.06 Å for **4**). There is thus no great framework change in going from **4** to **5**. Of real interest are the bond lengths and alternation pattern around the perimeter. These are shown in Table 2, using the atom numbering in Figure 1.

Table 2. Dihydropyrene Periphery Bond Lengths (Å) for **6**, **4**, **5**, **7**, and **33**

	6			**4**		**5**		**7**	**33**	
	Expt[a]	Calc[b] (C_2)	Calc[c,d] (C_i)	Expt[d]	Calc[d]	Expt[d]	Calc[d]	Calc[d]	Expt[a]	Calc[d]
C1-C2	1.402	1.401	1.408	1.389	1.405	1.439	1.435	1.419	1.354	1.376
C2-C3	1.387	1.401	1.395	1.400	1.396	1.357	1.373	1.385	1.431	1.421
C3-C4	1.397	1.397	1.403	1.404	1.400	1.426	1.426	1.411	1.351	1.377
C4-C5	1.389	1.407	1.400	1.394	1.402	1.366	1.378	1.391	1.429	1.423
C5-C6	1.393	1.397	1.404	1.376	1.400	1.430	1.426	1.411	1.367	1.377
C6-C7	1.388	1.401	1.392	1.407	1.398	1.359	1.373	1.386	1.429	1.421
C7-C8	1.399	1.401	1.411	1.388	1.404	1.440	1.434	1.417	1.359	1.376
C8-C9	1.402	1.418	1.408	1.421	1.414	1.372	1.386	1.402	1.437	1.443
C9-10	1.387	1.386	1.395	1.395	1.390	1.419	1.417	1.400	1.364	1.366
C10-C11	1.397	1.411	1.403	1.411	1.403	1.372	1.382	1.400	1.450	1.460
C11-C12	1.389	1.392	1.400	1.403	1.408	1.439	1.440	1.427	1.426	1.434
C12-C13	1.393	1.411	1.404	1.404	1.416	1.373	1.381	1.390	1.463	1.460
C13-C14	1.388	1.386	1.392	1.378	1.387	1.413	1.417	1.404	1.362	1.366
C14-C1	1.399	1.418	1.411	1.422	1.416	1.370	1.387	1.399	1.440	1.443
$\Delta\Sigma$[e]	0.000	0.016	0.000	0.018	0.007	-0.062	-0.048	-0.019	0.071	0.057

[a] Reference 1c. [b] Reference 24. [c] The structure of C_i symmetry obtained using Jaguar 4.0 (ref 1c) was reoptimized using Gaussian 98. [d] This work. Bond length standard deviations are given in full in the Supporting Information and are in the range 0.003−0.004 Å. [e] $\Delta\Sigma$ = average "red" bond length − average "blue" bond length.[8]

Blissfully obvious is the opposite alternation pattern of **5** and **33**, consistent[25] with **33** consisting of two fused [4n + 2] π systems while **5** is a [4n][4n + 2]-fused π system. It is interesting to note that the mild bond alternation in **4** is in the same sense as the strong alternation in **33** and opposite to that in **5**. Coupling constants require that for **33**, the C4−C5 bond is long (smaller $^3J_{H4,5}$), while for **5**, the C4−C5 bond is required to be short (larger $^3J_{H4,5}$). The $^3J_{H4,5}$ values of 6.9 and 8.7 Hz reported previously[4] for **5** and **33**, respectively, are supported by the X-ray data obtained here, namely, 1.366 versus 1.429 Å, although the crystals of **5** are disordered and only average bond lengths have been determined. Should the minor isomer be localized in an opposite sense, this would only reduce the observed alternation, not cancel it.

Clearly as well, the average bond length deviation, $\Delta\Sigma$, is consistent with the greater aromaticity of benzene relative to the antiaromaticity of cyclopentadienone. The ratio of these, 0.062/0.071 = 87%, which gives the effect of cyclopentadienone relative to that of benzene on the basis of bond alternation, is similar to the ratio (80%) based on chemical shift measurement. The calculated ratio of $\Delta\Sigma$ values (see below) suggests that the bond localizing effects of cyclopentadienone are ∼84% of those of benzene and is in good agreement with the experimental ratio. Unfortunately, we have not yet been able to secure crystals of **10** or **22** suitable for X-ray structure determination.

4. Computational Studies. If it is assumed that the observed changes in chemical shift ($\Delta\delta_{Me}$) for the fulvene-fused dihydropyrenes are entirely due to their aromaticities, the estimated aromaticities (relative to benzene) of the parent fulvenes **35** and **36** (13−16 and 22−25%, respectively) are unexpectedly large. These anomalous aromaticities together with the lack of

(24) Williams, R. V.; Edwards, W. D.; Mitchell, R. H.; Robinson, S. G. *J. Am. Chem. Soc.* **2005**, *127*, 16207–16214.
(25) (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.

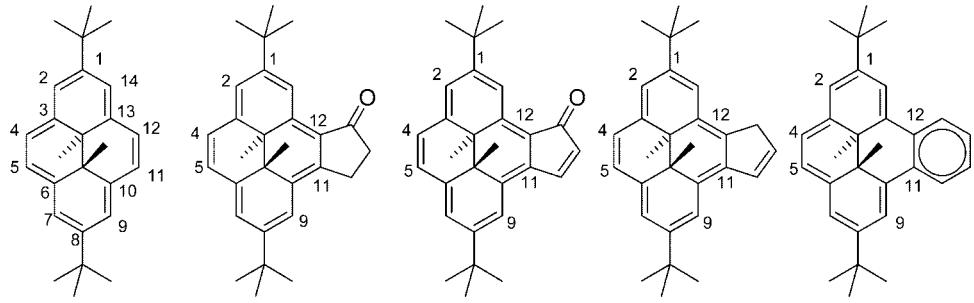


Figure 1. Carbon numbering around the dihydropyrene periphery for the bond length data in Table 2.

Table 3. NICS Values Calculated at the 5-Ring Centroid [NICS(0)] and 1 Å Vertically above/below This Point [NICS(1/1′)] for **17**, **35**, and **36**

	17	35	36
NICS(0)[a]	−2.09	−3.13	−2.39
NICS(0)[b]	+1.60		
NICS(0)[c]	−0.68	−1.77	
NICS(1), (NICS(1′))[a]	−4.60	−5.22	−4.44 (−4.86)
NICS(1)[b]	−1.90		
NICS(1)[c]	−3.93	−4.12	

[a] This work, calculated at the GIAO-HF/6-31G*//B3LYP/6-31G* level. [b] Reference 14g, calculated at the GIAO-BLYP/6-31G*//BLYP/6-31G* level. [c] Reference 14d, calculated at the GIAO-HF/6-31+G*//BLYP/6-311+G* level.

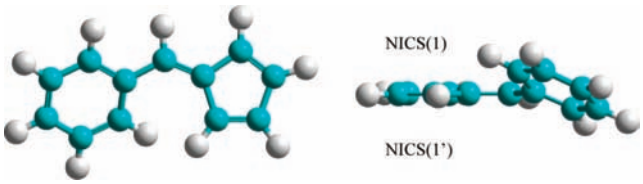
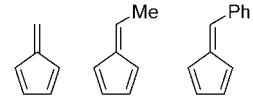


Figure 2. Optimized geometry and location of NICS points 1 and 1′ for 6-phenylfulvene (**36**).

structural data for **10** and **22** and the disordered nature of the crystals of **5** prompted us to examine these systems computationally.

As already mentioned, the status of fulvene **17** with respect to its aromaticity has been an area of some dispute.[14,15] Recent computational studies all provide evidence suggesting that **17** is not aromatic. Schleyer and co-workers[14g] concluded from the magnetic susceptibility exaltation, NICS, and aromatic stabilization energy (ASE) data that **17** is not aromatic.[14a] Similarly, the studies of Cyranski and co-workers[14c,d] [the harmonic oscillator model of aromaticity (HOMA), NICS, ASE, ^{3}He chemical shifts, magnetic susceptibility exaltation, and anisotropy of magnetic susceptibility] and Fowler and co-workers[15c] (principally the induced current densities) supported the classification of **17** as nonaromatic. There is, however, general agreement that electron-donating substituents at the 6-position of fulvene promote the aromatic character of the fulvene nucleus. Experimental efforts at verifying this prediction are ambiguous.[14,15] While Cyranski and co-workers[14c,d] made no pronouncement as to the aromaticity of 6-methylfulvene (**35**), their calculated data indicates that it is very slightly more aromatic than **17**. We are not aware of any computational studies attempting to divine the aromaticity of 6-phenylfulvene (**36**). Our own NICS calculations (this work) lead us to suggest that **36** is nonaromatic, with NICS values very similar to those of **17** and **35** (Table 3). As can be seen from Figure 2, the phenyl group in **36** is significantly twisted out of conjugation with the fulvene moiety and therefore functions as a poor electron donor. As is apparent from the fact that the NICS(1′) value is more shielded than the NICS(1) value, this twist places NICS point 1′ within the shielding cone of the phenyl group. Similarly, it is likely that NICS(0) is affected by the phenyl group's anisotropic deshielding. To augment our findings using the dimethyldihydropyrene meter to experimentally probe the aromaticities of **5**, **10**, and **22**, we initiated a computational study of these systems.

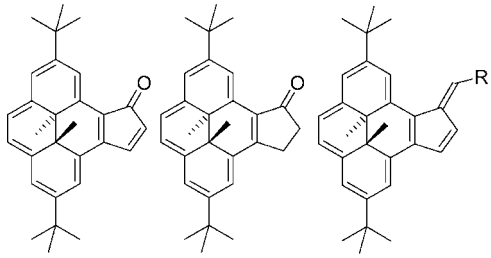


4.1. Computational Methods. We have previously shown that density functional theory (DFT) using the B3LYP/6-31G* method is very successful in modeling dimethyldihydropyrenes, validating our use of this level of theory in this study.[26] The geometries for all of the compounds in this study were optimized using the B3LYP/6-31G* method as implemented in the Gaussian 98 suite of programs.[27] All of the optimized structures were confirmed to be minima through their calculated energy second derivatives (no imaginary frequencies). Gaussian 98[27] was used to calculate NICS[28] values with the Hartree−Fock (HF) gauge-independent atomic orbital (GIAO) method on the B3LYP/6-31G* optimized geometry (GIAO-HF/6-31G*//B3LYP/6-31G*) and also to obtain NMR chemical shifts, which were calculated for ^{1}H (GIAO-HF/6-31G*//B3LYP/6-31G*) and ^{13}C (scaled[29] from GIAO-B3LYP/6-31G*//B3LYP/6-31G*) NMR at the optimized B3LYP/6-31G* geometries. Again, we have shown that these methods reliably provide excellent agreement with experimental data.[30]

4.2. Computational Results. In an extensive study correlating experimentally determined aromaticities of the dimethyldihydropyrene nucleus in a range of derivatives, we demonstrated that the use of NICS(14Av) (the average of the NICS values calculated at the centroids of the four six-membered rings constituting the dihydropyrene nucleus) provided the best calculated determination of DHPN.[1c] NICS(5) is the NICS value

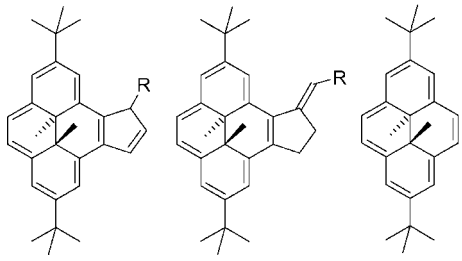
(26) For example, see: Ayub, K.; Zhang, R.; Robinson, S. G.; Twamley, B.; Williams, R. V.; Mitchell, R. H. *J. Org. Chem.* **2008**, *73*, 451–456, and references therein.
(27) Frisch, M. J.; et al. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.
(28) Schleyer, P. v. R.; Maerker, C.; Deansfeld, A.; Jial, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.
(29) Forsyth, D. A.; Sebag, A. B. *J. Am. Chem. Soc.* **1997**, *119*, 9483–9494.
(30) For example, see: Mitchell, R. H.; Blunden, R.; Hollett, G.; Bandyopadhyay, S.; Williams, R. V.; Twamley, B. *J. Org. Chem.* **2005**, *70*, 675–680, and references therein.

Table 4. NICS Values for **5**, **4**, **7**, **18**, **40**, **19**, **10**, **8**, **37**, **22**, **25**, **38**, and **6**



5 **4**

18 R=H
10 R=Me
22 R=Ph



7 R=H
40 R=Me
8 R=$MeCH_2$
25 R=$PhCH_2$

19 R=H
37 R=Me
38 R=Ph

6

compound	NICS(14Av)	NICS(5)
5	−7.35	6.67
4	−16.01	2.81
7	−14.90	1.40
18	−11.49	2.46
40	−14.42	1.06
19	−17.18	1.05
10	−14.21	2.35
8	−14.22	1.14
37	−17.30	1.18
22	−13.60	2.79
25	−14.01	1.33
38	−17.03	1.45
6 (C_2)	−15.87	
6 (C_i)	−18.29	

at the centroid of the five-membered ring. A summary of the results for some of the compounds in this study are shown in Table 4 (the complete set of NICS values is given Table S14 in the Supporting Information).

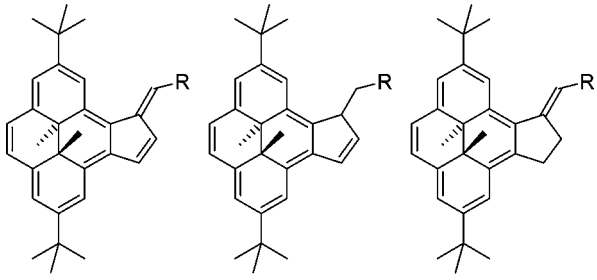
In previous studies, we obtained fully optimized structures for **6** with C_i and C_2 symmetries.[1c,24] These structures are essentially degenerate: the one having C_2 symmetry is 0.11 kcal/mol lower in total electronic energy than that having C_i symmetry. The structures are very similar, differing in peripheral bond lengths by a maximum of 0.009 Å (Table 2). It is therefore quite surprising that there is such a large difference in NICS values (Table 4) for these two geometries. This difference is reflected to a much lesser extent in the differences in their $\Delta\Sigma$ values (Table 2). In light of our earlier study correlating experimentally determined aromaticities with calculated NICS values,[1c] we consider the NICS values for **6**(C_i) to be a more accurate representation of this system. We plan a further investigation of these anomalously large differences in NICS values. In the current study, these differences are irrelevant, as we base our assignments of the fulvene aromaticities on the differences between the properties of the fulvene-fused dihydropyrenes and the corresponding nonaromatic models. The large negative NICS value of −18.29 (−15.87) for **6**, which is characteristic of a highly aromatic system, is dramatically reduced to −7.35 for **5**, indicating a sizable quenching of the aromaticity of **6**. Such a quenching is indicative of fusion by a strong (anti)aromatic system, in this case the cyclopentadienone. Similarly, the large positive NICS(5) value for **5** is consistent with the cyclopentadienone moiety exhibiting significant antiaromaticity. A better comparison to assess the antiaromaticity of cyclopentadienone is that between the NICS values for **5** and **4** and **5** and **7**. In both **4** and **7**, local anisotropies and other effects not associated with fusion by an (anti)aromatic system are taken into account. **4** and **7** do show smaller DHPNs [NICS(14Av) = −16.01 and −14.90, respectively] than **6**, but this reduction is minor when compared with the corresponding value for **5**. Clearly, our NICS calculations support our NMR- and X-ray structure-based assignments of the antiaromaticity of cyclopentadienone **1**. Nyulászi and Schleyer[31] determined that cyclopentadiene (**39**) is not aromatic; therefore, the sizable reduction in DHPN in **7** [δ −3.48 and −3.51 in C_6D_6,[2b] which, as expected, are very similar to δ −3.51 for **8** in C_6D_6 (average of both methyls and both diastereomers)] can be attributed to local anisotropies and Mills−Nixon-type effects. As these effects are larger than those found for the cyclopentanone moiety in **4** (δ −3.71 and −3.74 in $CDCl_3$ [4]), it is appropriate to revise our original comparison of the reduction of the DHPN in **5** by using **7** instead of **4** as the nonaromatic model. Comparison of the calculated bond alternations (Table 2) also shows that **7** has a greater effect than **4** ($\Delta\Sigma$ = 0.019 and 0.007, respectively). When **7** is used as the model, the effect of the cyclopentadienone relative to benzene, using experimentally determined chemical shifts, is 73% (compared with 78% when **4** was used as the model). Despite their disordered nature, our calculated geometries for **5** and **4** (Table 2) are in good agreement with the X-ray structures: the maximum differences between calculated and experimental bond lengths (Δr) are 0.016 and 0.024 Å for **5** and **4**, respectively, which are similar to the Δr of 0.028 Å we found previously for a series of dimethyldihydropyrene derivatives.[1c] The obvious bond alternation calculated for **5**, in the same sense as that in the X-ray results, lends compelling support for the antiaromaticity of **1**. It should be noted that both the X-ray (disordered) and calculated bond lengths of **4** show only mild alternation around the dihydropyrene periphery.

39

Further examination of Table 4 immediately reveals contradictory results for the fulvenes. The NICS(14Av) values across the series of fulvene-, methylfulvene-, and phenylfulvene-fused dihydropyrenes **18**, **10**, and **22** orders the DHPN as **10** > **22** > **18**, which implies that the order of aromaticity of these fulvenes is **17** > **36** > **35** if it is assumed that the NICS(14Av) value is only affected by the aromaticity of the annelating fulvene. Disconcertingly, the NICS(5) values for all of these fulvenes are *positive*, but their magnitudes are small enough that they could either be taken to indicate weak antiaromaticity or perhaps nonaromaticity of the annelating fulvene ring. In view of the results for the nonaromatic (fulvene annelation) models **8**, **19**, **25**, **37**, **38**, and **40**, it is apparent that "hydrogenation" of the exocyclic double bond (**8**, **25**, and **40**) significantly reduces the

(31) Nyulászi, L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1999**, *121*, 6872–6875.

Table 5. Calculated Dihydropyrene Periphery Bond Lengths (Å) for **18**, **40**, **19**, **10**, **8**, **37**, **22**, **25**, and **38**



18 R=H
10 R=Me
22 R=Ph

40 R=H
8 R=Me
25 R=Ph

19 R=H
37 R=Me
38 R=Ph

	18	40	19	10	8	37	22	25	38[a]
C1-C2	1.423	1.420	1.409	1.415	1.420	1.408	1.416	1.421	1.408
C2-C3	1.379	1.384	1.390	1.384	1.383	1.390	1.384	1.383	1.391
C3-C4	1.417	1.412	1.406	1.412	1.413	1.406	1.413	1.413	1.406
C4-C5	1.384	1.390	1.395	1.389	1.390	1.395	1.388	1.389	1.395
C5-C6	1.416	1.412	1.406	1.411	1.412	1.405	1.412	1.412	1.406
C6-C7	1.380	1.385	1.389	1.385	1.385	1.390	1.384	1.384	1.389
C7-C8	1.424	1.418	1.413	1.418	1.418	1.413	1.419	1.419	1.414
C8-C9	1.394	1.400	1.405	1.400	1.400	1.405	1.400	1.400	1.404
C9-C10	1.408	1.401	1.399	1.403	1.401	1.399	1.404	1.402	1.400
C10-C11	1.391	1.399	1.396	1.396	1.399	1.396	1.395	1.398	1.395
C11-C12	1.445	1.429	1.421	1.439	1.429	1.401	1.44	1.43	1.421
C12-C13	1.394	1.390	1.412	1.402	1.390	1.414	1.402	1.390	1.416
C13-C4	1.411	1.408	1.394	1.404	1.408	1.394	1.404	1.408	1.394
C14-C1	1.394	1.397	1.409	1.400	1.397	1.409	1.400	1.397	1.410
$\Delta\Sigma$[b]	-0.033	-0.022	-0.007	-0.021	-0.022	-0.004	-0.022	-0.023	-0.007

[a] Geometry optimized using Gaussian 03, revision D.01.[27] [b] $\Delta\Sigma$ = average "red" bond length − average "blue" bond length.

aromaticity of the dihydropyrene unit compared with **6**, while "hydrogenation" of the endocyclic double bond (**19**, **37**, and **38**) only slightly reduces the diatropicity compared with **6**. The NICS(14Av) values for the nonaromatic models **40**, **8**, and **25** are close to the corresponding values for the fulvene-fused dihydropyrenes **18**, **10**, and **22**, indicating that the parent fulvenes **17**, **35**, and **36** enjoy little or no aromaticity. This is obviously a case where "other effects" dominate any *weak* aromaticity-induced localization of the macrocyclic ring. Immediately apparent from Table 5 is the fact that the bond lengths around the [14]annulene periphery for every entry do indeed alternate. However, in each case, the alternation is not that expected for annelation with an aromatic system (where the "red" bonds would be longer than the "blue" bonds), but the one that would result from an *antiaromatic* annelation! The five-membered rings enforce Mills−Nixon-type localization on the dihydropyrene moiety, just as we previously reported for **14**−**16**. There is little difference in the reduction in DHPN, as determined from geometric parameters ($\Delta\Sigma$), for the nonaromatic models **8**, **25**, and **40** and the corresponding fulvene-fused dihydropyrenes **10**, **22**, and **18**, and as we concluded from our calculated NICS(Av14) values, our geometric analysis suggests that **17**, **35**, and **36** are not aromatic. A consistent picture emerges between the cyclopentadienone (**5**) and fulvene (**10**, **18** and **22**)-fused series: in both series, hydrogenation of the endocyclic double bonds results in minimal reduction of DHPN (compared with **6**), as evidenced by bond localization and NICS(Av14). In contrast, for **7**, **8**, **25**, and **40** with endocyclic double bonds, the DHPNs (again compared with **6**) are greatly reduced. These results clearly demonstrate the need for great care in selecting appropriate nonaromatic models in assessing relative aromaticities.

Tables S1 and S2 in the Supporting Information give experimental and calculated ^{1}H and ^{13}C NMR chemical shifts for the relevant molecules of this study. Our results for parent annulene **6** and the benzo derivative **33** were previously published.[1c]

Conclusions

On the basis of ring-current measurements, fulvenes show measurable apparent aromaticities (12−16% of that of benzene for methylfulvene, 22−25% for phenylfulvene) when dihydropyrene is used as the NMR probe with **8** and **25** as the nonaromatic models. NICS and bond length calculations also show a marked reduction in DHPN upon annelation of the parent dihydropyrene **6** with these fulvenes. However, there is little difference between either the NICS(Av14) or $\Delta\Sigma$ values of the fulvene-fused dihydropyrenes **10**, **18**, and **22** and those of the *appropriate* (exocyclic hydrogenated) nonaromatic models **8**, **25**, and **40**, which leads us to conclude that the fulvenes **17**, **35**, and **36** are nonaromatic. Using our calculated chemical shifts shows that the values of $\Delta\delta_{Me}$, the difference between the average chemical shift for the two internal methyl groups of a fulvene and the corresponding average for the appropriate nonaromatic model, are only 0.23 and −0.1 ppm for **10** (vs **8**) and **22** (vs **25**), respectively (i.e., the internal methyls of **22** are *more* shielded than those of **25**). Again, we interpret these calculated $\Delta\delta_{Me}$ values to indicate that 6-methylfulvene **35** and 6-phenylfulvene **36** lack any appreciable aromaticity. The noted reductions in DHPN in these compounds are principally a consequence of local anisotropies and especially Mills−Nixon-type effects of the annelating groups. This leaves a glaring contradiction between our experimental and computational results. Clearly, experiment cannot be wrong, but our calculations are of proven reliability. The probable origin of this dichotomy lies in the fact that the experimental results were obtained on solutions of the fulvene-fused dihydropyrenes, while the computations strictly apply to the isolated molecules in the gas phase. We have previously noted similar discrepancies and attempted, with only limited success (as others have also found), to computationally address the issue of solvation using various reaction-field models.[32] It is probable that differential solvation of fulvenes **10** and **22** compared with the nonaromatic models **8** and **25** leads to elevated $\Delta\delta_{Me}$ values from NMR, which erroneously support the assignment of **35** and **36** as aromatic. A further demonstration of the credibility of our computational results is provided by their current confirmation of the strong antiaromaticity of cyclopentadienone. This study confirms the paramount importance of using great care in selecting the appropriate nonaromatic models and of the vital synergy between experiment and calculation for the determination of relative aromaticities. When the exocyclic hydrogentated nonaromatic models (**8** and **25**) for methyl- and phenylfulvene-annelated dihydropyrenes (**10** and **22**) are used to estimate the relative aromaticities of **35** and **36**, it is apparent that they are essentially nonaromatic.

Bond length data for the cyclopentadienone-fused dihydropyrene **5** show about 80% of the bond alternation caused by

(32) (a) Williams, R. V. *Eur. J. Org. Chem.* **2001**, 227–235. (b) Seefelder, M.; Heubes, M.; Quast, H.; Edwards, W. D.; Armantrout, J. R.; Williams, R. V.; Cramer, C. J.; Goren, A. C.; Hrovat, D. A.; Borden, W. T. *J. Org. Chem.* **2005**, *70*, 3437–3449.

benzene when using the enone **4** as the nonaromatic model, in remarkable agreement with the chemical shift data obtained previously.[4] Again, calculations reveal that this constitutes a small overestimation of the antiaromaticity of cyclopentadienone and that the endocyclic hydrogenation model **4** is not the best choice. Using the better nonaromatic model **7,** we revise our original estimation of the antiaromaticity-induced effect on DHPN to be 73% compared with that of benzene.

Experimental Section

For general information and structure numbering for the spectral assignments, see the Supporting Information.

2,7-Di-*tert*-butyl-9-methylenyl-*trans*-11c,11d-dimethyl-10,11,11c,11d-tetrahydrocyclopenta[*e*]pyrene (19). *n*-Butyllithium (200 μL, 1.6 M solution in hexane, 0.32 mmol) was added to $(Ph)_3PCH_3^+Br^-$ (120 mg, 0.34 mmol) in dry THF (20 mL) under argon at −78 °C (dry ice/acetone bath). The color immediately changed to yellow. The dry ice/acetone bath was removed after 3 min, and the solution was warmed to room temperature (20 °C) and left to stir for 5 min. Next, a solution of cyclopentanone **4**[2b] (80 mg, 0.20 mmol) in dry THF (10 mL) was added dropwise, and the mixture was stirred at 20 °C for an additional hour. Hexanes (30 mL) were then added, and the solution was washed with water (4 × 50 mL). The organic layer was then dried over anhydrous Na_2SO_4 and evaporated to give a dark-green solid, which was chromatographed over silica gel with hexane to elute dihydropyrene **19** (57 mg, 71%) as a green crystalline solid, mp (dec). ^{1}H NMR (C_6D_6): δ 9.39 (s, 1H, H-1), 8.55 (d, J = 1.0 Hz, 1H, H-8), 8.49 (s, 1H, H-6), 8.48 (s, 1H, H-3), 8.30 (AB, J = 7.4 Hz, 1H, H-4), 8.28 (AB, J = 7.4 Hz, 1H, H-5), 6.46 (t, J = 2.2 Hz, 1H, H-12$_a$), 5.69 (t, J = 1.9 Hz, 1H, H-12$_b$), 3.69−3.64 and 3.59−3.53 (m, 1H each, H-11), 3.18−3.06 (m, 2H, H-10), 1.64 (s, 9H, 2−C(CH$_3$)$_3$), 1.62 (s, 9H, 7−C(CH$_3$)$_3$), −3.27 (s, 3H, 11c−CH$_3$), −3.29 (s, 3H, 11d−CH$_3$). ^{13}C NMR (C_6D_6): δ 153.04 (C-9), 146.08 (C-7), 144.32 (C-2), 141.24 (C-11a), 138.09 (C-3a), 136.57 (C-5a), 132.27 (C-11f), 131.48 (C-11e), 131.20 (C-11b), 123.05 (C-5), 122.57 (C-4), 121.29 (C-6), 120.47 (C-3), 118.69 (C-8), 118.59 (C-1), 106.54 (C-12), 36.08 (2,7−*C*(CH$_3$)$_3$), 34.91 (C-10), 31.89 (C-11c), 31.57 and 31.53 (2,7−C(*C*H$_3$)$_3$), 30.84 (C-11d), 29.12 (C-11), 15.18 (11c,11d−*C*H$_3$). EI MS: *m*/*z* 396 (M^+). HRMS: calcd for $C_{30}H_{36}$, 396.2817; found, 396.2813. Compound **19** was not stable and always contained some rearranged product **20** (internal methyl protons at δ −3.43 and −3.44, 12-Me at δ 2.88; see the spectra in the Supporting Information).

2,7-Di-*tert*-butyl-9-ethylidene-*trans*-11c,11d-dimethyl-11c,11d-dihydrocyclopenta[*e*]pyrene (10). Method A. This method followed Ottosson's procedure.[20] The preparation of anion **21** was carried out in a glovebox: the cyclopentadienyl-fused dihydropyrene **7**[2b] (100 mg, 0.26 mmol) and $LiCH_2SiMe_3$ (26 mg, 0.28 mmol) in toluene (10 mL) were stirred overnight at 20 °C in a glovebox. The color changed from green to red as the lithium cyclopentadienide-fused dihydropyrene **21** formed. Next, the reaction mixture was dried under vacuum. The pure lithium salt of **21** was obtained by washing the red residue three times with a small mount of hexane to remove the excess base. This salt (50 mg, 0.13 mmol) was placed in a Kontes flask with a stir bar and removed from the glovebox. Dry THF (10 mL) was then added, followed by acetaldehyde (0.14 mmol, 1.4 mL of a 1 M solution in dried THF, dried overnight over molecular sieve) using a syringe. The resulting mixture was then stirred at 20 °C for 30 min. The solvent was then removed under vacuum, and the dark-brown solid was chromatographed on deactivated silica gel with hexane to yield 36 mg (68%) of methylfulvene **10** as a dark-brown solid (properties below).

Method B. This method followed Shimizu's procedure.[21] Cyclopentadienyl-fused dihydropyrene **7**[2b] (50 mg, 0.13 mmol), aqueous NaOH (5 M, 3 mL), and cetyltrimethylammonium bromide (2 mg, 4 mol %) were stirred in THF (3 mL) at 20 °C, and a solution of acetaldehyde (0.4 mmol, 4 mL of a 0.1 M solution in dried THF) was added dropwise over 30 min, after which stirring was continued for an additional 30 min. Water (5 mL) was then added, and the reaction mixture was extracted with hexane. The extracts were washed with water, dried with anhydrous $MgSO_4$, and evaporated to give a dark-brown solid, which was chromatographed on deactivated silica gel with hexane to yield 16 mg (30%) of methylfulvene **10** that was identical to the sample from method A above.

Recrystallization from methanol gave a dark-brown solid, mp 124−125 °C. ^{1}H NMR (C_6D_6): δ 9.22 (s, 1H, H-8), 8.77 (d, J = 1.2 Hz, 1H, H-1), 8.45 (s, 1H, H-6), 8.44 (s, 1H, H-3), 8.31 (AB, J = 8.1 Hz, 1H, H-4), 8.29 (AB, J = 8.1 Hz, 1H, H-5), 7.86 (dd, J = 5.75, 1.6 Hz, 1H, H-11), 7.40 (q, J = 7.4 Hz, 1H, H-12), 7.174 (dd, J = 5.7 Hz, 0.7 Hz, 1H, H-10; in THF-d_8, these appeared at δ 7.21 and did not overlap the benzene signal), 2.14 (d, J = 7.4 Hz, 3H, H-13), 1.619 (s, 9H, 7−C(CH$_3$)$_3$), 1.618 (s, 9H, 2−C(CH$_3$)$_3$), −3.10 (s, 3H, 11c−CH$_3$), −3.13 (s, 3H, 11d−CH$_3$). ^{13}C NMR (C_6D_6): δ 147.47 (C-7/2), 146.03 (C-9), 145.61 (C-2/7), 139.33 (C-5a), 138.22 (C-11a), 137.62 (C-3a), 132.28 (C-11e), 130.44 (C-11), 129.84 (C-11b), 128.69 (C-10), 128.29 (C-11f), 127.61 (C-12), 125.05 (C-5), 124.41 (C-4), 122.42 (C-3), 121.30 (C-6), 117.61 (C-1), 116.92 (C-8), 36.55 and 36.35 (2,7−*C*(CH$_3$)$_3$), 33.64 (C-11c,d), 32.31 and 32.26 (2,7−C(*C*H$_3$)$_3$), 17.19 (11c−*C*H$_3$), 16.90 (C-13), 16.71 (11d−*C*H$_3$). EI MS: *m*/*z* 408 (M^+). HRMS: calcd for $C_{31}H_{36}$, 408.2817; found, 408.2814. This compound decomposed on standing.

9-Benzylidene-2,7-di-*tert*-butyl-*trans*-11c,11d-dimethyl-11c,11d-dihydrocyclopenta[*e*]pyrene (22). Method A. This method followed Ottosson's procedure,[20] and was carried out in a glovebox. The cyclopentadienyl-fused dihydropyrene **7**[2b] (50 mg, 0.13 mmol) and $LiCH_2SiMe_3$ (13 mg, 0.14 mmol) in toluene (10 mL) were stirred overnight at 20 °C, during which the color changed from green to red. Next, benzaldehyde (∼40 mg, 0.38 mmol, dried by molecular sieve, type 4A) was added, and the reaction mixture was stirred at 20 °C for 30 min. The solvent was then removed to give a reddish-brown solid, which was chromatographed on deactivated silica gel with hexane to yield 49 mg (80%) of phenylfulvene **22** as a reddish-brown solid (properties below).

Method B. This method followed Shimizu's procedure.[21] Cyclopentadiene **7**[2b] (50 mg, 0.13 mmol), benzaldehyde (∼40 mg, 0.38 mmol, excess), and cetyltrimethylammonium bromide (2 mg, 4 mol %) were added to THF (3 mL). Aqueous NaOH solution (5 M, 3 mL) was then added, and the resulting mixture was stirred at 20 °C for 1.5 h under argon. Water (5 mL) was then added, and the reaction mixture was extracted with hexane. The extracts were washed with water, dried with anhydrous $MgSO_4$, and evaporated to give a reddish-brown solid, which was chromatographed on deactivated silica gel with hexane to yield 45 mg (74%) of phenylfulvene **22** as a reddish-brown solid that was identical to the sample from method A.

Mp: 132−133 °C. ^{1}H NMR ($CDCl_3$): δ 8.96 (s, 1H, H-8), 8.49 (d, J = 1.1 Hz, 1H, H-1), 8.29 (s, 2H, H-3,6), 8.23 (AB, J = 8.1 Hz, 1H, H-4), 8.20 (AB, J = 8.1 Hz, 1H, H-5), 8.07 (s, 1H, H-12), 7.82 (dd, J = 5.7, 1.6 Hz, 1H, H-11), 7.70 (d, J = ∼8 Hz, 2H, H-14,18), 7.48 (t, J = ∼8 Hz, 2H, H-15,17), 7.34 (t, J = ∼8 Hz, 1H, H-16), 7.30 (dd, J = 5.7, 0.7 Hz, 1H, H-10), 1.66 (s, 9H, 7−C(CH$_3$)$_3$), 1.64 (s, 9H, 2−C(CH$_3$)$_3$), −3.29 (s, 3H, 11c−CH$_3$), −3.32 (s, 3H, 11d−CH$_3$). ^{1}H NMR (C_6D_6, 300 MHz): δ 9.29 (s, 1H, H-8), 8.69 (bs, 1H, H-1), 8.42 (s, 1H, H-3/6), 8.39 (s, 2H, H-3/6 and H-12), 8.26 (AB, J = 8 Hz, 1H, H-4), 8.22 (AB, J = 8 Hz, 1H, H-5), 7.90 (dd, J = 6, 2 Hz, 1H, H-11), 7.66 (d, J = 8 Hz, 2H, H-14,18), 7.50 (d, J = 6 Hz, H-10), 7.25 (t, J = ∼8 Hz, 2H, H-15,17), 7.12 (t, J = ∼8 Hz, 1H, H-16), 1.60 (s, 18H, 2,7−C(CH$_3$)$_3$), −2.90 and −2.94 (2s, 3H each, 11c,11d−CH$_3$). ^{13}C NMR ($CDCl_3$): δ 148.17 (C-7), 145.89 (C-2), 144.52 (C-9), 139.33 (C-5a), 138.89 (C-13), 137.42 (C-3a), 136.14 (C-11a), 132.52 (C-11e), 132.08 (C-11), 130.40 (C-14,18), 129.70 (C-10), 129.55 (C-11b), 129.26 (C-12), 128.78 (C-15,17), 127.52 (C-11f), 127.43 (C-16), 124.88 (C-4), 124.03 (C-5), 122.13 (C-3), 120.98 (C-6), 116.82

(C-1), 116.20 (C-8), 36.45 (7−*C*(CH_3)$_3$), 36.16 (2−*C*(CH_3)$_3$), 33.62 (C-11d), 32.12 (C-11c), 32.00 (7−C(*C*H_3)$_3$), 31.95 (2−C(*C*H_3)$_3$), 17.14 and 16.81 (11c,11d−CH_3). IR (KBr) ν (cm^{-1}): 3039, 2962, 2923, 2865, 1596, 1459, 1388, 1361, 1261, 886, 865, 701, 680. UV−vis (cyclohexane) λ_{max} [nm] (ϵ_{max}): 325 (32 400), 418 (41 300), ∼500 sh (10 000), 590 (1090), 651 (1450), 733 (4800). EI MS: *m*/*z* 470 (M^+); HRMS: calcd for $C_{36}H_{38}$, 470.2974; found, 470.2982.

2,7-Di-*tert*-butyl-9-hydroxymethyl-*trans*-11c,11d-dimethyl-11c,11d-dihydrocyclopenta[*e*]pyrene (23). (Attempted synthesis of **18** using Shimizu's procedure[21]). Cyclopentadiene **7** (50 mg, 0.13 mmol), formaldehyde (0.5 mL of a 37 wt % aqueous solution, 6.7 mmol, excess), and cetyltrimethylammonium bromide (2 mg, 4 mol %) were added to THF (3 mL). Aqueous NaOH solution (5 M, 3 mL) was then added. The resulting mixture was stirred at 20 °C for 1.5 h under argon. Water (5 mL) was then added, and the reaction mixture was extracted with hexane. The extracts were washed with water, dried with anhydrous $MgSO_4$, and evaporated to give a green solid, which was chromatographed on alumina (3% water-deactivated) with 2:1 hexane/ethyl ether to yield 20 mg (37%) of alcohol **23** as a green solid, mp 168−169 °C. ^{1}H NMR (C_6D_6): δ 8.86 (d, J = 0.9 Hz, 1H, H-1), 8.83 (d, J = 0.9 Hz, 1H, H-8), 8.60 (s, 1H, H-3), 8.58 (s, 1H, H-6), 8.47 (AB, J = 5.3 Hz, 1H, H-4), 8.44 (AB, J = 5.3 Hz, 1H, H-5), 7.87 (dd, J = 5.7, 1.5 Hz, 1H, H-11), 6.82 (dd, J = 5.7, 2.0 Hz, 1H, H-10), 4.65−4.62 (m, 1H, H-9), 4.27−4.24 and 3.78−3.75 (m, 1H each, H-12), 1.67 and 1.66 (s, 9H each, 2,7−C(CH_3)$_3$), −3.52 and −3.57 (s, 3H each, 11c,11d−CH_3). ^{13}C NMR (C_6D_6): δ 145.97 and 145.15 (C-2,7), 138.43 (C-11a), 137.83 (C-3a), 137.61 (C-10), 137.24 (C-5a), 136.57 (C-11f), 132.29 (C-11), 131.19 (C-11b), 129.43 (C-11e), 124.64 (C-4), 124.06 (C-5), 121.90 (C-3), 121.25 (C-6), 117.90 (C-1), 117.04 (C-8), 67.74 (C-12), 54.93 (C-9), 36.47 (2,7−*C*(CH_3)$_3$), 32.43 (2,7−C(*C*H_3)$_3$), 31.97 and 31.50 (C-11c,d), 15.68 and 15.28 (11c,11d−CH_3). IR (thin film) ν (cm^{-1}): 3440 (br, OH). LSI MS: *m*/*z* 412.2 (M^+). No product of structure **18** could be found. When alcohol **23** (35 mg, 0.073 mmol), dry pyridine (0.5 mL), dry CH_2Cl_2 (10 mL), and tosyl chloride (30 mg, 0.16 mmol) were stirred at 20 °C under argon for 1.5 h and the resulting product was reacted with potassium *tert*-butoxide, only decomposed products were obtained.

NMR Samples of Ethyl Derivatives 8 and 9. Compound **7** (20 mg) in toluene (2 mL) was converted to its anion **21** using $LiCH_2SiMe_3$ (6 mg), as described above for **22**. Ethyl bromide (1 drop, excess) was then added, after which the red solution quickly turned green. After 30 min, the solution was filtered through Celite and then evaporated. The product was extracted with C_6D_6, which was used directly in measuring the ^{1}H NMR data (300 MHz) for **8** (two diastereomers, shifts given as X/Y): δ 8.93/8.90 (s, 1H, H-1), 8.82/8.76 (s, 1H, H-8), 8.62/8.60 (s, 2H, H-3,6), 8.48−8.46 (m, 2H, H-4,5), 7.95/7.90 (dd, J = ∼6, 1 Hz, 1H, H-11), 6.76/6.72 (dd, J = ∼6, 1 Hz, 1H, H-10), 4.48/4.39 (m, 1H, H-9), 2.60−2.06 (m, 2H, H-12), 1.69 and 1.66 (s, 9H each, −C(CH_3)$_3$), ∼1.6 (m, 3H, H-13), −3.46, −3.51, −3.53, and −3.54 (s, 6H total, internal methyl protons). When this sample was evaporated, dissolved in THF-d_8, and reconverted to the anion with $LiCH_2SiMe_3$ (6 mg), the internal methyl protons shifted to about δ −2. Water was then added. The product was filtered through silica gel using hexane, and the green fraction then yielded the single isomer of **9**. ^{1}H NMR (500 MHz, C_6D_6): δ 9.31 (s, 1H, H-8), 8.77 (d, J = 1.0 Hz, 1H, H-1), 8.61 (s, 1H, H-6), 8.60 (s, 1H, H-3), 8.47 and 8.45 (AB, J = 7.8 Hz, 2H, H-4,5), 6.41 (t, J = ∼2 Hz, 1H, H-10), 4.13−3.96 (m, 2H, H-11), 3.48−3.33 (m, 2H, −CH_2−), 1.69 (s, 18H, C(CH_3)$_3$), 1.52 (t, J = 7.3 Hz, 3H, −CH_2CH_3), −3.43 and −3.42 (s, 3H each, internal −CH_3). ^{13}C NMR (C_6D_6): δ 150.65 (C-9), 145.39 (C-2/7), 144.63 (C-7/2), 139.41 (C-11a), 138.46 (C-11f), 137.59 (C-3a/5a), 137.42 (C-5a/3a), 131.58 (C-11a/11b), 130.58 (C-11b/11a), 129.67 (C-10), 124.20 (C-4/5), 123.27 (C-5/4), 121.45 (C-6), 120.92 (C-3), 118.47 (C-8), 116.64 (C-1), 36.93 (C-11), 36.57 (7−*C*(CH_3)$_3$), 36.45 (2−*C*(CH_3)$_3$), 32.54 and 32.51 (2,7−C(*C*H_3)$_3$), 32.38 (C-11d), 31.43 (C-11c), 26.34 (−CH_2−), 15.78 and 15.76 (11c,11d−*C*H_3), 13.99 (−CH_2CH_3). MS: *m*/*z* 410 (M^+).

NMR Samples of Benzyl Derivatives 25 and 28. Compound **7** (20 mg) in toluene (2 mL) was converted to its anion **21** using $LiCH_2SiMe_3$ (6 mg), as described above for **22**. Benzyl bromide (1 drop, excess) was then added, after which the red solution quickly turned green. After 30 min, the solution was filtered through Celite and then evaporated. The product was extracted with C_6D_6, which was used directly in measuring the ^{1}H NMR data (500 MHz, C_6D_6) of **25** (two diastereomers): δ 8.894, 8.889, 8.87, and 8.82 (4d, J = 1.3 Hz, 2H, H-1,8), 8.64, 8.62, 8.604, and 8.599 (4d, J = ∼1 Hz, 2H, H-3,6), 8.49−8.45 (m, 2H, H-4,5), 7.86 and 7.81 (2dd, J = 5.6, 1.5 Hz, 1H, H-11), 7.40−6.92 (m, 5H, phenyl ring), 6.81 and 6.74 (2dd, J = 5.6, 2.0 Hz, 1H, H-10), 4,73−4.68 and 4,63−4.59 (2m, 1H, H-9), 4.11 and 3.84 (2*AB*, J = 13.6, 4.3 Hz, 1H, −CH_AH$_B$−), 2.90 and 2.83 (2A*B*, J = 13.6, 10.4 Hz, 1H, −CH$_A$$H_B$−), 1.73, 1.71, 1.64, and 1.63 (4s, 18H, 2,7−C(CH_3)$_3$), −3.57, −3.54, and −3.53 (1:2:1 s, 6H, 11c,11d−CH_3). ^{13}C NMR: see the Supporting Information. When this sample was evaporated, dissolved in THF-d_8, and reconverted to the anion with $LiCH_2SiMe_3$ (6 mg), the internal methyl protons shifted to about δ −2. Water was then added. The product was filtered through silica gel using hexane, and the green fraction then yielded the isomer of **28**. ^{1}H NMR (300 MHz, THF-d_8): δ 8.9, 8.7, 8.5, 8.4, and 8.3 (s, (1,1,1,1,2, 6H total, DHP protons), 7.3−7.1 (m, 6H, H-9 and Ph), 6.4−6.3 (m, 1H, H-10), 4.8 and 3.6 (brs, 2H, H-11), 4.3−4.1 (m, 2H, CH_2Ph), 1.7 (s, 18H, 2,7−C(CH_3)$_3$), −3.9 (s, 6H, 11c,11d−CH_3).

***trans*-3-(2′,7′-Di-*tert*-butyl-4′-*trans*-10b′,10c′-dimethyl-10b′,10c′-dihydropyrenyl)acrylic Acid (29).** Ethyl 3-(2′,7′-di-*tert*-butyl-4′-*trans*-10b′,10c′-dimethyl-10b′,10c′-dihydropyrenyl) acrylate[2b] **30** (640 mg, 1.45 mmol) in THF (100 mL) was refluxed with 2 M NaOH (200 mL) for 18 h under argon. The solution was then cooled to room temperature, neutralized with 2 M HCl (200 mL), and extracted with CH_2Cl_2 (300 mL). The combined organic extracts were washed with water, dried, and evaporated to give a green residue, which was chromatographed over deactivated silica gel using 1:1 hexane/CH_2Cl_2 as the eluant. Eluted first was the starting ester **30** (132 mg, 21%). Eluted next with CH_2Cl_2 was the acid **29** as a brownish-green solid (430 mg, 72%), mp 239−241 °C. ^{1}H NMR: δ 9.31 (d, J = 15.5 Hz, 1H, H-3), 8.94 (s, 1H, H-3′), 8.74 (s, 1H, H-5′), 8.52 (s, 1H, H-6′), 8.50 (s, 1H, H-1′), 8.48 (s, 1H, H-8′), 8.44 (AB, J = 7.95 Hz, 1H, H-9′), 8.40 (AB, J = 7.95 Hz, 1H, H-10′), 6.90 (d, J = 15.5 Hz, 1H, H-2), 1.72 (s, 9H, 2−C(CH_3)$_3$), 1.67 (s, 9H, 7−C(CH_3)$_3$), −3.738 and −3.744 (s, 3H each, 10b′,10c′−CH_3). ^{13}C NMR: δ 173.02 (C-1), 148.41 (C-2′), 146.85 (C-7′), 143.78 (C-3), 139.49 (C-10a′), 137.74 (C-3a′), 137.38 (C-8a′), 136.70 (C-5a′), 125.23 (C-9′), 124.47 (C-4′), 124.18 (C-10′), 122.82 (C-8′), 122.19 (C-6′), 121.85 (C-1′), 119.97 (C-5′), 116.08 (C-3′,C-2), 36.72 (2′−*C*(CH_3)$_3$), 36.14 (7′−*C*(CH_3)$_3$), 32.10 and 31.99 (2′,7′−C(*C*H_3)$_3$), 31.86 (C-10b′), 30.12 (C-10c′), 15.66 and 15.57 (10b′,10c′−CH_3). IR (KBr) ν (cm^{-1}): ∼3400−2400 (vbr), 1681, 1599, 1298, 1202, 971, 885, 673. UV (methanol) λ_{max} [nm] (ϵ_{max}): 284 (9900), 356 (35 700), 396 (40 200), 492 (8700), 612 (440), 672 (1800). EI MS: *m*/*z* 414 (M^+). HRMS: calcd for $C_{29}H_{34}O_2$, 414.2559; found, 414.2556.

Improved Method for 2,7-Di-*tert*-butyl-*trans*-11c,11d-dimethyl-11c,11d-dihydro-9-oxo-9*H*-cyclopenta[*e*]pyrene (5). Oxalyl chloride (0.8 mL, 9 mmol) was added to the acid **29** (350 mg, 0.84 mmol) in dry dichloromethane (100 mL) under argon. The resulting solution was stirred at room temperature for 6 h, after which the solvent was removed under vacuum and the green residue evacuated for 1.5 h to get rid of the excess chlorinating reagent. The brown solid was then taken up in dry dichloromethane (200 mL), and BF_3·OEt_2 (0.3 mL, 2.4 mmol) was added to the mixture under argon. The solution was stirred at room temperature for an additional 12 h. Next, ice water was added, and the aqueous layer was extracted with dichloromethane. The combined organic extracts were washed with water, dried, and evaporated to give a reddish-brown solid, which was chromatographed on deactivated silica gel

with 1:1 hexane/CH_2Cl_2 to yield 266 mg (80%) of cyclopentadienone **5** as a green solid, mp ~210 °C (dec), with identical properties to the previously obtained sample.[4] Additional spectral information: ^{1}H NMR ($CDCl_3$; C_6D_6 values in parentheses): δ 8.91 (9.61) (d, J = 1.3 Hz, 1H, H-8), 8.07 (7.695) (d, J = 5.7 Hz, 1H, H-11), 7.74 (7.76) (s, 1H, H-1), 7.68 (7.70) (s, 1H, H-6), 7.671 (7.69) (s, 1H, H-3), 7.665 (7.57) (AB, J = 8.8 Hz, 1H, H-4), 7.63 (7.53) (AB, J = 8.8 Hz, 1H, H-5), 6.18 (6.24) (d, J = 5.7 Hz, 1H, H-10), 1.51 (1.42) (s, 9H, 7−C$(CH_3)_3$), 1.49 (1.40) (s, 9H, 2−C$(CH_3)_3$), −1.88 (−1.86) (s, 3H, 11d−CH_3), −1.92 (−1.91) (s, 3H, 11c−CH_3). ^{13}C NMR ($CDCl_3$; C_6D_6 values in parentheses): δ 197.34 (196.63) (C-9), 154.86 (154.45) (C-7), 148.9 (148.43) (C-2), 144.85 (144.93) (C-11), 142.95 (142.59) (C-5a), 142.66 (142.59) (C-11e), 139.95 (140.19) (C-3a), 133.02 (132.98) (C-11b), 132.07 (132.82) (C-10), 131.73 (132.39) (C-11a), 127.53 (127.66) (C-4), 126.24 (126.66) (C-5), 123.66 (123.82) (C-3), 122.29 (122.75) (C-6), 121.23 (122.27) (C-11f), 116.17 (117.43) (C-8), 114.89 (115.56) (C-1), 36.97 (36.96) (C-11d), 36.52 (36.68) (C-11c), 36.46 (36.62) (7−*C*$(CH_3)_3$), 35.95 (36.07) (2−*C*$(CH_3)_3$), 30.97 (31.19) and 30.96 (31.17) (2,7−C(*C*$H_3)_3$), 21.54 (21.34) (11d−CH_3), 20.39 (20.18) (11c−CH_3). IR: see ref 9. UV−vis (cyclohexane) λ_{max} [nm] (ϵ_{max}): 236 (10 000), 310 (45 100), 398 (31 400), 416 (28 100), 566 (1000), 620 (1200), 687 (1400). MS: see ref 9. Anal. Calcd for $C_{29}H_{32}O$: C, 87.83; H, 8.13. Found: C, 87.96; H, 8.09. The X-ray structure of **5** is given in the Supporting Information.

Crystallographic Experimental Procedures. Crystals of compound **5** (compound **4**) were removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was selected, mounted on a MiTeGen fiber (glass fiber for **4**), and placed in the low-temperature nitrogen stream.[33] Data for both compounds were collected at ~89(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low-temperature device. Data were measured using ω scans of 0.3° per frame for 40 s (60 s for **4**), and a full sphere of data was collected. A total of 2400 frames were collected, with a final resolution of 0.83 Å for both compounds. The first 50 frames were recollected at the end of data collection to check for decay. Cell parameters were retrieved using SMART[34] software and refined using SAINTPlus[35] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus[35] software. Both structures were solved by direct methods and refined by the least-squares method on F^2 using the SHELXTL[36] program package. The data for compound **3** were rotationally twinned with three components and were deconvoluted using CELL_NOW,[37] giving (1) a 10.5° rotation from the first domain about the reciprocal axis 1.000 −0.498 0.479 (real axis −0.336 1.000 −0.070) and (2) a 4.1° rotation from the first domain about the reciprocal axis 1.000 −0.003 0.015 (real axis 1.000 0.032 0.025), with twinning ratios of 0.053(2) and 0.037(1) respectively. Absorption corrections were applied using TWINABS.[38] The structure was solved in the space group $P2_1/c$ (No. 14) by analysis of systematic absences. There is disorder in the central atoms C26−C29 as well as the ketone O1. The occupancies of these disordered sites were refined as 69 and 91%, respectively, for the major disordered fraction. The structure of compound **4** was solved in the space group $P\bar{1}$ (No. 2) by analysis of systematic absences. Absorption corrections were applied using SADABS.[39] The central atoms C18−C21 were disordered above and below the molecular plane with refined occupancies of 80:20%. The ketone was disordered with a 91:9% refined occupancy. All of the non-hydrogen atoms were refined anisotropically in both **5** and **4**. No decomposition was observed during data collection. Details of the data collection and refinement are given in tables and CIF in the Supporting Information.

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Supporting Information Available: General experimental conditions; numbering system for proton and carbon NMR spectra and copies of experimental spectra; X-ray structure data and CIF for **4** and **5**; the complete set of NICS values for the compounds in Table 4; calculated energies and Cartesian coordinates for all of the optimized structures (**4**−**8**, **10**, **17**−**19**, **22**, **25**, **33**, **35**−**38**, **40**); and complete ref 27. This material is available free of charge via the Internet at http://pubs.acs.org.

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