JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
pubs.acs.org/JACS

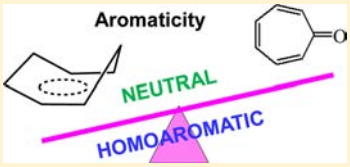
Experimental Verification of the Homoaromaticity of 1,3,5-Cycloheptatriene and Evaluation of the Aromaticity of Tropone and the Tropylium Cation by Use of the Dimethyldihydropyrene Probe

Richard Vaughan Williams,*[,†] W. Daniel Edwards,[†] Pengrong Zhang,[‡] David J. Berg,[‡] and Reginald H. Mitchell*[,‡]

[†] Department of Chemistry, University of Idaho, Post Office Box 442343, Moscow, Idaho 83844-2343, United States
[‡] Department of Chemistry, University of Victoria, Post Office Box 3065, Victoria, British Columbia V8W 3V6, Canada

Supporting Information

ABSTRACT: By use of a dimethyldihydropyrene experimental probe for aromaticity, 1,3,5-cycloheptatriene (**16**) is demonstrated to be a neutral homoaromatic hydrocarbon! On the basis of ^{1}H NMR results, **16** is judged to be ∼30%, tropone **18** ∼20%, and tropylium **22** ∼50% as aromatic as benzene. The latter result may be an underestimation because of charge delocalization. The B3LYP/6-31G* calculated geometries and GIAO-HF/6-31G*//B3LYP/6-31G* calculated NMR chemical shifts and nucleus-independent chemical shifts (NICS) support these conclusions. These estimates were obtained by synthesis of the annelated dihydropyrenes **7** (tropone fused), **9** (1,3,5-cycloheptatriene fused), and **10** (tropylium fused). [4 + 3] Cycloaddition of the isofuran **5** with an oxyallyl cation (prepared from 2,4-dibromopentan-3-one) gave the C7 fused dihydropyrene **6** in 77% yield. Elimination of water gave tropone **7** in 61% yield, which, via $LiAlH_4$ reduction to alcohol **8** (48% yield) and treatment with HBF_4, gave quantitatively tropylium cation **10**. When ketone **7** was reduced with AlH_3 (generated from $AlCl_3/LiAlH_4$) in ether/benzene at 25 °C, the isomeric cycloheptatrienes **11** (70% yield) and **9** (15% yield) were obtained.

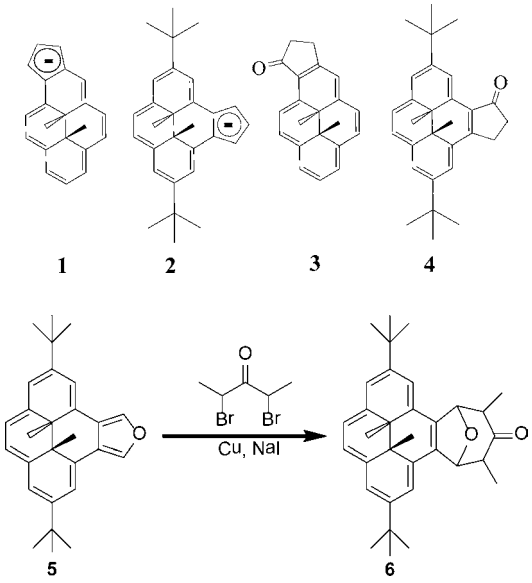


INTRODUCTION

Cyclopentadienide anion and tropylium cation are the archetype *non*-benzenoid 6π electron species considered to be "strongly aromatic" and are found in many textbook discussions of aromaticity.[1] Tropone is considered to be weakly aromatic or nonaromatic,[2] while 1,3,5-cycloheptatriene is calculated to be homoaromatic.[3] For several decades, we have used the dimethyldihydropyrene probe to *experimentally* compare relative aromaticities for a variety of aromatic species to that of benzene.[4] Cyclopentadienide anion was one of the first systems we studied,[5] and it was found to have about 50% of the bond-localizing ability of benzene. We equate the latter to "relative aromaticity"[6] in comparisons of different systems. Despite our early success with the C5 system, synthesis of suitably substituted C7-fused dihydropyrenes (DHPs) evaded us until recently. However, results for tropylium cation, tropone, and 1,3,5-cycloheptatriene are now available, and the C5/C7 comparison can be made. This paper describes our results.

SYNTHESES

The cyclopentadienide fused dihydropyrenes **1** and **2** were synthesized from the cyclopentanones **3** and **4**, respectively.[5,7] However, all attempts to use procedures starting with the corresponding cycloheptanones failed to yield tropylium or tropone fused DHPs. Klein's modification of the Hoffman procedure[8] of reacting a furan with an oxyallyl cation (prepared from 2,4-dibromopentan-3-one) in a [4 + 3] cycloaddition looked suitably mild for the DHP nucleus to withstand, and indeed reaction of the isofuran **5**[9] with 2,4-dibromopentan-3-one in situ with copper powder and NaI at room temperature for 24 h yielded 77% of the adduct **6** as a mixture of two diastereomers (each as a pair of enantiomers).



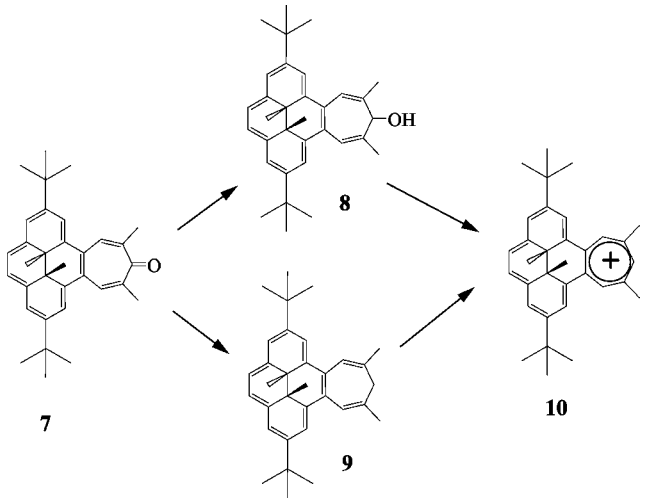
For characterization, these could be separated by chromatography on neutral alumina as **6a** and **6b** (2:3; less/more polar) in

Received: July 13, 2012
Published: September 21, 2012

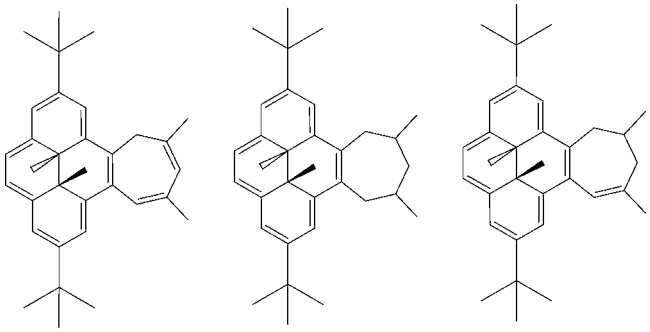
dx.doi.org/10.1021/ja306868r | J. Am. Chem. Soc. 2012, 134, 16742−16752

which the internal methyl protons appear at δ −3.62 and −3.84 for **6a** and at δ −3.75 and −3.78 for **6b**. The $^3J_{H-H}$ values for H_a and H_b were used to make the assignment and were found to be 0 and 4.7 Hz in **6a** and **6b**, respectively, consistent with model (Karplus) calculations (0 and 3.8 Hz). As well, an X-ray structure for **6b** was obtained (see Supporting Information). For synthetic purposes, the mixed isomers of **6**, upon elimination of water by use of *t*-BuOK in *t*-BuOH at 60 °C, gave 61% of the dark red tropone **7**. The structure was confirmed by high-resolution mass spectrometry (HRMS), elemental analysis, and an X-ray structure (see Supporting Information). The NMR spectra are discussed below. The conversion of tropone **7** to tropylium cation **10** could in theory proceed via the alcohol **8**, by loss of hydroxide or equivalent, or via triene **9**, by hydride abstraction (Scheme 1).

Scheme 1



In practice, the route through the alcohol **8** worked much better: reduction of tropone **7** with lithium aluminum hydride ($LiAlH_4$, LAH) in dry ether at 20 °C gave (some decomposition occurred during workup) 45% of alcohol **8** (IR at 3500 cm^{-1} and correct HRMS). Addition of 48% aqueous tetrafluoroboric acid to deuterated tetrahydrofuran (THF), benzene, chloroform, or acetone immediately and quantitatively gave a purple solution of the cation **10**·BF_4 in the respective solvent. The internal methyl protons of **8** at δ −3.24 and −3.21 were completely replaced by those of **10** at δ −2.62 (benzene-d_6). The spectra are fully discussed later. In the alternate route, ketone **7** was reduced with AlH_3 (generated from $AlCl_3/LiAlH_4$) in ether/benzene at 25 °C and gave a 70% yield of the 13*H*-isomer **11** and 15% of the 11*H*-isomer **9**. The major isomer **11** showed two internal methyl proton peaks at δ −3.65 and −3.89, while the higher symmetry minor isomer **9** showed only one at δ −3.32. Full characterization is given in the Experimental Section, and NMR details are discussed later. An X-ray structure of **9** is reported in the Supporting Information.

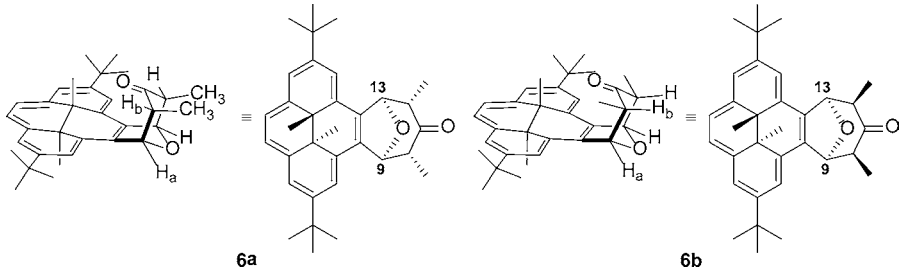


11 **12** **13**

Reaction of trityl cation (as the PF_6^- salt) with the "triene" **11** in toluene-d_8 at 20 °C in an NMR tube indicated that a very small amount of cation **10** was obtained but not in a synthetically useful yield. For model purposes, triene **11** was reduced with hydrogen over prereduced PtO_2 catalyst in ethyl acetate to yield (100% conversion) the products **12** and **13** in a 7:3 ratio (which depends upon the amount of hydrogen used). Each was obtained as a mixture of possibly three diastereomers, which were not necessary to separate for NMR model purposes. There is probably one isomer (C_1 symmetry) with two methyl peaks and two isomers (C_2 symmetry) with one peak each in equal amounts. The internal methyl protons of the major isomer of **12** were at δ −3.97 and −4.03 and for the minor isomer δ −3.98 and −3.99, which were in a 5:1 ratio and thus could easily be seen. The average = δ −4.00. Those for **13** (4:1 ratio) were at δ −3.83 and −3.90 (major isomer) and at δ −3.85 and −3.88 (minor isomer), with the average being δ −3.87.

COMPUTATIONAL STUDIES

We have previously shown that a wide variety of dihydropyrenes can be successfully modeled by use of B3LYP/6-31G* density functional theory. Using this level of theory, we have calculated structural and NMR data and relative aromaticities in excellent accord with the corresponding experimental data.[4c,d,10] On the basis of these calculations, we predicted synthetic targets, which proved to be highly effective photoswitches.[11] These successful studies justify our continued use of these methods. All structures reported in this study were fully optimized by the B3LYP/6-31G* method as implemented in the Gaussian 03 and 09 suite of programs.[12] All optimized geometries were confirmed to be minima (zero imaginary frequencies) through their calculated energy second derivatives. Nucleus-independent chemical shifts (NICS) were calculated using the Hartree−Fock (HF) gauge-independent atomic orbital (GIAO) method on the B3LYP/6-31G* optimized geometry (GIAO-HF/6-31G*//B3LYP/6-31G*)[13] and the ^{1}H (GIAO-HF/6-31G*//B3LYP/6-31G*)

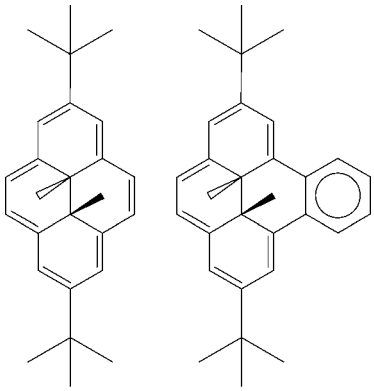


dx.doi.org/10.1021/ja306868r | J. Am. Chem. Soc. 2012, 134, 16742−16752

and ^{13}C (scaled[14] from GIAO-B3LYP/6-31G*//B3LYP/6-31G*) NMR chemical shifts were also calculated at the optimized B3LYP/6-31G* geometries.

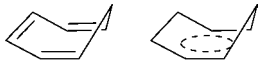
"AROMATICITY" DATA BASED UPON ^1H NMR SPECTRA

To estimate relative aromaticities, the two model compounds **14** and **15** are used.[4] Essentially, [e]-annelation of **14** with a benzene ring, as in **15**, reduces the aromatic ring current flowing in the 14-π ring of **14**, as indicated by the chemical shift of the internal methyl protons, δ −4.06 in **14** but δ −1.58 in **15.** The "relative aromaticity to benzene" for any other annelating ring can then be estimated by comparison of the change in shift from **14** for that fused ring to that caused by benzene (2.48 ppm).



14 **15**

Cycloheptatriene. Homoaromaticity, the observation of aromatic properties in compounds in which the cyclic electron delocalization is interrupted by saturated unit(s), is well established for charged systems but remains elusive in neutral compounds.[15] It is only recently that the first experimental characterization of homoaromaticity in a neutral carbocycle (semibullvalene) was reported.[16] The proposal that 1,3,5-cycloheptatriene **16** (monohomobenzene, tropilidene, or tropilidine) is homoaromatic predates the formal recognition and naming of this concept.[17−20] Early studies, including one by Williams et al.[21] indicated that **16** was not homoaromatic. However, by 2001,[15] the topic of its homoaromaticity or otherwise was still controversial, but one of us concluded "cycloheptatriene enjoys very weak homoaromatic stabilization which can easily be overwhelmed by other factors".[15] More recently the situation has clarified; computational studies by Chen and Schleyer and co-workers[3a] confirmed the weak homoaromaticity of cycloheptatriene, as did the induced current density calculations of Sundholm and co-workers.[3b] Until now, there has been no unequivocal experimental determination of the homoaromaticity of **16**.[3a,15,21]



16

Comparison of the ^1H NMR chemical shifts (Table 1) of parent DHP **14** with those of benzo-DHP **15** clearly shows that upon benzannelation the external protons are moved upfield (H-4 the most) and the internal methyl protons are shifted downfield, both caused by reduction in the DHP ring current.[4] However, conjugation through a σ bond can also cause a small reduction in the ring current of the DHP, for example, in phenyl-substituted dihydropyrenes.[22] Unlike in the case of **14** versus **15**, where the change in chemical shift is large, when small changes are observed, more care is required in attributing the change to any aromaticity of the annelating group.

Examination of the data in Table 1 for the internal methyl protons indicates large reductions in the ring current for benzo-DHP **15** and for the cation **10** but much smaller ones for the tropone **7** and trienes **9** and **11** relative to the "nonaromatic" models **12** and **13**. Comparison of the chemical shifts for H-4, which is farthest removed from the site of annelation and is least subject to through-space anisotropy effects, likewise indicates a small shielding from **14** for compounds **7**, **9**, and **11** relative to that observed for **12** and **13**. Nevertheless such small changes are "on the edge" for reliable aromaticity estimates.[4a] If the chemical shifts are taken at face value, then an estimate of the relative aromaticity of cycloheptatriene with respect to benzene can be made by comparing the change in chemical shift of the internal methyl protons on going from parent **14** to cycloheptatriene-annelated derivatives **9** (−4.06 to −3.32 = 0.74 ppm) and **11** [−4.06 to (−3.65 − 3.89)/2 = 0.29 ppm] with the change caused by benzene, that is, upon going from parent **14** to benz-annelated derivative **15** (−4.06 to −1.58 = 2.48 ppm). Thus the ratios, (0.74/2.48) × 100 = 30% and (0.29/2.48) × 100 = 12%, respectively, represent the homoaromaticity of cycloheptatriene relative to that of benzene.[4] If data for the external proton H-4 are used, then the relative aromaticities are found to be 35% and 17%, respectively, in excellent agreement with the values obtained from the internal methyl changes in chemical shift. In principle, the same values should be obtained for either isomeric triene **9** or **11**, assuming that no other factors come into play. We will discuss this difference after we have discussed the relevant calculated structures below, since unfortunately we were not able to obtain X-ray quality crystals for **11**, but we could for **9** (Figure 1). Full X-ray data for **9** are given in the Supporting Information, and bond lengths are shown in Table 2 below.

The DHP periphery is planar, and the C−C bond lengths average 1.398 Å. However, there is some bond alternation, with the sum of the modulus of deviation from the average bond length being 0.361 Å (14 carbons of DHP), which is substantially greater than the 0.069 Å found for **14** but less than that found (0.539 Å) for benzo-DHP **15**. Traditionally, when an aromatic system is annelated on to DHP, bond localization of the DHP ring is caused in proportion to the aromaticity of the annelating ring.[4a] The results for **9** certainly indicate that cycloheptatriene has a significant localizing effect, which we equate with "homoaromaticity".

Calculations. Given that the highest symmetry expected for any of the [e]-cyclohept-annelated dihydropyrenes is C_2, we began modeling the triene **9** by annelating the di-^{t}Bu-dihydropyrene **14**, which itself was optimized in rigorously C_2 symmetry (**14**:C_2). The resulting optimized geometry, of C_1 symmetry, gave NMR and bond length data in poorer agreement with the corresponding experimental data than we normally find when modeling dihydropyrenes at this level of theory (Table 2 and Table S1a,b in Supporting Information).[10,11] We therefore decided to consider different starting geometries of **9** for optimization. Careful examination of the optimized geometry of **14**:C_2 revealed that the two potential [e]-annelation sites have slightly different bond lengths (1.4067 and 1.3927 Å). The triene (**9**:C_2) above was formed by annelation on to the slightly longer side. Annelation on to the shorter side of **14**:C_2 and subsequent optimization gave a structure, **9**:C_2', of C_1 symmetry. Similarly, annelation and optimization of **14**:C_i gave a C_1 optimized

dx.doi.org/10.1021/ja306868r | J. Am. Chem. Soc. 2012, 134, 16742−16752

Table 1. Relevant ^{1}H NMR Shifts for Compounds in This Study

	shift (ppm, $CDCl_3$)							
proton	**7**	**9**	**10**	**11**	**12**	**13**	**14**[4c]	**15**[4c]
1	9.16	8.59	9.60	8.80	8.72	8.60	8.58	8.28
3	8.41	8.16	8.45	8.36	8.43	8.43	8.58	7.35
4	8.26	8.00	8.23	8.24	8.34	8.31	8.46	7.13
9	9.27	7.46	10.45	8.27				
11			8.81	5.91				
int-Me	−3.56	−3.32	−2.79	−3.65/−3.89	−4.00	−3.87	−4.06	−1.58

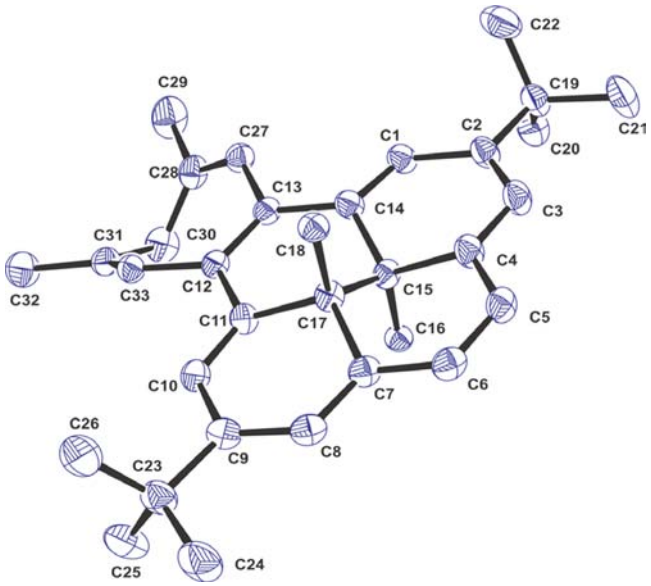


Figure 1. ORTEP3 drawing (50% probability level) of triene **9**.

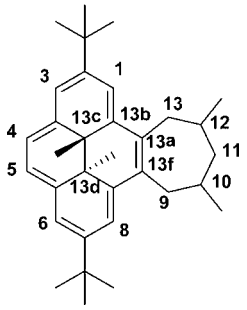
geometry (**9**:C_i) and optimization of the experimental X-ray geometry led to a C_1 fully optimized structure (**9**:X) essentially identical to **9**:C_2'. **9**:C_2' and **9**:X give the best match with the experimental NMR chemical shifts and bond lengths (Table 2 and Table S1a,b in Supporting Information). **9**:C_i is in better agreement with the experimental data than **9**:C_2 but worse than **9**:C_2'/**9**:X (Table 2 and Table S1a,b in Supporting Information). The optimized geometries were subjected to the stability test (keyword Stable) as instituted in the Gaussian suite of programs, and in each case the wave functions were found to be stable. The three calculated geometries **9**:C_2'/**9**:X, **9**:C_i, and **9**:C_2 are almost degenerate (all energies within <1 kcal/mol range) at the B3LYP/6-31G* level of theory. We did not carry out an exhaustive search for all local minima of **9** and fully expect that other minima exist for **9**. The abundance of calculated structures and their near degeneracy suggest that single-determinate methods, as used here, may not be ideal for modeling **9**. Unfortunately, such highly conjugated molecules are far too large for the feasible use of multiconfiguration self-consistent field (MCSCF) methods. The very good agreement of the **9**:C_2' data with the corresponding experimental quantities strongly supports the use of this geometry for the remainder of our study.

The starting geometry for **11** was generated by annelating on to the shorter side of **14**:C_2 and that for **13** by in silico "hydrogenation" of **9**:C_2'. The optimized structure for **11** (**11**:C_2') gave calculated NMR shifts in good agreement with experiment (Table S2a,b in Supporting Information). Comparison of experimental and calculated chemical shifts for **13** is not possible because it is isolated as a mixture of diastereomers, from which assignment of chemical shifts is not possible.

In an extensive study correlating experimentally determined aromaticities of the dimethyldihydropyrene nucleus (DDPN) in a range of derivatives, we demonstrated that the use of $NICS_{avg}$ (average of the NICS values calculated at the centroids of the four six-membered rings constituting the DDPN) provided the best calculated determination of the dihydropyrene aromaticity.[4c] As already mentioned, as a consequence of the aromaticity of the annelating ring, the "aromaticity" of the DPPN is reduced. This reduction in DPPN aromaticity is manifested in an increase in $NICS_{avg}$ (more positive). The larger the increase in $NICS_{avg}$, the greater the aromaticity of the annelating ring. $NICS_{Ann7}$ is the NICS value at the centroid of C9, C10, C12, C13, C13a, and C13f (the homobenzene moiety) for **9** and **13** and C9, C10, C11, C12, C13a, and C13f for **11** of the seven-membered annelating ring. The NICS values, reported in Table 3, clearly demonstrate the homoaromaticity of the cycloheptatriene moiety of **9**. The issue of choosing an appropriate nonaromatic model, one in which all effects (charge, strain, local anisotropies, conformational changes, etc.) other than the aromaticity of the annelating group are present, is always a challenge. Frequently, the computational "hydrogenation" of one of the double bonds of the annelating group to yield a dihydro derivative gives the best model.[4d] Compared with the parent di-^{t}Bu-DHP **14** ($NICS_{avg}$ −18.65), the aromaticity of the DDPN of benzoannelated **15** is significantly quenched ($NICS_{avg}$ −4.64) while that of the annelating benzene ring is little affected (NICS −10.80 compared with −11.5[13a] for benzene itself). It is entirely reasonable to attribute the majority, if not all, of this quenching to the aromaticity of the annelating benzene ring, as in silico "hydrogenation" of one of the benzene's double bonds to give **17** results in very little quenching of the DDPN aromaticity ($NICS_{avg}$ −16.06). A comparison of **9** and its dihydro derivative **13** reveals that the aromaticity of the DDPN in **9** is noticeably reduced compared to that in **13** ($NICS_{avg}$ −11.08 versus −14.65). $NICS_{Ann7}$ is almost the same in both **9** and **13** and appreciably more positive than for parent 1,3,5-cycloheptatriene **16**, indicating nearly complete quenching of the homoaromaticity of the cycloheptatriene moiety in **9**. A computational assessment of the relative homoaromaticity of cycloheptatriene **16** relative to the aromaticity of benzene can be gained by considering the change in $NICS_{avg}$ in going from cycloheptoannelated **9** to the dihydro model **13** (3.81) and the corresponding difference for the benzo series **15** and **17** (11.42) to give a relative homoaromaticity of 3.81/11.42 × 100 = 33%, which is in remarkably good agreement with the experimental value (30%) determined from ^{1}H NMR chemical shifts. In complete agreement with the experimental data, it is immediately apparent from Table 3 that the isomeric cycloheptoannelated **11** presents a less homoaromatic cycloheptatriene unit than in **9**. By the same approach as above, the relative

dx.doi.org/10.1021/ja306868r | J. Am. Chem. Soc. 2012, 134, 16742−16752

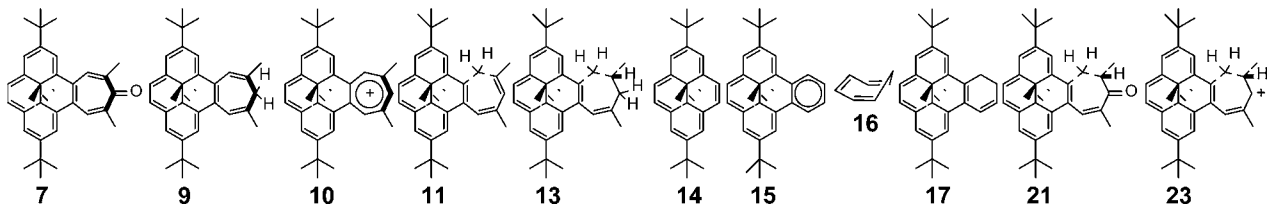
Table 2. Comparison of Selected Experimental and Calculated Bond Lengths of 9



	length (Å)								
bond	9exp	9:C_2'	9:X	9:C_i	9:C_2	Δ9 :C_2' [a]	Δ9:X[a]	Δ9:C_i[a]	Δ9:C_2[a]
C1−C2	1.436	1.4262	1.4262	1.4163	1.4095	−0.0098	−0.0098	−0.0197	−0.0265
C2−C3	1.3722	1.3904	1.3904	1.3995	1.4062	0.0182	0.0182	0.0273	0.034
C3−C3a	1.4057	1.4071	1.407	1.398	1.3918	0.0014	0.0013	−0.0077	−0.0139
C3a−C4	1.3731	1.3887	1.3887	1.3952	1.4016	0.0156	0.0156	0.0221	0.0285
C4−C5	1.4034	1.4117	1.4116	1.4051	1.3979	0.0083	0.0082	0.0017	−0.0055
C5−C5a	1.372	1.3886	1.3886	1.3941	1.4015	0.0166	0.0166	0.0221	0.0295
C5a−C6	1.3977	1.4077	1.4077	1.4019	1.3924	0.01	0.01	0.0042	−0.0053
C6−C7	1.3743	1.3892	1.3893	1.3947	1.4047	0.0149	0.015	0.0204	0.0304
C7−C8	1.4332	1.428	1.428	1.4218	1.4112	−0.0052	−0.0052	−0.0114	−0.022
C8−C8a	1.3605	1.3796	1.3797	1.3846	1.3937	0.0191	0.0192	0.0241	0.0332
C8a−C13f	1.4432	1.442	1.442	1.4361	1.4281	−0.0012	−0.0012	−0.0071	−0.0151
C13f−C13a	1.4012	1.4227	1.4227	1.4288	1.4358	0.0215	0.0215	0.0276	0.0346
C13a−C13b	1.4455	1.4383	1.4383	1.4306	1.4233	−0.0072	−0.0072	−0.0149	−0.0222
C13b-C1	1.3571	1.3827	1.3827	1.3909	1.3969	0.0256	0.0256	0.0338	0.0398
C13f−C9	1.4677	1.4666	1.4666	1.467	1.4683	−0.0011	−0.0011	−0.0007	0.0006
C9−C10	1.3364	1.3491	1.3491	1.3489	1.3484	0.0127	0.0127	0.0125	0.012
C10−C11	1.5011	1.5138	1.5139	1.5142	1.5146	0.0127	0.0128	0.0131	0.0135
C11−C12	1.4984	1.5155	1.5156	1.5159	1.5162	0.0171	0.0172	0.0175	0.0178
C12−C13	1.3319	1.3464	1.3464	1.3459	1.3455	0.0145	0.0145	0.014	0.0136
C13−C13a	1.4706	1.4706	1.4706	1.4721	1.4732	0.0000	0.0000	0.0015	0.0026
per-avg[b]	1.3982	1.4074	1.4074	1.4070	1.4068				
Σ(dev)[c]		0.250	0.250	0.198	0.148				
Σ(dev)[d]	0.361	0.268	0.268	0.186	0.157				

[a]Calculated bond length − experimental bond length. [b]Average bond length of DHP periphery. [c]Sum of the modulus of deviation from the appropriate calculated periphery average. [d]Sum of the modulus of deviation from the periphery experimental average.

Table 3. NICS Values for 7, 9, 11, and 13−17

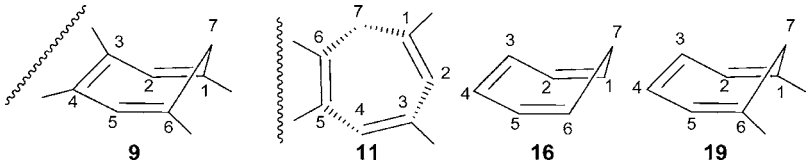


	7:C_2'	9:C_2'	10:C_2'	11:C_2'	13:C_2'	14:C_2[a]	15:C_2' [b]	16	17:C_2'	21:C_2'	23:C_2'
$NICS_{avg}$	−11.90	−11.08	−8.57	−12.96	−14.89	−18.65	−4.64		−16.06	−14.67	−3.25
$NICS_{Ann7}$		−1.19		−1.83	−1.25			−5.69[c]			
$NICS_{Ann6}$							−10.80[d]				

[a]From ref 4c. [b]These values are almost the same as those reported in ref 4c (−4.64 and −10.78) for **15**:C_2. [c]NICS value at the centroid of the six carbon atoms constituting the homobenzene portion of 1,3,5-cycloheptatriene (compare with ref 38, which reports a NICS value of −4.2 at the centroid of the complete 7-membered ring, and see also ref 3a). For comparison, the GIAO-HF/6-31G*//B3LYP/6-31G* NICS value for benzene is −11.5 (ref 13a). [d]NICS value at the centroid of the annelating benzene ring.

homoaromaticity of the cycloheptatriene in **11** is 1.73/11.42 × 100 = 15%, again in good agreement with the experimental value (12%). As already noted, one might expect the relative homoaromaticities of the cycloheptatriene in **9** and **11** to be the same. It is interesting to note that Ohkita et al.[23] observed a similar variation in NICS values depending upon the site of aryl fusion to tropone **18** (vide infra). It is apparent from the optimized structures of **9**:C_2' and **11**:C_2' that the cyclo-

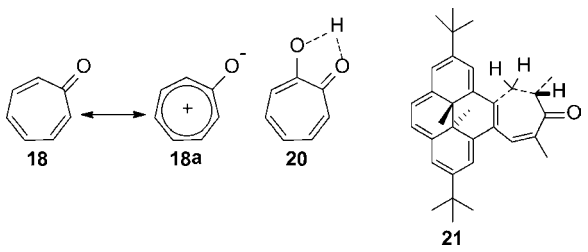
Table 4. Comparison of Selected Calculated Bond Lengths, Bond Angles, and Dihedral Angles of 9, 11, 16, and 19



	bond lengths (Å)					bond angles (deg)		dihedral angles (deg)	
	r_{1-2} (r_{5-6})	r_{1-7} (r_{6-7})	r_{2-3} (r_{4-5})	r_{3-4}	r_{1-6}	θ_{123} (θ_{654})	θ_{217} (θ_{567})	ϕ_{1256}	ϕ_{1234} (ϕ_{3456})
9	1.3464	1.5155	1.4706	1.4227	2.4446	126.99	119.43	1.19	−42.01
	(1.3491)	(1.5139)	(1.4666)			(127.64)	(120.10)		(35.42)
11	1.3496	1.5137	1.4570	1.3652	2.4775	124.43	118.66	−2.22	−34.24
	(1.4148)	(1.5165)	(1.4632)			(121.32)	(116.45)		(36.61)
16	1.3512	1.5094	1.3655	1.3655	2.4467	125.43	121.92	0.00	−30.52
19	1.3547	1.5154	1.4459	1.3657	2.4722	125.68	119.34	0.00	−30.44

heptatrienyl moieties in **9** and **11** are somewhat distorted compared with geometries of the parents **16** and **19** (Table 4). The C_s symmetry of **16** and **19** ensures that in these species $r_{1-2} = r_{5-6}$, $r_{1-7} = r_{6-7}$, $\theta_{123} = \theta_{654}$, $\theta_{217} = \theta_{567}$, $\phi_{1256} = 0.00$, and $\phi_{1234} = -\phi_{3456}$. The most significant differences between **9** and **11** are the hinge angles at the bow (θ_{217} and θ_{567}) and stern (θ_{123} and θ_{654}), the dihedral angles (ϕ_{1256}, ϕ_{1234}, and ϕ_{3456}) and the homoaromatic "*bond*" length (r_{1-6}). In most cases, **11** departs more than **9** from the corresponding values in **16** and **19**. Surprisingly, these small differences amount to a large difference in the calculated aromaticities of the DPPN in **9** and **11**. The more puckered (smaller hinge angles) and less coplanar (ϕ_{1256}) structure in **11** leads to a weaker homoaromatic interaction, as evidenced by the longer homoaromatic "*bond*" and more negative $NICS_{avg}$.

Tropone. Tropolone (**20**) holds a special place in the history of aromaticity, as it represents one of the first successes of the predictive powers of the Hückel rules.[24] Dewar[25] correctly predicted the structure of stipitatic acid and the partial structure of colchicine based on the anticipated special stability (aromaticity) of the tropolone motif. Similarly, tropone (**18**) was also considered to be aromatic.[2,26,27] The aromaticity of **18** and **20**, mediated through 6π-electron dipolar structures (e.g., **18a**), has been called into question.[2,26−28] The conclusion to be drawn from most recent computational studies is that tropone is moderately aromatic as determined by a wide variety of aromaticity indices.[29−31] However, Ohkita et al.[23] consider tropone itself to enjoy "little resonance stabilization", while aryl fusion at the 3,4-position of the tropone results in enhanced aromaticity of the tropone ring whereas 2,3- and 4,5-fusion diminishes this aromaticity.



By use of the ^{1}H NMR data in Table 1 for the internal methyl protons and H-4 of tropone **7**, parent **14**, and benzo derivative **15**, exactly as above for **9**, the relative aromaticity of tropone is found to be 20% and 15%, respectively, in good agreement with each other and somewhat smaller in magnitude than that found for cycloheptatriene!

An X-ray structure was obtained for the tropone **7** (full data in Supporting Information, bond lengths in Table 5), and an ORTEP3 drawing is shown in Figure 2.

Table 5. Comparison of Selected Experimental and Calculated Bond Lengths of 7

	length (Å)		
bond	7expt	7:C_2'	Δ7:C_2' [a]
C1−C2	1.425	1.4208	−0.0042
C2−C3	1.379	1.3932	0.0142
C3−C3a	1.398	1.4014	0.0034
C3a−C4	1.378	1.3921	0.0141
C4−C5	1.409	1.405	−0.004
C5−C5a	1.374	1.3921	0.0181
C5a−C6	1.402	1.4014	−0.0006
C6−C7	1.378	1.3932	0.0152
C7−C8	1.425	1.4208	−0.0042
C8−C13e	1.373	1.388	0.015
C13e−C13f	1.443	1.4416	−0.0014
C13f−C13a	1.413	1.4332	0.0202
C13a−C13b	1.447	1.4416	−0.0054
C13b−C1	1.377	1.388	0.011
C13f−C9	1.456	1.4471	−0.0089
C9−C10	1.347	1.3628	0.0158
C10−C11	1.472	1.4747	0.0027
C11−C12	1.466	1.4747	0.0087
C12−C13	1.349	1.3628	0.0138
C13−C13a	1.453	1.4471	−0.0059
per-avg [b]	1.4015	1.40803	
Σ(dev) [c]		0.196	
Σ(dev) [d]	0.307	0.217	

[a]Calculated bond length − experimental bond length. [b]Average bond length of DHP periphery. [c]Sum of the modulus of deviation from the appropriate calculated periphery average. [d]Sum of the modulus of deviation from the periphery experimental average.

All the carbons on the DHP framework are close to the mean plane with an average deviation of 0.028 Å. The average C−C distances in the DHP framework are 1.402 Å (Table 5) with the sum of the modulus of bond deviation from average[32] being 0.307 Å, somewhat less than that (0.361 Å) found for the

dx.doi.org/10.1021/ja306868r | J. Am. Chem. Soc. 2012, 134, 16742−16752

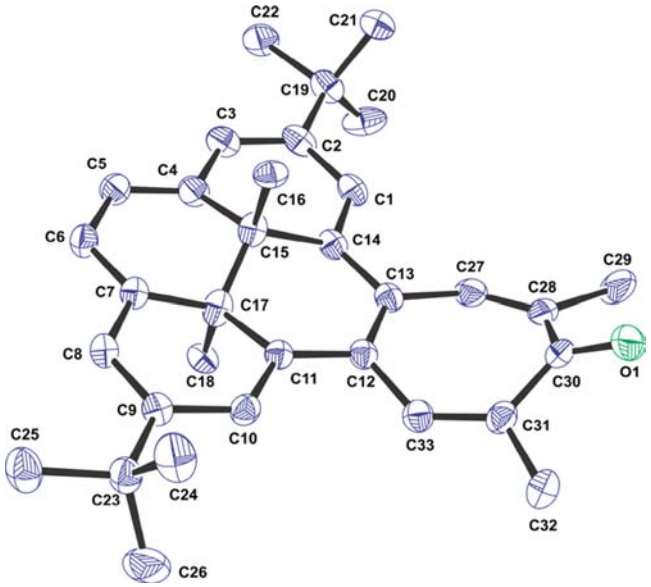


Figure 2. ORTEP3 drawing (50% probability level) of tropone **7**.

cycloheptatriene **9**, which is consistent with the NMR data suggestion that *tropone is less aromatic than cycloheptatriene!*

Calculations. Upon comparison of the calculated and experimental ^{1}H and ^{13}C chemical shifts for **7** (Table S3a,b in Supporting Information), it is once more apparent that annelating on to the shorter side of the parent di-^{t}Bu-dihydropyrene (**14**:C_2) gave the optimized structure **7**:C_2', whose chemical shifts most closely matched the experimental values. (Imposition of C_2 symmetry and reoptimization gave **7**:C_2'S, of similar energy to **7**:C_2' but with ^{1}H chemical shifts that deviate much more from experiment.) As with cycloheptatriene **9**, optimization of the X-ray structure of 7 resulted in a species essentially identical to **7**:C_2'. The NICS values for **7**:C_2' and its dihydro derivative, **21**:C_2' (Table 3), and the corresponding calculated chemical shifts for the internal methyl groups (Table S3a in Supporting Information) support tropone's designation as weakly aromatic. As was done for **16**, the relative aromaticity of **18** can be assessed computationally by considering the change in $NICS_{avg}$ in going from **7** to the dihydro model **21** (2.77) and the corresponding difference for the benzo series **15** and **17** (11.42) to give a relative aromaticity of 2.77/11.42 × 100 = 24%, in good agreement with the experimental value.

Tropylium Cation. Hückel predicted the now long-recognized and well-accepted aromaticity of the tropylium cation **22**.[2,26,27] Unlike for 1,3,5-cycloheptatriene and tropone, where their (homo)aromaticity has been disputed, the aromaticity of the tropylium cation remains unchallenged.[33] However, it is of significant value to locate **22**'s rank on an experimental scale of aromaticity. Despite the long history of the aromaticity of **22**, we are not aware of any experimental determinations of its relative aromaticity.

A comparison of the ^{1}H NMR spectra of cation **10**·BF_4 and alcohol **8** are shown in Figure 3.

Formation of the cation **10** is clearly evident from the downfield shift of all the external aromatic protons. As well, an electrospray mass spectrum at m/z 435 was obtained for **10**·BF_4. The internal methyl protons of **10** appeared at δ −2.62 in benzene-d_6 and −2.79 in $CDCl_3$, with less variation in other solvents (Table 6). A "simple" estimate of the relative aromaticity

Table 6. ^{1}H Chemical Shifts for Selected Protons of Cation 10 in Several Solvents

	shift (ppm)			
proton	acetone-d_6	THF-d_8	$CDCl_3$	benzene-d_6
1	10.06	9.84	9.60	9.78
3	8.79	8.61	8.45	8.10
4	8.54	8.35	8.23	7.62
9	11.00	10.75	10.45	10.50
11	9.17	9.04	8.81	8.30
int-CH_3	−2.74	−2.69	−2.79	−2.62

of the cation with respect to that of benzene can then be made by comparing the change in shift of the internal methyl protons upon going from parent **14** to cation-annelated derivative **10** (−4.06 to −2.79 = 1.27 ppm) with the change caused by benzene, that is, upon going from parent **14** to benz-annelated derivative **15** (−4.06 to −1.58 = 2.48 ppm). Thus the ratio (1.27/2.48) × 100 = 51% represents the aromaticity of the cation relative to that of benzene.[4] This estimate, however, does ignore any effect of charge (see below) and ring annelation on the DHP, but given that the models **12** and **13** have only minor effects, the latter assumption seems reasonable. The effect of charge is less obvious, since charge delocalization over the DHP ring is anticipated. The reduction of charge density on the tropylium ring reduces its incipient aromaticity, but in opposition, the

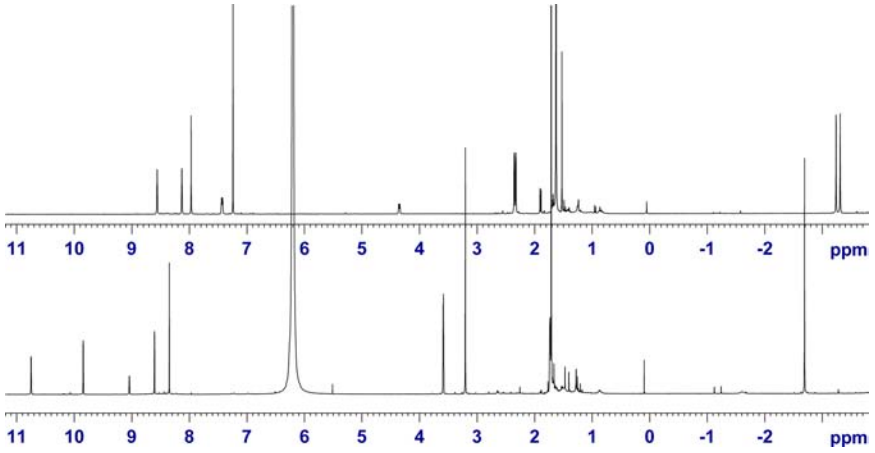


Figure 3. 500 MHz ^{1}H NMR spectra of cation **10**·BF_4 (in THF-d_8, lower spectrum) and alcohol **8** (in $CDCl_3$, upper spectrum).

dx.doi.org/10.1021/ja306868r | *J. Am. Chem. Soc.* 2012, 134, 16742−16752

partial positive charge on the DHP causes ^{1}H downfield shifts in the DDPN. On balance, we expect these factors to result in an underestimation of the aromaticity of the tropylium cation. Our computational results (vide infra) support this conclusion. The DHP ring protons are more affected by the charge than the internal methyl protons as evidenced by the comparison of the relative aromaticities obtained for tropylium via the internal methyl protons (51%) versus H-4 (17%); note that for the neutral systems **7** (20%, 15%), **9** (30%, 35%), and **11** (12%, 16%), the two estimates agreed well with each other. In our analysis[5] of the C5 anion **1**, we concluded that delocalization of the negative charge over the DHP resulted in about 0.07 unit of negative charge per periphery atom, which had only a small effect on the internal methyl protons. The chemical shifts of the relevant protons for **10** are given in Table 6.

If the positive charge were delocalized equally over all 19 periphery carbons, only 0.05 charge unit would be on each carbon, less than in the anion. Comparison of protons 4 and 11 in Table 6 suggests that since H-11 is the more deshielded, more of the charge resides in the C7 ring. In neutral DHPs, we have found a relationship between the chemical shifts of the internal methyl protons and the external H-4,5 protons in $CDCl_3$:[9]

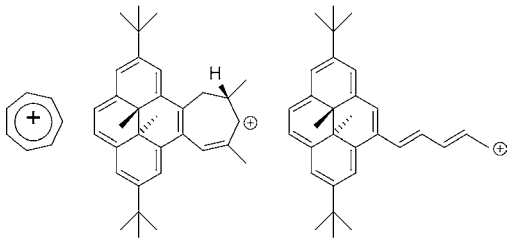
$$\delta(int\text{-Me}) = 13.050 - 2.038d(\text{H-4}) \quad (1)$$

Thus for δ(*int*-Me) −2.79, δ(H-4) is calculated from eq 1 to be 7.77, about 0.46 ppm less deshielded than it is. Since one whole charge deshields about 10.6 ppm,[35] it suggests that about 0.04 unit of charge is causing this, in quite good agreement with slightly more charge residing in the C7 ring than in the DHP. It is interesting that the chemical shift of the internal methyl protons of anion **1** was also about δ −2.8, and so by our NMR method, the Cp anion and the tropylium cation appear to have very similar relative aromaticities.

Calculations. As by now expected, the calculated ^{1}H shifts from the optimized geometry (**10**:C_2') resulting from annelation on to the shorter side of **14**:C_2 are in the best agreement with the experimental shifts (see Table S4 in Supporting Information). The NICS value (Table 3) for cation **10**:C_2' is −8.57, which at first sight seems quite reasonable, as it indicates that the cation is more aromatic than the cycloheptatriene in **9** and the tropone in **7** but less aromatic than benzene in **15**. However, the value found for its dihydro derivative **23**:C_2' (−3.25) instantly gives some concern and reveals that charge delocalization in this case has a very dominant effect. These NICS values would indicate, if only the aromaticity of the annelating group perturbed the DDPN NICS, that the *nonconjugated* dihydro group is *more* aromatic than the tropylium cation! To further confirm the origins of these unusual NICS values, we optimized the geometry of the pentadienyl cation **24**, generated by substituting on to the shorter side of **14**:C_2, and calculated its $NICS_{avg}$ (−5.11). Charge delocalization has once again resulted in a significant positive shift in $NICS_{avg}$ compared with those of **14** and the tropylium cation **10**. Of course, the fact that $NICS_{avg}$ for **10** is more negative than for **23** and **24** indicates that the tropylium cation is aromatic, retaining a much greater charge density on the 7-membered ring than the open chain in **24** or the dihydro moiety in **23**. From the calculated results, the relative aromaticity of the cation cannot be estimated with any certainty.

CONCLUSIONS

The most exciting result is the experimental demonstration that 1,3,5-cycloheptatriene is homoaromatic, based upon ^{1}H NMR results by use of the dimethyldihydropyrene probe. The



22 23 24

proposed (homo)aromaticity of cycloheptatriene (**16**) and tropone (**18**) have been disputed and, in the case of cycloheptatriene, is an area of quite some controversy. Our use of the DHP probe clearly demonstrates that both **16** and **18** are (homo)aromatic. The aromaticity of the tropylium cation **22** is well-accepted and our results fully support its aromaticity. Unfortunately, due to extensive charge delocalization in the DDPN of **23**, a NICS-based estimate of the relative aromaticity of **22** to that of benzene is not feasible. We consider our experimental estimate of the relative aromaticity of the tropylium cation (50%) to be a reasonable, but minimum value.

EXPERIMENTAL SECTION

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

2,7-Di-*tert*-butyl-11-oxo-*cis*-10,12-dimethyl-13c,13d-dimethyl-14-oxabicyclo[3.2.1]oct-13a-eno[13a:13f;*e*]-*trans*-13c,13d-dihydropyrene (6a) and 2,7-Di-*tert*-butyl-11-oxo-*trans*-10,12-dimethyl-13c,13d-dimethyl-14-oxabicyclo[3.2.1]-oct-13a-eno[13a:13f;*e*]-*trans*-13c,13d-dihydropyrene (6b). A solution of 2,4-dibromopentan-3-one[36] (0.10 mL, 1.5 g, 6.0 mmol) in dry acetonitrile (50 mL) was added to a mixture of the isofuran **5**[9] (2.06 g, 5.36 mmol), copper powder (1.27 g, 20.0 mmol), and sodium iodide (5.7 g, 38 mmol) in dry acetonitrile (150 mL) under argon. The purple reaction mixture was stirred overnight at 25 °C under argon, when the color had disappeared. The reaction mixture was then filtered through a Celite pad, and the filtrate was evaporated to give a green solid. This residue was redissolved in ethyl acetate and washed with 28% (concentrated aueous) ammonia solution, water, and aqueous NaCl solution. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under vacuum. The resulting green solid was chromatographed over neutral alumina, with benzene/hexanes (1:1) as eluant. Eluted first was unreacted isofuran **5** (0.32 g, 15% recovery). Eluted second and third were the green products **6a** and **6b** in a ratio of 2:3 from ^{1}H NMR, a total of 1.94 g (77.3% yield).

Adduct **6a** was recrystallized from toluene as green crystals, mp 211−212 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 8.60 (s, 1H, H-3), 8.57 (s, 1H, H-6), 8.45 (d, J = 1.2 Hz, 1H, H-1), 8.43 (d, J = 1.2 Hz, 1H, H-8), 8.41 (AB, J = 8.1 Hz, 1H, H-4), 8.40 (AB, J = 8.1 Hz, 1H, H-5), 6.18 (s, 1H, H-13), 6.16 (s, 1H, H-9), 3.09 (q, J = 7.5 Hz, 1H, H-10), 2.86 (q, J = 7.5 Hz, 1H, H-12), 1.64 (d, 3H, J = 7.4 Hz, 10-CH_3), 1.61 [s, 9H, 2/7-C(CH_3)$_3$], 1.60 (d, J = 7.4 Hz, 3H, 12-CH_3), 1.59 [s, 9H, 2/7-C(CH_3)$_3$], −3.62 (s, 3H, 13c-CH_3), −3.84 (s, 3H, 13d-CH_3). ^{13}C NMR (125 MHz, C_6D_6) δ 212.05 (C-11), 146.55 (C-2/7), 146.37 (C-2/7), 137.59 (C-3a), 137.53 (C-5a), 136.45 (C-13a), 135.88 (C-13f), 128.2 (C-13b,13e) [note: two indistinguishable peaks were beneath the solvent peak; these could be determined from the HMBC spectrum], 124.84 (C-4), 124.57 (C-5), 122.27 (C-6), 122.11 (C-3), 118.06 (C-8), 117.12 (C-1), 83.54 (C-13), 83.20 (C-9), 52.10 (C-10,12), 36.46 [2/7-C(CH$_3$)$_3$], 36.43 [2/7-C(CH$_3$)$_3$], 32.41 (C-13c/13d), 32.37 [2/7-C(CH$_3$)$_3$], 32.35 [2/7-C(CH$_3$)$_3$], 30.30 (C-13c/13d), 19.03 (10-CH$_3$), 18.96 (13-CH$_3$), 15.42 (13c-CH$_3$), 15.07 (13d-CH$_3$). IR (KBr) ν 3041, 2951, 2929, 2904, 2869, 1704, 1602, 1458, 1382, 1359, 1346, 1263, 1195, 1082, 1065, 961, 932, 888, 870, 674 cm^{-1}. UV−vis (cyclohexane) λ_{max}, nm (ε_{max}, L·mol^{-1}·cm^{-1}) 238 (7300), 330 (27 900), 347 (98 500), 361 (29 200, sh), 386 (46 800), 438 (4500, sh), 464 (7600, sh), 483 (10 200), 595 (200), 645 (900, sh), 615 (1100). EI MS m/z 468 (M$^+$). HRMS calcd for $C_{33}H_{40}O_2$, 468.3028; found, 468.3019.

dx.doi.org/10.1021/ja306868r | J. Am. Chem. Soc. 2012, 134, 16742−16752

Adduct **6b** was recrystallized from dichloromethane and methanol as green crystals, mp 203−204 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 8.54 (s, 2H, H-3 and H-6), 8.47 (d, 1H, J = 1.0 Hz, H-1), 8.41 (d, J = 1.0 Hz, 1H, H-8), 8.40 (AB, J = 7.8 Hz, 1H, H-5), 8.38 (AB, J = 7.8 Hz, 1H, H-4), 6.25 (d, J = 4.7 Hz, 1H, H-13), 6.22 (d, J = 4.8 Hz, 1H, H-9), 3.32 (dq, J = 6.8, 4.7 Hz, 1H, H-12), 3.20 (dq, J = 6.8, 4.7 Hz, 1H, H-10), 1.60 [s, 9H, 2/7-C(CH_3)$_3$], 1.59 [s, 9H, 2/7-C(CH_3)$_3$], 1.26 (d, J = 6.7 Hz, 3H, 12-CH_3), 1.10 (d, J = 6.7 Hz, 3H, 10-CH_3), −3.75 (s, 3H, 13d-CH_3), −3.78 (s, 3H, 13c-CH_3). ^{13}C NMR (125 MHz C_6D_6) δ 208.10 (C-11), 146.32 (C-2/7), 145.98 (C-2/7), 137.89 (C-3a), 137.14 (C-5a), 135.22 (C-13f), 134.85 (C-13a), 130.12 (C-13b), 129.58 (C-13e), 124.76 (C-4/5), 124.69 (C-4/5), 122.04 (C-3), 121.64 (C-6), 119.71 (C-1), 118.78 (C-8), 84.57 (C-9), 83.66 (C-13), 54.08 (C-12), 52.81 (C-10), 36.46 [2/7-C(CH_3)$_3$], 36.41 [2/7-C(CH_3)$_3$], 32.32 [2/7-C(CH_3)$_3$], 32.28 [2/7-C(CH_3)$_3$], 32.24 (C-13c), 30.57 (C-13d), 15.94 (13c-CH_3), 15.22 (13d-CH_3), 11.89 (12-CH_3), 11.70 (10-CH_3). IR (KBr) ν 3026, 2962, 2923, 2902, 2876, 1705, 1601, 1461, 1374, 1359, 1346, 1235, 1199, 1043, 1021, 887, 868, 852, 673 cm^{-1}. UV−vis (cyclohexane) λ_{max}, nm (ε_{max}, L·mol^{-1}·cm^{-1}) 205 (23 700), 239 (7600), 331 (27 800), 349 (99 300), 360 (34 800), 385 (46 100), 438 (5000), 461 (7600), 480 (9900), 537 (200), 600 (200), 644 (900), 651 (1100). Anal. Calcd for $C_{33}H_{40}O_2$: C, 84.57; H, 8.60. Found: C, 84.64; H, 8.64. X-ray structure: see Supporting Information.

2,7-Di-*tert*-butyl-11-oxo-10,12,13c,13d-tetramethylcycloheptatrieno[13a:13f;*e*]-*trans*-13c,13d-dihydropyrene (7). Mixed compounds **6a** and **6b** (2.2 g, 4.7 mmol) were stirred in *tert*-butanol (150 mL) at 60 °C until completely dissolved. The oil bath was removed and potassium *tert*-butoxide (6.0 g, 53 mmol) was added slowly with stirring under argon. Then the mixture was warmed to 60 °C and stirred for 40 min under argon. The reaction was then quenched by pouring it into a mixture of ether and water in a separatory funnel. The aqueous layer was extracted three times with ethyl acetate. The organic layers were combined, washed with aqueous NaCl solution, and dried over anhydrous $MgSO_4$. The solvent was then removed and the product was chromatographed over neutral aluminum oxide (deactivated with 5% water) with hexanes and dichloromethane (ratio 1:4 to 1:1) as eluant. The green starting material was eluted first (0.30 g, 14% recovery). Eluted next was product **7**, which was rechromatographed over silica gel with dichloromethane as eluant to afford 1.12 g (61% yield) of dark red crystals from benzene, mp 191−193 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.27 (s, 2H, H-9 and H-13), 9.16 (s, 2H, H-1 and H-8), 8.41 (s, 2H, H-3 and H-6), 8.26 (s, 2H, H-4 and H-5), 2.60 (s, 6H, 10,12-CH_3), 1.70 [s, 18H, 2,7-C(CH_3)$_3$], −3.56 (s, 6H, 13c,d-CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.35 (C-11), 146.73 (C-2,7), 138.68 (C-3a, 5a), 138.33 (C-10,12), 135.24 (C-13b,13e), 133.78 (C-9,13), 127.67 (C-13a,13f), 123.84 (C-4,5), 122.31 (C-3,6), 119.60 (C-1,8), 36.52 [2,7-C(CH_3)$_3$], 32.00 [2,7-C(CH_3)$_3$], 31.03 (C-13c,13d), 24.31 (10,12-CH_3), 15.01 (internal CH_3). IR (KBr) ν 2962, 2925, 2864, 1609, 1465, 1361, 1345, 1240, 1160, 1035, 895, 869, 674 cm^{-1}. UV−vis (cyclohexane) λ_{max}, nm (ε_{max}, L·mol^{-1}·cm^{-1}) 257 (13 900), 268 (16 400), 284 (13 800), 377 (32 900), 401 (39 600), 423 (56 400), 488 (6200), 513 (7200), 534 (6500), 627 (900), 696 (1700). EI MS m/z 450 (M$^+$). HRMS calcd for $C_{33}H_{38}O$, 450.2923; found, 450.2913. Anal. Calcd for $C_{33}H_{38}O$: C, 87.95; H, 8.50. Found: C, 87.74; H, 8.45.

2,7-Di-*tert*-butyl-10,12,13c,13d-tetramethyl-11*H*-11-hydroxycycloheptatrieno[13a:13f;*e*]-*trans*-13c,13d-dihydropyrene (8). $LiAlH_4$ (31 mg, 0.82 mmol) was added to tropone **7** (60 mg, 0.13 mmol) in dry ether (15 mL) in a dry Schlenk tube under argon, and the mixture was stirred at 20 °C for 1 h. The resulting mixture was diluted with ether and poured into a solution of NH_4Cl in ice water. The organic layer was washed with water and aqueous NaCl solution. The ether layer was dried over $MgSO_4$ for 1 h and the solvent was removed under vacuum to afford 25 mg (45%) of **8**. This was chromatographed on alumina, with dichloromethane and hexane (1:1) and then pure dichloromethane as eluants, to give a dark orange product. This was recrystallized by diffusing hexane into dichloromethane in a freezer to afford dark red crystals of **8**, mp 193−194 °C. ^{1}H NMR (500 MHz C_6D_6) δ 8.56 (m, 2H, H-1 and H-8), 8.14 (m, 2H, H-3 and H-6), 7.97 (s, 2H, H-4 and H-5), 7.44 (s, 1H, H-9), 7.42 (s, 1H, H-13), 4.35 (d, J = 5.0 Hz, 1H, H-11), 2.35 (s, 3H, 10-CH_3), 2.32 (s, 3H, 12-CH_3), 1.90 (d, J = 5.3 Hz, 1H, -O*H*), 1.63 [s, 18H, 2- and 7-C(CH_3)$_3$], −3.24 (s, 3H, 13d-CH_3), −3.31 (s, 3H, 13c-CH_3). ^{13}C NMR (125 MHz C_6D_6) δ 145.45 (C-2/7), 145.34 (C-2/7), 143.00 (C-10), 142.15 (C-12), 138.14 (C-5a), 137.41 (C-3a), 135.00 (C-13e), 134.65 (C-13b), 130.37 (C-13a), 129.70 (C-13f), 121.82 (C-4/5), 121.80 (C-4/5), 120.49 (C-3/6), 120.32 (C-9), 120.25 (C-1/3/6/8), 120.23 (C-1/3/6/8), 119.49 (C-1/8), 118.81 (C-13), 73.19 (C-11), 36.21 (C-2,7), 32.00 [2/7-C(CH_3)$_3$], 31.97 [2/7-C(CH_3)$_3$], 31.05 (C-13c/13d), 30.94 (C-13c/13d), 20.07 (10-CH_3), 19.73 (12-CH_3), 16.28 (13c-CH_3), 15.41 (13d-CH_3). IR (KBr) ν 3579, 2962, 2928, 2904, 2865, 1599, 1461, 1439, 1361, 1343, 1260, 1233, 1174, 1099, 1083, 1021, 884, 845, 669, 598 cm^{-1}. UV−vis (cyclohexane) λ_{max}, nm (ε_{max}, L·mol^{-1}·cm^{-1}) 362 (65 700), 402 (57 900), 488 (7490), 508 (7740), 598 (552), 666 (1220). EI MS m/z 452 (M$^+$). HRMS calcd for $C_{33}H_{40}O$, 452.3079; found, 452.3080. Anal. Calcd for $C_{33}H_{40}O$: C, 87.56; H, 8.91. Found: C, 86.34; H, 8.79.

2,7-Di-*tert*-butyl-10,12,13c,13d-tetramethyl-13*H*,13*H*-cycloheptatrieno[13a:13f;*e*]-*trans*-13c,13d-dihydropyrene (11) and 2,7-Di-*tert*-butyl-10,12,13c,13d-tetramethyl-11*H*,11*H*-cycloheptatrieno[13a:13f;*e*]-*trans*-13c,13d-dihydropyrene (9). Aluminum hydride was generated by a procedure adapted from the literature.[37] A three-necked flask was charged with lithium aluminum hydride (3.9 g, 0.10 mol) and dry ether (250 mL). The stirred slurry was warmed to reflux for 2 h under argon. Then the oil bath was replaced with an ice bath. Aluminum chloride (13.65 g, 0.10 mol) was added slowly under argon. The resulting slurry was then refluxed for another 2 h. The reaction mixture was then cooled to −78 °C in a dry ice/acetone bath. A solution of tropone **7** (0.50 g, 1.1 mmol) in ether (50 mL) and benzene (150 mL) was added dropwise. The resulting mixture was stirred for 12 h at 25 °C under argon, and then the reaction was quenched by addition of ethyl acetate and ice water sequentially with ice bath cooling. The product was extracted with ether three times and the organic layer was then washed with aqueous NaCl solution, dried over anhydrous $MgSO_4$, and evaporated. The products were chromatographed on a silica gel column with hexanes as the eluant. The first fraction contained the asymmetric isomer **11** (0.34 g, 70% yield) as dark orange crystals from benzene, mp 175−176 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (s, 1H, H-1), 8.79 (s, 1H, H-8), 8.36 (s, 1H, H-3), 8.35 (s, 1H, H-6), 8.27 (s, 1H, H-9), 8.24 (d, J = 7.2 Hz, 1H, H-4), 8.20 (d, J = 7.2 Hz, 1H, H-5), 5.91 (s, 1H, H-11), 4.38 (d, J = 12.4 Hz, 1H, H-13), 3.04 (d, J = 12.3 Hz, 1H, H-13), 2.38 (d, J = 0.9 Hz, 1H, 10-CH_3), 2.18 (d, J = 1.4 Hz, 1H, 12-CH_3), 1.70 [s, 9H, 2-C(CH_3)$_3$], 1.69 [s, 9H, 7-C(CH_3)$_3$], −3.65 (s, 3H, 13d-CH_3), −3.89 (s, 3H, 13c-CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.66 (C-7), 144.80 (C-2), 139.39 (C-12), 138.37 (C-10), 137.83 (C-5a), 136.38 (C-3a), 133.94 (C-13e), 132.45 (C-13b), 128.92 (C-13a), 128.83 (C-13f), 126.48 (C-9), 124.44 (C-11), 122.42 (C-4), 121.68 (C-5), 120.25 (C-3), 120.02 (C-6), 118.78 (C-1), 117.41 (C-8), 36.34 [7-C(CH_3)$_3$], 36.22 [2-C(CH_3)$_3$], 35.55 (C-13), 32.19 [7-C(CH_3)$_3$], 32.14 [2-C(CH_3)$_3$], 30.62 (C-13d), 30.54 (C-13c), 25.48 (10-CH_3), 24.58 (12-CH_3), 14.60 (13d-CH_3), 14.47 (13c-CH_3). IR (KBr) ν 3012, 2962, 2922, 2860, 1645, 1590, 1459, 1438, 1345, 1260, 1230, 1193, 886, 856, 831, 795, 672, 647 cm^{-1}. UV−vis (cyclohexane) λ_{max}, nm (ε_{max}, L·mol^{-1}·cm^{-1}) 227 (17 500), 287 (9600), 358 (64 000), 373 (36 600), 399 (57 500), 486 (8400), 501 (9400), 600 (300), 666 (1300). Anal. Calcd for $C_{33}H_{40}$: C, 90.77; H, 9.23. Found: C, 89.81; H, 9.19.

The second fraction contained the symmetric isomer **9** (75 mg, 15% yield) as dark orange crystals from benzene, mp 187−188 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, J = 1.0 Hz, 2H, H-1 and H-8), 8.16 (d, J = 1.0 Hz, 2H, H-3 and H-6), 8.00 (s, 2H, H-4 and H-5), 7.46 (q, J = 1.4 Hz, 2H, H-9 and H-13), 2.53 (d, J = 1.0 Hz, 2H, H-11), 2.34 (d, J = 1.4 Hz, 6H, 10- and 12-CH_3), 1.63 [s, 18H, 2- and 7-C(CH)$_3$], −3.32 (s, 6H, 13c,d-CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.10 (C-2,7), 140.44 (C-10,12), 137.72 (C-3a,5a), 135.16 (C-13b,13e), 130.75 (C-13a,13f), 121.83 (C-9,13), 121.61 (C-4,5), 120.12 (C-3,6), 119.11 (C-1,8), 38.54 (C-11), 36.19 [2,7-C(CH)$_3$], 32.04 [2,7-C(CH)$_3$], 31.14 (C-13c,13d), 26.08 (10,12-CH_3), 15.86 (internal-CH_3); UV−vis (cyclohexane) λ_{max}, nm (ε_{max}, L·mol^{-1}·cm^{-1}) 256 (13 400), 290 (6500), 359 (58 100), 374 (39 100), 399 (51 800), 455 (5600), 484 (7700), 504 (8100), 597 (400), 668 (1200). IR (KBr) ν 3052, 2960, 2947, 2926, 2899, 2863, 1601, 1459, 1433, 1372, 1360, 1345, 1239, 1224, 1199, 882, 870, 856,

848, 800, 681, 649 cm^{-1}. EI MS m/z 436 (M^+). HRMS calcd for $C_{33}H_{40}$, 436.3130; found, 436.3133. An X-ray-quality crystal of this isomer was obtained from benzene with slow diffusion of diethyl ether; see Supporting Information.

Tropylium Cation (10). Tetrafluoroboric acid (48% aq, 1 drop) was added to alcohol **8** (5.0 mg, 0.011 mmol) in 0.7 mL of each of the deuterated solvents (THF-d_8, $CDCl_3$, benzene-d_6, and acetone-d_6) in an NMR tube. The solution immediately turned purple and then the NMR spectrum was recorded, which indicated quantitative conversion to salt **10**·BF_4^-. ^{1}H NMR (500 MHz, C_6D_6) δ 10.50 (s, 2H, H-9 and H-13), 9.78 (s, 2H, H-1 and H-8), 8.30 (s, 1H, H-11), 8.10 (s, 2H, H-3 and H-6), 7.62 (s, 2H, H-4 and H-5), 2.93 (s, 6H, 10- and 12-CH_3), 1.68 [s, 18H, 2- and 7-C(CH_3)$_3$], −2.61 (s, 6H, 13c- and 13d-CH_3). ^{13}C NMR (125 MHz, C_6D_6) δ 151.79 (C-11), 151.04 (C-2,7), 148.56 (C-10,12), 145.00 (C-9,13), 142.06 (C-3a,5a), 140.76 (C-13a,13f), 135.23 (C-13b,13e), 130.90 (C-1,8), 127.91 (C-3,6), 127.44 (C-4,5), 37.00 [2,7-C(CH$_3$)$_3$], 33.95 (C-13c,13d), 31.46 [2,7-C(CH_3)$_3$], 28.63 (10,12-CH_3), 16.51 (13c,13d-CH_3). IR (KBr) ν 2963, 2926, 2866, 1599, 1512, 1462, 1437, 1384, 1364, 1345, 1305, 1237, 1198, 1171, 1112, 1081, 1052, 1020, 891, 872, 815, 670 cm^{-1}. UV−vis (dichloromethane) λ_{max} 242, 272, 352, 374, 498, 670, 728 nm. ESI m/z 435 (M^+). HRMS calcd for $C_{33}H_{39}$, 435.3052; found, 435.3054.

Procedure from **11**: Cycloheptatriene **11** (20 mg, 0.046 mmol) was dissolved in toluene (or THF) (5 mL) in a Erlenmeyer flask in a glovebox. Trityl tetrakis(pentafluorophenyl)borate (45 mg, 0.049 mmol) in toluene (1 mL) was added to the flask at 20 °C. The solution was stirred for 1 h, and then the solvent was removed on a rotavaporator and the dark brown film residual was dissolved in NMR solvent, which showed that only a very small amount of cation **10** was present.

Reduction of Triene 11 to 2,7-Di-*tert*-butyl-10,12,13c,13d-tetramethyl-*trans*-13c,13d-dihydro-{9,10,11,12,13-pentahydrocyclohepta}[13a:13f;*e*]pyrene (12) and 2,7-Di-*tert*-butyl-10,12,13c,13d-tetramethyl-*trans*-13c,13d-dihydro-{9,10,11-trihydrocyclohepta}[13a:13f;*e*]pyrene (13). Pt_2O (16 mg, 0.070 mmol) was suspended in ethyl acetate (5 mL) in a Schlenk tube sealed with a rubber septum. Hydrogen in a balloon was cannulated to the solution through the septum. The solution was stirred at 20 °C until it turned black. Then a solution of triene **11** (20 mg, 0.046 mmol) in ethyl acetate (2 mL) was added by syringe. The reaction was stirred for 1 h. The black catalyst was then removed by filtration through a Celite pad, and the solvent was removed to afford a green solid. Preparative TLC separated the two products (65:35 ratio) with hexane/dichloromethane (5:1) as eluant. The first band contained mixed isomers (4:1 ratio) of **12**. Major isomer: ^{1}H NMR (500 MHz $CDCl_3$) δ 8.74 (s, 1H, H-1/8), 8.71 (s, 1H, H-1/8), 8.44 (s, 1H, H-3/6), 8.43 (d, J = 0.7 Hz, 1H, H-3/6), 8.34 (s, 2H, H-4 and H-5), 4.00−3.90 (m, 2H, H-9 and H-13), 3.47−3.35 (m, 1H, H-9/13), 3.34−3.21 (m, 1H, H-9/13), 2.00−1.81 (m, 2H, H-10 and 12), 1.64−1.47 (m, 2H, H-11), 1.678 and 1.676 [s, 18H, 2- and 7-C(CH_3)$_3$], 1.35−1.24 (m, 3H, 10/12-CH_3), 1.22 (d, J = 6.7 Hz, 3H, 10/12-CH_3), −3.98 (s, 3H, internal-CH_3), −4.03 (s, 3H, internal-CH_3). ^{13}C NMR (125 MHz $CDCl_3$, selected and assigned where it is possible) δ 144.91 and 144.73 (C-2,7), 137.12 (C-3a/5a), 136.98 (C-3a/5a), 132.80 (C-13a/13f), 122.60 and 122.49 (C-4,5), 120.38 (C-3/6), 120.25 (C-3/6), 117.21, 116.94, 116.62 (C-1,8), 36.62, 34.62, 32.25. Minor isomer: ^{1}H NMR (500 MHz $CDCl_3$) δ 8.77 (d, J = 1.0 Hz, 1H), 8.74 (d, J = 1.0 Hz, 1H), 8.35 (s, 1H), 3.85 (dd, J = 14.4, 3.4 Hz, 1H), 3.82 (dd, J = 14.8, 3.4 Hz, 1H), 3.70 (dd, J = 14.4, 7.6 Hz, 1H), 3.62 (dd, J = 14.6, 7.4 Hz, 1H), 2.4−2.3 (m), 2.3−2.2 (m), 1.08 (d, J = 7.0 Hz, 3H) 0.96 (d, J = 7.0 Hz, 3H), −3.986 (s, 3H), −3.995 (s, 3H). Mixed isomers: UV−vis (cyclohexane) λ_{max} 352, 388, 482, 598, 652 nm. EI MS m/z 440 (M^+). HRMS calcd for $C_{33}H_{44}$, 440.3443; found, 440.3443.

The second band contained the monoene **13** as two isomers in a 4:1 ratio. Major isomer: ^{1}H NMR (500 MHz $CDCl_3$) δ 8.60 (d, J = 1.0 Hz, 1H), 8.44 (underneath peaks for isomer**11**, 1H), 8.43 (underneath peaks for isomer **11**, 1H), 8.41 (d, J = 1.0 Hz, 1H), 8.31 (s, 2H), 7.57−7.55 (m, 1H, H-13), −3.83 (internal-CH_3), −3.90 (internal-CH_3). Minor isomer: internal methyl protons at −3.85 (s) and −3.88 (s) (other peaks overlap with other products). As only the chemical shifts associated with the internal methyl protons were of interest to us, no effort was made to separate these products further.

■ ASSOCIATED CONTENT

Supporting Information

Part 1: General synthetic experimental conditions, numbering system for NMR assignments, X-ray structure determination of tropone **7** and triene **9**, and ^{1}H and ^{13}C NMR spectra of all new compounds. Part 2: Tables of comparisons of selected experimental and calculated ^{1}H and ^{13}C NMR chemical shifts for **7**, **9**, **10**, **11**; calculated Cartesian coordinates and energies for key compounds; and complete ref 12. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

regmitch@uvic.ca; williams@uidaho.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

R.V.W. thanks the National Science Foundation (CHE-0714761) for support of this work. R.H.M., D.J.B., and P.Z. thank the Natural Sciences and Engineering Research Council of Canada and the University of Victoria for financial support.

■ REFERENCES

(1) See for example *Organic Chemistry*, 8th ed.; Solomons, T. W. G., Fryhle, C. B., Eds.; John Wiley & Sons: New York, 2004; pp 636−637.

(2) See for example *Aromaticity*; Garratt, P. J., Ed.; John Wiley & Sons, New York, 1986; pp179−180.

(3) (a) Chen, Z.; Jiao, H.; Wu, J. I.; Herges, R.; Zhang, S. B.; Schleyer, P. v. R. *J. Phys. Chem. A* **2008**, *112*, 10586−10594. (b) Fliegl, H.; Sundholm, D.; Taubert, S.; Jusélius, J.; Klopper, W. *J. Phys. Chem. A* **2009**, *113*, 8668−8676.

(4) (a) Mitchell, R. H. *Chem. Rev.* **2001**, *101*, 1301−1315. (b) Mitchell, R. H.; Brkic, Z.; Berg, D. J.; Barclay, T. M. *J. Am. Chem. Soc.* **2002**, *124*, 11983−11988. (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.; Zhang, R.; Berg, D. J.; Twamley, B.; Williams, R. V. *J. Am. Chem. Soc.* **2009**, *131*, 189−199.

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

(6) Mitchell, R. H.; Iyer, V. S.; Khalifa, N.; Mahadevan, R.; Venugopalan, S.; Weerawarna, S. A.; Zhou, P. *J. Am. Chem. Soc.* **1995**, *117*, 1514−1532.

(7) Mitchell, R. H.; Fan, W.; Lau, D. Y. K.; Berg, D. J. *J. Org. Chem.* **2004**, *69*, 549−554.

(8) (a) Klein, S.; Roberts, S. M. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2686−2691. (b) Hoffmann, H. M. R. *Angew. Chem.* **1973**, *85*, 877−894.

(9) Mitchell, R. H.; Ward, T. R. *Tetrahedron* **2001**, *57*, 3689−3695.

(10) 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.

(11) (a) Ayub, K.; Zhang, R.; Robinson, S. G.; Twamley, B.; Williams, R. V.; Mitchell, R. H. *J. Org. Chem.* **2008**, *73*, 451. (b) Ayub, K.; Li, R.; Bohne, C.; Williams, R. V.; Mitchell, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 4040.

(12) (a) Frisch, M. J. et al. *Gaussian 03, Revision E.01*; Gaussian Inc., Wallingford, CT, 2004. (b) Frisch, M. J. et al. *Gaussian 09, Revision B.01*; Gaussian Inc., Wallingford, CT, 2010. See Supporting Information for full reference.

(13) (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317−6318. (b) Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2383−2386. (c) Subramanian, G.; Schleyer, P. v. R.; Jiao, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2638−2640.

(14) Forsyth, D. A.; Sebag, A. B. *J. Am. Chem. Soc.* **1997**, *119*, 9483−9494.

(15) Williams, R. V. *Chem. Rev.* **2001**, *101*, 1185−1204.
(16) Griffiths, P. R.; Pivonka, D. E.; Williams, R. V. *Chem.—Eur. J.* **2011**, *17*, 9193−9199.
(17) Thiele, J. *Liebigs Ann. Chem.* **1901**, *319*, 226−230.
(18) Applequist, D. E.; Roberts, J. D. *J. Am. Chem. Soc.* **1956**, *78*, 4012−4022.
(19) Doering, W. v. E.; Laber, G.; Vonderwahl, R.; Chamberlain, N. F.; Williams, R. B. *J. Am. Chem. Soc.* **1956**, *78*, 5448.
(20) Winstein, S. *J. Am. Chem. Soc.* **1959**, *81*, 6523−6524.
(21) (a) Williams, R. V.; Kurtz, H. A.; Farley, B. *Tetrahedron* **1988**, *44*, 7455−7460. (b) Williams, R. V.; Kurtz, H. A. *Adv. Phys. Org. Chem.* **1994**, *29*, 273−331.
(22) (a) Lai, Y.-H.; Chen, P.; Dingle, T. W. J. *J. Org. Chem.* **1997**, *62*, 916−924. (b) Lai, H.-Y.; Jiang, J. *J. Org. Chem.* **1997**, *62*, 4412−4417. (c) Mitchell, R. H.; Bohne, C.; Wang, Y. X.; Bandyopadhyay, S.; Wozniak, C. B. *J. Org. Chem.* **2006**, *71*, 327−336.
(23) (a) Ohkita, M.; Sano, K.; Suzuki, T.; Tsuji., T. *Tetrahedron Lett.* **2001**, *42*, 7295−7297. (b) Ohkita, O.; Sano, K.; Suzuki, T.; Tsuji, T.; Sato, T.; Niino, H. *Org. Biomol. Chem.* **2004**, *2*, 1044−1050.
(24) Hückel, E. Z. *Phys* **1931**, *70*, 204−286.
(25) (a) Dewar, M. J. S. *Nature* **1945**, *155*, 50−51. (b) Dewar, M. J. S. *Nature* **1945**, *155*, 141−142. (c) Dewar, M. J. S. *Nature* **1950**, *166*, 790−791.
(26) Balaban, A. R.; Banciu, M.; Ciorba, V. *Annulenes, Benzo-, Hetero-, Homo-Derivatives and their Valence Isomers*; CRC Press, Inc.: Boca Raton, FL, 1987.
(27) Lloyd, D. *Carbocyclic Non-Benzenoid Aromatic Compounds*; Elsevier: Amsterdam, 1984.
(28) (a) Bertelli, D. J.; Andrews, T. G., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 5280−5286. (b) Bertelli, D. J.; Andrews, T. G., Jr.; Crews, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 5286−5296. (c) Bertelli, D. J. In *Topics in Nonbenzenoid Aromatic Chemistry, Vol. 1*; Nozoe, T., Breslow, R., Hafner, K., Itô, S., Murata, I., Eds.; J. Wiley & Sons, Inc.: New York, 1973.
(29) Najafian, K.; Schleyer, P. v. R.; Tidwell, T. T. *Org. Biomol. Chem.* **2003**, *1*, 3410−3417.
(30) Feixas, F.; Matito, E.; Poater, J.; Solà, M. *J. Comput. Chem.* **2008**, *29*, 1543−1554.
(31) Noorizadeh, S.; Shakerzadeh, E. *Phys. Chem. Chem. Phys.* **2010**, *12*, 4742−4749.
(32) Zhang, P.; Brkic, Z.; Berg, D. J.; Mitchell, R. H.; Oliver, A. G. *Organometallics* **2011**, *30*, 5396−5407.
(33) For representative publications in support of the aromaticity of the tropylium cation **20**, see refs 2, 13a, 26, 27, 31, and 34 and citations therein.
(34) (a) Foroutan-Nejad, C.; Shahbazian, S.; Feixas, F.; Rashidi-Ranjbar, P.; Sola, M. *J. Comput. Chem.* **2011**, *32*, 2422−2431. (b) Stanger, A. *J. Org. Chem.* **2010**, *75*, 2281−2288. (c) Noorizadeh, S.; Dardab, M. *Chem. Phys. Lett.* **2010**, *493*, 376−380. (d) Pérez-Juste, I.; Mandado, M.; Carballeira, L. *Chem. Phys. Lett.* **2010**, *491*, 224−229. (e) Jursic, B. *J. Mol. Struct. (THEOCHEM)* **1999**, *468*, 171−179. (f) Jusélius, J.; Sundholm, D. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3429−3435. (g) Mo, Y.; Jiao, H.; Lin, Z.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1998**, *289*, 383−390. (h) Fowler, P. W.; Steiner, E. *J. Phys. Chem. A* **1997**, *101*, 1409−1413. (i) Jug, K. *J. Org. Chem.* **1983**, *48*, 1344−1348.
(35) (a) Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, *2*, 468−472. (b) Schaefer, T.; Schneider, W. G. *Can. J. Chem.* **1963**, *41*, 966−982.
(36) Doerr, R. G.; Skell, P. S. *J. Am. Chem. Soc.* **1967**, *89*, 4684−4687.
(37) Boekelheide, V.; Phillips, J. B. *J. Am. Chem. Soc.* **1967**, *89*, 1695−1704.
(38) Nishinaga, T.; Izukawa, Y.; Komatsu, K. *J. Phys. Org. Chem.* **1998**, *11*, 475.