First Examples of Stable Arenium Ions from Large Methylene-Bridged Polycyclic Aromatic Hydrocarbons (PAHs). Directive Effects and Charge Delocalization Mode

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In connection to a growing interest in developing structure/activity trends in *nonalternant* polyarenes, we report on the generation and NMR studies of the first series of persistent arenium ions from large methylene-bridged PAHs (mostly 22π six-fused ring systems). Low-temperature protonation (FSO_3H/SO_2ClF) and model nitration (with HNO_3/HOAc or NO_2^+ BF_4^-) were used as mimic reactions for generation of biological electrophiles. The site(s) of protonation (and nitration) were determined as a function of PAH structure. Charge delocalization mode in the resulting arenium ions of protonation are assessed based on detailed low-temperature NMR studies at 500 MHz. Systems studied were 1-methylcyclopenta[*def*]phenanthrene **2**, 11*H*-benz[*bc*]aceanthrylene **8**, 5*H*-benzo[*b*]cyclopenta[*def*]chrysene **9**, 13*H*-dibenzo-[*bc*,*l*]aceanthrylene **10**, 13*H*-cyclopenta[*rst*]-pentaphene **11**, 4*H*-benzo[*b*]cyclopenta[*mno*]chrysene **12**, 6*H*-cyclopenta[*ghi*]picene **13**, 4*H*-cyclopenta[*pqr*]picene **14**, 4*H*-cyclopenta[*def*]dibenz[*a*,*c*]anthracene **15**. For comparison, dibenzo[*a*,*c*]-anthracene **16** and dibenzo[*a*,*h*]anthracene **17** were also included (Figures 1 and 2). It is shown that the methano-bridge exerts a strong directive effect which diminishes as the bridge moves from the more central "inner" positions to more peripheral "outer" positions. Charge delocalization mode in the resulting carbocations are discussed based on the magnitude of $\Delta\delta$ ^{13}C values. Possible relationships with biological electrophiles formed by epoxide ring opening in the putative metabolites are also considered.

Introduction

Methylene-bridged PAHs constitute a novel class of *nonalternant* polyarenes whose chemistry and biological activity are relatively unexplored.[1] This class of compounds can be viewed as the "hierarchy" benzannelated derivatives of parent member cyclopenta[*def*]phenanthrene **1** (Figure 1). They are present in coal tar and crude petroleum and have been detected in significant levels in the atmosphere. Since the late 1980s, synthetic methods became available for the preparation of five- and six-ring fused methylene-bridged PAHs in reasonable quantities,[2−8] and for stereoselective synthesis of the putative reactive metabolite of 4*H*-cyclopenta[*def*]chysene **3**.[9−11] These advances have stimulated chemical and biological reactivity studies.

Introduction of a methylene bridge into chrysene increases electrophilic reactivity, even though one bay-region is removed. It also confers significant increase in tumorigenic and carcinogenic activity. The methylene-bridged bay-region derivatives of chrysene and benz[*a*]-anthracene are both mutagenic and tumorigenic.[12] Methanochrysene **3** is metabolically activated to diol-epoxides **5** and **6** which bind to DNA in human mammary carcinoma MCF-7 cell cultures.[13] An additional pathway involving oxidation of the bridge methylene to benzylic alcohol which is enzymatically converted to reactive sulfate-ester (precursor to the solvolytic carbocation) has also been proposed.[9] These studies focus attention on the possible importance of carbocations **5a**$^+$, **6a**$^+$, and **7a**$^+$ in the DNA-binding step for compound **3** (Figure 1). Electrophilic reactivity studies on large methano-PAHs are hitherto limited to bromination and formylation in **3**, **8**, **10**, and **12** (Figures 1 and 2).[14]

Using low-temperature protonation (FSO_3H/SO_2ClF) and model nitration (with HNO_3/HOAC or NO_2^+ BF_4^-) as mimic reactions for the formation of biological elec-

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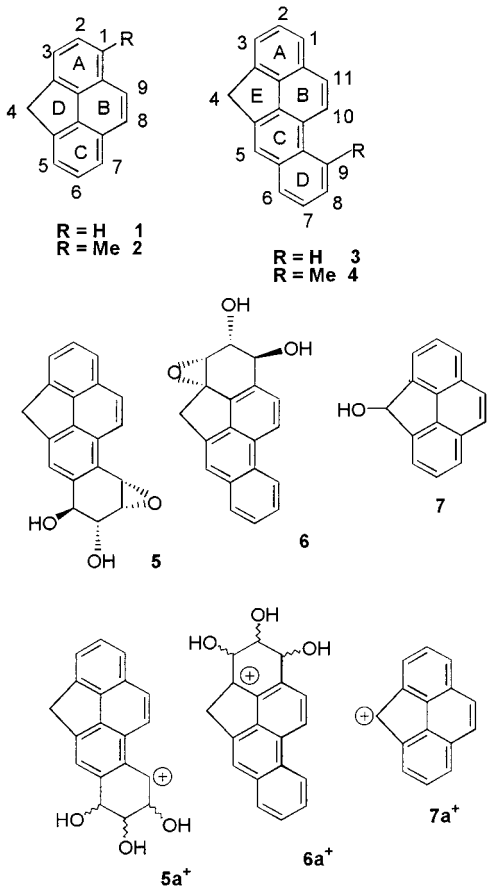


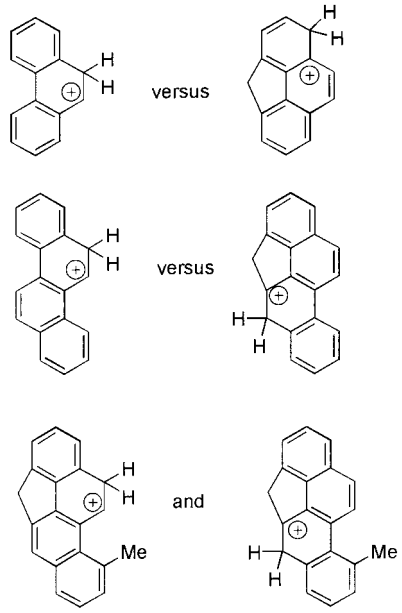
Figure 1. Cyclopenta[*def*]phenanthrene; cyclopenta[*def*]chrysene, its putative active metabolites, and proposed derived carbocations. A, B, C, D designations for the rings are arbitrary.

trophiles, we report here on the site(s) of attack and charge delocalization modes in the resulting long-lived arenium ions in a series of methylene-bridged PAHs as a function of structure and benzannelation mode.[15] Relative arenium ion energies for all possible protonation sites were computed by AM1 for comparison with experiment.

Results and Discussion

NMR Assignments. Detailed NMR assignments for the methano-PAHs, their carbocations, and the nitro derivatives were based on ^{1}H, ^{13}C, H/H COSY, HMQC, HMBC, and NOED spectra. The reported assignments of the proton resonances for the precursors[4−6] were expanded and fine-tuned (and corrected). A consistent feature in the ^{1}H NMR spectra of the methano-PAHs is the detection of *peri*-NOE effects which also include the methylene-bridge. Compound **10** exhibits the largest bay-region proton deshielding among this group (δ 8.92) due to increased compression and nonplanarity. There were no previous ^{13}C data in the literature for these PAHs.

Influence of Methano-Bridge in Directing Electrophilic Attack. Background. Whereas in phenanthrene the 9,10 (meso) positions are attacked by electrophiles, in cyclopenta[*def*]phenanthrene **1** the site of attack moves to C-1.[14,16] The site of attack in the parent chrysene (protonation, nitration, bromination) is C-5/C-11.[17,18] In the methano-derivative **3**, protonation is exclusively directed to C-5 (peri-to the bridge).[17] Bromination gave a 10:1 mixture of 5-Br and 11-Br.[14,16] Methyl introduction at the bay region (compound **4**) resulted in a 3:1 mixture of arenium ions of protonation at C-11 and C-5 (see structure).[18]



Stable Ion Studies and Model Nitration (Schemes 1−3 , Figure S1, Figure 3, Figure S2 and representative NMR spectra in Supporting Information). 1-Methylcyclopenta[*def*]phenanthrene 2. Although the focus of the present study is on six (and five)-ring fused systems, it was relevant (in relation to our previous studies with **1**, **3**, and **4**[16−18]) to determine the site of attack in **2** with a methyl group substituted at C-1, to explore if *ipso* attack would occur or whether electrophilic attack moves to another site. This gave a 3:1 mixture (at −70 °C) of **2aH**$^+$ and **2bH**$^+$ (Scheme 1) whose ratio remained unchanged at −30 °C (a dark-red solution). Cation **2aH**$^+$ represents a novel example of attack at C-2 in a phenanthrene skeleton. For both carbocations, the Me group exhibits NOE effect with its corresponding *ortho* and *peri* protons, and the most deshielded proton is H-6. The most deshielded carbon resonance in **2aH**$^+$ is C-1 (δ 199.1), whereas for **2bH**$^+$ C-6 is most downfield (δ 172.0). In **2bH**$^+$, additional NOE enhancements were observed between CH_2/H-8 and methylene-bridge/H-5. The charge delocalization path is similar for the two arenium ions (only charge localization at C-9 and C-9b are reversed), resulting in a biphenylium cation (A/C rings) (see Figure 3). AM1 calculations single out the carbocations derived from protonation at C-7 (**2bH**$^+$; lowest relative energy), C-8 (higher by ∼ 0.5 kcal/mol), and C-2 (**2aH**$^+$; higher by an additional 0.5 kcal/mol) as having distinctly lower relative energies as compared to other candidates, with a slight preference for **2bH**$^+$ over **2aH**$^+$(ca. 1 kcal/mol).

(15) For related recent studies of PAH carbocations and structure/activity relationships, see: Laali, K. K.; Okazaki, T.; Hansen, P. E. *J. Org. Chem*. **2000**, *65*, 3816; Laali, K. K.; Okazaki, T.; Coombs, M. M. *J. Org. Chem*. **2000**, *65*, 7399, and refs 16−19 below.

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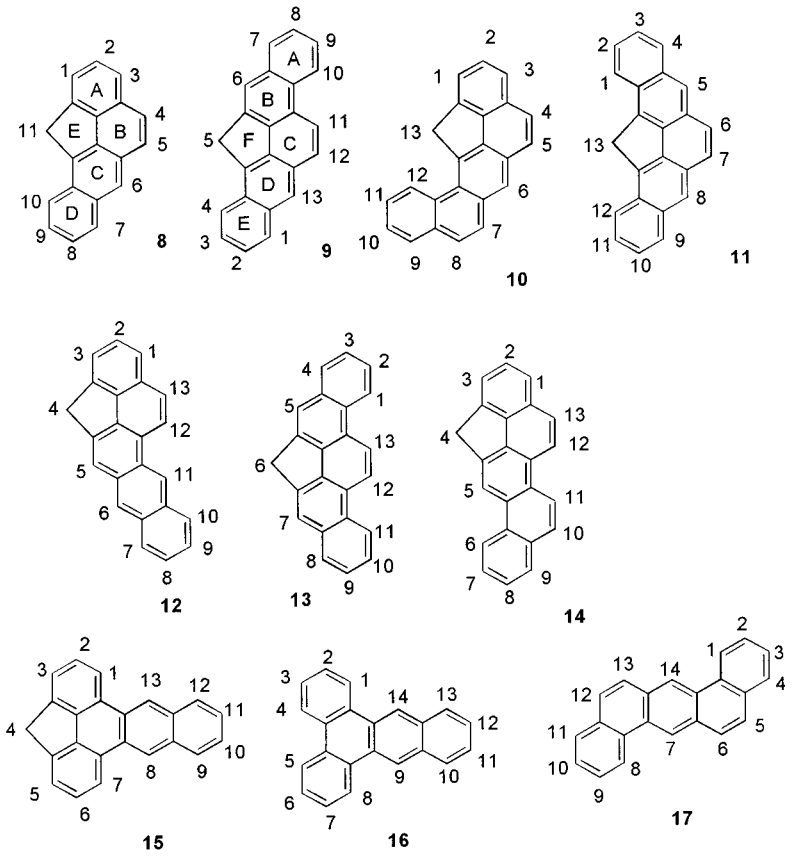

Figure 2. Six-ring fused methylene-bridged PAHs and analogues. A, B, C, D designations for the rings are arbitrary.

11*H*-Benz[*bc*]aceanthrylene 8. Compound **8** (18π) could be viewed as methanobenz[*a*]anthracene or a monobenzannelated derivative of parent **1**. It is cleanly protonated at C-6 (with FSO_3H/SO_2ClF) to give **8H**$^+$ as a dark-red solution at −70 °C (>95%). NOE enhancements were observed between the CH_2 group (at protonation site) and H-5/H-7, and between H-11 (methano-bridge)/H-1. The most deshielded proton is H-10 (δ 8.87; *peri* to methano-bridge). Positive charge is delocalized to a large extent into the anthracene moiety with limited delocalization into the A-ring (Figure 3). This charge alternation path is similar to those of C-7 protonated benz[*a*]anthracene (BA) and the C-12 (*ipso*) protonated 7,12-Me_2BA (included in Figure 3).[19] In concert with experiment, AM1 predicts that among all possible arenium ions, **8H**$^+$ has the lowest energy. Skeletally intact hydrocarbon **8** was recovered upon quenching of the superacid solution.

Protonation of Six-Ring Fused 22π Methano-PAHs 9−15. 5*H*-Benzo[*b*]cyclopenta[*def*]chrysene 9. This *nonalternant* hydrocarbon combines the features of **8** with an additional annelated ring that creates a bay-region. Its low-temperature protonation (FSO_3H/SO_2ClF) gave a dark-purple solution at −70 °C whose NMR spectral data are fully consistent with clean formation of arenium ion **9H**$^+$ by attack at C-13. The most deshielded proton is the H-11 (δ 9.44). NOE effects were detected between H-5/H-6 and H-6/H-7, and between H-13/H-1 and H-13/H-12. Positive charge is highly delocalized into the anthracenium moiety plus one other carbon in the B-ring. Although the site of attack is the same in **8H**$^+$ and **9H**$^+$ and their charge delocalization modes are analogous, they differ in the magnitude of $\Delta\delta$ ^{13}C values (Figure 3). AM1-minimizations concur with experiment showing that C-13 protonation is most favored. Quenching of the superacid solution led to the recovery of intact **9**.

Protonation and Nitration of 13*H*-Dibenzo[*bc,l*]-aceanthrylene 10. Compound **10** is cleanly protonated in FSO_3H/SO_2ClF to give **10H**$^+$ in near quantitative yield (a purple solution). A notable feature in the proton spectrum is the upfield shift of the bay-region H-12, whereas all other protons are deshielded. This implies a change in its relative orientation upon rehybridization at C-6. The methylene-bridge protons exhibit NOE with H-12/H-1, and the H-6 proton give rise to NOE with H-5/H-7. The most downfield carbon resonance is C-12c (δ 188.1). Charge delocalization in **10H**$^+$ is confined to the ring undergoing attack and two other conjugated carbons in the anthracene moiety. Reduced delocalization could stem from buckling at the annelated rings which diminishes π-participation. AM1 correctly predicts that among all possible protonation sites, arenium ion of attack at C-6 has the lowest energy. Intact **10** was obtained by quenching of the cation solution. In agreement with protonation and AM1 calculations, classical nitration of **10** gave the 6-nitro derivative **10NO$_2$** (removal of 8.31 ppm singlet for H-6), with high regioselectivity (>95%).

Protonation of 13*H*-Cyclopenta[*rst*]pentaphene 11. Low-temperature reaction of compound **11**, a symmetrically dibenzannelated derivative of parent **1**, with FSO_3H/SO_2ClF gave a dark-green solution whose NMR data are fully consistent with near quantitative formation of **11H**$^+$ by attack at C-5 (Scheme 2). This is also the

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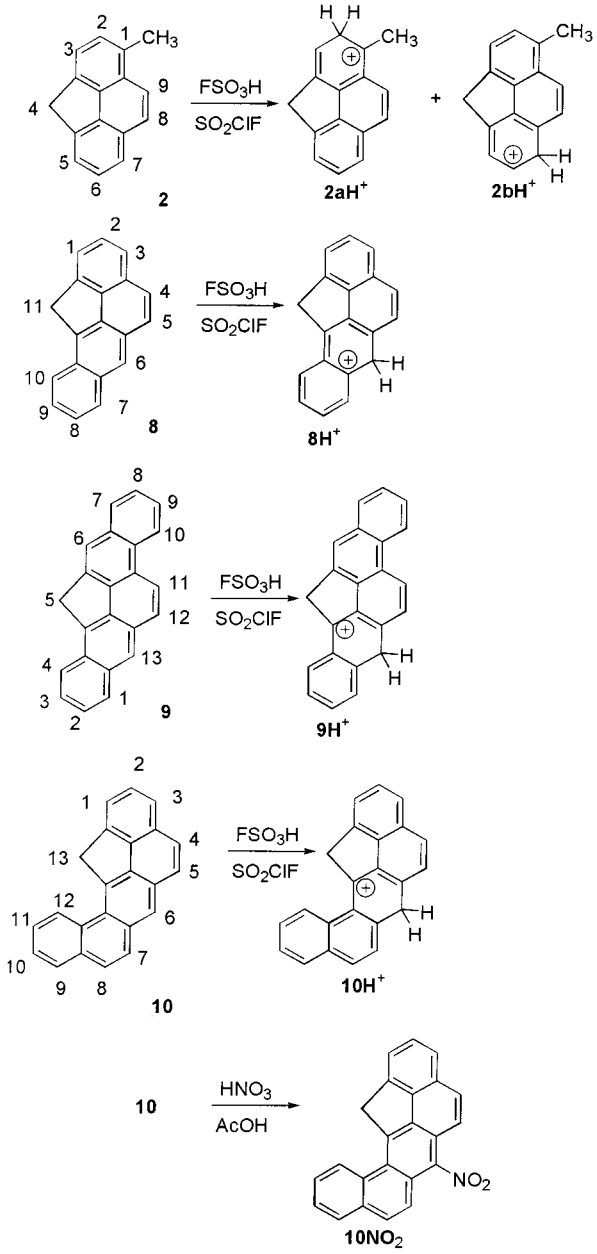
Scheme 1



AM1-predicted lowest energy carbocation. The most deshielded protons are H-6/H-7, and the most deshielded carbon is C-4a (δ 188.7). Methylene protons at C-5 exhibit NOE with H-4/H-6, whereas H-7 shows NOE with H-6/H-8. The bridge methylenes likewise exhibit *peri*-NOE effects. Another notable feature is the upfield shift of protons in the distal benzannelated ring. Positive charge is mostly retained within a naphthalenium cation plus one conjugated carbon. Intact precursor was isolated upon quenching of the superacid solution.

Protonation of 4*H*-Benzo[*b*]cyclopenta[*mno*]chrysene 12. Compound **12** reacted with FSO_3H/SO_2ClF to give a dark-red/purple solution at −70 °C. Detailed NMR analysis of the resulting complex spectra is consistent with the formation of **12aH**$^+$ and **12bH**$^+$ by attack at C-11 and C-6, in 2:1 ratio, respectively, which remained unchanged at −30 °C. Whereas AM1 calculations single out **12aH**$^+$ and **12bH**$^+$ as the most favored carbocations, there is a slight preference for **12bH**$^+$ (by ∼1 kcal/mol). In the proton spectrum, there are two distinct low field

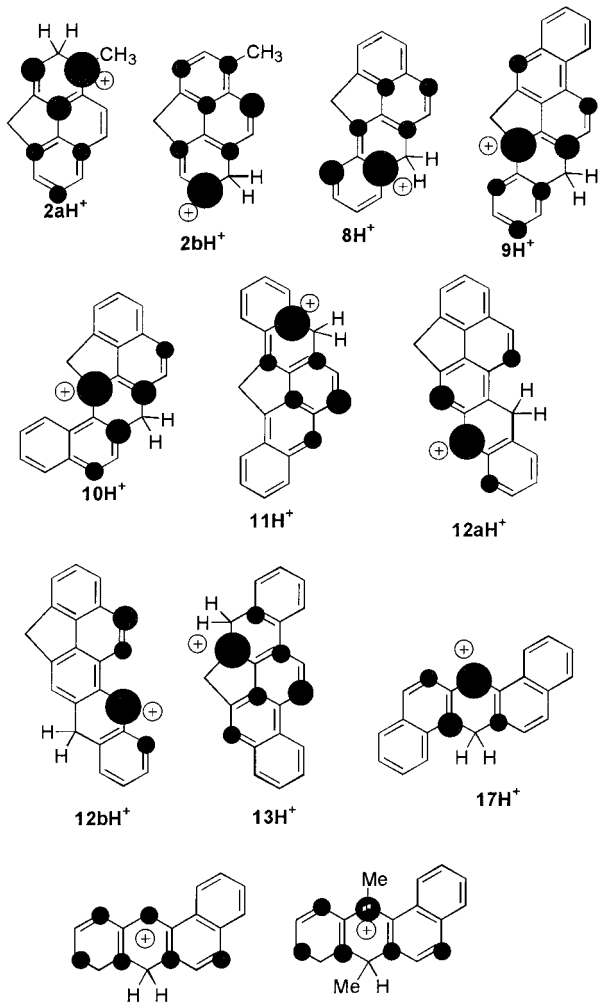


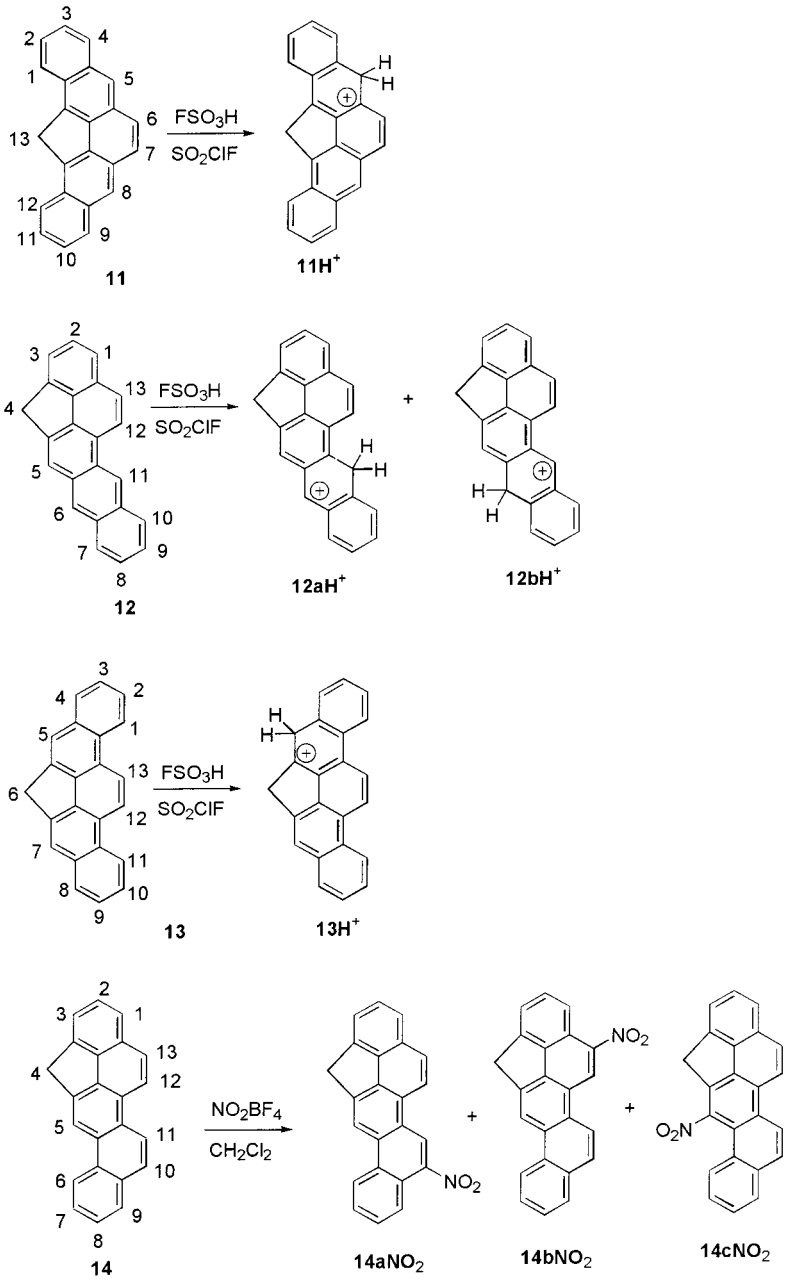
Figure 3. ^{13}C NMR-derived charge delocalization modes in the carbocations.

singlets at δ 10.10 and δ 9.57 which belong to the H-11 and H-6 of **12bH**$^+$ and **12aH**$^+$, respectively (*para* to the sites of attack). A notable feature is the paratropic shift of bay-region H-12 in **12aH**$^+$ and to a lesser extent H-11 in **12aH**$^+$. In the ^{13}C spectrum, the two methylenes in **12bH**$^+$ have the same chemical shift. Complexity of the ^{13}C spectra (42 aromatic resonances) precluded specific assignments of some of the quaternary carbons; nevertheless, it is seen that positive charge is highly localized on the anthracenium moiety for both carbocations (Figure 3). Once again, no skeletal rearrangements occurred upon quenching, and the intact substrate was isolated.

Protonation of 6*H*-Cyclopenta[*ghi*]picene 13. The mode of dibenzannelation in compound **13** creates two bay-regions on the same side. Its low-temperature protonation gave a single carbocation (a dark-green solution) resulting from attack at C-5 (*peri* to methano-bridge). The most deshielded proton (at δ 9.42) is due to H-12. The bay-region protons H-11, H-13, and H-1 are shifted upfield. In the ^{13}C NMR, the carbons *ortho* and *para* to the site of attack are most deshielded ($\Delta\delta$ 70.8). The charge alternation path is confined to two rings plus two conjugated carbons and confers naphthalenium ion character to the carbocation (Figure 3).

Protonation and Nitration of 4*H*-Cyclopenta[*pqr*]picene 14. This compound has two bay-regions on opposite sides. Low-temperature reaction of **14** with

Scheme 2



FSO_3H/SO_2ClF at −70 °C gave a purple solution accompanied by formation of a purple precipitate. ^1H NMR of the liquid phase exhibited very broad features, indicative of radical cation formation.[20] The purple precipitate is in all probability a radical cation salt rather than a dimer cation because quenching of the entire sample returned only the unchanged **14**. AM1 minimization predict that the most favored protonation sites are C-5, C-10, and C-13 whose computed energies are within 0.6 kcal/mol of each other.

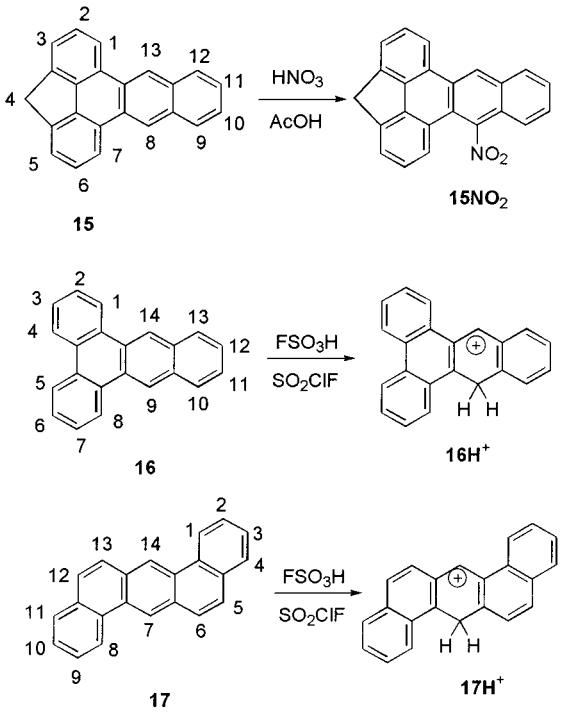
Nitronium tetrafluorborate nitration of **14** gave a mixture of three mononitro derivatives in 5:3:2 ratio (NMR). Since attempts to separate these isomers proved unsuccessful, they were analyzed directly in the mixture. The minor isomer is the 5-nitro derivative **14cNO₂** since irradiation of the methylene-bridge protons gave only NOE enhancement in H-3 (δ 7.77). The remaining isomers (**14aNO₂** and **14bNO₂**) each have one distinct low field singlet [at δ 9.22 (most abundant isomer) and δ 9.47]. Irradiation of methano-bridge protons gave *peri*-NOE enhancement in both isomers, and NOE was detected between H-11/H-12 for both isomers. The data are consistent with nitration at C-10 and C-13.[21]

Protonation of 4*H*-Cyclopenta[*def*]dibenzo[*a,c*]-anthracene 15. This hydrocarbon is the methano-analogue of **16**. AM1 minimizations predict that the presence of the methylene bridge does not alter the preference for attack at C-8 which is most favored in **16**. A dark-red/purple solution was obtained by low-temper-

(20) For previous examples of PAH radical cation formation in superacids, see: Laali, K. K. *Chem. Rev.* **1996**, *96*, 1873. Laali, K. K.; Hansen, P. E. *Res. Chem. Intermed.* **1996**, *22*, 737. Laali, K. K.; Hansen, P. E.; Gelerinter, E.; Houser, J. J. *J. Org. Chem.* **1993**, *58*, 4088. Laali, K. K.; Houser, J. J. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1303.

(21) The possibility that nitronium tetrafluoroborate nitration of this substrate may proceed via initial oxidation to the radical cation cannot be ruled out.

Scheme 3



ature reaction of **15** with FSO_3H/SO_2ClF at −70 °C whose ^1H NMR spectra exhibited broad and featureless resonances with paratropic shifts indicative of competing radical cation formation.[20] Quenching of the superacid solution returned the intact substrate.

In concert with AM1, nitration of **15** produces **15NO₂** as a major product by attack at C-8 (Scheme 3).[21] Nitro substitution causes paratropic shifts in H-7/H-9 and H-1, whereas H-13 (para) remains unchanged. In the ^{13}C NMR, nitro substituent effect on C-8 is 23.1 ppm. Electrospray mass spectrum of **15NO₂** (0.01% NH_4NO_3 in MeOH) showed *m/z* 336 $(M + H)^+$, whose MS/MS gave *m/z* 290 $(M + H - NO_2)^+$ as daughter ion.

Comparative Protonation Study of 16 and 17. Limited electrophilic substitution data (bromination and nitration) are available for **16** and **17** which point to the *meso*-region as the reactive site,[1,22] but there have been no previous protonation studies. In the present work, we find that the outcome of protonation of **16** is analogous to that of the methano-derivative **15**. A dark-purple solution resulted at −70 °C, which exhibited broad NMR features and paratropic shift of proton resonances with the most downfield proton resonance at δ 8.94 due to H-14. The protonation site was deduced to be C-9. This is in accord with AM1 calculations which very strongly prefer the C-9/C-14 positions.

Protonation of **17** gave a blue-purple solution whose NMR spectra, despite broadening especially of the protons, could be analyzed, and partial assignments were made. The most notable feature in the proton spectrum is a dramatic paratropic shift of the ring protons. The center of gravity in the neutral substrate is at δ 8.14 whereas in the carbocation it is at δ 7.49. This pronounced paratropic shift was not observed in the carbocations derived from methano-PAHs discussed above which are formally also 20π systems. A plausible explanation is increased planarity and reduced deformation in **16H⁺** as compared to the *nonalternant* methano-analogues which allow more extensive π-delocalization. Analysis of the $\Delta\delta$ ^{13}C values show that the central ring in the anthracene moiety plus a conjugated carbon become most positive. AM1 minimizations concur with experiment and point to C-7 as site of electrophilic attack.

Comparative Discussion. Directive influence of the methylene bridge is seen in compounds **8**, **9**, **10**, and **11**, where the site of attack is "pseudo-*para*". In **13** substitution occurs *peri* to the bridge. For compounds **12**, **14**, and **15** where the methano-bridge moves from more central "inner" positions to more peripheral "outer" positions substitution is directed to sites away from the methylene-bridge to the *meso* positions of the phenanthrene or anthracene subunits. The outcome of protonation of **15** and **16** is the same.

Figure 3 sketches the derived charge alternation paths for the arenium ions studied in this work based on the magnitude of $\Delta\delta$ ^{13}C values. It is apparent that both the benzannelation mode and the number of annelated benzene rings have a major impact on the charge delocalization mode in the derived carbocations (compare **8H⁺**, **9H⁺**, **10H⁺**, and **11H⁺**). Using these patterns it is possible to *speculate* on the preferred epoxidation sites and possible ring opening modes which could induce similar charge delocalization paths (Figure S2). These patterns point to the possible importance of K-region and M-region epoxides for some of the methano-PAHs. Charge delocalization mode in model carbocation **13H⁺** makes it possible to predict that epoxidation in a bridge-ring may be significant (similar to methano-chrysene **3**).[9] It should be noted, however, that these predictions do not take into account steric factors and accessibility issues which are bound to be important in the outcome of metabolic epoxidation and subsequent DNA adduct formation. Reliability of a carbocation-based structure/activity relationship to identify important epoxidation sites and carbocations in large methano-PAHs could be further tested as synthetic and metabolic studies on this class of compounds advance. The present stable ion study gave no indication for any skeletal rearrangement nor hydride shift to form benzylic carbocations at the bridge (as in **7a⁺**). Bridge alcohol (halide) or ketone derivatives[9,11] might be better substrates for direct access to these intermediates.

Experimental Section

Methylene-bridged PAHs were available from previous studies (in R.G.H laboratory). Their synthesis and characterizations had already been reported.[2−8]

FSO_3H (Allied and Aldrich) was freshly distilled in an all-glass distillation unit under a dry nitrogen atmosphere. SO_2ClF was synthesized from SO_2Cl_2, NH_4F and TFAH according to a modified procedure of Prakash et al.[23] Several distillations provided pure SO_2ClF.

NMR spectra were recorded on a 500 MHz instrument. Those of neutral substrates were recorded in $CDCl_3$ at room temperature. Carbocations were studied between −70° → −30 °C. NMR analyses included ^1H, ^{13}C, H/H COSY, HMQC and HMBC, and NOED experiments.

Mass Spectra. These were obtained using electrospray MS (using an ion-trap instrument with MS/MS capability). MeOH

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(23) Reddy, V. P.; Bellow, D. R.; Prakash, G. K. S. *J. Fluorine Chem.* **1992**, *56*, 195.

was used as solvent to which 0.01% NH_4NO_3 was added to protonate the PAH.

AM1 Calculations. These were carried out using standard methods as implemented in the Hyperchem package version 5.11 (Hypercube Inc, 1999) or Insight II Release 97.0 (MSI, 1999).

General Procedure for Stable Ion Generation. SO_2ClF (ca. 0.4 mL) was distilled into a 5 mm NMR tube containing the PAH (5−10 mg) cooled to dry ice−acetone temperature. To the resulting suspension was added cold FSO_3H/SO_2ClF, and the mixture was mixed (vortex) until homogeneous. Then two drops of cold CD_2Cl_2 were added on the top of the solution, and the mixture was thoroughly mixed (vortex).

Quenching Experiments. The superacid solution was poured into ice−$NaHCO_3$, and the mixture was extracted with CH_2Cl_2. The organic extract was washed (10% NaCl) and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue was analyzed by NMR.

Nitration of 13*H*-Dibenz[*bc*,*l*]aceanthrylene (10). To a solution of **10** (4 mg) in AcOH−CH_2Cl_2 (1:1) (0.2 mL) was added 50% HNO_3 (0.1 mL), and the mixture was stirred overnight. The solution was poured into water and extracted (CH_2Cl_2), and the organic layer was washed (10% NaOH) and dried ($MgSO_4$). Evaporation of the solvent gave **10NO₂** as a yellow solid (5 mg). mp 240 °C (dec); IR ($CHCl_3$) 1520, 1355 cm^{-1}. ES-MS data (see text), NMR (Figure S1).

Nitration of 4*H*-Cyclopenta[*pqr*]picene (14). To a solution of **14** (4 mg) in CH_2Cl_2 (0.5 mL) was added NO_2BF_4 (4 mg). After mixing for 5 min, the solution was poured into water and extracted (CH_2Cl_2). The organic layer was dried ($MgSO_4$). Evaporation of the solvent gave as yellow solid (5 mg), which was analyzed by NMR (Figure S1). The mixture contained three compounds (4 mg) with 5:3:2 ratio (see text).

Nitration of 13*H*-Cyclopenta[*rst*]pentaphene (15). A similar procedure as for **10** was utilized. Following the reaction of **15** (4 mg) and workup, removal of the solvent gave **15NO₂** (4 mg, yellow solid) as a major product. Purification attempts via recrystallization and SiO_2 column chromatography failed. IR ($CHCl_3$) 1529, 1363 cm^{-1}. NMR (Figure S1).

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Supporting Information Available: Figure S1; Figure S2. Selected NMR spectra for protonation of **8**−**13**. This material is available free of charge via the Internet at http://pubs.acs.org

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