Stable Ion Studies of the Chrysene Skeleton. Protonation of Chrysene, 6-Halochrysenes, 6-Acetylchrysene, and 4*H*-Cyclopenta[*def*]chrysene: NMR Studies of Charge Distribution in Chrysenium Cations and AM1 Calculations

Kenneth K. Laali,*[,†] Sandro Hollenstein,[†,‡] Ronald G. Harvey,[§] and Poul Erik Hansen*[,⊥]

Department of Chemistry, Kent State University, Kent, Ohio 44242, Ben May Institute, University of Chicago, Chicago, Illinois 60637, and Department of Chemistry and Life Science, Roskilde University, DK-4000, Roskilde, Denmark

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Chrysene (**1**), 6-fluorochrysene (**2**), 6-chlorochrysene (**3**), and 6-bromochrysene (**4**) are cleanly monoprotonated in $FSO_3H{\cdot}SbF_5$ (ca. 10:1)/SO_2ClF at the C-12 position. 6-Acetylchrysene (**5**) is CO-protonated in FSO_3H/SO_2ClF with significant charge delocalization into the chrysene and provides a model for a C-6-protonated chrysenium cation. 4*H*-Cyclopenta[*def*]chrysene (**6**) is protonated at C-5 (site of bromination and acetylation). The observed chrysenium (methanochrysenium) cations are those predicted by AM1 to have the lowest energies. The NMR characteristics of the resulting arenium ions are discussed and the $\Delta\delta$ ^{13}Cs are compared with AM1 calculated changes in charges [$\Delta q_c = q_c(\text{ion}) - q_c(\text{neutral})$]. Possible relationships between the charge delocalization path in chrysenium ions and metabolic activation of chrysenes by electrophilic pathways via the bay-region epoxide ring opening (→ PAH−DNA adduct) are evaluated.

Introduction

Parent chrysene (**1**) is a weakly active carcinogen with two identical bay regions. On the basis of metabolic studies, the bay-region *anti*-1,2-diol 3,4-epoxide **7** (Figure 1) was identified as the ultimate carcinogen.[1] Fu and Harvey have reported on synthetic routes to **7** and to other diol epoxides of chrysene and on their biological activity.[2,3] The same diol epoxide is the principle active form of **8** for which introduction of a *peri* methyl enhances carcinogenicity dramatically.[1] While **9** is also formed, it is thought to be biologically less important.[1] Bioassays on selectively fluorinated 5-methylchrysenes have narrowed down the active sites mostly to C-12, C-1, and C-3.[4,5]

Introduction of a methano-bridge into chrysene (→ **6**) increases electrophilic reactivity while at the same time removing one of the bay regions. Various synthetic strategies have been devised to produce **6** in satisfactory yields for further studies.[6,7] In **6**, apart from the diol epoxide activation pathway, a new reactive site for DNA binding may be formed by enzymatic hydroxylation on the relatively acidic bridge position followed by esterification and cleavage to a carbocation.[8]

The bay-region theory has provided a connection between higher metabolic activity of bay-region epoxides and increased stability of their derived carbocations,[9,10] which also correlates with their localization energies based on simple MO calculations.[11] The 6-position in chrysene is the site of electrophilic attack. Protiodetri-

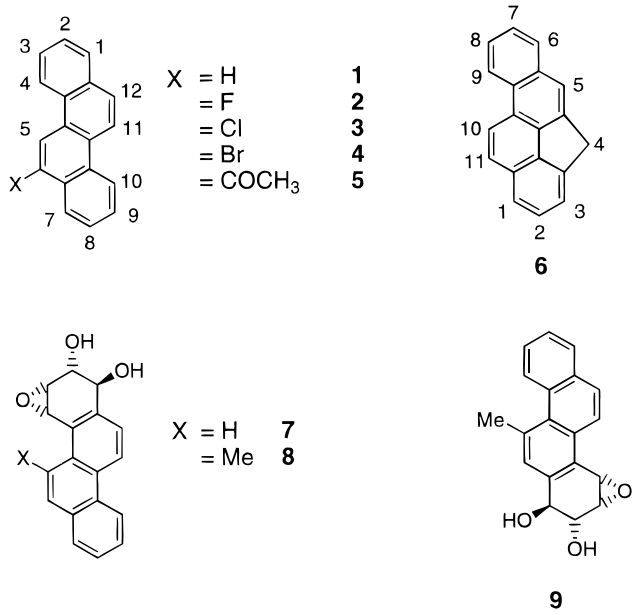

Figure 1. Chrysene (**1**), 6-halochrysenes (**2**−**4**), 6-acetylchrysene (**5**), 4*H*-methanochrysene (**6**), and metabolically significant diolepoxids of chrysene (**7**−**9**).

† Kent State.
‡ Postdoctoral research fellow 1996−1997.
§ University of Chicago.
⊥ Roskilde University.
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(1) Harvey, R. G. In *Polycyclic Hydrocarbons and Carcinogenesis*; Harvey, R. G. Ed.; ACS Symposium Series 283; American Chemical Society: Washington, DC, 1985; Chapter 3.
(2) Fu, P. P.; Harvey, R. G. *J. Chem. Soc., Chem. Commun.* **1978**, 585.
(3) Fu, P. P.; Harvey, R. G. *J. Org. Chem.* **1979**, *44*, 3778.
(4) Hecht, S. S.; Loy, M.; Mazzarese, R.; Hoffmann, D. *J. Med. Chem.* **1978**, *21*, 38.
(5) Hecht, S. S.; Mazzarese, R.; Amin, S.; LaVoie, E.; Hoffmann, D. in *Polynuclear Aromatic Hydrocarbons*; Jones, P. W., Leber, P., Eds.; Ann Arbor Science: Ann Arbor, MI, 1979; pp 733−752.
(6) Lee-Ruff, E.; Kruk, H.; Katz, M. *J. Org. Chem.* **1984**, *49*, 553.
(7) Harvey, R. G.; Pataki, J.; Cortez, C.; Di Raddo, P.; Yang, C. X. *J. Org. Chem.* **1991**, *56*, 1210. Yang, C. X.; Harvey, R. G. *Tetrahedron* **1992**, *48*, 3735.
(8) Dai, W. D.; Abu-Shqara, Harvey, R. G. *J. Org. Chem.* **1995**, *60*, 4905.
(9) Lehr, R. E.; Kumar, S.; Levin, W.; Wood, A. W.; Chang, R. L.; Conney, A. H.; Yagi, H.; Sayer, J. M.; Jerina, D. M. In *Polynuclear Aromatic Hydrocarbons and Carcinogenesis*; Harvey, R. G., Ed.; ACS Symposium Series 283; American Chemical Society: Washington, DC, 1985; Chapter 4.
(10) Wood, A. W.; Levin, W.; Chang, R. L.; Yagi, H.; Thakker, D. R.; Lehr, R. E.; Jerina, D. M.; Conney, A. H. In *Polycyclic Aromatic Hydrocarbons*; Jones, P. W., Leber, P. Eds.; Ann Arbor Science Publishers, Inc.: Ann Arbor, MI, 1979; pp 531−551.

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tation studies by Taylor and associates[12,13] gave the positional reactivity order 6 (12) > 5 (11) > 1 (7) > 4 (10) > 3 (9) > 2 (8). Hückel localization energies predict 6 > 1 > 5 ∼ 4 > 3 > 2.[12] For acetylation, the reactivity order 6 >> 5 > 1 > 3 ∼ 2 >>4 has been found.[14]

In relation to our previous and ongoing studies of PAH arenium ions under persistent ion conditions probing the charge distribution pattern in the resulting carbocations,[15−20] we report here on the generation of chrysenium cations **1H**$^+$−**4H**$^+$, CO-protonated 6-acetylchrysene **5H**$^+$, and methanochrysenium ion **6H**$^+$ and explore the charge delocalization mode in the resulting arenium ions by NMR studies and AM1 theory.

Results and Discussion

NMR Spectra of the Chrysenes. The ^{1}H NMR spectra (300 and 250 MHz) of chrysenes are complex due to extensive overlap of several protons and the narrow range of the chemical shifts coupled to low solubility in the case of **1** and **2**. The H−H COSY together with the C−H HETCOR relationships in the spectrum of **6** allowed more specific assignments of the reported data.[21] The H-9/H-10 bay region protons give rise to two low-field doublets at 8.70 and 8.52 ppm, respectively.

The one-bond and long-range C−F couplings aided the assignments of the ^{13}C NMR spectrum of **2**. These values compare well with those of 9-fluorophenanthrene.[22] 9-Chloro- and 9-bromophenanthrene served as models for determining substituent effects in **3** and **4**.[23] The data for **1** have been reported.[24]

The ^{13}C assignments for **6** were based on off-resonance decoupling experiments and long-range C−H couplings. The methylene bridge was used as a substituent in comparsion with parent chrysene. Similar results were obtained in comparing 4,5-methanophenanthrene with phenanthrene.[25] These assignments were subsequently enhanced via analysis of 2D-NMR spectra (H−H COSY and C−H HETCOR).

In the ^{1}H NMR spectrum of **5**, the bay-region H-7 appears as a distinct singlet at 9.07 ppm. Assignments of the proton and carbon resonances were made on the basis of proton chemical shifts in comparison with 6-halochrysenes, H−H couplings, carbon chemical shifts, and relative intensities (several carbons and protons may possibly be interchanged).

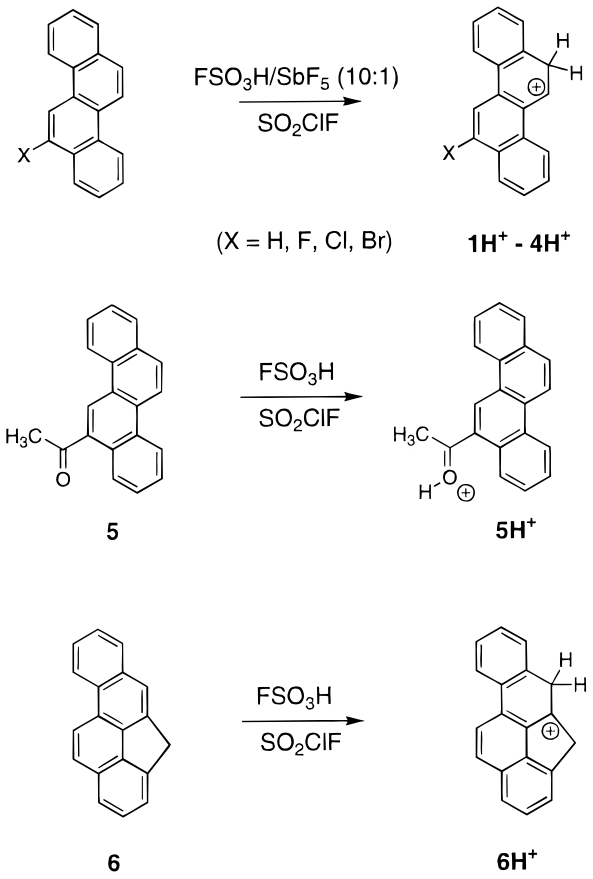

Figure 2. Protonation reactions of **1**−**6**.

Protonation Studies (Figures 2−5 and Supporting Information). To our surprise, neither chrysene **1** nor its 6-halo derivatives **2**−**4** were fully protonated in FSO_3H/SO_2ClF. Instead, heterogeneous solutions were formed with development of red color showing very broad proton resonances. Persistent chrysenium cations were cleanly obtained when the acidity (H_o) was increased by addition of a few drops of $FSO_3H{\cdot}SbF_5$ (4:1) to the heterogeneous mixture of the chrysenes in FSO_3H/SO_2ClF whereupon clear dark-red homogeneous solutions resulted. Thus, the needed superacid system is approximately $FSO_3H{\cdot}SbF_5$ (10:1). The chrysenium cations were stable between −70 and −40 °C. The resolution and the line widths in the ^{1}H NMR spectra were optimal for spectra recorded between −60 and −80 °C (−20 °C for **5H**$^+$ and −45 °C for **6H**$^+$).

The 6-acetyl derivative **5** is cleanly CO-protonated with FSO_3H/SO_2ClF with no NMR indication for arenium ion formation. The CO*H*$^+$ signal appears as a distinct singlet at ∼12.7 ppm below −45 °C. On raising the temperature, it gets very broad while acetyl rotation becomes more facile, giving rise to sharper and more resolved aromatic proton resonances.

The methylene-bridged chrysene **6** is fully protonated in FSO_3H/SO_2ClF forming a clear red solution of **6H**$^+$ that was stable for several days (−70 → −20 °C). Attempts to diprotonate **6** with $FSO_3H{\cdot}SbF_5$ (1:1)/SO_2ClF gave a blue-black solution exhibiting very broad ^{1}H NMR features indicative of oxidation to the radical cation. Indeed, the ESR spectrum exhibited a strong featureless absorption with $g = 2.0025$ and $\Delta H_{pp} = 10.4$ *g* at 225 K.

General Features of the NMR Spectra of the Protonated Chrysenes (Figure 3): The Proton NMR Spectra. The C*H*$_2$ (carbocation) resonance in the chry-

(11) Lowe, J. P.; Silverman, B. D. *J. Am. Chem. Soc.* **1984**, *106*, 5955. Lowe, J. P.; Silverman, B. D. *J. Am. Chem. Soc.* **1981**, *103*, 2852.
(12) Archer, W. J.; Taylor, R.; Gore, P. H.; Kamounah, F. S. *J. Chem. Soc., Perkin. Trans. 2* **1980**, 1828.
(13) Taylor, R. *Electrophilic Aromatic Substitution*; Wiley Interscience: Chichester, 1990; Chapter 3.
(14) Reference 13, Chapter 6.
(15) Review: Laali, K. K. *Chem. Rev.* **1996**, *96*, 1873.
(16) Laali, K. K.; Hansen, P. E. *Res. Chem. Intermed.* **1996**, *22*, 737.
(17) Laali, K. K.; Houser, J. J. *J. Chem. Soc., Perkin. Trans. 2* **1996**, 1265.
(18) Laali, K. K.; Hansen, P. E.; Laali, K. K.; Hansen, P. E.; Houser, J. J.; Zander, M. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1781.
(19) Laali, K. K.; Hansen, P. E. *J. Chem. Soc., Perkin Trans. 2* **1995**, 537.
(20) Laali, K. K.; Hansen, P. E. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2249 and references cited therein.
(21) Abu-Shaqara, E.; Yang, C. X.; Harvey, R. G. *J. Org. Chem.* **1992**, *57*, 3312.
(22) Hansen, P. E.; Berg, A.; Jakobson, H. J.; Manzara, A. P. *Org. Magn. Reson.* **1977**, *10*, 179.
(23) Martin, R. H.; Morian, J.; Defay, N. *Tetrahedron* **1974**, *30*, 179.
(24) Pouchert, C. J.; Behnke, J. *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra*; Aldrich Chemical Co.: Milwaukee, WI, 1993.
(25) Laali,K. K.; Hollenstein, S.; Hansen, P. E. *J. Org. Chem.*, submitted.

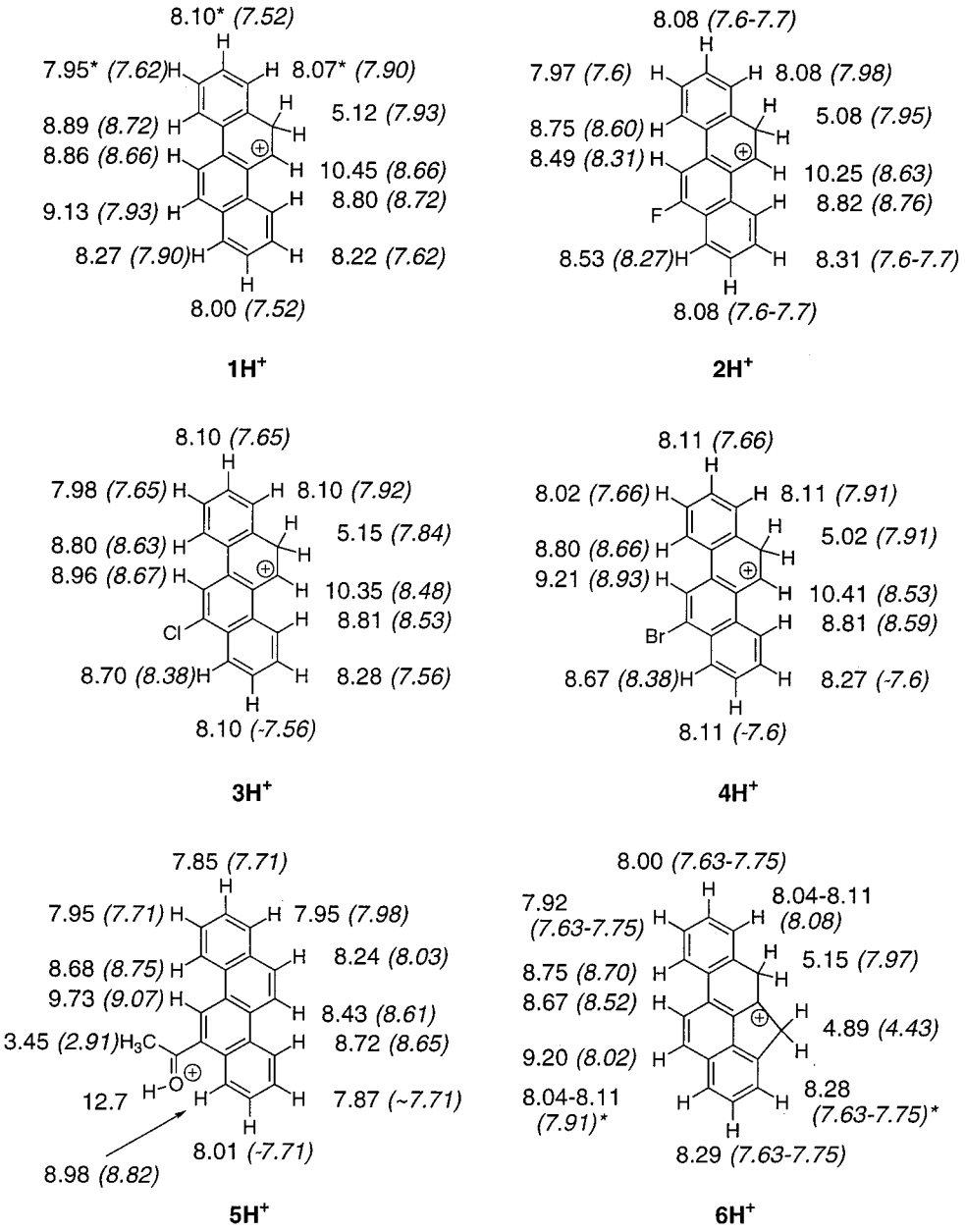

Figure 3. ^{1}H-chemical shifts of **1H**$^+$−**6H**$^+$ and starting materials (**1**−**6**, *italic*).

senium cations appear in the 5−5.15 ppm range. The proton chemical shifts change rather dramatically depending on the PAH/superacid ratio and the nature of the superacid system, whereas subsequent dilution with SO_2ClF had little effect.

The ^{1}H NMR spectrum of **2H**$^+$ was assigned on the basis of COSY and HETCOR spectra; H-5 was assigned on the basis of a three-bond coupling of 9 Hz, and the singlet at 10.25 was unambigously assigned to H-11. These resonances clearly show that C-12 is the site of protonation. The two-spin systems of A and D rings were assigned on the basis of COSY relationships. Specific assignments to each ring were based on H-7. C-7 shows a three-bond J_{C-F} of 7 Hz; this identified C-7. From the HETCOR spectrum H-7 was assigned, following which the remaining spins of the spin system could be assigned to protons of the D ring. For those of the A ring, the bay-region proton H-4 was taken as the most deshielded within the spin system.

The ^{1}H NMR spectra of **1H**$^+$, **3H**$^+$, and **4H**$^+$ are very similar except for differences due to substituent effect. The chemical shift of H-5 varies in a similar fashion as that of 9-substituted phenanthrenes;[26] likewise, the H-7 chemical shift depends on the substitutent (Figure 3).

The ^{1}H NMR spectrum of **5H**$^+$ exhibits a distinct very-low-field singlet at 9.73 for H-7. The carbonyl carbon moves from 202.1 in **5** to 211.8 ppm in the oxonium ion. Assignments of the aromatic protons were assisted by the COSY and HETCOR relationships.

The ^{1}H NMR spectrum of **6H**$^+$ exhibits two distinct broad pseudo singlets at 5.15 and 4.89 ppm for the CH_2 of the protonation site and the methylene-bridge, respectively. Coupling is within the line-broadenig limit and is apparent via H−H COSY. The most deshielded doublet at 9.20 ppm is due to H-11, whereas low-field doublets at 8.75 and 8.67 ppm are due to bay-region H-9/H-10 protons (H−H COSY and C−H HETCOR relationships).

The ^{13}C NMR Spectra (Figures 4 and 5). For **2H**$^+$, the assignments were based on a HETCOR spectrum for

(26) Bartle, K. D.; Smith, J. A. S. *Spectrochim. Acta* **1967**, *23A*, 1689.

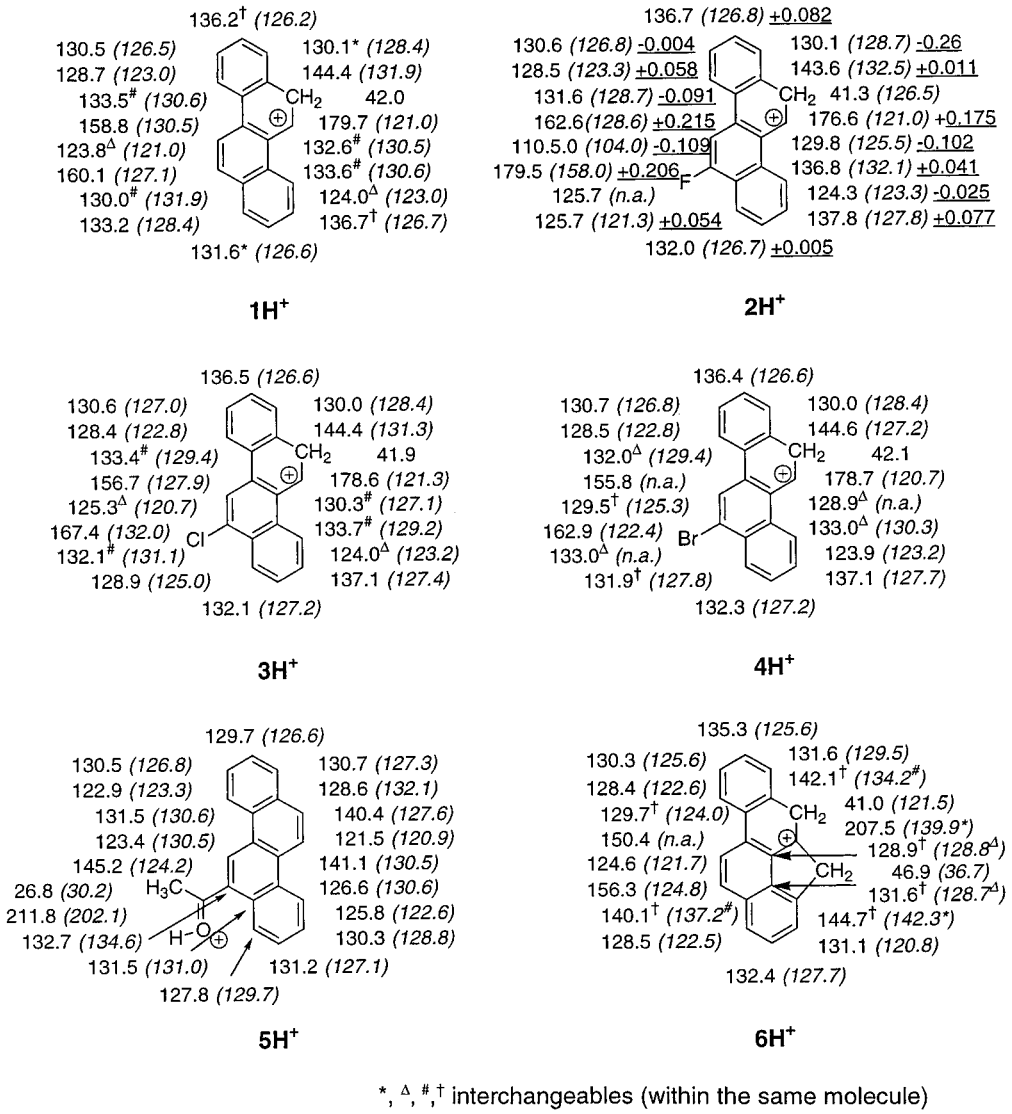

Figure 4. ^{13}C-chemical shifts of **1H**$^+$−**6H**$^+$ and starting materials (**1**−**6**, *italic*) and calculated Δq's for **2/2H**$^+$ (underlined).

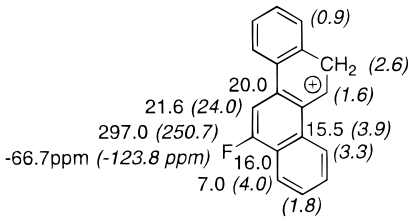

Figure 5. C−F coupling constants (Hz) and ^{19}F-chemical shifts of **2H**$^+$ and **2** (*italic*).

proton-bearing carbons, C−F couplings, and substitutent effects: C-6 was identified by means of its large $^1J_{C-F}$ coupling and C-6a by a $^2J_{C-F}$ of 16 Hz. The C−F coupling to C-4b is unusually large, probably because of the increased bond order of the C-4b/C-5 bond. A smaller $^3J_{C-F}$ of 15.5 Hz is observed at C-10a; of the remaining quaternary carbons, that of C-12a (*ortho* to the protonation site) is the most deshielded. Finally, assignments of C-4a/C-10a may be interchanged. For other halochrysenium ions the ^{13}C assignments were based on chemical shifts and comparison with **2H**$^+$ (see below). For **6H**$^+$, the assignments were based on a C−H HETCOR spectrum for proton-bearing carbons. The most deshielded quaternary carbon resonance is at 207.5 ppm and was assigned to C-4a.

Structure Assignments. A comparison of the ^{13}C NMR data for the chrysenium cations (**1H**$^+$−**4H**$^+$) clearly reveals variation due to the halogen substituents, but the overall picture is very similar, especially for **1H**$^+$, **3H**$^+$, and **4H**$^+$. The 6-fluoro substituents causes the largest effects. Taking into account the variations caused by substituents in other PAHs,[22,27] it is concluded that all four chrysenes are protonated at C-12.

For comparison, the relative energies and charges for **1** and **2** were calculated by the AM1 method (ref 15 and Supporting Information). In both cases, in agreement with superacid studies, the most stable chrysenium ions are formed by C-12 (C-6) protonation.

The AM1-calculated relative stability order is as follows: C-6 > C-1 > C-4 > C-5 > C-3 > C-2. The presence of fluorine at C-6 increases the stability of the C-5-protonated cation, thereby changing the sequence to C-12 > C-5 > C-1 > C-10 > C-4 ~ C-3 > C-11 > C-7 > C-8 > C-2 > C-9. For the most favored cations, AM1 changes in carbon charges [$\Delta q_c = q_c$(ion) − q_c(neutral)] shows a consistent pattern whereby C-5a, C-6, and C-11 carry the most positive charge.

In acetyl-protonated chrysene, the positive charge is

(27) Dewar, M. J. S.; Kelemen, J. *J. Chem. Phys.* **1968**, *49*, 499.

primarily delocalized into C-5, C-11a, and C-12. It is analogous to a C-6-protonated chrysenium ion.

For the methano-analogue **6H**$^+$, AM1 predicts protonation at C-11 and C-5 to be almost equally favored (0.3 kcal/mol difference; ref 15 and Supporting Information). Protonation at C-11 was excluded on the basis of the absence of two low-field aromatic singlets, whereas several other protonation sites could also be excluded on the basis of their predicted higher relative energies and NMR arguments. A distinction between C-5 and C-1 hinged on distinguishing a "singlet" in a highly overlapping region (8.11−7.92 ppm) of the ^{1}H NMR spectrum, where four protons appear. The problem was solved with the aid of low-temperature H−H COSY and C−H HETCOR analysis on a freshly prepared sample, showing that in agreement with AM1 predictions and in line with bromination and acetylation reactions on **6** protonation occurs at C-5 (Figure 2).[28a]

For all the studied cations, AM1-calculated changes in carbon charges were used as a guiding tool to enhance the assignments (reduce the number of interchangeable assignments), especially for ring junction carbons having very narrow chemical shift range.[28b]

Charge Delocalization Mode in Chrysenium (Methanochrysenium) Cations. The $\Delta\delta$ ^{13}C values can be used to map out the charge delocalization pathway in the resulting chrysenium cations. Correlation between $\Delta\delta$ ^{13}C and AM1 changes in carbon charges Δq for **2H**$^+$ (Supporting Information) shows significant deviation for carbons that are close to the protonation site (large $\Delta\delta$ ^{13}C values). The correlation does not improve when regional charges (carbon and hydrogen) are plotted against $\Delta\delta$ ^{13}C values. A similar picture emerged for C-6-protonated benzo[a]pyrene.[18]

Analysis of the $\Delta\delta$ ^{13}C values shows that **1H**$^+$ and **3H**$^+$ are very similar. For **4H**$^+$ more positive charge is found at C-6 and less at C-4b compared to **1H**$^+$ and **3H**$^+$, whereas the opposite is seen for **2H**$^+$. For sites like C-12a and C-11, a gradual change was found. For **2H**$^+$, both the observed $\Delta\delta$ ^{19}F (57.1 ppm) and the change in the magnitude of $^1J_{C-F}$ (from 250.7 to 297 Hz) may serve as gauge of back-bonding and fluoronium ion character. Both parameters are larger for the 6-fluorochrysenium cation than for the fluoropyrenium ions we previously reported.[29]

For the methanochrysenium cation **6H**$^+$, the charge alternation path for protonation at C-5 is very similar to those of C-6-protonated **1H**$^+$ and C-12-protonated **2H**$^+$ with the positive charge residing primarily on three-ring carbons (C-4a, C-9b, and C-11 in **6H**$^+$).

A Comparison of the Protonation Results and Connection to Biological Activation. In concert with Taylor's early protiodetritation results,[12] our stable ion and AM1 studies demonstrate that in the absence of steric factors, C-12 (C-6) is the most favored site for electrophilic attack in chrysene. Presence of halogen substituents at C-6 does not alter this preference nor the mode of charge delocalization in the resulting arenium ions.

The presence of fluorine at C-6 does lower the energy for C-5 protonation, but the C-12-protonated cation still has the lowest energy.

The positive charge in the chrysenium cation is located primarily at four carbon centers (*ortho* and *para* to the site attack and at C-12 (C-6)). Thus, for **1H**$^+$ and **5H**$^+$, C-5 and C-12 appear to be the most plausible site(s) for subsequent nucleophilic trapping.

The chrysenium cations generated in this study may be considered models for 11,12- (or 5,6)-bay-region epoxide ring opening. Metabolic studies, however, do not support the notion that these sites are the preferred biological epoxidation sites. The metabolites of 5-methylchrysene indicate epoxidations mainly at the 7,8-, 1,2-, and 9,10-positions. The phenols formed are at C-1, C-7, and C-9.[5]

It appears that accessibility of the A and D ring to cytochrome P450 might be an important factor. The resulting epoxide(s) would then open in such a way to generate the most highly delocalized carbocation(s) (bay-region theory).

In mapping out charge delocalization in carbocations formed from the bay-region epoxides of chrysenes, regioisomeric α-phenanthrene-substituted carbocations may represent better models. Generation and charge delocalization in this category of carbocations and ways to modulate π-participation by the PAH substitutent is underway and will be reported.

Experimental Section

FSO_3H (Linde) and SbF_5 (Fluorochem or Aldrich) were doubly-distilled at atmospheric pressure under argon in an all-glass distillation unit and stored in Nalgene bottles with Teflon seals under argon.

SO_2ClF was prepared by a modified procedure of Prakash et al.[30] from SO_2Cl_2, ammonium fluoride, and CF_3COOH. Several distillations provided pure SO_2ClF.

The halochrysene samples were gifts donated by Prof. Arne Berg (Aarhus University, Denmark). The chloro- and bromochrysenes had been synthesized by standard electrophilic halogenation,[31] whereas 6-fluorochrysene was made from the 6-nitro compound via the amino, diazo derivatives.[32] The halochrysenes were purified by crystalization. Purities were checked by ^{1}H and ^{13}C (and ^{19}F for **2**) NMR prior to protonation studies.

6-Acetylchrysene (**5**) was synthesized by standard Friedel−Crafts acylation[33] of **1** ($MeCOCl/AlCl_3$) and purified by column chromatography (pentane/ether 10:1−5:1).

4*H*-Cyclopenta[*def*]chrysene was synthesized at the University of Chicago according to ref 7.

Procedure for Stable Ion Generation. In a typical experiment, about 15−30 mg of the chrysenes was placed in a 5 mm NMR tube. The NMR-tube was then connected to the HV-line. After several cycles of degassing and flushing with argon, the NMR tube was evacuated for ca. 5 min. About 0.3 mL of SO_2ClF was then condensed into the NMR tube and cooled with liquid nitrogen. After completion of the SO_2ClF addition, the liquid nitrogen was exchanged for a dry ice/acetone bath, and about 0.05 mL of superacid (FSO_3H/SbF_5 10:1) was slowly added under argon. The color suddenly turned deep red. After vigorous stirring at −78 °C (vortex), about 0.1 mL of CD_2Cl_2 was slowly added and the cold sample was vortexed again.

(28) (a) The presence of a minor arenium ion (<10%) is decernable in both the ^{1}H and ^{13}C NMR spectra (Supporting Information). In the ^{1}H NMR, a deshielded doublet at 9.70 ppm, a singlet at 8.82 ppm, and a pseudotriplet at ca. 8.19 ppm are clearly seen; extensive overlap precludes a definitive assignment for the minor ion. (b) For these carbons correlation of Δq_c and $\Delta\delta^{13}$C is reasonable (see the supporting information); minor variations in the chemical shift of these carbons do not affect the deduced charge delocalization mode.

(29) Laali, K. K.; Hansen, P. E. *J. Org. Chem.* **1993**, *58*, 4096.

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

(31) Reference 13, Chapter 9, and references cited therein.

(32) Badger, G. M.; Stephens, J. F. *J. Chem. Soc.* **1956**, 3637.

(33) Gore, P. H.; Kamounah, F. S.; Miri, A. Y. *J. Chem. Res., Synop.* **1980**, 40.

Alternatively, the chrysenium cations were generated using our previously reported standard technique under argon without the HV-line (for details see ref 18).

NMR spectra were recorded on a GE-GN-300 MHz instrument at KSU and on a Bruker AC-250 MHz at Roskilde.

The procedures for low-temperature NMR studies were analogous to our previously reported methods.[34]

AM1 calculations were carried out using MOPAC 93 running under OS/2 at the University of Akron (Dr. John J. Houser, retired) and subsequently by using the Hyperchem package (Hypercube 1995) at KSU. The calculated energies and charges obtained using these packages were found to be the same within 0.1 kcal/mol.

(34) Laali, K. K.; Koser, G. F.; Subramanyam, S.; Forsyth, D. A. *J. Org. Chem.* **1993**, *58*, 1385.

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Supporting Information Available: Selected ^{1}H, H−H COSY, ^{13}C, and C−H HETCOR spectra of **1H**$^{+}$, **2H**$^{+}$, **5H**$^{+}$, and **6H**$^{+}$; calculated energies of all possible protonated chrysenes and Δq's of the C-atoms; and plot of Δq_c vs $\Delta\delta^{13}$C (16 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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