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Generation of the First Series of Oxonium−Annulenium Dications from *trans*-15,16-Dimethyldihydropyrene DMDHP: A Diatropic → Paratropic → Diatropic/Paratropic Manifold by Mono- and Diprotonation

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The 2-formyl derivative of *trans*-dimethyldihydropyrene DMDHP **5** is monoprotonated with FSO_3H/SO_2ClF and diprotonated with $FSO_3H{\cdot}SbF_5$ (4:1)/SO_2ClF to form persistent carboxonium monocation $\mathbf{5H}^+$ and carboxonium−annulenium dication $\mathbf{5H_2}^{2+}$, respectively. With the cyclohexenone-fused **8** and cyclopentenone-fused **9** derivatives, the tendency to diprotonate increases, whereby dications $\mathbf{8H_2}^{2+}$ and $\mathbf{9H_2}^{2+}$ are cleanly generated in FSO_3H/SO_2ClF. However, the monocation $\mathbf{8H}^+$ could be produced in $HOAc{\cdot}TFAH/CD_2Cl_2$ under exchanging conditions. For **9**, diprotonation competes even at these low acidities; the isomeric **10** behaved similarly. The biscyclopentenone-fused derivatives **11** and **12** form bisoxonium ions in $TFAH/CD_2Cl_2$ and Lewis acid complexes with $SnCl_4$. The transoid form has a stronger tendency to exist in equilibrium with ring protonation. The charge delocalization pathway in the annulene ring are deduced in the cations and compared with the previously studied ring protonated 12-annulenium ions derived from parent **1** and its 2-nitro and 2-bromo derivatives. Examination of the shielding/deshielding trends in the internal methyl protons and the annulene ring protons is used to shed light on the ring current effects in the mono- and dications. The charge delocalization mode at the periphery of the annulenium cation is also evaluated on the basis of magnitude of $\Delta\delta^{13}C$ values. AM1 calculations were used to obtain the relative protonation energies for various sites for comparison with the experiment. Diprotonation of the 2,7-dinitro derivative **13** and oxidation of parent **1** were also examined.

Introduction

Numerous recent studies have shown that Boekelheide's *trans*-15,16-dimethyl-dihydropyrene (DMDHP) **1**,[1] a 14π-diatropic annulene, with its highly shielded internal methyl groups is a sensitive probe for monitoring the ring current effects and aromaticity in annulenes (Figure 1).[2−6]

The syntheses of [a]ring- and [e]ring-benzannelated dihydropyrenes[2,3,7] and their PAH-fused analogues (e.g., naphtho-, pyreno-, phenanthro-, biphenyleno-, and acenaphthyleno-DMDHP) [4,8−10] have been accomplished. Several heteroaromatic-fused counterparts (e.g., furan and thiophene) were also synthesized, and their ring current effects were examined.[6,11]

Whereas the diatropicity in the macrocycle is reduced by benzannelation due to bond localization, fusion of nonconjugated carbocyclic rings does not significantly alter the ring current.[5]

Changes in the degree of diatropicity and the induced diamagnetic ring current in **1** as a function of substituents, e.g., nitro **2**, bromo **3**, aryl **4**, formyl **5** attached to the periphery of the macrocycle are rather small.[12−14]

The most dramatic effects observed in the ring current are in the dianion **6**.[15] In comparison, a much smaller effect was seen in the π-complexed example **7**, where a paratropic 16π-annulene is generated via metal back-bonding (Figure 1).[16]

In our previous study,[17] we showed that the [14]-annulenes **1**, **2**, and **3** are monoprotonated in FSO_3H/SO_2ClF to form persistent diamagnetic [12]annulenium ions with strong preference for attack at C-2 (Figure 2). The resulting induced paramagnetic ring current caused substantial deshielding of the internal methyl chemical

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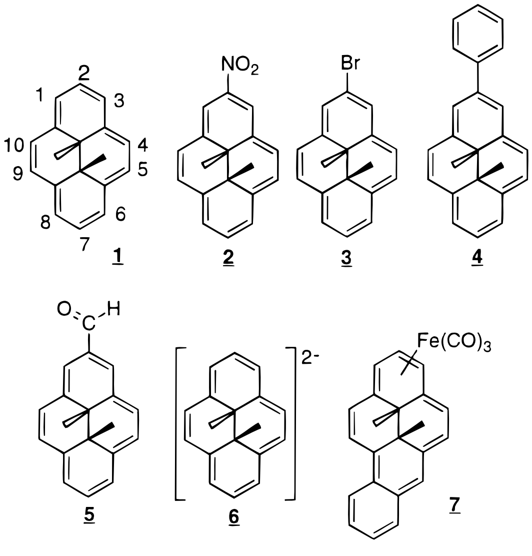


Figure 1. Dimethydihydropyrene **1**, its 2-nitro, 2-bromo, 2-phenyl, and 2-formyl derivatives (**2**−**5**), its dianion **6**, and the $Fe(CO)_5$-complexed benzo derivative **7**.

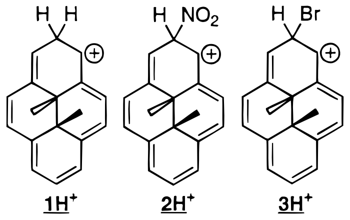


Figure 2. Persistent annulenium ions of ipso attack (ref 17).

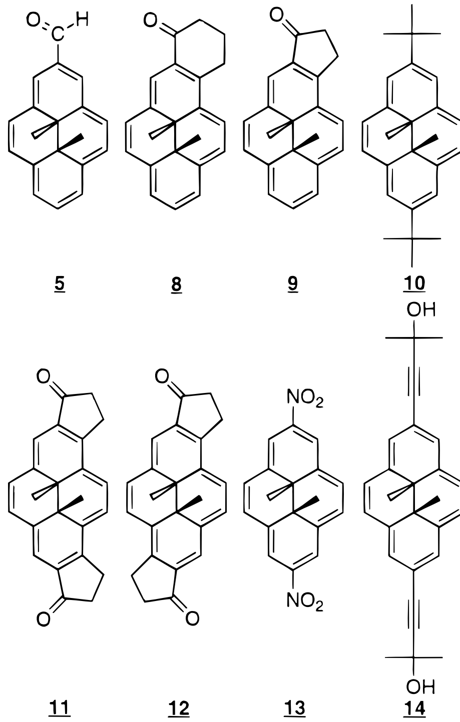


Figure 3. List of DMDHP derivatives studied.

shifts. NMR studies allowed not only the ring current effects but also the charge delocalization pathway at the periphery of the dihydropyrenium cation to be deduced in comparison with the pyrenium ions.

The availability of the 2-formyl **5** and the cyclopentenone- and cyclohexenone-fused derivatives **8**, **9**, **10**, **11**, and **12** (Figure 3) provided the impetus for the present stable ion study with particular interest in the possibility of creating a diatropic → paratropic → diatropic manifold by mono- and diprotonation to form carboxonium monocations and carboxonium−annulenium dications. Protonation of the 2,7-dinitro derivative **13** and of the 2,7-alkynyl-diol **14** and oxidation of **1** with SbF_5/SO_2ClF were also explored.

Results and Discussion

NMR Assignments of the Precursors (Figure 7) and the Resulting Annulenium Cations (Figure 5). The ^1H NMR spectra were assigned on the basis of chemical shifts, multiplicities, coupling constants, integrals, H/H COSY, and H/C HETCOR relationships, complemented in several cases by NOED spectra. The ^{13}C NMR spectral assignments were based on the chemical shifts and H/C HETCOR relationships. Depending on the annulene structure and the complexity of the systems, a number of quaternary carbons could not be specifically assigned and remain interchangeable.

AM1 Calculations. The inability of semiempirical methods (AM1, PM3) to predict C_{2h} structure (rather than C_2 symmetry) for the parent **1** has been discussed before.[6,17] On the other hand, for the annulenium ions, there is good qualitative agreement between the charge alternation path deduced on the basis of NMR and that predicted on the basis of changes in the Mulliken carbon charges Δq_C. Furthermore, the observed site of ring protonation is usually that predicted by AM1 to be the most favored.

Mono- and Diprotonation of the [14]Annulenes (Figure 4). Protonation of 5. Addition of cold FSO_3H to **5** in SO_2ClF gave the carboxonium ion $\mathbf{5H^+}$ as a persistent green solution. In the ^1H NMR spectrum (at −51 °C) the internal methyls appear at −1.95 and −1.87 ppm and the aldehydic C**H** at 8.84 ppm. Observation of an NOE between the H-1 singlet at 8.68 ppm and the aldehydic proton taken together with the 1.76 ppm shielding of the latter (syn to the lone pair) is indicative of the *Z* configuration of the carboxonium group (H,H anti). The $CO\mathbf{H}^+$ resonance is not observable as a separate signal in FSO_3H (at −51 °C) due to rapid exchange. Comparison of the ^1H NMR chemical shifts of **5** and $\mathbf{5H^+}$ shows that π-charge delocalization into the COH^+ group and contribution from a mesomeric (paratropic) 12π-annulenium ion (13π if the contribution of the exocyclic double bond is also included in the cyclic array) (see also Figure 8 and later discussion) induce a paramagnetic ring current which deshields the internal methyls and shields the protons of the macrocycle relative to the precursor (with the exception of H-7). In the ^{13}C NMR spectrum, the $\mathbf{C}OH^+$ appears at 177.0 ppm, shielded by 16.5 ppm. There is a clear charge alternation path through the periphery with C-5a, C-8a, C-7, C-4, C-10 (and C-1) becoming most positive. The nonequivalence of both C-1/C-3 and H-1/H-3 is noteworthy.

Protonation of **5** with $FSO_3H{\cdot}SbF_5$ (4:1)/SO_2ClF gave a green solution whose NMR spectral data are in full agreement with the formation of $\mathbf{5H_2^{2+}}$, a carboxonium−annulenium dication. In the ^1H NMR spectrum (−52 °C), the internal methyls appear at 0.48 and 0.10 ppm, and the $CO\mathbf{H}^+$ resonance gives rise to a broad singlet at 13.4 ppm. The $C\mathbf{H}_2$ (H-5,5′) is at 4.49 and shows a ca. 2.3 Hz

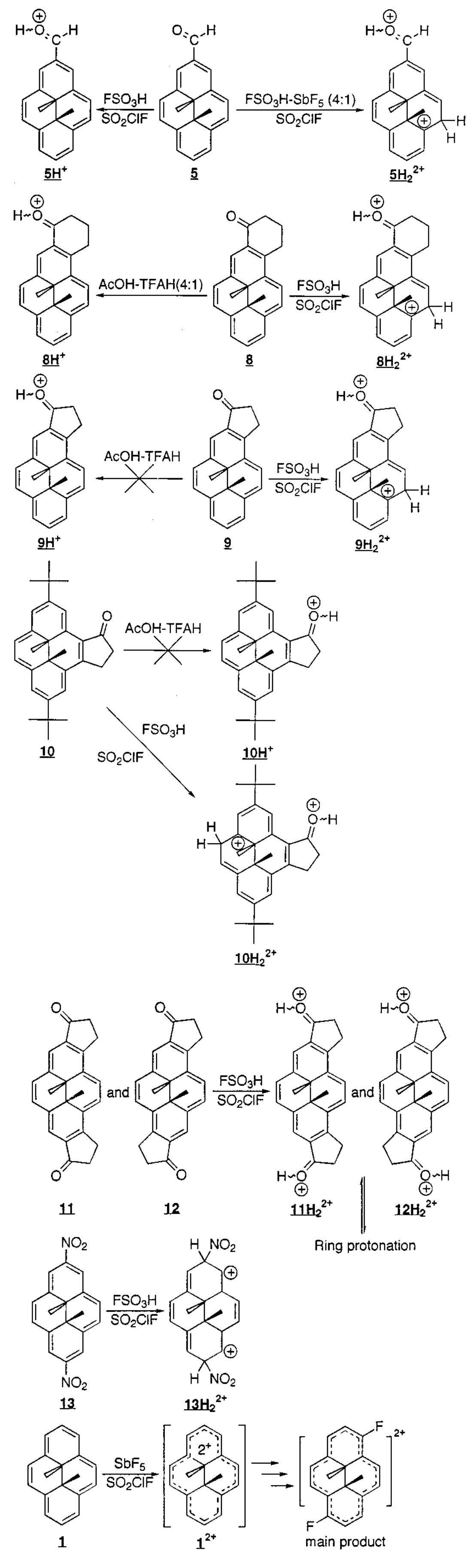


Figure 4. Protonation studies; formation of carboxonium ions and carboxonium–annulenium dications.

coupling to H-10. Observation of an NOE between the aldehydic proton at 9.45 ppm and H-1 at 9.05 ppm taken together with the absence of any visible coupling in the 9.45 ppm resonance and shielding of H-3 by ~1 ppm relative to H-1 (proximity of the lone pair) suggests an *E* configuration at the carboxonium group (H,H syn). In addition to the broad singlet at 13.4 ppm, the ^{1}H NMR showed another broad singlet at 10.36 ppm. If this is the CO**H**$^+$ of the *Z*-isomer, its **H**COH$^+$ must be burried under the acid peak. Diprotonation with FSO$_3$H•SbF$_5$ (1:1), however, gave a much sharper acid peak with no indication for another **H**COH$^+$ singlet, but more of the broad resonance at 10.36 ppm was produced in addition to other unresolved broad resonances between 8.5 and 8.70 ppm; it was concluded that the latter was due to a byproduct.

In the ^{13}C NMR, the **C**H$_2$ (C-5) appears at 37.4 ppm and the carboxonium carbon at 199.8 ppm (deshielded by 22.8 ppm relative to **5H**$^+$). The most deshielded annulenium carbons are the C-5a, C-8a, C-7, C-1, C-4, and C-10. The extent of charge delocalization into the carboxonium moiety from C-1/C-3 is clearly nonuniform; C-1 is at 169.2 ppm ($\Delta\delta$ = ca. 30 ppm), but C-3 is observed at 129.2 ppm, close to the value in the carboxonium ion.

The mesomeric form A of **5H$_2$**$^{2+}$ (Figure 8) is a 12π-paratropic annulenium ion, whereas B is a 10π-diatropic dication (11π if the exocyclic double bond is included). Comparison of the NMR data between **5H$_2$**$^{2+}$ and **1H**$^+$ (ref 17) clarifies that form A is a minor contributor, since the internal methyls are less deshielded and the protons of the macrocycle are overall more deshielded as compared to 12π-monoprotonated annulenium ions (**1H**$^+$, **2H**$^+$, and **3H**$^+$).[17] Such comparisons imply that form B of **5H$_2$**$^{2+}$ with a diamagnetic ring current is an important contributor. ^{13}C NMR chemical shifts and the $\Delta\delta$ values suggest some degree of bond fixation at C-3/C-3a, indicative of a dication made up of 6π (hexatrienyl cation) and 2π (allyl cation) moieties, with a double bond which does not significantly contribute to charge delocalization, as opposed to an 8π (4n) plus 2π (4n + 2) system. We will return to the discussion of the ring current effects in a comparative sense at the end of the discussion.

AM1 Calculations. For the carboxonium ion **5H**$^+$, AM1 predicted only a negligible difference in the *Z*/*E* energies (~0.1 kcal/mol). For comparison with the experiment, we calculated the relative energies of all possible ring-protonated dications; the results are sketched in Figure 6. Protonation at C-9 was most favored (as observed) followed by C-5. The *Z*/*E* configuration of the carboxonium group did not change this preference; only the energies of C-1/C-3 protonation increased for the *E*-carboxonium ion (H,H syn).

Protonation of 8. The cyclohexenone-fused derivative **8** shows a stronger tendency to diprotonate. Thus, under the conditions in which **5** is monoprotonated (FSO$_3$H/SO$_2$ClF), the carboxonium monocation **8H**$^+$ could not be obtained; instead, **8H$_2$**$^{2+}$ was cleanly formed.

By switching to the milder acid system HOAc/TFAH (4:1) in CD$_2$Cl$_2$ at room temperature, **8H**$^+$ could be generated under exchanging conditions as a green solution.

The internal methyls move downfield by approximately 1 ppm, but the $\Delta\delta$ ^{1}H values for the macrocycle are small

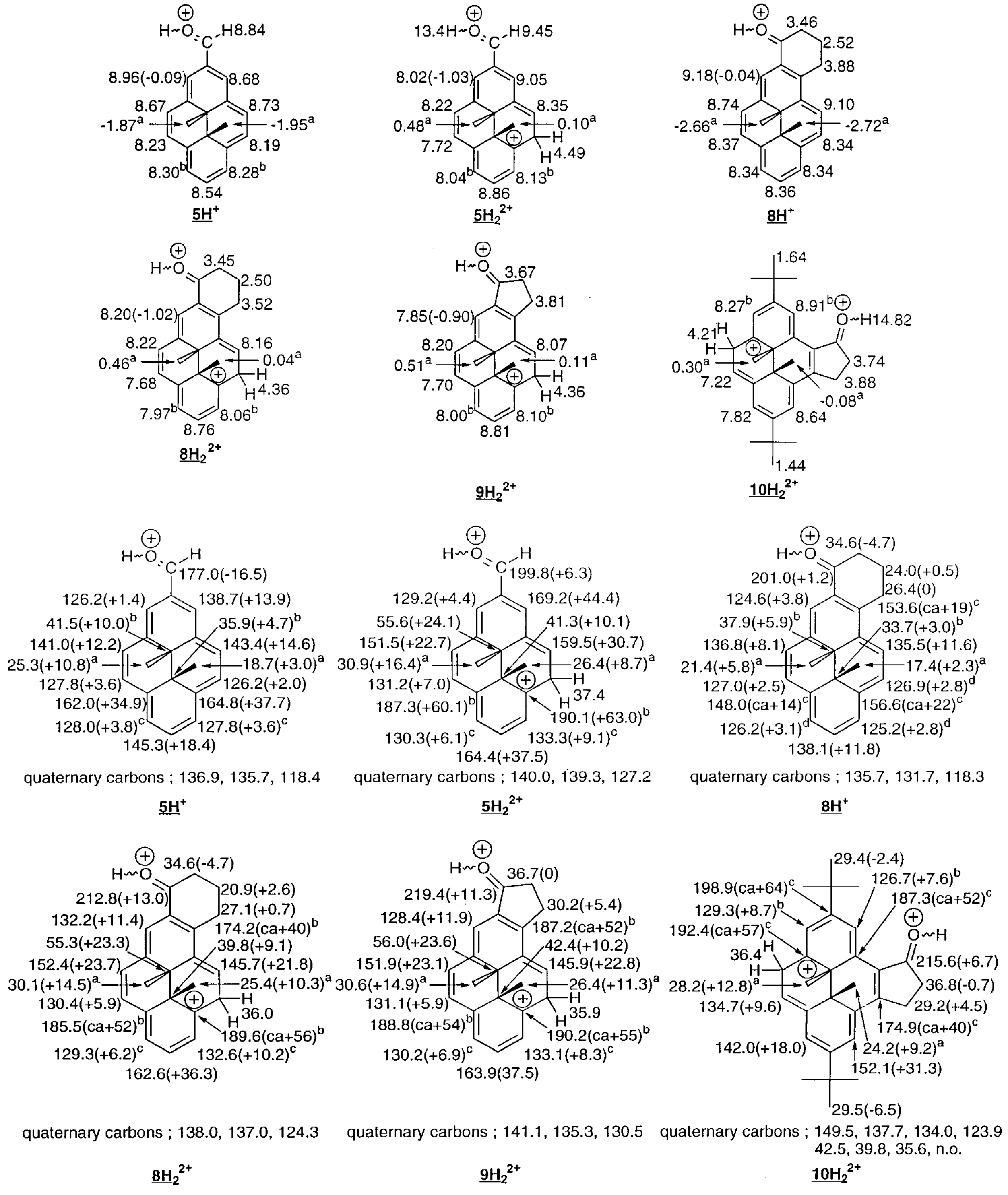
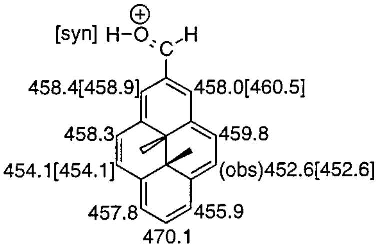


Figure 5. (a) ^{1}H NMR data for the mono- and dications. (b) ^{13}C NMR and $\Delta\delta$ values (in parentheses) for the mono- and dications. Superscripts a, b, and c denote pairs (or sets) of resonances whose assignments may be interchanged.

(showing an overall deshielding trend relative to the precursor); the $\Delta\delta$ ^{13}C values are also smaller than those for **5H**$^+$.

Focusing on the carboxonium–annulenium dication **8H**$_2$$^{2+}$ formed in FSO_3H/SO_2ClF as a persistent green solution, we found in the ^{1}H NMR spectrum that the internal methyls move to 0.46 and 0.04 ppm and the annulene protons exhibit strong shielding relative to the precursor (except for H-7 which is more downfield). There is, furthermore, a systematic shielding in the γ-CH$_2$ of the cyclohexenone ring in the sequence **8** → **8H**$^+$ → **8H**$_2$$^{2+}$ which also exhibits an NOE with H-4 in the sequence. The α-CH$_2$ is deshielded upon CO protonation, and the β-CH$_2$ is almost unchanged. The **C**H$_2$ (H-5,5′) is at 4.36 ppm and appears as a broadened doublet; the CO**H**$^+$ is not observed as a separate signal.

In the ^{13}C NMR, the **C**OH$^+$ signal is at 212.8 ppm deshielded by ca. 13 ppm from the precursor. The positive charge is heavily retained at C-5a, C-8a, C-3, C-4, and C-10. In comparison with the C-protonated annulenium ions,[17] the mesomeric form B (an enol–annulenium dication), a 10π-diatropic system with a diamag-



5H$^+$

Figure 6. AM1 energies (kcal/mol) for ring protonation of **5H**$^+$ [carboxonium group with H,H syn].

netic ring current, must be an important contributor. Analysis of the $\Delta\delta^{13}$C values once again suggests a system made up of a 6π (trienyl cation), a 2π (allyl cation), and a localized 2π (C-1–C-10a) bond, rather than a 12π (4n) paratropic annulenium dication.

In agreement with the NMR-based assignments, AM1 predicts that ring protonation of the carboxonium ion at C-5 should be favored over C-9 (by 4 kcal/mol).

Protonation of 9. Diprotonation of the cyclopentenone-fused derivative **9** is so favorable that all attempts to generate **9H**$^+$ led to equilibrium mixtures of **9H**$^+$ and **9H$_2$**$^{2+}$ depending on the acidity. With TFAH/HOAc/CD$_2$Cl$_2$, a purple solution was obtained whose ^{1}H NMR spectrum showed broadening and deshielding of the annulene protons. Increasing acidity (addition of more TFAH) led to more broadening, especially for the H-7 triplet. In pure TFAH/CD$_2$Cl$_2$, except for one doublet at 8.50 ppm all other resonances broadened and emerged with an overall downfield shift trend. The internal methyls appeared as five different singlets between −2.7 and −1.68 ppm. The latter also appeared very broad in the ^{13}C NMR spectra. These acidity-dependent broadening and shifting of the resonances are typical of a monoprotonation/diprotonation equilibrium.

Clean generation of the carboxonium–annulenium dication **9H$_2$**$^{2+}$ was achieved by a low-temperature reaction with FSO$_3$H/SO$_2$ClF. The same dication was also formed in "magic acid" (FSO$_3$H•SbF$_5$ (1:1))/SO$_2$ClF, where the CO**H**$^+$ was observable as a separate signal at 12.4 ppm. However, the magic acid solution had a much shorter lifetime, and decomposition set in before ^{13}C NMR data could be collected. The discussion, therefore, concentrates on the dication formed in FSO$_3$H/SO$_2$ClF (at −52 °C).

The shielding/deshielding patterns observed for **9H$_2$**$^{2+}$ are analogous to those observed for **8H$_2$**$^{2+}$ and **5H$_2$**$^{2+}$. Thus in the ^{1}H NMR, the internal methyls appear at 0.51 and 0.11 ppm, and the annulenium protons move upfield, except for H-7 which is deshielded in the dication. The shielding effects in the macrocycle are most pronounced for H-1 (0.9 ppm); the CH$_2$ (H-5,5′) appears somewhat broad, showing unresolved coupling to H-4. The methylenes in the cyclopentenone ring exhibit the same pattern observed with **8** including the NOE effect between γ-CH$_2$ and H-4. AM1 predicted a difference of only 0.1 kcal/mol in the energies of the two geometrical isomers of **9H$_2$**$^{2+}$.

In the ^{13}C NMR, the **C**OH$^+$ resonance is observed at 219.4 ppm, and the charge delocalization path in the annulenium moiety is similar to that in **8H$_2$**$^{2+}$. The system is best described as an enol–annulenium dication (10π) comprised of a 6π (hexatrienyl cation), a 2π (allyl cation), and a reasonably fixed 2π system.

AM1 calculations predicted that **8** with a puckered cyclohexene ring was ca. 11 kcal/mol more stable than the planar **9**. For the carboxonium ions, **8H**$^+$ was predicted to be 12.8 kcal/mol lower in energy as compared to **9H**$^+$, but the difference in the $\Delta\Delta H_f°$ (dication minus monocation) values was less than 2 kcal/mol. In addition, whereas O-protonation was favored over C-protonation (at C-5) for both **8** and **9** (→ **8H**$^+$/**9H**$^+$), the $\Delta\Delta H_f°$ values (annulenium minus carboxonium) were 3 and 2 kcal/mol, respectively. These trends may explain the difficulty in observing **9H**$^+$ directly.

Protonation of 10. Monoprotonation with HOAc/CD$_2$Cl$_2$ gave an exchange averaged carboxonium ion as a brown solution. In the ^{1}H NMR, whereas the two-doublet four-singlet aromatic pattern was intact, a new set of broad resonances appeared on the high-field side of the original peaks; a similar effect was seen in the aliphatic region, while the change in the position of the internal methyls was negligible. With the HOAc•TFAH/CD$_2$Cl$_2$ system, the two sets of resonances coalesced to give averaged broad signals for all protons. In the more highly acidic solvent TFAH/CD$_2$Cl$_2$ (a red-brown solution), the internal methyls appeared as a broad hump centered at ca. −2.50 ppm. These observations suggest equilibrium ring protonation. Protonation of **10** with FSO$_3$H/SO$_2$ClF cleanly produced the carboxonium–annulenium dication **10H$_2$**$^{2+}$. In the all-singlet ^{1}H NMR spectrum (Supporting Information), the internal methyls appeared at 0.30 and −0.08 and the CO**H**$^+$ at 14.8 ppm (slightly broad). Whereas all of the annulenium protons appear shielded, the effect is most pronounced for H-9, H-3, and H-8.

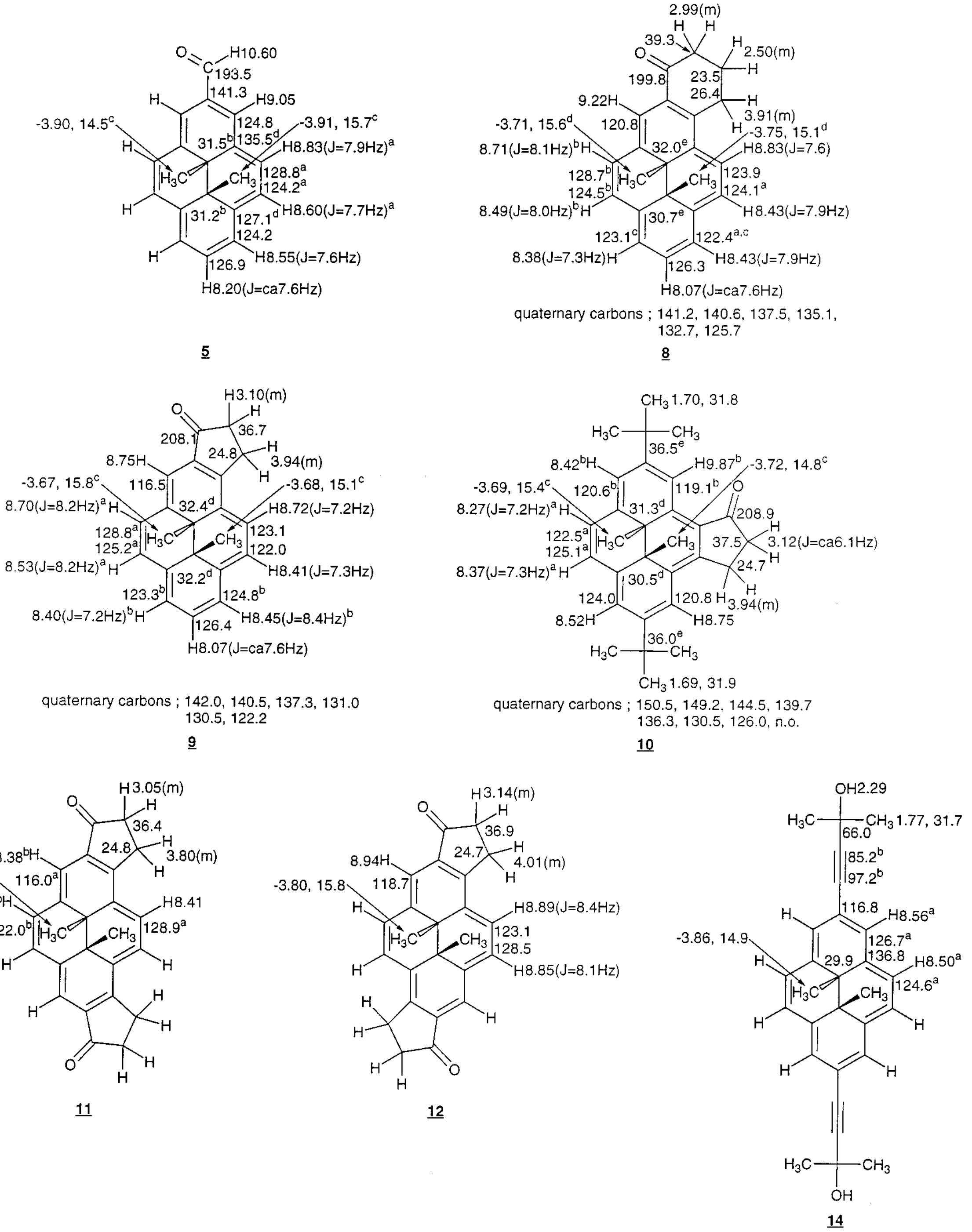
In the ^{13}C NMR spectrum, the **C**OH$^+$ appears at 215.6 ppm deshielded by only ca. 7 ppm relative to **10**. In the NOED spectra, NOE enhancement could be detected between the tBu methyls at C-7 and H-6/H-8.

Deriving a delocalization path based on the magnitude of $\Delta\delta^{13}$C is more difficult in this case because of the presence of eight quaternary ring carbons (all of which are, in fact seen).

By taking substituent effects into account and comparing other annulenium dications, reasonable (but tentative) assignments were made for C-2, C-3a, and C-10a, leading to a consistent pattern. In line with the NMR-based asssignments, AM1 predicts that protonation at C-10 is greatly preferred over that at C-9 (by 16 kcal/mol). The overall pattern of charge delocalization at the periphery of the annulene is also correctly predicted by AM1 based on the magnitude of Δq_C.

Protonation of 11/12 Mixture. The cisoid and the transoid diketones **11** and **12** having two cyclopentene-fused rings annulated to the DMDHP macrocycle were available as a ca. 1:1 mixture. For **12**, the internal methyls are at −3.80 ppm, whereas for the less diatropic **11**, they are at −2.88 ppm. Protonation with TFAH/CD$_2$Cl$_2$ gave a purple solution of the corresponding biscarboxonium ions **11H$_2$**$^{2+}$ and **12H$_2$**$^{2+}$. For the cisoid form, the internal methyls moved to −2.25 ppm, and the three singlets for the macrocycle became deshielded (by ca. 0.2 ppm) with no noticeable line broadening; the methylenes appeared as slightly broad pseudo singlets. These results are in line with an averaged dioxonium species.

For **12H$_2$**$^{2+}$, the AB and the singlet resonances of the macrocycle protons became broad and overlapping; the methylenes also appeared quite broad, but the internal methyls (now at −3.38 ppm) remained sharp. More



quaternary carbons ; 141.2, 140.6, 137.5, 135.1, 132.7, 125.7

quaternary carbons ; 142.0, 140.5, 137.3, 131.0 130.5, 122.2

quaternary carbons ; 150.5, 149.2, 144.5, 139.7 136.3, 130.5, 126.0, n.o.

Figure 7. ^{1}H and ^{13}C NMR assignments of the precursors. Superscripts a, b, and c denote pairs (or sets) of resonances whose assignments may be interchanged.

complete protonation occurs in the more acidic TFAH•H_2SO_4/CD_2Cl_2 system where the resonances due to $\mathbf{12H_2}^{2+}$ broadened further, merged, and disappeared into the baseline, except for the internal methyl which only slightly broadened (at −2.85). Finally, in FSO_3H/SO_2ClF (a green solution) at −48 °C, all resonances for $\mathbf{12H_2}^{2+}$ including that of the internal methyl collapsed into the baseline, whereas the signals for $\mathbf{11H_2}^{2+}$ remained sharp. For the latter, the internal methyls were at −1.50 ppm, and the annulene singlets were more deshielded (8.64, 8.26, 8.18 ppm); the methylene signals were also sharp. These results seem to suggest that $\mathbf{12H_2}^{2+}$ is in equilibrium with an oxonium−annulenium dication which becomes more favorable with increasing acidity.

For comparison, Lewis acid complexation of **11**/**12** with $SnCl_4$ was examined, forming the corresponding bis complexes. Upon complexation, the internal methyls moved to −2.42 and −3.54 ppm, respectively, the three annulene ring singlets of the cisoid form appeared very slightly deshielded, and for the transoid form, the AB and the singlet merged to give two pseudo-singlets (at 9.0 and 9.02 ppm). Unlike the spectra in TFAH, no broadening of the transoid bis complex is observable. This agrees

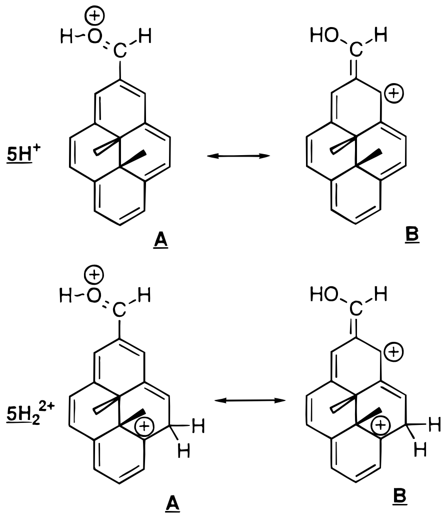


Figure 8.

with the suggestion that broadening of the transoid form may be due to competing ring protonation.

AM1 calculations predicted that whereas **$11H_2^{2+}$** is more stable than **$12H_2^{2+}$** (by 7.6 kcal/mol), their corresponding $\Delta\Delta H_f°$ values for further protonation (trication minus dioxonium ion) are nearly the same. This picture would be consistent with the observed, more facile, competing ring protonation for the *trans*-**12**.

Protonation of 13. In our previous work[17] we showed that **2** is ipso protonated to give the annulenium ion **$2H^+$**, a paratropic [12]annulenium cation. Synthesis of the 2,7-dinitro derivative provided the opportunity to find out if double ipso protonation can be affected to form a diatropic [10]annulenium dication. Slow addition of FSO_3H to **13** in SO_2ClF gave a *black* precipitate which could be dissolved in excess FSO_3H. In the ^1H NMR spectrum, two aromatic singlets were observed at 6.98 and 6.55 ppm, and in the aliphatic region, a broad resonance appeared at ca. 4.08 ppm (ca. 8H). The latter seems to be due to the two internal methyls overlapping with the two ipso protons. The data are compatible with the formation of di-ipso protonated species. Whereas attempts to obtain a ^{13}C spectrum were unsuccessful due to insufficient solubility, quenching of the ion solution did return the intact 2,7-dinitro derivative **13** (^1H NMR). Limited NMR data precluded a complete assignment; it is unclear why the second protonation had only little effect on the ring current (in comparison with **$2H^+$**).

Attempted Protonation of 14. We envisioned that controlled O-protonation/ionization should lead to an alkyne-substituted tertiary carbocation with the potential to obtain the mesomeric cumulene-type annulenium cation. Careful addition of cold FSO_3H to **14** in SO_2ClF gave a black solid on contact at dry ice−acetone temperature. Examination of the top liquid (^1H NMR at −61 °C) showed broad (and quite weak) resonances in a complex mixture [aromatics between 9.1 and 7.70 ppm, several deshielded tBu(Me) singlets, and several broad singlets between −1 and 2 ppm possibly due to internal methyls]. Rapid oligomerization prevented study of the carbocation. The resulting solid was not further investigated.

Reaction of DMDHP 1 with SbF_5/SO_2ClF. DMDHP reacted with SbF_5/SO_2ClF at dry ice−acetone temperature to give a green solution. NMR monitoring showed that, initially, a mixture of oxidized and ring protonated products were formed (plus other byproducts), but over time, the ^1H NMR spectrum simplified to one major product (δ_{Me} = 1.92 ppm). The annulene ring protons gave rise to just four doublets (no triplets). H/H COSY confirmed the couplings. The data are compatible with a 1,8-difluorinated dication (see also below); the ^{13}C NMR spectrum confirmed the presence of four different CH groups (δ ^{13}C = 170.4, 149.5, 148.1, and 142.1). After five weeks, additional products grew and increased with time. At this point, the sample was quenched, and the isolated organic residue was examined by ^{19}F NMR; it showed three fluorinated products in close environments (−117 to −118 ppm). The ^1H NMR of the quench indicated that the diagnostic shielded internal methyls had vanished, indicative of cleavage of the internal bond on exothermic quenching to presumably yield a mixture of fluorinated pyrenes.

A Comparative Discussion of the Annulenium Ions and Ring Current Effects. Depending on the acidity of the superacid, the 2-formyl-substituted derivative **5** is cleanly mono- and diprotonated to form a carboxonium ion **$5H^+$** and a carboxonium-annulenium dication **$5H_2^{2+}$**. Tendency for diprotonation increased in the cyclohexenone- and cyclopentenone-fused derivatives. Thus, under the conditions where **5** is monoprotonated, **8** and **9** gave the corresponding dications. Monoprotonation of **8** could be effected in more mildly acidic systems, but competing ring protonation could not be prevented in the case of **9** even under these conditions; isomeric cyclopentenone-fused **10** behaved similarly.

Analysis of the NMR data shows very similar charge delocalization patterns among the carboxonium−annulenium dications and within the carboxonium ions. The charge delocalization mode in the dications is very similar to the positive charge strongly localized at C-3, C-4, C-5a, C-7, C-8a, and C-10; it differs from the pattern in the ring protonated monocations only in significantly less deshielding at C-1 and the nonequivalent delocalization from C-3 and C-1.

In the carboxonium ions, the ring current must be changing as the observed changes in δ_{Me} are too large to be caused by the charge alone. By comparing the magnitude of the internal methyl deshielding and shielding of the ring protons in the mono- and dications with that of the ring protonated 12π-annulenium cations it can be inferred that, for the dications, the mesomeric form B, an enol−annulenium dication (10π-periphery; diatropic), contributes and thus lowers the paratropicity (decreasing the paramagnetic ring current). In the carboxonium ions, mesomeric form B makes a small contribution to reducing the diamagnetic ring current of **5**. Finally, the magnitude of $\Delta\delta^{13}C$'s suggests that the 10π-dications consist of hexatrienyl and allyl cation moieties and a relatively fixed double bond.

For the isomeric biscyclopentenone-fused derivatives, biscarboxonium ions are formed, but the NMR data suggest that the transoid form has a greater tendency for equilibrium ring protonation. The results with $SnCl_4$ complexations, which show bis complexes but no exchange broadening of either form, lend support to these arguments.

Based on limited data, double ipso protonation of **13** has been suggested. Similarly, two-electron oxidation of **1** followed by ring fluorination was oberved in reaction with SbF_5.

Reversal of the ring current effect from diatropic to paratropic is by no means comparable to what was observed in the dianion (now a classical NMR textbook example).[18]

Experimental Section

FSO_3H (Allied), SbF_5 (Aldrich or Fluorochem) were distilled in an all-glass distillation unit and stored in Nalgene bottles under argon. SO_2ClF was synthesized from SO_2Cl_2, NH_4F, and TFAH according to a modified procedure of Prakash et al.[19] TFAH and HOAc (both from Aldrich) were used without further purification. Superacid mixtures were prepared as previously described.[20] NMR spectra were recorded on a GE-GN300 widebore instrument using our previously established procedures.[20] Synthesis of the 2-formyl-fused **5**, the mono-fused **9**, and the biscyclopentanone-fused derivatives **11/12** have been previously reported.[21−23]

Cyclohexanone 8. Pyridinium dichromate[24] (2.11 g, 5.50 mmol) was added to *trans*-12b,12c-dimethyl-7,8,9,10,12b,12c-hexahydrobenzo[def]chrysene (see below) (400 mg, 1.40 mmol) in dry dichloromethane (40 mL), and the mixture was stirred for 4 h at 20 °C under argon. The mixture was filtered through Celite, washing the latter with more dichloromethane. The filtrate was evaporated and preabsorbed onto silica gel (mesh 40−200) and chromatographed on silica gel using dichloromethane−methanol (10:1) as eluant. The deep red band was recrystallized from dichloromethane−hexane (1:6) as reddish-brown crystals, 150 mg (36%): mp 141−142 °C. ^1H and ^{13}C NMR, see Figure 7; IR (KBr) 1645 cm^{-1}; HR-MS calcd for $C_{22}H_{20}O$ 300.1514, found 300.1521. Anal. Calcd: C, 87.96; H, 6.71. Found: C, 87.55; H, 6.65. *trans*-12b,12c-Dimethyl-7,8,9,10,12b,12c-hexahydrobenzo[def]chrysene was prepared from 5,7-bis(bromomethyl)-6-methyltetralin and 1,3-bis(mercaptomethyl)toluene using the same sequence which was described for *trans*-12b,12c-dimethyl-12b,12c-dihydrobenzo[*a*]pyrene[2] and which will be described in detail elsewhere.

Cyclopentanone 10. This was prepared using a sequence identical to that used for **9**,[21] starting from 2,7-di-*tert*-butyl-4-formyl-*trans*-10b,10c-dimethyldihydropyrene and was obtained in 25% overall yield as reddish-brown chunks: mp 180−182 °C; ^1H and ^{13}C NMR, see Figure 7; IR (KBr) 1665 cm^{-1}; HR-MS calcd for $C_{29}H_{34}O$ 398.2610, found 398.2643.

Diol 14. 2-Methyl-3-butyn-2-ol (1.25 mL, 13 mmol), copper(I) iodide (13 mg, 65 μmol), and $PdCl_2(PPh_3)_2$ (46 mg, 65 μmol) were added to a solution of 2,7-dibromo-*trans*-10b,10c-dimethyldihydropyrene (533 mg, 1.3 mmol) in diethylamine (40 mL) under argon, and then the solution was stirred for 8 h at 60 °C. After being cooled and evaporated, the residue was chromatographed over silica gel (40−200 mesh), using ethyl acetate−hexane (1:2) as eluant to yield first a small amount of a mono-ol and then the reddish-orange diol **14**, 360 mg (70%) as needles from ethyl acetate−hexane: mp 131−133 °C; ^1H and ^{13}C NMR, see Figure 7; IR (KBr) 3300 (bs), 2150 (w) cm^{-1}; HR-FAB-MS calcd for $C_{28}H_{29}O_2$ (MH^+) 397.2168, found 397.2171.

2,7-Dinitro-*trans*-10b,10c-dimethyldihydropyrene 13. $Cu(NO_3)_2{\cdot}3H_2O$ (70 mg) was added to a solution of **2**[12] (80 mg, 0.29 mmol) in $CHCl_3$ (20 mL) containing 2 drops of acetic anhydride under argon. After being stirred for 16 h, the mixture was filtered through a short column of silica gel and the filtrate rechromatographed over silica gel (40−200 mesh) using ethyl acetate−hexanes (1:1) as eluant, followed by fractional crystallization from dichloromethane−hexane to give 30 mg (32%) of purple **13**, mp ca. 221 °C (dec); ^1H NMR (360 MHz, $CDCl_3$) δ 9.49 (s, 4, H-1), 8.97 (s, 4, H-4), −3.74 (s, 6); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ 143.4, 138.9, 130.4 (C-4), 119.6 (C-1), 31.5, 15.7; UV ($CHCl_3$) λ_{max} (ϵ_{max}) nm 350 (21, 000), 396 (6400), 419 (7800), 564 (8200), 633 (1000), 698 (1100); HR-MS calcd for $C_{18}H_{14}N_2O_4$ 322.0953, found 322.0952.

Direct nitration of **1** produces greater quantities of higher nitrated products.

General procedure for Stable Ion Generation. Preparation of the Dications. A slurry of the substrate (30 mg) in SO_2ClF (0.3 mL) was prepared using an HV line. After addition of 0.5 mL of CD_2Cl_2 as an NMR lock, $FSO_3H{\cdot}SbF_5$ (4:1; 5 drops) or FSO_3H (5 drops) was added directly to the 5-mm NMR tube at dry ice−acetone temperature under argon. The resulting solution was vigorously mixed (vortexed) until homogeneous. For the monocations, HOAc (0.3 mL) or HOAc/TFAH (0.3 mL) and CD_2Cl_2 (0.1 mL) were added to the annulene substrate directly into a 5-mm NMR tube with efficient vortex mixing at room temperature.

For the oxidation reaction with **1**, SbF_5 (1 mL) was charged into a 10-mm NMR tube under argon; SO_2ClF (2 mL) was condensed into a 5-mm NMR tube using an HV line and was directly added to SbF_5 at dry ice−acetone temperature. By vigorous (vortex) mixing and slight periodic warming, a clear homogeneous solution resulted. The substrate (30 mg) was charged into another 5-mm NMR tube to which SO_2ClF was added via the HV line. The SbF_5/SO_2ClF solution (in the 10-nm tube) was then added to the 5-mm tube containing the slurry of the substrate in SO_2ClF under argon with efficient mixing.

AM1 calculations were performed with the Hyperchem package (Hypercube, 1995).

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Supporting Information Available: Selected ^1H, ^{13}C, and 2D-NMR spectra for $\mathbf{5H_2}^{2+}$, $\mathbf{5H}^{+}$, $\mathbf{8H_2}^{2+}$, $\mathbf{9H_2}^{2+}$, and $\mathbf{10H_2}^{2+}$ (23 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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