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Stable Ion NMR and GIAO-DFT Study of Novel Cations from 8,16-Dicyano[2.2]metacyclophanedienes and from Strategically Substituted/Benzannelated Dihydropyrenes: Charge-Induced Tropicity Modulation and π-Switching‡

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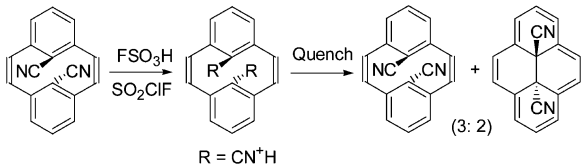

The dicyanometacyclophanediene **1** is diprotonated at the cyano groups ($\mathbf{1H_2}^{2+}$) in various superacid media. Upon quenching, intact **1** and the ring-closed CPD **2** were obtained in a 3:2 or 3:1 ratio, depending on the superacid system. Compound **2** undergoes ring opening in the superacid to give the *ipso*-monoprotonated $\mathbf{2H}^{+}$, which on quenching furnishes 1-cyanopyrene as a major product together with **2** and **1**. The dication $\mathbf{3}^{2+}$, with strongly deshielded internal methyls, was generated from the epoxyannulene **3**. Ketones **4**−**6** and ester **7** are O/C diprotonated to give paratropic carboxonium−annulenium dications ($\mathbf{4H_2}^{2+}$, $\mathbf{5H_2}^{2+}$, $\mathbf{6H_2}^{2+}$, and $\mathbf{7H_2}^{2+}$, respectively). Ester **8** gives a trication by two-electron oxidation and O-protonation. Conjugated carboxylic acid **9** gives a mixture of two dications by CO and ring protonation. The dibromo derivatives **10** and **11** form carboxonium ions, whereas the monobromo derivative **12** is O/C diprotonated to give an oxonium−annulenium dication. Charge delocalization modes and tropicity in the resulting species are evaluated by NMR and GIAO-DFT. Facile formation of **2** from **1** in quenching experiments indicates that thermal closing can be achieved with the diprotonated dinitrile, without imposing skeletal rearrangement.

Introduction

Extensive synthetic work and NMR studies by Mitchell and associates over the years have firmly established the dimethyldihydropyrene DMDHP [*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene] framework as a sensitive and reliable probe for monitoring the ring current effects and aromaticity in annulenes (Figure 1).[1−6] As a 14π-annulene, DMDHP exhibits a diatropic ring current which strongly shields the dangling methyl groups

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‡ Compound names: **1**, 8,16-dicyano[2.2]metacyclophane-1,9-diene; **2**, *trans*-10b,10c-dicyano-10b,10c-dihydropyrene; **3**, 2,7-bis(*tert*-butyl)-9,12,12c,12d-tetrahydro-*trans*-12c,12d-dimethyl- 9,12-epoxybenzo[e]pyrene; **4**, 2,7-bis(*tert*-butyl)-11c,11d-dihydro-*trans*-11c,11d-dimethyl-9*H*-cyclopenta[*e*]pyren-9-one; **5**, 2,7-bis(*tert*-butyl)- 10b,10c-dihydro-*trans*-10b,10c-dimethylpyren-4-yl 9-anthracenyl ketone; **6**, ethyl 2,7-bis(*tert*-butyl)-10b,10c-dihydro-*trans*-10b,10c-dimethylpyrene-4-carboxylate; **7**, ethyl 2,7-bis(*tert*-butyl)-12c,12d-dihydro-*trans*-12c,12d-dimethylbenzo[*e*]pyrene-4-carboxylate; **8**, ethyl 2,7-bis(*tert*-butyl)-12c,12d-dihydro-*trans*-12c,12d-dimethylbenzo[*e*]pyrene-10-carboxylate; **9**, 2,7-bis(*tert*-butyl)-10b,10c-dihydro-*trans*-10b,10c-dimethylpyrene-4-propenoic acid; **10**, 4,9-dibromo-7-*tert*-butyl-10b,10c-dihydro-*trans*-10b,10c-dimethylpyren- 2-yl 9-anthracenyl ketone; **11**, 4,9-dibromo-7-*tert*-butyl-10b,10c-dihydro-*trans*-10b,-10c-dimethylpyren-2-yl 1-naphthyl ketone; **12**, 4-bromo-2,7-bis(*tert*-butyl)-10b,-10c-dihydro-*trans*-10b,10c-dimethylpyren-10-yl 1-naphthyl ketone.

(1) Mitchell, R. H. *Chem. Rev.* **2001**, *101*, 1301−1315.

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(3) (a) Mitchell, R. H.; Williams, R. V.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2560−2571. (b) Mitchell, R. H.; Yan, J. S. H.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2551−2559. (c) Mitchell, R. H.; Williams, R. V.; Mahadevan, R.; Lai, Y.-H.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2571−2578. (d) Mitchell, R. H.; Carruthers, R. J.; Mazuch, L.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2544−2551.

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

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

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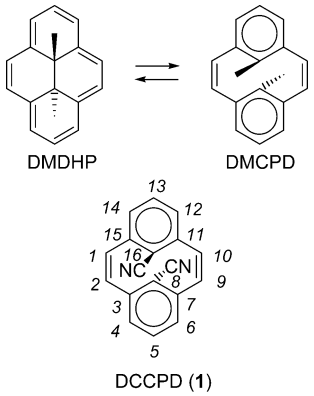

FIGURE 1. Structures of DMDHP, DMCPD, and DCCPD.

at the center of the macrocycle. Substitution and ring fusion can alter the diatropicity in DMDHP by bond localization. A wide variety of such molecules have been synthesized by Mitchell and co-workers and studied by NMR.[1−6]

Of strong current interest is the electrocyclic process that interconverts dihydropyrene DHP and metacyclophanediene CPD and the potential application of this process in designing reversible photochromic π-switches.[7−10] DMDHP is converted to DMCPD (Figure 1) by visible light, and the reverse reaction occurs by UV irradiation or thermally. The rate of thermal reaction has been shown to depend greatly on the substituents.[7] DFT study of the thermal reaction identified the 8,16-dicyano derivative DCCPD (see Figure 1) as a promising probe by raising the activation barrier for its return to DHP, therefore increasing its lifetime for photoswitching.[11] The focus of the preceding article[12] is on the synthesis and rearrangement of DCCPD. Introduction of nitrile substituents did increase thermal stability relative to the dimethyl analogue, but upon heating the closed compound rearranged by CN group migration.

We previously reported the first examples of persistent dimethyldihydropyrenium cations from DMDHP and some of its substituted derivatives (Figure 2a). Ring protonation transforms the diatropic[14]annulenes to paratropic[12]annulenium ions.[13]

In subsequent studies,[14] examples of annulenium−oxonium dications were reported from the 2-formyl derivative and several cyclcopentenone and cyclohexenone-fused derivatives of DMDHP (Figure 2b). The ring current effects were evaluated and charge delocalized modes in the resulting mono- and dications were determined. These studies showed that by charging the systems (via mono- and diprotonation) paratropic−diatropic manifolds could be generated.[14]

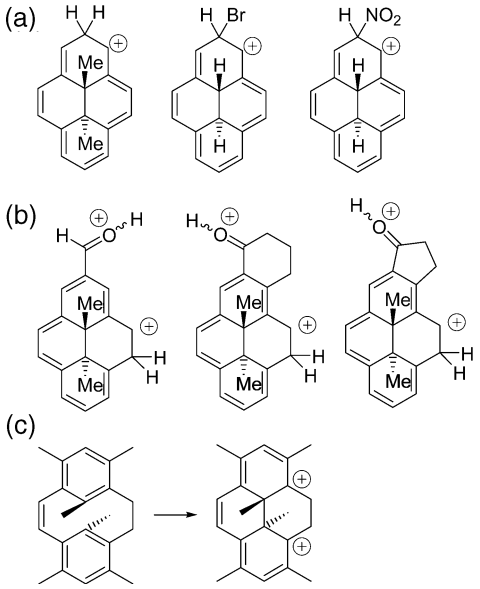

FIGURE 2. (a) Persistent dimethyldihydropyrenium cations from DMDHP. (b) Carboxonium−annulenium dications from DMDHP. (c) Formation of *trans*-dimethyldihydroethanophenanthrenium ions from methylated [2.2]metacyclophan-9-ene.

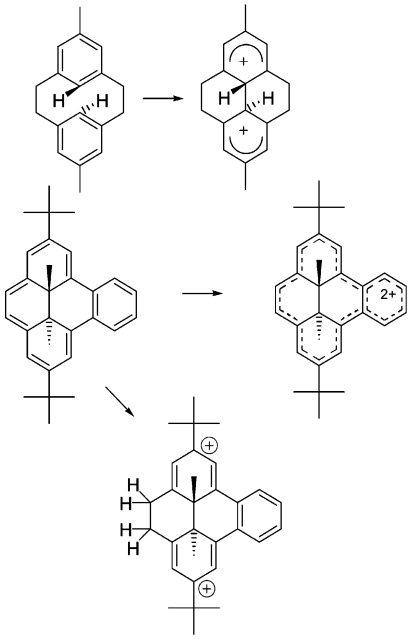

FIGURE 3. Diprotonated dication and oxidation dication.

More recently,[15] we reported on the formation of *trans*-dimethyldihydroethanophenanthrenium ions from methylated [2.2]metacyclophane monoenes and on the generation of a 14π diprotonated annulenium dication and a 16π oxidation dication from *trans*-12c,12d-dimethyl-12c,12d-dihydrobenzo[*e*]pyrene in superacids (Figures 2c and 3).[15]

The present study focuses on stable ion study of the cyclophanes and annulenes listed in Figure 4 (see footnote for complete IUPAC names). The recently synthesized dinitrile derivative **1** provided the opportunity to study ring closing via protonated intermediates. NMR and GIAO-NMR were used to

(6) Mitchell, R. H.; Iyer, V. S. *J. Am. Chem. Soc.* **1996**, *118*, 2903−2906.
(7) Mitchell, R. H. *Eur. J. Org. Chem.* **1999**, 2695−2703.
(8) Mitchell, R. H.; Bohne, C.; Wang, Y.; Bandyopadhyay, S.; Wozniak, C. B. *J. Org. Chem.* **2006**, *71*, 327−336.
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(10) Mitchell, R. H.; Iyer, V. S.; Mahadevan, R.; Venugopalan, S.; Zhou, P. *J. Org. Chem.* **1996**, *61*, 5116−5120.
(11) Williams, R. V.; Edwards, W. D.; Mitchell, R. H.; Robinson, S. G. *J. Am. Chem. Soc.* **2005**, *127*, 16207−16214.
(12) Ayub, K.; Zhang, R; Robinson, S. G.; Twamley, B.; Williams, R. V.; Mitchell, R. H. *J. Org. Chem.* **2008**, *73*, 451−456.
(13) Laali, K. K.; Bolvig, S.; Raeker, T. J.; Mitchell, R. H. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2635−2638
(14) Laali, K. K.; Tanaka, M.; Mitchell, R. H.; Lau, D. Y. K. *J. Org. Chem.* **1998**, *63*, 3059−3066.
(15) Laali, K. K.; Okazaki, T.; Mitchell, R. H.; Ward, T. R. *J. Org. Chem.* **2001**, *66*, 5329−5332.

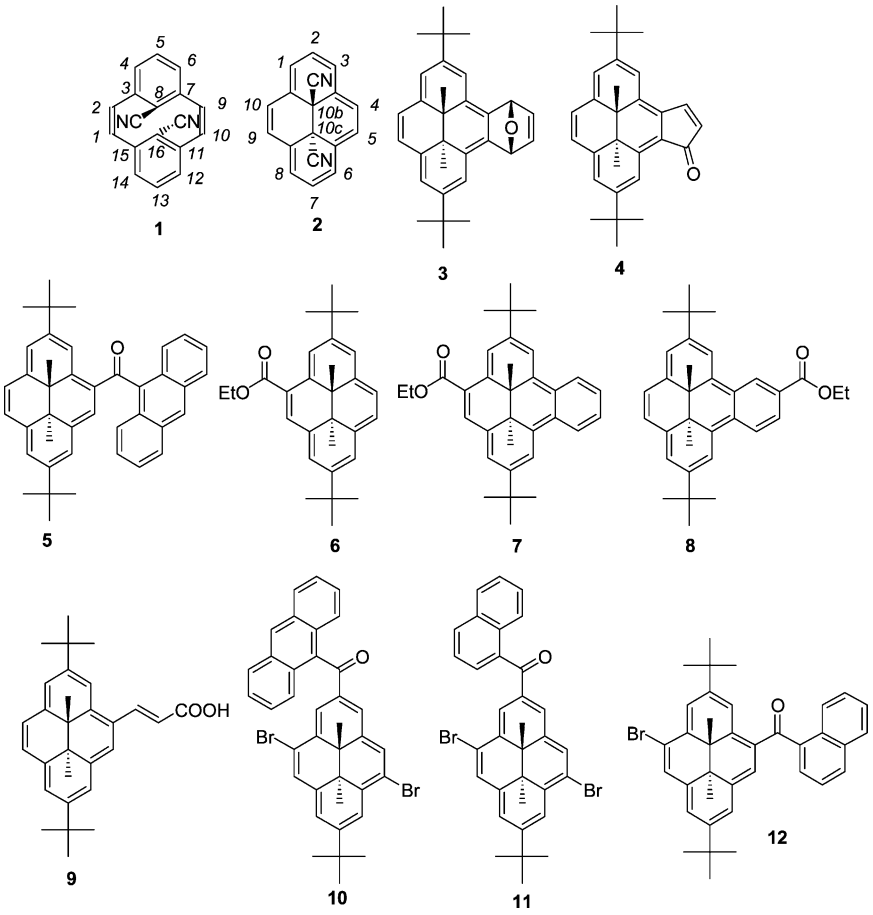
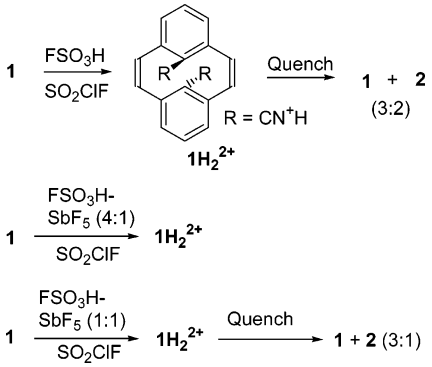


FIGURE 4. CPD and DHP compounds studied.

SCHEME 1. Protonation of 1 in Various Superacids and Quenching Outcomes

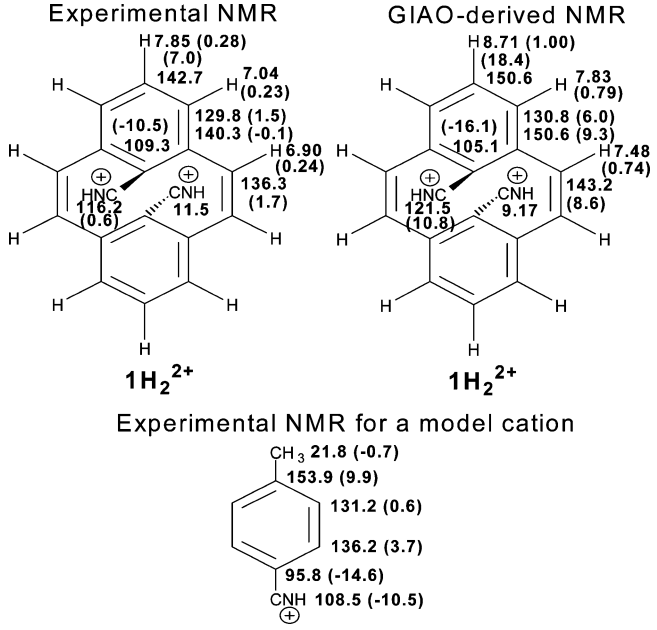


probe variations in the ring current effects (tropicity) and to determine charge delocalization modes in the resulting cations.

Results and Discussion

On the NMR Data for the Cyclophane and Annulene Precursors. The experimental and GIAO-derived ^{1}H and ^{13}C NMR assignments for the compounds listed in Figure 1 are complied in Chart S1 (Supporting Information). The computed ^{13}C NMR shifts compare rather well with the experimental data. On the ^{1}H NMR, whereas the computed values are typically more deshielded, the overall trends are similar. Moreover, the highly shielded nature of the internal methyl protons is well reproduced by GIAO-DFT.

CHART 1. Experimental and GIAO-Derived NMR Data for $1H_2^{2+}$ and Comparison with $MePhCNH^+$ as Model[a]



[a] $\Delta\delta^{13}$C and $\Delta\delta^{1}$H values relative to precursors in parentheses.

Stable Ion Study of DCCPD 1. Protonation of the dinitrile **1** was studied in FSO_3H/SO_2ClF, FSO_3H-SbF_5 (4:1)/SO_2ClF, and in FSO_3H-SbF_5 (1:1)/SO_2ClF. The NMR spectra of the resulting yellow solutions [yellow-brown with FSO_3H-SbF_5 (1:

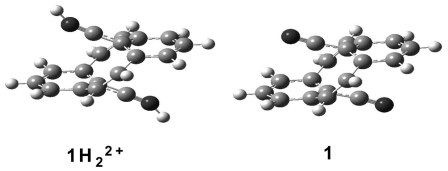


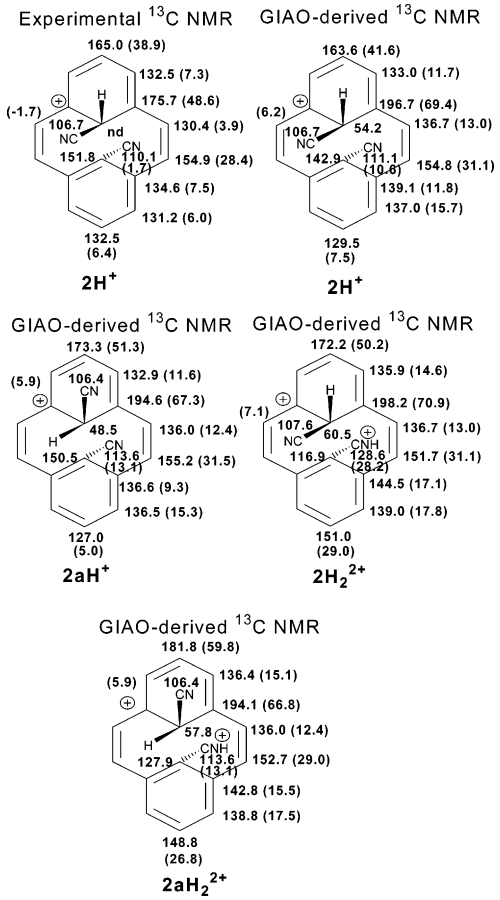
FIGURE 5. B3LYP/6-31+G(d,p)-optimized structures of **1** and $\mathbf{1H_2}^{2}$.

1)] in all cases were consistent with N-protonation at both CN groups to give $\mathbf{1H_2}^{2+}$ (Scheme 1). NMR data for $\mathbf{1H_2}^{2+}$ are summarized in Chart 1. In comparison with neutral **1**, the peripheral protons are deshielded, and there is limited charge delocalization into the *ortho*/*para* positions. The *ipso* carbon and *C*N are shielded relative to those in **1**, with the shielding magnitude increasing slightly by increasing acidity [from 109.3 and 116.2 ppm in FSO_3H to 107.3 and 114.7 ppm in FSO_3H-SbF_5 (4:1), and 103.4 and 111.4 ppm in FSO_3H-SbF_5 (1:1) respectively]. It is noteworthy that the observed shielding of the *ipso* carbon in $\mathbf{1H_2}^{2+}$ is analogous to that of CN-protonated *p*-cyanotoluene as model (data from ref 16) and that the optimized structure of $\mathbf{1H_2}^{2+}$ (Figure 5) shows significant pyramidalization at the *ipso* carbon. The GIAO-derived ^{13}C NMR shifts (Chart 1) agree with the experimental trends and with the observed shielding at the *ipso* carbon. Finally, the $-CNH^+$ was observable as a separate signal at 11.5 ppm at −30 °C.

Quenching of the superacid solutions of $\mathbf{1H_2}^{2+}$ furnished intact **1** along with the ring-closed analogue **2** in a 3:2 ratio (by NMR; via FSO_3H/SO_2ClF) and in a 3:1 ratio (by NMR; via FSO_3H-SbF_5 (1:1)/SO_2ClF). This finding is significant considering the observed lack of stability of **2** under thermal ring-closing conditions (see Introduction and preceding article[12]), implying that the activation barrier to electrocyclic ring closure (**1** → **2**) may be lowered by protonation of the nitrile groups.

Based on DFT, and consistent with its X-ray structure,[12] the isomer **1** (*anti*) is 10.6 kcal/mol less stable than isomer **2** (*trans*) but is favored over **1a** (*syn*) by 9.2 kcal/mol (Figure S1 and Table S1, Supporting Information). Dication $\mathbf{1H_2}^{2+}$ (with *anti* orientation of CNH groups) is 7.9 kcal/mol more stable than the *syn* isomer and 0.7 kcal/mol more stable than the ring-closed (*trans*) $\mathbf{2dH_2}^{2+}$.

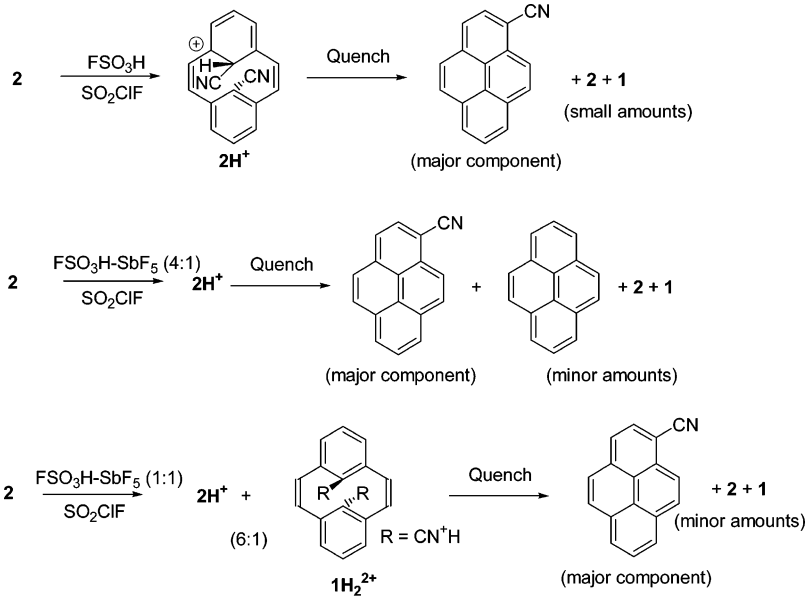
CHART 2. Experimental and GIAO-Derived ^{13}C NMR Data for $\mathbf{2H}^+$, $\mathbf{2aH}^+$, $\mathbf{2H_2}^{2+}$, and $\mathbf{2aH_2}^{2+}$ [a]



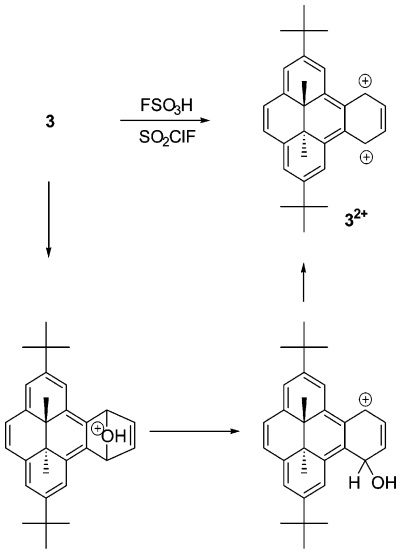
[a] $\Delta\delta^{13}C$ values relative to precursors in parentheses (nd = not detected).

Stable Ion Studies of Strategically Substituted/Benzannelated DHPs 2−11. (a) The Dinitrile 2. Protonation of **2** either with FSO_3H/SO_2ClF or with FSO_3H-SbF_5 (4:1)/SO_2ClF led to the formation the *ipso*-protonated [2.2]metacyclophanediene $\mathbf{2H}^+$ as an orange solution (Scheme 2). The nitrile carbons were

SCHEME 2. Protonation of 2 in Various Superacids and Quenching Outcomes



SCHEME 3. Suggested Pathway for the Formation of 3^{2+}



observed at 106.7 and 110.1 ppm with the C*H*CN at 4.64 ppm. Since a separate −CN*H*$^+$ signal was not detectable, equilibrium protonation at the other nitrile group could not be decided on this basis. Moreover, information as to relative orientation of the C−H and C−CN bonds at the sp^3-hybridzed center was needed. Structures shown in Figure S1 were computed by DFT (Table S1) (Supporting Information). Among the monocations, **2H**$^+$and **2aH**$^+$ were most preferred, and their relative energies were within 1 kcal/mol. Among the CPD dications, **2H$_2$**$^{2+}$and **2aH$_2$**$^{2+}$ were more stable (also within 1 kcal/mol of each other). NMR data for the monocations **2H**$^+$/**2aH**$^+$ and dications **2aH$_2$**$^{2+}$/**2aH$_2$**$^{2+}$ were computed by GIAO (see Charts 2 and S2, Supporting Information). The GIAO-derived data for **2H**$^+$ matched more closely with experiment (with ^{1}H NMR chemical shift for C*H*CN proton closest to experimental value). On this basis, relative conformation at the sp^3-center was selected as shown, and significant protonation at the *ipso* position of the second CN group (as in **2aH$_2$**$^{2+}$) was considered unlikely. Positive charge in **2H**$^+$ is delocalized into the *ortho*/*para* positions and the two conjugated bridge carbons.

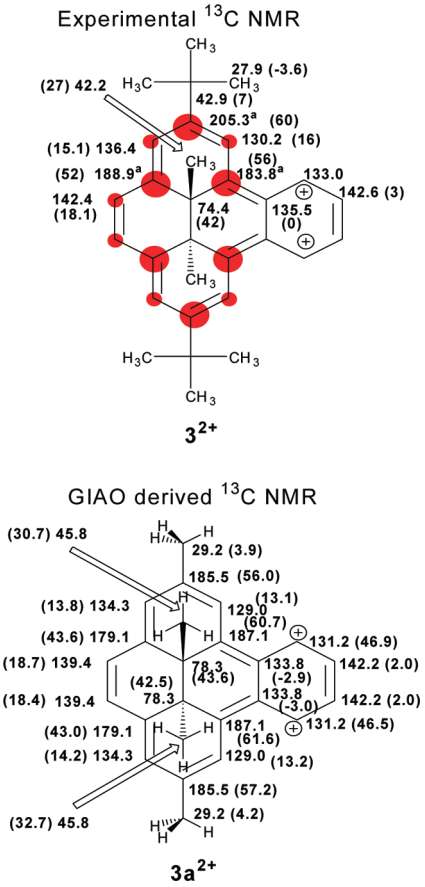
Quenching (for details see the Experimental Section) of the superacid solutions of **2H**$^+$ (via FSO_3H/SO_2ClF) led to the formation of 1-cyanopyrene as major product (>90% yield), accompanied by traces of **2** and **1**. Quenching of **2H**$^+$ (via FSO_3H-SbF_5 (4:1)/SO_2ClF)) again produced 1-cyanopyrene as major product, along with small amounts of **2**, **1**, and pyrene. Protonation of **2** with the higher acidity superacid FSO_3H-SbF_5 (1:1)/SO_2ClF (Scheme 2) gave **2H**$^+$as the major species, along with **1H$_2$**$^{2+}$ (in 6:1 ratio, respectively). Subsequent quenching furnished 1-cyanopyrene as a major product, together with **2** and **1** as very minor components. The identity of 1-cyanopyrene was confirmed by NMR and MS and by comparison with the reported spectral data.[17] Formation of 1-cyanopyrene can be explained by ring closure to form **2**, followed by sigmatropic shift of the CN group (as discussed in ref 12), elimination (loss of HCN), and aromatization.

(b) The Epoxybenzo[*e*]DHP 3. Low-temperature reaction of **3** with FSO_3H/SO_2ClF gave a dark orange solution whose

(16) Olah, G. A.; Forsyth, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 3137−3141.

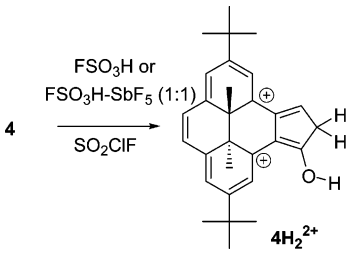
(17) Kitagawa, F.; Murase, M.; Kitamura, N. *J. Org. Chem.* **2002**, *67*, 2524−2531.

CHART 3. Specific ^{13}C NMR Assignments for 3^{2+} and Its Model Dication $3a^{2+}$ (tBu Replaced by Me)[a]



[a] $\Delta\delta^{13}$C values relative to precursors in parentheses; superscript a refers to interchangeable assignments; size of circles is roughly proportional to the magnitude of the $\Delta\delta^{13}$C values.

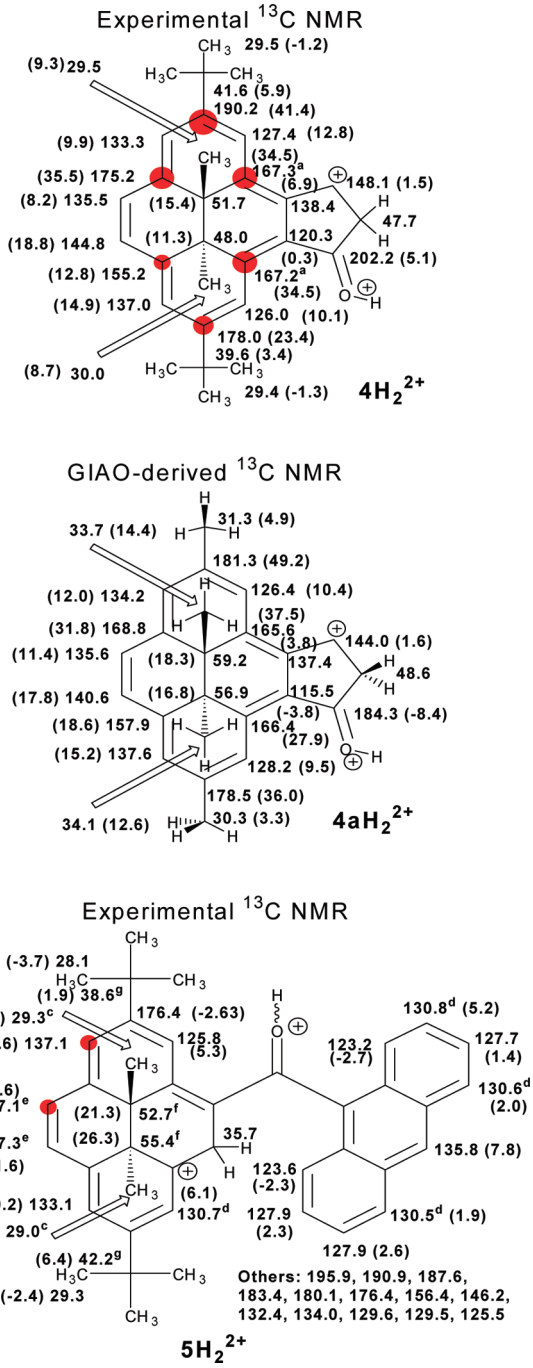
SCHEME 4. Formation of Carboxonium−Annulenium Dication $4H_2^{2+}$ from 4



NMR spectra indicated the formation of dication **3**$^{2+}$ (Scheme 3). The same dication was previously formed via the benzo[*e*]-derivative shown in Figure 3.[15] Its formation via **3** can be explained via the logical steps outlined in Scheme 3. Dication **3**$^{2+}$ is paratropic (16π), exhibiting strongly deshielded central methyls and shielded peripheral protons. Specific NMR assignments and charge delocalization mode for **3**$^{2+}$are included in Charts 3 and S3 (Supporting Information).

(c) Ketones 4 and 5. Low-temperature reaction of **4** with FSO_3H/SO_2ClF gave a dark-green solution whose NMR data were consistent with the formation of annulenium−carboxonium dication **4H$_2$**$^{2+}$ (Scheme 4). The same dication was also formed in FSO_3H-SbF_5 (1:1)/ SO_2ClF as a major species (dark-green solution). The NMR data are summarized in Charts 4 and S4 (Supporting Information). The internal methyls move from

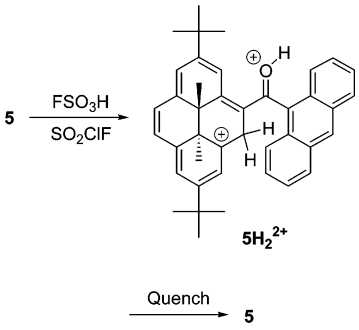
CHART 4. Specific ^{13}C NMR Assignments for $4H_2^{2+}$ and $5H_2^{2+}$ and GIAO-Derived ^{13}C NMR Data for the Model Cation $4aH_2^{2+}$ (tBu Replaced by Me)[a]



[a] $\Delta\delta^{13}C$ values relative to precursors in parentheses; superscript a−g refer to interchangeable assignments; size of circles is roughly proportional to magnitude of $\Delta\delta^{13}C$.

−1.89/−1.85 ppm in **4** to −0.46/−0.36 ppm in $\mathbf{4H_2}^{2+}$, and peripheral protons become deshielded. The C═OH^+ signal was observed at 13.2 ppm. This signal gave a larger NOE with the CH_2 protons at δ 4.89 and a small NOE enhancement with the annulene proton at δ 9.13. On this basis, the conformation of the carboxonium group was set as shown. Positive charge in the dication mainly resides in the annulenium moiety at alternating carbons, and there is little change in the chemical shift of the 5-membered ring. Chemical shift changes suggest

SCHEME 5. Protonation of 5 and Quenching



that the dication is best represented as the mesomeric diatropic (10π) annulenium species fused to a hydroxycyclopentadiene.

The parent ketone **5** bearing the bulky anthracene-C═O group at C-4 exhibits restricted rotation about the An-C═O bond at rt, causing H-5 not to be detectable and some other protons and several carbon signals to appear broad. Low-temperature reaction of **5** with FSO_3H/SO_2ClF gave a dark green solution. The NMR data were consistent with the formation of annulenium-carboxonium dication $\mathbf{5H_2}^{2+}$ as major species (Charts 4 and S4, Supporting Information), by protonation at C-5 (alpha to An-CO group), and at the carbonyl group. Due to restricted rotation at low temperature and signal broadening, complete assignment of the carbon resonances could not be achieved. The resulting annulenium dication is paratropic (12π), exhibiting notably deshielded internal methyls and shielded peripheral protons (protons in the anthracene moiety were deshielded). Quenching of the superacid solution of the dication returned the skeletally intact **5**.

(d) Esters 6−8. A dark-green solution was formed when **6** was reacted with FSO_3H/SO_2ClF. The NMR spectra were consistent with the formation of annulenium−carboxonium dications $\mathbf{6H_2}^{2+}$ (major) and $\mathbf{6aH_2}^{2+}$ (minor) by ring protonation at C-9 and C-4, respectively, and at the ester carbonyl (Scheme 6).

Shielding of the peripheral protons and significant deshielding of the internal methyls support the formation of a paratropic (12π) annulenium species. An interesting feature in the ^1H NMR of $\mathbf{6H_2}^{2+}$ is the diasterotopic nature of the CH_2 protons. A DFT-optimized model structure $\mathbf{6bH_2}^{2}$ (tBu replaced by Me) is shown in Figure 6.

For comparison, and in an effort to fine-tune the experimental NMR data, $\mathbf{6bH_2}^{2+}$ and $\mathbf{6cH_2}^{2+}$ were calculated by GIAO. The results are sketched in Charts 5 and S5 (Supporting Information). Interestingly, quenching of the superacid solution resulted in the formation of the chloro derivative **6a** as major component (Scheme 6), together with intact **6**. The origin of **6a** is likely via chlorination of **6** with SO_2ClF solvent during quenching. Chlorination of conjugated olefins with SO_2ClF has been reported in the literatures.[18]

The benz[*e*]annelated ester derivative **7** was diprotonated in FSO_3H/SO_2ClF to give the annulenium−carboxonium dication $\mathbf{7H_2}^{2+}$ (dark-green solution) (Scheme 7). The resulting annulenium species exhibits deshielded internal methyls, with mixed proton shielding/deshielding at the peripheral protons and the benz[*e*] ring (Charts 6 and S6, Supporting Information). Positive

(18) Grenier-Loustalot, M. F.; Iratcabal, P.; Meitras, F.; Petrissans, J. *Synthesis* **1976**, 33−35; Olah, G. A.; Ohannesian, L.; Arvanaghi, M.; Prakash, G. K. S. *J. Org. Chem.* **1984**, *49*, 2032−2034.

SCHEME 6. Protonation of 6 and Quenching Results

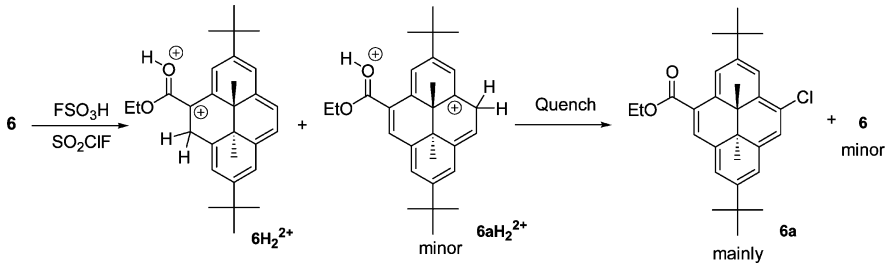
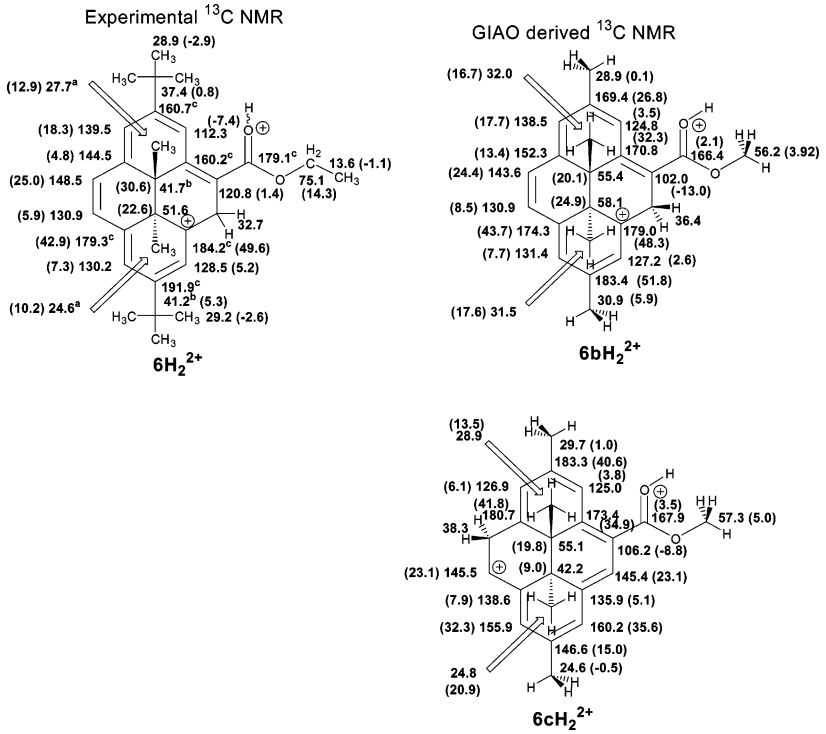
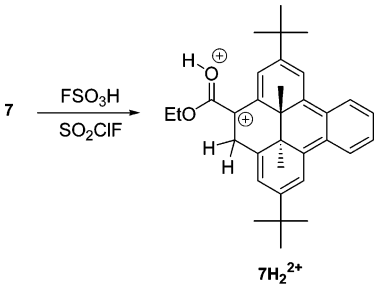


CHART 5. Experimental ^{13}C NMR Data for $6H_2^{2+}$ and GIAO-Derived ^{13}C NMR for Model Dications $6bH_2^{2+}$ and $6cH_2^{2+}$ [a]



[a] $\Delta\delta^{13}$C values relative to precursors in parentheses; superscript a−c refer to interchangeable assignments.

SCHEME 7. Protonation of 7



charge is more extensively delocalized into the annulene moiety than the [*e*]ring.

Moving the ester group from the DHP moiety (as in **7**) into the [*e*]ring (as in **8**) resulted in completely different protonation outcomes. Compound **8** reacted with FSO_3H/SO_2ClF to give a dark yellow solution whose NMR spectra were consistent with the formation of ethanophenanthrenium-carboxonium trication $\mathbf{8H_3}^{3+}$, formed by diprotonation at C-9/C-10 and ester protonation (Scheme 8). Formation of an ethanophenanthrenium dication from the [*e*]ring benzannelated 2,7-di-*tert*-butyl-DMDHP was observed previously (see Figure 3).

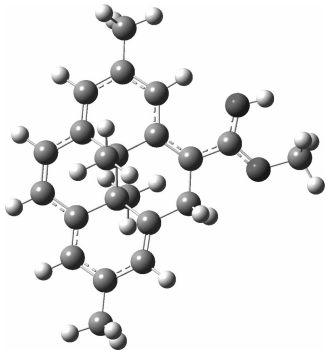
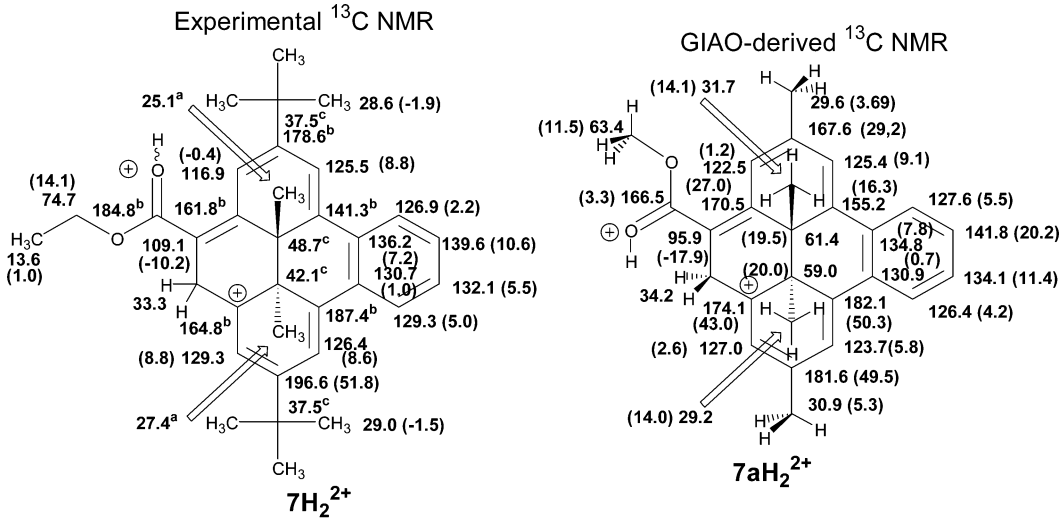


FIGURE 6. B3LYP/6-31+G(d,p)-optimized structure for the model dication $\mathbf{6bH_2}^{2+}$.

The trication was calculated by GIAO as a way to augment the assignments of the experimental NMR data (Charts 7 and S7, Supporting Information). Quenching the superacid solution returned the skeletally intact **8**, along with some unidentified degradation products.

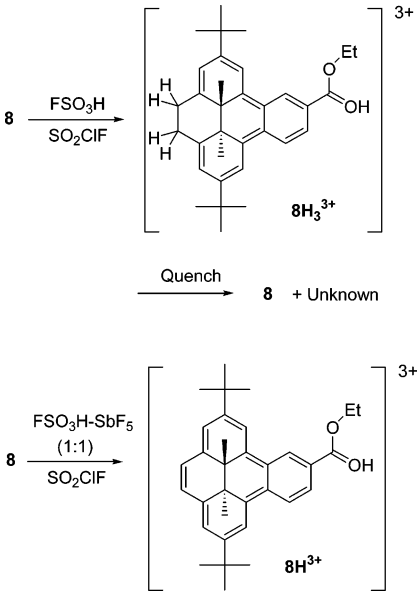
A different outcome was observed when **8** was reacted with FSO_3H-SbF_5 (1:1)/SO_2ClF. A dark-yellow solution resulted, whose NMR data were consistent with the formation of trication

CHART 6. Experimental ^{13}C NMR Data for $7H_2^{2+}$ and GIAO-Derived ^{13}C NMR Data for the Model Cation $7aH_2^{2+}$ [a]



[a] $\Delta\delta^{13}C$ values relative to precursors in parentheses; superscript a−c refer to interchangeable assignments).

SCHEME 8. Protonation of 8 in Different Superacids



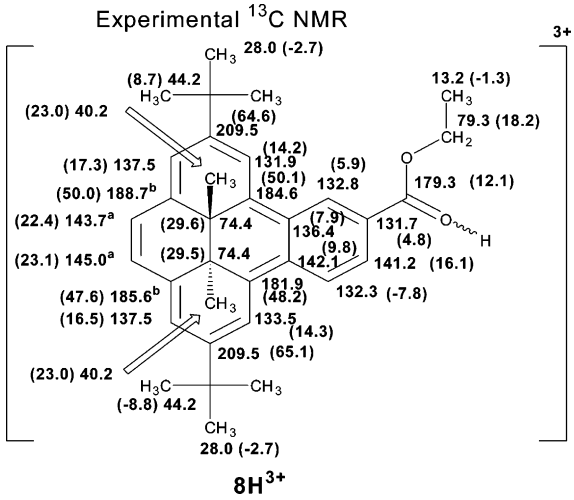
8H^{3+}, formed by 2-electron oxidation and ester carbonyl protonation (see Scheme 8).

The C═OH^+ signal was detected at 12.67 ppm (at −70 °C) and gave NOE with the *peri*-proton at δ 8.14 and the ethoxy $-CH_2$ group, suggesting that the carboxonium ion was not frozen as a single conformation in the triply charged species.

Positive charge in **8H$_3^{3+}$** is localized on the A/C rings within the ethanophenanthrenium moiety, with little delocalization into the benz[*e*]ring; by contrast, positive charge in **8H**$^{3+}$ is extensively spread out and includes the benz[e]ring. This pattern is similar to the earlier reported oxidation dication (see Figure 3).[15]

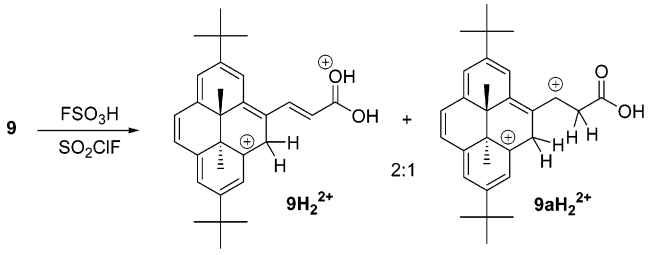
The triply charged **8H$_3^{3+}$**is overall diatropic (may be viewed as a 10π or a 14π system), but π-delocalization into the carboxonium moiety could induce some paratropic character (leading respectively to an 8π or a 12π system), with the net result being moderate diatropicity. In comparison, **8H**$^{3+}$ is strongly paratropic (16π). This is manifested in greatly increased internal methyl deshielding (∼6 ppm) and shielding of peripheral proton.

CHART 7. Experimental ^{13}C NMR Data for 8H^{3+} [a]



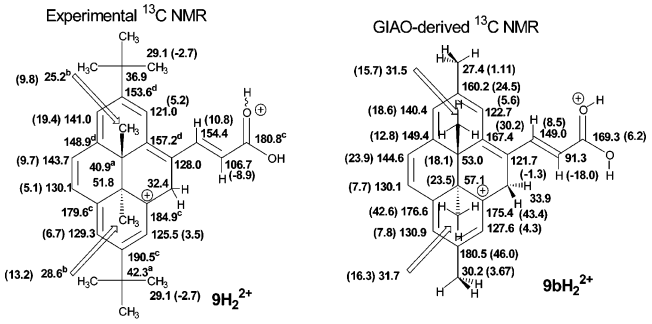
[a] $\Delta\delta^{13}C$ values relative to precursors in parentheses; superscript a and b refer to interchangeable assignments.

SCHEME 9. Protonation of 9



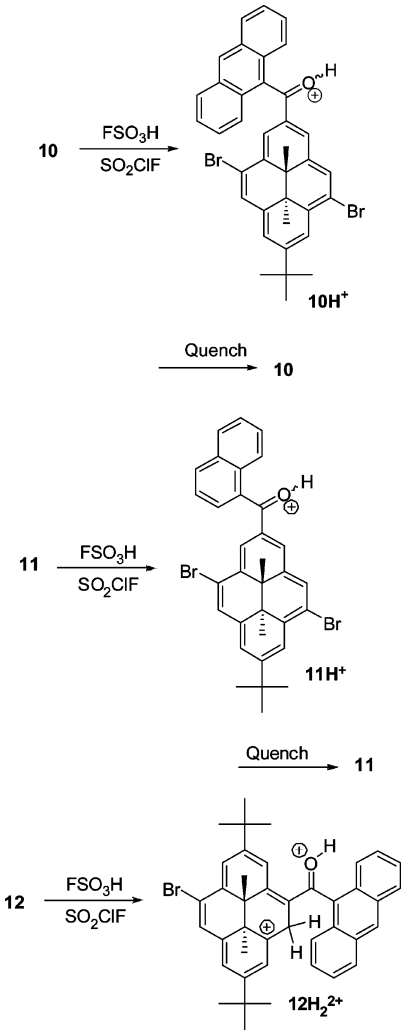
(e) Acrylic Acid 9. Compound **9** reacted with FSO_3H/SO_2ClF to give a brown-red solution. The NMR spectra were consistent with the formation of diprotonated dications **9H$_2^{2+}$**-(protonation at C-5 and at CO) as major species and **9aH$_2^{2+}$** as minor species (protonation at C-5 and at the exocyclic double bond) (Scheme 9). These dications constitute further examples of paratropic (12π) annulenium ions, with deshielded internal methyls and shielded peripheral protons. Complexity of the ^{13}C NMR data precluded specific assignment of some of the carbon

CHART 8. Experimental ^{13}C NMR Data for $9H_2^{2+}$ and GIAO-derived ^{13}C NMR for Model Systems $9bH_2^{2+}$ [a]



[a] $\Delta\delta^{13}$C values relative to precursors in parentheses; superscript a−d refer to interchangeable assignments.

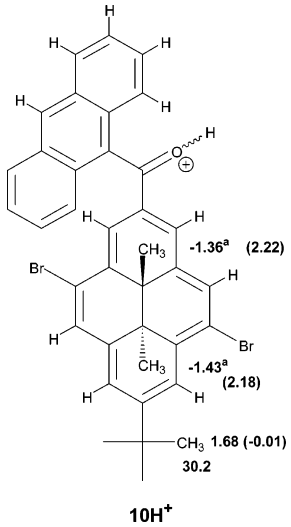
SCHEME 10. Protonation of Crowded Dibromo Ketones 10 and 11 and Monobromo Ketone 12



resonances, in particular those in the ring-junctions. As a guide to fine-tuning the assignments and for comparison, both dications were computed by GIAO. The experimental and GIAO NMR data are gathered in Charts 8 and S8, Supporting Information.

(f) Crowded Bromo Ketones 10−12. Low-temperature reaction of crowded dibromo ketones **10** and **11** in FSO_3H/SO_2ClF led to the formation of the corresponding carboxonium ions

CHART 9. Diagnostic ^{1}H (and ^{13}C) NMR Data for $10H^+$ [a]



[a] $\Delta\delta^1$H values relative to precursors in parentheses; superscript a refers to interchangeable assignments.

$\mathbf{10H}^+$ and $\mathbf{11H}^+$ by carbonyl protonation (dark green solutions) (Scheme 10). Restricted rotation around the Ar−CO bond in these crowded annulenes resulted in line-broadening; hence, limited specific NMR assignments could be made. The ^{1}H NMR data reveal significant changes in the ring current upon CO protonation leading to ∼2 ppm deshielding of the internal methyls. Diagnostic NMR data for $\mathbf{10H}^+$ and $\mathbf{11H}^+$ are summarized in Charts 9 and S9 (Supporting Information). Quenching of the carboxonium ion solutions in both cases returned the skeletally intact precursors.

Protonation of the monobromo ketone **12** led to O/C diprotonation to give the carboxonium−annulenium dication $\mathbf{12H_2}^{2+}$ (Scheme 10, Chart S9, Supporting Information). Dication $\mathbf{12H_2}^{2+}$ exhibits strongly deshielded methyl protons and shielded peripheral protons and is best viewed as a paratropic 12π-annulenium ion, with the positive charge from the carboxonium group mainly delocalized into the anthracene moiety.

Comparative Discussion and Concluding Remarks

We have shown that DCMCP **1** is diprotonated on the nitrile groups. Quenching of the resulting dinitrilium dication led to the formation of the ring closed DCDHP **2**, along with intact **1**. As discussed in the preceding article,[12] compound **1** has good thermal stability, requiring forcing conditions to induce ring closing, under which the resulting **2** was unstable and rearranged. The present results imply that the activation barrier for closing via $\mathbf{1H_2}^{2+}$ is lowered, allowing **2** to survive. Controlled protonation of DCDHP resulted in ring opening, with the formation of the *ipso*-protonated $\mathbf{2H}^+$, which on quenching gave cyanopyrene as the major product along with minor amounts of **2** and **1**. Similar outcomes were observed via controlled protonation of **2** with $FSO_3H{\cdot}SbF_5$ (4:1), except for the presence of minor amounts of pyrene in the quenching product mixture. The outcome of controlled protonation of **2** with $FSO_3H{\cdot}SbF_5$ (1:1) was the same as that in FSO_3H, except for the detection of $\mathbf{1H_2}^{2+}$.

Controlled protonation of the epoxy derivative **3** gave the paratropic dication $\mathbf{3}^{2+}$. Ketone **4** was diprotonated to a carboxonium−annulenium dication, thereby generating a diatropic dication (a 10π annulene fused to a cyclopentadiene moiety).

The carboxonium−annulenium dication formed by diprotonation of **5** has the characteristics of a paratropic (12π) species. Similarly, carboxonium−annulenium dications formed from esters **6** and **7**, are both paratropic.

The ester **8** reacted with FSO_3H to give ethanophenanthrenium−carboxonium trication $\mathbf{8H_3}^{3+}$. In the more oxidizing superacid $FSO_3H{\cdot}SbF_5$ (1:1), trication $\mathbf{8H}^{3+}$ was formed by two-electron oxidation and carbonyl protonation. The latter species exhibited strongly deshielded internal methyls. The acrylic acid **9** was also diprotonated, generating $\mathbf{9H_2}^{2+}$ as a paratropic species.

The diamagnetic ring current in the bromo ketones **10** and **11** is strongly diminished by CO protonation, which leads to internal methyl shielding. The monobromo-ketone derivative **12** was O/C diprotonated resulting in a paratropic annulenium ion.

In conclusion, the present study has greatly extended the available data on persistent annulenium ions derived from DHP and its benzannelated systems, further demonstrating the concept of tropicity modulation by charging. The stable ion work and the quenching experiments with the dicyano derivatives **1** and **2** imply that charged systems should be probed for π-switching.

Experimental Section

Computational Protocols. Structures were optimized using a C_1 molecular point group by the density function theory (DFT) method at B3LYP/6-31+G(d,p) level using the Gaussian 03 package.[19,20] All computed geometries were verified by frequency calculations to have no imaginary frequencies. Energies are summarized in Tables S1 and S2 (Supporting Information). NMR chemical shifts were calculated by the GIAO[21] method at the B3LYP/6-31+G(d,p) level. NMR chemical shifts were referenced to TMS (GIAO magnetic shielding tensor = 192.6 ppm for carbons and 31.65 ppm for protons in TMS), calculated with molecular symmetry of T_d at the same level of theory.

Preparation of the Solutions of the Carbocations in FSO_3H/SO_2ClF. The substrate (3−5 mg) was placed in a 5 mm NMR tube. The NMR tube was cooled in a dry ice acetone bath (−78 °C), and SO_2ClF (0.5 mL) was condensed. The superacid [FSO_3H, FSO_3H-SbF_5 (4:1), or FSO_3H-SbF_5 (1:1)] (2−3 drops) was then added at dry ice−acetone temperature under nitrogen. The resulting colored solution was efficiently mixed (vortex mixer). Finally, a few drops of cold CD_2Cl_2 were added to the NMR tube, and the solution was once again mixed (vortex) prior to NMR study.

Quenching Experiments. Cold solutions of the carbocations in NMR tubes were poured into ice−sodium bicarbonate with efficient mixing. After gas evolution ceased, the resulting mixture was extracted with CH_2Cl_2 and dried ($MgSO_4$). After evaporation of the solvent, the residue was analyzed by ^{1}H NMR.

1-Cyanopyrene: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, J = 9.5 Hz, 1H), 8.35 (d, J = 8.0 Hz, 1H), 8.33 (d, J = 8.0 Hz, 1H), 8.33 (d, J = 9.5 Hz, 1H), 8.28 (d, J = 8.0 Hz, 1H), 8.26 (d, J = 9.0 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H), 8.14 (dd, J = 8.0, 8.0 Hz, 1H), 8.12 (d, J = 9.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.2 (C), 133.0 (C), 130.9 (C), 130.6 (C and CH), 130.5 (CH), 129.6 (CH), 127.1 (CH), 127.00 (CH), 126.98 (CH), 126.9 (CH), 124.5 (CH), 124.1 (C), 124.0 (CH), 123.6 (C), 118.9 (C), 105.6 (C); ES-MS 228.1, 334.1, 336.1 561.0, 563.0 (288.1 calcd for M = [$C_{17}H_9N$ + H], 334.0, 336.1 (M + Ag)$^+$, 561.1/563.1 (2M + Ag)$^+$.

Compound 6a: brown oil; IR (NaCl) 2965, 1071, 1223, 1151, 1099; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.91 (s, 1H), 9.13 (s, 1H), 8.95 (s, 1H), 8.65 (s, 1H), 8.57 (s, 1H), 8.52 (s, 1H), 4.65 (q, J = 7.0 Hz, 2H), 1.74 (s, 9H), 1.68 (s, 9H), 1.63 (t, J = 7.0 Hz, 3H), −3.79 (s, 3H), −3.82 (s, 3H); ^{13}C NMR 168.6 (C=O), 150.3 (C), 147.1 (C), 136.7 (C), 136.1 (C), 135.2 (C), 133.0 (C), 125.6 (C), 125.4 (CH), 125.1 (CH), 124.0 (CH), 122.7 (CH), 120.7 (CH), 120.6 (C), 119.1 (CH), 61.0 (CH_2), 36.9 (C), 35.9 (CH), 32.7 (C), 31.9 ($3CH_3$), 31.7 ($3CH_3$), 29.2 (C), 14.7 ($3CH_3$); ES-MS 557.1/558.1/559.1/560.0/560.0/561.0/562.0/563.0 [M + Ag]$^+$.

On the Synthesis of Esters 6−8, the Carboxylic Acid 9, and Ketones 10 and 12. The esters **6** and **7** were prepared from the corresponding bromides by treatment with *n*-butyllithium and then ethyl chloroformate, respectively, and were obtained in 87% and 80% yields (for detailed procedure see the Supporting Information). The ester **8** was prepared by deoxygenation of its corresponding Diels−Alder adduct (prepared by Diels−Alder addition of the isofuran derivative with ethyl propriolate in ~70% yield as a mixture of two isomers with diiron nonacarbonyl in 72% yield (for detailed procedure see the Supporting Information). The acid **9** was prepared in 72% yield by hydrolysis of its corresponding ethyl ester (for detailed procedure see the Supporting Information). Anthracenyl ketone **10** and naphthyl ketone **12** were prepared by Friedel−Crafts reactions, and detailed procedures are given in the Supporting Information.

Acknowledgment. We thank the Ohio Board of Regents for the purchasing funds for the 500 MHz NMR instrument at KSU. R.H.M. thanks the Natural Sciences and Engineering Research Council of Canada and the University of Victoria for financial support.

Supporting Information Available: Energies and Cartesian coordinates for the optimized structures, experimental and GIAO-derived NMR data for the neutrals, carbocations, and their model compounds, general experimental methods, detailed synthetic procedures of neutrals, selected NMR spectra for the carbocations, and ^{1}H and ^{13}C NMR spectra for all new neutral compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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