

The first examples of persistent dimethyldihydropyrenium cations: reversal of ring current effects



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Diatropic [14]annulene *trans*-15,16-dimethyldihydropyrene **1** and its 2-bromo (**2**) and 2-nitro (**3**) derivatives are transformed into stable paratropic [12]annulenium ions (dimethyldihydropyrenium cations) by low temperature protonation with FSO₃H-SO₂ClF. Strong preference for *ipso* protonation (attack at C-2) is observed with **2** and **3**.

Stable ion studies provide the first charge delocalization mapping at the periphery of these [12]annulenium ions and a comparison with pyrenium cations.

The predicted (AM1 and PM3) annulenium ion energies and charges are compared with experiment. A theoretical study of **1** and 1H⁺ at the RHF/6-31G* level is included.

The annulenes, especially bridged annulenes, together with their protonated cations, dications (2e oxidation) and dianions (2e reduction), occupy a central position in organic chemistry as probes of 'aromaticity' and as a means to test experimentally the Hückel rule.^{1,2}

There is much current interest in molecules in which fusion of anti-aromatic or small strained rings to an aromatic core induces bond-localization.^{3,4}

Boekelheide's⁵ *trans*-15,16-dimethyldihydropyrene **1** (DMDHP),[‡] is a planar bridged [14]annulene with a very strong ring current. The highly shielded internal methyl protons are an excellent probe of π -electron delocalization and diatropicity.^{6,7} For example, benzannelation reduces diatropicity by increasing bond localization, with a dramatic change in the methyl chemical shift (Fig. 1).⁷⁻¹¹

Metal π -complexation (e.g. **4**→**5**) generates a paratropic 16 π species by metal back-donation,¹² but deshielding of the internal methyls is small compared to that in the dianion **6**.¹³

Aromatic substitution reactions of **1** (bromination, nitration, acylation) occur predominantly at the 2- (and 7) positions.¹⁴⁻¹⁶

Boekelheide's early chemical studies included equilibrium protonation of **1** in TFAH where methyl proton chemical shifts moved to 0.63 and 0.23 ppm.¹⁴

We report here the first examples of the fully protonated dimethyldihydropyrenium cations of **1**–**3**, with **2** and **3** showing strong preference for *ipso* attack (Fig. 2). Charge delocalization mapping at the periphery of these [12]annulenium ions are discussed and compared with persistent pyrenium cations.

As a guiding tool, AM1 (and PM3) energies and charges were also determined for comparison with NMR data; **1** and 1H⁺ were also probed at the RHF/6-31G* level of theory.

Results and discussion

The annulenium ions were generated by protonation with FSO₃H-SO₂ClF at dry ice-acetone temperature using the previously reported procedures for stable ion work.¹⁷ The NMR spectra were initially recorded at -67 °C, but no change in the spectra was observed up to ca. -35 °C.

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[‡] Chemical abstract uses *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene as the name for **1**.

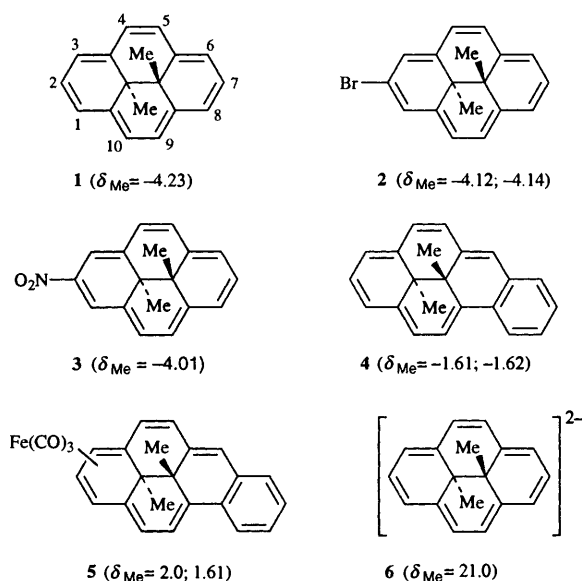


Fig. 1 Internal methyl proton chemical shifts in parent DMDHP, its substituted and benzannelated derivatives and the dianion

Protonation of **1** with FSO₃H-SO₂ClF gave a dark green solution whose ¹H and ¹³C NMR spectra were consistent with the formation of 1H⁺ as the major and 1aH⁺ as the minor annulenium ions (Fig. 2 and Table 1).

Similar low temperature protonation of **2** gave a mixture of 2H⁺ and 2aH⁺§ as a dark red solution in 70:30 ratio.

Low temperature protonation of **3** produced the *ipso*-protonated 3H⁺ almost exclusively, as a dark red solution. The actual ¹H NMR spectrum is shown in Fig. 3.

Attempts to prevent the formation of 1aH⁺ and 2aH⁺ by

§ Whereas formation of a skeletally intact C-4 protonated annulenium ion is more easily visualized for the minor cation, the doublet appearance of the sp³ (C) carbon in the H-coupled ¹³C NMR spectrum (see further discussion and Table 1) argues in favour of another *ipso*-protonated cation. On this basis formation of 2aH⁺ is tentatively suggested.

Table 1 NMR data for the annulenium cations

[6] Annulene and [14] annulenium ion	Solvent/Temp.	δ	
		^1H NMR	^{13}C NMR
1	$\text{CDCl}_3/\text{r.t.}$	8.65 ($\text{H}_4, \text{H}_5, \text{H}_9, \text{H}_{10}$); 8.60 ($\text{H}_1, \text{H}_3, \text{H}_6, \text{H}_8$); 8.12 (H_2, H_7) -4.23 (Me)	123.36; 123.30; 122.9 (C_2, C_7); 29.8 (C-Me); 136.6 ($\text{C}_{3a}, \text{C}_{5a}, \text{C}_{8a}, \text{C}_{10a}$); 13.9 (CH_3)
1H⁺	$\text{FSO}_3\text{H-SO}_2\text{ClF}/ -65^\circ\text{C}$	8.46 (H_1 ; $\Delta\delta = 0.34$); 7.48 (H_6, H_8 ; $\Delta\delta = -1.14$); 7.39 ($\text{H}_4, \text{H}_{10}$; $\Delta\delta = -1.26$); 7.05 (H_5, H_9 ; $\Delta\delta = -1.60$); 6.93 (s; H_1, H_3 ; $\Delta\delta = -1.67$); 4.83 (CH_2); 1.70 (Me; $\Delta\delta = 5.93$); 1.32 (Me; $\Delta\delta = 5.55$)	186.5 ($\text{C}_{3a}, \text{C}_{8a}$; $\Delta\delta = 49.9$); 166.2 (C_7 ; $\Delta\delta = 43.2$); 144.6 ($\text{C}_{3a}, \text{C}_{10a}$; $\Delta\delta = 10$); 145.4 ($\text{C}_4, \text{C}_{10}$; $\Delta\delta = 22.1$); 132.3 (C_6, C_8 ; $\Delta\delta = 9.0$); 129.9 (C_5, C_9 ; $\Delta\delta = 6.6$); 124.1 (C_1, C_3 ; $\Delta\delta = 0.8$); 60.3 (CH_2); 57.5 (C-Me ; $\Delta\delta = 27.7$); 47.7 (C-Me ; $\Delta\delta = 17.9$); 36.6 (Me; $\Delta\delta = 22.7$); 26.3 (Me; $\Delta\delta = 12.4$)
1aH⁺	$\text{FSO}_3\text{H-SO}_2\text{ClF}/ -65^\circ\text{C}$	~8.43 (H_2); 8.40 (H_7); 7.29 (H_6, H_8); 1.94 (Me; $\Delta\delta = 6.17$); 1.53 (Me; $\Delta\delta = 5.76$)	187.2 (C_{3a}); 166.8 (C_{10a}); 144.9 (C_5); ^c 62.0 (C-Me), 58.7 (C-Me); 50.4 ^c (CH_2); 38.0 (Me); 26.9 (Me)
2	$\text{CDCl}_3/\text{r.t.}$	8.73 (s; H_1, H_3); 8.61 ^a ($\text{H}_4, \text{H}_{10}$); 8.56 ^a (H_5, H_9); ~8.53 ^a (H_6, H_8); 8.12 (H_7); -4.14 (Me); -4.12 (Me)	136.8 ^a ($\text{C}_{3a}, \text{C}_{10a}$); 136.5 ^a ($\text{C}_{5a}, \text{C}_{8a}$); ~124.6 ^b (C_5, C_9), ~124.58 ^b ($\text{C}_4, \text{C}_{10}$); 122.7 (C_6, C_8); 125.5 (C_1, C_3); 123.3 (C_7); 118.0 (C_2); 30.14 (C-Me); 28.90 (C-Me); 14.14 (Me); 13.97 (Me)
2H⁺	$\text{FSO}_3\text{H-SO}_2\text{ClF}/ -63^\circ\text{C}$	7.64 (s; H_1, H_3 ; $\Delta\delta = -1.09$); 7.43 ($\text{H}_4, \text{H}_{10}$; $\Delta\delta = -1.18$); 6.91 ^a (H_5, H_9 ; $\Delta\delta = -1.65$); 6.83 ^a (H_6, H_8 ; $\Delta\delta = -1.70$); 6.81 (H_7 ; $\Delta\delta = -1.31$); 4.83 (CHBr); 1.71 (Me), 1.36 (Me)	181.9 ($\text{C}_{5a}, \text{C}_{8a}$; $\Delta\delta = 45.4$); 172.5 (C_7 ; $\Delta\delta = 49.2$); 146.2 ($\text{C}_4, \text{C}_{10}$; $\Delta\delta = \sim 21.6$); 144.4 ($\text{C}_{3a}, \text{C}_{10a}$; $\Delta\delta = 7.65$); 135.7 (C_1, C_3 ; $\Delta\delta = 10.2$); 128.7 (C_5, C_9 ; $\Delta\delta = \sim 4.1$); 124.5 (C_6, C_8 ; $\Delta\delta = \sim 1.8$); 60.8 (CHBr); 55.6 (C-Me); 47.2 (C-Me); 35.0 (Me); 26.0 (Me)
2aH⁺	$\text{FSO}_3\text{H-SO}_2\text{ClF}/ -63^\circ\text{C}$	7.57 (C_3); 7.35; 4.84 (CHBr); 1.94 (Me); 1.59 (Me)	182.5 ^a (C_{3a}), 173.3 ^a (C_{10a}); 62.5 (CHBr); 56.7 (C-Me); 49.7 (C-Me); 36.1 (Me); 26.6 (Me)
3	$\text{CDCl}_3/\text{r.t.}$	9.51 (H_1, H_3); 8.94 ($\text{H}_4, \text{H}_{10}$); 8.70 (H_5, H_9); 8.65 (H_6, H_8); 8.30 (H_7); -4.01 (Me); -3.99 (Me)	141.2 (C_2); 134.1 ($\text{C}_{3a}, \text{C}_{10a}$); 129.8 (C_1, C_3); ~129.8 ($\text{C}_{5a}, \text{C}_{8a}$); 127.9 (C_7); 124.9 ^a ($\text{C}_5, \text{C}_{10}$); 124.8 ^{a,b} (C_4, C_9); 118.6 ^b (C_6, C_8); 29.6 (C-Me); 15.8 (Me); 14.2 (Me)
3H⁺	$\text{FSO}_3\text{H-SO}_2\text{ClF}/ -62^\circ\text{C}$	7.97 (H_7 ; $\Delta\delta = -0.33$); 6.79 (H_1, H_3 ; $\Delta\delta = -2.72$); 6.78 (H_6, H_8 ; $\Delta\delta = -1.87$); 6.47 (H_5, H_9 ; $\Delta\delta = -2.23$); 6.30 ($\text{H}_4, \text{H}_{10}$; $\Delta\delta = -2.64$); 4.05 ^c (Me); 3.64 (Me)	190.9 ($\text{C}_{5a}, \text{C}_{8a}$; $\Delta\delta = 61.1$); 172.0 (C_7 ; $\Delta\delta = 44.1$); 161.5 ^d ($\text{C}_{3a}, \text{C}_{10a}$); 143.7 ($\text{C}_4, \text{C}_{10}$); $\Delta\delta = \sim 18.8$); 134.9 ^d (C_1, C_3 ; $\Delta\delta = \sim 5.1$); 134.8 ^a (C_6, C_8); 121.5 ($\text{C}_5, \text{C}_{10}$); 77.9 (CHNO_2); 67.3 (C-Me); 60.9 (C-Me); 42.6 (Me); 33.7 (Me)

^{a,b} Interchangeable groups of resonances. ^c CHNO_2 is buried under this signal. ^d Assignment uncertain; three other peaks (144.8, 141.8, 125.1) are present which did not show up in separate protonation experiments using a different batch of **3**.

protonation at lower temperatures to reduce local overheating were unsuccessful.

ipso-Protonation in **2H⁺**, **2aH⁺** and **3H⁺** cations was clearly established based on the H-coupled ^{13}C NMR spectra.

The resulting $4n\pi$ annulenium ions exhibit reversal of ring current effects, *i.e.* considerable deshielding of the methyl proton and carbon resonances (with much greater $\Delta\delta^1\text{H}$ values than the cation formed by TFAH protonation), and shielding of the annulenium protons (Table 1).

The magnitude of internal methyl deshielding ($\Delta\delta$) is in the range 5.5 to 8 ppm, with **3H⁺** showing the highest values. Methyl proton deshielding is accompanied by dramatic ring proton shielding. A large deshielding effect is observed for the internal methyl carbons (12–27 ppm), again with those in **3H⁺** being most deshielded.

Quenching of the ion solutions in all cases returned the skeletally intact [14]annulenes as the major product (^1H NMR), suggesting that for *ipso*-protonated annulenium ions deprotonation is more facile than denitration or debromination.

The positive charge in the annulenium cations is extensively delocalized away from the site of attack at the alternating carbons of the periphery (with C-4, C-5a, C-7, C-8a and C-10 being the most deshielded).

The $\Delta\delta^{13}\text{C}$ values for the parent pyrenium cation¹⁸ **7H⁺** are included for comparison (Fig. 4). Contrary to DMDHP, attack at C-2 is highly unfavourable for pyrene (by 20.5 kcal mol⁻¹);¹⁹

pyrenium ion from attack at C-2 cannot be generated under stable ion conditions.[¶]

Theoretical studies

Both semiempirical methods (AM1 and PM3) and the restricted Hartree–Fock at the DZV(d) level predict a cyclic polyene structure for **1** with significant bond alternation (C_2 symmetry). Only at the MP2 level is the experimentally observed C_{2h} structure predicted.⁴

Despite these limitations, AM1 correctly predicts the preference for attack at C-2 (relative annulenium ion stability: C-2 > C-4 > C-1) (Fig. 5).

For **2**, protonation at C-7 is predicted to be more favoured over *ipso* attack by 2.4 kcal mol⁻¹ (relative stability order: C-7 > C-5 > C-4 > C-2 > C-6 > C-1).

For **3**, *ipso* attack is 3.7 kcal mol⁻¹ lower in energy than attack at the unsubstituted C-7 (stability order: C-5 > C-2 > C-4 > C-7 > C-1).

In all cases, there is good correspondence between AM1 (and PM3) changes in carbon charges^{||} and the $\Delta\delta^{13}\text{C}$ values.

Although relative PM3 energies (Fig. 6) are higher than

[¶] For C-2 protonated pyrene, AM1 predicts very limited charge delocalization (*ortho* and *para* to the site of attack).

^{||} Based on ΔQ profiles [q_c (ion) - q_c (neutral)].

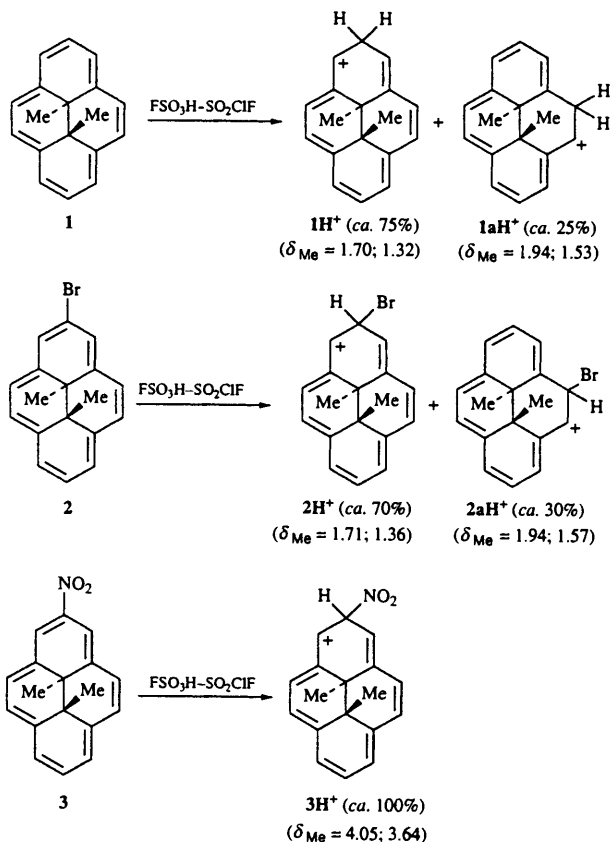


Fig. 2 Superacid protonation of 1-3

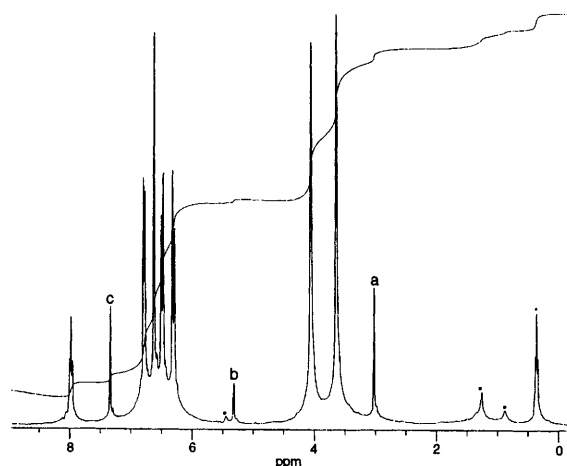


Fig. 3 ^1H NMR spectrum of 3H^+ [a: protonated acetone; b: CH_2Cl_2 ; c: CHCl_3 ; *: unknown impurities]

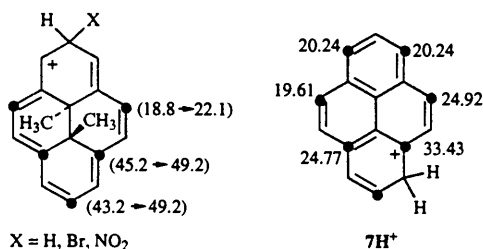


Fig. 4 Magnitude of $\Delta\delta^{13}\text{C}$ at the most deshielded carbons of the [14]annulene cations (a range is given depending on X) and comparison with parent pyrenium ion of α attack; circles indicate the ring carbon positions with largest $\Delta\delta^{13}\text{C}$ values

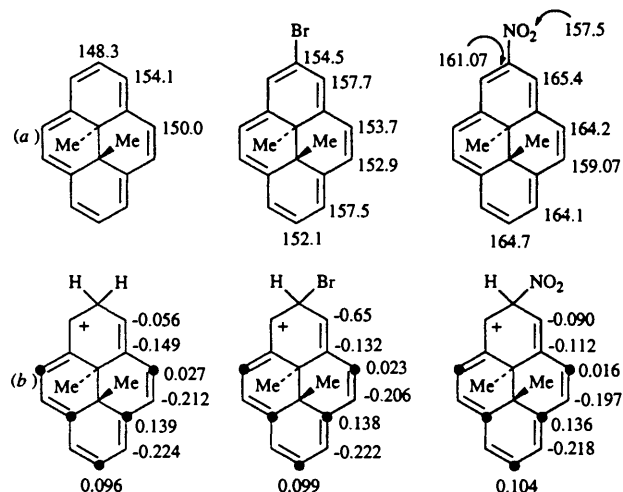


Fig. 5 (a) AM1 energies [ΔH^0 , (ion) - (neutral) in kcal mol^{-1}] for various monocations of [14]annulenes 1-3. (b) AM1 calculated carbon charges for the observed [12]annulene cations.

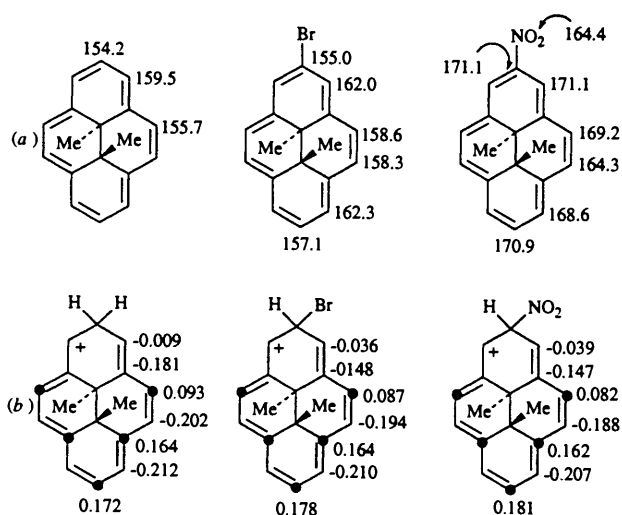


Fig. 6 (a) PM3 energies and (b) PM3 carbon charges for the observed monocations of 1-3

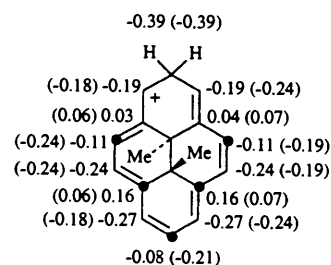


Fig. 7 Calculated charges for 1H^+ and **1** (in parentheses) at the RHF/6-31 G^* level

AM1, annulene ions stability order is correctly predicted for **1** and **2**. For **3**, PM3 fails to predict the preference for *ipso* attack.

Finally, for comparison we also calculated 1H^+ and **1** at the RHF/6-31 G^* level (in GAMESS) (Fig. 7). For **1**, as found previously,⁴ the [14]annulene is incorrectly predicted to have C_2 symmetry. For the [12]annulene cation, the charge delocalization pattern is similar to that predicted by semi-empirical methods and closely parallels the NMR-based conclusions.

In summary, monoprotection of dimethyldihydropyrenes

transforms the diatropic Hückel [14]annulenes 1–3 to paratropic $4n\pi$ [12]annulenium cations showing extensive charge delocalization away from the site of attack, analogous to pyrenium ions.

Additional studies aimed at diprotonation of 1 and its 2,7-disubstituted derivatives to generate diatropic dication, and protonation(alkylation) of benzannelated and cyclohexane-(cyclopentane-)fused derivatives of 1 have been initiated.

Experimental

The [14]annulenes 1–3 were synthesized and purified according to previously reported procedures.^{14–16}

FSO_3H (Linde) was doubly distilled in an all-glass distillation apparatus and stored in Nalgene bottles under argon. SO_2ClF (lecture bottle from PCR) was used without further purification.

NMR studies were carried out using a GE-GN300 MHz wide-bore instrument. The procedure for stable ion generation and low temperature NMR studies were similar to our previously published methods.^{17,18}

The AM1 and PM3 calculations were performed with the Hyperchem package (hypercube Inc., 1994) which uses Dewar's version.

The GAMESS package²⁰ (general atomic and molecular structure systems, version 1995) was used for RHF/6-31G* calculations.

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