Protonation of azuleno[1,2-*a*]acenaphthylene and 7-bromoazuleno[1,2-*a*]acenaphthylene in superacids: azulenium, acenaphthenium or naphthalenium cations?

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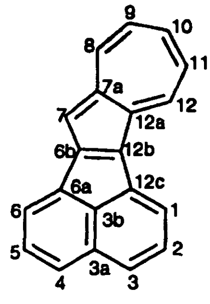
Persistent monocation 1aH$^+$ has been formed as the major product of low temperature protonation of azuleno[1,2-*a*]acenaphthylene 1 with FSO$_3$H·SO$_2$ClF or FSO$_3$H·SbF$_5$ (4:1)–SO$_2$ClF superacid media. Protonation at C-7 (→ 1bH$^+$) was observed only as a minor competing process (10–15%). Protonation of the 7-bromoazuleno[1,2-*a*]acenaphthylene 2 similarly gave the monocation 2aH$^+$; the *ipso*-protonated cation 2bH$^+$ was not observed.

The NMR characteristics of the resulting ions and their charge distribution patterns are discussed and compared with those of parent acenaphthenium 3H$^+$ and azulenium 4H$^+$ cations as models. Monocations 1a and 2a are best viewed as azulenium ions having strong tropylium ion character with limited charge delocalization into the naphthalene moiety. For comparison, the relative energies and changes in charge distribution Δq [q_c(ion) − q_c(neutral)] were calculated for cations 1a, 1b, 1c and 2a, 2b, 2c by the AM1 and PM3 methods.

The 20π azulenoid hydrocarbon 1 and its 7-bromo-derivative 2 have recently been synthesized by Kuroda *et al.*[1] Unlike azulene



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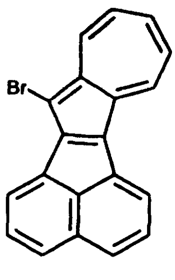

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and its derivatives which have an unmistakable blue colour, these polycyclic derivatives are both green. NMR studies revealed no contribution from a diatropic 20π system and indicated a condensed molecule made up of a 10π azulene and a 10π naphthalene pair, rather than an acenaphthylene–heptafulvene pair. This is in line with predictions based on π-calculations showing greater aromatic character in the azulene–naphthalene fused system.[2]

In relation to our previous and on-going work on long-lived arenium ions of large polycyclic aromatic hydrocarbons (PAHs) probing the charge distribution mode at the periphery of arenium ions and the influence of substituents like nitro and fluoro on charge modulation,[2–9] we report here a low temperature stable ion protonation study on 1 and 2. Our goal was to determine the site of protonation and the mode of charge distribution in the resulting cations.

Results and discussion

NMR studies on the precursors

The 600 MHz ^{1}H NMR and 150.9 MHz ^{13}C NMR spectra of the precursors 1 and 2 are shown in Figs. 1 and 2. The assignments, as summarized in Fig. 3, are based on COSY relationships and decoupling experiments in ^{1}H NMR and the HETCOR and COLOC relationships in ^{13}C NMR spectroscopy. In the latter case, some of the quaternary carbons could not be assigned with certainty.

An important feature in the ^{1}H NMR spectra of both compounds is the highly deshielded nature of the bay region hydrogens: 12-H and 8-H in the seven-membered ring, followed by those of 1-H and 6-H of the naphthalene ring.

As reported by Kuroda *et al.*[1] the vicinal coupling constants for the protons in the azulene moiety are between 9.8 and 9.2 Hz, whereas those in the naphthalene ring are much smaller (8.2–7.9 Hz).

Despite the complex nature of the proton NMR spectra, the 300 MHz NMR spectrum of 1 and 2 gave essentially the same information except that the region which contains resonances for 2-H, 3-H and 5-H was less resolved. The ^{13}C NMR spectra recorded at 75.5 MHz were also adequate, showing all the expected 20 aromatic resonances for each substrate. These studies suggested that stable ion studies at 300 MHz should be feasible.

Low temperature protonation studies

Careful addition of a clear solution of FSO$_3$H–SO$_2$ClF to a slurry of hydrocarbon 1 in SO$_2$ClF at dry ice–acetone temperature gave a clear red solution on contact, whose ^{1}H NMR spectrum [−65 °C; Fig. 4(*a*)] exhibited 11 resonances in the aromatic region 9.40–7.99 ppm (1 H each), five of which appeared as resolved doublets and six gave rise to three pairs of overlapping doublets (or doublet of doublets). The aliphatic region consisted of a sharp singlet at 6.46 ppm (1 H) and a broad singlet at *ca.* 4.2 ppm (slightly more than 1 H; see later).

These results are only compatible with protonation at the

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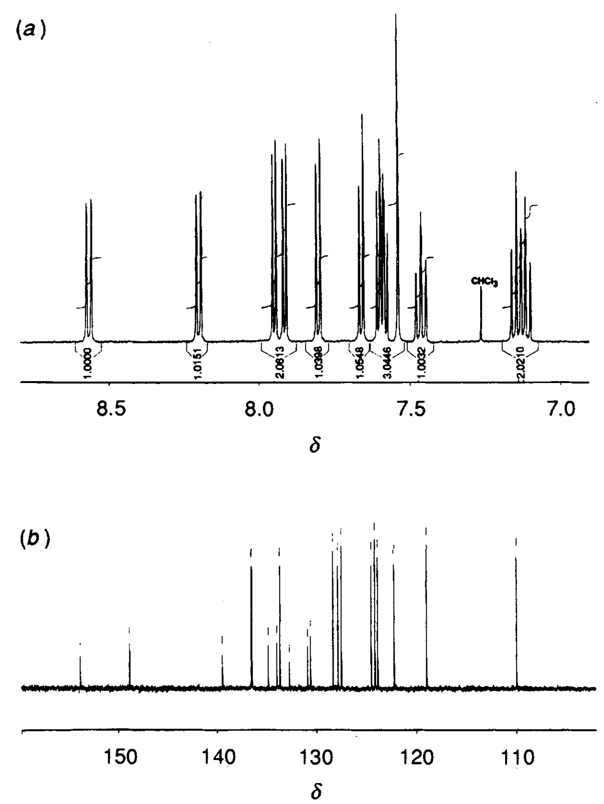


Fig. 1 (*a*) ^1H and (*b*) ^{13}C NMR spectra of parent compound **1**

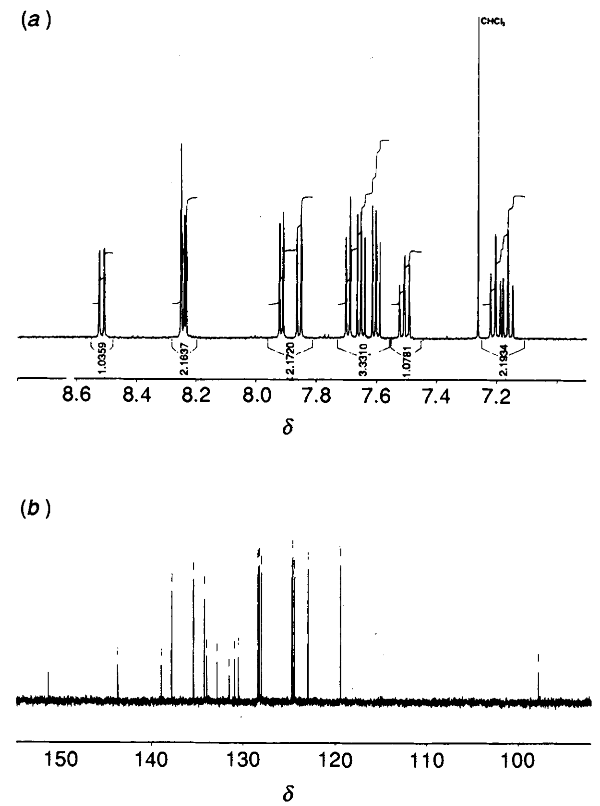


Fig. 2 (*a*) ^1H and (*b*) ^{13}C NMR spectra of **2**

acenaphthene double-bond (at C-12b or C-6b) to form **1aH**$^+$ or **1cH**$^+$ (Scheme 1); lack of vicinal coupling between the 6.46 and 4.2 ppm resonances argued against protonation at C-6b. The assignment of the aromatic protons (Fig. 5) were based on the magnitude of vicinal coupling constants, the Δδs and COSY relationships.

As required for a structure like **1aH**$^+$, the ^{13}C NMR

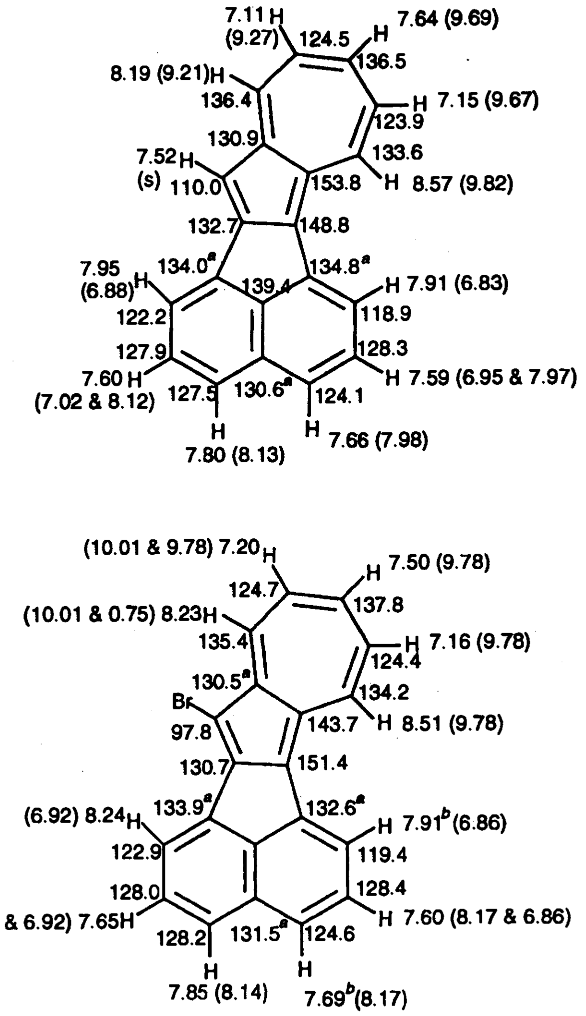


Fig. 3 NMR assignments for **1** and **2**. Coupling constants are given in parentheses. For each structure, interchangeable assignments are identified by superscript letters.

spectrum [Figs. 4(*b*) and 5] exhibited 19 aromatic resonances between 165.8 and 125.2 ppm with the three most deshielded resonances being non-hydrogen bearing assigned to 12a, 7a and 6b. The aliphatic region showed the sp^3 (CH^+) resonance at 68.4 ppm.

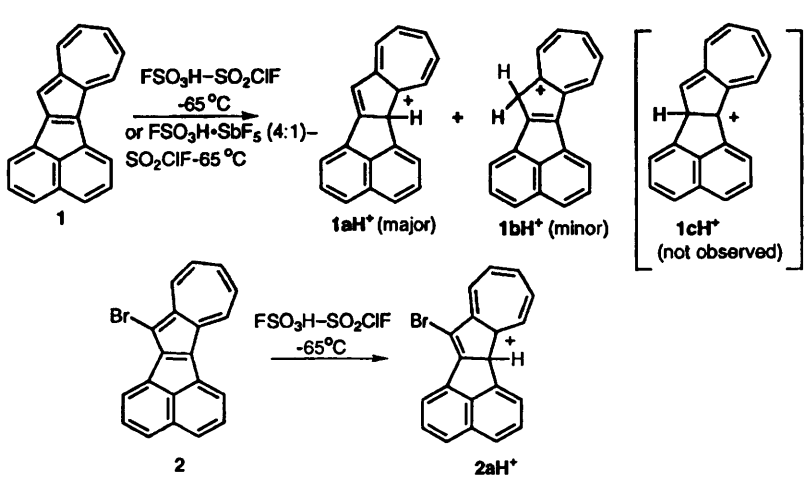
Minor amounts (15–20%) of a second arenium ion were also produced, which, based on the NMR data, could be assigned to the C-7 protonated azulenium ion **1bH**$^+$, whose sp^3 ($CH_2{}^+$) resonance coincides with the broad peak at *ca.* 4.2 ppm. This is corroborated from the relative integrals; more of the minor ion was formed in protonation experiments with $FSO_3H{\cdot}SbF_5$ (4:1)–SO_2ClF, in these spectra the $CH_2{}^+$ resonance was better resolved although still partially overlapping with the CH^+ of **1aH**$^+$.

Despite severe overlap [Fig. 4(*b*)], *ca.* 16 of the aromatic resonances for **1bH**$^+$ were discernible, the most deshielded of which at 172.6 ppm was assigned to C-6b. The $CH_2{}^+$ resonance for this cation was at 39.3 ppm (see Fig. 4, inset).

There was no change in the NMR spectra when the sample temperature was raised to −40 °C. Prolonged storage led to a slow increase in **1bH**$^+$. Furthermore, there is no indication in the NMR spectra for a rapid 1,2-hydrogen shift in **1aH**$^+$; its behaviour is similar to that of the parent acenaphthenium cation studied by Olah *et al.*[10]

Since an upfield shift of over 1 ppm for 7-H in **1aH**$^+$ appeared unusual, and in order to obtain further corroboratory evidence, the 7-bromo derivative **2** was studied (Scheme 1 and Fig. 5).

Thus a similar addition of cold $FSO_3H{\cdot}SO_2ClF$ to a green slurry of **2** in SO_2ClF at dry ice–acetone temperature produced



Scheme 1 Superacid protonation of 1 and 2

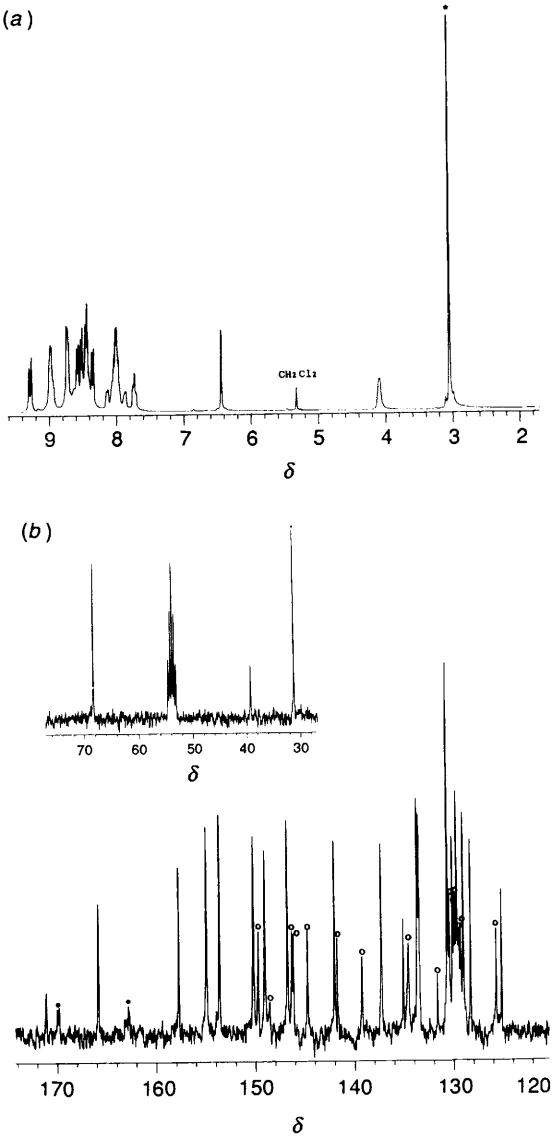


Fig. 4 (*a*) ^{1}H NMR spectrum (−65 °C) of **1aH**$^+$ and (*b*) the aromatic region of the ^{13}C NMR spectrum of **1aH**$^+$ (inset: the aliphatic region). * Protonated acetone; ○ = **1bH**$^+$.

a clear red solution. The aromatic region of its ^{1}H NMR spectrum indicated that despite some changes in the position of the aromatic resonances, essentially the same pattern of 11 protons consisting of five resolved 1 H doublets and three overlapping pairs of pseudo-doublets was obtained.

Table 1 Relative energies of various carbocations derived from **1** and **2**

Cation	Method	$\Delta\Delta_fH^\circ$/kcal mol^{-1}
1aH$^+$	AM1	143.06 (major ion observed)
1bH$^+$	AM1	141.05 (minor ion observed)
1cH$^+$	AM1	158.95 (not observed)
1aH$^+$	PM3	149.14
1bH$^+$	PM3	145.18
1cH$^+$	PM3	164.3
2aH$^+$	AM1	146.1 (the observed cation)
2bH$^+$	AM1	149.1
2cH$^+$	AM1	161.4
2aH$^+$	PM3	150.8
2bH$^+$	PM3	145.0
2cH$^+$	PM3	166.0

An important piece of information was the absence of the 6.46 ppm singlet in the ^{1}H NMR spectrum of **2aH**$^+$; the only aliphatic resonance was that of CH$^+$ observed at 5.16 ppm with its matching ^{13}C NMR absorption at 78.8 ppm. Hence the assignment of the 6.46 ppm singlet to 7-H of **1aH**$^+$ is correct. The observed chemical shifts for the (sp^3) CH$^+$ centre in these cations is rather extreme compared with other arenium ions.[9]

To explore if structural or conformational reasons may be responsible, the energies and conformations of cations **1a**, **1b**, **1c** and **2a**, **2b**, **2c** (Fig. 6) were calculated by the AM1 and PM3 methods.

Fig. 6(*a*) and (*b*) show the AM1 calculated structures for **1** and **2** together with their three different monocations. In **1aH**$^+$ and **2aH**$^+$ ions the sp^3 (CH) is located above the convex face of the arenium ion, whereas the hydrogen and bromine at C-7 appear to be approximately in the plane of the seven-membered ring. The modelling studies do not reveal anything unusual about the environment of 7-H which may lead to anisotropic shielding.

The $\Delta\Delta_fH^\circ$ data are summarized in Table 1. Calculations by AM1 and PM3 predict that **1bH**$^+$ (the minor cation observed) is more stable than **1aH**$^+$ by *ca.* 2 and *ca.* 4 kcal mol^{-1},‡ respectively. For **2**, the predicted (AM1) lowest energy cation is the same as that observed. In PM3, the observed ion is 5.8 kcal mol^{-1} higher in energy than the *ipso*-protonated ion **2bH**$^+$.

AM1 and PM3 calculations both predict that cations **1cH**$^+$ and **2cH**$^+$ are least favoured. In general the calculated $\Delta\Delta_fH^\circ$ values were higher in PM3 than in the AM1.

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‡ 1 cal = 4.184 J.

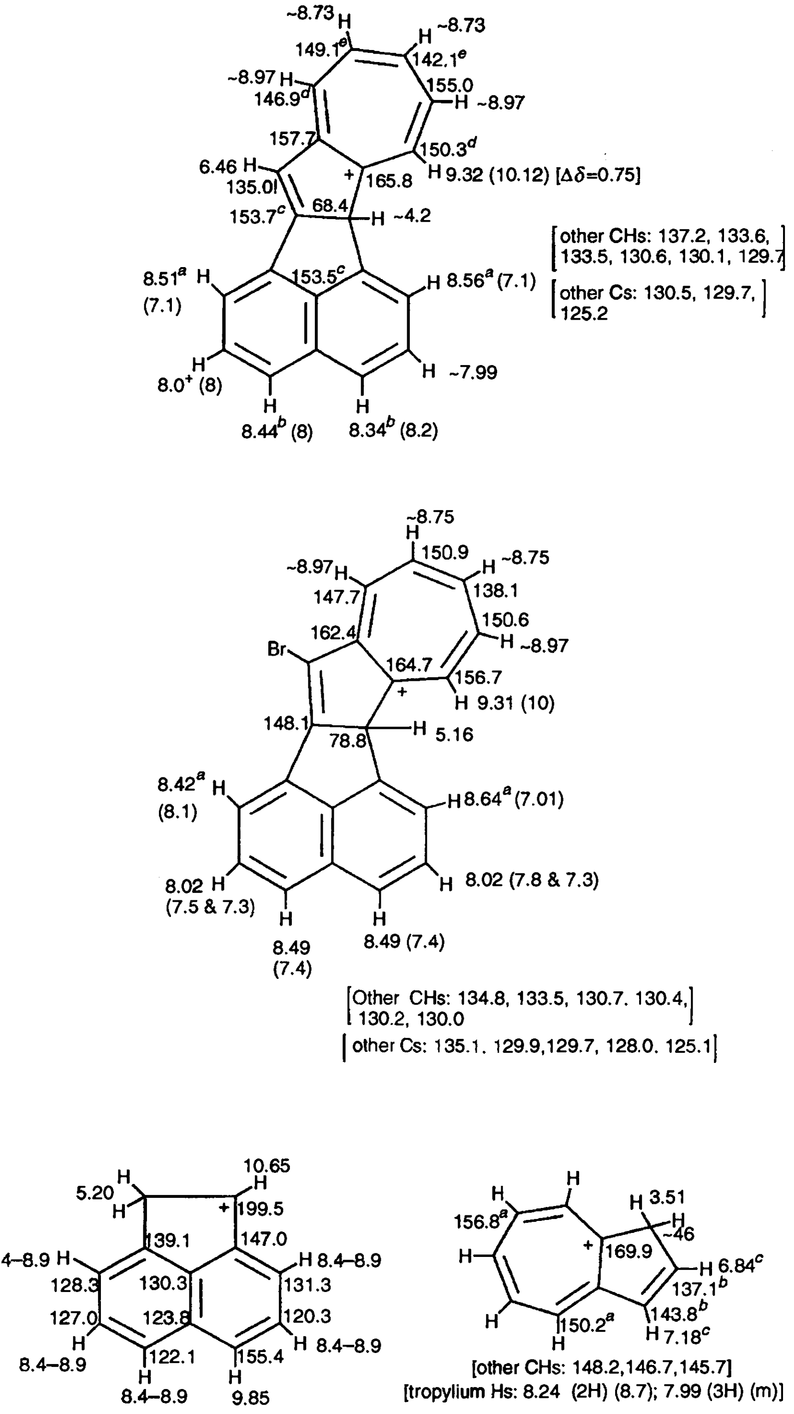
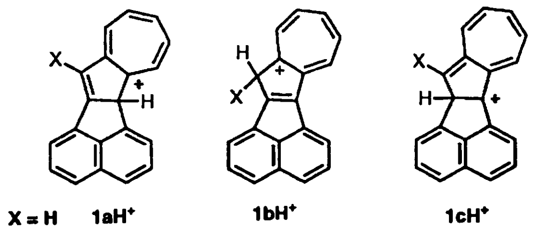


Fig. 5 NMR assignments for **1aH**$^+$, **2aH**$^+$, **3H**$^+$ and **4H**$^+$. Coupling constants are given in parentheses. For each structure, interchangeable assignments are identified by superscript letters.



X = H **1aH**$^+$ **1bH**$^+$ **1cH**$^+$

X = Br **2aH**$^+$ **2bH**$^+$ **2cH**$^+$

Attempted diprotonation

In an effort to induce a second protonation to generate an azulenium–naphthalenium dication species, the low temperature reaction of **1** with FSO$_3$H•SbF$_5$(1 : 1)–SO$_2$ClF was tried. The ^{1}H NMR spectrum of the resulting dark red solution showed essentially the same monocation but with substantial line broadening and loss of resolution, suggesting the coexistence of the monocation and the paramagnetic radical cation; a dication could not be obtained under these conditions.

Quenching experiments

Quenching of **2aH**$^+$ led to the recovery of **2** in *ca.* 95% yield (^{1}H NMR). However, quenching of **1aH**$^+$ gave, apart from **1**, a new compound which could not be separated from **1** by chromatography. The ^{1}H NMR spectrum of the mixture, despite its complexity, indicated that the quenching product resulted from substitution at C-7 (by the absence of the 7-H singlet in the new product). Fortunately, in two independent quenching experiments the ratio of the new compound to **1**

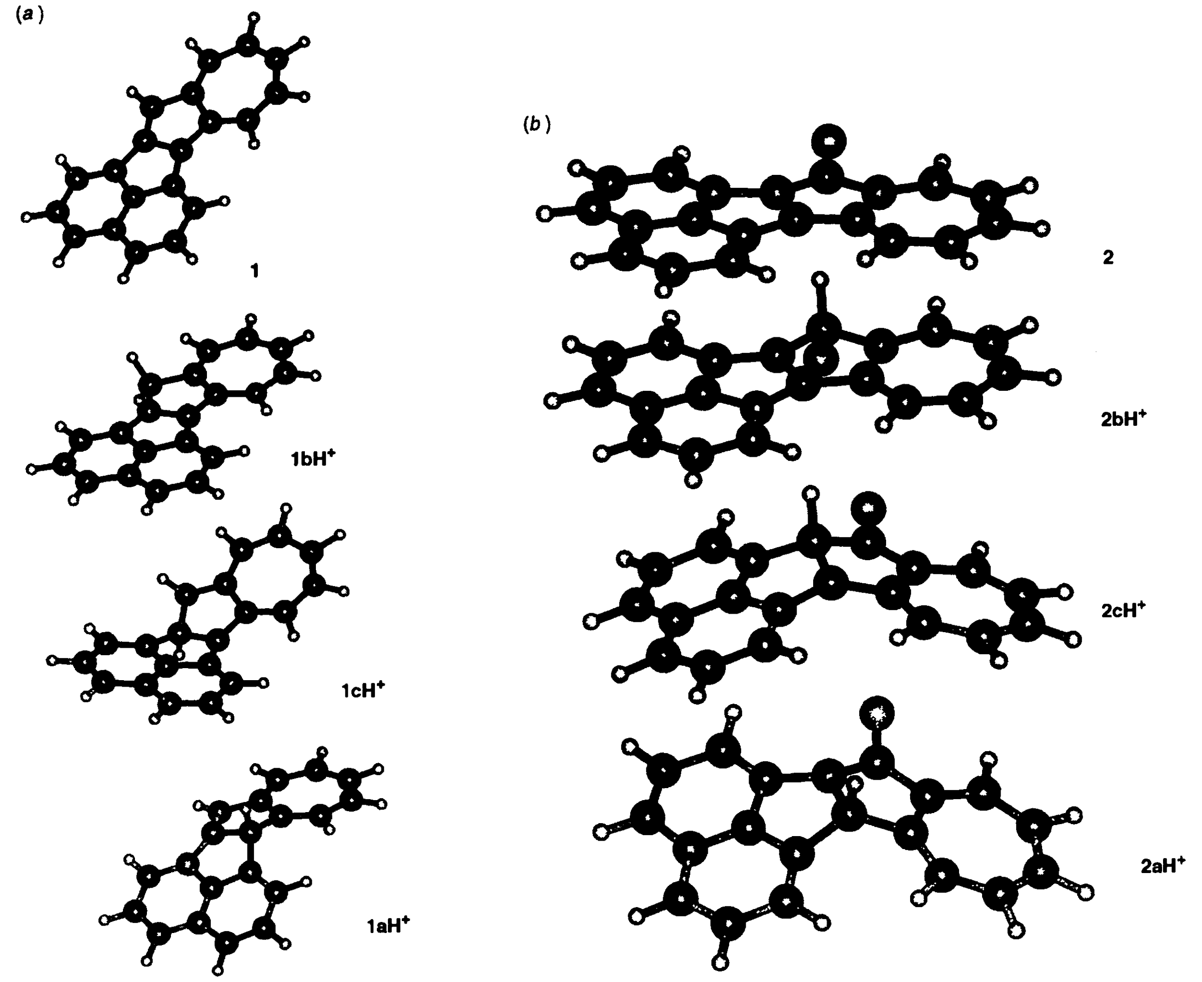


Fig. 6 AM1 predicted conformations of (*a*) **1** and (*b*) **2** and their carbocations

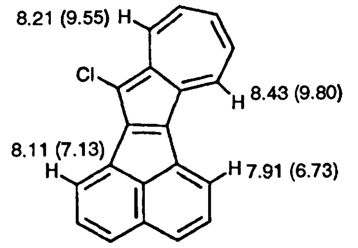


Fig. 7 Quenching product and its specific ^{1}H resonances

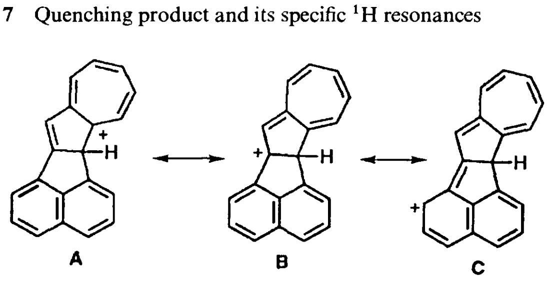


Fig. 8 Mesomeric forms of **1aH**$^+$

varied from 40:60 to 60:40 and this assisted partial NMR assignments, especially for the 8-H, 12-H, 1-H and 6-H resonances which were more distinct (Fig. 7). Based on a GCMS analysis the by-product was identified as the 7-chloro derivative [*m*/*z* 286 (M$^+$), appropriate M + 2 and a major ion at *m*/*z* 250 (M − HCl)]. The rather reactive C-7 position of **1** must undergo chlorination with SO_2ClF on exothermic quenching. When C-7 is substituted (as in **2**) there is no side-reaction.

On the nature of 1aH$^+$ and 2aH$^+$ cations

For both **1aH**$^+$ and **2aH**$^+$ the five protons in the seven-membered ring are the most deshielded and show larger vicinal coupling constants than those in the naphthalene moiety. The NMR assignments (Fig. 5), although incomplete, point to a strong azulenium ion character in these arenium ions (mesomeric form A; Fig. 8) with limited charge delocalization into the naphthalene moiety. The seven most deshielded carbon resonances for both ions are those of the tropylium moiety.

In order to comment further on the nature of the arenium ion derived from **1**, comparison was made with the parent acenaphthenium **3H**$^+$ and azulenium cations **4H**$^+$ as models. The ^{1}H and ^{13}C NMR data for **3H**$^+$ are available from the early work of Olah *et al.*[10] The data are included in Fig. 5.

As for **4H**$^+$, only its ^{1}H NMR data (100 MHz) in neat FSO_3H at −10 °C was available from the work of de Wit and Cerfontain.[11] We, therefore, re-examined the parent azulenium ion in $FSO_3H{\cdot}SO_2ClF$.

The blue colour of azulene immediately turns light brown on addition of the superacid at dry ice–acetone temperature. The 300 MHz ^{1}H NMR spectrum of the resulting cation shows the sp^3 (CH_2) at 3.51 ppm and the vinylic 2-H and 3-H protons as two distinct doublets at 6.84 and 7.18 ppm (coupling constant *ca.* 5.2 Hz). The tropylium cation protons give rise to a 2 H doublet at 8.24 ppm (8.7 Hz coupling) and a 3 H multiplet at 7.99 ppm. Our observed chemical shifts differ by *ca.* 1 ppm (more shielded) compared with the reported values;[11] this could in part originate from use of an external reference in the earlier work. In the ^{13}C NMR spectrum the sp^3 ($CH_2{}^+$) resonance is at 46.1 ppm and the vinylic carbons at 143.8 and 137.1 ppm. The H-bearing carbons of the tropylium moiety are between 156.8

and 143.8 ppm. The most deshielded ring junction carbon is at 169.9 ppm. There are minor amounts of a second ion present, tentatively assigned to a sulfonylation σ-complex[4,9,12] with its sp^3 (CH–SO$_2$H)$^+$ resonance at 72.2 ppm.

Examination of the AM1 and PM3 calculated Δq [q_c(ion) − q_c(neutral)] for the three different types of carbocations reveals that for **1aH**$^+$ and **2aH**$^+$, the tropylium ion character is more predominant over the naphthalenium character, whereas for **1bH**$^+$ and **2bH**$^+$ cations the opposite is observed. The energetically least favoured cations **1cH**$^+$ and **2cH**$^+$ appear to have the most acenaphthenium ion character.

Considering the observed NMR data for **1aH**$^+$ and **1bH**$^+$, taking into account the spectral data for **3H**$^+$ and **4H**$^+$ as models and bearing in mind the theoretical predictions of charge alternation mode (Δq), it can be concluded that **1aH**$^+$ and **2aH**$^+$ are best viewed as azulenium ions (mesomeric form A) with some naphthalenium ion character (mesomeric form C) and little or no acenaphthenium ion character (mesomeric form B).

Experimental

Synthesis of **1** and its electrophilic bromination (→**2**) have already been described.[1]

Azulene was a 99% purity sample purchased from Aldrich. FSO$_3$H (Linde) and SbF$_5$ (Fluorochem) were purified by distillation at atmospheric pressure under argon. SO$_2$ClF (lecture bottle from PCR Inc.) was used as received.

The ambient temperature NMR spectra and 2D NMR studies on the substrates **1** and **2** were performed on a 600 MHz Bruker instrument (at Tohoku University) and subsequently at 300 MHz with a GE-GN 300 MHz instrument (at KSU). The low temperature stable ion studies were all performed on a GE-GN 300 MHz NMR spectrometer.

The procedure for stable ion generation was similar to those already described.[4]

In quenching experiments the NMR tube containing the superacid solution was carefully poured into ice–hydrogen carbonate with efficient stirring. The organic phase was separated (CH$_2$Cl$_2$), dried (MgSO$_4$) and the solvent was removed under vacuum. The residue was dissolved in CDCl$_3$ for NMR studies.

The AM1 and PM3 calculations and energy minimizations were performed with the Hyperchem package (Hypercube Inc, 1994).

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