

Electrophilic and Oxidative Chemistry of 4-Methyl[6]helicene, [6]Helicene and Coronene; Persistent Ion Generation in Superacid Media, Gas Phase Mass Spectrometric Studies and AM1 Calculations

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4-Methyl[6]helicene **3** is protonated in FSO₃H–SO₂ at C-3 to give a persistent methylhexahelicenium cation; there is minor competing oxidation. The monoarenium ion of parent [6]helicene **2** was observed in the less oxidizing CF₃SO₃H (TfOH)–SO₂ClF. Competing oxidation is extensive and the arenium ion slowly disappears from the NMR spectrum. A monoprotonated coronene cation could not be observed. The coronene radical cation formed in attempted protonation was characterized by EPR.

The protonation, acetylation and trimethylsilylation of coronene and the [6]helicenes were studied in the gas phase by CI–MS and the decomposition of the resulting adducts were examined by tandem mass spectrometry. The oxidations of **1–3** were also probed by EI–MS and MS–MS experiments.

The energies of arenium ions of protonation of **2–3** were calculated by the AM1 method. The monocations observed under stable ion conditions are not the theoretically predicted lowest energy arenium ions. AM1 calculations were also performed on coronene radical cation, and its singlet and triplet dications. The previously observed singlet dication is predicted to be less stable than the triplet dication by 6.54 kcal mol⁻¹.†

As building blocks of the hierarchy helicenes, circulenes and kekulenes, the angularly fused chiral [6]helicene **1** and its planar analogue coronene **2** occupy an important position among larger fused polycyclic arenes.^{1–3}

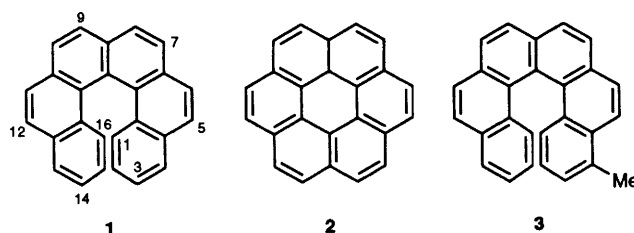
Recent interest in large helicenes, heterohelicenes and helicopodands stems from their potentiality in cation transport phenomenon and as chiral clefts in guest–host chemistry.^{1,2,4}

The classical stilbene photocyclization process, developed for the synthesis of [5]- and [6]-helicene and their derivatives,⁵ may be replaced by a more efficient Diels–Alder approach recently explored by Katz.⁶

In comparison to a wealth of information on structural–conformational aspects of parent [6]helicene and its substituted and benzannulated derivative,^{2,5–14} the electrophilic chemistry of [6]helicene and its substituted analogues is little explored.

As part of his extensive studies of [6]helicenes, Laarhoven examined the bromination, nitration and acetylation of **1**.¹⁴ The major products were those of monosubstitution at C-5 and disubstitution at C-5/C-12. In nitration and acetylation under mild conditions, the 8-substituted products were also isolated. It was found that bromine initially adds to **1**; HBr is subsequently eliminated either at higher temperature or on chromatography to give the 5-bromo- and 5,12-dibromo-hexahelienes. Bromination of [6]helicene with Br₂ (1 equiv.) in the presence of iodine gave 70% of 5-bromo- and 10% of 5,12-dibromo-hexahelienes.

Thus far, only crude semiempirical studies have been performed on [6]helicenes. The Mulliken overlap population μ_r , calculated by extended Hückel using the X-ray geometries, predict C-1 to be the most reactive. The simple Hückel, N_R , L_R calculations assign higher reactivity at C-5.^{14,5b} The positional reactivity order C-5 > C-7 > C-8 > C-1 > C-4 > C-6 > C-2 > C-3 for protiodetrition of [6]helicene has been established by Taylor and associates.¹⁵ In bromination and acetylation, attack at C-1 is not envisaged owing to steric inaccessibility.



As for the planar coronene **2**, its formation by loss of C₂H₄ from **1** in the gas phase in the EI mass spectrum of **1** has been studied by Dougherty, and rationalized as a thermal electrocyclic reaction.¹⁶ The electrophilic chemistry of **2** is little explored. Notable examples include halogenation, nitration and acylation.² Coronene oxidation to 2^{•+} in H₂SO₄ at room temp. has been reported,¹⁷ where the resulting radical cation has a degenerate ground state. Oxidation of **2** with SbCl₅ gave an unresolved EPR spectrum.^{18a} A trimer radical cation has been obtained by partial electrooxidation of **2** for which a resolved EPR spectrum was obtained at –100 °C.^{18b}

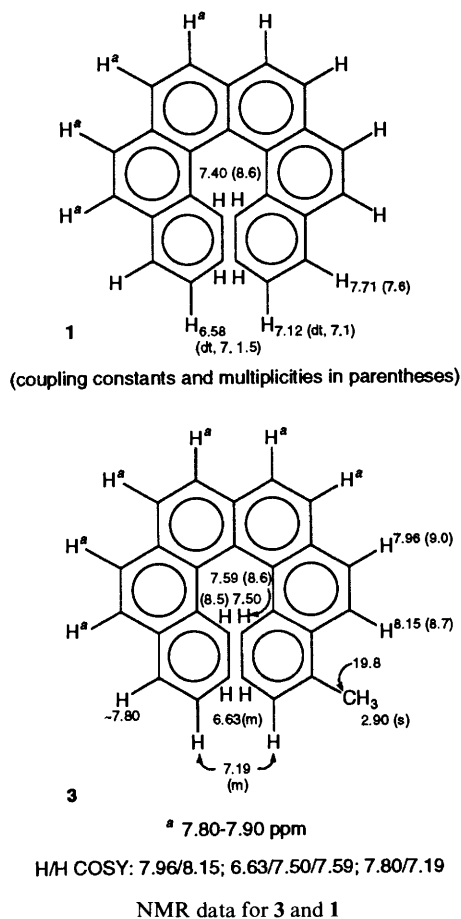
Recent EPR studies of 2^{•+} generated by oxidation with SbF₅–SO₂ClF showed it to be a triplet.¹⁹ *Ab initio* theory suggests that the dication is still planar.¹⁹

In continuation of our recent studies of protonation, sulfonylation and oxidation of fused polycyclic arenes^{20–25} and in relation to our recent gas phase electrophilic and oxidative reactions of janusene, fluorinated janusenes,²⁶ octamethylbiphenylene and dodecamethylbinaphthylene,²⁷ we have examined the protonation and oxidation of [6]helicenes **3** and **1**, and coronene **2** in superacid media. Parallel studies in the gas phase were conducted to probe the protonation, acetylation (MeCO⁺), and trimethylsilylation (Me₃Si⁺) of these compounds, where tandem mass spectrometry was utilized to examine the decomposition pathways of the resulting cations. Protonation and oxidation of **1–3** were also examined by the AM1 method in order to obtain the energies (and geometries) of the resulting cations.

† 1 kcal mol⁻¹ = 4.184 kJ mol⁻¹.

Results and Discussion

NMR of the [6]Helicenes and Coronene Substrates.—The ^1H NMR spectral data for parent **1**, and a large number of its mono-, dialkyl-substituted and benzannulated derivatives have been reported.^{11,5-7} Among the monomethyl derivatives, the anisotropic shielding order induced by the overlapping phenyl ring is 1-Me \gg 2-Me $>$ 3-Me $>$ 4-Me.^{11,6} For the ring protons, the shielding order H-2/H-15 $>$ H-3/H-14 $>$ H-1/H-16 $>$ H-4/H-13 has been established.^{11,6} The most deshielded protons are those of H-5 through H-8, and H-9 through H-12, located at its 'outer shell' and away from the overlapping phenyls. Our ^1H NMR data (300 MHz), backed by an H/H COSY analysis, fully supports the earlier assignments made for **1** and **3**. However, a noticeable solvent shift is observed in



CDCl_3 as compared to the previous data in CS_2 . The ^{13}C NMR spectral data for [6]helicene, and 5-deuterated [6]helicene had previously been analysed.^{5,28,29} Owing to the complexity and the narrow range that the carbon resonances occur in [6]helicenes, a full re-analysis was not attempted; the previous assignments were adopted. The symmetry element in **2** gives rise to just one proton resonance (δ 8.86) and three carbon resonances (δ 128.5, 126.0, 122.3).

The Superacid Chemistry of 4-Methyl[6]helicene 3, [5]Helicene 1 and Coronene 2; Protonation and Oxidation.—(a) **3** In superacids. Slow addition of a cold solution of $\text{FSO}_3\text{H-SO}_2$ to a yellow slurry of **3** in SO_2 at dry ice-acetone temperature gave a dark-blue solution. Careful analysis of its ^1H NMR spectrum [at -68°C ; Fig. 1(a)] clearly indicated that ring protonation had occurred at C-3, *ortho* to the methyl substituent to give a persistent 4-methyl[6]helicene monocation 3-H^+ .

The $\text{sp}^3(\text{CH}_2)$ protons are diastereotopic and give rise to two doublets at δ 5.31 and 4.85 with 30 Hz coupling, corresponding

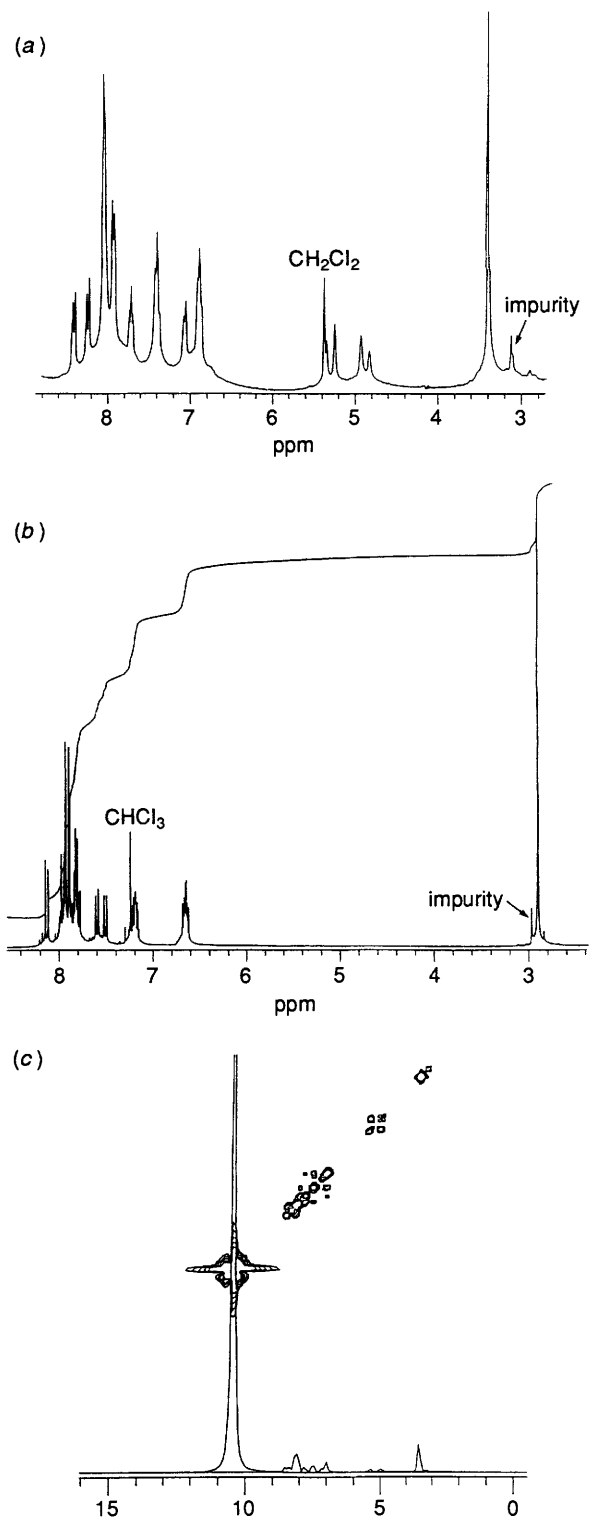


Fig. 1 (a) ^1H NMR spectrum of 3-H^+ ; (b) ^1H NMR spectrum of **3**; (c) H/H COSY analysis for 3-H^+

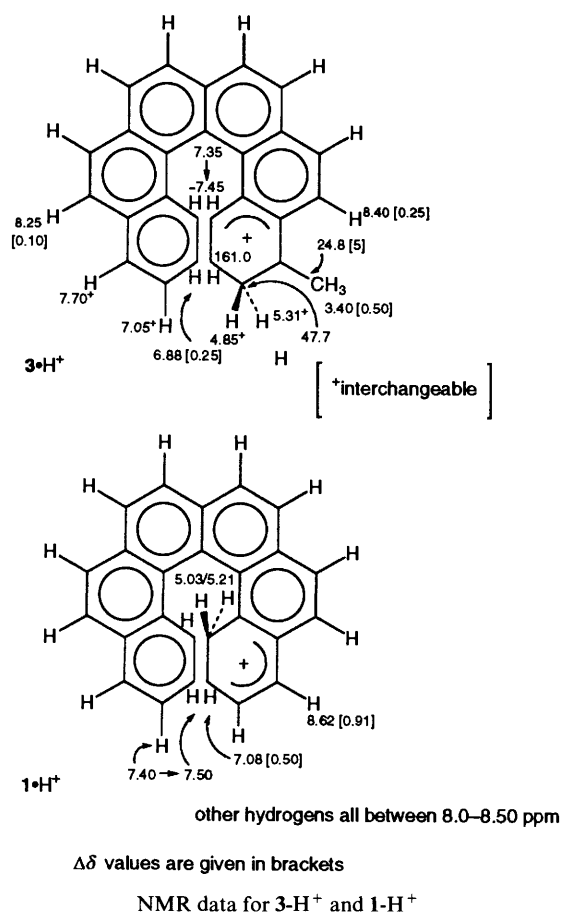
to a θ of ca. 102° on a Karplus plot.³⁰ The occurrence of a vicinal coupling between the non-equivalent $\text{sp}^3(\text{CH}_2)$ doublets was supported by a COSY experiment [Fig. 1(c)].

There is only one methyl absorption (singlet) present in the proton spectrum which is deshielded by 0.50 ppm relative to **1** [compare Figs. (a) and (b)], corroborating that C-3 is the site of attack.

The aromatic resonances occur between δ 6.80–8.40, their individual assignments are based on multiplicity, chemical shifts, relative integrals and COSY relationships. Thus the most shielded set of resonances appearing as overlapping doublets

(ca. δ 6.88; 2 H) are those of H-2/H-15. The latter are coupled to the doublet of doublet resonances appearing between δ 7.35–7.45 assigned to H-1/H-16. The expected charge-induced deshielding of H-2 (*ortho*) is apparently compensated for by the anisotropic shielding induced by the overlapping phenyl ring, giving rise to only modest overall deshielding in this region. The most downfield aromatic resonances are those of H-5/H-12, deshielded by 0.25 and 0.1 ppm, respectively relative to 3.

The assignments of the distorted doublet absorption at δ 7.07 (1 H) and the pseudo-triplet at δ 7.70 (showing a mutual H/H COSY) to H-14 and H-13 should be considered tentative, since although the $\Delta\delta$ s are reasonable, an 'interchanged assignment' appears to account more fully for their multiplicities. The remaining 'outer shell' hydrogens give rise to a broad singlet at δ 8.04 (4 H) and a broad doublet at δ 7.92. These resonances show no COSY cross peaks.



In agreement with the conclusions drawn based on ^1H NMR, the ^{13}C NMR spectrum exhibits a single deshielded methyl resonance at δ 24.8 and the $\text{sp}^3(\text{CH}_2)$ resonance at δ 47.7. The most deshielded carbon resonance is at δ 198 assigned to methyl-bearing C-4. It compares well with the 206.5 ppm chemical shift of the methyl-bearing ring carbon (*ortho*) in 2-methylnaphthalenium ion.³¹ The second most deshielded carbon absorption at δ 161 is attributed to C-2. As for the remaining carbon resonances, 14 signals are observed between δ 123–143.

In search of radical cations, the same ion solution was subsequently examined by EPR. A broad featureless signal ($g = 2.0022$) was detected, the appearance of which was not improved by subjecting the sample to a repeated freeze–thaw cycle. Therefore, a small concentration of the radical cation coexists with the [6]helicenium cation in this medium, without

causing noticeable line-broadening in the NMR. The coexistence of the arenium ions and radical cations of PAHs in superacid media was previously demonstrated by Davies,³² and by us with crowded alkylpyrenes.²³

Exothermic quenching of the superacid solution returned the structurally intact **3** (ca. 90% pure by NMR), and no coronene formation was seen.

In an attempt to effect the diprotonation of **3**, its reaction with $\text{FSO}_3\text{H}\cdot\text{SbF}_5$ (1:1) 'magic acid'^R– SO_2ClF was investigated: careful addition of a cold solution of magic acid^R– SO_2ClF to a cold slurry of **3** in SO_2ClF at dry ice–acetone temperature gave a dark-blue solution, whose ^1H NMR spectrum exhibited very broad aromatic and methyl resonances, indicative of oxidation to the radical cation. Indeed, an intense, broad EPR signal was observed having similar features as those seen in the $\text{FSO}_3\text{H}\text{--}\text{SO}_2$ solvent.

It is clear that with the SbF_5 -containing superacids, radical cation formation is much more extensive. The observed line broadening prohibits the analysis of the σ -complex formed.

(b) *1 In superacids.* Similar slow addition of a solution of $\text{FSO}_3\text{H}\text{--}\text{SO}_2$ to a slurry of **1** at dry ice–acetone temperature gave a dark-blue solution whose ^1H NMR spectrum exhibited very broad, deshielded, aromatic resonances, indicative of extensive oxidation.

In an effort to reduce the ease of oxidation, the protonation was carried out with $\text{CF}_3\text{SO}_3\text{H}$ (TfOH)– SO_2ClF . The ^1H NMR spectrum of the resulting deep-blue solution was immediately examined (at -55°C), showing monoprotection to give 1-H^+ . Within minutes at -55°C , oxidation sets in and the spectrum slowly disappears into the base line. Radical cation formation was corroborated by an EPR measurement showing an intense, broad resonance ($g = 2.002$, and $\Delta H_{\text{pp}} = 7.7$ gauss). To effect further oxidation to the dication, following the reaction of **1** with $\text{FSO}_3\text{H}\text{--}\text{SO}_2$, NO^+BF_4^- was added to the sample; the colour changed from deep-blue to black. In agreement with conversion of the RC to the dication, the EPR signal became less intense, but the ^1H NMR spectrum was still broad, more in accord with partial oxidation to the dication and the existence of a dication–radical cation equilibrium.

Returning to the analysis of the ^1H NMR spectrum of 1-H^+ (recorded at -55°C), it is most compatible with monoprotection at C-1. The diastereotopic $\text{sp}^3(\text{CH}_2)$ resonances appear as two doublets at δ 5.03 and 5.21. The most deshielded aromatic resonance in the spectrum is a doublet of doublet at δ 8.62 (1 H) assigned to H-4 (*para*). The most upfield aromatic resonance δ 7.08 (triplet of triplet appearance) is ascribed to H-2 (*ortho*) deshielded by 0.5 ppm from the precursor. The H-14/H-15 are between δ 7.40–7.50 and the remaining hydrogens all resonate between δ 8.0 and 8.50. The NMR spectrum is incompatible with protonation at C-5 or C-8 which are the observed sites of bromination of [6]helicene.

Quenching of the ion solution returned the intact **1** with ca. 87% purity (^1H NMR data); no coronene was formed on exothermic quenching.

(c) *3 In superacids.* Low temperature reaction of **3** with cold $\text{FSO}_3\text{H}\text{--}\text{SO}_2$ gave a deep-blue solution whose ^1H NMR spectrum indicated intervention by the radical cation exhibiting very broad aromatic resonances between δ 8.20–6.80.

The EPR spectrum of the superacid solution was subsequently examined. The coronene radical cation $3^{\bullet+}$ gave a well-resolved EPR signal at 203 K (Fig. 2) with $g = 2.0022$, and $a_{\text{H}} = 0.7 \pm 0.2$ gauss. Out of the 13 theoretically expected lines, 10 were clearly discernible. Increasing temperature (> 230 K) led to loss of hyperfine structure, some of the fine structure was recovered on recooling.

Thus facile oxidation of **3** and the resulting line-broadening in the NMR spectra prevents direct observation of its arenium ion.

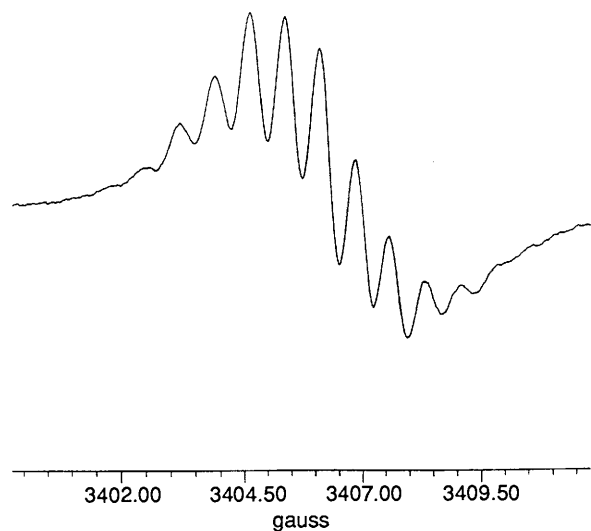


Fig. 2 EPR spectrum of coronene radical cation

Mass Spectral Studies.—In an effort to extend the electrophilic and oxidative chemistry of **1–3**, and to obtain insight into the decomposition modes of the resulting cations, their protonation, acetylation and trimethylsilylation were studied in the gas phase. For comparison, their oxidations were also probed. We began our studies with **2** for which solution NMR data on the corononium cation could not be obtained. The gas phase chemistry of **3** and **1** were subsequently examined.

Electrophilic and Oxidative Chemistry of 2.—The isobutane CI-MS of **2** shows the 2-H^+ ion in abundance (m/z 301); a protonation dication was not detected. Attempted collisional decomposition (CID) of m/z 301 ion shows it to be highly stable (no appreciable decomposition products).

Coronene is easily acetylated with MeCO^+ in the gas phase (acetone-CI)^{26,33–36} to give 2-COMe^+ ion (m/z 343). The major products of collisional decomposition of the acylated adduct are MeCO^+ (base peak) and 2-H^+ [Fig. 3(a)]. Preference for charge retention at the acetyl moiety is thus noted. Formation of 2-H^+ by decomposition of m/z 343 ion may be understood *via* homolysis of the acetylation complex and H^\bullet abstraction from acetyl radical (loss of ketene). Similar reactions have been observed previously with octamethylbiphenylene and dodecamethylbinaphthylene.²⁶ Loss of methyl from 2-COMe^+ ($\longrightarrow 2\text{-CO}^+$) upon CID is also seen as a minor pathway.

Reaction of Me_3Si^+ with **2** (TMS-CI)^{26,35,36} gives an abundant silylation adduct (m/z 373), decomposition of which shows exclusive formation of Me_3Si^+ ion (m/z 73), with no m/z 300 ion being seen. The EI mass spectrum of **2** shows an abundance of the radical cation (m/z 300). The oxidation dication 2^{+2} (with its $M + 1$ at m/z 150.5) is also formed. The relative intensities of m/z 150 : m/z 150.5 suggest that m/z 150 is a mixture (3^{+2} and a singly charged fragment ion). Three other dications (m/z 149, 148, 147) are also observed.

The coronene radical cation is rather resistant to collisional decomposition; small fragment ions owing to loss of CH fragments were obtained (m/z 287 and 274). Decomposition of 2^{+2} (m/z 150) occurs primarily by sequential acetylene loss ($\longrightarrow m/z$ 137, 124) and loss of CH_2 ($\longrightarrow m/z$ 143).

Gas Phase Electrophilic and Oxidative Chemistry of 3 and 1.—Gas phase protonation of 4-methyl[6]helicene **3** gives the protonated cation 3-H^+ (m/z 343). Loss of methyl ($\longrightarrow m/z$ 328) and ethylene ($\longrightarrow m/z$ 315) occur upon decomposition of protonated **3**.

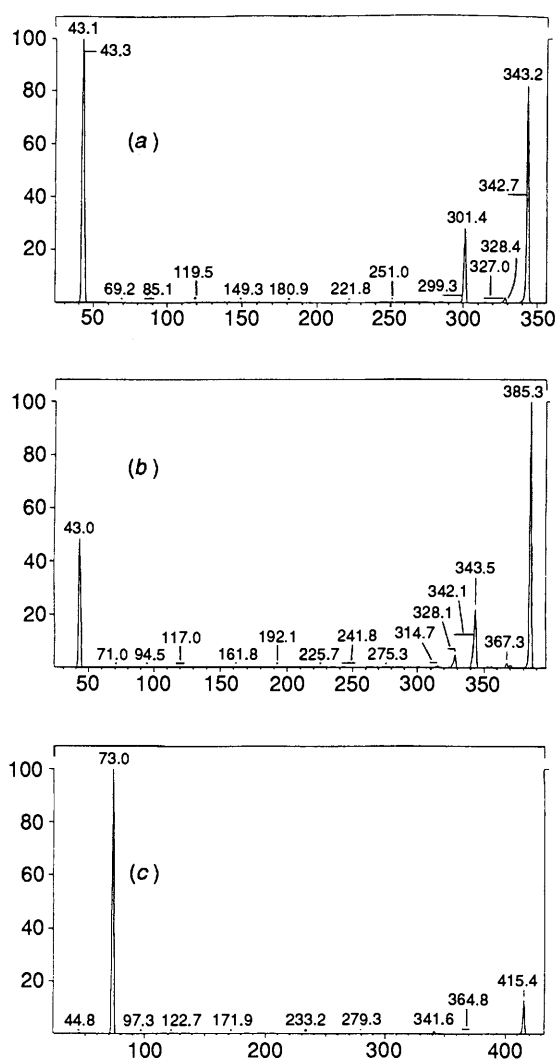


Fig. 3 (a) Collisional decomposition of 2-COMe^+ ion (m/z 343); (b) collisional decomposition of 3-COMe^+ ion (m/z 385); (c) collisional decomposition of 3-SiMe_3^+ ion (m/z 415)

Reaction of **3** with MeCO^+ gives the acetylation adduct 3-COMe^+ (m/z 385) and 3-H^+ . Collisional decomposition of the former cation [Fig. 3(b)] gives MeCO^+ and 3-H^+ (in ca. 2:1 ratio), again indicating a preference for charge retention at the acetyl fragment. Loss of methyl from 3-H^+ ($\longrightarrow m/z$ 328) is a minor pathway.

Similar reaction of **3** with Me_3Si^+ gave the 3-SiMe_3^+ ion in abundance (m/z 415; base peak). The silylated adduct decomposes on CID [Fig. 3(c)], forming m/z 73 (Me_3Si^+) and a trace of m/z 341 (corresponding to TMSH loss), thus exhibiting strong preference for charge retention at the silyl moiety.

Oxidation of **3** produces 3^{+2} in abundance (m/z 342), in addition to fragment ions at m/z 300 (2^{+2}), m/z 327 (Me loss from 3^{+2}), and m/z 314 (methylated coronene). In addition, the dication 3^{+2} (m/z 171) and the respective doubly-charged ions corresponding to further oxidation of the above mentioned singly-charged fragment ions, were also obtained [e.g. m/z 150 (coronene dication), m/z 149, m/z 157 (methyl-coronene dication), m/z 149, m/z 163.5].

Gas phase protonation of **1** (CI-MS) is extremely facile, leading to the m/z 329 ion as the only observable species. No diprotonation could be achieved under isobutane CI conditions. Collisional decomposition of 1-H^+ gives 2-H^+ (m/z 301), 2^{+2} and a fragment ion at m/z 314 (loss of methyl).

The [6]helicene **1** similarly reacts with MeCO^+ to give an acetylation adduct 1-COMe^+ (m/z 371) whose collisional

decomposition gives MeCO^+ and 1-H^+ in comparable amounts.

The 1^+ ion is abundantly produced in the EI mass spectrum (m/z 328). The most intense fragment ion produced from 1^{++} is coronene ion 2^{++} (m/z 300). The intact dication 1^{++} (m/z 164), and several other doubly charged [6]helicenes (at m/z 161, 162, 163, 165) were also detectable.

Collisional decomposition of m/z 328 ion (1^+) shows the loss of methyl (m/z 313) and ethylene ($\rightarrow 2^+$). The dication 1^{++} decomposes by sequential loss of CH_2S ($\rightarrow m/z$ 156, 150 and 143). Some coronene radical cations are also produced (m/z 300), presumably by concomitant reduction of 2^{++} (m/z 150).

AM1 Calculations.—The energies of the arenium ions of protonation of **2** and **3** were calculated by the AM1 method. The reactivity order [energies (kcal mol^{-1}) in parentheses] are shown below: For **2**: C-5 (163.1) > C-7 (163.5) > C-8 (163.6) > C-4 (165.6) > C-6 (167.1) > C-1 (167.6) > C-2 (167.9) > C-3 (178.7). For **3**: C-5 (283.6) > C-8 (284.1) > C-3 (286.3) > C-6 (287.0) > C-4 (290.5) (*exo*); 290.6 (*endo*) > C-1 (291.8) > C-7 (304.8) > C-2 (310.5).

For parent **2**, the arenium ion energies for attack at C-5, C-7 and C-8 are very close, as are those of C-6, C-1 and C-2. Attack at C-3 or C-4 is clearly unfavourable.

The predicted reactivity order closely parallels the positional reactivity order in protidetritiation¹⁵ except for the position of C-1 in the sequence.

The hexahelicenium cation observed under persistent ion conditions, is 4.5 kcal mol^{-1} higher in energy than the least energetic hexahelicenium cation produced by C-5 protonation.

For **3** a larger difference in the arenium ion energies are found. Attack at C-5 is most favoured and protonation at C-2, C-7 and C-1 are clearly unfavourable. AM1 calculations predict that the experimentally observed methylhexahelicenium cation is 2.7 kcal mol^{-1} less stable than the lowest energy arenium ion resulting from C-5 protonation.

Since diprotonation could not be effected in higher acidity superacid media owing to facile oxidation, it was of interest to predict the site of second protonation for the hexahelicenium monocations observed (Fig. 4). With C-3 protonated **3** [Fig. 4(a)], protonation at the other phenanthrene unit is definitely preferred, with C-11 calculated to be the favoured site of attack. For C-1 protonated **2** [Fig. 4(b)], a second protonation at C-11 (and C-13) are most favoured.

We also probed the charge distribution pattern in the monoarenium ions of attack at C-1, C-5 and C-8 in the parent hexahelicene [Figs. 5(a), 5(b), 5(c)] and in coronenium ion [Fig. 5(d)]. In all cases, substantial positive charge is sustained at the *para* position to the site of attack; the *ortho* carbons sustain little or no positive charge.

For the C-1 protonated **1** [Fig. 5(a)], the *ortho* carbon at the ring junction is clearly more positive. For the C-5 protonated cation [Fig. 5(b)], only one of the *ortho* carbons is slightly positive; the *para* position sustains most of the positive charge. This trend is also true for the arenium ion of attack at C-8 [Fig. 5(c)].

Unlike for pyrenium ions,^{20,21,24} charge delocalization/alternation at the periphery is not extensive in hexahelicenium cations and seems to be limited to the ring undergoing attack, extending only two carbons beyond the ring carbons *para* and *ortho* to the site of attack. Charge alternation at the planar coronene periphery in 3-H^+ is slightly more extended [Fig. 5(b)].

We also calculated the radical cation and the singlet and triple dications of coronene. The heat of formation of the radical cation is computed as 277.24 kcal mol^{-1} (coronene itself is 96.24 kcal mol^{-1}), those of the singlet and triplet dications are 535.92 and 542.46 kcal mol^{-1} respectively. Our AM1 calculations

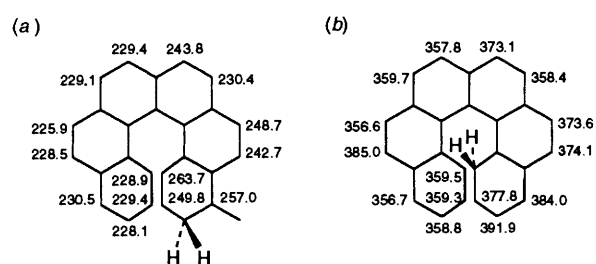


Fig. 4 Calculated energies (AM1) of arenium ions of diprotonation of 3-H^+ and 1-H^+

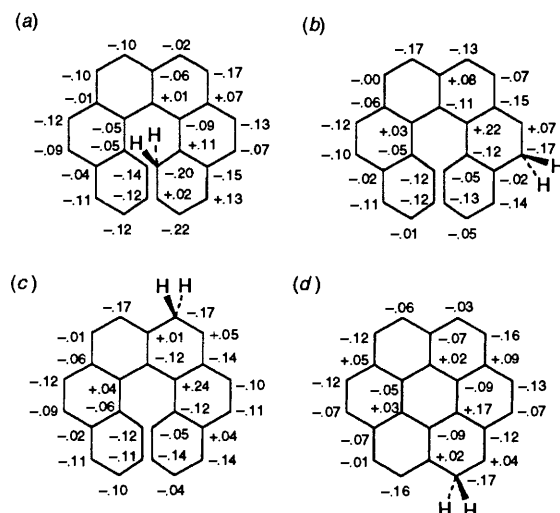


Fig. 5 Calculated charge distribution (AM1) in hexahelicenium of protonation at C-1, C-5 and C-8 and in the coronene monocation

suggest that the singlet dication is more stable than the experimentally observed triplet dication¹⁹ by 6.54 kcal mol^{-1} . In the singlet dication, 32% of the positive charge is taken up by the carbons and the rest by hydrogens. The charges in the triplet dication are close to zero. In the radical cation, only two of the carbons (at ring junctions) are positively charged and together bear 16% of the positive charge.

A Comparative Discussion of Electrophilic and Oxidative Processes Involving [6]Helicenes and Coronene.—Protonation of **3** under persistent ion conditions occurs at C-3, *ortho* to the methyl substituent. The arenium ion is sufficiently stable to be studied by NMR spectroscopy at low temperature. Competing oxidation to the paramagnetic radical cation is not extensive enough to affect the NMR line widths. AM1 calculations predict that the observed 3-H^+ ion is 2.7 kcal mol^{-1} less stable than the arenium ion of attack at C-5, which is calculated to be the most stable.

Low temperature protonation of **1** in mild superacids has been shown to take place at C-1. Oxidation is more rapid (as compared to **3**) and the arenium ion signals broaden in the NMR and disappear into the base line. Radical-cation formation is corroborated by EPR measurements. Attack at C-5 is again predicted to be most favoured, the arenium ion observed (1-H^+) is calculated to be 4.5 kcal mol^{-1} less stable than arenium ion of attack at C-5.

With coronene, oxidation is too rapid for an arenium ion to be observed by NMR spectroscopy. A complete EPR analysis of the formed coronene radical cation has been achieved.

Mass spectral studies demonstrate that facile protonation, acetylation and trimethylsilylation of [6]helicenes and coronene can be effected. Whereas the exact nature of the resulting adducts cannot be determined by this method, CID experiments exhibit strong preference for charge retention at the

electrophilic moiety. In line with solution observations, oxidations of 1–3 are quite facile in the gas phase; dications are also formed. Coronene and methylcoronene cations are formed by collisional decomposition of both the radical cations and the arenium ions of 1 and 2. In contrast, no indication for methylcoronene or coronene formation is found in quenching of the superacid solutions. AM1 calculations predict that the previously observed triplet dication of coronene is 6.54 kcal mol⁻¹ less stable than the singlet dication.

Experimental

Materials.—The [6]helicenes 3 and 1 were purchased from Aldrich. Their identities were established by NMR (¹H, ¹³C and H/H COSY) studies. Since their purities were estimated in the 95–97% range, they were utilized as received. Coronene 2 was also obtained from Aldrich and used without further purification. FSO₃H, CF₃SO₃H (TfOH) and SbF₅ (all Aldrich) were freshly distilled in an all-glass distillation unit under a dry nitrogen atmosphere prior to use. SO₂ClF (Aldrich) and SO₂ (anhydrous; Linde) were used without further purification. FSO₃H·SbF₅ (1:1) 'Magic acid'^R was freshly prepared as previously described.³⁷

The General Procedure for Stable Ion Generation.—Typically, a cold slurry of [6]helicene or coronene in SO₂ (or SO₂ClF) was prepared in a 10 mm NMR tube by adding ca. 0.5 cm³ of solvent to 25 mg of the aromatic substrate under nitrogen at dry ice–acetone temperature. A clear solution of the superacid (ca. 1 cm³) in SO₂ or SO₂ClF (ca. 1 cm³) was prepared in a second 10 mm NMR tube under nitrogen (vortex mixing). The superacid system was carefully poured into the cold aromatic with efficient vortex mixing. The protonated and oxidized [6]helicenes and coronene were all deep blue in colour. A cold aliquot was transferred into a pre-cooled 5 mm NMR tube under dry nitrogen either directly or *via* a cold pipette (SO₂ or SO₂ClF). The EPR samples were similarly prepared by transferring the cold ion solution *via* cold pipettes. CD₂Cl₂ served as reference and lock for the superacid samples.

The EPR samples were repeatedly flushed with a fast flow of dry nitrogen (repeated vortex mixing at low temperature). In some cases, the EPR samples were subjected to several freeze–thaw cycles and sealed.

NMR spectra were recorded on a GE GN-300 wide-bore instrument (¹H 300 MHz, ¹³C: 75.57 MHz). The probe was cooled while shimming on an [²H₆]acetone sample. The cold ion solution was quickly inserted and the sample spun for 3–5 min prior to establishing the lock and data collection.

X-Band EPR spectra were obtained using an IBM 200D-SRC spectrometer with a ER 4111 temperature controller (1 K precision).

Mass spectra were acquired on a Finnigan-Matt 95Q hybrid mass spectrometer. Collisional activation was carried out in the 'collision octapole' with translational energy of 50 eV and with air as the collision gas. The pressure in the collision cell was adjusted to ca. 0.2 Pa, which corresponds to a pressure in the quadrupole analyser region of 8 × 10⁻⁴ Pa. The acetone–CI and TMS–CI conditions were similar to our previously reported conditions adapted from literature procedures.^{33–36} The aromatics were introduced as solids.

The AM1 calculations were carried out with the MOPAC 6.0 version compiled for 80486 PCs (supplied by Serena Software).

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