Oxidative and Electrophilic Chemistry (Protonation, Acetylation, Trimethylsilylation) of Octamethylbiphenylene and Dodecamethylbinaphthylene; a Mass Spectral and Superacid Solution Study

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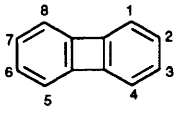
A mass spectral study of the cations formed by oxidation, protonation, acetylation ($MeCO^+$), trimethylsilylation (Me_3Si^+), and trifluoroacetylation–trifluoromethylation (CF_3CO^+–CF_3^+) of octamethylbiphenylene **4** (fully methylated [2]phenylene) and dodecamethylbinaphthylene **5** (fully methylated dibenzo[*b,h*]biphenylene) is reported, and the decomposition pathways of the resulting ions are probed by tandem mass spectrometry.

Collisional decompositions of the acylation and trimethylsilylation monocations are selective towards charge retention at the aromatic moiety. A bis-silylated monocation was formed *via* **5**. Doubly charged ions were only observed in oxidation reactions (EI/MS).

The greater solution stability of the arenium ion of ipso protonation of **5** as compared to **4** is borne out by its direct observation in FSO_3H–SO_2ClF at low temperature.

Synthesis and spectroscopic studies of [*n*]phenylenes in which biphenylene units are linerarly or angularly fused (as in **2** and **3**) have become topics of intense recent studies. Vollhardt and coworkers [1–4] have shown that the linear [*n*]phenylenes exhibit a diminishing HOMO–LUMO gap, increased paratropism of the inside phenyl hydrogens (^1H NMR) and nonadherence to the Hückel rule. The angular counterparts, on the other hand, exhibit a lesser decrease in the HOMO–LUMO gap, and deshielding of the internal phenyl hydrogens.



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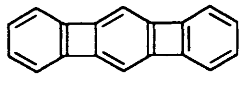

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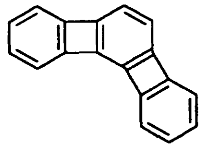

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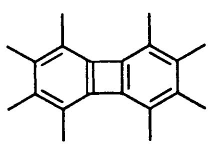

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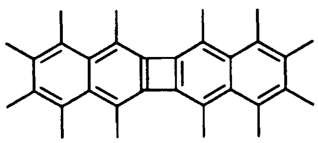

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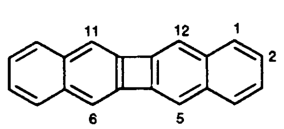

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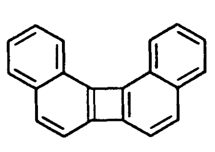

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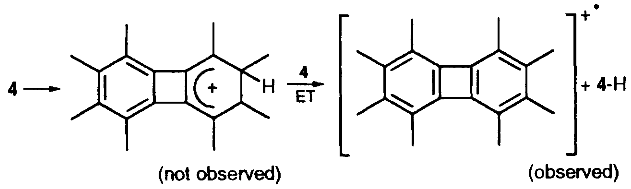
The aromaticity of the parent [2]phenylene **1** is well established based on MO calculations, spectroscopy and chemistry.[5,6]

Introduction of electron releasing substituents, for instance methyl groups, into linear [*n*]phenylenes represents an alternative approach to that of linear fusion of [*n*]phenylenes for lowering their HOMO–LUMO gap. Thus the oxidation potential of **4** is 11.8 kcal mol^{-1}* lower than [2]phenylene itself.[7]

Facile oxidation of **4** prevents direct observation of biphenylenium ions of protonation under stable ion conditions even in milder superacids *viz.* CF_3SO_3H and FSO_3H and $4^{+\bullet}$ is observed instead.[8]



Protonation of **4**

The spin density in $4^{+\bullet}$ is primarily located at the β-positions (C-2, 3, 6, 7). Thus the β-methyl resonance disappears in the ^1H NMR spectrum but the α-methyl signal remains.[7,8] This is consistent with theoretical predictions that free radical reactions of biphenylene, similar to its electrophilic reactions, should occur at the 2-position.[6]

The persistent radical cation of **4** can also be generated under much milder conditions with TFA–$CDCl_3$,[7] TFA–Tl$(TFA)_3$,[9] or TFA–diffuse daylight.[10] The EPR spectrum of $4^{+\bullet}$ has been studied in detail.[9,10]

In SbF_5–SO_2ClF or in FSO_3H·SbF_5 (1 : 1)–SO_2 two-electron oxidation of **4** occurs to give persistent 1^{2+}.[5,8] The less substituted dimethyl- and tetramethyl-biphenylene are also oxidized with SbF_5 to give stable dications.[11]

In [*n*]phenylenes, antiaromatic cyclobutadienes are fused to benzenes. With parent [2]phenylene this leads to a weakly coupled benzenoid system.[5,6] Theoretical studies and chemistry have suggested that fusing cyclobutadienes to naphthalene units in a dibenzo[*b,h*]biphenylene arrangement (as in **6**) increases the stability of the system relative to [2]phenylene, but angular annulation of phenyl groups to [*n*]phenylenes (as in **7**) reduces their stability.

Synthetically, Hart's aryne coupling method provides convenient access to both **4** and its higher homologue **5** *via* their dibromo derivatives.[12]

The present study demonstrates that arenium ions of ipso attack on **4** and **5** can be efficiently generated in the gas phase.

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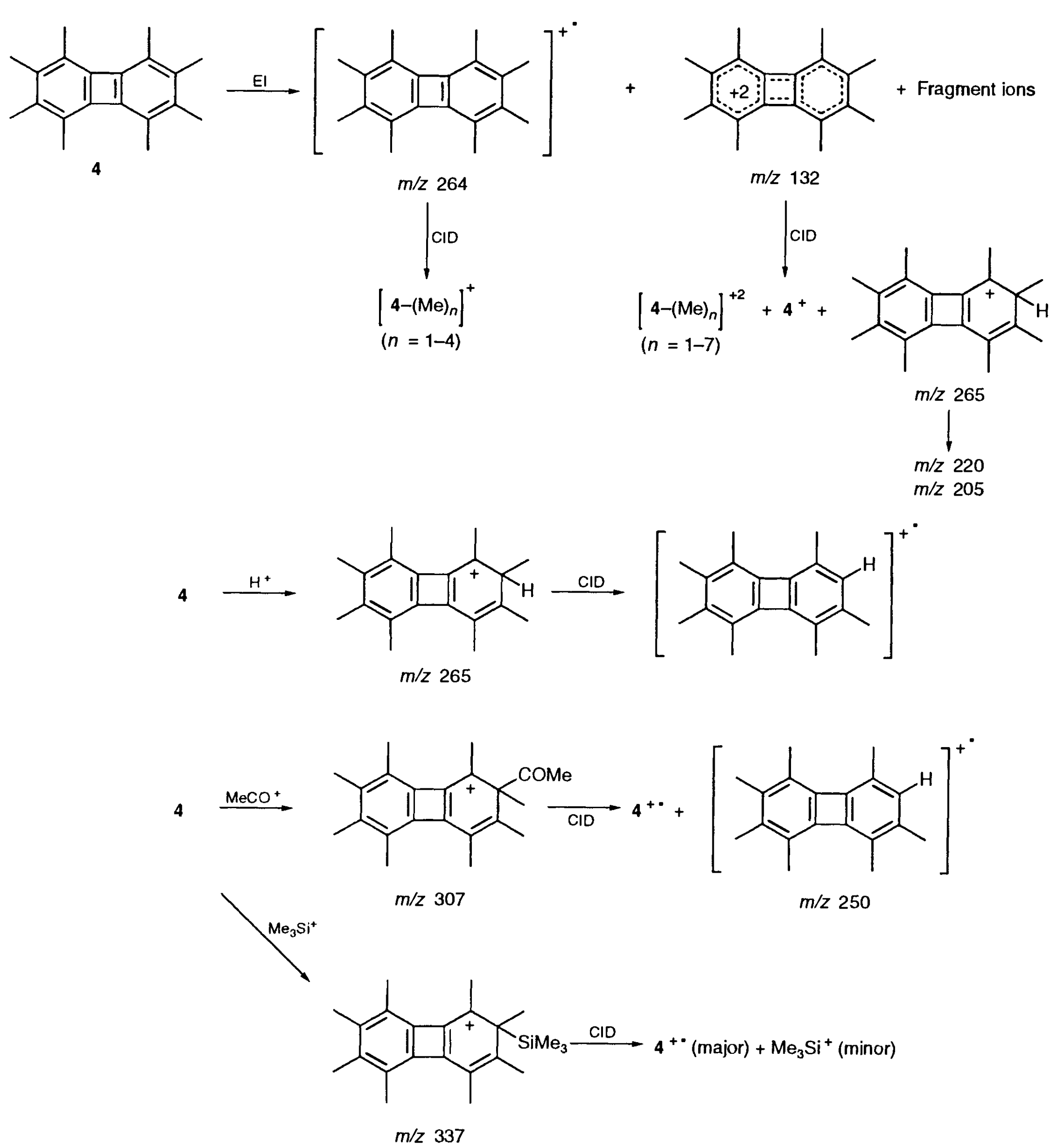
* 1 Cal = 4.18 J.



Scheme 1 Octamethylbiphenylene cations and their decomposition pathways in the gas phase

Comparison of the oxidative and electrophilic chemistry of **4** and **5** provides a means to address the possible role of phenyl annulation on the stability of [*n*]phenylene cations. We focus on oxidation, protonation, acylation ($MeCO^+$), trimethylsilylation (Me_3Si^+), as well as trifluoroacylation–trifluoromethylation (CF_3CO^+–$CF_3{}^+$) of **4** and **5**, and use tandem mass spectrometry to probe the decomposition pathways of the resulting cations.

To further explore the role of linear phenyl annulation on oxidative *versus* electrophilic chemistry in solution, low temperature protonation of **2** was carried out in FSO_3H–SO_2ClF for comparison with **1**.

Results and Discussion

MS Study of **4**.—The 70 eV EI mass spectrum of **4** shows the radical cation $\mathbf{4}^{+\bullet}$ (*m*/*z* 264) as the base peak and minor fragment ions due to consecutive loss of methyls (*m*/*z* 249, 234 and 219). A minor but distinct dication is also formed (*m*/*z* 132 with its M + 1 at *m*/*z* 132.5). The relative intensity ratios of *m*/*z* 132/132.5 indicated that the dication was a major contributor to *m*/*z* 132 ion, with minor contribution from a singly charged fragment ion, most likely tetramethylbenzyne cation formed by cycloreversion (Scheme 1).

The *m*/*z* 132/132.5 relative ion intensity ratios were examined as a function of the ionization energy (90–50 eV); in all cases the singly charged fragment ion was a contributor to *m*/*z* 132 and a 'pure dication' was not obtained.

Collisional decomposition of $\mathbf{4}^{+\bullet}$ (CID) leads to loss of methyls, exhibiting several fragment ions at *m*/*z* 249, 234, 219 and 204.

Consecutive loss of methyls from the dication is the major decomposition pathway for $\mathbf{4}^{2+}$ (*m*/*z* 132), with hydrogen atom abstraction and reduction as minor competing pathways to give $\mathbf{4}^{+\bullet}$ and $(\mathbf{4} + H)^+$. The latter ions demethylate to give singly-charged fragment ions in low abundance.

Gas phase mono-protonation of **4** (isobutane/CI–MS) is quite facile forming *m*/*z* 265 in 85% abundance. A diprotonated dication was not observed. Collisional decomposition of $(\mathbf{4} + H)^+$ gave two major fragment ions by methyl loss (*m*/*z* 250 and 235).

The biphenylene **4** also reacts with $MeCO^+$ (acetone/CI)[13–16] to give the acetylated adduct $(\mathbf{4} + COMe)^+$ (*m*/*z* 307, 22%), and $(\mathbf{4} + H)^+$ (as the base peak). No doubly acylated dication could be detected.

Collisional decomposition of the acetylated adduct (*m*/*z* 307) produced $\mathbf{4}^{+\bullet}$ (*m*/*z* 264) and $[\mathbf{4} - (Me) + H]^+$ (*m*/*z* 250)

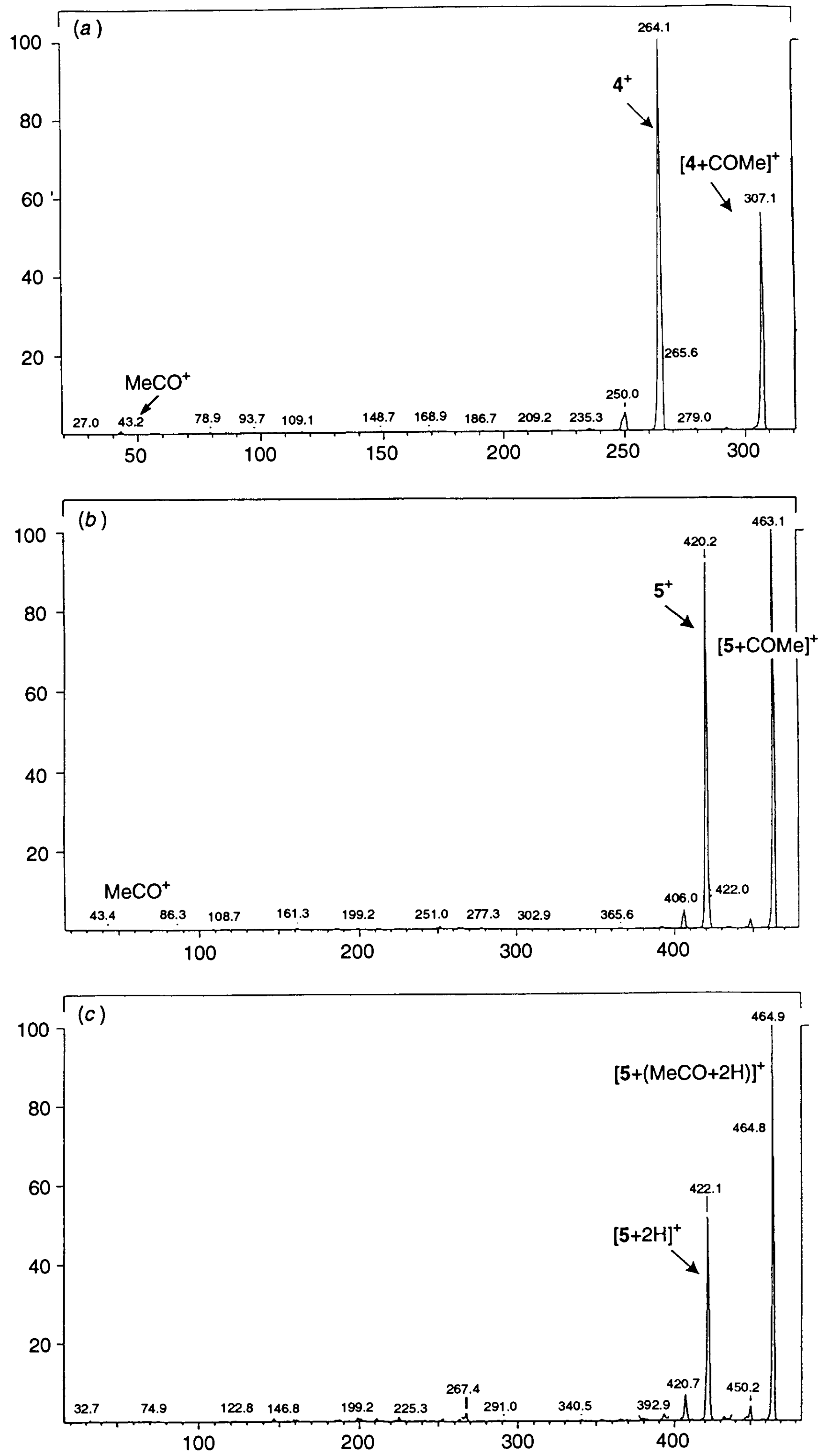


Fig. 1 (*a*) And (*b*), product ion scans of the mono-acylation cations of **4** and **5** (*m*/*z* 307 and *m*/*z* 463); (*c*) product ion scan of *m*/*z* 465 ion

as major products, and a tiny $MeCO^+$ cation *m*/*z* 43 [Fig. 1(*a*)].

It is interesting to note that collisional decomposition of $(\mathbf{4} + COMe)^+$ is quite different from that of (janusene + COMe)$^+$ which we recently studied,[17] for which the charge resided predominantly on the acyl fragment.

Regarding the origin of the minor *m*/*z* 250 ion, it is conceivable that $\mathbf{4}^{+\bullet}$ formed by loss of acetyl radical will abstract $H^\bullet$ from $MeCO^\bullet$ to give $(\mathbf{4} + H)^+$ and ketene. The ipso-protonated cation will then undergo loss of methyl (→ *m*/*z* 250) in accord with the protonation results on **4**.

Trimethylsilylation of **4** with Me_3Si^+ (TMS/CI-MS)[18,19] gave the $(\mathbf{4} + SiMe_3)^+$ adduct in high abundance (*m*/*z* 337, 100%).

Collisional decomposition of the silylated adduct [Fig. 2(*a*)] gave the *m*/*z* 263 cation as the major product and Me_3Si^+ (*m*/*z* 73) as the minor product, again indicating a preference for charge retention at the octamethylbiphenylene moiety as

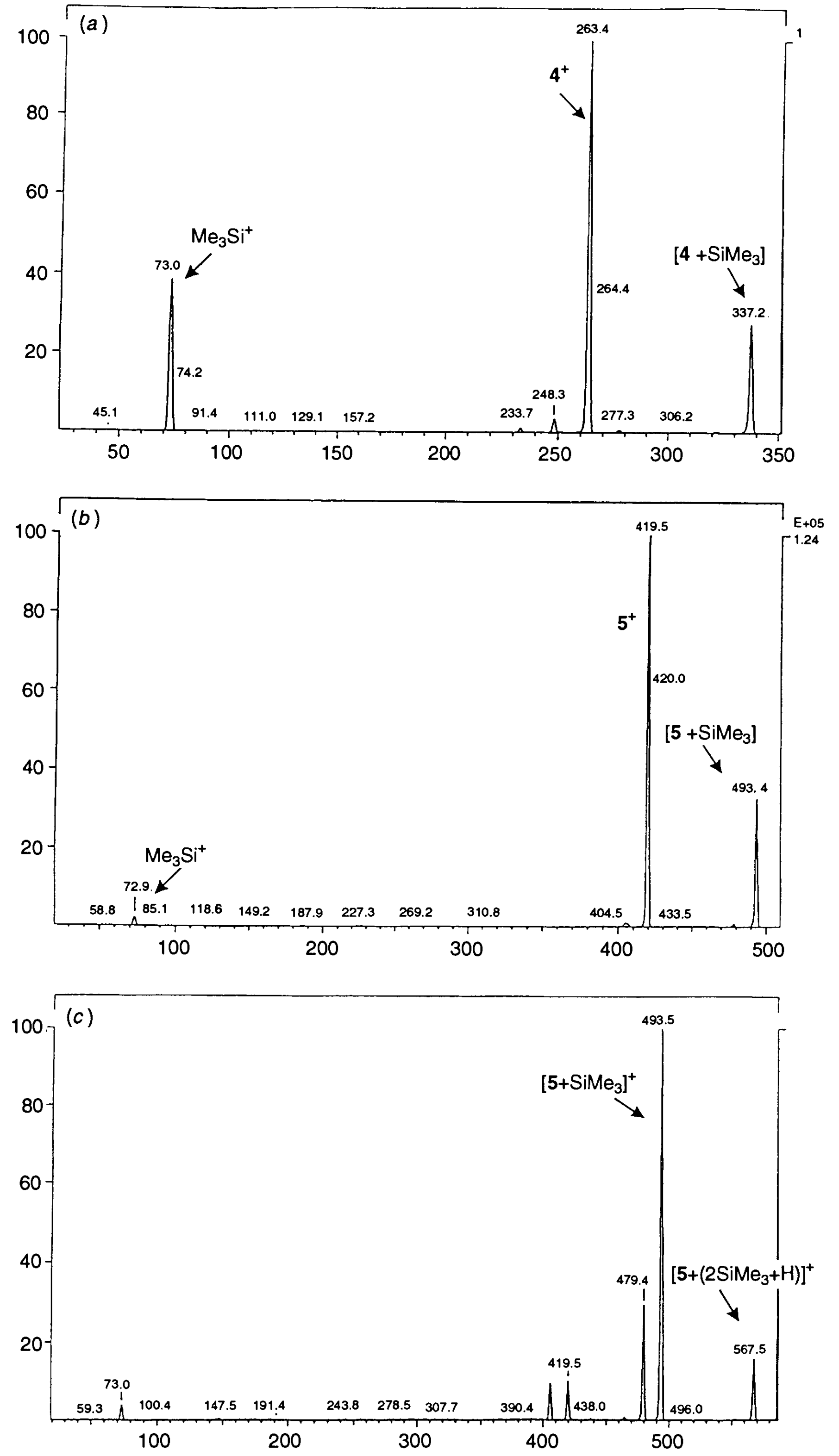


Fig. 2 (*a*), (*b*) and (*c*), product ion scans of *m*/*z* 337, 493 and 567 cations

opposed to the TMS (Me_4Si) moiety when the silylated adduct is decomposed.* A small *m*/*z* 248 (loss of Me from 263) was also detectable.

Trifluoroacetylation–trifluoromethylation of **4** with CF_3CO^+ and $CF_3{}^+$ (produced under TFA/CI conditions) gave only a minor ion due to $(\mathbf{4} + CF_3)^+$ (*m*/*z* 333).

MS Study of **5**.— The 70 eV EI mass spectrum of **5** gives the radical cation in abundance (*m*/*z* 420, 100%) together with minor demethylation fragment ions (up to six methyls; *m*/*z* 405, 390, 375, 360, 345 and 330). In addition, a distinct ion at *m*/*z* 210 is present with an M + 1 peak at *m*/*z* 210.5. The relative

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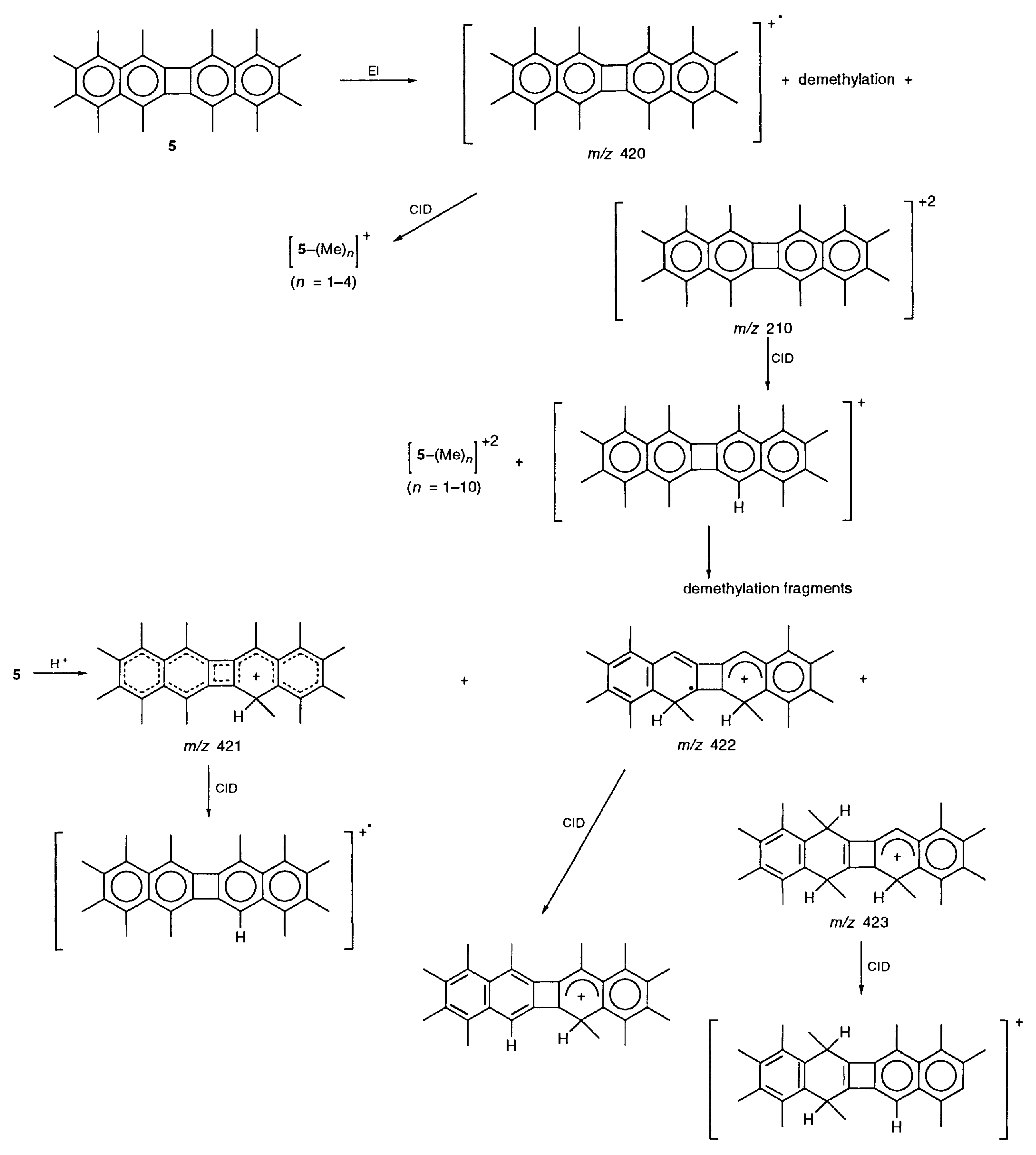
* Both σ and π complexes have been invoked in studies of arene–TMS^+ association complexes (see *e.g.* A. C. M. Wojtyniak and J. A. Stone, *Int. J. Mass. Spectrom. Ion Processes*, 1986, **74**, 59; J. S. Fornarini, *J. Org. Chem.*, 1988, **53**, 1314; J. A. Stone, *Research on Chemical Intermediates*, 1991, **16**, 257).



Scheme 2 Dodecamethylbinaphthylene cations and their decomposition pathways in the gas phase

intensity ratios of the latter cations confirm that the m/z 210 ion is due to the almost pure 5^{2+}. Increasing the ionization energy (90 eV) enhances the fragmentation leading to an overall lower dication/fragment ion ratio (*ca.* 80:20). Decreasing the ionization energy (50 eV) also lowers this ratio as dication formation becomes more difficult.

Collisional decomposition of $5^{+\bullet}$ leads to consecutive demethylation (up to four being detected) to give m/z 405, 390, 375 and 360 ions.

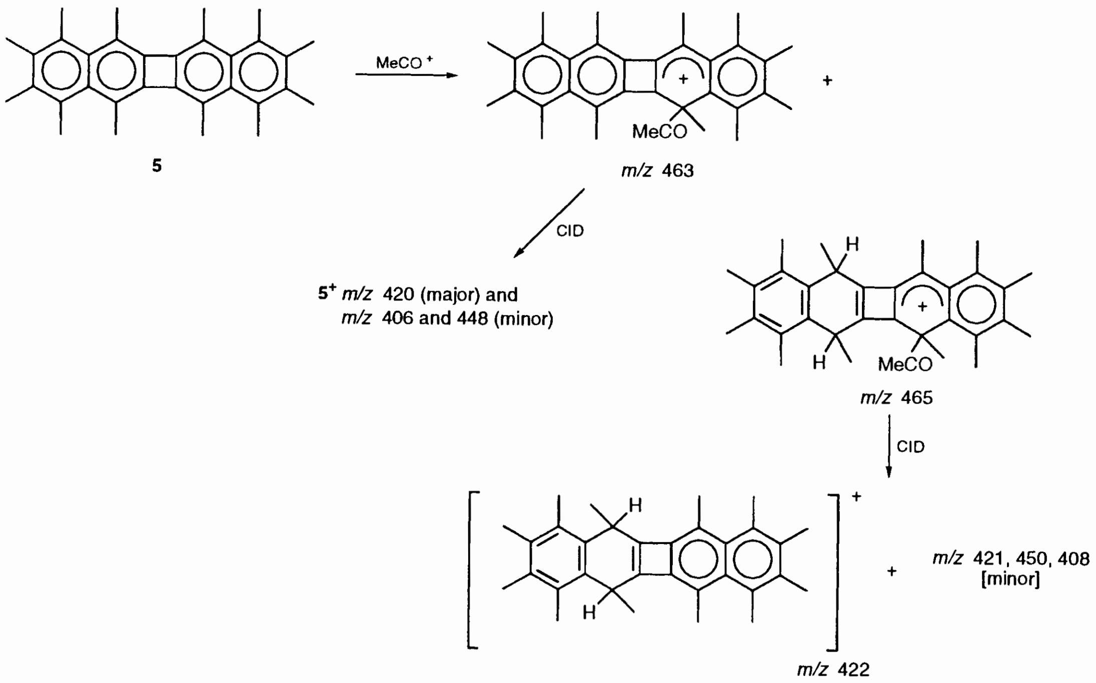
The predominant decomposition pathway for 5^{2+} is consecutive methyl loss to give doubly charged demethylated binaphthylenes (the loss of up to ten methyl groups were detectable). A minor event involving hydrogen atom abstraction and reduction to give $[5 - (Me)_n + H]^+$, *viz.* singly charged demethylated binaphthylene cations, was also detectable.

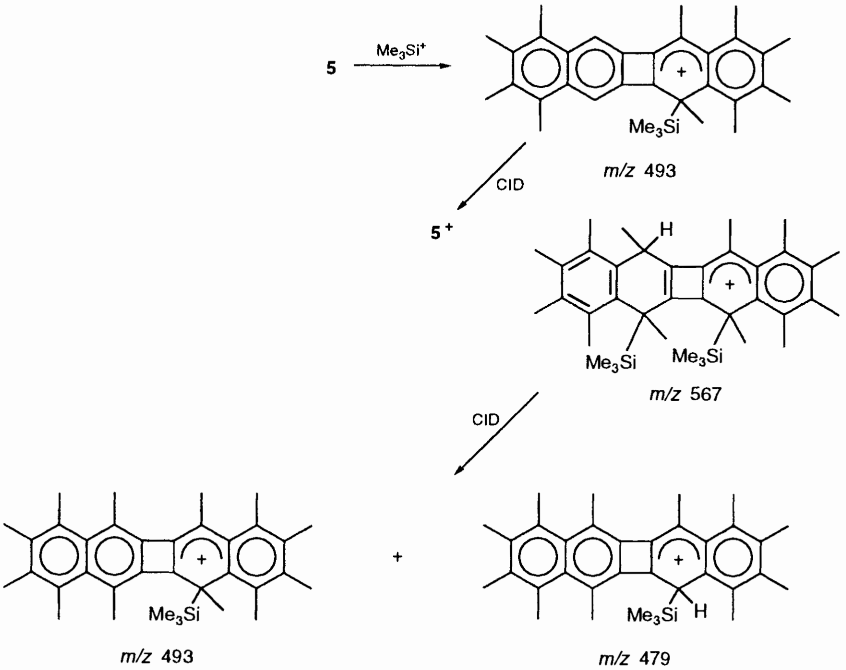
The isobutane/CI mass spectrum of **5** shows m/z 421 $(M + H)^+$, 422 $(M + 2H)^+$ and 423 $(M + 3H)^+$ ions in abundance, with no indication for a doubly charged protonated ion.

The $(5 + H)^+$, $(5 + 2H)^+$ and $(5 + 3H)^+$ ions are rather stable to collisional decomposition forming demethylated ions at m/z 406, 391, m/z 407, 392 and m/z 408, 393 respectively.

Reactions of **5** with $MeCO^+$ (acetone/CI-MS)[13–16] produces the mono-acetylated singly charged adducts: $(5 + COMe)^+$ (m/z 463, 28%) and $[5 + (COMe + 2H)]^+$ (m/z 465; 32%), as well as the protonated singly charged ions at m/z 421, 423 (and a minor one at m/z 425).

Collisional decomposition of the acetylated cations (5 +



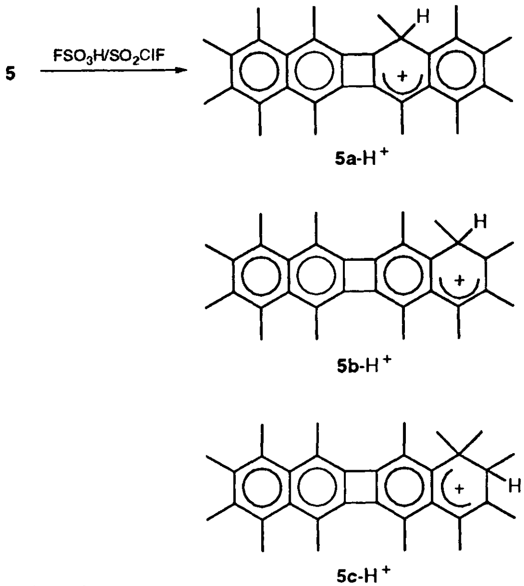


COMe)$^+$ and [**5** + (COMe + 2H)]$^+$ [Fig. 1(*b*) and 1(*c*)] leads to predominant loss of the acyl fragment to give **5**$^+$ (*m*/*z* 420) and (**5** + 2H)$^+$ (*m*/*z* 422) respectively and a barely visible MeCO$^+$ ion. Therefore, the decomposition is very selective towards charge retention at the aromatic moiety.

Reaction of **5** with SiMe$_3{}^+$ gives an abundant silylated adduct (**5** + SiMe$_3$)$^+$ at *m*/*z* 493, and a minor ion corresponding to [**5** + (2SiMe$_3$ + H)]$^+$ at *m*/*z* 567. Similar to the electrophilic reactions of **4**, strong preference for charge retention at the aromatic moiety is observed in collisional decomposition of the silylated adducts of **5** [Fig. 2(*b*)]. Thus with (**5** + SiMe$_3$)$^+$ ion, **5**$^+$ is formed and Me$_3$Si$^+$ ion is small. With the bis-silylated adduct, collisional decomposition [Fig. 2(*c*)] leads to loss of Me$_3$SiH (→ *m*/*z* 493). A less abundant fragment ion at *m*/*z* 479 corresponds to demethylation (*via m*/*z* 493), and H$^\bullet$ abstraction, likely from TMSH, to give [**5** + (SiMe$_3$ + H) − Me]$^+$. Minor fragment ions due to further demethylations are also detectable.

Finally, reaction of **5** with CF$_3$CO$^+$/CF$_3{}^+$ ions (generated *via* TFA/CI) gave weak (**5** + CF$_3$CO)$^+$ *m*/*z* 517 and [**5** + (CF$_3$H)]$^+$ *m*/*z* 490 adduct ions.

Protonation of **5** *with* FSO$_3$H–SO$_2$ClF *in Solution*.—Low temperature reaction of a cold slurry of **5** in SO$_2$ClF with FSO$_3$H–SO$_2$ClF at dry ice–acetone temperature gave a purple solution whose ^{1}H NMR spectrum (recorded at −68 °C) clearly indicated that a persistent σ-complex of monoprotonation was formed. The spectrum shows the ipso proton as an unresolved multiplet at 4.73 ppm, the ipso methyl at 1.46 ppm and seven methyl singlet absorptions between 3.15–2.40



Protonation of 5

ppm. The methyl resonances in the precursor **5** are at 2.62, 2.50 and 2.24 ppm.[12] Diprotonation can be ruled out based on the relative integrals. Whereas the exact site of attack under stable ion conditions remains to be determined, based on the number of methyl absorptions observed and in analogy with the known reactivity of benzo-biphenylene derivatives, **5a**-H$^+$ formation appears most reasonable.*

Thus unlike **4** for which an ipso protonated cation could not be detected due to concomitant oxidation, with **5** formation of a binaphthylenium ion of ipso attack was established.

A Comparative Discussion of the Electrophilic and Oxidative Chemistry of **4** *and* **5**.—(a) *Mass spectral studies.* Under electron impact **4** and **5** are easily oxidized to give radical cations, dications, and singly charged fragment ions. The latter being formed by demethylation and cycloreversion. The resulting radical cations $\mathbf{4}^{+\bullet}$ and $\mathbf{5}^{+\bullet}$ when subjected to collisional decomposition undergo loss of methyls.

For the dications, in addition to demethylation, hydrogen-abstraction and reduction is noted to give singly charged ions. Formation of singly charged ions (and their demethylation cations) are more significant for **5**.

Under CI conditions, **4** and **5** are readily monoprotonated; protonation dications are not detected. Demethylation of the protonated **4** and **5** is the only significant decomposition pathway, and collisional cycloreversion is unimportant.

Whereas both **4** and **5** react with MeCO$^+$ to give acylation cations, acetylation of **5** is more efficient. With **4** apart from (**4** + COMe)$^+$, [**4** + (COMe + 2H)]$^+$ cation is formed. These acylation adducts decompose selectively with the loss of MeCO, forming $\mathbf{4}^+$ and (**4** + 2H)$^+$ cations.

Trimethylsilylation of **4** and **5** with Me$_3$Si$^+$ gives abundant silylated adducts. With **5** a bis-silylated singly charged adduct is also formed. The decomposition of the trimethylsilylation cations is selective towards the loss of Me$_3$Si and formation of $\mathbf{4}^+$ and $\mathbf{5}^+$ with little Me$_3$Si$^+$ being formed. This selectivity towards charge retention at the aromatic moiety is even more pronounced for the silylated cation of **5**. A predominant decomposition pathway for the bis-silylated adduct is loss of TMSH.

Our choice of the site(s) of electrophilic attack for **4** and **5** as depicted in Schemes 1 and 2 are in line with the available information on solution reactivity of the parent **1** and **6**.[6] The electrophilic chemistry of **6** is not widely investigated and direct substitution has usually failed, but the 5-position is predicted to be most reactive.[6] Addition of hydrogen to the central benzene ring in [3]phenylene **2** in solution was observed by Vollhardt *et al.*[2]

The suggested structures for *m*/*z* 423 and 465 cations correspond to σ-complexes of mono-acetylation and mono-protonation with formal addition of H$_2$ at a naphthalene moiety. Similarly, the suggested structure for the bis-silylated adduct of **5** (*m*/*z* 567; Scheme 2) corresponds to a mono-trimethylsilylation σ-complex which has also undergone formal addition of TMSH at a naphthalene unit. A logical driving force for facile loss of TMSH from *m*/*z* 567 on collisional decomposition (→*m*/*z* 493) is re-aromatization of the naphthalene moiety.

Unlike reaction with MeCO$^+$, reaction of **4** and **5** with CF$_3$CO$^+$ and/or CF$_3{}^+$ is not very efficient, only weak adduct ions were formed.

(b) *Condensed phase protonation in superacids.* A persistent ipso-protonated cation is observed for **5**, unlike for **4** for which only the radical cation or the dication is formed depending on the superacid system used. Phenyl annulation appears to have increased the stability of the protonation σ-complex presumably because of its enhanced aromatic character, and electron transfer from the precursor to the arenium ion is less significant as compared to that for **4**.

In summary, our studies demonstrate that **4** and **5** undergo electrophilic attack in the gas phase by a variety of electrophiles to form stable adducts whose decompositions provide insight into their possible structures.

Experimental

Octamethylbiphenylene **4** was synthesized according to Hart[7] by benzyne coupling of dibromotetramethylbenzene in BuLi–THF. Dodecamethylbinaphthylene was a gift donated by Prof. Hart, whose synthesis has already been described.[7] FSO$_3$H (Allied) was freshly distilled in an all-glass distillation unit under dry nitrogen at atmospheric pressure. SO$_2$ClF (Aldrich) was used without further purification.

The procedure for stable ion generation was according to our previously published methods.[20] Low temperature ^{1}H NMR spectra were recorded on a GE/GN-300 wide-bore instrument. A Finnigan-Matt 95Q hybrid mass spectrometer was used for the MS studies. Collisional activation was carried out in the 'collision octapole' using air as collision gas. The aromatics were introduced as solids. The acetone/CI–MS and TMS/CI–MS conditions were analogous to the reported procedures.[13–19] For 'TFA/CI' experiments CF$_3$CO$_2$H was used as CI reagent to produce CF$_3$CO$^+$ (*m*/*z* 96) and CF$_3{}^+$ (*m*/*z* 69).

Acknowledgements

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* Dynamic proton transfer leading to a mixture of ipso-protonated arenium ions in a rapid equilibrium is not envisaged, since this would have resulted in methyl broadening or averaging.

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