Protonation–oxidation manifold in large PAHs. Benzo[a]coronene and benzo[ghi]perylene; stable ion studies in superacid media and AM1 calculations

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Low temperature protonations of benzo[a]coronene 5 and benzo[ghi]perylene 3 have been studied in FSO₃H–SO₂ClF and CF₃SO₃H–SO₂ClF superacids. For 5, rapid competing oxidation to the radical cation (RC) prevents the observation of 5H⁺ by NMR spectroscopy; the RC was probed by EPR spectroscopy. For 3, competing oxidation is less problematic and a persistent arenium ion 3H⁺ could be seen by NMR spectroscopy which was line-broadened due to presence of the RC.

Protonation of a mixture of 5 and 4,5-dihydropyrene 8 produced the C-3 protonated 8H⁺ and 5H·⁺. Addition of 8 to the superacid solution containing 3H⁺ and 3·⁺ led to detection by NMR spectroscopy of C-3 protonated 8H⁺ and the disappearance of 3H⁺.

Arenium ion energies (ΔΔH ion − neutral) and changes in carbon charges [ΔQ = q_c (ion) − q_c (neutral)] for protonation of 5 and 3 were probed by the AM1 method. The singlet oxidation dication of 5 was also calculated. The charge delocalization mode in the PAH arenium ions are discussed and compared.

Introduction

There is much current interest in the chemistry of [m]circulenes: most notably corannulene† 1, a dynamic bowl-shaped [5]circulene and its derivatives, and coronene 2, a flat rigid [6]circulene with D_{6h} symmetry.[1] Whereas 1 is a building block of C_{60}, 2 is a fragment of graphite sheets. Theory predicts increased aromatic stabilization for 2 compared with benzo-[ghi]perylene 3 and benzo[e]pyrene 4.[2]

Synthetically, 2 is readily available in reasonable quantities either from perylene[3] (by Diels–Alder strategy) or by photochemical ring closure of an appropriate cyclophene.[4]

During the 1950s Clar and Zander prepared various benzannellated derivatives of 2 (e.g. 5).[5] Its naphtho and anthraceno derivatives were also synthesized by Friedel–Crafts chemistry.[6]

More recently, Zander and co-workers have prepared both the alternant and non-alternant coronene dimers (6 and 7) by Scholl-type condensation.[7]

Introduction of significant peri strain in perchlorocoronene leads to marked non-planarity (close to D_{3d}).[8] Derivatives of perchlorocoronene have found application in host–guest chemistry.[9]

Nitrocoronene has been prepared by nitration with NO_2^+-BF_4^-–MeCN.[10] It is an environmental pollutant and mutagenic in the Ames assay.[10]

Coronene oxidation dication has been generated in highly oxidizing superacids and was shown to be a triplet.[11]

In a previous study,[12] we reported on electrophilic and oxidative chemistry of [6]helicenes and coronene. A persistent coronenium ion could not be generated in superacids due to facile oxidation; its persistent radical cation was probed by EPR spectroscopy. Facile protonation, acetylation and trimethylsilylation of coronene were effected in the gas phase (CI–MS). The coronenium cation and its singlet and triplet dications were also probed by the AM1 method.

In relation to these studies and our previous and ongoing

† IUPAC name: dibenzo[ghi,mno]fluoranthene.
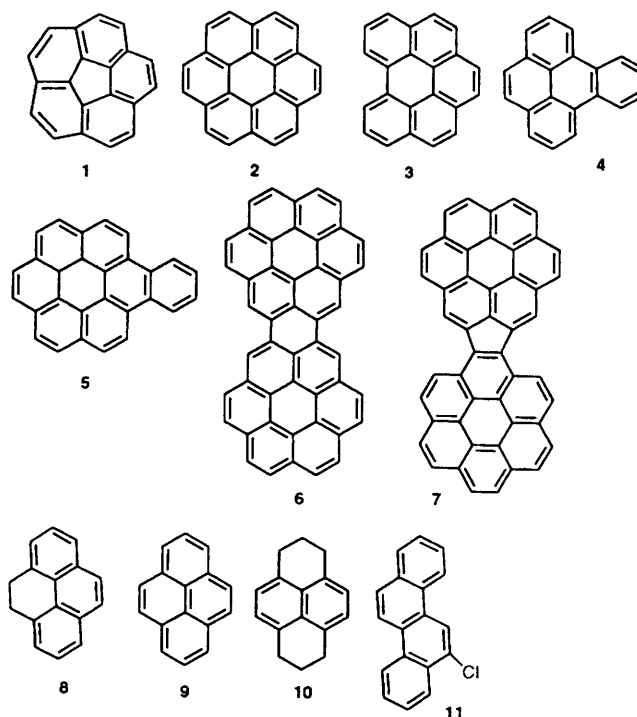
work on arenium ions of large PAHs probing charge delocalization at their periphery and charge perturbation by various substituents,[12–19] and in an effort to identify a relationship between certain charge delocalization modes and the magnitude of carcinogenic activity, we report here a stable ion and AM1 study on benzo[a]coronene 5 and benzo[ghi]-perylene 3.

Results and discussion

NMR spectra of 5 and 3

The D_{6h} symmetry in 2 which gives rise to a single proton

resonance at 8.86 ppm is lost in the benzo[a]annellated 5 whose ^{1}H NMR spectrum[20] exhibits six sets of signals with the bay region hydrogens H-8/H-13 and H-9/H-12 being most deshielded due to *peri*-strain (Fig. 1).

Both ^{1}H and ^{13}C NMR spectra of 3 have been reported, but specific assignments have not been made.[21] The most deshielded proton resonance is a doublet at 8.95 ppm for the bay-region H-9/H-10 followed by the singlet at 8.31 ppm for H-3/H-4 *meso* protons. The remaining resonances occur in a narrow region between 8.17 and 7.96 ppm and were partially assigned with the help of a COSY spectrum (Fig. 1). Limited solubility of 5 prevented the detection of quaternary carbons in the ^{13}C NMR spectrum (in CS_2–$CDCl_3$); the H-bearing carbons occur in a narrow range 127–121 ppm.

Solution studies in superacids

Low temperature reaction of 5 slurried in SO_2ClF with FSO_3H–SO_2ClF gave a dark green solution whose ^{1}H NMR spectrum (at *ca.* −65 °C) showed no absorptions for the arenium ion; only the resonances for the superacid and CH_2Cl_2 (from CD_2Cl_2 lock) were present. Similar observations were made in the less oxidizing CF_3SO_3H–SO_2ClF superacid. These results indicate the coexistence of paramagnetic 5·[+] in sufficient concentrations to prohibit detection of the arenium ion by NMR spectroscopy. Indeed, when a cold aliquot was transferred into a quartz EPR tube and examined by EPR spectroscopy, an intense but featureless signal was observed with g = 2.002 and ΔH_{pp} = 5.0 G. Variation in temperature and degassing of the sample by repeated freeze–thaw cycles did not improve the EPR signal.

Low temperature protonation of 3 with FSO_3H–SO_2ClF gave a green solution at dry ice–acetone temperature whose ^{1}H NMR spectrum (at −65 °C) (Fig. 2) exhibited a broad peak at *ca.* 4.60 ppm (2 H) for the $sp^3(CH_2^+)$, corroborating the formation of the arenium ion 3H[+]. However, the broad appearance of the aromatic resonances and limited deshielding of aromatic protons is strongly indicative of concomitant formation of 3·[+] in the superacid. The centre of gravity of the aromatic protons was at 8.20 ppm; more shielded than that of the neutral precursor (8.45 ppm) due to RC-induced paramagnetic shielding.

In our recent studies of protonated dihydropyrenes (ethanophenanthrenes),[22] we showed that the nature and concentration of the paramagnetic RC influences the position and resolution of the NMR spectra. Our work suggested the possible utility of a second RC as a 'pseudo-shift reagent' to spread out the signals of the PAH arenium ions. Furthermore, we found that H· transfer from protonated dihydropyrene 8H[+] to the pyrene radical cation 9·[+] can occur leading to 9H[+] (NMR) and 8·[+] (EPR).

In an attempt to produce 5H[+] by H· transfer to 5·[+] in the superacid, in the present study a *ca.* 5:1 mixture of 5 and 8 was protonated in FSO_3H–SO_2ClF at dry ice–acetone temperature. A persistent rose red solution resulted. The ^{1}H NMR spectrum (*ca.* −68 °C) of a cold aliquot transferred into a 5 mm NMR tube (cold CD_2Cl_2 was added) was consistent with C-3 protonated dihydropyrenium monocation 8H[+],[22] with no signals being observed for 5 (→5·[+]). Despite the presence of paramagnetic RC, the NMR linewidths (both ^{1}H and ^{13}C) were quite narrow and the spectra remained well resolved for *ca.* 1 h at low temperature. Subsequently, the lock signal (CD_2Cl_2) was diminished and eventually lost! The cold NMR tube was ejected and found to have turned into a dark brown polymeric solid. Since the stock solution of the carbocation was still intact in the cold bath, methylene chloride must have catalysed radical cation polymerization.

To the remaining cold stock solution of the superacid (8H[+] and 5·[+]) was added a cold slurry of 1,2,3,6,7,8-hexahydropyrene 10 in SO_2ClF. The ^{1}H NMR spectrum of the resulting clear red solution was consistent with a mixture of 8H[+] and 10H[+]
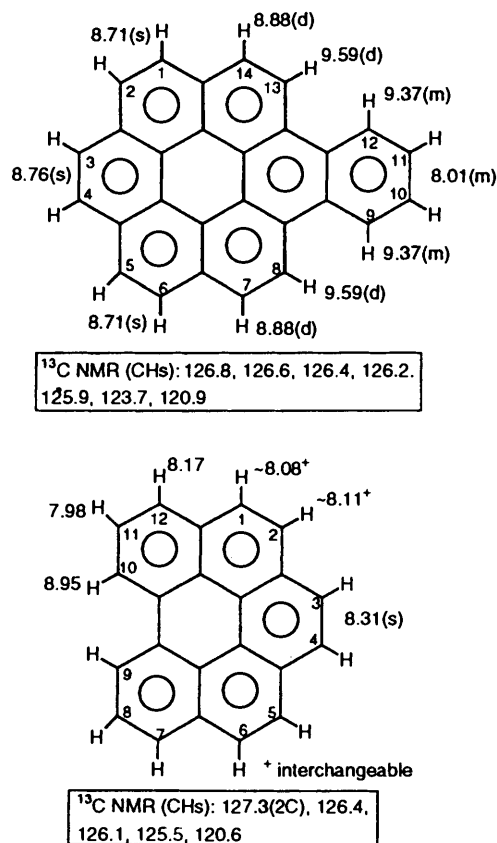

13C NMR (CHs): 126.8, 126.6, 126.4, 126.2, 125.9, 123.7, 120.9

13C NMR (CHs): 127.3(2C), 126.4, 126.1, 125.5, 120.6

[+] interchangeable

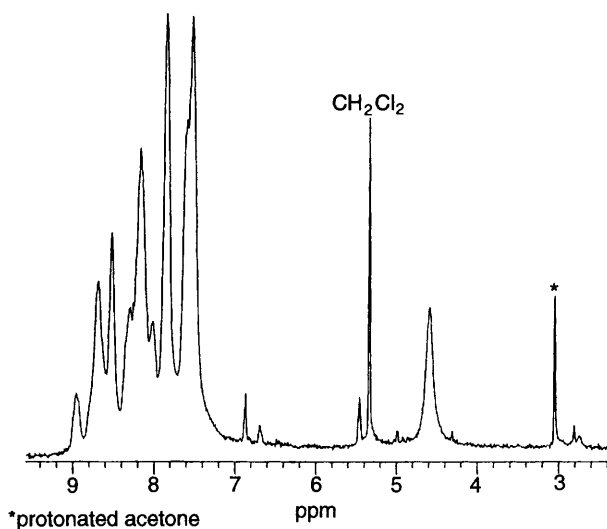**Fig. 1** NMR data for 5 and 1

*protonated acetone   ppm

Fig. 2 ^{1}H NMR spectrum of 3H[+]

(minor ion), again with no resonances observable for 5H[+] (Fig. 3, at −55 °C).

In further attempts to decrease the paramagnetic character of the superacid solutions and to obtain better NMR spectra, cold 8 was added at dry ice–acetone temperature to the superacid solution containing 3H[+]/3·[+]. Upon mixing, the green solution immediately turned red. The ^{1}H NMR spectrum (Fig. 4) showed clean formation of 8H[+] and disappearance of the resonances due to 3H[+] which were replaced by a featureless broad hump in the aromatic region.

These findings are similar to protonation of the 8 and 6-chlorochrysene 11 mixtures we previously studied,[22] and can be explained by H· transfer in the opposite direction to that desired, namely from 3H[+] to 8·[+] to form 3·[+] and 8H[+].
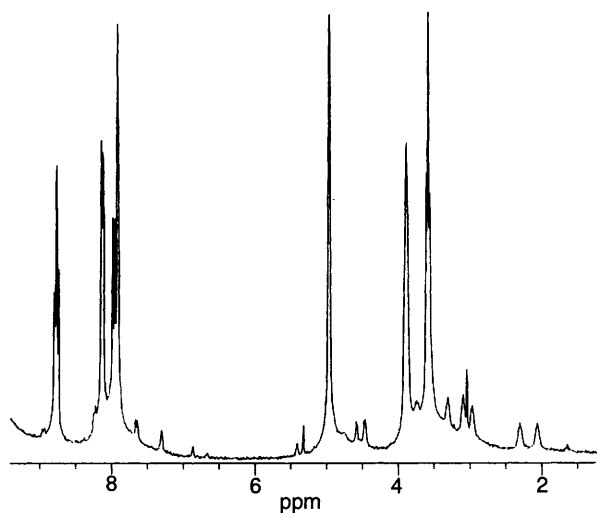
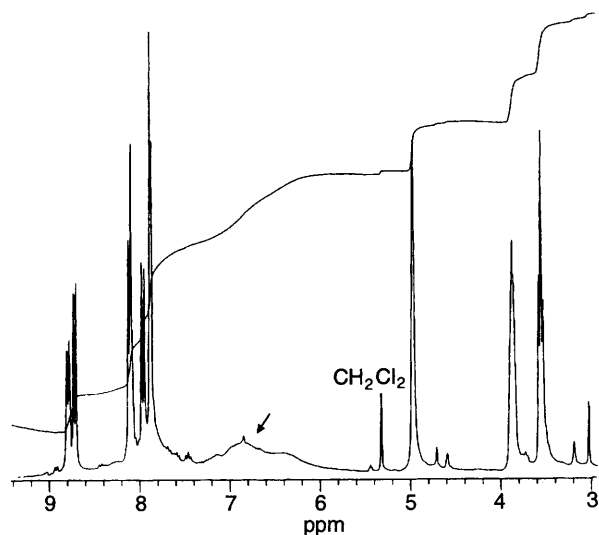Fig. 3   ¹H NMR spectrum for protonation of a mixture of 5, 8 and 9

Fig. 4   ¹H NMR spectrum for protonation of a mixture of 3 and 8

AM1 Calculations

Protonation and oxidation of 5. We calculated the arenium ion energies $(\Delta\Delta_f H^\circ)$ and changes in carbon charges $\Delta Q = [q_c$ (ion) $- q_c$ (neutral)] for monoprotonation of **5**. The results are displayed in Fig. 5. For comparison, the results for $2H^+$ are also shown.

The arenium ion stabilities are similar, with the most stable (**A**) and the least likely (**G**) carbocations separated by 7 kcal mol⁻¹. The ΔQ profiles show that the benzannellated ring does not participate in charge delocalization and that the mode of charge alternation remains very similar to coronenium cation itself.

Protonation of the benzannellated ring is least favoured, the resulting cations show limited charge delocalization paths with the π-electron density highly localized *para* and *ortho* to the site of attack and limited delocalization into four other conjugated carbons in the coronene unit.

As was the case for arenium ions of benzo[*a*]pyrene and benzo[*e*]pyrene,[19] for cations **A→E** the benzannellated *ortho* positions always carry less positive charge.

In relation to previous studies[11,12] with 2^{2+}, for comparison we calculated the singlet oxidation dication of **5** [$\Delta\Delta H$ (ion − neutral) = 426.6 kcal mol⁻¹].‡ Its ΔQ profile is shown in Fig.

‡ 1 cal = 4.184 J.

6. The charge is extensively delocalized at the 'rim' of the coronene moiety, primarily within a perylene unit; inner carbons do not contribute to the charge alternation path.

The calculated forms of the HOMO–LUMO for 5^{2+} are shown in Fig. 7. The AM1 predicted HOMO–LUMO energy gap for the singlet dication is merely 4.61 eV (the open shell biradical would not converge and could not be calculated).

Protonation of 3. The arenium ion stability order **A→F** was established for protonation of **3** based on AM1 energies (Fig. 8). Arenium ions **A, B** and **C** show extensive charge delocalization at alternating carbons of the periphery. Cation **D** exhibits a charge alternation path within an α protonated benzo[*e*]pyrene fragment. The least favoured cations **E** and **F** exhibit significant phenanthrenium ion character with minor delocalization into additional conjugated carbons.

A comparative discussion

Benzannellation in coronene does not significantly alter the charge delocalization mode in the arenium ion. Protonation at the coronene moiety remote from the benzannellated ring is clearly preferred and *peri* protonation (→**E**) is not favourable.

In solution, oxidation of **5** (→**RC**) is too rapid even in mild superacids, and the concentration of the radical cation is sufficiently high to wipe out the NMR spectrum of the arenium ion. Whereas the RC is easily detectable by EPR spectroscopy, the signal is broad and featureless, hence no hyperfine coupling could be obtained.

For **5**, protonation at C-14 and C-12 are the most favoured based on AM1 calculations, but the arenium ion energies for protonation at other sites are rather close, except for those of the benzannellated ring which are clearly not favoured.

AM1 calculations predict that the oxidation dication 5^{2+} exhibits significant charge alternation at the carbons of the rim within a perylene unit.

An observable monoprotonated benzo[*ghi*]perylene cation could be generated in $FSO_3H–SO_2ClF$, but the concomitant presence of the RC reduces the quality of the NMR spectra.

Protonation of a mixture **5** and **8** led to the observation by NMR spectroscopy of only $8H^+$. Addition of **8** to $3H^+–3^{\cdot+}$ led to NMR observation of $8H^+$ and the disappearance of $3H^+$ (→$3^{\cdot+}$). These findings are similar to our previous observations with a mixture of **8** and **10**.[22] We have not yet found a suitable H⁺ source to transform *in situ* the coexisting PAH radical cations to their arenium ions in superacids.

Relative stabilities of the arenium ions of protonation of **3** were determined by the AM1 method. Protonation at the non-annellated C-12 and C-10 are the most favoured. In these ions, the positive charge is very extensively delocalized. The less stable cations of **3** show more limited charge alternation. Those which have the highest energy exhibit phenanthrenium ion character.

The AM1 studies indicate that benzo[*a*]coronene cations are less delocalized than benzo[*ghi*]perylene ions. Benzannellation (**3→2**) severely limits the conjugation path in the carbocations despite the fact that **2** is still planar. Further benzannellation (**2→5**) has a minimal effect on the charge delocalization mode.

Experimental

Benzo[*a*]coronene synthesized by the method of Clar and Zander[3] was supplied by Rutgerswerke. Benzo[*ghi*]perylene was purchased from Aldrich. FSO_3H (Allied) and CF_3SO_3H (Aldrich) were distilled under argon and stored in Nalgene bottles with teflon seals. SO_2ClF (lecture bottle from PCR) was used without further purification.

AM1 calculations on **5** were carried out at University of Akron using MOPAC 93 version running under OS/2. AM1 calculations on **3** were carried out at KSU with the Hyperchem package (Hypercube Inc., 1994), which uses Dewar's version.
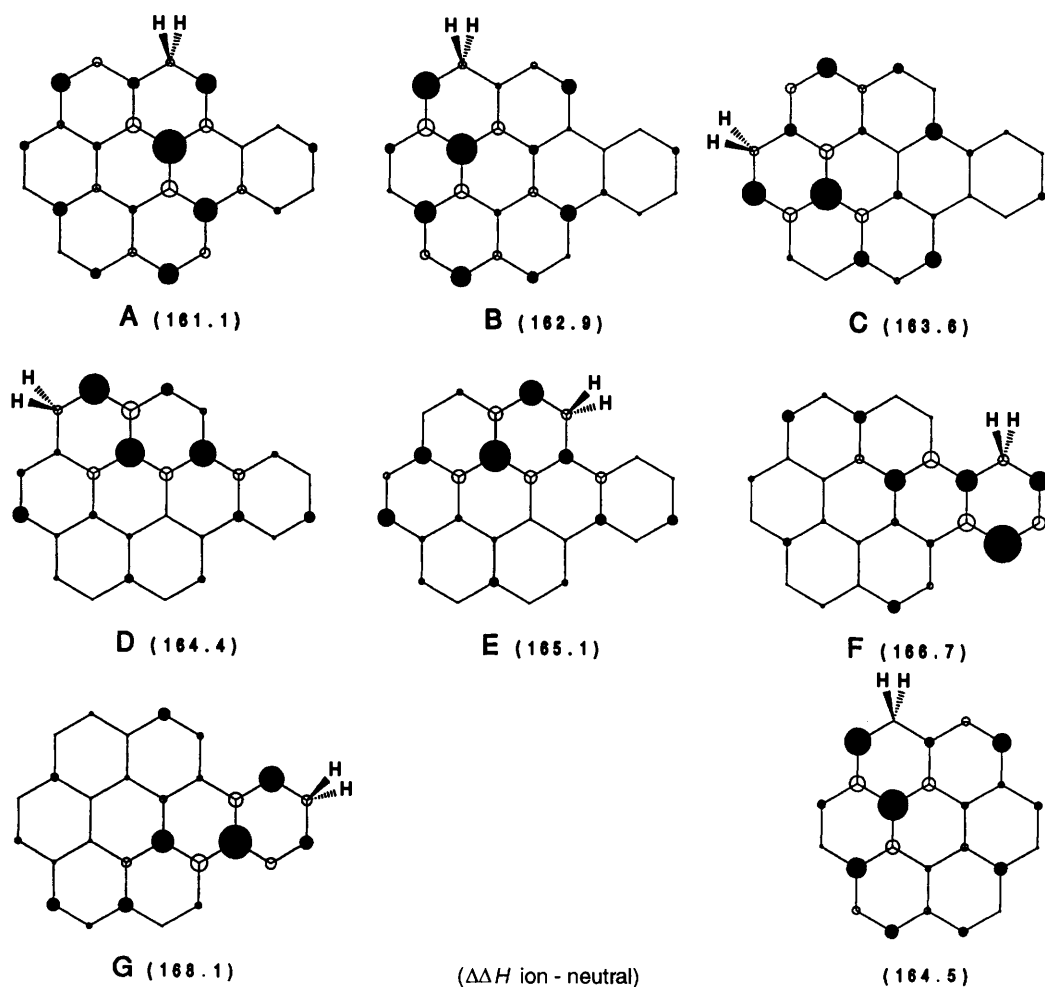
A (161.1) B (162.9) C (163.6)

D (164.4) E (165.1) F (166.7)

G (168.1) (ΔΔH ion - neutral) (164.5)

Fig. 5 AM1 energies and ΔQ profiles for protonation of 5 and 2

Fig. 6 AM1 ΔQ profile for 5^{2+}

Oxidation Dication

HOMO LUMO
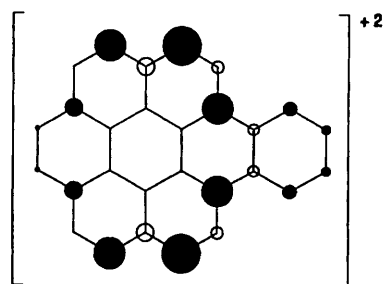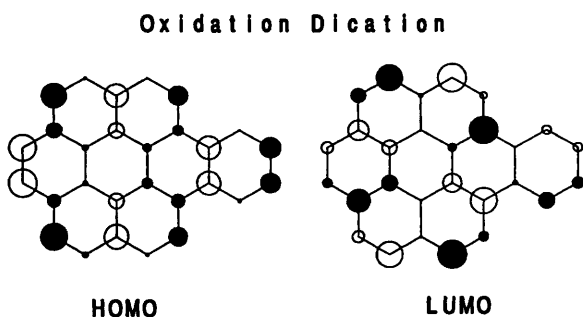
Fig. 7 Forms of the HOMO–LUMO in 5^{2+}

NMR spectra were recorded on a GE-GN300 MHz spectrometer. The X-band EPR spectra were obtained using an IBM 200D-SRC spectrometer with an ER 4111 temperature controller with 1 K precession. Procedures for low temperature NMR studies and stable ion generation were analogous to our previously published methods.
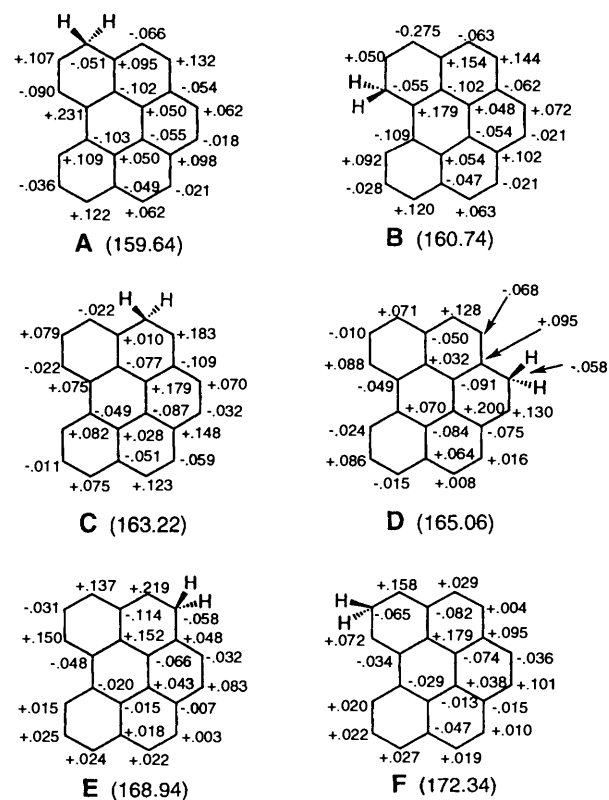
A (159.64) B (160.74)

C (163.22) D (165.06)

E (168.94) F (172.34)

Fig. 8 AM1 energies (kcal mol^{-1}) and changes in carbon charges ΔQ for protonation of 3

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