Superacid protonation of dihydrocyclobuta[*e*]pyrene and its C_{60}–*o*-quinodimethane adduct. An NMR, *ab initio*/GIAO and AM1/PM3 study

Kenneth K. Laali,*[a] Sandro Hollenstein,[a] Sergio E. Galembeck,[b] Yosuke Nakamura[c] and Jun Nishimura[c]

[a] *Department of Chemistry, Kent State University, Kent, OH 44242, USA*
[b] *LAMMOL, Departamento de Quimica, FFCLRP-USP, Ribeirao Preto, SP, Brazil*
[c] *Department of Chemistry, Gunma University, Kiryu, Japan*

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Dihydrocyclobuta[*e*]pyrene **1** is protonated in $FSO_3H–SO_2ClF$ to give a *ca.* 2:1 mixture of two arenium ions of α-protonation $\mathbf{1H^+}$ and $\mathbf{1aH^+}$. *Ab initio*/GIAO theory at the B3LYP/6-31G(d,p) level was utilized to calculate the NPA charges, relative energies and to predict the NMR chemical shifts for $\mathbf{1H^+}$ and $\mathbf{1aH^+}$ as a means to enhance the solution NMR-based assignments. The resulting regioisomeric arenium ions are highly delocalized and exhibit a uniform charge alternation path within a pyrenium moiety. Reasonable predictions of their relative energies and the overall charge delocalization mode can also be obtained at the AM1/PM3 levels. In an attempt to determine the influence of C_{60} on tropicity in an anchored-pyrenium ion, the C_{60}–*o*-quinodimethane adduct **2** was protonated in $FSO_3H{\cdot}SbF_5–SO_2ClF$; formation of regioisomeric bound-arenium ions ($\mathbf{2H^+}$, $\mathbf{2aH^+}$) which are very poorly soluble in superacid media was inferred from ^1H NMR and AM1/PM3 calculations were used to model these cations. Further model studies using a fragment of C_{60} bound to regioisomeric pyrenium ions were realized at the LSDA/DN level of theory with electrostatic potential derived charges at the B3LYP/6-31G(d,p) level.

Introduction

Dihydrocyclobuta[*e*]pyrene **1** was synthesized by Nishimura *et al.* in a synthetic sequence involving [2 + 2] photocyclization of the styrene derivative to cyclobutane-ring-bridged cyclophane followed by transannulation and aromatization.[1] This compound serves as an *in situ* source of *o*-quinodimethane by cycloreversion and this method was exploited to prepare C_{60}-PAH adducts including **2** by a [4 + 2]cycloaddition with C_{60}, whereby the arene becomes chemically attached to C_{60} *via* a flexible cyclohexene unit (Fig. 1).[2] The dynamics of the cyclohexene-anchor involve a half-boat to half-boat interconversion and can be probed *via* the methylene protons in the ^1H NMR spectrum which appear as an averaged broad singlet at room temperature that splits into an AB system on cooling.[2] Whereas the activation energy for ring inversion is variable as a function of the arene structure, there is little perturbation in the electronic properties of C_{60} upon adduct formation, therefore, the origin of the variable dynamics is more likely steric rather than electronic.[3] In the C_{60}-PAH adduct **2**, the proximal H-1/H-8 protons in the pyrene moiety are clearly deshielded,[3] showing that attachment to C_{60} increases diatropicity and this is in line with the known deshielding effect of the fullerene nucleus.

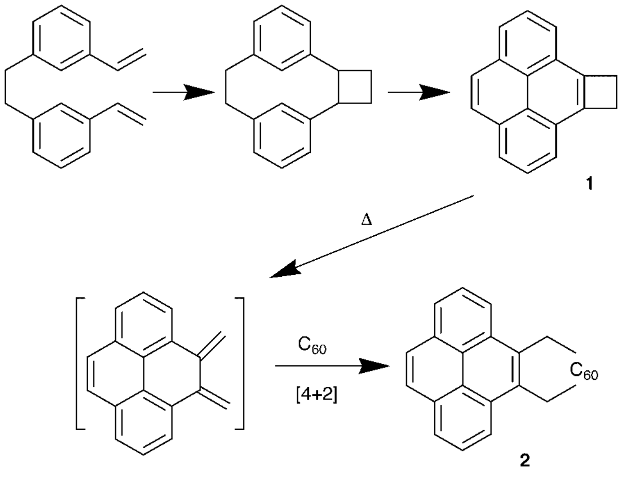


Fig. 1 Synthesis of **1** and **2**.

In relation to our stable ion studies of arenium ions and PAH dications,[4–6] we had previously studied a host of substituted pyrenium mono- and dications and examined the influence of alkyl, cycloalkyl, fluoro and nitro substituents on charge delocalization. It was, therefore, of interest to examine the cyclobutene (CB)-fused derivative **1** to gauge the influence of the CB ring and the C_{60}-bound pyrene **2** with the goal of exploring steric and electronic effects of C_{60} as a means to probe the tropicity issue for a bound-arenium ion.

Results and discussion

Low temperature protonation of **1** with $FSO_3H–SO_2ClF$ at dry ice–acetone temperature produced a dark blue–green solution whose ^1H NMR spectrum (recorded at −80 °C) is consistent with the formation of a *ca.* 2:1 mixture of two regioisomeric pyrenium ions of α-protonation (Fig. 2). Specific assignments within each group of proton resonances were made on the basis of relative intensities, multiplicities, chemical shifts, $\Delta\delta^1H$ values and with the help of H/H COSY analysis. The resulting assignments (Fig. 3) fit in quite well with the previously established general patterns of proton chemical shifts in other pyrenium ions.[4] As expected, the aliphatic region of the ^{13}C NMR spectrum of the mixture exhibited two sets of three resonances for the CH_2 groups. Out of the possible maximum of 30 aromatic resonances, 21 were clearly visible. These occurred between 175.8 and 124.6 ppm. There was no noticeable change with time in the relative proportions of the two arenium ions. In order to *specifically* assign each set of resonances to a given regioisomer (an attempt to settle this issue *via*

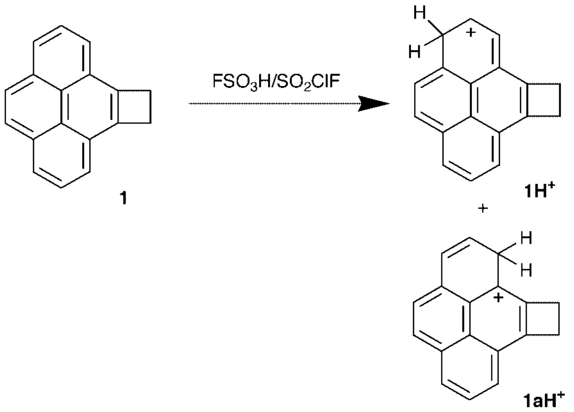


Fig. 2 Superacid protonation of **1**.

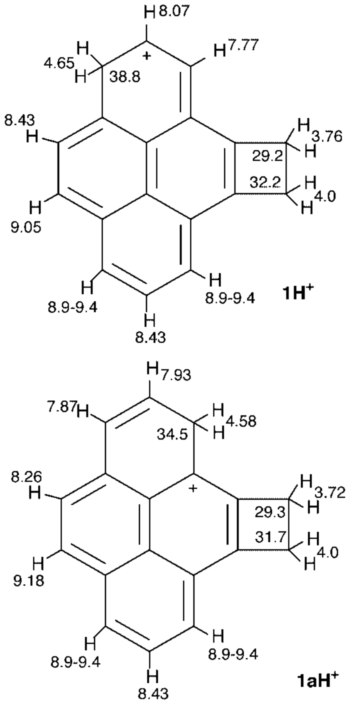


Fig. 3 NMR assignments for **1H**$^+$/**1aH**$^+$ (only the aliphatic carbon resonances are specifically assigned; there are 21 aromatic resonances between 175.8 and 124.6 ppm).

an NOED experiment proved unsuccessful) and because of the complexity of the system and low concentration of the carbocation solutions (substrate economy), at this point we resorted to high level *ab initio* theory.

Parent **1** and the regioisomeric arenium ions **1H**$^+$ and **1aH**$^+$ were studied using the hybrid density function method B3LYP/6-31G(d,p). Fig. 4 is a summary of the changes in the charges obtained by natural population analysis NPA (cation minus precursor) for the arenium ions **1H**$^+$ and **1aH**$^+$, showing extensive positive charge delocalization and a regular pattern of charge alternation within a pyrenium ion moiety. The charge delocalization mode is analogous to other pyrenium ions of α-attack illustrating that fusion to the cyclobutene ring has minimal effect. Protonation at C-3 (*peri* to CB ring) is predicted to be slightly less favorable (0.17 kcal mol^{-1}); thus relief of steric strain by rehybridization at C-3 cannot be a contributing stabilizing factor.

On this basis, the major regioisomer was assigned to **1H**$^+$ and the minor isomer to **1aH**$^+$. A larger difference in relative stabilities observed in solution could stem from preferential solvation and possibly also a counter ion effect (FSO$_3^-$ position relative to the CB ring) which might contribute to raising the energy of **1aH**$^+$.[7]

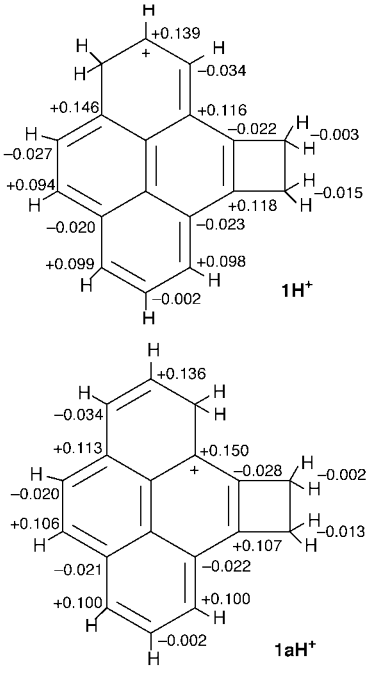
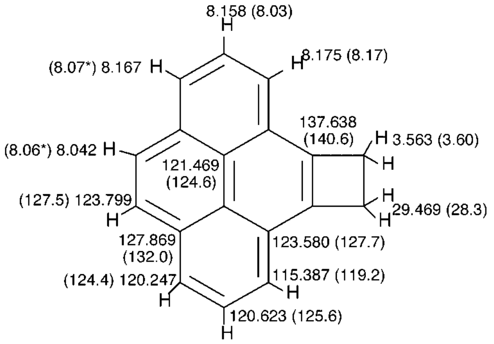


Fig. 4 Changes in NPA charges for **1H**$^+$/**1aH**$^+$.



* not specifically assigned (may be interchangeable)

Fig. 5 ^{13}C and ^{1}H NMR chemical shifts for parent **1** calculated by B3LYP/6-31G(d,p); experimental chemical shifts (in parentheses) are taken from ref. 1.

In recent years, *ab initio*/IGLO and MP2-GIAO calculations have successfully been applied to predict NMR spectra for a host of small carbocations.[8] These high-level calculations have not so far been extended to larger carbocations such as PAH arenium ions and dications probably because of computational resource constraints.

Fig. 5 shows the predicted and the experimental solution ^{1}H and ^{13}C chemical shifts for parent compound **1**. Fig. 6 illustrates the *ab initio*/GIAO calculated ^{1}H and ^{13}C NMR chemical shifts for the arenium ions **1H**$^+$ and **1aH**$^+$ as well as the predicted $\Delta\delta^{13}$C values for the most highly deshielded carbons at the periphery. It can be seen that the overall fit between the experimental and theoretical proton data is quite acceptable (compare Fig. 3 with Fig. 6). The established pattern of shielded H-3/H-7 and deshielded H-6/H-8/H-9 is clearly revealed from GIAO calculations. In the ^{13}C NMR, the fit for the aliphatic carbons is excellent. For the aromatic carbons even though specific assignments are not made, judging from the spread of the aromatic resonances in comparison to the predicted chemical shifts, the correspondence seems satisfactory. Furthermore, *ab initio*/GIAO calculations correctly predict the overall charge distribution pattern in the pyrenium cations.

For comparison, relative energies for **1H**$^+$ and **1aH**$^+$ were calculated by the AM1 and PM3 methods; they were predicted to be within 0.5 kcal mol^{-1} of each other. The overall pattern of

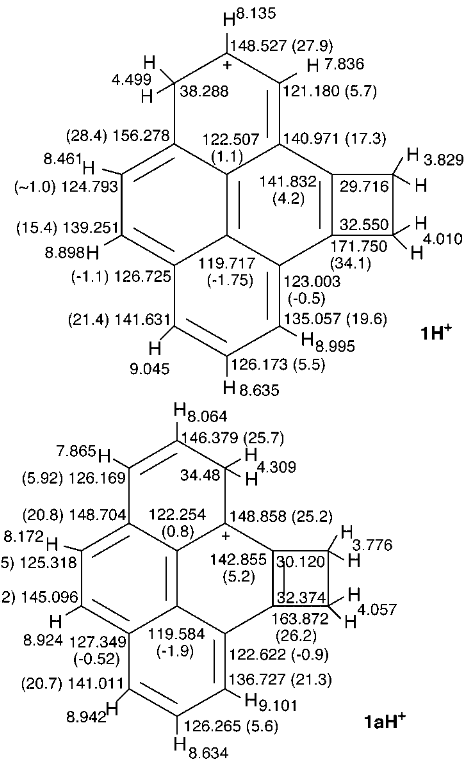


Fig. 6 ^{13}C and ^{1}H NMR chemical shifts calculated by B3LYP/6-31G(d,p) and the theoretical $\Delta\delta^{13}C$ values (cation minus neutral; given in parentheses) for **1H**$^+$/**1aH**$^+$ (point group: C_s for both).

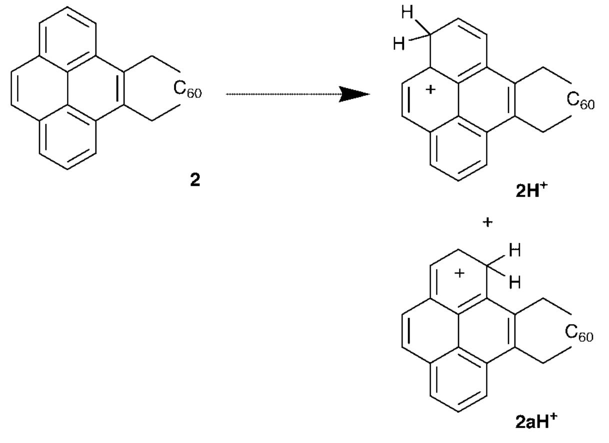


Fig. 7 Protonation of **2**.

charge alternation and pyrenium ion character of the resulting monoarenium ions was also correctly predicted.

Compound **2** in which a pyrene unit is anchored to C_{60} *via* a flexible cyclohexene ring is a potentially interesting probe to examine distal *versus* proximal α-protonation (**2H**$^+$and **2aH**$^+$) and the influence of C_{60} on tropicity in the pyrenium cations (Fig. 7).

Low temperature protonation of **2** was first examined in $FSO_3H–SO_2ClF$; a brown color developed but the substrate was hardly soluble in the superacid. Its ^1H NMR spectrum exhibited very broad but deshielded aromatic features. Addition of a few drops of $FSO_3H{\cdot}SbF_5$ (4:1) to this solution did not improve the solubility. An optimal ^1H NMR spectrum could be obtained at −50 °C after addition of a few drops of $FSO_3H{\cdot}SbF_5$ (1:1) to the same sample. The aromatic resonances appeared between *ca.* 8.0 and 9.40 ppm as seven, roughly equal intensity, resonances which due to solubility difficulties were broadened at the baseline. The cyclohexene CH_2's and the CH_2 (carbocation) resonances were unresolved, appearing as a broad envelope between *ca.* 4.30–5.0 ppm. A trace of protonated acetone served to ensure correct referencing of the spectrum. The results are compatible with a **2H**$^+$–**2aH**$^+$ mixture which is more downfield shifted than **1H**$^+$–**1aH**$^+$. These observations point to a deshielding effect from C_{60} on the arenium ion. Whereas AM1 favored distal protonation by ~1 kcal mol^{-1}, PM3 preferred proximal protonation by ~1 kcal mol^{-1}. This energy difference is compatible with the formation of an arenium *mixture* as deduced from NMR. Furthermore, both AM1 and PM3 agree on the pyrenium ion character of the resulting arenium ions and reveal the already established charge alternation path.

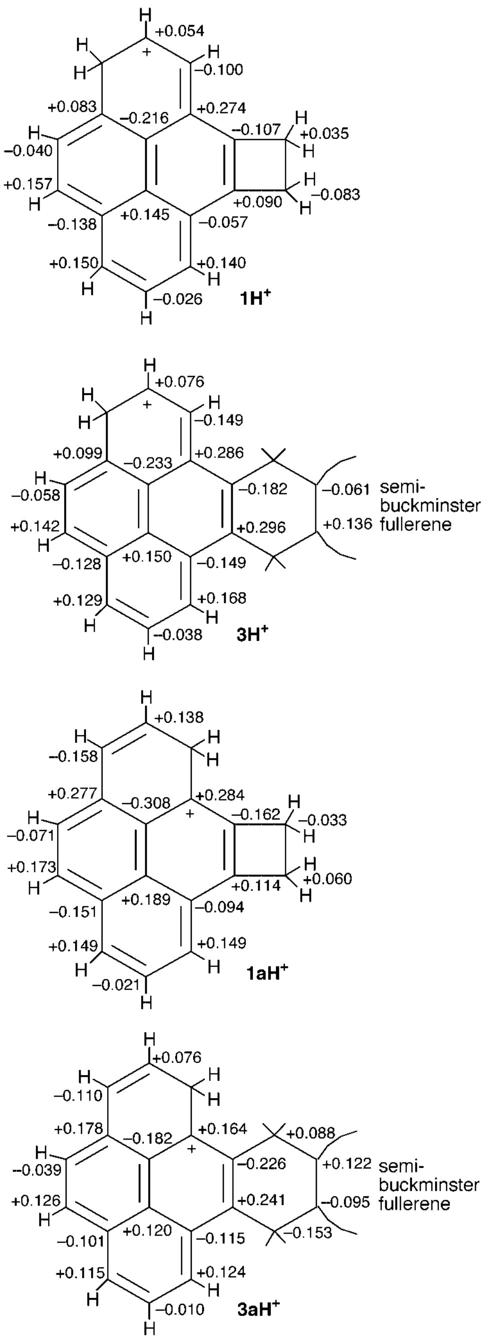


Fig. 8 Differences in the MK charges (cation minus neutral) for **1H**$^+$/**3H**$^+$ and **1aH**$^+$/**3aH**$^+$.

In an effort to obtain a more rigorous theoretical picture, a semibuckminsterfullerene–pyrene adduct was used as a model to calculate the corresponding regioisomeric pyrenium ions **3H**$^+$/**3aH**$^+$ at the B3LYP/6-31G(d,p)//LSDA/DN level of theory and their electrostatic potential derived charges were calculated by the Merz–Singh–Kollman algorithm (MK). Differences in the MK charges (cation minus neutral) for the bound pyrenium ions are gathered in Fig. 8 and compared with those of $\mathbf{1H}^+/\mathbf{1aH}^+$. Attempts to calculate the charges by the NPA method were unsuccessful. Whereas the overall charge alternation path and the pyrenium ion character are maintained in $\mathbf{3H}^+/\mathbf{3aH}^+$ it is apparent that attachment to the C_{60} fragment influences the magnitude of charge delocalization in the arenium ions. The generality of this feature requires further theoretical studies. It should be noted that at this level of theory the difference in relative stabilities is 0.91 kcal mol^{-1} in favor of proximal protonation which is in remarkable agreement with PM3.

In summary, the reliability of *ab initio*/GIAO calculations has been tested for predicting the NMR spectra and the charge delocalization mode in large arenium ions. Combination of *ab initio*/GIAO theory and NMR experiments could greatly facilitate solving complex structures and analysis of carbocation mixtures. Despite poor solubility, formation of C_{60}-anchored arenium ions has been shown. In line with previous studies in neutral systems, C_{60} appears to exhibit a deshielding effect on a chemically anchored arenium ion.

Experimental

Compounds **1** and **2** were synthesized and purified according to the literature procedures.[1,2]

FSO_3H (Allied) was triply distilled in an all glass distillation unit and stored in Nalgene bottles with Teflon seals under argon. SO_2ClF was prepared according to a modified procedure of Prakash *et al.*[9] from SO_2Cl_2, NH_4F and TFAH.

Preparation of the superacid solutions and procedures for stable ion work and low temperature NMR measurements were analogous to our previously published methods.[5] *Ab initio* calculations (hybrid density function method B3LYP/6-31G (d,p)[10,11] and GIAO[12]) were performed using the GAUSSIAN94 package software.[13] NPA charges[14] were obtained by NBO 3.1,[15] whereas AM1/PM3 calculations and energy minimizations were carried out with the Hyperchem 5 package (Hypercube, 1997). Geometry optimization on the semibuckminsterfullerene-bound pyrenium ions was performed using local density functional method SVWN and DN basis sets, equivalent to 6-31G, in Spartan 5.1.2.[16] Charges were fitted to electrostatic potentials as points selected to the Merz–Singh–Kollman scheme (MK),[17] with hybrid functional B3LYP[10] and 6-31G(d,p) basis sets[11] in the GAUSSIAN98 software.[18]

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