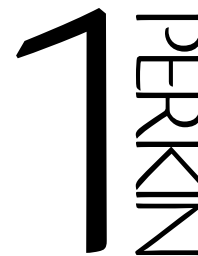# Synthesis and properties of stable heteroazulene analogues of a triphenylmethyl cation

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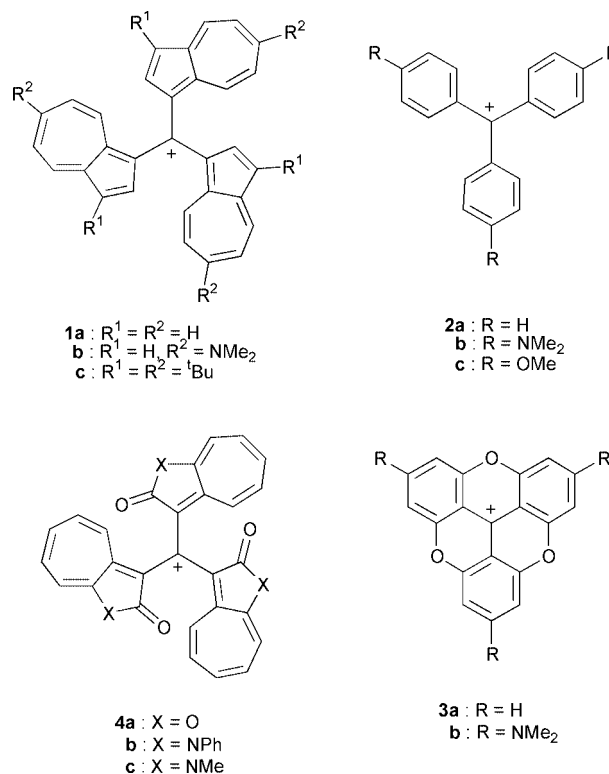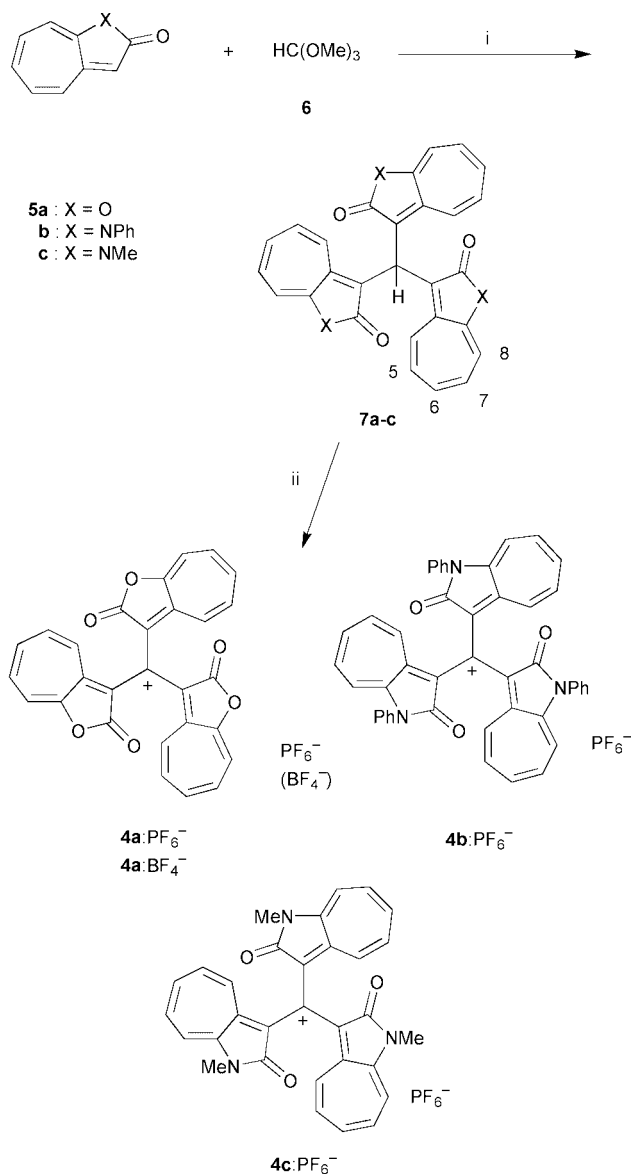
A general synthetic route to a novel type of fairly stable heteroazulene analogues of triphenylmethyl cations, tris(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)-, tris(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]pyrrol-3-yl)-, and tris(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]pyrrol-3-yl)methyl cations, **4a–c**, is reported. The synthetic method is based on a simple, TFA-catalyzed electrophilic aromatic substitution on the heteroazulenes 2*H*-cyclohepta[*b*]furan-2-one and 1,2-dihydro-*N*-phenyl-2*H*-, and 1,2-dihydro-*N*-methyl-2*H*-cyclohepta[*b*]pyrrol-2-one with trimethyl orthoformate, followed by oxidative hydrogen abstraction with DDQ and subsequent exchange of the counter-anion by using aq. HPF$_6$ solution. The stability of the cations **4a–c** is expressed as the pK_{R^+}-value, which is determined spectrophotometrically as 9.7, 12.2, and 13.1, respectively. The electrochemical reduction of **4a–c** exhibits reversible waves and low reduction potentials at −0.31, −0.58, and −0.62 (V *vs.* Ag/Ag$^+$) upon cyclic voltammetry (CV), which values are lower than that of tri(azulen-1-yl)methyl cations.

Introduction

Recently, Asao and co-workers have reported the synthesis of a series of azulene analogues of triphenylmethyl cations, *i.e.*, tri(azulen-1-yl)methyl,[1–7] di(azulen-1-yl)phenyl-methyl,[1,4,6–10] and (azulen-1-yl)diphenylmethyl cations[1,4,6,7,9] and their derivatives. Among the stable carbocations, much attention has been focused on triarylmethyl cations such as **2** and 4,8,12,12c-tetrahydro-4,8,12-trioxadibenzo[*cd,mn*]pyrenylium cations **3**. Many of them are used as textile dyes despite their low light-fastness, whereas others serve as laser dyes. Thus, their photophysical properties have also been extensively studied.[11] The tris(dimethylamino)-substituted cation **2b** and the cation **3a** show almost the same pK_{R^+}-value of 9.36[12] and 9.05,[13] respectively. The pK_{R^+}-value expresses the reactivity of the cation toward hydroxide ions.[14] The high stability of the cation **2b** as compared with **2a** (pK_{R^+} −6.4)[15] can be explained by the strong electron-donating ability of the dimethylamino substituents, which by simple resonance delocalize the charge. When compared with other carbocations such as the tris(4-methoxyphenyl)methyl cation **2c** (pK_{R^+} 0.82),[13] it becomes obvious that the high stability of the cation **3a** does not rely merely on the presence of the three oxygen atoms but also on the complete planarity of the molecular framework, which allows substantial delocalization of the positive charge. The reaction with the hydroxide ion becomes even further unfavorable due to destabilization of the corresponding methanol by strain when the central carbon is forced into sp^3 hybridization.[14] Thus, 2,6,10-tris-(dimethylamino)-4,8,12,12c-tetrahydro-4,8,12-trioxadibenzo-[*cd,mn*]pyrenylium cation **3b** has been synthesized recently as an extremely stable carbocation with the pK_{R^+}-value of 19.7.[16] Regarding the azulene-substituted methyl cations **1a–c**, theoretical calculations and the large dipole moment of azulene reasonably predict that azulene should stabilize carbocations attached at the 1-position, and indeed they exhibited good stabilities with high pK_{R^+}-values, 11.3 for **1a**,[1,4] and 14.3 for **1c**,[2,4] respectively. The cation **1b** (pK_{R^+} 24.4) is highly stabilized by three dimethylamino substituents, which by simple resonance stabilize the positive charge.[7] A *tert*-butyl substituent effectively stabilizes the cation **1c** by steric effects

1a : R^1 = R^2 = H
b : R^1 = H, R^2 = NMe$_2$
c : R^1 = R^2 = ^{t}Bu

2a : R = H
b : R = NMe$_2$
c : R = OMe

4a : X = O
b : X = NPh
c : X = NMe

3a : R = H
b : R = NMe$_2$

and also by the inductive electronic effects induced by C–C hyperconjugation with the π-system.[2,4] Since heteroazulenes such as 2*H*-cyclohepta[*b*]furan-2-one **5a**, as well as 1,2-dihydro-*N*-phenyl- and 1,2-dihydro-*N*-methylcyclohepta[*b*]pyrrol-2-ones **5b** and **5c** (Scheme 1) have a molecular framework similar to that of azulene and undergo electrophilic attack at the 3-position,[17,18] the heteroazulenes **5a–c** should stabilize cations attached at the 3-position by electronic and steric factors with the bulky molecular framework. In order to clarify the stabilizing effect of heteroazulenes toward the cationic center, we studied an efficient synthesis, large pK_{R^+}-values

Scheme 1 *Reagents and conditions*: i, CH$_2$Cl$_2$, TFA (5:1), r.t.; ii, (a) DDQ in CH$_2$Cl$_2$, (b) 60% aq. HPF$_6$ or 42% aq. HBF$_4$.

Table 1 Results for the preparation of methane derivatives **7a–c** and methylium salts **4a–c·PF$_6$⁻** and **4a·BF$_4$⁻**

Run	Compound 5	Substitution		Hydride abstraction	
		Product	Yield/%	Product	Yield/%
1	**5a**	**7a**	81	**4a·PF$_6$⁻**	25
2				**4a·PF$_6$⁻**	99
3	**5b**	**7b**	89	**4b·PF$_6$⁻**	97
4	**5c**	**7c**	76	**4c·PF$_6$⁻**	95
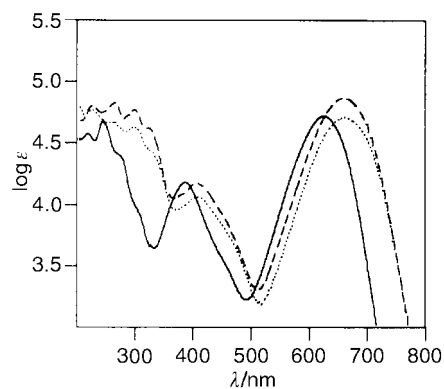
Fig. 1 UV–visible spectra of cations **4a** (solid line), **4b** (dotted line) and **4c** (broken line) in acetonitrile.

of 60% aq. HPF$_6$ solution gave the salts **4a–c·PF$_6$⁻** in the yields listed also in Table 1. Although the yield of **4a·PF$_6$⁻** is low, the attempted reaction of **7a** with DDQ and subsequent anion-exchange reaction with 42% aq. HBF$_4$ in acetic anhydride afforded a salt **4a·PF$_4$⁻** in good yield (Table 1, entry 2). Thus, the high solubility of **4a·PF$_6$⁻** in CH$_2$Cl$_2$ would be attributable to its low yield.

Spectroscopic properties of 4a–c·PF$_6$⁻ and 4a·BF$_4$⁻

The salts **4a–c·PF$_6$⁻** and **4a·BF$_4$⁻** crystallized easily to give complexes containing HPF$_6$ and HBF$_4$ molecules, respectively, in the crystal lattice. Thus, satisfactory analytical data of these salts were not obtained. However, the mass spectra of the salts **4a–c·PF$_6$⁻** and **4a·BF$_4$⁻** ionized by FAB exhibited the correct M⁺ − PF$_6$ and M⁺ − BF$_4$ ion peaks, which are indicative of the cationic structure of these compounds. The characteristic bands for the counter-ions PF$_6$⁻ and BF$_4$⁻ are observed at 838–839 cm⁻¹ and 1084 cm⁻¹ in the IR spectra of **4a–c·PF$_6$⁻** and **4a·BF$_4$⁻**, respectively. These features also support the cationic nature of the compounds. UV-vis spectra of cations **4a–c** in acetonitrile are shown in Fig. 1. The spectra resemble each other, but the spectrum of the cation **4a** shows appreciable blue shift by 38 and 35 nm in the longest-absorption maximum as compared with those of the other cations. The ¹H NMR chemical shifts of the methine protons (δ 5.46, 6.26, and 6.75) of methane derivatives **7a–c** disappeared in the ¹H NMR spectra of **4a–c·PF$_6$⁻** and **4a·BF$_4$⁻**. Thus, the ¹H NMR spectra also support the ionic structures of these compounds. The proton signals on the seven-membered ring of **4a–c·PF$_6$⁻** appear as broad signals. Thus, slow conformational change of the heteroazulene moieties of these cations occurs on the ¹H NMR time-scale at room temperature. Attempted measurement of the ¹H NMR spectra of **4c·PF$_6$⁻** at temperatures ranging from −30 °C (in CDCl$_3$) to 150 °C (in DMSO-d$_6$) exhibited no appreciable change in the broad signals. This feature is completely different from that of tri(azulen-1-yl)-methyl cations, which undergo rapid isomerization at high temperature (60 °C) but exist as two types of propeller conformations (at −60 °C).[4] The ¹³C NMR spectra of **4a–c·PF$_6$⁻** show more than ten carbon signals; this feature is in accord with that of the ¹H NMR spectra.

and low reduction potentials of novel heteroazulene analogues of the tri(azulen-1-yl)methyl cation; tris(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methylium, tris(1,2-dihydro-2-oxo-*N*-phenyl-cyclohepta[*b*]pyrrol-3-yl)methylium, and tris(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]pyrrol-3-yl)methyl cations, **4a–c**. We report herein our results in detail.

Results and discussion

Synthesis

The synthesis of tris(heteroazulene)-substituted methyl hexa-fluorophosphates **4a–c·PF$_6$⁻** was accomplished by hydride abstraction of tris(heteroazulene)-substituted methanes **7a–c**. The attempted reaction of heteroazulenes **5a**[19] with trimethyl orthoformate **6** in CH$_3$CO$_2$H at room temperature for 96 h did not proceed and the starting material **5a** was recovered quantitatively.[4] On the other hand, the reaction of heteroazulenes **5a**,[19] **5b**,[20] and **5c**[18,21] with **6** in a mixture of CH$_2$Cl$_2$–CF$_3$CO$_2$H (5:1) at room temperature for 24 h afforded **7a–c** in fairly good yields (Table 1). The compounds **7a–c** form powdery, reddish orange crystals, the structure of which was assigned on the basis of their IR, ¹H and ¹³C NMR spectral data, as well as elemental analyses and mass spectral data. Hydride abstraction from **7a–c** with DDQ in CH$_2$Cl$_2$ at room temperature followed by addition

Table 2 pK_{R^+}-Values and reduction potentials[a] of cations **4a**–**c**[b] and reference compounds **1a**,**c**

Compound	pK_{R^+}	$E1_{red}$	(E_{cathod}, E_{anod})	$E2_{red}$	(E_{cathod}, E_{anod})
4a	9.7	−0.31	(−0.33, −0.28)	−0.95	(−0.98, −0.92)
4b	12.2	−0.58	(−0.60, −0.55)	−1.27	(−1.30, −1.24)
4c	13.1	−0.62	(−0.65, −0.59)	−1.33	(−1.36, −1.30)
1a[c]	11.3	−0.78		−1.56[d]	
1c[c]	14.3	−0.91		−1.72[d]	

[a] V *vs.* Ag/Ag$^+$; a mean value of the cathodic and anodic peaks. [b] Salts **4a**–**c·**PF$_6^-$ were used for the measurement. [c] Ref. 4. [d] Irreversible process.

Stability of the methyl cations: pK_{R^+}-values and reduction potentials

The affinity of the carbocation toward hydroxide ions, expressed by the pK_{R^+}-value, is the most common criterion of carbocation stability.[14] The pK_{R^+}-values of the cations **4a**–**c** are summarized in Table 2 along with those of the tri(azulen-1-yl)methyl cations **1a**,**c**.[4] The neutralization of the cations **4a**–**c** is not completely reversible. This feature may be ascribed to the instability of neutralized products under the conditions of the pK_{R^+} measurement. Immediate (*ca.* 5 s) acidification of an alkaline solution (pH *ca.* 14) of **4a**–**c** with TFA regenerated the absorption maxima of the cations in the visible region to the extent of 85–90%. As expected, the heteroazulenes effectively stabilize the cations, and the pK_{R^+}-values of **4a**–**c** are extremely high for methyl cations such as **2a**–**c** and **3a**. Although the pK_{R^+}-value of **4a** is slightly lower by 0.6 pH units than that of the tris[3-(methoxycarbonyl)azulen-1-yl]methyl cation (pK_{R^+}-value 10.3),[4] **4b**,**c** exhibit higher pK_{R^+}-values than those of tri(azulen-1-yl)methyl cation **1a**, and lower values by 2.1 and 1.2 pH units, respectively, than that of **1c**. The relatively high stabilization effect of the cations **4b**,**c** compared with that of **4a** is attributable to the low electronegativity of the nitrogen atom as compared with the oxygen atom in the five-membered ring of **4a**.

The reduction potentials of **4a**–**c** determined by cyclic voltammetry (CV) in CH$_3$CN are also summarized in Table 2 together with those of the reference cations **1a**,**c**.[4,6] The reduction behavior of the cations is affected by the heteroazulene moiety. The waves of **4a**–**c** were reversible under the conditions of the CV measurements. The reduction of **4a**–**c** showed two reversible waves at −0.31 to −0.62 V ($E1_{red}$) and −0.95 to −1.33 V ($E2_{red}$), respectively. The two waves are ascribed to the formation of radicals **8a**–**c** and anions **9a**–**c**, respectively (Scheme 2).[4] Thus, the heteroazulene rings should stabilize not

Scheme 2
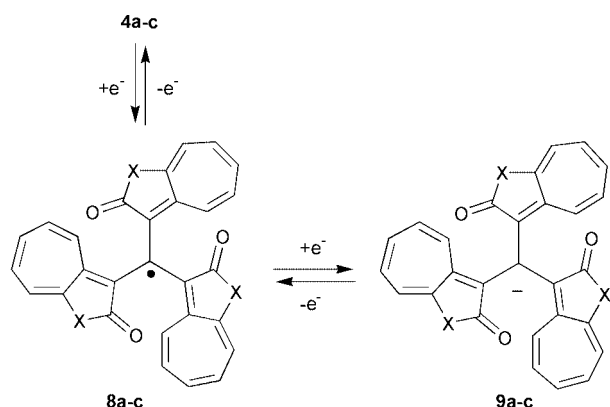
only the carbocations, but also the radical species **8a**–**c** and anions **9a**–**c** These values are less negative as compared with those of the azulene analogues **1a**,**c**. Furthermore, the reduction potential ($E1_{red}$) of **4a**–**c** is in the order of **4a** < **4b** < **4c**. This feature is in accordance with the order of pK_{R^+}-values (stability of cations), **4a** < **4b** < **4c**. The pK_{R^+}-value of **1a** (11.3)

is smaller than those of **4b**,**c** but larger than that of **4a**; however, the values of $E1_{red}$ and $E2_{red}$ are larger than those of **4a**–**c**. It may be considered that the electronic effect as well as the steric effect of the bulky heteroazulene unit bearing the carbonyl group and the substituent on the nitrogen atom contribute to the high pK_{R^+}-values of **4a**–**c**. The stabilizing effect of the heteroazulenes **5a**–**c** will be further investigated.

In summary, efficient synthesis of a fairly stable novel type of tris(heteroazulene)-substituted methyl cation **4a**–**c** was studied. The stabilities of the cations were also examined by the pK_{R^+}-values and their reduction potentials measured by CV. The cations **4b**,**c** exhibited larger pK_{R^+}-values than that of tri(azulen-1-yl)methyl cation **1a**, the pK_{R^+}-value of which is larger than that of **4a**. A good correlation between the pK_{R^+}-values and reduction potentials was obtained for the cations **4a**–**c**. Further studies concerning the synthesis and properties of stable heteroazulene-substituted cations are underway.

Experimental

IR spectra were recorded on a Perkin-Elmer 1640 spectrometer. Mass spectra and high-resolution mass spectra were run on a JMS-AUTOMASS 150 and a JMS-SX102A spectromer. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a JNM-lambda 500 spectrometer using CDCl$_3$ as solvent, and the chemical shifts are given relative to internal SiMe$_4$ standard; *J*-values are given in Hz. Mps were recorded on a Yamato MP-21 apparatus and are uncorrected. The heteroazulenes, 2*H*-cyclohepta[*b*]furan-2-one **5a**,[19] 1,2-dihydro-*N*-phenylcyclohepta[*b*]pyrrol-2-one **5b**,[20] and 1,2-dihydro-*N*-methylcyclohepta[*b*]pyrrol-2-one **5c**[18,21] were prepared as described previously.

General synthetic procedure for heteroazulene-substituted methane derivatives 7a–c

A solution of a heteroazulene **5** (3 mmol) and trimethyl orthoformate **6** (106 mg, 1 mmol) in a mixture of CH$_2$Cl$_2$ (10 cm^3) and trifluoroacetic acid (2 cm^3) was stirred at rt for 24 h. After the reaction was complete, the mixture was poured into aq. NaHCO$_3$. The mixture was extracted with CH$_2$Cl$_2$, and the extract was dried over Na$_2$SO$_4$ and concentrated *in vacuo*. The resulting residue was purified through column chromatography on Al$_2$O$_3$ by using hexane–ethyl acetate (1 : 1) as the eluent to give the products **7a**–**c**. The results are summarized in Table 1.

For **7a**. Reddish orange needles; mp 263–264 °C (from EtOH); δ_H (500 MHz) 5.46 (1H, s, CH), 6.77–6.83 (3H, m, H-6), 6.94–7.02 (9H, m, H-5, -7, -8), 7.38 (3H, d, *J* 11.7, H-4); δ_C (125.7 MHz) 26.9, 106.3, 114.1, 127.2, 130.7, 132.7, 135.2, 148.4, 157.5, 168.5; ν_{max} (KBr)/cm^{-1} 1735, 1269; *m/z* (rel. int.) 448 (M$^+$, 67%), 189 (100) (Found: C, 74.3; H, 3.5. C$_{28}$H$_{16}$O$_6$·$\frac{1}{2}$H$_2$O requires C, 74.25; H, 3.67%).

For **7b**. Reddish orange powder; mp 276–277 °C (from CHCl$_3$–CH$_3$CN); δ_H (500 MHz) 6.26 (1H, s, CH), 6.70 (3H, d, *J* 9.1, H-8), 6.73 (3H, dd, *J* 9.9, 8.5, H-6), 6.84 (3H, dd, *J* 9.9, 9.1, H-7), 6.94 (3H, dd, *J* 11.5, 8.5, H-4), 7.36 (6H, d, *J* 8.4, Ph *o*,*o'*), 7.41 (3H, t, *J* 7.4, Ph *p*), 7.49 (6H, dd, *J* 8.4, 7.4, Ph *m*,*m'*), 7.80 (3H, d, *J* 11.5, H-4); δ_C (125.7 MHz) 28.1, 112.3, 112.3, 128.1, 128.3, 128.8, 128.8, 129.3, 130.7, 130.9, 134.6, 141.2,

145.4, 168.2; ν_{max} (KBr)/cm^{-1} 1685; m/z (FAB) 673 (M$^+$, 100%) (Found: C, 80.8; H, 4.4; N, 6.3. C$_{46}$H$_{31}$N$_3$O$_3$·$\frac{1}{2}$H$_2$O requires C, 80.92; H, 4.72; N, 6.15%).

For **7c**. Reddish orange powder; mp 260–261 °C (from CH$_3$CN); δ_H (500 MHz) 3.51 (9H, s, Me), 6.09 (1H, s, CH), 6.75 (3H, dd, J 10.8, 8.7, H-6), 6.80 (3H, d, J 9.2, H-8), 6.88 (3H, dd, J 11.3, 8.7, H-5), 6.97 (3H, dd, J 10.8, 9.2, H-7), 7.61 (3H, d, J 11.3, H-4); δ_C (125.7 MHz) 26.5, 63.4, 110.6, 113.3, 127.7, 128.1, 130.1, 130.4, 140.8, 145.0, 168.4; ν_{max} (KBr)/cm^{-1} 1654; m/z (rel. int.) 487 (M$^+$, 3.5%), 149 (100) (Found: C, 76.1; H, 5.1; N, 8.7. C$_{31}$H$_{25}$N$_3$O$_3$ requires C, 76.37; H, 5.17; N, 8.62%).

General synthetic procedure for the methylium hexafluorophosphates 7a–c·PF$_6$$^-$

To a stirred solution of heteroazulene-substituted methane derivative **5** (0.25 mmol) in CH$_2$Cl$_2$ (10 cm^3) was added DDQ (70 mg, 0.3 mmol) and the mixture was stirred at rt for 1 h until the reaction was complete. To the reaction mixture was added 60% aq. HPF$_6$ (1 cm^3) and the resulting mixture was filtered. The filtrate was extracted with CH$_2$Cl$_2$ and the extract was dried over Na$_2$SO$_4$ and concentrated. The resulting residue was dissolved in CH$_2$Cl$_2$ and diethyl ether was added to the solution. The precipitated crystals were collected by filtration, washed with diethyl ether to give the salts **4a–c·PF$_6$$^-$**. The results are summarized in Table 1.

For **4a·PF$_6$$^-$**. Reddish brown powder; mp 208–210 °C (decomp.) (from CH$_2$Cl$_2$–Et$_2$O); δ_H (500 MHz; CD$_3$CN) 7.75–8.25 (13H, br m), 8.28–8.60 (2H, br m); δ_C (125.7 MHz; CD$_3$CN) 106.0, 127.1, 135.4, 136.7, 140.9, 141.3, 143.4, 143.9, 144.3, 150.9, 155.4, 163.1, 163.5, 164.6; ν_{max} (KBr)/cm^{-1} 1744, 838; λ_{max} (CH$_3$CN)/nm (log ε) 218 (4.57), 245 (4.67), 280 (4.36), 310 (sh, 3.90), 386 (4.18), 626 (4.72); m/z (FAB) 447 (M$^+$ − PF$_6$) (Found: M$^+$ − PF$_6$, 447.0891. C$_{28}$H$_{15}$F$_6$O$_6$P requires M − PF$_6$, 447.0869) (Found: C, 45.21; H, 1.87. C$_{28}$H$_{15}$F$_6$O$_6$P·HPF$_6$ requires C, 45.55; H, 2.18%).

For **4b·PF$_6$$^-$**. Reddish brown powder; mp 241–243 °C (decomp.) (from CH$_2$Cl$_2$–Et$_2$O); δ_H (500 MHz; CD$_3$CN) 7.35–7.88 (27H, br m), 8.08–8.26 (2H, m), 8.56–8.64 (1H, m); δ_C (125.7 MHz; CD$_3$CN) 112.0, 118.3, 122.9, 129.4, 130.7, 131.0, 131.1, 133.3, 134.6, 134.7, 137.2, 140.5, 140.7, 140.8, 141.9, 149.4, 150.3, 152.0, 152.4, 165.4, 165.5, 166.5, 172.1; ν_{max} (KBr)/cm^{-1} 1685, 839; λ_{max} (CH$_3$CN)/nm (log ε) 226 (4.76), 263 (4.67), 300 (4.62), 330 (sh, 4.43), 400 (4.07), 664 (4.71); m/z (FAB) 672 (M$^+$ − PF$_6$) (Found: M$^+$ − PF$_6$, 672.2313. C$_{46}$H$_{31}$F$_6$N$_3$O$_3$P requires M − PF$_6$, 672.2289) (Found: C, 61.3; H, 3.0; N, 4.9. C$_{46}$H$_{31}$F$_6$N$_3$O$_3$P·$\frac{1}{2}$HPF$_6$ requires C, 62.03; H, 3.45; N, 4.72%).

For **4c·PF$_6$$^-$**. Reddish brown powder; mp 251–253 °C (decomp.) (from CH$_2$Cl$_2$–Et$_2$O); δ_H (500 MHz; CD$_3$CN) 3.56 (9H, s), 7.37–7.70 (6H, br m), 7.78–7.98 (9H, br m); δ_C (125.7 MHz; CD$_3$CN) 27.9, 121.9, 132.4, 133.6, 136.2, 140.0, 140.4, 141.7, 152.1, 166.2, 172.3; ν_{max} (KBr)/cm^{-1} 1654, 838; λ_{max} (CH$_3$CN)/nm (log ε) 226 (4.80), 266 (4.82), 300 (4.77), 326 (4.62), 408 (4.17), 661 (4.87); m/z (FAB) 486 (M$^+$ − PF$_6$) (Found: M$^+$ − PF$_6$, 486.1788. C$_{31}$H$_{24}$F$_6$N$_3$O$_3$P requires M − PF$_6$, 486.1818) (Found: C, 52.1; H, 2.8; N, 6.9. C$_{31}$H$_{24}$F$_6$N$_3$O$_3$P·$\frac{1}{2}$HPF$_6$ requires C, 52.85; H, 3.51; N, 5.96%).

Preparation of the methylium tetrafluoroborate 4a·BF$_4$$^-$

To a stirred solution of a compound **7** (112 mg, 0.25 mmol) in CH$_2$Cl$_2$ (10 cm^3) was added DDQ (70 mg, 0.30 mmol) and the mixture was stirred for 1 h. After evaporation of the CH$_2$Cl$_2$, the residue was dissolved in acetic anhydride (5 cm^3) containing 42% HBF$_4$ (1 cm^3) at 0 °C and the mixture was stirred for 1 h. To the mixture was added Et$_2$O (100 cm^3) and the precipitate was collected by filtration to give **4a·BF$_4$$^-$** (Table 1, run 2) as a brown powder; mp 277–278 °C (decomp.) (from CH$_2$Cl$_2$–Et$_2$O); δ_H (500 MHz) 7.80–8.25 (14H, br m), 8.35–8.47 (1H, br d); ν_{max} (KBr)/cm^{-1} 1749, 1084; λ_{max} (CH$_3$CN)/nm (log ε) 218 (4.57), 245 (4.67), 280 (4.36), 310 (sh, 3.90), 386 (4.18), 626 (4.72); m/z (FAB) 447 (M$^+$ − BF$_4$) (Found: M$^+$ − BF$_4$, 447.0891. C$_{28}$H$_{15}$BF$_4$O$_6$ requires M − BF$_4$, 447.0869) (Found: C, 58.7; H, 2.3. C$_{28}$H$_{15}$BF$_4$O$_6$·$\frac{1}{2}$BF$_4$ requires C, 58.17; H, 2.70%).

Determination of pK_{R^+}-value of the methyl cations 4a–c

Buffer solutions of slightly different acidities were prepared by mixing aqueous solutions of KH$_2$PO$_4$ (0.1 M) and NaOH (0.1 M) (for pH 6.0–8.0), Na$_2$B$_4$O$_7$ (0.025 M) and HCl (0.1 M) (for pH 8.2–9.0), Na$_2$B$_4$O$_7$ (0.025 M) and NaOH (0.1 M) (for pH 9.2–10.8), Na$_2$HPO$_4$ (0.05 M) and NaOH (0.1 M) (for pH 11.0–12.0), and KCl (0.2 M) and NaOH (0.1 M) (for pH 12.0–14.0) in various portions. For the preparation of sample solutions, 1 cm^3 portions of the stock solution, prepared by dissolving 3–5 mg of a cation **4a–c·PF$_6$$^-$** in MeCN (20 cm^3), were diluted to 10 cm^3 with the buffer solution (8 cm^3) and MeCN (1 cm^3). The UV–visible spectrum was recorded for each cation **4a–c** in 10 different buffer solutions. Immediately after recording of the spectrum, the pH of each solution was determined on a pH meter calibrated with standard buffers. The observed absorbance at the specific absorption wavelengths (611 nm for **4a**; 642 nm for **4b**; 637 nm for **4c**) of each cation **4a–c** was plotted against pH to give a classical titration curve, whose midpoint was taken as the pK_{R^+}-value.

Cyclic voltammetry of the methyl cations 4a–c

The reduction potentials of **4a–c** were determined by means of a CV-27 voltammetry controller (BAS Co). A three-electrode cell was used, consisting of Pt working and counter electrodes and a reference Ag/AgNO$_3$ electrode. Nitrogen was bubbled through an acetonitrile solution (4 cm^3) of each compound (0.5 mmol dm^{-3}) and Bu$_4$NClO$_4$ (0.1 mol dm^{-3}) to deaerate it. The measurements were made at a scan rate of 0.1 V s^{-1} and the voltammograms were recorded on a WX-1000-UM-019 (Graphtec Co) X-Y recorder. Immediately after the measurements, ferrocene (0.1 mmol) ($E_{1/2}$ +0.083 V) was added as the internal standard, and the observed peak potentials were corrected with reference to this standard. The compounds exhibited reversible reduction–oxidation waves; the results are summarized in Table 2.

Acknowledgements

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