The Most Stable Methylcation. Tris(6-methoxy-1-azulenyl)methyl Hexafluorophosphate

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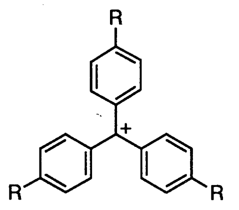
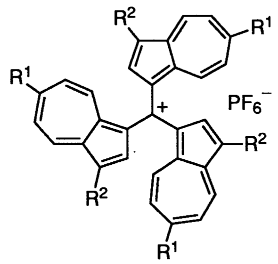
Extremely stable carbocations, tris(6-methoxy-1-azulenyl)methyl, bis(6-methoxy-1-azulenyl)(4-methoxyphenyl)methyl, and (6-methoxy-1-azulenyl)bis(4-methoxyphenyl)methyl cations were prepared and their $pK_R{}^+$ values were determined spectrophotometrically as >14.0, >14.0, and 13.2, respectively. The extreme stability of these methyl cations are attributable to dipolar structures of azulene rings in addition to the contribution of mesomeric effect of three methoxy groups.

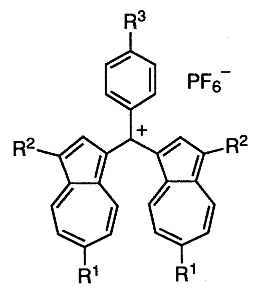
We have recently reported that the synthesis of a series of azulene analogues of triphenylmethyl cation (**1a**), i.e., (tri-1-azulenyl)methyl (**2a**), (di-1-azulenyl)phenylmethyl (**3a**), and (1-azulenyl)diphenylmethyl (**4a**) hexafluorophosphates.[1,2] These cations (**2a**—**4a**) showed extreme stabilities with extraordinary high $pK_R{}^+$ values (**2a**; 11.3, **3a**; 10.5, and **4a**; 3.0) and effectively stabilized by *t*-butyl substituents on their azulene rings by their steric and also by their inductive electronic effects induced by the contribution of C-C hyperconjugations with the π systems.[2-5] The $pK_R{}^+$ value (14.3) of **2b** was the highest value for a methyl cation substituted with only hydrocarbon groups ever reported, and is 3.0 p*K* units higher than that of **2a** and 20.7 p*K* units higher than that of **1a** ($pK_R{}^+$ −6.4).[6] In our continuing efforts to prepare extremely stable carbocations, we synthesized an azulene analogue of tris(4-methoxyphenyl)methyl cation (**1b**), i.e., tris(6-methoxy-1-azulenyl)methyl hexafluorophosphate (**2c**·$PF_6{}^-$). The three methoxy substituents on



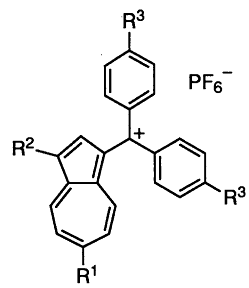
1a: R=H
1b: R=OMe



2a·$PF_6{}^-$: $R^1=R^2=H$
2b·$PF_6{}^-$: $R^1=R^2=t$-Bu
2c·$PF_6{}^-$: R^1=OMe, R^2=H



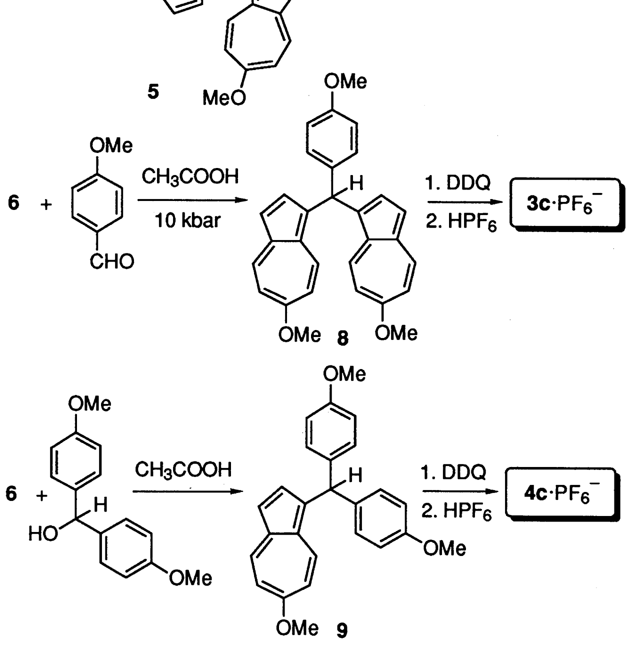
3a·$PF_6{}^-$: $R^1=R^2=R^3=H$
3b·$PF_6{}^-$: $R^1=R^2=t$-Bu, R^3=H
3c·$PF_6{}^-$: $R^1=R^3$=OMe, R^2=H



4a·$PF_6{}^-$: $R^1=R^2=R^3=H$
4b·$PF_6{}^-$: $R^1=R^2=t$-Bu, R^3=H
4c·$PF_6{}^-$: $R^1=R^3$=OMe, R^2=H

1b ($pK_R{}^+$ +0.82)[6] stabilized the parent triphenylmethyl cation (**1a**) by over 7.0 p*K* units so that **2c** was expected to show extremely high stability with large $pK_R{}^+$ value. In the present paper we will report the synthesis and some properties of **2c**, particularly, its high stability, as well as the corresponding 4-methoxyphenyl analogues (**3c** and **4c**) for comparison.

The synthesis of the cation **2c**·$PF_6{}^-$ was accomplished by hydride abstraction from the corresponding methane derivative (**5**) (Scheme 1). The reaction of two molar equivalents of 6-methoxyazulene (**6**) with 6-methoxyazulene-1-carboxaldehyde (**7**) in acetic acid at room temperature did not afford satisfactory results. These conditions were similar to those for the preparation of alkyl substituted tri(1-azulenyl)methanes.[2] However, we found that the high-pressure reaction (10 kbar) of **6** with **7** in a 50% acetic acid solution of dichloromethane at 30 °C for 2 d, afforded the desired **5** in 2.5% yield. Hydride abstraction reaction of **5** with DDQ in dichloromethane at room temperature proceeded under similar conditions for the formation of **2a**.[1-5]



Scheme 1.

The addition of a 60% aqueous HPF_6 solution to the reaction mixture yielded **2c**·PF_6^- in almost quantitative yield.[7] Similarly, **3c**·PF_6^- and **4c**·PF_6^- were also synthesized in high yields by hydride abstraction from bis(6-methoxy-1-azulenyl)-(4-methoxyphenyl)methane (**8**) and (6-methoxy-1-azulenyl)bis-(4-methoxyphenyl)methane (**9**), which were obtained by the reaction of **6** with *p*-anisaldehyde or 4,4'-bismethoxybenzhydrol in 9 and 40% yields, respectively (Scheme 1).[7]

Mass spectra of **2c**—**4c** ionized by FAB showed the correct M^+–PF_6 ion peaks, which indicated that the cationic structure of **2c**—**4c**. The characteristic bands of hexafluorophosphate were observed at around 839 — 841 (strong) and 558 (medium) cm^{-1} in the IR spectra of **2c**—**4c**, which also supported the cationic structure of these compounds. **2c**—**4c** showed strong absorption in the visible region at 620 (log ε 4.87), 624 (4.83), and 535 nm (4.34), respectively. Although the absorption maxima of **2c** and **3c** are comparable with those of the corresponding parent cations (**2a** and **3a**),[2] that of **4c** showed a bathochromic shift of 48 nm. The chemical shifts (^{13}C NMR) of central cationic carbon in **2c**—**4c** (156.31, 164.25, and 172.17 ppm, respectively) are comparable with those in the stable carbocations **2b**—**4b** (157.40, 165.54, and 168.58 ppm, respectively).[2]

The pK_R^+ values of **2c**—**4c** were determined spectrophotometrically at 25 °C in a buffer solution prepared in 50% aqueous MeCN.[2] The values of **2c**—**4c** were summarized in Table 1 along with those of the corresponding parent cations (**2a**—**4a**).[1,2] The exact values of **2c** and **3c** could not be determined by this method. Because these cations did not show any neutralization even in the solution of pH 14. The value of **2b** was extrapolated to be 14.3 by the slight neutralization below pH 14. Therefore, the values for **2c** and **3c** should be higher than that of **2b**. The value of **4c** was determined as 13.2, which is higher by 10.2 p*K* units than that of **4a**. The value of **3c** is beyond 14.0. The value of **2a** (11.3) is much higher than that of **3a** (10.5). Therefore, the value of **2c** is estimated far beyond 14.0.

The redox potentials (V vs. Ag/Ag^+) of **2c**—**4c** measured by cyclic voltammetry in MeCN are also summarized in Table 1 together with those of **2a**—**4a**.[2] The oxidation of **2c** showed waves around +0.90 — +0.98 V, which is due to the oxidation of two azulene rings to form a trication radical. The reduction of **2c** showed a reversible wave at –0.88 V and an irreversible wave at –1.64 V. The more negative reduction potentials of the methoxy derivatives (**2c**—**4c**) than those of **2a**—**4a** correspond to their high pK_R^+ values.

The tropylium ion substituted with bicyclo[2.2.2]octene units[8] and cyclopropenylium ion substituted with dialkylamino groups[9] were reported as stable cyclic cations with high pK_R^+ values around 13. To the best of our knowledge, **2c** and **3c** are the most stable methyl cations which have the highest pK_R^+ values ever reported. This unusual stability of **2c**—**4c** is ascribed to dipolar structures of azulene rings in addition to the contribution of mesomeric effect of the three methoxy groups.

Table 1. pK_R^+ values and redox potentials (V vs. Ag/Ag^+)[a] of **2c**—**4c** and those of **2a**—**4a**[1-3]

	pK_R^+	E_1^{red}	E_2^{red}	E_1^{ox}	E_2^{ox}
2c	>14.0	–0.88	(–1.64)	(+0.90)	(+0.98)
3c	>14.0	–0.80	(–1.63)	(+0.94)	-
4c	13.2	–0.69	(–1.62)	(+1.33)	-
2a	11.3	–0.78	(–1.56)	(+0.98)	(+1.07)
3a	10.5	–0.66	(–1.52)	(+1.04)	-
4a	3.0	(–0.48)	-	(+1.41)	-

[a] Irreversible processes are shown in parentheses.

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7 All new compounds were characterized by their IR, UV, ^1H NMR, and ^{13}C NMR spectral data and elemental analyses and/or mass spectroscopy. Selected physical and spectral data for **2c**, **3c**, and **4c** are given below.
2c; Brown powder; mp 206.0 - 208.0 °C; UV-vis (MeCN) λ_{max}, nm 228 (log ε 4.65), 297 (4.66), 337 (4.62), 430 (4.09), and 620 (4.87); ^1H NMR (600 MHz, DMSO-d_6, 80 °C) δ 8.831 (d, *J*=11.1 Hz, 3H, H_4), 7.753 (d, *J*=11.2 Hz, 3H, H_8), 7.726 (d, *J*=4.3 Hz, 3H, H_3), 7.665 (d, *J*=4.3 Hz, 3H, H_2), 7.622 (dd, *J*=11.1, 4.3 Hz, 3H, H_5), 7.182 (dd, *J*=11.2, 4.3 Hz, 3H, H_7), and 4.099 (s, 9H. 6-OMe).
3c; Brown powder; mp 204.0 - 205.5 °C; UV-vis (MeCN) λ_{max}, nm 224 (log ε 4.60), 250 (4.52), 278 (4.40), 304 (4.60), 345 (4.39), 423 (4.30), 472 (4.25), and 624 (4.83); ^1H NMR (500 MHz, $CDCl_3$) δ 8.572 (d, *J*=11.2 Hz, 2H, H_4), 7.742 (d, *J*=11.2 Hz, 2H, H_8), 7.549 (d, *J*=4.6 Hz, 2H, H_2), 7.505 (dd, *J*=11.2, 2.9 Hz, 2H, H_5), 7.492 (d, *J*=4.6 Hz, 2H, H_3), 7.358 (d, *J*=8.6 Hz, 2H, $H_{2',6'}$), 7.094 (d, *J*=8.6 Hz, 2H, $H_{3',5'}$), 7.046 (dd, *J*=11.2, 2.9 Hz, 2H, H_7), 4.039 (s, 6H, 6-OMe), and 3.996 (s, 3H, 4'-OMe).
4c; Brown powder; mp 104.0 - 106.0 °C; UV-vis (MeCN) λ_{max}, nm 223 (log ε 4.49), 296 (4.54), 352 (4.02), 421 (4.18), and 535 (4.34); ^1H NMR (500 MHz, $CDCl_3$) δ 8.655 (d, *J*=11.2 Hz, 1H, H_4), 7.973 (d, *J*=11.2 Hz, 1H, H_8), 7.831 (dd, *J*=11.2, 2.7 Hz, 1H, H_5), 7.568 (d, *J*=4.9 Hz, 1H, H_2), 7.532 (d, *J*=4.9 Hz, 1H, H_3), 7.456 (dd, *J*=11.2, 2.7 Hz, 1H, H_7), 7.403 (d, *J*=8.8 Hz, 2H, $H_{2',6'}$), 7.309 (d, *J*=8.8 Hz, 2H, $H_{2'',6''}$), 7.130 (d, *J*=8.8 Hz, 2H, $H_{3'',5''}$), 7.121 (d, *J*=8.8 Hz, 2H, $H_{3',5'}$), 4.157 (s, 3H, 6-OMe), 4.021 (s, 3H, 4''-OMe), and 3.988 (s, 3H, 4'-OMe).

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