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Tris(3,6-di-*t*-butyl-1-azulenyl)methyl Cation; Hydrocarbon Cation with the Highest pK_R+ Value

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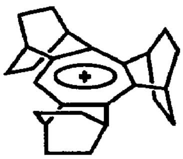
Abstract: Tris(3,6-di-*t*-butyl-1-azulenyl)methyl (**5**), tri(3-*t*-butyl-1-azulenyl)methyl (**10**), and tri(6-*t*-butyl-1-azulenyl)methyl (**11**) hexafluorophosphates were synthesized. Their pK_R^+ values were determined as 14.3, 13.2, and 13.7, respectively, and the value of **5** showed the highest one as carbocation ever reported. The extreme stability of methyl cation **5** is mainly attributable to steric effects of six bulky *t*-butyl groups in addition to the contribution of dipolar structure of three azulene rings.

The syntheses of extremely stable cyclic hydrocarbon carbocation **1** (pK_R^+ 13.5),[1] which consists of tropylium ion annelated with three bicyclo[2.2.2]octene units, tri(3-guaiazulenyl)cyclopropenylium ion (pK_R^+ >10)[2], and tricyclopropylcyclopropenylium ion (pK_R^+ 10.0)[3] have been reported. We recently reported[4] that the synthesis of a series of azulene analogs (**2**, **3**, **4**) of triphenylmethyl cation, and that these cations showed extraordinary high pK_R^+ values (e.g. **2**, R = H, 11.3; R = Me, 11.4) as methyl cations. We also reported the analogous stable dication species.[5]



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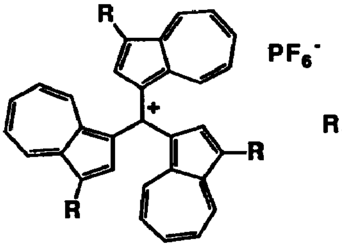

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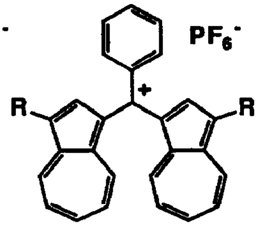

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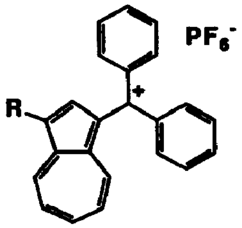

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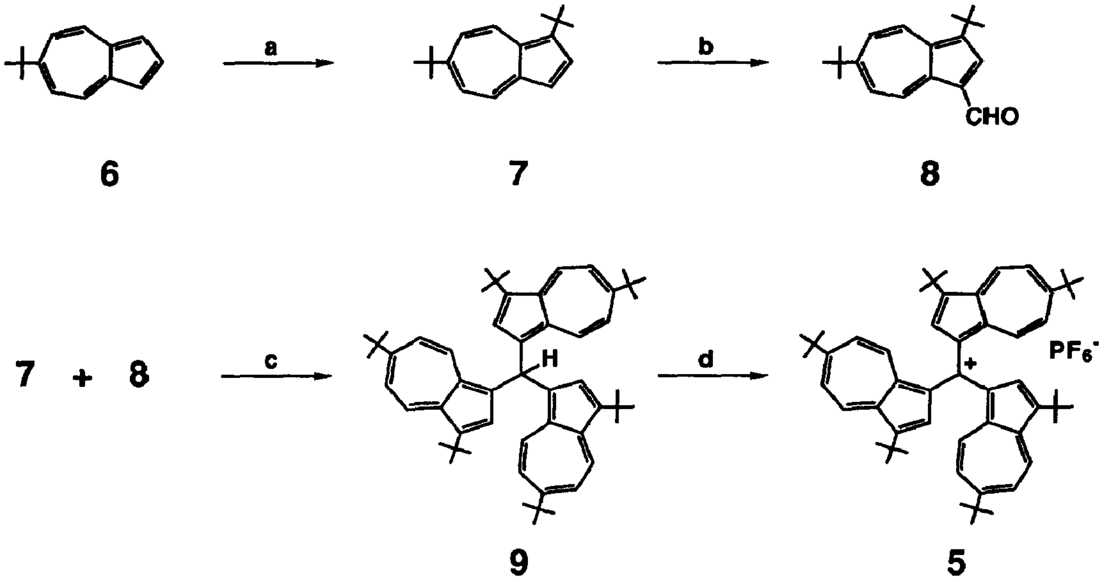
In order to enhance the stability of these triazulenylmethyl cations (**2**), we introduced bulky *t*-butyl groups to each of the three azulene rings. *t*-Butyl groups are expected stabilize **2** by their steric effects, and also by their inductive effects induced by the contribution of C-C hyperconjugation.

Here we report the synthesis of tris(3,6-di-*t*-butyl-1-azulenyl)methyl hexafluorophosphate (5), which shows pK_R^+ 14.3 the highest value ever reported, and also report the synthesis of tri(3-*t*-butyl-1-azulenyl)- and tri(6-*t*-butyl-1-azulenyl)methyl cations.

The synthesis of the cation 5 was accomplished as follows. The reaction of 1,6-di-*t*-butylazulene (7)[6], which was obtained by *t*-butylation[7] of 6-*t*-butylazulene (6),[8] and 1,6-di-*t*-butylazulene-3-carboxaldehyde (8)[6] in acetic acid at room temperature afforded tris(3,6-di-*t*-butyl-1-azulenyl)methane (9)[6] in 71% yield. Hydride abstraction of 9 with DDQ in CH_2Cl_2 followed by addition of 60% HPF_6 solution yielded 5 in quantitative yield.

Scheme I [a]



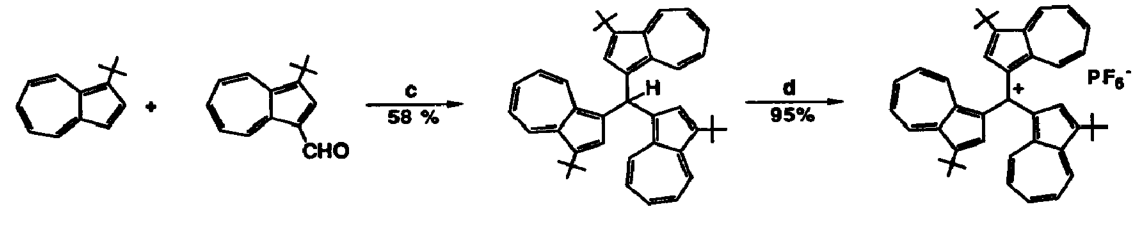
[a] (a) *t*-BuCl, $AlCl_3$, CH_2Cl_2, room temperature, 30 min, 52%; (b) $POCl_3$, DMF, room temperature, 30 min, 83%; (c) AcOH, room temperature, 3 weeks, 71%; (d) DDQ, CH_2Cl_2, room temperature, 60 min, then HPF_6 (aqueous, 60%), 15 min, 100%.

The chemical shift (^{13}C NMR) of central cationic carbon in 5 (151.82 ppm in DMSO-d_6) slightly upfields compared with those in 2 (R=H, 157.40; R=Me, 154.17 in $CDCl_3$) and does considerable upfield shift compared with those in 3 (R=H, 165.54; R=Me, 161.58 in $CDCl_3$). The upfield shifts observed in triazulenylmethyl cations are indicative of decreased charge densities on the cationic carbons and their enhanced thermodynamic stability.

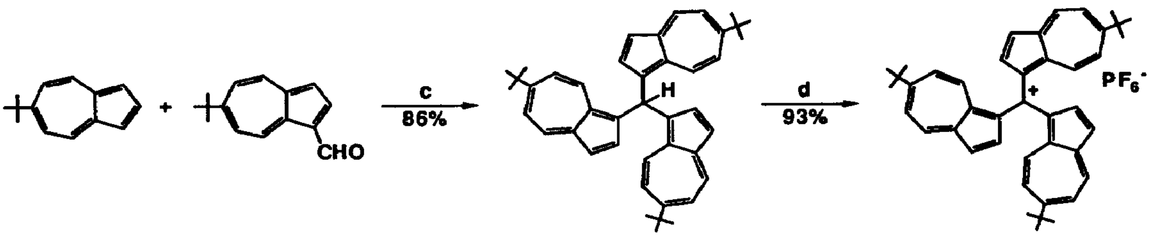
The pK_R^+ value of 5 was determined spectrophotometrically at 24°C in a glycine (0.1M) - NaOH (0.1M) buffer solution (pH 10) prepared in 50% aqueous CH_3CN. By further alkalification with 20% NaOH, the half-neutralization point of 5 was beyond 14, and pK_R^+ value was determined as 14.3.[9] The pK_R^+ value of 5 is much higher than that of 1, and the highest one as carbocation ever reported.

Tri(3-*t*-butyl-1-azulenyl)methyl hexafluorophosphate (**10**)[6] and tri(6-*t*-butyl-1-azulenyl)methyl hexafluorophosphate (**11**)[6] were similarly synthesized starting from 1-*t*-butylazulene, 6-*t*-butylazulene, and their 3- and 1-formyl derivatives, in good yields, respectively.

Scheme II



10



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The pK_R^+ values of **10** and **11** were also determined to be 13.2 and 13.7, respectively, by the similar method for **5**. These pK_R^+ values of **10** and **11** are rather close to that of **5**, and fairly larger than that of **2** (R=Me).

The stability of **5** is also demonstrated by its highly negative reduction potential (E_1 = -0.65 V versus SEC in MeCN by cyclic voltammetry using a Pt electrode with a scan rate of 100 mVs^{-1}) as compared with **10** (-0.59), **11** (-0.61) or **2** (R=H, -0.53; R=Me, -0.59; R=COOMe, -0.35).

Large difference of pK_R^+ values between **10** and **2** (R=Me) is indicating that the extreme stability of **10** is largely attributable to the steric effects of bulky *t*-butyl groups at 3-position. Since the contribution of C-C hyperconjugation of 3-*t*-butyl groups would be fairly small, it is unthinkable that the t-butyl groups effectively stabilize **10** by only its inductive effects. A little high pK_R^+ value of **11** than that of **10** show that the inductive electron donating effect of 6-*t*-butyl groups by C-C hyperconjugation fairly contribute to the stability in addition to the steric effects of *t*-butyl groups. Therefore *t*-butyl group at 6-position largely stabilizes cation than one at 3-position by addition of its inductive effect. Consequently, the high pK_R^+ value of **5** is mainly attributable to steric effects of six bulky *t*-butyl groups in addition to the contribution of dipolar structure of three azulene rings.

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5. Ito, S.; Morita, N.; Asao, T. *Tetrahedron Lett.* **1992**, *33*, 3773.
6. All new compounds were characterized by their IR, UV, ^{1}H NMR, and ^{13}C NMR spectral data and elemental analyses and/or mass spectroscopy. Selected spectral data for the new cations are given below.
   5; Brown powder; mp >300°C; UV (MeCN) λ_{max} 237 nm (log ε 4.71 sh), 248 (4.74), 300 (4.61), 335 (4.36 sh), 389 (4.13 sh), 409 (4.07 sh), 428 (4.00 sh), 611 (4.52 sh), 650 (4.62), and 670 (4.60 sh); ^{1}H NMR (600MHz, DMSO-d_6, 90°C) δ 9.11 (3H, d, J=10.9, H$_4$), 8.07 (3H, dd, J=10.4 and J=2.0, H$_5$), 7.75 (3H, d, J=10.6, H$_8$), 7.56 (3H, dd, J=10.6 and J=2.0, H$_7$), 7.56 (3H, s, H$_2$), 1.54 (27H, s, 6-*t*-Bu), and 1.40 (27H, s, 6-*t*-Bu); ^{13}C NMR (150MHz, DMSO-d_6, 90°C) δ 166.14 (s), 151.82 (s), 144.82 (s), 144.65 (s), 143.70 (s), 141.63 (d), 138.11 (d), 136.51 (d), 129.45 (s), 128.76 (d), 128.47 (d), 38.25 (s), 32.43 (s), 30.80 (q), and 30.63 (q).
   10; Brown powder; mp 252.0 - 255.0°C; UV (MeCN) λ_{max} 244 nm (log ε 4.75), 294 (4.55), 332 (4.27 sh), 370 (4.18 sh), 400 (4.11 sh), 427 (3.93 sh), 578 (4.36 sh), 616 (4.56 sh), 650 (4.61), and 675 (4.54 sh); ^{1}H NMR (400MHz, DMSO-d_6, 80°C) δ 9.18 (3H, d, J=10.2, H$_4$), 8.04 (3H, dd, J=10.0 and J=10.0, H$_6$), 7.91 (3H, dd, J=10.2 and J=10.0, H$_5$), 7.78 (3H, d, J=10.2, H$_8$), 7.72 (3H, s, H$_2$), 7.40 (3H, dd, J=10.2 and J=10.0, H$_7$), and 1.57 (27H, s, 3-*t*-Bu); ^{13}C NMR (22.5MHz, CDCl$_3$, 50°C) δ 154.28 (s), 147.14 (s, 2C), 145.53 (s), 143.61 (d), 142.11 (d), 139.37 (d), 138.03 (d), 131.23 (d), 130.92 (d and s), 33.48 (s), and 31.68 (s).
   11; Brown powder; mp 225.0 - 230.0°C; UV (MeCN) λ_{max} 230 nm (log ε 4.65 sh), 243 (4.66), 261 (4.58 sh), 283 (4.57 sh), 294 (4.59), 323 (4.45 sh), 343 (4.38 sh), 377 (4.16 sh), 415 (4.04 sh), 543 (4.25 sh), 578 (4.51 sh), 615 (4.64), and 632 (4.62 sh); ^{1}H NMR (400MHz, DMSO-d_6, 80°C) δ 8.84 (3H, d, J=10.2, H$_4$), 8.09 (3H, dd, J=10.2 and J=2.0, H$_5$), 7.81 (3H, d, J=4.4, H$_2$), 7.79 (3H, d, J=10.2, H$_8$), 7.72 (3H, d, J=4.4, H$_3$), 7.63 (3H, dd, J=10.2 and J=2.0, H$_7$), and 1.40 (27H, s, 6-*t*-Bu); ^{13}C NMR (22.5MHz, CDCl$_3$, 50°C) δ 167.60 (s), 156.69 (s), 149.83 (s), 144.80 (d), 144.25 (s), 139.77 (d), 137.45 (d), 132.36 (s), 130.65 (d), 129.40 (d), 123.70 (s), 39.36 (s), and 31.68 (q).
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9. Since pH of half-neutralization point was beyond 14, it was determined by extrapolation using the following equation. pH = p$K_R{}^+$ + log[ROH]/[R$^+$]

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