Tris[6-(dimethylamino)-1-azulenyl]methyl Hexafluorophosphate. Extremely Stable Methyl Cation with the Highest pK_R^+ Value

Shunji Ito,* Shigeru Kikuchi, Noboru Morita, and Toyonobu Asao

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

Received January 5, 1999

Extremely stable carbocations, tris[6-(dimethylamino)- and 6-morpholino-1-azulenyl]methyl (**2e** and **2f**), bis[6-(dimethylamino)-1-azulenyl][4-(dimethylamino)phenyl]methyl (**3e**), and [6-(dimethylamino)-1-azulenyl]bis[4-(dimethylamino)phenyl]methyl (**4e**) cations, were prepared, and their properties were fully characterized. These cations showed extremely high stabilities with high pK_R^+ values. The values of **2e** and **3e** were determined spectrophotometrically in DMSO/water as 24.3 ± 0.3 and 21.5 ± 0.2, respectively, which are higher than those of tri(1-azulenyl)methyl and di(1-azulenyl)phenylmethyl cations (**2a** and **3a**) by 13.0 and 11.0 pK units. The value of **4e** was determined to be 14.0 ± 0.1 in 50% aqueous acetonitrile and 14.3 ± 0.2 in DMSO/water, which is higher than that of (1-azulenyl)diphenylmethyl cation (**4a**) by 11.0−11.3 pK units. The extreme stability of these methyl cations is attributable to the dipolar structure of the azulene rings, in addition to the contribution of the mesomeric effect of three dimethylamino groups. The electrochemical reduction of **2e**, **3e**, and **4e** showed a wave at −1.26, −1.22, and −1.14 V (V vs Ag/Ag^+), respectively, upon cyclic voltammetry (CV). The relatively high reduction potentials, compared with those of unsubstituted parent 1-azulenylmethyl cations (**2a**, −0.78; **3a**, −0.66; and **4a**, −0.48 V), also exhibited the electrochemical stabilization of these methyl cations by the dimethylamino substituents. The oxidation of **2e**, **3e**, and **4e** exhibited an irreversible, barely separated two-step, one-electron oxidation wave to generate a trication species at a potential range of 0.50−0.75 V upon CV.

Introduction

Recently, we have reported the synthesis of a series of azulene analogues of triphenylmethyl cation (**1**), i.e., tri(1-azulenyl)methyl, di(1-azulenyl)phenylmethyl, and (1-azulenyl)diphenylmethyl hexafluorophosphates (**2a**·PF_6^-, **3a**·PF_6^-, and **4a**·PF_6^-) and their derivatives (e.g., **2b**,**c**·PF_6^-, **3b**,**c**·PF_6^-, and **4b**,**c**·PF_6^-) (Chart 1).[1] These cations (**2a**−**c**, **3a**−**c**, and **4a**−**c**) showed extreme stabilities with high pK_R^+ values (e.g., **2a**, 11.3; **3a**, 10.5; and **4a**, 3.0). *tert*-Butyl substituents on each azulene ring effectively stabilized these cations by their steric effect and also by their inductive electronic effects induced by the C−C hyperconjugations with the π systems, although the inductive electronic effect of the methyl substituent was small. The value (14.3) of **2c** is the highest for a methyl cation substituted with only hydrocarbon groups ever reported and is 3.0 pK units higher than that of **2a** and 20.7 pK units higher than that of **1** (pK_R^+ −6.4).[2]

In our continuing efforts to prepare extremely stable carbocations, we have investigated the introduction of three methoxy substituents on both the azulenyl and phenyl rings of 1-azulenylmethyl cations (**2a**, **3a**, and **4a**), i.e., tris(6-methoxy-1-azulenyl)methyl, bis(6-methoxy-1-azulenyl)(4-methoxyphenyl)methyl, and (6-methoxy-1-azulenyl)bis(4-methoxyphenyl)methyl hexafluorophosphates (**2d**·PF_6^-, **3d**·PF_6^-, and **4d**·PF_6^-) (Chart 1).[3] The methoxy groups of **2d** (pK_R^+ >14.0), **3d** (pK_R^+ >14.0), and **4d** (pK_R^+ 13.2) stabilized the parent 1-azulenylmethyl cations (**2a**, **3a**, and **4a**) by over 2.7, 3.5, and 10.2 pK units, respectively.

Very recently, Lauresen et al. reported 2,6,10-tris(diethylamino)-4,8,12-trioxa-4,8,12,*12c*-tetrahydrodibenzo[*cd*,*mn*]pyrenylium hexafluorophosphate as an extremely stable carbocation with the highest pK_R^+ value (19.7) for a carbonium ion.[4] Triphenylmethyl cation is also effectively stabilized by dimethylamino substituents. The pK_R^+ value of tris[4-(dimethylamino)phenyl]methyl cation is 9.36,[5] which is much higher than that of tris(4-methoxyphenyl)methyl cation (pK_R^+ 0.82).[2] Amino substituents on both azulenyl and phenyl rings (**2e**, **3e**, and **4e**) are expected to stabilize the methyl cations (**2a**, **3a**, and **4a**) much more effectively. Our recent work on the higher stability of the cations **3f**−**h** and **4f**−**h** (pK_R^+ 13.2−13.8 and 12.5−13.3, respectively),[6] compared with that of **3i**−**k** and **4i**−**k** (pK_R^+ 11.7−13.4 and 5.2−7.0, respectively),[3b] is also in agreement with this postulation.

In this paper, we will report the synthesis and extreme stabilities of tris[6-(dimethylamino)- and 6-morpholino-1-azulenyl]methyl hexafluorophosphates (**2e**,**f**·PF_6^-), as well as the corresponding 4-(dimethylamino)phenyl analogues, i.e., bis[6-(dimethylamino)-1-azulenyl][4-(dimeth-

(1) (a) Ito, S.; Morita, N.; Asao, T. *Tetrahedron Lett.* **1991**, *32*, 773. (b) Ito, S.; Morita, N.; Asao, T. *Tetrahedron Lett.* **1994**, *35*, 751. (c) Ito, S.; Morita, N.; Asao, T. *Tetrahedron Lett.* **1994**, *35*, 3723. (d) Ito, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1409. (e) Ito, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2011. (f) Ito, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2639. (g) Ito, S.; Fujita, M.; Morita, N.; Asao, T. *Chem. Lett.* **1995**, 475. (h) Ito, S.; Fujita, M.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3611. (i) Ito, S.; Morita, N.; Asao, T. *J. Org. Chem.* **1996**, *61*, 5077.

(2) Arnett, E. M.; Bushick, R. D. *J. Am. Chem. Soc.* **1964**, *86*, 1564.

(3) (a) Ito, S.; Kikuchi, S.; Morita, N.; Asao, T. *Chem. Lett.* **1996**, 175. (b) Ito, S.; Kikuchi, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 839.

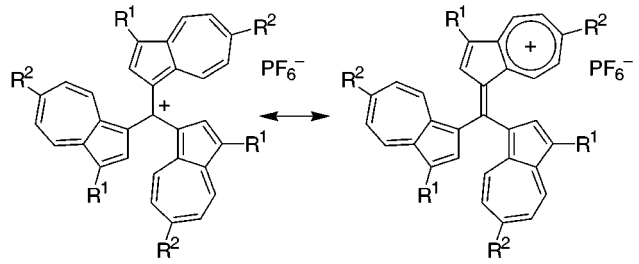
(4) Laursen, B. W.; Krebs, F. C.; Nielsen, M. F.; Bechgaard, K.; Christensen, J. B.; Harrit, N. *J. Am. Chem. Soc.* **1998**, *120*, 12255.

(5) (a) Goldacre, R. J.; Phillips, J. N. *J. Chem. Soc.* **1949**, 1724. (b) Deno, N. C.; Schriesheim, A. *J. Am. Chem. Soc.* **1955**, *77*, 3051.

(6) Ito, S.; Kobayashi, H.; Kikuchi, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 3225.

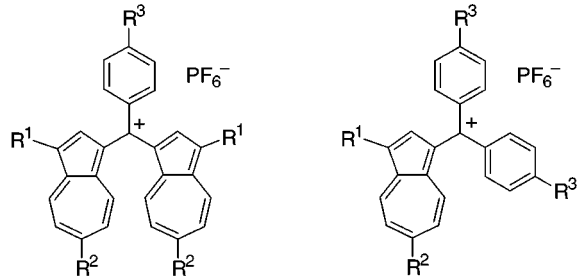
10.1021/jo990029p CCC: $18.00
Published on Web 07/21/1999

Chart 1



2a—f·PF_6^- **2'**·PF_6^-

a: $R^1=R^2=H$
b: $R^1=Me$, $R^2=H$
c: $R^1=R^2=$*tert*-Bu
d: $R^1=H$, $R^2=OMe$
e: $R^1=H$, $R^2=NMe_2$
f: $R^1=H$, $R^2=N(C_2H_4)_2O$



3a—k·PF_6^- **4a—k**·PF_6^-

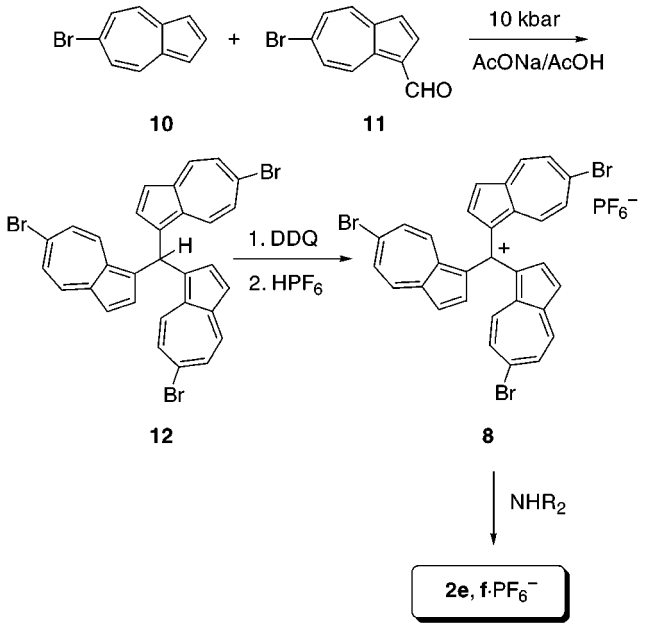
a: $R^1=R^2=R^3=H$
b: $R^1=Me$, $R^2=R^3=H$
c: $R^1=R^2=$*tert*-Bu, $R^3=H$
d: $R^1=H$, $R^2=R^3=OMe$
e: $R^1=H$, $R^2=R^3=NMe_2$
f: $R^1=R^2=H$, $R^3=NMe_2$
g: $R^1=Me$, $R^2=H$, $R^3=NMe_2$
h: $R^1=R^2=$*tert*-Bu, $R^3=NMe_2$
i: $R^1=R^2=H$, $R^3=OMe$
j: $R^1=Me$, $R^2=H$, $R^3=OMe$
k: $R^1=R^2=$*tert*-Bu, $R^3=OMe$

ylamino)phenyl]methyl and [6-(dimethylamino)-1-azulenyl]bis[4-(dimethylamino)phenyl]methyl hexafluorophosphates (**3e**·PF_6^- and **4e**·PF_6^-), for comparison.

Results and Discussion

Synthesis. The successive sequence[1,3,6] of the acid-catalyzed condensation of azulenes with aldehydes and hydride abstraction of the condensation products using DDQ could not be utilized for the synthesis of the salts **2e**·PF_6^- and **3e**·PF_6^-, although this sequence was effective for the synthesis of the salts **2a**·PF_6^- and **3a**·PF_6^-. Neither high- nor normal-pressure reaction of 6-(dimethylamino)azulene (**5**)[7] with 6-(dimethylamino)-1-azulenecarbaldehyde (**6**), which was synthesized from **5** by Vilsmeier formylation in 91% yield, and 4-(dimethylamino)benzaldehyde (**7**) in the presence of acetic acid afforded the desired condensation products, tris[6-(dimethylamino)-1-azulenyl]methane and bis[6-(dimethylamino)-1-azulenyl][4-(dimethylamino)phenyl]methane. However, we found that the tris(6-bromo-1-azulenyl)methyl and bis(6-bromo-1-azulenyl)[4-(dimethylamino)phenyl]methyl hexafluorophosphates (**8**·PF_6^- and **9**·PF_6^-) could be readily replaced by the secondary amines to give the salts **2e**·PF_6^- and **3e**·PF_6^-.

Scheme 1



10 **11** **12** **8** **2e, f**·PF_6^-

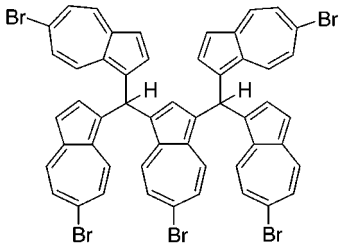
High pressure (10 kbar) was required for the reaction of 6-bromoazulene (**10**)[8] with 6-bromo-1-azulenecarbaldehyde (**11**) to prepare tris(6-bromo-1-azulenyl)methane (**12**) as shown in Scheme 1. This condition was effective for the acid-catalyzed condensation of azulenes with relatively low reactive aldehydes.[1c,1f,3,6] The high-pressure reaction of **10** with **11** in the presence of sodium acetate at 40 °C for 2 d in 50% acetic acid/dichloromethane afforded the desired **12** in 18% yield, together with 1,3-bis[bis(6-bromo-1-azulenyl)methyl]azulene (**13**) (Chart 2) in 24% yield. Addition of the sodium acetate was essential for this reaction. Without addition of the base, the yield of **12** decreased considerably as a result of the decomposition of both products (**12** and **13**) and starting materials (**10** and **11**) in the reaction conditions. Hydride abstraction reaction of **12** with DDQ in dichloromethane at room temperature proceeded under similar conditions for the preparation of **2a**.[1,3,6] Addition of a 60% aqueous solution of HPF_6 afforded the salt **8**·PF_6^- in quantitative yield. The reaction of **8**·PF_6^- with dimethylamine in acetonitrile at room temperature afforded the desired salt **2e**·PF_6^- in 18% yield. Tris(6-morpholino-1-azulenyl)methyl hexafluorophosphate (**2f**·PF_6^-) was also prepared by the similar treatment of **8**·PF_6^- with morpholine in 18% yield.

Salt **3e**·PF_6^- was also synthesized in moderate yield by the similar reaction of bis(6-bromo-1-azulenyl)[4-(dimethylamino)phenyl]methyl hexafluorophosphate (**9**·PF_6^-) with dimethylamine. High-pressure reaction (10 kbar) of 2 molar amounts of **10** with **7** at 40 °C for 1 d in the presence of sodium acetate in 50% acetic acid/dichloromethane afforded bis(6-bromo-1-azulenyl)[4-(dimethylamino)-phenyl]methane (**14**) in 11% yield, together with a diastereomeric mixture of 1,3-bis{(6-bromo-1-azulenyl)-[4-(dimethylamino)phenyl]methyl}-6-bromoazulene (**15a** and **15b**) in 11% yield in a ratio of ca. 1:1. Compounds **15a** and **15b** were readily separable by silica gel column chromatography. Hydride abstraction reaction of **14** with DDQ in dichloromethane at room temperature followed by addition of a 60% aqueous solution of HPF_6 yielded

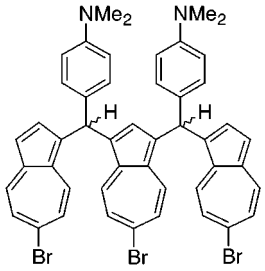
(7) 6-(Dimethylamino)azulene (**5**) was prepared in four steps starting from 4-pyrone in 25% yield according to the literature: (a) Zeller, K.-P. In *Houben-Weyl Methoden der Organischen Chemie*; Müller, E., Ed.; Georg Thiem Verlag: Stuttgart, 1985; Vol. 5, Part 2c, 127. (b) Bauer, W.; Müller-Westerhoff, U. *Tetrahedron Lett.* **1972**, 1021.

(8) McDonald, R. N.; Richmond, J. M.; Curtis, J. R.; Petty, H. E.; Hoskins, T. L. *J. Org. Chem.* **1976**, *41*, 1811.

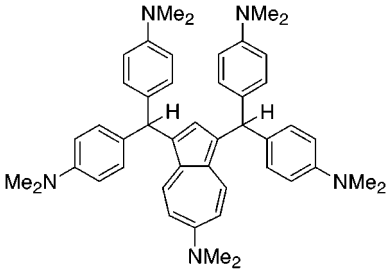
Chart 2



13

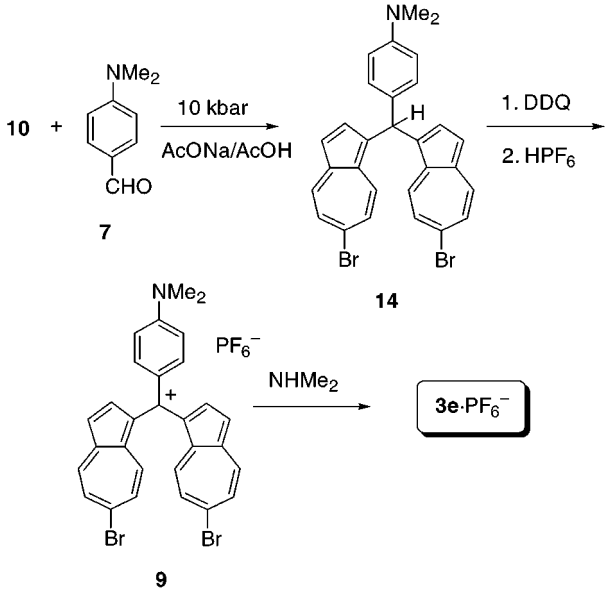


15a, b



18

Scheme 2

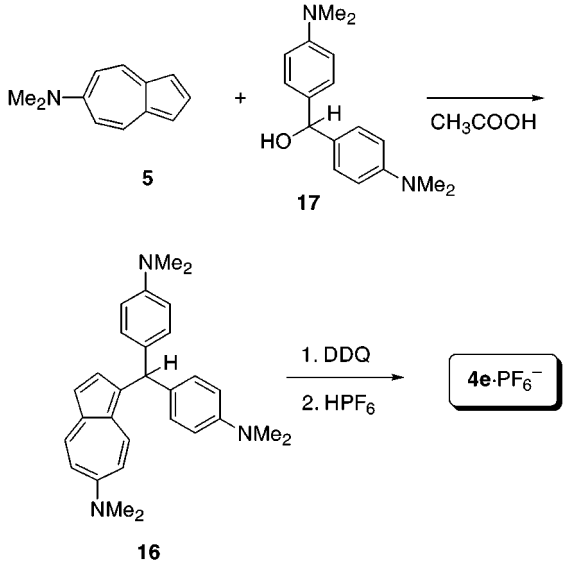


9

9·PF_6^- in 97% yield. The reaction of **9**·PF_6^- with dimethylamine in acetonitrile at room temperature afforded the salt **3e**·PF_6^- in 27% yield (Scheme 2).

In contrast to the synthesis of **2e**·PF_6^- and **3e**·PF_6^-, salt **4e**·PF_6^- was prepared in high yield by the hydride abstraction of [4-(dimethylamino)-1-azulenyl]bis[4-(dimethylamino)phenyl]methane (**16**), which was obtained by the similar acid-catalyzed condensation of 6-(dimethylamino)azulene (**5**) with 4,4′-bis(dimethylamino)benzhydrole (**17**) (Scheme 3). The reaction of **5** with **17** in acetic acid at room temperature for 10 min afforded the desired methane **16** in 61% yield, together with 1,3-bis{bis[4-(dimethylamino)phenyl]methyl}azulene (**18**) in 54% yield. Hydride abstraction of **16** with DDQ in dichloromethane at room temperature followed by addition of a 60% aqueous solution of HPF_6 afforded the salt **4e**·PF_6^- in 95% yield.

Scheme 3



16

Table 1. Longest Wavelength Absorptions and Coefficients of 2e, 3e, and 4e and Those of 2a,d, 3a,d, and 4a,d, for Comparison[1d,3]

sample	λ_{max}, nm	log ϵ	sample	λ_{max}, nm	log ϵ
2a	614	4.70	**3d**	624	4.83
2d	620	4.87	**3e**	614	4.88
2e	617	4.95	**4a**	487	4.16
2f	624	4.96	**4d**	535	4.34
3a	639	4.57	**4e**	594	4.92

Spectroscopic Properties. Mass spectra of **2e**·PF_6^-, **3e**·PF_6^-, and **4e**·PF_6^- ionized by FAB showed the correct $M^+ - PF_6$ ion peaks, which indicated the ionic structure of these compounds. The characteristic bands of hexafluorophosphate were observed at 845 (strong) and 558 (medium) cm^{-1} in their IR spectra, which also supported their ionic structure. These salts **2e**·PF_6^-, **3e**·PF_6^-, and **4e**·PF_6^- also showed strong absorption in visible region, as did the salts **2a**·PF_6^-, **3a**·PF_6^-, and **4a**·PF_6^-, and so on.[1,3,6] Their absorption maxima (nm) and coefficients (log ϵ) are summarized in Table 1. UV−vis spectra of **2e**, **3e**, and **4e** in acetonitrile and those of the related unsubstituted and 6-methoxy analogues (**2a**,**d**, **3a**,**d**, and **4a**,**d**) are shown in Figures 1−3.[1d,3b] Although absorption maxima of tri(1-azulenyl)methyl cations (**2a**) were little influenced by the electron-donating substituents, cations **3e** and **4e** exhibited a hypsochromic shift of 25 nm and a bathochromic shift of 107 nm, respectively, compared with those of the parent unsubstituted cations **3a** and **4a**.[1d] The magnitude of the shifts by the dimethylamino substituents were much larger than those by methoxy substituents. The coefficient tends to increase upon substitution with dimethylamino, as well as with methoxy substituents. These results are in agreement with those of substituted triphenylmethyl cations. The longest

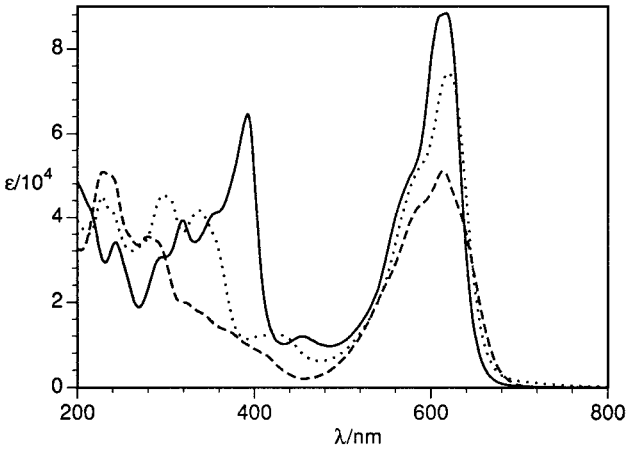


Figure 1. UV−vis spectra of cations **2e** (solid line), **2a** (broken line), and **2d** (dotted line) in acetonitrile.

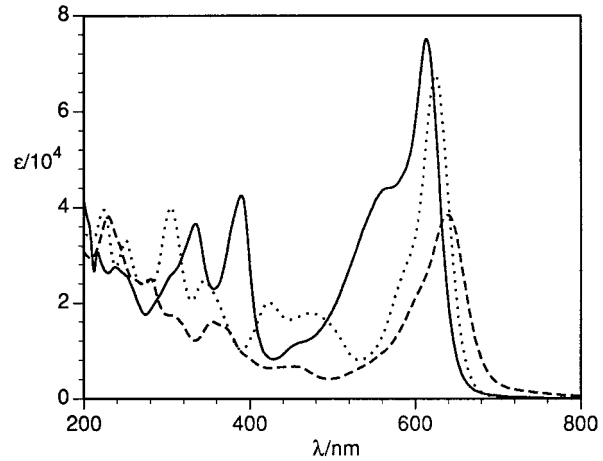


Figure 2. UV−vis spectra of cations **3e** (solid line), **3a** (broken line), and **3d** (dotted line) in acetonitrile.

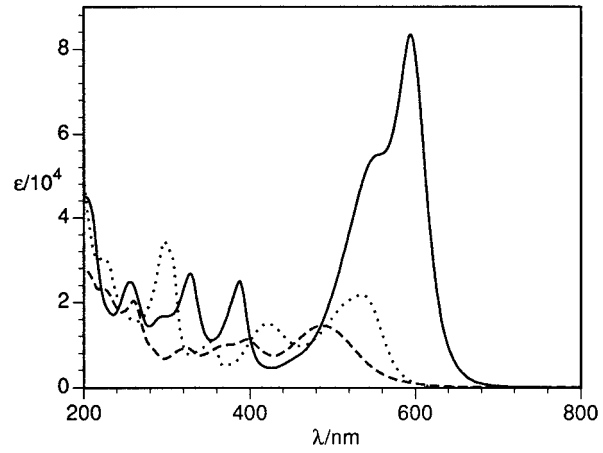


Figure 3. UV−vis spectra of cations **4e** (solid line), **4a** (broken line), and **4d** (dotted line) in acetonitrile.

absorption maximum and coefficient of the triphenylmethyl cation (431 nm (log ϵ 4.60)) increase by substitution with electron-donating groups. Those of the tris(4-dimethylaminophenyl)methyl and tris(4-methoxyphenyl)-methyl cations are 621 (log ϵ 5.02) and 483 nm (log ϵ 5.02), respectively.[9]

In contrast to the high stabilities, the chemical shifts (^{13}C NMR) of the cationic carbons for **2e**, **3e**, and **4e** (156.44, 162.08, and 169.98 ppm, respectively) are almost comparable with those for **2a**, **3a**, and **4c** (157.40, 165.54, and 168.58 ppm, respectively). However, the ^{13}C NMR of cations **2e**, **3e**, and **4e** exhibited considerable upfield shifts in the positions of C-2 (4.66−10.31 ppm), C-3a (9.74−13.64 ppm), C-5 (17.40−22.94 ppm), C-7 (18.50−24.91 ppm), and C-8a (9.17−15.43 ppm) compared with **2a**, **3a**, and **4c**.[1d] Salt **2f**·PF_6^- also showed spectroscopic properties similar to those of **2e**·PF_6^- (see Experimental Section).

Table 2. pK_R^+ Values and Redox Potentials[a] of 2e, 3e, and 4e and Those of 2a,d, 3a,d, and 4a,d, for Comparison[1d,3]

sample	pK_R^+	$E_{1(red)}$	$E_{2(red)}$	$E_{1(ox)}$	$E_{2(ox)}$
2e	24.3 ± 0.3	−1.26	(−1.92)	(+0.50)	(+0.64)
3e	21.5 ± 0.2	−1.22	(−1.89)	(+0.56)	(+0.63)
4e	14.0 ± 0.1	−1.14	(−1.84)	(+0.65)	(+0.75)
2d	>14.0	−0.88	(−1.64)	(+0.90)	(+0.98)
3d	>14.0	−0.80	(−1.63)	(+0.94)	
4d	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] The redox potentials were measured by cyclic voltammetry (V vs Ag/Ag$^+$, 0.1 M Et_4NClO_4 in acetonitrile, Pt electrode, and scan rate 100 mV s^{-1}). In the case of irreversible waves, which are shown in parentheses, E_{ox} and E_{red} were calculated as E_{pa} (anodic peak potential) −0.03 V and E_{pc} (cathodic peak potential) +0.03 V, respectively.

pK_R^+ Values and Redox Potentials. The pK_R^+ value of **4e** was determined spectrophotometrically at 25 °C in a buffer solution prepared in 50% aqueous acetonitrile.[10] The value of **4e** determined in these conditions was 14.0 ± 0.1, which is higher than that of **4a** by 11.0 pK units.[1d] The exact pK_R^+ values of cations **2e** and **3e** could not be determined by these conditions because of their high stabilities. Therefore the system of dimethyl sulfoxide (DMSO)/water/tetramethylammonium hydroxide (0.011 M) was used for the measurement.[11] The H_- scale (Hammet acidity scale) in the system ranges from 12 in water up to 26.2 in 99.6 mol % DMSO/water. The values of **2e** and **3e** could be determined in this system as 24.3 ± 0.3 and 21.5 ± 0.2, respectively. The value of **4e** could also be determined in this system as 14.3 ± 0.2. The neutralization of cations **2e**, **3e**, and **4e** was not completely reversible because of the instabilities of the neutralized products in the basic conditions. Acidification of the alkaline solution of **2e**, **3e**, and **4e** with HCl regenerated the absorption maxima in the visible region by 32%, 57%, and 89%, respectively. The values of **2e** and **3e** are extremely high for a methyl cation. These values are higher than those of **2a** and **3a** by 13.0 and 11.0 pK units (Table 2).[1d] The extreme stability of these methyl cations is attributable to the dipolar structure of the azulene rings, in addition to the contribution of the mesomeric effect of three dimethylamino groups.

The redox potentials (V vs Ag/Ag$^+$) of **2e**, **3e**, and **4e** measured by cyclic voltammetry (CV) in acetonitrile are also summarized in Table 2, together with those of the corresponding unsubstituted and 6-methoxy analogues (**2a**,**d**, **3a**,**d**, and **4a**,**d**).[1d,3] The reduction of **2e**, **3e**, and **4e** showed a reversible wave at −1.14 to −1.26 V and an

(9) (a) Barker, C. C.; Bride, M. H.; Hallas, G.; Stamp, A. *J. Chem. Soc.* **1961**, 1285. (b) Deno, N. C.; Jaruzelshi, J. J.; Schriesheim, A. *J. Am. Chem. Soc.* **1955**, *77*, 3044.

(10) (a) Kerber, R. C.; Hsu, H. M. *J. Am. Chem. Soc.* **1973**, *95*, 3239. (b) Komatsu, K.; Masumoto, K.; Waki, Y.; Okamoto, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2470.

(11) Dolman, D.; Stewart, R. *Can. J. Chem.* **1967**, *45*, 911.

irreversible wave at −1.84 to −1.92 V. The more negative reduction potentials of the dimethylamino derivatives (**2e**, **3e**, and **4e**), lower than those of **2a**, **3a**, and **4a** by 0.48−0.66 V, correspond to their high electrochemical stabilities. The reduction of **2e** also showed a small irreversible wave (−1.51 V) upon CV, just after the reversible wave and before the irreversible wave.

The oxidation of **2e**, **3e**, and **4e** exhibited voltammograms that were characterized by barely separated irreversible waves at 0.50−0.75 V due to the oxidation of two rings to generate a trication radical. The first oxidation potentials of **2e**, **3e**, and **4e** are less positive than those of **2a**,**d**, **3a**,**d**, and **4a**,**d** by 0.48−0.76 V. This behavior resembles the reported two-electron oxidation of 2,6,10-tris(diethylamino)-4,8,12-trioxa-4,8,12,*12c*-tetrahydrodibenzo[*cd*,*mn*]pyrenylium hexafluorophosphate at 1.30 and 1.37 V vs SCE.[4] In the oxidation of **2e**, **3e**, and **4e**, another irreversible wave was observed at 1.27, 1.36, and 1.52 V, respectively, upon CV, after the irreversible two waves.

As expected, these cations showed high stabilities with extremely high pK_R^+ values. These results indicate that the three dimethylamino substituents on both azulenyl and phenyl rings stabilized the methyl cations effectively. The pK_R^+ values of **3e** and **4e** were well beyond 20. To the best of our knowledge, the values of **3e** and **4e** are the highest ones for carbocations ever reported. This unusual stability of **2e**, **3e**, and **4e** is ascribed to the dipolar structures of the azulene rings, in addition to the contribution of the mesomeric effect of the three dimethylamino groups.

Experimental Section

General Procedures. Melting points were determined on a micro melting point apparatus and are uncorrected. Mass spectra were usually obtained at 70 eV. ^{1}H NMR spectra (^{13}C NMR spectra) were recorded at 90 (22.5), 400 (100), 500 (125), or 600 MHz (150 MHz). Voltammetry measurements were carried out with an electrochemical workstation equipped with Pt working and auxiliary electrodes and a reference electrode formed from $Ag/AgNO_3$ (0.01 M) and tetraethylammonium perchlorate (TEAP) as a supporting electrolyte, at the scan rate of 100 mV s^{-1}. Elemental analyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University. High-pressure reactions were carried out using a high-pressure apparatus purchased from Hikari-High Press Inc. ***Caution***: Although there was no report of the explosion of the high-pressure apparatus, proper safty measures should be adopted when handling the high-pressure apparatus.

6-Bromo-1-azulenecarbaldehyde (11). $POCl_3$ (2.2 mL, 24 mmol) was slowly added at 0 °C to a solution of 6-bromoazulene (**10**) (4.15 g, 20.0 mmol) in DMF (80 mL). The solution was stirred at room temperature for 30 min. The resulting solution was poured into ice−water, made alkaline with 2 M aqueous NaOH, and then extracted with CH_2Cl_2. The organic layer was washed with water, dried with $MgSO_4$, and concentrated in vacuo. Purification of the residue by column chromatography on silica gel with CH_2Cl_2 gave the azulene **11** (4.39 g, 93%): violet plates; mp 86.0−87.0 °C; MS *m*/*z* (relative intensity) 234 (M^+, 85); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 242 (4.13), 271 (3.88), 319 (4.74), 362 (3.82), 381 (3.88), 393 (3.86), 538 (2.70); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.35 (s, 1H), 9.27 (d, J = 10.5 Hz, 1H), 8.27 (d, J = 4.2 Hz, 1H), 8.19 (d, J = 10.5 Hz, 1H), 7.92 (dd, J = 10.5, 1.7 Hz, 1H), 7.82 (dd, J = 10.5, 1.7 Hz, 1H), 7.35 (d, J = 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.84 (d), 144.14 (s), 142.46 (d), 138.48 (s), 137.44 (s), 136.96 (d), 135.74 (d), 132.63 (d), 131.52 (d), 127.30 (s), 120.48 (d). Anal. Calcd for $C_{11}H_7OBr$: C, 56.20; H, 3.00. Found: C, 56.55; H, 3.14.

Tris(6-bromo-1-azulenyl)methane (12). A mixture of 6-bromoazulene (**10**) (1.04 g, 5.00 mmol), 6-bromo-1-azulenecarbaldehyde (**11**) (590 mg, 2.51 mmol), and sodium acetate (1.03 g, 1.26 mmol) was placed into a sealed Teflon vessel (9.1 mL) and the vessel was filled with 50% acetic acid solution of CH_2Cl_2. The mixture was left at 10 kbar (40 °C) for 24 h. The reaction mixture was diluted with CH_2Cl_2. The organic solution was washed with 5% aqueous $NaHCO_3$ and water, dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ to afford the methane **12** (199 mg, 18%), 1,3-bis[bis(6-bromo-1-azulenyl)methyl]-6-bromoazulene (**13**) (290 mg, 24%), the recovered **10** (332 mg, 32%), and the recovered **11** (22 mg, 3.7%).

12: blue crystals; mp 236.0−239.0 °C dec; MS *m*/*z* (relative intensity) 628 (M^+, 1.1); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 240 (4.55), 275 (4.93), 297 (5.04), 345 (4.27), 358 (4.28), 629 (3.88); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.974 (d, J = 10.3 Hz, 3H), 7.899 (d, J = 10.5 Hz, 3H), 7.432 (dd, J = 10.3, 1.8 Hz, 3H), 7.348 (d, J = 3.9 Hz, 3H), 7.291 (dd, J = 10.5, 1.8 Hz, 3H), 7.259 (d, J = 3.9 Hz, 3H), 7.198 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.650 (s), 138.579 (d), 135.378 (s), 134.865 (d), 134.786 (s), 133.267 (s), 131.716 (d), 125.985 (d), 125.435 (d), 118.707 (d), 35.975 (d). Anal. Calcd for $C_{31}H_{19}Br_3$: C, 58.99; H, 3.03. Found: C, 58.40; H, 3.33.

13: blue crystals; mp 232.5−235.0 °C dec; MS (FAB) *m*/*z* (relative intensity) 1050 (M^+, 11); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 240 (4.74), 295 (5.29), 358 (4.45), 605 (3.18); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.901 (d, J = 10.3 Hz, 4H), 7.867 (d, J = 10.8 Hz, 2H), 7.739 (d, J = 10.5 Hz, 4H), 7.395 (dd, J = 10.3, 1.8 Hz, 4H), 7.193 (d, J = 10.8 Hz, 2H), 7.171 (d, J = 3.9 Hz, 4H), 7.163 (dd, J = 10.5, 1.8 Hz, 4H), 7.144 (d, J = 3.9 Hz, 4H), 7.081 (s, 2H), 6.935 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.781 (d), 139.590 (s), 138.453 (d), 135.100 (s), 134.927 (s), 134.808 (d), 134.745 (s), 134.123 (s), 134.025 (s), 133.181 (s), 131.897 (d), 131.802 (d), 125.999 (d), 125.244 (d), 125.198 (d), 118.510 (d), 36.163 (d). Anal. Calcd for $C_{52}H_{31}Br_5$: C, 59.18; H, 2.96. Found: C, 59.23; H, 3.42.

Bis(6-bromo-1-azulenyl)[6-(dimethylamino)phenyl]-methane (14). A teflon vessel (9.1 mL) was filled with 6-bromoazulene (**10**) (1.04 g, 5.02 mmol), 4-(dimethylamino)-benzaldehyde (**7**) (382 mg, 2.56 mmol), sodium acetate (1.07 g, 13.0 mmol), and a 50% acetic acid solution of CH_2Cl_2. The mixture was left at 10 kbar (40 °C) for 24 h. The reaction mixture was diluted with CH_2Cl_2. The organic solution was washed with 5% aqueous $NaHCO_3$ and water, dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel with 20% ethyl acetate/CH_2Cl_2 and GPC with $CHCl_3$ to afford the methane **14** (94 mg, 11%), 1,3-bis{(6-bromo-1-azulenyl)[4-(dimethylamino)phenyl]methyl}-6-bromoazulene (**15a** and **15b**) (95 mg, 11%), and the recovered **10** (409 mg, 39%). Compounds **15a** (fr. 1, 32 mg, 3.6%) and **15b** (fr. 2, 20 mg, 2.2%) were separable by column chromatography on silica gel with ethyl acetate/CH_2Cl_2/hexane (2:5:5).

14: greenish blue crystals; mp 156.0−158.0 °C; MS *m*/*z* (relative intensity) 543 (M^+, 51); ES (MeCN) λ_{max}, nm (log ϵ) 235 (3.26), 286 (3.73), 359 (2.75), 607 (4.05); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 10.1 Hz, 2H), 7.91 (d, J = 10.5 Hz, 2H), 7.45 (d, J = 3.8 Hz, 2H), 7.39 (dd, J = 10.1, 1.9 Hz, 2H), 7.29 (dd, J = 10.5, 1.9 Hz, 2H), 7.26 (d, J = 3.8 Hz, 2H), 6.97 (d, J = 8.7 Hz, 2H), 6.63 (d, J = 8.7 Hz, 2H), 6.55 (s, 1H), 2.89 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.04 (s), 139.57 (s), 138.78 (d), 135.99 (s), 134.62 (d), 134.56 (s), 133.53 (s), 132.92 (s), 131.86 (d), 129.25 (d), 125.73 (d), 125.27 (d), 118.59 (d), 112.58 (d), 41.85 (d), 40.66 (q). Anal. Calcd for $C_{29}H_{23}NBr_2$: C, 63.87; H, 4.25; N, 2.57. Found: C, 63.72; H, 4.53; N 2.65.

15a: green crystals; mp 219.0−224.0 °C dec; MS (FAB) *m*/*z* 880 (M^+); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 289 (5.17), 359 (4.22), 610 (2.96); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.906 (d, J = 10.8 Hz, 2H), 7.902 (d, J = 10.3 Hz, 2H), 7.744 (d, J = 10.5 Hz, 2H), 7.375 (dd, J = 10.3, 1.8 Hz, 2H), 7.341 (d, J = 3.9 Hz, 2H), 7.236 (dd, J = 10.5, 1.8 Hz, 2H), 7.212 (d, J = 10.8 Hz, 2H), 7.192 (d, J = 3.9 Hz, 2H), 7.983 (s, 1H), 6.839 (d, J = 8.7 Hz, 4H), 6.552 (d, J = 8.7 Hz, 4H), 6.463 (s, 2H), 2.880 (s, 12H);

^{13}C NMR (150 MHz, $CDCl_3$) δ 148.968 (s), 140.094 (d), 139.617 (s), 138.829 (d), 135.970 (s), 134.700 (s), 134.593 (d), 134.404 (s and s), 134.352 (s), 133.566 (s), 132.521 (s), 132.204 (d), 131.725 (d), 129.188 (d), 125.633 (d), 125.041 (d), 124.875 (d), 118.490 (d), 112.518 (d), 41.833 (d), 40.694 (q). Anal. Calcd for $C_{48}H_{39}N_2Br_3$: C, 65.25; H, 4.45; N, 3.17. Found: C, 65.43; H, 4.72; N, 3.19.

15b: green crystals; mp 160.0−163.0 °C; MS (FAB) *m*/*z* (relative intensity) 880 (M^+, 31); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 243 (4.64), 287 (5.16), 358 (4.22), 610 (2.95); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.890 (d, J = 10.3 Hz, 2H), 7.872 (d, J = 10.5 Hz, 2H), 7.742 (d, J = 10.5 Hz, 2H), 7.373 (dd, J = 10.3, 1.9 Hz, 2H), 7.306 (d, J = 3.9 Hz, 2H), 7.194 (d, J = 10.5 Hz, 2H), 7.175 (dd, J = 10.5, 1.9 Hz, 2H), 7.169 (d, J = 3.9 Hz, 2H), 7.124 (s, 1H), 6.904 (d, J = 8.7 Hz, 4H), 6.332 (d, J = 8.7 Hz, 4H), 6.467 (s, 2H), 2.889 (s, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.973 (s), 140.152 (d), 139.527 (s), 138.709 (d), 135.822 (s), 134.637 (s), 134.544 (d), 134.461 (s), 134.434 (s), 134.321 (s), 133.468 (s), 132.697 (s), 131.912 (d), 131.811 (d), 129.198 (d), 125.700 (d), 125.025 (d), 124.837 (d), 118.467 (d), 112.581 (d), 41.786 (d), 40.692 (q). Anal. Calcd for $C_{48}H_{39}N_2Br_3$: C, 65.25; H, 4.45; N, 3.17. Found: C, 65.22; H, 4.63; N, 3.16.

[6-(Dimethylamino)-1-azulenyl]bis[4-(dimethylamino)-phenyl]methane (16). A solution of 6-(dimethylamino)-azulene (**5**) (343 mg, 2.00 mmol) and 4,4′-(dimethylamino)-benzhydrole (**17**) (541 mg, 2.00 mmol) in glacial acetic acid (12 mL) and CH_2Cl_2 (12 mL) was stirred at room temperature for 10 min under an argon atmosphere. The solvent was removed in vacuo. The residue was diluted with CH_2Cl_2. The organic solution was washed with 5% aqueous $NaHCO_3$ and water. The layer was dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel with ethyl acetate/CH_2Cl_2 to afford the methane **16** (378 mg, 61%), 1,3-bis{bis[4-(dimethylamino)phenyl]-methyl}-6-(dimethylamino)azulene (**18**) (367 mg, 54%), and the recovered **5** (93 mg, 27%).

16: purple needles; mp 234.0−236.0 °C dec; MS *m*/*z* (relative intensity) 423 (M^+, 100); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 265 (4.51), 336 (4.82), 404 (4.29), 504 (2.83); ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.95 (d, J = 11.2 Hz, 1H), 7.94 (d, J = 11.2 Hz, 1H), 7.03 (d, J = 8.8 Hz, 4H), 6.94 (s, 1H), 6.63 (d, J = 8.8 Hz, 4H), 6.38 (dd, J = 11.2, 2.4 Hz, 1H), 6.33 (dd, J = 11.2, 2.4 Hz, 1H), 5.84 (s, 1H), 3.17 (s, 6H), 2.88 (s, 12H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 157.83 (s), 148.62 (s), 136.15 (d), 134.72 (s), 134.05 (s), 133.53 (d), 133.25 (s), 129.96 (d), 129.63 (d), 128.16 (s), 116.15 (d), 112.55 (d), 106.85 (d), 106.70 (d), 48.03 (d), 41.85 (q), 40.87 (q). Anal. Calcd for $C_{29}H_{33}N_3$: C, 82.23; H, 7.85; N, 9.92. Found: C, 82.24; H, 7.72; N, 9.91.

18: violet prisms; mp 229.0−231.5 °C dec; MS *m*/*z* (relative intensity) 675 (M^+, 95); ES (CH_2Cl_2) λ_{max}, nm (log ϵ) 264 (4.77), 347 (4.90), 392 (4.07), 408 (4.11), 539 (2.88); ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.87 (d, J = 11.3 Hz, 2H), 6.99 (d, J = 8.8 Hz, 8H), 6.76 (s, 1H), 6.60 (d, J = 8.8 Hz, 8H), 6.22 (d, J = 11.3 Hz, 2H), 5.80 (s, 2H), 3.10 (s, 6H), 2.87 (s, 24H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 157.46 (s), 148.44 (s), 134.72 (s), 133.01 (d), 132.00 (s), 131.58 (d), 129.50 (d), 128.71 (s), 112.49 (d), 105.87 (d), 47.91 (d), 41.51 (q), 40.81 (q). Anal. Calcd for $C_{46}H_{53}N_5$: C, 81.74; H, 7.90; N, 10.36. Found: C, 81.83; H, 8.02; N, 10.11.

Tris(6-bromo-1-azulenyl)methyl Hexafluorophosphate (8·PF_6^-). DDQ (272 mg, 1.20 mmol) was added at room temperature to a solution of tris(6-bromo-1-azulenyl)methane (**12**) (472 mg, 0.748 mmol) in CH_2Cl_2 (100 mL). After the solution was stirred at the same temperature for 5 min, 60% HPF_6 (10 mL) was added. After an additional 5 min of stirring at room temperature, water was added to the mixture. The resulting suspension was filtered with suction. The organic layer was separated, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (5 mL) and added to ether (100 mL). The precipitated crystals were collected by filtration, washed with ether, and dried in vacuo to give the salt **8**·PF_6^- (580 mg, 100%): purple powder; mp 221.0−224.0 °C dec; MS (FAB) *m*/*z* 627 ($M^+ - PF_6$); ES (MeCN) λ_{max}, nm (log ϵ) 237 (4.77), 289 (4.67), 334 (4.56), 622 (4.75); ^{1}H NMR (600 MHz, MeCN-d_3, 63 °C) δ 8.612 (d, J = 10.6 Hz, 3H), 8.232 (dd, J = 10.6, 1.9 Hz, 3H), 7.983 (br d, J = 4.4 Hz, 3H), 7.829 (d, J = 4.4 Hz, 3H), 7.754 (dd, J = 10.7, 1.9 Hz, 3H), 7.586 (d, J = 10.7 Hz, 3H); ^{13}C NMR (150 MHz, MeCN-d_3, 63 °C) δ 158.610 (s), 150.459 (s), 146.810 (d), 144.876 (s), 140.012 (s), 139.094 (d), 137.064 (d), 136.178 (d), 135.307 (d), 134.750 (s), 125.852 (d). Anal. Calcd for $C_{31}H_{18}Br_3 \cdot PF_6$: C, 48.03; H, 2.34. Found: C, 48.31; H, 2.60.

Tris[6-(dimethylamino)-1-azulenyl]methyl Hexafluorophosphate (2e·PF_6^-). A solution of dimethylamine (406 mg, 9.01 mmol) in acetonitrile (25 mL) was added to a solution of **8**·PF_6^- (234 mg, 0.302 mmol) in acetonitrile (50 mL). After the reaction mixture was stirred at 0 °C for 10 min, the mixture was concentrated in vacuo. After the residue was dissolved in CH_2Cl_2, a 60% HPF_6 solution (3 mL) and water (30 mL) were added to the mixture. The organic layer was separated, washed with water, dried with $MgSO_4$, and concentrated in vacuo. The residue was crystallized from CH_2Cl_2/ether to give the salt **2e**·PF_6^- (37 mg, 18%): deep purple powder; mp 210.0−213.0 °C dec; MS (FAB) *m*/*z* 667 (M^+) and 522 ($M^+ - PF_6$); ES (MeCN) λ_{max}, nm (log ϵ) 243 (4.53), 319 (4.60), 392 (4.81), 455 (4.08), 617 (4.95); ^{1}H NMR (600 MHz, MeCN-d_3, 63 °C) δ 8.218 (d, J = 11.5 Hz, 3H), 7.376 (d, J = 11.8 Hz, 3H), 7.211 (d, J = 4.2 Hz, 3H), 7.185 (d, J = 4.2 Hz, 3H), 7.011 (dd, J = 11.5, 2.8 Hz, 3H), 6.430 (dd, J = 11.8, 2.8 Hz, 3H), 3.273 (s, 18H); ^{13}C NMR (150 MHz, MeCN-d_3, 63 °C) δ 161.022 (s), 156.438 (s), 141.533 (s), 138.799 (d), 137.328 (d), 136.546 (s), 136.372 (d), 133.907 (s), 122.112 (d), 115.268 (d), 113.353 (d), 41.847 (q). Anal. Calcd for $C_{37}H_{36}N_3 \cdot PF_6 \cdot 1/2H_2O$: C, 65.67; H, 5.51; N, 6.21. Found: C, 65.84; H, 5.00; N, 5.89.

Tris[6-(1-morpholino)-1-azulenyl]methyl Hexafluorophosphate (2f·PF_6^-). A solution of morpholine (530 mg, 6.08 mmol) in acetonitrile (20 mL) was added to a solution of **8**·PF_6^- (155 mg, 0.200 mmol) in acetonitrile (30 mL). After the reaction mixture was stirred at 0 °C for 10 min, the mixture was concentrated in vacuo. After the residue was dissolved in CH_2Cl_2, a 60% HPF_6 solution (3 mL) and water (30 mL) were added to the mixture. The organic layer was separated, washed with water, dried with $MgSO_4$, and concentrated in vacuo. The residue was crystallized from $CHCl_3$ to give the salt **2f**·PF_6^- (28 mg, 18%): deep purple powder; mp 223.0−224.0 °C; MS (FAB) *m*/*z* 793 (M^+) and 648 ($M^+ - PF_6$); ES (MeCN) λ_{max}, nm (log ϵ) 244 (4.56), 324 (4.61), 397 (4.83), 459 (4.16), 624 (4.96); ^{1}H NMR (600 MHz, MeCN-d_3, 63 °C) δ 8.318 (d, J = 11.5 Hz, 3H), 7.450 (d, J = 11.7 Hz, 3H), 7.324 (d, J = 4.1 Hz, 3H), 7.300 (d, J = 4.1 Hz, 3H), 7.215 (dd, J = 11.5, 2.9 Hz, 3H), 6.694 (dd, J = 11.7, 2.9 Hz, 3H), 3.835 (t, J = 4.9 Hz, 12H), 3.695 (t, J = 4.9 Hz, 12H); ^{13}C NMR (150 MHz, MeCN-d_3, 63 °C) δ 161.603 (s), 156.507 (s), 142.898 (s), 139.245 (d), 137.837 (s), 137.771 (d and d), 134.005 (s), 122.554 (d), 117.191 (d), 115.458 (d), 66.163 (t), 48.895 (t). Anal. Calcd for $C_{43}H_{42}N_3O_3 \cdot PF_6 \cdot 3/2H_2O$: C, 62.92; H, 5.53; N, 5.12. Found: C, 62.98; H, 5.22; N, 5.13.

Bis(6-bromo-1-azulenyl)[4-(dimethylamino)phenyl]-methyl Hexafluorophosphate (9·PF_6^-). DDQ (87 mg, 0.38 mmol) was added at room temperature to a solution of bis(6-bromo-1-azulenyl)[4-(dimethylamino)phenyl]methane (**14**) (165 mg, 0.303 mmol) in CH_2Cl_2 (30 mL). After the solution was stirred at the same temperature for 5 min, 60% HPF_6 (3 mL) was added. After an additional 5 min of stirring at room temperature, water was added to the mixture. The resulting suspension was filtered with suction. The organic layer was separated, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (3 mL) and added to ether (50 mL). The precipitated crystals were collected by filtration, washed with ether, and dried in vacuo to give the salt **9**·PF_6^- (202 mg, 97%): purple crystals; mp 137.5−140.0 °C; MS (FAB) *m*/*z* 542 ($M^+ - PF_6$); ES (MeCN) λ_{max}, nm (log ϵ) 235 (4.56), 286 (5.03), 346 (4.02), 359 (4.05), 607 (2.75), 659 (2.65); ^{1}H NMR (600 MHz, MeCN-d_3, 63 °C) δ 8.545 (d, J = 10.3 Hz, 2H), 8.133 (d, J = 10.3 Hz, 2H), 8.005 (d, J = 3.2 Hz, 2H), 7.782 (d, J = 3.2 Hz, 2H), 7.742 (d, J = 10.0 Hz, 2H), 7.599 (d, J = 10.0 Hz, 2H), 7.449 (d, J = 8.2 Hz, 2H), 7.053 (d, J = 8.2 Hz, 2H), 3.391 (s, 6H); ^{13}C NMR (150 MHz, MeCN-d_3, 63 °C) δ 164.042 (s), 157.551 (s), 148.663 (s), 145.985 (d), 143.929 (s), 141.408 (d), 139.090 (s), 138.596 (d), 136.664 (d), 134.522 (d), 133.676 (d), 133.288 (s), 129.280 (s), 124.444 (d),

114.422 (d), 40.709 (q). Anal. Calcd for $C_{29}H_{22}NBr_2 \cdot PF_6$: C, 50.53; H, 3.22; N, 2.03. Found: C, 50.08; H, 3.19; N, 2.42.

Bis[6-(dimethylamino)-1-azulenyl][6-(dimethylamino)-phenyl]methyl Hexafluorophosphate (3e·PF_6^-). A solution of dimethylamine (406 mg, 9.01 mmol) in acetonitrile (25 mL) was added to a solution of **9**·PF_6^- (207 mg, 0.300 mmol) in acetonitrile (50 mL). After the reaction mixture was stirred at 0 °C for 10 min, the mixture was concentrated in vacuo. After the residue was dissolved in CH_2Cl_2, a 60% solution of HPF_6 (3 mL) and water (30 mL) were added to the mixture. The organic layer was separated, washed with water, dried with $MgSO_4$, and concentrated in vacuo. The residue was crystallized from CH_2Cl_2/ether to give the salt **3e**·PF_6^- (51 mg, 27%): purple powder; mp 182.0−184.0 °C; MS (FAB) *m*/*z* 617 (M^+) and 472 ($M^+ - PF_6$); ES (MeCN) λ_{max}, nm (log ϵ) 238 (4.44), 334 (4.57), 390 (4.63), 614 (4.88); ^{1}H NMR (600 MHz, MeCN-d_3, 63 °C) δ 8.237 (d, J = 11.6 Hz, 2H), 7.416 (d, J = 11.8 Hz, 2H), 7.364 (d, J = 8.9 Hz, 2H), 7.241 (d, J = 4.4 Hz, 2H), 7.210 (d, J = 4.4 Hz, 2H), 7.112 (dd, J = 11.6, 3.0 Hz, 2H), 6.990 (d, J = 8.9 Hz, 2H), 6.588 (dd, J = 11.8, 3.0 Hz, 2H), 3.309 (s, 12H), 3.219 (s, 6H); ^{13}C NMR (150 MHz, MeCN-d_3, 63 °C) δ 162.08 (br s), 161.478 (s), 153.54 (br s), 142.882 (s), 138.991 (d), 137.868 (d), 137.771 (d), 137.581 (s), 136.331 (d), 133.576 (s), 130.91 (br s), 132.412 (d), 116.862 (d), 114.651 (d), 112.871 (d), 41.960 (q), 40.383 (q). Anal. Calcd for $C_{33}H_{34}N_3 \cdot PF_6 \cdot 2H_2O$: C, 60.64; H, 5.86; N, 6.43. Found: C, 60.53; H, 5.29; N, 6.23.

[6-(Dimethylamino)-1-azulenyl]bis[4-(dimethylamino)-phenyl]methyl Hexafluorophosphate (4e·PF_6^-). DDQ (137 mg, 0.604 mmol) was added at room temperature to a solution of [6-(dimethylamino)-1-azulenyl]bis[4-(dimethylamino)-phenyl]methane (**16**) (212 mg, 0.500 mmol) in CH_2Cl_2 (50 mL). After the solution was stirred at the same temperature for 5 min, 60% HPF_6 (5 mL) was added. After 5 min of stirring at room temperature, water (50 mL) was added to the mixture. The resulting suspension was filtered with suction. The organic layer was separated, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (5 mL) and added to ether (80 mL). The precipitated crystals were collected by filtration, washed with ether, and dried in vacuo to give the salt **4e**·PF_6^- (271 mg, 95%): deep purple powder; mp 249.0−251.0 °C; MS (FAB) *m*/*z* 567 (M^+) and 422 ($M^+ - PF_6$); ES (MeCN) λ_{max}, nm (log ϵ) 204 (4.65), 255 (4.40), 328 (4.43), 387 (4.40), 594 (4.92); ^{1}H NMR (500 MHz, MeCN-d_3) δ 8.127 (d, J = 11.9 Hz, 1H), 7.337 (d, J = 11.9 Hz, 1H), 7.198 (br, 4H), 7.144 (d, J = 4.9 Hz, 1H), 7.137 (dd, J = 11.9, 3.1 Hz, 1H), 7.098 (d, J = 4.9 Hz, 1H), 6.809 (d, J = 8.9 Hz, 4H), 6.674 (dd, J = 11.9, 3.1 Hz, 1H), 3.282 (s, 6H), 3.130 (s, 12H); ^{13}C NMR (125 MHz, MeCN-d_3) δ 169.977 (s), 162.389 (s), 155.536 (s), 145.430 (s), 139.841 (d), 139.404 (s), 139.380 (br d), 138.941 (d), 137.787 (d), 134.460 (s), 128.344 (s), 125.869 (d), 119.719 (d), 116.624 (d), 112.694 (d), 43.060 (q), 40.525 (q). Anal. Calcd for $C_{29}H_{32}N_3 \cdot PF_6$: C, 61.37; H, 5.68; N, 7.40. Found: C, 61.08; H, 5.69; N, 7.57.

pK_R^+ Values of 2e and 3e. Each 1 mL portion of stock solution, prepared by dissolving 2−3 mg of the salts **2e**·PF_6^- and **3e**·PF_6^- in DMSO (20 mL), was pipetted out and added to a 0.11 M (1 mL) or 1.1 M (0.1 mL) aqueous solution of tetramethylammonium hydroxide and an appropriate amount of water. The solution was made up to 10 mL by adding DMSO. The H_- value of the sample solution was calculated by the concentration (mol %) of DMSO in water. The concentration of cations **2e** and **3e** was determined spectrophotomerically. The observed absorbances at the specific absorption maxima of cations **2e** and **3e** were plotted against the *H*-value, giving classical titration curves whose midpoints were taken as the pK_R^+ values.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas "Creation of Delocalization Electronic Systems" (10146204) from the Ministry of Education, Science, Sports and Culture, Japan.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra for all mentioned compounds (**2e**,**f**·PF_6^-, **3e**·PF_6^-, **4e**·PF_6^-, **8**·PF_6^-, **9**·PF_6^-, **11**−**16**, and **18**) and the cyclic voltammograms of **2e**·PF_6^-, **3e**·PF_6^-, and **4e**·PF_6^-. This material is available free of charge via the Internet at http://pubs.acs.org.

JO990029P