Syntheses and Properties of Extremely Stable Di(1-azulenyl)phenylmethyl and (1-Azulenyl)diphenylmethyl Cations Having Dimethylamino Substituents on Their Phenyl Groups

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(Received April 16, 1996)

A series of extremely stable di(1-azulenyl)phenylmethyl and (1-azulenyl)diphenylmethyl cations having dimethylamino substituents on their phenyl groups, i.e., di(1-azulenyl)[4-(dimethylamino)phenyl]methyl (**5a**) and (1-azulenyl)bis[4-(dimethylamino)phenyl]methyl (**6a**) cations and their 3-methyl-1-azulenyl (**5b** and **6b**) and 3,6-di-*t*-butyl-1-azulenyl (**5c** and **6c**) homologs, were synthesized by hydride abstraction from the corresponding hydrides. Their properties were fully characterized. As expected, the pK_{R^+} values of these cations dramatically increased with the dimethylamino substituents on their phenyl groups. The values of **5a**—**c** (pK_{R^+} 13.2—13.8) and **6a**—**c** (pK_{R^+} 12.6—13.3) are higher by 1.4—2.7 and 8.7—9.6 pK units than those of the corresponding analogous phenyl- and diphenylmethyl cations. The redox behavior of each cation was also affected by the substituents. The oxidation of **5a**—**c** in acetonitrile exhibited a barely separated two-step oxidation wave at potential ranges of +0.75— +0.87 and +0.89— +1.01 V vs. Ag/Ag^+ upon cyclic voltammetry (CV), as occurs in the oxidation of tri(1-azulenyl)methyl cations. The wave is ascribed to the oxidation of the two azulene rings to generate a trication species. The oxidation of **6a**—**c** also showed two waves at a narrow potential range at +0.74—+0.92 V. Although the reduction of **6a**—**c** exhibited an irreversible wave at −0.94 V, that of **5a**—**c** showed a reversible wave at −0.87— −0.95 V upon CV. The temperature-dependent ^{1}H NMR spectra of **5b** and **6b** were also examined to clarify their stereochemistries. Stereoisomerizations due to the pyramidal dimethylamino substituents in addition to the propeller conformations of three aromatic rings were observed by low-temperature NMR studies. At higher temperature the NMR reflects the rapid isomerization of these stereoisomerisms.

We have recently reported the synthesis and properties of a series of azulene analogs of triphenylmethyl cation (**1**): i.e., tri(1-azulenyl)methyl (**2a**), di(1-azulenyl)phenylmethyl (**3a**), and (1-azulenyl)diphenylmethyl (**4a**) hexafluorophosphate and their derivatives (e.g., **2b**—**c**, **3b**—**c**, and **4b**—**c**) (Chart 1).[1] These cations were synthesized by hydride abstraction of the corresponding hydrocarbons. They showed extreme stabilities with high pK_{R^+} values (e.g., **2a**; 11.3, **3a**; 10.5, and **4a**; 3.0, respectively).[1a—1c] The high stabilities of these cations can be explained by the large π-conjugative effect between the central cationic carbon and the azulene rings (e.g. **2′**). Although the pK_{R^+} values of the methyl derivatives (**2b**, **3b**, and **4b**) were comparable with those of the parent cations (**2a**, **3a**, and **4a**), bulky *t*-butyl substituents on the azulene rings effectively stabilized these cations by steric and also inductive electronic effects, the latter being induced by the contribution of C–C hyperconjugation.[1a—1c] The pK_{R^+} value (14.3) of the hexa-*t*-butyl derivative **2c** is the highest one ever reported for a methyl cation substituted with only hydrocarbon groups, and is 3.0 pK units higher than that of **2a** and 20.7 pK units higher than that of **1** (pK_{R^+} − 6.44).[2]

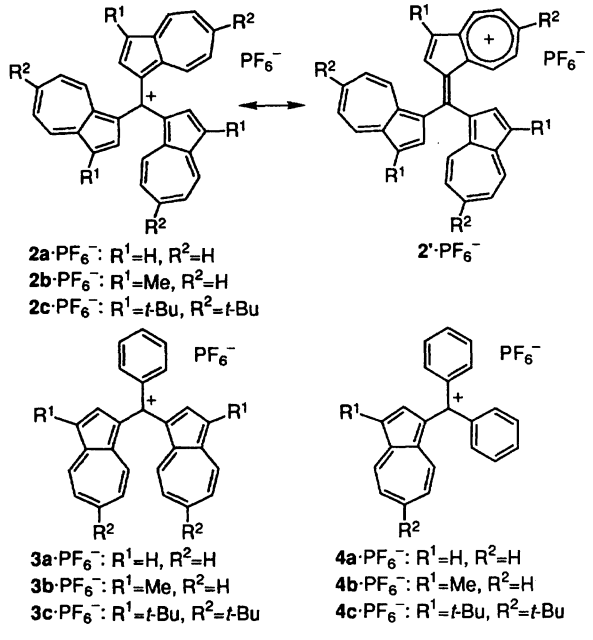


Chart 1.

As part of our continuing effort to construct extremely stable carbocations, we herein report the synthesis and properties of a series of di(1-azulenyl)phenylmethyl and (1-azulenyl)diphenylmethyl hexafluorophosphates having dimeth-

ylamino substituents on their phenyl groups: i.e., di(1-azulenyl)[4-(dimethylamino)phenyl]methyl (**5a**) and (1-azulenyl)bis[4-(dimethylamino)phenyl]methyl (**6a**) hexafluorophosphate and their derivatives (**5b**—**c** and **6b**—**c**) (Chart 2). The electron donating substituents will reflect the enlargement of the pK_{R^+} values owing to the contribution of dimethyl(4-methylidene-2,5-cyclohexadien-1-ylidene)ammonium structures such as **5′** and **6′**.[3] The redox behaviors of these cations will also be affected by the dimethylamino substituents, which will not only increase the reduction potentials due to the stabilization of the cations, but will also facilitate the oxidation of the carbocations:[4] e.g., both of **5a**—**c** and **6a**—**c** will produce a trication species by the oxidation of the two aromatic rings due to the contribution of the ammonium structures (**5′** and **6′**), as occurs in the oxidation of tri(1-azulenyl)methyl cations.[1c] Therefore the substitution of the dimethylamino groups on the phenyl rings will provide the cations (**3a**—**c** and **4a**—**c**) with both high thermodynamic stabilities and multistage redox properties.[5] The temperature-dependent NMR spectra of **5b** and **6b** were also examined to clarify their stereochemistries. These studies revealed a pyramidal structure of the dimethylamino substituents in addition to a propeller conformation of the three aromatic rings. The pyramidal structure of the substituents of **5b** and **6b** suggested that the high thermodynamic stabilities of the cations **5a**—**c** and **6a**—**c** were due to the high contribution of azulenium ion structures (**5″** and **6″**).

Results and Discussion

Synthesis. The syntheses of the cations **5a**—**c** and **6a**—**c** were accomplished by hydride abstraction from the corresponding hydrides (**7a**—**c** and **8a**—**c**) according to the procedure which had been reported for the preparation of **3a**—**c** and **4a**—**c** (Scheme 1).[1] The reaction of two molar amounts of azulene (**9a**) and its 1-methyl (**9b**) and 1,6-di-*t*-butyl (**9c**)[1c] derivatives with 4-(dimethylamino)benzaldehyde in acetic acid at 60 °C for 1—2 d did not afford satisfactory results (Table 1) because of the low reactivities of the aldehyde with these azulenes (**9a**—**c**) and the instabilities of the products (**7a**—**c**) under the reaction conditions. However, the high-pressure reaction (10 kbar) of **9a**—**c** with

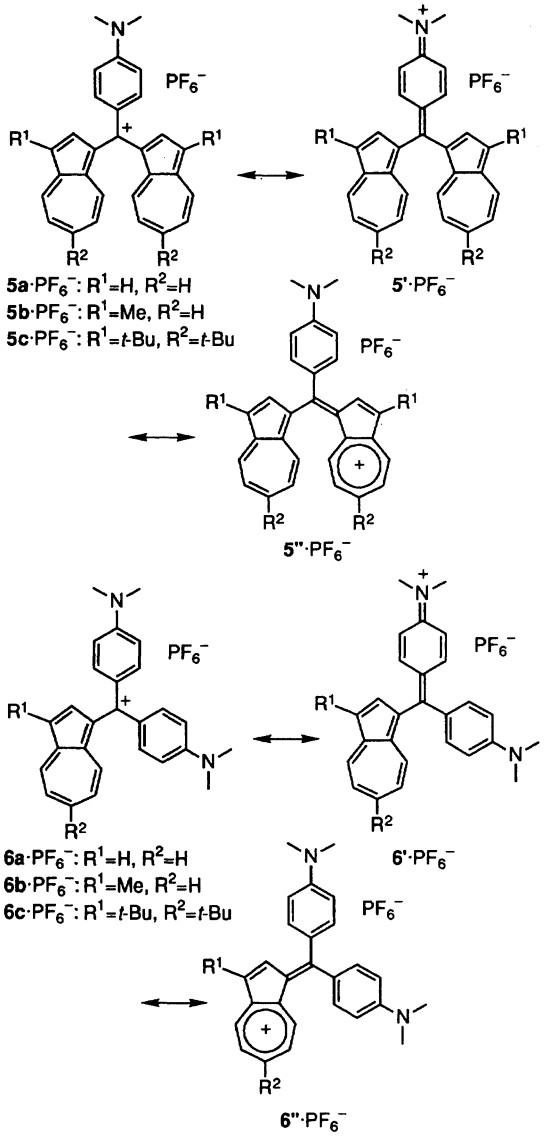
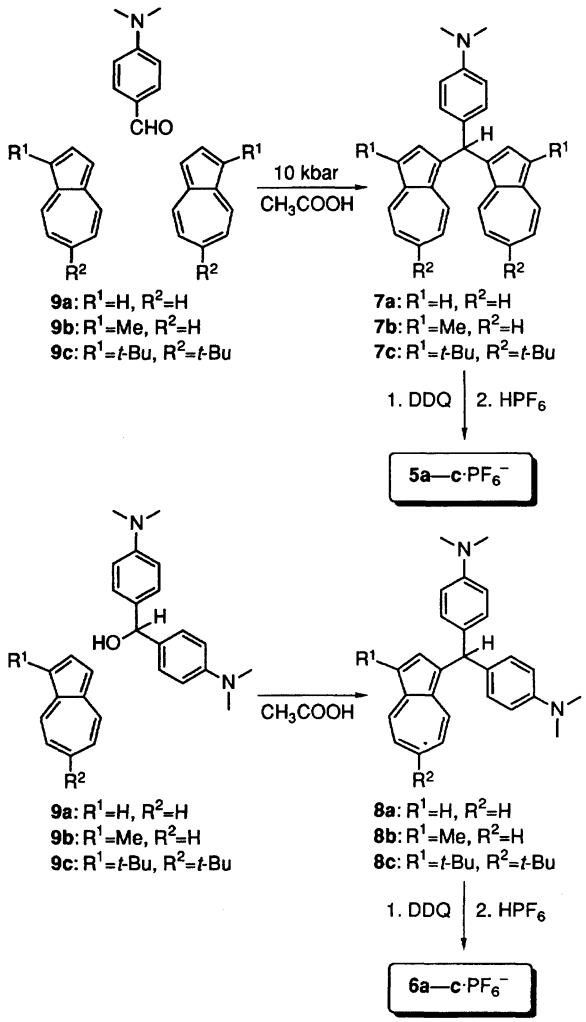


Chart 2.



Scheme 1.

Table 1. The Reaction of Azulenes **9a—c** with 4-(Dimethylamino)benzaldehyde or Bis[4-(dimethylamino)-phenyl]methanol in the Presence of Acetic Acid and the Synthesis of **5a—c** and **6a—c**

Entry	R^1	R^2	Conditions	Yield (%) of **7** and **8**		Yield (%) of **5**·PF_6^- and **6**·PF_6^-	
1	H	H	—	**7a**	24	**5a**·PF_6^-	91
2			10 kbar	**7a**	28		
3	Me	H	—	**7b**	24	**5b**·PF_6^-	99
4			10 kbar	**7b**	76		
5	*t*-Bu	*t*-Bu	—	**7c**	23	**5c**·PF_6^-	98
6			10 kbar	**7c**	57		
7	H	H	—	**8a**	66	**6a**·PF_6^-	99
8	Me	H	—	**8b**	88	**6b**·PF_6^-	98
9	*t*-Bu	*t*-Bu	—	**8c**	71	**6c**·PF_6^-	85

the aldehyde in a 50% acetic acid solution of dichloromethane at 30 °C for 1 d, afforded **7a—c** in 28—76% yields, along with 1,3-bis{(1-azulenyl)[4-(dimethylamino)phenyl]-methyl}azulene (**10**) in 18% yield, in the case of **9a** (Chart 3). Hydride abstraction[1] of **7a—c** with DDQ in dichloromethane at room temperature, followed by the addition of a 60% aqueous HPF_6 solution, yielded **5a—c** (91—99%) as a hexafluorophosphate (Table 1).

The reaction of azulenes (**9a—c**) with bis[4-(dimethylamino)phenyl]methanol in acetic acid at room temperature afforded **8a—c** in 66—88% yields, together with 1,3-bis{bis[4-(dimethylamino)phenyl]methyl}azulene (**11**) in 17% yield, in the case of **9a** (Chart 3). Hydride abstraction of **8a—c** with DDQ in dichloromethane at room temperature, followed by the addition of a 60% aqueous HPF_6 solution, yielded **6a—c**·PF_6^- in 85—98% yields (Table 1). These cations (**5a—c** and **6a—c**) were extremely stable and storable in the crystalline state.

Thermodynamic Stability. As a criterion of thermodynamic stabilities, the pK_{R^+} values of these cations (**5a—c** and **6a—c**) were determined spectrophotometrically at 25 °C in a buffer solution prepared in 50% aqueous acetonitrile.[1,6] Their pK_{R^+} values and those of the analogous phenyl derivatives (**3a—c** and **4a—c**) are summarized in Table 2. As expected by the stabilizing effect of the dimethylamino substituent,[3] the stabilities of **3a—c** and **4a—c** are considerably increased by the introduction of the substituents on each phenyl group. The pK_{R^+} values of **5a** (13.2±0.1) and **6a** (12.6±0.1) are extremely high for a methyl cation and are comparable with each other. These values are higher by 2.7 and 8.0 pK units than those of **3a** and **4a**, respectively, and higher by 1.9 and 1.3 pK units than that of tri(1-azulenyl)methyl cation (**2a**; 11.3).[1a—1c] The stabilizing ability of 1-azulenyl groups must be considerably higher than that of 4-(dimethylamino)phenyl groups, because the pK_{R^+} value of **2a** is larger than that of tris[4-(dimethylamino)phenyl]methyl cation (pK_{R^+} 9.36).[3] However, the stability of the cations **5a** and **6a** was appreciably higher than that of **2a**. These results are explained if the steric hindrance between the three azulene rings of **2a** contributes to the weakening the stabilization. Consequently, the high stabilizing effect of substituted methyl cations was available from the combination of 1-azulenyl and 4-(dimethylamino)phenyl groups.

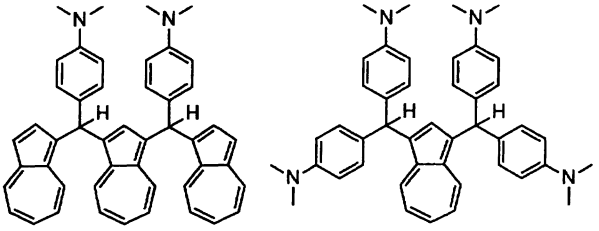


Chart 3.

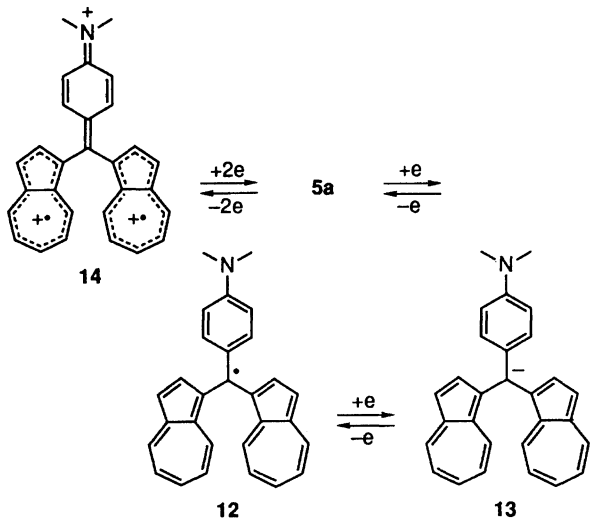
The stabilities of these cations were also little affected by the methyl substituents on their azulene rings. The pK_{R^+} values of the methyl derivatives **5b** (13.4±0.1) and **6b** (12.5±0.1) are comparable with those of **5a** and **6a**. In contrast to the methyl substituents, *t*-butyl substituents on the azulene rings stabilized these cations (**5a** and **6a**). The pK_{R^+} values of the *t*-butyl derivatives **5c** (13.8±0.1) and **6c** (13.3±0.1) are higher by 0.6 and 0.7 pK units than those of **5a** and **6a**, respectively. The neutralization of these cations (**5a—c** and **6a—c**) was not completely reversible. This may due to the instability of the neutralized products under the conditions of the pK_{R^+} measurement. After the pK_{R^+} measurement, acidification of the alkaline solution of **5a—c** and **6a—c** with HCl regenerated the characteristic absorption of the cations in visible region in 66—100% (Table 2).

Redox Behaviors. The redox potentials (V vs. Ag/Ag^+) of **5a—c** and **6a—c** measured by cyclic voltammetry (CV) in acetonitrile together with those of the analogous phenyl derivatives (**3a—c** and **4a—c**), are also summarized in Table 2.[1c] The reduction behaviors of **5a—c** are identical to those of the phenyl analogues (**3a—c**). The reduction of **5a—c** in acetonitrile showed a reversible wave at −0.87— −0.95 V and an irreversible wave at −1.64— −1.72 V upon the CV. These two waves are ascribed to the formation of a radical and an anion species such as **12** and **13**, respectively (Scheme 2). The reduction potentials of **5a—c** are more negative than those of **3a—c** by about 0.2 V; this indicates the stabilization of the methyl cations by the dimethylamino substituent on the phenyl groups. The most negative reduction potential of the *t*-butyl derivatives **5c** among these compounds corresponds to its high electrochemical stability. All the first reduction waves (−0.94 V) of **6a—c** were in the potential range comparable with those of **5a—c**. These results indicate the high electrochemical

Table 2. pK_{R^+} Values and Redox Potentials[a] of **5a—c**, **6a—c**, **3a—c**, and **4a—c**[1a—1c]

	pK_{R^+} [b]	E_1^{ox}	E_2^{ox}	E_1^{red}	E_2^{red}
5a	13.2(90%)	(+0.87)	(+1.01)	−0.87	(−1.64)
5b	13.4(90%)	(+0.82)	(+0.99)	−0.89	(−1.69)
5c	13.8(66%)	+0.75	+0.89	−0.95	(−1.72)
6a	12.6(100%)	(+0.76)	(+0.92)	(−0.94)	—
6b	12.5(78%)	(+0.74)	(+0.86)	(−0.94)	—
6c	13.3(97%)	(+0.74)	(+0.83)	(−0.94)	—
3a	10.5	(+1.04)	—	−0.66	(−1.52)
3b	10.8	(+0.90)	—	−0.70	(−1.57)
3c	12.4	+0.88	(+1.38)	−0.78	(−1.64)
4a	3.0	(+1.41)	—	−0.48	—
4b	3.7	—	—	—	—
4c	4.6	(+1.53)	—	−0.59	(−1.54)

a) The redox potentials were measured by cyclic voltammetry (V vs. Ag/Ag^+, 0.1 M Et_4NClO_4 in MeCN, Pt electrode, and scan rate 100 mV s^{-1}) (1 M = 1 mol dm^{-3}). Irreversible processes were shown in parentheses. b) Regenerated absorption maxima (%) of the cations in visible region by immediate acidification of the alkaline solution with HCl after the pK_{R^+} measurement were shown in parentheses.



Scheme 2.

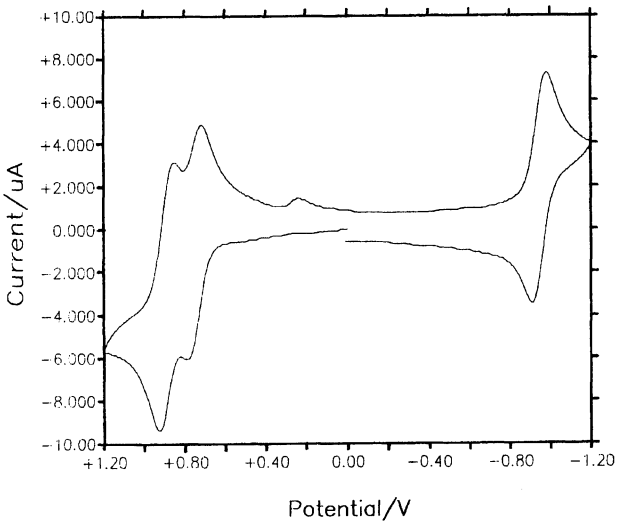


Fig. 1. Cyclic voltammogram of cation **5c** in acetonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate, 100 mV s^{-1}.

stabilities of **6a—c**. In contrast to the reduction of the analogous phenyl derivatives (**4a—c**), all the reduction waves of **6a—c** were irreversible under the conditions of the CV measurement.

As expected, the oxidation behaviors of **5a—c** were apparently distinct from those of the phenyl analogues (**3a—c**) and rather comparable with those of the related tri(1-azulenyl)methyl cations (**2a—c**). The oxidation of **5a—c** exhibited voltammograms that were characterized by a barely separated two-step oxidation wave at +0.75—+0.87 and +0.89—+1.01 V. These oxidation potentials are in the potential range comparable with those of **3a—c**. The two waves for the oxidation of **5a** and **5b** were irreversible under the condition of the CV measurement. The *t*-butyl substituent on the azulene rings apparently stabilizes the oxidation states, as indicated by the oxidation of **5c**. The oxidation of **5c** exhibited a barely separated two-step reversible wave upon the CV, as shown in Fig. 1. The two-step oxidation processes are due to generating a trication diradical species such as **14**. The dimethylamino substituent facilitated the oxidation of the two azulene rings of **5a—c**, owing to the contribution of dimethyl(4-methylidene-2,5-cyclohexadien-1-ylidene)ammonium structure (**5′**). These results are in contrast to those of **3a—c**.

The oxidation behavior of **6a—c** was identical to that of **5a—c**. The oxidation of **6a—c** showed a barely separated two-step oxidation wave at +0.74—+0.76 and +0.83—+0.92 V, which was in the potential range comparable with those of **5a—c**. The two-step oxidation processes are also attributable to the oxidation of both 1-azulenyl and 4-(dimethylamino)-phenyl rings. In contrast to the oxidation of **5a—c**, all the oxidation waves of **6a—c** were irreversible under the conditions of the CV measurement. These results clearly indicate that the dimethylamino substituents on the phenyl groups of **5a—c** and **6a—c** effectively stabilize the cations by their mesomeric effects and facilitate the oxidation of the other two rings. As expected, the dimethylamino substituents provided multistage redox properties to the di(1-azulenyl)phen-

ylmethyl and (1-azulenyl)diphenylmethyl cations (**3a**—**c** and **4a**—**c**).

Spectroscopic Properties. High-resolution mass spectra of **5a**—**c** and **6a**—**c** ionized by FAB showed the correct M^+–PF_6 ion peaks, which indicated the cationic structure of these compounds. The characteristic bands for the counter ion (PF_6^-) were observed around 840 (strong) and 558 (medium) cm^{-1} in their IR spectra, which also supported the cationic structure of these compounds. UV-vis spectra of **5a** and **6a** in acetonitrile along with those of the related phenyl analogues (**3a** and **4a**) were shown in Figs. 2 and 3. The strong absorption of **5a**—**c** in the visible region (**5a**; 615 (log ε 4.74), **5b**; 631 (4.75), and **5c**; 627 nm (4.77)) exhibited a hypsochromic shift by 24, 45, and 54 nm, respectively, compared with those of **3a**—**c**. However, those of **6a**—**c** (**6a**; 608 (log ε 4.86), **6b**; 605 (4.86), and **6c**; 606 nm (4.87)) showed an appreciable bathochromic shift by 121, 110, and 117 nm, respectively, compared with those of **4a**—**c**.[7]

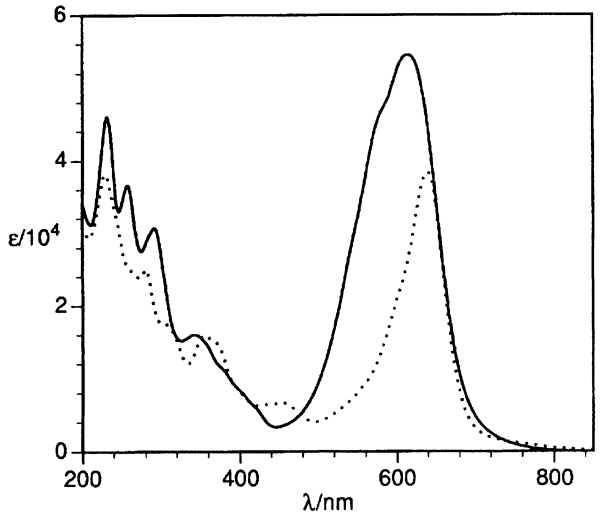


Fig. 2. UV-vis spectra of cation **5a** (solid line) and cation **3a** (broken line) in acetonitrile.

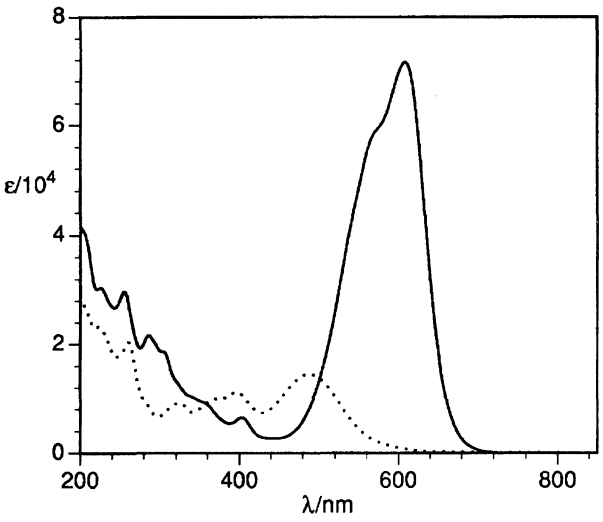
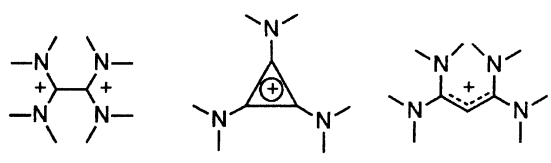


Fig. 3. UV-vis spectra of cation **6a** (solid line) and cation **4a** (broken line) in acetonitrile.

The ^{1}H NMR chemical shift of the methine protons of **7a**—**c** was slight upfield, compared with those of di(1-azulenyl)phenylmethane and its related derivatives. The methine proton signals of **8a**—**c** showed a similar behavior to those of **7a**—**c**. These signals disappeared on the ^{1}H NMR spectra of **5a**—**c** and **6a**—**c**. Thus, the ^{1}H NMR spectra also indicated a cationic structure of these compounds. In contrast to the high stabilities, the chemical shift (^{13}C NMR) of the central cationic carbons for **5a**—**c** (**5a**; 164.17, **5b**; 161.58, and **5c**; 161.49 ppm) and **6a**—**c** (**6a**; 170.54, **6b**; 169.69, and **6c**; 169.75 ppm) was comparable with those of **3a**—**c** (**3a**; 165.54, **3b**; 161.58, and **3c**; 161.11 ppm) and **4c** (168.58 ppm), respectively.[1c]

Stereochemistry of 5b and 6b. The temperature-dependent ^{1}H NMR spectra of 3,3′-dimethyl and 3-methyl derivatives (**5b** and **6b**) were examined to clarify their stereochemistries. The three aromatic rings of **5b** and **6b** should take propeller conformations, as the analogous **3b** and **4b** were revealed to exist in such a conformation by temperature-dependent ^{1}H NMR spectra.[1c—1h,8] It may be that the dimethylamino substituents of **5b** and **6b** exist in a planar geometry owing to the contribution of the dimethyl(4-methylidene-2,5-cyclohexadien-1-ylidene)ammonium structures (**5′** and **6′**), e.g., those of 1,1,2,2-tetrakis(dimethylamino)ethane-1,2-diylium (**15**),[9] 1,2,3-tris(dimethylamino)cyclopropenylium (**16**),[10] and 1,1,3,3-tetrakis(dimethylamino)allylium (**17**)[11] exist in an almost planar geometry, as indicated by their X-ray crystallographic analyses (Chart 4). The high stabilities of **5b** and **6b** suggested that the azulenium ion structures such as **5″** and **6″** made relatively large contribution to the stabilization. Thus, there is interest in the stereochemistry of the dimethylamino substituents of **5b** and **6b**. The point of these analyses is to determine whether the dimethylamino substituents of **5b** and **6b** should take a planar or a pyramidal geometry.

In order to freeze the internal rotations, we lowered the temperature of an NMR sample of **5b** and **6b** in 50% CD_2Cl_2/CS_2 and followed the spectral changes by 600 MHz ^{1}H NMR spectroscopy. The ^{1}H NMR spectra (methyl and dimethylamino region) of **5b**·PF_6^- at various temperatures are shown in Fig. 4. At −80 °C, the NMR consists, in the methyl region, of six signals, as indicated in Fig. 4. When the sample was warmed, all the six lines showed noticeable line broadening. Further warming resulted in coalescence of all the signals to a singlet, which became sharp at 40 °C. Although in the dimethylamino region the NMR consist of two signals with a broad signal at −80 °C, these signals had similar temperature-dependence to those of the methyl signals on the two azulene rings. The temperature-dependence of



15 **16** **17**

Chart 4.

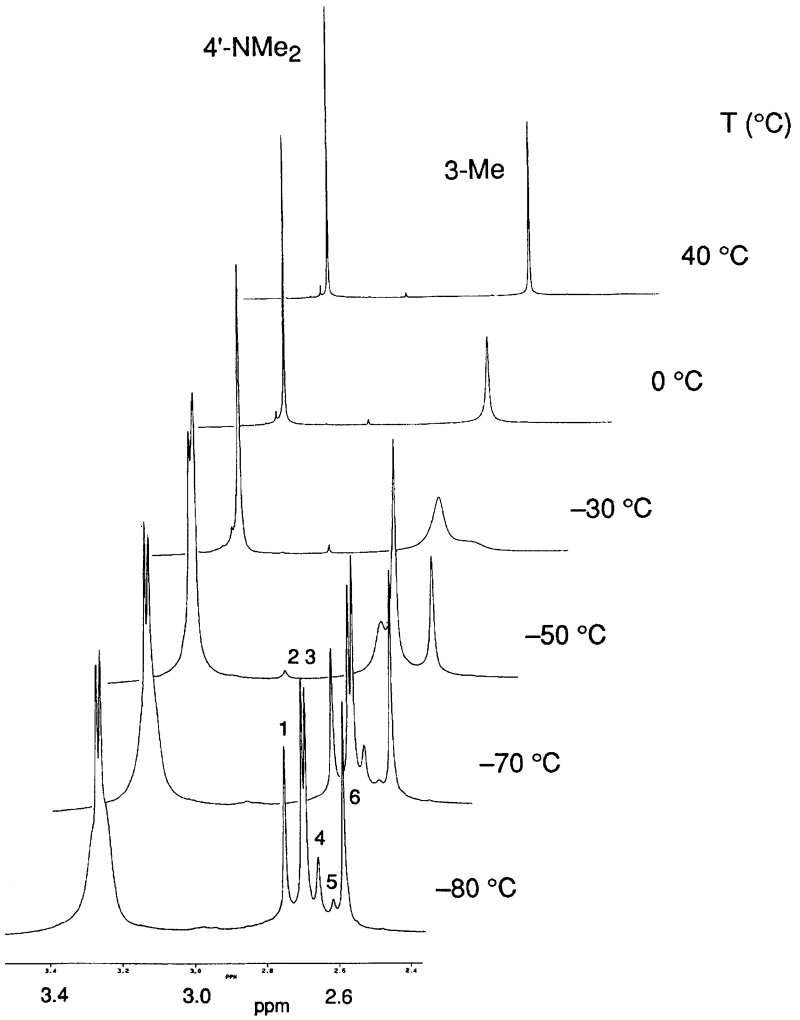


Fig. 4. ^{1}H NMR spectra of cation **5b** (600 MHz, methyl region) in 50% CH_2Cl_2/CS_2 at various temperatures.

the ^{1}H NMR spectra of **5b** was completely reversible under the conditions of these measurements.

If we assume that the dimethylamino substituent of **5b** exists in a nonplanar (pyramidal) geometry, four isomeric propeller conformations (***A***, ***B***, ***C***, and ***D***) and their enantiomers ($\overline{A}$, $\overline{B}$, $\overline{C}$, and $\overline{D}$) are possible for a molecule of this type (**5b**) (Fig. 5). Each enantiomer has C_1 symmetry and has two magnetically distinguishable methyl groups arising from those on the two azulene rings, as shown in Fig. 5. Therefore, when the interconversions among the four isomeric propeller conformations ($A\overline{A}$, $B\overline{B}$, $C\overline{C}$, and $D\overline{D}$) are frozen at the time scale of NMR, the ^{1}H NMR of **5b**, in the methyl region, is expected to consist of eight signals. The dimethylamino substituent of **5b** is supposed to behave similar to those of the methyl groups on the two azulene rings at the temperature-dependent NMR spectra, as shown in Fig. 5.

If we suppose that the dimethylamino substituent of **5b** exists in a planar geometry, the two methyl substituents on the two azulene rings of the propeller conformation ***A*** (a and b) become magnetically equivalent with those of ***B*** (c and d). Each methyl substituent on the two azulene rings of the conformations ***C*** (e and f) and ***D*** (g and h) also becomes magnetically equivalent. Therefore, when the internal rotations of **5b** are frozen at the time scale of NMR on the assumption of the planar geometry of the dimethylamino substituent, the low temperature ^{1}H NMR spectrum of **5b** should exhibit four signals in the methyl and dimethylamino region.

Therefore, the six signals in the methyl region at the low temperature NMR of **5b**, as indicated in Fig. 4, clearly indicate that the dimethylamino substituent of **5b** does not exist in a planar geometry, but it takes a pyramidal structure. The lack of two methyl signals from the expectation, in the methyl region, is assumed to be due to an accidental chemical shift equivalent or to the absence of a set of unstable enantiomers. The temperature-dependent NMR of **5b** revealed the restricted rotation and inversion of a pyramidal dimethylamino substituent, in addition to propeller conformations of the three aromatic rings. At the higher temperature, the NMR of **5b** reflects the rapid isomerization of these stereoisomerisms.

The ^{1}H NMR (aromatic region) spectra of **6b**·PF_6^- in 50% CD_2Cl_2/CS_2 at various temperatures are shown in Fig. 6. At −80 °C, the NMR for the two 4-(dimethylamino)phenyl groups of **6b** consists, in the aromatic region, of seven doublet signals, as indicated by the letters 1—7 in Fig. 6 (−80 °C), with a ratio of ca. 1 : 1 : 1 : 1 : 1 : 2 : 1. When the sample

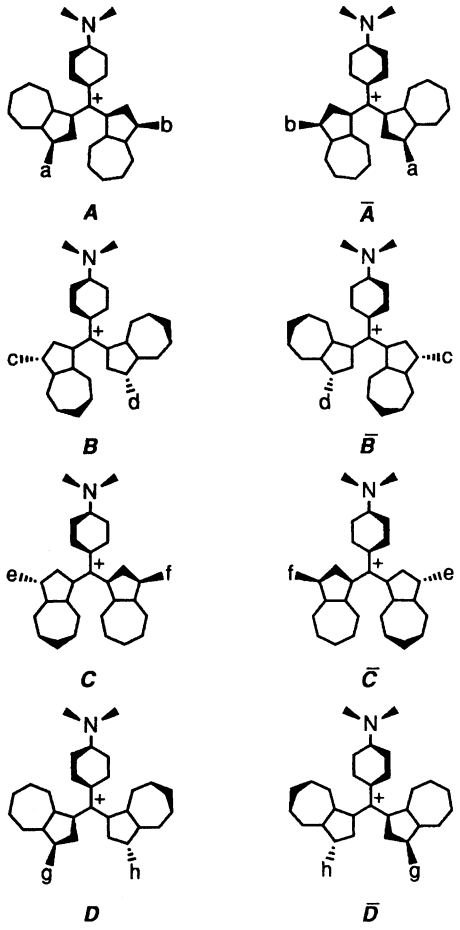


Fig. 5. Four isomeric propeller conformations (*A*, *B*, *C*, and *D*) and their enantiomers ($\bar{A}$, $\bar{B}$, $\bar{C}$, and $\bar{D}$) for **5b**. The magnetically distinguishable methyl groups arising from those on the azulene rings are tentatively labeled by the letters a—h.

was warmed, all the lines showed noticeable line broadening. Further warming resulted in coalescence of all the seven signals into two doublet signals. The NMR signals for the azulene ring did not show any temperature-dependence between −80—20 °C, except for the slight movement of the chemical shift to the direction of lower field according to the depression of the temperature. The NMR consists, in the dimethylamino region at −80 °C, of three broad signals, which had similar temperature-dependence to that in the aromatic region. The temperature-dependence of the ^{1}H NMR spectra of **6b** was also completely reversible under the conditions of the measurements.

If we assume that the dimethylamino substituents of **6b** exist in a nonplanar (pyramidal) geometry, four isomeric propeller conformations (*E*, *F*, *G*, and *H*) and their enantiomers ($\bar{E}$, $\bar{F}$, $\bar{G}$, and $\bar{H}$) are possibile for a molecule of this type (**6b**) (Fig. 7). Each enentiomer has C_1 symmetry and has two nonequivalent (dimethylamino)phenyl groups. Therefore, when the interconversions among the four isomeric propeller conformations (*E*$\bar{E}$, *F*$\bar{F}$, *G*$\bar{G}$, and *H*$\bar{H}$) are frozen at the time scale of NMR, the ^{1}H NMR for the two (dimethylamino)phenyl groups of **6b**, in the aromatic region, is expected to consist of thirty-two doublet signals.

There are two descriptions of the observed seven doublet signals in the aromatic region for the two (dimethylamino)-phenyl groups of **6b**, as discussed below. (i) If we suppose that the two dimethylamino substituents of **6b** exist in a planar geometry, the four isomeric propeller conformations (*E*$\bar{E}$, *F*$\bar{F}$, *G*$\bar{G}$, and *H*$\bar{H}$) of **6b** become equivalent with each other. Therefore, when the internal rotations of the three aromatic rings of **6b** are frozen at the time scale of NMR on the assumption of the planar geometry of the dimethylamino substituents, the low temperature ^{1}H NMR for the two (dimethylamino)phenyl groups of **6b**, in the aromatic region, should exhibit eight doublet signals with equal intensities. The three signals of **6b**, in the dimethylamino region, are described by the restricted rotation of the planar dimethylamino substituents. The results are comparable with the accidental chemical shifts equivalent of these four propeller conformations. (ii) The second description includes some dynamic processes. The rotation or inversion of the pyramidal dimethylamino substituents averages the four magnetically distinguishable positions (e.g., a, f, i, and n) of the four isomeric propeller conformations (*E*$\bar{E}$, *F*$\bar{F}$, *G*$\bar{G}$, and *H*$\bar{H}$) during the course of the interconversions, as illustrated in Fig. 8. If we assume the rapid rotation and/or inversion of the dimethylamino substituents, the low temperature ^{1}H NMR for the two (dimethylamino)phenyl groups of **6b**, in the aromatic region, is also expected to show eight doublet signals with equal intensities. The three signals of **6b**, in the dimethylamino region, are ascribed to either rotation or inversion of the dimethylamino substituents. The rapid interconversion of the four isomeric propeller conformations (*E*$\bar{E}$, *F*$\bar{F}$, *G*$\bar{G}$, and *H*$\bar{H}$) by a one-ring flip mechanism[12] of the two (dimethylamino)phenyl groups while retaining their pyramidal structures also affords a comparable result with the rotation or inversion of the pyramidal dimethylmino substituents, as illustrated in Fig. 9.

In both cases, the low temperature ^{1}H NMR of the two (dimethylamino)phenyl groups of **6b**, in the aromatic region, is expected to consist of eight doublet signals with equal intensities. Therefore, these two descriptions for the observed seven resonance signals in the aromatic region for the (dimethylamino)phenyl groups of **6b** could not be distinguished by the temperature-dependent NMR spectra. However, by considering the pyramidal structure of the dimethylamino substituent of **5b**, we suppose that the dimethylamino substituents of **6b** should take a pyramidal geometry. Therefore, the low temperature ^{1}H NMR spectrum of **6b** must be reflected by the rotation, inversion of the pyramidal dimethylamino substituents, or a one-ring flip of the two (dimethylamino)phenyl groups while retaining their pyramidal structures, in addition to the propeller conformations of the three aromatic rings. The lack of a resonance signal, in the aromatic region for the (dimethylamino)phenyl groups, is ascribed to an accidental chemical shift equivalent of a resonance signal. At the higher temperature, the NMR of **6b** also reflects the rapid isomerization of these stereoisomerisms. Consequently, the dynamic behavior of **5b** and **6b** detected

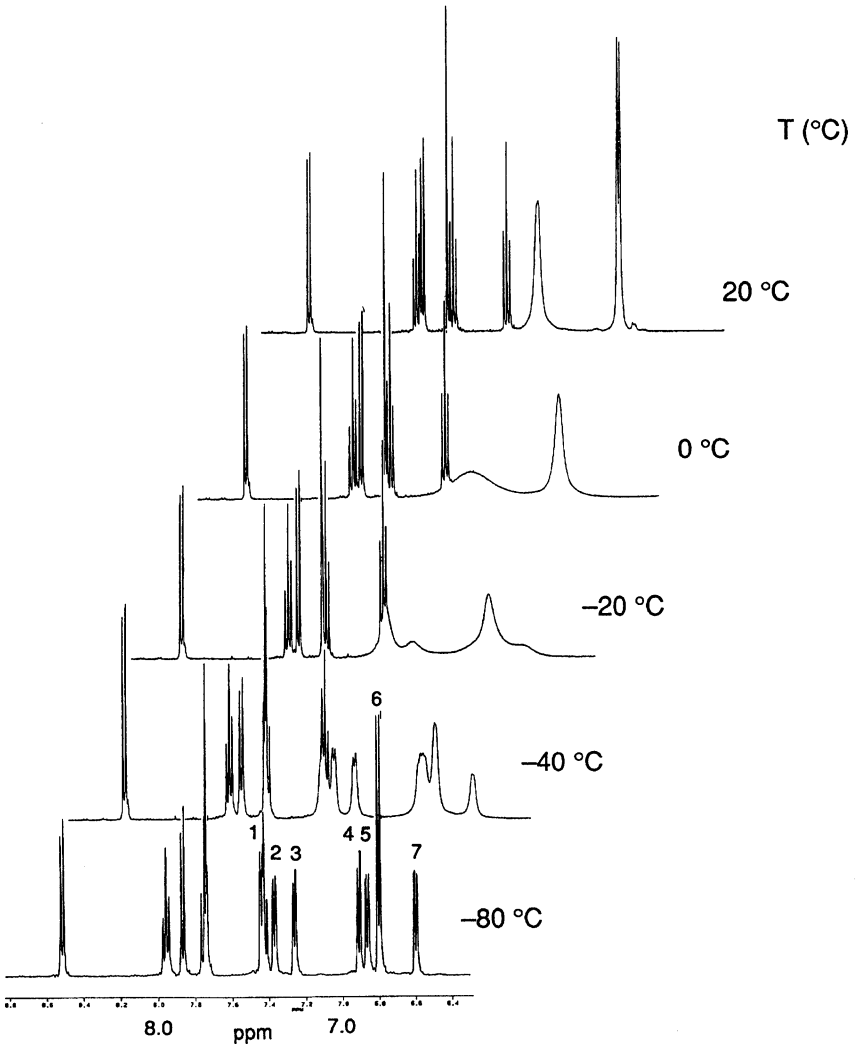


Fig. 6. ^{1}H NMR spectra of cation **6b** (600 MHz, aromatic region) in 50% CH_2Cl_2/CS_2 at various temperatures.

by the temperature-dependent NMR spectra should be concluded to be a result from a pyramidal structure of the dimethylamino substituents, in addition to propeller conformations of the three aromatic rings.

The pyramidal structure of the dimethylamino substituents of **5b** and **6b** suggests that the high thermodynamic stability of these cations **5a—c** and **6a—c** is attributable to the high contribution of the azulenium ion structures (**5″** and **6″**). The multiredox properties of these cations (**5a—c** and **6a—c**) is due to the contribution of the dimethyl(4-methylidene-2,5-cyclohexadien-1-ylidene)ammonium structures (**5′** and **6′**). Therefore, the high stabilizing effect of the substituted methyl cations (**5a—c** and **6a—c**) is attributable to the high contribution of the azulenium ion structures (**5″** and **6″**), in addition to the electron-donating properties of the less hindered 4-(dimethylamino)phenyl groups.

Experimental

General. Melting points were determined on a Yanagimoto micro melting point apparatus MP-S3 and are uncorrected. Mass spectra were obtained with a JEOL HX-110 or a Hitachi M-2500S instrument, usually at 70 eV. IR and UV spectra were measured on a Shimadzu FTIR-8100M and a Hitachi U-3410 spectrophotometer, respectively. ^{1}H NMR spectra were recorded on a Hitachi R-90H at 90 MHz, a JEOL JNM A500 at 500 MHz, or a Bruker AM 600 spectrometer at 600 MHz. ^{13}C NMR spectra were recorded on a Hitachi R-90H at 22.5 MHz, a JEOL JNM A500 at 125 MHz, or a Bruker AM 600 spectrometer at 150 MHz. Gel permeation chromatography (GPC) was performed on a TSKgel G2000H_6. Voltammetry measurements were carried out with a BAS100B/W electrochemical workstation equipped with Pt working and auxiliary electrodes, and a reference electrode formed from $Ag/AgNO_3$ (0.01 M, M=mol dm^{-3}) and tetraethylammonium perchlorate (TEAP) as a supporting electrolyte, at the scan rate of 100 mV s^{-1}. In the case of irreversible waves, E^{OX} and E^{red} were calculated as E_{pa} (anodic peak potential) −0.03 and E_{pc} (cathodic peak potential) +0.03, respectively. Elemental analyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University.

General Procedure for the Synthesis of Di(1-azulenyl)[4-(dimethylamino)phenyl]methanes (7a—c). A solution of azulenes (**9a—c**) and 4-(dimethylamino)benzaldehyde in a 50% acetic acid solution of CH_2Cl_2 (9.1 ml) was pressed at 10 kbar for 24 h at 30 °C. The solvent was removed in vacuo. The residue was diluted

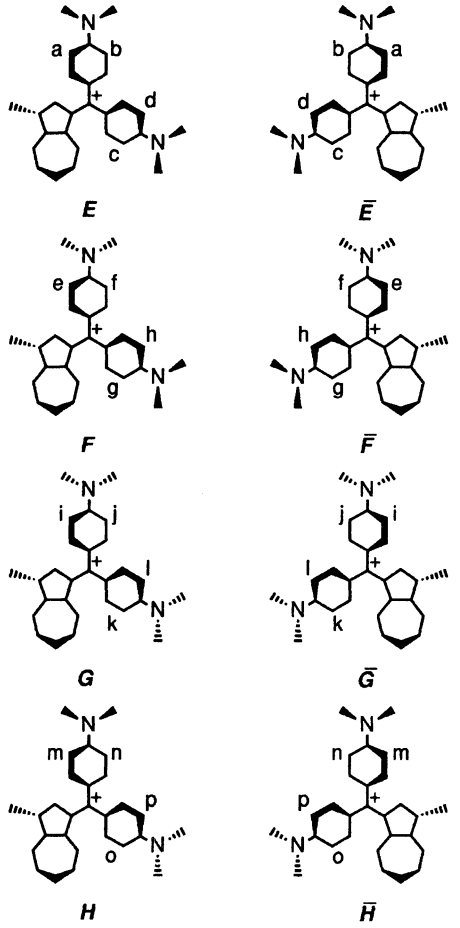


Fig. 7. Four isomeric propeller conformations (*E*, *F*, *G*, and *H*) and their enantiomers ($\bar{E}$, $\bar{F}$, $\bar{G}$, and $\bar{H}$) for **6b**. The magnetically distinguishable positions of the two 4-(dimethylamino)phenyl groups are tentatively labeled by the letters a—p.

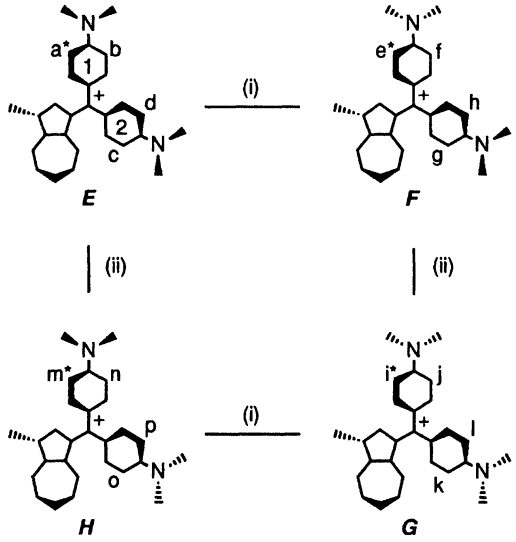


Fig. 8. The consequence of the stereoisomerization of the four isomeric propeller conformations (*E*$\bar{E}$, *F*$\bar{F}$, *G*$\bar{G}$, and *H*$\bar{H}$) for **6b** by the rotation or inversion of the pyramidal dimethylamino substituents. (i) That of ring 1. (ii) That of ring 2. The asterisks indicate the four magnetically distinguishable positions that are averaged during the course of interconversion.

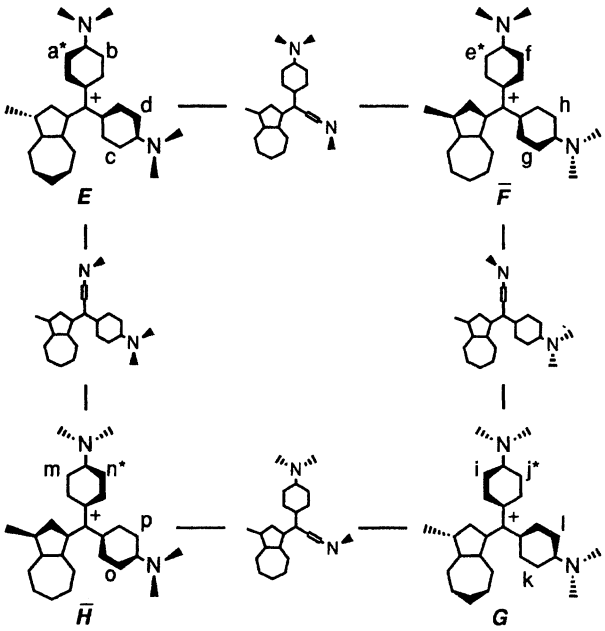


Fig. 9. The one-ring flip of the two 4-(dimethylamino)phenyl groups of **6b** while retaining their pyramidal structures. The processes averages the four magnetically distinguishable positions (e.g. a, n, j, and e) of the four isomeric propeller conformations (*E*$\bar{E}$, *F*$\bar{F}$, *G*$\bar{G}$, and *H*$\bar{H}$) during the course of interconversions.

with CH_2Cl_2. The organic layer 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 ethyl acetate/CH_2Cl_2/hexane and/or GPC with $CHCl_3$. The product was further purified by recrystallization.

Di(1-azulenyl)[4-(dimethylamino)phenyl]methane (7a). The general procedure was followed using azulene (**9a**) (1.28 g, 10.0 mmol) and 4-(dimethylamino)benzaldehyde (746 mg, 5.00 mmol). Column chromatography on silica gel with ethyl acetate/CH_2Cl_2 and GPC with $CHCl_3$ afforded the recovered **9a** (185 mg, 14%), the methane **7a** (467 mg, 28%), and a diastereomeric mixture of 1,3-bis{(1-azulenyl)[4-(dimethylamino)phenyl]methyl}azulenes (**10a** and **10b**) (292 mg, 18%). **10a** and **10b** were separable by column chromatography on silica gel with 2% ethyl acetate/CH_2Cl_2.

7a: Blue prisms; mp 167.0—169.0 °C (ethyl acetate/hexane); MS (70 eV) *m/z* (rel intensity) 387 (M^+; 100), 386 (31), 265 (30), and 215 (22); IR (KBr disk) ν_{max} 1611, 1574, 1518, 1393, 1348, and 772 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 241 (4.62), 280 (4.95), 350 (4.06), 364 (3.99), and 603 nm (2.85); ^1H NMR (90 MHz, $CDCl_3$) δ = 8.26 (d, J = 9.5 Hz, 2H, H_8), 8.24 (d, J = 9.5 Hz, 2H, H_4), 7.48 (d, J = 3.7 Hz, 2H, H_2), 7.46 (dd, J = 9.7, 9.7 Hz, 2H, H_6), 7.25 (d, J = 3.7 Hz, 2H, H_3), 7.02 (dd, J = 9.7, 9.5 Hz, 2H, H_5), 7.01 (d, J = 8.6 Hz, 2H, $H_{2',6'}$), 6.94 (dd, J = 9.7, 9.5 Hz, 2H, H_7), 6.67 (s, 1H, CH), 6.62 (d, J = 8.6 Hz, 2H, $H_{3',5'}$), and 2.87 (s, 6H, 4′-NMe_2); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 148.77 (s), 140.97 (s), 138.28 (d, C_2), 137.03 (d, C_6), 136.42 (d, C_4), 134.87 (s), 134.11 (s), 133.89 (s), 133.62 (d, C_8), 129.29 (d, $C_{2',6'}$), 122.22 (d, C_5), 121.70 (d, C_7), 116.48 (d, C_3), 112.58 (d, $C_{3',5'}$), 41.88 (d, CH), and 40.72 (q, 4′-NMe_2). Found: 89.62; H, 6.77; N, 3.42%. Calcd

for $C_{29}H_{25}N$: C, 89.88; H, 6.50; N, 3.61%.

10a: Greenish blue crystals; mp 239.0—241.0 °C (ethyl acetate/hexane); MS (70 eV) *m/z* (rel intensity) 646 (M^+; 39), 388 (22), 387 (82), 386 (83), 261 (73), 260 (100), 215 (27), and 128 (72); IR (KBr disk) ν_{max} 1613, 1574, 1518, 1395, 1350, 945, 776, 750, 735, and 743 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 242 (4.77), 280 (5.09), 351 (4.20), 365 (4.19), and 606 nm (2.95); ^1H NMR (600 MHz, $CDCl_3$) δ = 8.246 (d, J = 9.4 Hz, 2H, $H_{4,8}$), 8.241 (d, J = 9.4 Hz, 2H, $H_{4'}$), 8.205 (d, J = 9.6 Hz, 2H, $H_{8'}$), 7.502 (dd, J = 9.9, 9.8 Hz, 2H, $H_{6'}$), 7.409 (d, J = 3.8 Hz, 2H, $H_{2'}$), 7.399 (t, J = 9.9 Hz, 1H, H_6), 7.247 (s, 1H, H_2), 7.245 (d, J = 3.8 Hz, 2H, $H_{3'}$), 7.062 (dd, J = 9.8, 9.4 Hz, 2H, $H_{5'}$), 6.955 (dd, J = 9.9, 9.6 Hz, 2H, $H_{7'}$), 6.906 (d, J = 8.7 Hz, 4H, $H_{2'',6''}$), 6.883 (dd, J = 9.9, 9.4 Hz, 2H, $H_{5,7}$), 6.618 (s, 2H, CH), 6.551 (d, J = 8.7 Hz, 4H, $H_{3'',5''}$), and 2.871 (s, 12H, 4″-NMe_2); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 148.754 (s, $C_{4''}$), 141.035 (s, $C_{3'a}$), 139.980 (d, C_2), 138.401 (d, $C_{2'}$), 137.086 (d, C_6), 137.010 (d, $C_{6'}$), 136.440 (d, $C_{4'}$), 135.782 (s, $C_{3a,8a}$), 134.969 (s, $C_{8'a}$), 134.082 (s, $C_{1'}$), 133.906 (d, $C_{8'}$), 133.817 (s, $C_{1''}$), 133.486 (d, $C_{4,8}$), 132.464 (s, $C_{1,3}$), 129.268 (d, $C_{2'',6''}$), 122.166 (d, $C_{5'}$), 121.659 (d, $C_{7'}$), 121.326 (d, $C_{5,7}$), 116.435 (d, $C_{3'}$), 112.554 (d, $C_{3'',5''}$), 41.703 (d, CH), and 40.773 (q, 4″-NMe_2). Found: C, 88.60; H, 6.75; N, 4.12%. Calcd for $C_{48}H_{42}N_2$: C, 89.13; H, 6.54; N, 4.33%.

10b: Greenish blue crystals; mp 133.0—135.0 °C (ethyl acetate/hexane); MS (70 eV) *m/z* (rel intensity) 646 (M^+; 0.2), 387 (37), 261 (51), 260 (34), and 128 (100); IR (KBr disk) ν_{max} 1613, 1574, 1518, 1393, 1348, 945, 770, 750, and 733 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 242 (4.76), 279 (5.09), 351 (4.19), 366 (4.18), and 607 nm (2.96); ^1H NMR (600 MHz, $CDCl_3$) δ = 8.230 (d, J = 9.4 Hz, 2H, $H_{4,8}$), 8.191 (d, J = 9.4 Hz, 2H, $H_{4'}$), 8.140 (d, J = 9.7 Hz, 2H, $H_{8'}$), 7.449 (dd, J = 9.9, 9.9 Hz, 2H, $H_{6'}$), 7.386 (t, J = 9.9 Hz, 1H, H_6), 7.316 (d, J = 3.8 Hz, 2H, $H_{2'}$), 7.206 (s, 1H, H_2), 7.149 (d, J = 3.8 Hz, 2H, $H_{3'}$), 7.024 (dd, J = 9.9, 9.4 Hz, 2H, $H_{5'}$), 6.945 (d, J = 8.7 Hz, 4H, $H_{2'',6''}$), 6.870 (dd and dd, J = 9.9, 9.4 Hz and J = 9.9, 9.7 Hz, 4H, $H_{5,7}$ and $H_{7'}$), 6.598 (s, 2H, CH), 6.598 (d, J = 8.7 Hz, 4H, $H_{3'',5''}$), and 2.873 (s, 12H, 4″-NMe_2); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 148.749 (s, $C_{4''}$), 140.920 (s, $C_{3'a}$), 139.865 (d, C_2), 138.318 (d, $C_{2'}$), 137.085 (d, C_6), 137.035 (d, $C_{6'}$), 136.399 (d, $C_{4'}$), 135.732 (s, $C_{3a,8a}$), 134.852 (s, $C_{8'a}$), 133.991 (s, $C_{1'}$), 133.819 (d, $C_{1''}$), 133.798 (s, $C_{8'}$), 133.494 (d, $C_{4,8}$), 132.426 (s, $C_{1,3}$), 129.290 (d, $C_{2'',6''}$), 122.141 (d, $C_{5'}$), 121.628 (d, $C_{7'}$), 121.311 (d, $C_{5,7}$), 116.307 (d, $C_{3'}$), 112.577 (d, $C_{3'',5''}$), 41.669 (d, CH), and 40.786 (q, 4″-NMe_2). Found: C, 89.37; H, 6.52; N, 4.47%. Calcd for $C_{48}H_{42}N_2$: C, 89.13; H, 6.54; N, 4.33%.

Bis(3-methyl-1-azulenyl)[4-(dimethylamino)phenyl]methane (7b). The general procedure was followed using 1-methylazulene (**9a**) (711 mg, 5.00 mmol) and 4-(dimethylamino)benzaldehyde (388 mg, 2.60 mmol). Column chromatography on silica gel with CH_2Cl_2/hexane afforded the methane **7b** (787 mg, 76%). Green needles; mp 189.5—190.5 °C (ethyl acetate/hexane); MS (70 eV) *m/z* (rel intensity) 415 (M^+; 100), 400 (32), and 258 (20); IR (KBr disk) ν_{max} 1574, 1520, 1348, and 725 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 244 (4.60), 281 (4.94), 358 (4.07), 375 (4.01), and 634 nm (2.96); ^1H NMR (90 MHz, $CDCl_3$) δ = 8.14 (d, J = 9.5 Hz, 2H, H_8), 8.10 (d, J = 9.5 Hz, 2H, H_4), 7.39 (dd, J = 9.7, 9.7 Hz, 2H, H_6), 7.32 (s, 2H, H_2), 7.00 (d, J = 8.6 Hz, 2H, $H_{2',6'}$), 6.91 (dd, J = 9.7, 9.5 Hz, 2H, H_5), 6.81 (dd, J = 9.7, 9.5 Hz, 2H, H_7), 6.62 (d, J = 8.6 Hz, 2H, $H_{3',5'}$), 6.59 (s, 1H, CH), 2.87 (d, 6H, 4′-NMe_2), and 2.55 (s, 6H, 3-Me); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 148.68 (s), 139.35 (d, C_2), 136.97 (d and s, C_6), 135.02 (s), 134.08 (s), 133.28 (d, C_4), 132.98 (d, C_8), 132.49 (s), 129.26 (d, $C_{2',6'}$), 124.35 (s), 120.81 (d, C_7), 120.48 (d, C_5), 112.52 (d, $C_{3',5'}$), 41.39 (d, CH), 40.69 (q, 4′-NMe_2), and 12.73 (q, 3-Me). Found: C, 89.37; H, 7.26; N, 3.49%. Calcd for $C_{31}H_{29}N$: C, 89.60; H, 7.03; N, 3.37%.

Bis(3,6-di-*t*-butyl-1-azulenyl)[4-(dimethylamino)phenyl]methane (7c). The general procedure was followed using 1,6-di-*t*-butylazulene (**9c**) (1.20 g, 4.99 mmol) and 4-(dimethylamino)benzaldehyde (388 mg, 2.60 mmol). Column chromatography on silica gel with CH_2Cl_2/hexane afforded the methane **7c** (865 mg, 57%). Blue crystals; mp 243.0—245.0 °C (hexane); MS (70 eV) *m/z* (rel intensity) 611 (M^+; 64), 555 (45), 554 (100), 358 (21), 225 (28), and 57 (72); IR (KBr disk) ν_{max} 2961, 1574, 1518, 1362, and 1225 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 242 (4.70), 286 (5.00), 360 (4.13), 377 (4.03), and 630 nm (3.25); ^1H NMR (90 MHz, $CDCl_3$) δ = 8.51 (d, J = 11.0 Hz, 2H, H_4), 8.18 (d, J = 10.8 Hz, 2H, H_8), 7.42 (s, 2H, H_2), 7.11 (dd, J = 11.0, 2.0 Hz, 2H, H_5), 7.02 (dd, J = 10.8, 2.0 Hz, 2H, H_7), 6.97 (d, J = 8.9 Hz, 2H, $H_{2',6'}$), 6.61 (d, J = 8.9 Hz, 2H, $H_{3',5'}$), 6.55 (s, 1H, CH), 2.88 (s, 6H, 4′-NMe_2), 1.49 (s, 18H, 3-*t*-Bu), and 1.39 (s, 18H, 6-*t*-Bu); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 159.90 (s, C_6), 148.59 (s), 137.43 (s), 136.27 (d, C_2), 134.66 (s), 134.56 (s), 134.17 (d and s, C_4), 132.06 (d, C_8), 131.33 (s), 129.26 (d, $C_{2',6'}$), 118.95 (d, C_7), 117.92 (d, C_5), 112.58 (d, $C_{3',5'}$), 40.99 (d, CH), 40.84 (q, 4′-NMe_2), 38.16 (s, 6-*t*-Bu), 33.31 (s, 3-*t*-Bu), 32.33 (q, 3-*t*-Bu), and 31.88 (q, 6-*t*-Bu). Found: C, 87.42; H, 10.24; N, 2.31%. Calcd for $C_{45}H_{57}N$: C, 88.32; H, 9.39; N, 2.29%.

General Procedure for the Synthesis of (1-Azulenyl)bis[4-(dimethylamino)phenyl]methanes (8a—c). A solution of azulenes (**9a—c**) and bis[4-(dimethylamino)phenyl]methanol in glacial acetic acid was stirred at room temperature under an N_2 atmosphere until the reaction was completed. The solvent was removed in vacuo. The residue was diluted with CH_2Cl_2. The organic layer 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 ethyl acetate/CH_2Cl_2. The product was further purified by recrystallization.

(1-Azulenyl)bis[4-(dimethylamino)phenyl]methane (8a). The general procedure was followed using azulene (**9a**) (1.28 g, 10.0 mmol) and bis[4-(dimethylamino)phenyl]methanol (1.35 g, 4.99 mmol) in glacial acetic acid (60 ml). The mixture was stirred at room temperature for 4 h. Column chromatography on silica gel with ethyl acetate/CH_2Cl_2 afforded the recovered **9a** (608 mg, 48%), the methane **8a** (1.26 g, 66%), and 1,3-bis{bis[4-(dimethylamino)phenyl]methyl}azulene (**11**) (261 mg, 17%).

8a: Green needles; mp 182.0—183.5 °C (ethyl acetate); MS (70 eV) *m/z* (rel intensity) 380 (M^+; 100), 379 (39), 260 (31), and 215 (29); IR (KBr disk) ν_{max} 1615, 1518, 1350, and 795 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 281 (4.81), 350 (3.81), 367 (3.69), and 604 nm (2.53); ^1H NMR (90 MHz, $CDCl_3$) δ = 8.23 (d and d, J = 9.2 and 9.2 Hz, 2H, H_4 and H_8), 7.53 (d, J = 3.8 Hz, 1H, H_2), 7.46 (dd, J = 9.7, 9.7 Hz, 1H, H_6), 7.26 (d, J = 3.8 Hz, 1H, H_3), 7.01 (dd, J = 9.7, 9.2 Hz, 1H, H_5), 7.00 (d, J = 8.8 Hz, 4H, $H_{2',6'}$), 6.96 (dd, J = 9.7, 9.2 Hz, 1H, H_7), 6.62 (d, J = 8.8 Hz, 4H, $H_{3',5'}$), 5.96 (s, 1H, CH), and 2.87 (s, 12H, 4′-NMe_2); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 148.74 (s), 140.94 (s), 138.25 (d, C_2), 137.03 (d, C_6), 136.36 (d, C_4), 135.14 (s), 133.96 (s), 133.83 (s), 133.68 (d, C_8), 129.56 (d, $C_{2',6'}$), 122.16 (d, C_5), 121.70 (d, C_7), 116.45 (d, C_3), 112.52 (d, $C_{3',5'}$), 47.88 (d, CH), and 40.75 (q, 4′-NMe_2). Found: C, 85.42; H, 7.52; N, 7.45%. Calcd for $C_{27}H_{28}N_2$: C, 85.22; H, 7.42; N, 7.36%.

11: Greenish blue prisms; mp 209.5—211.0 °C (ethyl acetate/hexane); MS (70 eV) *m/z* (rel intensity) 632 (M^+; 50), 380 (28), 379 (58), 254 (35), and 253 (100); IR (KBr disk) ν_{max} 1615, 1520, and 1352 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 271 (4.91), 363 (3.90), 624 (2.57), and 694 nm (2.40); ^1H NMR (90 MHz, $CDCl_3$) δ = 8.16 (d, J = 9.5 Hz, 2H, $H_{4,8}$), 7.37 (dd, J = 9.5, 9.5 Hz, 1H, H_6),

7.35 (s, 1H, H_2), 6.96 (d, J = 8.8 Hz, 8H, $H_{2',6'}$), 6.84 (dd, J = 9.5, 9.5 Hz, 2H, $H_{5,7}$), 6.60 (d, J = 8.8 Hz, 8H, $H_{3',5'}$), 5.91 (s, 2H, CH), and 2.87 (d, 24H, 4′-NMe_2); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 148.71 (s), 139.75 (d, C_2), 136.88 (d, C_6), 136.03 (s), 133.96 (s), 133.38 (d, $C_{4,8}$), 132.12 (s), 129.53 (d, $C_{2',6'}$), 121.18 (d, $C_{5,7}$), 112.58 (d, $C_{3',5'}$), 47.82 (d, CH), and 40.84 (q, 4′-NMe_2). Found: C, 83.22; H, 7.64; N, 8.80%. Calcd for $C_{44}H_{48}N_4$: C, 83.50; H, 7.65; N, 8.85%.

(3-Methyl-1-azulenyl)bis[4-(dimethylamino)phenyl]methane (8b). The general procedure was followed using 1-methylazulene (**9b**) (711 mg, 5.00 mmol) and bis[4-(dimethylamino)phenyl]methanol (1.39 g, 5.14 mmol) in glacial acetic acid (30 ml). The mixture was stirred at room temperature for 100 min. Column chromatography on silica gel with ethyl acetate/CH_2Cl_2 afforded the methane **8b** (1.74 g, 88%). Green needles; mp 137.5—138.0 °C (ethyl acetate/hexane); MS (70 eV) m/z (rel intensity) 394 (M^+; 100), 393 (40), 379 (49), 274 (30), 258 (35), 252 (20), 197 (28), and 190 (23); IR (KBr disk) ν_{max} 1611, 1516, 1354, 1341, 1202, and 729 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 280 (4.76), 358 (3.80), 374 (3.71), and 630 nm (2.53); ^{1}H NMR (90 MHz, $CDCl_3$) δ = 8.12 (d, J = 9.2 Hz, 1H, H_8), 8.10 (d, J = 9.7 Hz, 1H, H_4), 7.39 (dd, J = 9.8, 9.8 Hz, 1H, H_6), 7.37 (s, 1H, H_2), 7.00 (d, J = 8.8 Hz, 4H, $H_{2',6'}$), 6.91 (dd, J = 9.8, 9.7 Hz, 1H, H_5), 6.83 (dd, J = 9.8, 9.2 Hz, 1H, H_7), 6.63 (d, J = 8.8 Hz, 4H, $H_{3',5'}$), 5.93 (s, 1H, CH), 2.88 (s, 12H, 4′-NMe_2), and 2.57 (s, 3H, 3-Me); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 148.74 (s), 139.38 (d, C_2), 136.97 (d, C_6), 136.91 (s), 135.36 (s), 133.96 (s), 133.25 (d, C_4), 133.10 (d, C_8), 132.28 (s), 129.59 (d, $C_{2',6'}$), 124.38 (s), 120.84 (d, C_7), 120.48 (d, C_5), 112.55 (d, $C_{3',5'}$), 47.67 (d, CH), 40.78 (q, 4′-NMe_2), and 12.76 (q, 3-Me). Found: C, 85.25; H, 7.95; N, 7.18%. Calcd for $C_{28}H_{30}N_2$: C, 85.24; H, 7.66; N, 7.10%.

(3,6-Di-*t*-butyl-1-azulenyl) bis [4-(dimethylamino) phenyl]-methane (8c). The general procedure was followed using 1,6-di-*t*-butylazulene (**9c**) (1.21 g, 5.03 mmol) and bis[4-(dimethylamino)-phenyl]methanol (1.38 g, 5.10 mmol) in glacial acetic acid (30 ml). The mixture was stirred at room temperature for 10 min. Column chromatography on silica gel with ethyl acetate/CH_2Cl_2 afforded the methane **8c** (1.77 g, 71%). Blue crystals; mp 192.5—193.5 °C (ethyl acetate/hexane); MS (70 eV) m/z (rel intensity) 492 (M^+; 100), 477 (26), 436 (31), 435 (84), and 57 (49); IR (KBr disk) ν_{max} 2961, 1613, 1578, 1516, and 1345 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ε) 292 (4.78), 301 (4.79), 360 (3.86), 379 (3.68), and 617 nm (2.64); ^{1}H NMR (90 MHz, $CDCl_3$) δ = 8.51 (d, J = 10.8 Hz, 1H, H_4), 8.12 (d, J = 10.8 Hz, 1H, H_8), 7.39 (s, 1H, H_2), 7.11 (dd, J = 10.8, 1.8 Hz, 1H, H_5), 7.04 (dd, J = 10.8, 1.8 Hz, 1H, H_7), 7.00 (d, J = 8.7 Hz, 4H, $H_{2',6'}$), 6.64 (d, J = 8.7 Hz, 4H, $H_{3',5'}$), 5.90 (s, 1H, CH), 2.89 (s, 12H, 4′-NMe_2), 1.51 (s, 9H, 3-*t*-Bu), and 1.39 (s, 9H, 6-*t*-Bu); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 160.02 (s, C_6), 148.68 (s), 137.37 (s), 136.12 (d, C_2), 134.90 (s), 134.26 (d, C_4), 134.20 (s), 134.02 (s), 132.25 (d, C_8), 130.97 (s), 129.63 (d, $C_{2',6'}$), 119.01 (d, C_5), 118.07 (d, C_7), 112.58 (d, $C_{3',5'}$), 47.76 (d, CH), 40.84 (q, 4′-NMe_2), 38.16 (s, 6-*t*-Bu), 33.31 (s, 3-*t*-Bu), 32.36 (q, 3-*t*-Bu), and 31.91 (q, 6-*t*-Bu). Found: C, 85.18; H, 9.25; N, 5.81%. Calcd for $C_{35}H_{44}N_2$: C, 85.31; H, 9.00; N, 5.69%.

General Procedure for the Synthesis of Di(1-azulenyl)[4-(dimethylamino)phenyl]methyl (5a—c) and (1-Azulenyl)bis[4-(dimethylamino)phenyl]methyl (6a—c) Hexafluorophosphates. DDQ was added at room temperature to a solution of di(1-azulenyl)-[4-(dimethylamino)phenyl]methanes (**7a—c**) and (1-azulenyl)bis-[4-(dimethylamino)phenyl]methanes (**8a—c**) in CH_2Cl_2. The solution was stirred at the same temperature for 5—10 min until the reaction was completed. A 60% aqueous HPF_6 solution was added slowly to the reaction mixture. After stirring at room temperature for an additional 5 min, water was added to the mixture. The resulting suspension was filtered with suction. The organic layer was separated, washed with water, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (3—5 ml) and then ether or hexane (50—100 ml) was added to the solution. The precipitated crystals were collected by filtration, washed with ether or hexane, and dried in vacuo to give the hexafluorophosphates **5a—c**·PF_6^- and **6a—c**·PF_6^-. The product was further purified by recrystallization from CH_2Cl_2/ether or CH_2Cl_2/hexane.

Di(1-azulenyl)[4-(dimethylamino)phenyl]methyl Hexafluorophosphate (5a·PF_6^-). The general procedure was followed using DDQ (136 mg, 0.599 mmol), di(1-azulenyl)[4-(dimethylamino)phenyl]methane (**7a**) (193 mg, 0.498 mmol), and 60% HPF_6 (5 ml) in CH_2Cl_2 (50 ml). Recrystallization from CH_2Cl_2/ether gave the hexafluorophosphate **5a**·PF_6^- (240 mg, 91%). Brown powder; mp 149.0—151.0 °C (CH_2Cl_2/ether); MS (FAB) m/z 386 (M^+-PF_6); IR (KBr disk) ν_{max} 1601, 1458, 1379, 1279, 1169, 841, and 558 cm^{-1}; UV (MeCN) λ_{max} (log ε) 231 (4.67), 257 (4.57), 291 (4.49), 343 (4.21), and 615 nm (4.74); ^{1}H NMR (500 MHz, $CDCl_3$, 55 °C) δ = 8.671 (d, J = 9.5 Hz, 2H, H_4), 7.951 (dd, J = 9.5, 9.5 Hz, 2H, H_6), 7.866 (d and br, J = 3.7 Hz, 4H, H_2 and H_8), 7.769 (dd, J = 9.5, 9.5 Hz, 2H, H_5), 7.620 (d, J = 3.7 Hz, 2H, H_3), 7.439 (br, 2H, H_7), 7.306 (d, J = 8.3 Hz, 2H, $H_{2',6'}$), 6.864 (d, J = 8.3 Hz, 2H, $H_{3',5'}$), and 3.311 (s, 6H, 4′-NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$, 55 °C) δ = 164.165 (s, C^+), 156.222 (s, $C_{4'}$), 150.714 (s, C_{3a}), 145.861 (s, C_{8a}), 145.616 (d, C_2), 142.171 (d, C_6), 140.445 (d, C_4), 140.290 (d, $C_{2',6'}$), 138.591 (d, C_8), 131.902 (d, C_5), 131.775 (s, C_1), 131.375 (d, C_7), 128.494 (s, $C_{1'}$), 123.513 (d, C_3), 113.389 (d, $C_{3',5'}$), and 40.584 (q, 4′-NMe_2). Found: C, 65.69; H, 4.78; N, 3.01%. Calcd for $C_{29}H_{24}NPF_6$: C, 65.54; H, 4.55; N, 2.63%.

Bis(3-methyl-1-azulenyl)[4-(dimethylamino)phenyl]methyl Hexafluorophosphate (5b·PF_6^-). The general procedure was followed using DDQ (276 mg, 1.22 mmol), bis(3-methyl-1-azulenyl)[4-(dimethylamino)phenyl]methane (**7b**) (419 mg, 1.01 mmol), and 60% HPF_6 (5 ml) in CH_2Cl_2 (100 ml). Recrystallization from CH_2Cl_2/ether gave the hexafluorophosphate **5b**·PF_6^- (560 mg, 99%). Brown powder; mp 161.0—165.0 °C (CH_2Cl_2/ether); MS (FAB) m/z 414 (M^+-PF_6); IR (KBr disk) ν_{max} 1601, 1426, 1408, 1393, 1354, 841, and 558 cm^{-1}; UV (MeCN) λ_{max} (log ε) 236 (4.67), 259 (4.56), 291 (4.47), 355 (4.15), and 631 nm (4.75); ^{1}H NMR (90 MHz, $CDCl_3$) δ = 8.58 (d, J = 11.0 Hz, 2H, H_4), 7.94 (dd, J = 9.7, 9.7 Hz, 2H, H_6), 7.79 (d, J = 10.1 Hz, 2H, H_8), 7.76 (dd, J = 11.0, 9.7 Hz, 2H, H_5), 7.74 (d, 2H, H_2), 7.34 (dd, J = 10.1, 9.7 Hz, 2H, H_7), 7.26 (d, J = 9.2 Hz, 2H, $H_{2',6'}$), 6.83 (d, J = 9.2 Hz, 2H, $H_{3',5'}$), 3.28 (d, 6H, 4′-NMe_2), and 2.68 (s, 6H, 3-Me); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 161.58 (s, C^+), 155.21 (s), 148.32 (s), 146.43 (s), 145.27 (d, C_2), 141.79 (d, C_6), 139.44 (d, $C_{2',6'}$), 137.80 (d, C_8), 137.31 (d, C_4), 132.10 (s), 131.06 (d, C_5), 130.97 (d, C_7), 130.33 (s), 128.31 (s), 112.73 (d, $C_{3',5'}$), 40.38 (q, 4′-NMe_2), and 12.76 (q, 3-Me). Found: C, 66.09; H, 5.36; N, 2.64%. Calcd for $C_{31}H_{28}NPF_6$: C, 66.55; H, 5.04; N, 2.50%.

Bis(3,6-di-*t*-butyl-1-azulenyl)[4-(dimethylamino)phenyl]methyl Hexafluorophosphate (5c·PF_6^-). The general procedure was followed using DDQ (137 mg, 0.604 mmol), bis(3,6-di-*t*-butyl-1-azulenyl)[4-(dimethylamino)phenyl]methane (**7c**) (308 mg, 0.503 mmol), and 60% HPF_6 (10 ml) in CH_2Cl_2 (50 ml). Recrystallization from CH_2Cl_2/hexane gave the hexafluorophosphate **5c**·PF_6^- (371 mg, 98%). Dark purple powder; mp 211.0—214.0 °C (CH_2Cl_2/hexane); MS (FAB) m/z 610 (M^+-PF_6); IR (KBr disk) ν_{max} 2961, 1601, 1472, 1464, 1433, 1418, 1366, 1345, 1237, 1188, 841, and 558 cm^{-1}; UV (MeCN) λ_{max} (log ε) 237 (4.71), 261 (4.64), 301 (4.59),

420 (4.03), and 627 nm (4.77); ^{1}H NMR (90 MHz, $CDCl_3$) δ = 8.97 (d, J = 11.0 Hz, 2H, H_4), 7.95 (dd, J = 11.0, 1.8 Hz, 2H, H_5), 7.70 (d, J = 11.0 Hz, 2H, H_8), 7.62 (s, 2H, H_2), 7.52 (dd, J = 11.0, 1.8 Hz, 2H, H_7), 7.31 (d, J = 9.0 Hz, 2H, $H_{2',6'}$), 6.81 (d, J = 9.0 Hz, 2H, $H_{3',4'}$), 3.30 (s, 6H, 4′-NMe_2), 1.58 (s, 18H, 3-*t*-Bu), and 1.46 (s, 18H, 6-*t*-Bu); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 166.95 (s, C_6), 161.49 (s, C^+), 155.05 (s), 146.46 (s), 145.85 (s), 144.53 (s), 142.61 (s, C_2), 138.92 (d, $C_{2',6'}$), 138.16 (d, C_4), 137.25 (d, C_8), 129.93 (s), 128.86 (d and d, C_5 and C_7), 127.92 (s), 112.52 (d, $C_{3',5'}$), 40.35 (q, 4′-NMe_2), 39.07 (s, 6-*t*-Bu), 33.19 (s, 3-*t*-Bu), 31.57 (q, 6-*t*-Bu), and 31.42 (q, 3-*t*-Bu). Found: C, 71.09; H, 7.53; N, 2.09%. Calcd for $C_{45}H_{56}NPF_6$: C, 71.50; H, 7.47; N, 1.85%.

(1-Azulenyl)bis[4-(dimethylamino)phenyl]methyl Hexafluorophosphate (6a·PF_6^-). The general procedure was followed using DDQ (272 mg, 1.20 mmol), (1-azulenyl)bis[4-(dimethylamino)phenyl]methane (**8a**) (382 mg, 1.00 mmol), and 60% HPF_6 (10 ml) in CH_2Cl_2 (100 ml). Recrystallization from CH_2Cl_2/ether gave the hexafluorophosphate **6a**·PF_6^- (521 mg, 99%). Brown powder; mp 147.0—151.0 °C (CH_2Cl_2/ether); MS (FAB) *m/z* 379 (M^+-PF_6); IR (KBr disk) ν_{max} 1584, 1375, 1364, 1171, 841, and 558 cm^{-1}; UV (MeCN) λ_{max} (log ε) 226 (4.48), 255 (4.47), 285 (4.34), 403 (3.82), and 608 nm (4.86); ^{1}H NMR (90 MHz, $CDCl_3$) δ = 8.63 (d, J = 9.0 Hz, 1H, H_4), 8.00 (dd, J = 10.1, 9.0 Hz, 1H, H_6), 7.98 (d, J = 9.9 Hz, 1H, H_8), 7.92 (d, J = 4.2 Hz, 1H, H_2), 7.74 (dd, J = 9.0, 9.0 Hz, 1H, H_5), 7.59 (d, J = 4.2 Hz, 1H, H_3), 7.52 (dd, J = 10.1, 9.9 Hz, 1H, H_7), 7.30 (d, J = 9.1 Hz, 1H, $H_{2',6'}$), 6.83 (d, J = 9.1 Hz, 4H, $H_{3',5'}$), and 3.27 (s, 12H, 4′-NMe_2); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 170.54 (s, C^+), 155.48 (s), 150.02 (s), 145.79 (s), 145.24 (d, C_2), 141.73 (d, C_6), 139.96 (d, C_4), 139.57 (d, $C_{2',6'}$), 138.35 (d, C_8), 131.30 (d, C_5), 130.63 (d, C_7), 130.36 (s), 127.22 (s), 122.67 (d, C_3), 112.55 (d, $C_{3',5'}$), and 40.32 (q, 4′-NMe_2). Found: C, 61.77; H, 5.49; N, 5.51%. Calcd for $C_{27}H_{27}N_2PF_6$: C, 61.83; H, 5.19; N, 5.34%.

(3-Methyl-1-azulenyl)bis[4-(dimethylamino)phenyl]methyl Hexafluorophosphate (6b·PF_6^-). The general procedure was followed using DDQ (273 mg, 1.20 mmol), (3-methyl-1-azulenyl)bis[4-(dimethylamino)phenyl]methane (**8b**) (395 mg, 1.00 mmol), and 60% HPF_6 (10 ml) in CH_2Cl_2 (100 ml). Recrystallization from CH_2Cl_2/ether gave the hexafluorophosphate **6b**·PF_6^- (526 mg, 98%). Brown powder; mp 157.0—159.0 °C (CH_2Cl_2/ether); MS (FAB) *m/z* 393 (M^+-PF_6); IR (KBr disk) ν_{max} 1586, 1366, 1186, 1173, 843, and 558 cm^{-1}; UV (MeCN) λ_{max} (log ε) 230 (4.50), 260 (4.49), 288 (4.34), 414 (3.91), and 605 nm (4.86); ^{1}H NMR (90 MHz, $CDCl_3$) δ = 8.54 (d, J = 9.5 Hz, 1H, H_4), 7.96 (dd, J = 9.7, 9.7 Hz, 1H, H_6), 7.90 (d, J = 9.5 Hz, 1H, H_8), 7.78 (s, 1H, H_2), 7.75 (dd, J = 9.7, 9.5 Hz, 1H, H_5), 7.48 (dd, J = 9.7, 9.5 Hz, 1H, H_7), 7.28 (d, J = 9.2 Hz, 4H, $H_{2',6'}$), 6.82 (d, J = 9.2 Hz, 4H, $H_{3',5'}$), 3.26 (s, 12H, 4′-NMe_2), and 2.67 (s, 3H, 3-Me); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 169.69 (s, C^+), 155.33 (s), 148.32 (s), 147.22 (s), 145.51 (d, C_2), 141.73 (d, C_6), 139.47 (d, $C_{2',6'}$), 138.19 (d, C_8), 137.06 (d, C_4), 131.67 (s), 130.97 (d, C_5), 130.91 (d, C_7), 129.44 (s), 127.43 (s), 112.49 (d, $C_{3',5'}$), 40.38 (q, 4′-NMe_2), and 12.76 (q, 3-Me). Found: C, 62.29; H, 5.70; N, 5.46%. Calcd for $C_{28}H_{29}N_2PF_6$: C, 62.45; H, 5.43; N, 5.20%.

(3,6-Di-*t*-butyl-1-azulenyl)bis[4-(dimethylamino)phenyl]methyl Hexafluorophosphate (6c·PF_6^-). The general procedure was followed using DDQ (273 mg, 1.20 mmol), (3,6-di-*t*-butyl-1-azulenyl)bis[4-(dimethylamino)phenyl]methane (**8c**) (494 mg, 1.00 mmol), and 60% HPF_6 (10 ml) in CH_2Cl_2 (100 ml). Recrystallization from CH_2Cl_2/ether gave the hexafluorophosphate **6c**·PF_6^- (544 mg, 85%). Brown powder; mp 183.5—187.0 °C (CH_2Cl_2/ether); MS (FAB) *m/z* 491 (M^+-PF_6); IR (KBr disk) ν_{max} 1586, 1366, 1356, 1184, 1173, 843, and 558 cm^{-1}; UV (MeCN) λ_{max} (log ε) 231 (4.51), 261 (4.55), 310 (4.43), 419 (3.96), and 606 nm (4.87); ^{1}H NMR (90 MHz, $CDCl_3$) δ = 8.94 (d, J = 11.0 Hz, 1H, H_4), 7.97 (d, J = 10.8 Hz, 1H, H_8), 7.95 (dd, J = 11.0, 2.0 Hz, 1H, H_5), 7.73 (s, 1H, H_2), 7.63 (dd, J = 10.8, 2.0 Hz, 1H, H_7), 7.29 (d, J = 9.1 Hz, 4H, $H_{2',6'}$), 6.84 (d, J = 9.1 Hz, 4H, $H_{3',5'}$), 3.27 (s, 12H, 4′-NMe_2), 1.60 (s, 9H, 3-*t*-Bu), and 1.48 (s, 9H, 6-*t*-Bu); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 169.75 (s, C^+), 167.19 (s, C_6), 155.18 (s), 147.68 (s), 146.21 (s), 144.47 (s), 142.55 (d, C_2), 139.29 (d, $C_{2',6'}$), 138.07 (d, C_4), 137.58 (d, C_8), 129.23 (d and d, C_5 and C_7), 129.14 (s), 127.49 (s), 112.34 (d, $C_{3',5'}$), 40.35 (q, 4′-NMe_2), 39.16 (s, 6-*t*-Bu), 33.16 (s, 3-*t*-Bu), 31.45 (q, 6-*t*-Bu), and 31.27 (q, 3-*t*-Bu). Found: C, 65.66; H, 6.93; N, 4.56%. Calcd for $C_{35}H_{43}N_2PF_6$: C, 66.03; H, 6.81; N, 4.40%.

The pK_{R^+} Value. The sample solutions of the hexafluorophopshates **5a**—**c**·PF_6^- and **6a**—**c**·PF_6^- were prepared by dissolving in a glycine (0.1 M) solution (50 ml) and made up to 100 ml by adding MeCN; the sample solution with lower acidity was made by further alkalification with 20% aqueous NaOH. The pH of each sample was measured on a Horiba pH meter F-13 calibrated with standard buffers before use. The observed absorbances at the specific absorption maxima of the cation **5a**—**c** and **6a**—**c** were plotted against the pH, giving a classical titration curve whose midpoint was taken as the pK_{R^+} value.

The complete spectral data of MS, IR, UV, ^{1}H, ^{13}C NMR spectra, and detailed synthetic procedures (18 pages) for the reported compounds (hexafluorophosphates of **5a**—**c** and **6a**—**c**, **7a**—**c**, **8a**—**c**, **10a**—**b**, and **11**). ^{1}H NMR and ^{13}C NMR spectra for all mentioned compounds (39 pages). This materials is deposited as Document No. 69061 at the Office of the Editor of Bull. Chem. Soc. Jpn.

This work was supported by the Nishida Research Fund for Fundamental Organic Chemistry and a Grant-in-Aid for Scientific Research No. 07740482 from the Ministry of Education, Science, Sports and Culture.

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