Synthesis and Dynamic Stereochemistry of Di-1-azulenyl-(1- and 2-naphthyl)methyl Hexafluorophosphates. Clear Evidence of the One-Ring Flip Mechanism of a Molecular Propeller by Controlling the Flipping Ring[1)]

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In order to control the flipping ring of a molecular propeller and to obtain clear evidence of a one-ring flip mechanism, stable carbocations, di-1-azulenyl(1-naphthyl and 2-naphthyl)methyl cations, bis(3-methyl-1-azulenyl)(1-naphthyl (**5b**) and 2-naphthyl (**6b**))methyl cations, and bis(3,6-di-*t*-butyl-1-azulenyl)-(1-naphthyl and 2-naphthyl)methyl cations were synthesized by hydride abstraction of the corresponding hydrocarbons. These cations showed extreme stabilities with high pK_{R+} values (10.3—12.7). The dynamic stereochemistries of **5b** and **6b** were studied by temperature-dependent ^{1}H NMR spectra, which were analyzed by a flip mechanism. While the ^{1}H NMR signals of **6b** did not resolve satisfactorily, the low-temperature ^{1}H NMR spectra of **5b** showed that the flipping ring of the molecular propeller was controlled by a one-ring flip of the 1-naphthyl group. These analyses afforded clear evidence of the one-ring flip mechanisms of (1-azulenyl)methyl cations.

The correlated rotation of a molecular propeller is commonly analyzed in terms of the flip mechanism postulated by Kurkland et al.[2—4)] In this mechanism, a ring flip is defined by the rotation of the ring through the plane which is perpendicular to a reference plane (the plane which is defined by three arylic ipso carbons). The nonflipping ring rotates concomitantly with the ring flip in the opposite direction, which passes through the reference plane. Depending on the number of flipping rings during the rotation, the mechanisms are designated as zero-, one-, two-, or three-ring flips. Each of these mechanisms involves helicity reversal. The lowest energy (threshold) rotation mechanism for the conformational change of the system was limited to a sterically most favorable two-ring flip.[5,6)] Recently, we have reported the synthesis and the dynamic stereochemistry of azulene analogues of triphenylmethyl cations (**4**), i.e., (tri-1-azulenyl)methyl (**1a**), (di-1-azulenyl)phenylmethyl (**2a**), and (1-azulenyl)diphenylmethyl (**3a**) hexafluorophosphates and their derivatives (**1b**—**g**·PF_6^-, **2b**—**f**·PF_6^-, and **3b**—**f**·PF_6^-) (Chart 1).[7—10)] These cations (**1a**—**g**, **2a**—**f**, and **3a**—**f**) were synthesized by hydride abstraction of the corresponding hydrocarbons, and showed extreme stabilities with high pK_{R+} values. The dynamic stereochemistries of **1b** and **1g** showed that the threshold rotation mechanism for the conformational change of the system was not uniformly a two-ring flip. The mechanism was variable between a one-ring flip and a two-ring flip due to the contribution of the conjugative effect of the central cation with the azulene rings and of the steric effect among the three rings.[8—11)]

The rotation mechanisms for **1b** and **1g** were determined by comparison of the two different activation energies ($\Delta G^{\neq}$) among their four stereoisomers.[8—11)] If it is possible to control the flipping ring, the one-ring flip will appear more clearly in the temperature-dependent NMR spectra. The one-ring flip mechanism of **1b** arises from the large conjugative interaction between the central cation (C^+) and the three azulene rings. In case one of the three azulene rings of **1** is replaced by a ring whose conjugative effect is less than the azulene ring, the ring will flip predominantly. Unsymmetrical 1- and 2-naphthyl substituents allow the investigation of the rotation of the naphthyl ring by the substituents on the azulene rings in the temperature-dependent NMR spectra. Therefore, we synthesized the 1- and 2-naphthyl analogues of the (tri-1-azulenyl)methyl cations (**1**), i.e., di-1-azulenyl(1- and 2-naphthyl)methyl hexafluorophosphates (**5a**·PF_6^- and **6a**·PF_6^-) and their 3,3′-dimethyl (**5b**·PF_6^- and **6b**·PF_6^-) and 3,6,3′,6′-tetra-*t*-butyl derivatives (**5c**·PF_6^- and **6c**·PF_6^-) by hydride abstraction of the corresponding methane derivatives, i.e., di-1-azulenyl(1- and 2-naphthyl)methanes (**7a** and **8a**) and their 3,3′-dimethyl (**7b** and **8b**) and 3,6,3′,6′-tetra-*t*-butyl derivatives (**7c** and **8c**). The dynamic stereochemistries of **5b** and **6b** were studied by temperature-

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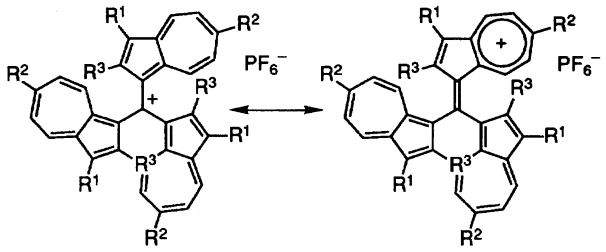
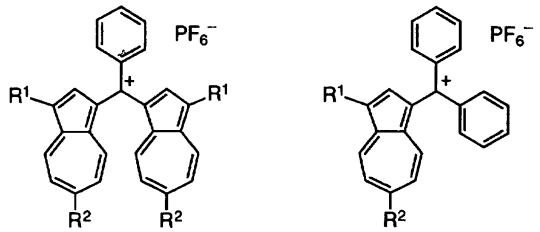
dependent ^{1}H NMR spectra, which were analyzed by the flip mechanism (Chart 2).[2—4]

Results and Discussion

Synthesis. The synthesis of **5a**—**c**·PF_6^- and **6a**—**c**·PF_6^- was accomplished by hydride abstraction from the corresponding methane derivatives (**7a**—**c** and **8a**—**c**) (Scheme 1). The reaction of two molar equivalents of azulene (**9a**) and its 1-methyl (**9b**) and 1,6-di-*t*-butyl derivatives (**9c**)[8] with 1- or 2-naphthaldehydes in acetic acid at room temperature for 24 h afforded **7a**—**c** and **8a**—**c** in 29—86% yields (Table 1),



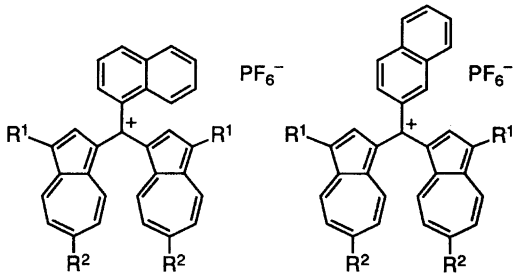
1a·PF_6^-: R^1=H, R^2=H, R^3=H
1b·PF_6^-: R^1=Me, R^2=H, R^3=H
1c·PF_6^-: R^1=COOMe, R^2=H, R^3=H
1d·PF_6^-: R^1=*t*-Bu, R^2=*t*-Bu, R^3=H
1e·PF_6^-: R^1=H, R^2=*t*-Bu, R^3=H
1f·PF_6^-: R^1=*t*-Bu, R^2=H, R^3=H
1g·PF_6^-: R^1=H, R^2=H, R^3=Me



2a·PF_6^-: R^1=H, R^2=H
2b·PF_6^-: R^1=Me, R^2=H
2c·PF_6^-: R^1=COOMe, R^2=H
2d·PF_6^-: R^1=*t*-Bu, R^2=*t*-Bu
2e·PF_6^-: R^1=H, R^2=*t*-Bu
2f·PF_6^-: R^1=*t*-Bu, R^2=H

3a·PF_6^-: R^1=H, R^2=H
3b·PF_6^-: R^1=Me, R^2=H
3c·PF_6^-: R^1=COOMe, R^2=H
3d·PF_6^-: R^1=*t*-Bu, R^2=*t*-Bu
3e·PF_6^-: R^1=H, R^2=*t*-Bu
3f·PF_6^-: R^1=*t*-Bu, R^2=H

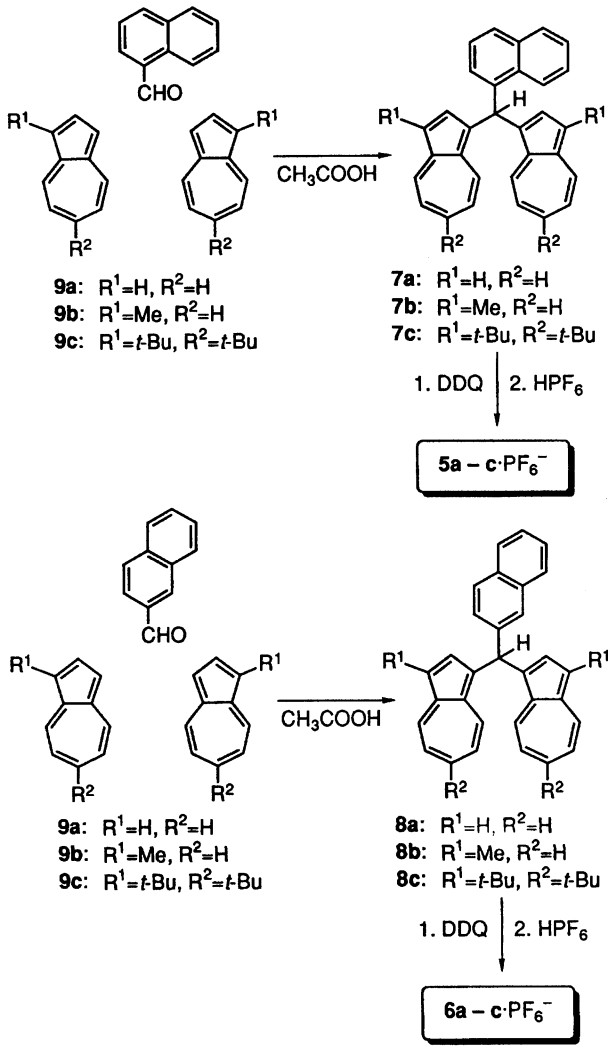
Chart 1.



5a·PF_6^-: R^1=H, R^2=H
5b·PF_6^-: R^1=Me, R^2=H
5c·PF_6^-: R^1=*t*-Bu, R^2=*t*-Bu

6a·PF_6^-: R^1=H, R^2=H
6b·PF_6^-: R^1=Me, R^2=H
6c·PF_6^-: R^1=*t*-Bu, R^2=*t*-Bu

Chart 2.



Scheme 1.

together with 1,3-bis[(1-azulenyl)(1- and 2-naphthyl)-methyl]azulenes (**10** and **11**) in 22 and 20% yields, respectively, in the case of **9a**. Hydride abstraction[7—10] of **7a**—**c** and **8a**—**c** with DDQ in dichloromethane at room temperature followed by addition of a 60% aqueous HPF_6 solution yielded **5a**—**c**·PF_6^- and **6a**—**c**·PF_6^- in 89—99% yields (Table 1).

pK_{R+} Values and Redox Potentials. The pK_{R+} values of **5a**—**c** and **6a**—**c** were determined spectrophotometrically at 25 °C in a buffer solution prepared in 50% aqueous MeCN.[8,10] The pK_{R+} values of **5a** (10.7) and **6a** (10.3) are extremely high for a methyl cation substituted with only hydrocarbon groups. The methyl substituents on the azulene rings slightly increase the pK_{R+} values (**5b**; 11.0 and **6b**; 11.3). Introduction of bulky *t*-butyl groups at the 3,3′,6,6′-positions stabilized the cations (**5a** and **6a**) effectively. The pK_{R+} values of the *t*-butyl derivatives (**5c** and **6c**) are higher by 1.9 and 2.4 pK_{R+} units than those of **5a** and **6a**, respectively. The pK_{R+} values of **5a**—**c** and **6a**—**c** are summarized in Table 2 along with those of the phenyl derivatives (**2a**, **b**, and **d**).[7,8] There are small differ-

Table 1. Reaction of Azulenes (**9a**—**c**) with 1- or 2-Naphthaldehyde in Acetic Acid, and Synthesis of Di-1-azulenyl(1- and 2-naphthyl)methyl Hexafluorophosphates (**5a**—**c**·PF_6^- and **6a**—**c**·PF_6^-)

Entry	R^1	R^2	Yield (%) of **7** and **8**		Yield (%) of **5**·PF_6^- and **6**·PF_6^-	
1	H	H	**7a**	34	**5a**·PF_6^-	94
2	Me	H	**7b**	76	**5b**·PF_6^-	94
3	*t*-Bu	*t*-Bu	**7c**	80	**5c**·PF_6^-	89
4	H	H	**8a**	29	**6a**·PF_6^-	94
5	Me	H	**8b**	86	**6b**·PF_6^-	99
6	*t*-Bu	*t*-Bu	**8c**	86	**6c**·PF_6^-	98

Table 2. The pK_{R+} Values and the Redox Potentials[a] of **5a**—**c** and **6a**—**c**, Together with Those of **2a**, **b**, and **d**[7,8]

	pK_{R+}[b]	E_1^{ox}	E_2^{ox}	E_1^{red}	E_2^{red}
5a	10.7 (81%)	(+1.02)	—	−0.64	(−1.55)
5b	11.0 (77%)	(+0.88)	—	−0.69	(−1.59)
5c	12.6 (12%)	+0.87	(+1.38)	−0.77	(−1.64)
6a	10.3 (81%)	(+1.03)	—	(−0.63)	—
6b	11.3 (75%)	(+0.89)	—	−0.70	(−1.55)
6c	12.7 (29%)	+0.87	(+1.39)	−0.77	(−1.61)
2a	10.5	(+1.04)	—	−0.66	(−1.52)
2b	10.8	(+0.90)	—	−0.70	(−1.57)
2d	12.4	+0.88	(+1.38)	−0.78	(−1.64)

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 were shown in parentheses.

ences in the pK_{R+} values of **5**, **6**, and **2**. The 1- and 2-naphthyl substituents slightly increase the pK_{R+} values, compared with the phenyl substituent, except for **6a**. Neutralization of these cations (**5a**—**c** and **6a**—**c**) is not completely reversible due to the instability of the neutralized products under basic conditions. Immediate acidification of the alkaline solutions of **5a**—**c** and **6a**—**c** with HCl regenerated the absorption maxima of the cations in the visible region in 12—81%; this is also summarized in Table 2.

The redox potentials (V vs. Ag/Ag^+) of **5a**—**c** and **6a**—**c** measured by cyclic voltammetry in MeCN are also summarized in Table 2 together with those of the phenyl derivatives (**2a**, **b**, and **d**).[8] The oxidation of **5a**—**c** and **6a**—**c** showed a wave around +0.87—+1.03 V, which is due to the oxidation of one azulene ring to give a dication radical. The reduction of **5a**—**c** and **6a**—**c** showed a reversible wave around −0.64—−0.77 V and an irreversible wave around −1.55—−1.64 V, except for **6a**. The more negative reduction potentials of the *t*-butyl derivatives (**5c**; −0.77 and **6c**; −0.77 V) correspond to their high pK_{R+} values. These redox potentials are almost equal to those of the phenyl derivatives (**2**).

Dynamic Stereochemistries of 5b and 6b. 3, 3′-Dimethyl derivatives (**5b** and **6b**) were utilized for the analyses of the dynamic stereochemistries of **5a**—**c** and **6a**—**c** to avoid the complexities of the temperature-dependent NMR spectra. The ^1H NMR (600 MHz, methyl region) spectra of **5b** in 50% CD_2Cl_2/CS_2 at various temperatures are shown in Fig. 1. At −85 °C the NMR spectrum in the methyl region consists of four sets of two signals with equal intensities (ab, cd, ef, and gh, as indicated in Fig. 1) in intensity ratios of ca. 2.6 : 2.0 : 1 : 1.9. Four isomeric propeller conformations (***A***, ***B***, ***C***, and ***D***) and their enantiomers ($\overline{\boldsymbol{A}}$, $\overline{\boldsymbol{B}}$, $\overline{\boldsymbol{C}}$, and $\overline{\boldsymbol{D}}$) are possible for a molecule of this type. These stereoisomers (***A*$\overline{\boldsymbol{A}}$**, ***B*$\overline{\boldsymbol{B}}$**, ***C*$\overline{\boldsymbol{C}}$**, and ***D*$\overline{\boldsymbol{D}}$**) are illustrated in Fig. 2. Each set of enantiomers has C_1 symmetry and has two nonequivalent methyl groups. Therefore, the eight resonance signals in the methyl region at −85 °C are attributable to a mixture of these diastereomers, and the two methyl signals with equal intensities arise from the methyl groups of a set of enantiomers.

When the sample was warmed to ca. −70 °C, the two signals (g and h) with equal intensities at the lower field coalesced to a singlet, while the other signals (ab, cd, and ef) at the higher field did not change very much. Upon further warming of the sample, noticeable line broadening occurred in these NMR signals and resulted in coalescence of all eight signals to a singlet, which became sharp at 40 °C. The temperature-dependence of the ^1H NMR spectra of **5b** was completely reversible.

Possibilities for the isomerization of **5b** can be an-

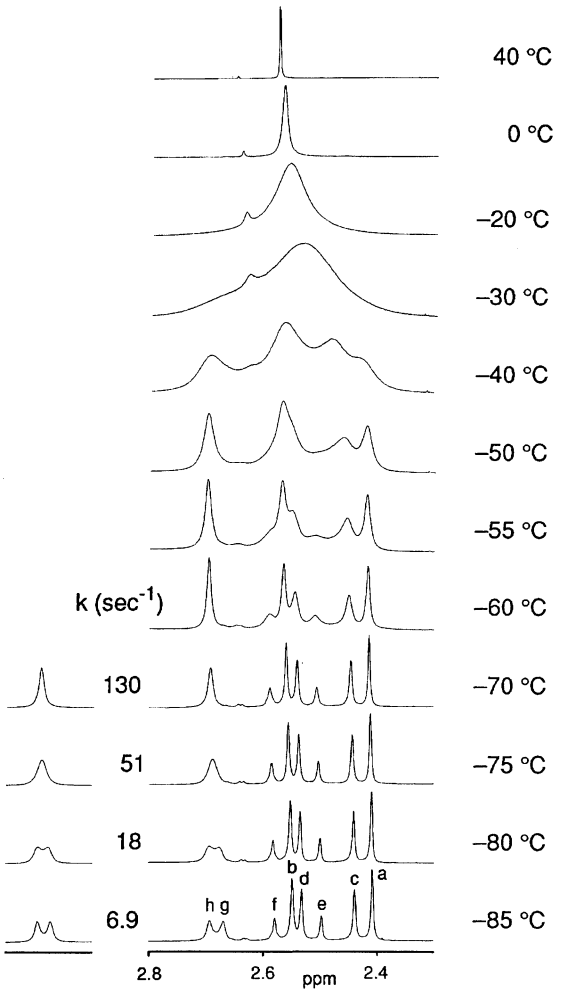


Fig. 1. ^{1}H NMR spectra of **5b** (600 MHz, methyl region) at various temperatures. The right panel displays the experimental spectra. The left panel shows the calculated spectra for the $D \rightarrow \overline{D}$ interconversion of a one-ring flip mechanism.

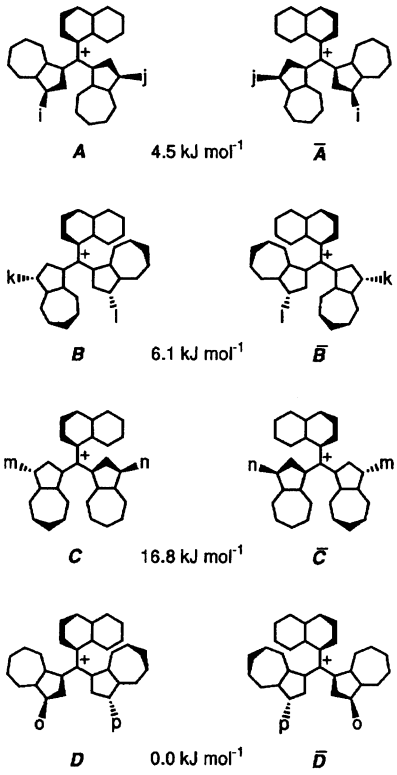


Fig. 2. Four isomeric propeller conformations of **5b**, and calculated (PM3) relative heats of formation for these conformations. Letters i—p are tentatively attached to the methyl groups, corresponding to the low-temperature NMR spectrum.

alyzed by flip mechanisms. The four flip mechanisms and the idealized transition state for **5b** are illustrated in Fig. 3. There are a total of 20 distinct pathways in the four kinds of flip mechanisms (four in zero-ring flip, seven in one-ring flip, six in two-ring flip, and three in three-ring flip). The diastereomeric environments of the 3,3′-methyl groups of the azulene rings are labeled with the letters i—p for convenience, as shown in Fig. 2. The resulting site exchanges for the 3,3′-methyl groups of the stereoisomers ($A\overline{A}$, $B\overline{B}$, $C\overline{C}$, and $D\overline{D}$) of **5b** by the four flip mechanisms are summarized in Table 3. The processes which averaged the 3,3′-methyl signals with equal intensities at the lower field (signals g and h) were $C \rightarrow \overline{C}$ and $D \rightarrow \overline{D}$ interconversions of the one-ring flip mechanism and $A \rightarrow \overline{A}$ and $B \rightarrow \overline{B}$ interconversions of the three-ring flip mechanism. Therefore, the mechanism that can explain the observed coalescence of the two signals (g and h) at the low temperatures (−85——70 °C) was limited to those four processes.

The three-ring flip processes (Fig. 3e) are readily excluded from the analysis of the dynamic behavior of **5b**. The three transition states of the three-ring flip processes (all three rings rotate through planes perpendicular to the reference plane) are unfavorable on steric grounds[12,13] because the steric interactions among the 8-positions of the azulene rings and the 8-position of the 1-naphthyl group are essential for the transition states of $A \rightarrow \overline{A}$ and $B \rightarrow \overline{B}$, as shown in Fig. 3f. Consequently, the threshold rotation mechanism for **5b** was either a one-ring flip process of $C \rightarrow \overline{C}$ or that of $D \rightarrow \overline{D}$.

The idealized transition state of $C \rightarrow \overline{C}$ at the one-ring flip entails the placement of the 8-position of the two azulene rings in essentially the same location, as shown in Fig. 3c. This situation is obviously unreasonable for the observed coalescence of the two signals (g and h). Furthermore, consideration of the stabilities of the stereisomers ($A\overline{A}$, $B\overline{B}$, $C\overline{C}$, and $D\overline{D}$) using molecular models and the calculated (PM3)[14] relative heats of formation, as shown in Fig. 2, demonstrates that $C\overline{C}$ is the most unstable stereoisomer, so that the methyl signals of e and f should be assigned to those of $C\overline{C}$. Therefore, the observed coalescence of the g and h signals at low temperatures (−85——70 °C) arises from the $D \rightarrow \overline{D}$ interconversion of the one-ring flip mechanism.

The $D \rightarrow \overline{D}$ interconversion of the one-ring flip mechanism clearly appeared in the low-temperature NMR

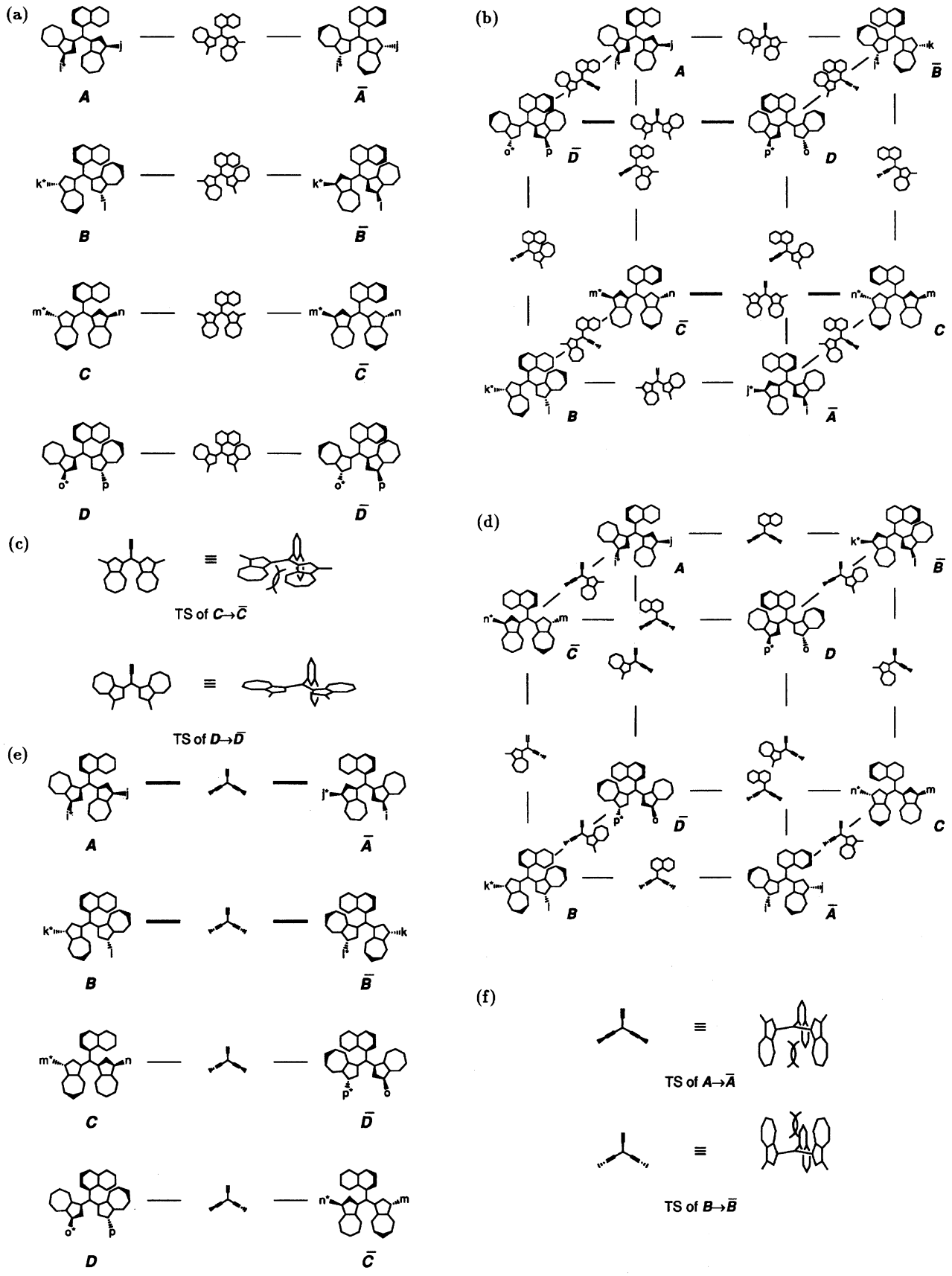


Fig. 3. The four flip mechanisms and the idealized transition states (TS) for the stereoisomers of **5b**. (a) Zero-ring flip mechanism for **5b**; (b) One-ring flip mechanism for **5b**; (c) TS of the $C \rightarrow \overline{C}$ and $D \rightarrow \overline{D}$ interconversions of the one-ring flip mechanism; (d) Two-ring flip mechanism; (e) Three-ring flip mechanism; (f) TS of the $A \rightarrow \overline{A}$ and $B \rightarrow \overline{B}$ interconversions of the three-ring flip mechanism.

Table 3. Resulting Site Exchanges for 3,3′-Methyl Groups of the Stereoisomers ($A\overline{A}$, $B\overline{B}$, $C\overline{C}$, and $D\overline{D}$) of **5b** by the Four Flip Mechanisms

Mechanism	Isomerization process	Resulting site exchanges[a]
Zero-ring flip	[***A***→$\overline{A}$] or [$\overline{A}$→***A***]	[i→i] [j→j]
	[***B***→$\overline{B}$] or [$\overline{B}$→***B***]	[k→k] [l→l]
	[***C***→$\overline{C}$] or [$\overline{C}$→***C***]	[m→m] [n→n]
	[***D***→$\overline{D}$] or [$\overline{D}$→***D***]	[o→o] [p→p]
One-ring flip	[***A***→$\overline{B}$] or [$\overline{A}$→***B***]	[i→l] [j→k]
	[***A***→$\overline{C}$] or [$\overline{A}$→***C***]	[i→m] [j→n]
	[***A***→$\overline{D}$] or [$\overline{A}$→***D***]	[i→o] [j→p]
	[***B***→$\overline{C}$] or [$\overline{B}$→***C***]	[k→m] [l→n]
	[***B***→$\overline{D}$] or [$\overline{B}$→***D***]	[k→o] [l→p]
	[***C***→$\overline{C}$] or [$\overline{C}$→***C***][b]	[m→n] [n→m]
	[***D***→$\overline{D}$] or [$\overline{D}$→***D***][b]	[o→p] [p→o]
Two-ring flip	[***A***→$\overline{B}$] or [$\overline{A}$→***B***]	[i→k] [j→l]
	[***A***→$\overline{C}$] or [$\overline{A}$→***C***]	[i→n] [j→m]
	[***A***→$\overline{D}$] or [$\overline{A}$→***D***]	[i→p] [j→o]
	[***B***→$\overline{C}$] or [$\overline{B}$→***C***]	[k→n] [l→m]
	[***B***→$\overline{D}$] or [$\overline{B}$→***D***]	[k→p] [l→o]
	[***C***→$\overline{D}$] or [$\overline{C}$→***D***]	[m→o] [n→p]
Three-ring flip	[***A***→$\overline{A}$] or [$\overline{A}$→***A***][b]	[i→j] [j→i]
	[***B***→$\overline{B}$] or [$\overline{B}$→***B***][b]	[k→l] [l→k]
	[***C***→$\overline{D}$] or [$\overline{C}$→***D***]	[m→p] [n→o]

a) The letters in brackets represent 3,3′-methyl groups whose environments are averaged by the process indicated. b) The process averaged the 3,3′-methyl signals of identical conformer.

spectra. These results showed that only the 1-naphtyl ring was the flipping ring in **5b** at the low temperatures, and the threshold rotation mechanism of **5b** was a one-ring flip of this ring. The mechanism that can explain the observed coalescence at higher temperatures is a combination of the one-ring flip of the 1-naphthyl ring (***D***→$\overline{D}$ interconversion) with other pathways, such as a one-azulene ring flip mechanism for **2b**.[14]

Simulation of the low-temperature ^{1}H NMR spectra of **5b** was accomplished by the program DNMR3K,[16] and the results are also shown in Fig. 1. The rate data was used to calculate the free energy of the activation for the enantiomerization of ***D*** and $\overline{D}$ at −70 °C. The barrier for the enantiomerization of ***D*** and $\overline{D}$ is $\Delta G^{\neq}_{-70\,^\circ C}=41.1\pm2.1$ kJ mol^{-1} ($\Delta H^{\neq}=57.5\pm1.5$ kJ mol^{-1}, $\Delta S^{\neq}=81\pm7.4$ J K^{-1} mol^{-1}) which is lower than the $\Delta G^{\neq}_{-70\,^\circ C}$ values for the flip of an azulene ring of **2b** ($\Delta G^{\neq}_{-70\,^\circ C}=47.3\pm3.5$ and 48.3 ± 3.5 kJ mol^{-1}).

The ^{1}H NMR (600 MHz, methyl region) spectra of **6b** in 50% CD_2Cl_2/CS_2 at various temperatures are shown in Fig. 4. At −85 °C the NMR spectra in the methyl region consists of seven signals (as indicated by the letters a—g in Fig. 4) in an intensity ratio of ca. 2.0 : 2.3 : 2.3 : 2.8 : 2.8 : 1 : 1. Eight isomeric propeller conformations including the stereoisomers are possible for **6b**, similar to the case of **5b**. Each set of two signals with equal intensities (bc, de, and fg) is attributable to

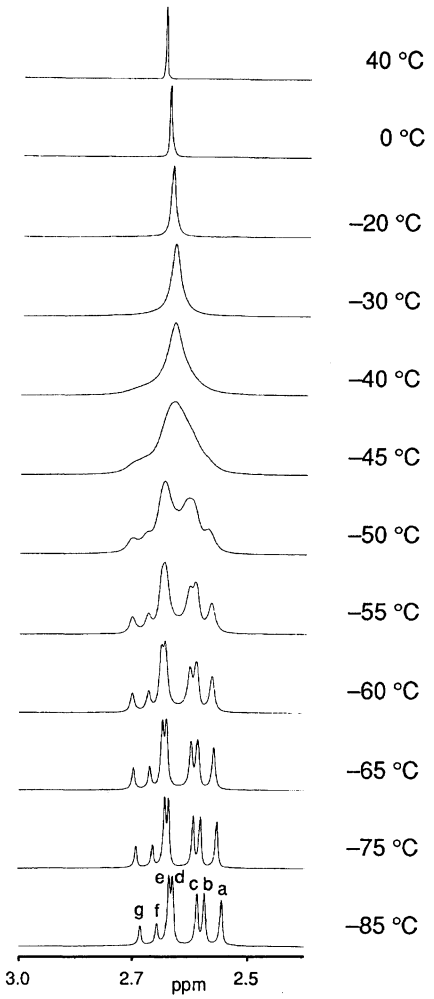


Fig. 4. ^{1}H NMR spectra of **6b** (600 MHz, methyl region) at various temperatures.

the methyl signals of the enantiomers. The remaining one signal (a) indicates an accidental chemical shift equivalent or coalescence of the two methyl signals in a set of enantiomers at that temperature. When the sample was warmed to ca. −50 °C, noticeable line broadening and coalescence of all seven signals (a—g) to a singlet occurred simultaneously, and the signal became sharp at 40 °C.

Possibilities of stereoisomerism and isomerization of **6b** by the flip mechanism are compatible with those of **5b**. While the g and h signals of **5b** coalesced to a singlet at lower temperatures, each set of two signals of **6b** (bc, de, and fg) did not coalesce to a singlet at lower temperatures, as shown in Fig. 4. Therefore, signal a of **6b** at the higher field should arise from stereoisomers of $D\overline{D}$. The 2-naphthyl substituent does not effectively affect the separation of the methyl signals of **6b**, compared with the 1-naphthyl substituent of **5b**. The temperature-dependence of the observed signals of **6b** is consistent with the one-ring flip mechanism of the 1-naphthyl ring for **5b**.

The threshold rotation mechanism for **5b**, which

clearly appeared in the temperature-dependent NMR spectra, was a one-ring flip of the 1-naphthyl ring. The NMR signals of **6b** did not resolve satisfactorily. However, the temperature-dependence of the signals of **6b** showed tendencies similar to those of **5b**. The analysis of the dynamic stereochemistry of **5b** afforded clear evidence of the one-ring flip mechanism of (1-azulenyl)-methyl cations. The one-ring flip mechanism of the 1-naphthyl ring for **5b** is attributed to the large conjugative effect of azulene rings with the cationic carbon.

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-2500 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 or a Bruker AM 600 spectrometer at 600 MHz. ^{13}C NMR spectra were recorded on a Hitachi R-90H at 22.5 MHz or a Bruker AM 600 spectrometer at 150 MHz. Gel permeation chromatographies (GPC) were performed on Showadenko Shodex K2001 and K2002. 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 a scan rate of 100 m V s^{-1}. 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(1- and 2-naphthyl)methanes (7a—c and 8a—c). A solution of azulenes (**9a—c**) and 1- or 2-naphthaldehyde in glacial acetic acid was stirred at room temperature under an Ar atmosphere until the reaction was completed. The solvent was removed in vacuo and 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 CH_2Cl_2 and/or GPC with $CHCl_3$. The product was further purified by recrystallization.

Di-1-azulenyl(1-naphthyl)methane (7a). The general procedure was followed using azulene (**9a**) (1.28 g, 10.0 mmol) and 1-naphthaldehyde (390 mg, 2.50 mmol) in glacial acetic acid (60 ml). The reaction mixture was stirred for 48 h at room temperature. Column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ afforded recovered **9a** (643 mg, 50%), methane **7a** (330 mg, 34%), and 1,3-bis[(1-azulenyl)(1-naphthyl)methyl]azulene (**10**) (185 mg, 22%).

7a: Blue crystals; mp 220.0—221.0 °C (EtOAc/hexane); MS (70 eV) *m/z* (rel intensity) 394 (M^+; 87), 393 (26), 267 (43), 266 (39), 265 (100), and 263 (21); IR (KBr disk) 1574, 1395, 789, 772, 737, and 731 cm^{-1}; UV (CH_2Cl_2) 228 (log ε 4.85), 284 (4.92), 294 (4.91), 349 (4.06), 365 (3.96), 601 (2.85), and 650 nm (2.77); ^{1}H NMR (90 MHz, $CDCl_3$) δ=8.25 (d, J=9.5 Hz, 4H, $H_{4,8}$), 8.07—6.87 (m, 14H), 7.05 (dd, J=10.5, 9.5 Hz, 2H, H_5), and 6.94 (dd, J=10.1, 9.5 Hz, 2H, H_7); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ=141.36 (s), 141.06 (s), 138.74 (d, C_2), 137.19 (d, C_6), 136.61 (d, C_4), 134.81 (s), 133.89 (s), 133.44 (d, C_8), 133.10 (s), 131.76 (s), 128.62 (d), 126.88 (d), 126.67 (d), 125.91 (d), 125.45 (d), 125.23 (d), 124.14 (d), 122.46 (d, C_5), 121.94 (d, C_7), 116.61 (d, C_3), and 39.35 (d, CH). Found: C, 94.35; H, 5.76%. Calcd for $C_{31}H_{22}$: C, 94.38; H, 5.62%.

10: Blue crystals; mp > 300 °C (toluene/hexane); MS (70 eV) *m/z* (rel intensity) 660 (M^+; 100), 394 (46), 268 (29), 267 (39), 266 (25), and 265 (70); IR (KBr disk) 1574, 1395, 787, 774, and 729 cm^{-1}; UV (CH_2Cl_2) 228 (log ε 5.06), 283 (5.07), 349 (4.17), 365 (4.14), and 605 nm (2.98); ^{1}H NMR (90 MHz, $CDCl_3$) δ=8.18 (d, J=10.5 Hz, 6H, $H_{4,8,4',8'}$) and 8.06—6.61 (m, 30H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ=141.03 (s), 140.97 (s), 140.75 (s), 138.80 (d, $C_{2,2'}$), 137.31 (d, C_6), 137.10 (d, $C_{6'}$), 136.49 (d, $C_{4'}$), 135.75 (s), 134.78 (s), 133.80 (s), 133.59 (d, $C_{4,8}$ or $C_{8'}$), 133.50 (d, $C_{4,8}$ or $C_{8'}$), 132.70 (s), 132.64 (s), 131.76 (s), 131.67 (s), 128.53 (d), 126.79 (d), 126.61 (d), 125.69 (d), 125.30 (d), 125.08 (d), 124.35 (d), 122.37 (d), 121.79 (d, 2C), 116.39 (d, $C_{3'}$), and 39.59 (d, CH). Found: C, 94.07; H, 5.96%. Calcd for $C_{52}H_{36}$·toluene: C, 94.11; H, 5.89%.

Bis(3-methyl-1-azulenyl)(1-naphthyl)methane (7b). The general procedure was followed using 1-methylazulene (**9b**) (703 mg, 4.95 mmol) and 1-naphthaldehyde (398 mg, 2.55 mmol) in glacial acetic acid (30 ml). The reaction mixture was stirred for 45 h at room temperature. Column chromatography on silica gel with CH_2Cl_2 afforded methane **7b** (797 mg, 76%). Blue crystals; mp 265.0—266.5 °C decomp (EtOAc/hexane); MS (70 eV) *m/z* (rel intensity) 422 (M^+; 100), 407 (38), 295 (25), 280 (27), 279 (54), 266 (24), and 265 (69); IR (KBr disk) 1572, 789, 776, and 731 cm^{-1}; UV (CH_2Cl_2) 228 (log ε 4.82), 286 (4.91), 357 (4.03), 374 (4.01), 631 (2.85), and 687 nm (2.76); ^{1}H NMR (600 MHz, $CDCl_3$) δ=8.143 (d, J=9.7 Hz, 4H, $H_{4,8}$), 8.033 (d, J=8.5 Hz, 1H, $H_{8'}$), 7.854 (d, J=7.7 Hz, 1H, $H_{5'}$), 7.715 (d, J=8.2 Hz, 1H, $H_{4'}$), 7.415 (dd, J=9.8, 9.7 Hz, 2H, H_6), 7.401 (dd, J=7.7, 6.9 Hz, 1H, $H_{6'}$), 7.381 (s, 1H, CH), 7.298 (dd, J=8.5, 6.9 Hz, 1H, $H_{7'}$), 7.272 (dd, J=8.2, 7.5 Hz, 1H, $H_{3'}$), 7.175 (s, 2H, H_2), 6.969 (dd, J=9.7, 9.7 Hz, 2H, H_5), 6.911 (dd, J=7.5 Hz, 1H, $H_{2'}$), 6.826 (dd, J=9.8, 9.7 Hz, 2H, H_7), and 2.507 (s, 6H, 3-Me); ^{13}C NMR (150 MHz, $CDCl_3$) δ=141.651 (s, $C_{1'}$), 139.874 (d, C_2), 137.187 (d, C_6), 137.034 (s, C_{3a}), 134.920 (s, C_{8a}), 133.880 (s, $C_{4'a}$), 133.543 (d, C_4), 132.839 (d, C_8), 131.747 (s, $C_{8'a}$), 131.577 (s, C_1), 128.613 (d, $C_{5'}$), 126.801 (d, $C_{4'}$), 126.685 (d, $C_{2'}$), 125.975 (d, $C_{7'}$), 125.499 (d, $C_{3'}$), 125.247 (d, $C_{6'}$), 124.583 (s, C_3), 124.221 (d, $C_{8'}$), 121.073 (d, C_7), 120.720 (d, C_5), 38.658 (d, CH), and 12.652 (q, 3-Me). Found: C, 92.44; H, 6.41%. Calcd for $C_{33}H_{26}$·1/3H_2O: C, 92.48; H, 6.27%.

Bis(3,6-di-*t*-butyl-1-azulenyl)(1-naphthyl)methane (7c). The general procedure was followed using 1,6-di-*t*-butylazulene (**9c**) (1.20 g, 5.00 mmol) and 1-naphthaldehyde (398 mg, 2.55 mmol) in glacial acetic acid (30 ml). The reaction mixture was stirred for 54 h at room temperature. Column chromatography on silica gel with CH_2Cl_2 afforded methane **7c** (1.23 g, 80%). Blue crystals; mp 265.0—266.0 °C decomp (EtOAc/hexane); MS (70 eV) *m/z* (rel intensity) 618 (M^+; 93), 562 (46), 561 (100), 294 (24), and 57 (90); IR (KBr disk) 2963 and 1576 cm^{-1}; UV (CH_2Cl_2) 228 (log ε 4.89), 289 (4.97), 302 (4.95), 359 (4.10), 376 (4.03), and 616 nm (2.86); ^{1}H NMR (90 MHz, $CDCl_3$) δ=8.54 (d, J=10.6 Hz, 2H, H_4), 8.14 (d, J=10.6 Hz, 2H, H_8), 8.06—6.87 (m,

8H), 7.22 (s, 2H, H_2), 7.13 (d, J=10.6 Hz, 2H, H_5), 7.01 (d, J=10.6 Hz, 2H, H_7), 1.44 (s, 18H, 3-*t*-Bu), and 1.39 (s, 18H, 6-*t*-Bu); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ=160.08 (s, C_6), 141.94 (s), 137.52 (s), 136.67 (d, C_2), 134.38 (s), 134.32 (d, C_4), 134.20 (s), 133.80 (s), 131.94 (d, C_8), 130.54 (s), 128.44 (d), 126.67 (d), 126.55 (d), 125.75 (d), 125.51 (d), 125.05 (d), 124.41 (d), 119.20 (d, C_7), 118.19 (d, C_5), 38.70 (d, CH), 38.22 (s, 6-*t*-Bu), 33.28 (s, 3-*t*-Bu), 32.27 (q, 3-*t*-Bu), and 31.91 (q, 6-*t*-Bu). Found: C, 91.32; H, 8.91%. Calcd for $C_{47}H_{54}$: C, 91.21; H, 8.79%.

Di-1-azulenyl(2-naphthyl)methane (8a). The general procedure was followed using azulene (**9a**) (1.28 g, 10.0 mmol) and 2-naphthaldehyde (391 mg, 2.50 mmol) in glacial acetic acid (60 ml). The reaction mixture was stirred for 44 h at room temperature. Column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ afforded recovered **9a** (664 mg, 52%), methane **8a** (288 mg, 29%), and 1,3-bis[(1-azulenyl)(2-naphthyl)methyl]azulene (**11**) (163 mg, 20%).

8a: Blue crystals; mp 181.5—183.5 °C (EtOAc/hexane); MS (70 eV) m/z (rel intensity) 394 (M^+; 100), 393 (33), 267 (53), 266 (46), 265 (99), 252 (26), 128 (23), and 55 (20); IR (KBr disk) 1574, 1391, 776, 764, and 735 cm^{-1}; UV (CH_2Cl_2) 230 (log ε 4.81), 283 (4.94), 325 (3.96), 349 (4.08), 365 (3.99), and 599 nm (2.85); ^{1}H NMR (90 MHz, $CDCl_3$) δ=8.28 (d, J=9.7 Hz, 2H, H_8), 8.26 (d, J=9.7 Hz, 2H, H_4), 7.82—7.25 (m, 13H), 7.05 (dd, J=9.7, 9.0 Hz, 2H, H_5), 6.94 (dd, J=9.7, 9.5 Hz, 2H, H_7), and 6.90 (s, 1H, CH); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ=143.25 (s), 141.06 (s), 138.41 (d, C_2), 137.28 (d, C_6), 136.70 (d, C_4), 135.08 (s), 133.65 (d, C_8), 133.53 (s), 132.98 (s), 132.10 (s), 127.80 (d, 3C), 127.49 (d), 126.76 (d), 125.72 (d), 125.27 (d), 122.52 (d, C_5), 121.97 (d, C_7), 116.64 (d, C_3), and 43.10 (d, CH). Found: C, 94.33; H, 5.74%. Calcd for $C_{31}H_{22}$: C, 94.38; H, 5.62%.

11: Blue crystals; mp 220.0—222.0 °C decomp (EtOAc/hexane); MS (70 eV) m/z (rel intensity) 660 (M^+; 22), 394 (52), 393 (35), 268 (65), 267 (69), 266 (34), 265 (78), 252 (26), 141 (30), 128 (100), 57 (38), 56 (31), and 55 (23); IR (KBr disk) 1574 (s), 1395 (s), 774 (s), 762 (s), and 735 (s) cm^{-1}; UV (CH_2Cl_2) 228 (log ε 5.03), 282 (5.02), 349 (4.13), 365 (4.10), and 604 nm (2.90); ^{1}H NMR (90 MHz, $CDCl_3$) δ=8.30 (d, J=9.0 Hz, 2H, $H_{4'}$), 8.20 (d, 4H, $H_{4,8,8'}$), 7.77—6.80 (m, 28H), and 6.83 (s, 2H, CH); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ=142.95 (s), 141.06 (s), 139.99 (d, C_2), 138.28 (d, $C_{2'}$), 137.43 (d, $C_{6'}$), 137.16 (d, C_6), 136.64 (d, $C_{4'}$), 135.97 (s), 135.08 (s), 133.74 (d, $C_{4,8}$ or $C_{8'}$), 133.59 (d, $C_{4,8}$ or $C_{8'}$), 133.38 (s), 132.74 (s), 132.00 (s), 131.61 (s), 127.77 (d), 127.67 (d), 127.58 (d), 127.40 (d), 126.73 (d), 125.57 (d), 124.14 (d), 122.46 (d), 121.82 (d, 2C), 116.55 (d, $C_{3'}$), and 43.00 (d, CH). Found: C, 92.38; H, 5.88%. Calcd for $C_{52}H_{36}$:H_2O: C, 92.00; H, 5.64%.

Bis(3-methyl-1-azulenyl)(2-naphthyl)methane (8b). The general procedure was followed using 1-methylazulene (**9b**) (705 mg, 4.95 mmol) and 2-naphthaldehyde (394 mg, 2.52 mmol) in glacial acetic acid (30 ml). The reaction mixture was stirred for 46 h at room temperature. Column chromatography on silica gel with CH_2Cl_2 afforded methane **8b** (903 mg, 86%). Blue crystals; mp 196.0—197.5 °C decomp (EtOAc/hexane); MS (70 eV) m/z (rel intensity) 422 (M^+; 100), 407 (40), 295 (24), 280 (24), 279 (48), and 265 (60); IR (KBr disk) 1574, 749, and 735 cm^{-1}; UV (CH_2Cl_2) 228 (log ε 4.83), 282 (4.93), 357 (4.05), 374 (4.04), and 630 nm (2.85); ^{1}H NMR (90 MHz, $CDCl_3$) δ=8.17 (d, J=9.5 Hz, 4H, $H_{4,8}$), 7.86—7.36 (m, 9H), 7.32 (s, 2H, H_2), 6.96 (dd, J=9.9, 9.5 Hz, 2H, H_5), 6.83 (dd, J=9.7, 9.5 Hz, 2H, H_7), 6.83 (s, 1H, CH), and 2.56 (s, 6H, 3-Me); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ=143.47 (s), 139.50 (d, C_2), 137.16 (d, C_6), 137.03 (s), 135.21 (s), 133.53 (d, C_4), 133.01 (d, C_8), 132.06 (s), 131.39 (s), 127.83 (d, 2C), 127.67 (d), 127.46 (d), 126.70 (d), 125.66 (d), 125.20 (d), 124.56 (s), 121.06 (d, C_7), 120.78 (d, C_5), 42.61 (d, CH), and 12.73 (q, 3-Me). Found: C, 93.41; H, 6.39%. Calcd for $C_{33}H_{26}$: C, 93.80; H, 6.20%.

Bis(3,6-di-*t*-butyl-1-azulenyl)(2-naphthyl)methane (8c). The general procedure was followed using 1,6-di-*t*-butylazulene (**9c**) (1.20 g, 5.00 mmol) and 2-naphthaldehyde (399 mg, 2.55 mmol) in glacial acetic acid (30 ml). The reaction mixture was stirred for 28 h at room temperature. Column chromatography on silica gel with CH_2Cl_2 afforded methane **8c** (1.33 g, 86%). Blue crystals; mp 241.0—242.5 °C decomp (EtOAc/hexane); MS (70 eV) m/z (rel intensity) 618 (M^+; 97), 562 (46), 561 (100), and 294 (22); IR (KBr disk) 2963, 1578, 1364, 1227, and 833 cm^{-1}; UV (CH_2Cl_2) 228 (log ε 4.92), 287 (4.98), 359 (4.12), 376 (4.05), and 613 nm (2.84); ^{1}H NMR (90 MHz, $CDCl_3$) δ=8.55 (d, J=11.0 Hz, 2H, H_4), 8.20 (d, J=10.8 Hz, 2H, H_8), 7.82—7.28 (m, 7H), 7.41 (s, 2H, H_2), 7.15 (dd, J=11.0, 1.8 Hz, 2H, H_5), 7.04 (dd, J=10.8, 1.8 Hz, 2H, H_7), 6.79 (s, 1H, CH), 1.49 (s, 18H, 3-*t*-Bu), and 1.40 (s, 18H, 6-*t*-Bu); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ=160.21 (s, C_6), 143.96 (s), 137.64 (s), 136.36 (d, C_2), 134.78 (s), 134.44 (d, C_4), 134.23 (s), 133.53 (s), 132.16 (d, C_8), 132.03 (s), 130.30 (s), 127.98 (d), 127.89 (d), 127.46 (d, 2C), 126.61 (d), 125.51 (d), 125.02 (d), 119.23 (d, C_7), 118.28 (d, C_5), 42.33 (d, CH), 38.22 (s, 6-*t*-Bu), 33.34 (s, 3-*t*-Bu), 32.33 (q, 3-*t*-Bu), and 31.91 (q, 6-*t*-Bu). Found: C, 90.60; H, 9.12%. Calcd for $C_{47}H_{54}$·1/3H_2O: C, 90.33; H, 8.82%.

General Procedure for the Synthesis of Di-1-azulenyl(1- and 2-naphthyl)methyl Hexafluorophosphates (5a—c·PF_6^- and 6a—c·PF_6^-). DDQ was added at room temperature to a solution of di-1-azulenyl(1- and 2-naphthyl)methanes (**7a**—**c** and **8a**—**c**) in CH_2Cl_2. The solution was stirred at the same temperature for 10—20 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 Et_2O (50—100 ml) was added to the solution. The precipitated crtystals were collected by filtration, washed with Et_2O, and dried in vacuo to give hexafluorophosphates **5a**—**c**·PF_6^- and **6a**—**c**·PF_6^-. The products were further purified by recrystallization from CH_2Cl_2/ether.

Di-1-azulenyl(1-naphthyl)methyl Hexafluorophosphate (5a·PF_6^-). The general procedure was followed using DDQ (137 mg, 0.60 mmol), di-1-azulenyl(1-naphthyl)-methane (**7a**) (197 mg, 0.50 mmol), and 60% HPF_6 (5 ml) in CH_2Cl_2 (50 ml). Recrystallization from CH_2Cl_2/ether gave hexafluorophosphate **5a**·PF_6^- (254 mg, 94%). Brown powder; mp 150.0—151.0 °C decomp (CH_2Cl_2/ether); MS (FAB) m/z 393 (M^+−PF_6); IR (KBr disk) 1468, 1460, 1375, 1360, 1314, 1275, 839, 801, and 558 cm^{-1}; UV (MeCN) 221 (log ε 4.89), 301 (4.47), 504 (4.01), 566 (4.02), and 647 nm (4.71); ^{1}H NMR (90 MHz, $CDCl_3$) δ=8.76 (d, J=10.6 Hz,

2H, H_4) and 8.26—7.17 (m, 19H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ=162.71 (s, C^+), 154.20 (s), 147.25 (s), 146.15 (d, C_2), 143.62 (d, C_6), 141.49 (d, C_4), 139.29 (d, C_8), 138.77 (s), 136.00 (d, C_5), 134.90 (d, C_7), 134.23 (s), 133.56 (s), 133.44 (d), 133.13 (d), 132.89 (s), 128.80 (d), 127.86 (d), 127.09 (d, C_3), 126.94 (d), 125.30 (d), and 124.69 (d). Found: C, 69.29; H, 4.10%. Calcd for $C_{31}H_{21}PF_6$: C, 69.15; H, 3.93%.

Bis(3-methyl-1-azulenyl)(1-naphthyl)methyl Hexafluorophosphate (5b·PF$_6^-$). The general procedure was followed using DDQ (273 mg, 1.20 mmol), bis(3-methyl-1-azulenyl)(1-naphthyl)methane (**7b**) (423 mg, 1.00 mmol), and 60% HPF_6 (10 ml) in CH_2Cl_2 (100 ml). Recrystallization from CH_2Cl_2/ether gave hexafluorophosphate **5b**·PF$_6^-$ (535 mg, 94%). Brown powder; mp >300 °C (CH_2Cl_2/ether); MS (FAB) m/z 421 (M^+-PF_6). IR (KBr disk) 1478, 1441, 1410, 1395, 1341, 1310, 1285, 839, and 558 cm^{-1}; UV (MeCN) 221 (log ε 4.90), 301 (4.50), 397 (4.06), 508 (3.93), and 684 nm (4.70); ^{1}H NMR (600 MHz, $CDCl_3$) δ=8.621 (d, J=9.5 Hz, 2H, H_4), 8.177 (d, J=8.2 Hz, 1H, $H_{2'}$), 8.030 (dd, J=9.6, 9.6 Hz, 2H, H_6), 7.985 (d, J=7.6 Hz, 1H, $H_{5'}$), 7.972 (dd, J=9.6, 9.5 Hz, 2H, H_5), 7.923 (d, J=9.7 Hz, 2H, H_8), 7.617 (dd, J=8.2, 7.1 Hz, 1H, $H_{3'}$), 7.584 (s, 2H, H_2), 7.475 (dd, J=7.6, 7.3 Hz, 1H, $H_{6'}$), 7.454 (dd, J=9.7, 9.6 Hz, 2H, H_7), 7.426 (d, J=7.1 Hz, 1H, $H_{4'}$), 7.274 (d, J=8.5 Hz, 1H, $H_{8'}$), 7.219 (dd, J=8.5, 7.3 Hz, 1H, $H_{7'}$), and 2.605 (s, 6H, 3-Me); ^{13}C NMR (150 MHz, $CDCl_3$) δ=159.292 (s, C^+), 152.356 (s, C_{3a}), 148.193 (s, C_{8a}), 145.300 (d, C_2), 143.418 (d, C_6), 139.520 (s, $C_{1'}$), 139.078 (d, C_8), 138.439 (d, C_4), 135.992 (s, C_3), 135.179 (d, C_5), 134.994 (d, C_7), 133.822 (s, $C_{4'a}$), 133.387 (s, C_1), 133.229 (s, $C_{8'a}$), 132.859 (d, $C_{2'}$), 132.812 (d, $C_{4'}$), 128.870 (d, $C_{5'}$), 127.951 (d, $C_{7'}$), 127.015 (d, $C_{6'}$), 125.368 (d, $C_{3'}$), 125.105 (d, $C_{8'}$), and 12.834 (q, 3-Me). Found: C, 70.10; H, 4.89%. Calcd for $C_{33}H_{25}PF_6$: C, 69.96; H, 4.45%.

Bis(3,6-di-*t*-butyl-1-azulenyl)(1-naphthyl)methyl Hexafluorophosphate (5c·PF$_6^-$). The general procedure was followed using DDQ (272 mg, 1.20 mmol), bis(3,6-di-*t*-butyl-1-azulenyl)(1-naphthyl)methane (**7c**) (618 mg, 1.00 mmol), and 60% HPF_6 (10 ml) in CH_2Cl_2 (100 ml). Recrystallization from CH_2Cl_2/ether gave hexafluorophosphate **5c**·PF$_6^-$ (681 mg, 89%). Brown powder; mp 282.0—283.0 °C (CH_2Cl_2/ether); MS (FAB) m/z 617 (M^+-PF_6). IR (KBr disk) 2963, 1476, 1418, 1333, 1312, 1244, 841, and 558 cm^{-1}; UV (MeCN) 221 (log ε 4.89), 309 (4.57), 399 (4.05), 500 (3.93), and 686 nm (4.78); ^{1}H NMR (90 MHz, $CDCl_3$) δ=9.02 (d, J=11.0 Hz, 2H, H_4), 8.27—7.29 (m, 9H), 8.13 (d, J=11.0 Hz, 2H, H_5), 7.90 (d, J=11.0 Hz, 2H, H_8), 7.46 (s, 2H, H_2), 1.51 (s, 18H, 3-*t*-Bu), and 1.43 (s, 18H, 6-*t*-Bu); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ=168.74 (s, C_6), 158.41 (s, C^+), 149.32 (s), 147.71 (s), 147.64 (s), 142.19 (d, C_2), 139.20 (d, C_4), 138.86 (s), 137.92 (d, C_8), 133.62 (s), 132.92 (s), 132.77 (d, 3C, C_5), 132.37 (s), 132.03 (d, C_7), 128.77 (d), 127.49 (d), 126.76 (d), 125.39 (d), 125.02 (d), 39.31 (s, 6-*t*-Bu), 33.25 (s, 3-*t*-Bu), 31.45 (q, 6-*t*-Bu), and 30.99 (q, 3-*t*-Bu). Found: C, 74.02; H, 6.95%. Calcd for $C_{47}H_{53}PF_6$: C, 74.00; H, 7.00%.

Di-1-azulenyl(2-naphthyl)methyl Hexafluorophosphate (6a·PF$_6^-$). The general procedure was followed using DDQ (82 mg, 0.36 mmol), di-1-azulenyl(2-naphthyl)methane (**8a**) (118 mg, 0.30 mmol), and 60% HPF_6 (3 ml) in CH_2Cl_2 (50 ml). Recrystallization from CH_2Cl_2/ether gave hexafluorophosphate **6a**·PF$_6^-$ (151 mg, 94%). Brown powder; mp 145.0—147.0 °C decomp (CH_2Cl_2/ether); MS (FAB) m/z 393 (M^+-PF_6); IR (KBr disk) 1468, 1377, 1277, 841, and 558 cm^{-1}; UV (MeCN) 221 (log ε 4.84), 287 (4.53), 372 (4.28), 490 (4.17), and 643 nm (4.65); ^{1}H NMR (90 MHz, $CDCl_3$) δ=8.81 (d, J=10.6 Hz, 2H, H_4) and 8.10—7.39 (m, 19H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ=164.69 (s, C^+), 153.74 (s), 147.55 (s), 146.27 (d, C_2), 143.53 (d, C_6), 141.52 (d, C_4), 139.23 (d, C_8), 138.56 (s), 137.03 (d), 135.48 (d, C_5), 135.17 (s), 134.32 (d, C_7), 133.38 (s), 132.40 (s), 129.90 (d), 129.53 (d), 129.41 (d), 128.74 (d), 127.83 (d), 127.55 (d), and 126.55 (d, C_3). Found: C, 69.47; H, 4.25%. Calcd for $C_{31}H_{21}PF_6$: C, 69.15; H, 3.93%.

Bis(3-methyl-1-azulenyl)(2-naphthyl)methyl Hexafluorophosphate (6b·PF$_6^-$). The general procedure was followed using DDQ (273 mg, 1.20 mmol), bis(3-methyl-1-azulenyl)(2-naphthyl)methane (**8b**) (423 mg, 1.00 mmol), and 60% HPF_6 (10 ml) in CH_2Cl_2 (100 ml). Recrystallization from CH_2Cl_2/ether gave hexafluorophosphate **6b**·PF$_6^-$ (560 mg, 99%). Brown powder; mp >300 °C (CH_2Cl_2/ether); MS (FAB) m/z 421 (M^+-PF_6). IR (KBr disk) 1410, 1341, 1311, 1287, 839, and 558 cm^{-1}; UV (MeCN) 219 (log ε 4.80), 290 (4.55), 310 (4.41), 371 (4.30), 507 (4.10), and 680 nm (4.60); ^{1}H NMR (90 MHz, $CDCl_3$) δ=8.68 (d, J=10.8 Hz, 2H, H_4), 8.05—7.33 (m, 15H), 7.71 (s, 2H, H_2), and 2.69 (s, 6H, 3-Me); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ=161.12 (s, C^+), 151.64 (s), 148.35 (s), 145.48 (d, C_2), 143.22 (d, C_6), 139.17 (s), 138.77 (d, C_8), 138.44 (d, C_4), 136.52 (d), 135.36 (s), 135.05 (s), 134.60 (d, C_5), 134.17 (d, C_7), 132.55 (s), 132.34 (s), 130.05 (d), 129.38 (d), 129.26 (d), 128.62 (d), 127.89 (d), 127.49 (d), and 12.94 (q, 3-Me). Found: C, 69.69; H, 4.52%. Calcd for $C_{33}H_{25}PF_6$: C, 69.69; H, 4.45%.

Bis(3,6-di-*t*-butyl-1-azulenyl)(2-naphthy)methyl Hexafluorophosphate (6c·PF$_6^-$). The general procedure was followed using DDQ (272 mg, 1.20 mmol), bis(3,6-di-*t*-butyl-1-azulenyl)(2-naphthyl)methane (**8c**) (618 mg, 1.00 mmol), and 60% HPF_6 (10 ml) in CH_2Cl_2 (100 ml). Recrystallization from CH_2Cl_2/ether gave hexafluorophosphate **6c**·PF$_6^-$ (747 mg, 98%). Brown powder; mp 253.0—255.0 °C (CH_2Cl_2/ether); MS (FAB) m/z 617 (M^+-PF_6). IR (KBr disk) 2963, 1476, 1466, 1333, 1312, 1244, 839, and 558 cm^{-1}; UV (MeCN) 220 (log ε 4.77), 295 (4.55), 365 (4.30), 496 (4.06), and 685 nm (4.68); ^{1}H NMR (90 MHz, $CDCl_3$) δ=9.07 (d, J=11.2 Hz, 2H, H_4), 8.16 (dd, J=11.2, 1.5 Hz, 2H, H_5), 8.10—7.46 (m, 7H), 7.87 (d, J=10.8 Hz, 2H, H_8), 7.57 (s, 2H, H_2), 7.56 (dd, J=10.8, 1.5 Hz, 2H, H_7), 1.58 (s, 18H, 3-*t*-Bu), and 1.44 (s, 18H, 6-*t*-Bu); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ=168.77 (s, C_6), 160.73 (s, C^+), 149.05 (s), 148.16 (s), 147.31 (s), 142.77 (d, C_2), 139.26 (d, C_4), 138.80 (s), 138.10 (d, C_8), 135.97 (d), 135.08 (s), 132.70 (s), 132.37 (d, C_5), 131.76 (s), 131.55 (d, C_7), 129.93 (d), 129.35 (d), 129.14 (d), 128.74 (d), 128.01 (d), 127.49 (d), 39.35 (s, 6-*t*-Bu), 33.31 (s, 3-*t*-Bu), 31.48 (q, 6-*t*-Bu), and 31.11 (q, 3-*t*-Bu). Found: C, 73.92; H, 7.01%. Calcd for $C_{47}H_{53}PF_6$: C, 74.00; H, 7.00%.

The pK_{R^+} Value. Sample solutions of hexafluorophosphates **5a**—**c**·PF$_6^-$ and **6a**—**c**·PF$_6^-$ were prepared by dissolving each compound in a glycine (0.1 M) solution (50 ml) and adding MeCN up to 100 ml. Sample solutions with lower acidity were prepared by further alkalification with 20% aqueous NaOH. The pH of each sample was deter-

mined on a Horiba pH meter F-13 calibrated with standard buffers before use. The observed absorbance at the specific absorption maxima of cations **5a**—**c** and **6a**—**c** were plotted against the pH, giving classical titration curves whose midpoints were taken as the pK_{R+} values.

^{1}H NMR and ^{13}C NMR spectra (32 pages) and the complete MS, IR, and UV spectral data (8 pages) for the reported compounds (hexafluorophosphates of **5a**—**c** and **6a**—**c**, **7a**—**c**, **8a**—**c**, **10**, and **11**) are deposited as Document No. 68067 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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