Synthesis and Dynamic Stereochemistry of a Tri(1-azulenyl)methyl Cation Containing a Different Substituent on Each Azulene Ring

Shunji Ito, Noboru Morita, and Toyonobu Asao*

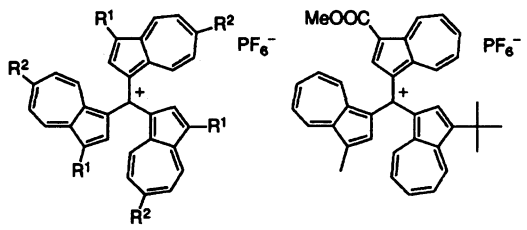
Department of Chemistry, Faculty of Science, Tohoku University, Kawauchi, Aoba-ku, Sendai 980-77

(Received December 27, 1994)

The first example of a tri(1-azulenyl)methyl cation (**2**) containing a different substituent on each azulene ring was synthesized, and the dynamic stereochemistry was studied by temperature-dependent ^{1}H NMR spectra. The dynamic behavior of **2** supported a one-ring flip mechanism and the validity of the flip mechanism for the analysis of the conformational change of the tri(1-azulenyl)methyl cations.

The lowest energy (threshold) rotation mechanism for the conformational change of molecular propellers, such as triphenylmethyl cations, was uniformly a two-ring flip.[1,2] Recently, we reported the syntheses of tri(1-azulenyl)methyl hexafluorophosphate (**1a**) and its 3,3′,3″-trimethyl (**1b**), 3,3′,3″-tris(methoxycarbonyl) (**1c**), and *t*-butyl derivatives (**1d**—**f**) by hydride abstraction of the corresponding methane derivatives (Chart 1).[3—5] The analysis of the temperature-dependent ^{1}H NMR spectra of **1b** using a flip mechanism showed that the threshold rotation mechanism for **1b** was the first example of a one-ring flip mechanism.[5—7] Here we report the dynamic behavior of the first example of a tri(1-azulenyl)-methyl cation (**2**) containing a different substituent on each azulene ring.

The synthesis and conformational analysis of the molecular propellers having different three aryl substituents without local C_2 symmetry, i.e., ArAr′Ar″X type propellers, have been reported by Mislow et al.[8,9] The molecular propellers showed residual diastereoisomerism by the rapid two-ring flip. In the case of mechanisms including the one-ring flip, it is expected that the residual diastereoisomerism is not observed in the temperature-dependent NMR spectra. Therefore, the results will provide further evidence of the one-ring flip mechanism for the tri(1-azulenyl)methyl cations (e.g. **1b**). In the one- or two-ring flip mechanism for **2**, which was considered similar to the conformational analysis of **1b**, all the vertices (stereoisomers) of the cube become different, in contrast to **1b**. Therefore, the conformational analysis of **2** will also show the validity of the flip mechanism for the analysis of the dynamic stereochemistry of tri(1-azulenyl)methyl cations, because the analysis shows that all stereoisomers interconvert along each side of the cube.



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

2

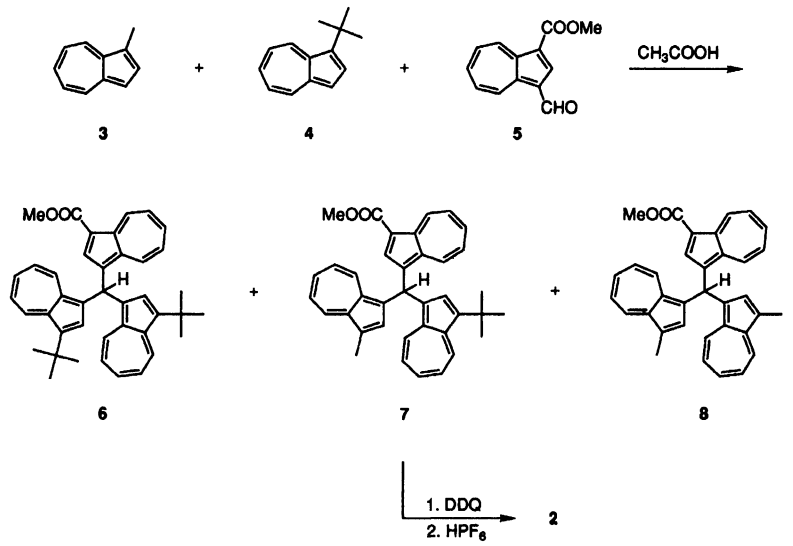
Chart 1.

Results and Discussion

Synthesis. The reaction of an equimolar amount of 1-methylazulene (**3**)[10] and 1-*t*-butylazulene (**4**) [5,11] with methyl 3-formylazulene-1-carboxylate (**5**)[5] in acetic acid at room temperature for 7 d, afforded a mixture of tri(1-azulenyl)methane derivatives **6**, **7**, and **8** (Scheme 1). The mixture was separated by gel-permeation chromatography to give **6**, **7**, and **8** in 17, 43, and 21% yields, respectively. The oxidative hydride abstraction[3—5] of **7** with DDQ in dichloromethane at room temperature followed by the addition of 60% HPF_6 yielded a stable 3-*t*-butyl-3′-methoxycarbonyl-3″-methyltri(1-azulenyl)methyl hexafluorophosphate (**2**) in 91% yield.

The pK_{R+} value and the redox potentials of **2** are summarized in Table 1 along with those of the parent tri(1-azulenyl)methyl cation (**1a**).[3,5] The high stability of **2** was shown in the high pK_{R+} value (11.8), which was slightly higher than that of **1a** (11.3), and in the more negative reduction potential (−0.76 V vs. Ag/Ag^+ using a Pt electrode in MeCN containing 0.1 M Et_4NClO_4) (1 M=1 mol dm^{-3}).

Dynamic Stereochemistry. The ^{1}H NMR (600



Scheme 1.

Table 1. The pK_{R+} Values[a] and the Redox Potentials[b] of **2** and **1a**[3,5]

	pK_{R+}	E_1^{red}	E_2^{red}	E_1^{ox}	E_2^{ox}
2	11.8	−0.76	(−1.45)	(+0.89)	(+1.20)
1a	11.3	−0.78	(−1.56)	(+0.98)	(+1.07)

a) The pK_{R+} values were determined spectrophotometrically at 24 °C in buffer solution prepared in 50% aqueous MeCN. b) The redox potentials were measured by cyclic volammetry (V vs. Ag/Ag^+, 0.1 M Et_4NClO_4 in MeCN, Pt electrode, and scan rate 100 $mV\,s^{-1}$). Irreversible processes were shown in parentheses.

MHz) spectra of **2** in $CDCl_3$ at 60 °C and −30 °C, and those in the *t*-butyl region at various temperatures are shown in Figs. 1 and 2, respectively. At −30 °C, the NMR consists, in the *t*-butyl region, of seven signals (as indicated by the letters 1—7). When the sample was warmed, all the lines broadened simultaneously and further warming resulted in coalescence of all seven peaks to a singlet, which became sharp at 60 °C. The NMR consists, in methyl and methoxycarbonyl regions, of five and six signals at −30 °C, respectively, and these signals had similar behavior to the *t*-butyl signals.

Sixteen isomeric propeller conformations are possible for a molecule of this type including enantiomeric isomers, as shown in Figs. 3 and 4. $\boldsymbol{A_1}$ and $\boldsymbol{A_2}$ and their enantiomers, which are shown with an overbar, have pseudo C_3 symmetries (concerning the three azulene rings), and those enantiomers have two nonequivalent *t*-butyl groups. The other six sets of enantiomers ($\boldsymbol{B_1}$—$\boldsymbol{B_6}$ and their enantiomers) are of C_1 symmetries, and each enantiomer has a nonequivalent *t*-butyl group. Therefore, the low temperature ^1H NMR spectrum of **2** is expected to have eight resonance signals in the *t*-butyl region attributable to a mixture of diastereomers. The lack of one signal for **2** in the *t*-butyl region is due to either an accidental chemical shift equivalent or absence of a set of unstable enantiomers.

Possible interconversions of the stereoisomers of **2** are represented by four processes according to the flip mechanism, i.e., from a zero- to a three-ring flip.[1] However, the zero- and the three-ring flip will be excluded from the analysis of dynamic behavior of **2** on steric grounds, as similar to **1b**.[5—7] Therefore, the possible interconversion mechanism for **2** is either a one- or a two-ring flip. The one- and two-ring flip connecting $\boldsymbol{B}$ and $\overline{\boldsymbol{B}}$ are composed of two sets of hexagonal cyclic interconversions, and each $\boldsymbol{B}$ and $\overline{\boldsymbol{B}}$ is interconverted to $\boldsymbol{A}$ or $\overline{\boldsymbol{A}}$ by each mechanism. Therefore, these consist of two sets of cubic-type interconversions, as illustrating in Figs. 3 and 4, respectively.

Each set of the interconversions of the one-ring flip includes one of all the sets of enantiomers. In contrast to the one-ring flip, the two sets of the interconversion of the two-ring flip consisted of two diastereomeric forms, as shown in Fig. 4. Therefore, rapid interconversion by the two-ring flip is expected to show residual diastereoisomerism,[8,9] which will show two *t*-butyl signals in temperature-dependent ^1H NMR spectra. However, the temperature-dependent ^1H NMR spectra of **2** showed no evidence of residual diastereoisomerism by the rapid two-ring flip, as shown in Fig. 2. Therefore, the contribution of the one-ring flip must be considerable in extent in the rotation mechanism for **2**. These results support the one-ring flip mechanism for the tri(1-azulenyl)methyl cations (**1a**—**f**).

The dynamic behavior of **2** also supported the existence of the cubic-type interconversion, such as a one-ring flip for **2** (Fig. 3), which was proposed by the flip mechanism. The observed seven signals in the *t*-butyl region at the low temperature correspond to the seven stereoisomers at the vertices of the cube. The coalescence of the seven signals to a singlet indicates that all stereoisomers interconvert along each side of the cube. These results also validate the flip mechanism in the analysis of the dynamic stereochemistry of the tri(1-

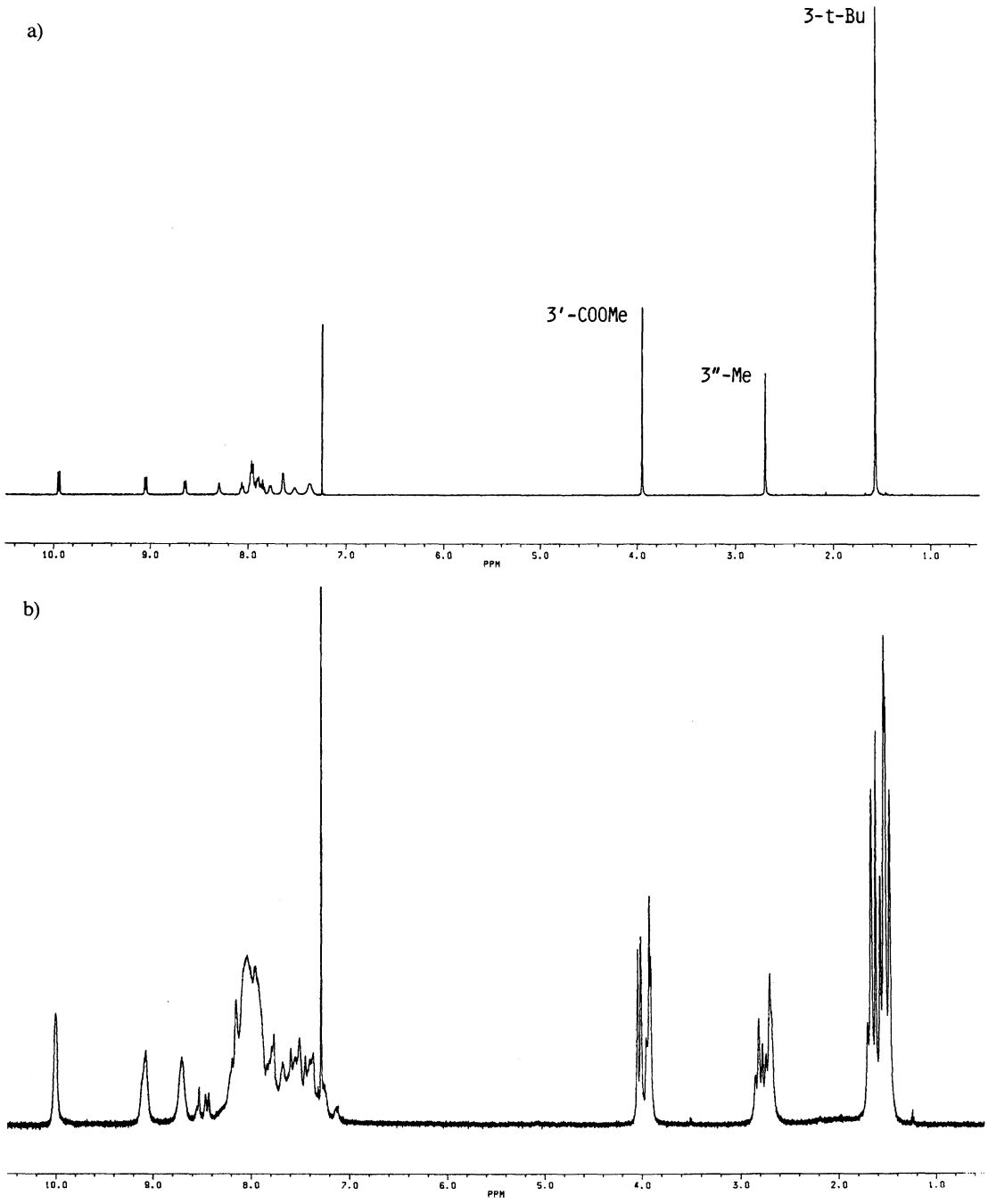


Fig. 1. ^{1}H NMR spectra of **2** (600 MHz) in $CDCl_3$. (a) at 60 °C; (b) at −30 °C.

azulenyl)methyl cations (**1a**—**f**).

Experimental

General. The melting points were determined on a Yanagimoto micro melting-point apparatus (MP-S3) and are uncorrected. Electron-impact mass spectra were obtained with a JEOL HX-110 instrument, usually at 70 eV. IR and UV spectra were measured on a Hitachi 270-30 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 with Pt working and auxiliary electrodes, and a reference electrode formed from $Ag/AgNO_3$ (0.01 M) and tetrabutylammonium perchlorate solution (0.1 M) in MeCN. All measurements were made under argon on a 1 mM sample of the substrate in 10 ml of dry MeCN containing 0.1 M tetraethylammonium perchlorate (TEAP) as a supporting electrolyte, at a scan rate of 100 $mV\,s^{-1}$. Elemental analyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University.

3- *t*- Butyl- 3′- methoxycarbonyl- 3″- methyltri(1-

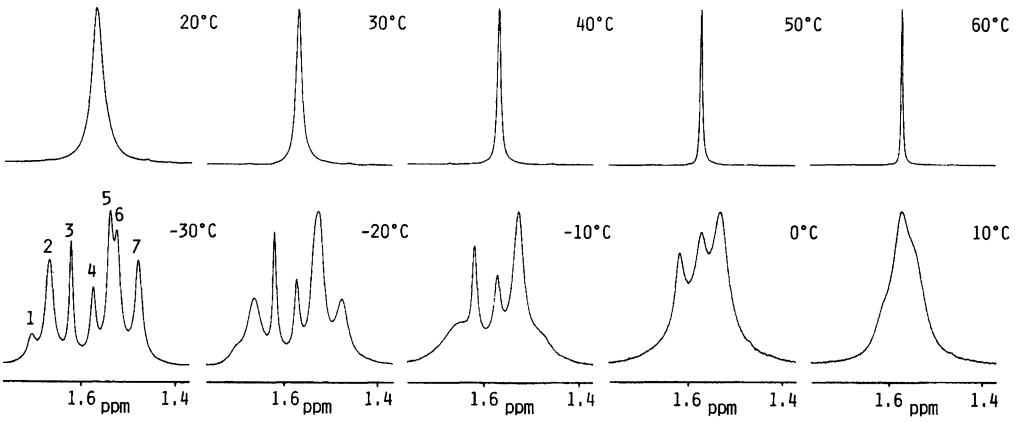


Fig. 2. ^{1}H NMR spectra of **2** (600 MHz, *t*-butyl region) in $CDCl_3$ at various temperatures.

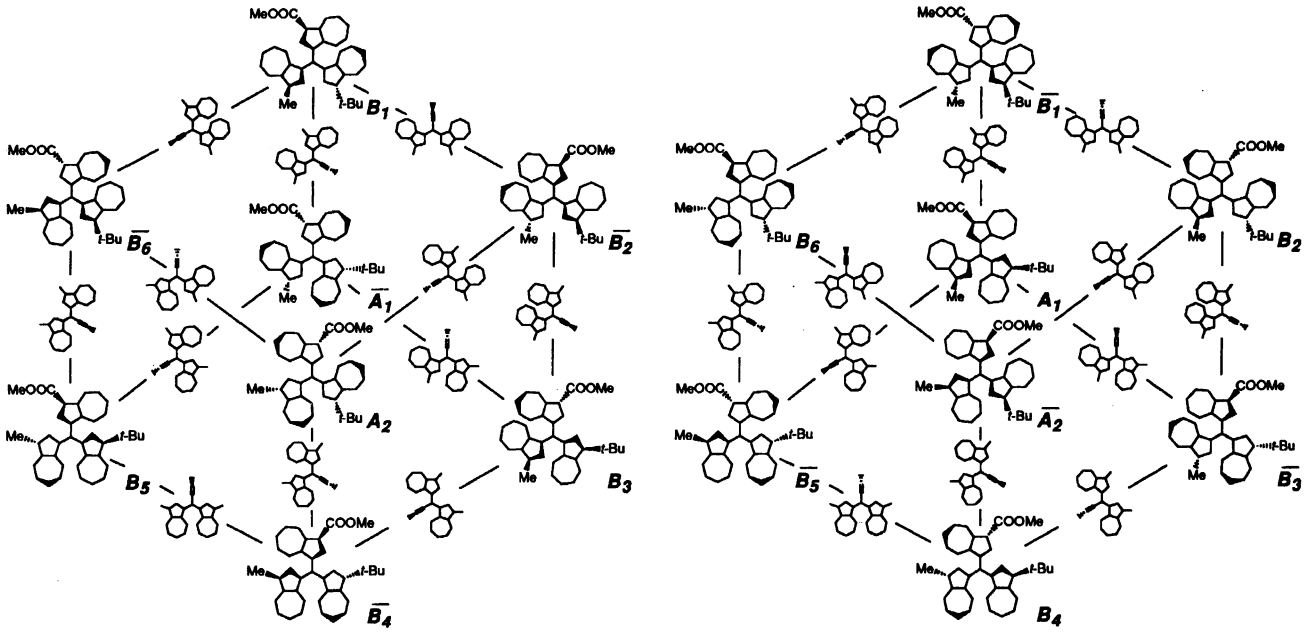


Fig. 3. One-ring flip mechanism for **2**.

azulenyl)methane (7). A solution of 1-methylazulene (**3**) (488 mg, 3.43 mmol), 1-*t*-butylazulene (**4**) (631 mg, 3.42 mmol), and methyl 3-formylazulene-1-carboxylate (**5**) (735 mg, 3.43 mmol) in glacial acetic acid (20 ml) was stirred at room temperature under an Ar atmosphere for 7 d. The violet solution turned to a violet suspension. The crystals were collected by filtration and purified by column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ to afford 3,3′-di-*t*-butyl-3″-methoxycarbonyltri(1-azulenyl)-methane (**6**) (333 mg, 17%), the tri(1-azulenyl)methane **7** (763 mg, 43%), and 3-methoxycarbonyl-3′,3″-dimethyltri(1-azulenyl)methane (**8**) (349 mg, 21%).

6: Greenish-blue prisms; mp 146.0—149.5 °C (toluene/hexane); MS (70 eV) *m/z* (rel intensity) 564 (M^+; 40), 508 (42), 507 (100), 184 (33), and 169 (87); IR (KBr disk) 2960, 1698, 1570, 1444, 1420, 1392, 1366, 1226, 1206, and 740 cm^{-1}; UV (CH_2Cl_2) 241 ($\log\varepsilon$ 4.66), 293 (4.93), 374 (4.15), and 613 nm (2.95); ^{1}H NMR (90 MHz, $CDCl_3$) δ= 9.61 (d, J=9.2 Hz, 1H, $H_{4''}$), 8.60 (d, J=9.9 Hz, 2H, $H_{4,4'}$), 8.31 (d, J=9.7 Hz, 1H, $H_{8''}$), 8.18 (d, J=9.2 Hz, 2H, $H_{8,8'}$), 7.78—6.71 (m, 13H), 3.83 (s, 3H, 3″-COOMe), and 1.46 (s, 18H, 3,3′-*t*-Bu); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ=165.73 (s, 3″-COOMe), 141.58 (s, $C_{3''a}$), 140.82 (d, $C_{2''}$), 139.78 (s, $C_{8''a}$), 138.62 (d, $C_{6''}$), 137.95 (s, $C_{3,3'}$), 137.49 (d, $C_{4''}$), 137.10 (d, $C_{2,2'}$), 136.88 (d, $C_{6,6'}$), 135.57 (s, $C_{3a,3'a}$), 135.48 (s, $C_{8a,8'a}$), 135.30 (d, 2C, $C_{4,4'}$ and $C_{8''}$), 133.83 (s, $C_{1''}$), 132.86 (d, $C_{8,8'}$), 130.72 (s, $C_{1,1'}$), 127.22 (d, $C_{5''}$), 125.88 (d, $C_{7''}$), 120.91 (d, $C_{7,7'}$), 120.39 (d, $C_{5,5'}$), 114.87 (s, $C_{3''}$), 50.87 (q, 3″-COOMe), 35.50 (d, CH), 33.31 (s, 3,3′-*t*-Bu), and 32.24 (q, 3,3′-*t*-Bu). Found: *m/z* 564.3029. Calcd for $C_{41}H_{40}O_2$: M, 564.3029. Found: C, 87.05; H, 7.21%. Calcd for $C_{41}H_{40}O_2$: C, 87.19; H, 7.14%.

7: Greenish-blue prisms; mp 229.0—230.0 °C decomp (toluene/hexane); MS (70 eV) *m/z* (rel intensity) 522 (M^+;

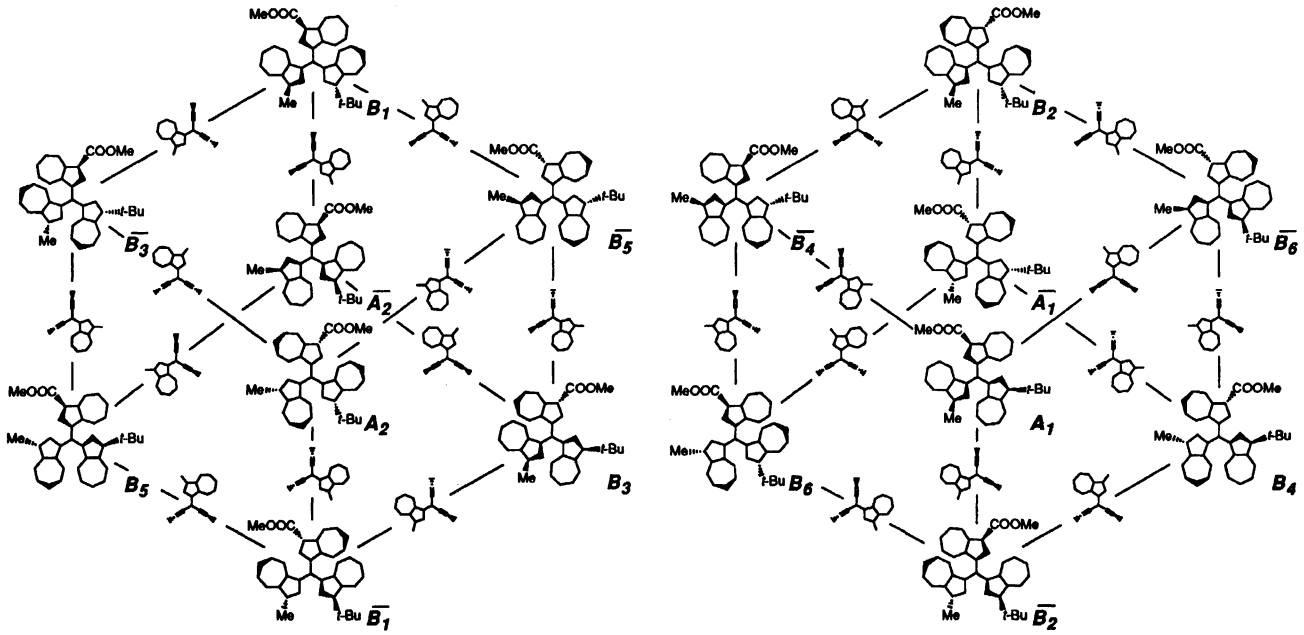


Fig. 4. Two-ring flip mechanism for **2**.

100), 507 (22), and 465 (60); IR (KBr disk) 1696, 1456, 1444, 1418, and 1200 cm^{-1}; UV (CH_2Cl_2) 240 (log ε 4.65), 293 (4.93), 358 (4.13), 374 (4.14), 614 (2.92), and 614 nm (2.95); ^1H NMR (600 MHz, $CDCl_3$) δ=9.618 (d, J=9.9 Hz, 1H, $H_{4'}$), 8.607 (d, J=9.8 Hz, 1H, H_4), 8.357 (d, J=9.7 Hz, 1H, $H_{8'}$), 8.186 (d, J=9.7 Hz, 1H, H_8), 8.137 (d, J=9.5 Hz, 1H, $H_{8''}$), 8.132 (d, J=9.5 Hz, 1H, $H_{4''}$), 7.808 (s, 1H, $H_{2'}$), 7.665 (dd, J=9.9, 9.8 Hz, 1H, $H_{6'}$), 7.454 (dd, J=9.9, 9.9 Hz, 1H, $H_{5'}$), 7.415 (dd, J=9.9, 9.7 Hz, 1H, H_6), 7.402 (dd, J=9.7, 9.7 Hz, 1H, $H_{6''}$), 7.348 (s, 1H, H_2), 7.229 (s, 1H, $H_{2''}$), 7.219 (s, 1H, CH), 7.196 (dd, J=9.8, 9.7 Hz, 1H, $H_{7'}$), 6.977 (dd, J=9.9, 9.8 Hz, 1H, H_5), 6.956 (dd, J=9.7, 9.5 Hz, 1H, $H_{5''}$), 6.821 (dd, J=9.7, 9.7 Hz, 1H, H_7), 6.814 (dd, J=9.7, 9.5 Hz, 1H, $H_{7''}$), 3.816 (s, 3H, 3'-COOMe), 2.522 (s, 3''-Me), and 1.459 (s, 9H, 3-*t*-Bu); ^{13}C NMR (150 MHz, $CDCl_3$) δ=165.856 (s, 3'-COOMe), 141.664 (s, $C_{3'a}$), 140.910 (d, $C_{2'}$), 139.752 (s, $C_{8'a}$), 139.432 (d, $C_{2''}$), 138.780 (d, $C_{6'}$), 138.043 (s, C_3), 137.594 (d, $C_{4'}$), 137.134 (s, $C_{3''a}$), 137.134 (d, $C_{6''}$), 137.063 (d, C_2), 136.986 (d, C_6), 135.516 (s, C_{3a}), 135.516 (s, C_{8a}), 135.429 (d, C_4), 135.313 (d, $C_{8'}$), 134.764 (s, $C_{8''a}$), 133.846 (s, $C_{1'}$), 133.530 (d, $C_{4''}$), 132.969 (d, C_8), 132.722 (d, $C_{8''}$), 131.576 (s, $C_{1''}$), 130.872 (s, C_1), 127.349 (d, $C_{5'}$), 126.040 (d, $C_{7'}$), 124.694 (s, $C_{3''}$), 121.009 (d, C_7), 120.916 (d, $C_{7''}$), 120.678 (d, $C_{5''}$), 120.409 (d, C_5), 114.849 (s, $C_{3'}$), 50.899 (q, 3'-COOMe), 35.264 (d, CH), 33.242 (s, 3-*t*-Bu), 32.184 (q, 3-*t*-Bu), and 12.673 (q, 3''-Me). Found: m/z 522.2561. Calcd for $C_{38}H_{34}O_2$: M, 522.2559. Found: C, 82.68; H, 6.83%. Calcd for $C_{38}H_{34}O_2 \cdot 3/2H_2O$: C, 83.03; H, 6.78%.

8: Greenish-blue prisms; mp 231.0—232.0 °C decomp (toluene/hexane); MS (70 eV) m/z (rel intensity) 480 (M^+; 29), 86 (64), 84 (100), and 51 (24); IR (KBr disk) 1694, 1576, 1456, 1444, 1420, 1208, and 728 cm^{-1}; UV (CH_2Cl_2) 240 (log ε 4.26), 293 (4.54), 358 (3.74), 373 (3.74), and 613 nm (2.95); ^1H NMR (90 MHz, $CDCl_3$) δ=9.62 (d, J=9.5 Hz, 1H, H_4), 8.38 (d, J=9.2 Hz, 1H, H_8), 8.14 (d, J=9.5 Hz, 4H, $H_{4',4''}$ and $H_{8',8''}$), 7.83—6.70 (m, 13H), 3.82 (s, 3H, 3-COOMe), and 2.53 (s, 6H, 3',3''-Me); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ=165.66 (s, 3-COOMe), 141.58 (s, C_{3a}), 140.78 (d, C_2), 139.63 (s, C_{8a}), 139.26 (d, $C_{2,2''}$), 138.71 (d, C_6), 137.58 (d, C_4), 137.10 (s and d, 2C, $C_{3'a,3''a}$ and $C_{6',6''}$), 135.17 (d, C_8), 134.72 (s, $C_{8'a,8''a}$), 133.80 (s, C_1), 133.53 (d, $C_{4',4''}$), 132.67 (d, $C_{8',8''}$), 131.61 (s, $C_{1',1''}$), 127.28 (d, C_5), 126.00 (d, C_7), 124.63 (s, $C_{3',3''}$), 120.94 (d, $C_{7',7''}$), 120.69 (d, $C_{5',5''}$), 114.90 (s, C_3), 50.87 (q, 3-COOMe), 35.20 (d, CH), and 12.73 (q, 3',3''-Me). Found: m/z 480.2090. Calcd for $C_{35}H_{28}O_2$: M, 480.2089. Found: C, 85.65; H, 6.08%. Calcd for $C_{35}H_{28}O_2 \cdot 1/2H_2O$: C, 85.86; H, 5.97%.

3- *t*- Butyl- 3'- methoxycarbonyl- 3''- methyltri(1-azulenyl)methyl Hexafluorophosphate (2). DDQ (64 mg, 0.28 mmol) was added at room temperature to a solution of 3-*t*-butyl-3'-methoxycarbonyl-3''-methyltri(1-azulenyl)methane (**7**) (105 mg, 0.20 mmol) in CH_2Cl_2 (40 ml). The blue color turned to deep blue. After the solution was stirred at the same temperature for 1 h, 60% HPF_6 (2 ml) was added slowly. After stirring at room temperature for an additional 15 min, water (20 ml) 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 (1 ml) and Et_2O (30 ml) was added to the solution. The precipitated crystals were filtered off, washed with hexane, and dried in vacuo to give the tri(1-azulenyl)methyl cation **2** (121 mg, 91%). Deep brown powder; mp 233.5—239.0 °C (CH_2Cl_2/ether); MS (FAB) m/z 521 ($M^+ - PF_6$); IR (KBr disk) 1472, 1446, 1414, 1366, 1344, 1228, 1214, 840, and 558 cm^{-1}; UV (MeCN) 297 (log ε 4.59) and 588 nm (4.44); ^1H NMR (600 MHz, DMSO-d_6, 90 °C) δ=9.966 (d, J=10.0 Hz, 1H, $H_{4'}$), 9.316 (d, J=10.0 Hz, 1H, H_4), 8.919 (d, J=9.8 Hz, 1H, $H_{4''}$), 8.367 (s, 1H, $H_{2'}$), 8.311 (dd, J=9.8, 9.7 Hz, 1H, $H_{6'}$), 8.228 (dd, J=10.0, 9.7 Hz, 1H, $H_{5'}$), 8.208 (dd, J=9.9, 9.8 Hz, 1H, $H_{6''}$), 8.191 (dd, J=9.8, 9.8 Hz, 1H, H_6), 8.099 (dd, J=10.0, 9.8 Hz, 1H, H_5), 8.099 (dd, J=9.9, 9.8 Hz, 1H,

$H_{5''}$), 8.034 (d, J=10.0 Hz, 1H, $H_{8'}$), 8.014 (d, J=10.0 Hz, 1H, H_8), 7.931 (d, J=9.8 Hz, 1H, $H_{8''}$), 7.922 (s, 1H, $H_{2''}$), 7.804 (s, 1H, H_2), 7.717 (dd, J=10.0, 9.8 Hz, 1H, $H_{7'}$), 7.611 (dd, J=9.8, 9.8 Hz, 1H, $H_{7''}$), 7.575 (dd, J=10.0, 9.8 Hz, 1H, H_7), 4.004 (s, 3H, 3′-COOMe), 2.778 (s, 3H, 3″-Me), and 1.670 (s, 9H, 3-*t*-Bu); ^{13}C NMR (150 MHz, DMSO-d_6, 90 °C) δ=163.804 (s, 3′-COOMe), 153.824 (s, C^+), 149.557 (s, $C_{3''a}$), 147.503 (s, C_{3a}), 147.321 (s, C_{8a}), 146.842 (d, $C_{2'}$), 146.603 (s, $C_{8''a}$), 145.885 (s, $C_{3'a}$), 145.555 (s, C_3), 145.284 (s, $C_{8'a}$), 144.791 (d, $C_{2''}$), 143.120 (d, $C_{6'}$), 142.615 (d, C_2), 142.435 (d, $C_{6''}$), 142.375 (d, C_6), 139.816 (d, $C_{4'}$), 139.508 (d, C_4), 138.604 (d, $C_{8'}$), 137.937 (d, $C_{8''}$), 137.891 (d, C_8), 137.866 (d, $C_{4''}$), 133.424 (s, $C_{3''}$), 133.126 (d, $C_{5'}$), 132.853 (d, C_5 of $C_{5''}$), 132.486 (d, 2C, C_7 and $C_{7''}$), 132.223 (d, C_5 or $C_{5''}$), 132.139 (d, $C_{7'}$), 131.491 (s, $C_{1''}$), 130.542 (s, C_1), 129.691 (s, $C_{1'}$), 119.135 (s, $C_{3'}$), 50.889 (q, 3′-COOMe), 32.512 (s, 3-*t*-Bu), 30.548 (q, 3-*t*-Bu), and 11.848 (q, 3″-Me). Found: m/z 521.2437. Calcd for $C_{38}H_{33}O_2^+$: $M^+ - PF_6$, 521.2480. Found: C, 67.70; H, 4.70%. Calcd for $C_{35}H_{28}O_2PF_6 \cdot 1/2H_2O$: C, 67.55; H, 5.07%.

Complete spectral data of MS, IR, UV, ^{1}H NMR, and ^{13}C NMR for the reported compounds (**2**, **6**, **7**, and **8**) are deposited as Document No. 68029 at the Office of the Editer of Bull. Chem. Soc. Jpn.

This work was supported by a Grant-in-Aid for Scientific Research No. 03854053 to S. I. and that on Priority Areas No. 02230103 to T. A. from the Ministry of Education, Science and Culture, and the Research Aid of Inoue Foundation for Science.

References

1) K. Mislow, *Acc. Chem. Res.*, **9**, 26 (1976).
2) E. E. Wille, D. S. Stephenson, P. Capriel, and G. Binsch, *J. Am. Chem. Soc.*, **104**, 405 (1982).
3) S. Ito, N. Morita, and T. Asao, *Tetrahedron Lett.*, **32**, 773 (1991).
4) S. Ito, N. Morita, and T. Asao, *Tetrahedron Lett.*, **35**, 751 (1994).
5) S. Ito, N. Morita, and T. Asao, *Bull. Chem. Soc. Jpn.*, **68**, 1409 (1995).
6) S. Ito, N. Morita, and T. Asao, *Tetrahedron Lett.*, **33**, 6669 (1992).
7) S. Ito, N. Morita, and T. Asao, *Tetrahedron Lett.*, **35**, 3723 (1994).
8) R. Glaser, J. F. Blount, and K. Mislow, *J. Am. Chem. Soc.*, **102**, 2777 (1980).
9) P. Finocchiaro, D. Gust, and K. Mislow, *J. Am. Chem. Soc.*, **96**, 3198 (1973).
10) M. Yasunami, S. Miyoshi, N. Kanegawa, and K. Takase, *Bull. Chem. Soc. Jpn.*, **66**, 892 (1993).
11) H. Franke and M. Mühlstädt, *J. Prakt. Chem.*, **35**, 249 (1967).