

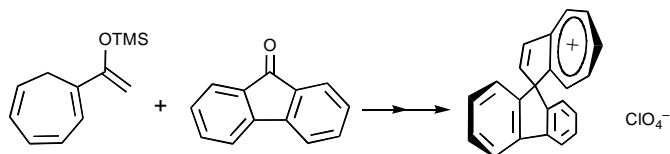
## Graphical Abstract

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**Spiro[1*H*-azulenium-1,9'-fluorene]  
perchlorate. Intramolecular charge-transfer  
interaction between orthogonally arranged  
units of the azulenium cation and fluorene**

Mitsunori Oda<sup>a,\*</sup> Nobue Nakajima,<sup>b</sup> Nguyen  
Chung Thanh<sup>b</sup> and Shigeyasu Kuroda<sup>b</sup>  
<sup>a</sup> Department of Chemistry, Faculty of Science,  
Shinshu University, Asahi 3-1-1, Matsumoto,  
Nagano, 390-8621 Japan; <sup>b</sup> Department of Applied  
Chemistry, Faculty of Engineering, University of  
Toyama, Gofuku 3190, Toyama, 930-8555 Japan.

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## Spiro[1*H*-azulenium-1,9'-fluorene] perchlorate. Intramolecular charge-transfer interaction between orthogonally arranged units of the azulenium cation and fluorene

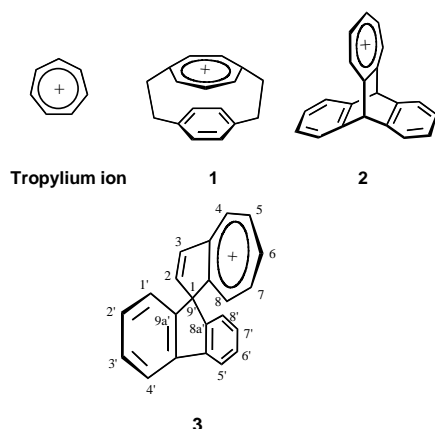
Mitsunori Oda,<sup>a,\*</sup> Nobue Nakajima,<sup>b</sup> Nguyen Chung Thanh<sup>b</sup> and Shigeyasu Kuroda<sup>b</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Shinshu University, Asahi 3-1-1, Matsumoto, Nagano, 390-8621, Japan

<sup>b</sup> Department of Applied Chemistry, Faculty of Engineering, University of Toyama, Gofuku 3190, Toyama, 930-8555, Japan

**Abstract**—Spiro[1*H*-azulenium-1,9'-fluorene] (**3**) perchlorate was synthesized in five steps starting from fluorenone and trimethylsilyl enol ether of 1-acetylcycloheptatriene. The  $pK_{R+}$  value of **3** was determined to be 7.8. A characteristic absorption band of **3** in acetonitrile was observed at 430 nm, which shows a bathochromic shift in dichloromethane, indicating the first example of the intramolecular charge transfer interaction between orthogonally arranged units of an azulenium ion having a tropylium ion ring and fluorene having two benzene rings. © 2009 Elsevier Science. All rights reserved

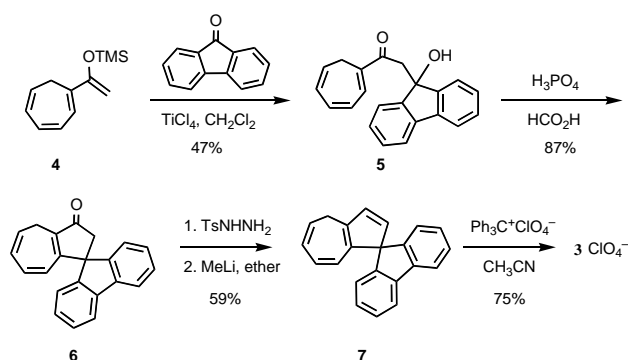
A typical absorption band based on the intramolecular charge-transfer (CT) interaction<sup>1</sup> between the tropylium cation and benzene has been observed in UV-Vis spectra of cyclophane **1**<sup>2</sup> and a triptycene-type compound **2**.<sup>3,4,5</sup> The dihedral angles between the tropylium cation ring and the benzene ring in **1** and **2** are approximately 180° and 120°, respectively. However, a compound, composed of these rings arranged orthogonally, has never been synthesized. In this paper we describe synthesis of the title compound **3**, which is composed of a fluorene part having two benzene rings and the azulenium cation part having a tropylium ion ring, and also its intramolecular CT interaction.



**Figure 1.** Tropylium ion and cations composed of the tropylium ion and at least one benzene ring.

The title cation **3** was synthesized by our previously reported method,<sup>6,7</sup> as shown in Scheme 1. The Mukaiyama aldol reaction<sup>8</sup> of **4** with fluorenone in dichloromethane

gave **5** in 47% yield. The Nazarov cyclization<sup>9</sup> of **5** produced tetrahydroazulenone **6** in 87% yield. The subsequent Shapiro reaction<sup>10</sup> via the tosylhydrazone resulted in **7** in 59% yield. Hydride abstraction from **7** with trityl perchlorate gave **3** in 75% yield. The perchlorate salt of **3** was isolated as yellow solids (Table 1). The  $pK_{R+}$  value of **3** was determined to be 7.8 by the UV method in 50% aqueous acetonitrile.<sup>11</sup> Thus, the stability of **3** is greater than that of the tropylium ion (3.9)<sup>11</sup> and less by about 2  $pK_{R+}$  units than that of the spiroannulated azulenium ion **8** (9.9).<sup>6c,12</sup>



**Scheme 1.** Synthetic method for preparing **3**.

A perpendicular relationship between two five-membered rings in **3** is expected from the bisected spiroannulation at the central 1(9') carbon atom. Also, calculations of **3** at the B3LYP/6-311+G(d,p) level of theory predict that it has an

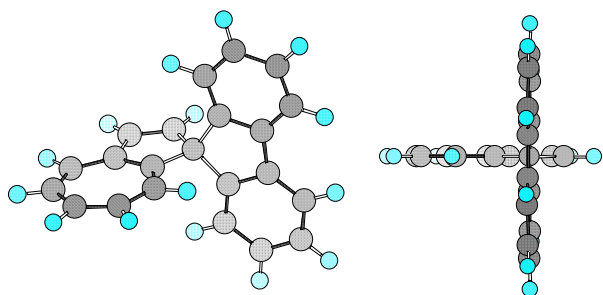
arrangement with planar azulenyl and fluorenyl rings, as depicted in Fig. 2.<sup>14,15</sup> In the <sup>1</sup>H NMR spectrum of **3**, the

Corresponding author. Tel.: +81 263-37-3343; fax: +81 263-37-3343; e-mail: mituoda@shinshu-u.ac.jp

**Table 1.** Physical properties of cations **3** and **8**

Cation	p <i>K</i> <sub>R</sub> <sup>+</sup>	UV-Vis (CH <sub>3</sub> CN) λ <sub>max</sub> (log ε) nm	<sup>1</sup> H NMR δ <sub>ppm</sub> (CD <sub>3</sub> CN)
<b>3</b> ClO <sub>4</sub> <sup>-</sup> Yellow solids, mp = 98–100 °C	7.8	212sh (4.18), 220 (4.40), 226sh (4.39), 233sh (4.24), 255 (4.32), 266sh (4.15), 280sh (4.01), 291sh (3.77), 303 (3.80), 360 (3.56), 430sh (2.99)	6.98 (dd, <i>J</i> = 7.8, 1.0 Hz, H-1',8'), 7.30 (dt, <i>J</i> = 7.8, 1.1 Hz, H-3',6'), 7.52 (d, <i>J</i> = 5.4 Hz, H-2), 7.57 (dt, <i>J</i> = 7.8, 1.1 Hz, H-2',7'), 7.77 (d, <i>J</i> = 5.4 Hz, H-3), 7.95 (d, <i>J</i> = 9.5 Hz, H-8), 8.05 (td, <i>J</i> = 7.8 Hz, 0.7 Hz, H-4',5'), 8.45 (dt, <i>J</i> = 10.0, 1.2 Hz, H-7), 8.67 (tt, <i>J</i> = 10.0, 1.2 Hz, H-6), 8.96 (dt, <i>J</i> = 10.0, 1.2 Hz, H-5), 9.12 (dd, <i>J</i> = 10.0, 1.2 Hz, H-4)
<b>8</b> BF <sub>4</sub> <sup>-a</sup> A dark green oil	9.9	230 (4.30), 270(4.42), 287sh (3.88), 363 (3.94)	1.97(m, 2H), 2.01(m, 2H), 2.14 (m, 2H), 2.30 (m, 2H), 7.33 (d, <i>J</i> = 5.4 Hz, H-3), 7.72 (d, <i>J</i> = 5.4 Hz, H-2), 8.75 (tt, <i>J</i> = 8.8, 0.4 Hz, H-6), 8.77 (t, <i>J</i> = 8.8 Hz, H-7), 8.90 (t, <i>J</i> = 8.8 Hz, H-5), 8.96 (dd, <i>J</i> = 8.8, 0.4 Hz, H-4), 9.00 (dm, <i>J</i> = 8.8 Hz, H-8) <sup>b</sup>

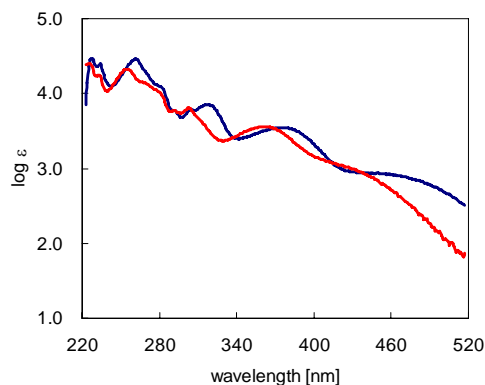
<sup>a</sup> Taken from ref. 5c. <sup>b</sup> Data of **8** PF<sub>6</sub><sup>-</sup>



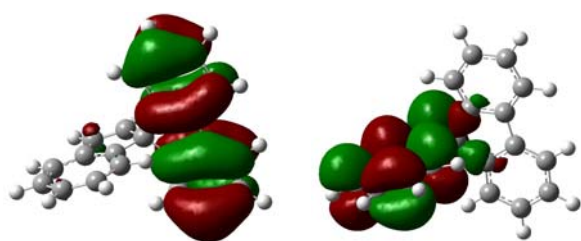
**Figure 2.** Structure (Chem3D output) of cation **3** calculated at the B3LYP/6-311+G(d,p) level of theory.

hydrogens at the 2 and 8 positions resonate at a slightly higher magnetic field compared with those of other 1,1-substituted azulenium ions,<sup>6,16</sup> probably due to a shielding effect of the benzene rings of the fluorene part. There is a weak NOE correlation (2%) between the H-8 and H1'(8') hydrogen atoms, indicating relatively short distance between them. An interesting spectroscopic feature of **3** was found in its UV-Vis absorption spectrum. While UV spectra of spiroannulated and dialkylazulenium ions in acetonitrile show three absorption bands at 220–230, 260–270 and 350–365 nm<sup>6c,6d</sup> and the spectrum of fluorene has a band at 300 nm,<sup>17</sup> the UV-Vis absorption spectrum of **3** in acetonitrile shows four slightly complex bands at 200–380 nm and a weak broad band around 430 nm (Fig. 3). The latter band shifts to 446 nm in the less polar solvent of dichloromethane and the molar absorption coefficient does not change in the concentrations of the cation, indicating that this absorption band is due to the intramolecular CT interaction between the fluorene part and the azulenium cation part. Calculated HOMO and LUMO orbitals are shown in Fig. 4, which indicate that the fluorene part mainly contributes to the HOMO of **3** and the azulenium cation part contributes to the LUMO. To the best of our

knowledge, this is the first synthesis of a cation composed of the tropylium ion and benzene rings arranged orthogonally, and the intramolecular CT interaction between these parts has been confirmed. Unfavorable matching between coefficients at the C2 and C8a positions in the LUMO and those at the C8a' and C9a' positions in the HOMO<sup>18</sup> suggests that an orbital interaction between them via through space in its ground state can be excluded to stabilize this molecule.<sup>19</sup> In the calculated structures of **3** and the isoelectronic neutral compound **9**, single bond lengths of C1–C2 and C1–C8a are shorter and those of C8a'–C9' and C9'–C9a' are longer in **3** than the corresponding bonds in **9** (Table 2). These results imply that σ-electrons of the C8a'–C9' and C9'–C9a' bonds tend to be donated to the cationic part in **3**, even though the C8a' and C9a' carbons are relatively electronegative sp<sup>2</sup> hybridized atoms. Thus, the tropylium ion part in **3** is stabilized not only by π–π conjugation with the C2–C3



**Figure 3.** UV-Vis absorption spectra of cation **3** in acetonitrile (red) and dichloromethane (blue).

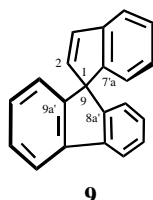


**Figure 4.** HOMO (left) and LUMO (right) of cation **3** calculated at the B3LYP/6-311+G(d,p) level of theory.

ethylene unit but also by  $\sigma$ - $\pi$  conjugation between the  $\sigma$ -bonds of the C8a'-C9' and C9'-C9a' and p-orbitals at the C2 and C8a positions. However, **3** is less stable than **8** probably due to a less effective  $\sigma$ - $\pi$  conjugation of the relatively electronegative C8a' and C9a'  $sp^2$  carbon atoms.

**Table 2.** Calculated C-C bond lengths (Å) around the spiro center carbon atoms in **3** and **9**

<b>3</b>		<b>9</b>	
C1-C2	1.502	C1-C2	1.525
C1-C8a	1.524	C1-C7a	1.528
C9'-C9a'	1.540	C9'-C9a'	1.532
C8a'-C9'	1.540	C8a'-C9'	1.532



## Acknowledgments

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- All new compounds are characterized by spectroscopic and combustion analyses. Selected data are as follows. **4**: Colorless solids, mp 126-128 °C;  $\nu_{\max}$  (KBr) = 1626s, 1388s, 1203s, 1172s, 771s, 740s, 708s  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) = 2.67 (d,  $J$  = 7.2 Hz, 2H), 3.26 (s, 2H), 5.46 (br, 1H), 5.60 (dt,  $J$  = 9.2, 7.2 Hz, 1H), 6.26 (dd,  $J$  = 9.2, 6.0 Hz, 1H), 6.54 (dd,  $J$  = 11.3, 6.0 Hz, 1H), 6.81 (dd,  $J$  = 11.3, 5.8 Hz, 1H), 6.86 (d,  $J$  = 5.8 Hz, 1H), 7.23 (td,  $J$  = 7.5, 1.2 Hz, 2H), 7.33 (td,  $J$  = 7.5, 1.2 Hz, 2H), 7.50 (d,  $J$  = 7.5 Hz, 2H), 7.61 (d,  $J$  = 7.5 Hz, 2H) ppm;  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) = 25.1, 45.7, 80.9, 112.0, 124.1, 125.8, 127.4, 127.9, 128.9, 128.97,

- 131.1, 134.0, 136.7, 139.1, 148.3, 200.8 ppm;  $m/z$  (rel. int) = 314 ( $M^+$ , 15 %), 181 (40), 180 (100), 152 (44), 134 (25), 133 (23), 118 (30), 91 (43), 76 (13), 65 (13).
- 5**: An viscous yellow oil;  $\nu_{\max}$  (KBr) = 1692s, 1613s, 1447s, 1274s, 770s, 752m, 735s  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) = 2.90 (d,  $J$  = 6.3 Hz, 1H), 3.03 (s, 2H), 5.56 (d,  $J$  = 11.4 Hz, 1H), 5.73 (dt,  $J$  = 10.0, 6.3 Hz, 1H), 6.07 (dt,  $J$  = 10.0, 6.2 Hz, 1H), 6.42 (dd,  $J$  = 11.4, 6.2 Hz, 1H), 7.17 (d,  $J$  = 7.3 Hz, 2H), 7.28 (m, 2H), 7.40 (t,  $J$  = 7.3 Hz, 2H), 7.76 (d,  $J$  = 7.3 Hz, 2H) ppm;  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) = 22.1, 48.8, 57.0, 120.1, 123.1, 125.5, 127.8, 127.9, 128.0, 132.9, 137.5, 140.5, 148.4, 167.0, 205.8 ppm;  $m/z$  (rel. int) = 296 ( $M^+$ , 100 %), 267 (22), 265 (23), 254 (47), 253 (45), 252 (51), 126 (19), 118 (43), 90 (34).
- 6**: An air-sensitive yellow oil;  $\nu_{\max}$  (KBr) = 2924s, 759s, 732s  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) = 2.90 (d,  $J$  = 6.5 Hz, 2H), 5.44 (td,  $J$  = 9.5, 6.5 Hz, 1H), 5.68 (d,  $J$  = 11.0 Hz, 1H), 6.07 (m, 2H), 6.25 (d,  $J$  = 5.3 Hz, 1H), 6.49 (d,  $J$  = 5.3 Hz, 1H), 6.92 (d,  $J$  = 7.6 Hz, 2H), 7.17 (td,  $J$  = 7.6, 1.0 Hz, 2H), 7.32 (td,  $J$  = 7.6, 1.0 Hz, 2H), 7.75 (d,  $J$  = 7.6 Hz, 2H) ppm;  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) = 27.9, 70.6, 120.1, 120.6, 123.3, 125.3, 127.4, 127.5, 127.8, 128.4, 135.6, 136.6, 141.7, 142.1, 143.1, 143.2 ppm;  $m/z$  (rel. int) = 281 ( $M^{+1}$ , 34 %), 280 ( $M^+$ , 100), 279 (100), 278 (45), 277 (38), 276 (42), 266 (25), 265 (77), 252 (25), 138 (28), 133 (21), 132 (20).
- 3**:  $\nu_{\max}$  (KBr) = 1448s, 1091s  $\text{cm}^{-1}$ ;  $\delta_{\text{C}}$  ( $\text{CD}_3\text{CN}$ ) = 74.7, 122.7, 124.8, 129.8, 131.2, 136.5, 138.7, 144.9, 146.4, 146.5, 150.7, 151.1, 153.9, 159.5, 173.0, 176.9 ppm;  $m/z$  (rel. int) = 280 ( $\text{C}_{22}\text{H}_{15}^{+1}$ , 55 %), 279 ( $\text{C}_{22}\text{H}_{15}^+$ , 100), 278 (68), 277 (33), 276 (34), 265 (35); Found: C, 69.35; H, 4.24 %, calcd for  $\text{C}_{22}\text{H}_{15}\text{ClO}_4$ : C, 69.79; H, 3.99 %.
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  12. Also the reduction potential (-0.37 V vs. SCE, irreversible) of **3** obtained by cyclic voltammetry evidences relative instability compared with that (-0.41 V vs. SCE, irreversible) of **8**.
  13. Despite many efforts X-ray analysis of **3** was unsuccessful so far.
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