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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

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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.

A typical absorption band based on the intramolecular charge-transfer (CT) interaction[1] between the tropylium cation and benzene has been observed in UV–vis spectra of cyclophane **1**[2] and a triptycene-type compound **2**.[3–5] 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 Letter, 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 (Fig. 1).

The title cation **3** was synthesized by our previously reported method,[6,7] as shown in Scheme 1. The Mukaiyama aldol reaction[8] of **4** with fluorenone in dichloromethane gave **5** in 47% yield. The Nazarov cyclization[9] of **5** produced tetrahydroazulenone **6** in 87% yield. The subsequent Shapiro reaction[10] 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.[11] Thus, the stability of **3** is greater than that of the tropylium ion (3.9)[11] and is less by about 2 pK_R+ units than that of the spiroannulated azulenium ion **8** (9.9).[6c,12]

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 Figure 2.[13,14] In the ^{1}H NMR spectrum of **3**, the hydrogens at the 2 and 8 positions resonate at a slightly higher magnetic field compared with those of other 1,1-substituted azulenium ions,[6,15] 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

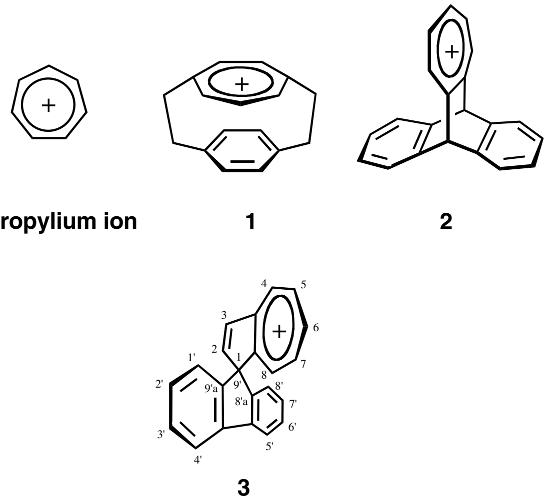

Figure 1. Tropylium ion and cations composed of the tropylium ion and at least one benzene ring.

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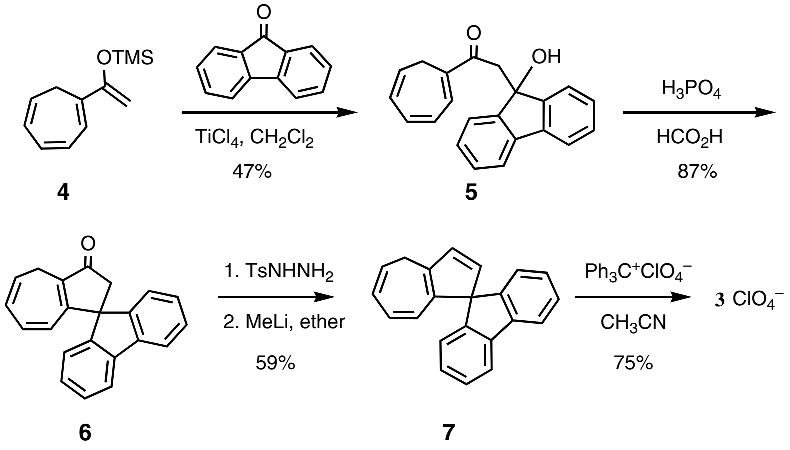
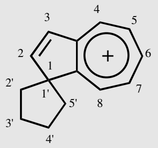


Scheme 1. Synthetic method for preparing **3**.

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

Cation	pK_{R^+}	UV–vis (CH$_3$CN) λ_{max}(log ε) nm	^{1}H NMR δ_{ppm} (CD$_3$CN)
3 ClO$_4^-$ 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, J = 7.8, 1.1 Hz, H-1′,8′), 7.30 (dt, J = 7.8, 1.1 Hz, H-3′,6′), 7.52 (d, J = 5.4 Hz, H-2), 7.57 (dt, J = 7.8, 1.1 Hz, H-2′,7′), 7.77 (d, J = 5.4 Hz, H-3), 7.95 (d, J = 10.0 Hz, H-8), 8.05 (td, J = 7.8 Hz, 1.0 Hz, H-4′,5′), 8.45 (dt, J = 10.0, 1.0 Hz, H-7), 8.67 (tt, J = 10.0, 1.0 Hz, H-6), 8.96 (dt, J = 10.0, 1.0 Hz, H-5), 9.12 (dd, J = 10.0, 1.0 Hz, H-4)
8 BF$_4^-$ [a] 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, J = 5.4 Hz, H-3), 7.72 (d, J = 5.4 Hz, H-2), 8.75 (tt, J = 8.8, 0.4 Hz, H-6), 8.77 (t, J = 8.8 Hz, H-7), 8.90 (t, J = 8.8 Hz, H-5), 8.96 (dd, J = 8.8, 0.4 Hz, H-4), 9.00 (dm, J = 8.8 Hz, H-8)[b]

[a] Taken from Ref. 6c.
[b] Data of **8**PF$_6^-$.

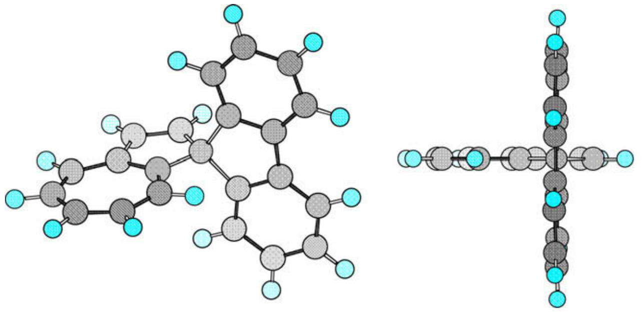


Figure 2. Structure (Chem3D output) of cation **3** calculated at the B3LYP/6-311+G(d,p) level of theory.

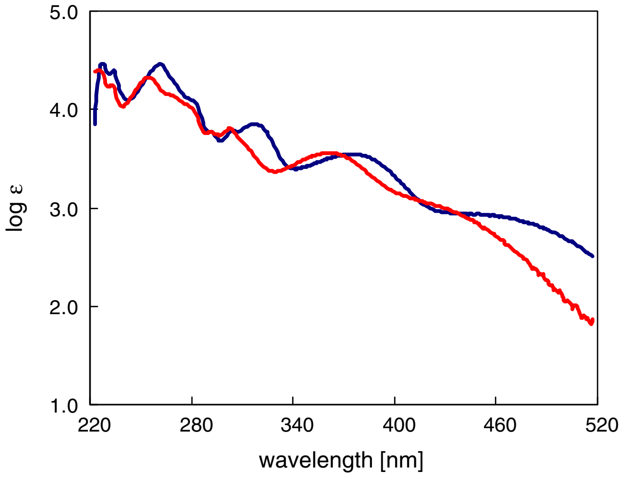


Figure 3. UV–vis absorption spectra of cation **3** in acetonitrile (red) and dichloromethane (blue).

ions in acetonitrile show three absorption bands at 220–230, 260–270, and 350–365 nm[6c,d] and the spectrum of fluorene has a band at 300 nm,[16] 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

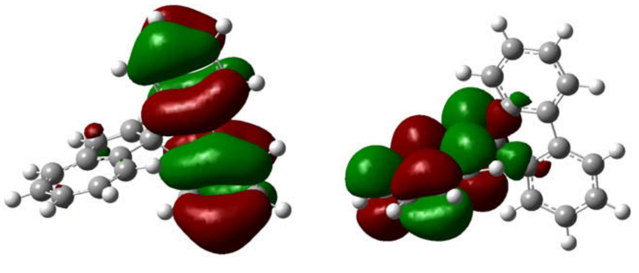
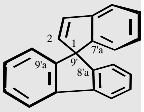


Figure 4. HOMO (left) and LUMO (right) of cation **3** calculated at the B3LYP/6-311+G(d,p) level of theory.

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

3		**9**		
C1–C2	1.502	C1–C2	1.525	 **9**
C1–C8a	1.524	C1–C7a	1.528	
C9′–C9a′	1.540	C9′–C9a′	1.532	
C8a′–C9′	1.540	C8a′–C9′	1.532	

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.[17] Calculated HOMO and LUMO orbitals are shown in Figure 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[18] suggests that an orbital interaction between them via space in its ground state can be excluded to stabilize this molecule.[19] 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^2 hybridized atoms. Thus, the tropylium ion part in **3** is stabilized not only by π–π conjugation with the C2–C3 ethylene unit but also by σ–π conjugation between the σ-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 σ–π conjugation of the relatively electronegative C8a′ and C9a′ sp^2 carbon atoms.

Acknowledgments

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7. All new compounds are characterized by spectroscopic and combustion analyses. Selected data are as follows. Compound **4**: Colorless solids, mp 126–128 °C; ν_{max} (KBr) = 1626s, 1388s, 1203s, 1172s, 771s, 740s, 708s cm^{-1}; δ_H ($CDCl_3$) = 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; δ_C ($CDCl_3$) = 25.1, 45.7, 80.9, 112.0, 124.1, 125.8, 127.4, 127.9, 128.9, 129.0, 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). Compound **5**: A viscous yellow oil; ν_{max} (KBr) = 1692s, 1613s, 1447s, 1274s, 770s, 752m, 735s cm^{-1}; δ_H ($CDCl_3$) = 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; δ_C ($CDCl_3$) = 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). Compound **6**: An air-sensitive yellow oil; ν_{max} (KBr) = 2924s, 1446s, 759s, 732s cm^{-1}; δ_H ($CDCl_3$) = 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; δ_C ($CDCl_3$) = 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). Compound **3**: ν_{max} (KBr) = 1448s, 1091s cm^{-1}; δ_C (CD_3CN) = 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 ($C_{22}H_{15}{}^{+}$+1, 55%), 279 ($C_{22}H_{15}{}^{+}$+1, 100), 278 (68), 277 (33), 276 (34), 265 (35). Calcd for $C_{22}H_{15}ClO_4$: C, 69.79: H, 3.99. Found: C, 69.35: H, 4.24. *Caution! The perchlorate salt is potentially explosive.*
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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**.
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