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SYNTHESIS AND PROPERTIES OF (1-AZULENYL)DI(3-INDOLYL)-METHYLIUM HEXAFLUOROPHOSPHATES [+]

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Abstract – (1-Azulenyl)di(3-indolyl)methanes (**3a**-**c**;**5a**,**b**) were synthesized by the acid-catalyzed condensation of methyl 3-formylazulene-1-carboxylate (**1**) with indoles (**2a**-**d**) and converted to the corresponding (1-azulenyl)di(3-indolyl)methylium hexafluorophosphates (**6a**-**d**). On the basis of their pK_{R+} values (~ 13), the methyl cations (**6a**-**d**) were found to be comparably stable to tri(1-azulenyl)methyl cations.

INTRODUCTION

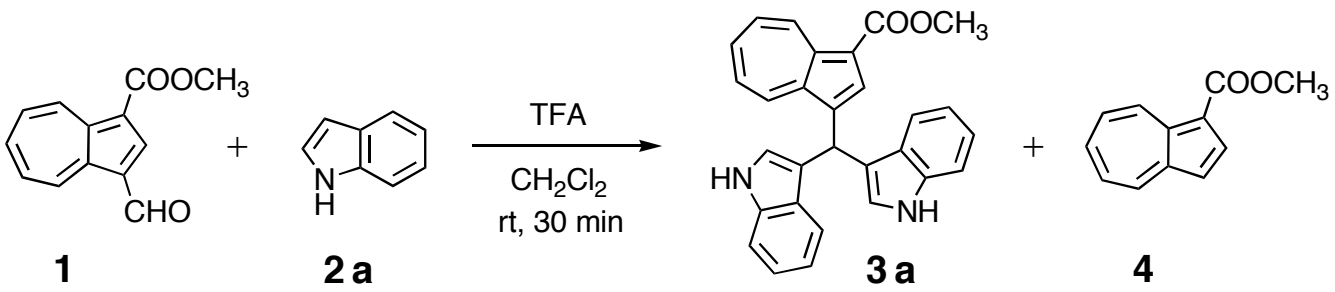
On the polarizability and electron-donating character of azulene ring, very stable 1-azulenyl-substituted methyl cations were prepared and their physicochemical properties have been investigated.[1] It has been found that the 1-azulenyl group stabilized carbocations and gave high pK_{R+} values[1a] as (1-azulenyl)-biphenylmethyl cation (pK_{R+} 3.0), di(1-azulenyl)phenylmethyl cation (10.5), and tri(1-azulenyl)methyl cation (11.3) in comparison with triphenylmethyl cation (-6.4).[2] Furthermore, the introduction of three strongly electron-donating dimethylamino groups into the three 6-positions of the tri(1-azulenyl)methyl cation brought the highest pK_{R+} value (24.3).[1c] On the other hand, indole has an isoelectronic structure with azulene. It is expected that the 3-indolyl group is able to conjugate with cationic carbon on the basis of electron-donating effect of the nitrogen atom and gives highly stable carbocations. We report here the first synthesis and physicochemical properties of (1-azulenyl)di(3-indolyl)methyl cations.

[+] Dedicated to the memory of Professor Kenji Koga

RESULTS AND DISCUSSION

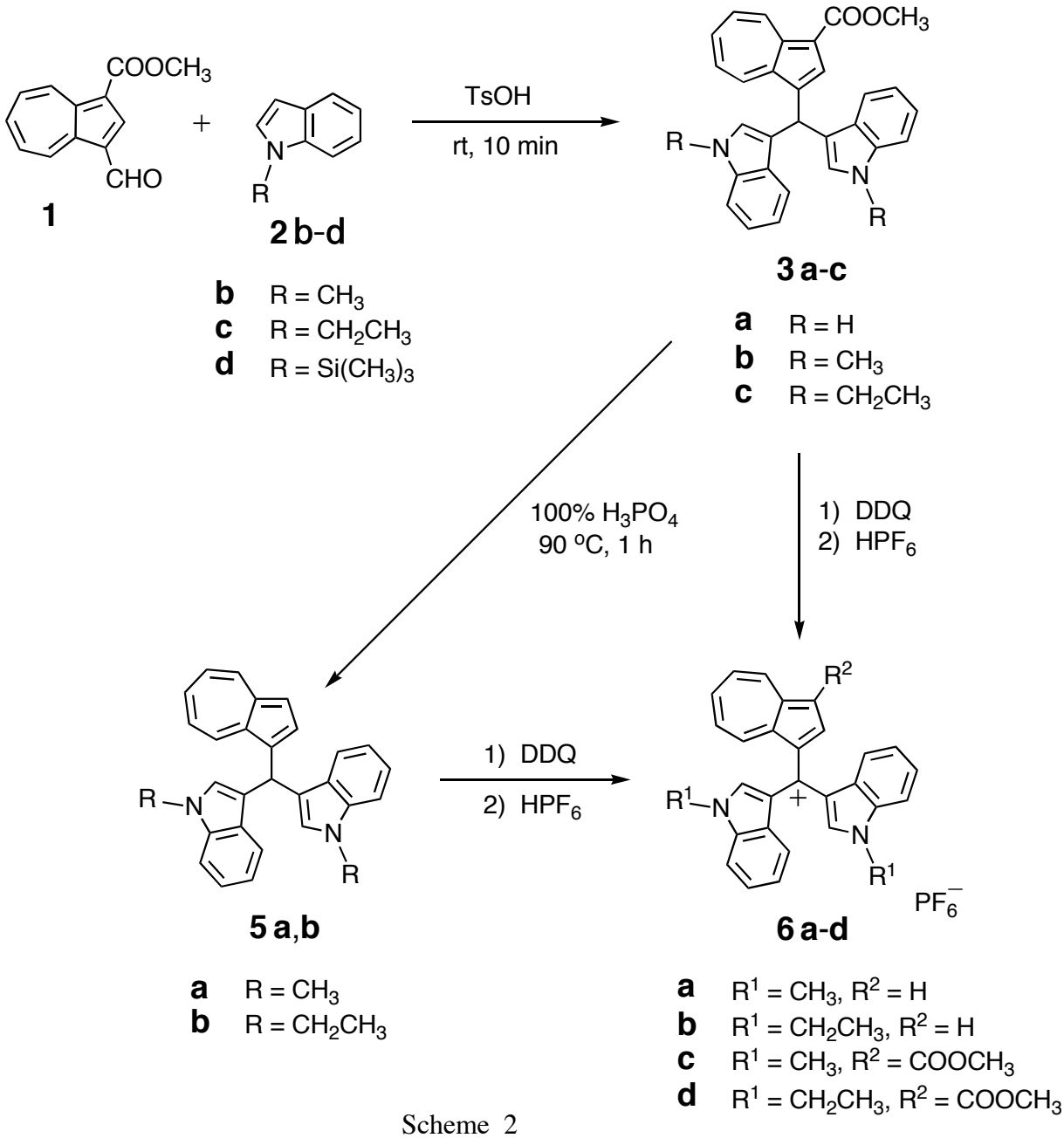
Synthesis

It is reported that the sequence of the acid-catalyzed condensation of azulenes with aldehydes and hydride abstraction of the condensed products with DDQ is useful method for preparation of methyl cations containing 1-azulenyl group.[1] The reaction of methyl 3-formylazulene-1-carboxylate (**1**) with three molar equivalents of indole (**2a**) in acetic acid gave no condensation product after stirring for 2 h at rt. When trifluoroacetic acid (TFA) was added into this mixture, the condensation began to afford (3-methoxycarbonyl-1-azulenyl)di(3-indolyl)methane (**3a**) (27%) after stirring for 30 min. The structure was confirmed spectrophotometrically (see: EXPERIMENTAL). The TFA-catalyzed reaction in dichloromethane gave the product (**3a**) (22%) and methyl azulene-1-carboxylate (**4**) (9%), which was a deformylated product from the azulene (**1**).



Scheme 1

On the other hand, it was reported as one of very convenient methods that the solid-state condensation of aryl aldehydes with nitrogen heterocycles in the presence of *p*-toluenesulfonic acid[3] or *N*-bromosuccinimide.[4] A mixture of methyl 3-formylazulene-1-carboxylate (**1**) and three molar equivalents of 1-trimethylsilylindole (**2d**) was ground in a mortar in the presence of five molar equivalents of *p*-toluenesulfonic acid to give (3-methoxycarbonyl-1-azulenyl)di(3-indolyl)methane (**3a**) in 38% yield. In a similar manner, the reactions of the azulene (**1**) with 1-methylindole (**2b**) or 1-ethylindole (**2c**) gave (3-methoxycarbonyl-1-azulenyl)di(1-methyl-3-indolyl)methane (**3b**) (70%) and (3-methoxycarbonyl-1-azulenyl)di(1-ethyl-3-indolyl)methane (**3c**) (70%), respectively. When compound (**3a**) were heated for 1 h at 90 ºC in 100% phosphoric acid in order to remove the methoxycarbonyl group, any desired product was not obtained. Similarly, compounds (**3b**,**c**) were treated to give (1-azulenyl)di(1-methyl-3-indolyl)methane (**5a**) (13%) and (1-azulenyl)di(1-ethyl-3-indolyl)methane (**5b**) (24%) as blue microcrystals, respectively.



Scheme 2

The hydride abstraction from these (1-azulenyl)di(3-indolyl)methanes (**3b**,**c**;**5a**,**b**) with DDQ in dichloromethane, followed by adding 60% hexafluorophosphoric acid yielded the corresponding (1-azulenyl)di(3-indolyl)methylium hexafluorophosphates (**6a**-**d**) in moderate to good yields, by an exchange of the counter anion with PF_6^-

Spectroscopic Properties

The HRMS spectra of methyl cations (**6a**-**d**) showed correct M^+ - PF_6 ion peaks, which were revealed their cationic structures. In the ^1H NMR spectra, the methane signals for the of neutral compounds (**3b**,**c**;**5a**,**b**) at δ 6.42-6.45 were disappeared in spectra of cations (**6a**-**d**). The downfield shifts of the

azulenic protons were observed by *ca*. 0.5 ppm in the cations (**6a**-**d**). Similar behaviors were also observed in the indole ring protons. This means that not only the azulene ring but also the indole ring contribute towards the stabilization of the cations (**6a**-**d**). In the ^{13}C NMR spectra of the cations (**6a**-**d**), the signals for the methyl cationic carbons were observed at δ 151-160. These δ values are comparable to those for tri(1-azulenyl)methyl cations.[1] In the UV-VIS spectra, the cations (**6a**-**d**) showed strong characteristic absorption maxima in the visible 513-520 nm region.

pK_R+ Values

The pK_R+ values were determined spectrophotometrically in 0.1 M glycine buffered solution prepared in 50% aqueous acetonitrile at 25 °C[1,5] and listed in Table 1. The pK_R+ values of cations (**6a-d**) are very high (*ca*. 13) and comparable to those of tri(1-azulenyl)methyl cations.[1] The high stabilities of these cations were attributed to an extended conjugative effect among the central cation and the azulene and indole ring, as shown in Figure 1. Namely, it was found that the electron-donating character of the nitrogen atoms in the indole rings stabilizes these methyl cations (**6a-d**).

Table 1. pK_R+ Values of (1-Azulenyl)di(3-indolyl)methyl Cations (**6a**-**d**)

	R^1	R^2	pK_R+
6a	CH_3	H	13.5
6b	CH_2CH_3	H	13.8
6c	CH_3	$COOCH_3$	12.8
6d	CH_2CH_3	$COOCH_3$	13.0

CONCLUSION

Four (1-azulenyl)di(3-indolyl)methylium hexafluorophosphates (**6a**-**d**) were synthesized from methyl 3-formylazulene-1-carboxylate (**1**) and indoles (**2a**-**d**) *via* (1-azulenyl)di(3-indolyl)methanes (**5a**,**b**;**3b**,**c**). It was found that these methyl cations (**6a**-**d**) have high stabilities based on a nitrogen conjugative effect in the indole ring in addition to the electron-donating effect of the 1-azulenyl moiety.

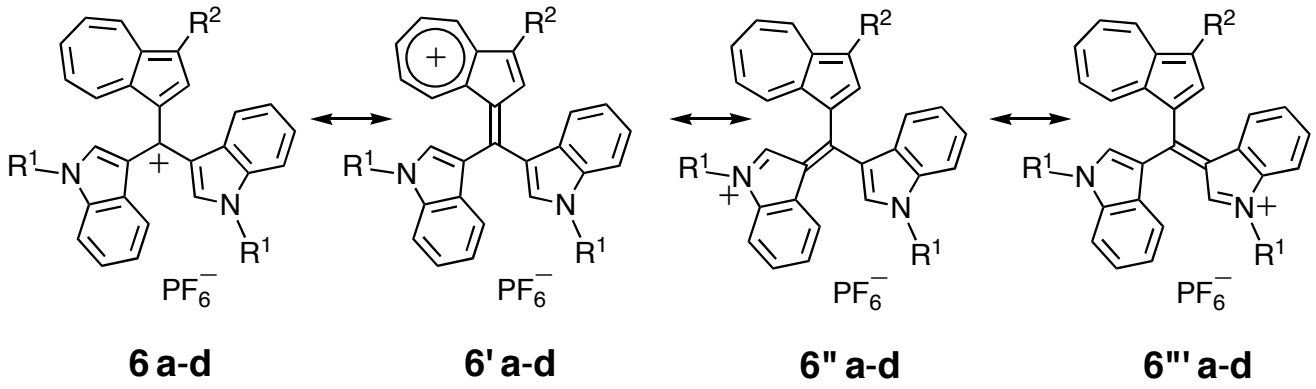


Figure. 1

EXPERIMENTAL

The melting points were determined with a Yanaco MP JP-3 apparatus and are uncorrected. The IR spectra were taken on a Perkin-Elmer Pragon 1000 spectrophotometer. The UV-VIS spectra were measured on a Shimadzu MultiSpec-1500 spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded with a JEOL JNM-AL 300 spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C). The MS spectra were obtained with JEOL JMS-01-SG instrument.

Materials. Methyl 3-formylazulene-1-carboxylate (**1**)[1a] was prepared from 3-methoxycarbonyl-2*H*-cyclohepta[*b*]furan-2-one *via* methyl 3-methylazulene-1-carboxylate.[6] Indole (**2a**) and 1-methylindole (**2b**) were commercially available and 1-ethyl- (**2c**)[7] and 1-trimethylsilylindole (**2d**)[8] were prepared according to the literatures.

Reactions of Methyl 3-Formylazulene-1-carboxylate (1) with Indoles (2a-d). a) A solution of methyl 3-formylazulene-1-carboxylate (**1**) (202 mg, 1.0 mmol) and indole (**2a**) (351 mg, 3.0 mmol) in acetic acid (30 mL) was stirred for 30 min at rt in the presence of TFA (0.25 mL, 3.0 mmol). The reaction mixture was dissolved in chloroform (50 mL) and neutralized with a saturated sodium hydrogencarbonate solution. The solution was washed with water and dried over sodium sulfate. The evaporation residue was purified by column chromatograpgy on silica gel (150 g) with chloroform to afford (3-methoxycarbonyl-1-azulenyl)di(3-indolyl)methane (**3a**) and methyl azulene-1-carboxylate (**4**).

(3-Methoxycarbonyl-1-azulenyl)di(3-indolyl)methane (3a). Yield, 95 mg (22%); violet micro-crystals (from chloroform); mp 239-240 °C; IR (KBr) ν_{max} 3414 (NH), 1667 cm^{-1} (C=O); UV-VIS ($CHCl_3$) λ_{max} (log ε) 244 (5.56), 292 (5.68), 372 (4.93), 386 (4.96), 558 nm (2.67); ^{1}H NMR ($CDCl_3$) δ 3.83 (3H, s, $COOCH_3$), 6.48 (1H, s, -CH<), 6.52 (2H, d, *J* = 3.3 Hz, 4'-,4"-H), 6.52 (2H, dd, *J* = 8.1, 8.1 Hz, 5'-,5"-H), 6.98 (2H, dd, *J* = 8.1, 8.1 Hz, 6'-,6"-H), 7.28-7.38 (5H, m), 7.48 (1H, dd, *J* = 9.9, 9.3 Hz, 6-H), 7.73 (1H, dd, *J* = 9.9, 9.9 Hz, 5-H), 7.78 (2H, s, NH x 2), 8.07 (1H, s, 2-H), 8.58 (1H, d, *J* = 9.9 Hz,

8-H), 9.60 (1H, d, *J* = 9.9 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ 32.24 (-CH<), 50.94 (CH_3), 111.08 (=CH-), 114.85 (=C<), 119.18 (=CH-), 119.49 (=C<), 119.71 (=CH-), 121.88 (=CH-), 123.62 (=CH-), 126.05 (=CH-), 126.96 (=C<), 127.37 (=CH-), 132.18 (=C<), 135.17 (=CH-), 136.71 (=C<), 137.49 (=CH-), 138.87 (=CH-), 140.11 (=C<), 140.82 (=CH-), 141.65 (=C<), 166.42 (C=O); MS (FAB) *m/z* (%) 430 (M^+, 100), 429 (37). HRMS (FAB). Calcd for $C_{29}H_{22}N_2O_2$: M, 430.1681. Found: M^+ 430.1679.

Methyl Azulene-1-carboxylate (4). Yield, 17 mg (9 %); violet oil.[6]

b) A mixture of the formylazulene (**1**) (202 mg, 1.0 mmol) and indole (**2b**-**d**) (3.0 mmol) was ground in a mortar in the presence of *p*-toluenesulfonic acid (1.05 g, 5.5 mmol) and allowed to stand for 30 min at rt. The reaction mixture was worked up, as described above, to give (3-methoxycarbonyl)di(3-indolyl)-methanes (**3b**-**c**). The reaction of compound (**1**) with 1-trimethylsilylindole (**2d**) gave the product (**3a**) (38%).

(3-Methoxycarbonyl-1-azulenyl)di(1-methyl-3-indolyl)methane (3b). Yield, 450 mg (38%); violet microcrystals (from chloroform); mp 250-251 °C; IR (KBr) ν_{max} 1690 cm^{-1} (C=O); UV-VIS ($CHCl_3$) λ_{max} (log ε) 240 (4.58), 294 (4.58), 375 (3.92), 559 nm (3.31); ^{1}H NMR ($CDCl_3$) δ 3.57 (3H, s, CH_3), 3.76 (3H, s, $COOCH_3$), 6.39 (2H, s, 2'-,2"-H), 6.42 (1H, s, -CH<), 6.98 (2H, dd, *J* = 8.1, 6.9 Hz, 5'-,5"-H), 7.12 (2H, dd, *J* = 7.2, 6.9 Hz, 6'-,6"-H), 7.20-7.29 (5H, m), 7.42 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 7.67 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 8.01 (1H, s, 2-H), 8.52 (1H, d, *J* = 9.6 Hz, 8-H), 9.55 (1H, d, *J* = 9.9 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ 32.04 (-CH<), 32.67 (1'-CH_3), 50.91 (COO*C*H_3), 109.07 (=CH-), 114.81 (=C<), 118.07 (=C<), 118.59 (=C<), 119.79 (=CH-), 121.36 (=CH-), 126.01 (=CH-), 127.29 (=CH-), 127.32 (=C<), 128.23 (=CH-), 132.61 (=C<), 135.15 (=CH-), 137.41 (=CH-), 137.44 (=C<), 138.82 (=CH-), 139.99 (=C<), 140.72 (=C<), 141.65 (=C<), 165.89 (C=O); MS (FAB) *m/z* (%) 458 (M^+, 100), 457 (28). HRMS (FAB). Calcd for $C_{31}H_{26}N_2O_2$: M, 458.1994. Found: M^+ 458.1996.

(3-Methoxycarbonyl-1-azulenyl)di(1-ethyl-3-indolyl)methane (3c). Yield, 484 mg (98%); violet microcrystals (from chloroform); mp 105-106 °C; IR (KBr) ν_{max} 1690 cm^{-1} (C=O); UV-VIS ($CHCl_3$) λ_{max} (log ε) 243 (5.58), 293 (5.66), 373 (4.89), 386 (4.90), 557 nm (3.98); ^{1}H NMR ($CDCl_3$) δ 1.24 (6H, t, *J* = 7.5 Hz, CH_3 x 2), 3.81 (2H, q, *J* = 7.5 Hz, CH_2 x 2), 3.74 (3H, s, $COOCH_3$), 6.41-6.44 (3H, m, -CH< + 2'-,2"-H), 6.86 (2H, dd, *J* = 7.5, 7.2 Hz, 5'-,5"-H), 7.10 (2H, dd, *J* = 7.5, 7.2 Hz, 6'-,6"-H), 7.18-7.27 (5H, m), 7.39 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 7.63 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 8.01 (1H, s, 2-H), 8.51 (1H, d, *J* = 9.9 Hz, 8-H), 9.54 (1H, d, *J* = 9.9 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ 15.46 (CH_3), 32.24 (-CH<), 40.79 (CH_2), 50.87 (COO*C*H_3), 109.15 (=CH-), 114.80 (=C<), 118.03 (=C<), 118.49 (=C<), 119.94 (=CH-), 121.71 (=CH-), 125.92 (=CH-), 126.61 (=CH-), 127.23 (=CH-), 127.51 (=C<), 132.63 (=C<), 135.15 (=CH-), 136.39 (=CH-), 137.36 (=CH-), 138.78 (=CH-), 140.78 (=CH-), 141.62 (=C<), 165.87 (C=O); MS (FAB) *m/z* (%) 486 (M^+, 100), 485 (59). HRMS (FAB). Calcd for $C_{33}H_{30}N_2O_2$: M, 486.2307.

Found: M^+ 486.2313.

Preparation of (1-azulenyl)di(3-indolyl)methanes (5a,b): A suspension of (3-methoxycarbonyl-1-azulenyl)di(3-indolyl)methane (**3b,c**) (1.0 mmol) in 100% phosphoric acid (30 mL) was heated at 90 ºC for 1 h. The reaction mixture was quenched with water, neutralized with 2M sodium hydroxide solution, and extracted with chloroform. After drying over sodium sulfate, the evaporation residue was chromatographed on a Wakogel B-10 plate (30 x 30 cm) with hexane-diethyl ether (1 :1) to afford (1-azulenyl)di(3-indolyl)methanes (**5a,b**).

(1-Azulenyl)di(1-methyl-3-indolyl)methane (5a). Yield, 52 mg (13%); blue microcrystals (from chloroform); mp 105 ºC; UV-VIS ($CHCl_3$) λ_{max} (log ε) 242 (4.50), 283 (4.65), 349 (3.68), 365 (3.47), 600 nm (2.51); ^{1}H NMR ($CDCl_3$) δ 3.62 (6H, s, CH_3 x 2), 6.48 (2H, s, 2'-,2"-H), 6.55 (1H, s, -CH<), 6.95 (2H, dd, *J* = 7.5, 7.2 Hz, 5'-,5"-H), 7.02-7.36 (9H, m), 7.51 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 7.68 (1H, d, *J* = 3.6 Hz, 2-H), 8.26 (1H, d, *J* = 9.3 Hz, 8-H), 8.46 (1H, d, *J* = 9.3 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ 32.39 (-CH<), 32.62 (CH_3), 108.99 (=CH-), 116.48 (=CH-), 118.46 (=CH-), 118.84 (=C<), 120.05 (=CH-), 121.24 (=CH-), 121.67 (=CH-), 122.18 (=CH-), 127.46 (=C<), 128.09 (=CH-), 133.16 (=C<), 133.51 (=CH-), 134.78 (=C<), 136.35 (=CH-), 137.12 (=CH-), 137.39 (=C<), 139.08 (=CH-), 141.04 (=C<); MS (FAB) *m/z* (%) 400 (M^+, 100), 399 (36), 270 (47), 268 (20), 149 (29), 144 (23). HRMS (FAB). Calcd for $C_{29}H_{24}N_2$: M, 400.1939. Found: M^+ 400.1978.

(1-Azulenyl)di(1-ethyl-3-indolyl)methane (5b). Yield, 103 mg (24%); blue microcrystals (from chloroform); mp 74 ºC; UV-VIS ($CHCl_3$) λ_{max} (log ε) 243 (4.44), 280 (4.56), 349 (3.61), 365 (3.41), 600 nm (2.47); ^{1}H NMR ($CDCl_3$) δ 1.33 (6H, s, CH_3 x 2), 4.03 (4H, s, CH_2 x 2), 6.54 (3H, s, -CH< + 2'-,2"-H), 6.93 (2H, dd, *J* = 7.8, 6.9 Hz, 5'-,5"-H), 6.99-7.33 (9H, m), 7.52 (1H, dd, *J* = 9.9, 9.6 Hz, 6-H), 7.68 (1H, d, *J* = 3.6 Hz, 2-H), 8.27 (1H, d, *J* = 9.3 Hz, 8-H), 8.47 (1H, d, *J* = 9.3 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ 15.53 (CH_3), 32.55 (-CH<), 40.77 (CH_2), 109.08 (=CH-), 116.46 (=CH-), 118.35 (=CH-), 118.83 (=C<), 120.21 (=CH-), 121.04 (=CH-), 121.62 (=CH-), 122.15 (=CH-), 127.65 (=C<), 133.21 (=C<), 133.35 (=CH-), 134.79 (=C<), 136.30 (=CH-), 136.36 (=C<), 137.09 (=CH-), 139.19 (=CH-), 141.05 (=C<); MS (FAB) *m/z* (%) 428 (M^+, 39), 307 (36), 154 (100), 136 (59). HRMS (FAB). Calcd for $C_{31}H_{28}N_2$: M, 428.2252. Found: M^+ 428.2292.

Preparation of (1-Azulenyl)di(3-indolyl)methylium Hexafluorophosphates (6a-d). A suspended solution of (1-azulenyl)di(3-indolyl)methane (**5a,b**) or (3-methoxycarbonyl-1-azulenyl)di(3-indolyl)-methane (**3b,c**) (1.0 mmol) and DDQ (227 mg, 1.0 mmol) in dichloromethane (35 mL) was stirred for 1 h at rt. After adding 60% hexafluorophosphoric acid solution (0.45 mL, 3.00 mmol), the solution was stirred for additional 5 min, diluted with water, and filtered. The filtrate was dried over sodium sulfate. The evaporation residue was recrystallized from dichloromethane-hexane to give (1-azulenyl)di(3-

indolyl)methylium hexafluorophosphates (**6a**-**d**).

(1-Azulenyl)di(1-methyl-3-indolyl)methylium Hexafluorophosphate (6a). Yield, 424 mg (78%); reddish violet microcrystals (from dichloromethane-hexane); mp > 300 °C; UV-VIS ($CHCl_3$) λ_{max} (log ε) 240 (4.50), 293 (4.60), 328 (4.00), 514 nm (4.67); ^{1}H NMR ($CDCl_3$) δ 4.18 (6H, s, CH_3 x 2), 6.56 (2H, br, 2'-,2"-H), 6.98 (2H, m, 6'-,6"-H), 7.26-7.38 (7H, m), 7.62 (1H, d, *J* = 3.8 Hz, 3-H), 7.74 (1H, dd, *J* = 9.6, 9.3 Hz, 7-H), 7.90 (1H, dd, *J* = 9.9, 9.0 Hz, 6-H), 8.24 (1H, d, *J* = 9.9 Hz, 8-H), 8.69 (1H, d, *J* = 9.0 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ 34.60 (CH_3), 112.68 (=CH-), 113.90 (=CH-), 120.25 (=CH-), 122.76 (=C<), 124.00 (=CH-), 125.29 (=CH-), 127.47 (=C<), 127.60 (=CH-), 129.29 (=C<), 131.49 (=C<), 131.70 (=C<), 138.43 (=CH-), 139.89 (=C<), 140.67 (=CH-), 142.23 (=CH-), 146.69 (=C<), 151.01 (=CH-), 158.07 (C^+); MS (FAB) *m/z* (%) 399 (M^+, 100), 307 (26), 154 (64), 136 (38). HRMS (FAB). Calcd for $C_{29}H_{23}N_2^+$: M, 399.1861. Found: M^+ 399.1896.

(1-Azulenyl)di(1-ethyl-3-indolyl)methylium Hexafluorophosphate (6b). Yield 275 mg (48%); reddish violet microcrystals (from dichloromethane-hexane); mp > 300 °C; UV-VIS ($CHCl_3$) λ_{max} (log ε) 236 (4.94), 292 (4.60), 327 (4.00), 513 nm (4.57); ^{1}H NMR ($CDCl_3$) δ 1.68 (6H, t, *J* = 7.2 Hz, CH_3 x 2), 4.61 (4H, q, *J* = 7.2 Hz, CH_2 x 2), 6.80 (2H, br, 2'-,2"-H), 7.10-7.44 (4H, m, 5'-,5"-,6'-,6"-H), 7.47-7.85 (5H, m, 4'-,4"-,7-,7'-,7"-H), 7.82 (1H, d, *J* = 4.0 Hz, 3-H), 7.96 (1H, dd, *J* = 9.9, 9.6 Hz, 5-H), 8.13 (1H, d, *J* = 9.9, 9.6 Hz, 6-H), 8.44 (1H, d, *J* = 9.9 Hz, 8-H), 8.50 (1H, d, *J* = 4.0 Hz, 2-H), 8.97 (1H, d, *J* = 9.6 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ 15.33 (CH_3), 43.60 (CH_2), 102.78 (=C<), 113.08 (=CH-), 113.62 (=C<), 121.64 (=C<), 121.65 (=CH-), 123.54 (=CH-), 123.61 (=CH-), 124.75 (=CH-), 126.13 (=CH-), 129.04 (=C<), 132.18 (=CH-), 132.49 (=CH-), 139.52 (=CH-), 140.06 (=C<), 141.33 (=CH-), 142.83 (=CH-), 145.50 (=CH-), 151.55 (=C<), 159.75 (C^+); MS (FAB) *m/z* (%) 427 (M^+, 100), 307 (14), 154 (39), 136 (24). HRMS (FAB). Calcd for $C_{31}H_{27}N_2^+$: M, 427.2174. Found: M^+ 427.2198.

(3-Methoxycarbonyl-1-azulenyl)di(1-methyl-3-indolyl)methylium Hexafluorophosphate (6c). Yield, 536 mg (89%); reddish violet microcrystals (from dichloromethane-hexane); mp 141-142 °C; UV-VIS ($CHCl_3$) λ_{max} (log ε) 241 (4.58), 294 (4.79), 346 (4.09), 518 (4.75), 655 nm (2.38); ^{1}H NMR ($CDCl_3$) δ 3.94 (6H, s, CH_3 x 2), 4.21 (3H, s, $COOCH_3$), 6.47 (2H, br, 2'-,2"-H), 6.97 (2H, dd, *J* = 7.5, 7.2 Hz, 5'-,5"-H), 7.34 (2H, dd, *J* = 7.5, 7.2 Hz, 6'-,6"-H), 7.45-7.54 (5H, m), 7.92-8.06 (2H, m, 5-,6-H), 8.38 (1H, d, *J* = 9.6 Hz, 8-H), 8.61 (1H, s, 2-H), 10.01 (1H, d, *J* = 9.3 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ 35.01 (CH_3), 51.67 (COO*C*H_3), 111.99 (=CH-), 119.52 (=C<), 119.94 (=C<), 120.69 (=C<), 120.90 (=CH-), 124.50 (=CH-), 125.46 (=C<), 125.77 (=CH-), 127.55 (=C<), 132.26 (=CH-), 132.82 (=CH-), 139.20 (=CH-), 140.35 (=C<), 140.52 (=CH-), 142.41 (=CH-), 143.89 (=C<), 146.65 (=CH-), 146.99 (=CH-), 159.76 (C^+), 164.95 (C=O); MS (FAB) *m/z* (%) 457 (M^+, 100), 154 (41), 136 (33). HRMS (FAB). Calcd for $C_{31}H_{25}N_2O_2^+$: M, 457.1916. Found: M^+ 457.1919.

(3-Methoxycarbonyl-1-azulenyl)di(1-ethyl-3-indolyl)methylium Hexafluorophosphate (6d). Yield, 611 mg (97%); red microcrystals (from dichloromethane-hexane); mp 160-161 °C; UV-VIS ($CHCl_3$)

λ_{max} (log ε) 241 (4.57), 294 (4.66), 348 (4.10), 520 (4.64), 658 nm (2.59); ^{1}H NMR ($CDCl_3$) δ 1.68 (6H, t, *J* = 7.2 Hz, CH_3 x 2), 3.91 (3H, s, $COOCH_3$), 4.62 (4H, d, *J* = 7.2 Hz, CH_2 x 2), 6.65 (2H, br, 2'-,2"-H), 7.05 (2H, m, 5'-,5"-H), 7.41 (2H, m, 6'-,6"-H), 7.67-7.85 (5H, m), 8.10-8.32 (2H, m, 5-,6-H), 8.62 (1H, d, *J* = 9.0 Hz, 8-H), 8.64 (1H, s, 2-H), 10.03 (1H, d, *J* = 9.6 Hz, 4-H); ^{13}C NMR ($CDCl_3$) δ 15.20 (CH_3), 43.87 (CH_2), 51.83 ($COOCH_3$), 113.37 (=CH-), 113.72 (=C<), 120.21 (=C<), 121.90 (=CH-), 125.17 (=CH-), 126.45 (=CH-), 128.71 (=C<), 129.14 (=C<), 133.85 (=CH-), 134.39 (=CH-), 140.44 (=CH-), 140.55 (=CH-), 141.28 (=CH-), 144.31 (=CH-), 146.84 (=CH-), 146.88 (=C<), 147.34 (=C<), 147.78 (=C<), 151.60 (C^+), 165.31 (C=O); MS (FAB) *m/z* (%) 485 (M^+, 47), 307 (25), 289 (14), 154 (100), 136 (67). HRMS (FAB). Calcd for $C_{33}H_{29}N_2O_2^+$: M, 485.2229. Found: M^+ 485.2249.

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