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Synthesis of Trication Stabilized by Azulene Rings

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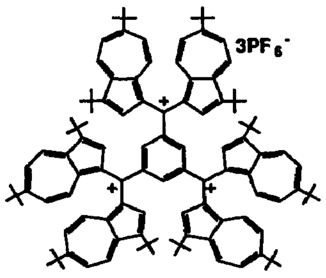
Abstract: Extraordinary stable trication of 1,3,5-tris[bis(3,6-di-*t*-butyl-1-azulenyl)methylio]benzene trishexafluorophosphate (**6**) was synthesized, and the p$K_R$$^{+++}$, p$K_R$$^{++}$, and p$K_R$$^{+}$ values were determined as 9.1, 10.9 and 12.7, respectively.

Recently we reported the synthesis of azulene analogs of triphenylmethyl cation, i.e., tri(1-azulenyl)methyl cation (**1**), di(1-azulenyl)phenylmethyl cation (**2**), and (1-azulenyl)diphenylmethyl cation (**3**), and their derivatives by hydride abstraction of the corresponding hydro derivatives with DDQ in good yields.[1] The methyl cation stabilized by two azulene rings (**2**) or more (**1**) showed extraordinary stability with high p$K_R$$^+$ values.[1] These observation indicates the combination of methyl cations stabilized by two azulene rings makes up the high stable polycations. In this concept, we synthesized dications species of tetraazulenyl-*m*-xylylene (**4**) and tetraazulenyl-*p*-xylylene (**5**), and showed their high stabilities.[2] We now extended the synthetic method to the trication species, and the trication (**6**) stabilized by six azulene rings was synthesized, which will be reported in this paper.



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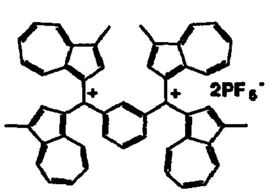

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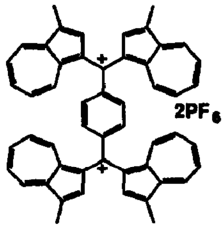

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The reaction of six molar equivalents of 1,3-di-*t*-butylazulene[3] with one equivalent of 1,3,5-triformylbenzene[4] in a 1 : 1 mixture of dichloromethane and acetic acid at room temperature for 24 h, afforded 1,3,5-tris[bis(3,6-di-*t*-butyl-1-azulenyl)methyl]benzene (**7**)[5] and 3,5-bis[bis(3,6-di-*t*-butyl-1-azulenyl)methyl]-benzaldehyde (**8**)[5] in 42% and 20% yields, respectively.[6] The oxidative hydride abstraction of **7** with DDQ in dichloromethane at room temperature followed by the addition of 60% HPF_6 solution yielded stable trications, 1,3,5-tris[bis(3,6-di-*t*-butyl-1-azulenyl)methylio]benzene trishexafluorophosphate (**6**)[5] in 99% yield.

The pK_R values of **6** were determined spectrophotometrically at 24°C in buffer solution prepared in 50% aqueous MeCN, and were summarized in Table I together with those of the dications (**4** and **5**).[7] We could not determine separately the pK_R^{++} and pK_R^{+} values of dications (**4** and **5**).[2] However, the trication (**6**) showed the pK_R^{+++}, pK_R^{++} and pK_R^{+} values, separately. The Table shows pK_R^{+++} value of trication (**6**) is slightly lower than the pK_R values of dications (**4** and **5**). However, the pK_R^{+} values of **6** are slightly higher than those of the dications (**4** and **5**), which may be attributable to the introduction of *t*-butyl groups.[3] Consequently, the trication (**6**) is effectively stabilized by azulene rings as in the case of dications. The reduction potentials of **6** determined by cyclic voltammetry were also shown in Table I. The first (E_1), second (E_2) and third (E_3) reduction potentials for **6** show small negative values and fairly close each other.

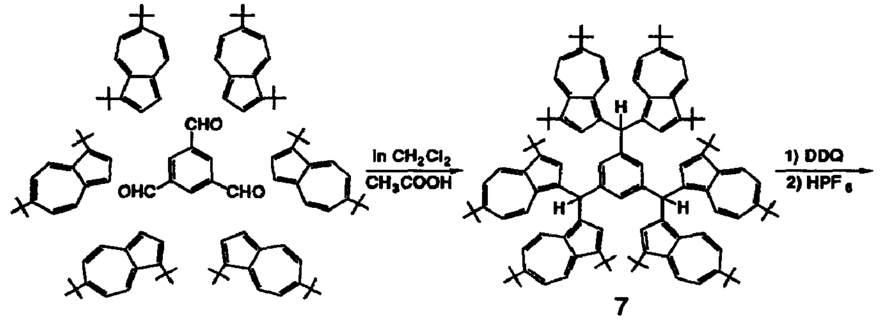

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Table I. pK_R values and reduction potentials[a] of **6**, **4** and **5**

	pK_R^{+++}	pK_R^{++}	pK_R^{+}	E_1	E_2	E_3
6	9.1	10.9	12.7	-0.31	-0.41	-0.52
4		11.5		-0.35	-0.44	
5		11.2		-0.15	-0.21	

a) V vs. SCE, 0.1 mol d^{-3} Et_4NClO_4 in MeCN, Pt electrode, scan rate 100 mV s^{-1}.

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5. All new compounds were characterized by their IR, UV, ^1H and ^{13}C NMR spectral data, and mass spectroscopy, selected spectral data for **6**, **7**, and **8** are given below.

   6; Black powder; mp 265.5 - 268.0°C (dec); UV (MeCN) λ_{max} 245 nm (log ε 5.09), 272 (4.98 sh), 299 (4.95), 320 (4.97), 358 (4.83), 391 (4.69 sh), 485 (4.33), 642 (4.76 sh), and 693 (5.03); ^1H NMR (90MHz, $CDCl_3$, 50°C) δ 8.89 (d, 6H, J=11.0, H_4), 8.02 (s, 3H, $H_{2',4',6'}$), 7.98 (d, 6H, J=11.0, H_5), 7.81 (d, 6H, J=11.0, H_7), 7.65 (s, 6H, H_2), 7.71 (d, 6H, J=11.0, H_7), 1.44 (s, 54H, 3-*t*-Bu), and 1.40 (s, 54H, 6-*t*-Bu).

   7; Blue crystals; mp 247.0 - 248.5°C (dec); UV (CH_2Cl_2) λ_{max} 243 nm (log ε 4.97), 290 (5.40), 303 (5.34), 346 (4.44 sh), 359 (4.51), 376 (4.42), 562 (3.13 sh), 616 (3.28), 672 (3.19 sh), and 751 (2.67 sh); ^1H NMR (90MHz, $CDCl_3$) δ 8.42 (d, 6H, J=10.6, H_4), 8.02 (d, 6H, J=10.6, H_8), 7.09 (s, 6H, H_2), 7.05 (dd, 6H, J=10.6 and J=1.5, H_5), 6.97 (s, 3H, $H_{2',4',6'}$) 6.91 (dd, 6H, J=10.6 and J=1.5, H_7), 6.37 (s, 3H, CH), 1.37 (s, 54H, 6-*t*-Bu), and 1.29 (s, 54H, 3-*t*-Bu).

   8; Blue crystals; mp 296.0 - 298.0°C (dec); UV (CH_2Cl_2) λ_{max} 244 nm (log ε 4.79), 287 (5.18), 304 (5.15), 344 (4.26 sh), 358 (4.31), 375 (4.23), 565 (2.95 sh), 612 (3.08), 747 (2.48 sh); ^1H NMR (90MHz, $CDCl_3$) δ 9.79 (s, 1H, 1'-CHO), 8.51 (d, 4H, J=10.6, H_4), 8.08 (d, 4H, J=10.5, H_8), 7.50 (s, 2H, $H_{2',6'}$), 7.19 (s, 4H, H_2), 7.13 (dd, 4H, J=10.6 and J=1.8, H_5), 7.01 (dd, 4H, J=10.5 and J=1.8, H_7), 6.58 (s, 2H, CH), and 1.39 (s, 74H, 3-*t*-Bu and 6-*t*-Bu).
6. In only acetic acid solution, trace amount of **7** was produced, and tetrasubstituted product (**8**) became a major product and about two molar equivalents of 1,3-di-*t*-butylazulene were recovered, because of the low solubility of **8** in acetic acid.
7. The pK_R values of **4**, **5** and **6** were measured in 50% aqueous MeCN solution prepared by 0.1N aqueous glycine solution, and titrated with 20% aqueous sodium hydroxide solution.

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