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SYNTHESIS OF DICATION SPECIES STABILIZED BY AZULENE RINGS

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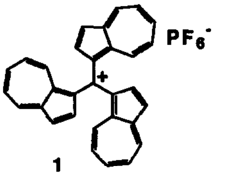
Abstract: *Extraordinary stable dications of tetraazulenyl-m-xylylene and tetraazulenyl-p-xylylene were synthesized, and their* pK_R^+ *values were determined as 11.5 and 11.2, respectively.*

We recently reported the synthesis of azulene analogues of triphenylmethyl cation, i.e., tri(1-azulenyl)methyl cation (**1**), di(1-azulenyl)phenylmethyl cation (**2**), and 1-azulenyldiphenylmethyl cation (**3**), and their derivatives by hydride abstraction of the corresponding hydro derivatives with DDQ in good yields.[1] We also reported that these cation have extraordinary stability with high pK_R^+ values.[1] We now extended the synthetic method to dication species, and two dications stabilized by azulene rings were obtained, which will be reported in this paper.



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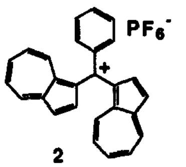

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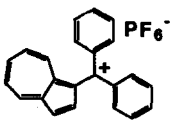

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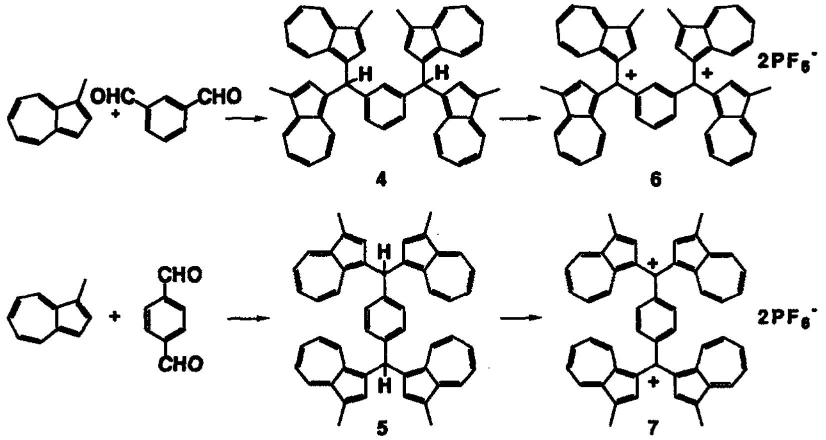
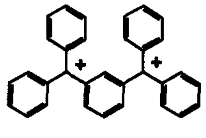
The reaction of four molar equivalents of 1-methylazulene with one equivalent of isophthalaldehyde in acetic acid at room temperature for 12h, afforded 1,3-bis[di(3-methyl-1-azulenyl)methyl]benzene (**4**) and *m*-[di(3-methyl-1-azulenyl)methyl]-benzaldehyde in 88% and 13% yields, respectively. Similarly, the reaction of 1-methylazulene with terephthalaldehyde yielded 1,4-bis[di(3-methyl-1-azulenyl)-methyl]benzene (**5**) and *p*-[di(3-methyl-1-azulenyl)methyl]benzaldehyde in 24% and 25% yields, respectively.[2] The oxidative hydride abstraction of **4** and **5** with DDQ in dichloromethane at room temperature followed by the addition of 60% HPF_6 solution yielded stable dications 1,3-bis[di(3-methyl-1-azulenyl)methylium]benzene bishexa-fluorophosphate (**6**) and 1,4-bis[di(3-methyl-1-azulenyl)methylium]benzene bis-hexafluorophosphate (**7**), in quantitative yields, respectively.[2]

The pK_R^+ values of **6** and **7** were determined spectrophotometrically at 24°C in buffer solutions prepared in 50% aqueous MeCN, and are shown in Table I together with those of the corresponding benzene analogues (**8**, **9**).[3] We could not determine pK_R^+ and pK_R^{++} values separately. The Table shows pK_R of *m*-dication **6** is slightly higher than that of *p*-dication **7**, and both dications are almost 10^{20} times more stable than the corresponding benzene analogues. The reduction potentials of **6** and **7** determined by cyclic voltammetry were also shown in Table I. Both the first reduction potential (E_1) and the second one (E_2) for two cations show small negative values and fairly close each other. Attempted generations of the corresponding diradicals from these dications are now in progress.



4 **6** **5** **7**



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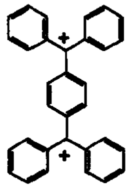

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Table I. pK_R values of **6**, **7**, **8**, and **9** and reduction potentials[a)] of **6** and **7**

	pK_R^{++}	pK_R^{+}	E_1	E_2
6	11.5		-0.35	-0.44
7	11.2		-0.15	-0.21
8	-9.9	-7.9		
9	-10.5	-8.1		

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

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References and Notes

(1) S. Ito, N. Morita, and T. Asao, *Tetrahedron Lett.*, **32**, 773 (1991).

(2) All new compounds were characterized by their IR, UV, ^1H NMR spectral data and elemental analyses and/or mass specroscopy, selected spectral data for **6** and **7** are given below.
6; Black powder; mp >300°C; ES (MeCN) λ_{max} 234 nm (log ε 4.83), 267 (4.67 sh), 284 (4.64), 315 (4.49 sh), 367 (4.47), 399 (4.33 sh), 470 (3.99 sh), 496 (4.04), 645 (4.56 sh), 681 (4.67); ^1H NMR (400MHz, DMSO-d_6, 80°C) δ 8.87 (d, 4H, J=10.0, H_8), 8.24 (dd, 4H, J=10.0, 10.0, H_6), 8.11(dd, 4H, J=10.0, 10.0, H_7), 7.97 (d, 4H, J=10.0, H_4), 7.92 (t, 1H, J=8.0, $H_{5'}$), 7.91 (d, 4H, J=1.0, H_2), 7.85 (dd, 2H, a=9.0, 1.8, $H_{4',6'}$), 7.71 (dd, 4H, J=10.0, 10.0, H_5), 7.49 (t, 1H, J=1.8 $H_{2'}$), 2.67 (d, 12H, J=1.0, Me).
7; Black powder; mp >300°C; ES (MeCN) λ_{max} 230 nm (log ε 4.81), 259 (4.68 sh), 270 (4.64 sh), 284 (4.58 sh), 318 (4.39 sh), 347 (4.24), 377 (4.27 sh), 398 (4.31), 518 (4.18), 598 (4.14 sh), 681 (4.46); ^1H NMR (400MHz, DMSO-d_6, 80°C) δ 8.87 (d, 4H, J=9.8, H_8), 8.26 (dd, 4H, J=9.8, 9.8, H_6), 8.13 (dd, 4H, J=9.8, 9.8, H_7), 8.06 (d, 4H, J=9.8, H_4), 7.95 (d, 4H, J=1.0, H_2), 7.75 (dd, 4H, J=9.8, 9.8, H_5), 7.67 (s, 4H, $H_{2',3',5',6'}$), 2.72 (d, 12H, J=1.0, Me).

(3) H. Hart, T. Sulzberg, and R. R. Rafos, *J. Am. Chem. Soc.*, **85**, 1800 (1963).

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