PERKIN 2

Dication species stabilized by heteroazulenes: synthesis and properties of 1,3- and 1,4-bis[bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyliumyl]-, bis[bis(1,2-dihydro-*N*-methyl-2-oxocyclohepta-[*b*]pyrrol-3-yl)methyliumyl]benzene, and their related dications

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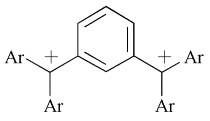
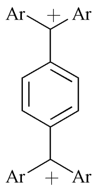
A general synthetic route to a novel type of heteroazulene analogue of exceptionally stable dimethyliumbenzenes (**16a–c**·$\mathbf{2PF_6^-}$ and **17a–c**·$\mathbf{2PF_6^-}$) bearing 1,3-di- and 1,4-dimethylium groups substituted with four 2*H*-cyclohepta-[*b*]furan-2-one **9a**, four 1,2-dihydro-*N*-methylcyclohepta[*b*]pyrrol-2-one **9b**, and two **9a** and two **9b**, is reported. The synthetic method is based on a single and stepwise TFA-catalyzed electrophilic aromatic substitution on the heteroazulenes **9a** and **9b** with isophthalaldehyde and terephthalaldehyde to afford the corresponding 1,3- and 1,4-dimethylbenzene derivatives, followed by oxidative hydrogen abstraction with DDQ, and subsequent exchange of the counter-anion by using aq. HPF_6 solution. In spite of the dicationic nature of **16a–c** and **17a–c**, they exhibited high stability with large $\mathrm{p}K_{\mathrm{R}^+}$ values due to the stabilizing effect of the heteroazulene units; however, we could not determine $\mathrm{p}K_{\mathrm{R}^+}$ and $\mathrm{p}K_{\mathrm{R}^{++}}$ values separately. Thus, the $\mathrm{p}K_{\mathrm{R}^+}$ values correspond to the average of the pH used to form neutralized dications and half-neutralized monocations. The electrochemical reduction of the cations exhibits irreversible waves and low reduction peak potentials upon cyclic voltammetry (CV); the values are discussed on the basis of the comparison with those of the related monocation species.

Introduction

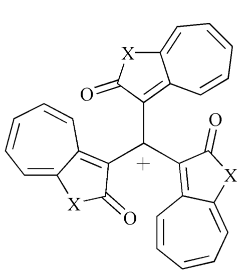
The first aryl-stabilized carbodications, 1,3-bis(diphenylmethyliumyl)benzene **1** and 1,4-bis(diphenylmethyliumyl)benzene **2** in solution were independently reported by Hart *et al.*[1,2] and Volz and Volz de Lecea[3] more than three decades ago. It is remarkable that Asao and his co-workers have reported recently the synthesis and properties of azulene analogues of **1** and **2**, *i.e.*, 1,3-bis[bis(3-methylazulen-1-yl)methyliumyl]benzene **3**, 1,4-bis[bis(3-methylazulen-1-yl)methyliumyl]benzene **4**, and their related derivatives. The dications are extraordinarily stable with high $\mathrm{p}K_{\mathrm{R}^+}$ values (11.5 for **3** and 11.2 for **4**).[4,5] The $\mathrm{p}K_{\mathrm{R}^+}$ values seem to be reasonable because azulene derivatives stabilize cations, *i.e.*, triazulen-1-ylmethyl,[6,12] diazulen-1-yl(phenyl)-methyl,[6,9,11–15] and azulen-1-yl(diphenyl)methyl cations[6,9,11,12,14] and their derivatives, to a great extent as studied extensively by Asao and his co-workers. Much of the motivation for studying the properties of organic molecules stems from manipulation of the primary chemical structure. Strategies for raising or lowering the HOMO and LUMO levels include conjugation length control, as well as the introduction of an electron-donating or -withdrawing group to the parent molecular skeleton.



1: Ar = Ph
3: Ar = 3-Me-azulen-1-yl

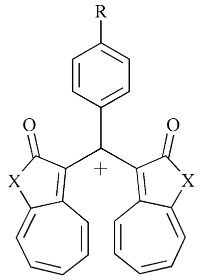


2: Ar = Ph
4: Ar = 3-Me-azulen-1-yl



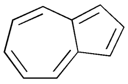
5a-c

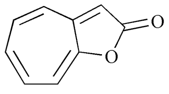
a : X = O; **b** : X = NPh; **c** : X = NMe

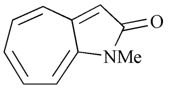


6a-e : X = O **7a-e** : X = NPh
a : R = NMe$_2$; **b** : R =OMe; **c** : R = H
d : R = Cl; **e** : R = CN

Based on this concept, we have studied previously the synthesis and properties of heteroazulene analogues of the triphenylmethyl cation, *i.e.,* tris(2-oxo-2*H*-cyclohepta-[*b*]furan-3-yl)-, tris(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]-pyrrol-3-yl)-, and tris(1,2-dihydro-2-oxo-*N*-methylcyclohepta-[*b*]pyrrol-3-yl)methyl cations, **5a–c**,[16] as well as bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)(phenyl)methyl and bis(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]pyrrol-3-yl)(phenyl)methyl cations **6a**–**c** and **7a**–**c**.[17] The MO calculations (AM1: MOPAC97)[18] predict the heteroazulenes **9a** and **9b** have lower HOMO and LUMO energies as compared with those of azulene **8**. The cations are very stable with $\mathrm{p}K_{\mathrm{R}^+}$ values of 9.7–13.1 for **5a–c**, 12.4–7.9 for **6a**–**c**, 13.5–11.1 for **7a**–**c**, which are considerably







	8	**9a**	**9b**
LUMO (eV)	-0.87	-1.19	-0.88
HOMO (eV)	-8.02	-8.69	-8.25

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Table 1 Results for the preparation of dimethylbenzene derivatives **12a–c** and **13a–c**, and dimethylium salts **16a–c·2PF$_6^-$** and **17a–c·2PF$_6^-$**

			Condensation		Hydride abstraction	
Run	Heteroazulene	Aldehyde	Product	Yield (%)	Product	Yield (%)
1	**9a**[a]	**10**	**12a**	88	**16a·2PF$_6^-$**	91
2	**9b**[a]	**10**	**12b**	100	**16b·2PF$_6^-$**	70
3	**9a**[a]	**11**	**13a**	83	**17a·2PF$_6^-$**	96
4	**9b**[a]	**11**	**13b**	100	**17b·2PF$_6^-$**	69
5	**9a**[b]	**10**	**14**	74	—	—
			12a	13	—	—
6	**9b**	**14**	**12c**	98	**16c·2PF$_6^-$**	94
7	**9a**[b]	**11**	**15**	81	—	—
			13a	9	—	—
8	**9b**	**15**	**13c**	100	**17c·2PF$_6^-$**	75

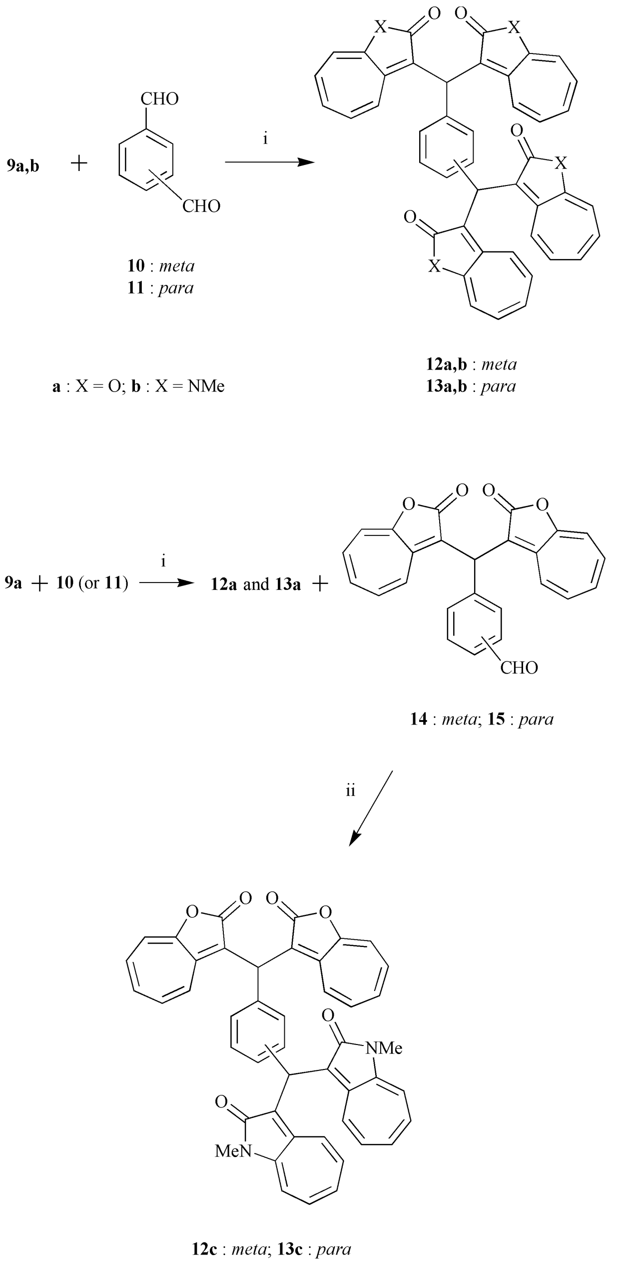
[a] Four equiv. heteroazulene. [b] Two equiv. heteroazulene.

larger than that of the triphenylmethyl cation (pK_{R^+} = −6.44)[19] and similar to that of the triazulen-1-ylmethyl cation (pK_{R^+} = 11.3)[6–12] Furthermore, the electrochemical reduction of **5a–c** exhibited reversible waves and low reduction potentials, $E1_{red}$ and $E2_{red}$, upon cyclic voltammetry (CV), respectively, and they are more positive as compared with those of the triazulen-1-ylmethyl cation.[6] Thus, heteroazulenes, such as **9a** and **9b**, are suggested to stabilize not only cations but also radical species and anions. Thus, in connection with our previous study of heteroazulene-substituted methylium ions,[16,18] we studied an efficient synthesis of heteroazulene analogues of dications **1**–**4**, 1,3-bis[bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)-methyliumyl]- and 1,3-bis[bis(1,2-dihydro-2-oxo-*N*-methyl-cyclohepta[*b*]pyrrol-3-yl)methyliumyl]benzenes **16a** and **16b**, and their 1,4-isomers **17a** and **17b**, as well as 1-[bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyliumyl]-3-[bis(1,2-dihydro-2-oxo-*N*-methylcyclohepta[*b*]pyrrol-3-yl)methyliumyl]benzene **16c** and its 1,4-analogue **17c**. The dications exhibited quite large pK_{R^+} values and low reduction potentials. We report herein the results in detail.

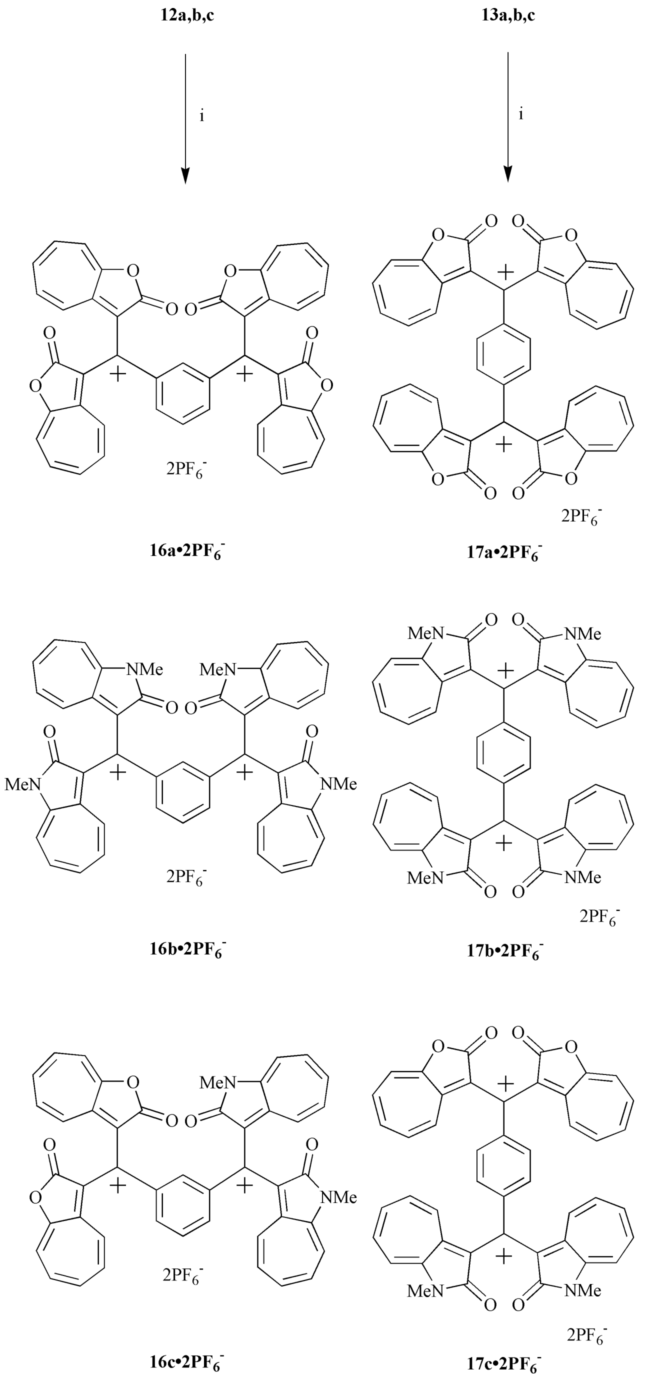
Results and discussion

Synthesis

The reactions of four molar equivalent amounts of 2*H*-cyclohepta[*b*]furan-2-one **9a**[20] and 1,2-dihydro-*N*-methylcyclohepta[*b*]pyrrol-2-one **9b**[21,22] with one equivalent amount of isophthalaldehyde **10** in CH_2Cl_2–TFA (10 : 1) at rt for 48 h afforded 1,3-bis[bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyl]-benzene **12a** and the corresponding pyrrole derivative **12b** in moderate to good yields (Scheme 1; Table 1, Runs 1 and 2). Similarly, the reactions of compounds **9a** and **9b** with terephthalaldehyde **11** yielded 1,4-bis[bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyl]benzene **13a** and the corresponding pyrrole derivative **13b** in similar yields (Table 1, Runs 3 and 4). On the other hand, controlled reactions of two molar equivalent amounts of **9a** with one molar equivalent amount of isophthalaldehyde **10** and terephthalaldehyde **11** in CH_2Cl_2–TFA (10 : 1) at rt afforded the desired 3-[bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyl]benzaldehyde **14** and 4-[bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyl]benzaldehyde **15**, in addition to small amounts of **12a** and **13a**, respectively (Table 1, Runs 5 and 7). The aldehydes **14** and **15** reacted with heteroazulene **9b** in a similar fashion to afford 1-[bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyl]-3-[bis(1,2-dihydro-2-oxo-*N*-methylcyclohepta[*b*]pyrrol-3-yl)methyl]benzene **12c** and the corresponding 1,4-disubstituted isomer **13c** in excellent yields, respectively (Table 1, Runs 6 and 8). The compounds **12a–c** and **13a–c** formed powdery, orange or yellow crystals, the structures of which were assigned on the basis of their IR, ^{1}H and ^{13}C NMR spectral data, as well as elemental analyses and mass spectral data. The oxidative hydrogen abstraction of **12a–c** and **13a–c** with DDQ in CH_2Cl_2 at rt for 1 h, followed by addition of aqueous 60% HPF_6 solution afforded stable dicationic salts **16a–c·2PF$_6^-$** and **17a–c·2PF$_6^-$** in the yields listed also in Table 1 (Scheme 2).



Scheme 1 *Reagents and conditions*: i CH_2Cl_2–TFA (10 : 1), rt; ii CH_2Cl_2–TFA (10 : 1), **9b**, rt.



Scheme 2 *Reagents and conditions*: i (a) DDQ in CH_2Cl_2 (b) 60% aq. HPF_6.

Spectroscopic properties

Dications **16a–c** and **17a–c** were fully characterized by the spectral data, as shown in the Experimental section. The salts **16a–c·2PF$_6^-$** and **17a–c·2PF$_6^-$** were easily crystallized to give complexes containing CH_2Cl_2 or HPF_6 molecules, respectively, in the crystal lattice. Thus, some of the salts did not give satisfactory analytical data; however, the mass spectra of the salts **16a–c·2PF$_6^-$** and **17a–c·2PF$_6^-$** ionized by FAB exhibited the correct ion peaks, $M^+ - 2PF_6$, which are indicative of the dicationic structure of these compounds. The characteristic bands for the counter anion PF_6^- are observed at 836–843 and 837–843 cm^{-1} in the IR spectra of **16a–c·2PF$_6^-$** and **17a–c·2PF$_6^-$**, respectively. These features also support the dicationic nature of the compounds. The UV–vis spectra of cations **16a–c** and **17a–c** in CH_3CN are shown in Figs. 1 and 2, respectively. The longest wavelength absorption maxima of the series of dications **16a** (610 nm), **16b** (630 nm), and **16c** (612 nm), and the series of **17a** (612 nm), **17b** (639 nm), and **17c** (620 nm) resemble each other. The longest wavelength absorption maxima of dications **16a**,**c** and **17a**,**c** are even shorter than those of the related monocations **6b**,**c** (621 nm), while those of **16b** and **17b** are shorter than those of similar phenyl-substituted monocations **7b–e** (652 nm). Thus, the UV–vis spectra of dications **16a–c** and **17a–c** do not suggest the presence of appreciable conjugation among the methylium units. This feature seems to be reasonable based on our previous study considering the longest wavelength absorption maxima of **6b–e** (621 nm) and **7b–e** (652 nm) as well as on the calculations of the stable conformations of **6a–c** and **7a–c** with reference to the dihedral angles, θ_1, θ_2, and θ_3, which express deviation of the plane of the phenyl groups and heteroazulenes from the reference plane (the plane which is defined by the three aromatic *ipso* carbons, Fig. 3).[17]

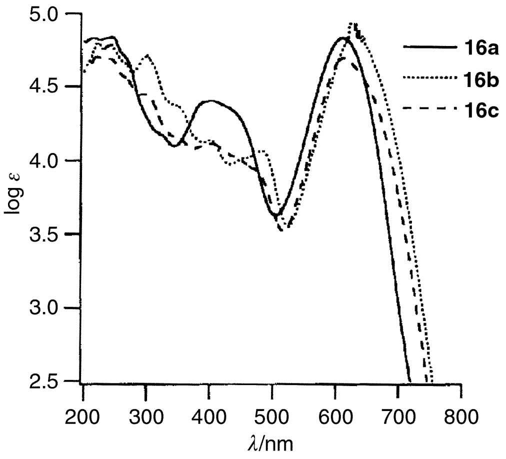


Fig. 1 UV–vis spectra of cations **16a–c** in CH_3CN.

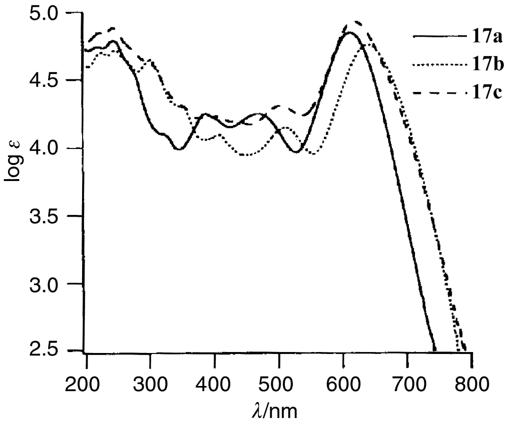


Fig. 2 UV–vis spectra of cations **17a–c** in CH_3CN.

The signals of the methine protons of methane derivatives **12a–c** and **13a–c** disappeared in the ^1H NMR spectra of **16a–c·2PF$_6^-$** and **17a–c·2PF$_4^-$**. Thus, the ^1H NMR spectra also support the dicationic structures of these compounds. Proton signals on the seven-membered rings of **16a–c·2PF$_6^-$** and **17a–c·2PF$_6^-$** appear as broad signals. Attempted measurement of the ^1H NMR spectra of **16b·2PF$_6^-$** and **17b·2PF$_6^-$** at temperatures ranging from rt to 70 °C (in CD_3CN) exhibited no appreciable change in the broad signals. Thus, slow conformational change of the heteroazulene moieties of these cations occurs in the ^1H NMR time scale at these temperatures.

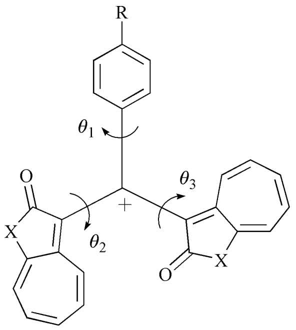
Stability of the dications: pK_{R^+} values and reduction potentials

The affinity of the carbocation toward hydroxide ions, expressed by the pK_{R^+} value, is the most common criterion of carbocation stability.[23] The pK_{R^+} values of the dications **16a–c** and **17a–c** were determined spectrophotometrically in buffer

Table 2 pK_{R^+} values and reduction potentials[a] of dications **16a–c**,[b] and **17a–c**[b]

Compd.	pK_{R^+}	$E1_{\mathrm{red}}$	$E2_{\mathrm{red}}$	$E3_{\mathrm{red}}$	$E4_{\mathrm{red}}$
16a	9.0	−0.33		−1.05	
16b	12.1	−0.60		−1.37	
16c	12.7	−0.34	−0.62	−0.96	−1.37
17a	9.3	−0.04	−0.34	−1.06	−1.34
17b	11.5	−0.30	−0.50	−1.10	−1.38
17c	12.0	−0.19	−0.57	−0.95	−1.32
6c	9.3	(−0.31)	(−1.03)		
7c	12.0	(−0.53)	(−1.29)		
3[c]	11.5 ± 0.2				
4[c]	11.2 ± 0.1				

[a] Peak potentials V *vs.* Ag/Ag$^+$. Reversible processes are shown in parentheses. [b] **16a–c·2PF$_6^-$** and **17a–c·2PF$_6^-$** were used for the measurement. [c] Ref. 4 and 5.

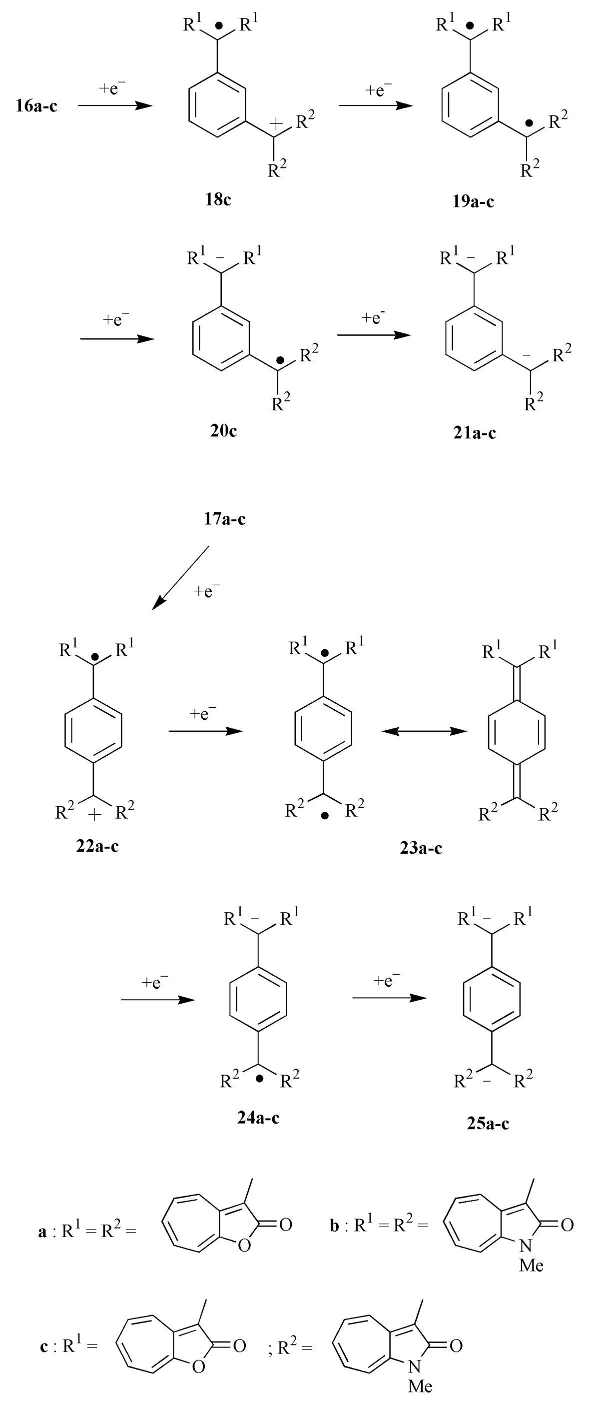


6a-e: X = O
7a-e: X = NPh
a : R = NMe$_2$; **b**: R = OMe; **c** : R = H
d : R = Cl; **e** : R = CN

Fig. 3

solutions prepared in 20% aqueous CH$_3$CN and summarized in Table 2 along with those of reference compounds **3**, **4**, **6c**, and **7c**.[4,5,17] We could not determine pK_{R^+} and p$K_{\mathrm{R}^{++}}$ values separately. The two methylium units of the dications **16a–c** and **17a–c** were neutralized simultaneously by using buffer solutions of pH ranging from 8.3 to 14.0. Thus, the pK_{R^+} values correspond to the average of the pH used to form neutralized dications and half-neutralized monocations. The neutralization of the dications **16a–c** and **17a–c** is not completely reversible. This feature may be ascribed to the instability of the neutralized products under the conditions of the pK_{R^+} measurement. Immediate acidification of an alkaline solution of **16a–c** and **17a–c** with TFA regenerated the absorption maxima of the cations in the visible regions to 85–90%. As expected, the heteroazulenes effectively stabilize the dications, and the pK_{R^+} values of **16a–c** and **17a–c** are extremely high as compared with those of dications **1** and **2** (**1**: p$K_{\mathrm{R}^{++}}$ −9.9 and pK_{R^+} −7.9; **2**: p$K_{\mathrm{R}^{++}}$ −10.5 and pK_{R^+} −8.1).[2,3] Although the pK_{R^+} values of **16a** and **17a** are similar to that of monocation **6c**, the values of **16b**,**c** and **17b**,**c** are similar to that of **7c**. The pyrrole substituent **9b** stabilizes dications **16b**,**c** and **17b**,**c** slightly more as compared with azulene analogues **3** and **4** (Table 2). The relatively high stability of the dications **16b**,**c** and **17b**,**c** as compared with those of **16a** and **17a** is attributable to the low electronegativity of the nitrogen atom as compared with the oxygen atom in the five-membered ring of the heteroazulene unit.

The reduction potentials of dications **16a–c** and **17a–c** were determined by cyclic voltammetry (CV) in CH$_3$CN. The reduction waves of both series of **16a–c** and **17a–c** were irreversible under the conditions of CV measurements, and thus, the peak potentials are summarized in Table 2 together with those of the reference monocations **6c** and **7c**.[17] The reduction behavior of dications is affected by the heteroazulene units and their substitution patterns. The reduction of a series of dications **16a–c** is expected to give a non-Kekulé-type electronic structure upon reduction. Actually, dication **16c**, which has two different methylium units, exhibited four reduction potentials, $E1_{\mathrm{red}}$–$E4_{\mathrm{red}}$ (Table 2 and Scheme 3). The values of $E1_{\mathrm{red}}$ and $E2_{\mathrm{red}}$ are similar to those of $E1_{\mathrm{red}}$ of related monocations **6c** and **7c**, respectively, and the values of $E3_{\mathrm{red}}$ and $E4_{\mathrm{red}}$ are close to the values of $E2_{\mathrm{red}}$ of monocations **6c** and **7c**, respectively. Thus, the values of $E1_{\mathrm{red}}$–$E4_{\mathrm{red}}$ for **16c** could correspond to those obtained in the process giving **18c**, **19c**, **20c**, and **21c**, respectively. On the other hand, dications **16a** and **16b**, both of which have the same two methylium units, exhibited two-step reduction peaks at −0.33 and −1.05, and −0.60 and −1.37; the former values are very similar to those of $E1_{\mathrm{red}}$ and $E2_{\mathrm{red}}$ for monocation **6c**, as well as $E1_{\mathrm{red}}$ and $E3_{\mathrm{red}}$ for **16c**, respectively. These last two values for **16b**, are similar to those of $E1_{\mathrm{red}}$ and $E2_{\mathrm{red}}$ for monocation **7c**, as well as $E2_{\mathrm{red}}$ and $E4_{\mathrm{red}}$ for dication **16c**, respectively. Thus, the reduction process of **16a**,**b**



Scheme 3

is rationalized to proceed *via* two steps, two-electron reductions affording diradical species **19a**,**b** and dianions **21a**,**b**, respectively (Scheme 3). Furthermore, this feature indicates that **16a**–**c** give non-Kekulé-type electronic structures upon reduction and reflects the absence of conjugation between the two methylium units. On the other hand, the CV of the series **17a**–**c** exhibited four reduction potentials, and they are suggestive of four steps, four-electron reduction of **17a**–**c** giving **22a**–**c**, **23a**–**c**, **24a**–**c**, and **25a**–**c**, respectively (Scheme 3), as in the case of dication **16c**. The less negative reduction potentials, $E1_{red}$ and $E2_{red}$, for **17a**–**c**, as compared with those of $E1_{red}$ and $E2_{red}$ for **16a**–**c**, as well as $E1_{red}$ for **6c** and **7c**, respectively, are attributable to the destabilization arising from the through-bond electronic repulsion of the two methylium units in **17a**–**c**. The reduction potentials, $E3_{red}$ and $E4_{red}$, for **17a**–**c** are similar, and also similar to those of dication **16c**. This feature may be ascribed to the contribution of a common closed-shell structure for **23a**–**c**.

In summary, efficient synthesis of two series of fairly stable heteroazulene-substituted dications **16a**–**c** and **17a**–**c** has been accomplished. Their stabilities were determined by their pK_{R^+} values and the reduction potentials measured by CV. The pK_{R^+} values of dications **16a** and **17a** were shown to be smaller than those of azulene analogues **3** and **4**, while the values of **16b**,**c** and **17b**,**c** are larger than those of **3** and **4**. Further studies concerning the synthesis and properties of stable heteroazulene-substituted polycations are underway.

Experimental

IR spectra were recorded on a Horiba FT-710 spectrometer. Mass spectra and high-resolution mass spectra were run on JMS-AUTOMASS 150 and JMS-SX102A spectrometers. Unless otherwise specified, ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a JNM-lambda 500 spectrometer using $CDCl_3$ as the solvent, and the chemical shifts are given relative to internal $SiMe_4$ standard: *J*-values are given in Hz. The abbreviations, Fr and Py, in the ^{1}NMR data denote 2-oxo-2*H*-cyclohepta[*b*]furan-3-yl and 1,2-dihydro-*N*-methyl-2-oxo-cyclohepta[*b*]pyrrol-3-yl moieties, respectively. Mps were recorded on a Yamato MP-21 apparatus and are uncorrected. The heteroazulenes, 2*H*-cyclohepta[*b*]furan-2-one **9a**[20] and 1,2-dihydro-*N*-phenylcyclohepta[*b*]pyrrol-2-one **9b**[21,22] were prepared as described previously.

Preparation of 1,3- and 1,4-bis[bis(2-oxo-2*H*-cyclohepta[*b*]-furan-3-yl)methyl]benzenes 12a and 13a

A solution of **9a** (4 mmol) and **10** or **11** (1 mmol) in a mixture of CH_2Cl_2 (10 cm^3) and TFA (2 cm^3) was stirred at rt for 48 h. After the reaction was complete, the mixture was poured into aqueous $NaHCO_3$ solution. The mixture was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified through column chromatography on Al_2O_3 by using hexane–ethyl acetate (1 : 1) as the eluent to give the products **12a** or **13a**. The results are summarized in Table 1.

For **12a**. Orange powder; mp 280–282 °C (from CH_2Cl_2–EtOH); δ_H (500 MHz) 5.61 (2H, s, CH), 6.76–6.80 (4H, m, H-6), 6.90–6.96 (12H, m, H-5, 7, 8), 7.03 (1H, s, Ph-2), 7.15 (2H, d, *J* 7.8, Ph-4, 6), 7.30 (1H, t, *J* 7.8, Ph-5), 7.40 (4H, d, *J* 11.7, H-4); δ_C (125.7 MHz) 35.2, 108.8, 114.0, 126.4, 126.8, 128.1, 129.3, 130.9, 132.2, 134.8, 137.7, 148.6, 157.5, 169.2; ν_{max} ($CHCl_3$)/cm^{-1} 1735, 1268; *m*/*z* (rel. int.) 682 (M$^+$, 100%) (Found: C, 75.8; H, 3.8. $C_{44}H_{26}O_8\cdot\frac{2}{3}H_2O$ requires C, 76.07; H, 3.97%).

For **13a**. Yellow powder; mp 304–305 °C (from CH_2Cl_2–EtOH); δ_H (500 MHz) 5.69 (2H, s, CH), 6.79–6.84 (4H, m, H-6), 6.93–7.01 (12H, m, H-5, 7, 8), 7.18 (4H, s, Ph), 7.47 (4H, d, *J* 11.3, H-4); δ_C (125.7 MHz; DMSO-d$_6$) 34.7, 108.0, 114.1, 127.0, 128.0, 131.1, 132.9, 135.1, 136.1, 147.8, 156.6, 168.0; ν_{max} ($CHCl_3$)/cm^{-1} 1745, 1271; *m*/*z* (rel. int.) 682 (M$^+$, 100%) (Found: C, 59.9; H, 2.7. $C_{44}H_{26}O_8\cdot 2CH_2Cl_2$ requires C, 59.96; H, 3.06%).

Preparation of 1,3- and 1,4-bis[bis(1,2-dihydro-2-oxo-*N*-methylcyclohepta[*b*]pyrrol-3-yl)methyl]benzenes 12b and 13b

A solution of **9b** (4 mmol) and **10** or **11** (1 mmol) in a mixture of CH_2Cl_2 (10 cm^3) and TFA (2 cm^3) was stirred at rt for 48 h. After the reaction was complete, the mixture was poured into aqueous $NaHCO_3$ solution. The mixture was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified through column chromatography on Al_2O_3 by using hexane–ethyl acetate (1 : 1) as the eluent to give the products **12b** or **13b**. The results are summarized in Table 1.

For **12b**. Yellow powder; mp 302–304 °C (from $CHCl_3$); δ_H (500 MHz) 3.43 (12H, s, Me), 6.03 (2H, s, CH), 6.75 (4H, d, *J* 8.6, H-8), 6.76 (4H, dd, *J* 10.2, 8.5, H-6), 6.83 (4H, dd, *J* 11.0, 8.5, H-5), 6.96 (4H, dd, *J* 10.2, 8.6, H-7), 7.04 (1H, s, Ph-2), 7.08 (2H, d, *J* 7.6, Ph-4, 6), 7.18 (1H, t, *J* 7.6, Ph-5), 7.71 (4H, d, *J* 11.0, H-4); δ_C (125.7 MHz) 26.4, 35.9, 110.9, 114.3, 125.9, 128.1, 128.4, 128.7, 128.8, 129.7, 130.2, 140.0, 141.0, 144.8, 168.7; ν_{max} ($CHCl_3$)/cm^{-1} 1663; *m*/*z* (FAB) 735 (M$^+$ + 1) (Found: C, 77.7 H, 4.7; N, 7.5. $C_{48}H_{38}N_4O_4\cdot\frac{1}{2}H_2O$ requires C, 77.50; H, 5.28; N, 7.53%).

For **13b**. Yellow powder; mp >330 °C (from TFA–EtOH); δ_H (500 MHz) 3.52 (12H, s, Me), 6.13 (2H, s, CH), 6.81 (4H, d, *J* 8.7, H-8), 6.82 (4H, dd, *J* 8.7, 8.2, H-6), 6.94–7.01 (8H, m, H-5, 7), 7.10 (4H, s, Ph-2, 3, 5, 6), 7.80 (4H, d, *J* 11.2, H-4); δ_C (125.7 MHz) 26.5, 35.4, 111.2, 114.4, 128.0, 128.8, 128.8, 129.9, 130.4, 137.6, 141.0, 144.8, 168.8; ν_{max} ($CHCl_3$)/cm^{-1} 1663; *m*/*z* (FAB) 735 (M$^+$ + 1) (Found: C, 72.0; H, 5.1; N, 6.5. $C_{48}H_{38}N_4O_4\cdot CH_2Cl_2$ requires C, 71.79; H, 4.92; N, 6.83%).

Preparation of 3- and 4-[bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)-methyl]benzaldehydes 14 and 15

A solution of **9** (2 mmol) and **10** or **11** (1 mmol) in a mixture of CH_2Cl_2 (20 cm^3) and TFA (2 cm^3) was stirred at rt for 1 h. The reaction mixture was poured into aqueous $NaHCO_3$ solution. The mixture was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified through column chromatography on Al_2O_3 by using hexane–ethyl acetate (1 : 1) as the eluent to give the products **14** and **12a**, or **15** and **13a**. The results are summarized in Table 1.

For **14**. Yellow powder; mp 127–128 °C (from CH_2Cl_2–EtOH); δ_H (500 MHz) 5.76 (1H, s, CH), 6.83–6.88 (2H, m, H-6), 6.99–7.04 (6H, m, H-5, 7, 8), 7.51 (2H, d, *J* 11.3, H-4), 7.51 (2H, d, *J* 4.8, Ph-4,6), 7.72 (1H, s, Ph-2), 7.81 (1H, t, *J* 4.8, Ph-5), 9.97 (1H, s, CHO); δ_C (125.7 MHz) 34.7, 108.1, 114.6, 128.0, 128.5, 128.7, 129.5, 131.3, 132.6, 133.7, 135.2, 136.9, 138.3, 148.9, 157.7, 169.4, 192.2; ν_{max} ($CHCl_3$)/cm^{-1} 1742, 1707; *m*/*z* (FAB) 408 (M$^+$) (Found: C, 74.6; H, 3.8. $C_{26}H_{16}O_5\cdot\frac{1}{2}H_2O$ requires C, 74.81; H, 4.10%).

For **15**. Yellow powder; mp 191–192 °C (from AcOEt); δ_H (500 MHz) 5.75 (1H, s, CH), 6.83–6.89 (2H, m, H-6), 6.99–7.05 (6H, m, H-5, 7, 8), 7.40 (2H, d, *J* 8.2, Ph-2, 6), 7.50 (2H, d, *J* 11.4, H-4), 7.95 (2H, d, *J* 8.2, Ph-3, 5); δ_C (125.7 MHz) 35.2, 108.1, 114.6, 128.1, 128.3, 130.2, 131.3, 132.6, 135.2, 144.2, 148.8, 157.7, 169.4, 191.7; ν_{max} ($CHCl_3$)/cm^{-1} 1746, 1705; *m*/*z* (FAB) 408 (M$^+$) (Found: C, 76.1; H, 3.6. $C_{26}H_{16}O_5$ requires C, 76.46; H, 3.95%).

Preparation of 1-[bis(1,2-dihydro-2-oxo-*N*-methylcyclohepta-[*b*]pyrrol-3-yl)methyl]-3-[bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyl]benzene 12c and its 1,4-analogue 13c

A solution of **14** or **15** (1 mmol) and **9b** (2 mmol) in a mixture of CH_2Cl_2 (10 cm^3) and TFA (2 cm^3) was stirred at rt for 6 h. After the reaction was complete, the mixture was poured into aqueous $NaHCO_3$ solution. The mixture was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified through column chromatography on Al_2O_3 by using hexane–ethyl acetate (1 : 1) as the eluent to give the product **12c** or **13c**. The results are summarized in Table 1.

For **12c**. Yellow powder; mp 234–235 °C (from $CHCl_3$–AcOEt); δ_H (500 MHz) 3.46 (6H, s, NMe), 5.57 (1H, s, FrCH), 6.08 (1H, s, PyCH), 6.72–6.76 (2H, m, Fr-6), 6.77 (2H, d, *J* 9.6, Fr-8), 6.79 (2H, d, *J* 9.5, Py-8), 6.84–6.92 (8H, m, Fr-5, 7, Py-5, 6), 6.98 (2H, dd, *J* 10.0, 9.8, Py-7), 7.03 (1H, s, Ph-2), 7.09 (1H, d, *J* 7.6, Ph-4), 7.14 (1H, d, *J* 7.8, Ph-6), 7.24 (1H, dd, *J* 7.8, 7.6, Ph-5), 7.34 (2H, d, *J* 11.6, Fr-4), 7.76 (2H, d, *J* 11.4, Py-4); δ_C (125.7 MHz) 26.4, 35.2, 35.7, 109.0, 111.2, 113.7, 114.1, 125.5, 126.8, 127.5, 128.3, 128.5, 128.8, 128.9, 130.0, 130.5, 130.8, 131.9, 134.5, 137.2, 140.5, 141.0, 144.7, 148.5, 157.6, 168.6, 169.3; ν_{max} ($CHCl_3$)/cm^{-1} 1744, 1670, 1268; *m*/*z* (FAB) 709 ($M^+ + 1$) (Found: C, 77.2; H, 4.1; N, 3.9. $C_{46}H_{32}N_2O_6\cdot\frac{1}{2}H_2O$ requires C, 76.97; H, 4.63; N, 3.9%).

For **13c**. Yellow powder; mp 291–292 °C (from $CHCl_3$–AcOEt); δ_H (500 MHz) 3.46 (6H, s, NMe), 5.57 (1H, s, FrCH), 6.08 (1H, s, PyCH), 6.72–6.76 (2H, m, Fr-6), 6.77 (2H, d, *J* 9.6, Fr-8), 6.79 (2H, d, *J* 9.5, Py-8), 6.84–6.92 (8H, m, Fr-5, 7, Py-5, 6), 6.98 (2H, dd, *J* 10.0, 9.8, Py-7), 7.03 (1H, s, Ph-2), 7.09 (1H, d, *J* 7.6, Ph-4), 7.14 (1H, d, *J* 7.8, Ph-6), 7.24 (1H, dd, *J* 7.8, 7.6, Ph-5), 7.34 (2H, d, *J* 11.6, Fr-4), 7.76 (2H, d, *J* 11.4, Py-4); δ_C (125.7 MHz) 26.4, 35.2, 35.7, 109.0, 111.2, 113.7, 114.1, 125.5, 126.8, 127.5, 128.3, 128.5, 128.8, 128.9, 130.0, 130.5, 130.8, 131.9, 134.5, 137.2, 140.5, 141.0, 144.7, 148.5, 157.6, 168.6, 169.3; ν_{max} ($CHCl_3$)/cm^{-1} 1745, 1675, 1268; *m*/*z* (FAB) 709 ($M^+ + 1$) (Found: C, 70.0; H, 3.8; N, 3.4. $C_{46}H_{32}N_2O_6\cdot\frac{2}{3}CHCl_3$ requires C, 70.19; H, 4.31; N, 3.67%).

General synthetic procedure for the 1,3- and 1,4-bis[bis(heteroazulene-substituted)methyliumyl]benzene bis(hexafluorophosphates) 16a–c·2PF$^-$ and 17a–c·2PF$_6^-$

To a stirred solution of bis[bis(heteroazulene-substituted)-methylbenzenes **12a–c** or **13a–c** (0.2 mol) in CH_2Cl_2 (10 cm^3) was added DDQ (140 mg, 0.6 mmol) and the mixture was stirred at rt for 1 h until the reaction was complete. To the reaction mixture was added 60% aqueous HPF_6 solution (2 cm^3) and the resulting mixture was filtered. The filtrate was extracted with CH_2Cl_2 and the extract was dried over Na_2SO_4 and concentrated. The resulting residue was dissolved in CH_2Cl_2 and ether was added to the solution. The precipitated crystals were collected by filtration, washed with ether to give the salts **16a·2PF$_6^-$**, **16b·2PF$_6^-$**, and **16c·2PF$_6^-$** or **17a·2PF$_6^-$**, **17b·2PF$_6^-$**, and **17c·2PF$_6^-$**.

For **16a·2PF$_6^-$**. Dark-brown powder; mp 209–210 °C (from CH_2Cl_2–Et_2O); δ_H (500 MHz; CD_3CN) 7.53–8.43 (24H, br m); ν_{max} (KBr)/cm^{-1} 1749, 1261, 839; *m*/*z* (FAB) 681 ($M^+ + 1 - 2PF_6$) (Found: $M + 1 - 2PF_6$, 681.1589. $C_{44}H_{24}O_8P_2F_{12}$ requires $M + 1 - 2PF_6$ 681.1530) (Found: C, 49.7; H, 2.1. $C_{44}H_{24}O_8P_2F_{12}\cdot\frac{3}{2}CH_2Cl_2$ requires C, 49.77; H, 2.48%).

For **16b·2PF$_6^-$**. Dark-brown powder; mp 235–236 °C (from CH_2Cl_2–Et_2O); δ_H (500 MHz; CD_3CN) 3.53 (12H, br m, Me), 7.58–7.71 (2H, m), 7.79–7.98 (18H, br m), 8.15 (4H, t, *J* 10.3); ν_{max} (KBr)/cm^{-1} 1685, 839; *m*/*z* (FAB) 732 ($M^+ - 2PF_6$) (Found: $M^+ - 2PF_6$, 732.2672. $C_{48}H_{36}N_4O_4P_2F_{12}$ requires $M - 2PF_6$ 732.2760) (Found: C, 51.6; H, 3.0; N, 5.0. $C_{48}H_{36}N_4O_4P_2F_{12}\cdot\frac{3}{2}CH_2Cl_2$ requires C, 51.70; H, 3.42; N, 4.87%).

For **16c·2PF$_6^-$**. Dark-brown powder; mp 204–205 °C (from acetone–Et_2O); δ_H (500 MHz; CD_3CN) 3.39, 3.48, 3.51, 3.57 (6H, br s, Me), 7.71 (2H, t, *J* 7.9), 7.78–8.07 (12H, br m), 8.12–8.33 (8H, br m), 8.38 (2H, t, *J* 10.1); ν_{max} (KBr)/cm^{-1} 1752, 1685, 1262, 843; *m*/z (FAB) 706 ($M^+ - 2PF_6$) (Found: $M^+ - 2PF_6$, 706.2126. $C_{46}H_{30}N_2O_6P_2F_{12}$ requires $M - 2PF_6$, 706.2094) (Found: C, 53.5; H, 2.6; N, 3.2. $C_{46}H_{30}N_2O_6P_2F_{12}\cdot\frac{1}{2}CH_2Cl_2$ requires C, 53.75; H, 3.01; N, 2.70%).

For **17a·2PF$_6^-$**. Dark-brown powder; mp >330 °C (from CH_2Cl_2–Et_2O); δ_H (500 MHz; CD_3CN) 7.88–7.90 (4H, br m), 7.91 (4H, s, Ph), 8.18–8.22 (4H, br m), 8.36–8.39 (4H, br m), 8.43–8.49 (8H, br m); ν_{max} (KBr)/cm^{-1} 1763, 1262, 839; *m*/*z* (FAB) 681 ($M^+ + 1 - 2PF_6$) (Found: $M^+ + 1 - 2PF_6$, 681.1605. $C_{44}H_{24}O_8P_2F_{12}$ requires $M + 1 - 2PF_6$ 681.1530) (Found: C, 47.2; H, 2.0. $C_{46}H_{32}N_2O_6P_2F_{12}\cdot HPF_6$ requires C, 47.33; H, 2.26%).

For **17b·2PF$_6^-$**. Dark-brown powder; mp >330 °C (from CH_2Cl_2–Et_2O); δ_H (500 MHz; CD_3CN) 3.59 (12H, s, Me), 7.67 (4H, br s), 7.82–7.96 (12H, br m), 7.96–8.05 (4H, br m), 8.15–8.22 (4H, br m); ν_{max} (KBr)/cm^{-1} 1685, 837; *m*/*z* (FAB) 732 ($M^+ - 2PF_6$) (Found: $M^+ - 2PF_6$, 732.2650. $C_{48}H_{36}N_4O_4P_2F_{12}$ requires $M - 2PF_6$, 732.2760) (Found: C, 47.0; H, 3.0; N, 4.5. $C_{48}H_{36}N_4O_4P_2F_{12}\cdot\frac{3}{2}HPF_6$ requires C, 46.43; H, 3.04; N, 4.51%).

For **17c·2PF$_6^-$**. Dark-brown powder; mp 196–198 °C (from CH_3CN–Et_2O); δ_H (500 MHz; CD_3CN) 3.55–3.62 (6H, br m), 7.65–8.45 (24H, br m); ν_{max} (KBr)/cm^{-1} 1735, 1685, 1262, 843; *m*/*z* (FAB) 706 ($M^+ - 2PF_6$) (Found: $M^+ - 2PF_6$, 706.2128. $C_{46}H_{30}N_2O_6P_2F_{12}$ requires $M - 2PF_6$ 706.2094) (Found: C, 54.5; H, 2.7; N, 3.0. $C_{46}H_{30}N_2O_6P_2F_{12}$ requires C, 55.43; H, 3.03; N, 2.81%).

Determination of pK_{R^+} values of dications 16a–c and 17a–c

Buffer solutions of slightly different acidities were prepared by mixing aqueous solutions of KH_2PO_4 (0.1 M) and NaOH (0.1 M) (for pH 6.0–8.0), $Na_2B_4O_7$ (0.025 M) and HCl (0.1 M) (for pH 8.2–9.0), $Na_2B_4O_7$ (0.025 M) and NaOH (0.1 M) (for 9.2–10.8), Na_2HPO_4 (0.05 M) and NaOH (0.1 M) (for pH 11.0–12.0), and KCl (0.2 M) and NaOH (0.1 M) (for pH 12.0–14.0) in various portions. For the preparation of sample solutions, 1 cm^3 portions of the stock solution, prepared by dissolving 3–5 mg of cation **16a–c·PF$_6^-$** in MeCN (20 cm^3), were diluted to 10 cm^3 with the buffer solution (8 cm^3) and MeCN (1 cm^3). The UV–vis spectrum was recorded for each cation **16a–c** and **17a–c** in 10 different buffer solutions. Immediately after recording the spectrum, the pH of each solution was determined on a pH meter calibrated with standard buffers. The observed absorbance at the specific absorption wavelengths (609 nm for **16a**; 622 nm for **16b**; 622 nm for **16c**, 609 nm for **17a**, 624 nm for **17b**, 620 nm for **17c**) of each cation was plotted against pH to give a classical titration curve, whose midpoint was taken as the pK_{R^+} value. The results are summarized in Table 2.

Cyclic voltammetry of dications 16a–c and 17a–c

The reduction potentials of **16a–c** and **17a–c** were determined by means of a CV-27 voltammetry controller (BAS Co). A three-electrode cell was used consisting of Pt working and counter electrodes and a reference $Ag/AgNO_3$ electrode. Nitrogen was bubbled through an acetonitrile solution (4 cm^3) of each compound (0.5 mmol dm^{-3}) and Bu_4NClO_4 (0.1 mol dm^{-3}) to deaerate it. The measurements were made at a scan rate of 0.1 V s^{-1} and the voltammograms were recorded on a WX-1000-UM-019 (Graphtec Co) X-Y recorder. Immediately after the measurements, ferrocene (0.1 mmol, $E_{1/2} = +0.083$) was added as the internal standard, and the observed peak potentials were corrected with reference to this standard. The compounds exhibited no reversible reduction wave: each of the reduction potentials was measured through independent scans, and they are summarized in Table 2.

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