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Tetrahedron 59 (2003) 4157–4165

TETRAHEDRON

Synthesis and properties of bis(heteroazulen-3-yl)methyl cations and bis(heteroazulen-3-yl)ketones

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Received 19 February 2003; revised 1 April 2003; accepted 3 April 2003

Abstract—The synthesis and properties of a novel type of bis(heteroazulen-3-yl)methyl cations, bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyl cation salt and nitrogen analogues, (**9a**–**c**·PF_6^-) and (**9a**–**c**·BF_4^-), as well as bis(heteroazulen-3-yl)ketones (**12a**–**d**) are studied. The synthetic method was based on a TFA-catalyzed electrophilic aromatic substitution on the heteroazulenes (**6a**–**d**) with paraformaldehyde to afford the corresponding disubstituted methane derivatives **7a**–**d**, followed by oxidative hydrogen abstraction with DDQ, and subsequent exchange of the counter-anion by using aq. HPF_6 or aq. HBF_4. In addition, the reaction of **7a**–**d** with 2.2 equiv. amounts of DDQ afforded carbonyl compounds **12a**–**d**. The delocalization of the positive charge of **9a**–**c** was evaluated by the ^1H and ^{13}C NMR spectral data. The thermodynamic stability of cations **9a**–**c** was evaluated to be in the order **9a**<**9b**<**9c** on the basis of their reduction potentials measured by cyclic voltammetry (CV) and pK_{R+} values (2.6–10.3) obtained spectrophotometrically. The reduction waves of cations **9a**–**c** were irreversible, suggesting the dimerization of the radical species generated by one-electron reduction. This was demonstrated by the reduction of **9a**·BF_4^- with Zn powder to give dimerized product **14a**. In addition, the quenching of **9a**·BF_4^- with MeOH/$NaHCO_3$ gives ether derivative **15a**, which is proposed for the precursor for synthesizing tris(heteroazulene)-substituted methyl cations bearing two different heteroazulene-units. © 2003 Published by Elsevier Science Ltd.

1. Introduction

Recently, Asao and co-workers have reported the synthesis and properties of tris(azulene-3-yl)methyl cation and its derivatives (**1a**–**c**).[1–7] The pK_{R+} values of **1a**–**c** (pK_{R+}=10.3–11.4) are remarkably higher than that of the triphenylmethyl cation (pK_{R+}=−6.44).[8] This feature shows that azulenes have large stabilizing effect toward methyl cations. In the studies, attempted hydride abstraction of tri(azulen-3-yl)methanes with $Ph_3C^+\cdot PF_6^-$ experience extrusion of an azulene moiety to give bis(azulen-3-yl)methyl cations (**2a**–**c**) (Fig. 1). The pK_{R+} values of **2a**–**c** (pK_{R+}=2.1–8.7) are lower than those of **1a**–**c** and remarkably higher than that of the diphenylmethyl cation (pK_{R+}=−13.3).[9] Thus, methyl cations **3a**–**c** have been synthesized, and their crystal structures revealed that the best plane of the isopropylbenzene ring twists by 40.1°, 21.3°, and 20.7°, respectively, from the best plane of the guaiazulenylmethylium substituent owing to the influence of steric hindrance.[10a,b] On the other hand, we have studied the synthesis and properties of heteroazulene analogues of the triphenylmethyl cation, i.e. the tris(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyl cation and pyrrole analogues (**4a**–**c**),[11] as well as the bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)phenylmethyl cation and pyrrole analogues.[12] Thus, heteroazulenes **6a**–**c** (Scheme 1) are demonstrated to stabilize not only cations but also radical species and anions on the basis of their pK_{R+} values and reduction potentials.[12] The stabilizing effect can be ascribed to the electronic effect expressed by π-electron donation and the steric effect of the bulky heteroazulene-units. The reaction of **4a**–**c** with the hydroxide ion becomes unfavorable due to destabilization of the corresponding alcohol owing to strain when the central carbon is forced into sp^3 hybridization. An independent evaluation of these two stabilizing effects seems to be difficult. In this relation, we have also reported the synthesis and properties of heteroazulene-substituted 1,3-bismethyliumbenzene derivatives[13] and 1,3,5-tris-methyliumbenzene derivatives.[14] In the studies, two or three methylium units of dications or trications are twisted against the central phenyl group, respectively, and no conjugation among the methylium units is permitted. In order to evaluate the electronic effect of heteroazulenes, we have studied the synthesis and properties of (heteroazulen-3-yl)tropylium ions (**5a**–**d**), which are expected to have smaller steric effect.[15] In these studies, we have established that the electron-donating ability of heteroazulenes to the tropylium ion is larger in the order **6d**<**6a**<**6b**<**6c** (Scheme 1).[15] From this viewpoint, we investigated the synthesis and properties of the bis(heteroazulen-3-yl)methyl cations (**9a**–**c**), which are expected to have smaller steric effect than the corresponding triheteroazulene-substituted cations (**4a**–**c**), via bis(heteroazulene)-substituted methanes

Keywords: bis(heteroazulen-3-yl)methyl cation; bis(heteroazulen-3-yl)ketone; pK_{R+}; redox potential.

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0040–4020/03/$ - see front matter © 2003 Published by Elsevier Science Ltd.
doi:10.1016/S0040-4020(03)00546-5

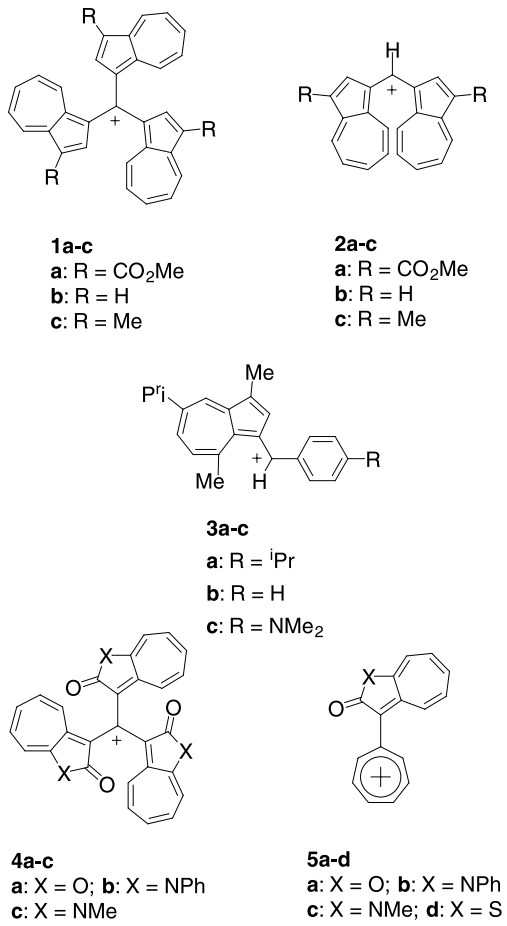


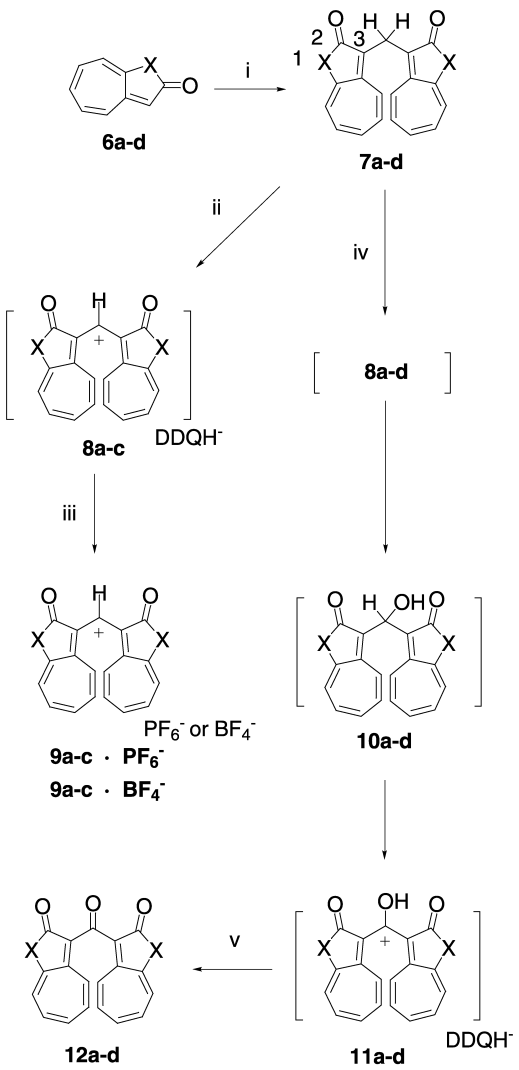
Figure 1.

(**7a**–**c**). The thermodynamic stability of cations **9a**–**c** is evaluated to be in the order **9a**<**9b**<**9c** on the basis of their reduction potentials and pK_{R+} values. To gain insight into the reactivity of **9a**, the one-electron reduction with Zn powder and the quenching reaction with MeOH/$NaHCO_3$ were carried out to result in the formation of radical-coupling product **14a** and ether **15a**, respectively. On the other hand, although bis(azulen-3-yl)ketone was synthesized by the reaction of azulene with oxalyl chloride,[16] bis(heteroazulen-3-yl)ketone has not been synthesized so far. Since the alkyl group on the 1- or 3-position of the azulene nucleus can be converted to a carbonyl function upon treatment with 2 molar equiv. amounts of DDQ in the presence of H_2O,[17] compounds **7a**–**d** are allowed to react with DDQ in the presence of H_2O to give bis(heteroazulen-3-yl)ketones (**12a**–**d**). In addition, we propose a possible methodology for synthesizing heteroazulene-substituted methyl cations bearing two different heteroazulene units. We report herein the results in detail.

2. Results and discussion

2.1. Synthesis

Preparation of bis(heteroazulen-3-yl)methyl cations was easily accomplished by the TFA-catalyzed electrophilic substitution of heteroazulenes with paraformaldehyde and subsequent oxidative hydrogen abstraction. The reactions of



Scheme 1. *Reagents and conditions*: (i) $(CH_2)_n$, CH_2Cl_2–TFA (1:1), rt, 24 h; (ii) DDQ, CH_2Cl_2, rt, 1 h; (iii) 60% HPF_6 or 42% HBF_4, Ac_2O, 0°C, 1 h; (iv) DDQ (2.2 equiv.), H_2O, CH_2Cl_2, CH_3CN, rt, 24 h; (v) aq. $NaHCO_3$.

paraformaldehyde with 2 molar equiv. amounts of 2*H*-cyclohepta[*b*]furan-2-one (**6a**),[18] 1,2-dihydro-*N*-phenylcyclohepta[*b*]pyrrol-2-one (**6b**),[19] 1,2-dihydro-*N*-methylcyclohepta[*b*]pyrrol-2-one (**6c**),[20] and 2*H*-cyclohepta[*b*]thiophen-2-one (**6d**)[21] in CH_2Cl_2–TFA (5:1) at rt for 24 h afforded bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methane (**7a**), bis(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]pyrrol-3-yl)methane (**7b**), bis(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]pyrrol-3-yl)methane (**7c**), and bis(2-oxo-2*H*-cyclohepta[*b*]thiophen-3-yl)methane (**7d**) in good yields, respectively (Scheme 1, Table 1, runs 1, 4, 7, and 10). The compounds **7a**–**d** are powdery, orange or yellow crystals, the structures of which were assigned on the basis of their IR, ^1H and ^{13}C NMR spectral data, as well as mass spectral data and elemental analyses. The oxidative hydrogen abstraction of **7a**–**c** with 1.2 molar equiv. amounts of DDQ in CH_2Cl_2 at rt to give **8a**–**c**, followed by addition of aq. 60% HPF_6 solution afforded salts **9a**–**c**·PF_6^- in the yields listed also in Table 1 (runs 1, 4, and 7). Although the yield of **9a**·PF_6^- is poor, the attempted reaction of **7a**–**c** with DDQ and subsequent

Table 1. Results for the preparation of methane derivatives **7a–d** and methylium salts **9a–c**·PF_6^- **9a–c**·BF_4^-, and **12a–d**

Run	Compound **6**	Substitution		Hydride abstraction		
		Product	Yield (%)	Condition	Product	Yield (%)
1	**6a**	**7a**	97	A	**9a**·PF_6^-	15
2	–	–	–	A	**9a**·BF_4^-	87
3	–	–	–	B	**12a**	71
4	**6b**	**7b**	82	A	**9b**·PF_6^-	90
5	–	–	–	A	**9b**·BF_4^-	99
6	–	–	–	B	**12b**	76
7	**6c**	**7c**	100	A	**9c**·PF_6^-	78
8	–	–	–	A	**9c**·BF_4^-	100
9	–	–	–	B	**12c**	72
10	**6d**	**7d**	87	B	**12d**	71

(A) **7a–c** (0.25 mmol) and DDQ (1.2 equiv.) in CH_2Cl_2 (10 cm^3). (B) **7a–d** (0.25 mmol), H_2O (0.1 cm^3), and DDQ (2.2 equiv.) in CH_2Cl_2 (10 cm^3) and CH_3CN (10 cm^3).

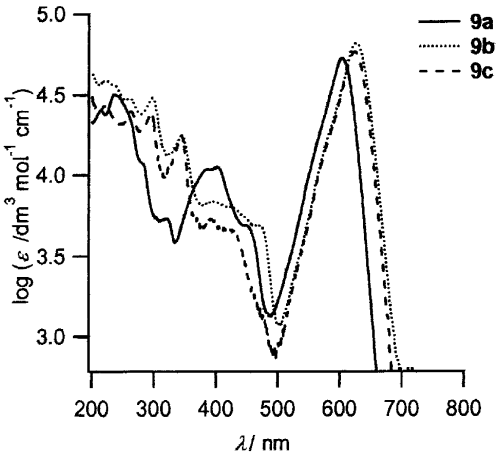


Figure 2. UV–vis spectra of **9a–c** in CH_3CN.

anion-exchange reaction with 42% aq. HBF_4 in acetic anhydride afforded salts **9a–c**·BF_4^- in good yields, respectively (Scheme 1, Table 1, runs 2, 5, and 8). Thus, the low yield of **9a**·PF_6^- would be attributable to its high solubility in CH_2Cl_2. On the other hand, the reaction of **7a–d** with 2.2 molar equiv. amounts of DDQ in moist CH_3CN and CH_2Cl_2 afforded bis(heteroazulen-3-yl)ketones (**12a–d**) in good yields, respectively (Scheme 1, Table 1, runs 3, 6, 9, and 10). These reactions are considered to proceed as follows: the intermediates **8a–d**, generated by the oxidative hydrogen abstraction of **7a–d** with DDQ, react with H_2O to give alcohols **10a–d**. The subsequent oxidative hydrogen abstraction of **10a–d** with another DDQ gives **11a–d**, which is converted to give **12a–d** by addition of aq. $NaHCO_3$.[17] In addition, the reaction of **7d** with even 1.2 molar equiv. amounts of DDQ afforded only **12d** in lower yield. Since the cation **8d** would be unstable because of the low electron-donating property of **6d** as compared with **6a–c**,[15] H_2O-addition of **8d** in the presence of stray H_2O is considered to proceed rapidly to give **10d** (vide infra). Thus, we could not isolate cation salt **9d**·BF_4^-.

2.2. Properties

The structures of **9a–c**·PF_6^-, **9a–c**·BF_4^-, and **12a–d** are assigned on the basis of their spectral data and elemental analyses. Mass spectra of the salts **9a–c**·PF_6^- and **9a–c**·BF_4^- ionized by FAB exhibit the correct M^+-PF_6 or M^+-BF_4 ion peaks, which are indicative of the cationic structure of these compounds. The characteristic bands for the counter ion PF_6^- are observed at 839 cm^{-1} in the IR spectra of **9a–c**·PF_6^-, and the characteristic bands for the counter ion BF_4^- of **9a–c**·BF_4^- are observed at 1084–1058 cm^{-1}. These features also support the cationic nature of **9a–c**. The UV–vis spectra of cations **9a–c** in acetonitrile are shown in Figure 2, and the longest wavelength absorption maxima of **9a–c** are also summarized in Table 2. The spectra of **9a–c** are similar to each other, and the longest wavelength absorption maximum of **9a** shows a blue-shift by 21 and 22 nm as compared with those of **9b** and **9c**, respectively. Moreover, the longest wavelength absorption maxima of **9a–c** exhibit blue-shift by 23, 38, and 37 nm as compared with those of tris(heteroazulene)-substituted cations **4a–c** (**4a**, 626 nm; **4b**, 664 nm; **4c**, 661 nm), respectively. In the ^1H NMR spectra, proton signals on the seven-membered ring of **9a–c**·PF_6^- and **9a–c**·BF_4^- appear as broad signals. However, these signals become sharp at 50–70°C. Thus, rapid conformational change of the heteroazulene moieties in these cations occurs at high temperature in the NMR time scale. This feature is completely different from that of heteroazulene-substituted bulky methyl cations **4a–c**, which exhibit broad signals even at high temperature,[4,5,7,8] thus, suggesting that the heteroazulene moieties of cations **9a–c** experience less steric hindrance. The chemical shifts of methylene protons of **7a–c** and methylium protons of **9a–c** as well as the chemical shift-difference ($\Delta\delta_H$) between them, respectively, are summarized in Table 2. The ^{13}C NMR spectra of **9a–c** were recorded and assigned by using the C–H Cosy spectra. The chemical shifts of methylene carbons of **7a–c** and methylium carbons of **9a–c** as well as the chemical shift-difference ($\Delta\delta_C$) between them, respectively, are also summarized in Table 2. The signal of methylium carbons of **9a–c** appear remarkably higher-field than that of the diphenylmethyl cation (δ_c 200.2 at −60°C in SO_2–SbF_5).[22] In the ^1H NMR as well as in the ^{13}C NMR, the chemical shift-differences ($\Delta\delta_H$ and $\Delta\delta_C$) are smaller in the order **9a**>**9b**>**9c**, suggesting that the positive charge is delocalized to the heteroazulene moiety more largely in the order **9a**<**9b**<**9c**. These features are similar to the heteroazulene-substituted tropylium ions **5a–d**.[15] Consequently, it was clarified that the electron-donating ability of heteroazulenes to the methyl cation is larger in the order **6a**<**6b**<**6c**.

The UV–vis spectra of ketones **12a–d** in acetonitrile are shown in Figure 3 and the longest wavelength absorption maxima of **12a–d** are summarized in Table 2. The values show a remarkable blue-shift as compared with those of **9a–c**, respectively, and they are in the order **12a**<**12d**<**12b**=**12c**. The feature is similar to those of **5a–d**. Furthermore, the chemical shifts of carbonyl-carbons of **12a–d** are also summarized in Table 2. While these chemical shifts are slightly higher than that of benzophenone (δ_C 195.2), the values are much lower than those of cations **9a–c**. In the ^1H NMR spectra at rt, all protons of **12a–d** appear as sharp signals. These features show that the heteroazulene moiety undergoes fast conformational change in the NMR time scale.

Table 2. The longest wavelength absorption maxima of **9a–c** and **12a–d** and ^{1}H NMR and ^{13}C NMR spectral data of **7a–c**, **9a–c**, and **12a–d**

Compound	λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1})		^{1}H NMR/δ			^{13}C NMR/δ			
	9	**12**	**7**	**9**	$\Delta\delta_H$[a]	**7**	**9**	$\Delta\delta_C$[b]	**12**
a	603 (4.73)	453 (4.63)	3.66	8.83	5.17	16.3	143.5	127.2	182.2
b	626 (4.82)	473 (4.63)	4.07	8.92	4.85	16.9	140.4	123.5	186.0
c	624 (4.77)	473 (4.62)	3.97	8.73	4.76	16.7	138.9	122.2	185.7
d	–	459 (4.46)	–	–	–	–	–	–	187.3

9a–c·PF_6^- were used for the measurement.
[a] $\Delta\delta_H$: chemical shifts difference between δ_H (methine of **7**) and δ_H (methylium of **9**).
[b] $\Delta\delta_C$: chemical shifts difference between δ_C (methine of **7**) and δ_C (methylium of **9**).

The reduction potentials of cations **9a–c** are determined by cyclic voltammetry (CV) in CH_3CN. The reduction waves are irreversible under the conditions of the CV measurements, respectively; and thus, the peak potentials ($E1_{red}$) are summarized in Table 3 along with those of the reference compound **4a–c**[11] and **5a–d**.[4] The values ($E1_{red}$) of cation **9a–c** are more positive in the order **9a**>**9b**>**9c**, and they are more positive than the corresponding tris(heteroazulene)-substituted cations (**4a–c**) and heteroazulene-substituted tropyrium cations (**5a–c**), respectively. While

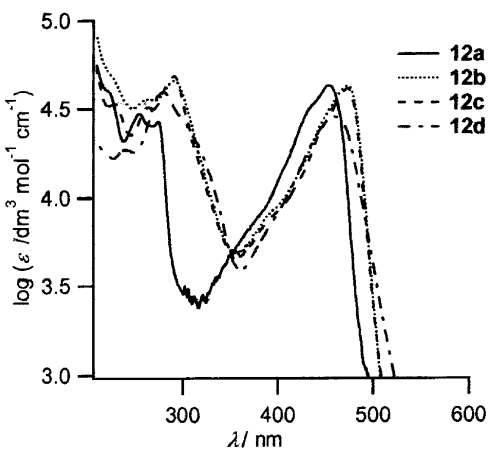


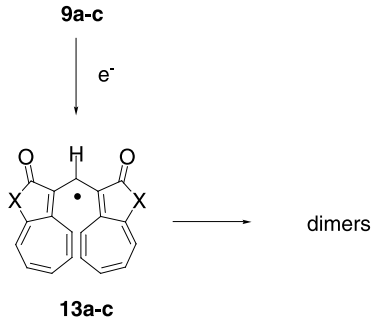
Figure 3. UV–vis spectra of **12a–d** in CH_3CN.

Table 3. Reduction potentials and pK_{R+} values of **9a–c**, **4a–c**, and **5a–d**

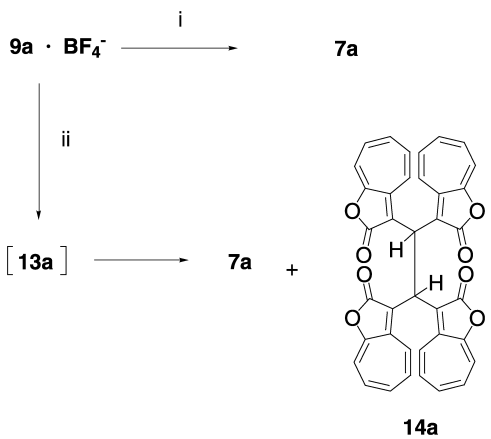
compound	Reduction potentials[a]		pK_{R+}	Δ[b]
	$E1_{red}$	$E2_{red}$		
9a	(−0.27)	–	2.6	7.1
9b	(−0.51)	–	9.9	2.3
9c	(−0.52)	–	10.3	2.8
4a[d]	−0.31	−0.95	9.7	–
4b[c]	−0.58	−1.27	12.2	–
4c[c]	−0.62	−1.33	13.1	–
5a[d]	(−0.50)	–	3.8	–
5b[d]	(−0.65)	–	5.3	–
5c[d]	(−0.66)	–	5.7	–
5d[d]	(−0.49)	–	3.2	–

9a–c·PF_6^- were used for the measurement.
[a] V vs Ag/$AgNO_3$; a mean value of the cathodic and anodic peaks. Irreversible processes were shown in parentheses.
[b] pK_{R+} difference between **9** and **4**.
[c] Ref. 11.
[d] Ref. 15.

cations **4a–c** show two reversible waves ($E1_{red}$ and $E2_{red}$), respectively, cations **9a–c** as well as cations **5a–d** exhibit only one irreversible wave ($E1_{red}$). The feature is similar to that of azulene analogues of trisubstituted cations and disubstituted cations **1a–c** and **2a–c**.[4] Moreover, the cations **3a–c** showed similar feature.[10a,b] The irreversible nature is probably due to the formation of methyl radicals **13a–c** and their dimerization reactions (Scheme 2). In order to confirm this point, the chemical reduction of **9a** was carried out (Scheme 3). The reaction of **9a** with $NaBH_4$ afforded **7a** in 92% yield, while one-electron reduction of **9a** by using Zn afforded **7a** and dimerized product **14a** in 10% and 54% yields, respectively; the latter compound **14a** plausibly arises from the dimerization of **13a**. One-electron reduction of **3b** is also known to give dimerized product,



Scheme 2.



Scheme 3. *Reagents and conditions*: (i) $NaBH_4$, CH_3CN, rt, 1 h; (ii) Zn, CH_3CN, rt, 0.5 h.

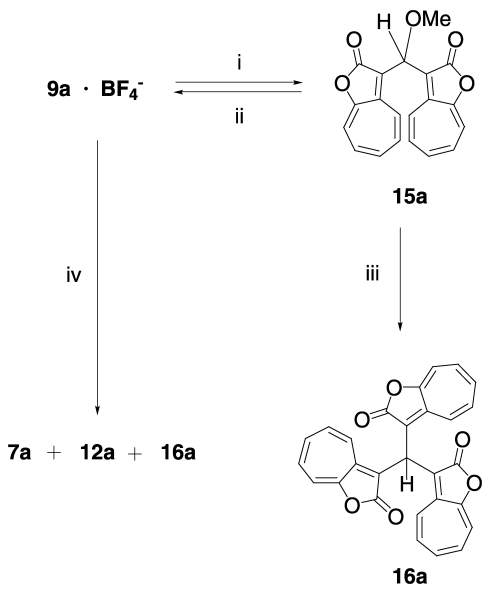
1,2-di(3-guaiazulenyl)-1,2-diphenylehtane.[10b] Thus, the $E1_{red}$ of **9a**–**c** would become to be irreversible. This fact suggests that the steric hindrance for dimerization would be small for **9a**–**c**. The structure of **14a** is assigned on the basis of the IR, ^{1}H and ^{13}C NMR spectral data as well as elemental analysis and mass spectral data.

The affinity of the carbocation towards the hydroxide ion, expressed by the pK_{R+} value, is the most common criterion of carbocation stability.[23] The pK_{R+} values of the cations **9a**–**c** are obtained spectrophotometrically and are summarized also in Table 3, together with those of the reference compounds **4a**–**c**[11] and **5a**–**d**.[13] The neutralization of the cations **9a**–**c** is not completely reversible. This feature is ascribed to the instability of the neutralized products under the conditions of the pK_{R+} measurement. Rapid (after 10 s) acidification of an alkaline solution (ca. pH 14) of **9a**–**c** with TFA regenerated the absorption maxima of the cations in the visible regions in ca. 80% yield. Although the pK_{R+} values of **9a**–**c** are smaller than those of **4a**–**c**, respectively, the values become larger in the order **9a**≪**9b**<**9c**. Thus, the stabilizing ability of the heteroazulenes **6a**–**c** to the methyl cations is considered to be larger in the order **6a**≪**6b**<**6c**. This feature has also been observed in the pK_{R+} values of **5a**–**c** (Table 3).[13] The pK_{R+} value of **5d** is smaller than that of **5a**. Thus, the salt **8d** would be unstable and collapse to **10d** in the presence of stray water (vide supra, Scheme 1). The pK_{R+} difference (Δ) between **9a**–**c** and **4a**–**c** are also summarized in Table 3. The Δ values for cations **9a** and **4a** are large (7.1), while those of cations **9b**,**c** and **4b**,**c** are small Δ (2.3 and 2.8, respectively). This feature suggests that heteroazulenes **6b**,**c** have large stabilizing ability arising from the electronic effect. While heteroazulene **6a** has small stabilizing ability arising from the electronic effect as compared with **6b**,**c**, a large stabilizing effect by steric effect in trisubstituted cation **4a**–**c** is clearly suggested.

The reaction of **3a** with MeONa/MeOH gives the 1-isopropyl-4-(3-guaiazulenylmethoxymethyl)benzene.[10a] Thus, the neutralized product **15a** (90% yield) is isolated by the reaction of **9a** with MeOH/$NaHCO_3$ (Scheme 4). The structure was clearly identified on the basis of the spectroscopic data as well as elemental analysis. Compound **15a** regenerated **9a** in good yield upon treatment with aq. HBF_4 in Ac_2O. On the other hand, the reaction of **15a** with **6a** in the presence of TFA afforded **16a**, which was a precursor of cation **4a**[4] in 97% yield. Since the reaction of **6a** with **9a** in the presence of $NaHCO_3$ gives **16a** along with **7a** and **12a**, both of which plausibly arise from a disproportionation reaction of **10a** generated from **9a** and stray water, the present method is applicable to the preparation of trisubstitutedmethyl cations bearing mixed heteroazulene-units.

3. Conclusion

Convenient preparations of fairly stable bis(heteroazulen-3-yl)methyl salts (**9a**–**c**·PF_6^-) and (**9a**–**c**·BF_4^-), and bis(heteroazulen-3-yl)ketones (**12a**–**d**) were accomplished. The delocalization of the positive charge of cations **9a**–**c** was suggested by the ^{1}H and ^{13}C NMR spectra. The stability



Scheme 4. *Reagents and conditions*: (i) MeOH, CH_2Cl_2, $NaHCO_3$, rt, 0.5 h; (ii) 42% HBF_4, Ac_2O, 0°C, 1 h; (iii) **6a**, CH_2Cl_2–TFA (1:1), rt, 5 min; (iv) **6a**, $NaHCO_3$, CH_3CN, rt, 1 h.

of the methyl cation derivatives **9a**–**c** is clarified to be in the order **9a**<**9b**<**9c** based on the reduction potentials and the pK_{R+} values. Furthermore, electronic effect and steric effect in the cation-stabilizing heteroazulene-units are discussed. The irreversibility of reduction waves of **9a**–**c** was suggested by dimerization of the postulated radical species generated by Zn-reduction. In addition, quenching of cation **9a** with MeOH/$NaHCO_3$ giving **16a** is proposed to provide a new preparative method of trisubstituted methylcations bearing two different heteroazulene units. Further studies concerned with this project will be continued.

4. Experimental

4.1. General

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 JNM-lambda 500 spectrometers using $CDCl_3$ as the solvent, and the chemical shifts are given relative to internal $SiMe_4$ standard: *J*-values are given in Hz. Mps were recorded on a Yamato MP-21 apparatus and are uncorrected. The heteroazulenes, 2*H*-cyclohepta[*b*]furan-2-one (**6a**),[18] 1,2-dihydro-*N*-phenylcyclohepta[*b*]pyrrol-2-one (**6b**),[19] 1,2-dihydro-*N*-methylcyclohepta[*b*]pyrrol-2-one (**6c**),[20] and 2*H*-cyclohepta[*b*]thiophen-2-one (**6d**),[21] were prepared as described previously.

4.2. General synthetic procedure for heteroazulene-substituted methane derivatives (7a–d)

A solution of heteroazulene **6a**–**d** (2 mmol) and paraformaldehyde (30 mg, 1 mmol) in a mixture of CH_2Cl_2 (10 mL) and trifluoroacetic acid (2 mL) was stirred at rt for 24 h. After the reaction was completed, 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/AcOEt (1:1) as the eluent to give the products **7a–d** (Table 1, run 1, 4, 7, and 10).

4.2.1. Bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methane (7a). Yellow powder; mp 244–245°C (from EtOH); ^{1}H NMR (500 MHz) δ 3.66 (2H, s, CH_2), 6.78 (1H, dd, J=9.5, 8.5 Hz, H-6), 6.89 (1H, d, J=8.9 Hz, H-8), 6.92 (1H, dd, J=9.5, 8.5 Hz, H-7), 7.07 (1H, dd, J=11.4, 8.5 Hz, H-5), 7.76 (1H, d, J=11.4 Hz, H-4); ^{13}C NMR (125.7 MHz) δ 16.3, 107.9, 113.6, 127.6, 130.7, 132.0, 134.9, 148.5, 157.5, 170.2; IR (KBr) ν 1731, 1257 cm^{-1}; MS (rel. int.) m/z 304 (M^+, 94.2), 220 (100%). Anal. calcd for $C_{19}H_{12}O_4$: C, 74.99; H, 3.97. Found: C, 74.7; H, 3.5.

4.2.2. Bis(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]-pyrrol-3-yl)methane (7b). Reddish-orange powder; mp 261–262°C (from AcOEt); ^{1}H NMR (500 MHz) δ 4.07 (2H, s, CH_2), 6.68 (2H, d, J=8.8 Hz, H-8), 6.78 (2H, dd, J=10.8, 8.2 Hz, H-6), 6.83 (2H, dd, J=10.8, 8.8 Hz, H-7), 7.06 (2H, dd, J=11.3, 8.2 Hz, H-5), 7.33 (4H, d, J=8.3 Hz, Ph-2, 6), 7.46 (2H, t, J=7.3 Hz, Ph-4), 7.54 (4H, dd, J=8.3, 7.3 Hz, Ph-3, 5), 8.28 (2H, d, J=11.3 Hz, H-4); ^{13}C NMR (125.7 MHz) δ 16.9, 112.5, 112.9, 128.5, 128.6, 128.8, 129.2, 129.5, 130.3, 131.1, 134.6, 141.5, 145.2, 169.1; IR (KBr) ν 1711 cm^{-1}; MS (FAB) m/z 455 (M^++H). Anal. calcd for $C_{31}H_{22}N_2O_2$: C, 81.92; H, 4.88; N, 6.16. Found: C, 81.5; H, 4.7; N, 6.0.

4.2.3. Bis(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]-pyrrol-3-yl)methane (7c). Yellow powder; mp 256–257°C (from EtOH); ^{1}H NMR (500 MHz) δ 3.53 (6H, s, CH_3), 3.97 (2H, s, CH_2), 6.79 (2H, d, J=9.0 Hz, H-8), 6.80 (2H, dd, J=10.8, 8.6 Hz, H-6), 6.96 (2H, dd, J=10.8, 9.0 Hz, H-7), 7.06 (2H, dd, J=11.2, 8.6 Hz, H-5), 8.13 (2H, d, J=11.3 Hz, H-4); ^{13}C NMR (125.7 MHz) δ 16.7, 26.5, 110.8, 113.6, 128.1, 128.6, 129.8, 130.5, 140.9, 144.6, 169.2; IR (KBr) ν 1663 cm^{-1}; MS (FAB) m/z 331 (M^++H). Anal. calcd for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.0; H, 5.0; N, 8.3.

4.2.4. Bis(2-oxo-2*H*-cyclohepta[*b*]thiophen-3-yl)methane (7d). Dark orange needles; mp 230–231°C (from CH_2Cl_2/EtOH); ^{1}H NMR (500 MHz) δ 3.90 (2H, s, CH_2), 6.83–6.89 (4H, m, H-6, 8), 7.02–7.06 (2H, m, H-5), 7.26–7.28 (2H, m, H-7), 7.90 (2H, d, J=11.6 Hz, H-4); ^{13}C NMR (150.9 MHz) δ 20.3, 125.4, 130.3, 131.0, 131.4, 133.2, 133.4, 150.2, 153.1, 190.2; IR (KBr) ν 1628 cm^{-1}; MS (FAB) m/z 337 (M^++H). Anal. calcd for $C_{19}H_{12}O_2S_2$+1/2H_2O: C, 66.06; H, 3.79. Found: C, 65.7; H, 3.3.

4.3. General synthetic procedure for methylium hexafluorophosphates (9a–c·PF_6^-)

To a stirred solution of **7a–c** (0.25 mol) in CH_2Cl_2 (10 mL) was added DDQ (70 mg, 0.3 mmol) and the mixture was stirred at rt for 1 h until the reaction completed. To the reaction mixture was added 60% aqueous HPF_6 (1 mL) solution 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 precipitates were collected by filtration, washed with ether to give the salts **9a–c·PF_6^-** (Table 1, run 1, 4, and 7).

4.3.1. Bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyl hexafluorophosphate (9a·PF_6^-). Reddish-brown powder; mp 221–222 (from CH_3CN/Et_2O); ^{1}H NMR (500 MHz, CD_3CN, 50°C) δ 8.31 (2H, dd, J=10.1, 9.4 Hz, H-6), 8.39 (4H, d, J=10.2 Hz, H-4, 8), 8.49 (2H, dd, J=10.2, 10.1 Hz, H-7), 8.51 (2H, dd, J=10.2, 9.4 Hz, H-5), 8.83 (1H, s, CH); ^{13}C NMR (125.7 MHz, CD_3CN, 50°C) δ 108.6, 129.2, 132.6, 139.0, 142.7, 143.5, 145.3, 146.4, 151.1, 165.5; IR (KBr) ν 1734, 1261, 839 cm^{-1}; MS (FAB) m/z 303 (M^+-PF_6). HRMS calcd for $C_{19}H_{11}O_4PF_6$: 303.0657 ($M-PF_6$). Found: 303.0682 (M^+-PF_6).

4.3.2. Bis(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]-pyrrol-3-yl)methyl hexafluorophosphate (9b·PF_6^-). Reddish-brown powder; mp 187–188°C (from CH_2Cl_2/Et_2O, decomp.); ^{1}H NMR (500 MHz, CD_3CN, 50°C) δ 7.49 (4H, d, J=8.2 Hz, Ph-2, 6), 7.64 (2H, t, J=7.2 Hz, Ph-4), 7.68 (4H, dd, J=8.2, 7.2 Hz, Ph-3, 5), 7.80 (2H, d, J=10.3 Hz, H-8), 7.99 (2H, dd, J=10.1, 9.6 Hz, H-6), 8.13 (2H, dd, J=10.1, 10.0 Hz, H-5), 8.18 (2H, dd, J=10.3, 9.6 Hz, H-7), 8.26 (2H, d, J=10.0 Hz, H-4), 8.92 (1H, s, CH); ^{13}C NMR (125.7 MHz, CD_3CN, 50°C) δ 113.4, 125.8, 129.2, 129.6, 131.2, 131.3, 134.2, 138.4, 139.7, 140.4, 142.1, 144.5, 146.7, 155.8; IR (KBr) ν 1696, 839 cm^{-1}; MS (FAB) m/z 453 (M^+-PF_6). HRMS calcd for $C_{31}H_{21}N_2O_2PF_6$: 453.1604 ($M-PF_6$). Found: 453.1588 (M^+-PF_6). Anal. calcd for $C_{31}H_{21}N_2O_2PF_6$: C, 62.21; H, 3.54; N, 4.68. Found: C, 62.8; H, 3.2; N, 4.8.

4.3.3. Bis(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]-pyrrol-3-yl)methyl hexafluorophosphate (9c·PF_6^-). Reddish-brown powder; mp 206–207°C (from CH_2Cl_2/Et_2O, decomp.); ^{1}H NMR (600 MHz, CD_3CN, 50°C) δ 3.59 (6H, s, Me), 7.97 (2H, dd, J=10.1, 9.6 Hz, H-6), 8.06 (2H, d, J=9.8 Hz, H-8), 8.07–8.12 (4H, m, H-4, 5), 8.27 (2H, dd, J=10.1, 9.8 Hz, H-7), 8.73 (1H, s, CH); ^{13}C NMR (150.9 MHz, CD_3CN, 50°C) δ 27.5, 112.5, 124.2, 136.8, 138.1, 138.9, 141.0, 143.4, 145.5, 154.7, 165.8; IR (KBr) ν 1701, 839 cm^{-1}; MS (FAB) m/z 329 (M^+-PF_6). HRMS calcd for $C_{21}H_{17}N_2O_2PF_6$: 329.1290 ($M-PF_6$). Found: 329.1287 (M^+-PF_6). Anal. calcd for $C_{21}H_{17}N_2O_2PF_6$: C, 53.17; H, 3.02; N, 5.96. Found: C, 53.2; H, 3.6; N, 5.9.

4.4. Preparation of methylium tetrafluoroborates (9a–c·BF_4^-)

To a stirred solution of **7a–c** (0.25 mmol) in CH_2Cl_2 (10 mL) was added DDQ (70 mg, 0.30 mmol), and the mixture was stirred at rt for 1 h. After evaporation of the CH_2Cl_2, the residue was dissolved in Ac_2O (5 mL) and 42% HBF_4 (1 mL) at 0°C and the mixture was stirred for 1 h. To the mixture was added Et_2O (100 mL) and the precipitates were collected by filtration to give **9a–c**·BF_4^- (Table 1, run 2, 5, and 8).

4.4.1. Bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyl tetrafluoroborate (9a·BF_4^-). Greenish yellow powder; mp 224–225°C (from CH_2Cl_2/Et_2O, decomp.); ^{1}H NMR

(600 MHz, CD_3CN, 70°C) δ 8.31 (2H, t, J=9.7 Hz, H-6), 8.38 (2H, d, J=10.2 Hz, H-4), 8.39 (2H, d, J=10.0 Hz, H-8), 8.48 (2H, dd, J=10.0, 9.7 Hz, H-7), 8.50 (2H, dd, J=10.2, 9.7 Hz, H-5), 8.82 (1H, s, CH); ^{13}C NMR (150.9 MHz, CD_3CN, 70°C) δ 111.9, 130.1, 137.5, 137.6, 139.8, 143.6, 144.3, 146.2, 147.2, 168.3; IR (KBr) ν 1806, 1792, 1769, 1736, 1261, 1060 cm^{-1}; MS (FAB) m/z 303 (M^+-BF_4). HRMS calcd for $C_{19}H_{11}O_4BF_4$: 303.0657 ($M-BF_4$). Found: 303.0645 (M^+-BF_4). Anal. calcd for $C_{19}H_{11}O_4BF_4$: C, 58.50; H, 2.84. Found: C, 58.6; H, 2.5.

4.4.2. Bis(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]-pyrrol-3-yl)methyl tetrafluoroborate (9b·BF_4^-). Reddish-brown powder; mp 232–234°C (from CH_3CN/Et_2O, decomp.); ^{1}H NMR (600 MHz, CD_3CN, 70°C) δ 7.52 (4H, d, J=8.3 Hz, Ph-2, 6), 7.66 (2H, t, J=7.4 Hz, Ph-4), 7.70 (4H, dd, J=8.3, 7.4 Hz, Ph-3, 5), 7.82 (2H, d, J=10.5 Hz, H-8), 8.01 (2H, t, J=9.7 Hz, H-6), 8.15 (2H, dd, J=10.5, 9.7 Hz, H-7), 8.20 (2H, dd, J=10.5, 9.7 Hz, H-5), 8.29 (2H, d, J=10.5 Hz, H-4), 8.95 (1H, s, CH); ^{13}C NMR (150.9 MHz, CD_3CN, 70°C) δ_C 113.2, 121.0, 125.7, 129.1, 129.4, 131.0, 131.2, 134.0, 139.6, 140.2, 142.0, 144.3, 155.5, 166.4; IR (KBr) ν 1701, 1685, 1084 cm^{-1}; MS (FAB) m/z 453 (M^+-BF_4). HRMS calcd for $C_{31}H_{21}N_2O_2BF_4$: 453.1604 ($M-BF_4$). Found: 453.1628 (M^+-BF_4). Anal. calcd for $C_{31}H_{21}N_2O_2BF_4+H_2O$: C, 66.69; H, 4.18; N, 5.02. Found: C, 66.4; H, 3.9; N, 4.8.

4.4.3. Bis(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]-pyrrol-3-yl)methyl tetrafluoroborate (9c·BF_4^-). Reddish-brown powder; mp 241–244°C (from CH_3CN/Et_2O, decomp.); ^{1}H NMR (600 MHz, CD_3CN, 70°C) δ 3.64 (6H, s, Me), 8.06 (2H, t, J=9.7 Hz, H-6), 8.15 (2H, d, J=10.0 Hz, H-8), 8.20 (2H, dd, J=10.0, 9.7 Hz, H-7), 8.28–8.35 (4H, m, H-4, 5), 8.85 (1H, s, CH); ^{13}C NMR (150.9 MHz, CD_3CN, 70°C) δ 28.6, 113.5, 125.6, 137.8, 139.4, 140.2, 142.2, 144.5, 147.0, 155.8, 167.2; IR (KBr) ν 1719, 1694, 1084 cm^{-1}; MS (FAB) m/z 329 (M^+-BF_4). HRMS calcd for $C_{21}H_{17}N_2O_2BF_4$: 329.1290 ($M-BF_4$). Found: 329.1291 (M^+-BF_4). Anal. calcd for $C_{21}H_{17}N_2O_2$-BF_4+HBF_4: C, 50.05; H, 3.60; N, 5.56. Found: C, 50.1; H, 3.9; N, 5.5.

4.5. Preparation of bis(heteroazulen-3-yl)ketones (12a–d)

To a stirred solution of **7a–d** (0.5 mmol) in H_2O (0.1 mL), CH_2Cl_2 (10 mL), and CH_3CN (10 mL) was added DDQ (257 mg, 1.1 mmol) and the mixture was stirred at rt for 24 h. After evaporation of the solvent, the residue was dissolved in Ac_2O (5 mL) and 42% HBF_4 (1 mL) at 0°C and the mixture was stirred for 1 h. To the mixture was added Et_2O (100 mL) and the precipitates were collected by filtration. Then the precipitates were dissolved in aqueous $NaHCO_3$ solution, extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4 and concentrated in vacuo to give the products **12a–d** (Table 1, run 3, 6, 9, and 10).

4.5.1. Bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)ketone (12a). Orange powder; mp>300°C (from CH_2Cl_2/EtOH); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.54 (2H, dd, J=10.3, 9.3 Hz, H-6), 7.71 (2H, dd, J=10.3, 9.5 Hz, H-7), 7.78 (2H, d, J=9.5 Hz, H-8), 7.81 (2H, dd, J=11.2, 9.3 Hz, H-5), 8.51 (2H, d, J=11.2 Hz, H-4); ^{13}C NMR (150.9 MHz, DMSO-d_6) δ 105.7, 119.9, 129.3, 135.1, 137.0, 140.7, 152.1, 158.0, 165.1, 182.2; IR ($CHCl_3$)/ν_{max} 1776, 1744, 1469, 1268 cm^{-1}; MS (rel. int.) m/z 318 (M^+, 72), 173 (100%). Anal. calcd for $C_{19}H_{10}O_5+1/5H_2O$: C, 68.78; H, 3.13. Found: C, 68.9; H, 2.9.

4.5.2. Bis(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]-pyrrol-3-yl)ketone (12b). Orange prisms; mp 273–275°C (from CH_2Cl_2/EtOH); ^{1}H NMR (500 MHz) δ 7.09 (2H, d, J=9.4 Hz, H-8), 7.16 (2H, dd, J=9.8, 9.2 Hz, H-6), 7.24 (2H, dd, J=9.8, 9.4 Hz, H-7), 7.37 (4H, d, J=8.0 Hz, *o*-Ph), 7.46 (2H, t, J=7.4 Hz, *p*-Ph), 7.46 (2H, dd, J=11.1, 9.2 Hz, H-5), 7.52 (4H, dd, J=8.0, 7.4 Hz, *m*-Ph), 8.86 (2H, d, J=11.1 Hz, H-4); ^{13}C NMR (125.7 MHz) δ 112.7, 116.3, 128.7, 128.8, 129.6, 130.1, 131.7, 133.8, 134.2, 135.9, 146.4, 147.3, 166.2, 186.0; IR ($CHCl_3$) ν 1684, 1458 cm^{-1}; MS (rel. int.) m/z 468 (M^+, 100%). Anal. calcd for $C_{31}H_{20}N_2O_3+1/3H_2O$: C, 78.47; H, 4.39; N, 5.90. Found: C, 78.6; H, 4.2; N, 5.8.

4.5.3. Bis(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]-pyrrol-3-yl)ketone (12c). Orange powder; mp>300°C (from CH_2Cl_2/EtOH); ^{1}H NMR (500 MHz) δ 3.58 (6H, s, Me), 7.20 (2H, dd, J=10.0, 9.7 Hz, H-6), 7.24 (2H, d, J=9.5 Hz, H-8), 7.42 (2H, dd, J=10.0, 9.5 Hz, H-7), 7.44 (2H, dd, J=11.0, 9.7 Hz, H-5), 8.80 (2H, d, J=11.0 Hz, H-4); ^{13}C NMR (150.9 MHz) δ 26.6, 113.1, 115.0, 129.8, 131.2, 133.5, 135.7, 146.4, 146.7, 166.4, 185.7; IR ($CHCl_3$) ν 1670, 1593, 1468 cm^{-1}; MS (FAB) m/z 345 (M^++H). HRMS calcd for $C_{21}H_{16}N_2O_3$: 345.1239 (M+H). Found: 345.1246 (M^++H). Anal. calcd for $C_{21}H_{16}N_2O_3+1/2H_2O$: C, 71.38; H, 4.85; N, 7.93. Found: C, 71.3; H, 4.3; N, 7.9.

4.5.4. Bis(2-oxo-2*H*-cyclohepta[*b*]thiophen-3-yl)ketone (12d). Orange powder; mp 274–277°C (from CH_2Cl_2/EtOH, decomp); ^{1}H NMR (500 MHz) δ 7.19–7.23 (4H, m, H-6, 7), 7.33–7.37 (2H, m, H-5), 7.69 (2H, d, J=10.1 Hz, H-8), 8.57 (2H, d, J=11.6 Hz, H-4); ^{13}C NMR (150.9 MHz) δ 125.0, 132.4, 133.3, 133.6, 136.0, 137.0, 152.9, 156.8, 187.0, 187.3; IR ($CHCl_3$) ν 1672, 1643, 1449 cm^{-1}; MS (FAB) m/z 351 (M^++H). HRMS calcd for $C_{19}H_{10}O_3S_2$: 351.0150 (M+H). Found: 351.0126 (M^++H). Anal. calcd for $C_{19}H_{10}O_3S_2+H_2O$: C, 61.94; H, 3.28. Found: C, 61.6; H, 2.8.

4.6. Reduction of 9a·BF_4^- with $NaBH_4$

A solution of **9a**·BF_4^- (19.5 mg, 0.05 mmol) and $NaBH_4$ (1.9 mg, 0.05 mmol) in CH_3CN (1 mL) was stirred at rt for 1 h. To the mixture was added saturated aqueous NH_4Cl solution, and the mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 and concentrated in vacuo to give **7a** (14.0 mg, 92%).

4.7. Reduction of 9a·BF_4^- with Zn

To a solution of **9a**·BF_4^- (195 mg, 0.5 mmol) in CH_3CN (20 mL) was added powdery Zn (325 mg, 5.0 mmol) and the mixture was stirred at rt for 24 h. After filtration, the filtrate was concentrated in vacuo. The resulting residue was separated by column chromatography on SiO_2 (hexane/

AcOEt=1:2) to give **7a** (15 mg, 10%) and **14a** (83 mg, 54%).

4.7.1. 1,1,2,2-Tetrakis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)ethane (14a). Orange powder; mp 282–283°C (from CH_2Cl_2/EtOH, decomp); ^{1}H NMR (500 MHz) δ 6.25 (2H, s, CH), 6.81 (4H, dd, J=10.2, 8.5 Hz, H-6), 6.82 (4H, d, J=9.4 Hz, H-8) 6.89 (4H, dd, J=10.2, 9.4 Hz, H-7), 7.16 (4H, dd, J=11.6, 8.5 Hz, H-5), 8.18 (4H, br s, H-4); ^{13}C NMR (125.7 MHz) δ 29.3, 106.6, 114.1, 128.8, 131.4, 132.1, 135.3, 143.6, 157.4, 169.6; IR (KBr) ν 1742, 1273 cm^{-1}; MS (FAB) m/z 607 (M^++H). HRMS calcd for $C_{38}H_{22}O_8$: 607.1393 (M+H). Found: 607.1388 (M^++H). Anal. calcd for $C_{38}H_{22}O_8$+3/2H_2O: C, 72.03; H, 3.98. Found: C, 71.8; H, 3.7.

4.8. Reaction of 9a·BF_4^- with MeOH

To a suspension of **9a**·BF_4^- (39 mg, 0.1 mmol) and $NaHCO_3$ (24 mg, 0.3 mmol) in CH_3CN (1 mL) was added MeOH (3 mL) and the mixture was stirred at rt for 0.5 h. After evaporation of the solvent, the resulting residue was purified through column chromatography on SiO_2 using hexane/AcOEt (1:1) as the eluent to give **15a** (30 mg, 90%).

4.8.1. Bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)-methoxymethane (15a). Orange needles; mp 174–175°C (from EtOH); ^{1}H NMR (500 MHz) δ 3.43 (3H, s, Me), 5.62 (1H, s, CH), 6.85–6.91 (1H, m, H-6), 6.98–7.03 (2H, m, H-7, 8), 7.16 (1H, dd, J=11.3, 8.5 Hz, H-5), 8.04 (1H, d, J=11.3 Hz, H-4); ^{13}C NMR (125.7 MHz) δ 57.1, 70.2, 107.0, 114.7, 128.4, 131.3, 132.4, 135.4, 149.0, 157.4, 168.1; IR (KBr) ν 1749, 1271 cm^{-1}; MS (rel. int.) m/z 334 (M^+, 20), 303 (100%). Anal. calcd for $C_{20}H_{14}O_5$: C, 71.85; H, 4.22. Found: C, 71.4; H, 4.2.

4.9. Reaction of compound 15a with HBF_4

The compound **15a** (84 mg, 0.25 mmol) was dissolved in a mixture of Ac_2O (5 mL) and aq. 42% HBF_4 (1 mL), and the mixture was stirred at 0°C for 1 h. To the mixture was added Et_2O (100 mL) and the precipitates were collected by filtration to give **9a**·BF_4^- (98 mg, 100%).

4.10. Reaction of 15a with 6a

To a solution of **15a** (10 mg, 0.03 mmol) and **6a** (4 mg, 0.03 mmol) in CH_2Cl_2 (1 mL) was added TFA (0.2 mL) and the mixture was stirred at rt for 5 min. 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, concentrated in vacuo to give the product **16a** (13 mg, 97%), which was identical with the authentic sample.[11]

4.11. Reaction of 9a with 6a

To a solution of **9a** (39 mg, 0.1 mmol) and **6a** (15 mg, 0.1 mmol) in CH_3CN (2 mL) was added $NaHCO_3$ (83 mg, 1.0 mmol), and the mixture was stirred at rt for 1 h. To the mixture was added MeOH (1 mL) and the mixture was further stirred at rt for 0.5 h. After evaporation of the solvent, the resulting residue was dissolved in CH_2Cl_2 and filtered to remove excess $NaHCO_3$ and $NaBF_4$. The filtrate was washed by H_2O and the CH_2Cl_2 extract was dried over Na_2SO_4, concentrated in vacuo to give a mixture of **6a**,**7a**,**12a**, and **16a** (47 mg) in a molar ratio in 29:10:6:84 as determined by ^{1}H NMR spectrum.

4.12. Determination of pK_{R+} value of methyl cations 9a–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 mL portions of the stock solution, prepared by dissolving 3–5 mg of cation **9a**–**c**·PF_6^- in CH_3CN (20 mL), were diluted to 10 mL with the buffer solution (8 mL) and CH_3CN (1 mL). The UV–vis spectrum was recorded for each cation **9a**–**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 (597 nm for **9a**; 609 nm for **9b**; 605 nm for **9c**) of each cation **9a**–**c** was plotted against pH to give a classical titration curve, whose midpoint was taken as the pK_{R+} value.

4.13. Cyclic voltammetry of methyl cations 9a–c

The reduction potentials of **9a**–**c** were determined by means of 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 mL) 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 scan, and they are summarized in Table 3.

Acknowledgements

Financial support from a Waseda University Grant for Special Research Project and 21COE 'Practical Nanochemistry' from MEXT, Japan is gratefully acknowledged. We thank the Materials Characterization Central Laboratory, Waseda University, for technical assistance with the spectral data and elemental analyses.

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