Synthesis and Properties of α,α-Bis(heteroazulen-3-yl)-1,4-benzoquinonemethides

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The synthesis and properties of a novel type of α,α-bis(heteroazulen-3-yl)-1,4-benzoquinonemethides **11a–f** are studied. The synthetic method was based on a TFA-catalyzed electrophilic aromatic substitution on the heteroazulenes with 4-hydroxybenzaldehyde to afford the corresponding methane derivatives, followed by oxidative hydrogen abstraction with DDQ, and subsequent exchange of the counter-anion by using aq. HBF_4 or aq. HPF_6 and neutralization. The polarization of **11a–f** was evaluated by their ^{13}C NMR and UV–vis spectral data. The thermodynamic stability of the conjugated acid of **11a–f** was evaluated to be in the order **11a** < **11b** < **11c** and in the order **11d** < **11e** < **11f** based on their pK_a values (<0–5.4) obtained spectrophotometrically. The substituent effect of *t*-Bu was discussed based on the UV–vis spectra and pK_a values. In CV measurements, the reduction waves of quinonemethides **11a–f** were reversible, suggesting a stabilizing effect of heteroazulenes toward the radical and anion species. Moreover, quinonemethides **11a–f** showed two oxidation waves, and that the first oxidation potentials ($E1_{ox}$) of **11a–c**, which have two *t*-Bu groups, are reversible.

Conjugated π-electron chromophores containing a donor and an acceptor group have attracted current interest in terms of optoelectronic materials,[1] such as nonlinear optics[2] and near-infrared dyes.[3] Among numerous classes of these chromophores, compounds containing a quinonoid unit as a spacer are especially promising,[4] because such conjugated systems have generally been recognized to possess marked push–pull electronic effects, which induce large dipole moments, leading to a high nonlinear response[5] and ready intramolecular charge-transfer transitions, leading to deep coloration.[6] In this regard, the parent compound, α,α-diphenyl-1,4-benzoquinonemethide, has been known for many years;[7] numerous substituted compounds have been described in the literature.[8] In this context, the synthesis and properties of compounds **1a**,**b** have been investigated.[9] Moreover, benzoquinonoid compounds have hitherto played a most important role in the development of organic redox chemistry due to their multistage redox properties.[10] Recently, Ito, Asao, and co-workers have reported the synthesis and properties of α,α-bis(azulen-1-yl)-1,4-benzoquinonemethides **2a**,**b** and their derivatives.[11] These quinonemethides **2a**,**b** are highly polarized by the extreme electron-donating properties of the azulenyl group, and the highly polarized properties of **2a**,**b** are reflected in the high pK_a values of their conjugated acid. In addition, the solvatochromic effect and redox properties of **2a**,**b** were also reported. On the other hand, we 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,[12] as well as the bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)phenylmethyl cations **3a–e** and pyrrole analogues **4a–e**[13] (Fig. 1).

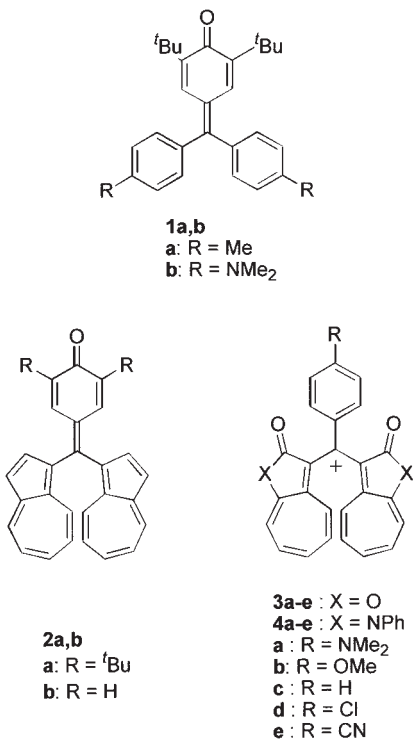

Fig. 1.

In these reports, we clarified the stabilizing ability of heteroazulenes **5a–c** (Scheme 1) toward methyl cations and the remarkable substituent effect of cations **3a–e** and **4a–e**. In this context, we also reported on the synthesis and properties of heteroazulene-substituted benzene-1,3-bismethylium derivatives[14] and benzene-1,3,5-trismethylium derivatives.[15] In the studies, two or three methylium units of dications or trications were twisted against the central phenyl group, respectively, and no conjugation among the methylium units is suggested. In order to evaluate the electronic effect of heteroazulenes,

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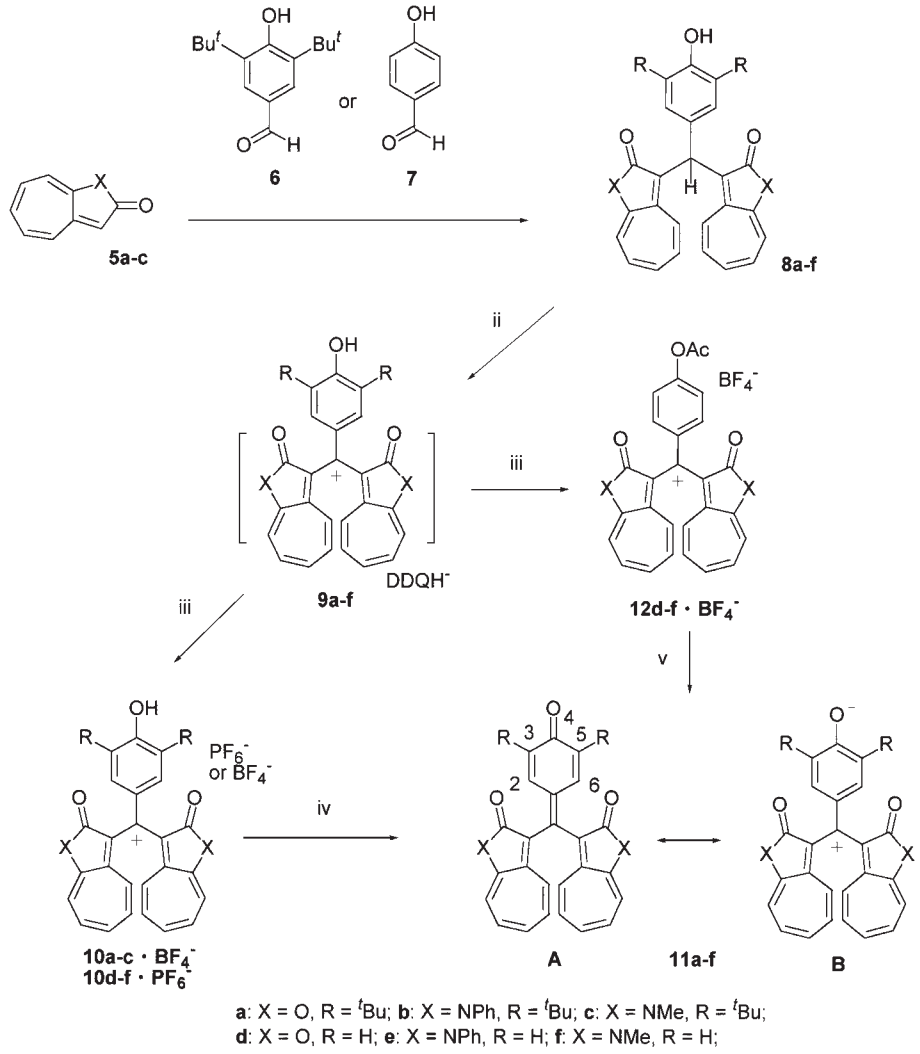


Scheme 1. Reagents and conditions: i, $CHCl_3$–TFA (5:1), reflux, 8 h; ii, DDQ, CH_2Cl_2, rt, 1 h; iii, 60% HPF_6 or 42% HBF_4, Ac_2O, 0 °C, 1 h; iv, aq. $NaHCO_3$; v, K_2CO_3.

we also studied the synthesis and properties of (heteroazulen-3-yl)tropylium ions[16] and bis(heteroazulen-3-yl)methyl cations,[17] which are expected to have a smaller steric effect. In these studies, we clarified that the heteroazulenes **5a–c** can be demonstrated to stabilize not only cations, but also radical species and anions based on their pK_{R+} values and reduction potentials.[13,16] From this viewpoint, we investigated the synthesis and properties of α,α-bis(heteroazulen-3-yl)-1,4-benzoquinonemethides **11a–f**, which are expected to have a highly polarized structure and multistage redox properties. To gain insight into the polarized structure of **11a–f**, the chemical shifts of quinone carbonyl carbon and solvatochromic effects as well as the pK_a values of the conjugate acids of **11a–f** were studied. Based on a measurement of a CV, the redox property of the quinonemethides **11a–f** was also clarified. We report herein on the results in detail.

Results and Discussion

Synthesis. The preparation of α,α-bis(heteroazulen-3-yl)-1,4-benzoquinonemethides was easily accomplished by the TFA-catalyzed electrophilic substitution of heteroazulenes with 4-hydroxybenzaldehyde and subsequent oxidation. The acid-catalyzed condensation of 4-hydroxybenzaldehyde with heteroazulene at room temperature proceeded slowly; thus, the reactions were carried out at 80 °C. The reactions of 3,5-di-*t*-butyl-4-hydroxybenzaldehyde **6** or 4-hydroxybenzaldehyde **7** with two molar equivalent amounts of 2*H*-cyclohepta[*b*]furan-2-one **5a**,[18] 1,2-dihydro-*N*-phenylcyclohepta[*b*]pyrrol-2-one **5b**,[19] and 1,2-dihydro-*N*-methylcyclohepta[*b*]pyrrol-2-one **5c**[20] in $CHCl_3$–TFA (5/1) at 80 °C for 8 h afforded (3,5-di-*t*-butyl-4-hydroxyphenyl)bis(heteroazulen-3-yl)methane derivatives **8a–c** or bis(heteroazulen-3-yl)(4-hydroxyphenyl)methane derivatives **8d–f** in good yields, respectively (Scheme 1, Table 1, Runs 1–4, 6, and 8). Compound **8a** was obtained in modest yield and the starting material **5a** was recovered in 55% yield. Compounds **8a–f** were powdery, orange or yellow crystals, the structures of which were assigned based on their IR, ^{1}H and ^{13}C NMR spectral data, as well as the mass spectral data and elemental analyses. The oxidative hydrogen abstraction of **8a–c** with 1.2 molar equivalent amounts of DDQ in CH_2Cl_2 at rt gave **9a–c**, followed by the addition of an aq. 42% HBF_4 solution (Table 1, Condition A) afforded salts **10a–c**•BF_4^- in the yields (also listed in Table 1 (Runs 1–3)). Since the cations **10a–c**•BF_4^- were un-

Table 1. Results for the Preparation of Methane Derivatives **8a–f**, Cations **10a–c•BF$_4^-$**, **12d–f•BF$_4^-$**, and **10d–f•PF$_6^-$** and Quinone Methides **11a–f**

Run	Heteroazulene **5**	Aldehyde **6** or **7**	Substitution Product	Substitution Yield/%	Hydride abstraction Conditions	Hydride abstraction Product	Hydride abstraction Yield/%	Neutralization Product	Neutralization Yield/%
1	**5a**	**6**	**8a**	45	A	**10a•BF$_4^-$**	100	**11a**	92
2	**5b**	**6**	**8b**	86	A	**10b•BF$_4^-$**	98	**11b**	93
3	**5c**	**6**	**8c**	89	A	**10c•BF$_4^-$**	90	**11c**	100
4	**5a**	**7**	**8d**	100	A	**12d•BF$_4^-$**	100	**11d**	71
5					B	**10d•PF$_6^-$**	100	**11d**	100
6	**5b**	**7**	**8e**	92	A	**12e•BF$_4^-$**	100	**11e**	44
7					B	**10e•PF$_6^-$**	93	**11e**	100
8	**5c**	**7**	**8f**	83	A	**12f•BF$_4^-$**	100	**11f**	71
9					B	**10f•PF$_6^-$**	100	**11f**	100

a) Conditions A: 1) **8a–f** and DDQ in CH_2Cl_2, 2) 42% HBF_4 and Ac_2O. Conditions B: 1) **8d–f** and DDQ in CH_2Cl_2, 2) 60% HPF_6.

stable (vide infra), further purification was not carried out. Neutralization of **10a–c•BF$_4^-$** with a saturated aq. $NaHCO_3$ solution afforded quinonemethides **11a–c** in good yields (Table 1, Runs 1–3). On the other hand, a similar treatment of **8d–f** afforded acetylated compounds **12d–f•BF$_4^-$** (Table 1, Runs 4, 6, and 8). The treatment of cations **12d–f•BF$_4^-$** with K_2CO_3 for 16 h afforded quinonemethides **11d–f** in poor yields. Thus, 60% aq. HPF_6 was used for exchange of the counter ion to give **10d–f•PF$_6^-$** (Table 1, Condition B). Neutralization of **10d–f•PF$_6^-$** with a 4% aq. NaOH solution afforded quinonemethides **11d–f** in good yields (Table 1, Runs 5, 7, and 9). This feature suggests that the *t*-Bu groups have a large steric hindrance to prevent acetylation.

Properties. The deprotonation reaction of the cations **10a–c•BF$_4^-$**, and **10d–f•PF$_6^-$** proceeded gradually under recrystallization. The deacetylation reaction of the cations **12d–f•BF$_4^-$** also proceeded gradually under recrystallization. Thus, satisfactory analytical data of these cations were not obtained. However, the structures of **10a–c•BF$_4^-$**, **12d–f•BF$_4^-$**, and **10d–f•PF$_6^-$** were assigned based on their spectral data. Mass spectra of the salts **10a–c•BF$_4^-$**, **12d–f•BF$_4^-$**, and **10d–f•PF$_6^-$**, ionized by FAB, exhibit the correct $M^+ - PF_6$ or $M^+ - BF_4$ ion peaks, indicative of the cationic structure of these compounds. The characteristic bands for the counter ion BF_4^- of **10a–c•BF$_4^-$** and **12d–f•BF$_4^-$** were observed at 1058–1084 cm^{-1}, and the characteristic bands for the counter ion PF_6^- of **10d–f•PF$_6^-$** were observed at 840–845 cm^{-1} in the IR spectra. These features also support the cationic nature of **10a–c**, **12d–f**, and **10d–f**.

The structures of quinonemethides **11a–f** were assigned based on their spectral data and elemental analyses. The quinonemethides **11a–f** were easily crystallized to give complexes containing H_2O or the solvent molecule in the crystal lattice; this feature is similar to the cases of heteroazulene-substituted methyl cations and Crystal Violet [tris(4-dimethylaminophenyl)methyl chloride], which forms two crystal structures containing H_2O as the monohydrate and the nonahydrate.[21] In the ^1H NMR spectra at room temperature, proton signals on the seven-membered ring of **11a–f** appear as broad signals. However, these signals become sharp at elevated temperature (50–70 °C). Thus, a rapid conformational change of the heteroazulene moieties in these quinonemethides occurs at those temperatures on the NMR time scale. The ^{13}C NMR spectra of **11a–f** were recorded and the chemical shifts of the quinone carbonyl carbon were assigned by using the C–H COSY spectra (HMBC). The chemical shifts of the quinone carbonyl carbon of **11a–f** as well as those of the reference compounds **2a**,**b** are summarized in Table 2. These values of **11a–f** are similar to those of **2a**,**b** and **1a**,**b** (**1a**: δ_C 186.2, **1b**: δ_C 185.9). These values become higher in the order **11a** < **11b** < **11c** and **11d** <

Table 2. ^{13}C NMR Spectral Data, the Longest Wavelength Absorption Maxima of UV–Vis Spectra, and pK_a Values of **11a–f** and Reference Compound **2a**,**b**

Compd	^{13}C NMR/δ[a]	λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}) CH_3CN	CH_3CN + TFA[b]	CH_2Cl_2	MeOH	$\Delta\lambda$[c]	pK_a[d]
11a	187.0	453 (4.41)	620 (4.75)	452 (4.51)	454 (4.42)	+2	<0
11b	186.3	486 (4.49)	654 (4.73)	480 (4.46)	478 (4.42)	−2	1.6
11c	185.9	486 (4.46)	650 (4.73)	481 (4.47)	481 (4.49)	0	1.9
11d	187.4	467 (4.50)	618 (4.78)	471 (4.53)	483 (4.32)	+12	4.2
11e	186.3	508 (4.36)	651 (4.59)	508 (4.39)	543 (4.38)	+35	5.3
11f	185.2	512 (4.42)	646 (4.65)	511 (4.34)	548 (4.33)	+37	5.4
2a[e]	185.6	—	—	507 (4.42)	521 (4.45)	+14	3.4
2b[e]	186.6	—	—	522 (4.43)	549 (4.55)	+27	6.5

a) Chemical shift of 4-position. b) Generation of cations **10a–f**. c) Difference in wavelength between the values in CH_2Cl_2 and in MeOH. d) The pK_a values of the conjugate acids of **11a–f** were determined spectrophotometrically in a buffered solution prepared in 50% aqueous CH_3CN. e) Ref. 11.

11e < **11f** and two quinonemethides having the same heteroazulene show similar values, respectively. Thus, the contribution of the charge-separated ionic forms **11a–f-B** (Scheme 1) becomes larger in this order; however, these low chemical shifts suggest that the contribution of the charge-separated ionic forms **11a–f-B** is not very large in the ground state.

The UV–vis spectra of quinonemethides **11a–f** in acetonitrile are shown in Figs. 2 and 3. The longest wavelength absorption maxima of **11a–f** are also summarized in Table 2. The spectra of **11a–c** are similar, and the longest wavelength absorption maximum of **11a** shows a blue-shift by 33 nm, compared with those of **11b** and **11c** in a CH_3CN solution. The spectra of **11d–f** are also similar, and the longest wavelength absorption maximum of **11d** shows a blue-shift by

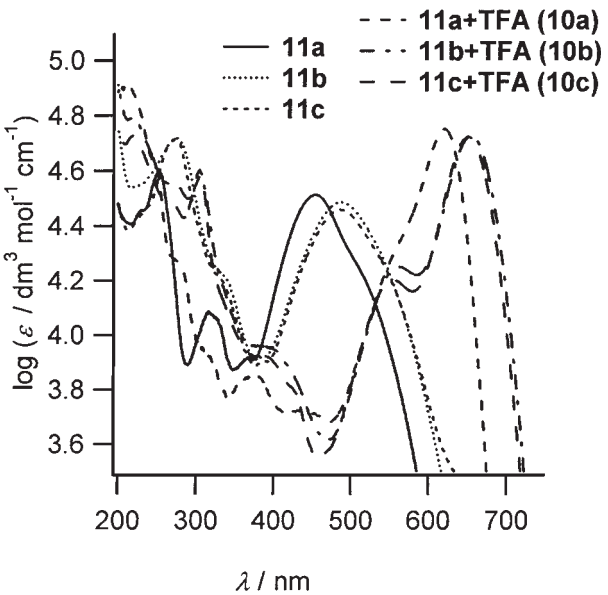


Fig. 2. UV–vis spectra of **11a–c** in CH_3CN and in CH_3CN and TFA.

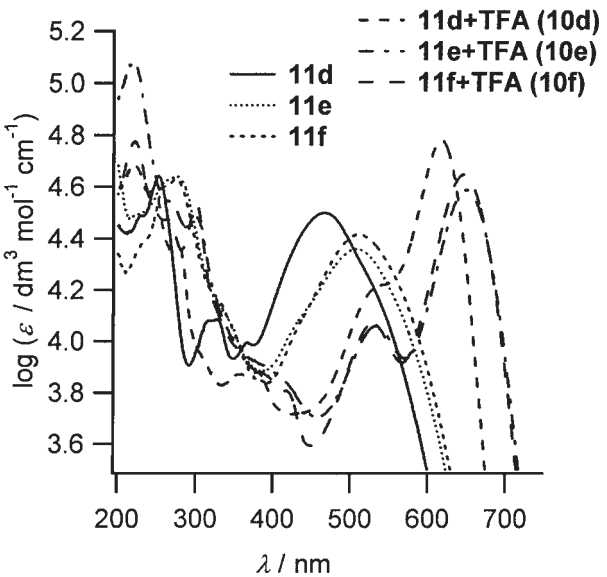


Fig. 3. UV–vis spectra of **11d–f** in CH_3CN and in CH_3CN and TFA.

41 and 45 nm compared with those of **11e** and **11f**, respectively. In addition, the longest wavelength absorption maxima of *t*-Bu-substituted **11a–c** show a blue-shift compared with those of unsubstituted **11d–f**, respectively. By additing a drop of TFA, compounds **11a–f** were completely protonated to give cations **10a–f**. Moreover, these cations **10a–f** regenerated quinonemethides **11a–f** quantitatively upon the addition of a drop of Et_3N. Thus, the protonation–deprotonation cycle is completely reversible. The longest wavelength absorption maxima of **10a–f** are also summarized in Table 2. Pairs of quinonemethides having the same heteroazulene-unit show similar values, respectively, suggesting no substituent effect of the *t*-Bu group. Moreover, the values of **10a**,**d** are similar to those of **3b–e** (621 nm) and the values of **10b**,**e** are similar to those of **4b–e** (652 nm). This feature seems to be reasonable based on our previous study considering the longest wavelength absorption maxima of **3a–e** and **4a–e** as well as the calculation of the stable conformations of **3a–e** and **4a–e**. Regarding the charge-separated ionic forms **11a–f-B**, the phenoxide-moiety has a larger electron-donating ability than the heteroazulene-moiety. Thus, the phenoxide-moiety has a more planar conformation and the heteroazulene-moiety is twisted against the cationic plane. On the contrary, the heteroazulene-moiety has a larger electron-donating ability than the hydroxyphenyl-moiety in cations **10a–f**. Since the heteroazulene-moiety has a more planar conformation and the hydroxyphenyl-moiety is twisted against the cationic plane, conjugation between the hydroxyphenyl-moiety and the methylium carbon becomes smaller. Thus, the substituent effect of the *t*-Bu group on the hydroxyphenyl-moiety becomes less important.

It is well known that highly polarized compounds, such as quinonemethides, show large solvatochromic effects.[4] The large solvatochromic effects of **2a**,**b** were also reported.[11] Thus, the UV–vis spectra of **11a–f** were measured in CH_2Cl_2 and in MeOH. The longest wavelength absorption maxima of **11a–f** in CH_2Cl_2 and in MeOH as well as the difference in these wavelengths ($\Delta\lambda$) are summarized in Table 2. Compounds **11d–f** show large solvatochromic effects, although *t*-Bu-substituted compounds **11a–c** show weak or no solvatochromic effects due to the steric effect of the *t*-Bu group, which hinders the solvation of protic solvents as well as protonation. The negative solvatochromic effects of **11d–f** can be rationalized by stabilization of their excited states by hydrogen bonding of the quinonemethides with protic solvents.[22] Thus, the contribution of the charge-separated ionic forms **11a–f-B** seems to be larger in their excited states compared with their ground state. The solvatochromic effects are larger in the order **11d** < **11e** < **11f**, which are rationalized by the electron-donating ability of the heteroazulenes **5a–c** (**5a** < **5b** < **5c**).[12–17]

The pK_a values of the conjugate acids of **11a–f** provide a criterion of stability of the protonated forms of **11a–f**. The pK_a values of the conjugated acids of **11a–f** (**10a–f**) were determined spectrophotometrically in buffer solutions prepared in 50% aqueous CH_3CN, and are summarized in Table 2. Compound **11a** in all buffer solutions was not protonated completely, and the pK_a value of **11a** was estimated to be <0. The relatively low pK_a values for conjugate acids of **11a–c**, as

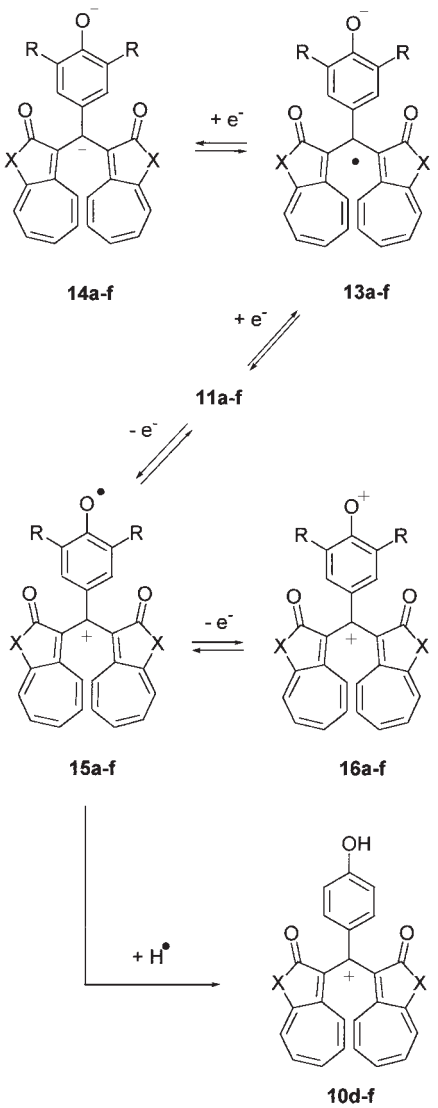
Table 3. Redox Potentials of **11a–f** and Reference Compounds **2a**,**b**, and Reduction of **11a–f** with Zn Powder

	Redox potentials[a]					Reduction with Zn powder	
Compd	$E1_{red}$	$E2_{red}$	$E3_{red}$	$E1_{ox}$	$E2_{ox}$	Product	Yield/%
11a	−1.24	−1.56	—	+0.74	(+1.09)	**8a**	100
11b	−1.40	−1.77	—	+0.55	(+0.95)	**8b**	98
11c	−1.42	−1.83	—	+0.51	(+0.92)	**8c**	93
11d	−1.07	−1.44	−1.66	(+0.78)	(+1.47)	**8d**	100
11e	−1.22	−1.63	—	(+0.59)	(+1.11)	**8e**	100
11f	−1.26	−1.65	—	(+0.55)	(+1.06)	**8f**	94
2a[b]	(−1.55)	—	—	+0.47	(+0.95)		
2b[b]	−1.38	(−1.75)	—	(+0.45)	—		

a) V vs $Ag/AgNO_3$; mean value of the cathodic and anodic peaks. Irreversible processes are shown in parentheses. b) Ref. 11.

compared with those of **11d–f**, indicate the steric effects of the *t*-Bu group, which hinder the protonation of the quinonemethides **11a–c**. The pK_a values of the conjugated acids of **11a–c** are larger in the order **11a** < **11b** < **11c**, while the pK_a values of the conjugated acids of **11d–f** are larger in the order **11d** < **11e** < **11f**. This feature is rationalized by the electon-donating ability of heteroazulenes **5a–c** (**5a** < **5b** < **5c**).[12–17]

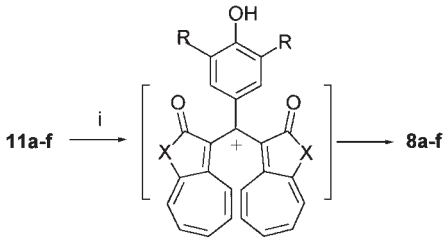
The reduction and oxidation potentials of quinonemethides **11a–f** determined by cyclic voltammentry (CV) in CH_3CN are summarized in Table 3 along with those of reference compounds **2a**,**b**.[11] The reduction waves of **11a–f** are reversible under the conditions of the CV measurements, and quinonemethides **11a–c** and **11e**,**f** showed two reversible waves. The quinonemethide **11d** showed three reversible waves. The two waves ($E1_{red}$ and $E2_{red}$) are explained by the formation of stable radical anions **13a–f** and dianions **14a–f**, rescpectively (Scheme 2). The additional wave ($E3_{red}$) of **11d** is rationalized by reduction of the heteroazulene-moiety of **14d**. These characteristics are due to the heteroazulenes which stabilize the radical species and anion species.[13] On the other hand, two oxidation waves were recorded in the measurements of quinonemethides **11a–f**, as summarized in Table 3. The first oxidation waves ($E1_{ox}$) of **11a–c** are reversible, while the second oxidation waves ($E2_{ox}$) of **11a–c** and the two oxidation waves of **11d–f** are irreversible. The two waves can also be explained by the formation of radical cations **15a–f** and dications **16a–f**, respectively (Scheme 2). The reversible oxidation waves ($E1_{ox}$) of **11a–c** suggest stabilization of the phenoxyl radicals by the steric hindrance of the *t*-Bu group. On the contrary, after the first cycle of CV measurements of **11d–f**, other reduction waves were recorded at −0.32 V, −0.57 V, and −0.61 V, respectively. These waves are suggested to be the reduction waves of **10d–f**, which are generated by the hydrogen abstraction of phenoxyl radicals **15d–f**. On the other hand, we recently reported that the one-electron reduction of the bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyl cation by using Zn powder afforded a radical species, which rapidly dimerizes to give 1,1,2,2-tetrakis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)-ethane.[17] Thus, the reaction of **11a–f** with Zn powder was carried out (Scheme 3). The quinonemethides **11a–f** were protonated in HCl/AcOH to give cations **10a–f**, which were reduced to afford the methane derivative **8a–f** in good yield (Table 3). This feature shows that the quinonemethides **11a–f** have good redox properties.



a: X = O, R = ^{t}Bu; **b**: X = NPh, R = ^{t}Bu;
c: X = NMe, R = ^{t}Bu; **d**: X = O, R = H;
e: X = NPh, R = H; **f**: X = NMe, R = H;

Scheme 2.

In summary, a convenient preparation of fairly stable α,α-bis(heteroazulen-3-yl)-1,4-benzoquinonemethides **11a–f** was accomplished. The properties of **11a–f** were clarified by mea-



a: X = O, R = ^{t}Bu; **b**: X = NPh, R = ^{t}Bu;
c: X = NMe, R = ^{t}Bu; **d**: X = O, R = H;
e: X = NPh, R = H; **f**: X = NMe, R = H;

Scheme 3. Reagents and conditions: i, Zn, 3% HCl, AcOH, reflux, 8 h.

suring the ^{13}C NMR and UV–vis spectra and the solvatochromic effects as well as the pK_a values of their conjugate acids. The contribution of the polarized structure of quinonemethides **11a–f** was clarified to be small in the ground state, but larger in the excited state. Owing to the stabilizing ability of heteroazulenes toward the radical and anion species, quinonemethides **11a–f** show two or three reversible reduction waves in the CV measurements. Moreover, the quinonemethides **11a–f** showed two oxidation waves, and the first oxidation potentials ($E1_{ox}$) of **11a–c**, which have *t*-Bu substituents, were reversible. Further studies concerning the synthesis and properties of heteroazulene-substituted quinonemethide analogues 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 JNM-lambda 500 spectrometers, 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 were uncorrected. The heteroazulenes, 2*H*-cyclohepta[*b*]furan-2-one **5a**,[18] 1,2-dihydro-*N*-phenylcyclohepta[*b*]pyrrol-2-one **5b**,[19] and 1,2-dihydro-*N*-methylcyclohepta[*b*]pyrrol-2-one **5c**[20] were prepared as described previously.

General Synthetic Procedure for Heteroazulene-Substituted Methane Derivatives 8a–f. A solution of heteroazulene **5a–c** (2 mmol) and 3,5-di-*t*-butyl-4-hydroxybenzaldehyde **6** (234 mg, 1 mmol) [or 4-hydroxybenzaldehyde **7** (122 mg, 1 mmol)] in a mixture of $CHCl_3$ (10 cm^3) and trifluoroacetic acid (2 cm^3) was stirred at 80 °C for 6 h. After the reaction was completed, the mixture was poured into an 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 by recrystallization to give products **8a–c** [or products **8d–f**] (Table 1, Runs 1–4, 6, and 8).

3,5-Di-*t*-butyl-4-hydroxyphenyl-bis(2-oxo-2*H*-cyclohepta[*b*]-furan-3-yl)methane (8a): Orange powder; mp 237–238 °C (from CH_2Cl_2/EtOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (18H, s, Bu), 5.10 (1H, s, OH), 5.65 (1H, s, CH), 6.76 (2H, dd, J = 8.7, 8.3 Hz, H-6), 6.88–6.95 (6H, m, H-5,7,8), 7.01 (2H, s, Ph-2,6), 7.38 (2H, d, J = 12.0 Hz, H-4); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 30.3, 34.4, 35.2, 109.8, 113.7, 124.3, 126.9, 128.4, 130.8, 131.9, 134.1, 136.2, 148.3, 152.6, 157.7, 169.5; IR (KBr) ν 1635, 1236 cm^{-1}; MS (rel, int.) *m*/*z* 508 (M$^+$, 26), 51 (100%). Anal. Calcd for $C_{33}H_{32}O_5$: C, 77.55; H, 6.31%. Found: C, 77.93; H, 6.34%.

3,5-Di-*t*-butyl-4-hydroxyphenyl-bis(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]pyrrol-3-yl)methane (8b): Orange powder; mp 272–273 °C (from CH_2Cl_2/EtOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.40 (18H, s, Bu), 5.20 (1H, s, OH), 6.20 (1H, s, CH), 6.70 (2H, d, J = 8.9 Hz, H-8), 6.75 (2H, dd, J = 10.6, 8.5 Hz, H-6), 6.82 (2H, dd, J = 10.6, 8.9 Hz, H-7), 6.88 (2H, dd, J = 11.5, 8.5 Hz, H-5), 7.13 (2H, s, Ph-2,6), 7.30 (4H, d, J = 8.1 Hz, NPh-2,6), 7.41 (2H, t, J = 7.7 Hz, NPh-4), 7.50 (4H, dd, J = 8.1, 7.7 Hz, NPh-3,5), 7.80 (2H, d, J = 11.5 Hz, H-4); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 30.4, 34.4, 35.9, 112.6, 114.3, 124.8, 128.4, 128.8, 129.3, 129.4, 129.5, 129.6, 130.1, 130.3, 134.7, 135.6, 141.2, 145.5, 152.1, 168.9; IR (KBr) ν 1679 cm^{-1}; MS (rel, int.) *m*/*z* 659 (M$^+$, 46), 658 (100%). Anal. Calcd for $C_{45}H_{42}N_2O_3 \cdot 1/3H_2O$: C, 81.18; H, 6.43; N, 4.09%. Found: C, 81.30; H, 6.47; N, 4.21%.

3,5-Di-*t*-butyl-4-hydroxyphenyl-bis(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]pyrrol-3-yl)methane (8c): Yellow powder; mp 242–243 °C (from CH_2Cl_2/EtOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 (18H, s, Bu), 3.50 (6H, s, NMe), 5.05 (1H, s, OH), 6.05 (1H, s, CH), 6.80 (2H, dd, J = 11.0, 9.9 Hz, H-6), 6.81 (2H, d, J = 9.8 Hz, H-8), 6.90 (2H, dd, J = 11.0, 9.8 Hz, H-7), 6.96 (2H, dd, J = 11.3, 9.9 Hz, H-5), 6.99 (2H, s, Ph-2, 6), 7.74 (2H, d, J = 11.3 Hz, H-4); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 26.4, 30.3, 34.3, 35.8, 110.8, 115.0, 124.7, 128.7, 128.9, 129.6, 129.7, 129.9, 135.6, 140.7, 144.8, 152.0, 168.8; IR (KBr) ν 1669 cm^{-1}; MS (rel, int.) *m*/*z* 534 (M$^+$, 23), 57 (100%). Anal. Calcd for $C_{35}H_{38}N_2O_3 \cdot 1/2H_2O$: C, 77.14; H, 7.20; N, 5.11%. Found: C, 77.32; H, 7.23; N, 5.15%.

4-Hydroxyphenyl-bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)-methane (8d): Yellow powder; mp 250–252 °C (from CH_2Cl_2/EtOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.40 (1H, s, CH), 6.71 (2H, d, J = 8.7 Hz, Ph-3,5), 6.91 (2H, dd, J = 9.6, 8.1 Hz, H-6), 6.98 (2H, d, J = 8.7 Hz, Ph-2,6), 7.02–7.15 (6H, m, H-5,7,8), 7.19 (2H, d, J = 11.5 Hz, H-4), 9.37 (1H, s, OH); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 26.9, 31.3, 35.2, 112.3, 114.9, 115.8, 128.2, 129.1, 130.8, 131.3, 140.7, 144.8, 156.1, 168.1; IR (KBr) ν 1653, 1221 cm^{-1}; MS (ESI) *m*/*z* 395 (M$^+$, 100%). Anal. Calcd for $C_{25}H_{16}O_5 \cdot 1/2H_2O$: C, 73.78; H, 3.88%. Found: C, 74.07; H, 4.23%.

Bis(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]pyrrol-3-yl)(4-hydroxyphenyl)methane (8e): Yellow powder; mp 216–218 °C (from CH_2Cl_2/EtOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.98 (1H, s, OH), 6.19 (1H, s, CH), 6.72–6.78 (6H, m, H-6,7,8), 6.85 (2H, d, J = 8.3 Hz, Ph-3,5), 6.90 (2H, dd, J = 11.1, 8.3 Hz, H-5), 7.18 (2H, d, J = 8.3 Hz, Ph-2,6), 7.35 (4H, d, J = 8.2 Hz, NPh-2, 6), 7.43 (2H, t, J = 8.3 Hz, NPh-4), 7.50 (4H, dd, J = 8.3, 8.2 Hz, NPh-3,5), 7.86 (2H, d, J = 8.3 Hz, H-4); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 35.9, 113.8, 114.4, 116.1, 129.1, 129.4, 129.9, 130.0, 130.1, 130.2, 131.0, 131.5, 131.8, 135.1, 142.1, 146.0, 155.1, 169.5; IR (KBr) ν 1684 cm^{-1}; MS (ESI) *m*/*z* 545 (M$^+$, 100%). Anal. Calcd for $C_{37}H_{26}N_2O_3 \cdot 3/2H_2O$: C, 77.28; H, 5.41; N, 4.50%. Found: C, 77.47; H, 5.10; N, 4.88%.

Bis(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]pyrrol-3-yl)(4-hydroxyphenyl)methane (8f): Yellow powder; mp 272–273 °C (from CH_2Cl_2/EtOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.25 (6H, s, NMe), 5.80 (1H, s, CH), 6.64 (2H, d, J = 8.2 Hz, Ph-2,6), 6.84–6.90 (4H, m, Ph-3,5, H-8), 6.94 (2H, dd, J = 9.6, 8.2 Hz, H-6), 7.05–7.15 (4H, m, H-5,7), 7.62 (2H, d, J = 10.9 Hz, H-4), 9.25 (1H, s, OH); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 26.1, 30.6, 34.4, 110.1, 111.6, 114.1, 115.0, 127.5, 128.4, 130.1, 130.6, 140.0,

144.1, 155.4, 167.4; IR (KBr) ν 1653 cm^{-1}; MS (ESI) m/z 421 (M^+, 100%). Anal. Calcd for $C_{27}H_{22}N_2O_3 \cdot 1/2H_2O$: C, 75.09; H, 5.20; N, 6.16%. Found: C, 75.16; H, 5.37; N, 6.49%.

Preparation of Methylium Tetrafluoroborates 10a–c·BF_4^-. To a stirred solution of **8a–c** (0.25 mmol) in CH_2Cl_2 (10 cm^3) 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 cm^3) and 42% HBF_4 (1 cm^3) at 0 °C and the mixture was stirred for 1 h. To the mixture was added Et_2O (100 cm^3) and the precipitates were collected by filtration to give **10a–c·BF_4^-** (Table 1, Runs 1–3).

3,5-Di-*t*-butyl-4-hydroxyphenyl-bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)methyl tetrafluoroborate (10a·BF_4^-): Dark brown powder; mp 230–232 °C (from CH_3CN/Et_2O, decomp.); ^{1}H NMR (400 MHz, CD_3CN) δ 1.40 (18H, s, Bu), 7.53 (2H, s, Ph-2,6), 7.60–8.20 (11H, m, OH, H-4,5,6,7,8); IR (KBr) ν 1628, 1084 cm^{-1}; MS (FAB) m/z 507 ($M^+ - BF_4$); HRMS Calcd for $C_{33}H_{31}BF_4O_5$: 507.2187 ($M - BF_4$). Found: 507.2191 ($M^+ - BF_4$).

3,5-Di-*t*-butyl-4-hydroxyphenyl-bis(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]pyrrol-3-yl)methyl tetrafluoroborate (10b·BF_4^-): Dark brown powder; mp 260–263 °C (from CH_3CN/Et_2O, decomp.); ^{1}H NMR (400 MHz, CD_3CN) δ 1.48 (18H, s, Bu), 6.63 (1H, bs, OH), 7.45 (2H, bs, Ph-2,6), 7.58–7.90 (20H, m, NPh-2,3,4,5,6, H-4,5,6,7,8); IR (KBr) ν 1636, 1083 cm^{-1}; MS (FAB) m/z 657 ($M^+ - BF_4$); HRMS Calcd for $C_{45}H_{41}BF_4N_2O_3$: 657.3113 ($M - BF_4$). Found: 657.3114 ($M^+ - BF_4$).

3,5-Di-*t*-butyl-4-hydroxyphenyl-bis(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]pyrrol-3-yl)methyl tetrafluoroborate (10c·BF_4^-): Dark brown powder; mp 250–255 °C (from CH_3CN/Et_2O, decomp.); ^{1}H NMR (400 MHz, CD_3CN) δ 1.30 (18H, s, Bu), 3.57 (6H, s, NMe), 5.50 (1H, s, OH), 7.38 (2H, s, Ph-2,6), 7.52–7.65 (6H, m), 7.86 (2H, m), 8.00 (2H, m); ^{13}C NMR (125.7 MHz, CH_3CN) δ 27.9, 30.4, 35.4, 115.3, 123.2, 128.5, 132.5, 134.6, 137.8, 139.8, 140.0, 142.0, 149.8, 153.5, 162.4, 163.1, 165.6; IR (KBr) ν 1636, 1083 cm^{-1}; MS (FAB) m/z 533 ($M^+ - BF_4$); HRMS Calcd for $C_{35}H_{37}BF_4N_2O_3$: 533.2840 ($M - BF_4$). Found: 533.2848 ($M^+ - BF_4$). Anal. Calcd for $C_{35}H_{37}BF_4N_2O_3 \cdot 1/3BF_4$: C, 64.63; H, 5.70; N, 4.17%. Found: C, 64.70; H, 5.79; N, 4.31%.

Preparation of Methylium Tetrafluoroborates 12d–f·BF_4^-. To a stirred solution of **8d–f** (0.25 mmol) in CH_2Cl_2 (10 cm^3) 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 cm^3) and 42% HBF_4 (1 cm^3) at 0 °C and the mixture was stirred for 1 h. To the mixture was added Et_2O (100 cm^3) and the precipitates were collected by filtration to give **12d–f·BF_4^-** (Table 1, Runs 4, 6, and 8).

4-Acetoxyphenyl-bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)-methyl tetrafluoroborate (12d·BF_4^-): Dark green powder; mp 150–155 °C (from CH_3CN/Et_2O, decomp.); ^{1}H NMR (400 MHz, CD_3CN) δ 2.30 (3H, s, OAc), 7.35 (2H, d, J = 10.4 Hz, Ph-3,5), 7.68–7.83 (4H, m), 7.91–8.13 (4H, m), 8.25–8.40 (4H, m); IR (KBr) ν 1752, 1083 cm^{-1}; MS (FAB) m/z 437 ($M^+ - BF_4$); HRMS Calcd for $C_{27}H_{17}BF_4O_6$: 437.1036 ($M - BF_4$). Found: 437.1028 ($M^+ - BF_4$). Anal. Calcd for $C_{27}H_{17}BF_4O_6 \cdot H_2O$: C, 59.94; H, 3.48%. Found: C, 59.81; H, 3.53%.

4-Acetoxyphenyl-bis(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]pyrrol-3-yl)methyl tetrafluoroborate (12e·BF_4^-): Dark green powder; mp 190–195 °C (from CH_3CN/Et_2O, decomp.); ^{1}H NMR (400 MHz, CD_3CN) δ 2.25 (3H, s, OAc), 6.47 (2H, d, J = 10.9 Hz, Ph-3,5), 6.85–8.00 (22H, m); IR (KBr) ν 1630, 1083 cm^{-1}; MS (FAB) m/z 587 ($M^+ - BF_4$); HRMS Calcd for $C_{39}H_{27}BF_4N_2O_4$: 587.1964 ($M - BF_4$). Found: 587.1965 ($M^+ - BF_4$).

4-Acetoxyphenyl-bis(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]pyrrol-3-yl)methyl tetrafluoroborate (12f·BF_4^-): Dark green powder; mp 175–180 °C (from CH_3CN/Et_2O, decomp.); ^{1}H NMR (400 MHz, CD_3CN) δ 2.30 (3H, s, OAc), 3.57 (6H, s, NMe), 6.48 (2H, d, J = 10.7 Hz, Ph-3,5), 6.80–8.20 (12H, m); IR (KBr) ν 1600, 1083 cm^{-1}; MS (FAB) m/z 463 ($M^+ - BF_4$); HRMS Calcd for $C_{29}H_{23}BF_4N_2O_4$: 463.1697 ($M - BF_4$). Found: 463.1690 ($M^+ - BF_4$).

General Synthetic Procedure for Methylium Hexafluorophosphates 10d–f·PF_6^-. To a stirred solution of **8d–f** (0.25 mol) in CH_2Cl_2 (10 cm^3) 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 a 60% aqueous HPF_6 (1 cm^3) 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 in vacuo. 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 **10d–f·PF_6^-** (Table 1, Runs 5, 7, and 9).

4-Hydroxyphenyl-bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)-methyl hexafluorophosphate (10d·PF_6^-): Dark brown powder; mp 170–172 °C (from CH_3CN/Et_2O, decomp.); ^{1}H NMR (400 MHz, CD_3CN) δ 5.35 (1H, s, OH), 6.98 (2H, d, J = 9.8 Hz, Ph-3,5), 7.65 (2H, d, J = 9.8 Hz, Ph-2,6), 7.76 (2H, m), 7.90–8.01 (4H, m), 8.15–8.27 (4H, m); IR (KBr) ν 1737, 840 cm^{-1}; MS (FAB) m/z 395 ($M^+ - PF_6$); HRMS Calcd for $C_{25}H_{15}F_6O_5P$: 395.0949 ($M - PF_6$). Found: 395.0943 ($M^+ - PF_6$).

Bis(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]pyrrol-3-yl)(4-hydroxyphenyl)methyl hexafluorophosphate (10e·PF_6^-): Dark brown powder; mp 180–185 °C (from CH_3CN/Et_2O, decomp.); ^{1}H NMR (400 MHz, CD_3CN) δ 5.35 (1H, s, OH), 6.98 (2H, d, J = 9.3 Hz, Ph-3,5), 7.45 (4H, d, J = 9.3 Hz, NPh-2,6), 7.59–7.95 (18H, m, Ph-2,6, NPh-3,4,5, H-4,5,6,7,8); IR (KBr) ν 1675, 845 cm^{-1}; MS (FAB) m/z 545 ($M^+ - PF_6$); HRMS Calcd for $C_{37}H_{25}F_6N_2O_3P$: 545.1873 ($M - PF_6$). Found: 545.1868 ($M^+ - PF_6$).

Bis(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]pyrrol-3-yl)(4-hydroxyphenyl)methyl hexafluorophosphate (10f·PF_6^-): Dark brown powder; mp 155–157 °C (from CH_3CN/Et_2O, decomp.); ^{1}H NMR (400 MHz, CD_3CN) δ 3.55 (6H, s, NMe), 5.10 (1H, s, OH), 6.88 (2H, d, J = 10.5 Hz, Ph-3,5), 7.45 (2H, d, J = 10.5 Hz, Ph-2,6), 7.60–7.75 (6H, m, H-6,7,8), 7.92 (2H, d, J = 11.6 Hz, H-4), 8.09 (2H, dd, J = 11.6, 10.5 Hz, H-5); IR (KBr) ν 1634, 845 cm^{-1}; MS (FAB) m/z 421 ($M^+ - PF_6$); HRMS Calcd for $C_{27}H_{21}F_6N_2O_3P$: 421.1576 ($M - PF_6$). Found: 421.1571 ($M^+ - PF_6$).

Preparation of α,α-Bis(heteroazulen-3-yl)-1,4-benzoquinonemethides 11a–c from 10a–c·BF_4^-. The cation **10a–c·BF_4^-** (0.25 mmol) was dissolved in aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 and concentrated in vacuo to give the products **11a–c** (Table 1, Runs 1–3).

3,5-Di-*t*-butyl-α,α-bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)-1,4-benzoquinonemethides (11a): Dark green powder; mp 228–230 °C (from CH_2Cl_2/AcOEt); ^{1}H NMR (500 MHz, DMSO-d_6, 80 °C) δ 1.18 (18H, s, Bu), 7.01 (2H, s, Ph-2,6), 7.19 (2H, d, J = 11.2 Hz, H-4), 7.16–7.20 (2H, m, H-6), 7.37–7.43 (6H, m, H-5,7,8); ^{13}C NMR (125.7 MHz, DMSO-d_6) δ 30.3, 31.6, 35.9, 55.7, 60.6, 118.1, 128.8, 130.7, 134.3, 136.3, 138.9, 147.3,

150.6, 158.5, 171.2, 187.0; IR (KBr) ν 1652 cm^{-1}; MS (rel, int.) m/z 657 (M^+, 18), 84 (100%). Anal. Calcd for $C_{33}H_{30}O_5 \cdot 3/2H_2O$: C, 74.49; H, 6.55%. Found: C, 74.28; H, 6.23%.

3,5-Di-*t*-butyl-α,α-bis(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]pyrrol-3-yl)-1,4-benzoquinonemethides (11b): Dark green powder; mp 279–280 °C (from CH_2Cl_2/AcOEt); ^{1}H NMR (500 MHz, DMSO-d_6, 80 °C) δ 1.30 (18H, s, Bu), 6.94 (2H, d, $J = 9.5$ Hz, H-8), 7.07 (2H, dd, $J = 10.5$, 9.5 Hz, H-6), 7.18 (2H, s, Ph-2,6), 7.27 (4H, dd, $J = 10.5$, 9.5 Hz, H-5,7), 7.36 (2H, d, $J = 10.5$ Hz, H-4), 7.36 (4H, d, $J = 7.4$ Hz, NPh-2,6), 7.53 (2H, t, $J = 7.2$ Hz, NPh-4), 7.60 (4H, dd, $J = 7.4$, 7.2 Hz, NPh-3,5); ^{13}C NMR (125.7 MHz, DMSO-d_6) δ 29.7, 33.1, 35.1, 112.1, 114.7, 128.0, 128.7, 129.0, 129.7, 130.4, 130.8, 131.0, 133.9, 134.5, 137.7, 143.7, 146.0, 146.3, 166.1, 186.3; IR (KBr) ν 1680 cm^{-1}; MS (ESI) m/z 657 ($M^+ + H$, 100%). Anal. Calcd for $C_{45}H_{40}N_2O_3 \cdot 1/5CH_2Cl_2$: C, 80.79; H, 6.02; N, 4.00%. Found: C, 80.57; H, 6.04; N, 4.16%.

3,5-Di-*t*-butyl-α,α-bis(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]pyrrol-3-yl)-1,4-benzoquinonemethides (11c): Dark green powder; mp 235–236 °C (from CH_2Cl_2/AcOEt); ^{1}H NMR (500 MHz, DMSO-d_6, 80 °C) δ 1.14 (18H, s, Bu), 3.48 (6H, s, NMe), 7.03 (2H, s, Ph-2,6), 7.08 (2H, dd, $J = 10.2$, 8.7 Hz, H-6), 7.20 (2H, dd, $J = 10.7$, 8.7 Hz, H-5), 7.25 (2H, d, $J = 10.7$ Hz, H-4), 7.34 (2H, d, $J = 8.5$ Hz, H-8), 7.39 (2H, dd, $J = 10.2$, 8.5 Hz, H-7): ^{13}C NMR (125.7 MHz, DMSO-d_6) δ 26.4, 29.4, 34.8, 112.2, 113.9, 127.3, 129.9, 130.7, 131.9, 133.1, 133.2, 143.1, 145.5, 145.6, 165.9, 177.9, 185.9; IR (KBr) ν 1662 cm^{-1}; MS (ESI) m/z 421 (M^+, 100%). Anal. Calcd for $C_{35}H_{36}N_2O_3 \cdot H_2O$: C, 76.21; H, 6.74; N, 5.09%. Found: C, 76.34; H, 6.96; N, 5.09%.

Preparation of α,α-Bis(heteroazulen-3-yl)-1,4-benzoquinonemethides 11d–f from 12d–f•BF_4^-. To a solution of **12d–f**•BF_4^- (0.25 mmol) in CH_2Cl_2 (1 cm^3) was added K_2CO_3 (138 mg, 1 mmol), and the mixture was stirred at rt for 48 h. After the reaction was completed, the mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 and concentrated in vacuo to give **11d–f** (Table 1, Runs 4, 6, and 8).

α,α-Bis(2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)-1,4-benzoquinonemethides (11d): Dark green powder; mp 260–263 °C (from CH_2Cl_2/AcOEt, decomp.); ^{1}H NMR (500 MHz, DMSO-d_6, 50 °C) δ 6.25 (2H, d, $J = 10.0$ Hz, Ph-3,5), 7.20–7.26 (2H, m, H-6), 7.27 (2H, d, $J = 11.3$ Hz, H-4), 7.32 (2H, d, $J = 10.0$ Hz, Ph-2,6), 7.40–7.51 (6H, m, H-5,7,8); ^{13}C NMR (125.7 MHz, DMSO-d_6) δ 118.8, 128.0, 128.8, 134.8, 136.7, 138.1, 138.2, 139.6, 151.6, 151.7, 158.8, 166.8, 166.9, 187.4; IR (KBr) ν 1617 cm^{-1}; MS (ESI) m/z 395 ($M^+ + H$, 100%). Anal. Calcd for $C_{25}H_{14}O_5 \cdot CH_2Cl_2$: C, 66.05; H, 3.05%. Found: C, 66.00; H, 3.28%.

α,α-Bis(1,2-dihydro-2-oxo-*N*-phenylcyclohepta[*b*]pyrrol-3-yl)-1,4-benzoquinonemethides (11e): Dark green powder; mp 272–275 °C (from CH_2Cl_2/AcOEt, decomp.); (500 MHz, DMSO-d_6, 50 °C) δ 6.27 (2H, d, $J = 9.9$ Hz, Ph-3,5), 7.03 (2H, d, $J = 9.3$ Hz, H-8), 7.17 (2H, dd, $J = 10.1$, 9.3 Hz, H-7), 7.34–7.46 (12H, m, H-4,5,6, Ph-2,6, NPh-2,6), 7.55 (2H, t, $J = 7.5$ Hz, NPh-4), 7.62 (4H, dd, $J = 7.8$, 7.5 Hz, NPh-3,5); ^{13}C NMR (125.7 MHz, DMSO-d_6) δ 31.0, 54.8, 59.7, 115.6, 126.4, 127.8, 128.5, 129.2, 129.5, 131.3, 133.8, 134.4, 134.8, 138.2, 144.4, 146.2, 165.4, 186.2; IR (KBr) ν 1688 cm^{-1}; MS (ESI) m/z 545 ($M^+ + H$, 100%). Anal. Calcd for $C_{37}H_{24}N_2O_3 \cdot 2H_2O$: C, 76.56; H, 4.94; N, 4.59%. Found: C, 76.54; H, 4.86; N, 4.82%.

α,α-Bis(1,2-dihydro-*N*-methyl-2-oxocyclohepta[*b*]pyrrol-3-yl)-1,4-benzoquinonemethides (11f): Dark green powder; mp 220–223 °C (from CH_2Cl_2/AcOEt, decomp.); ^{1}H NMR (500 MHz, DMSO-d_6, 50 °C) δ 3.50 (6H, s, NMe), 6.23 (2H, d, $J = 9.6$ Hz, Ph-3,5), 7.16 (2H, dd, $J = 9.0$, 8.7 Hz, H-6), 7.25 (2H, d, $J = 9.6$, Ph-2,6), 7.28 (2H, dd, $J = 10.8$, 8.7 Hz, H-5), 7.31 (2H, d, $J = 10.8$ Hz, H-4), 7.46 (2H, d, $J = 9.5$ Hz, H-8), 7.49 (2H, dd, $J = 9.5$, 9.0 Hz, H-7); ^{13}C NMR (125.7 MHz, DMSO-d_6) δ 26.6, 60.0, 111.4, 115.4, 125.8, 127.5, 128.5, 130.9, 134.2, 134.4, 138.0, 144.3, 146.1, 165.4, 185.2; IR (KBr) ν 1663 cm^{-1}; MS (ESI) m/z 421 ($M^+ + H$, 100%). Anal. Calcd for $C_{27}H_{20}N_2O_3 \cdot 1/2CH_2Cl_2$: C, 71.41; H, 4.79; N, 6.03%. Found: C, 71.35; H, 4.57; N, 6.05%.

Preparation of α,α-Bis(heteroazulen-3-yl)-1,4-benzoquinonemethides 11d–f from 10d–f•PF_6^-. The cation **10d–f**•PF_6^- (0.25 mmol) was dissolved in a 4% aqueous NaOH solution and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 and concentrated in vacuo to give the products **11d–f** (Table 1, Runs 5, 7, and 9).

Determination of pK_a Value of Conjugate Acids of Quinonemethides 11a–f. Buffer solutions of slightly different acidities were prepared by mixing aqueous solutions of potassium hydrogen phthalate (0.1 M) and HCl (0.1 M) (for pH 0.0–4.0), potassium hydrogen phthalate (0.1 M) and NaOH (0.1 M) (for pH 4.1–5.9), KH_2PO_4 (0.1 M) and NaOH (0.1 M) (for pH 6.0–8.0) in various portions. For preparing of sample solutions, 1 cm^3 portions of the stock solution, prepared by dissolving 3–5 mg of quinonemethides **11a–f** 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 quinonemethide **11a–f** in 50 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 of each quinonemethide **11a–f** (453 nm for **11a**; 489 nm for **11b**; 487 nm for **11c**; 467 nm for **11d**; 509 nm for **11e**; 507 nm for **11f**) was plotted against the pH to give a classical titration curve, whose midpoint was taken as the pK_a value.

Cyclic Voltammetry of Quinonemethides 11a–f. The reduction potentials of **11a–f** 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 oxidation–reduction waves, which are summarized in Table 3.

Reduction of 11a–f with Zn Powder. To a solution of **11a–f** (0.1 mmol) in AcOH (1 cm^3) and 3% HCl (0.1 cm^3) was added powdery Zn (65 mg, 1.0 mmol), and the mixture was stirred at 80 °C for 8 h. After filtration, the filtrate was concentrated in vacuo. The mixture was poured into an aqueous $NaHCO_3$ solution; this new mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 and concentrated in vacuo to give products **8a–f** (Table 3).

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